Instructions

1) Complete this report for:
   - Research Competitiveness Subprogram grants
   - Industrial Ties Research Subprogram
   - LaSER grants

2) All pages of this report must be numbered consecutively.

3) If this is a final report, complete sections I, II, and IIIB comprehensively for the cumulative project period.

4) Sections I and II are to be completed by the principal investigator(s). Section III is to be completed by the authorized fiscal officer.

5) Submit electronically in pdf format.

6) Attach additional pages if necessary; clearly label as Narrative form and give the LEQSF contract number.

Date: 5/15/00        LEQSF Contract #:  LEQSF (1997-00)-RD-A-14

Type of report: Annual_____ Final (cumulative)_____ X _____

Principal Investigator ______ Gary L. Findley

Department/Unit and Institution ______ Chemistry/Univ. of LA at Monroe ______ Phone # ______ (318) 342-1835 ______

Other Principal Investigator(s) ______ N/A ______

Title of Project ______ An NLU Collaborative Research Program in Physical Chemistry Using VUV ______

Synchrotron Radiation ______

Current Reporting Period: July 1, 1997 ______ through ______ June 30, 2000 ______

Signature(s) of Lead Principal Investigator(s): ______

Signature of Authorized Institutional Representative: ______
I. ABSTRACT

A collaborative research program in physical chemistry has been initiated. This program makes use of monochromatic synchrotron radiation at the University of Wisconsin Synchrotron Radiation Center (Aluminum Seya beamline 083) to study the host density dependence of dopant excited states in molecular systems. Photoionization and photoabsorption spectral measurements of CH₃I doped into varying number densities of SF₆ were performed in order to determine the electron scattering length in SF₆, and to investigate the nature of subthreshold photoionization in CH₃I/SF₆. This initial investigation has now been extended to the perturbers Ar, N₂, CO₂, CF₄, and C₄F₈, and to other dopants (benzene, ethyl iodide, and hydrogen iodide). One overall goal of this work was to establish a viable spectroscopy group effort at ULM (formerly NLU) in order to bolster the research capabilities in physical chemistry at both the graduate (M.S.) and undergraduate levels. A solid foundation for this goal has now been achieved.

One graduate student, Ms. Cherice M. Evans, has been involved in this initial collaboration. Ms. Evans received her M.S. degree in Chemistry from ULM in May 1998, working on a problem in nonlinear dynamics, while simultaneously participating in experimental measurements at the University of Wisconsin. Ms. Evans' original experimental studies at the University of Wisconsin, which were directly supported by this grant, served as a foundation for the Ph.D. research program she began in August 1998 at the LSU Center for Advanced Microstructures and Devices (CAMD) and the LSU Department of Chemistry. Ms. Evans continued to participate in this collaborative program for the duration of the LEQSF grant, and the research carried out under this project constitutes her Ph.D. dissertation. During the past year, Ms. Evans has completed her general examination for the Ph.D. degree, and is on track for graduation in May 2001.

The following milestones have been achieved during years 1 - 3:

• Six measurement quanta have been awarded by the University of Wisconsin Synchrotron Radiation Center. All of these measurement periods have been used by us.

• One M.S. student has graduated from ULM and is currently at LSU-CAMD as a Ph.D. Candidate in Chemistry. This provides a basis for the extension of the ULM/Wisconsin collaboration to CAMD.

• Seven research papers have been published (or are in the process of publication), and four others are currently in preparation.

• Seven scientific presentations have been made at national and/or regional conferences.

Increased opportunity for modern research in physical chemistry has thereby been provided at ULM, leading to a diversification of the research base for the State of Louisiana in general, and northeast Louisiana in particular.

LEQSF (1997-00)-RD-A-14
II. PROJECT REPORT

A. ACCOMPLISHMENTS

1. Personnel

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Graduate Student/Ph.D. Candidate  
Louisiana State University/Department of Chemistry and CAMD  
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2. Presentations

(i) Analytic Solutions to the Lotka-Volterra Model for Sustained Chemical Oscillations

Oral defense of M.S. Thesis
Department of Chemistry, Northeast Louisiana University, Monroe, LA
C. M. Evans

Thesis defense
February 9, 1998

(ii) Analytic Solutions to the Lotka-Volterra Problem

1998 Joint Meeting of the American Physical Society and the American Association of Physics Teachers, Columbus, OH
C. M. Evans and G. L. Findley

Contributed paper
April 18–21, 1998

(iii) Synchrotron Radiation in Chemistry

1998 Southwest Regional Meeting of the American Chemical Society, Baton Rouge, LA
G. L. Findley

Invited lecture
November 1–3, 1998
(iv) **Photoionization Spectra of CH$_3$I Perturbed by SF$_6$: Electron Scattering in SF$_6$ Gas**

1998 Southwest Regional Meeting of the American Chemical Society, Baton Rouge, LA

C. M. Evans, R. Reininger and G. L. Findley  Contributed paper

November 1-3, 1998

(v) **Subthreshold Photoionization Spectra of CH$_3$I Perturbed by SF$_6$**

American Physical Society Centennial Meeting, Atlanta, GA

C. M. Evans, R. Reininger and G. L. Findley  Contributed paper

March 20–26, 1999

(vi) **Subthreshold Photoionization of CH$_3$I in Ar, N$_2$ and CO$_2$**

218$^{th}$ National Meeting of the American Chemical Society, New Orleans, LA

C. M. Evans, R. Reininger and G. L. Findley  Contributed paper

August 22–26, 1999

(vii) **Subthreshold Photoionization Spectra of CH$_3$I in Pertruber Gases: Ar, N$_2$, CO$_2$ and SF$_6$**

Department of Chemistry, Louisiana Tech University, Ruston, LA

G. L. Findley  Invited lecture

April 26, 2000
(viii) A New Family of Lotka-Volterra Related Differential Equations

Year 2000 International Conference on Dynamical Systems and Differential Equations, Kennesaw, GA

C. M. Evans and G. L. Findley Invited paper

May 18–21, 2000

(ix) Photoionization Spectra of CH₃I and C₂H₅I Perturbed by CF₄ and c-C₄F₈: Electron Scattering in Halocarbon Gases

2000 Annual Meeting of the American Physical Society Division of Atomic, Molecular and Optical Physics, Storrs, CT

C. M. Evans, E. Morikawa and G. L. Findley Contributed paper

June 14–17, 2000

3. Publications

(i) Analytic Solutions to the Lotka-Volterra Model for Sustained Chemical Oscillations

C. M. Evans

M.S. Thesis, Northeast Louisiana University

May, 1998

Reprint attached to this Report.
(ii) **Photoionization Spectra of CH₃I Perturbed by SF₆: Electron Scattering in SF₆ Gas**

C. M. Evans, R. Reininger and G. L. Findley


Reprint attached to this Report.

(iii) **Subthreshold Photoionization Spectra of CH₃I Perturbed by SF₆**

C. M. Evans, R. Reininger and G. L. Findley

Chemical Physics **241** (1999) 239–246  Peer reviewed article

Reprint attached to this Report.

(iv) **A New Transformation for the Lotka-Volterra Problem**

C. M. Evans and G. L. Findley

Journal of Mathematical Chemistry **25** (1999) 105-110  Peer reviewed article

Reprint attached to this Report.

(v) **Analytic Solutions to a Family of Lotka-Volterra Related Differential Equations**

C. M. Evans and G. L. Findley

Journal of Mathematical Chemistry **25** (1999) 181-189  Peer reviewed article

Reprint attached to this Report.
(vi) **Subthreshold Photoionization of CH$_3$I in Ar, N$_2$ and CO$_2$**

C. M. Evans, R. Reininger and G. L. Findley

Chemical Physics Letters, in press  Peer reviewed article

Page proofs attached to this Report.

(vii) **Photoionization Studies of C$_2$H$_5$I and C$_6$H$_6$ Perturbed by Ar and SF$_6$**

C. M. Evans, J. D. Scott, F. H. Watson and G. L. Findley

Chemical Physics, submitted  Peer reviewed article

Preprint attached to this Report.

(viii) **Photoionization Spectra of CH$_3$I and C$_2$H$_2$I Perturbed by CF$_4$ and c-C$_4$F$_8$: Electron Scattering in Halocarbon Gases**

C. M. Evans, E. Morikawa and G. L. Findley

Physical Review A, submitted  Peer reviewed article

Preprint attached to this Report.

4. **Patents**

None
5. **External Funding Activity**

**Impurity Photoionization in Molecular Hosts**

G. L. Findley


Approved May 1998 and May 1999

These proposals provided for at least 6 weeks of beamtime each year on the Al-Seya beamline (083) at the University of Wisconsin Synchrotron Radiation Center during 1998–1999 and 1999–2000. The sample chamber, sample cells, pumping systems and measurement electronics that were previously maintained by Dr. Ruben Reininger are now assigned to Dr. G. L. Findley.

1999–2000 Proposal attached to this Report.

**Molecular Photoionization in Dense Gases and Simple Fluids**

G. L. Findley, E. Morikawa and J. D. Scott

National Science Foundation, in preparation for submission (August, 2000)

The submission of this proposal has hinged upon the construction of the NIM beamline at LSU-CAMD. The completion of this beamline, which has suffered considerable delays, is currently underway. The above proposal reflects our intent to continue measurements at SRC until the NIM beamline is fully commissioned.

6. **Specific Technical Accomplishments**

a. **Statement of Goals**

We have established a collaborative research program in physical chemistry using vacuum ultraviolet (VUV, 5-40 eV) synchrotron radiation at the Synchrotron Radiation Center (SRC, Aladdin) at the University of Wisconsin-Madison. Based upon our earlier work on the electronic structure of molecules in dense rare gases, we have
investigated photoionization and photoabsorption of CH$_3$I doped into varying number densities of SF$_6$. One overall intent of this effort was to establish a viable spectroscopy group at ULM in order to bolster the research capabilities at both the graduate (M.S.) and undergraduate levels. The work at the Wisconsin Synchrotron Radiation Center is a short-term opportunity that will provide an ongoing program that can be transferred in the future to the LSU Center for Advanced Microstructures and Devices (CAMD) after the VUV beamline that is to be constructed there is finished.

In the original proposal for this project, the goals and benchmarks were as follows.

**year 1**

- 4 - 6 weeks measurement time
- participation by Ms. Cherice Evans

**benchmarks**: Completion of T-dependent studies of CH$_3$I/Ar. Beginning of CH$_3$I/SF$_6$ measurements. Publication of one paper on molecular solvation in the rare gases. One presentation at a scientific conference.

**year 2**

- 4 - 6 weeks measurement time
- participation by Ms. Cherice Evans
- selection of a second graduate student

**benchmarks**: Completion of M.S. thesis by Ms. Evans (*completed in year 1*). Completion of CH$_3$I/SF$_6$ measurements and, if warranted, T-dependent studies of CH$_3$I/SF$_6$. Beginning of CH$_3$I/CH$_4$ measurements. Publication of at least one paper on CH$_3$I/SF$_6$. Two presentations at scientific conferences. Submission of a proposal to NSF on photoconduction in molecular liquids.

**year 3**

- 4 - 6 weeks measurement time
- participation by a second graduate student
- selection of a third graduate student
- initial movement of program
benchmarks: Completion of CH$_3$I/CH$_4$ measurements and, if warranted, T-dependent studies of CH$_3$I/CH$_4$. Publication of at least one paper on CH$_3$I/CH$_4$. Two presentations at scientific conferences. Submission of a proposal to DOE (Basic Energy Sciences) in the general area of electronic structure of liquids.

b. Activities Conducted in the Project

The principal investigator made one preliminary visit to SRC (September 1996) to schedule the first measurement period (December 19, 1996 - January 2, 1997). This initial two-week measurement period, which was supported by ULM, resulted in a study of field ionization spectra of CH$_3$I/Ar as a function of temperature, for a fixed Ar number density near the triple point liquid, in order to investigate solvent effects. Subsequent to this visit, the LEQSF grant supported two measurement periods (July 7, 1997 - July 27, 1997 and May 22, 1998 - June 14, 1998), for a total of 6 weeks of beamtime during year 1 of the project. The year 2 beamtime proposal was approved by SRC for two measurement periods, December 13, 1998 - January 15, 1999 and June 3, 1999 - July 2, 1999 (split over two Fiscal Years), for a total of 6 weeks of beamtime during year 2 of the project. The year 3 beamtime proposal, which was attached to the 1998-1999 Annual Report, was approved for two measurement periods (December 27, 1999 - January 15, 2000 and May 22, 2000 - June 10, 2000), for a total of 6 weeks of beamtime during year 3 of the project. All of these measurements employed the Al-Seya beamline at SRC.

One ULM graduate student, Ms. Cherice M. Evans, was selected to work on this project for the first year. At the time of her selection, Ms. Evans was a ULM undergraduate Chemistry major who had worked with the principal investigator on a theoretical problem for one year in preparation for beginning her graduate studies (M.S. degree) at ULM in January 1997. While participating in all of the above measurements, Ms. Evans continued her theoretical work in nonlinear dynamics, with the result that she graduated with the M.S. degree in May 1998 (year 1). Ms. Evans’ early experimental work at SRC served as a foundation for her Ph.D. studies, which began in August 1998 at LSU-CAMD (in the LSU Department of Chemistry) under the direction of Dr. John D. Scott, CAMD Scientific Director. By agreement with Dr. Scott, Ms. Evans’ involvement in the present project has continued and will result in her Ph.D. dissertation.

All of the goals described in Section 6.a were met or exceeded, with the following modifications:
• No suitable additional graduate students were found for this project. Since Ms. Evans, Dr. Scott and the principal investigator agreed that the research described in this Report was suitable for Ms. Evans’ Ph.D. dissertation at LSU, however, the absence of additional graduate students was no impediment to the project.

• As described in the 1997-1998 Annual Report, CF₄ was substituted for CH₄, as a result of new directions arising from the year 1 work.

• Proposal submission has been delayed recently as a result of uncertainties pertaining to the construction of the NIM beamline at LSU-CAMD. One proposal concerning photoconduction in molecular liquids is currently in preparation for submission to NSF. Moreover, two SRC beamtime proposals have been prepared and approved during the course of this project.

Specific technical results are as follows.

Studies in nonlinear dynamics: The Lotka-Volterra dynamical system
\[
\begin{align*}
\dot{\phi} &= a x_1 - b x_1 x_2; \\
\dot{\phi} &= -c x_2 + b x_1 x_2
\end{align*}
\] was reduced to a single second-order autonomous ordinary differential equation by means of a new variable transformation. Formal analytic solutions were presented for this latter differential equation for both \(c = a\) and \(c \neq a\) cases.

An initial formal analysis of the above analytic solutions was presented. A family of first-order autonomous ordinary differential equations related to the Lotka-Volterra system was derived, and the analytic solutions to these systems were given. Invariants for the latter systems were introduced, and a simple transformation which allows these systems to be reduced to Hamiltonian form was provided.

Electron scattering in SF₆ gas: A photoionization study of CH₃I in the presence of SF₆ perturbers (up to the perturber density \(9.75 \times 10^{19} \text{ cm}^{-3}\)) disclosed a red shift of autoionizing features that depends linearly on the perturber number density. From the perturber induced energy shifts of the CH₃I nd Rydbergs (\(n=9,10,11,12\)), the electron scattering length of SF₆ was found to be \(A=-0.484 \text{ nm}\), which accords with cross section data.

Subthreshold photoionization of CH₃I perturbed by SF₆: We have measured pressure-dependent and temperature-dependent subthreshold photoionization spectra of pure CH₃I (up to 200 mbar) and CH₃I doped into SF₆ (up to 1 bar). At the high pressures studied, no temperature effect was observed for the subthreshold structure, thus ruling out vibrational autoionization of CH₃I as an ionization mechanism.
Moreover, analysis of photocurrent intensities as a function of CH$_3$I number density (pure CH$_3$I) and SF$_6$ number density (CH$_3$I doped into SF$_6$) revealed a quadratic dependence in the former case and a linear dependence in the latter case. These dependencies were explained in terms of dopant (D)/perturber (P) interactions involving the excited state process $D^* + P \rightarrow [DP]^+ + e$, where $D^*$ is a discrete Rydberg state of the dopant (CH$_3$I). From the density dependence of the subthreshold structure of CH$_3$I/SF$_6$, the electron scattering length in SF$_6$ was determined and compared to a value recently obtained from autoionizing states in the same system.

**Subthreshold photoionization of CH$_3$I in Ar, N$_2$ and CO$_2$:** We have measured pressure-dependent subthreshold photoionization spectra of CH$_3$I doped into varying number densities of the perturber gases Ar, N$_2$ and CO$_2$. The intensity of the observed subthreshold structure was discussed in terms of two different interactions, namely electron attachment and associative ionization. Effective rate constants for these two processes were analyzed, and the variation in these constants was discussed in terms of the properties of the dopant excited state and the perturber ground state.

**Photoionization of C$_2$H$_5$I and C$_6$H$_6$ perturbed by Ar and SF$_6$:** We have measured photoionization spectra of C$_2$H$_5$I and C$_6$H$_6$ doped into Ar and SF$_6$, and photoabsorption spectra of C$_2$H$_5$I doped into Ar. The observation of subthreshold photoionization in C$_2$H$_5$I/SF$_6$ and C$_6$H$_6$/SF$_6$ was discussed in terms of dopant (D)/perturber (P) interactions involving the excited state process $D^* + P \rightarrow [DP]^+ + e^-$, where $D^*$ is a discrete Rydberg state of the dopant. The density-dependent energy shifts of high-n Rydberg states observed in the subthreshold photoionization spectra were used to obtain the zero-kinetic energy electron scattering length for SF$_6$. Similarly, the zero-kinetic-energy electron scattering length of Ar was obtained from the density-dependent energy shifts of C$_2$H$_5$I Rydberg states.
Photoionization of CH$_3$I and C$_2$H$_5$I perturbed by CF$_4$ and c-C$_4$F$_8$: Photoionization spectra of CH$_3$I and C$_2$H$_5$I doped into perturber halocarbon gases CF$_4$ (up to a perturber number density of $6.1 \times 10^{20}$ cm$^{-3}$) and c-C$_4$F$_8$ (up to a perturber number density of $2.42 \times 10^{19}$ cm$^{-3}$) disclosed a red shift of the dopant autoionizing features that depends linearly on the perturber number density. In the case of CF$_4$, which is transparent in the spectral region of interest, this red shift was verified from the dopant photoabsorption features as well. From the perturber-induced energy shifts of the dopant Rydberg states and ionization energies, the zero-kinetic-energy electron scattering lengths for CF$_4$ and c-C$_4$F$_8$ were found to be $-0.180 \pm 0.003$ nm and $-0.618 \pm 0.012$ nm, respectively. (To our best knowledge, these are the first measurements of zero-kinetic-energy electron scattering lengths for both CF$_4$ and c-C$_4$F$_8$.)

7. **Stimulus Assessment**

a. **Assessment of Action Plan to Eliminate Barriers to National Competitiveness**

The original plan to eliminate barriers to national competitiveness involved the following elements.

- Establish an ongoing research effort at SRC.
- Explore the transfer of this effort to CAMD.
- Begin submission of competitive proposals.

Major components of this plan have been achieved and are having an effect in eliminating competitiveness barriers. This is evidenced by an extension of our project to CAMD by virtue of Ms. C. M. Evans’ continuance as a Research Assistant and Ph.D. Candidate at CAMD, and by the acceptance of two of our competitive beamtime proposals by SRC.

b. **Assessment of Progress Made in Attempts to Achieve National Competitiveness**

Acceptance of our competitive beamtime proposals for year 2 and year 3 by SRC is categorically equivalent to the receipt of federal funding for this project and represents a significant milestone, one which foreshadows potential success in the NSF proposal currently in preparation.

In 1999, the principal investigator gave an invited keynote address at a synchrotron radiation symposium held in concert with a regional meeting of the
American Chemical Society. This invitation reflects the increasing competitiveness of the principal investigator in applied synchrotron radiation research.

c. Human Resource Development Achievements

The success of Ms. C. M. Evans in obtaining her M.S. degree in record time (1 and 1/2 years) at ULM, and her success in submitting for publication the results of her research, made a positive impression on the ULM Chemistry Department. New standards have thereby been set both for quality and for hard work. The continued success of Ms. Evans as an LSU graduate student serves as an exemplar for both graduate and undergraduate ULM Chemistry students, and has elicited several preliminary inquiries from other students who desire to emulate Ms. Evans’ experience.

B. VARIANCE FROM ORIGINAL WORK PLAN

Our original work plan was accomplished in full and ahead of schedule, with only minor modifications as described in Section 6. b.

C. PROBLEMS ENCOUNTERED

No problems were encountered in the pursuit of the research goals for this project. As described in Section 6. b, however, suitable additional graduate students were not identified for this project.

D. “NUGGETS”

A ULM presence is now fully established at SRC as an expected user group. Efforts to duplicate this achievement at CAMD are underway. Moreover, the principal investigator has continued his work in Washington to secure funding for the proposed ULM Applied Sciences Laboratory (to be co-located with CAMD). These more intangible accomplishments were certainly aided by the LEQSF funding that the principal investigator has received.

E. OTHER COMMENTS

None
F. NEXT REPORTING PERIOD

None.

G. FUTURE RESEARCH PLANS

1. Describe Plans for Securing/Continuing to Secure Consistent External Funding in the Future on a Consistent Basis

   An NSF proposal is nearing completion for submission. Since the NIM beamline at LSU-CAMD is now close to commissioning, the substantial body of research accomplished under the present LEQSF grant has provided a number of different avenues for funding VUV spectroscopy on this beamline. Future proposals will focus, for example, on problems related to chemical reactivity at surfaces.

2. Describe Future Research Directions

   The following papers are currently in preparation:


   These efforts will be followed by studies of photoionization of molecular impurities in liquid Ar and liquid CF$_4$. New work in the area of simple fluids will be an outgrowth of the following paper, which is in preparation:

3. Other Comments

None.

III. EXPENDITURE REPORT

The final expenditure report will be transmitted separately by the ULM Office of Business Affairs.

APPENDICES


Photoionization spectra of CH$_3$I perturbed by SF$_6$: electron scattering in SF$_6$ gas

C.M. Evans $^{a,b}$, R. Reininger $^a$, G.L. Findley $^{a,*}$

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Received 13 July 1998; in final form 24 September 1998

Abstract

A photoionization study of CH$_3$I in the presence of SF$_6$ perturbers (up to the perturber density $9.75 \times 10^{19}$ cm$^{-3}$) disclosed a red shift of autoionizing features that depends linearly on the perturber number density. From the perturber induced energy shifts of the CH$_3$I $n$d$^r$ Rydbergs ($n=9,10,11,12$), the electron scattering length of SF$_6$ was found to be $A=-0.484$ nm, which accords with previously reported (but less precise) cross-section data. An assessment is made of the validity of the impact approximation used in the data analysis presented here. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Perturber pressure effects on dopant Rydberg state energies and ionization energies continue to generate interest as a means of measuring electron scattering lengths in the perturber medium. Dopant/perturber systems have included CH$_3$I/rare gases [1–3], CH$_3$I/H$_2$ [3], CH$_3$I/alkanes [4], CH$_3$I/CO$_2$ [5], CH$_3$I/N$_2$ [6], benzene/rare gases [3,7], and benzene/H$_2$ [3]. Both photoabsorption and photoionization spectra have been measured. (At high perturber number densities, however, photoabsorption measurements can become limited if both the perturber and the dopant absorb in the same spectral region.) Thus, pressure effects have been analyzed for discrete and autoionizing dopant Rydberg states [1–7] and for subthreshold photoionization structure [5,6], and a synopsis of data pertaining to electron scattering lengths has been given [8].

The extraction [1–8] of the electron scattering length in a perturber medium from the density-dependent energy shift of dopant Rydberg states follows the theory by Fermi [9], as modified by Aleksiev and Sobel’man [10]. According to these authors [9,10], the total energy shift $\Delta$ may be written as a sum of contributions

$$\Delta = \Delta_s + \Delta_p,$$

where $\Delta_s$, the ‘scattering shift,’ is due to the interaction of the Rydberg electron with the perturber molecule, while $\Delta_p$, the ‘polarization shift,’ results
from the interaction of the positive core of the Rydberg molecule with the perturber molecule. \( \Delta_p \) can be calculated from \([2,10]\)

\[
\Delta_p = -10.78 \left( \frac{1}{2} \alpha e^2 \right)^{2/3} (\hbar v)^{1/3} \rho.
\]  \(2\)

In this equation, \( \rho \) is the perturber number density, \( \alpha \) is the polarizability of the perturber molecule, \( e \) is the charge on the electron, \( \hbar \) is the reduced Planck constant, and \( v \) is the relative thermal velocity of the dopant and perturber molecules. \( \Delta_{\infty} \) results from a measurement of \( \Delta_p \) after calculating \( \Delta_p \). Then, the electron scattering length \( A \) of the perturber, which gauges the electron–perturber interaction, can easily be determined from \([9]\)

\[
\Delta_{\infty} = \left( \frac{2 \pi \hbar^2}{m} \right) A \rho,
\]  \(3\)

where \( m \) is the mass of the electron.

In the present Letter, we report photoionization spectra of CH\(_3\)I perturbed by up to 4 bar of SF\(_6\). Since SF\(_6\) absorbs weakly in the region of the first \( (I_1 = I'(E_{1/2}) = 9.54 \text{ eV} \) \([2]\)) and second \( (I_2 = I'(E_{1/2}) = 10.16 \text{ eV} \) \([2]\)) ionization energies of CH\(_3\)I, photoabsorption measurements are not possible except at very low SF\(_6\) pressures. From the photoionization spectra, however, we were able to assign autoionizing \( nd \) Rydberg states of CH\(_3\)I, and to follow the energy shifts of these states as a function of increasing SF\(_6\) number density. By fitting the autoionizing state energies to the Rydberg equation, we were then able to determine \( I_2 \) as a function of increasing SF\(_6\) number density. As described above, these shifts can then be used to extract the electron scattering length in SF\(_6\).

SF\(_6\) is of interest as a perturber medium because of the large size and high symmetry of this molecule. In addition, SF\(_6\) has been the subject of studies of collisional effects (e.g., \( I \) changing collisions) involving Rydberg atoms \([11]\). However, even though SF\(_6\) is widely used as a high-pressure electrical insulator, only one measurement \([12]\) of the zero-energy scattering cross-section \( \sigma \) is known to us, a value \([12]\) determined by very slow electron attachment cross-section measurements in an electron beam collision chamber method. Since the zero-energy scattering cross-section is related to the electron scattering length as \( \sigma = 4 \pi A^2 \), the results presented here yield a much more precise determination of this parameter.

The experimental method employed in this Letter provides an excellent means for the precise determination of the electron scattering length in gaseous perturbers \([1–8]\). Recently, Al-Omari et al. \([13]\) have called into question the use of Eq. (2), which involves the impact approximation, in determining \( \Delta_p \). In the discussion below, therefore, we provide a brief description of these authors’ \([13]\) results as they pertain to our continued use of Eq. (2) in the following analysis.

2. Experiment

Details of the experimental cell have been published previously \([14]\). Briefly, photoionization spectra were measured with monochromatized synchrotron radiation (with a resolution of 0.13 nm, or \(~10 \text{ meV} \) in the spectral range of interest) that entered a copper experimental cell through a LiF window. The window had a thin (7 nm) coating of gold to act as an electrode. A second electrode (stainless steel) was placed parallel to the window with a spacing of 1.05 mm. The cell was connected to a cryostat and heater system allowing the temperature to be controlled to within 1 K. The applied electric field was 100 V, with the negative electrode being the LiF window. (The reported spectra are current saturated, which was verified by measuring selected spectra at different electric field strengths.)

CH\(_3\)I (Aldrich Chemical, 99%) and SF\(_6\) (Matheson Gas Products, 99.996%) were used without further purification. The gas handling system has been described previously, as well as the procedures employed to ensure a homogeneous mixing of CH\(_3\)I with SF\(_6\) \([4]\).

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the photoemission current from a metallic grid intercept-
3. Results and discussion

Photoionization spectra of CH$_4$I and CH$_3$I doped into varying number densities of SF$_6$ are presented in Fig. 1 in the autoionizing region ($I < h\nu < \lambda$) of CH$_4$I. Energy positions of a number of nd$'$ states for selected perturber number densities $\rho$ are given in Table 1, as well as the values of $I_2$ extracted from a fit of the assigned spectra to the Rydberg equation. A plot of nd$'$ energies and $I_2$ as a function of perturber number density is shown in Fig. 2, where the red shift of all spectral features is readily apparent. Fig. 2 demonstrates that the peak positions depend linearly on the perturber number density (cf. Eqs. (1)–(3)), and that the resulting linear fits (obtained by regression analysis) are essentially parallel to one another.

Since the slopes of the straight lines of Fig. 2 are essentially equal, one may assume that the average slope ($-24.72 \times 10^{-23}$ eV cm$^3$) closely approximates the asymptotic shift rate of the Rydberg series. Using the value [15] $\alpha = 6.54 \times 10^{-24}$ cm$^3$ for SF$_6$, one finds from Eqs. (1)–(3) an electron scattering length for SF$_6$ of $\lambda = -0.484$ nm. Since the zero-energy scattering cross-section $\sigma$ is given by

$$\sigma = 4\pi\lambda^2,$$

we have $\sigma = 2.94 \times 10^{-14}$ cm$^2$ for SF$_6$. This should be compared to the value $\sigma = 2 \times 10^{-14}$ cm$^2$ determined by very slow electron attachment cross-section measurements in an electron beam collision chamber method [12]. To our best knowledge, this is the first determination of the electron scattering length in SF$_6$ using high-$n$ Rydberg states.

Eq. (1) is an expression of the statistical independence of Rydberg electron scattering and core ion scattering off of the perturber atoms or molecules for high-$n$ Rydberg states [2,9,10,16]. Eq. (2), however, also requires the validity of the impact approximation, which assumes that the time between core ion/perturber collisions is long in comparison to the collision time [2,10,16]. At high densities, the impact approximation fails [16,17].

Fermi [9] originally estimated the polarization shift by assuming an $R^{-4}$ interaction between the core ion and an individual perturber atom or molecule. For high-$n$ Rydbergs and high density, Fermi then averaged this polarization potential by

<table>
<thead>
<tr>
<th>$\rho$ (10$^{19}$ cm$^{-3}$)</th>
<th>9d$'$</th>
<th>10d$'$</th>
<th>11d$'$</th>
<th>12d$'$</th>
<th>$I_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>9.867</td>
<td>9.937</td>
<td>9.988</td>
<td>10.022</td>
<td>10.162</td>
</tr>
</tbody>
</table>

Fig. 1. Photoionization spectra ($T = 27^\circ$C) of pure CH$_4$I (0.1 mbar) and CH$_3$I (5 mbar) doped into varying number densities ($10^{19}$ cm$^{-3}$) of SF$_6$: (a) 0.12; (b) 1.97; (c) 5.02; and (d) 9.75.
calculations for NO in Ar [18], and they concluded that their results should remain quantitatively valid for \( \rho \leq 1.6 \times 10^{22} \text{ cm}^{-3} \).

If one assumes that the maximum in \( P(W) \) gives the polarization shift, Eq. (1) becomes

\[
\Delta = \left( \frac{2\pi \hbar^2}{m} \right) \rho - 18.9 \left( \frac{a e^2}{2} \right) \rho^{2/3} \tag{7}
\]

as opposed to the impact approximation result described above, namely

\[
\Delta = \left( \frac{2\pi \hbar^2}{m} \right) \rho - 10.78 \left( \frac{a e^2}{2} \right)^{2/3} (\hbar c)^{1/3} \rho . \tag{8}
\]

A nonlinear least-squares fit of Eq. (7) to the present SF\(_6\) data yields the value \( A = -0.426 \text{ nm} \), which is within \( \sim 10\% \) of the value found from the fit to Eq. (8) (i.e., \( A = -0.484 \text{ nm} \)). Clearly, a larger density range than that provided here for SF\(_6\) is required in order to assess the relative applicability of Eqs. (7) and (8). Such a range is provided by data given in [2] for the system CH\(_3\)I/Ar.

Fig. 3. Shift in the first vertical ionization energy of CH\(_3\)I in varying number densities of Ar (\( \bullet \) = data from [2]; \( \cdots \cdots \) = nonlinear least-squares fit to Eq. (7); \( \cdots \cdots \cdots \) = linear least-squares fit to Eq. (8)). See text for discussion.
Table 2

Total shift rates $\Delta \rho$ and scattering lengths $A$ (from Eq. (8)) determined by means of photoionized Rydberg lines: Al, in the autoionization region; ST, in the subthreshold region.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\Delta \rho$ ($10^{-15}$ eV cm$^2$)</th>
<th>$A$ (nm)</th>
<th>Region</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.0</td>
<td>0.019</td>
<td>Al</td>
<td>[6]</td>
</tr>
<tr>
<td>Ar</td>
<td>$-4.75$</td>
<td>$-0.082$</td>
<td>Al</td>
<td>[21]</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$-7.86$</td>
<td>$-0.138$</td>
<td>Al</td>
<td>[4]</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>$-10.05$</td>
<td>$-0.176$</td>
<td>Al</td>
<td>[4]</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$-11.8$</td>
<td>$-0.224$</td>
<td>ST</td>
<td>[5]</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>$-12.93$</td>
<td>$-0.228$</td>
<td>Al</td>
<td>[4]</td>
</tr>
<tr>
<td>Xe</td>
<td>$-16.8$</td>
<td>$-0.324$</td>
<td>ST</td>
<td>[22]</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>$-24.72$</td>
<td>$-0.484$</td>
<td>Al</td>
<td>this Letter</td>
</tr>
</tbody>
</table>

In Fig. 3 we have plotted the shift [2] in the vertical ionization energy $I_v$ of CH$_4$ vs. Ar number density $\rho$, as determined from the measured shifts in the energy positions of high-$n$ Rydberg states. We have also plotted the results of a nonlinear least-squares fit to Eq. (7) and a linear least-squares fit to Eq. (8), yielding scattering lengths of $A = -0.061$ nm (Eq. (7)) and $A = -0.091$ nm (Eq. (8)) for this data set. While both Eqs. (7) and (8) are within the error bars of Fig. 3, the scattering lengths differ by more than 30% from one another. Moreover, the scattering length of Eq. (8) compares favorably to the value $A = -0.089$ nm determined by the electron swarm method [19].

From Fig. 3 we conclude that Eq. (8) provides a better description of the energy shift in the low-density region than does Eq. (7), and that we remain justified in our continued use of Eq. (8) in the analysis of the SF$_6$ data presented here. One possible problem with Eq. (7) is that $A_0$ was identified with the polarization energy that maximizes $P(W)$, rather than with that which would result from first convoluting $P(W)$ with the pure dopant spectrum, as discussed in [20] for the case of field ionization of CH$_4$ in Ar.

In summary, we have presented the first determination of the electron scattering length in SF$_6$, using high-$n$ Rydberg states, and have provided an analysis supporting the continued use of the impact approximation for the polarization energy (i.e., Eqs. (2) and (8)) in the extraction of this scattering length. Since the use of dopant Rydberg energy shifts in perturbed photoionization spectra as a means of determining scattering lengths is relatively new, we have summarized in Table 2 recent data on total shift rates and electron scattering lengths for various perturbers. Clearly, the largest scattering length so far measured by this method is that for SF$_6$.

Acknowledgements

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References


Subthreshold photoionization spectra of CH$_3$I perturbed by SF$_6$

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Abstract

We present pressure- and temperature-dependent subthreshold photoionization spectra of pure CH$_3$I (up to 200 mbar) and CH$_3$I doped into SF$_6$ (up to 1 bar). At the high pressures studied, no temperature effect was observed for the subthreshold structure, thus ruling out vibrational autoionization of CH$_3$I as an ionization mechanism. Moreover, analysis of photocurrent intensities as a function of CH$_3$I number density (pure CH$_3$I) and SF$_6$ number density (CH$_3$I doped into SF$_6$) shows a quadratic dependence in the former case and a linear dependence in the latter case. This is discussed in terms of dopant (D)/perturber (P) interactions involving the excited state processes D$^+$ + P → D$^+$ + P$^-$ and D$^+$ + P → [DP]$^+$ + e$^-$. Where D$^+$ is a discrete Rydberg state of the dopant (CH$_3$I). From the density dependence of the subthreshold structure of CH$_3$I/SF$_6$, the electron scattering length in SF$_6$ is determined and compared to a value recently obtained from autoionizing states in the same system. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Methyl iodide (CH$_3$I) has served as a convenient probe in studies of high-\(n\) Rydberg dopant–perturber interactions [1–7]. Dopant/perturber systems have included CH$_3$I/rare gases [1–4], CH$_3$I/H$_2$ [4], CH$_3$I/alkanes [5], CH$_3$I/CO$_2$ [6] and CH$_3$I/N$_2$ [7]. Both photoabsorption and photoionization spectra have been measured, and perturber pressure effects have been analyzed for discrete and autoionizing dopant Rydberg states [1–7], as well as for subthreshold photoionization structure [3,6,7].

Photoionization spectra of CH$_3$I [8–11] and of CH$_3$I doped into Xe [3], CO$_2$ [6] and N$_2$ [7] exhibit rich subthreshold structure beginning 0.17 eV before the ionization limit \(I = R^2E_{1/2}\). From the observed energy spacing and linear shift (as a function of perturber number density) of these peaks, the subthreshold structure has been identified as arising from high-\(n\) Rydberg states of CH$_3$I, which permitted the evaluation of electron scattering lengths in highly absorbing perturber media [3,6,7].

Ivanov and Vilesov [9] discussed vibrational autoionization as a possible source of the subthreshold signal in pure CH$_3$I at pressures below 10$^{-3}$ mbar. At higher pressures, however, they proposed [8,9] that subthreshold photoionization results from the Hornbeck–Molnar [12] process, namely,

\[
\begin{align*}
\text{CH}_3\text{I} + h\nu & \rightarrow \text{CH}_3\text{I}^+ , \\
\text{CH}_3\text{I}^+ + \text{CH}_3\text{I} & \rightarrow (\text{CH}_3\text{I})^+_2 + e^- ,
\end{align*}
\]

as observed in the rare gases. (Here, \(h\nu\) is the photoexcitation energy and CH$_3$I$^+$ represents a Rydberg state.)
From a study of the temperature dependence of the relative peak heights of the subthreshold structure in pure CH$_3$I, Meyer et al. [11] were able to demonstrate that the ionization mechanism is vibrational autoionization at pressures up to $15 \times 10^{-3}$ mbar. This pressure is one order of magnitude greater than the pressure limit cited by Ivanov and Vilesov [9], after which these authors [9] claimed to have observed a quadratic dependence of photocurrent signal on CH$_3$I pressure [in accord with process (1), above].

In a recent work [13], we measured the linear shift of autoionizing states of CH$_3$I perturbed by SF$_6$, in the region $I < h\nu < I [\approx KE_{1/2}]$, as a function of SF$_6$ number density in order to extract the electron scattering length in SF$_6$. In the present paper, we report both pressure- and temperature-dependent subthreshold photoionization spectra of pure CH$_3$I (up to 200 mbar) and CH$_3$I doped into SF$_6$ (up to 1 bar). Our results confirm a quadratic dependence of photocurrent signal upon CH$_3$I pressure in the subthreshold region of pure CH$_3$I at high pressure, with no temperature dependence indicative of vibrational autoionization. For CH$_3$I/SF$_6$, we observe a linear dependence of photocurrent signal upon SF$_6$ pressure in the subthreshold region, again with no temperature effect. This latter result suggests a possible analog of process (1), namely

$$\text{CH}_3\text{I} + \text{SF}_6 \rightarrow [(\text{CH}_3\text{I})(\text{SF}_6)]^+ + e^- .$$  \hspace{1cm} (2)

Finally, we have used the subthreshold structure of CH$_3$I/SF$_6$ photoionization to extract the electron scattering length in SF$_6$ and find that this value accords with our previously reported result [13].

2. Experiment

Photoionization and photoabsorption spectra were measured with monochromatized synchrotron radiation having a resolution of 0.13 nm (200 μm slits), or $\sim 10$ meV in the spectral range of interest. Two different cells were used: cell 1 [14] is equipped with entrance and exit MgF$_2$ windows and a pair of parallel-plate electrodes (stainless steel, 3.0 mm spacing) oriented perpendicular to the windows, thus permitting the simultaneous recording of transmission and photoionization spectra. The light path inside the cell is 1.0 cm. Cell 2 [15] is equipped with an entrance LiF window coated with a thin (7 nm) layer of gold to act as an electrode. A second electrode (stainless steel) is placed parallel to the window with a spacing of 1.05 mm. The bodies of both cells are fabricated from copper and are capable of withstandout up to 100 bar. Each cell was connected to a cryostat and heater system allowing the temperature to be controlled to within $\pm 1$ K [14]. The applied electric field was 100 V, with the negative electrode being the LiF window in cell 2. (The reported spectra are current saturated, which was verified by measuring selected spectra at different field strengths.) Photocurrents within the cell were of the order of $10^{-10}$ A.

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the photoemission current from a metallic grid intercepting the beam prior to the experimental cell. All photoionization spectra are normalized to this current. Transmission spectra (which are reported as absorption = 1 – transmission) were normalized both to the incident light intensity and to the empty cell transmission.

CH$_3$I (Aldrich Chemical, 99%+) and SF$_6$ (Matheson Gas Products, 99.996%) were used without further purification. The gas handling system has been described previously, as well as the procedures employed to ensure a homogeneous mixing of CH$_3$I with SF$_6$ [5].

3. Results and discussion

Representative subthreshold photoionization spectra for pure CH$_3$I at varying CH$_3$I pressures (number densities) are presented in Fig. 1 in comparison to the low-pressure photoabsorption spectrum of CH$_3$I. Similar spectra are shown in Fig. 2 for CH$_3$I doped into varying number densities of SF$_6$. (All of the photoionization spectra presented are normalized to unity at the same spectral feature above the CH$_3$I $^2E_{1/2}$ threshold.) In both systems, one observes subthreshold photoionization structure that correlates with nd Rydberg states of CH$_3$I converging on the $^2E_{3/2}$ ionization limit. In order to ascertain whether
or not the high-pressure subthreshold structure arises from the vibrational autoionization mechanism demonstrated by Meyer et al. [11] in low-pressure pure CH$_3$I (where the photocurrent signals are at least two orders of magnitude less than those reported here), we measured photoionization spectra for one sample pressure at different temperatures. These results are shown in Fig. 3 for pure CH$_3$I, and in Fig. 4 for CH$_3$I/Se$_6$. Clearly, there is no temperature effect on the relative intensities of the subthreshold peaks, thus ruling out vibrational autoionization as the ionization mechanism in the high-pressure case.

We extracted peak areas (by gaussian fits to the photoionization spectra) for the density-dependent subthreshold structure of pure CH$_3$I and CH$_3$I doped into Se$_6$. These data are collected in Table 1 (CH$_3$I) and Table 2 (CH$_3$I/Se$_6$), and plotted in Fig. 5 (CH$_3$I) and Fig. 6 (CH$_3$I/Se$_6$). Fig. 5 clearly shows a quadratic dependence on CH$_3$I number density, as claimed by Ivanov and Vilesov [9], in accord with process (1). Equally clearly, Fig. 6 exhibits a linear dependence on Se$_6$ number density, which accords with the suggested process (2). (An analysis of peak heights as opposed to peak areas gives rise to plots identical in shape to those shown here.)

Since the subthreshold photoionization structure of Figs. 1 and 2 is superimposed upon a rising exponential background, as discussed by Ivanov and Vilesov [8,9], we have subtracted an exponential background fitted to the zero baseline and the sharp photocurrent step at threshold. The resulting spectra, when analyzed for peak area (or peak height), yield
polarizable perturber, the electron attachment contribution to the photocurrent is given by
\[ i_{ea} = k_1 \rho_D, \]  \hspace{1cm} (6)
where the effective rate constant \( k_1 \) is proportional to the (saturated) electron attachment cross-section, and we have assumed for the dopant number densities that \( \rho_D \propto \rho_D \) in the linear absorption regime. Likewise, the associative ionization [process (4)] contribution to the photocurrent is given by
\[ i_{ai} = k_2 \rho_D \rho_P, \]  \hspace{1cm} (7)
where the effective rate constant \( k_2 \) is proportional to the associative ionization cross-section, \( \rho_P \) is the perturber number density, and we have again assumed that \( \rho_D \propto \rho_D \).

In the absence of any significant photochemical contribution [i.e., process (5)] to the observed signal,

plots identical in shape to those presented in Figs. 5 and 6.

Ivanov and Vilesov [8,9] discussed three bimolecular processes which, for a general dopant (D)/perturber (P) system, can be symbolized as
\[ \text{D}^- + \text{P} \rightarrow \text{D}^+ + \text{P}^-, \]  \hspace{1cm} (3)
\[ \rightarrow [\text{DP}]^+ + e^-, \]  \hspace{1cm} (4)
\[ \rightarrow \text{R}_1^- + \text{R}_2 + e^-. \]  \hspace{1cm} (5)
Process (3) represents electron attachment [16], while process (4) is associative ionization [16] (i.e., the Hornbeck–Molnar [12] process). Process (5) represents a photochemical rearrangement leading to charged species. In their discussion of pure CH\(_3\)I (D = P = CH\(_3\)I), Ivanov and Vilesov [8,9] discounted process (5) on the basis of energetic considerations.

If we assume that process (3) is saturated (i.e., independent of the perturber pressure) for a highly
Table 1
Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 1) of pure CH$_3$I at varying number densities $\rho$ (10$^{10}$ cm$^{-3}$)

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>10d</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0024</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.025</td>
<td>0.00836</td>
<td>0.0128</td>
<td>0.0178</td>
<td>0.0254</td>
</tr>
<tr>
<td>0.12</td>
<td>0.0538</td>
<td>0.171</td>
<td>0.306</td>
<td>0.524</td>
</tr>
<tr>
<td>0.24</td>
<td>0.151</td>
<td>0.549</td>
<td>0.996</td>
<td>1.69</td>
</tr>
<tr>
<td>0.49</td>
<td>0.520</td>
<td>1.78</td>
<td>3.26</td>
<td>6.08</td>
</tr>
</tbody>
</table>

Regression coefficients:

$\alpha = 0.00 \quad 0.00 \quad 0.00 \quad 0.00$

$\beta = 0.229 \quad 0.863 \quad 1.41 \quad 1.99$

$\gamma = 1.73 \quad 5.63 \quad 10.9 \quad 21.1$

The regression coefficients are for a least-squares second-order polynomial fit, $i = \alpha \rho^2 + \beta \rho + \gamma$, as shown in Fig. 5.

Then, the subthreshold photocurrent should be given by

$$i = (k_1 + k_2 \rho_D) \rho_D,$$

which accords with the data presented here for pure CH$_3$I ($\rho_P = \rho_D = \rho$) (cf. Fig. 5 and Table 1).

$$i = \alpha \rho + \beta \rho^2,$$

and for CH$_3$I/SF$_6$ ($\rho_P = \rho, \rho_D = \text{constant}$) (cf. Fig. 6 and Table 2).

$$i = b_0 + b_1 \rho.$$

From the analysis presented above, $\alpha$ and $b_0$ should depend upon the dopant Rydberg electron attachment cross-section in CH$_3$I and SF$_6$, respectively. These cross-sections scale linearly with the principal quantum number $n$ for the CH$_3$I excited state [16]. A plot of $\alpha$ vs. $n$ and $b_0$ vs. $n$ is presented in Fig. 7a and Fig. 8a, respectively, and the linearity is indeed striking. Since $\alpha$ and $b_0$ are reflective of a molecular interaction, these parameters should depend upon the excited state polarizability of CH$_3$I [17], which in turn scales according to $n^5$ [16]. A plot of $\alpha$ vs. $n^5$ and $b_0$ vs. $n^5$ is presented in Fig. 7b and Fig. 8b, respectively, and the linearity is again striking.

Clearly, the mechanisms of electron attachment and associative ionization are sufficient to explain the observed density dependence of subthreshold
Fig. 6. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 2) of 0.1 mbar CH₃I doped into SF₆ as a function of SF₆ number density $\rho$ ($10^{15}$ cm$^{-3}$). ○, 11d; ■, 12d; ▲, 13d; ▼, 14d. The solid lines represent a least-squares fit to the function $b_1 \rho + b_0$ (cf. Table 2).

The above result accords with the theory by Fermi [18], as modified by Alekseev and Sobel’man [19]. According to these authors [18,19], the total energy shift $\Delta$ is due to a sum of contributions

$$\Delta = \Delta_{\text{sc}} + \Delta_p,$$

where $\Delta_{\text{sc}}$, the 'scattering shift', is due to the interaction of the Rydberg electron with the perturber molecule, while $\Delta_p$, the 'polarization shift', results from the interaction of the positive core of the Rydberg molecule with the perturber molecule. $\Delta_p$ can be calculated from [2,13,19]

$$\Delta_p = -10.78 \left( \frac{1}{2} \alpha e^2 \right)^{2/3} (\hbar \omega)^{1/3} \rho.$$

In this equation, $\rho$ is again the perturber number density, $\alpha$ the polarizability of the perturber.

Fig. 7. (a) Linear and (b) quadratic regression coefficients for the subthreshold photoionization density dependence of pure CH₃I (Table 1) plotted vs. the CH₃I excited state principal quantum number $n$ and $n'$, respectively. The straight lines are least-squares fits to the data. See text for discussion.
Finally, the electron scattering length $A$ of the perturber, which gauges the electron–perturber interaction, can easily be determined from [18]

$$
\Delta_{sc} = \left( \frac{2 \pi \hbar^2}{m} \right) A \rho,
$$

(13)

where $m$ is the mass of the electron.

Since the slopes of the straight lines of Fig. 9 are essentially equal, one may assume that the average slope $(-25.14 \times 10^{-23}$ eV cm$^2$) closely approximates the asymptotic shift rate of the Rydberg series. Using the value [20] $\alpha = 6.54 \times 10^{-24}$ cm$^3$ for SF$_6$, one finds from Eqs. (11)–(13) an electron scattering length for SF$_6$ of $A = 0.492$ nm. This compares favorably to our recent measurement [13] of $A =$

![Graph showing the relationship between $b$ and $n$ for two different ranges of $n'$ and $n$.](image)

Fig. 8. (a) Constant and (b) linear regression coefficients for the subthreshold photoionization density dependence of CH$_4$I/SF$_6$ (Table 2) plotted vs. the CH$_4$I excited state principal quantum number $n$ and $n'$, respectively. The straight lines are least-squares fits to the data. See text for discussion.

![Graph showing Rydberg states of CH$_4$I as a function of number density $\rho$.](image)

Fig. 9. Energy shifts of $n\ell$ Rydberg states of CH$_4$I as a function of SF$_6$ number density $\rho$ (10$^{10}$ cm$^{-3}$). The fitted ionization energy $I_\ell$ is denoted $^1E_{1/2}$. All straight lines are least-squares fits.

### Table 3

<table>
<thead>
<tr>
<th>$\rho$ (10$^{10}$ cm$^{-3}$)</th>
<th>1d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
<th>$I_\ell$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.73</td>
<td>9.365</td>
<td>9.399</td>
<td>9.426</td>
<td>9.444</td>
<td>9.539</td>
</tr>
</tbody>
</table>
from the analysis of autoionizing states in CH$_3$I/SeF$_6$.

In summary, we have presented pressure- and temperature-dependent subthreshold photoionization spectra of pure CH$_3$I and CH$_3$I doped into SeF$_6$. On the basis of these measurements, we were able to rule out vibrational autoionization as the mechanism of subthreshold ionization at high pressures, in contrast to the low-pressure case in pure CH$_3$I [9,11]. Moreover, we demonstrated a quadratic dependence on number density for the photocurrent signal in pure CH$_3$I, as reported previously [9], and a linear dependence on number density for the photocurrent signal in CH$_3$I doped into SeF$_6$. We then analyzed these dependences within a model that invoked both (saturated) electron attachment and associative ionization and found that the data presented are consistent with a Hornbeck–Molnar [12] mechanism leading to subthreshold photoionization in both cases. Nevertheless, only a mass analysis of photo-products will conclusively resolve this issue, as originally pointed out by Ivanov and Vilesov [9]. (This is particularly of interest in the case of SeF$_6$, since this molecule weakly absorbs to a dissociative final state in this spectral region [21].) No photocurrent was detected in pure SeF$_6$ in the energy region reported here, however.) Finally, we were able to evaluate the electron scattering length in SeF$_6$ from the perturber density-dependent subthreshold photoionization data. The value presented is in accord with our previous measurement resulting from autoionization studies in CH$_3$I/SeF$_6$ [13].

Acknowledgements

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References

A new transformation for the Lotka–Volterra problem

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The Lotka–Volterra dynamical system \( \dot{x}_1 = ax_1 - bx_1x_2, \dot{x}_2 = -cx_2 + bx_1x_2 \) is reduced to a single second-order autonomous ordinary differential equation by means of a new variable transformation. Formal analytic solutions are presented for this latter differential equation.

The Lotka–Volterra (LV) problem consists of the following pair of first-order autonomous ordinary differential equations:

\[
\begin{align*}
\dot{x}_1 &= ax_1 - bx_1x_2, \\
\dot{x}_2 &= -cx_2 + bx_1x_2,
\end{align*}
\]

where \( x_1(t) \) and \( x_2(t) \) are real functions of time, \( \dot{x}_i := dx_i/dt \), and \( a, b, c \) are positive real constants. This system was originally introduced by Lotka [8] in 1920 as a model of undamped oscillations in autocatalytic chemical reactions, and was later applied by Volterra [17] to treat predator–prey interactions in ecology. Other applications have followed in the intervening years in physics [13], chemistry [11], population biology [15] and epidemiology [14]. Indeed, the LV dynamical system is today a standard textbook example in the theory of nonlinear ordinary differential equations [10,16].

Since the original publication by Lotka [8], it has been known that equations (1) possess a dynamical invariant, namely,

\[
\Lambda = bx_1 + bx_2 - c \ln x_1 - a \ln x_2.
\]

By means of a logarithmic transformation, Kermer [5] showed that \( \Lambda \) serves to reduce equations (1) to a Hamiltonian system. This has recently sparked a resurgence of interest in the LV problem (including a rediscovery of some previously known results [6,12]), particularly with regard to dynamical invariants of generalizations of equations (1) [7,13].

Although the existence of a dynamical invariant for equations (1) implies that this system is solvable, very little is known about the analytic form of these solutions, with the exception of a Lie series analysis [3,4]. The purpose of the present note is to present a new transformation that reduces the LV system to a single second-order autonomous ordinary differential equation, and to reduce the solution of this equation...
to an integral quadrature. Thus, formal analytic solutions to equations (1) will be presented.

We begin by defining new coordinates \( z_1(t) \) and \( z_2(t) \) as follows:

\[
\begin{align*}
    z_1 &= \Lambda^{-1/2}(b x_1 + b x_2)^{1/2}, \\
    z_2 &= \Lambda^{-1/2}(-c \ln x_1 - a \ln x_2)^{1/2},
\end{align*}
\]

where the positive square root is implied in each case. From equations (1)–(3) we find

\[
\begin{align*}
    x_1 &= \frac{\Lambda}{b(a + c)}(cz_1^2 - 2z_2 z_2), \\
    x_2 &= \frac{\Lambda}{b(a + c)}(az_1^2 + 2z_2 z_2),
\end{align*}
\]

and

\[
    z_1^2 + z_2^2 = 1.
\]

Equation (5) permits the definition of an angle \( \phi \) such that

\[
    z_1 = \sin \phi, \quad z_2 = \cos \phi.
\]

From equations (2), (4) and (6), then, we find

\[
\begin{align*}
    \ddot{w} + \left[ \cot \phi - \tan \phi - \frac{2 \Lambda}{a + c} \cos \phi \sin \phi \right] \dot{w}^2 + (c - a)\left( 1 - \frac{\Lambda}{a + c} \sin^2 \phi \right) \dot{w} \\
    - \frac{1}{2} ac \left( 1 - \frac{\Lambda}{a + c} \right) \tan \phi - \frac{1}{2} \frac{ac \Lambda}{a + c} \sin \phi \cos \phi = 0.
\end{align*}
\]

Making the substitution

\[
    w = \frac{\Lambda}{2(a + c)} (1 + \cos 2\phi),
\]

equation (7) becomes

\[
    \ddot{w} - \dot{w}^2 - (c - a)(w - 1)\dot{w} + acw(w - 1) = 0.
\]

Moreover, from equations (4), (6) and (8) it follows that

\[
\begin{align*}
    x_1 &= \frac{1}{b} (cw + \dot{w}), \\
    x_2 &= \frac{1}{b} (aw - \dot{w}).
\end{align*}
\]

Equation (9) is fully equivalent to the LV dynamical system (i.e., equations (1)). A fourth-order Runge–Kutta [1] integration of equation (9) is shown in figure 1 for a typical trajectory, and the usual phase-plane plot of equations (10) for this same trajectory is given in figure 2. (These results are identical with those we have obtained from a direct numerical integration of equations (1), the plots of which are not shown for the sake of brevity.)

If we now set \( c = \alpha a \), equation (2) can be rearranged to yield

\[
\begin{align*}
    bx_1 x_2 &= -\frac{k^2}{b} x_1^{1-\alpha} e^{k(x_1 + x_2)/a}, \\
    k^2 &= -b^2 e^{-\alpha/a},
\end{align*}
\]
Figure 1. Fourth-order Runge-Kutta solution to equation (9) of the text for $a = 0.50$, $b = 1.30$, $c = 0.67$. Initial data for this trajectory are $w(t = 0) = 2.00$, $\dot{w}(t = 0) = 0.50$. The invariant (equation (2) of text) is $\Lambda = 2.5850$.

Figure 2. Phase-plane plot of equations (10) of the text for the trajectory specified in figure 1.

which reduces equations (1) to

$$\dot{x}_1 = ax_1 + \frac{k^2}{b} x_1^{1-\alpha} e^{b(x_1+x_2)/a},$$

$$\dot{x}_2 = -ax_2 - \frac{k^2}{b} x_1^{1-\alpha} e^{b(x_1+x_2)/a}.$$  

(12)
Substituting equations (10) into equations (12) gives
\[ \ddot{w} = a^2 a w + a(1 - \alpha) \omega + k^2 \left[ \frac{1}{b} (\alpha a w + \omega) \right]^{1-\alpha} e^{(\alpha+1)w}. \] (13)

Folding equation (13) into equation (9) (with \( c = \alpha a \)) yields the following equation for the first integral:
\[ \dot{w}^2 + a(\alpha - 1)w \dot{w} - \alpha a^2 w^2 - k^2 \left[ \frac{1}{b} (\alpha a w + \omega) \right]^{1-\alpha} e^{(\alpha+1)w} = 0. \] (14)

For the case \( c = a \ (\alpha = 1) \), equation (14) reduces to
\[ \dot{w}^2 - (a^2 w^2 + k^2 e^{2w}) = 0, \] (15)
or
\[ \dot{w} = \pm \left[ a^2 w^2 + k^2 e^{2w} \right]^{1/2}. \] (16)

Formal integration of equation (16) leads to the quadrature
\[ t - t_0 = \pm \int \left[ a^2 w'^2 + k^2 e^{2w'} \right]^{-1/2} dw'. \] (17)

Equation (17) represents an analytic solution to the \( c = a \) LV problem. Moreover, an analysis of the form of this integral [2] shows its relationship to the family of elliptic integrals, and leads to a new class of LV related differential equations.

In order to provide a similar quadrature for the \( c \neq a \) case, an alternative form of the first integral may be found by writing equations (11) as
\[ -\frac{k^2}{b} x_1^{-\alpha} e^{(x_1+x_2)/a} = bx_2, \] (18)
or, using equations (10),
\[ -\frac{k^2}{b} \left[ \frac{1}{b} (\alpha a w + \omega) \right]^{-\alpha} e^{(\alpha+1)w} = aw - \dot{w}. \] (19)

If we now define a function \( \rho(w) \) such that
\[ \alpha a w + w = \alpha a e^\rho, \] (20)
and write \( aw - \dot{w} = a(\alpha + 1)w - (\alpha a w + \omega) \), equation (19) becomes
\[ -\frac{k^2}{b} \left[ \frac{\alpha a}{b} \right]^{-\alpha} e^{(\alpha+1)w} e^{-\alpha \rho} = a(\alpha + 1)w - \alpha a e^\rho. \] (21)
or
\[ ba(\alpha + 1)w - b\alpha a e^\rho + k^2 \left[ \frac{\alpha a}{b} \right]^{-\alpha} e^{(\alpha+1)w} e^{-\alpha \rho} = 0. \] (22)
Since $\rho(u)$ can be determined from equation (22), we have from equation (20) the first integral

$$\dot{w} = \alpha a (\varepsilon^0 - w).$$  \hspace{1cm} (23)

Formal integration of equation (23) yields the quadrature

$$t - t_0 = \int_{w}^{w'} \frac{1}{\alpha a (\varepsilon^0 - w')} \, dw'.$$  \hspace{1cm} (24)

Equation (24) represents an analytic solution to the general LV problem. As in the $c = a$ case, an analysis of the form of equation (24) [2] shows the relationship of this integral to the family of elliptic integrals, and leads to a new class of LV related differential equations.

Finally, it is worth noting that we have integrated equation (13) directly using a symbolic processor [9], and that this integration results in the same formal solution presented above (i.e., equation (24), with $\rho$ being given by equation (22)). Using the same symbolic processor [9], we have also shown that equation (24) reduces to equation (17) under the assumption $\alpha = 1$ ($c = a$), which demonstrates the consistency of these solutions.

In summary, we have presented a transformation for the LV dynamical system that reduces this system to a single second-order autonomous ordinary differential equation. We have also provided formal analytic solutions to the LV problem by means of integral quadratures. An analytic investigation of these integrals will be presented separately [2].

Acknowledgements

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References


[9] Maple V, Rel. 4.00a (Waterloo Maple, Inc., Waterloo, Ontario, Canada).


Analytic solutions to a family of Lotka–Volterra related differential equations

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An initial formal analysis of the analytic solutions (C.M. Evans and G.L. Findley, J. Math. Chem. 25 (1999) 105–110) to the Lotka Volterra (LV) dynamical system is presented. A family of first-order autonomous ordinary differential equations related to the LV system is derived, and the analytic solutions to these systems are given. Invariants for the latter systems are introduced, and a simple transformation which allows these systems to be reduced to Hamiltonian form is provided.

1. Introduction

The Lotka–Volterra (LV) problem, originally introduced in 1920 by Lotka [8] as a model for undamped oscillating chemical reactions, and later applied by Volterra [18] to predator–prey interactions, consists of the following pair of first-order autonomous ordinary differential equations:

\[
\begin{align*}
\dot{x}_1 &= ax_1 - bx_1 x_2, \\
\dot{x}_2 &= cx_2 - bx_1 x_2,
\end{align*}
\]

where \(x_1(t)\) and \(x_2(t)\) are real functions of time, \(\dot{x}_i = dx_i/\text{dt}\), and \(a, b, c\) are positive real constants. Since that time, the LV model has been applied to problems in population biology (see, for example, [16]), chemical kinetics (see, for example, [13]), neural networks (see, for example, [12]) and epidemiology [15], and has become a classic example for nonlinear dynamical systems [11,17]. In the 1960s, Kerner [6] showed that the dynamical invariant, known since the original publication by Lotka [8] and having the form

\[
\Lambda = bx_1 + bx_2 - c \ln x_1 - a \ln x_2,
\]

could reduce equations (1), by means of a logarithmic transformation, to a Hamiltonian system. This initial discovery has been expanded by Kerner [6,7] and Plank [14] to multi-dimensional Lotka–Volterra equations, and Dutt [3] has analyzed the Hamiltonian form of equation (2) using Hamiltonian–Jacobi theory.

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Recently, equations (1) were shown [4] to have the solution

\[
x_1 = \frac{1}{b}(a\alpha w + \dot{w}),
\]

\[
x_2 = \frac{1}{b}(aw - \dot{w}),
\]

where \(a\alpha = c\) and \(w\) is given by the solution to

\[
\ddot{w} - \dot{w}^2 - a(\alpha - 1)(w - 1)\dot{w} + a^2\alpha w(w - 1) = 0.
\]

With the use of equation (2), equation (4) can be written as

\[
\ddot{w} - a(1 - \alpha)\dot{w} - a^2\alpha w - k^2 \left[ \frac{1}{b}(a\alpha w + \dot{w}) \right]^{1-\alpha} e^{(\alpha+1)w} = 0,
\]

where \(k^2 = -\frac{b^2}{e^{-A/a}}\). In [4] we showed that the formal analytic solution to equation (5) is

\[
t - t_0 = \int_{w}^{w'} \left[ a\alpha (e^\rho - e^{\rho'}) \right]^{-1} dw',
\]

where \(e^\rho\) solves

\[
ba(\alpha + 1)w' - b\alpha w e^\rho + k^2 \left( \frac{aa}{b} \right)^{-\alpha} e^{(\alpha+1)w'} e^{-\alpha\rho} = 0.
\]

Equation (6) represents a complete reduction of the LV problem to an integral quadrature which, however, is not reducible to elementary functions. The purpose of the present paper is to begin an exploration of this quadrature.

In section 2, we provide an initial analysis of equation (5) (and, therefore, of equation (6)) by means of a power series expansion of the exponential \(e^{(\alpha+1)w}\), for small integer values of \(\alpha\) (\(\alpha = 1, 2, 3\)). Moreover, for the case \(\alpha = 1\), the relationship of the solutions provided by equation (6) to the family of elliptic functions will be explored. In section 3, an inverse transformation of equations (3), along with the solutions to equation (5) provided in section 2, is used to develop a family of LV related first-order autonomous ordinary differential equations, and the dynamical invariant for each of these systems is derived. Finally, a simple transformation of these invariants which permits each system to be placed into Hamiltonian form is presented.

2. Power series analysis

Our analysis begins by expanding the exponential term in equation (5) in a power series to give

\[
\ddot{w} - a(1 - \alpha)\dot{w} - a^2\alpha w - k^2 \left[ \frac{1}{b}(a\alpha w + \dot{w}) \right]^{1-\alpha} \sum_{m=0}^{\infty} \frac{1}{m!}(\alpha + 1)^m w^m = 0.
\]
Truncation of the power series in equation (8) gives approximate solutions to the LV problem (cf. figure 1). As will be shown below, the truncation of equation (8) leads to a family of differential equations, each seemingly more complex than the original LV problem, which can be solved in terms of known functions. For finite integer \( n \), equation (8) can be approximated as

\[
\dot{w} - a(1 - \alpha) \dot{w} - a^2 \alpha w - k^2 \left[ \frac{1}{b}(a \alpha w + \dot{w}) \right]^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} (\alpha + 1)^m w^m = 0,
\]

which has the solution

\[
t - t_0 = \int_{w'}^{w} \left[ a \alpha (\rho - w') \right]^{-1} dw',
\]

where \( \rho \) is given by the solution to

\[
(n + 1) \left[ -ba \alpha \rho^{\alpha + 1} + ba(\alpha + 1)w' \rho^\alpha + k^2 \left( \frac{b}{a \alpha} \right)^\alpha \sum_{m=0}^{n+1} \frac{1}{m!} (\alpha + 1)^m w'^m \right] = 0.
\]
When $\alpha$ is an integer, equation (11) reduces to an $\alpha + 1$ degree polynomial which can be solved in terms of radicals for $\alpha \leq 3$ with the aid of a symbolic processor [9].

For $\alpha = 1$, the solution to equation (11) is

$$\rho = w' \pm \frac{1}{a} \left[ a^2 w'^2 + k^2 \sum_{m=0}^{n+1} \frac{2^m}{m!} w'^m \right]^{1/2}.$$ 

which, when substituted into equation (10), gives the solution

$$t - t_0 = \pm \int^w \left[ a^2 w'^2 + k^2 \sum_{m=0}^{n+1} \frac{2^m}{m!} w'^m \right]^{-1/2} \, dw'.$$  \hspace{1cm} (12)

With the use of a symbolic processor [9,10], equation (12) can be integrated in terms of known functions for $n \leq 3$, these solutions are given in table 1. The solutions for $n - 0$ and $n - 1$ are exponential, although the solution for $n - 1$ can become periodic when $a^2 < 2k^2$. When $n = 2$ or $n = 3$, the solutions are elliptic functions of the first kind [2].

When $\alpha = 2$, the solution of equation (11) leads to three values for $\rho$ which can then be substituted into equation (10) to yield the analytic solutions

$$t - t_0 = \int^w \left[ \frac{1}{2} p_2^{1/3} + 2a^2 w'^2 p_2^{-1/3} - aw' \right]^{-1} \, dw'$$

and

$$t - t_0 = \int^w \left[ -\frac{1}{4} (1 \pm i\sqrt{3}) p_2^{1/3} - a^2 (1 \mp i\sqrt{3}) w'^2 p_2^{-1/3} - aw' \right]^{-1} \, dw',$$

where $p_2$ is defined as

$$p_2 = 8a^2 w'^3 + 4k^2 b \sum_{m=0}^{n+1} \frac{3^m}{m!} w'^m$$

$$+ 4 \left( \frac{bk^2}{m!} \sum_{m=0}^{n+1} \frac{3^m}{m!} w'^m \left( 4a^2 w'^3 + \frac{3^m}{m!} bk^2 w'^m \right) \right)^{1/2}.$$ 

Substituting the four solutions of equation (11) when $\alpha = 3$ into equation (10) gives the analytic solutions

$$t - t_0 = \int^w \left[ -2aw' \pm 12a^3 w'^3 (3b^2 k^2 S p_3^{-1/3} - p_3^{1/3} - 6a^2 w'^2) \right]^{-1/2}$$

$$+ \frac{\sqrt{6}}{6} \left[ (3b^2 k^2 S p_3^{-1/3} - p_3^{1/3} - 6a^2 w'^2)^{1/3} \right.$$ 

$$\pm \left( 3b^2 k^2 S p_3^{1/3} - p_3^{1/3} - 12a^2 w'^2 \right) \right]^{-1} \, dw'.$$
Table 1

Analytic solutions to equation (12) of text for \(\alpha = 1\) and \(n \leq 3\).

<table>
<thead>
<tr>
<th>(n)</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(w(t) = \frac{1}{\sqrt{2}} e^{\lambda (t-t_0)} + \frac{k^2}{\sqrt{2}} (k^2 - \alpha) e^{\lambda (t-t_0)} - \frac{k^2}{2})</td>
</tr>
<tr>
<td>1</td>
<td>(w(t) = \frac{1}{\sqrt{2}} e^{\lambda (t-t_0)} + \frac{k^2}{\sqrt{2}} (k^2 - \lambda) e^{\lambda (t-t_0)} - \frac{k^2}{2}), where (\lambda = \sqrt{a^2 + 2k^2})</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{\sqrt{5}}{2} k \sqrt{3h} - \beta_{\pi}(t-t_0) = F \left( \sin^{-1} \left( \frac{\beta_2 - \beta_3}{\beta_2 - \beta_1} \right) \right) ), where (F) is an elliptic function of the first kind and (\beta_i) and (\beta_j) are defined as</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{\sqrt{5}}{2} k[\beta_2 - \beta_3]^{1/2} (t-t_0) = F \left( \sin^{-1} \left( \frac{2a^2 - 2k^2}{2(a^2 + k^2)} \right) \right)^{1/2} ), where (\beta_i) and (\beta_j) are defined as</td>
</tr>
</tbody>
</table>

\(^{a}\) Abramowitz and Stegun [2].

and

\[ t - t_0 = \int_{0}^{w'} \left[ -2a w' \pm 12 a^3 w^3 \left( 3b^2 k^2 S p_3^{1/3} - p_3^{1/3} - 6 a^2 w'^2 \right)^{-1/2} \right] \]
\[ -\frac{\sqrt{6}}{6} \left( (3b^2 k^2 S p_1^{-1/3} - p_1^{1/3} - 6a^2 w^2) \right)^{1/2} \]
\[ = \left( 3b^2 k^2 S p_1^{-1/3} - p_1^{1/3} - 12a^2 w^2 \right) \]^{-1} \, dw',

where
\[ p_3 = 3k^2 b^2 S \left[ -9a^2 w^2 + (3k^2 b^2 S + 81a^4 w^4)^{1/2} \right] \]

and
\[ S = \sum_{m=0}^{n+1} \frac{4^m}{m!} w^m. \]

When \( \alpha > 3 \), the polynomial can no longer be solved in terms of radicals.

The solutions of equation (9) represent analytic solutions to a family of first-order autonomous ordinary differential equations. The next section develops this family of differential equations from an inverse transformation of equations (3) coupled with the knowledge of equation (9).

3. Systems of LV related differential equations

In this section, an inverse transformation of equations (3) is used to develop the family of first-order autonomous ordinary differential equations which are equivalent to equation (9). Equation (10) represents the analytic solutions to this family of equations which, as shown in section 2, can be solved in terms of known functions for \( \alpha = 1 \) and \( n < 3 \). The phase space trajectories (cf. figure 1) indicate that these systems are conservative since closed orbits exist. Later in this section, the constant of the motion for each system will be derived, and a transformation will be presented which allows this family of equations to be placed into Hamiltonian form.

The inverse transformation of equations (3) is given by
\[ w = \frac{b}{a} (\alpha + 1)^{-1} (x_1 + x_2), \]
\[ \dot{w} = b (\alpha + 1)^{-1} (x_1 - \alpha x_2). \]

Substituting \( \dot{w} \) obtained from equation (9) into the time derivative of equations (3), and employing the transformation given by equations (13) yields the following system of first-order autonomous ordinary differential equations:
\[ \dot{x}_1 = ax_1 + \frac{k^2}{b} x_1^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m, \]
\[ \dot{x}_2 = -\alpha ax_2 - \frac{k^2}{b} x_1^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m. \]
Although these equations appear to be more complicated than the original LV system given in equations (1), equations (14) can be solved analytically in terms of known functions for $\alpha - 1$ and $n \leq 3$. When $n = 2$ and $\alpha - 1$, equations (14) have the quadratic coupling term which appears in the LV predator-prey model (i.e., equations (1)) as well as quadratic terms dependent only on $\tau_1$ and $\tau_2$ (which is reminiscent of the LV competition model (see, for example, [1])).

The phase space trajectories of equations (14) are determined by
\[
\frac{dx_1}{dt} = \frac{\alpha x_1 + \frac{k^2}{b} x_1^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m}{-a \alpha x_2 - \frac{k^2}{b} x_1^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m},
\]
which can be integrated to give
\[
I_n = a x_1^\alpha x_2 + \frac{k^2}{b} \sum_{m=1}^{n+1} \frac{1}{m!} a^{1-m} b^m (x_1 + x_2)^m.
\]

That $I_n$ is an invariant for the system, thereby explaining the closed-orbit nature of the phase-space trajectories of figure 1, may be shown by induction as follows.

The condition that $I_n$ be constant is
\[
\frac{dI_n}{dt} = \partial_1 I_n x_1^{(n)} + \partial_2 I_n x_2^{(n)} = 0,
\]
where $\partial_i I_n = \partial I_n / \partial x_i$ and $\dot{x}_i^{(n)} - \dot{x}_i$, for some specific value of $n$. For $n = 0$, equation (17) becomes
\[
\frac{dI_0}{dt} = \left( \alpha x_1^{\alpha-1} x_2 + \frac{k^2}{b} \right) \left( \alpha x_1 + \frac{k^2}{b} x_1^{\alpha-1} \right) + \left( \alpha x_1^{\alpha} + \frac{k^2}{b} \right) \left( -a \alpha x_2 - \frac{k^2}{b} x_1^{\alpha-1} \right),
\]
which simplifies to
\[
\frac{dI_0}{dt} = 0.
\]

When $n = j + 1$, equations (14) can be written recursively as
\[
\dot{x}_1^{(j+1)} = \dot{x}_1^{(j)} + (j + 1)! \left[ j^2 b a^{-j-1} (x_1 + x_2)^j \right]^{(j+1)},
\]
\[
\dot{x}_2^{(j+1)} = \dot{x}_2^{(j)} - (j + 1)! \left( -j^2 b a^{-j-1} (\tau_1 + \tau_2)^j \right)^{(j+1)},
\]
and $I_{j+1}$ (equation (16)) can be rewritten as
\[
I_{j+1} = I_j + [(j + 2)!]^{-1} k^2 b^j a^{-j-1} (x_1 + x_2)^{j+2}.
\]
Substituting equations (18) and the derivatives of equation (19) into equation (17) and rearranging gives
\[
\frac{dI_{j+1}}{dt} = \left( \partial_1 I_j \dot{x}_1^{(j)} + \partial_2 I_j \dot{x}_2^{(j)} \right) + [(j + 1)!]^{-1} k^2 (x_1 + x_2)^j b^j a^{-j-1}
\times \left[ (x_1^{(j)} + x_2^{(j)}) \right].
Since \( \partial I_j \hat{x}^{(j)}_1 \parallel \partial I_j \hat{x}^{(j)}_2 = 0 \) by assumption, \( \frac{dI_{j+1}}{dt} \) reduces to

\[
\frac{dI_{j+1}}{dt} = [(j+1)!]^{-1} k^2 j!^j a^{-j-1}(x_1 + x_2)^{j+1} [x_1^{1-\alpha}(a_0 x_1^{\alpha-1} x_2 - a x_1^{\alpha}) + (a x_1 - a_0 x_2)].
\]

which simplifies to \( \frac{dI_{j+1}}{dt} = 0 \), thus completing the proof.

The invariant of equation (16) can be written in Hamiltonian form by introducing \((q, p)\) variables

\[
q = x_1 \quad \text{and} \quad p = x_1^{\alpha-1} x_2.
\]

This transformation allows the system represented by equations (14) and (16) to be written as

\[
\dot{q} = aq + k^2 q^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{m-1} (q + p q^{1-\alpha})^m,
\]

\[
\dot{p} = -ap - k^2 [1 + (1 - \alpha) pq^{-\alpha}] \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{m-1} (q + p q^{1-\alpha})^m,
\]

with the function

\[
H_n = aqp + k^2 \sum_{m=0}^{n+1} \frac{1}{m!} a^{1-m} b^{m-2} (q + p q^{1-\alpha})^m
\]

serving as a Hamiltonian, which may be shown simply as follows. The derivatives of equation (22) with respect to \(q\) and \(p\) are

\[
\frac{\partial H_n}{\partial p} = aq + k^2 q^{1-\alpha} \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{m-1} (q + p q^{1-\alpha})^m,
\]

\[
\frac{\partial H_n}{\partial q} = ap + k^2 [1 + (1 - \alpha) pq^{-\alpha}] \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{m-1} (q + p q^{1-\alpha})^m.
\]

Directly comparing equations (23) with equations (21) gives

\[
\frac{\partial H_n}{\partial p} = \dot{q} \quad \text{and} \quad \frac{\partial H_n}{\partial q} = -\dot{p},
\]

which are, of course, Hamilton’s equations.

4. Conclusion

In this paper, we have presented an initial analysis of the analytic solution [4] to the Lotka–Volterra problem and have shown, for the special case of \(\alpha = 1\), the relationship between this solution and the family of elliptic functions. We also have provided the form of the integral quadrature (equation (6)) for the cases of \(\alpha \leq 3\). The truncation of the power series used in our analysis of the analytic solution has been
shown to lead to a new family of LV related differential equations which, for \( \alpha = 1 \) and \( n \leq 3 \), can be solved in terms of known functions. The constant of the motion for this family was given, and a simple transformation was found to take this invariant into Hamiltonian form.

Acknowledgements

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References

[9] Maple V, Rel. 4.00a (Waterloo Maple, Inc., Waterloo, ON).
[10] Mathematica, Rel. 3.0 (Wolfram Research, Inc., Champaign, IL).
Subthreshold photoionization of CH$_3$I in Ar, N$_2$ and CO$_2$

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Abstract

We present pressure-dependent subthreshold photoionization spectra of CH$_3$I doped into varying number densities of the perturber gases Ar, N$_2$ and CO$_2$. The intensity of the observed subthreshold structure is discussed in terms of two different interactions, namely electron attachment and associative ionization. Effective rate constants for these two processes are analyzed, and the variation in these constants is discussed in terms of the properties of the dopant excited state. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Perturber effects on the electronic structure of molecules continue to generate considerable interest using a variety of experimental techniques, including photoabsorption, photoionization and field ionization spectroscopies. Methyl iodide (CH$_3$I) has served as the dopant in many such studies because of the atomic-like Rydberg series and the low ionization energy ($I_1 = 5.0 E_3/2$) = 9.54 eV [1] observed for this molecule. Perturbers have included rare gases [1–5], H$_2$ [4], alkanes [6], CO$_2$ [7], N$_2$ [8] and SF$_6$ [9,10]. Both photoabsorption and photoionization spectra have been measured, and perturber pressure effects have been analyzed for discrete and autoionizing dopant Rydberg states [1–9], as well as for subthreshold photoionization structure [3,5,7,8,10].

Photoionization spectra of CH$_3$I [5,10–12] and of CH$_3$I doped into Ar [5], Xe [3], CO$_2$ [7], N$_2$ [8] and SF$_6$ [10] exhibit rich subthreshold structure beginning 0.17 eV before the ionization limit I$_1$. From the observed energy spacing and linear energy shift (as a function of perturber number density) of the peaks, this structure has been identified as arising from high-n Rydberg states of CH$_3$I. This identification permits the evaluation of electron scattering lengths in highly absorbing perturber media [3,7,8,10]. Indeed, all of the techniques mentioned above provide a high-precision adjunct [1–10] to the measurement of electron scattering lengths by low-energy electron scattering [13] and electron swarm [14] experiments.

The low energy onset of CH$_3$I subthreshold ionization rules out collisional transfer of translational or rotational energy from a perturber molecule at room temperature as the ionization mechanism. Therefore, Ivanov and Vilesov [11,12] discussed three bimolecular processes leading to subthreshold struc-
ture which, for a general dopant (D)/perturber (P) system, can be symbolized as

\[ D^* + P \rightarrow D^+ + P^- \]  
(1)
\[ D^* + P \rightarrow [DP]^+ + e^- \]  
(2)
\[ D^* + P \rightarrow R_1^+ + R_2 + e^- \]  
(3)

Eq. (1) represents electron attachment [15], Eq. (2) is associative ionization [15] (i.e., the Hornbeck–Molnar [16] process), and Eq. (3) describes a photochemical rearrangement leading to charged particles. In their discussion of pure CH₃I (D = P = CH₃I), Ivanov and Vilesov [11,12] attributed the presence of subthreshold structure in the pure CH₃I photoionization spectra at high pressures of CH₃I to Eq. (2), since the intensity was quadratically dependent upon the pressure of CH₃I and showed no temperature effect indicative of vibrational autoionization. Eq. (3), namely photochemical rearrangement leading to charged particles, was ruled out by Ivanov and Vilesov [11,12] on the basis of energetic considerations.

Recently [10], we also showed that the intensity of the subthreshold structure in pure methyl iodide depends quadratically on the CH₃I pressure (in accord with the experiments by Ivanov and Vilesov [12]), while the intensity of the subthreshold structure in CH₃I doped into SF₆ depends linearly on the SF₆ pressure. This was explained [10] by assuming that Eq. (1) was saturated (i.e., independent of perturber pressure) for a highly polarizable perturber, allowing the electron attachment contribution to the photocurrent to be written as [10]

\[ i_{ea} = k_1 \rho_D. \]  
(4)

In Eq. (4), the effective rate constant \( k_1 \) is proportional to the (saturated) attachment cross-section, and we have assumed for the dopant number densities that \( \rho_D \propto \rho_D \) in the linear absorption regime. Likewise, the associative ionization (Eq. (2)) contribution to the photocurrent can be written as [10]

\[ i_{ai} = k_2 \rho_D \rho_P, \]  
(5)

where the effective rate constant \( k_2 \) is proportional to the associative ionization cross-section, and where \( \rho_P \) is the perturber number density. In the absence of any significant photochemical contribution (i.e., Eq. (3)) to the observed photocurrent, then, the subthreshold photocurrent is given by [10]

\[ i = (k_1 + k_2 \rho_P) \rho_D. \]  
(6)

Assuming that the attachment cross-section scales linearly [15] with the principal quantum number \( n \) for the CH₃I excited state, \( k_1 \) should vary linearly with \( n \). The parameter \( k_2 \), on the other hand, is reflective of a molecular interaction, and therefore should depend upon the excited state polarizability of CH₃I [17], which in turn scales according to \( n^7 \) [15]. For the case of CH₃I doped into SF₆ [10], we indeed found that \( k_1 \) varies linearly with \( n \), while \( k_2 \) varies linearly with \( n^7 \). Eq. (6) also applies in the case of pure CH₃I [10], but now \( \rho_P = \rho_D \), leading to

\[ i = k_1 \rho_D + k_2 \rho_D^2. \]  
(7)

For pure CH₃I, we again found [10] that \( k_1 \) varies linearly with \( n \), while \( k_2 \) varies linearly with \( n^7 \).

In the present paper, we report the pressure-dependent subthreshold photoionization spectra of CH₃I doped into Ar, N₂, and CO₂, and compare these results to our previous SF₆ study [10]. In all cases, we observe a linear dependence of the photocurrent intensity upon the perturber number density, with no temperature effect. For the perturbers discussed here, however, as opposed to the strongly electron-attaching perturber SF₆, Eq. (1) cannot be the mechanism leading to the photocurrent contribution represented by Eq. (4). In addition, since the energy onset for subthreshold photoionization is the same for Ar, N₂, and CO₂, as will be shown below, Eq. (2) is doubtful as the mechanism leading to the photocurrent contribution represented by Eq. (5). In order to model the pressure dependence of the subthreshold photoionization spectra reported here, we invoke a modification of the explanation given for subthreshold photoionization in pure CH₃I [10], namely,

\[ CH_3I^* + CH_3I \rightarrow CH_3I^* + CH_3I^- \]  
(8)
\[ CH_3I^* + CH_3I + P \rightarrow CH_3I_2^+ + P + e^- \]  
(9)

As was the case in pure CH₃I (and CH₃I/SF₆), we continue to assume that the electron attachment (i.e., Eq. (8)) is saturated. In line with recent electron swarm studies of halocarbons perturbed by N₂ and
CO₂ [18], however, we invoke a perturber stabilization of the associative ionization step, as indicated in Eq. (9). In this case, then, Eq. (7) becomes

\[ i = k_1 \rho_D + k_2 \rho_D^2 \rho_P. \]  

(10)

As will be shown below, Eq. (10) is sufficient to explain the pressure dependences observed in the present work.

2. Experiment

Photoionization and photoabsorption spectra were measured using monochromatized synchrotron radiation with a resolution of 0.13 nm (200 µm slits), or \( \sim 10 \) meV in the spectral range of interest. Two different experimental cells were used: Cell 1 [19] is equipped with entrance and exit MgF₂ windows and a pair of parallel plate electrodes (stainless steel, 3.0 mm spacing) oriented parallel to the incoming radiation and perpendicular to the windows, thus permitting the simultaneous recording of photoionization and transmission spectra. The light path inside the cell is 1.0 cm. Cell 2 [20] is equipped with an entrance LiF window coated with a thin (7 nm) layer of gold to act as an electrode. The second electrode (stainless steel) is placed parallel to the window with a spacing of 1.05 mm. The bodies of both cells are fabricated from copper and are capable of withstand-}

---

**Fig. 1** Subthreshold photoionization (cell 2, 200 µm slits) of 5.0 mbar CH₃I in various perturbers (at a number density of 0.12 \( \times 10^{19} \) cm⁻³): (a) Ar, (b) N₂, (c) CO₂; (d) SF₆ [10]. Absorption of pure CH₃I (cell 1, 200 µm slits): 0.1 mbar. Each photoionization spectrum is normalized to unity at the same spectral feature above the \( ^2E_{3/2} \) ionization threshold.

**Fig. 2** Subthreshold photoionization spectra of CH₃I/Ar at 298 K. Photoionization (cell 2, 200 µm slits) of 5.0 mbar CH₃I in varying Ar number densities (10¹⁹ cm⁻³): (a) 0.12; (b) 0.24; (c) 0.48; (d) 1.23. Each photoionization spectrum is normalized to unity at the same spectral feature above the \( ^2E_{3/2} \) ionization threshold. In (a), the dotted lines are an example of the Gaussian fits used to obtain peak intensities.
Table 1
Peak areas (by Gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 2) of 5.0 mbar CH$_3$I in varying number densities $\rho$ (10$^{19}$ cm$^{-3}$) of Ar

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.0543</td>
<td>0.203</td>
<td>0.379</td>
<td>0.544</td>
</tr>
<tr>
<td>0.24</td>
<td>0.0615</td>
<td>0.216</td>
<td>0.398</td>
<td>0.579</td>
</tr>
<tr>
<td>0.48</td>
<td>0.0722</td>
<td>0.255</td>
<td>0.449</td>
<td>0.676</td>
</tr>
<tr>
<td>0.73</td>
<td>0.0851</td>
<td>0.269</td>
<td>0.501</td>
<td>0.753</td>
</tr>
<tr>
<td>1.23</td>
<td>0.107</td>
<td>0.330</td>
<td>0.602</td>
<td></td>
</tr>
</tbody>
</table>

Regression coefficients

$b_0$ 0.0482 0.189 0.351 0.502
$b_1$ 0.0498 0.113 0.204 0.342

The regression coefficients are for a least-squares linear fit, $b_1 \rho + b_0$, as shown in Fig 3a.

electrode being the LiF window in cell 2. (The reported spectra were current saturated, which was verified by measuring selected spectra at different electric field strengths.) Photocurrents within the cell were of the order of 10$^{-10}$ A.

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the photoemission current from a metallic grid intercepting the beam prior to the experimental cell. All photoionization spectra are normalized to this current. Transmission spectra (which are reported as absorption = 1-transmission) were normalized both to the incident light intensity and to the empty cell transmission.

CH$_3$I (Aldrich Chemical, 99%), Ar (Matheson Gas Products, 99.9999%), N$_2$ (Matheson Gas Products, 99.9999%) and CO$_2$ (Matheson Gas Products, 99.995%) were used without further purification. The gas handling system has been described previously, as well as the procedures employed to ensure a homogeneous mixing of CH$_3$I with the perturber gases [6].

3. Results and discussion

Subthreshold photoionization spectra for CH$_3$I doped into Ar, N$_2$ and CO$_2$ (measured at the same pressure of CH$_3$I and the same perturber number density) are presented in Fig. 1 in comparison to the low-pressure photoabsorption spectrum of CH$_3$I. We have also included our previously reported [10] CH$_3$I/SF$_6$ spectrum in this figure. (All of the photoionization spectra presented are normalized to unity

Table 2
Peak areas (by Gaussian fits to the photoionization spectra) for the subthreshold photoionization structure of 5.0 mbar CH$_3$I in varying number densities $\rho$ (10$^{19}$ cm$^{-3}$) of N$_2$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.0686</td>
<td>0.234</td>
<td>0.434</td>
<td>0.596</td>
</tr>
<tr>
<td>0.25</td>
<td>0.0823</td>
<td>0.241</td>
<td>0.475</td>
<td>0.645</td>
</tr>
<tr>
<td>0.49</td>
<td>0.101</td>
<td>0.290</td>
<td>0.545</td>
<td>0.769</td>
</tr>
<tr>
<td>0.73</td>
<td>0.128</td>
<td>0.313</td>
<td>0.602</td>
<td>0.868</td>
</tr>
<tr>
<td>1.22</td>
<td>0.159</td>
<td>0.412</td>
<td>0.744</td>
<td>1.10</td>
</tr>
<tr>
<td>2.50</td>
<td>0.285</td>
<td>0.598</td>
<td>1.09</td>
<td></td>
</tr>
</tbody>
</table>

Regression coefficients

$b_0$ 0.0574 0.215 0.397 0.541
$b_1$ 0.0910 0.153 0.285 0.449

The regression coefficients are for a least-squares linear fit, $b_1 \rho + b_0$, as shown in Fig 3b.
Table 3
Peak areas (by Gaussian fits to the photoionization spectra) for the subthreshold photoionization structure of 5.0 mbar CH$_3$I in varying number densities $\rho$ (10$^{10}$ cm$^{-3}$) of CO$_2$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.0906</td>
<td>0.309</td>
<td>0.504</td>
<td>0.731</td>
</tr>
<tr>
<td>0.37</td>
<td>0.120</td>
<td>0.358</td>
<td>0.561</td>
<td>0.852</td>
</tr>
<tr>
<td>0.73</td>
<td>0.165</td>
<td>0.401</td>
<td>0.689</td>
<td>0.997</td>
</tr>
<tr>
<td>1.10</td>
<td>0.183</td>
<td>0.472</td>
<td>0.805</td>
<td>1.20</td>
</tr>
<tr>
<td>1.46</td>
<td>0.213</td>
<td>0.531</td>
<td>0.906</td>
<td></td>
</tr>
</tbody>
</table>

Regression coefficients

$b_0 = 0.0778$, $b_1 = 0.289$, $b_2 = 0.467$, $b_3 = 0.673$, $b_4 = 0.475$

The regression coefficients are for a least-squares linear fit, $b_1 \rho + b_0$, as shown in Fig. 3c.

at the same spectral feature above the CH$_3$I $^2$E$_{3/2}$ threshold.) From Fig. 1, one observes that the subthreshold photoionization structure correlates in all cases with the nd Rydberg states of CH$_3$I converging on the $^2$E$_{3/2}$ ionization limit, and that the intensity of the subthreshold structure increases as Ar < N$_2$ < CO$_2$ < SF$_6$. Representative subthreshold photoionization spectra for CH$_3$I doped into varying number densities of Ar are presented in Fig. 2. (The perturbers N$_2$ and CO$_2$ give rise to spectra which are qualitatively similar to those of Fig. 2. For brevity, we have not reproduced those spectra here.) As was observed for CH$_3$I/SF$_6$ [10], photoionization spectra for one dopant/perturber sample pressure, measured at different temperatures for each perturber gas, show no temperature effect on the subthreshold structure, thus ruling out vibrational autoionization as the subthreshold ionization mechanism.

We have extracted peak areas (by Gaussian fits to the photoionization spectra) for the density-dependent subthreshold structure of CH$_3$I doped into Ar, N$_2$, and CO$_2$. These data are collected in Table 1 (CH$_3$I/Ar), Table 2 (CH$_3$I/N$_2$) and Table 3 (CH$_3$I/CO$_2$). Since $\rho_D$ is constant, Eq. (10) may be rewritten as

$$i = b_0 + b_1 \rho$$

(11)

where $b_0 = k_1 \rho_D$ and $b_1 = k_2 \rho_D^2$. These linear correlation coefficients are also collected in Tables 1–3, and the photoionization peak areas are plotted versus $\rho_D$ for each perturber gas in Fig. 3a (CH$_3$I/Ar), Fig. 3b (CH$_3$I/N$_2$) and Fig. 3c (CH$_3$I/CO$_2$). The linearity of these plots is indeed striking, as was also the case for CH$_3$I/SF$_6$ [10]. (An analysis of photoionization peak heights as opposed to peak areas gives rise to plots identical in shape to those shown in Fig. 3.)

Fig 3 Peak areas (by Gaussian fits to the photoionization spectra) for the subthreshold photoionization structure of 5.0 mbar CH$_3$I doped into (a) Ar (cf. Fig 2), (b) N$_2$, and (c) CO$_2$ as a function of density $\rho$ (10$^{10}$ cm$^{-3}$)  i.e., 11d, 12d, 13d, 14d. The solid lines represent a least-squares fit to the function $b_1 \rho + b_0$ (cf. Table 1, Table 2, Table 3).
Since the subthreshold photoionization structure is superimposed upon a rising exponential background (cf. Figs. 1 and 2), as discussed by Ivanov and Vilesov [11,12], we have subtracted an exponential background fitted to the zero baseline and the sharp photocurrent step at threshold. The resulting spectra, when analyzed for peak area (or peak height), yield plots identical in shape to those shown in Fig. 3.

As discussed in the introduction, \( b_0 \) should scale as \( n \) (since \( k_1 \) scales as \( n \) [10]), while \( b_1 \) should scale as \( n^2 \) (since \( k_2 \) scales as \( n^2 \) [10]), where \( n \) is the principal quantum number for the CH\(_3\)I excited state. In Fig. 4, we have plotted \( b_0 \) versus \( n \) and \( b_1 \) versus \( n_0 \) for the Ar, N\(_2\) and CO\(_2\) data presented here, and have compared these plots to our earlier results for SF\(_6\) [10]. Clearly, Fig. 3 and 4 demonstrate that the mechanisms of electron attachment and associative ionization are sufficient to explain the observed density dependence and \( n \) dependence of the subthreshold photoionization structure in Ar, N\(_2\) and CO\(_2\), as was also the case for CH\(_3\)I/SF\(_6\) [10].

In summary, we have presented pressure-dependent subthreshold photoionization spectra of CH\(_3\)I doped into Ar, N\(_2\) and CO\(_2\). We demonstrated a linear dependence on perturber number density for the dopant subthreshold photocurrent signal. We then analyzed these dependences within a model that invoked both (saturated) electron attachment and associative ionization and found that the data are consistent with a perturber-stabilized Hornbeck–Molnar [16] mechanism leading to subthreshold photoionization in all cases. (Nevertheless, as mentioned in the case of CH\(_3\)I/SF\(_6\) [10] and as originally pointed out by Ivanov and Vilesov [12], only a mass analysis of photoproducts will conclusively resolve this issue.) Finally, the subthreshold ionization effective rate constants \( k_1 \) and \( k_2 \), in terms of the regression coefficients \( b_0 \) and \( b_1 \), respectively, were shown to depend in simple ways upon the excited state of the dopant.

For Ar, N\(_2\) and CO\(_2\) perturbers we invoked electron attachment to form CH\(_3\)I\(^-\) (Eq. (8)), while for SF\(_6\) we invoked electron attachment to form SF\(_6\)^- (Eq. (1)). Clearly, the mechanism of Eq. (8) must be present in the case of SF\(_6\) as well, but perhaps only as a minor contributor. In order to separate these two mechanisms by the methods employed here, other dopants must be considered. (For example, ethyl iodide (CH\(_2\)CH\(_2\)I) doped into these same perturbers exhibits subthreshold photocurrent structure only for the SF\(_6\) perturber [21].) In addition, measurements of subthreshold photoionization intensities as a function of \( \rho_M \), for fixed \( \rho_P \), for various dopants and perturbers will be required to assess the general applicability of Eq. (10). Such studies are currently in progress by us.

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References

Photoionization studies of C$_2$H$_5$I and C$_6$H$_6$
perturbed by Ar and SF$_6$

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submitted 1 May 2000

Abstract

We present photoionization spectra of C$_2$H$_5$I and C$_6$H$_6$ doped into Ar and SF$_6$, and photoabsorption spectra of C$_2$H$_5$I doped into Ar. The observation of subthreshold photoionization in C$_2$H$_5$I/SF$_6$ and C$_6$H$_6$/SF$_6$ is discussed in terms of dopant (D)/perturber (P) interactions involving the excited state processes of D$^+$ + P $\rightarrow$ D$^+$ + P$^-$ and D$^+$ + P $\rightarrow$ [DP]$^+$ + e$^-$, where D$^+$ is a discrete Rydberg state of the dopant. The density-dependent energy shifts of high-n Rydberg states observed in the subthreshold photoionization spectra are used to obtain the zero-kinetic-energy electron scattering length for SF$_6$. Similarly, the zero-kinetic-energy electron scattering length of Ar obtained from the density-dependent energy shifts of C$_2$H$_5$I Rydberg states is presented. (Electron scattering lengths obtained here for SF$_6$ and Ar accord with values previously obtained using the density-dependent energy shifts of high-n Rydberg states of CH$_3$I doped into these two perturber gases.)

1. Introduction

Numerous photoabsorption [1-5], photoionization [2,6-15] and field ionization [16] studies of dopant/perturber (D/P) systems have exploited perturber pressure effects on molecular dopant Rydberg state energies and ionization energies as a means of measuring electron scattering lengths in the perturber medium. In many of these systems [2,8,10-12,14,15], photoionization structure has been observed to occur at energies lower than the unperturbed dopant ionization threshold. This subthreshold photoionization structure, which tracks the photoabsorption of discrete dopant Rydberg states in the same energy region, has been used [8,10,14] in the evaluation of perturber pressure effects necessary for the extraction of electron scattering lengths. The nature of those processes leading to sub-threshold photoionization is not well understood, however. Subthreshold photoionization has traditionally been explained as resulting from the collisional transfer of translational, rotational or vibrational energy from a perturber to an excited-state dopant [6]. However, photoionization spectra of CH$_3$I [11,12,14] and of CH$_3$I doped into Xe [10], Ar [2,15], CO$_2$ [8,15], N$_2$ [15] and SF$_6$ [14] exhibit rich subthreshold structure beginning 0.17 eV below the CH$_3$I ionization limit, which is much too low an onset to be accounted for by collisional transfer of perturber translational energy to an excited-state dopant molecule. Moreover, the observation of similar subthreshold spectra in systems containing both atomic and molecular perturbers apparently excludes rotational and vibrational energy transfer as potential mechanisms as well. (Vibrational autoionization, however, has been found to give rise to a weak subthreshold structure in CH$_3$I at very low perturber pressures [11,12,17]. At higher perturber
pressures, this vibrational autoionization is supplanted by a subthreshold structure having a much lower energy onset [11,12,14].) Finally, CHI photochemistry has been ruled out on the basis of energetics in these systems by Ivanov and Vilesov [11,12]. It becomes important, then, to study subthreshold photoionization as a function of temperature, dopant number density and perturber number density in order to explore the nature of those mechanisms leading to subthreshold structure.

We recently measured subthreshold photoionization of CHI doped into Ar, N2, CO2 [15] and SF6 [14]. In the absence of any temperature effect indicative of vibrational autoionization, we proposed two possible pathways leading to subthreshold structure [14,15]. The first pathway requires direct dopant/perturber interactions leading both to charge transfer and to dimer ion formation [14]:

\[
D^* + P \rightarrow D^* + P^-  \quad (1)
\]

\[
\rightarrow [DP]^* + e^- ,  \quad (2)
\]

where D* is a Rydberg state of the dopant molecule. Since the first process [i.e., eq. (1)] of this pathway invokes electron attachment to the perturber, this mechanism should be enhanced in perturbers exhibiting a large electron attachment cross-section. The second process [i.e., eq. (2)] constitutes associative ionization, which should lead to a perturber-dependent onset energy as a result of dopant/perturber dimerization.

The second pathway, namely [15],

\[
D^* + D \rightarrow D^* + D^-  \quad (3)
\]

\[
D^* + D + P \rightarrow D_2^* + P + e^- ,  \quad (4)
\]

differs significantly with regard to dopant/perturber interactions. In the first process [i.e., eq. (3)] of this pathway, electron attachment is now to the dopant rather than to the perturber. Therefore, if the dopant itself has a large enough electron attachment cross-section, subthreshold structure should be observed even when the perturber has a low electron attachment cross-section. In the second process [i.e., eq. (4)], since the associative ionization is now only stabilized by the perturber [18], the onset energy should remain constant even if the perturber is varied.

For either of the above pathways, the subthreshold photocurrent will be given by a sum of two contributions, namely [14,15],

\[
i = i_{ea} + i_{ai} , \quad (5)
\]

where \(i_{ea}\) is the photocurrent contribution resulting from electron attachment, and \(i_{ai}\) is the photocurrent contribution resulting from associative ionization. In pathway 1, the electron attachment contribution \(i_{ea}\) is given by [cf. eq. (1)]

\[
i_{ea} = k_{1}^{(1)} \rho_{D^*} \rho_{P} , \quad (6)
\]

while in pathway 2 this contribution is given by [cf. eq. (3)]

\[
i_{ea} = k_{1}^{(2)} \rho_{D^*} \rho_{D} .  \quad (7)
\]

In eqs. (6, 7), \(k_{1}^{(1,2)}\) is the effective rate constant for the electron attachment process, and \(\rho_{A}\) is the number density of species A. If we now assume that the electron attachment is saturated (i.e., dependent only upon \(\rho_{D}\)), and if we further assume that \(\rho_{D^*} \% \rho_{D}\) in the linear absorption regime, eqs. (6,7) both reduce to [14,15]

\[
i_{ea} = k_{1} \rho_{D} , \quad (8)
\]

where \(k_{1}\) is an empirical rate constant for saturated electron attachment. Under these assumptions, then, the electron attachment contribution to the total subthreshold photocurrent has the same form for both pathways 1 and 2.

Pathways 1 and 2 differ with regard to the associative ionization contribution to the subthreshold photocurrent, however. If we again assume that \(\rho_{D^*} \% \rho_{D}\) in the linear absorption regime, the associative ionization contribution from pathway 1 [cf. eq. (2)] is given by [14]

\[
i_{ai} = k_{2}^{(1)} \rho_{D} \rho_{P} , \quad (9)
\]
while the same contribution from pathway 2 [cf. eq. (4)] is given by [15]

$$i_{at} = k_2^{(2)} D P_P$$ \hspace{1cm} (10)

where $k_2^{(1.2)}$ is the effective rate constant for associative ionization.

By combining eqs. (8-10) and by replacing $k_2^{(1.2)}$ with an empirical associative ionization rate constant $k_2$, we find that the total subthreshold photocurrent is

$$i = (k_1 + k_2 D_P) P_D$$ \hspace{1cm} (11)

for pathway 1, and

$$i = (k_1 + k_2 D_P D) P_D$$ \hspace{1cm} (12)

for pathway 2. Clearly, when a dopant/perturber system exhibits subthreshold photoionization, both pathways 1 and 2 may be operative simultaneously. However, in a system where both pathways are available [cf. eqs. (1,3) and eqs. (2,4)], pathway 1 will dominate when $D_P >> D_D$. Therefore, if the perturber has a large electron attachment cross-section, one should expect that the subthreshold photocurrent will be modeled by eq. (11), with little contribution from pathway 2. We have indeed shown this to be the case for a constant number density of $CH_3$I doped into varying number densities of $SF_6$ [14]. Moreover, we have also shown [14] that eq. (11) holds for the degenerate case (D = P = $CH_3$I) of varying number densities of pure $CH_3$I, in which eq. (1) of pathway 1 is identical to eq. (3) of pathway 2.

If the perturber has a small electron attachment cross-section, one should expect that the subthreshold photocurrent will be modeled by eq. (12), with little contribution from pathway 1. In fact, we have indeed found that eq. (12) is sufficient to explain the subthreshold photocurrent of a constant number density of $CH_3$I doped into varying number densities of Ar, $N_2$ and $CO_2$ [15].

Since $k_1$ is proportional to the (saturated) electron attachment cross-section which, in turn, scales as the principal quantum number $n$ of the dopant Rydberg state [6], $k_1$ should vary linearly with $n$. $k_2$, on the other hand, is determined by molecular interactions which are dependent upon the excited state polarizability of the dopant molecule [19]. Since Rydberg state polarizability scales as $n^7$ [6], $k_2$ should also scale as $n^7$. We have shown that the $n$ and $n^7$ scaling of $k_1$ and $k_2$, respectively, holds for pure $CH_3$I [14], as well as for the $CH_3$I/P systems with $P = Ar, N_2, CO_2$ [15] and $SF_6$ [14]. Therefore, the processes of electron attachment [i.e., eqs. (1,3)] and associative ionization [i.e., eqs. (2,4)] are sufficient to explain the density dependence and $n$ dependence of the observed subthreshold photoionization structure. (We should note, however, that other mechanisms can not positively be ruled out, provided that such mechanisms scale as $n$ (and are saturated) or as $n^7$.)

In a previous study [14], we observed subthreshold photoionization structure in pure $CH_3$I that was quadratically dependent on $CH_3$I number density. As mentioned above, this structure was modeled within pathway 1 [i.e., eqs. (1,2)] by setting $P = D = CH_3$I. We have also observed subthreshold photoionization structure in $CH_3$I/$SF_6$ that was linearly dependent on the $SF_6$ number density [14]. This $CH_3$I/$SF_6$ subthreshold structure was explained within pathway 1, since $SF_6$ has a large electron attachment cross-section [6,20]. However, the existence of subthreshold structure in pure $CH_3$I implies that, in the presence of a perturber with a small electron attachment cross-section, subthreshold photoionization of $CH_3$I can proceed through pathway 2 [i.e., eqs. (3,4)]. The availability of pathway 2 was also indicated by the presence of subthreshold photoionization for $CH_3$I doped into Ar, $N_2$ and $CO_2$ [15] which was linearly dependent upon the perturber number density at constant $CH_3$I pressure. (Subthreshold photoionization structure has also been observed in HI [21]. However, this structure has not been studied in detail due to the complexity of the observed subthreshold current.) Additional studies involving different dopant molecules are needed in order to develop
a better understanding of those properties necessary for a dopant/perturber system to exhibit subthreshold photoionization, and to probe the general applicability of pathway 1 [i.e., eqs. (1, 2)] and pathway 2 [i.e., eqs. (3, 4)].

The origin of subthreshold photoionization structure in high-n Rydberg states has also permitted the determination of zero-kinetic-energy electron scattering lengths of highly absorbing perturbers [8,10,14]. This determination of electron scattering lengths from perturber-induced energy shifts of high-n Rydberg states follows from a theory by Fermi [22], as modified by Alekseev and Sobel’man [23]. These authors [22,23] concluded that the total perturber-induced energy shift is a sum of two contributions,

\[ \Delta = \Delta_{sc} + \Delta_p, \]  

(13)

where \( \Delta_{sc} \) is the ‘scattering’ shift and \( \Delta_p \) is the ‘polarization’ shift. The polarization shift \( \Delta_p \), which results from the interaction of the cationic core of the Rydberg molecule with the perturber molecule, is given by [2,23]

\[ \Delta_p = -10.78 \left( \frac{1}{2} \alpha e^2 \right)^{2/3} (\hbar \nu)^{1/3} \rho_p, \]  

(14)

where \( \alpha \) is the polarizability of the perturber molecule, \( e \) is the charge of the electron, \( \nu \) is the relative thermal velocity of the molecules and \( \hbar \) is the reduced Planck constant. Since \( \Delta_p \) is easily calculated and \( \Delta_{sc} \) is determined from the experimental spectra, \( \Delta_{sc} \) can be obtained from eq. (13). However, the scattering shift \( \Delta_{sc} \), which is due to the interaction between the quasi-free electron and the perturber medium, is given by [22]

\[ \Delta_{sc} = \left( \frac{2 \pi}{m} \right) A \rho_p, \]  

(15)

where \( m \) is the mass of the electron and \( A \) is the zero-kinetic-energy electron scattering length of the perturber. Therefore, the value for \( \Delta_{sc} \) obtained from eq. (13) can be used to determine the zero-kinetic-energy electron scattering length \( A \) via eq. (15).

In the present Paper, we present a photoionization study of \( \text{C}_2\text{H}_5\text{I} \) and \( \text{C}_6\text{H}_6 \) doped into \( \text{Ar} \) and \( \text{SF}_6 \). The dopant \( \text{C}_2\text{H}_5\text{I} \) was chosen because of the similarity of its electronic structure to that of \( \text{CH}_3\text{I} \) [14,15]. The dopant \( \text{C}_6\text{H}_6 \), on the other hand, was chosen because of the lack of any similarity to \( \text{CH}_3\text{I} \). The perturber \( \text{Ar} \) was selected because of its small electron affinity, which makes this perturber a prime candidate for investigating pathway 2 [i.e., eqs. (3, 4)]. The perturber \( \text{SF}_6 \), on the other hand, was selected because of its large electron affinity, which makes this perturber a prime candidate for investigating pathway 1 [i.e., eqs. (1,2)]. As will be reported below, pure \( \text{C}_2\text{H}_5\text{I} \) and pure \( \text{C}_6\text{H}_6 \) (unlike pure \( \text{CH}_3\text{I} \)) do not exhibit subthreshold photocurrent, which indicates that pathway 2 should not be available in these systems. This inability to access pathway 2 is further substantiated here by the absence of subthreshold photoionization in \( \text{C}_2\text{H}_5\text{I} \) and \( \text{C}_6\text{H}_6 \) doped into \( \text{Ar} \). However, both \( \text{C}_2\text{H}_5\text{I} \) and \( \text{C}_6\text{H}_6 \) doped into \( \text{SF}_6 \) exhibit rich subthreshold photoionization structure which will be modeled within the confines of pathway 1 [eqs. (1, 2 and 11)]. Since we can assign the subthreshold photoionization structure to high-n Rydberg states of the dopant, we have also extracted the electron scattering length of \( \text{SF}_6 \) from the density-dependent energy shifts of the subthreshold structure of \( \text{C}_2\text{H}_5\text{I} \) and \( \text{C}_6\text{H}_6 \). The values obtained from the measurements presented here accord well with those values obtained from a similar analysis of the subthreshold photocurrent of \( \text{CH}_3\text{I}/\text{SF}_6 \) [14], as well as from the autoionization spectra of \( \text{CH}_3\text{I}/\text{SF}_6 \) [13]. Since \( \text{Ar} \) is transparent in the spectral region of interest, we were also able to obtain the electron scattering length of \( \text{Ar} \) from both the absorption spectra and the autoionization spectra of \( \text{C}_2\text{H}_5\text{I} \) doped into \( \text{Ar} \). The value extracted from these measurements agrees nicely with that obtained from similar absorption studies of \( \text{CH}_3\text{I} \) [2,3] and \( \text{C}_6\text{H}_6 \) [5] in
Ar, as well as with that obtained from field ionization measurements of CH₃I in dense Ar [16,24].

2. Experiment

The experimental apparatus has been described in detail previously [14,25]. Briefly, photoionization and photoabsorption spectra were measured using monochromatized synchrotron radiation having a resolution of 0.09 nm (100 : slits), or ~ 8 meV in the spectral region of interest. The copper experimental cell, which has a path length of 1.0 cm, was equipped with entrance and exit MgF₂ windows and a pair of parallel-plate electrodes (stainless steel, 3.0 mm spacing) oriented perpendicular to the windows. This arrangement of electrodes and windows allowed for the simultaneous recording of transmission and photoionization spectra. The cell, which is capable of withstanding pressures up to 100 bar, was connected to a cryostat and heater system allowing the temperature to be controlled to within ± 1 K. The applied electric field was 100 V, and all reported spectra are current saturated. (Current saturation was verified by measuring selected spectra at different electric field strengths. Photocurrents within the cell were of the order of 10⁻¹⁰ A.)

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the photoemission current from a metallic grid intercepting the beam prior to the experimental cell. All photoionization spectra are normalized to this current. Transmission spectra (which are reported as absorption = 1 - transmission) are normalized both to the incident light intensity and to the empty cell transmission.

C₂H₅I (Sigma, 99%), C₆H₆ (Aldrich Chemical, 99.9+%), SF₆ (Matheson Gas Products, 99.996%) and Ar (Matheson Gas Products, 99.9999%) were used without further purification. The gas handling system has been described previously, as have the procedures employed to ensure a homogenous mixing of dopant and perturber [6].

3. Results and Discussion

In Fig. 1 and Fig. 2, we present subthreshold photoionization spectra of C₂H₅I and C₆H₆, respectively, doped into SF₆, in comparison to the low pressure photoabsorption spectra of the dopant. Over the same number density ranges as those given in Figs. 1 and 2, C₂H₅I and C₆H₆ doped into Ar exhibited no subthreshold photoionization structure. Therefore, these spectra are not reproduced here. (All C₂H₅I spectra presented are normalized to unity at the same spectral feature above the X₁ ²E₁/₂ [26, 27] ionization threshold. All C₆H₆ spectra are normalized to unity at the same spectral feature.)

![Fig. 1. Subthreshold photoionization spectra of C₂H₅I/SF₆ at 300 K. Absorption of pure C₂H₅I: 0.5 mbar. Photoionization of 0.1 mbar C₂H₅I in varying SF₆ number densities (10⁹ cm⁻³): a, 0.12; b, 0.73; c, 1.5; d, 2.2. Each spectrum is normalized to unity at the same spectral feature above the X₁ ²E₁/₂ ionization threshold. In (a), the dotted lines are an example of the gaussian fits used to obtain peak intensities.]
Absorption

Fig. 2. Subthreshold photoionization spectra of C₆H₆/SF₆ at 300 K. Absorption of pure C₆H₆: 1.0 mbar. Photoionization of 1.0 mbar C₆H₆ in varying SF₆ number densities (10¹⁹ cm⁻³): a, 0.12; b, 0.49; c, 1.1; d, 2.2. Each spectrum is normalized to unity at the same spectral feature above the ²E₁g ionization threshold. Above the ²E₁g [28] ionization threshold.) Since the onset of the subthreshold photocurrent signal is far below the first ionization limit of the dopant at room temperature (0.27 eV below for C₂H₅I, 0.22 eV below for C₆H₆), the collisional transfer of translational, rotational or vibrational energy from the perturber to the dopant can be discounted as a possible ionization mechanism leading to this structure. Furthermore, as was also the case for CH₃I/Ar [15] and CH₃I/SF₆ [14], we observed no temperature effect on the relative intensities of the subthreshold structure, thereby ruling out vibrational autoionization as a possible mechanism. (The absence of any temperature dependence was verified by measuring subthreshold photoionization spectra for various dopant/perturber sample pressures at various temperatures (in the range -40°C to 80°C) for both systems. With the exception of a temperature dependent background (see below), no change was observed in these subthreshold spectra. For the sake of brevity, these spectra are not shown here.) We also observed no subthreshold features in pure C₂H₅I (0.1 mbar - 160 mbar) and pure C₆H₆ (1 mbar - 100 mbar). (Again for the sake of brevity, we do not reproduce these spectra here.) Therefore, as discussed in the introduction, the most probable mechanisms leading to sub-threshold photoionization are those of pathway 1 [i.e., eqs. (1, 2)].

We have obtained peak areas for the subthreshold photocurrent shown in Figs. 1 and 2 by integrating a gaussian deconvolution of various peaks. (An example of part of a gaussian deconvolution used to obtain the peak areas is shown in Fig. 1a.) The values for these peak areas are plotted in Fig. 3 versus the number density of SF₆, and are listed in Table 1.

Fig. 3. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure of (a) 0.1 mbar C₂H₅I and (b) 1.0 mbar C₆H₆ as a function of SF₆ number density. In (a): ë, 10d; ë, 11d; ñ, 12d; ñ, 13d; õ, 14d. In (b): ð, 8R'; 9R'; 9R'; 10R'; 11R'; 12R'. The solid lines represent a least-squares fit to the function b₀ + b₁D.
Table 1. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 3) of 0.1 mbar C\(_2\)H\(_5\)I in varying SF\(_6\) number densities D(10\(^{19}\) cm\(^{-3}\)).

<table>
<thead>
<tr>
<th>D</th>
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<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
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<tr>
<td>2.2</td>
<td>0.640</td>
<td>1.19</td>
<td>1.95</td>
<td>2.94</td>
<td></td>
</tr>
</tbody>
</table>

Regression Coefficients*

\[
b_0 = 0.0118, \quad b_1 = 0.286
\]

*The regression coefficients are for a least-squares linear fit, \(b_0 + b_1D\), as shown in Fig. 5a.

(C\(_2\)H\(_5\)I /SF\(_6\)) and Table 2 (C\(_6\)H\(_6\)/SF\(_6\)). Clearly, the intensity of the subthreshold photoionization is linearly dependent on the perturber number density, which is in accord with pathway 1 [cf. eq. (11)]. Since the subthreshold structure is superimposed on a rising exponential background (as discussed by Ivanov and Vilesov [11,12]), we have also subtracted an exponential background fitted to the zero baseline and the photocurrent step at threshold. The resulting spectra, when analyzed for peak areas, yields plots similar in detail to the ones shown in Fig. 3.

The linear plots of Fig. 3 are in accord with pathway 1 [i.e., eqs. (1,2, and 11)] for \(D_0\) constant, and may be expressed as

\[
i = b_0 + b_1P_P. \tag{16}
\]

The linear correlation coefficients \(b_0 (= k_1 D_0)\) and \(b_1 (= k_2 D_0)\) are given in Table 1 (C\(_2\)H\(_5\)I/SF\(_6\)) and Table 2 (C\(_6\)H\(_6\)/SF\(_6\)). Since the linear
correlation coefficients $b_0$ and $b_1$ are proportional to $k_1$ and $k_2$, respectively, $b_0$ and $b_1$ should have the same $n$ dependence as $k_1$ and $k_2$. In Fig. 4 ($C_2H_5I/SF_6$) and Fig. 5 ($C_6H_6/SF_6$), we have plotted $b_0$ versus $n$ and $b_1$ versus $n^7$. The linearity of these figures, when coupled with the analysis of Fig. 3, allows one to conclude that pathway 1 [i.e., eqs. (1, 2 and 11)] is sufficient to explain the behavior of the subthreshold photoionization in both $C_2H_5I/SF_6$ and $C_6H_6/SF_6$. (However, as mentioned in the introduction, other mechanisms are possible so long as these mechanisms scale as $n$ (and are saturated) or as $n^7$.) Unlike the case of $CH_3I$, which exhibits subthreshold photoionization structure in pure $CH_3I$ [14], $CH_3I/Ar$ [15] and $CH_3I/SF_6$ [14], the dopants $C_2H_5I$ and $C_6H_6$ appear to exhibit subthreshold photoionization in $C_2H_5I/SF_6$ and $C_6H_6/SF_6$ arising only from pathway 1 [i.e., eqs. (1, 2, and 11)] in the absence of pathway 2 [i.e., eqs. (3, 4 and 12)].

Since we can assign the subthreshold photoionization structure to high-$n$ Rydberg states of the dopant, we have used the density-dependent energy shifts of this structure to obtain the zero-kinetic-energy electron scattering length of SF$_6$. In Table 3, the energy positions of a number of $C_2H_5I$ nd Rydberg states [26,27], as assigned from the photoionization spectra, are given for selected SF$_6$ number densities. Ionization energies $I_1$ [$I(\tilde{X}_1^1{E}_{2/2})$] extracted from a fit of the assigned spectra to the Rydberg equation are also given in Table 3. The energy positions of a number of $C_6H_6$ nR' states [5,27,28], as well as the values of $I_1$ [$I(\tilde{X}_1^1{E}_{1g})$] extracted from a fit of the assigned spectra to the Rydberg equation, are presented in Table 4 for selected SF$_6$ number densities. The shift data are summarized in Figs. 6a and 6b, where we have plotted the energy positions of nd $C_2H_5I$ and nR' $C_6H_6$ Rydberg

<table>
<thead>
<tr>
<th>D</th>
<th>10d</th>
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<th>13d</th>
<th>14d</th>
<th>$I_1$</th>
</tr>
</thead>
</table>

Table 4. nR' and $I_1$ [$I(\tilde{X}_1^1{E}_{1g})$] photoionization energies (eV) of $C_6H_6$ in selected number densities $D(10^{19} \text{cm}^{-3})$ of SF$_6$.  

<table>
<thead>
<tr>
<th>D</th>
<th>8R'</th>
<th>9R'</th>
<th>10R'</th>
<th>11R'</th>
<th>12R'</th>
<th>$I_1$</th>
</tr>
</thead>
</table>
Fig. 6. Energy shifts of (a) nd Rydberg states of C$_2$H$_5$I and (b) the nR' Rydberg states of C$_2$H$_6$ as a function of SF$_6$ number density $D$ ($10^{19}$ cm$^{-3}$). In (a): $\cdot$, 10d; $\cdot$, 11d; $\cdot$, 12d; $\cdot$, 13d; $\cdot$, I$_1$ ($X_1^2E_{1g}$). In (b): $\circ$, 8R'; $\ast$, 9R'; $\triangle$, 10R'; $\nabla$, 11R'; $\ast$, 12R'; $\odot$, I$_1$ ($2E_{1g}$). The solid lines represent a least-squares linear fit.

Fig. 7. Photoabsorption spectra of C$_2$H$_5$I/Ar at 300 K. Photoabsorption spectra of (a) 0.5 mbar C$_2$H$_5$I and C$_2$H$_5$I doped into varying number densities of Ar ($10^{20}$ cm$^{-3}$): b, 0.024; c, 2.38; d, 4.87. The concentration of C$_2$H$_5$I was kept below 10 ppm in Ar. All absorption spectra are corrected for the empty cell transmission. The assignment given at the bottom corresponds to the pure C$_2$H$_5$I spectrum.

Since Ar is transparent in the region of the first (I$_1$ / I$_2$ ($X_1^2E_{1g}$) = 9.349 eV [27,28]) and second (I$_1$ / I$_2$ ($X_2^2E_{1g}$) = 9.932 eV [27,28]) ionization energies of C$_2$H$_5$I, we were also able to obtain the perturber-induced energy shifts of C$_2$H$_5$I doped into Ar from both the autoionization spectra and the photoabsorption spectra of C$_2$H$_5$I/Ar. These data allowed us to determine the zero-kinetic-energy electron scattering length of Ar. In Fig. 7, we present photoabsorption spectra of C$_2$H$_5$I doped into varying number densities of Ar. (For brevity, we have not presented the autoionization spectra for C$_2$H$_5$I/Ar since these spectra reproduce the photoabsorption structure in the autoionizing region.) The energy shifts obtained from the photoabsorption measurements are

and $A = -0.484$ nm determined from the perturber-induced energy shift of CH$_3$I autoionization spectra [13].

Similarly, the value $D = -24.21 \times 10^{-23}$ eV cm$^3$ obtained from C$_2$H$_6$/SF$_6$ yields a zero-kinetic-energy electron scattering length of $A = -0.473$ nm. Both scattering lengths obtained in the present study accord well with the scattering length $A = -0.492$ nm determined by an analysis of the subthreshold structure of CH$_3$I/SF$_6$ [14].
Table 5. nd and I₁ / I(\tilde{X}_1^{2}E_{1/2}) as well as nd' and I₂ / I(\tilde{X}_2^{2}E_{1/2}) photoabsorption energies (eV) of C₂H₅I in selected number densities D(10²⁰ cm⁻³) of Ar.

<table>
<thead>
<tr>
<th>D</th>
<th>10d</th>
<th>11d</th>
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<th>I₁</th>
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<tr>
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<th>12d'</th>
<th>13d'</th>
<th>14d'</th>
<th>I₂</th>
</tr>
</thead>
</table>

summarized in Table 5 and plotted in Fig. 8. (Since the energy shifts obtained from the autoionization spectra are identical (to within experimental error) to the energy shifts extracted from the photoabsorption spectra, we have not included these data here.) Using the perturber induced energy shifts of C₂H₅I in Ar extracted from the photoabsorption spectra, and using eqs. (13) - (15) with the value [30] \(A = 1.66 \times 10^{-24} \text{ cm}^³\), we obtain an electron scattering length for Ar of \(A = 0.086 \text{ nm}\). This value agrees well with \(A = 0.089 \text{ nm}\) obtained from similar measurements involving CH₃I [2,3] and C₆H₇ [5] doped into Ar, and \(A = 0.082 \text{ nm}\) obtained from field ionization measurements of CH₃I doped into dense Ar [16,24].

In summary, we have measured photoionization and photoabsorption spectra of C₂H₅I/Ar and C₆H₆/Ar and photoionization spectra of C₂H₅I/SF₆ and C₆H₆/SF₆, as a function of the perturber number density. We have shown that pathway 1 [i.e., eqs. (1, 2 and 11)], which depends upon direct dopant/perturber interactions, is sufficient to explain the origin of subthreshold photoionization in both C₂H₅I and C₆H₆ doped into SF₆. We have also shown that pathway 2 [i.e., eqs. (3, 4 and 12)] is likely unavailable as a subthreshold photoionization mechanism in both C₂H₅I and C₆H₆, since subthreshold photoionization is absent in pure C₂H₅I, pure C₆H₆, C₂H₅I/Ar and C₆H₆/Ar. (The inaccessibility of pathway 2 may be due, in part, to the inability of C₂H₅I and C₆H₆ to form stable dimers in a static system. However, resolving this issue completely will require a detailed mass analysis (as originally discussed by Ivanov and Vilesov [11] for CH₃I in a molecular beam experiment.) We have shown that the correlation coefficients \(b₀ \) and \(b₁ \) scale in a simple fashion according to the principal
quantum number of the dopant Rydberg state, which allows us to conclude that the mechanisms of electron attachment to SF$_6$, and associative ionization with SF$_6$, are sufficient to explain the behavior of the subthreshold photocurrent. Additional measurements where the perturber number density is held constant while the dopant number density is varied will provide a further test of the applicability of pathway 1 [i.e., eqs. (1, 2 and 11)] and pathway 2 [i.e., eqs. (3, 4 and 12)] for general dopant/perturber systems. (These measurements are currently in progress by us for CH$_3$I/Ar and CH$_3$I/SF$_6$ [31], for example.)

Finally, we have used the density-dependent energy shifts of high-n Rydberg states, extracted from the subthreshold photoionization spectra of C$_2$H$_5$I and C$_6$H$_6$ doped into SF$_6$, to determine the zero-kinetic-energy scattering length of SF$_6$. The values obtained from these measurements were shown to agree with that obtained by similar measurements of CH$_3$I/SF$_6$ [13,14]. We also presented photoabsorption spectra of C$_2$H$_5$I doped into Ar and used these spectra to obtain the zero-kinetic-energy electron scattering length of Ar. This value was shown to accord both with the scattering lengths obtained from photoabsorption measurements of CH$_3$I/Ar [2,3] and C$_6$H$_6$/Ar [5], as well as with the value extracted from field ionization measurements of CH$_3$I doped into dense Ar [16,24].

Acknowledgements

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References

27. G. Herzberg, Electronic Spectra and Electronic
Photoionization spectra of CH3I and C2H5I perturbed by CF4 and c-C4F8: Electron scattering in halocarbon gases

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Photoionization spectra of CH3I and C2H5I doped into perturber halocarbon gases CF4 (up to a perturber number density of 6.1 x 10^20 cm^-3) and c-C4F8 (up to a perturber number density of 2.42 x 10^19 cm^-3) disclosed a red shift of the dopant autoionizing features that depends linearly on the perturber number density. In the case of CF4, which is transparent in the spectral region of interest, this red shift was verified from the dopant photoabsorption features as well. From the perturber-induced energy shifts of the dopant Rydberg states and ionization energies, the zero-kinetic-energy electron scattering lengths for CF4 and c-C4F8 were found to be -0.180 ± 0.003 nm and -0.618 ± 0.012 nm, respectively. To our best knowledge, these are the first measurements of zero-kinetic-energy electron scattering lengths for both CF4 and c-C4F8. From these zero-kinetic-energy electron scattering lengths, we find that the zero-kinetic-energy electron scattering cross-sections are F = 4.1 ± 0.2 x 10^{-15} cm^2 and 4.8 ± 0.2 x 10^{-14} cm^2 for CF4 and c-C4F8, respectively.

PACS number(s): 33.20.Ni, 34.80.-i

1. Introduction

The interaction of halocarbon gases like CF4 and c-C4F8 with low energy [1-4] and high energy electrons [3,5,6] has received increasing attention, primarily due to the importance of these gases to the semiconductor industry [3], and to the involvement of these gases in stratospheric photochemistry [7]. In fact, many of the perfluoronated halocarbons are used as sources for reactive species in plasma etching [8,9], and halocarbons have the potential to be used as insulators in high voltage switches [4].

In order to model accurately the behavior of halocarbon gases in both plasma etching and stratospheric photochemistry, the interaction between halocarbons and low energy electrons must be better understood. However, the measurement of low energy electron scattering cross-sections and low energy electron attachment rates for halocarbons can be extremely difficult because of the large electronegativities of these molecules. For example, a typical method for studying electron/gas interactions, the electron swarm method, depends on the electron number density remaining constant throughout the experiment [10]. When a molecule has a large electronegativity, however, the electron number density will vary during the experiment as a result of electron attachment in addition to electron induced ionization, thus complicating the interpretation of data [10]. For such molecular species, the measurement of zero-kinetic-energy electron scattering cross-sections is particularly problematic [3,4,10]. As a result, many numerical calculations have predicted the zero-kinetic-energy cross-section of CF4[1,3,5,11,12] with an emphasis on extension to other halogenated gases. However, the accuracy of these calculated values is currently unknown since, to the best of our knowledge, no zero-kinetic-energy electron scattering cross-section measurements have been obtained for CF4.

An alternative method for determining the zero-kinetic-energy electron scattering cross-section of a gas involves perturber-induced energy shifts of high-n Rydberg states [13-19] of
a dopant molecule. In this method, a dopant molecule having a Rydberg series observable in photoabsorption and/or photoionization spectroscopy is mixed with a perturber gas of interest. As the perturber concentration is increased, the dopant high-n Rydberg state energies shift as a result of dopant/perturber interactions. These energy shifts can then be modeled using a theory by Fermi [14], as modified by Alekseev and Sobel’man [15]. According to these authors [14,15], the total energy shift $\Delta$ can be written as a sum of contributions

$$\Delta = \Delta_{sc} + \Delta_p,$$  \hspace{1cm} (1)

where $\Delta_{sc}$ is the scattering shift resulting from the interactions of the optical electron with the perturber medium, and $\Delta_p$ is the polarization shift resulting from the interaction of the dopant core with the perturber medium. $\Delta_p$ can be computed from [13,15]

$$\Delta_p = -10.78 \left( \frac{1}{2} \alpha e^2 \right)^{2/3} \left( \hbar \nu \right)^{1/3} \rho,$$ \hspace{1cm} (2)

where $\alpha$ is the polarizability of the perturber molecule, $e$ is the charge on the electron, $\hbar$ is the reduced Planck constant, and $\nu$ is the relative thermal velocity of the dopant and perturber molecules. $\Delta_{sc}$ results from a measurement of $\Delta_p$, after calculating $\Delta_p$. Finally, the electron scattering length $A$ of the perturber, which gauges the electron-perturber interactions, can be determined from [14]

$$\Delta_{sc} = \left( \frac{2 \pi \hbar^2}{m} \right) A \rho,$$ \hspace{1cm} (3)

where $m$ is the mass of the electron. The zero-kinetic-energy electron scattering cross-section is then related to the zero-kinetic-energy electron scattering length by [14]

$$\sigma = 4 \pi A^2.$$ \hspace{1cm} (4)

The perturber-induced energy shifts of high-n Rydberg states have been used to obtain the zero-kinetic-energy electron scattering lengths of numerous gases [16,17], including the electronegative gases CO$_2$ [18] and SF$_6$ [17,19].

In the present Paper, we present photoionization spectra of the dopant molecules CH$_3$I and C$_2$H$_5$I perturbed by CF$_4$, as well as photoionization spectra of CH$_3$I perturbed by c-C$_4$F$_8$. Since c-C$_4$F$_8$ weakly absorbs in the same energy region as the first and second ionization energies of both CH$_3$I and C$_2$H$_5$I, measurements of photoabsorption spectra are not possible with this perturber except for very low pressures of c-C$_4$F$_8$. CF$_4$, however, is transparent in this spectral region and, therefore, photoabsorption spectra of CH$_3$I and C$_2$H$_5$I doped into CF$_4$ are also presented.

From the measured perturber-induced energy shifts of dopant high-n Rydberg states, and from the corresponding dopant ionization energy shifts obtained by fitting energy levels to the Rydberg equation, we extract the zero-kinetic-energy electron scattering lengths of CF$_4$ and c-C$_4$F$_8$, which are then used to compute the zero-kinetic-energy electron scattering cross-sections. To the best of our knowledge, this is the first measurement of the zero-kinetic-energy electron scattering length for either of these gases. For the case of CF$_4$, we compare our measured zero-kinetic-energy electron scattering cross-section with the theoretical values computed from various methods [3,12].

2. Experiment

Photoionization and photoabsorption spectra were measured with monochromatic synchrotron radiation [20] (with a resolution of 0.09 nm, or ~8 meV in the spectral region of interest), which entered a copper experimental cell [17,21] equipped with entrance and exit MgF$_2$ windows. This cell, which is capable of withstanding pressures of up to 100 bar, possesses two parallel plate electrodes (stainless steel, 3 mm spacing) aligned perpendicular to the windows, thus allowing for the simultaneous measurement of photoionization and transmission spectra. The light path within the
cell is 1.0 cm. The cell was connected to a cryostat and heater system which allows the temperature to be controlled to within ±1 K. The applied voltage was 100 V, and all photoionization spectra were current saturated (which was verified by measuring selected spectra at different applied voltages). Photocurrents within the cell were of the order of $10^{-10}$ A.

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the current across a metallic mesh intercepting the beam prior to the experimental cell. All photoionization spectra are normalized to this current. All transmission spectra (reported here as absorption = 1 - transmission) are normalized both to the incident light intensity and to the empty cell transmission.

CH$_3$I (Aldrich Chemical, 99.5%), C$_2$H$_5$I (Sigma, 99%), CF$_4$ (Matheson Gas Products, 99.999%) and c-C$_4$F$_8$ (Matheson Gas Products, 99.98%) were used without further purification. Both the gas handling system and the procedures employed to ensure homogeneous mixing of the dopant and perturber have been described previously [17,22].

3. Results and Discussions

Photoionization measurements of CH$_3$I and CH$_3$I doped into varying number densities of CF$_4$ are presented in Fig. 1 in the autoionizing region [16] ($I_1 < h < I_2$) of CH$_3$I. In Fig. 2, photoabsorption measurements of C$_2$H$_5$I and C$_2$H$_5$I doped into varying number densities of CF$_4$ are shown. (The measured photoionization spectra of C$_2$H$_5$I doped into CF$_4$, and the photoabsorption spectra of CH$_3$I doped into CF$_4$ are not shown for the sake of brevity.) The values of $I_1$ (I/I$(2E_{1/2})$ [16]) obtained from fitting the assigned CH$_3$I photoionization spectra to the Rydberg equation are given in Table 1, along with the values for $I_2$ (I/I$(2E_{1/2})$ [23,24]) extracted from the C$_2$H$_5$I photoionization spectra. Although the measured spectra are not

FIG 1. Photoionization spectra (T = 25°C) of pure CH$_3$I (0.1 mbar), and CH$_3$I (0.1 mbar) doped into varying number densities ($10^{20}$ cm$^{-3}$) of CF$_4$: (a) 0.073; (b) 0.23; (c) 0.74 and (d) 1.30. All spectra are intensity normalized to the same spectral feature above the CH$_3$I $^2E_{3/2}$ ionization limit.

FIG 2. Photoabsorption spectra of C$_2$H$_5$I/CF$_4$ at 25°C. Photoabsorption spectra of (a) 0.5 mbar C$_2$H$_5$I, and C$_2$H$_5$I doped into varying number densities of CF$_4$ ($10^{20}$ cm$^{-3}$): b, 1.22; c, 2.43; d, 6.08. The concentration of C$_2$H$_5$I was kept below 10 ppm in CF$_4$. All absorption spectra are corrected for the empty cell transmission. The assignment given at the bottom corresponds to the pure C$_2$H$_5$I spectrum.
shown here, we have also included in Table 1 the values of $I_1$ and $I_2$ extracted from the C$_2$H$_5$I photoabsorption measurements, and $I_1'$ and $I_2'$ extracted from the CH$_3$I photoabsorption measurements. In Fig. 3 we present the photoionization spectra of CH$_3$I and CH$_3$I doped into varying number densities of c-C$_4$F$_8$. Photoabsorption measurements, however, were not possible due to the absorption of c-C$_4$F$_8$ in this spectral region. In Table 2, the values of $I_2$ extracted from fitting the assigned CH$_3$I photoionization spectra to the Rydberg equation are given.

A plot of the shift in ionization energy $\Delta I$ as a function of the number density $D$ of CF$_4$ is shown in Fig. 4. Fig. 4 demonstrates that the red shift of the ionization energy depends linearly upon the perturber number density and, therefore, can be analyzed within the Fermi model (cf. eqs. (1) - (3)). The slope of the linear fit (obtained by regression analysis) of Fig. 4 is $\Delta I / D = -8.648 \pm 0.172 \times 10^{-23}$ eV cm$^3$. Using the value [25] $\alpha = 3.838 \times 10^{-24}$ cm$^3$ for CF$_4$ in eq. (2) gives a polarization shift of $\Delta \alpha / D = -3.38 \times 10^{-26}$ eV cm$^3$. Substituting $\Delta \alpha / D$ and $\Delta I / D$ into eq. (1) leads to $\Delta \alpha / D = 8.546 \pm 0.172 \times 10^{-23}$ eV cm$^3$ which, when substituted into eq. (3), gives a zero-kinetic-energy scattering length of $\lambda = -0.180 \pm 0.003$ nm. Therefore, the zero-kinetic-energy electron scattering cross-section [cf. eq. (4)] is $F = 4.1 \pm 0.2 \times 10^{-15}$ cm$^2$. Current estimates of low energy electron scattering

<table>
<thead>
<tr>
<th>D</th>
<th>$I_1$ (PA)</th>
<th>$I_1$ (PA)</th>
<th>$I_2$ (PA)</th>
<th>$I_2$ (PI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.039</td>
<td>9.537</td>
<td>10.164</td>
<td>10.164</td>
<td></td>
</tr>
<tr>
<td>0.073</td>
<td>9.536</td>
<td>10.163</td>
<td>10.163</td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>9.535</td>
<td>10.162</td>
<td>10.162</td>
<td></td>
</tr>
<tr>
<td>0.74</td>
<td>9.532</td>
<td>10.158</td>
<td>10.158</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Selected first ionization energies (obtained from photoabsorption (PA) measurements) and second ionization energies (obtained from photoabsorption and photoionization (PI) measurements) of CH$_3$I and C$_2$H$_5$I doped into various number densities $D$(10$^{20}$ cm$^{-3}$) of CF$_4$. All ionization energies are in eV.

<table>
<thead>
<tr>
<th>D</th>
<th>$I_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>10.163</td>
</tr>
<tr>
<td>0.36</td>
<td>10.162</td>
</tr>
<tr>
<td>0.73</td>
<td>10.161</td>
</tr>
<tr>
<td>1.45</td>
<td>10.158</td>
</tr>
<tr>
<td>1.81</td>
<td>10.157</td>
</tr>
<tr>
<td>2.42</td>
<td>10.156</td>
</tr>
</tbody>
</table>

Table 2. Selected second ionization energies (obtained from photoionization measurements) of CH$_3$I doped into various number densities $D$(10$^{19}$ cm$^{-3}$) of c-C$_4$F$_8$.

![Graph](image-url)
FIG 4. Shifts of the ionization energies of CH$_3$I and C$_2$H$_5$I, obtained from fitting the assigned spectra (e.g., Figs. 1 and 2) to the Rydberg equation, as a function of CF$_4$ number density. $\bullet$, I, CH$_3$I photoabsorption; $\blacksquare$, I$_2$, CH$_3$I photoabsorption; I$, I$, CH$_3$I photoionization; $\circ$, I; C$_2$H$_5$I photoabsorption; $\triangle$, I; C$_2$H$_5$I photoionization. (The error in the energy for each point is $\pm 3$ meV.)

cross-sections for CF$_4$ range from a low of $1.269 \times 10^{-15}$ cm$^2$, obtained by averaging all of the currently known low energy electron scattering cross-section measurements [3], to a high of $8 \times 10^{-15}$ cm$^2$ [12] computed using the continuum MS-X" method described by Davenport [26]. The value we obtain for the zero-kinetic-energy cross-section, therefore, falls within these two limits.

Similar to the above analysis, Fig. 5 presents the change in the ionization energy of CH$_3$I as a function of $c$-C$_4$F$_8$ number density $D$. As was the case for CF$_4$, a red shift which is linearly dependent upon the $c$-C$_4$F$_8$ number density is observed. The slope of the straight line (obtained from regression analysis) is $\Delta I/ D = -29.57 \pm 0.51 \times 10^{-23}$ eV cm$^3$. Using the value [27] $n = 7.37 \times 10^{-24}$ cm$^3$ for $c$-C$_4$F$_8$, and following the same prescription as that described above for CF$_4$ gives a zero-kinetic-energy electron scattering length of $A = -0.618 \pm 0.012$ nm for $c$-C$_4$F$_8$. Therefore, the zero-kinetic-energy electron scattering cross-section for $c$-C$_4$F$_8$ is $F = 4.8 \pm 0.2 \times 10^{-14}$ cm$^2$ from eq. (4).

Recent attempts by Sanabia and co-workers [28] to measure the low energy electron scattering cross-section gave $F = 4.8 \times 10^{-15}$ cm$^2$ for an electron energy of 1 eV. However, the sharp increase in the electron scattering cross-section of $c$-C$_4$F$_8$ below 1 eV made these low energy electron measurements unreliable [28].

In summary, we have presented photoionization and photoabsorption spectra of CH$_3$I and C$_2$H$_5$I doped into CF$_4$ and $c$-C$_4$F$_8$. From the perturber-induced density-dependent energy shifts of the ionization energies of the dopant molecules, we obtained the zero-kinetic-energy electron scattering lengths and electron scattering cross-sections for both CF$_4$ and $c$-C$_4$F$_8$. We have also illustrated that the method of perturber-induced energy shifts of dopant high-n Rydberg states and ionization energies continues to be an accurate means for determining the zero-kinetic-energy electron scattering lengths when other methods (e.g., the electron swarm method) fail.
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Analytic Solutions to the Lotka-Volterra Model for Sustained Chemical Oscillations*

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ABSTRACT

The Lotka-Volterra (LV) model of oscillating chemical reactions, characterized by the rate equations

\[ \begin{align*}
\dot{x}_1 &= a x_1 - b x_1 x_2 \\
\dot{x}_2 &= -c x_2 + b x_1 x_2,
\end{align*} \]

has been an active area of research since it was originally posed in the 1920s. In this Thesis, we present a simple transformation which reduces the two-dimensional LV system to a one-dimensional system modeled by a second-order nonlinear autonomous ordinary differential equation. The formal analytic solutions to the LV problem are then derived for the first time. An introductory analysis of these solutions is given which leads to the development of an LV-related family of dynamical systems. Analytic solutions to this family of differential equations are presented, for certain cases, in terms of known functions that exhibit oscillatory behavior. The Hamiltonian nature of both the LV model and the related family of differential equations is developed, and future extensions of this treatment are discussed.

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*A thesis submitted to the faculty of Northeast Louisiana University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
CHAPTER 1

INTRODUCTION

1. Description of Intent

In this work, we present analytic solutions to the Lotka-Volterra (LV) model for sustained chemical oscillations. During the analysis of these solutions, a family of LV-related nonlinear autonomous ordinary differential equations, all of which can be solved analytically (some in terms of known functions) are developed. The Hamiltonian forms of both the LV model and its related family are explored in order to gain more insight into the nature of dynamical systems which possess invariants.

An oscillating chemical system is one in which some macroscopic feature of the system undergoes periodic temporal or spatial variations. (The LV system, for example, exhibits sustained oscillations in time.) In recent years, an increasing amount of attention has been paid to oscillating chemical reactions because of the discovery of oscillatory homogeneous biochemical and inorganic systems [1,2].

Although much research has been done on the nature of oscillating systems, such as the study by Prigogine and co-workers on the thermodynamic and kinetic requirements for the existence of oscillations [3,4], little is known analytically about such systems. This lack of knowledge is a result of the complexity of the differential models used. Thus, the development of a systematic technique for the solution of a set of n nonlinear first-order differential equations could lead to new insights into the nature of conservative systems which possess sustained oscillations. Because of the highly nonlinear nature of the differential equations used to model chemical oscillators [5,6], much of the current research has been aimed at analyzing the qualitative behavior of the rate laws (e.g., [7]). The qualitative properties of differential equations, including the requirements for a system to be considered conservative, will be discussed in more detail in Chapter 2, and applied throughout the remainder of this work. In Chapter 3, reaction schemes used to model some common chemical oscillators will be described, and the phenomenological rate laws will be developed.

In Chapter 4, we present a method which allows a two-dimensional nonlinear conservative system, namely the LV model, to be reduced to a one-dimensional system modeled by a second-order nonlinear ordinary differential equation. (The generalization of this method to systems with dimensionality greater than 2 is briefly discussed in Chapter 6.) The main reasons for the choice of the LV model for our study are that it is the simplest known model of a two-component system which exhibits sustained oscillations, and it has wide applicability in many fields. The analytic solution to
the LV model, which is presented in Chapter 4, has a doubly periodic nature which implies that it represents a new type of elliptic function. An introductory analysis of this function is presented in Chapter 5 in terms of the analytic solutions to a LV-related family of differential equations. This family, which appears initially to be more complicated than the LV model, is capable in some cases of being solved analytically in terms of known functions, with the solutions representing approximations to the solution of the LV system.

The Hamiltonian form of the LV model is investigated in Chapter 4, leading to the definition of a new Hamiltonian in a four-dimensional phase space. A brief discussion of the further extension of this Hamiltonian to n-dimensional systems is presented in Chapter 6. The LV-related family of differential equations is also shown to possess a Hamiltonian, although the function constructed is not a traditional Hamiltonian.

2. Plan of Presentation

Since oscillating chemical reactions are modeled by nonlinear differential equations [8-10], the mathematical theory of dynamical systems is briefly reviewed in Chapter 2. Chapter 3 presents a discussion of phenomenological chemical kinetics, with the development of rate laws for chemical reactions ranging from simple chemical reaction schemes to the complex reaction schemes which show sustained chemical oscillations. Current techniques for generating analytic solutions to these rate laws are also presented. The Lotka-Volterra model is introduced and solved both numerically and analytically in Chapter 4. Several different methods for the development of Hamiltonians for the LV model, one of which leads to the discovery of a new invariant, are also presented. Chapter 5 uses the analysis of the analytic solution to the LV model to develop a family of LV-related differential equations which, in some instances, can be solved analytically in terms of known functions. Finally, these equations are shown to be conservative and to possess a Hamiltonian structure. The generalization of the techniques used to solve the two-dimensional LV model to an n-dimensional conservative system are discussed briefly in Chapter 6.

CHAPTER 2

DYNAMICAL SYSTEMS

1. Qualitative Properties of Dynamical Systems

A dynamical system, by which any homogeneous chemical reaction is modeled [8-10], consists of a set of first-order ordinary differential equations. In this Section, we present a review of the qualitative properties of such systems. (A qualitative property, such as stability, of a dynamical system is one which may be determined without explicitly solving the system.) The mathematical results presented here will be used throughout the remainder of this work.

Consider a system of first-order ordinary differential equations (ODEs) represented by

$$\dot{x}_i = f_i(t, x_1, ..., x_n), \quad \forall i = 1, ..., n \quad (2.1)$$

where \(\dot{x}_i = \frac{dx_i}{dt}\). By allowing \(x_1, ..., x_n\) to be components of a n-dimensional vector \(x\), eq. (2.1) can be written as

$$\dot{x} = f(t, x), \quad (2.2)$$

where \(f(t, x)\) is a vector-valued function. In order to be well defined, eq. (2.2) requires that the function \(f\) be continuous in both the one-dimensional real Euclidean space of the scalar \((t \in \mathbb{R})\) and the n-dimensional real Euclidean space of the vector \((x \in \mathbb{R}^n)\). The function \(f\) maps an open subset \(G\) of \(\mathbb{R}^{n+1}\) to \(\mathbb{R}^n\), which can be written symbolically as \(f: G \to \mathbb{R}^n\) where \(G \subset \mathbb{R}^{n+1}\) [11,12].

A solution to eq. (2.2) is a function \(\phi(t)\) which
is defined on an interval I of the t-axis (I ⊂ R), such that \( \phi: I \rightarrow \mathbb{R}^n \) is continuously differentiable and \( \phi(t) \) satisfies eq. (2.2) [12]. The solution of eq. (2.2) is the curve \( \Gamma \) lying in region \( G \), where each point of the curve has the coordinates \( (t, \phi(t)) \), and where the tangent to \( \Gamma \) at each point is represented by \( \mathbf{f}(t, \phi(t)) \) [11].

One of the most important conditions that \( \mathbf{f}(t,x) \) must satisfy is the Lipschitz condition for continuous differentiability. The condition for a function to be Lipschitz continuous in the neighborhood of a certain point \( p_0 \) is that

\[
\| \mathbf{f}(t,x) - \mathbf{f}(t,x') \| \leq L \| x - x' \|, \tag{2.3}
\]

where \( L \) is a constant and \( \| r \| \) is the Euclidean length (norm) of the vector given by

\[
\| r \| = \left( \sum_{i=1}^{n} r_i^2 \right)^{1/2}, \tag{2.4}
\]

and where \( x, x' \) belong to a bounded domain \( D \subset \mathbb{R}^n \) [13,14]. The neighborhood of a point \( p_0 \) defined by the coordinates \( (t_0, x^0) \) in \( \mathbb{R}^{n+1} \) \( \{ p_0 := (t_0, x^0) \in \mathbb{R}^{n+1} \} \) is the set of points \( N(t_0, x^0) \) satisfying the conditions that for every \( (t, x), |t-t_0| < \tau \) and \( \| x-x^0 \| < \rho \), where \( \tau \) and \( \rho \) are positive constants. A boundary point of \( G \) is defined as the point \( (t_0, x^0) \) in \( \mathbb{R}^{n+1} \) such that every neighborhood of \( (t_0, x^0) \) contains both points in \( G \) and points outside of \( G \). The set \( G \subset \mathbb{R}^{n+1} \) is open if and only if it contains none of its boundary points, and is closed if it contains all of its boundary points [11].

The requirement of Lipschitz continuity in the neighborhood of the point \( p_0 \) implies that there exists a unique solution to the initial value problem, namely, the problem of finding a solution to eq. (2.2) which satisfies the condition \( \phi(t_0) = x^0 \) [12-14]. This existence-uniqueness theorem may also be stated as follows: there exists one and only one solution \( x = \phi(t, p_0) \) of eq. (2.2) which satisfies the initial condition \( \phi(t_0, p_0) = x^0 \) if \( \mathbf{f}(t,x) \) and its first partial derivatives \( \frac{\partial \mathbf{f}}{\partial x} \) are continuous in \( G \subset \mathbb{R}^{n+1} \). Thus, each solution \( \phi(t,p_0) \) exists and is continuous on some interval \( I \subset \mathbb{R} \) containing \( t_0 \), and every solution is continuous with respect to variations in the values of the initial condition \( p_0 \) [11,15].

If eq. (2.2) is autonomous, \( \mathbf{f} \) is not an explicit function of time:

\[
\mathbf{x} = \mathbf{f}(\mathbf{x}). \tag{2.5}
\]

This is a special case of eq. (2.2), where the domain of \( \mathbf{f} \) is some real \( n \)-dimensional region \( G \subset \mathbb{R}^n \) instead of an \( (n+1) \)-dimensional region. Throughout the remainder of this discussion, \( \mathbf{f}(\mathbf{x}) \) and its first partial derivatives will be assumed to be continuous so that the existence-uniqueness theorem discussed above applies. If, for aid of visualization, we assume that eq. (2.5) governs the motion of a physical system, then the components of \( \mathbf{x} \) may be viewed as the generalized coordinates for the system. This set of coordinates, \( \{ x_i \mid i = 1, \ldots, n \} \), constitutes the configuration space for the system. The solution curves for this system, referred to as trajectories or orbits, represent the history of the positional variations of the system, since the position \( \mathbf{x} \) of the system at any given time will lie on one of these trajectories [13]. The trajectory that the position \( \mathbf{x} \) moves along as time advances is determined by the initial conditions chosen for the system.

The velocity of the point \( \mathbf{x} \) at any given time along the trajectory is the tangent vector to the point [i.e., eq. (2.5)]. Thus the solution to eq. (2.5) can be viewed as a point moving along a curve in an \( n \)-dimensional space with a position dependent velocity given by eq. (2.5). (By convention, the orientation of trajectories is in the direction of increasing time.) A trajectory which passes through the initial point \( x^0 \in \mathbb{R}^n \) represents an infinite set of solutions \( \{ \phi(t+c,x^0) \mid c \in \mathbb{R} \} \) which differ from each other in phase. The invariance of the solutions of autonomous systems to translations of the independent variable \( t \) can be shown as follows.

If \( \alpha(t) = \phi(t,x^0) \) is a solution to eq. (2.5) on the interval \( (a,b) \), then \( \beta(t) = \phi(t-c,x^0) \) is a solution on the interval \( (a-c,b-c) \), where \( c \) is any real constant.
Since for every \( \tau \in (a,b) \), \( \alpha(\tau) = \beta(\tau-c) \), \( \alpha(\tau) \) and \( \beta(\tau) \) define identical trajectories in configuration space [11]. Thus, the solutions of eq. (2.5) are invariant to translations in time.

The solution \( \alpha(t) = \phi(t,x^0) \) of eq. (2.5) is periodic with period \( T \) if there exists some real finite positive number \( T \) such that \( \alpha(t+T) = \alpha(t) \ \forall \ t \in \mathbb{R} \) (excluding the trivial case of \( \alpha(t) = \text{constant} \)). A system has periodic solutions if and only if it possess trajectories which are closed curves [16]. (Let \( \gamma \) be a closed curve that solves eq. (2.5) and is defined by \( \alpha \ \forall \ t \in \mathbb{R} \). Since \( \gamma \) is closed, there exists a time \( t_1 \) and a number \( T > 0 \) such that \( \alpha(t_1) = \alpha(t_1+T) \). Therefore \( \alpha \) is periodic [11,17].)

A point \( x^c \in G \) is a critical point of a system (which physically corresponds to a stationary or equilibrium state of a system) if \( f(x^c) = 0 \). If a solution of eq. (2.5) generates a trajectory \( \gamma \) which passes through at least one point with a non-zero velocity, then \( \gamma \) cannot pass through a critical point in finite time [13,16]. The behavior of trajectories in a sufficiently small neighborhood around the critical point determines the nature or stability of the critical point \( x^c \). A critical point \( x^c \) is Lyapunov stable [12], usually referred to as stable, if for all \( \varepsilon > 0 \), there exists some \( \delta(\varepsilon) > 0 \) such that for any solution \( \phi(t,x^0) \) of eq. (2.5), a stronger condition for stability is that there exist some \( \delta > 0 \) such that

\[
\| x^0 - x^c \| < \delta(\varepsilon) \quad \Rightarrow \\
\| \phi(t,x^0) - x^c \| < \varepsilon \quad \forall \ t \geq t_0 .
\]

A critical point which satisfies this condition for stability is said to be asymptotically stable [13]. A critical point which does not meet any of the criteria for stability is said to be unstable.

\[
\| x^0 - x^c \| < \delta \quad \Rightarrow \quad \lim_{t \to \infty} \| \phi(t,x^0) - x^c \| = 0 .
\]

To develop a better understanding of stability, let us consider the two-dimensional autonomous system

\[
x = f(x)
\]

where \( x=(x_1,x_2) \) and \( f(x)=(f_1(x), f_2(x)) \), and investigate the geometric implications of stability for this system. In a two-dimensional system, the neighborhood of a point is a circle centered about that point with some radius \( \rho > 0 \), which will be referred to as the \( \rho \)-neighborhood of the point. For a critical point to be stable, there must exist a sufficiently small \( \delta \)-neighborhood \( N(\delta) \) of \( x^c \) contained in any \( \varepsilon \)-neighborhood \( N(\varepsilon) \) of \( x^c \) such that every trajectory which passes

![Fig. 2.1 Example of a trajectory which shows Lyapunov stability.](image1)

![Fig. 2.2 Example of a trajectory which is asymptotically stable.](image2)
through $N(\tilde{\delta})$ at some time $t = t_0$, remains in $N(\epsilon)$ for all future times [12,17] (see Fig. 2.1). The critical point is asymptotically stable if there exists a sufficiently small $N(\tilde{\delta})$ of $x^c$ such that every trajectory which passes through $N(\tilde{\delta})$ at some time $t = t_0$ approaches the critical point as $t$ approaches infinity (see Fig. 2.2). All critical points which are asymptotically stable are also Lyapunov stable; however, the converse is not true. For a critical point to be unstable, a trajectory must exist which passes through $N(\tilde{\delta})$ but does not remain in $N(\epsilon)$ (see Fig. 2.3).

The stability of critical points is important in the analysis of physical systems since, for example, an equilibrium state of a chemical system corresponds to an asymptotically stable critical point. Thus, if a system is perturbed from its equilibrium point by a small amount, the system will return to the equilibrium point in a sufficiently long period of time. This is an example of Le Châtelier's Principle.

2. Conservative Systems

A conservative system is defined as a system given by eq. (2.5) which possesses at least one first integral on a region $R \subset G$. A first integral is a differentiable function $F(x)$ on $R$ such that for any solution $x = \phi(t, x^0) \in \mathbb{R}$ of eq. (2.5),

$$F(\phi(t, x^0)) = C \equiv \text{constant, } \forall \ t \in I, \quad (2.6)$$

such that $x = \phi(t, x^0) \in \mathbb{R}$. (The trivial case of $F$ identically constant is excluded.) The integral represented in eq. (2.6) defines a family of $(n-1)$-dimensional surfaces, referred to as level surfaces, on which each trajectory lies [11]. A trajectory lies on a level surface $L_s$ if that trajectory touches the surface at at least one point. This can be seen by allowing $F$ to be an integral on $R \subset G$ and defining the level surface $L_s = \{x \mid F(x) = C\}$ where $C$ is some constant. Let $\phi(t, x^0) \in \mathbb{R}$ be a solution of eq. (2.5) on the interval $J$, $\forall \ t \in J$. Then for some $t_1 \in J$, $\phi(t_1, x^0) = x^1 \in L_s$ implies that $\phi$ will define a trajectory $\gamma$ which touches $L_s$ at the point $x^1 \in \mathbb{R}$. The condition that $x^1 \in L_s$ implies that

$$F(\phi(t_1, x^0)) = F(x^1) = C, \quad (2.7)$$

but since $F$ is an integral of $R$ by hypothesis, the above relationship must hold for all $t \in J$. This allows eq. (2.7) to be written as

$$F(\phi(t, x^0)) = C, \quad \forall \ t \in J,$$

which implies that $F$ is equal to a constant on every point of the trajectory $\gamma$. Thus, every point of $\gamma$ is an element of $L_s$, implying that the trajectory must lie completely on the level surface $L_s$. An integral, therefore, represents a special constraint on the system of equations which reduces the dimensionality of the system by one. (In classical mechanics, general constraints are referred to as holonomic when the variable $x$ represents spatial coordinates [18].) Since for a two-dimensional system ($n=2$) the level surfaces reduce to trajectories [16], the trajectories of a conservative two-dimensional autonomous system are completely defined by a single integral.

In order to illustrate this, let us consider the two-dimensional system

$$\dot{x}_1 = f_1(x_1, x_2), \quad \dot{x}_2 = f_2(x_1, x_2), \quad (2.9)$$

where $f_i$ and $\partial f_i/\partial x_j$ $(i, j = 1, 2)$ are continuous in
A set of integrals is independent if no integral of the set is derivable from the other integrals of the set or, in other words, if there does not exist a function having the form \( \Phi(F_1, \ldots, F_{n-1}) = 0 \), where \( F_i \) are the integrals. The independence of a set of integrals is determined by the existence of a nonzero functional determinant or Jacobian [20],

\[
\begin{vmatrix}
\frac{\partial F_1}{\partial x_2} & \cdots & \frac{\partial F_1}{\partial x_n} \\
\vdots & \ddots & \vdots \\
\frac{\partial F_{n-1}}{\partial x_2} & \cdots & \frac{\partial F_{n-1}}{\partial x_n}
\end{vmatrix} \neq 0 .
\]

If this condition is satisfied, the variables \( x_i, \forall \ i = 2, \ldots, n \), can be expressed as unique, continuous, differentiable functions of the one independent variable \( x_1 \) [19]:

\[
x_i = \psi_i(x_1), \quad \forall \ i = 2, \ldots, n .
\]

As a final note, conservative systems cannot possess asymptotically stable singular points [13]. This can be illustrated by defining an invariant \( F \) for eq. (2.9) and letting \( F(x_1^c, x_2^c) = C_0 \), where \( C_0 \) is a known constant. The condition for \( (x_1^c, x_2^c) \) to be an asymptotically stable point is that every trajectory in a sufficiently small neighborhood of the critical point approaches this point as \( t \to \infty \). But, by hypothesis, \( F \) is an invariant, implying that \( F \) is a constant on every trajectory in the \((x_1, x_2)\) plane. If \( \gamma \) is a trajectory which approaches the point \((x_1^c, x_2^c)\) as \( t \to \infty \), and \( F(x_1^c, x_2^c) = C_1 \) along every point of \( \gamma \), then

\[
\lim_{t \to \infty} F(x_1^c, x_2^c) = F(x_1^c, x_2^c) = C_1 = C_0 .
\]

Since every trajectory in a sufficiently small neighborhood approaches the point \((x_1^c, x_2^c)\) as \( t \to \infty \), \( F \) attains the value of \( C_0 \) for every trajectory in some small region \( R \) about the point \((x_1^c, x_2^c)\). This contradicts the hypothesis that \( F \) is invariant, since the value of \( F \) should change for each trajectory. Although the previous argument is for a two-dimensional system, similar arguments can be
applied to systems with higher dimensionality.

The fact that no conservative system can possess an asymptotically stable critical or equilibrium point has many implications for oscillating chemical reactions. The major implication is that oscillating chemical systems occur far from equilibrium. On the other hand, some systems which possess asymptotically stable points in configuration space may possess invariants in the reaction coordinate space, which is a space defined not only by the position but also by the velocity [11]. These systems may be completely specified by a reaction Hamiltonian, which is a conservative integral of the motion. The next Section will discuss the nature of conservative integrals which possess Hamiltonian structure, and how these integrals can be used to determine the phase-space trajectories of a system.

3. The Hamiltonian

Although the Hamiltonian approach to dynamical systems adds nothing new to the physical nature of the problem, it does allow for the development of new and more powerful approaches to working with physical properties of the system which have already been established. The Hamiltonian can be developed either from the properties of work done on a conservative physical system, or from a variational calculus approach applied to Hamilton’s principle [22]. The latter approach will be presented in this Section.

For a 2n-dimensional dynamical system which can be written in the form

\[ \dot{x} = a \, y, \quad \dot{y} = g(x,y) \quad (2.16) \]

where \( a \) is a proportionality constant, the components of the vector \( x \in \mathbb{R}^n \) are the coordinates of the system, and the components of the vector \( y \in \mathbb{R}^n \) are the momenta of the system. The 2n-dimensional real Euclidean space in which the solution curves to eq. (2.16) lie will be referred to as the phase space of the system, with the n-dimensional spaces in which the solution curves of \( x = a \, y \) and \( \dot{y} = g(x,y) \) lie being referred to as configuration space and momentum space, respectively. For convenience, the proportionality constant \( a \), which in a mechanical system would be related inversely to mass, will be assumed to be one. The velocity of the system represented by eq. (2.16) is \( \dot{x} \) and the acceleration is \( \ddot{x} \). Kinetic energy is the energy that the system possesses as a result of the motion of the system, and is classically defined as

\[ T = \frac{1}{2} \sum_{i=1}^{n} \dot{x}_i^2. \quad (2.17) \]

The potential energy \( V \) is the energy that a system possesses as a result of the configuration of the system. (A system which is subject to dissipative forces can have a potential linearly dependent on the velocity; in general, forces in a conservative system are derivable from the negative gradient of the potential energy.)

One immediate result of eq. (2.16) is

\[ x = \dot{y} = g(x,x) \quad , \quad (2.18) \]

implying that any 2n-dimensional system having the form of eq. (2.16) can be written as a n-dimensional system of second-order autonomous differential equations. The converse of this argument is also true. In general, a set of \( n \)th order differential equations can be expressed as a set of \( mn \) first-order differential equations [13]. Thus, any second-order differential equation can be viewed as a system which models a fictitious particle with a position and momentum defined by eq. (2.16).

Hamilton’s principle [21] states that out of all possible paths along which a dynamical system may travel from one point to another in a specific amount of time, the actual path followed is the one which minimizes the time integral of the difference between the kinetic and potential energies. Hamilton’s principle can be summarized by stating that the action integral,
where $L = T - V$, is constant for the actual path of motion. Thus, the variation [22] of eq. (2.19) is

$$
\delta I = \delta \int_{t_1}^{t_2} L(x, \dot{x}) \, dt = 0 ,
$$

(2.20)

which is a sufficient condition for deriving the equations of motion for a dynamical system having the form of eq. (2.16) [18]. The function $L(x, \dot{x})$ is termed the Lagrangian of the system.

The variation of $I$ is obtained by considering $I$ as a function of some parameter $\alpha$ which labels a set of curves $x_i(t, \alpha)$ such that

$$
x_i(t, \alpha) = x_i(t, 0) + \alpha \eta_i(t) , \quad \forall \ i = 1, \ldots, n ,
$$

(2.21)

where $x_i(t, 0)$ are the solutions to the extremum problem (to be obtained), and $\eta_i$ are independent functions of $t$ which vanish at the end points and are continuous up through second derivatives ($C^2$) [18,22]. With the use of eq. (2.21), eq. (2.20) becomes

$$
\delta I = \int_{t_1}^{t_2} \sum_{i=1}^{n} \left( \frac{\partial L}{\partial x_i} \frac{\partial x_i}{\partial \alpha} \right) \, d \alpha \, dt = 0 ,
$$

(2.22)

which can be integrated by parts to give

$$
\frac{\partial I}{\partial \alpha} \, d\alpha = \int_{t_1}^{t_2} \sum_{i=1}^{n} \left( \frac{\partial L}{\partial \dot{x}_i} \frac{\partial \dot{x}_i}{\partial \alpha} \right) \, d\alpha \, dt = 0 ,
$$

where

$$
\delta x_i = \left( \frac{\partial x_i}{\partial \alpha} \right)_0 \, d\alpha .
$$

The fundamental lemma from variational calculus [22] states that if

$$
\int_{x^{(1)}}^{x^{(2)}} M(x) \, \eta(x) \, dx = 0
$$

then
for any arbitrary function \( \eta(x) \in C^2 \), then \( M(x) \) must vanish identically in the interval \((x^{(1)},x^{(2)})\). Applying this lemma to eq. (2.23) gives

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{x}_i} - \frac{\partial L}{\partial x_i} = 0, \quad \forall \ i = 1, \ldots, n. \tag{2.24}
\]

This system of equations [eq. (2.24)] is referred to as Lagrange’s equations and is equivalent to the original equations of motion [eq. (2.16)]. Thus, the dynamical system is now defined by a Lagrangian,

\[
L = \frac{1}{2} \sum_{i=1}^{n} \dot{x}_i^2 + V(x,\dot{x}), \tag{2.25}
\]

which satisfies Lagrange’s equations [eq. (2.24)]. The conjugate momentum is now given by

\[
y_i = \frac{\partial L}{\partial \dot{x}_i} = \dot{x}_i + \frac{\partial V}{\partial x_i}, \tag{2.26}
\]

which reduces to the form of eq. (2.16) if the system does not have a velocity-dependent potential. The transition from a Lagrangian formulation to a Hamiltonian formulation is mathematically equivalent to a coordinate transformation from \((x,\dot{x})\) to \((x,y)\). This switch in coordinates is accomplished by performing a Legendre transformation on the Lagrangian.

A Legendre transformation, in general, concerns a function \( f \) of two variables \((x,y)\) which has a total differential given by

\[
df = \frac{\partial f}{\partial x} \, dx + \frac{\partial f}{\partial y} \, dy = u \, dx + v \, dy.
\]

In order to change the coordinates from \((x,y)\) to \((u,y)\), with the differential quantities expressed in terms of \(du\) and \(dy\), a new function \( g \) is defined such that

\[
g = f - u \, x.
\]

Direct differentiation of \( g \) gives

\[
dg = df - u \, dx - x \, du,
\]

which, upon substituting in the relationship for \( df \), reduces to

\[
dg = v \, dy - x \, du.
\]

By direct comparison of the last equation to the total differential of \( g \), the functional form of \( x \) and \( v \) must satisfy the relationships

\[
x = -\frac{\partial g}{\partial x} \quad \text{and} \quad v = \frac{\partial g}{\partial y}.
\]

Applying this transformation to eq. (2.25) gives the Hamiltonian as

\[
H(x,y) = \sum_{i=1}^{n} y_i x_i - L(x,\dot{x}),
\]

which, if the potential is linear in the velocity, reduces to

\[
H(x,y) = \frac{1}{2} \sum_{i=1}^{n} \left( y_i - \frac{\partial V}{\partial y_i} \right)^2 + V(x,y) \tag{2.27}
\]

where

\[
\frac{\partial H}{\partial y_i} = \dot{x}_i, \quad \frac{\partial H}{\partial x_i} = -\dot{y}_i \tag{2.28}
\]

\( \forall \ i = 1, \ldots, n. \) The Hamiltonian, which is the sum of the potential and kinetic energy of a system, represents the total energy. Eq. (2.28) are Hamilton’s equations, which completely define the motion of the system. It is important to note that not all systems of first-order autonomous differential equations can be placed into Hamiltonian form, although all conservative systems should possess a transformation which allows the equations to be placed into a form which solve Hamilton’s equations. If a system can be placed into a form which solves Hamilton’s equations, and if

\[
\frac{\partial^2 H}{\partial x_i \partial y_j} = \frac{\partial^2 H}{\partial y_i \partial x_j}, \quad \forall \ i, j = 1, \ldots, n,
\]

where \( i \neq j \), the system possesses a Hamiltonian.

The invariance of the Hamiltonian is easily shown for a system with a velocity-independent
potential by a direct time differentiation of eq. (2.27). When the potential is velocity independent, eq. (2.27) reduces to
\[ H(x,y) = \frac{1}{2} \sum_{i=1}^{n} y_i^2 + V(x) = T + V, \tag{2.29} \]
which has the time derivative
\[ \frac{dH}{dt} = y \dot{y} + \frac{dV}{dt} \dot{x}. \tag{2.30} \]

Using eq. (2.26) and Hamilton’s equations [eq. (2.28)], reduces eq. (2.30) to
\[ \frac{dH}{dt} = \dot{x} \dot{y} - \dot{\dot{x}} \dot{y} = 0. \]

Since \( H \) represents an invariant, similar to the invariants discussed in the previous Section, it defines a family of curves in the phase plane which are the possible trajectories of the particle. The particular trajectory of the particle is determined as soon as the initial position and momentum of the particle are specified.

Although the form of the potential \( V(x) \) has not been given, several qualitative properties of the trajectories can be determined from eq. (2.29). Since \( H \) is quadratic in \( y \) and \( y \in \mathbb{R}^n \), \( H(x,y) = H(x,-y) \), which implies that the trajectories will be symmetric with respect to reflection across the \( x \)-axis. Furthermore, since \( T > 0 \), the potential must be less than or equal to the total energy of the system, thus confining the trajectories to that region of phase space.

The equilibrium points for a Hamiltonian system [i.e., a system solving eq. (2.28)] are \( y = 0 \) and \( dV/dx = -g(x) = 0 \). This implies that the singular points of eq. (2.16), or equivalently eq. (2.28), lie on the \( x \)-axis and must be at a point where the potential energy is an extremum. If the potential energy attains a maximum at the singular point, the singular point is unstable; if the potential is at a minimum, the singular point will be stable [13,17].

The existence of a Hamiltonian for a given dynamical system can be used to discover the other constants of the motion, since the Poisson bracket of the Hamiltonian with a function \( \phi(x,y) \) is the time derivative of \( \phi \). The Poisson bracket of \( H \) with \( \phi \) is defined by
\[ [H,\phi] = \sum_{i=1}^{n} \left( \frac{\partial H}{\partial y_i} \frac{\partial \phi}{\partial x_i} - \frac{\partial H}{\partial x_i} \frac{\partial \phi}{\partial y_i} \right) = \frac{d\phi}{dt}. \tag{2.31} \]

Later in this work, a new approach to obtaining Hamiltonians for the Lotka-Volterra model will be presented. Also, the existence of a Hamiltonian structure for a family of nonlinear differential equations related to the Lotka-Volterra model will be shown. The ability to write a Hamiltonian for a dynamical system allows the application of new techniques, such as Hamilton-Jacobi theory [18], in an attempt to develop analytic solutions.

CHAPTER 3

THE DYNAMICS OF CHEMICAL SYSTEMS

1. Introduction

The dynamics of chemical systems (i.e., chemical kinetics) is the study of the mechanism and rate of transformation of one set of compounds (the reactants) into another set (the products). As mentioned in Chapter 2, the rate of reaction of a system is modeled by a set of first-order autonomous differential equations [10], which are referred to as the rate laws. Recall from the previous Chapter that the variables \( x_i \in \mathbb{R}^n, \forall i = 1,…,n \), were taken to be the generalized coordinates of a system modeled by a set of \( n \) first-order differential equations, and that the vector \( x \) in configuration space completely specified the state of the system at a given time. The generalized coordinates \( x_i \) of the dynamical system [eq. (2.5)] can be interpreted as composite variables of the
amount of the chemical components in a system and are then referred to as reaction coordinates.

The reaction coordinates for a system are defined chemically as follows. The total mass of a system of r components at any given time can be written

\[ m(t) = \sum_{\alpha=1}^{r} m_\alpha(t) , \]

where \( m_\alpha(t) \) is the mass of the \( \alpha \)th component at time \( t \). The change of the \( \alpha \)th component can be expressed as

\[ \mathrm{d} m_\alpha = d_1 m_\alpha + d_E m_\alpha, \quad \forall \ \alpha = 1, \ldots, r, \]

(3.1)

where \( d_1 m_\alpha \) and \( d_E m_\alpha \) are the (differential) mass changes of the \( \alpha \)th component resulting from reactions within the system, and from mass transfer with the exterior, respectively. The conservation of mass during a reaction implies that

\[ d_1 m = \sum_{\alpha=1}^{r} d_1 m_\alpha = 0 , \]

(3.2)

and, therefore, that

\[ \mathrm{d} m = \mathrm{d}_E m = \sum_{\alpha=1}^{r} d_E m_\alpha . \]

(3.3)

The differential reaction coordinate for a chemical system is defined by

\[ \mathrm{d} x_i = \frac{1}{v_{i\alpha}} \mathrm{d} n_{i\alpha} , \]

(3.4)

where \( \mathrm{d} n_{i\alpha} \) is the change in the number of moles of the \( \alpha \)th component due to the \( i \)th reaction, and \( v_{i\alpha} \) is the stoichiometric coefficient of the \( \alpha \)th component in the \( i \)th reaction [11]. (By convention, the sign of \( v_{i\alpha} \) is positive if the component is a product and negative if it is a reactant.) Converting to moles and substituting eqs. (3.2) and (3.4) into eq. (3.1) gives

\[ \mathrm{d} n_{i\alpha} = \sum_{i=1}^{n} v_{i\alpha} \mathrm{d} x_i + d_E n_{i\alpha}, \quad \forall \ \alpha = 1, \ldots, r. \]

(3.5)

If \( d_E n_{i\alpha} = 0 \) for some component \( \beta \), then eq. (3.5) can be integrated to give

\[ n_{i\beta}(t) - n_{i\beta}(0) = \sum_{j=1}^{n} v_{i\beta} [ x_j(t) - x_j(0) ] , \]

which, if the component \( x_j \) only appears in the \( i \)th reaction, reduces to

\[ x_i(t) = \frac{1}{v_{i\beta}} [ n_{i\beta}(t) - n_{i\beta}(0) ] + x_i(0) . \]

(3.6)

When the change in volume during the course of the reaction is negligible, this reaction coordinate [eq. (3.6)] can be expressed in terms of the molar concentrations of the components.

Chemical reactions are classified by how eqs. (3.2) and (3.3) are related, the type of mechanism followed, and the order of the system. An open chemical reaction is a reaction where some of the components gain or lose mass by interaction with sources external to the system (\( d_E m \neq 0 \)). If the mass of some of the components in the reaction is maintained constant via interactions with an external reservoir, while the remaining components undergo mass changes due only to reactions within the system, the reaction is said to be simply open. In this case,

\[ d_1 m_\alpha = d_1 m_\alpha , \quad \forall \ \alpha = 1, \ldots, s < r \]

\[ d_1 m_\alpha = -d_E m_\alpha , \quad \forall \ \alpha = s+1, \ldots, r . \]

A system is closed if the total change in mass is zero, implying that the mass of the system is conserved during the course of the reaction. In most kinetic studies, only simply open or closed systems are considered.

The general mechanisms which are used to construct a model for a chemical system are either reversible or irreversible simple chemical reactions, or autocatalytic chemical reactions. A simple chemical reaction is a closed single step reaction having the form

\[ \sum_{\alpha=1}^{r} A_\alpha \rightleftharpoons \sum_{\alpha=r+1}^{s} A_\alpha \]

(3.7)
where \( k_i \) and \( k_i' \) are rate constants, which are independent of the concentrations of the components but dependent on temperature [23]. If \( k_i' = 0 \), the reaction is irreversible; otherwise it is classified as a reversible reaction. The order of a system refers to the highest power to which the concentrations of the components are raised (e.g., a second-order reaction will have at least one quadratic term) in the rate law. When a single-step reaction creates, as a product, one of the reactants, such that the total concentration of that reactant is constant for the reaction, the reaction is said to be autocatalytic. An oscillating chemical system is a complicated system modeled by a combination of simple and autocatalytic reactions with at least one autocatalytic reaction, since an autocatalytic step is a necessary condition for chemical oscillations to exist [3,4].

The solutions to the rate laws, usually referred to as integrated rate laws, give the concentrations of the chemical components of a system as functions of time, thus allowing for predictions of the amount of a specific compound in the reaction vessel at any given time. Two approaches for obtaining these solutions are the phenomenological approach [10,23] and the Hamiltonian approach [11,24-26], with the latter being a simple mathematical extension of the former. The phenomenological approach to chemical kinetics involves writing the rate law for each reaction in terms of one component for that reaction and solving the resulting system of differential equations. This approach can become complicated even for systems containing a small number of chemical reactions. The Hamiltonian approach develops a set of reaction coordinates and their conjugate momenta, and uses these to write a reaction Hamiltonian for the system. Once a reaction Hamiltonian is defined, powerful solution techniques, such as Hamilton-Jacobi theory, can be applied in order to obtain analytic solutions.

The reaction Hamiltonian for a system can in principle be derived as follows. Let a system of \( n \) chemical reactions possess the set of \( n \) corresponding rate equations

\[
\dot{x} = f(x) \tag{3.8}
\]

where \( x = (x_1, \ldots, x_n) \) and \( f(x) = (f_1(x), \ldots, f_n(x)) \).

The second time derivative of eq. (3.8) is

\[
\ddot{x} = \sum_{j=1}^{n} \frac{\partial f}{\partial x_j} \dot{x}_j = \sum_{j=1}^{n} \frac{\partial f}{\partial x_j} f_j(x) = g(x), \tag{3.9}
\]

which, using the same line of reasoning as that presented in Chapter 2, can be expressed as a set of \( 2n \) first-order differential equations

\[
\dot{x} = f(x), \quad \dot{y} = g(x),
\]

thus defining the reaction coordinates \( x \) and the reaction momenta \( y \) of the system. If the system possesses a potential \( V(x) \) such that

\[
g_i(x) = -\frac{\partial V}{\partial x_i}, \quad \forall \ i = 1, \ldots, n, \tag{3.10}
\]

then a reaction Hamiltonian, defined by

\[
H(x,y) = \frac{1}{2} \sum_{i=1}^{n} y_i^2 + V(x) \tag{3.11}
\]

exists. The existence of a Hamiltonian guarantees that the dynamical behavior of the system will be described by eq. (2.28), and that the solutions to the system will define closed curves in the reaction phase space. The particular phase space trajectory of the system is fixed by the specification of a set of \( 2n \) initial conditions. Both the phenomenological and the Hamiltonian approaches to the solution of the rate laws of simple and autocatalytic reactions will be presented in the following sections. The formalism developed will then be used to set up the dynamical equations for the complex systems of some common chemical oscillators.

2. Simple Chemical Reactions

As mentioned in the previous Section, a simple chemical reaction is a closed or simply open single-step reaction having the form [eq. (3.7)]
where the forward reaction is of order \( r \) and the reverse reaction is of order \( s-r \). Processes which are modeled by simple chemical reactions include radioactive decay, absorption and emission of electromagnetic radiation, and some formation and degradation reactions.

For an irreversible reaction \( (k_1' = 0) \), the phenomenological rate law is

\[
\dot{x} = k_1 \sum_{\alpha=1}^{r} \left( n_\alpha(0) - x \right),
\]

(3.12)

where \( n_\alpha(0) \) is the number of moles of the \( \alpha \)th component at \( t = 0 \), and \( x \) is the reaction coordinate as given in eq. (3.6) with \( x(0) = 0 \). The integrated rate law is

\[
k_1 t = \int_0^x \left( \sum_{\alpha=1}^{r} \left[ n_\alpha(0) - x' \right] \right)^{-1} \, dx',
\]

(3.13)

the solution of which depends upon the initial concentrations of the components \( n_\alpha(0) \) for \( r > 1 \). When \( r = 1 \), the solution to eq. (3.13) is

\[
x(t) = n_1(0) \left[ 1 - e^{-k_1 t} \right],
\]

or, equivalently,

\[
n_1(t) = n_1(0) e^{-k_1 t},
\]

which is the familiar equation for first-order exponential decay. If the initial concentrations of all the components in the reaction are equal [i.e., \( n_\alpha(0) = n_{\alpha+1}(0) = n(0), \forall \alpha = 1, \ldots, r-1 \)], eq. (3.13) can be integrated and solved for \( x \) to give

\[
x = n(0) - n(0)^{1-r} + (1-r) k_1 t^{\frac{1}{1-r}}, \quad \forall \ r > 1.
\]

(3.14)

When the reaction is a reversible reaction, the phenomenological rate law is

\[
\dot{x} = k_1 \sum_{\alpha=1}^{r} \left[ n_\alpha(0) - x \right] - k_1' \sum_{\beta=r+1}^{s} \left[ n_\beta(0) + x \right],
\]

(3.12)

which when written in integral form becomes

\[
t = \int_0^x \left( k_1 \sum_{\alpha=1}^{r} \left[ n_\alpha(0) - x' \right] - k_1' \sum_{\beta=r+1}^{s} \left[ n_\beta(0) + x' \right] \right)^{-1} \, dx'.
\]

(3.15)

Eq. (3.15) can be integrated only in very limited cases, such as the second-order \( (r = 2, s = 4) \) case, where the values of \( n_\alpha (\alpha = 1,2) \) are equal, and the initial concentrations of \( n_\beta (\beta = 3,4) \) are zero.

The Hamiltonian approach [11,24,25] to the solution of an irreversible reaction modeled by eq. (3.7) when \( k_1' = 0 \) begins with the reaction rate defined by eq. (3.12) where the reaction coordinate \( x \) is defined by eq. (3.6) without the assumption of \( x(0) = 0 \). Eq. (3.10) implies that the second time derivative of eq. (3.12) is equal to the negative gradient of the potential for the system. Thus, the reaction potential is given by [11,24,25]

\[
V(x) = \frac{1}{2} k_1^2 \sum_{\alpha=1}^{r} \left[ x - x(0) - n_\alpha(0) \right]^2,
\]

which implies that the reaction Hamiltonian is

\[
H(x,y) = \frac{1}{2} y^2 - \frac{1}{2} k_1^2 \sum_{\alpha=1}^{r} \left[ x - x(0) - n_\alpha(0) \right]^2.
\]

(3.17)
The dynamical equations for the chemical reaction are now given by the solution to Hamilton’s equations [eq. 2.28]. The analytic solutions to these equations can be obtained by solving eq. (3.17) using Hamilton-Jacobi theory [18] and, in every instance, agree with those solutions obtained using the phenomenological approach [24,25]. For a reversible reaction [eq. (3.7) with \(k_1' \neq 0\)], the reaction Hamiltonian has the form of eq. (3.11) with a potential given by [11,24,25]

\[
V(x) = -\frac{1}{2} \left[ k_1^2 \sum_{\alpha=1}^{r} \left[ x(x(0) - n_\alpha(0)) \right] \right] \\
+ k_1^2 \sum_{\beta=r+1}^{s} \left[ -x(x(0) - n_\beta(0)) \right] \\
+ k_1 k_1' \sum_{\alpha=1}^{r} \sum_{\beta=r+1}^{r} \left[ x(x(0) - n_\alpha(0)) \right] \\
\times \left[ -x(x(0) - n_\beta(0)) \right].
\]

Although the Hamiltonian formulation of chemical kinetics initially appears more complicated, as the complexity of a chemical system increases, the ability to write a reaction Hamiltonian and to use the solution techniques developed for solving Hamiltonian systems [18,22] improves the chance of obtaining analytic solutions to the rate equations.

### 3. Autocatalytic Reactions [11,26]

Consider a chemical system having a fixed number of reactions \(n\) which are coupled via a single intermediate \(X\):

\[
a_{i\alpha} A_\alpha + c_i^{(1)} X \rightleftharpoons a_{i\alpha}' A'_\alpha + c_i^{(2)} X, \quad (3.18)
\]

\(\forall i = 1,\ldots,n\), where the components \(A_\alpha\) and \(A'_\alpha\), \(\alpha = 1,\ldots,r\), are maintained constant, and the coefficients \(a_{i\alpha}, a_{i\alpha}'\) and \(c_i^{(j)} (j = 1,2)\) for the \(i\)th reaction are non-negative integers [11,26]. An autocatalytic reaction is a reaction which produces as a product a larger quantity of one of the reactants than is used in the reaction. An autocatalytic scheme is a special case of eq. (3.18), where for at least one of the reactions \(c_i^{(2)} > c_i^{(1)}\).

The phenomenological rate law for the above reaction scheme, if \(k_1' = 0\), is

\[
\frac{d[X]}{dt} = \sum_{i=1}^{n} \frac{d[X]^{(i)}}{dt}, \quad (3.19)
\]

where

\[
\frac{d[X]^{(i)}}{dt} = \pm k_1 \left[ A_{\alpha_0} \right]^{a_{i\alpha}} [X]^{c_i^{(1)}} (3.20)
\]

is the rate of change of the concentration of component \(X\) (denoted by \([X]\)) in the \(i\)th reaction. The sign of eq. (3.20) is positive if \(c_i^{(2)} > c_i^{(1)}\) and negative if \(c_i^{(1)} > c_i^{(2)}\). If the reaction scheme is reversible, eq. (3.20) becomes

\[
\frac{d[X]^{(i)}}{dt} = \pm k_1' \left[ A_{\alpha_0}' \right]^{a_{i\alpha}'} [X]^{c_i^{(i)}} \quad (3.21)
\]

\(\pm k_1' \left[ A_{\alpha_0}' \right]^{a_{i\alpha}'} [X]^{c_i^{(2)}}\).

In general eq. (3.19) can only be solved for small \(n\) in terms of known functions.

The development of a reaction Hamiltonian for the chemical system of eq. (3.18) with \(k_1' = 0\) [11,26] begins by defining the reaction coordinate for the system,

\[
x = n_0 + \sum_{i=1}^{n} v_{iX} (x_i - x_0^i),
\]

where \(n_0\) is the initial number of moles of component \(X\), \(x_i\) is the reaction coordinate of the \(i\)th reaction [as defined by eq.(3.6)], and \(v_{iX}\) is the stoichiometric coefficient of \(X\) in the \(i\)th reaction [11,26]. The reaction Hamiltonian for the chemical system represented by eq. (3.18) when \(k_1' = 0\) is [11,26]
\[ H(x,y) = \frac{1}{2} y^2 + \sum_{i=1}^{n} V^i(x) + \sum_{i,j=1 \atop i \neq j}^{n} V^{ij}(x), \]
\[ (3.22) \]

where the potential \( V^i(x) \), given by
\[ V^i(x) = -k^2_1 A^2_{i0} x^2 \epsilon^{(i)}, \]
constitutes the contribution from the \( i \)th reaction, and the potential \( V^{ij}(x) \), given by
\[ V^{ij}(x) = \pm \left[ 4 V^i(x) V^j(x) \right]^{1/2}, \]
represents the coupling between the \( i \)th and \( j \)th reactions, with the sign being determined by the particular set of reactions under consideration. Since every possible combination of binary coupling appears in the Hamiltonian, the total number of coupling terms for a set of \( n \) reactions is \( [11,26] C^{(n)} = n! \left[ 2! \left( n - 2 \right)! \right]^{-1} \). Eq. (3.22) can also be used for reversible reactions by realizing that a set of \( n \) reversible reactions can be written as a set of \( 2n \) irreversible reactions \([11,26]\). Once a reaction Hamiltonian is known, the solution techniques employed in Hamiltonian dynamics can be used to analytically solve the dynamical system \([18,21,22]\).

In the next Section, the phenomenological approach to the solution of simple and autocatalytic reactions will be used to set up dynamical models for some common chemical oscillators.

4. Oscillating Chemical Reactions

In this Section, a brief introduction to chemical systems which exhibit sustained oscillations is presented. This introduction will be expanded in Chapter 4 to a more thorough investigation of one of the models presented below, namely the Lotka-Volterra model. Oscillating chemical reactions are multi-component, multi-step systems which must possess at least one autocatalytic step and have a component which exhibits sustained oscillations in space or time. The autocatalytic step creates a feed-back loop which, in a sequence of chemical reactions, is defined as the inhibition or activation of one step in the reaction by a product of a later step in the reaction.

The simplest reaction scheme which exhibits sustained oscillations in time is the Lotka-Volterra system. This system, originally introduced in 1920 by A. Lotka [27], and later modified by V. Volterra [28] for use in ecology, is modeled by the following set of reactions:

\[ \begin{align*}
A_1 + X_1 & \rightarrow 2 X_1 \\
X_1 + X_2 & \rightarrow 2 X_2 \quad \text{(LV)} \\
A_2 + X_2 & \rightarrow A_2 + A_3.
\end{align*} \]

We assume here that the concentration of \( A_1 \) is held constant by contact with an external reservoir, the concentration of \( A_2 \) is constant during the course of the reaction, and \( A_3 \) is unreactive. Under these conditions, the dynamics of the system are completely defined by the changes in the concentrations of the two autocatalytic intermediates \( X_1 \) and \( X_2 \).

The phenomenological rate laws for the LV reaction scheme are

\[ \begin{align*}
\dot{x}_1 &= a x_1 - b x_1 x_2 \\
\dot{x}_2 &= -c x_2 + b x_1 x_2, \quad (3.23)
\end{align*} \]

where, if the volume of the reaction remains constant during the course of the reaction, \( x_i = [X_i] \) (i=1,2), \( a = k_1 [A_{i0}] \), \( b = k_2 \), and \( c = k_3 [A_{20}] \), with \([A_{i0}]\) symbolizing the initial concentration of the component \( A_i \). Numerical integration of eq. (3.23),
which will be considered further in Chapter 4, shows that the LV model has closed trajectories (see Fig. 3.1), indicating the existence of periodic solutions. Until recently [29], however, the analytic form of these solutions was not known. In Chapter 4, we present the technique used to obtain the analytic solutions to eq. (3.23).

Continued interest in the LV problem is a result of the ease with which it can be modified to model a variety of systems in many different fields. Today, one of the main applications of the Lotka-Volterra system is in modeling the interaction of biological species [30,31], not chemical reactions. However, G. Rabal and co-workers [1] have used the LV scheme, and a modification of this scheme, to model pH regulated oscillating systems which were designed for a continuously stirred tank reactor. The modified reaction scheme which they [1] used is

\[
\begin{align*}
A_1 + A_2 & \rightarrow X_2 \\
A_1 + A_2 + X_1 & \rightarrow A_3 \\
A_1 + X_1 + X_2 & \rightarrow 2X_1 + A_4 .
\end{align*}
\]

The dynamical equations for this system are

\[
\begin{align*}
\dot{x}_1 &= -ax_1 + bx_1x_2 \\
\dot{x}_2 &= c - bx_1x_2 ,
\end{align*}
\]

(3.24)

where \(a = k_2 [A_{10}] [A_{20}]\), \(b = k_3 [A_{10}]\), and \(c = k_1 [A_{10}] [A_{20}]\). This system, which is similar to Lotka’s 1910 reaction scheme [32], has an unstable critical point at \((c/a, a/b)\) [see Fig. 3.2], indicating that the intermediates exhibit forced oscillations (i.e., oscillations that increase in amplitude over time).

The next major advance in the study of chemical oscillators was in 1952, when A. M. Turing [33] showed that a chemical reaction coupled with diffusion could exhibit stable spatial patterns. Later, Prigogine and co-workers [34,35] illustrated this phenomenon with the reaction mechanism

\[
\begin{align*}
A_1 & \rightarrow X_1 \\
A_2 + X_1 & \rightarrow X_2 + A_3 \\
2X_1 + X_2 & \rightarrow 3X_1 \\
X_1 & \rightarrow A_4 .
\end{align*}
\]

Fig. 3.1 Solution curves to eq. (3.23) of text showing the closed trajectories indicative of periodic solutions.

Fig. 3.2 Solution curves to eq. (3.24) of text indicating growing oscillations
This mechanism, and any modifications to this mechanism which possess a 3\textsuperscript{rd} order autocatalytic step, are referred to as the Brusselator [36] (since Prigogine and his associates were working in Brussels at the time). The intermediates $X_1$ and $X_2$ show sustained oscillations in time without including diffusion. If diffusion terms are included, however, spatial patterns also develop.

The phenomenological rate laws, if diffusion is not considered and if the concentrations of $A_i$ ($i=1,\ldots,4$) are constant throughout the course of the reaction, are

$$
\begin{align*}
\dot{x}_1 &= a - b x_1 + c x_1^2 x_2 - d x_1 \\
\dot{x}_2 &= b x_1 - c x_1^2 x_2 ,
\end{align*}
\tag{3.25}
$$

where $a = k_1 \left[A_{10}\right]$, $b = k_2 \left[A_{20}\right]$, $c = k_3$ and $d = k_4$. The solution curves of eq. (3.25) exhibit a stable limit cycle (see Fig. 3.3). A limit cycle is a closed trajectory in configuration space which has the property that every trajectory sufficiently near the limit cycle approaches this cycle either as $t \to \infty$ (a stable limit cycle) or as $t \to -\infty$ (an unstable limit cycle) [13]. When a stable limit cycle exists, the structure of the oscillation will be stable for small perturbations of the initial values of $x_1$ and $x_2$ [13], implying that the qualitative behavior of the oscillations is less dependent on the initial concentrations of the system.

Until recently [37], the LV reaction scheme and the Brusselator were the only two-component reaction mechanisms known which had intermediates exhibiting sustained oscillations. N. Samardzija and co-workers [37] have developed a method which allows them to transform the Van der Pol [12,13] rate equations,

$$
\begin{align*}
\dot{x}_1 &= x_2 \\
\dot{x}_2 &= -x_1 + \mu (1 - x_1^2) x_2 ,
\end{align*}
\tag{3.26}
$$

where $\mu$ is a positive constant, into phenomenological rate laws which can be modeled by a complex (10 step) reaction scheme with intermediates that show sustained oscillations.

The first reaction known to exhibit both spatial and temporal oscillations is the three-component reaction of the cerium-ion catalyzed oxidation of malonic acid by bromate in a sulfuric acid medium [38,39]. The reaction mechanism proposed by Field, Körös, and Noyes (FKN) for this so-called Belousov-Zhabotinksii reaction [2] consists of two processes, as summarized in Table 3.1. The first process, process A, is the reduction of bromate ions by bromide ions through a series of oxygen transfers. When the concentration of the bromide level goes below a certain critical concentration, the reaction switches to the second process, process B, which is the oxidation of Ce(III) by the radical $\text{BrO}_2^-$ species. This reaction autocatalytically produces bromous acid, which is a component in the first process. The Ce(IV) produced by the oxidation of Ce(III) reacts with one of the products of process A to produce the bromide ion. As the concentration of the bromide ion increases past the critical concentration, the reaction switches back to process A. Thus, the bromide ion can be viewed as a delayed negative feed back component [2,5].
Table 3.1  FKN [2,5] mechanism for the Belousov-Zhabotinskii reaction

<table>
<thead>
<tr>
<th>Process A</th>
<th>Process B</th>
<th>Net Reaction</th>
<th>Side Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br}^- + \text{BrO}_3^- + 2 \text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr} )</td>
<td>( \text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2 \text{Br}_2' + \text{H}_2\text{O} )</td>
<td>( \text{BrO}_3^- + 4 \text{Ce(III)} + \text{CH}_2(\text{COOH})_2 + 5 \text{H}^+ \rightarrow 4 \text{Ce(IV)} + 3 \text{H}_2\text{O} + \text{BrCH(COOH)}_2 )</td>
<td>( 6 \text{Ce(IV)} + \text{CH}_2(\text{COOH})_2 + \text{H}_2\text{O} \rightarrow 6 \text{Ce(III)} + \text{HCOOH} + 2 \text{CO}_2 + 6 \text{H}^+ )  ( 4 \text{Ce(IV)} + \text{BrCH(COOH)}_2 + \text{H}_2\text{O} \rightarrow 4 \text{Ce(III)} + \text{HCOOH} + 2 \text{CO}_2 + 5 \text{H}^+ + \text{Br}^- )</td>
</tr>
</tbody>
</table>
A generalization of the FKN mechanism, generally referred to as the Oregonator, leads to the following reaction scheme [2,5]:

\[
\begin{align*}
A_1 + X_2 & \xrightleftharpoons[k_1']{k_1} X_1 \\
X_1 + X_2 & \xrightleftharpoons[k_2']{k_2} X_2 + A_3 \quad \text{(OREG)} \\
A_2 + X_1 & \xrightleftharpoons[k_4']{k_4} 2X_1 + X_3 \\
2X_1 & \xrightleftharpoons[k_5']{k_5} A_4 \\
X_3 & \xrightleftharpoons[k_5']{f} fX_2 ,
\end{align*}
\]

where \( f \) is a stoichiometric factor [5]. If the rate constants for the reverse reactions are close to zero, and the concentrations of \( A_i \), \( i = 1, \ldots, 4 \), are held constant, then the rate laws for the Oregonator can be written

\[
\begin{align*}
\dot{x}_1 &= a x_2 - k_2 x_1 x_2 + b x_1 - 2 k_4 x_1^2 \\
\dot{x}_2 &= -a x_2 - k_2 x_1 x_2 + f k_5 x_3 \quad \text{(3.26)} \\
\dot{x}_3 &= k_3 x_1 - k_5 x_3 ,
\end{align*}
\]

where \( a = k_1 [A_{10}] \) and \( b = k_3 [A_{20}] \). The solutions of eq. (3.26) exhibit stable limit cycle behavior.

Using the law of mass action, N. Samardzija and co-workers [36] have transformed numerous well known multi-dimensional dynamical systems, such as the Rössler rate equations [40], the Lorenz attractor rate equations [41], and the rate equations for the forced Duffing system [42], into phenomenological rate laws which can be used to model large multi-step chemical reaction schemes. The intermediates in these schemes not only show oscillatory behavior but also show chaotic behavior like period-doubling (when the period of the limit cycle successively doubles, causing the system to circulate twice around the cycle before the initial concentrations are restored).

Since the first introduction of chemical reaction schemes which possess rate equations exhibiting sustained oscillations [27], and the discovery of an actual oscillating chemical system [38,39], the theory of oscillating chemical reactions has been an extremely active area of research. Nevertheless, oscillatory phenomena are still not well understood, mainly due to the lack of a sufficiently developed mathematical treatment of the highly nonlinear first-order differential equations which model these systems. In the next chapter, a method for obtaining analytic solutions to conservative dynamical systems possessing two degrees of freedom will be developed and applied to the Lotka-Volterra (LV) model.

**CHAPTER 4**

**THE LOTKA-VOLTERRA MODEL**

1. Introduction

Since the Lotka-Volterra problem was originally posed in 1920 by Lotka [27], it has been one of the most studied models for a two-dimensional dynamical system exhibiting sustained oscillations. Among the reasons for the popularity of this model are the relative simplicity of the differential equations which characterize the system, and the wide applicability of this system to a variety of different physical, chemical and biological problems.

The chemical reaction scheme originally developed by Lotka [27] is
which, when the concentrations of $A_1$, $A_2$, and $A_3$ are assumed to be constant, leads to the rate equations given by eq. (3.23), namely

$$
\dot{x}_1 = a x_1 - b x_1 x_2 , \\
\dot{x}_2 = -c x_2 + b x_1 x_2 ,
$$

where $a$, $b$, and $c$ are as defined in Chapter 3. V. Volterra [28] later recast this model in terms of the populations of two interacting biological species, where one species preys upon the other. Both Lotka [27] and Volterra [28] generalized the two species model [eq. (3.23)] to an n-dimensional system (GLV) modeled by the rate equations

$$
\dot{x}_i = \varepsilon_i x_i + \frac{1}{\beta_i} \sum_{j=1}^{n} \alpha_{ij} x_i x_j , \forall i=1,\ldots,n , \quad (4.1)
$$

where $\varepsilon_i$ is the coefficient of increase or decrease of the $i$th species, $\beta_i$ measures the strength of coupling of the $i$th species to predator-prey interactions, and $\alpha_{ij}$ gauges the interaction between the $i$th and the $j$th species.

The LV and GLV models have been adapted and applied to neural networks [43], epidemiology [44], and mode-specific coupling in lasers [45], as well as being used in population biology [30,46] and chemical kinetics [1,47]. Recently, V. Fairen and B. Hernández-Bermejo [48] showed that any set of kinetic equations can be associated to an equivalent GLV representation by the introduction of suitable collective variables. These results have later been expanded for application to general nonlinear systems [49].

Despite the increasing number of LV applications, the analytic solutions to this problem have never been explicitly determined until the present work. Since the original publications [27,28], the system was known to be conservative, thus implying that the solutions are periodic, but the analytic form of the solutions was unknown. Many different techniques have been applied and developed in the attempt to derive analytic solutions to the LV model. One of the first methods applied when trying to determine the nature of the solutions to an ordinary differential equation is numerical integration, since the numerical integration of an equation generates data which can then be plotted allowing for the visualization of solution curves. The technique of numerical integration will be discussed and applied to the LV model later in this Chapter. Another traditional approach is linearization of the rate equations in order to simplify the system [50]. The linearization of the LV model [51] leads to the rate equations

$$
\dot{x}_1 = -c x_2 + \frac{a c}{b} , \\
\dot{x}_2 = a x_1 - \frac{a c}{b} ,
$$

which are the familiar differential equations for the harmonic oscillator, and which have the general solutions [51]

$$
x_1(t) = A + B \cos \omega t + C \sin \omega t , \\
x_2(t) = D + E \cos \omega t + F \sin \omega t ,
$$

where $A$, $B$, $C$, $D$, $E$, $F$ (not all independent) are determined by the initial conditions, and $\omega$ is determined by $a$, $b$, and $c$. Other methods used in order to attempt to determine directly analytic solutions to eq. (3.23) have included decomposition methods [52], iterative solution techniques [53], and perturbation techniques [54,55]. None of these methods leads directly to
analytic solutions to the LV model. Later in this Chapter, we present a direct method involving a transformation which uses the invariant of the LV system to derive the form of the analytic solutions to eq. (3.23).

Another approach to obtaining analytic solutions to the LV problem is to analyze the invariant, or first integral, of the system, since the existence of a first integral reduces the system to a one-dimensional problem. Since Lotka’s 1920 paper [27], the form of the first integral of eq. (3.23), namely

$$\Lambda = b x_1 + b x_2 - c \ln x_1 - a \ln x_2 , \quad (4.2)$$

has been known. Normally when the invariant for a two-dimensional system is known, the invariant can be used to eliminate one of the variables. However, eq. (4.2) cannot be easily solved for either $x_1$ or $x_2$ once given a fixed $\Lambda$. The inability to solve eq. (4.2) in a straightforward manner has led to the development of Hamiltonian forms for the LV model. In the 1960s, E. H. Kerner [56] showed that a simple logarithmic transformation of eq. (3.23) allows the LV model to be written in Hamiltonian form with the transformed eq. (4.2) being the Hamiltonian. Kerner then expanded this logarithmic transformation to make it applicable to the GLV system [eq. (4.1)]. Recent interest in the Hamiltonian nature of the LV problem has led to the rediscovery of this transformation for both the two-dimensional and multi-dimensional cases [57-60]. The ability to write a Hamiltonian for the LV model led R. Dutt [61] in the 1970s to apply Hamilton-Jacobi theory to Kerner’s Hamiltonian, but because of the nontraditional form of the Hamiltonian, only approximate solutions to the rate equations could be obtained. In an attempt to develop a traditional Hamiltonian for the LV model, T. Georgian and G. L. Findley [11] transformed the two-dimensional LV system into a four dimensional system involving both the rate equations and the acceleration equations. Later in this Chapter the Hamiltonian nature of the two-dimensional LV model will be discussed in greater detail.

The form of the invariants for the GLV model [eq. (4.1)] has been an important area of research in the past few years. L. Cairó and M. R. Feix [62] used a Carleman embedding method [63] to develop the linear polynomial family of invariants for the GLV model, whereas B. Grammaticos and co-workers [64] used a method based on the Frobenius integrability theorem [65] to develop the same invariants for the three-dimensional case.

The study done by Grammaticos and co-workers was later clarified by S. Labrunie [66], who derived the conditions which must be satisfied by polynomial first-integrals for the three dimensional LV system. Another technique used by M. A. Almeida and co-workers [67] to determine the invariants for the GLV model is a Lie symmetry analysis [68]. The Lie symmetry method permitted M. A. Almeida and co-workers to determine conditions on the constants $\epsilon_i$, $\beta_i$, $\alpha_{ij}$ in eq. (4.1) which allow for the existence of first integrals. As in the two-dimensional case, the existence of invariants for the GLV system has led to the study of the Hamiltonian nature of the GLV system [69,70] in an attempt to develop analytic solutions to the GLV model.

Although a large amount of research has been done on the conservative nature and Hamiltonian forms of the LV and GLV systems, none of this research has led to analytic solutions for either model until now. In this Chapter, we present (for background purposes) a simple technique for numerically integrating eq. (3.23). Then, with the use of eq. (4.2), a coordinate transformation is introduced to reduce the LV system to a one-dimensional problem, which can be modeled by a second-order nonlinear ordinary differential equation. This characteristic differential equation is then formally integrated to give the quadrature which represents the analytic solution to the LV problem. Finally, the Hamiltonian nature of the LV model is explored from a novel perspective.
2. Numerical Integration

In the study of nonlinear differential equations, analytic solutions are usually unknown; therefore, one of the first steps in analyzing a nonlinear system is the numerical integration of the differential equations for different initial conditions. Numerical integration generates a set of data which can be plotted, thus allowing visualization of the solution curves which can help to determine the stability of the system (as well as other qualitative properties). Because of the frequency with which this technique is used, many different methods for numerical integration have been developed; all of these techniques can be placed into one of three subdivisions, however: extrapolation/interpolation, single-step methods, or multi-step methods [71]. In this Section, a brief introduction to these methods will be given, and then a detailed explanation of one type of single-step method, namely the Runge-Kutta method, will be presented and applied to the LV model.

**Extrapolation/interpolation** methods involve the approximation of an integral of the function \( f(t) \) over some interval \((a,b)\) by a summation. In other words [72],

\[
\int_{a}^{b} f(t) \, dt \approx \sum_{i=0}^{n} c_{i} f(t_{i}) ,
\]

where the form of \( c_{i} \) and \( t_{i} \) are determined by the method used, and where \( n \) determines the level of approximation. (For example, in the Newton-Cotes (NC) methods \( t_{i} = t_{0} + i \, h, \quad \forall \, i = 0, \ldots, n \), with \( h = (b-a)/n \), \( t_{0} = a \) and \( t_{n} = b \) for a closed NC method, and \( h = (b-a)/(n+2) \), \( t_{0} = a+h \), and \( t_{n} = b-h \) for an open NC method.) This method can only be used if the differential equation can be written as a first-order, separable differential equation. (A *separable* differential equation in this context is a differential equation which can be written in the form \( \dot{x} = f(t) \, g(x) \).)

**Single-step and multi-step** methods use weighted average values of \( f(x,t) \) taken at different points in the interval \( t_{0} \leq t \leq t_{n+1} \). This weighted average is defined by [71]

\[
x_{n+k} = \sum_{i=1}^{k} \alpha_{i} x_{n+i} + h \sum_{i=1}^{k} \beta_{i} \dot{x}_{n+i} ,
\]

where \( h \) is the step size, or distance between the points along an interval, and \( \alpha_{i} \) and \( \beta_{i} \) are constants \( \forall \, i = 1, \ldots, k \). If \( k = 1 \), implying that the value of \( x \) is dependent on the previous step only, the method is a single-step method. If \( k > 1 \), the value of \( x \) is dependent on several previous steps, and the method is known as multi-step. The technique used for determining the constants \( \alpha_{i} \) and \( \beta_{i} \) separate the different single-step or multi-step methods [71]. Common single-step methods include the Euler, or tangent-line method, and the Runge-Kutta method. Common multi-step methods are the Milne Predictor-Corrector method and the Adams-Moulton methods. The most popular method for numerical integration, because of the accuracy and ease of programming, is the single-step Runge-Kutta method which will now be discussed in more detail.

The single-step Runge-Kutta method involves the general equation [71]

\[
x_{n+1} = x_{n} + \sum_{i=1}^{r} w_{i} k_{i} ,
\]

where \( w_{i} \) is a weighting coefficient to be determined, \( r \) is the number of \( f(t,x) \) substitutions, and

\[
k_{i} = h \left\{ t_{n} + c_{i} \, h , \quad x_{n} + \sum_{j=1}^{i-1} a_{ij} k_{j} \right\} ,
\]

\[
c_{i} = 0 , \quad \forall \, i = 1, \ldots, r .
\]

The determination of the parameters \( w_{i}, c_{i}, \) and \( a_{ij} \) is done by Taylor series expansion of \( x_{n+1} \) in powers of \( h \), such that this expansion agrees with the solution of the differential equations to a specified number of terms in the Taylor series [71].
The number $r$ of terms in the Taylor series defines
the order of the Runge-Kutta method. The local
truncation error for a general Runge-Kutta method
is proportional to $h^{r+1}$, and the global truncation
error for a finite interval is proportional to $h^r$ [51].
Since both the error and the stability of the
numerical integration using a Runge-Kutta method
are related to the step-size $h$ chosen for the
integration [71], J. B. Rosser [73] has developed
techniques which allow the step-size to be adjusted
during the numerical integration. This modification
allows the Runge-Kutta methods to be used for stiff
differential equations. (A stiff differential equation
is one which has at least one rapidly decaying
solution [50,71].)

The most common Runge-Kutta method used
for numerical integration is the classic fourth-order
Runge-Kutta. This method can be applied to both
first-order and second-order differential equations
with only slight modifications to the general Runge-
Kutta formula. The general fourth-order Runge-
Kutta formula for numerical integration of a first
order differential equation $[\ddot{x} = f(t, x)]$ is [74]

$$ x^{(n+1)} = x^{(n)} + h \left( \frac{k_1^{(n)}}{6} + k_2^{(n)} + 2 k_3^{(n)} + k_4^{(n)} \right), \tag{4.3} $$

where

$$ k_1^{(n)} = f(t^{(n)}, x^{(n)}) $$

$$ k_2^{(n)} = f\left( t^{(n)} + \frac{h}{2}, x^{(n)} + \frac{h}{2} k_1^{(n)} \right) $$

$$ k_3^{(n)} = f\left( t^{(n)} + \frac{h}{2}, x^{(n)} + \frac{h}{2} k_2^{(n)} \right) $$

$$ k_4^{(n)} = f\left( t^{(n)} + h, x^{(n)} + h k_3^{(n)} \right). $$

When the differential equation is a second-order
differential equation $[\ddot{x} = f(t, x, \dot{x})]$, the numerical
integration formula becomes

$$ x^{(n+1)} = x^{(n)} + h \left( \frac{\dot{x}^{(n)}}{6} + \frac{h}{6} \left( k_1^{(n)} + 2 k_2^{(n)} + k_3^{(n)} + k_4^{(n)} \right) \right), \tag{4.4} $$

where

$$ k_1^{(n)} = f(t, x^{(n)}, \dot{x}^{(n)}) $$

$$ k_2^{(n)} = f\left( t + \frac{h}{2}, x^{(n)} + \frac{h}{2} \dot{x}^{(n)} + \frac{h}{8} k_1^{(n)} \right) $$

$$ k_3^{(n)} = f\left( t + \frac{h}{2}, x^{(n)} + \frac{h}{2} \dot{x}^{(n)} + \frac{h}{8} k_2^{(n)} \right) $$

$$ k_4^{(n)} = f\left( t + h, x^{(n)} + h \dot{x}^{(n)} + \frac{h}{2} k_3^{(n)} \right). $$

All of the solution curves which are used as figure
illustrations in the present work were obtained by
numerically integrating the relevant differential
equations using one of the two Runge-Kutta
methods presented above.

The numerical integration of the LV system can
be accomplished in three different ways using a
fourth-order Runge-Kutta technique. Each of these
methods produces the same numerical results, although the stability of the integration for different initial conditions differs for each method. The first method is the direct numerical integration of eq. (3.23) using eq. (4.3). This method is easily coded as an executable program (cf. Appendix 2), or even as a macro in a spreadsheet, making the data easily accessible for analysis. This integration of the rate equations is stable over a wide range of initial conditions. The second method involves the numerical integration of the second time derivatives of eq. (3.23), namely
\[
\begin{align*}
\dot{x}_1 &= a^2 x_1 - b^2 x_1^2 x_2 + b^2 x_1 x_2^2 \\
&\quad + b (c - 2a) x_1 x_2 \\
\dot{x}_2 &= c^2 x_2 + b^2 x_1^2 x_2 - b^2 x_1 x_2^2 \\
&\quad + b (a - 2c) x_1 x_2 ,
\end{align*}
\]
(4.5)
using a modification of eq. (4.4). Although this method produces the same numerical results, it is not as stable as the first method, which means that this method cannot be used for extreme initial conditions. The final method numerically integrates the four-dimensional system derived by expressing eq. (4.5) as a system of first-order differential equations. This method proved to be the least stable of the three methods used for numerical integration. The full equations employed in the numerical integration for all three methods are given in Appendix 1.

The numerical integration of the LV system [eq. (3.23)] allows for the shape of the solution curves to be visualized. The solution curves for \(x_1\) and \(x_2\) are doubly periodic functions, with the solution of \(x_2\) being slightly out of phase with respect to \(x_1\) (see Fig. 4.1). This double periodicity suggests that the solutions to eq. (3.23) are related to the family of elliptic functions [74]. Later in this work, the relationship between the analytic solutions to the LV problem, which will be derived in the next section, and the elliptic functions will be shown.

Fig. 4.1 The solutions of eq. (3.23) of text showing the doubly periodic nature of \(x_1\) and \(x_2\). (Curves are for the constant values \(a = 0.50\), \(b = 1.30\), and \(c = 0.67\) and the initial conditions \(x_i(0) = 0.90\) and \(x_i(0) = 0.30\).)

3. Analytic Solutions [29]

The numerical integration of the LV problem allows the solution curves to be visualized, but does not give the form of the analytic solution. In this section, a simple coordinate transformation will be presented which reduces the LV system to a one-dimensional problem characterized by a second-order nonlinear autonomous ordinary differential equation. The integral quadrature which represents the solution to this differential equation is then derived.

The development of the analytic solution to eq. (3.23) begins by using the invariant \(\Lambda\) [eq. (4.2)] to define new coordinates \(z_1(t)\) and \(z_2(t)\) such that
\[
z_1^2 + z_2^2 = 1
\]
(4.6)
Several different ways of partitioning eq. (4.2) into two new coordinates consistent with eq. (4.6) are possible. We choose to define the new coordinates by placing the linear terms of the invariant into one coordinate, and the nonlinear terms of the invariant into another, to give
\[
\begin{align*}
z_1 &= \left(\frac{b}{\Lambda} (x_1 + x_2)\right)^{1/2} \\
z_2 &= \left(-\frac{1}{\Lambda} (c \ln x_1 + a \ln x_2)\right)^{1/2}
\end{align*}
\]
(4.7)
This choice allows for the original coordinates \(x_1\)
and \( x_2 \) to be expressed in terms of the new coordinates as

\[
x_1 = \frac{\Lambda}{b(a + c)}(c z_1^2 - 2 z_2 \dot{z}_2) \quad (4.8)
\]

\[
x_2 = \frac{\Lambda}{b(a + c)}(a z_1^2 + 2 z_2 \dot{z}_2).
\]

Because of eq. (4.6), the new coordinates can be written as a single angle \( \Phi \) defined by

\[
\tan \Phi = \frac{z_1}{z_2}.
\]

With \( z_1 \) and \( z_2 \) now being defined as

\[
z_1 = \sin \Phi \quad z_2 = \cos \Phi,
\]

both eq. (3.23) and the time derivative of eq. (4.2) reduce to the same second-order nonlinear autonomous ordinary differential equation, namely

\[
\ddot{\Phi} + \left[ \cot \Phi - \tan \Phi - \frac{2 \Lambda}{a + c} \cos \Phi \sin \Phi \right] \dot{\Phi}^2
\]

\[
+ (c - a) \left( 1 - \frac{\Lambda}{a + c} \sin^2 \Phi \right) \dot{\Phi}
\]

\[
- \frac{1}{2} a c \left( 1 - \frac{\Lambda}{a + c} \right) \tan \Phi
\]

\[
- \frac{1}{2} a c \frac{\Lambda}{a + c} \sin \Phi \cos \Phi = 0.
\]

Since solving eq. (4.10) is equivalent to solving the rate equations for the LV model [i.e., eq. (3.23)], simplification of eq. (4.10) is in order. By defining a new angle \( \Phi = 2 \Phi \), and by using the half-angle formulas [72], eq. (4.10) reduces to

\[
\ddot{\Phi} + \left[ \cot \Phi - \frac{1}{2} \frac{\Lambda}{a + c} \sin \Phi \right] \dot{\Phi}^2 + \frac{1}{2} (c - a) \left[ 2 - \frac{\Lambda}{a + c} (1 - \cos \Phi) \right] \dot{\Phi}
\]

\[
+ \frac{1}{2} a c \left[ 2 - \frac{\Lambda}{a + c} (1 - \cos \Phi) \right] (\cot \Phi - \csc \Phi) = 0.
\]

Eq. (4.11) still cannot be solved formally as yet, but it can be further simplified by defining a new variable \( w \) as

\[
w = \frac{1}{2} \frac{\Lambda}{a + c} (1 - \cos \Phi),
\]

which reduces eq. (4.11) to

\[
\ddot{w} - \dot{w}^2 - (c - a) (w - 1) \dot{w}
\]

\[
+ a c w (w - 1) = 0.
\]

Transforming eq. (4.8) to the new variable gives the values of the original coordinates \( x_1 \) and \( x_2 \) as

\[
x_1 = \frac{1}{b} (c w + \dot{w}),
\]

\[
x_2 = \frac{1}{b} (a w - \dot{w}).
\]

Eq. (4.13) can be formally integrated using a symbolic processor [75] for the special case of \( a = c \) to give the analytic solution (via quadrature)

\[
t - t_0 = \pm \int_0^w \frac{dw'}{\left[ \frac{a^2}{w'^2} + w_0 e^{2 w'} \right]^{1/2}},
\]

where \( t_0 \) and \( w_0 \) are dependent on initial data. Eq. (4.15) represents a new function. Numerical analysis of eq. (4.13) using eq. (4.3) shows that the implicit function \( w \) is doubly periodic (see Fig. 4.2), indicating a relationship to the Jacobian elliptic functions [74]. This relationship will be explored further in the next Chapter.

When \( c \neq a \), the solution of eq. (4.13) is more problematic, but straightforward. The first step in solving eq. (4.13) is the rearrangement of
where \( t_0 \) is an initial datum and \( \rho \) solves
\[
\alpha a \left[ b a (\alpha + 1) w' - b \alpha a e^p \right] + k^2 \left( \frac{\alpha a}{b} \right)^{-\alpha} e^{(\alpha + 1) w'} e^{-\alpha \rho} = 0 .
\]

When \( \alpha = 1 \) (\( a = c \)), eq. (4.19) reduces to eq. (4.15), with \( w_0 = k^2 \).

Even though eq. (4.18) cannot be integrated in terms of known elementary functions, it does represent the analytic solution to the LV problem, since substitution of the values of \( w \) and \( \dot{w} \) obtained from a numerical integration of eq. (4.18) into eq. (4.14) generates the same solutions as a direct numerical integration of eq. (3.23). An introductory analysis of eq. (4.18) using a power series expansion will be presented in the next Chapter in the context of generating analytical solutions to a LV-related family of differential equations.

4. Hamiltonians

As mentioned in Section 4.1, a great deal of interest has been expressed in the Hamiltonian form of the LV model, mainly because of the powerful solution techniques which can be applied if a Hamiltonian exists. Although the analytic solution to the LV model was derived in the last Section without using a Hamiltonian technique, in this Section we will review different approaches to developing Hamiltonians for the LV problem, since Hamiltonian methods are important when considering the symmetry of the system.

In the 1960s, while studying the dynamical aspects of chemical kinetics, E. H. Kerner [56] showed that the LV model could be placed into Hamiltonian form using a simple logarithmic transformation. This transformation defined the position \( q \) and the momentum \( p \) as [56]
\[
q = \ln x_2 , \quad p = \ln x_1 ,
\]
which allowed the rate equations to be written as
\[
\dot{q} = - (b \ e^p - a), \quad \dot{p} = b \ e^q - c.
\]
The invariant for the transformed system is the Hamiltonian and is defined by [56]
\[
H = b \ e^q + b \ e^p - c p - a q, \quad (4.21)
\]
which by direct differentiation with respect to q and p yields Hamilton’s equations. This Hamiltonian, however, because of its nontraditional nature, cannot be solved using Hamilton-Jacobi theory or any of the other advanced solution techniques that Hamiltonian dynamics allows. (A traditional Hamiltonian is defined by an invariant having the form of eq. (2.27).)

In an attempt to develop a more traditional Hamiltonian, T. Georgian and G. L. Findley defined a possible reaction Hamiltonian as [11]
\[
H = \frac{1}{2} (y_1^2 + y_2^2) - \frac{1}{2} (a^2 x_1^2 + c^2 x_2^2)
\]
\[
+ b^2 x_1^2 x_2^2 - b \ zeta x_1 x_2, \quad (4.22)
\]
where \( y_i = \dot{x}_i \), and
\[
\zeta = - b x_1^2 + (c - 2 a) x_1
\]
\[
= - b x_2^2 + (a - 2 c) x_2, \quad (4.23)
\]
which comes from assuming that \( \partial_2 \dot{x}_1 = \partial_1 \dot{x}_2 \) (\( \partial_i \) = \( \partial/\partial x_i \) for i = 1,2). Eq. (4.23) was proposed initially as a holonomic constraint [11]. However, the Hamiltonian represented by eq. (4.22) is not constant because the condition implied by eq. (4.23) does not hold for any arbitrary trajectory (although it does hold for the critical point). This approach does allow, however, for modifications in terms of a coordinate transformation and an integrating factor.

We begin the modification of eq. (4.22) by defining new coordinates \( q_1 \) and \( q_2 \) such that
\[
q_1 = \ln x_1, \quad q_2 = \ln x_2, \quad (4.24)
\]
which transform the rate equations [eq. (3.23)] to
\[
\dot{q}_1 = - (b \ e^{q_2} - a), \quad \dot{q}_2 = b \ e^{q_1} - c. \quad (4.25)
\]
This transformation is similar to the transformation which Kerner applied [56], except that both of the original coordinates are kept as position coordinates. The Hamiltonian for the system can now be defined by
\[
H = \frac{\mu}{2} (p_1^2 + p_2^2) + V(q_1, q_2), \quad (4.26)
\]
where the form of the conjugate momenta \( p_i (i = 1,2) \) will be discussed below, \( \mu = \mu(p_1, p_2) \) is an integrating factor which will also be discussed below, and V is a potential which solves
\[
\frac{dV}{V} = V_{q_1} \, dq_1 + V_{q_2} \, dq_2 = 0 \quad (4.27)
\]
with \( \ddot{q}_i \) being the accelerations and \( \xi = \xi(q_1, q_2) \). The acceleration equations, derived by taking the second time derivative of eq. (4.25), are
\[
\ddot{q}_1 = - b \ e^{q_1} (b \ e^{q_2} - c), \quad (4.28)
\]
\[
\ddot{q}_2 = - b \ e^{q_2} (b \ e^{q_1} - a).
\]
In order for eq. (4.27) to be satisfied and for dV to be an exact differential, the second derivatives of the potential must commute. In other words,
\[
\partial_2 (\xi \dot{q}_1) = \partial_1 (\xi \dot{q}_2), \quad (4.29)
\]
which gives the characteristic partial differential equation in terms of \( \xi \) as
\[
\xi_{q_2} \ddot{q}_1 - \xi_{q_1} \ddot{q}_2 = \xi \left[ b \ e^{q_1} (b \ e^{q_2} - c)
\]
\[
- b \ e^{q_1} (b \ e^{q_2} - a) \right]. \quad (4.30)
\]
The solution of eq. (4.30) for \( \xi \), which defines the potential since
\[ V = b \, e^{q_1} \int \xi (b \, e^{q_1} - c) \, dq_1 + b \, e^{q_1} \int \xi (b \, e^{q_2} - a) \, dq_2 - \int \partial_1 \left[ \xi b \, e^{q_1} (b \, e^{q_2} - a) \right] dq_1 \, dq_2 , \]

\[(4.31)\]

begins by defining a new function \( \beta(q_1, q_2) \) such that

\[ \frac{V_1}{V_2} = \left( \frac{b \, e^{q_1} - c}{e^{q_1}} \right) \times \left( \frac{e^{q_2}}{b \, e^{q_2} - a} \right) = \frac{\beta_1}{\beta_2} , \]

\[(4.32)\]

which is solved by

\[ \beta = b \, q_1 + b \, q_2 + \frac{a}{e^{q_2}} + \frac{c}{e^{q_1}} . \]

\[(4.33)\]

If the potential is defined as \( V = -\beta \), then the accelerations \([eq. (4.28)]\) can be written as

\[ \ddot{q}_1 = -\frac{\beta_1}{\xi} , \quad \ddot{q}_2 = -\frac{\beta_2}{\xi} , \]

\[(4.34)\]

with \( \xi \) being defined as

\[ \xi = -\frac{1}{b \, e^{q_1} e^{q_2}} . \]

\[(4.35)\]

Thus, the Hamiltonian is now

\[ H = \frac{\mu}{2} (p_1^2 + p_2^2) - b \, q_1 - b \, q_2 - \frac{a}{e^{q_2}} - \frac{c}{e^{q_1}} . \]

\[(4.36)\]

Hamilton’s equations \([eq. (2.28)]\) imply that

\[ \dot{q}_1 = \frac{1}{2} ( p_1^2 + p_2^2 ) \frac{\partial \mu}{\partial p_1} + \mu p_1 \]

\[ \dot{q}_2 = \frac{1}{2} ( p_1^2 + p_2^2 ) \frac{\partial \mu}{\partial p_2} + \mu p_2 \]

\[(4.37)\]

\[ \dot{p}_1 = -b + \frac{c}{e^{q_1}} , \]

\[ \dot{p}_2 = -b + \frac{a}{e^{q_2}} , \]

which can be used to develop relationships for \( p_i (i = 1, 2) \), as well as the form of the function \( \mu \). At this time, we have not investigated the functional form for either \( p_i \) or \( \mu \) other than the relationships given in eq. \((4.37)\).

Another method which can be used to develop a Hamiltonian for the LV system also uses the coordinate transformation represented by eq. \((4.24)\). G. D. Birkoff \[76\] showed that any dynamical system with two degrees of freedom can be transformed into a system possessing a Lagrangian

\[ L = \frac{1}{2} ( \dot{q}_1^2 + \dot{q}_2^2 ) + \alpha_1 \dot{q}_1 + \alpha_2 \dot{q}_2 + \gamma , \]

\[(4.38)\]

where \( \alpha_i (i = 1, 2) \) and \( \gamma \) are functions of \( q_1 \) and \( q_2 \) only, and satisfy the following conditions:

\[ (I) \quad \ddot{q}_1 + \lambda \, \dot{q}_2 = \frac{\partial \gamma}{\partial q_1} \]

\[(4.39)\]

\[ (II) \quad \ddot{q}_2 - \lambda \, \dot{q}_1 = \frac{\partial \gamma}{\partial q_2} \]

\[ (III) \quad \lambda = \frac{\partial \alpha_1}{\partial q_2} - \frac{\partial \alpha_2}{\partial q_1} . \]

A Legendre transformation of eq. \((4.38)\) defines the Hamiltonian as
\[ H = \frac{1}{2} \left[ (p_1 - \alpha_1)^2 + (p_2 - \alpha_2)^2 \right] - \gamma, \quad (4.40) \]

where the conjugate momenta \( p_i \) are defined by

\[ p_1 = \frac{\partial L}{\partial \dot{q}_1} = \dot{q}_1 + \alpha_1, \quad (4.41) \]
\[ p_2 = \frac{\partial L}{\partial \dot{q}_2} = \dot{q}_2 + \alpha_2, \quad (4.41) \]

and where the potential \( \gamma \) is determined by eq. (4.39). If we want the system to satisfy the condition that the time derivative of the momenta equal the accelerations, then \( \alpha_1 \) and \( \alpha_2 \) must be constants for any set of initial conditions. Therefore, we define \( \alpha_1 \) and \( \alpha_2 \) as

\[ \alpha_1 = \Lambda, \quad \alpha_2 = -\Lambda, \quad (4.42) \]

since \( \Lambda \) is invariant for any set of initial conditions. Substitution of eq. (4.42) into eq. (4.39) gives the partial differential equations which the potential must solve. Since the second derivatives of \( \gamma \) commute, eq. (4.39) can be integrated to define the potential as

\[ \gamma = \frac{1}{2} b^2 \left( e^{2 q_1} + e^{2 q_2} \right) - b \left( c e^{q_1} + a e^{q_2} \right) - (a + c) \Lambda. \quad (4.43) \]

With this definition of the potential, the Hamiltonian becomes

\[ H = \frac{1}{2} \left[ (p_1 - \Lambda)^2 + (p_2 + \Lambda)^2 \right] - \frac{1}{2} b^2 \left( e^{2 q_1} + e^{2 q_2} \right) + b \left( c e^{q_1} + a e^{q_2} \right) + (a + c) \Lambda, \quad (4.44) \]

with the derivatives being given as follows:

\[ \frac{\partial H}{\partial p_1} = p_1 - \Lambda = \dot{q}_1 \]
\[ \frac{\partial H}{\partial p_2} = p_2 + \Lambda = \dot{q}_2 \]
\[ \frac{\partial H}{\partial q_1} = \left[ (p_2 + \Lambda) - (p_1 - \Lambda) \right] \times \left( b e^{q_1} - c \right) - \frac{\partial \gamma}{\partial q_1} = -\dot{p}_1 \]
\[ \frac{\partial H}{\partial q_2} = \left[ (p_2 + \Lambda) - (p_1 - \Lambda) \right] \times \left( b e^{q_2} - a \right) - \frac{\partial \gamma}{\partial q_2} = -\dot{p}_2. \quad (4.45) \]

The partial derivatives of the potential \( \gamma \) are:

\[ \frac{\partial \gamma}{\partial q_1} = (b e^{q_1} - c) \left[ (b e^{q_1} - c) + (b e^{q_2} - a) - b e^{q_2} \right] \]
\[ + (b e^{q_2} - a) - b e^{q_1} \]
\[ \frac{\partial \gamma}{\partial q_2} = (b e^{q_2} - a) \left[ (b e^{q_1} - c) + (b e^{q_2} - a) - b e^{q_1} \right]. \]

The Hamiltonian represented by eq. (4.44) is in the traditional form, but with a velocity dependent potential.

Since the system being characterized by eq. (4.44) is a four-dimensional system, three constants of the motion should exist. Two of the constants, namely the original invariant [eq. (4.2)] and the Hamiltonian [eq. (4.44)], have now been developed. As discussed in Chapter 2, the Hamiltonian for a dynamical system can be used to find the other constants of the motion by
construction of a Poisson bracket. If $f(q,p)$ is an invariant for the dynamical system, then the Poisson bracket of $f(q,p)$ with $H$ [eq. (4.44)] can be reduced using eq. (4.45) to the condition

$$\left( \frac{\partial f}{\partial q_1} + b e^{q_1} \frac{\partial f}{\partial p_2} \right) \dot{q}_1 + \left( \frac{\partial f}{\partial q_2} - b e^{q_2} \frac{\partial f}{\partial p_1} \right) \dot{q}_2 = 0 .$$

(4.46)

One approach to solving eq. (4.46) is to define a function $\Psi$ such that

$$\frac{\partial \Psi}{\partial q_1} + b e^{q_1} \frac{\partial \Psi}{\partial p_2} = b e^{q_1} - c ,$$

$$\frac{\partial \Psi}{\partial q_2} - b e^{q_2} \frac{\partial \Psi}{\partial p_1} = b e^{q_2} - a ,$$

which is solved by

$$\Psi = p_2 - p_1 - c q_1 - a q_2 .$$

(4.47)

The existence of three independent invariants (represented by $\Lambda$ [eq. (4.2)], $H$ [eq. (4.44)] and $\Psi$ [eq. (4.47)]) implies that the system is completely integrable. (The linear independence of the three invariants was checked by computing the Jacobian of the system, which is non-zero.) Complete integrability implies that the LV system can be represented by one independent variable, which was shown explicitly in the last section.

CHAPTER 5

LOTKA-VOLTERRA RELATED FAMILY OF DIFFERENTIAL EQUATIONS

1. Development [77]

As mentioned in Chapter 4, the technique used to solve the LV model leads to a family of LV-related differential equations. In this Chapter, this family will be derived, and the analytic solutions (which represent approximate solutions to the LV model) will be presented. The family of invariants for this system will be developed, and a simple transformation will be shown which allows these systems to be written in Hamiltonian form.

In Section 4.3, the rate equations for the LV model were rewritten as [eq. (4.17)]

$$\dot{x}_1 = a x_1 + \frac{k^2}{b} x_1^{1-\alpha} e^{b(x_1 + x_2)/a}$$

$$\dot{x}_2 = -a x_2 - \frac{k^2}{b} x_1^{1-\alpha} e^{b(x_1 + x_2)/a} ,$$

where $k^2 = -b^2 e^{-\Lambda/a}$. Introducing a power series expansion for the exponential term yields

$$\dot{x}_1 = a x_1 + \frac{k^2}{b} x_1^{1-\alpha}$$

$$\times \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m ,$$

(5.1)

$$\dot{x}_2 = -a x_2 - \frac{k^2}{b} x_1^{1-\alpha}$$

$$\times \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m .$$

A family of differential equations related to the LV model can be derived by truncating the power series in eq. (5.1) to give

$$\dot{x}_1 = a x_1 + \frac{k^2}{b} x_1^{1-\alpha}$$

$$\times \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m ,$$

(5.2)

$$\dot{x}_2 = -a x_2 - \frac{k^2}{b} x_1^{1-\alpha}$$

$$\times \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m ,$$
for $n = 0, \ldots, \infty$, with $n = \infty$ corresponding to the LV model. (Although the value of $k^2$ can be any negative number, for the system to become the LV model as $n \to \infty$, $k$ must be defined by $k^2 = - b^2 \ e^{-\Lambda/a}$, where $\Lambda$ is the value of eq. (4.2) at $t = 0$.) The family of differential equations represented by eq. (5.2), even though it appears to be more complicated than the original LV problem, will be shown in the next Section to possess analytic solutions in terms of known functions for the cases when $\alpha = 1$ and $n \leq 3$. The integral quadrature for the cases of $n = 2$ and $n = 3$ will also be presented. Numerical integration of eq. (5.2) shows that for $n \geq 2$, the solution curves are closed, which implies the existence of periodic solutions (see Fig. 5.1). Thus, eq. (5.2) represents a family of two-dimensional dynamical systems which show sustained oscillations.

Eq. (5.2) may have applications in a variety of areas. In the 1970s, J. J. Tyson and J. C. Light [6] developed a technique for deriving two-component reaction schemes modeled by equations similar to this family. (Due to the complexity of the rate laws, however, no attempt was made to obtain analytic solutions.) Another area in which this family may have applications is population biology, since eq. (5.2), when $n = 2$ and $\alpha = 1$, has the quadratic coupling term which appears in the LV predator-prey model

$$\ddot{w} - a \ (1 - \alpha) \dot{w} - a^2 \alpha \ w$$

$$- k^2 \left[ \frac{1}{b} \left( a \ \alpha \ w + \dot{w} \right) \right]^{1 - \alpha}$$

$$\times \sum_{m = 0}^{n} \frac{1}{m!} (\alpha + 1)^{m} \ w^{m} = 0,$$

for $n = 0, \ldots, \infty$. Eq. (5.3), which as $n \to \infty$ becomes the characteristic differential equation for the LV model [eq. (4.18)], can be integrated using a symbolic processor [75] to give the quadrature

$$t - t_0 = \int_{0}^{w} \left[ a \ \alpha \left( \rho - w' \right) \right]^{-1} \ dw', \quad (5.4)$$

where $\rho$ is given by the solution to the polynomial
Eq. (5.5) can be solved in terms of radicals for $\alpha \leq 3$ with the aid of a symbolic processor [75]. Numerical integration of eq. (5.3) for a specified value of $\alpha > 0$ and $n > 1$ shows that the solution curves are doubly periodic functions with the same general shape as that for the LV model (see Fig. 5.2). As the value of $n$ increases, the solution curves of eq. (5.4) become better approximations to the LV model.

When $\alpha = 1$, eq. (5.5) is a second order polynomial which can be solved using the quadratic formula to give

$$t - t_0 = \pm \int_0^w \left[ a^2 w'^2 + k^2 \sum_{m=0}^{n-1} \frac{2^m w^m}{m!} \right]^{-1/2} \, dw'. $$

Eq. (5.6), which reduces to eq. (4.15) when $n = \infty$, can be solved in terms of known functions for $n \leq 3$ (with the use of a symbolic processor [75,79]); these solutions are presented in Table 5.1. From these solutions it becomes obvious that the doubly periodic nature of the LV problem appears as a result of the higher-order terms in the power series expansion, since the solutions for the $n = 0$ and $n = 1$ case are exponential (although the solution for the $n = 1$ case can become periodic when $a^2 < 2 k^2$). Elliptic functions, like the solutions to the $n = 2$ and $n = 3$ case, are known for their doubly periodic nature [74].

For the case of $\alpha = 2$, the solution of eq. (5.5) has three branches which, when substituted back into eq. (5.4), give

$$t - t_0 = \int_0^w \left[ \frac{1}{2} p_{2}^{1/3} + 2 a^2 w'^2 p_{2}^{-1/3} \right]^{-1} \, dw', $$

and

$$t - t_0 = \int_0^w \left[ -\frac{1}{4} (1 \pm i \sqrt{3}) p_{2}^{1/3} - a^2 (1 + i \sqrt{3}) w'^2 p_{2}^{-1/3} - a w' \right]^{-1} \, dw', $$

Fig. 5.2 The solution curves of eq. (5.3) of text when $\alpha = 1$ for $n = 4$ and $n = \infty$, showing both the doubly periodic nature of the solutions as well as the order of approximation to the LV model.
TABLE 5.1. Analytic Solutions to Eq. (5.6) of Text for n ≤ 3.

<table>
<thead>
<tr>
<th>n</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[ w(t) = \frac{1}{2a} e^{\pm a(t-t_0)} + \frac{k^2}{2a^2} (k^2 - a) e^{\pm a(t-t_0)} - \frac{k^2}{a^2} ]</td>
</tr>
<tr>
<td>1</td>
<td>[ w(t) = \frac{1}{2\lambda} e^{\pm \lambda(t-t_0)} + \frac{k^2}{2\lambda^2} (k^2 - \lambda) e^{\pm \lambda(t-t_0)} - \frac{k^2}{\lambda^2} ] where ( \lambda = \sqrt{a^2 + 2k^2} )</td>
</tr>
</tbody>
</table>
| 2 | \[ \pm \frac{\sqrt{2}}{3} k \sqrt{b_1 - b_3} (t - t_0) = F \left( \sin^{-1} \left( \frac{w - b_3}{b_1 - b_3} \right), \frac{b_2 - b_3}{b_1 - b_3} \right) \] where \( F \) is an elliptic function of the first kind and 

\[ b_1 = -\frac{1}{4} \frac{a^2 + 2k^2}{k^2} - \frac{1}{8} (1 + \sqrt{3}) k^2 p_2^{1/3} + \frac{1}{8} (1 - \sqrt{3}) k^2 (a^4 + 4a^2 k^2 - 4k^4) p_2^{-1/3} \]

\[ b_2 = -\frac{1}{4} \frac{a^2 + 2k^2}{k^2} - \frac{1}{8} (1 - \sqrt{3}) k^2 p_2^{1/3} + \frac{1}{8} (1 + \sqrt{3}) k^2 (a^4 + 4a^2 k^2 - 4k^4) p_2^{-1/3} \]

\[ b_3 = -\frac{1}{4} \frac{a^2 + 2k^2}{k^2} - \frac{1}{4} k^{-2} p_2^{1/3} - \frac{1}{4} k^2 (a^4 + 4a^2 k^2 - 4k^4) p_2^{-1/3} \] \] with \( p_2 \) defined as

\[ p_2 = -a^6 - 6a^4 k^2 - 8k^6 + 4\sqrt{3a^2 k^2 (5a^2 - 4k^2)} + k^4 (3a^6 + 8k^6) \] \] continued on next page

where \( p_2 \) is defined as

\[ p_2 = 8 a^3 w'^3 + 4 k^2 b \sum_{m=0}^{n+1} \frac{3^m}{m!} w'^m \]

\[ + 4 \left( b k^2 \sum_{m=0}^{n+1} \frac{3^m}{m!} w'^m \left( 4 a^3 w'^3 \right. \right. \]

\[ \left. + \frac{3^m}{m!} b k^2 w'^m \right) \right)^{1/2}. \] When the summation in eq. (5.9) is allowed to go to infinity, eqs. (5.7) and (5.8) represent the integral quadratures for the LV model when \( a = 2c \).

When \( \alpha = 3 \), the four solutions to eq. (5.5), upon substitution into eq. (5.4), lead to the integral quadratures presented below:
TABLE 5.1 continued.

<table>
<thead>
<tr>
<th>n</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>[ \frac{\sqrt{6}}{2} k [\beta_2 - \beta_3] (\beta_1 - \beta_3)]^{1/2} (t - t_0) = F \left{ \sin^{-1} \left( \frac{(\beta_2 - \beta_3)(w - \beta_1)}{(\beta_1 - \beta_3)(w - \beta_2)} \right) \right}^{1/2} \left( \frac{(\beta_1 - \beta_4)(\beta_2 - \beta_3)}{(\beta_4 - \beta_1)(\beta_3 - \beta_2)} \right)</td>
</tr>
</tbody>
</table>

where

\[
\beta_1 = -\frac{1}{2} + \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2}
\]

\[
+ \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} + 4(a^2 + k^2) \right]
\]

\[
+ 2\sqrt{k} (2k^2 - 3a^2) \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2} \]

\[
\beta_2 = -\frac{1}{2} + \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2}
\]

\[
- \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} + 4(a^2 + k^2) \right]
\]

\[
+ 2\sqrt{k} (2k^2 - 3a^2) \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2} \]

\[
\beta_3 = -\frac{1}{2} - \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2}
\]

\[
+ \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} + 4(a^2 + k^2) \right]
\]

\[
+ 2\sqrt{k} (2k^2 - 3a^2) \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2} \]

\[
\beta_4 = -\frac{1}{2} - \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2}
\]

\[
- \frac{\sqrt{p}}{4} k^{-1} \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} + 4(a^2 + k^2) \right]
\]

\[
+ 2\sqrt{k} (2k^2 - 3a^2) \left[ p_3^{1/3} + (a^2 + 2k^2)^2 p_3^{-1/3} - 2(a^2 + k^2) \right]^{1/2} \]

with \( p \) defined by

\[
p_3 = a^6 + 6a^4k^2 - 24k^4a^2 - 4k^6 + 2k^2 \sqrt{72a^4k^4 - 12k^6 - 114a^6k^2 - 18a^8} \]

*M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, Dover, New York, 1965.*
These analytic solutions to eq. (5.3) also represent the solutions to the LV model when \( a = 3 \), if the summation is allowed to go to infinity.

The integral quadratures presented above, although not reducible to known functions, do represent analytic solutions to eq. (5.3) for finite \( n \), and to eq. (4.18) for infinite \( n \). The numerical integration of these quadratures leads to periodic solutions which are indicative of a conservative system. In the next Section, the invariants for eq. (5.2) will be derived, and a simple transformation which allows this system to be written in Hamiltonian form will be presented.

3. Invariants and Hamiltonians [77]

The fact that eq. (5.2) possesses closed curves as solutions (see Fig. 5.1) is indicative of the existence of an invariant for the system. The derivation of the invariant for any two-dimensional system modeled by a set of first-order differential equations begins by taking the ratio of the rate equations. For the system represented by eq. (5.2), this ratio is

\[
\frac{dx_1}{dx_2} = \left[ a x_1 + \frac{k^2}{b} x_1^{1-\alpha} \right] \times \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m 
\]

where

\[
p_3 = 3 k^2 b^2 S \left[ -9 a^2 w'^2 + (3 k^2 b^2 S + 81 a^4 w'^4) \right]
\]

and

\[
S = \sum_{m=0}^{n+1} \frac{4^m}{m!} w'^m.
\]
\[
\left\{ \begin{array}{c}
- a x_2 - \frac{k^2}{b} x_1^{1-\alpha} \\
\times \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m \end{array} \right\} dx_1 \\
- \left\{ a x_1 + \frac{k^2}{b} x_1^{1-\alpha} \right\}
\times \sum_{m=0}^{n} \frac{1}{m!} \left( \frac{b}{a} \right)^m (x_1 + x_2)^m \left\} \right. dx_2 \\
\right.
\]

(5.10)

Eq. (5.10) can be integrated to give

\[
I_n = a x_1^\alpha x_2 + \frac{k^2}{b} \sum_{m=1}^{n} \frac{1}{m!} a^{1-m} b^{m-2} (x_1 + x_2)^m.
\]

(5.11)

which can be shown by induction to be the first integral of the system as follows.

The condition for eq. (5.11) to be invariant is

\[
\frac{dI_n}{dt} = \partial_1 I_n \dot{x}_1^{(n)} + \partial_2 I_n \dot{x}_2^{(n)} = 0, \quad (5.12)
\]

where \(\partial_1 I_n = \partial I_n/\partial x_1\) and \(\dot{x}_1^{(n)} = \dot{x}_1\) for some specific value of \(n\). When \(n = 0\), eq. (5.12) can be written as

\[
\frac{dI_0}{dt} = \left( a x_1^{\alpha-1} x_2 + \frac{k^2}{b} \right) \left( a x_1 + \frac{k^2}{b} x_1^{1-\alpha} \right) \\
+ \left( a x_1^\alpha + \frac{k^2}{b} \right) \left( -a x_2 - \frac{k^2}{b} x_1^{1-\alpha} \right),
\]

which simplifies to zero. Now, eq. (5.2) can be written recursively as

\[
\dot{x}_1^{(j+1)} = \dot{x}_1^{(j)} + \left[ (j+1)! \right]^{-1} \\
x_2^{(j+1)} = x_2^{(j)} - \left[ (j+1)! \right]^{-1} \\
x_1^{1-\alpha} (x_1 + x_2)^{j+1},
\]

(5.13)

and \(I_{j+1}\) [eq. (5.11)] can be rewritten as

\[
I_{j+1} = I_j + \left[ (j+2)! \right]^{-1} \\
x_2^{(j+1)} \\
x_1^{1-\alpha} (x_1 + x_2)^{j+2}.
\]

(5.14)

Substitution of eq. (5.13) and the derivatives of eq. (5.14) into eq. (5.12) gives, upon rearrangement,

\[
\frac{dI_{j+1}}{dt} = \left( \partial_1 I_j \dot{x}_1^{(j)} + \partial_2 I_j \dot{x}_2^{(j)} \right) \\
+ \left[ (j+1)! \right]^{-1} k^2 (x_1 + x_2)^{j+1} b^j a^{-j-1} \\
x_1^{1-\alpha} \left( \partial_1 I_j - \partial_2 I_j + (\dot{x}_1^{(j)} + \dot{x}_2^{(j)}) \right),
\]

which (since \(\partial_1 I_j \dot{x}_1^{(j)} + \partial_2 I_j \dot{x}_2^{(j)} = 0\) by assumption) reduces to

\[
\frac{dI_{j+1}}{dt} = \left[ (j+1)! \right]^{-1} k^2 b^j a^{-j-1} \\
x_1^{1-\alpha} \left[ x_1^{1-\alpha} \left( a x_1^{\alpha-1} x_2 \right) \\
- a x_1^\alpha \right] + \left( a x_1 - a x_2 \right)
\]

(5.15)

Expansion and rearrangement simplifies eq. (5.15) to zero, thus completing the proof that eq. (5.11) is invariant.
Another method leading to the characteristic differential equation [eq. (5.3)] for eq. (5.2) begins by defining new coordinates $z_1$ and $z_2$ in the same manner as developed in Chapter 4 for the solution to the LV problem. The coordinate $z_1$ is defined such that it contains only the terms linear in $x_1$ and $x_2$ in the invariant, while the coordinate $z_2$ contains the remaining terms of the invariant. Applying the remaining coordinate transformations of Chapter 4 reduces eq. (5.2) to eq. (5.3).

The transformation of eq. (5.2) into Hamiltonian form begins by introducing new variables $q$ and $p$ such that

$$ q = x_1 \quad \text{and} \quad p = x_1^{-1} x_2. \quad (5.16) $$

This transformation allows the rate equations [eq. (5.2)] for the system to be written as

$$ \dot{q} = a q + k^2 q^{1-\alpha} $$
$$ \times \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{-m} (q + p q^{1-\alpha})^m $$

$$ \dot{p} = -a p - k^2 [1 + (1 - \alpha) p q^{-\alpha}] $$
$$ \times \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{-m} (q + p q^{1-\alpha})^m, \quad (5.17) $$

and the invariant [eq. (5.11)] to be rewritten as

$$ H_n = a q p + k^2 $$
$$ \times \sum_{m=1}^{n+1} \frac{1}{m!} a^{-m} b^{-m-2} (q + p q^{1-\alpha})^m. \quad (5.18) $$

The derivation of Hamilton’s equations from eq. (5.18) may be shown simply as follows. The derivatives of eq. (5.18) with respect to $q$ and $p$ are

$$ \frac{\partial H_n}{\partial p} = a q + k^2 q^{1-\alpha} $$
$$ \times \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{-m} (q + p q^{1-\alpha})^m $$

$$ \frac{\partial H_n}{\partial q} = a p + k^2 [1 + (1 - \alpha) p q^{-\alpha}] $$
$$ \times \sum_{m=0}^{n} \frac{1}{m!} a^{-m} b^{-m} (q + p q^{1-\alpha})^m. \quad (5.19) $$

which by direct comparison with eq. (5.17) leads to Hamilton’s equations, namely

$$ \frac{\partial H_n}{\partial p} = \dot{q} \quad \text{and} \quad \frac{\partial H_n}{\partial q} = -\dot{p}. $$

The Hamiltonian of eq. (5.18), like Kerner’s Hamiltonian for the original LV problem, does not treat both coordinates equally. An extension of this system to a full four-dimensional space in order to develop a more traditional Hamiltonian has not been attempted. If a more traditional Hamiltonian can be developed for this general family of functions, the nature of the third invariant for the general system could be compared to the third invariant of the LV model [eq. (4.47)] to perhaps give more insight into the symmetry of both the LV problem and its related family.

**CHAPTER 6**

**CONCLUSION**

In this Thesis, we presented for the first time the analytic solutions to the Lotka-Volterra problem. Our presentation began with a brief discussion of the qualitative properties of dynamical systems in Chapter 2. This treatment was then used in Chapter 3 for the development and solution
of the rate laws pertaining to various chemical reaction schemes. Chapter 3 also provided a brief introduction to the study of systems which exhibit sustained chemical oscillations. Our study of chemical oscillations was then expanded in Chapter 4 to a more thorough investigation of the LV model, which led ultimately to the development of a new coordinate transformation for the LV system. This transformation [eq. (4.7)] reduced the dimensionality of the LV problem by one and allowed for the development of an equivalent second-order differential equation [eq. (4.13)], which was then solved analytically via quadratures. These quadratures [eqs. (4.15) and (4.19)], although not capable of being integrated in terms of known elementary functions, define new functions which represent the analytic solutions to the Lotka-Volterra problem. In Chapter 5, an introductory analysis of these analytic solutions was provided, one which led to the development of a new family of LV-related dynamical systems [eq. (5.2)]. This family of dynamical systems, although appearing more complex than the LV system, could in some instances be solved in terms of known functions (Table 5.1). The Hamiltonian forms for both the LV problem (Section 4.4) and the LV-related family [eq. (5.18)] were also explored.

The analytic solutions to the LV problem represent, if fully analyzed, the definition of new elliptic-type functions. The full analysis of any quadrature begins by comparing the form of its solutions to the solutions of known functions. This comparison leads to the development of approximations to the quadrature in terms of known functions, as well as to insight into the nature of the function. For the analytic solutions to the LV problem [eq. (4.19)], we began this comparison by performing a power series expansion on the exponential term in the quadrature. When $a = c$, truncation of this expansion led to a relationship (given in Table 5.1) between this function and the family of elliptic functions [74]. A future full analysis of eq. (4.19) will involve showing that eq. (4.19) is convergent, determining the exact nature of the two periods of the solution, and defining the singularities of the function (see, for example, E. T. Whittaker and G. N. Watson’s book on modern analysis [80]).

The coordinate transformation employed to solve the LV model [eq. (4.7)], which involved the first integral of the system [eq. (4.2)], may have the capability of being generalized to an n-dimensional system such as GLV (cf. Chapter 4). For example, an integrable four-dimensional system will possess three invariants. If two of these invariants were known, four new coordinates $z_i (i = 1, \ldots, 4)$ could be defined such that the system could be represented by two angles $\Psi$ and $\Omega$, with these angles being given by

$$\tan \Psi = \frac{z_1}{z_2} \quad \text{and} \quad \tan \Omega = \frac{z_3}{z_4}. \quad (6.1)$$

With eq. (6.1), the old system could be represented by the solution to two second-order characteristic differential equations in terms of $\Psi$ and $\Omega$, which may or may not be coupled. (The coupling would depend upon the nature of the original invariants, and on how the coordinates $z_i$ are defined.) If the differential equations are coupled, it might be possible to use the same technique to reduce the system to one dimension if an invariant in terms of $\Psi$ and $\Omega$ can be found.

The determination of the invariants of any n-dimensional system, however, is a problem in its own right. This problem can be solved in part if the system can be written in Hamiltonian form, since once a Hamiltonian is known, the construction of the Poisson bracket with a general function can lead to insight into the form of other invariants. The Lagrangian that Birkhoff [76] developed for a two-dimensional system [cf. eq. (4.38)] can be generalized to an n-dimensional Lagrangian given by

$$L = \sum_{i=1}^{n} \left[ \frac{1}{2} \dot{q}_i^2 + \alpha_i \dot{q}_i \right] + \gamma, \quad (6.2)$$
where \( \alpha_i, \forall i = 1, \ldots, n \), and \( \gamma \) are functions dependent only upon the coordinates \( q_i \). These functions can be determined as follows. For eq. (6.2) to truly define a Lagrangian, Lagrange’s equations [i.e., eq. (2.24)] must be satisfied. This condition leads to the function \( \gamma \) being defined by a system of \( n \) partial differential equations, namely

\[
\frac{\partial \gamma}{\partial q_i} = \ddot{q}_i + \sum_{j=1}^{n} \left( \frac{\partial \alpha_i}{\partial q_j} - \frac{\partial \alpha_j}{\partial q_i} \right) \dot{q}_j, \quad \forall \ i = 1, \ldots, n.
\]  

(6.3)

If there exists a set of functions \( \alpha_i (i = 1, \ldots, n) \) such that \( \gamma \) possesses a complete differential (in other words, if all of the mixed partial derivatives of \( \gamma \) commute), the system will be able to be written in Lagrangian form. Once the Lagrangian is defined, a Legendre transformation (defined in Section 2.3, above) of eq. (6.2) leads to a Hamiltonian having the form

\[
H = \frac{1}{2} \sum_{i=1}^{n} \left( p_i - \alpha_i \right)^2 - \gamma,
\]

(6.4)

where the momenta of the system \( p_i \) are defined by

\[
p_i = \frac{\partial L}{\partial \dot{q}_i} = \dot{q}_i + \alpha_i.
\]

(6.5)

Once eq. (6.4) is determined for the system, the Poisson bracket [i.e., eq. (2.31)] can be constructed and analyzed in order to develop the other invariants for the system. The existence of eq. (6.4) can also be used to determine the analytic solutions to the system by applying Hamilton-Jacobi theory [22].

The family of LV-related differential equations developed in Chapter 5 [eq. (5.2)] represents a set of two-dimensional systems which show sustained oscillations (see Fig. 5.2). The applications for which these systems may provide models have not yet been explored. It may be possible (using the techniques of J. J. Tyson and J. C. Light [6], or the approach of N. Samardzija and co-workers [37]) to develop oscillating chemical reaction schemes, modeled by eq. (5.2), in which the analytic solutions to the rate laws are known in terms of well-defined functions. Eq. (5.2) should also be able to be recast in terms of complex interactions between populations of biological species. This family of dynamical systems clearly provides a rich analytical ground for a plethora of future model studies.

**APPENDICES**

1. **4th ORDER RUNGE-KUTTA EQUATIONS FOR THE LV MODEL**

**1. Method 1**

The first method used in this Thesis to numerically integrate the LV problem was a direct fourth order Runge-Kutta integration [eq. (4.3)] of eq. (3.23),

\[
\dot{x}_1 = a x_1 - b x_1 x_2
\]

\[
\dot{x}_2 = -c x_2 + b x_1 x_2,
\]

where \( a, b, \) and \( c \) are positive constants. Given an initial value of \( x_1 \) and \( x_2 \), and the values for the constants \( a, b, \) and \( c \), the recursion relation for obtaining the next value is

\[
x_1^{(n+1)} = x_1 + \frac{h}{6} \left( k_1 + 2 k_2 + 2 k_3 + k_4 \right)
\]

\[
x_2^{(n+1)} = x_2 + \frac{h}{6} \left( m_1 + 2 m_2 + 2 m_3 + m_4 \right),
\]

where \( x_j (j=1,2) \), \( k_i \) and \( m_i \) denote their respective values for the \( n \)th step unless otherwise noted, and \( k_i \) and \( m_i \) (\( i=1, \ldots, 4 \)) are defined as follows:
Repeated use of the above recursion relation generates a set of data points which can then be plotted using a standard spreadsheet (such as [81]) or a symbolic processor [75].

2. Method 2

The second technique used to numerically integrate the LV model was the numerical integration of the acceleration equations [eq. (4.5)],

\[
\begin{align*}
\ddot{x}_1 &= a^2 x_1 - b^2 x_1^2 x_2 \\
&\quad + b^2 x_1 x_2^2 + b (c - 2 a) x_1 x_2 \\
\ddot{x}_2 &= c^2 x_2 + b^2 x_1^2 x_2 \\
&\quad - b^2 x_1 x_2^2 + b (a - 2 c) x_1 x_2 ,
\end{align*}
\]

using a modification of eq. (4.4), since the accelerations do not depend implicitly on the rate equations. This method requires four initial conditions: the initial values of \(x_1\) and \(x_2\) and the initial rates \(\dot{x}_1\) and \(\dot{x}_2\) calculated by substituting the initial values of \(x_1\) and \(x_2\) into eq. (3.23). The velocity dependent recursion relation for \(x_1\) and \(x_2\) given the initial conditions are:

\[
\begin{align*}
\dot{x}_1^{(n+1)} &= x_1 + h \left[ \dot{x}_1 + \frac{h}{6} \left( k_1 + 2 k_2 \right) \right] \\
\dot{x}_2^{(n+1)} &= x_2 + h \left[ \dot{x}_2 + \frac{h}{6} \left( m_1 + 2 m_2 \right) \right],
\end{align*}
\]

and the recursion relation for the velocities are:

\[
\begin{align*}
\dot{x}_1^{(n+1)} &= \dot{x}_1 + \frac{h}{6} \left( k_1 + 4 k_2 + k_3 \right) \\
\dot{x}_2^{(n+1)} &= \dot{x}_2 + \frac{h}{6} \left( m_1 + 4 m_2 + m_3 \right)
\end{align*}
\]

with \(x_j (j=1,2)\) and \(k_i, m_i (i=1,\ldots,3)\) denoting their
respective values for the nth step unless otherwise noted and \( k_i \) and \( m_i \) being defined below. The values for \( k_i \) and \( m_i \) \((i=1,…,3)\) are given by:

\[
\begin{align*}
   k_1 &= a^2 x_1 - b^2 x_1^2 x_2 + b^2 x_1 x_2^2 + b (c - 2a) x_1 x_2 \\
   m_1 &= c^2 x_2 + b^2 x_1 x_2 - b^2 x_1 x_2^2 + b (a - 2c) x_1 x_2 \\
   k_2 &= a^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right) + b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right)^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right) \\
   &\quad - b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right)^2 \\
   &\quad + b (c - 2a) \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right) \\
   m_2 &= c^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right) - b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right)^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right) \\
   &\quad + b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right)^2 \\
   &\quad + b (a - 2c) \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_1 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_1 \right) \\
   k_3 &= a^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right) + b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right)^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right) \\
   &\quad - b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right)^2 \\
   &\quad + b (c - 2a) \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right) \\
   m_3 &= c^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right) - b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right)^2 \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right) \\
   &\quad + b^2 \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right)^2 \\
   &\quad + b (a - 2c) \left( x_1 + \frac{h}{2} \dot{x}_1 + \frac{h}{8} k_2 \right) \left( x_2 + \frac{h}{2} \dot{x}_2 + \frac{h}{8} m_2 \right)
\end{align*}
\]
\[ k_4 = a^2 \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right) + b^2 \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right)^2 \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) \]
\[- b^2 \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right) \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) + b (c - 2a) \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right) \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) \]
\[ m_4 = c^2 \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) - b^2 \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right)^2 \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) \]
\[ + b^2 \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right) \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right)^2 \]
\[ + b (a - 2c) \left( x_1 + h \dot{x}_1 + \frac{h}{2} k_3 \right) \left( x_2 + h \dot{x}_2 + \frac{h}{2} m_3 \right) \].

Just as in Method 1, continuous application of the above recursion relation generates a set of data consisting of the numerical values of \( x_1 \) and \( x_2 \), as well as the numerical values of \( \dot{x}_1 \) and \( \dot{x}_2 \).

3. Method 3

The development of the third method begins by expressing eq. (4.5) as a system of four first-order differential equations represented by

\[ \dot{x}_1 = x_3 \]
\[ \dot{x}_2 = x_4 \]
\[ \dot{x}_3 = a^2 x_1 - b^2 x_1^2 x_2 + b (c - 2a) x_1 x_2 \]
\[ \dot{x}_4 = c^2 x_2 + b^2 x_1^2 x_2 - b^2 x_1 x_2^2 + b (a - 2c) x_1 x_2 \].

The initial conditions for the problem are the initial values of \( x_1 \) and \( x_2 \), and the initial values for the rates \( x_3 \) and \( x_4 \) determined by substituting the initial values for \( x_1 \) and \( x_2 \) into eq. (3.23). The recursion relation for the four variables, developed by applying eq. (4.3), are

\[ x_1^{(n+1)} = x_1 + \frac{h}{6} (j_1 + 2j_2 + 2j_3 + j_4) \]
\[ x_2^{(n+1)} = x_2 + \frac{h}{6} (k_1 + 2k_2 + 2k_3 + k_4) \]
\[ x_3^{(n+1)} = x_3 + \frac{h}{6} (m_1 + 2m_2 + 2m_3 + m_4) \]
\[ x_4^{(n+1)} = x_4 + \frac{h}{6} (n_1 + 2n_2 + 2n_3 + n_4) \],

where the values for \( x_i \) (\( i = 1, \ldots, 4 \)) and \( j_i, k_i, m_i, n_i \) (\( i = 1, \ldots, 4 \)) denote their respective values for the \( n \)th step unless otherwise noted, and \( j_i, k_i, m_i, n_i \) are defined below. The weighting coefficients \( j_i, k_i, m_i, n_i \) are determined by:
\[ j_1 = x_3 \]
\[ k_1 = x_4 \]
\[ m_1 = a^2 x_1 - b^2 x_1^2 x_2 + b^2 x_1 x_2^2 + b (c - 2 a) x_1 x_2 \]
\[ n_1 = c^2 x_2 + b^2 x_1^2 x_2 - b^2 x_1 x_2^2 + b (a - 2 c) x_1 x_2 \]
\[ j_2 = x_3 + \frac{1}{2} m_1 \]
\[ k_2 = x_4 + \frac{1}{2} n_1 \]
\[ m_2 = a^2 \left( x_1 + \frac{1}{2} j_1 \right) - b^2 \left( x_1 + \frac{1}{2} j_1 \right)^2 \left( x_2 + \frac{1}{2} k_1 \right) \]
\[ + b^2 \left( x_1 + \frac{1}{2} j_1 \right) \left( x_2 + \frac{1}{2} k_1 \right)^2 + b (c - 2 a) \left( x_1 + \frac{1}{2} j_1 \right) \left( x_2 + \frac{1}{2} k_1 \right) \]
\[ n_2 = c^2 \left( x_2 + \frac{1}{2} k_1 \right) + b^2 \left( x_1 + \frac{1}{2} j_1 \right)^2 \left( x_2 + \frac{1}{2} k_1 \right) \]
\[ - b^2 \left( x_1 + \frac{1}{2} j_1 \right) \left( x_2 + \frac{1}{2} k_1 \right)^2 + b (a - 2 c) \left( x_1 + \frac{1}{2} j_1 \right) \left( x_2 + \frac{1}{2} k_1 \right) \]
\[ j_3 = x_3 + \frac{1}{2} m_2 \]
\[ k_3 = x_4 + \frac{1}{2} n_2 \]
\[ m_3 = a^2 \left( x_1 + \frac{1}{2} j_2 \right) - b^2 \left( x_1 + \frac{1}{2} j_2 \right)^2 \left( x_2 + \frac{1}{2} k_2 \right) \]
\[ + b^2 \left( x_1 + \frac{1}{2} j_2 \right) \left( x_2 + \frac{1}{2} k_2 \right)^2 + b (c - 2 a) \left( x_1 + \frac{1}{2} j_2 \right) \left( x_2 + \frac{1}{2} k_2 \right) \]
Application of the above recursion relation generates a set of data which contains the numerical solutions for $x_1$ and $x_2$ as well as $x_{00}^1(x_3)$ and $x_{00}^2(x_3)$.

2. COMPUTER CODE FOR NUMERICAL INTEGRATION

The classic fourth-order Runge-Kutta method is a popular integration technique because it can be easily coded. The pseudo-code for an algorithm which numerically integrates eq. (3.23), and calculates the invariant for the system [eq. (4.2)] is given below.

Algorithm: Runge_Kutta_LV

BEGIN Mainline

CONSTANT $t_0 = 0$

VARIABLES $a$, $b$, $c$, $h$, $iter$, $k_1$, $k_2$, $k_3$, $k_4$, $m_1$, $m_2$, $m_3$, $m_4$, $X1$, $X2$, kerner, COUNT

OUTPUT (“Runge Kutta Fourth Order Numerical Integration”)
OUTPUT (“Of the Lotka-Volterra Model”)
OUTPUT ( )
OUTPUT (“The equations which are solved are the rate equations”)
OUTPUT (“dX1/dt = a X1 - b X1 X2 and”)
OUTPUT (“dX2/dt = -c X2 + b X1 X2.”)
OUTPUT ( )
OUTPUT ( )
OUTPUT (“Enter the values for a, b, and c.”)
INPUT (a,b,c)
OUTPUT (“Enter the initial values for X1 and X2.”)
INPUT (X1, X2)
OUTPUT (“Enter the step size.”)
INPUT (h)
OUTPUT (“Enter the number of iterations wanted.”)
INPUT (iter)
kerner = b*(X1+X2) - c*ln(X1) - a*ln(X2)
OUTPUT ( )

\[
\begin{align*}
n_3 &= c^2 \left( x_2 + \frac{1}{2} k_2 \right) + b^2 \left( x_1 + \frac{1}{2} j_2 \right)^2 \left( x_2 + \frac{1}{2} k_2 \right) \\
&\quad - b^2 \left( x_1 + \frac{1}{2} j_2 \right) \left( x_2 + \frac{1}{2} k_2 \right)^2 + b \left( a - 2 c \right) \left( x_1 + \frac{1}{2} j_2 \right) \left( x_2 + \frac{1}{2} k_2 \right) \\
\end{align*}
\]

\[
\begin{align*}
\frac{j_4}{4} &= x_3 + m_3 \\
\frac{k_4}{4} &= x_4 + n_3 \\
m_4 &= a^2 \left( x_1 + j_3 \right) - b^2 \left( x_1 + j_3 \right) \left( x_2 + k_3 \right) \\
&\quad + b^2 \left( x_1 + j_3 \right) \left( x_2 + k_3 \right)^2 + b \left( c - 2 a \right) \left( x_1 + j_3 \right) \left( x_2 + k_3 \right) \\
n_4 &= c^2 \left( x_2 + k_3 \right) + b^2 \left( x_1 + j_3 \right) \left( x_2 + k_3 \right)^2 \\
&\quad - b^2 \left( x_1 + j_3 \right) \left( x_2 + k_3 \right)^2 + b \left( a - 2 c \right) \left( x_1 + j_3 \right) \left( x_2 + k_3 \right)
\end{align*}
\]
The above pseudo-code can be translated into any standard computer language such as Basic, Fortran, or C++. The C++ code is given below.

```cpp
#include<iostream.h>                              // calls the libraries needed
#include<iomanip.h>
#include<math.h>

void main(void)
{
  int iter, COUNT;                                // sets variables and precision
  double a, b, c, h;
  long double k_1, m_1, k_2, m_2, k_3, m_3, k_4, m_4, X_1, X_2, t, kerner;

  COUNT = 0;

  const double t_0=0.00000;                      // defines any constants used
  const double frac1 = (1.00/2.00);
  const double frac2 = (1.00/6.00);

  cout << "Runge-Kutta Fourth Order Numerical Intergration\n";
  cout << "Of the Lotka-Volterra Model";
  cout << "The rate equations which are solved are given by\n";

  k_1 = a*X1 - b*X1*X2
  m_1 = -c*X2 + b*X1*X2
  k_2 = a*(X1 + 0.5*k_1) - b*(X1 + 0.5*k_1)*(X2 + 0.5*m_1)
  m_2 = -c*(X2 + 0.5*m_1) + b*(X1 + 0.5*k_1)*(X2 + 0.5*m_1)
  k_3 = a*(X1 + 0.5*k_2) - b*(X1 + 0.5*k_2)*(X2 + 0.5*m_2)
  m_3 = -c*(X2 + 0.5*m_2) + b*(X1 + 0.5*k_2)*(X2 + 0.5*m_2)
  k_4 = a*(X1 + k_3) - b*(X1 + k_3)*(X2 + m_3)
  m_4 = -c*(X2 + m_3) + b*(X1 + k_3)*(X2 + m_3)

  t = t_0 + h*COUNT
  X1 = X1 + (h/6)*(k_1 + 2*k_2 + 2*k_3 + k_4)
  X2 = X2 + (h/6)*(m_1 + 2*m_2 + 2*m_3 + m_4)
  kerner = b*(X1 + X2) - c*ln(X1) - a*ln(X2)

  cout << "t \t \t X1 \t \t X2 \t \t kerner\n";
  cout << "----- \t ---------- \t ---------- \t \------\n";
  cout << t_0, X1, X2, kerner << endl;
  COUNT = COUNT + 1
}
END WHILE
END Mainline.
```

The pseudo-code translates into:

1. Initialize variables and precision.
2. Define constants.
3. Print initialization and rate equations.
4. Implement Runge-Kutta fourth-order method iteratively.
5. Calculate new values of `X1` and `X2` using the updated rates.
6. Update `kerner` with updated values of `X1` and `X2`.
7. Print updated values of `t`, `X1`, `X2`, and `kerner`.
8. Increment `COUNT`.
9. Repeat steps 4-8 until all iterations are completed.

This code snippet demonstrates the implementation of the Runge-Kutta fourth-order method for solving the Lotka-Volterra model numerically. It is designed to be flexible and adaptable to different programming environments.
cout << "dX1/dt = a \times X1 - b \times X1 \times X2 and\n";
cout << "dX2/dt = - c \times X2 + b \times X1 \times X2.\n";
cout << "Enter the values for a, b, and c.\n";
cin >> a >> b >> c;
cout << "Enter the step size.\n";
cin >> h;
cout << "Enter the initial values for X1 and X2.\n";
cin >> X1 >> X2;
cout << "Enter the number of iterations wanted.\n";
cin >> iter;

kerner = b*(X_1 + X_2) - c*log(X_1) - a*log(X_2);

cout << "Numerical Solution to the LV Model\n";
cout << "t X1 X2 kerner\n";
cout << "------- --------- --------- ---------\n";
cout << setiosflags(ios::showpoint) << setprecision(6) << setiosflags(ios::left) <<
setw(14) << t_0

cout << setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_1

cout << setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_2

cout << setiosflags(ios::showpoint) << setprecision(6) << setiosflags(ios::left) <<
setw(8) << kerner <<"\n";

while (COUNT < iter)
{
    k_1 = a*X_1 - b*X_1*X_2;
m_1 = - c*X_2 + b*X_1*X_2;
k_2 = a*(X_1 + frac1*k_1) - b*(X_1 + frac1*k_1)*(X_2 + frac1*m_1);
m_2 = - c*(X_2 + frac1*m_2) + b*(X_1 + frac1*k_1)*(X_2 + frac1*m_1);
k_3 = a*(X_1 + frac1*k_2) - b*(X_1 + frac1*k_2)*(X_2 + frac1*m_2);
m_3 = - c*(X_2 + frac1*m_2) + b*(X_1 + frac1*k_2)*(X_2 + frac1*m_2);
k_4 = a*(X_1 + k_3) - b*(X_1 + k_3)*(X_2 + m_3);
m_4 = - c*(X_2 + m_3) + b*(X_1 + k_3)*(X_2 + m_3);

t = t_0 + (h*(COUNT + 1));

X_1 = X_1 + h*frac2*(k_1 + 2.0*k_2 + 2.0*k_3 + k_4);
X_2 = X_2 + h*frac2*(m_1 + 2.0*m_2 + 2.0*m_3 + m_4);

kerner = b*(X_1 +X_2) -c*log(X_1) - a*log(X_2);

if (COUNT <= 8)
cout << setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << t
<< setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_1
<< setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_2
<< setiosflags(ios::showpoint) << setprecision(6) << setiosflags(ios::left) <<
setw(8) << kerner
<< “
”;

else
  cout << setiosflags(ios::showpoint) << setprecision(6) << setiosflags(ios::left) <<
setw(14) << t
<< setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_1
<< setiosflags(ios::showpoint) << setprecision(5) << setiosflags(ios::left) <<
setw(14) << X_2
<< setiosflags(ios::showpoint) << setprecision(6) << setiosflags(ios::left) <<
setw(8) << kerner
<< “
”;

COUNT++;
}
}

The output of this C++ code is a table of values for time, $x_1$, $x_2$, and the value for the invariant for a given initial value of $x_1$ and $x_2$, and a user defined set of constants $a$, $b$, and $c$.

ACKNOWLEDGEMENTS

I would like to thank Dr. Gary L. Findley for the time, patience and support which he has given to me over the past two years. I would also like to thank Dr. Fred Watson and the rest of the NLU Chemistry Faculty for their encouragement. Finally, I want to thank my parents and family, since without their support and encouragement I would not have had this opportunity to further my education.

Program Title: Impurity Photoionization in Molecular Hosts

Program Leader Name: Dr. Gary L. Findley

Is program leader a PRT member: _____ Yes    __ X __ No
If yes, complete the PRT supplement form.

Affiliation (complete mailing address):
Department of Chemistry
Northeast Louisiana University
Monroe, LA 71209

Phone: (318) 342-1835    FAX: (318) 342-1755    Email: chfindley@alpha.nlu.edu

ABSTRACT of Program Description:

Photoionization and field ionization of hydrogen iodide (HI) impurity doped into rare gas hosts and molecular hosts (e.g., Ar, SF₆, CF₄) will be measured as a function of host number density. These studies will focus on (i) subthreshold photoionization structure as a sensitive probe of solvation effects due to van der Waals interactions, and (ii) shifts in field ionization thresholds at very high host number densities.

This work, which is an extension of our previous studies of methyl iodide (CH₃I) at SRC, is intended to complete the Ph.D. dissertation of one student.

A. Requested Beam Time, starting August, 1999 (please check one box):

☐ 6 months    ☑ 12 months    ☐ 18 months

<table>
<thead>
<tr>
<th>3-week quantum of beam time</th>
<th>Beamline (see attached list)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 quanta</td>
<td>Al Seya</td>
<td>Dec, 1999 and June, 2000</td>
</tr>
</tbody>
</table>
**B. Collaborators on the SRC Experiments Only, Including Students** (please list education level, i.e. Faculty, Scientist, Staff/Engineer, Post Doc/Res. Associate, Graduate Student, Project Asst/Assoc/Tech, Undergraduate Student):

<table>
<thead>
<tr>
<th>Name of Collaborator</th>
<th>Education Level</th>
<th>Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cherice M. Evans</td>
<td>Graduate Student</td>
<td>Louisiana State University</td>
</tr>
</tbody>
</table>

**A. Experimental Requirements and Equipment**

C1: List any equipment that is needed from SRC, shared with other Users, or used in collaboration with a PRT that needs to be considered during scheduling:

> I continue to use equipment that was formerly provided at SRC by Dr. Ruben Reininger. This equipment has been kept together at SRC for the purpose of these experiments.

**C.2 End Stations Available:**

- [ ] Check here if the SRC-CMA photoemission system is needed. (Complete SRC-CMA form.)
- [ ] Check here if the Scienta analyzer photoemission system is needed. (Complete Scienta form.)
- [ ] Check here if the infrared microscope is needed.
- [ ] Check here if the spin polarized photoemission system is needed.
- [ ] Check here if the magnetic dichroism chamber is needed.
- [ ] Check here if the X-ray absorption chamber is needed.
NOTE: For the benefit of the reviewers, who may not be experts in your field, please include an introductory paragraph placing your work in a broader context. Please add a paragraph justifying the number of quanta you need for your experiments.

A. Introduction

Methyl iodide (CH$_3$I) has served as a convenient probe in studies of high-n Rydberg dopant-perturber interactions [1-7]. Dopant/perturber systems have included CH$_3$I/rare gases [1-4], CH$_3$I/H$_2$ [4], CH$_3$/alkanes [5], CH$_3$I/CO$_2$ [6] and CH$_3$I/N$_2$ [7]. Both photoabsorption and photoionization spectra have been measured, and perturber pressure effects have been analyzed for discrete and autoionizing dopant Rydberg states [1-7], as well as for subthreshold photoionization structure [3,6,7].

Photoionization spectra of CH$_3$I [8-11] and of CH$_3$I doped into Xe [3], CO$_2$ [6] and N$_2$ [7] exhibit rich subthreshold structure beginning 0.17 eV before the ionization limit $I_1$ ≡ $I$ ($^2E_{1/2}$). From the observed energy spacing and linear shift (as a function of perturber number density) of these peaks, the subthreshold structure has been identified as arising from high-n Rydberg states of CH$_3$I, which permitted the evaluation of electron scattering lengths in highly absorbing perturber media [3,6,7].

Ivanov and Vilesov [9] discussed vibrational autoionization as a possible source of the subthreshold signal in pure CH$_3$I at pressures below 10$^{-3}$ mbar. At higher pressures, however, they proposed [8,9] that subthreshold photoionization results from the Hornbeck-Molnar [12] process, namely, (Here, hv is the photoexcitation energy and CH$_3$I$^*$ represents a Rydberg state.)

From a study of the temperature dependence of the relative peak heights of the subthreshold structure in pure CH$_3$I, Meyer, Asaf and Reininger [11] were able to demonstrate that the ionization mechanism is vibrational autoionization at pressures up to 15 x 10$^{-3}$ mbar. This pressure is one order of magnitude greater than the pressure limit cited by Ivanov and Vilesov [9], after which these authors [9] claimed to have observed a quadratic dependence of photocurrent signal on CH$_3$I pressure (in accord with process (1), above).

In a recent work [13], based upon studies carried out at SRC, we measured the linear shift of autoionizing states of CH$_3$I perturbed by SF$_6$, in the region $I_1 < hv < I_2 [≡ I (^2E_{1/2})]$, as a function of SF$_6$ number density in order to extract the electron scattering length in SF$_6$. In this proposal, we report both pressure-dependent and temperature-dependent subthreshold photoionization spectra of pure CH$_3$I (up to 200 mbar) and CH$_3$I doped into SF$_6$ (up to 1 bar). Our results confirm a quadratic dependence of photocurrent signal upon CH$_3$I pressure in the subthreshold region of pure CH$_3$I at high pressure, with no temperature dependence indicative of vibrational autoionization. For CH$_3$I/SF$_6$, we observe a linear dependence of photocurrent signal upon SF$_6$ pressure in the subthreshold region, again with no temperature effect. This latter result suggests a possible analog of process (1), namely

$$\text{CH}_3\text{I}^* + \text{SF}_6 \rightarrow [(\text{CH}_3\text{I})(\text{SF}_6)]^* + \text{e}^- ,$$  \hspace{1cm} (2)

We propose to extend these measurements to HI in an attempt to ascertain the general applicability of these results to other molecules.

B. Experiment

Photoionization and photoabsorption spectra were measured with monochromatized synchrotron radiation having a resolution of 0.13 nm (200 μ slits), or ~ 10 meV in the spectral range of interest. Two different cells
were used: Cell 1 [14] is equipped with entrance and exit MgF$_2$ windows (which will be replaced with LiF windows for the proposed HI studies) and a pair of parallel-plate electrodes (stainless steel, 3.0 mm spacing) oriented perpendicular to the windows, thus permitting the simultaneous recording of transmission and photoionization spectra. The light path inside the cell is 1.0 cm. Cell 2 [15] is equipped with an entrance LiF window coated with a thin (7 nm) layer of gold to act as an electrode. A second electrode (stainless steel) is placed parallel to the window with a spacing of 1.05 mm. The bodies of both cells are fabricated from copper and are capable of withstanding up to 100 bar. Each cell was connected to a cryostat and heater system allowing the temperature to be controlled to within 1 K [14]. The applied electric field was 100 V, with the negative electrode being the LiF window in cell 2. (The reported spectra are current saturated, which was verified by measuring selected spectra at different electric field strengths.) Photocurrents within the cell were of the order of $10^{-10}$ A.

The intensity of the synchrotron radiation exiting the monochromator was monitored by measuring the photoemission current from a metallic grid intercepting the beam prior to the experimental cell. All photoionization spectra are normalized to this current. Transmission spectra (which are reported as absorption $= 1 - \text{transmission}$) were normalized both to the incident light intensity and to the empty cell transmission.

CH$_3$I (Aldrich Chemical Company, 99%) and SF$_6$ (Matheson Gas Products, 99.996%) were used without further purification. The gas handling system has been described previously, as well as the procedures employed to ensure a homogeneous mixing of CH$_3$I with SF$_6$ [5].

C. Results in Methyl Iodide

Representative subthreshold photoionization spectra for pure CH$_3$I at varying CH$_3$I pressures (number densities) are presented in Fig. 1 in comparison to the low-pressure photoabsorption spectrum of CH$_3$I. Similar spectra are shown in Fig. 2 for CH$_3$I doped into varying number densities of SF$_6$.

To ascertain whether or not the high-pressure subthreshold structure arises from the vibrational autoionization mechanism demonstrated by Meyer, Asaf and Reininger [11] in low-pressure pure CH$_3$I (where the photocurrent signals are at least two orders of magnitude less than those reported here), we measured photoionization spectra for one sample pressure at different temperatures. These results are shown in Fig. 3 for pure CH$_3$I, and in Fig. 4 for CH$_3$I/SF$_6$. Clearly, there is no temperature effect on the relative intensities of the subthreshold peaks, thus ruling out vibrational autoionization as the ionization mechanism in the high-pressure case.

We extracted peak areas (by gaussian fits to the photoionization spectra) for the density-dependent subthreshold structure of pure CH$_3$I and CH$_3$I doped into SF$_6$. These data are collected in Table I (CH$_3$I) and Table II (CH$_3$I/SF$_6$), and plotted in Fig. 5 (CH$_3$I) and Fig. 6 (CH$_3$I/SF$_6$). Figure 5 clearly shows a quadratic dependence on CH$_3$I.
number density, as claimed by Ivanov and Vilesov [9], in accord with process (1). Equally clearly, Fig. 6 exhibits a linear dependence on SF$_6$ number density, which accords with the suggested process (2). (An analysis of peak heights as opposed to peak areas gives rise to plots identical in shape to those shown here.)

Since the subthreshold photoionization structure of Figs. 1 and 2 is superimposed upon a rising exponential background, as discussed by Ivanov and Vilesov [8,9], we have subtracted an exponential background fitted to the zero baseline and the sharp photocurrent step at threshold. The resulting spectra, when analyzed for peak area (or peak height), yield plots identical in shape to those presented in Figs. 5 and 6.

Ivanov and Vilesov [8,9] discussed three bimolecular processes which, for a general dopant (D)/perturber (P) system, can be symbolized as

\[
\begin{align*}
\text{D}^+ + \text{P} & \rightarrow \text{D}^+ + \text{P}^- \quad (3) \\
& \rightarrow [\text{DP}]^- + \text{e}^- \quad (4) \\
& \rightarrow \text{R}_1^- + \text{R}_2 + \text{e}^- \quad (5)
\end{align*}
\]

Eq. (3) represents electron attachment [16], while eq. (4) is associative ionization [16] (i.e., the Hornbeck-Molnar [12] process). Eq. (5) represents a photochemical rearrangement leading to charged species. In their discussion
of pure CH\textsubscript{3}I (D = P = CH\textsubscript{3}I), Ivanov and Vilesov [8, 9] discounted process (5) on the basis of energetic considerations.

If we assume that process (3) is saturated (i.e., independent of the perturber pressure) for a highly polarizable perturber, the electron attachment contribution to the photocurrent is given by

$$ i_{ea} = k_1 \rho_D, \quad (6) $$

where the effective rate constant $k_1$ is proportional to the (saturated) electron attachment cross section, and we have assumed for the dopant number densities that $\rho_{D*} \propto \rho_D$ in the linear absorption regime. Likewise, the associative ionization [process (4)] contribution to the photocurrent is given by

$$ i_{ai} = k_2 \rho_D \rho_P, \quad (7) $$

where the effective rate constant $k_2$ is proportional to the associative ionization cross section, $\rho_P$ is the perturber number density, and we have again assumed that $\rho_{D*} \propto \rho_D$.

In the absence of any significant photochemical contribution [i.e., process (5)] to the observed signal, then, the subthreshold photocurrent should be given by

$$ i = (k_1 + k_2 \rho_P) \rho_D, \quad (8) $$

which accords with the data presented here for pure CH\textsubscript{3}I ($\rho_P \equiv \rho_D \equiv \rho$) [cf. Fig. (5) and Table I],

$$ i = a_1 \rho + a_2 \rho^2, \quad (9) $$

and for CH\textsubscript{3}I/SF\textsubscript{6} ($\rho_P \equiv \rho$, $\rho_D = \text{constant}$) [cf. Fig. (6) and Table II],

$$ i = b_0 + b_1 \rho + b_2 \rho^2. \quad (10) $$

### Table I. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 1) of pure CH\textsubscript{3}I at varying number densities $\rho$ ($10^{19}$ cm\textsuperscript{-3}). The regression coefficients are for a least-squares second-order polynomial fit, $a_2 \rho^2 + a_1 \rho + a_0$, as shown in Fig. 5.

<table>
<thead>
<tr>
<th>$\rho/10^{19}$ cm\textsuperscript{-3}</th>
<th>10d</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0024</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.025</td>
<td>0.00836</td>
<td>0.0128</td>
<td>0.0178</td>
<td>0.0254</td>
</tr>
<tr>
<td>0.12</td>
<td>0.0538</td>
<td>0.171</td>
<td>0.306</td>
<td>0.524</td>
</tr>
<tr>
<td>0.24</td>
<td>0.151</td>
<td>0.549</td>
<td>0.996</td>
<td>1.69</td>
</tr>
<tr>
<td>0.49</td>
<td>0.520</td>
<td>1.78</td>
<td>3.26</td>
<td>6.08</td>
</tr>
</tbody>
</table>

**Regression Coefficients**

- $a_0$: 0.00
- $a_1$: 0.229
- $a_2$: 1.73

### Table II. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 2) of 0.1 mbar CH\textsubscript{3}I in varying number densities $\rho$ ($10^{19}$ cm\textsuperscript{-3}) of SF\textsubscript{6}. The regression coefficients are for a least-squares linear fit, $b_1 \rho + b_0$, as shown in Fig. 6.

<table>
<thead>
<tr>
<th>$\rho/10^{19}$ cm\textsuperscript{-3}</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>0.225</td>
<td>0.436</td>
<td>0.901</td>
<td>1.29</td>
</tr>
<tr>
<td>0.49</td>
<td>0.365</td>
<td>0.708</td>
<td>1.42</td>
<td>2.16</td>
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<tr>
<td>0.73</td>
<td>0.452</td>
<td>0.843</td>
<td>1.68</td>
<td>2.71</td>
</tr>
<tr>
<td>0.97</td>
<td>0.572</td>
<td>1.06</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>1.22</td>
<td>0.670</td>
<td>1.21</td>
<td>2.30</td>
<td></td>
</tr>
</tbody>
</table>

**Regression Coefficients**

- $b_0$: 0.101
- $b_1$: 0.444
- $b_2$: 0.990

- $b_1$: 0.768
- $b_2$: 1.40
- $b_3$: 2.39
Fig. 5. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 1) of pure CH$_3$I as a function of CH$_3$I number density $\rho$ ($10^{19}$ cm$^{-3}$). ○, 10d; ■, 11d; ▲, 12d; ▼, 13d. The solid lines represent a least-squares fit to the function $a_2 \rho^2 + a_1 \rho + a_0$ (cf. Table I).

Fig. 6. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 2) of 0.1 mbar CH$_3$I doped into SF$_6$ as a function of SF$_6$ number density $\rho$ ($10^{19}$ cm$^{-3}$). ○, 11d; ■, 12d; ▲, 13d; ▼, 14d. The solid lines represent a least-squares fit to the function $b_1 \rho + b_0$ (cf. Table II).

Fig. 7. (a) Linear and (b) quadratic regression coefficients for the subthreshold photoionization density dependence of pure CH$_3$I (Table I) plotted versus the CH$_3$I excited state principal quantum number $n$ and $n^7$, respectively. The straight lines are least-squares fits to the data. See text for discussion.

Fig. 8. (a) Constant and (b) linear regression coefficients for the subthreshold photoionization density dependence of CH$_3$I/SF$_6$ (Table II) plotted versus the CH$_3$I excited state principal quantum number $n$ and $n^7$, respectively. The straight lines are least-squares fits to the data. See text for discussion.
From the analysis presented above, $a_1$ and $b_0$ should depend upon the dopant Rydberg electron attachment cross section in CH$_3$I and SF$_6$, respectively. These cross sections scale linearly with the principal quantum number $n$ for the CH$_3$I excited state [16]. A plot of $a_1$ vs. $n$ and $b_0$ vs. $n$ is presented in Fig. 7(a) and Fig. 8(a), respectively, and the linearity is indeed striking. Since $a_2$ and $b_1$ are reflective of a molecular interaction, these parameters should depend upon the excited state polarizability of CH$_3$I [17], which in turn scales according to $n^7$ [16]. A plot of $a_2$ vs. $n^7$ and $b_1$ vs. $n^7$ is presented in Fig. 7(b) and Fig. 8(b), respectively, and the linearity is again striking.

Clearly, the mechanisms of electron attachment and associative ionization are sufficient to explain the observed density dependence of subthreshold photoionization. (A photochemical contribution [i.e., process (5)] is not positively ruled out, however, provided that such a mechanism scales as $n$ (and is saturated) or as $n^7$.)

The energy positions of a number of CH$_3$I nd Rydberg states, as assigned from the photoionization spectra, for selected SF$_6$ number densities are given in Table III, as well as the values of $I_1$ extracted from a fit of the assigned spectra to the Rydberg equation. A plot of nd energies and $I_1$ as a function of SF$_6$ number density is shown in Fig. 9, where the red shift of all spectral features is readily apparent. Fig. 9 demonstrates that the peak positions depend linearly on the SF$_6$ number density, and that the resulting linear fits (obtained by regression analysis) are essentially parallel to one another.

The above result accords with the theory by Fermi [18], as modified by Alekseev and Sobel’man [19]. According to these authors [18,19], the total energy shift $\Delta$ is due to a sum of contributions

$$\Delta = \Delta_{sc} + \Delta_p ,$$

where $\Delta_{sc}$, the “scattering shift,” is due to the interaction of the Rydberg electron with the perturber molecule, while $\Delta_p$ the “polarization shift,” results from the interaction of the positive core of the Rydberg molecule with the perturber molecule. $\Delta_{sc}$ can be calculated from [2,13,19]

$$\Delta_p = -10.78 \left( \frac{1}{2} e^2 \frac{\alpha}{\pi} \right)^{2/3} (\hbar \nu)^{1/3} \rho .$$

In this equation, $\rho$ is again the perturber number density, $\alpha$ the polarizability of the perturber molecule, $e$ is the charge on the electron, $\hbar$ is the reduced Planck constant, and $\nu$ is the relative thermal velocity of the dopant and perturber molecules. $\Delta_{sc}$ results from a measurement of $\Delta$, after calculating $\Delta_p$.

Finally, the electron scattering length $A$ of the perturber, which gauges the electron-perturber interaction, can easily be determined from [18]

$$\Delta_{sc} = \left( \frac{2 \pi \hbar^2}{m} \right) A \rho ,$$

where $m$ is the mass of the electron.

**Table III.** nd and $I_1 \equiv 1 (^2E_{3/2})$ photoionization energies (eV) of CH$_3$I in selected number densities $\rho$ (10$^{19}$ cm$^{-3}$) of SF$_6$.

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
<th>$I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.73</td>
<td>9.365</td>
<td>9.399</td>
<td>9.426</td>
<td>9.444</td>
<td>9.539</td>
</tr>
</tbody>
</table>
Since the slopes of the straight lines of Fig. 9 are essentially equal, one may assume that the average slope
\((-25.14 \times 10^{-23} \text{ eV cm}^3)\) closely approximates the asymptotic shift rate of the Rydberg series. Using the value [20]
\(\alpha = 6.54 \times 10^{-24} \text{ cm}^3\) for SF\(_6\), one finds from Eqs. (11-13) an electron scattering length for SF\(_6\) of \(A = -0.492 \text{ nm}\).
This compares favorably to our recent measurement [13] of \(A = -0.484 \text{ nm}\), from the analysis of autoionizing states in CH\(_3\)I/SF\(_6\).

D. 1999-2000 SRC Measurements

We propose to extend the measurements described above to hydrogen iodide doped into Ar, SF\(_6\), and CF\(_4\).
(CF\(_4\) is transparent in the spectral region of interest.) Both of the first two ionization energies of HI lie below the
LiF cutoff, thus permitting a complete comparison of CH\(_3\)I and HI results in both the autoionizing and subthreshold regions. We will determine whether or not subthreshold structure is observed in HI analogous to
that seen in CH\(_3\)I and, if it is observed, we will study the nature of the HI pressure dependence. We will also
measure the effect of varying number densities of Ar, SF\(_6\), and CF\(_4\) on HI in both the subthreshold and
autoionizing regions. Finally, we will measure field ionization of HI in all of the target perturber gases, as well as
in pure HI.

These measurements are intended to complete the initial data collection for the Ph.D. dissertation of Ms.
Cherice M. Evans.

All of these measurements will be carried out on the Aluminum Seya-Namioka beamline at Aladdin (SRC, University of Wisconsin), which has an energy range of 5-35 eV and a minimum bandpass of 0.003 – 0.1 eV.
The endstation electronics, sample chamber and gas-handling system are in place (previously maintained by Dr.
Ruben Reininger’s group) at the SRC. Thus, no additional equipment is needed to perform these experiments.
Bibliography for Program Description (Reference List – one page maximum)

GARY L. FINDLEY

Education:

Ph.D. (Physical Chemistry) Louisiana State University 1978
B.S. (Biology & Chemistry) University of Arkansas at Little Rock 1974

Professional:

Northeast Louisiana University

Professor of Chemistry 1998 –
Associate Professor of Chemistry 1995 – 1998
Adjunct Professor 1993 – 1995

University of Arkansas

Adjunct Associate Professor 1990 – 1993

Louisiana State University

CAMD Project Director 1986 – 1989
Adjunct Associate Professor 1986 – 1989
Visiting Assistant Professor 1978 – 1982

New York University

Associate Professor 1982 – 1986

Research Interests:

Experimental applications of synchrotron radiation; photoionization, photoconduction and photoemission in condensed phase van der Waals systems; nonlinear dynamics of chemical reactions; model Hamiltonians for molecular problems.

Memberships/Appointments:

American Physical Society; American Chemical Society; Fellow, American Institute of Chemists; Editor, Wiley Monographs in Chemical Physics.

Publications:

Approximately seventy research papers and two books.
SRC-Related Publications (past two years)


Papers in preparation:


