Subthreshold Photoionization Spectra of CH$_3$I Perturbed by SF$_6$

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We present 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). At the high pressures studied, no temperature effect is 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 $D^* + P \rightarrow D^+ + P^-$ and $D^* + P \rightarrow [DP]^+ + e^-$, 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$_6$ is determined and compared to a value recently obtained from autoionizing states in the same system.

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 $I_{1s} = I (^2E_{3/2})$. 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,

$$\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3\text{I}^* \quad (1)$$

$$\text{CH}_3\text{I}^* + \text{CH}_3\text{I} \rightarrow (\text{CH}_3\text{I})_2^* + e^-,$$

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, Asaf and Reininger [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 $I_1 < h \nu < I_2$ [$= I (2E_{1/2})$, as a function of SF$_6$ number density in order to extract the electron scattering length in SF$_6$. In the present paper, 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

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

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 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 LiF 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 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 - 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].

### 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 $2E_{3/2}$ threshold.) In both systems, one observes
subthreshold photoionization structure that correlates with nd Rydberg states of CH$_3$I converging on the $^{2}E_{3/2}$ ionization limit. In order to ascertain whether or not the high-pressure subthreshold structure arises from the vibrational autoionization mechanism demonstrated by Meyer, 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

\[ \text{Eq. (3)} \quad \text{D}^* + \text{P} \rightarrow \text{D}^+ + \text{P}^- \]

\[ \text{Eq. (4)} \quad [\text{DP}]^+ + \text{e}^- \]

\[ \text{Eq. (5)} \quad \text{R}_1^* + \text{R}_2 + \text{e}^- . \]

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 CH₃I (D = P = CH₃I), 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

\[ i_{ea} = k_1 \rho_D, \]

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 \( \rho_D = \rho_D^* \) in the linear absorption regime. Likewise, the associative ionization [process (4)] contribution to the photocurrent is given by

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

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 \( \rho_P^* \propto \rho_P \).

In the absence of any significant photochemical contribution [i.e., process (5)] to the
observed signal, then, the subthreshold photocurrent should be given by
\[ I = (k_1 + k_2 \rho_D) \rho, \]
(8)

which accords with the data presented here for pure CH\(_3\)I \((\rho_0 = \rho_D)\) [cf. Fig. (5) and Table I],
\[ I = a_1 \rho + a_2 \rho^2, \]
(9)

Table I. 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 \(\rho\) \((10^{19}\text{ cm}^{-3})\). 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.

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Regression Coefficients

\(a_0\) \hspace{1cm} 0.00 \hspace{1cm} 0.00 \hspace{1cm} 0.00 \hspace{1cm} 0.00
\(a_1\) \hspace{1cm} 0.229 \hspace{1cm} 0.863 \hspace{1cm} 1.41 \hspace{1cm} 1.99
\(a_2\) \hspace{1cm} 1.73 \hspace{1cm} 5.63 \hspace{1cm} 10.9 \hspace{1cm} 21.1

Table II. 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 \(\rho\) \((10^{19}\text{ cm}^{-3})\). The regression coefficients are for a least-squares linear fit, \(b_1 \rho + b_0\), as shown in Fig. 6.

<table>
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Regression Coefficients

\(b_0\) \hspace{1cm} 0.101 | 0.376 | 0.690 | 0.990
\(b_1\) \hspace{1cm} 0.444 | 0.768 | 1.40  | 2.39
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 and 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’mann [19]. According to these authors [18,19], the total energy shift $\Delta$ is due to a sum...
Fig. 9. Energy shifts of nd Rydberg states of CH$_3$I as a function of SF$_6$ number density $D$ (10$^{19}$ cm$^{-3}$). The fitted ionization energy $I_1$ is denoted $2E_{3/2}$. All straight lines are least-squares fits.

of contributions

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

(11)

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. $\Delta_p$ can be calculated from [2,13,19]

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

(12)

In this equation, $\rho$ is again the number density of the perturber molecule, $\alpha$ 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. $\Delta_{sc}$ 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]

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

(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 x 10$^{-23}$ eV cm$^3$) 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 $A = -0.484$ nm, from the analysis of autoionizing states in CH$_3$I/SF$_6$.

In summary, we have presented pressure-dependent and temperature-dependent subthreshold photoionization spectra of pure CH$_3$I and CH$_3$I doped into SF$_6$. On the basis of these measurements, we were able to rule out vibrational autoionization as the mechanism of subthreshold ionization at high pressures, in contradistinction 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 SF$_6$. 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 photoproducts will

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conclusively resolve this issue, as originally pointed out by Ivanov and Vilesov [9]. (This is particularly of interest in the case of SF$_6$, since this molecule weakly absorbs to a dissociative final state in this spectral region [21]. No photocurrent was detected in pure SF$_6$ in the energy region reported here, however.) Finally, we were able to evaluate the electron scattering length in SF$_6$ 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/SF$_6$ [13].

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