

PHOTOIONIZATION SPECTRA OF CH<sub>3</sub>I PERTURBED BY SF<sub>6</sub>:  
ELECTRON SCATTERING IN SF<sub>6</sub> GAS

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ABSTRACT

A photoionization study of CH<sub>3</sub>I in the presence of SF<sub>6</sub> 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 CH<sub>3</sub>I nd' Rydbergs (n=9,10,11,12), the electron scattering length of SF<sub>6</sub> was found to be  $A = -0.484 \text{ nm}$ , 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.

## 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<sub>3</sub>I/rare gases [1-3], CH<sub>3</sub>I/H<sub>2</sub> [3], CH<sub>3</sub>I/alkanes [4], CH<sub>3</sub>I/CO<sub>2</sub> [5], CH<sub>3</sub>I/N<sub>2</sub> [6], benzene/rare gases [3,7], and benzene/H<sub>2</sub> [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 Alekseev and Sobel'man [10]. According to these authors [9,10], the total energy shift  $\Delta$  may be written as a sum of contributions

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

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 [2,10]

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

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  $\nu$  is the relative

thermal velocity of the dopant and perturber molecules.  $\Delta_{sc}$  results from a measurement of  $\Delta$ , 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]

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

where  $m$  is the mass of the electron.

In the present paper, we report photoionization spectra of  $\text{CH}_3\text{I}$  perturbed by up to 4 bar of  $\text{SF}_6$ . Since  $\text{SF}_6$  absorbs weakly in the region of the first ( $I_1 \equiv I^2E_{3/2} = 9.54$  eV [2]) and second ( $I_2 \equiv I^2E_{1/2} = 10.16$  eV [2]) ionization energies of  $\text{CH}_3\text{I}$ , photoabsorption measurements are not possible except at very low  $\text{SF}_6$  pressures. From the photoionization spectra, however, we were able to assign autoionizing  $nd'$  Rydberg states of  $\text{CH}_3\text{I}$ , and to follow the energy shifts of these states as a function of increasing  $\text{SF}_6$  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  $\text{SF}_6$  number density. As described above, these shifts can then be used to extract the electron scattering length in  $\text{SF}_6$ .

$\text{SF}_6$  is of interest as a perturber medium because of the large size and high symmetry of this molecule. In addition,  $\text{SF}_6$  has been the subject of studies of collisional effects (e.g.,  $\ell$  changing collisions) involving Rydberg atoms [11]. However, even though  $\text{SF}_6$  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 paper provides an excellent means for the precise determination of the electron scattering length in gaseous perturbers [1-8]. Recently, Al-Omari, Reininger and Huber [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  $\sim 10$  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 1K. The applied electric field was 100V, 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<sub>3</sub>I (Aldrich Chemical Company, 99%) and SF<sub>6</sub> (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<sub>3</sub>I with SF<sub>6</sub> [4].

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. Photocurrents within the cell were of the order of  $10^{-10}$  A.

### 3. RESULTS AND DISCUSSION

Photoionization spectra of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{I}$  doped into varying number densities of  $\text{SF}_6$  are presented in Fig. 1 in the autoionizing region ( $I_1 < h\nu < I_2$ ) of  $\text{CH}_3\text{I}$ . Energy positions of a number of  $nd'$  states for selected perturber number densities  $\rho$  are given in Table I, 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  $\text{cm}^3$ ) closely approximates the asymptotic shift rate of the Rydberg series. Using the value [15]  $\alpha = 6.54 \times 10^{-24}$   $\text{cm}^3$  for  $\text{SF}_6$ , one finds from Eqs. (1-3) an electron scattering length for  $\text{SF}_6$  of  $A = -0.484$  nm. Since the zero-energy scattering cross section  $\sigma$  is given by

$$\sigma = 4\pi A^2, \quad (4)$$

we have  $\sigma = 2.94 \times 10^{-14}$   $\text{cm}^2$  for  $\text{SF}_6$ . This should be compared to the value  $\sigma \approx 2 \times 10^{-14}$   $\text{cm}^2$  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<sub>6</sub> 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<sup>-4</sup> 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 integrating over R (with a lower limit given by the Wigner-Seitz radius) to find [2,9]

$$\Delta_p = - 20.3 \left( \frac{\alpha e^2}{2} \right) \rho^{4/3}. \quad (5)$$

Recently, Al-Omari, Reininger and Huber [13] calculated the polarization energy distribution P(W) of impurity molecules in dense gases using a static approximation. In the infinite temperature limit, these authors derived an approximate expression for P(W) which has a maximum at

$$W_M = - 18.9 \left( \frac{\alpha e^2}{2} \right) \rho^{4/3}, \quad (6)$$

which is essentially the Fermi result but without the high density restriction. They [13] also found that their high temperature expression for P(W) compared favorably to finite-temperature Monte Carlo 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

$$\Delta = \left( \frac{2\pi\hbar^2}{m} \right) A \rho - 18.9 \left( \frac{\alpha e^2}{2} \right) \rho^{4/3} \quad (7)$$

as opposed to the impact approximation result described above, namely

$$\Delta = \left( \frac{2\pi\hbar^2}{m} \right) A \rho - 10.78 \left( \frac{\alpha e^2}{2} \right)^{2/3} (\hbar\nu)^{1/3} \rho. \quad (8)$$

A nonlinear least-squares fit of Eq. (7) to the present  $SF_6$  data yields the value  $A = -0.426$  nm, which is within approximately 10% of the value found from the fit to Eq. (8) [i.e.,  $A = -0.484$  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  $CH_3I/Ar$ .

In Fig. 3 we have plotted the shift [2] in the vertical ionization energy  $I_1$  of  $CH_3I$  versus 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  $\Delta_p$  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  $\text{CH}_3\text{I}$  in Ar.

In summary, we have presented the first determination of the electron scattering length in  $\text{SF}_6$  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 II 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  $\text{SF}_6$ .

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TABLE I.  $nd'$  and  $I_2 \equiv I(^2E_{1/2})$  photoionization energies (eV) of  $\text{CH}_3\text{I}$  in selected number densities  $\rho$  ( $10^{19} \text{ cm}^{-3}$ ) of  $\text{SF}_6$ .

$\rho$	9d'	10d'	11d'	12d'	$I_2$
0.12	9.868	9.938	9.987	10.022	10.164
0.96	9.867	9.937	9.988	10.022	10.162
1.97	9.866	9.936	9.986	10.020	10.162
5.02	9.863	9.933	9.980	10.013	10.153
9.75	9.856	9.923	9.968	10.002	10.139

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

Gas	$\Delta/\rho$ ( $10^{-23} \text{ eV cm}^3$ )	$A$ (nm)	Region	Reference
$\text{N}_2$	0.0	0.019	AI	a
Ar	-4.75	-0.082	AI	b
$\text{CH}_4$	-7.86	-0.138	AI	c
$\text{C}_2\text{H}_6$	-10.05	-0.176	AI	c
$\text{CO}_2$	-11.8	-0.224	ST	d
$\text{C}_3\text{H}_8$	-12.93	-0.228	AI	c
Xe	-16.8	-0.324	ST	e
$\text{SF}_6$	-24.72	-0.484	AI	This work

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## FIGURE CAPTIONS

Figure 1. Photoionization spectra ( $T=27^{\circ}\text{C}$ ) of pure  $\text{CH}_3\text{I}$  (0.1 mbar) and  $\text{CH}_3\text{I}$  (5 mbar) doped into varying number densities ( $10^{19} \text{ cm}^{-3}$ ) of  $\text{SF}_6$ : a, 0.12; b, 1.97; c, 5.02; d, 9.75.

Figure 2. Energy shifts of  $nd'$  Rydberg states of  $\text{CH}_3\text{I}$  as a function of  $\text{SF}_6$  number density. The fitted ionization energy  $I_2$  is denoted  ${}^2E_{1/2}$ . All straight lines result from a linear regression analysis.

Figure 3. Shift in the first vertical ionization energy of  $\text{CH}_3\text{I}$  in varying number densities of Ar. ●, data from [2]; - - - nonlinear least-squares fit to Eq. (7); — linear least-squares fit to Eq. (8). See text for discussion.

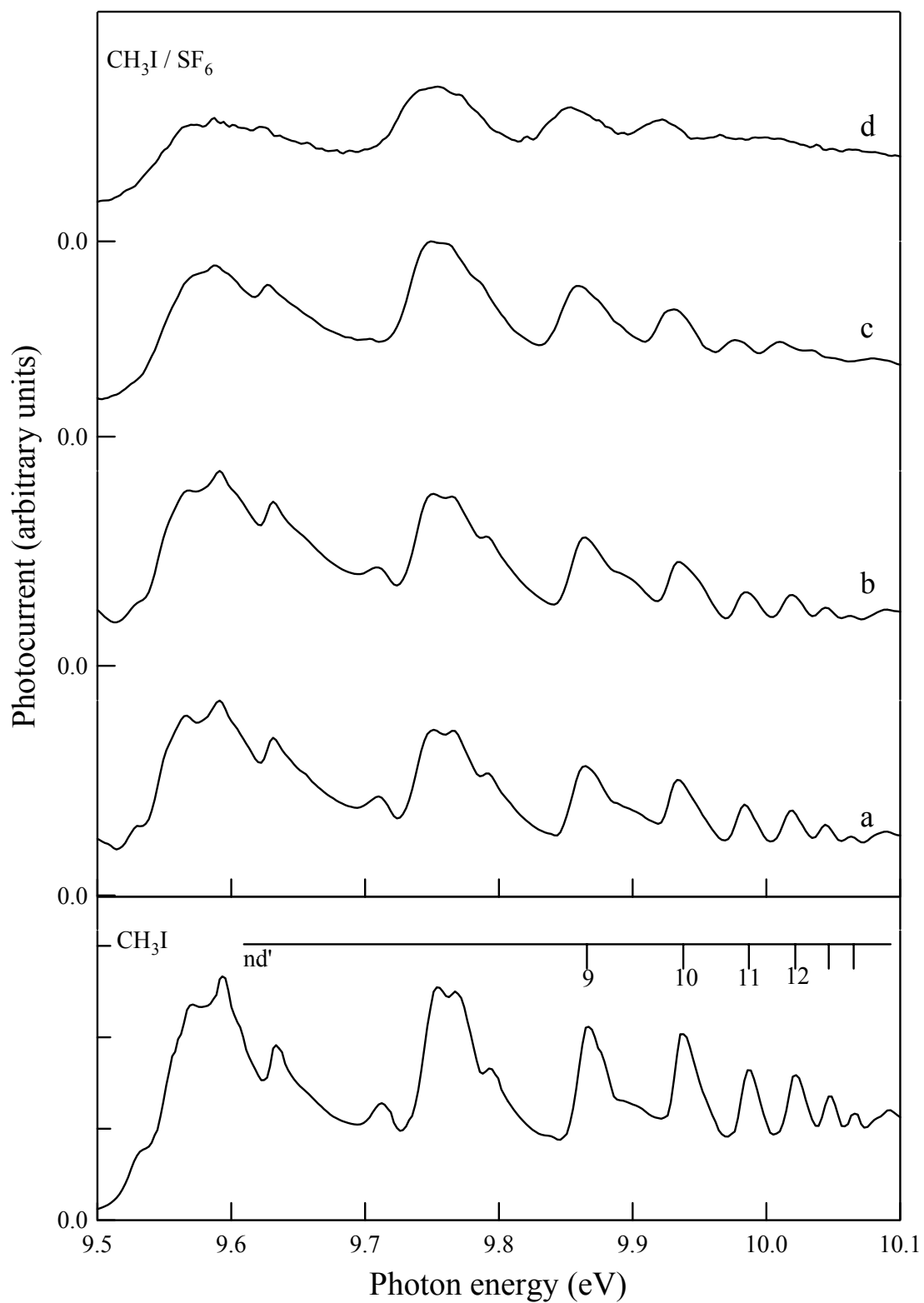


Figure 1. Evans, Reininger and Findley, "Photoionization Spectra of  $\text{CH}_3\text{I}$  Perturbed by  $\text{SF}_6$ "

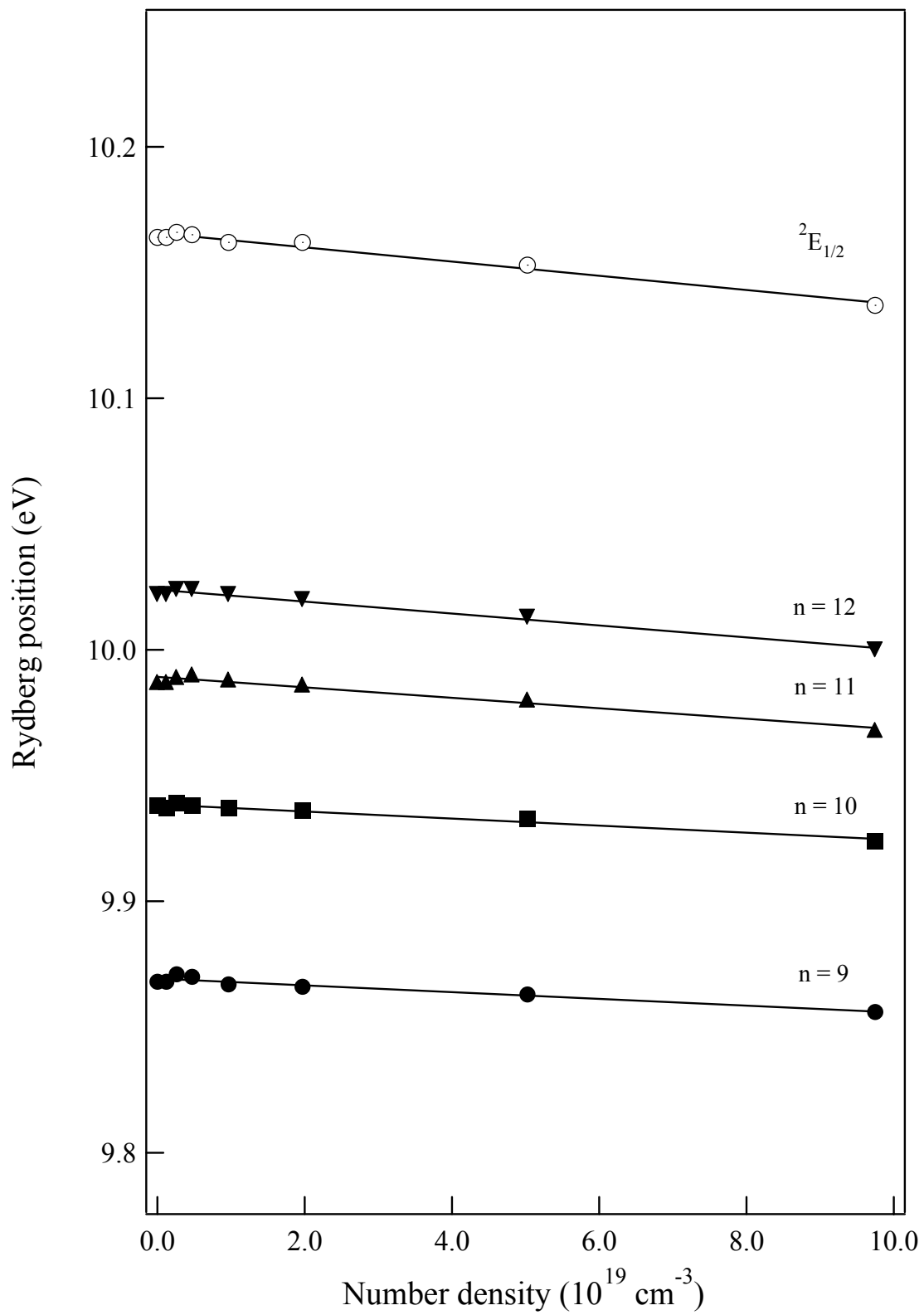


Figure 2. Evans, Reininger and Findley, "Photoionization Spectra of  $\text{CH}_3\text{I}$  Perturbed by  $\text{SF}_6$ "

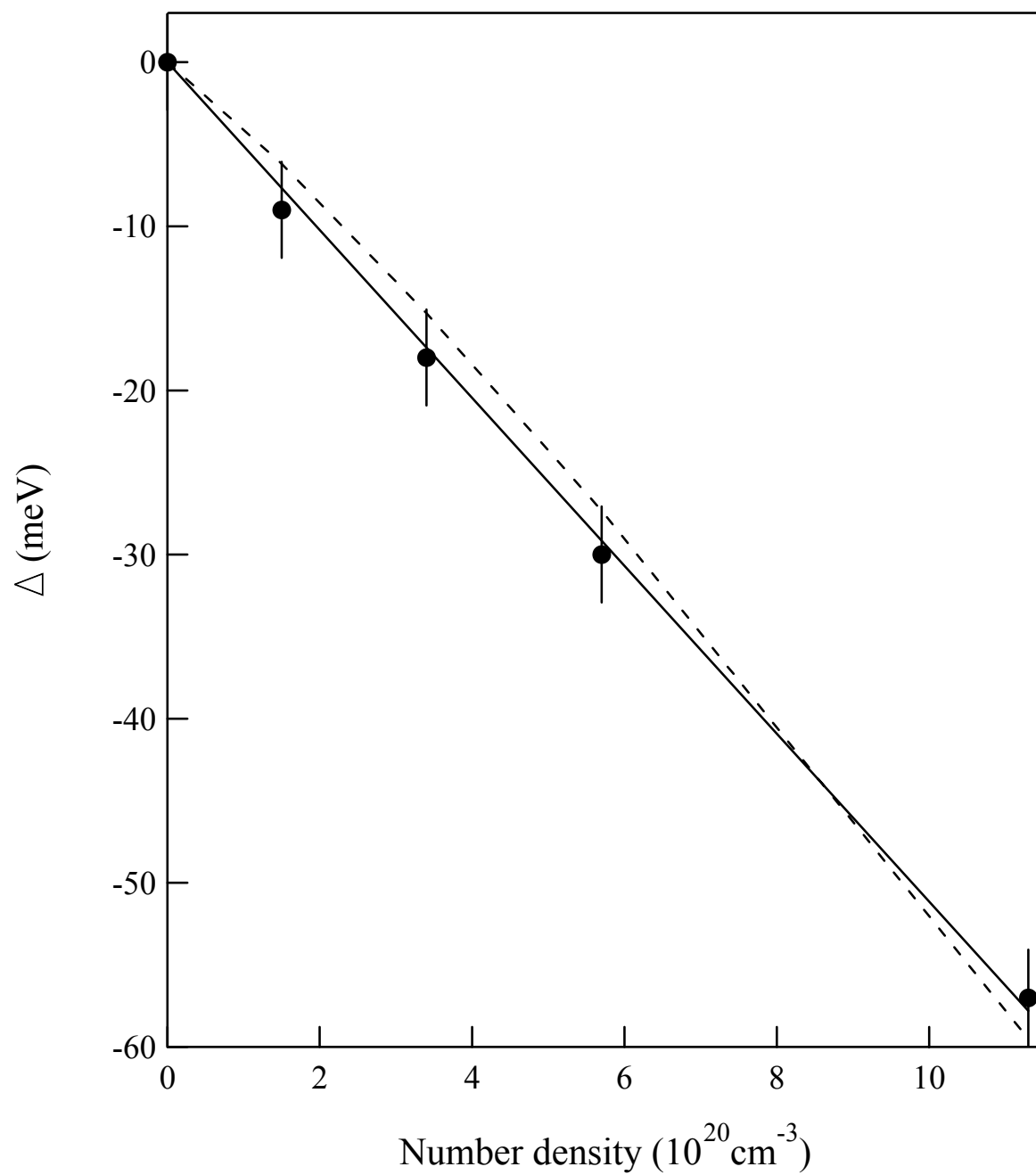


Figure 3. Evans, Reininger and Findley, "Photoionization Spectra of  $\text{CH}_3\text{I}$  Perturbed by  $\text{SF}_6$ "