Subthreshold photoionization of CH₃I in Ar, N₂ and CO₂

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Abstract

We present pressure-dependent subthreshold photoionization spectra of CH₃I doped into varying number densities of the perturber gases Ar, N₂ and CO₂. 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.

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 (CH₃I) has served as the dopant in many such studies because of the atomic-like Rydberg series and the low ionization energy (I₁ = I(2Δ₁E) = 9.54 eV [1]) observed for this molecule. Perturbers have included rare gases [1-5], H₂ [4], alkanes [6], CO₂ [7], N₂ [8] and SF₆ [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 CH₃I [5,10-12] and of CH₃I doped into Ar[5], Xe [3], CO₂ [7], N₂ [8] and SF₆ [10] exhibit rich subthreshold structure beginning 0.17 eV before the ionization limit I₁. 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 CH₃I. 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 CH₃I 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 structure which, for a general dopant (D)/perturber (P) system, can be symbolized as

\[ D^+ + P \rightarrow D^+ + P^- \]  \hspace{1cm} (1)

\[ \rightarrow [DP]^+ + e^- \]  \hspace{1cm} (2)
\[ \rightarrow R_1^* + R_2 + e^- \] (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 CH\textsubscript{3}I (D = P = CH\textsubscript{3}I), Ivanov and Vilesov [11,12] attributed the presence of subthreshold structure in the pure CH\textsubscript{3}I photoionization spectra at high pressures of CH\textsubscript{3}I to eq. (2), since the intensity was quadratically dependent upon the pressure of CH\textsubscript{3}I 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 CH\textsubscript{3}I pressure (in accord with the experiments by Ivanov and Vilesov [12]), while the intensity of the subthreshold structure in CH\textsubscript{3}I doped into SF\textsubscript{6} depends linearly on the SF\textsubscript{6} 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]

\[ i_{af} = k_2 \rho_D \rho_P, \] (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 CH\textsubscript{3}I 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 CH\textsubscript{3}I [17], which in turn scales according to \( n^7 \) [15]. For the case of CH\textsubscript{3}I doped into SF\textsubscript{6} [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 CH\textsubscript{3}I [10], but now \( \rho_P = \rho_D \), leading to

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

For pure CH\textsubscript{3}I, 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 CH\textsubscript{3}I doped into Ar, N\textsubscript{2} and CO\textsubscript{2}, and compare these results to our previous SF\textsubscript{6} 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 SF\textsubscript{6}, 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, N\textsubscript{2} and CO\textsubscript{2}, 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 CH$_3$I [10], namely,

$$\text{CH}_3\text{I}^+ + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{I}^+ + \text{CH}_3\text{I}^-$$  \hspace{1cm} (8)

$$\text{CH}_3\text{I}^+ + \text{CH}_3\text{I} + \text{P} \rightarrow (\text{CH}_3\text{I})_2^+ + \text{P} + e^-$$ \hspace{1cm} (9)

As was the case in pure CH$_3$I (and CH$_3$I/SF$_6$), 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 N$_2$ and CO$_2$ [18], however, we invoke a perturber stabilization of the associative ionization step, as indicated in eq. (9). In this case, then, eq. (7) becomes

$$i = k_1 \rho_D + k_2 \rho_D^2 \rho_P.$$ \hspace{1cm} (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 µ slits), or ~ 10 meV in the spectral range of interest. Two different experimental cells were used: Cell 1 [19] is equipped with entrance and exit MgF$_2$ 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 withstanding pressures up to 100 bar. Each cell was connected to a cryostat and heater system allowing the temperature to be controlled to within ± 1 K [19]. The applied electric field was 100 V, with the negative 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 1$^{10}$ 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%), 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
Fig. 1. Subthreshold photoionization (cell 2, 200 μ slits) of 5.0 mbar CH₃I in various perturbers (at a number density of 0.12 x 10¹⁹ cm⁻³): a, Ar; b, N₂; c, CO₂; d, SF₆ [10]. Absorption of pure CH₃I (cell 1, 200 μ slits): 0.1 mbar. Each photoionization spectrum is normalized to unity at the same spectral feature above the 2E₃/₂ ionization threshold.

also included our previously reported [10] CH₃I/SF₆ spectrum in this figure. (All of the photoionization spectra presented are normalized to unity at the same spectral feature above the CH₃I 2E₃/₂ threshold.) From Fig. 1, one observes that the subthreshold photoionization structure correlates in all cases with the nd Rydberg states of CH₃I converging on the 2E₃/₂ ionization limit, and that the intensity of the subthreshold structure increases as Ar < N₂ < CO₂ < SF₆. Representative subthreshold photoionization spectra for CH₃I doped into varying number densities of Ar are presented in Fig. 2. (The perturbers N₂ and CO₂ 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 CH₃I/SF₆ [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 CH₃I doped into Ar, N₂ and CO₂. These data are collected in Table 1 (CH₃I/Ar), Table 2 (CH₃I/N₂) and Table 3 (CH₃I/CO₂). Since ρ₀ is constant, eq. (10) may be rewritten as

\[ i = b_0 + b_1 \rho_P, \]

(11)

where \( b_0 = k_j \rho_0 \) and \( b_1 = k_2 \rho_0^2 \). These linear correlation coefficients are also collected in

![Fig. 2. Subthreshold photoionization spectra of CH₃I/Ar at 298K. Photoionization (cell 2, 200 μ 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 2E₃/₂ ionization threshold. In (a), the dotted lines are an example of the Gaussian fits used to obtain peak intensities.](image)
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 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>
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<tr>
<td>1.23</td>
<td>0.107</td>
<td>0.330</td>
<td>0.602</td>
<td></td>
</tr>
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</table>

Regression Coefficients

$b_0 = 0.0482$  
$b_1 = 0.0498$

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

Tables 1-3, and the photoionization peak areas are plotted versus $\rho$, for each perturber gas in Fig. 3a (CH$_3$I/Ar), b (CH$_3$I/N$_2$) and c (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.)

Since the subthreshold photoionization structure is superimposed upon a rising

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 $\rho$ ($10^{19}$ cm$^{-3}$) of CO$_2$.

<table>
<thead>
<tr>
<th>$\rho$</th>
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<th>12d</th>
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<th>14d</th>
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<tr>
<td>0.12</td>
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<td>0.504</td>
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<tr>
<td>0.73</td>
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<td>0.997</td>
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<tr>
<td>1.10</td>
<td>0.183</td>
<td>0.472</td>
<td>0.805</td>
<td>1.20</td>
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<tr>
<td>1.46</td>
<td>0.213</td>
<td>0.531</td>
<td>0.906</td>
<td></td>
</tr>
</tbody>
</table>

Regression Coefficients

$b_0 = 0.0778$  
$b_1 = 0.104$

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

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$_2$; c, CO$_2$ as a function of number density $\rho$ ($10^{19}$ cm$^{-3}$). dots, 11d; ■, 12d; ▲, 13d; ▼, 14d. The solid lines represent a least-squares fit to the function $b_1 \rho + b_0$ (cf. Tables 1-3).
Fig. 4. (a) Constant and (b) linear regression coefficients for the subthreshold photoionization density dependence of CH$_3$I in varying perturbers versus the CH$_3$I excited state principal quantum number $n$ and $n^7$, respectively. •, Ar (Table 1); ■, N$_2$ (Table 2); ▲, CO$_2$ (Table 3); ▼, SF$_6$ [10]. The solid lines represent a least-squares linear fit to the data. See text for discussion.

As discussed in the introduction, $b_0$ should scale as $n$ (since $k_1$ scales as $n$ [10]), while $b_1$ should scale as $n^7$ (since $k_2$ scales as $n^7$ [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 $n^7$ 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, Figs. 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$_3$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 \( \rho_D \), 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.

Acknowledgments

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References