Photoionization studies of C\textsubscript{2}H\textsubscript{5}I and C\textsubscript{6}H\textsubscript{6} perturbed by Ar and SF\textsubscript{6}

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submitted 20 April 2000

Abstract

We present photoionization spectra of C\textsubscript{2}H\textsubscript{5}I and C\textsubscript{6}H\textsubscript{6} doped into Ar and SF\textsubscript{6}, and photoabsorption spectra of C\textsubscript{2}H\textsubscript{5}I doped into Ar. The observation of subthreshold photoionization in C\textsubscript{2}H\textsubscript{5}I/SF\textsubscript{6} and C\textsubscript{6}H\textsubscript{6}/SF\textsubscript{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\textsubscript{6}. Similarly, the zero-kinetic-energy electron scattering length of Ar obtained from the density-dependent energy shifts of C\textsubscript{2}H\textsubscript{5}I Rydberg states is presented. (Electron scattering lengths obtained here for SF\textsubscript{6} and Ar accord with values previously obtained using the density-dependent energy shifts of high-n Rydberg states of CH\textsubscript{3}I doped into these two perturber gases.)

1. Introduction

Numerous photoabsorption \cite{1-5}, photoionization \cite{2,6-15} and field ionization \cite{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 \cite{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 \cite{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 subthreshold 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 \cite{6}. However, photoionization spectra of CH\textsubscript{3}I \cite{11,12,14} and of CH\textsubscript{3}I doped into Xe \cite{10}, Ar \cite{2,15}, CO\textsubscript{2} \cite{8,15}, N\textsubscript{2} \cite{15} and SF\textsubscript{6} \cite{14} exhibit rich subthreshold structure beginning 0.17 eV below the CH\textsubscript{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\textsubscript{3}I at very low perturber pressures \cite{11,12,17}. At

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higher perturber pressures, this vibrational autoionization is supplanted by a subthreshold structure having a much lower energy onset [11,12,14].) Finally, CH\textsubscript{3}I 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 CH\textsubscript{3}I doped into Ar, N\textsubscript{2}, CO\textsubscript{2} [15] and SF\textsubscript{6} [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]:

\begin{equation}
D^* + P \rightarrow D^* + P^- \rightarrow [DP]^* + e^-, \tag{1}
\end{equation}

where D\textsuperscript{*} 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],

\begin{equation}
D^* + D \rightarrow D^+ + D^- \tag{3}
\end{equation}

\begin{equation}
D^* + D + P \rightarrow D_2^+ + P + e^- \tag{4}
\end{equation}

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],

\begin{equation}
i = i_{ea} + i_{ai}, \tag{5}
\end{equation}

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)]

\begin{equation}
i_{ea} = k_1^{(1)} \rho_{D^*} \rho_P, \tag{6}
\end{equation}

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

\begin{equation}
i_{ea} = k_1^{(2)} \rho_{D^*} \rho_D. \tag{7}
\end{equation}

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 \(\rho_{D^*} \approx \rho_D\) in the linear absorption regime, eqs. (6,7) both reduce to [14,15]

\begin{equation}
i_{ea} = k_1 \rho_D, \tag{8}
\end{equation}

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 \(\rho_{D^*} \approx \rho_D\) in the linear absorption regime, the associative ionization contribution from pathway 1 [cf. eq. (2)] is given by [14]

\begin{equation}
i_{ai} = k_2^{(1)} \rho_D \rho_P, \tag{9}
\end{equation}

while the same contribution from pathway 2 [cf.
eq. (4)] is given by [15]

\[ i_{at} = k_2^{(2)} p_p p_D, \]  

(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

\[ i = (k_1 + k_2 p_D) p_D \]  

(11)

for pathway 1, and

\[ i = (k_1 + k_2 p_D) p_D \]  

(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 \( p_D >> p_p \). 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 CH₃I doped into varying number densities of SF₆ [14]. Moreover, we have also shown [14] that eq. (11) holds for the degenerate case \( (D = P = CH₃I) \) of varying number densities of pure CH₃I, 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 CH₃I doped into varying number densities of Ar, N₂ and CO₂ [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 CH₃I [14], as well as for the CH₃I/P systems with \( P = Ar, N₂, CO₂ [15] \) and SF₆ [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 \( n^7 \).)

As mentioned above, we have observed [14] subthreshold photoionization structure in pure CH₃I that is quadratically dependent on CH₃I number density, and that can be modeled within pathway 1 [i.e., eqs. (1,2)] by setting \( P = D = CH₃I \). We have also observed subthreshold photoionization structure in CH₃I/SF₆ that is linearly dependent on the SF₆ number density [14]. This CH₃I/SF₆ subthreshold structure was explained within pathway 1, since SF₆ has a large electron attachment cross-section [6,20]. However, the existence of subthreshold structure in pure CH₃I implies that, in the presence of a perturber with a small electron attachment cross-section, subthreshold photoionization of CH₃I 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 CH₃I doped into Ar, N₂ and CO₂ [15] which was linearly dependent upon the perturber number density at constant CH₃I 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)].

In the present Paper, we present a photoionization study of C₂H₅I and C₆H₆ doped into Ar and SF₆. The dopant C₂H₅I was chosen because of the similarity of its electronic structure to that of CH₃I [14,15]. The dopant C₆H₆, on the other hand, was chosen because of the lack of any similarity to CH₃I. The perturber 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 SF₆, 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 C₂H₅I and pure C₆H₆ (unlike pure CH₃I) 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 C₂H₅I and C₆H₆ doped into Ar. However, both C₂H₅I and C₆H₆ doped into SF₆ exhibit rich subthreshold photoionization structure which will be modeled within the confines of pathway 1 [eqs. (1, 2 and 11)].

Finally, 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]. Briefly, 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 [22,23]

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

(14)

where \( \alpha \) is the polarizability of the perturber molecule, \( e \) is the charge of the electron, \( v \) is the relative thermal velocity of the molecules and \( \hbar \) is the reduced Planck constant. Since \( \Delta_p \) is easily calculated and \( \Delta \) 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]

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

(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, since we can assign the subthreshold photoionization structure to high-n Rydberg states of the dopant, we have extracted the electron scattering length of SF₆ from the density-dependent energy shifts of the subthreshold structure of C₂H₅I and C₆H₆. The values obtained from the measurements presented here accord well with those values obtained from a similar analysis of the subthreshold photocurrent of CH₃I/SF₆ [14], as well as from the autoionization spectra of CH₃I/SF₆ [13]. Since Ar is transparent in the spectral region of interest, we were also able to obtain the electron scattering length of Ar from both the absorption spectra and the autoionization spectra of C₂H₅I doped into Ar. The value extracted from these measurements agrees nicely with that obtained from similar absorption studies of CH₃I [2,3] and C₆H₆ [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, 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 [7].

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. (All C₂H₅I spectra presented are normalized to unity at the same spectral feature above the \( \tilde{X}_1^2E_{1/2} \) [26,27] ionization threshold. All C₆H₆ spectra are normalized to unity at the same spectral feature above the \( ^2E_{1g} \) [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 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.) We also observed no subthreshold features in pure C₂H₅I (0.1 mbar - 160 mbar) and pure C₆H₆ (1 mbar - 100 mbar). Therefore, as discussed in the introduction, the most probable mechanisms leading to subthreshold 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 (C₂H₅I/SF₆) and Table 2 (C₆H₆/SF₆). 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
Table 1. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 3) of 0.1 mbar C₂H₅I in varying SF₆ number densities ρ (10¹⁹ cm⁻³)

<table>
<thead>
<tr>
<th>ρ</th>
<th>10d</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.0301</td>
<td>0.242</td>
<td>0.497</td>
<td>0.785</td>
<td>1.14</td>
</tr>
<tr>
<td>0.24</td>
<td>0.0710</td>
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<td>0.594</td>
<td>0.940</td>
<td>1.33</td>
</tr>
<tr>
<td>0.49</td>
<td>0.142</td>
<td>0.433</td>
<td>0.784</td>
<td>1.20</td>
<td>1.76</td>
</tr>
<tr>
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<td>0.483</td>
<td>0.848</td>
<td>1.30</td>
<td>1.92</td>
</tr>
<tr>
<td>0.73</td>
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<td>0.543</td>
<td>0.941</td>
<td>1.42</td>
<td>2.12</td>
</tr>
<tr>
<td>1.09</td>
<td>0.336</td>
<td>0.683</td>
<td>1.20</td>
<td>1.80</td>
<td>2.73</td>
</tr>
<tr>
<td>1.5</td>
<td>0.445</td>
<td>0.856</td>
<td>1.47</td>
<td>2.19</td>
<td>3.36</td>
</tr>
<tr>
<td>1.8</td>
<td>0.526</td>
<td>1.02</td>
<td>1.70</td>
<td>2.51</td>
<td>3.41</td>
</tr>
<tr>
<td>2.2</td>
<td>0.640</td>
<td>1.19</td>
<td>1.95</td>
<td>2.94</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Regression Coefficients*

\[ b_0 = 0.0118 + 0.207 D \]
\[ b_1 = 0.286 + 0.427 D \]

*The regression coefficients are for a least-squares linear fit, \( b_0 + b_1 \rho \), as shown in Fig. 5.

Table 2. Peak areas (by gaussian fits to the photoionization spectra) for the subthreshold photoionization structure (cf. Fig. 4) of 1.0 mbar C₆H₆ in varying SF₆ number densities ρ (10¹⁹ cm⁻³)

<table>
<thead>
<tr>
<th>ρ</th>
<th>8R'</th>
<th>9R'</th>
<th>10R'</th>
<th>11R'</th>
<th>12R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.407</td>
<td>1.16</td>
<td>1.95</td>
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<tr>
<td>0.24</td>
<td>0.443</td>
<td>1.22</td>
<td>2.09</td>
<td>3.00</td>
<td>4.17</td>
</tr>
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<td>0.49</td>
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<td>2.48</td>
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<tr>
<td>0.72</td>
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<td>2.76</td>
<td>4.05</td>
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</tr>
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<td>4.89</td>
<td>7.69</td>
</tr>
<tr>
<td>1.4</td>
<td>0.778</td>
<td>1.98</td>
<td>3.65</td>
<td>5.68</td>
<td>8.81</td>
</tr>
<tr>
<td>2.2</td>
<td>1.15</td>
<td>2.60</td>
<td>4.72</td>
<td>7.42</td>
<td>10.18</td>
</tr>
</tbody>
</table>

Regression coefficients*

\[ b_0 = 0.356 + 1.05 \rho \]
\[ b_1 = 0.351 + 0.690 \rho \]

*The regression coefficients are for a least-squares linear fit, \( b_0 + b_1 \rho \), as shown in Fig. 5b.

Fig. 4. (a) Constant and (b) linear regression coefficients for the subthreshold density dependence of C₂H₅I/SF₆ (Table 2) plotted versus the C₂H₅I excited state principal quantum number \( n \) and \( n' \), respectively. The straight lines are least-squares fits to the data. See text for discussion.

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

\[ i = b_0 + b_1 \rho \beta. \]  

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 (C₂H₅I/SF₆) and Fig. 5 (C₆H₆/SF₆), we have plotted \( b_0 \) versus \( n \) and \( b_1 \) versus \( n' \). 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 C₂H₅I/SF₆ and C₆H₆/SF₆. (However, as mentioned in the
Fig. 5. (a) Constant and (b) linear regression coefficients for the subthreshold density dependence of C₂H₅/SF₆ (Table 3) plotted versus the C₂H₅ excited state principal quantum number n and n', respectively. The straight lines are least-squares fits to the data. See text for discussion.

Table 3. nd and I₁ = I(\tilde{X}_1 \tilde{2}E_{1/2}) photoionization energies (eV) of C₂H₅I in selected number densities ρ (10¹⁹ cm⁻³) of SF₆.

<table>
<thead>
<tr>
<th>ρ</th>
<th>10d</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>14d</th>
<th>I₁</th>
</tr>
</thead>
</table>

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 SF₆. In Table 3, the energy positions of a number of C₂H₅I nd Rydberg states [26,27], as assigned from the photoionization spectra, are given for selected SF₆ number densities. Ionization energies I₁ = I(\tilde{X}_1 \tilde{2}E_{1/2}) 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 C₆H₆ nR' states [27,28], as well as the values of I₁ (\tilde{C}_1 \tilde{E}_{1g}) extracted from a fit of the assigned spectra to the Rydberg equation, are presented in Table 4 for selected SF₆ number densities. The shift data are summarized in Figs. 6a and 6b, where we have plotted the energy positions of nd C₂H₅I and nR' C₆H₆ Rydberg states, respectively, versus SF₆ number density. Fig. 6 shows that the energy shifts are linearly dependent on the perturber number density and can therefore be analyzed by the Fermi model given in eqs. (13-15) of the introduction. Using the value [29] α = 6.54 x 10⁻²⁴ cm³ for SF₆, and the value Δ/ρ = -25.36 x 10⁻¹³ eV cm³ obtained from the subthreshold photoionization spectra of C₂H₅I doped into SF₆, one finds a zero-
Fig. 6. Energy shifts of (a) nd Rydberg states of C$_2$H$_5$I and (b) the nR' Rydberg states of C$_6$H$_6$ as a function of SF$_6$ number density $\rho$ (10$^{19}$ cm$^{-3}$). In (a): $\bullet$, 10d; $\Box$, 11d; $\blacktriangle$, 12d; $\blacktriangledown$, 13d; $\blacklozenge$, 14d; $\bigstar$, I$_1$ ($\tilde{X}$,$I_{1/2}$). In (b): $\bigcirc$, 8R'; $\Box$, 9R'; $\blacktriangle$, 10R'; $\blacktriangledown$, 11R'; $\bigstar$, 12R'; $\blacklozenge$, I$_1$ ($\tilde{E}$,$I_{3/2}$). 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.
Table 5. $n_d$ and $I_1 = I(\tilde{X}_2^{2}E_{1/2})$ as well as $n_d'$ and $I_2 = I(\tilde{X}_2^{2}E_{1/2})$ photoabsorption energies (eV) of C$_2$H$_5$I in selected number densities $\rho$ (10$^{20}$ cm$^{-3}$) of Ar.

<table>
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<tr>
<th>$\rho$</th>
<th>10d</th>
<th>11d</th>
<th>12d</th>
<th>13d</th>
<th>$I_1$</th>
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</table>

<table>
<thead>
<tr>
<th>$\rho$</th>
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<th>11d'</th>
<th>12d'</th>
<th>13d'</th>
<th>14d'</th>
<th>$I_2$</th>
<th>$I_1$</th>
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</table>

CH$_3$I doped into dense Ar [16,24].

In summary, we have measured photoionization and photoabsorption spectra of C$_2$H$_5$I/Ar and C$_6$H$_6$/Ar and photoionization spectra of C$_2$H$_5$I/SF$_6$ and C$_6$H$_6$/SF$_6$, 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 C$_2$H$_5$I and C$_6$H$_6$ doped into SF$_6$. We have also shown that pathway 2 [i.e., eqs. (3, 4 and 12)] is likely unavailable as a subthreshold photoionization mechanism in both C$_2$H$_5$I and C$_6$H$_6$, since subthreshold photoionization is absent in pure C$_2$H$_5$I, pure C$_6$H$_6$, C$_2$H$_5$I/Ar and C$_6$H$_6$/Ar. (The inaccessibility of pathway 2 may be due, in part, to the inability of C$_2$H$_5$I and C$_6$H$_6$ 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 CH$_3$I in a molecular beam experiment.) We have shown that the correlation coefficients $b_0$ and $b_1$ 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 C2H5I and C6H6 doped into SF6, to determine the zero-kinetic-energy scattering length of SF6. The values obtained from these measurements were shown to agree with that obtained by similar measurements of CH3I/SF6 [13,14]. We also presented photoabsorption spectra of C2H5I 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 CH3I/Ar [2,3] and C6H6/Ar [5], as well as with the value extracted from field ionization measurements of CH3I doped into dense Ar [16,24].

Acknowledgements

This work was carried out at the University of Wisconsin Synchrotron Radiation Center (NSF DMR95-31009) and was supported by a grant from the Louisiana Board of Regents Support Fund (LEQSF (1997-00)-RD-A-14).

References