

Polarization Energy Distribution of a Positive Ion in Liquid Argon

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We show that the polarization energy distribution of an ion in a dense medium can be obtained from photoionization spectra recorded at two values of the applied electric field. The experimental width of the polarization energy distribution is in very good agreement with the width calculated from the computed first and second moments of the theoretical distribution. The experimental spectra are simulated using the calculated moments and the photoionization spectra of the pure dopant. The simulation yields the energy of the quasifree electron in the medium.

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The evolution of electronic levels as the density of a fluid is increased from that of a dilute gas to that of a dense liquid has attracted considerable interest lately both experimentally and theoretically. Several theoretical models have addressed the line shifts and broadening induced by the increasing density in pure and doped samples [1]. Various groups have recently reported theoretical results on the density dependence of the quasifree electron energy V_0 in the media [2]. A problem interconnecting the above mentioned theoretical work concerns the change in the ionization potential of a solute as the density of the solvent is changed from the gas to the dense liquid. This problem has been investigated by several groups in various systems using single photon [3,4] and multiphoton [5] photoconductivity techniques. The experimentally observed shift in the extrinsic photoconductivity threshold, $E_{pc}(\rho)$, due to the solvent at a density ρ , has been explained in terms of a formula proposed by Raz and Jortner [6]:

$$E_{pc}(\rho) - I_g = w(\rho) + V_0(\rho), \quad (1)$$

where I_g is the gas phase ionization potential of the solute and $w(\rho)$ is the density dependent polarization energy between the positive ion and the media. Equation (1) combined with experimental values for I_g and $V_0(\rho)$ were used in determining the polarization energy between the positive ion and the media. This was also done by several groups in experiments performed at one liquid density [7,8].

The main purpose of the present Letter is to report on an experimental technique which yields the polarization energy *distribution* of a positive ion in a dense media. Furthermore, we show that the experimental results are in good agreement with calculations based on the first and second moments of the polarization energy distribution using realistic interaction potentials. Finally, the value of V_0 is deduced from the energy shift between the experimental data and a simulation using the calculated distribution and the spectra of pure CH_3I .

The system chosen to demonstrate the experimental technique consist of CH_3I doped in liquid argon at a density of $1.65 \times 10^{22} \text{ cm}^{-3}$. The choice of the molecule is

based on its atomiclike photoionization spectrum, which is very similar to that of Xe [9], and on the fact that its ionization limit is well below the first resonance line of argon. The measurements were performed using monochromatized synchrotron radiation ($\Delta\lambda = 0.065 \text{ nm}$). The experimental cell is equipped with entrance and exit MgF_2 windows and a pair of parallel electrodes separated by 3 mm. The electrodes are oriented parallel to the plane of the storage ring and almost in contact with the windows. The cell can withstand pressures up to 100 bars and can be cooled down below 70 K.

Figure 1(a) presents the photoionization of pure CH_3I gas recorded with electric fields of 833 and 9633 V/cm. The structure in the spectra above the first ionization limit ($I_{g1} = 9.538 \text{ eV}$) is due to the autoionizing ns' , np' , and nd' Rydberg states converging to the second ionization limit ($I_{g2} = 10.164 \text{ eV}$). The effects caused by increasing the applied electric field have been described in detail in Ref. [10]. Classically, Rydberg states within $2\sqrt{F}$ (a.u.) below the zero field ionization limit will ionize due to the presence of the field. We note in passing that in the

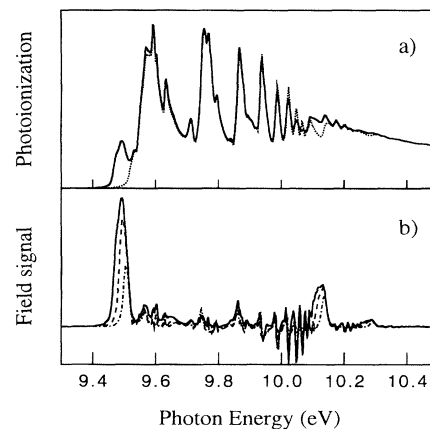


FIG. 1. (a) Photoionization of pure CH_3I (0.1 mbar) recorded with 9633 (solid line) and 833 V/cm (dotted line). (b) Field signals (see text) for 9633 (solid line), 5633 (dashed line), and 2700 V/cm (dot-dashed line).

above mentioned work [10] we found a smaller constant, 1.42 a.u. The main feature in Fig. 1(a) is the additional current below the first and second ionization limits. Figure 1(b) presents the field signals, $FS_G(F, F_1, h\nu)$, i.e., the spectra obtained by subtracting the spectrum recorded with the lowest field ($F_1 = 833$ V/cm) from those recorded with $F = 2700, 5633, \text{ or } 9633$ V/cm. As seen in the figure, maxima are observed below the first and second ionization limits. The maxima at low (high) energy correspond to the Rydberg states converging to I_{g1} (I_{g2}) which are ionized by F but not by F_1 . The strong oscillations around 10 eV are due to the increasing Stark broadening of the high Rydberg states converging to the second ionization limit with increasing the applied field [see also Fig. 1(a)]. Additional small maxima observed in the field signal spectra are due to Rydberg states converging to vibrationally excited states of the ion, which, as before, are ionized by F but not by F_1 .

The photoionization of CH_3I doped in liquid argon is displayed in Fig. 2(a). As expected, the spectra recorded in the liquid differ considerably from those shown in Fig. 1(a). The high density induces a considerable energy shift and a smearing of the rich autoionization structure. As seen in the figure, field ionization also occurs in the liquid in the threshold region and around 9.25 eV. The field signals obtained in the liquid, $FS_L(F, F_1, h\nu)$, are displayed in Fig. 2(b). As in Fig. 1(b), there are two main peaks in each spectra as well as small maxima at

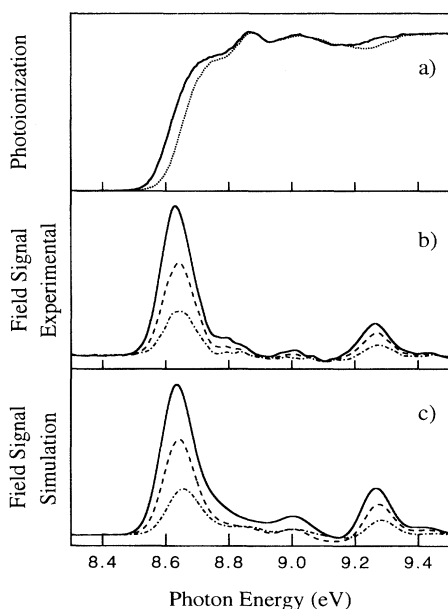


FIG. 2. (a) Photoionization of CH_3I doped in liquid argon ($\rho = 16.5 \times 10^{21} \text{ cm}^{-3}$) recorded with 9633 (solid line) and 833 V/cm (dotted line). (b) As in Fig. 1(b). (c) Simulated field signals using Eq. (10) (see text) for 9633 (solid line), 5633 (dashed line), and 2700 V/cm (dot-dashed line).

around 8.8, 9.0, and 9.42 eV. The peaks correspond to CH_3I Rydberg states converging to the (shifted) ionization potentials in liquid argon and which are field ionized by F but not by F_1 [11]. We note that also in dense argon gas the lowering of the ionization potential as a function of the applied field follows a \sqrt{F} law [11]. The energy separation between the two main peaks, at around 8.6 and 9.3 eV, corresponds to the spin orbit splitting which does not change with the sample density within the accuracy of our measurements. Comparing Figs. 1(b) and 2(b), one realizes that the peaks in the liquid are considerably broader than in the gas. Examination of Fig. 2(b) reveals that the FWHM of all the main peaks in the figure are, approximately the same, 0.11 eV.

The polarization energy given in Eq. (1) depends, actually, on the position \mathbf{r}_i of the host atoms relative the dopant at the moment of excitation, i.e., $w(\mathbf{r}_1 \dots \mathbf{r}_N)$. Under the assumption that the interactions are spherically symmetric, the polarization energy can be approximated as a sum of pair potentials [12,13]

$$w(\mathbf{r}_1 \dots \mathbf{r}_N) = \frac{-\alpha e^2}{2} \sum_{i=1}^N \frac{f(r_i)}{r_i^4}, \quad (2)$$

where α is the polarizability of the solvent atom, e is the electron charge, and $f(r_i)$ is the screening function which accounts for the repulsive interactions between the induced dipoles in the solvent. Based on the canonical distribution, the probability of finding a polarization energy W can be expressed as

$$P(W) = \frac{\int \dots \int \delta(W - w(\mathbf{r}_1 \dots \mathbf{r}_N)) \exp(-\beta U(\mathbf{r}_1 \dots \mathbf{r}_N)) \prod_i d\mathbf{r}_i}{\int \dots \int \exp(-\beta U(\mathbf{r}_1 \dots \mathbf{r}_N)) \prod_i d\mathbf{r}_i}, \quad (3)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T the temperature. $U(\mathbf{r}_1 \dots \mathbf{r}_N)$ represents the potential energy of the system before the ionization. As in the case of line shapes of allowed optical transitions at high perturber densities [14], $P(W)$ can be approximated as

$$P(W) \propto \exp[-(W - m_1)^2 / 2(m_2 - m_1^2)], \quad (4)$$

where the first and second moments of the distribution are given by [14]

$$\begin{aligned} m_1 &= 4\pi\rho \int_0^\infty g_{12}(r)w(r)r^2 dr, \quad (5) \\ m_2 &= m_1^2 + 4\pi\rho \int_0^\infty g_{12}(r)w(r)^2 r^2 dr \\ &\quad + 8\pi^2\rho^2 \int_0^\infty \int_0^\infty g_{12}(r_1)w(r_1)r_1^2 dr_1 \\ &\quad \times \int_0^\infty g_{12}(r_2)w(r_2)r_2^2 dr_2 \\ &\quad \times (1/r_1 r_2) \int_{|r_1-r_2|}^{r_1+r_2} [g_{11}(s) - 1] s ds, \quad (6) \end{aligned}$$

respectively. In Eqs. (5) and (6), g_{11} and g_{12} are the host-host and host-solvent radial distribution functions. We

should point out that Messing and Jortner [13] calculated the density dependence of the polarization energy of Xe^+ in argon based on Eq. (5).

The radial distribution functions were computed based on the Percus-Yevick integral equations for Lennard-Jones (LJ) potentials, as given in Ref. [15]. The LJ parameters for Ar-Ar, $\sigma_{11} = 0.3405$ nm and $\epsilon_{11} = 119.7$ K, were taken from Ref. [16]. Since, to our best knowledge, accurate LJ parameters for Ar- CH_3I are not available, we obtained the $\text{CH}_3\text{I-CH}_3\text{I}$ LJ parameters ($\sigma_{22} = 0.467$ nm and $\epsilon_{22} = 407$ K) from the critical point data of CH_3I [17] as described in Ref. [18]. The Ar- CH_3I LJ parameters were then calculated according to Sikora's combining rule [19], obtaining $\sigma_{12} = 0.4063$ nm and $\epsilon_{12} = 160.6$ K. The screening function $f(r)$ was evaluated numerically, as described in Ref. [13], using our results for the radial distribution functions and $\alpha = 1.64 \times 10^{-24}$ cm³ [20]. Finally, the values obtained for m_1 and the FWHM of the polarization distribution are -0.603 and 0.105 eV, respectively.

The above discussion makes evident that the ionization potential of a solute in a dense media has to be represented, as well, by a distribution. Since V_0 corresponds to the energy of a delocalized electron in the media, the probability that the ionization potential of the solute in the liquid is I_p is given by

$$L(I_p) = P(I_p - (I_g + V_0)). \quad (7)$$

As mentioned above, $FS_L(F, F_1, h\nu)$ is due to the field ionization of Rydberg states having excitation energies $I_{pj} - c\sqrt{F} < h\nu < I_{pj} - c\sqrt{F_1}$, where c is a constant, and the index j represents the different ionization potentials. In the simplifying case of a single ionization potential, this implies that the field signal spectrum is proportional to the convolution between a square function of width $c(\sqrt{F} - \sqrt{F_1})$ and the probability distribution of the ionization potential

$$FS_L(F, F_1, h\nu) \propto \int_{h\nu+c\sqrt{F_1}}^{h\nu+c\sqrt{F}} L(I_p) dI_p. \quad (8)$$

Using Eq. (7) and assuming that $c(\sqrt{F} - \sqrt{F_1})$ is much smaller than the width of $P(W)$, Eq. (8) can be approximated as

$$FS_L(F, F_1, h\nu) \propto c(\sqrt{F} - \sqrt{F_1})P\left(h\nu - I_g - V_0 + \frac{c}{2}(\sqrt{F} + \sqrt{F_1})\right). \quad (9)$$

Equation (9) implies that the width of the peaks in the field signal do not depend on F and are equal to the width of the polarization distribution. This was pointed out when discussing Fig. 2(b). Equation (9) also predicts a small redshift equal to $c(\sqrt{F} + \sqrt{F_1})/2$ in the field signal with increasing F , as observed in Fig. 2(b). Taking this

correction into account allows us to identify the maximum in the field ionization signal to the *vertical ionization potential* in a dense media.

In Eq. (8) we implicitly assumed that the lowering of the ionization potential by the field is a steplike function. As seen in Fig. 1(a), this is not the case in the pure molecule and it is caused by field induced autoionization and hot bands effects [10]. These effects, and the presence of more than one ionization potential, can be accounted for by convoluting the polarization distribution with the field ionization spectra obtained for the bare molecule, namely,

$$FS_L(F, F_1, h\nu) = \int P(W)FS_G[F/\epsilon, F_1/\epsilon, (h\nu - V_0) - W]dW. \quad (10)$$

We included in FS_G the shift in the ionization limit due to V_0 and the fact that the electric field of the ion in the liquid is screened by the dielectric constant ϵ .

The field signals in the liquid were generated from Eqs. (10) and (4), using $V_0 = 0$ and the field signals recorded in pure CH_3I [21]. The resulting field signals, shifted by -0.26 eV, are displayed in Fig. 2(c). We should stress at this point that the shift, which corresponds to V_0 and the vertical scale in Fig. 1(c) (which is the same for the three simulated spectra), is the *only* free parameter in the calculated spectra. A comparison between the experimental and simulated field signals reveals that the calculations reproduce closely almost all the features in the experimental results, including the relative energy positions. In particular, the experimental FWHM of the first peaks, ≈ 0.11 eV, are in very good agreement with the simulated ones, ≈ 0.12 eV. This corroborates our model and the approximation used in calculating $P(W)$. The presently determined value for V_0 is in good agreement with the one obtained by using a photoinjection technique, -0.27 ± 0.02 eV [22], and most of the theoretical values [2].

In summary, we have described an experimental technique which yields the polarization energy distribution of an ion in a dense medium. We have also calculated this distribution and obtained excellent agreement with the experimental results. Furthermore, from the comparison between the calculations and the experiment, we deduced the energy of the quasifree electron in the media. We should point out that, due to space limitations, we restricted ourselves in describing the experimental results and calculations to only one density in the liquid. In fact, similar agreement between the experimental data and the calculations were obtained for argon densities from the gas to the triple point liquid [23].

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