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Photoionization quantum yields of organic molecules in liquid argon and xenon

Akira Hitachi
Department of Physics, Kochi Medical School, Oko-cho, Nankoku-shi, Kochi 783, Japan

Hideo Ichinose,* Jun Kikuchi, and Tadayoshi Doke
Advanced Research Institute for Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Kimiaki Masuda and Eido Shibamura
Saitama College of Health, Kamiokubo, Urawa-shi, Saitama 338, Japan

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Photoionization quantum yields of organic molecules in liquid argon and xenon have been measured. The liquid rare gases are excited by α particles, and vacuum ultraviolet photons emitted from the respective excimer ionize the organic molecules. The quantum yields for TMA (trimethylamine) and TEA (triethylamine) in liquid xenon are observed to be as large as 80% in contrast to much smaller values in the gases in the same excess energy region. [S0163-1829(97)06510-7]

I. INTRODUCTION

Rare gas liquids can approach the ideal solvent for many organic molecules[1,2] because they are not chemically or structurally disruptive and they are optically transparent in most of the vacuum ultraviolet (vuv) and in all of the ultraviolet, visible, and infrared spectral regions. Also, they are suitable in many kinds of radiation detectors using ionization and/or scintillation signals.[3]

Recently, many studies have been performed in high pressure gases or condensed rare gases doped with molecules in order to study fundamental processes of photoionization in these media. Synchrotron radiation provides a powerful and useful vuv source.[4] Many experiments have measured the photoconductivity and obtained information concerning the ionization potential.[5,6] However, only a few studies have determined the photoionization quantum yield ϕ in these media because of experimental difficulties in estimating the amount of photons absorbed. We have developed an experimental method to obtain the quantum yield ϕ of organic molecules in liquid xenon[7] and argon,[8] using an ionization chamber and α particles. The vuv emission from the rare gas excimer produced by α particles is used as an excitation source. Since the energy of an α particle is known, the amount of photons absorbed can be determined accurately. Some values of ϕ in liquid xenon were briefly reported previously; however, a multiwire chamber was used and the values obtained had relatively large uncertainties. Therefore, we have reinvestigated these molecules. The quantum yield is found to behave quite differently as a function of photon energy in liquid phase as compared with that in gas phase.

II. EXPERIMENTAL METHOD

The ionization chambers used in the experiments were described elsewhere[7–9] and therefore only briefly described here. Three chambers were used in a series of experiments. A multiwire chamber with a MgF_2 window was used for the observation of vuv photons.[7] The second chamber is a large gridded ionization chamber with a Pyrex window.[8] A sodium salicylate wavelength shifter was used to observe vuv photons. The third chamber is a small ionization chamber mainly used to measure the photoionization yield in liquid Xe and the energy resolution in both liquid Ar (Ref. 9) and Xe.[10] The detection areas of three chambers were 15 to 40 mm in diameter and 2 to 7 mm thick. ^{207}Bi, ^{210}Po, ^{252}Cf, or their mixture was deposited at the center of the cathode.

Ar and Xe gases were purified using a Ti-Ba getter purifier. Allene (96.8%) was obtained from PCR Inc., TMA (trimethylamine) (99.8%) from Kodak, and TEA (triethylamine) (99.5%) from Wako-Junyaku. The organic compounds were purified using molecular sieves. Details of the purification method used for the organic compounds and the gas handling system are described in Ref. 8.

III. PHOTOIONIZATION OF DOPANTS IN A LIQUID IONIZATION CHAMBER

The charge collection for high LET (linear energy transfer) particles, such as α particles, in a liquid is inefficient because many ions are produced in a small volume along the particle track. The recombination of ions and the relaxation of free excitons produce the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ self-trapped excitons in liquid rare gases. These self-trapped excitons decay to the $^1\Sigma_g^+$ repulsive ground states giving vuv photons with a broad structureless second emission continuum peaked at 128 and 175 nm (9.7 and 7.1 eV) for liquid Ar and Xe, respectively.[11] The widths of the emissions are about 0.6 and 0.5 eV FWHM (full width at half maximum), for condensed argon[11] and xenon,[12] respectively. When a small amount of organic molecules (1–200 ppm) are added to the liquid rare gases, these vuv photons can ionize the doped molecules. The ion pairs produced by absorption of the vuv photons are scattered in a large volume of the ionization chamber and electrons can be collected by a relatively low electric field E. The charge collection in the doped liquids is increased dramatically and this phenomenon is used as the basis of photoionization detectors for heavy ions. The photoabsorption cross section σ and the photoionization quantum yield ϕ can be obtained from the difference in the charge collected in pure and in doped liquid rare gases.

The ionization threshold I_s of a molecule is reduced in solution. In nonpolar liquids such as alkanes and liquid rare gases, I_s can be estimated by the relation,[13]

$$I_s = IP + P_+ + V_0, \tag{1}$$

where IP is the ionization potential in gas phase and V_0 is the energy of the quasifree electron at the bottom of conduction band of the liquid ($V_0 = -0.17$ and -0.65 eV for argon and xenon, respectively[14]). The polarization energy P_+ of the positive ion is given by the Born equation:[15]

$$P_+ = -\frac{e^2}{2r_+}(1-\varepsilon^{-1}). \tag{2}$$

In this classic approximation, a liquid is treated as a uniform continuum with the optical dielectric constant ε (1.52 for liquid argon and 1.94 for liquid xenon[16]), and the positive ion is regarded as a sphere with radius r_+ and charge e.

There are some cases which show Eq. (1) does not apply in supercritical fluids in the low pressure region because of strong interactions between the doped molecules and host atoms.[17] Even in these systems I_s values are well described by Eq. (1) at high densities. Also, photoionization phenomena are dynamic processes because of the difference between the time scales of optical transitions (10^{-16} s) and adiabatic polarization (10^{-12} s). These effects are observed in nonpolar solvents at a much lower density region (10^{20} atoms/cm^3) (Refs. 18 and 19) than in liquid Ar and Xe (10^{22} atoms/cm^3). In spite of its approximate nature, it is known that Eq. (1) is generally found to be valid for organic molecules in nonpolar liquids.[20,21]

It has been reported by several authors that the Born equation describes the polarization energy well.[6,22] Messing and Jortner[23] reported that Eq. (2) shows only a 10% difference from that obtained by a quantum-mechanical calculation for Xe$^+$ in fluid Ar. The difficulty mainly lies in the measurement of I_s, V_0 and the evaluation of P_+. For example, most authors use an empirical power law, $i(h\nu) = C(h\nu - I_s)^m$, where i is the photocurrent, C is an empirical constant, and $m = 5/2$ or $3/2$, to determine I_s. The values reported for I_s coincide well because of the very sharp increase in photocurrent near the threshold.

Most authors have used the Wigner-Seitz radius $r_{\mathrm{WZ}} = (3/4\pi N)^{1/3}$, where N is the number density of liquid, for the radius of positive ion r_+ in Eq. (2). Recently, Katoh *et al.*[24] compared the van der Waals radius $r_{\mathrm{VDW}} = (3V_{\mathrm{VDW}}/4\pi)^{1/3}$ and r_{WZ} with experimental value of r_+ for several aromatic cations in alkane solutions. The van der Waals volume V_{VDW} is calculated as the sum of the van der Waals increments of all atoms in the molecule.[25] They reported that values of r_+ agree better with r_{VDW} than with r_{WZ} for these relatively large molecules. The result implies that the positive charge is delocalized over the whole cation.

Another method to obtain r_+ is to use a radius r_n derived from the molar refraction, $M_r = \{(n^2-1)/(n^2+2)\}(M/\rho)$, where n is the refractive index, M is the molecular weight, and ρ is the density. Since M_r provides an approximate measure of the actual total volume (without free space) of the molecules in one gram mole, we obtain, $r_n = (3M_r/4\pi N_A)^{1/3}$, where N_A is the Avogadro's number. This formula assumes a perfect conductor for a spherical molecule. We can obtain M_r from n, or, since M_r is ideally an additive property, we can add values of M_r assigned to individual atoms or types of bonds.

TABLE I. Ionization potential IP in the gas phase and the estimated values of I_s in liquid Ar and Xe for organic molecules used in the experiment. The values are in eV. The ion radii r_+ are in Å.

Molecules	IP	r_+	I_s in liquid Ar	I_s in liquid Xe
Ethylene	10.51	2.61	9.4	8.5
Allene	9.53	2.82	8.5	7.6
Trimethylamine	7.82	3.28	6.9	6.1
Triethylamine	7.50	3.81	6.7	5.9

We calculated r_n for the molecules quoted in Ref. 24 and compared r_+ with r_{WZ}, r_{VDW}, and r_n. For most molecules r_{VDW} gives the best values. The values of r_{WZ} seem to be too large for these relatively large molecules. The values of r_n are too small for most molecules except naphthalene and triphenylamine for which r_n gives the best values. Molecules doped in liquid rare gases give somewhat large r_+ values,[26] and r_{WZ} may give the best values in these systems. However, the measurements have large errors (± 0.5 Å).[26]

More investigations are needed to conclude which model gives the best value for r_+ in liquid rare gases. We do not measure I_s. We just need to estimate I_s in order to know the trend of the quantum yield as a function of the excess energy given to the electron. Also, for small molecules the differences in the methods for calculating the radius are not large, so we use r_{WZ} here for r_+ in Eq. (2) as most authors do.

The calculated values of I_s for the molecules used in the experiments are listed in Table I. Because of the reduction of ionization potential in solution, photons can ionize some molecules which would not be ionized in gas phase.

The charge $Q(E)$ collected for α particles in doped liquid Ar or Xe can be written as

$$Q(E) = Q_\alpha(E) + \eta'[qN_i - Q_\alpha(E)]Y_{\mathrm{iso}}(E) + \eta' q N_{\mathrm{ex}} Y_{\mathrm{iso}}(E), \tag{3}$$

at low concentrations of dopant where collisional processes are negligible.[8] Here the charge is measured in electrons. N_i and N_{ex} are the numbers of ion pairs and excitons, respectively, produced by an incident particle. N_i is calculated by dividing the energy deposited in the liquid rare gas by the W value, an average energy required to produce an ion pair. We use W values of 23.6 and 15.6 eV, respectively, for liquid Ar (Ref. 27) and Xe,[28] and $N_{\mathrm{ex}}/N_i = 0.21$ and 0.06 for liquid Ar and for liquid Xe, respectively.[29] The first term, $Q_\alpha(E)$, is a contribution from direct ionization and the saturation characteristics for α particles in pure liquid Ar (Ref. 30) or Xe (Ref. 10) was used. The second term is the contribution from recombination, and the third term is that from excitation. η' is the apparent photoionization yield expressed as

$$\eta' = g\phi_{\mathrm{vuv}}\phi, \tag{4}$$

where ϕ_{vuv} is the quantum yield for vuv photon emission for liquid Ar or Xe. We take $\phi_{\mathrm{vuv}} = 1$.[7,8] ϕ is the photoionization quantum yield of the doped molecules in question. We assume here that ϕ does not depend on the external electric field. g expresses the fraction of vuv photons absorbed in the detection area and it is determined by the value of σ and the chamber geometry. Previously, the maximum value for g was assumed to be $\frac{1}{2}$ since the ranges of α particles in liquid Ar and Xe are short. Nearly half the photons produced are absorbed by the cathode wall. The range of α particles [52 and 44 μm for liquid Ar and Xe, respectively, for 5.305 MeV α's (Ref. 31)] are taken into consideration in the present analysis. The energy spectra then becomes asymmetric because the absorbed photon number depends on the angle of the ejected α particle particularly when the dopant concentration is large. The value of the center of gravity was compared to the experimental value.

$Y_{\mathrm{iso}}(E)$ is the fraction of collected charge expected for isolated ion pairs in an external field E. For $Y_{\mathrm{iso}}(E)$ we substituted the value for 1 MeV electrons $Y_{\beta}(E)$,[28,32] since no experimental values are available for $Y_{\mathrm{iso}}(E)$ in condensed rare gases. Generally, $Y_{\mathrm{iso}}(E)$ is higher than $Y_{\beta}(E)$.

The factor q expresses the fraction of ionization and excited species which survive high-excitation-density quenching ($q = 1$ for no quenching). The value of q in liquid argon was determined to be 0.71 at $E = 0$ using the scintillation and ionization yield obtained for relativistic heavy ions[33] and its field dependence is reported in Ref. 30. A value of 0.75 is taken for q in Xe (Ref. 34) and it is assumed to be constant.

The value of σ was obtained by three methods: (i) observing the change in the fraction of transmitted photons as a function of molecular concentration, (ii) using the positive charge effect in ionization chambers, and (iii) measuring the ionization yield as a function of dopant concentration and comparing with Eq. (3). The relative light yield with or without dopant is observed in method (i).

The charge collected with or without a grid is observed in method (ii). In a diode chamber, the positive charge effect reduces the charge signal due to photoionization $Q_{\mathrm{PID}}(E)$, the second and third terms in Eq. (3), to $Q^{+}_{\mathrm{PID}}(E)$. When photons are emitted from a point source on a cathode and absorbed with an absorption length $l_0 = [\sigma N_d]^{-1}$, where N_d is the number of doped molecules in unit volume, we have

$$\frac{Q^{+}_{\mathrm{PID}}(E)}{Q_{\mathrm{PID}}(E)} = \int^{\mathrm{chamber}} \frac{e^{-r/l_0}}{l_0 r^2} \times \left(1 - \frac{r\cos\theta}{d}\right) dV \bigg/ \int^{\mathrm{chamber}} \frac{e^{-r/l_0}}{l_0 r^2}\, dV, \tag{5}$$

where r is the distance from the point source, θ is the angle of the photon emitted, and d is the distance between the two electrodes. Since the range of α particles in liquid rare gases is much smaller than the distance between the two electrodes, we can ignore the range of α particles here. Nevertheless, we have taken the range of α particles into account in calculating the positive charge effect. Equation (5) is a function of l_0 and σ can be estimated by measuring the charge collected with or without the grid.

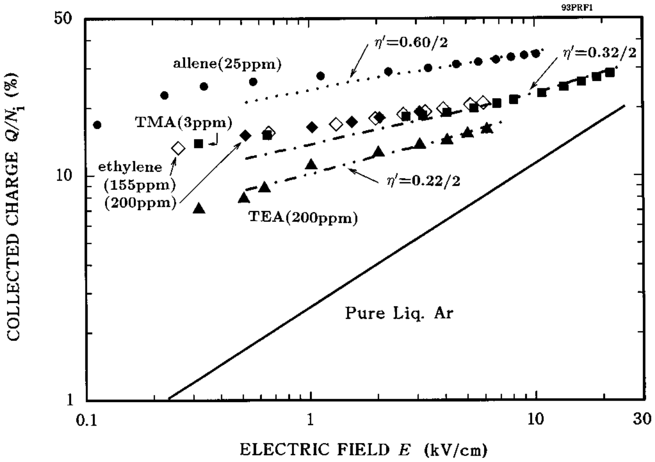

FIG. 1. Collected charge Q/N_i, where N_i is the total ionization (in unit of electrons) for ^{210}Po and ^{252}Cf α particles as a function of applied electric field in pure liquid Ar and liquid Ar doped with ethylene (◇ : 155; ◆ : 200 ppm), allene (●: 25 ppm), TMA (■: 3 ppm), and TEA (▲: 200 ppm). Curves give the calculated results from Eq. (3). The geometry of the sensitive regions of chambers used are ●,■,▲, ◆ : 38 mmϕ and 4.6 mm thick; ◇ : 15 mmϕ and 3.8 mm thick.

IV. RESULTS

The data were fit to Eq. (3) and typical results for liquid argon and xenon are shown in Figs. 1 and 2, respectively. The agreement for liquid Xe is good. However, the data for liquid Ar at low electric fields lie systematically above the curve predicted by Eq. (3).[8] We substituted the saturation characteristics for an isolated ion pairs by that for 1 MeV electrons. The thermalization length of electrons in condensed rare gases is very large and the ion pair produced by

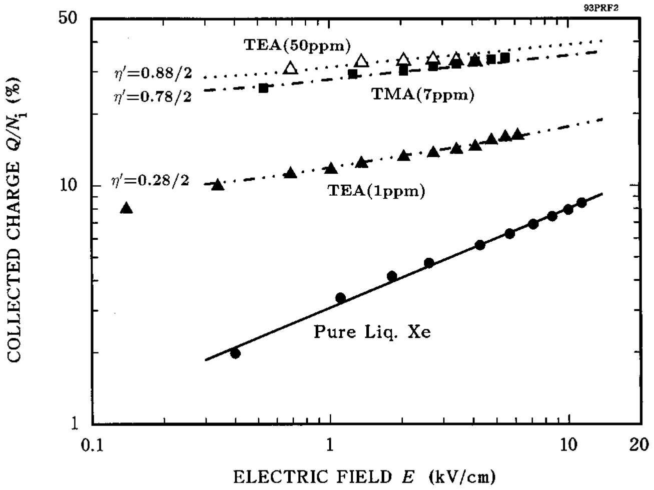

FIG. 2. Collected charge Q/N_i, where N_i is the total ionization (in unit of electrons) for ^{210}Po α particles as a function of applied electric field in pure liquid Xe and liquid Xe doped with TMA (■: 7 ppm) and TEA (▲: 1 ppm; △: 50 ppm). Curves give the calculated results from Eq. (3). The geometry of the sensitive region of the chamber used is 15 mmϕ and 3.8 mm thick.

TABLE II. Photoabsorption cross section σ and photoionization quantum yield ϕ for molecules in liquid Ar and Xe. [Small differences in some values from those reported before (Refs. 7 and 8) are mainly due to the estimation of the fraction of photons absorbed in the detection region. See the text.] σ is in units of 10^{-18} cm^2.

	Ar		Xe	
Molecules	σ	ϕ	σ	ϕ
Ethylene	7 7 [b]	>0.30 [a]		
Allene	25 52 [d]	0.60		
Trimethylamine	50	0.30	40	0.80
Triethylamine		0.20 [c]	40	0.80
Tetramethylgermanium	147 [d]			

[a] Some vuv photons from liquid argon are not absorbed due to the high IP of ethylene. The value of ϕ is a lower limit.

[b] Reference 39. The value is calculated from the photoabsorption length.

[c] σ was assumed to be about the same as that for trimethylamine.

[d] Reference 38. The values are calculated from the photoabsorption length reported at 10 ppm.

ionizing particles cannot be treated as isolated even for the minimum ionizing charged particles. Therefore, the real curve can be higher than the predicted curve at a low E. The difference between $Y_{\mathrm{iso}}(E)$ and $Y_\beta(E)$ in liquid Xe may be small since $Y_\beta(E)$ saturates faster than in Ar. An addition of a small concentration of molecular solute in liquid rare gases leads to an increase in the electron drift velocity[35,36] even at low concentrations.[37] This effect may also lead to more charge collection in the low electric field region and change $Q_\alpha(E)$ and $Y_{\mathrm{iso}}(E)$ in Eq. (3).

The shape of $Q(E)$ and consequently $Y_{\mathrm{iso}}(E)$ do not seem to depend on the kind of dopants when the concentration of dopant is small. This is demonstrated clearly by comparing $Q(E)$ curves for TMA and ethylene in liquid Ar. The curves are almost identical for TMA doping of 3 ppm and an ethylene doping of 155 and 200 ppm in liquid Ar as shown in Fig. 1. Here, an ethylene concentration of 155 or 200 ppm can be regarded as low since ethylene is a small molecule and the collisional energy transfer cross section will be small. The excess energies $h\nu - I_s$ are about 3 eV for TMA and less than 0.5 eV for ethylene. Equation (3) shows that if the product of the amount of photons absorbed and ϕ is the same, then $Q(E)$ has the same dependence on E for all molecules.

The values of σ and ϕ for organic molecules doped in liquid Ar and Xe are shown in Table II together with the values reported by other groups.[38,39] A value of σ for TEA in liquid Ar is missing from the table, but ϕ can be evaluated to certain extent without an accurate knowledge of σ as long as most of the vuv photons are absorbed in the detection region. With this method, measurement of ϕ is easier than that of σ. In fact, it is difficult to determine the actual concentration of dopants in liquid rare gases. We assume that all the molecules introduced into the chamber are dissolved in the liquid. However, some molecules are attached into the wall or make aggregates when their concentration becomes high. The values of ϕ obtained here are much larger than those reported in the gas phase.[40–44] Particularly ϕ values for TMA and TEA in liquid Xe are as large as 80%.

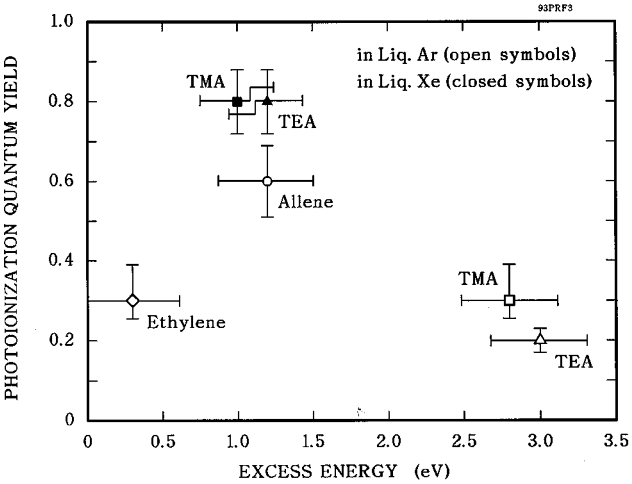

FIG. 3. Photoionization quantum yield obtained for molecules in liquid argon and xenon as a function of excess energy available for the ejected electron.

Values of ϕ in liquid Ar and Xe are plotted as a function of the excess energy, $h\nu - I_s$, of the ejected electron in Fig. 3. We can observe that ϕ decreases with increasing excess energy except for ethylene. Since the IP for ethylene is high, some vuv photons in the broad Ar emission spectrum escape without being absorbed by the ethylene and therefore limits the increase in charge collected. In fact, we observed some light even at high concentrations of ethylene. The excess energy dependence of ϕ observed in liquid rare gases is very different from that reported in gas phase. Generally ϕ increases slowly with energy in gas phase as discussed in next section.

Anderson[45] has observed the photoionization effect for many organic compounds in liquid Ar. The value of ϕ cannot be determined from his early data since the organic compounds were not purified. However, the increase in charge collected for doped liquid Ar shows an interesting trend. Those molecules that show large photoionization effects tend to have small excess energies. His results are in accord with our measurements.

V. DISCUSSION

The shape of $Q(E)$ as a function of E does not depend on the kind of molecules added to liquid rare gases. The value of $Y_{\mathrm{iso}}(E)$ in Eq. (3) strongly depends on the ratio of the thermalization distance to the Onsager radius. An ejected electron loses its energy by collisions. The energy loss processes for photoionized electrons in liquid rare gases are inefficient and most of the thermalization time is spent in the very low energy region. Therefore the thermalization distance does not strongly depend on the excess energy and it is determined mainly by inefficient elastic scattering at an energy much lower than 1 eV in contrast to organic liquids. Also, the thermalization distance is much longer than the Onsager radius in liquid rare gases. As a result, the fraction of electrons collected as a function of E can be independent of the kind of molecules doped in liquid rare gases. Therefore the values of $Y_{\rm iso}(E)$ in Eq. (3) are almost the same for all doped molecules. We also have the same dependence of $Q(E)$ on E for most molecules. The difference in $Q(E)$ for doped molecules appears through the differences in photoabsorption length and ϕ.

Schmidt *et al.*[46] reported a strong dependence of ''quantum'' yields of photoionization on the excess energy in hydrocarbon solutions. The results show that the yield increases with the excess energy. However, values reported are the overall ionization yields, $\phi Y_{\rm iso}(E)$, the number of separated charges divided by the number of photons absorbed. The overall ionization yield in organic solutions is relatively small and is dominated by the germinate recombination of electrons and ions because the thermalization length in most organic liquids is generally shorter than the Onsager radius. As the excess energy increases, the thermalization length increases and as a result the ''apparent'' ionization yield increases.

A general trend of ϕ as the function of photon energy in gas phase is that ϕ is small near the ionization threshold and increases gradually with photon energy. ϕ reaches close to unity at about twice the ionization energy. Koizumi *et al.*[47] have measured ϕ for many organic compounds. They reported that the ionization yield curve as a function of excitation photon energy $h\nu$ depends on the energy difference $\Delta I_{1,2}$ between the first and second ionization potentials. For molecules with large $\Delta I_{1,2}$, alkenes and ethers [$\Delta I_{1,2}=2.2$–2.6 eV (Ref. 48)], the ionization yield curve shows a peak or shoulder in the energy region just above the threshold and begins to increase again with increasing the photon energy near the second threshold. For molecules with small $\Delta I_{1,2}$, cyclopropane and cyclohexane ($\Delta I_{1,2}=0.6$–0.7 eV), the curves have no peak or shoulder but increase monotonically. Ethylene and TMA have large $\Delta I_{1,2}$ [2.3–4 eV (Ref. 48)] and therefore belong to the former group. The ϕ curve for ethylene in the gas phase has a shoulder at about 2 eV above the IP.[41] The ϕ curves for TMA and TEA show a peak at <1 eV above the IP.[40] On the other hand, allene with $\Delta I_{1,2}\sim 0.5$ eV belongs to the latter.

The values of ϕ for TMA and TEA obtained in liquid Ar are similar or larger than those in the gas phase. The values for allene and ethylene are very large if one considers the fact that the photon energy is close to or almost the same as I_s. The large values of about 0.8 measured for TMA and TEA in liquid Xe are quite exotic and require a new explanation.

The ionization yield in a gas is determined by the competition between ionization and dissociation to neutral products. Reductions in photodissociation quantum yield have been observed in the liquid rare gases[49] and also in mixed rare gas halogen clusters.[50] These phenomena[51,52] have been discussed in terms of a cage effect. For example, Schriever *et al.*[53] reported the cage effect for the abstraction of a H atom from H_2O in Ar matrices. They reported an additional barrier of 1.8 eV due to the matrix cage for the permanent dissociation of H_2O into OH and H. The fragments recoil from their solvent neighbors with a high probability and recombine.[49] The excess energy is expended as heat.

The cage effect can also influence photoionization. If the superexcited dissociative state can find a path that leads to ionization while trapped in the cage, there will be higher values of ϕ in the condensed media. The values of ϕ for TMA and TEA in liquid Xe are much larger than those in liquid Ar. The molecular weights for TMA and TEA are 59 and 101, respectively, and they are between those of Ar ($A=40$) and Xe ($A=131$). Allene has the same weight as Ar and has a larger ϕ than heavier molecules such as TMA and TEA in liquid Ar. These facts support the cage effect. The excess energy dependence observed here may be apparent. Generally, a small molecule has a larger IP than a large molecule. Therefore, the excess energy dependence can be due to the molecular weight dependence.

Recently, Hasegawa *et al.*[54] have measured ϕ for TMA in Xe doped liquid Ar. The idea was to ionize TMA by vuv photons whose energy is close to that in liquid Xe. They expected a large ϕ in liquid Ar by assuming the similar photon energy dependence of ϕ as that in liquid Xe. The photon energy shifts from Ar emission to Xe emission by adding Xe into condensed Ar.[11] However, they did not observe any enhancement of ϕ by adding Xe in liquid Ar.

Another explanation for the large value of ϕ for TMA and TEA is due to Rydberg states. The IP becomes lower as the density of the gas increases towards its value in solution I_s. This shift of the ionization potential results in progressively more and more of the higher-lying states of the isolated molecule becoming autoionizing (superexcited).[5] However, it is difficult to explain the excess energy dependence of ϕ. This model should give a large ϕ for higher excess energy.

The ionization quantum yield due to collisional energy transfer is reported to be slightly larger than that due to photoexcitation in the gas phase.[55] One may think the large values of ϕ obtained in liquid rare gases is due to collisional processes. The energy transfer in condensed rare gases can also take place by collisional mechanisms. The rate for collisional energy transfer can be estimated[56] for ''free'' exciton dynamic motion or self-trapped exciton diffusion controlled mechanism. These processes can occur when the concentration of dopant is high (>10 ppm) for the triplet state of liquid Ar depending on the reaction rate constants.

The collisional process has an effect on the saturation characteristics. The charge distribution due to collisional ionization may not be advantageous for charge collection. Ion pairs produced by the collisional energy transfer will be distributed near the particle track. The diffusion length for the $\mathrm{Ar}_2(^3\Sigma_u^+)$ state is about 1000 Å and those for the $\mathrm{Ar}_2(^1\Sigma_u^+)$, $\mathrm{Xe}_2(^1\Sigma_u^+)$, and $\mathrm{Xe}_2(^3\Sigma_u^+)$ states are only a few hundred Å. These ranges are much shorter than the range of the α track (40–50 μm). The charge distribution can be regarded as cylindrical. The collection of charges distributed in a cylindrical geometry is less efficient than that for isolated ion pairs. Also, the excitation density of α particles is high. Therefore the charge collected should increase with field strength much slower than those obtained for electron excitation $Y_\beta(E)$. On the other hand, experimental evidence, particularly in liquid Ar, shows an upward deviation from Eq. (3) at a low E. This result suggests that the contribution from collisional ionization is small.

VI. CONCLUSIONS

(a) Quantum yields for photoionization in liquid rare gases as a function of the excess energy available for the ejected electron show a sharp contrast to that reported in gas phase. (b) The quantum yields obtained for TMA and TEA in liquid Xe are as large as 0.8 in spite of the excess energy being only 1 eV. Allene has the largest yield reported so far in liquid Ar with an excess energy of also about 1 eV. The large values of ϕ obtained in liquid rare gases may be attributed to the cage effect. (c) The saturation characteristics, $Y_{\text{iso}}(E)$ reflected upon $Q(E)$ in Eq. (3), for dopant ionization in the liquid rare gases do not depend very much on the excess energy which is contrary to that reported in organic liquids. The reason may be that the thermalization length in condensed rare gases is very large and determined mainly by inefficient elastic scattering at energies much lower than 1 eV.

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[*] Present address: Toshiba Corporation, Shibaura, Minato-ku, Tokyo 105, Japan.

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