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# Ionization of Pyrene in Nonpolar Hydrocarbon Solvents as Studied by Simultaneous Two-Photon Ionization Spectra

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Pyrene has two photoconductivity thresholds in the wavelength region of 360–435 nm (two-photon energy: 5.70–6.89 eV) in nonpolar hydrocarbon and tetramethylsilane. The first one is located at 6.04–6.44 eV and the second one at 5.18–6.11 eV. The former was assigned to direct ionization and the latter to an ion-pair formation process. Direct ionization is the major process.

The ionization potential in a liquid ($IP_L$) is lower by a few electronvolts than that in the gas phase ($IP_G$), because the ions and the electrons may be stabilized in solvents.[1,2] The difference can be expressed as

$$IP_L = IP_G + P_+ + V_0, \tag{1}$$

where the polarization energy ($P_+$) of the cation is typically $-1$ to $-2$ eV and the electron affinity ($V_0$) of the solvent is typically $-0.6$ to $+0.1$ eV.[1–4] Thus, $IP_L$ is typically smaller by 1–2 eV than $IP_G$.

The ionization potential in a liquid can be determined as the photoconductivity threshold by either direct photoionization using VUV photons[3–7] or by successive two-photon ionization using an intense laser.[2,8–12] The first photoconductivity threshold due to the ionization of pyrene in solutions was reported to be 6.20 eV[4] in neopentane using synchrotron radiation, and 4.80 eV[8] in pentane and 4.79 eV[9] in hexane using a dye laser, while that in the gas phase lies at 7.41 eV.[13] The VUV measurement may be affected by an instability of the light source (discharge lamp) or by a weakness of the light source (synchrotron radiation) and/or by the photoionization of solvent molecules. Two-photon measurements using a dye laser may be affected by three-photon processes because of tight focusing. A high-power tunable laser has recently been improved so that the photoconductivity signal can be measured without tight focusing, and the simultaneous two-photon process based on new tunable lasers may be more advantageous in the determination of the photoconductivity threshold.[11,12]

In the present study, we measured the two-photon ionization spectra (wavelength dependence of the photoionization efficiency) of pyrene in several saturated hydrocarbons and tetramethylsilane in the wavelength region 360–435 nm (two-photon energy of 5.70–6.89 eV). We found two photoconductivity thresholds in the spectra, as in the case of aniline,[12] and studied their assignments and ionization processes.

## Experimental

The experimental apparatus was essentially identical to that described in a previous paper.[12] In brief, the second harmonic (12 mJ/pulse at 400 nm, 4–5 ns pulse width) of a Ti-sapphire laser (Continuum TS60: 700–900nm, 10 Hz) was focused softly into a stainless-steel ionization cell using a cylindrical lens. The pulse energy of the laser beam was continuously monitored and calibrated. The electrode spacing was 3 mm and the applied voltage was 1 kV. The photocurrent (1–1000 pA) was measured as the dc current averaged over 150–300 laser pulses using a picocammeter (Takeda Riken TR8652; time resolution: 5–20 ms).

Pyrene (Janssen Chem. 99%) was used as supplied. The solvents were used after distillation with $CaCl_2$.

## Results and Discussion

The photocurrent was quadratically proportional to the laser pulse energy under weak focusing and a reasonable laser pulse energy. This finding indicates that the photocurrent originates from a two-photon process; all of the measurements described below were carried out in this range. A more intense laser beam or a tighter focusing induced an appreciable three-photon process, and should carefully be avoided. The photocurrent was proportional to the concentrations of pyrene. This finding indicates that only one pyrene molecule should be involved in the photoconductivity and that any bimolecular secondary process should be negligible.

Typical two-photon ionization spectra of pyrene ($1\times10^{-4}$ M; 1 M = 1 mol dm$^{-3}$) in hexane, octane, 2,2-dimethylbutane, and 2,2,4-trimethylpentane are shown in Fig. 1: the laser pulse energy was 0.4–2.2 mJ/pulse, depending on the wavelength used, and the photocurrent was normalized to the laser pulse energy. The photocurrent was larger in a solvent with a low $V_0$ value (for example: 2,2,4-trimethylpentane) and smaller in a solvent with a high $V_0$ value (for example: hexane).

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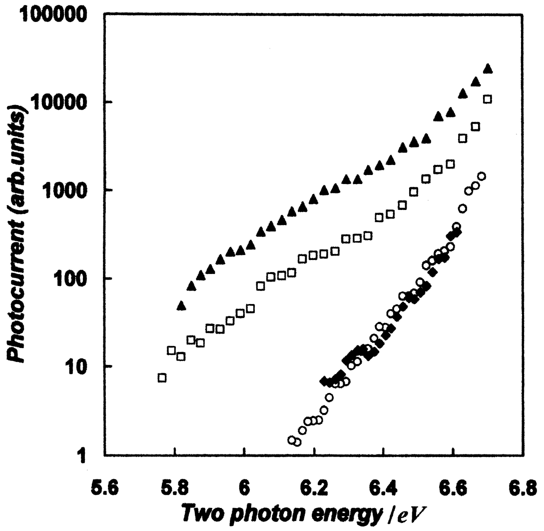

Fig. 1. Two-photon ionization spectra of pyrene ($1 \times 10^{-4}$ M).
Solvent: (◆) hexane, (○) octane, (□) 2,2-dimethylbutane, (▲) 2,2,4-trimethylpentane.

The photocurrent ($I$) is proportional to the 5/2 power of the excess energy for photoionization[3] near to the ionization threshold,

$$I = c(2h\nu - \mathrm{IP_L})^{5/2}, \tag{2}$$

where $c$ is a proportionality constant, and $h\nu$ is the photon energy. Although this equation is empirical, it holds good up to 1.5 eV above the first photoconductivity threshold,[5,6,11,12] and even when there are two thresholds.[12] ($2h\nu - \mathrm{IP_L}$) represents the excess energy that the molecule has after the formation of ionized species. Thus, a plot of $I^{2/5}$ over $2h\nu$ should give a straight line, and its intersection with the abscissa and a bending point should give the photoconductivity threshold. Two typical plots are shown in Fig. 2; both of them have two thresholds.

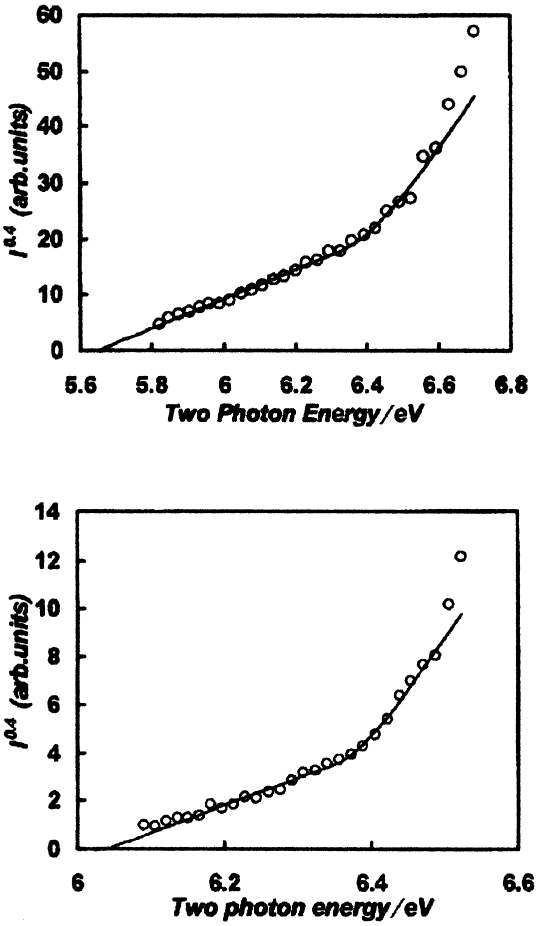

Fig. 2. Dependence of the 2/5 power of photocurrent of pyrene on two-photon energy.
Solvent: (a) 2,2,4-trimethylpentane, (b) cyclohexane.

There are two photoconductivity thresholds of pyrene in all of the solvents used: pentane, hexane, octane, 2,2-dimethylbutane, 2,2,4-trimethylpentane, cyclohexane, and tetramethylsilane. These thresholds can be assigned to a simultaneous two-photon process, because pyrene has no absorption band in the region of these thresholds. There seems to be an additional threshold at about 6.6 eV in Fig. 2 (above) and 6.5 eV in Fig. 2 (below). These thresholds should be assigned to a stepwise two-photon process through the $S_1$ state of pyrene, and will not be discussed in this paper. Thus, there are two simultaneous two-photon processes in the observed range of the energy. The $I^{2/5} - 2h\nu$ plots were analyzed using

$$I^{2/5} = c_1(2h\nu - \mathrm{IP_{L1}}) + c_2(2h\nu - \mathrm{IP_{L2}}), \tag{3}$$

where the relative value of $c_1$ to $c_2$ should indicate the relative contribution of the two processes. A wide linear range for both processes justified the linear additivity of the two processes.[12] The analysis was carried out using two $c$'s as parameters; the best fit is shown as the solid line in Fig. 2. The observed points agreed well with the simulated line. The observed values of $\mathrm{IP_{L1}}$, $\mathrm{IP_{L2}}$, $c_1$ and $c_2$ obtained in the analysis are summarized in Table 1. The accuracy of the observed values of $\mathrm{IP_L}$ would be 0.01–0.13 eV, as shown in Table 1. This Table shows that $c_2$ is much larger than $c_1$, which indicates that the second process is the major process of photoconductivity formation. The effect of impurity was investigated as shown in the previous paper,[12] and was found to be negligible.

The polarization energy ($P_+$) can be calculated based on the Born equation.[14] The calculated values of $P_+$ are given in Table 2 together with the dielectric constant ($\varepsilon$),[13] the electron affinity ($V_0$)[15] and the electron mobility ($\mu$)[16] of the solvent. It is then possible to calculate $\mathrm{IP_L}$ of the direct ionization of pyrene based on Eq. 1 using $V_0$, $P_+$ and $\mathrm{IP_G}$ (7.41 eV[13]); the results are given in the sixth column of Table 2. The observed and calculated values of $\mathrm{IP_L}$ are compared in Fig. 3. The solid line indicates an agreement of the two values. As shown in this Figure, the second photoconductivity threshold ($\mathrm{IP_{L2}}$) agrees with the calculated value, and should be assigned to the direct ionization of pyrene. The agreement between the observed value of $\mathrm{IP_{L2}}$ and the calculated value of $\mathrm{IP_L}$ is excellent for those solvents with a large $\mu$ value.

Table 1. Observed Values of Photoconductivity Thresholds of Pyrene in Various Solvents

| Solvent | $IP_{L1}$/eV | $IP_{L2}$/eV | $c_1$/arb. unit | $c_2$/arb. unit |
|---|---|---|---|---|
| Pentane | 6.11±0.04 | 6.44±0.01 | 2.6±1.4 | 400±100 |
| Hexane | 5.87±0.09 | 6.34±0.03 | 0.9±0.3 | 42±15 |
| Octane | 6.05±0.05 | 6.41±0.05 | 3.8±1.3 | 110±50 |
| 2,2-Dimethylbutane | 5.68±0.13 | 6.31±0.06 | 8.6±3.6 | 330±120 |
| 2,2,4-Trimethylpentane | 5.65±0.06 | 6.31±0.03 | 36±8 | 1000±200 |
| Cyclohexane | 6.04±0.05 | 6.34±0.04 | 4.3±1.5 | 150±70 |
| Tetramethylsilane | 5.18±0.05 | 6.04±0.10 | 29±4 | 730±400 |

Table 2. Estimation of Photoconductivity Thresholds of Pyrene in Various Solvents

| Solvent | $V_0$/eV[a] | $1-1/\varepsilon$[b] | $\mu$/cm$^2$V$^{-1}$s$^{-1}$[c] | $P_+$(cal) /eV | $IP_L$(cal) /eV |
|---|---|---|---|---|---|
| Pentane | −0.01 | 0.457 | 0.154 | −0.83 | 6.6 |
| Hexane | 0.04 | 0.468 | 0.074 | −0.85 | 6.6 |
| Octane | 0.13 | 0.487 | 0.038 | −0.88 | 6.7 |
| 2,2-Dimethylbutane | −0.20 | 0.465 | 12 | −0.84 | 6.4 |
| 2,2,4-Trimethylpentane | −0.18 | 0.487 | 6.5 | −0.88 | 6.4 |
| Cyclohexane | 0.01 | 0.505 | 0.28 | −0.91 | 6.5 |
| Tetramethylsilane | −0.55 | 0.479 | 103 | −0.87 | 6.0 |

a) Ref. 14. b) Ref. 12. c) Ref. 15.

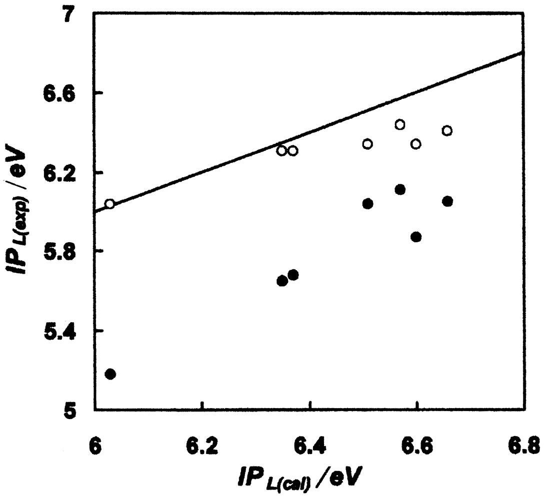

Fig. 3. Comparison of the observed and the calculated photoconductivity thresholds.

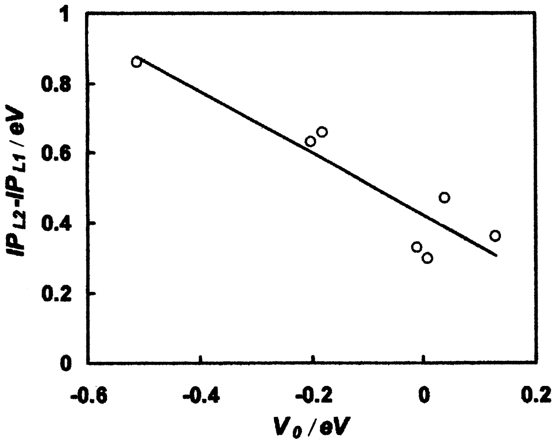

Fig. 4. Differences of the two photoconductivity thresholds and their dependence on the electron affinity ($V_0$) of the solvent.

The first ionization potential of pyrene in solutions was reported to be 6.20 eV[4] in neopentane using synchrotron radiation, and 4.80 eV[8] in pentane and 4.79 eV[9] in hexane using a dye laser. The present data agree with the VUV measurement. The two-photon measurements using a dye laser may be affected by three-photon processes because of tight focusing.

The first threshold observed in the present study was, however, not reported in the VUV measurements.[4] This is probably due to their weaker signals, because synchrotron radiation is weaker than a laser.[7] The first photoconductivity threshold ($IP_{L1}$) may be assigned to an ion-pair formation process, as discussed in detail in the previous paper; this process is not due to any impurities.[12] The present data and those in ref. 12 indicate that the 5/2 power law holds good in the process which shows the first threshold.

The difference of the two photoconductivity thresholds can be related to $V_0$, as shown in Fig. 4. Their relation can be expressed as

$$IP_{L1} - IP_{L2} = -0.89\ V_0 + 0.42. \tag{4}$$

This finding indicates that a large negative value of the electron affinity of the solvent stabilizes the ion-pair formation relative to photoionization.

The values of $c_1$ and $c_2$ are plotted over $\mu$ in Fig. 5. This plot shows that the apparent ionization efficiency is larger in a solvent of high electron mobility, probably because the electron can escape easily from the cage when $\mu$ is large.

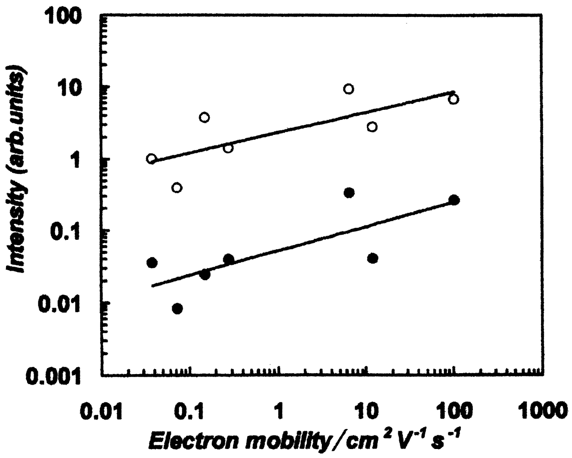

Fig. 5. The relative contribution of the two processes of photoconductivity formation and the electron mobility of solvents.
(●) $c_1$, (○) $c_2$.

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