Characteristics of the Slow Conductivity Signals of Pyrene Produced by Pulsed Laser Irradiation in Non-Polar Hydrocarbon Solvents

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Characteristics of the Slow Conductivity Signals of Pyrene Produced by Pulsed Laser Irradiation in Non-Polar Hydrocarbon Solvents

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Conductivity signals induced by pulsed laser irradiation of pyrene in non-polar hydrocarbon solvents consist of fast signal (first few milliseconds) associated with electrons and a slow signal (after some milliseconds) with ions. Characteristics of the slow signal have been investigated by changing the laser pulse energy, the bias voltage, the electric field, the electrode spacing and the irradiation position. The time profile of the slow signal was affected by space charge effects and by competition between interionic recombination of ions and their escape from the irradiation region.

1. Introduction

Dynamics of electrons, ions, and geminate ion-electron pairs produced in pulse radiolysis,[1] have been the subject of many experimental and theoretical studies, but those in photoionization remain almost unexplored. The pulsed laser photoionization technique makes it possible to ionize one solute selectively by appropriately choosing the excitation wavelength and to produce charged species at a specified region in a solution. The conductivity measurement is a simple and sensitive technique. Thus, the conductivity signal produced by photoionization will offer valuable information about dynamics of electrons, molecular ions, and geminate ion-electron pairs.

Several researchers have measured the time profile of conductivity signals produced by pulsed laser irradiation on some aromatic molecules in non-polar hydrocarbon solvents[2-9] and in tetrahydrofuran.[10,11] We have recently reported that the conductivity signal in the ns-s region and the signal consisted of a fast signal associated with electrons[8] and a slow signal associated with ions.[12]

In the present study, we have observed the conductivity signal induced by pulsed laser irradiation on pyrene in non-polar hydrocarbon solvents, and specially examined its dependence on several experimental parameters for elucidating the behavior of the slow signal.

2. Experimental

2.1 Instrumentation

The experimental apparatus is almost identical with those described previously.[8] The photoionization cell described previously[8] was used for most of the measurements.

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Another cell was designed and used for temperature variation measurements as is illustrated in **Fig. 1.** A pair of phosphor bronze electrodes (5 × 5 mm) were fixed in parallel on stainless steel tubes, and were supported in a square quartz cell (4 × 1 × 1 cm). The cell was held in a quartz dewar flask; liquid nitrogen was added into methanol for a low temperature measurement. The temperature of the solution was measured with a chromel-alumel thermocouple. The temperature during a measurement was maintained to be $< \pm 1$ K.
A high dc voltage (0.4–1.5 kV) was applied to the top electrode and the bottom electrode collected the signal.

2.2 Reagents

Pyrene (Nakarai Chemicals) was purified as described previously.[13] All solvents, n-pentane, n-hexane (liquid chromatographic grade for HPLC, Kishida Chemicals), n-octane, n-decane, n-dodecane, and n-hexadecane (reagent grade, Kishida Chemicals) were kept over molecular sieves. A sample solution was prepared just before use from stock solutions (10^{-2}–10^{-3} M). A portion of the sample solution was pippeted into the cell.

3. Results

3.1 General feature

The conductivity signal of pyrene extends from the laser flash to subsecond region as typically shown in **Fig. 2** (time resolution: 50 μs); it could be classified into the fast signal (first few milliseconds) associated with electrons[8] and the slow signal (after some milliseconds) with ions.[12]

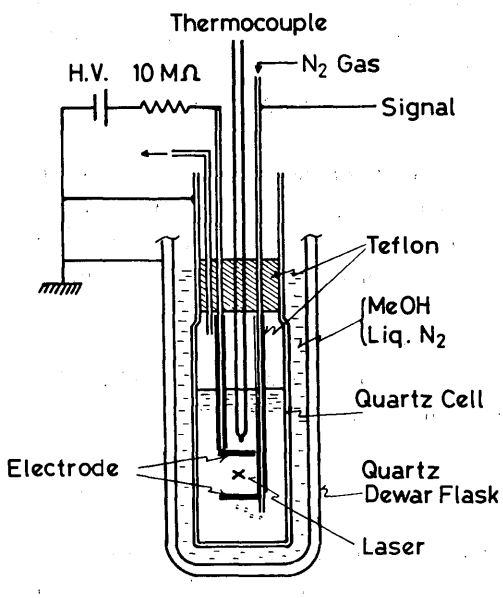

Fig. 1 Schematic diagram of the photoionization cell.

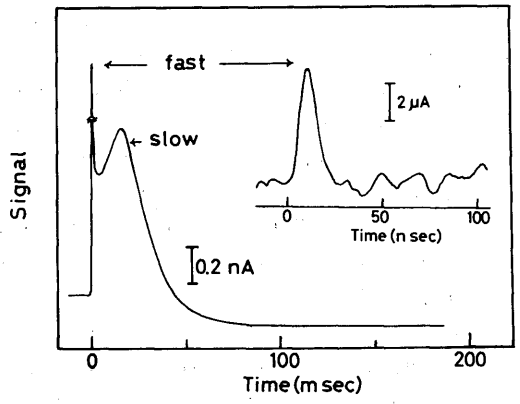

Fig. 2 A typical conductivity signal of pyrene (1×10^{-5} M) in n-pentane (time resolution: about 50 μs). The fast signal is very intense and is out of scale. The bias voltage and the electrode spacing are 2 kV and 3 mm, respectively. The laser is focused and irradiates in the middle between electrodes. The insert shows the fast signal at the time resolution of 3.5 ns.

In an aerated condition, the fast signal decayed rapidly and its shape was almost identical to the square of that of the laser pulse as shown in the upper right of **Fig. 2** (time resolution: 3.5 ns). The fast signal was assignable[8] to the drift of electrons and the displacement[5] (polarization[6]) current of geminate ion-electron pairs produced by two-photon ionization of pyrene. Rise and fall of the fast signal exceeded the time resolution of the system (3.5 ns).[8]

On the other hand, the time profile of the slow signal was unique and showed a maximum typically when the laser irradiated in the middle between the electrodes. Addition of air or a small amount of water showed no substantial change compared with a deaerated condition. The peak time (t_m), which is defined as the time until the slow signal reaches its maximum, tended to be longer for a molecule with a high molecular weight, and was shorter for a solvent with low viscosity.[12] These findings show that the slow signal originates from ions.

3.2 Laser power

Peak intensities of both fast and slow signals increased quadratically with increasing the laser pulse energy of less than about 0.2 mJ. When the laser is focused, the fast signal is about 5 times as large as the slow signal. However, the slow signal saturated more rapidly because of space charge effects,[12] and could be generated by a defocused laser beam where the fast signal was much smaller than the slow signal. These findings suggest that the slow signal is induced by both two- and one- photon processes, and that dynamics of ions are different from those of electrons.

3.3 Bias voltage and electrode spacing

The area intensity of the slow signal increased linearly with the bias voltage (0.4−1.5 kV) as shown in **Fig. 3a**, where the electrode spacing was kept constant (6 mm). It decreased linearly with increasing the electrode spacing under the constant bias voltage (−1 kV), but showed no substantial change under the constant electric field (−2.5 kV/cm) as

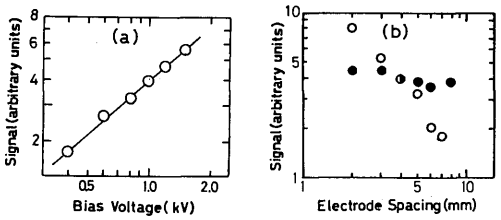

Fig. 3 Effects of bias voltage (a) and electrode spacing (b) on the area intensity of the slow signal of pyrene (1×10^{-5} M) in n-pentane.
(a) Constant electrode spacing (6 mm): (b) constant bias voltage (− 1 kV) (○) and constant electric field (−2.5 kV/cm) (●).

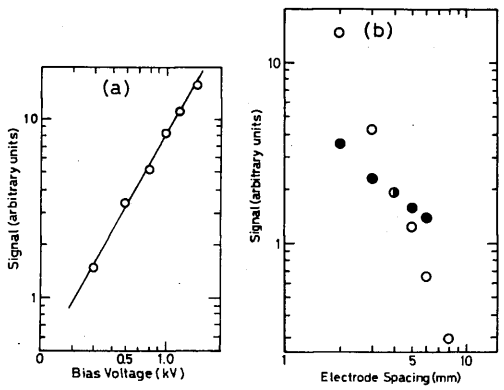

Fig. 4 Effects of bias voltage (a) and electrode spacing (b) on the peak intensity of the slow signal of pyrene (1×10^{-5} M) in n-pentane.
(a) Constant electrode spacing (6 mm): (b) constant bias voltage (− 1 kV) (○) and constant electric field (−2.5 kV/cm) (●).

shown in **Fig. 3b.** These findings suggest that the area intensity, that is, the total number of cations and anions increases linearly with the bias voltage, as is expected from the Onsager theory,[14] and that the ions are collected effectively under the present condition.

The peak intensity of the slow signal (~nA—~10 pA), and thus, the number of ions ($\sim 10^{12}$—$\sim 10^{10}$ cm^{-3}) are considerably large; thus, the time profile of the slow signal depends on space charge effects.[12] The peak intensity of the slow signal showed typical behaviors for the space charge limited current;[15] it was proportional to the twice power of the bias voltage (**Fig. 4a**), inversely proportional to the cube of the electrode spacing under the constant bias voltage (−1 kV) (**Fig. 4b**), and inversely proportional to the electrode spacing under the constant electric field (−2.5 kV/cm) (**Fig. 4b**). While, the peak intensity of the fast signal increased linearly with the bias voltage.[8]

3.4 Irradiation Position

Typical sets of slow signals at three irradiation positions of the laser beam under forward (+1 kV) and reverse (−1 kV) biased fields are shown in **Fig. 5.** The signal was

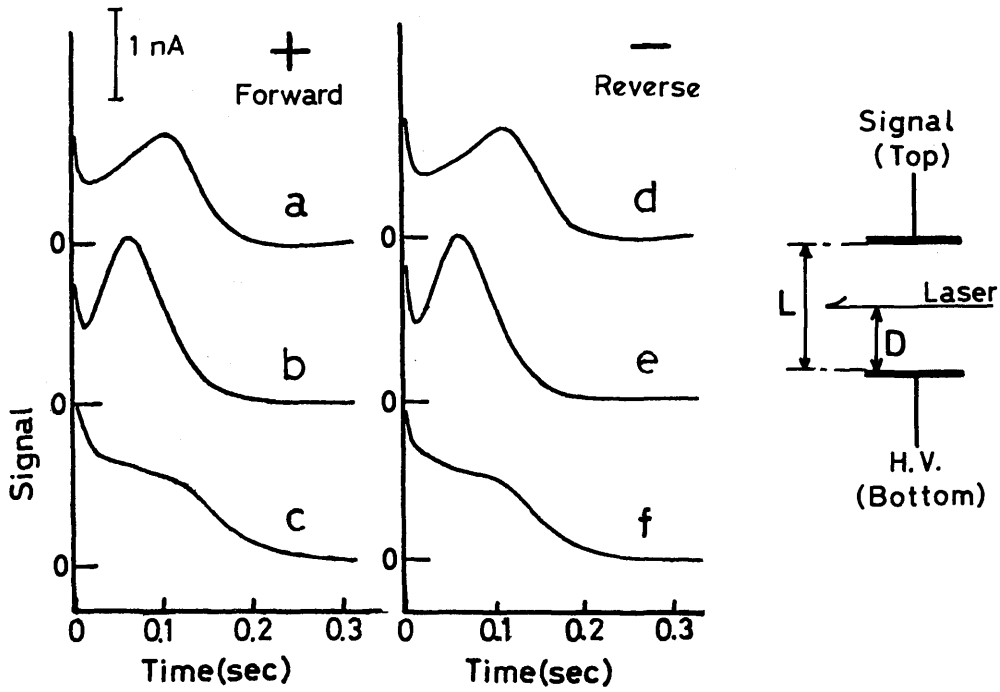

Fig. 5 Effects of irradiation position of the laser beam between the electrodes on the slow signal for a pyrene (1×10^{-5} M) in n-pentane.
Left (+), forward biased field: right (−), reverse biased field. The laser irradiates close to the bottom electrode (a,b), in the middle between the electrodes (c,d), and close to the top electrode (e,f). The bias voltage and the electrode spacing are +0.75 kV and 3 mm, respectively.

opposite in direction (positive for the forward and negative for the reverse biased fields), but its shape and absolute intensity were almost identical in each irradiation position. When the laser irradiated close to the bottom electrode, t_m was about 110 ms (**Fig. 5a, b**).

However, t_m (60 ms) was about half when the laser irradiated in the middle between theelectrodes (**Fig. 5c, d**). While, the signal showed no appreciable peak when the laser irradiated close to the top electrode; a shoulder was observed at about 120 ms (**Fig. 5e, f**), which was almost identical with t_m in **Fig. 5a** and **b**, and was twice as much as t_m in **Fig. 5c** and **d.** The peak time, t_m, increased linearly with increasing the electrode spacing under the constant electric field (−2.5 kV/cm). These findings show that the slow signal is due to the drift of cations and anions and that the maximum and the shoulder represent the discharge of the ions at the electrodes. Thus, the mobility of an anion (μ_-) and a cation (μ_+) can be obtained from these figures ($\mu_-=1.1\times10^{-3}$ and $\mu_+=1.1\times10^{-3}$ $cm^2V^{-1}s^{-1}$).

3.5 Temperature dependence and viscosity

The peak time of the slow signal increased with decreasing temperature. While, intensities of both fast and slow signals decreased with decreasing temperature. Logarithmic plots of the intensity versus the reciprocal of the absolute temperature gave a straight line with an activation energies of 3 (fast) and 2 (slow) kcal/mol in n-hexane (**Fig. 6**). Similar results were obtained for other solvents, and are summarized in **Table 1.**

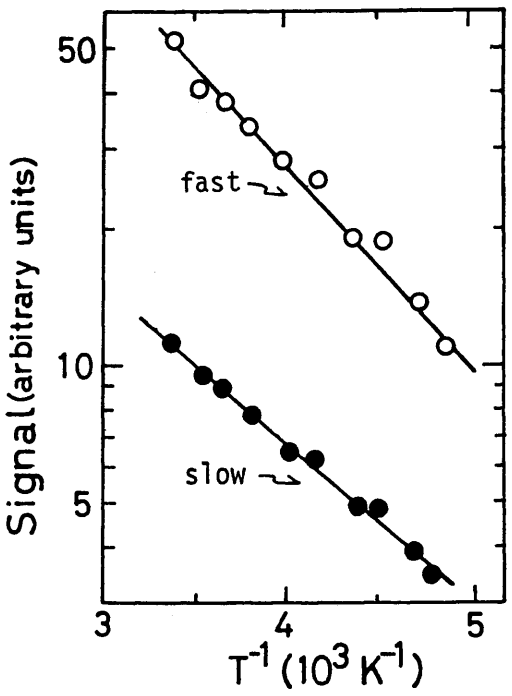

Fig. 6 Effects of temperature on the area intensities of the fast (○) and the slow (●) signals of pyrene (1×10^{-5} M) in n-hexane. The laser is focused and irradiates in the middle between the electrodes. The bias voltage and the electrode spacing are 1 kV and 4 mm, respectively.

Table 1 Activation energy of conductivity signals induced by pulsed laser irradiation of pyrene (1×10^{-5} M) in n-alkanes.

solvent	viscosity[19] cP (25℃)	activation energy (kcal/mol)	
		fast	slow
n-hexane	0.30	3 ± 1	2 ± 1
n-octane	0.52	3 ± 1	2 ± 1
n-decane	0.86	4 ± 1	3 ± 1
n-dodecane	1.38	5 ± 2	4 ± 1
n-hexadecane	3.34	4 ± 1	6 ± 2

Both fast and slow signals tended to decrease but their activation energies tended to increase for n-alkanes with high viscosity. These findings also suggest that the conductivity signal is due to the drift of ions.

4. Discussion

Upon irradiation of the nitrogen laser, a pyrene molecule consecutively absorbs two photons to produce a geminate ion-electron pair. Although most of geminate pairs recombine within one nanosecond,[16] some of them dissociate into free pyrene cations and electrons. The fast signal is due to the drift of electrons and displacement of the dipole moment of the geminate pairs.[8] Electrons are quickly captured by pyrene,[8] oxygen,[3] or residual impurities[4,5,8,10] to produce anions. The slow signal is associated with both cations and anions; their mobilities should be much smaller than those of electrons.

Charge separation reactions between monophotonically excited singlet and/or triplet states, such as triplet-triplet annihilation[10,11] also should occur in the present condition, since the slow signal could be observed at a low photon density of the laser when a two-photon process is unlikely to occur and the fast signal is very small.

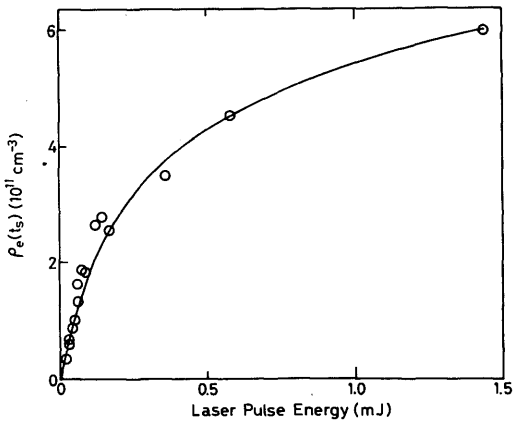

Fig. 7 Effects of laser pulse energy on the slow signal of pyrene (1×10^{-5} M) in n-pentane. The bias voltage and the electrode spacing are 1 kV and 6 mm, respectively. The laser irradiates in the middle between the electrodes. The solid curve was estimated by equation 7.

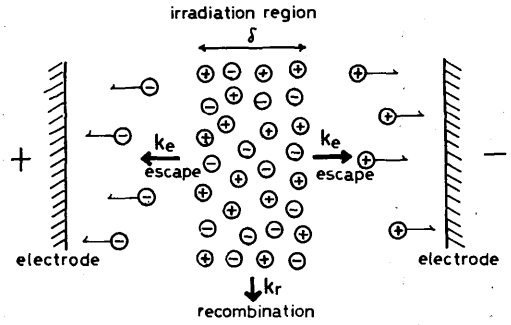

Fig. 8 Schematic illustration for the generation of the slow signal. Positive (+) and negative (−) ions either recombine (k_r) in the irradiation region or escape (k_e) from it.

The area intensity of the slow signal increased with increasing the laser pulse energy, as shown in **Fig. 7.** The following model can interpret this dependence. Cations and anions produced by laser irradiation either recombine (rate constant: k_r) in the irradiation region or escape (rate constant: k_e) toward the electrodes, as is illustrated in **Fig. 8.** Here ions located near the surface of the irradiation region can escape from the recombination and drift along the electric field. The drift velocity is small in the irradiation region because of space charge and becomes larger outside the region; the increase in the drift velocity induces increase in the slow signal. The interionic recombination would occur within the time t_s,[11]

$$t_s = \delta L / \mu V, \qquad (2)$$

where δ is the irradiation width ($\sim$0.4 mm), L the electrode spacing (6 mm), $\mu = \mu_+ + \mu_-$ (2.2×10^{-3} $cm^2V^{-1}s^{-1}$), and V the bias voltage (1 kV); then, we obtain t_s=11 ms.

The initial density (ρ (0)) of the total ions in the irradiation region decreases to ρ (t) at a time t by interionic recombination as:

$$\rho(t) = \rho(0)\ (1+k_r\rho(0)t)^{-1}, \qquad (3)$$

if the escape of ions is negligible except the surface of the irradiation region. Thus, the density ($\rho_e(t)$) of free ions, which have escaped from the recombination, can be expressed as:

$$d\rho_e(t)/dt = k_e\rho(t) = k_e\rho(0)\ (1+k_r\rho(0)t)^{-1}. \qquad (4)$$

Then at $t=t_s$,

$$\rho_e(t_s) = (k_e/k_r)\ \ln\ (1+k_r\rho(0)t_s). \qquad (5)$$

The area intensity of the slow signal after t_s corresponds approximately to the total number of free ions, since no interionic recombination would occur. The maximum value of $\rho_e(t_s)$ for a very intense laser would be 7×10^{11} cm^{-3} by extrapolation on **Fig. 7** and $\rho_e(t_s)$ is 6×10^{11} cm^{-3} at the laser pulse energy (I) is 1.44 mJ.

The initial density of ions, ρ (0), in the irradiation region should be proportional to the square of the laser pulse energy, I, as:

$$\rho(0) = bI^2, \qquad (6)$$

where b is a proportionality constant.

According to the Onsager theory,[14] the probability of ions escaping from geminate recombination is estimated to be 2% in n-pentane for a electric field of 1.67 kV/cm at a room temperature; thus the maximum value of ρ (0) is estimated to be 2.4×10^{14} cm^{-3} for 1×10^{-5} M (6×10^{15} cm^{-3}) of pyrene. Therefore, we can evaluate $\rho(0) = 7\times10^{13}$ cm^{-3} at I=1.44 mJ from equation 5 since $\rho(0) = 2.4\times10^{14}$ cm^{-3}, $\rho_e(t_s) = 7\times10^{11}$ cm^{-3} and $k_r = 1.9\times10^{-9}$ $cm^{-3}s^{-1}$;[2] thus, $b = 3.4\times10^{13}$ $cm^{-3}mJ^{-2}$ from equation 6. Then we obtain

$$(k_r/k_e)\ \rho_e(t_s) = \ln\ (1+710I^2). \qquad (7)$$

The theoretical curve (shown in the solid line in **Fig. 7**) is in good agreement with the experimental result. These findings show that most ions recombine in the irradiation region and the time profile of the slow signal is due to competition between interionic recombination and ion drift. The drift velocity of ions will be effectively small in the recombination region, and will increase to induce current rise outside the recombination region.

5. Conclusion

We have demonstrated that the slow conductivity signal induced by pulsed laser irradiation in non-polar hydrocarbon solvents originated from ions, and that its time profile resulted from space charge effects and from competition between interionic recombination of ions and their escape from the irradiation region.

Acknowledgment

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