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Characteristics of Escape Probabilities in Single- and Two-Color Multiphoton Ionization of Anthracene in *n*-Alkanes

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Synopsis

Single- and two-color multiphoton ionization of anthracene have been compared in *n*-alkane solvents. The simultaneous action of 10-ns laser lights at 355 (UV) and 1064 nm (IR) gave a substantially larger time-integrated photocurrent signal (thus, the escape probability of a geminate cation-electron pair based on the Onsager model) as compared with that obtained when the UV light acted alone. It is suggested that the IR light acts through the geminate cation-electron pair to give its longer thermalization distance. For a solvent with higher electron mobility, escape probabilities for both photoionization methods tended to be larger but the relative increase in the escape probability by the additional action of the IR light tended to be smaller.

Introduction

Multiphoton ionization (MPI) is a unique and powerful technique for investigating the dynamics of ions and electrons in nonpolar solvents, since it can produce a cation and an electron by ionizing a solute selectively and softly at a specified region; the comparison of MPI and pulse radiolysis results is very interesting¹⁾. Also, this technique is promising analytically²⁾.

In solution, it is generally assumed that photoionization of molecules initially produces geminate cation-electron pairs, and they either recombine geminately or escape into free ions and electrons; free electrons will be rapidly captured by a solute, oxygen, or residual im-

purities, and will generate anions¹⁾. The escape probability P of ions (electrons) from geminate recombination is given first order by,

$$P = \exp(-r_c/r)(1 + er_e E/2kT) \quad (1)$$

where e is the electron charge, E the electric field, k the Boltzmann constant, T the temperature, r the initial separation distance of the ion and the electron of the geminate cation-electron pair, and $r_c (= e^2/\epsilon kT$, where ϵ is the dielectric constant of the solvent) the Onsager radius³⁾.

Most of MPI researches are based on single-color laser excitation. On the other hand, MPI with the use of two-color laser lights is a relatively new technique photophysically^{1,4)} and is very useful analytically⁵⁾, although

mechanistic studies have not yet been made in detail. In recent MPI of aromatic molecules in *n*-alkane solvents, the simultaneous action of UV and IR 10-ns laser lights at room temperature enhanced the peak intensity of the photocurrent signal as compared with that obtained when the UV light acted alone; the results suggested that the IR light excited the geminate cation-electron pair rather than an excited neutral parent molecule produced by absorption of two UV photons⁹⁾. However, the peak intensity of the photocurrent signal is attributed mainly to formation and decay processes of the geminate cation-electron pair and depends both on the mobility of an electron and on the quantum yield of the geminate cation-electron pair; it does not give the escape probability (Eq. 1). The total charge or the time-integrated photocurrent should be measured in order to evaluate the escape probability and to elucidate such IR-assisted photocurrent increase in the framework of the Onsager model; it is also important for extending analytical applications of this two-color MPI technique. In this case the number of charge carriers should be kept extremely low (at most in a few tenths of picoamperes) in order to avoid possible interionic recombination of cations and anions produced by escaping geminate recombination in the laser irradiation region⁶⁻⁹⁾.

From these viewpoints, very weak time-integrated photocurrent signals induced by two-color (UV+IR) and single-color (UV) MPI of anthracene were measured in *n*-alkane solvents, in order to evaluate the escape probability and compare the characteristics of the two MPI methods in the framework of the Onsager model.

Experimental

The experimental apparatus with UV (355 nm) and IR (1064 nm) laser excitation (Fig. 1) is similar with the previous one⁹⁾. The fundamental and the third harmonic radiation of a Nd:YAG laser (Quantel YG 580 A, pulse duration 10 ns) were used as IR and UV light sources, respectively, at a repetition rate of 5 Hz. Both UV and IR laser beams (diameter 3.5 mm) were combined collinearly by a dichroic mirror D. They were focused by a

Fig. 1. Schematic diagram of the experimental apparatus.

P: prism, R: resistor, S: slit, D: dichroic mirror, UV: 355 nm, VS: 532 nm, IR: 1064 nm.

quartz lens and irradiated the solution simultaneously. The initial current was detected by an electrometer (Advantest TR 8641, gain 10^{10}) and was integrated (averaged) by an appropriate RC filter (RC time constant 3 s) to give a time-integrated photocurrent signal. Its output was recorded by a recorder (RDK R-02). The laser pulse energies were about 15 μ J at 355 nm (UV) and 26 mJ at 1064 nm (IR).

The photoionization cell⁹⁾ has a pair of brass disc electrodes (diameter 0.5 cm) with 0.2 cm separation. Anthracene and *n*-alkanes (the number of chain length $N=5, 6, 7, 8, 10, 12$) of reagent grade were used as received. The concentration of anthracene was 1×10^{-5} M. All measurements were carried out at room temperature.

Results and Discussion

The simultaneous action of the UV and the IR lights generated a larger time-integrated photocurrent signal, $i(\text{UV}+\text{IR})$, than that obtained when the UV light acted alone, $i(\text{UV})$, as typically shown in Fig. 2. Neither the sample solution nor the solvent showed no appreciable photocurrent signals when the IR light acted alone. With decreasing the chain length of the *n*-alkane solvent, $i(\text{UV})$ increased more rapidly than $i(\text{UV}+\text{IR})$.

Plots of the photocurrent signal against the electric field E yielded a straight line in both MPI methods; typical results in *n*-hexane and

Fig. 2. Typical changes of the time-integrated photocurrent signals of anthracene (1×10^{-5} M) in *n*-decane (left) and *n*-hexane (right) induced by the additional action of the IR light. Bias voltage: -0.5 kV,

Fig. 3. Effects of electric field on the photocurrent signal of anthracene (1×10^{-5} M). $\circ$: UV+IR in *n*-hexane, $\triangle$: UV+IR in *n*-decane, $\bullet$: UV in *n*-hexane, $\blacktriangle$: UV in *n*-decane.

n-decane are shown in Fig. 3. The value of the slope-to-intercept ratio K was found to lie in the $(6-9) \times 10^{-5}$ cm/V and showed reasonable agreement with the predicted K value ($=e^3/2\epsilon k^2 T^2$) from Eq. (1), $(5.7-6.1) \times 10^{-5}$ cm/V. The result shows that the Onsager model is applicable for both MPI methods and $i(\text{UV}+\text{IR})$ and $i(\text{UV})$ are proportional to the charge of free ions (thus, the escape probability), and that the effect of interionic recombination is negligible under the present condition. Thus, Eq. (1) may be rewritten as¹³:

$$i = i_0(1 + KE) \quad (2)$$

Fig. 4. Effects of intercept values $i_0(\text{UV}+\text{IR})$ ($\circ$) and $i_0(\text{UV})$ ($\bullet$) and the relative increase in the intercept value $\Delta i_0/i_0(\text{UV})$ ($\square$) on the electron mobility¹⁰.

where i_0 corresponds to the intercept value in Fig. 3 and to the number of free ions generated at $E=0$.

As shown in Fig. 4, the values of $i_0(\text{UV}+\text{IR})$ as well as $i_0(\text{UV})$ were larger for higher electron mobility of the *n*-alkane solvent obtained from pulse radiolysis¹⁰. This implies that the thermalization length tends to be larger for higher electron mobility of the *n*-alkane solvent in both MPI methods. In addition, $i_0(\text{UV}+\text{IR})$ was larger than $i_0(\text{UV})$ in each solvent (Fig. 2), and the slope of the logarithmic plots of $i(\text{UV}+\text{IR})$ versus T^{-1} was negatively smaller than that in the case of $i(\text{UV})$ versus T^{-1} ¹¹. These aspects indicate that the additional action of the IR light gives a larger thermalization distance of the geminate cation-electron pair than that in the case of the UV light alone.

On the other hand, the relative increase in the photocurrent signal at $E=0$, $\Delta i_0/i_0(\text{UV}) = \{i_0(\text{UV}+\text{IR}) - i_0(\text{UV})\}/i_0(\text{UV})$, increased steeply with decreasing the electron mobility, while Δi_0 tended to become larger (Fig. 2). These aspects suggest that $\Delta i_0/i_0(\text{UV})$ corresponds to the relative efficiency of photoexcitation of the geminate cation-electron pair by the IR light; it was substantially affected by the electron mobility, probably because the time for recombination (or escape into free ions) of the geminate cation-electron pair must be longer

and the thermalization distance of the geminate cation-electron pair would be shorter for lower electron mobility of the *n*-alkane solvent.

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