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ELECTRON ATTACHMENT AS A PROBE OF PHOTOIONIZATION PROCESSES IN LIQUID MEDIA<sup>1</sup>

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ABSTRACT

The effects of electron attaching additives on the photoionization threshold of pyrene in seven liquid media comprising a dielectric hydrocarbon liquid and an electron attaching additive, A, were studied. The photoionization threshold,  $I_L^1$ , was found to be independent of the dielectric hydrocarbon liquid and the concentration of each A used. On the basis of these data it was concluded that in the presence of an efficient A at high concentrations, the photoejected electron is captured by A at times shorter than those required for electron solvation (or any possible trapping by the solvent) and that the photoionization process for a solute molecule in these dielectric liquids is probably completed at times  $<10^{-14}$  and  $>10^{-16}$  s and its "energetics" are rather independent of the bulk properties of these liquids.

KEYWORDS

Photoionization; photoionization threshold of pyrene in dielectric liquids; electron attachment as a probe of photoionization in liquids; dynamics of the photoionization process in dielectric liquids in the presence of electron attaching additives.

INTRODUCTION

The determination of the ionization threshold of molecules in liquid media is important in efforts to link the properties of isolated molecules with those in the liquid phase and in efforts to assess the effect of the medium on charge-separated states. For this reason it has been the subject of many studies over the last two decades (Bernas, 1980). Despite these efforts, basic questions still remain concerning on the one hand the accurate determination of the photoionization threshold,  $I_L^1$  (Siomos, 1981a) and the effect of the medium on it, and on the other hand the

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theoretical understanding of the relationship between  $I_L^1$  and  $I_G^1$ , the photoionization threshold of the molecule in the gas phase (Siomos, 1981b).

As a part of our effort to understand the photoionization process of molecules in liquids, we developed two different but complementary techniques [the integrated fluorescence (Siomos, 1980a) and the laser two-photon ionization technique (Siomos, 1980b)] to measure  $I_L^1$ . In this paper we report on the effect of the bulk properties of the dielectric liquids and electron attaching additives on  $I_L^1$  using the integrated fluorescence technique. With this technique the  $I_L^1$  of a fluorescent molecule, M, is established by monitoring its total fluorescence intensity,  $I_F(\lambda_{exc})$ , as a function of the excitation wavelength,  $\lambda_{exc}$ , or photon energy,  $h\nu_{exc}$ , in the absence and in the presence of an appropriate A. In the absence of A the preponderance of ion pairs recombine and little, if any, change in  $I_F(h\nu_{exc})$  around  $I_L^1$  is observed although a decrease in  $I_F(h\nu_{exc})$  usually is observed at  $h\nu_{exc}$  well above  $I_L^1$  (Fig. 1). In the presence of A, a rather pronounced decrease in  $I_F(h\nu_{exc})$  is observed for  $h\nu_{exc} > I_L^1$  (Fig. 1) effected through the removal of the photoejected electron,  $e^-$ , by A (i.e.,  $A + e^- \rightarrow A^-$ ), thereby preventing recombination fluorescence. In this manner the value of  $I_L^1$  of pyrene was determined in seven nonpolar liquids comprising a dielectric liquid and an electron attaching additive at rather high concentrations. The dielectric liquids were the six hydrocarbons n-hexane (n-H), n-pentane (n-P), n-heptane (n-Hp), isopentane (i-P), cyclopentane (c-P), neohexane (neo-H), and tetramethylsilane (TMSi). The electron attaching molecules used were the cyclic perfluorocarbons perfluoromethyl cyclohexane (c-C<sub>7</sub>F<sub>14</sub>), perfluoro-1,2-dimethyl cyclobutane (c-C<sub>6</sub>F<sub>12</sub>), perfluoro-1,3-dimethyl cyclohexane (c-C<sub>8</sub>F<sub>16</sub>), and the linear perfluorocarbon perfluoro-n-hexane (PFn-H). The concentration of A used was rather high; it was varied in steps of 0.25 mol dm<sup>-3</sup> and was in the range 0.25-1.50 mol dm<sup>-3</sup>. The concentration of pyrene was 10<sup>-2</sup> mol dm<sup>-3</sup>. The experimental apparatus employed is similar to that described earlier (Siomos, 1980a).

## RESULTS AND DISCUSSION

Figure 1 shows typical integrated fluorescence intensity spectra of pyrene in liquid n-pentane. The integrated fluorescence intensity,  $I_F(\lambda_{exc})$ , is plotted vs the excitation wavelength for a 10<sup>-2</sup> mol dm<sup>-3</sup> solution of pyrene in liquid n-pentane in the absence of the A (curve 1), in the presence of PFn-H (curves 2-4), and in the presence of c-C<sub>7</sub>F<sub>14</sub> (curves 5-7). All spectra were normalized at 2700 Å. (Any other normalization point in the wavelength range ~2300-2800 Å would have been equally appropriate.) The absorption spectrum of pyrene (Kourouklis, 1981) is shown in the figure by the dashed curve. The  $I_F(\lambda_{exc})$  for 10<sup>-2</sup> mol dm<sup>-3</sup> pyrene solutions is independent of the molar extinction coefficient variations and no correction for the fraction of photons absorbed as a function of  $\lambda_{exc}$  is necessary (Siomos, 1980a). For the PFn-H containing solutions,  $I_F(\lambda_{exc})$  decreases considerably for  $\lambda_{exc} < 2100$  Å, while for the c-C<sub>7</sub>F<sub>14</sub>-containing solutions this decrease starts around 2300 Å. Similar results to those in Fig. 1 were obtained for all the solvents and all the electron attaching additives studied.

In order to determine  $I_L^1$  the ratio  $R_{[A]}(\lambda_{exc})$  of the  $I_F(\lambda_{exc})$  function in the presence of A to that in the absence of A was determined and plotted as a function of  $\lambda_{exc}$ . Figure 2 shows a typical example for a 10<sup>-2</sup> mol dm<sup>-3</sup> solution of pyrene in n-P at a PFn-H concentration of 1.01 mol dm<sup>-3</sup>. By means of a least-squares fit (Siomos, 1981b) to the experimental data (solid line) the function indicated by the dashed line was calculated, which allows accurate location of the  $I_L^1$ . From such analyses we determined the  $I_L^1$  values in Table 1 for pyrene in seven dielectric liquids utilizing PFn-H and c-C<sub>7</sub>F<sub>14</sub> as A. In Table 1 are presented also the  $I_L^1$  values of pyrene in neohexane determined using c-C<sub>6</sub>F<sub>12</sub> and c-C<sub>8</sub>F<sub>16</sub> as A.

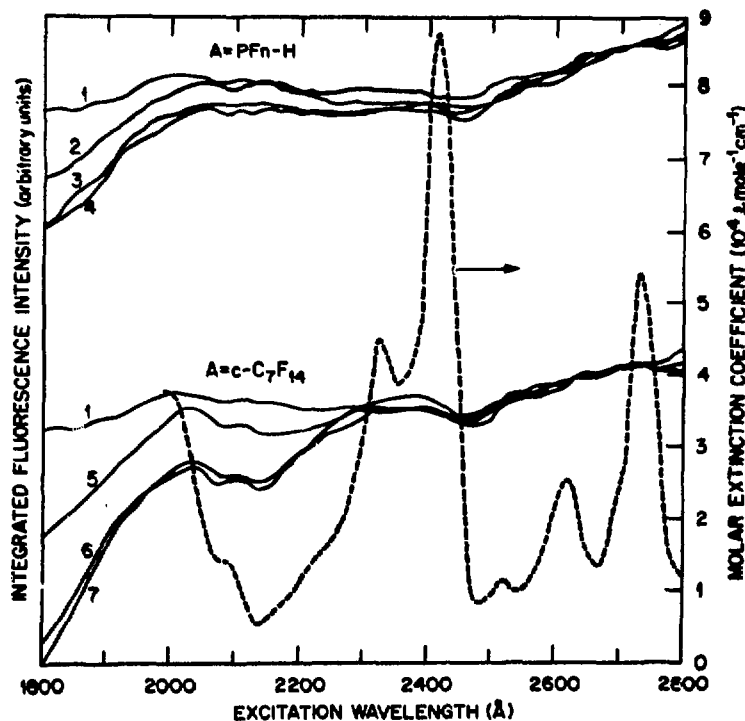


Fig. 1. Integrated fluorescence intensity vs excitation wavelength for a  $10^{-2}$  mol  $\text{dm}^{-3}$  solution of pyrene in liquid n-pentane at room temperature. [A] (perfluoro-n-hexane): 0.0 mol  $\text{dm}^{-3}$  (curve 1), 0.25 mol  $\text{dm}^{-3}$  (curve 2), 1.01 mol  $\text{dm}^{-3}$  (curve 3), 1.48 mol  $\text{dm}^{-3}$  (curve 4), and [A] (perfluoromethylcyclohexane): 0.26 mol  $\text{dm}^{-3}$  (curve 5), 1.04 mol  $\text{dm}^{-3}$  (curve 6), and 1.51 mol  $\text{dm}^{-3}$  (curve 7). The spectra were normalized at 2700 Å. The dashed curve represents the absorption spectrum of pyrene.

The following observations can be made on the basis of the  $I_L^1$  data in Table 1: (1) The  $I_L^1$  values of pyrene in the dielectric hydrocarbon liquids used with PFn-H as the A are higher than the  $I_L^1$  values using c-C<sub>7</sub>F<sub>14</sub>, c-C<sub>6</sub>F<sub>12</sub>, and c-C<sub>8</sub>F<sub>16</sub> as A. (2) For all electron attaching additives the  $I_L^1$  values are independent of the bulk properties of the dielectric liquid. (3) The  $I_L^1$  values are independent of the concentration of A used (0.25–1.50 mol  $\text{dm}^{-3}$ ).

In an effort to rationalize these experimental findings we considered the electron capturing characteristics of the A's used and also the time evolution of the photoionization and electron attachment processes. From the magnitude and energy dependence of the gaseous electron attachment rates ( $k_{\text{cap}}(\epsilon)$ ) of the A's used in the present study (Fig. 3) can be seen that in the gas phase the cyclic perfluorocarbons attach electrons with near-thermal energies with higher efficiency (by about a factor of 50) than the linear PFn-H molecule, which attaches electrons most efficiently at  $\sim 1$  eV. From these gaseous properties of the A's, the possible effect of the dielectric liquid medium on these data (Siomos, 1981b) and the concentrations of the A's used, we estimated the mean electron capture time to be  $(\tau_{\text{cap}}) \sim 10^{-14}$  s. This time is longer than the time required for the isolated molecule direct photoionization process ( $\sim 10^{-16}$  s) but shorter than the solvation time,  $\tau_{\text{solv}}$  (or any other trapping process by the solvent medium) of the photoejected electron, which for liquid water was found to be  $\sim 3 \times 10^{-13}$  s (Wiesenfeld

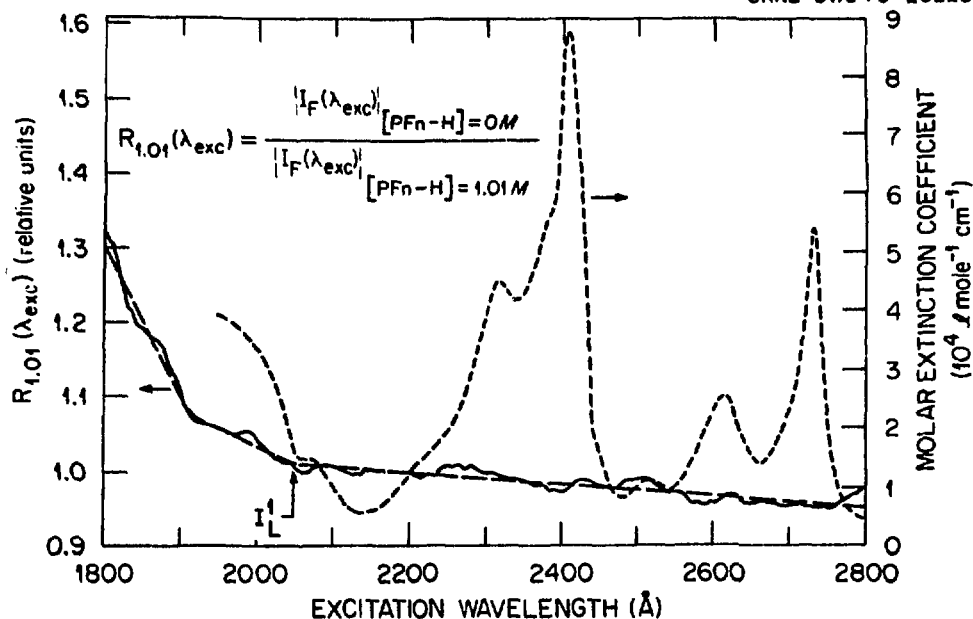


Fig. 2. The ratio of pyrene integrated fluorescence intensity ( $10^{-2}$  mol  $\text{dm}^{-3}$  solution in *n*-pentane) in the absence of perfluoro-*n*-hexane (the electron attaching compound) to that in the presence of 1.01 mol  $\text{dm}^{-3}$  of perfluoro-*n*-hexane as a function of the excitation wavelength. The long dashed line (---), through the experimental data (solid line) was obtained by a least-squares fitting procedure (see text). The pyrene absorption spectrum is represented by the (----) line. The symbol M = mol  $\text{dm}^{-3}$ .

Table 1 Values of  $I_L^1$  for Pyrene in Dielectric Liquids

Dielectric Liquid	$I_L^1$ (eV)*			
	PFn-H	c-C <sub>7</sub> F <sub>14</sub>	c-C <sub>6</sub> F <sub>12</sub>	c-C <sub>8</sub> F <sub>16</sub>
<i>n</i> -Hexane	5.99 ± 0.03	5.43 ± 0.03		
<i>n</i> -Pentane	6.04 ± 0.03	5.46 ± 0.03		
<i>n</i> -Heptane	5.77 ± 0.03	5.46 ± 0.03		
Isopentane		5.50 ± 0.03		
Cyclopentane	5.81 ± 0.03	5.50 ± 0.03		
Neohexane	5.92 ± 0.03	5.50 ± 0.03	5.45 ± 0.08	5.39 ± 0.08
TMSi		5.50 ± 0.03		

\* $I_L^1$  values for the highest concentration of A ( $\approx 1.50$  mol  $\text{dm}^{-3}$ ). The  $I_L^1$  values corresponding to the mean value for six different concentrations of PFn-H and c-C<sub>7</sub>F<sub>14</sub> in the range 0.25–1.50 mol  $\text{dm}^{-3}$  in 0.25 mol  $\text{dm}^{-3}$  steps were similar within the experimental error.

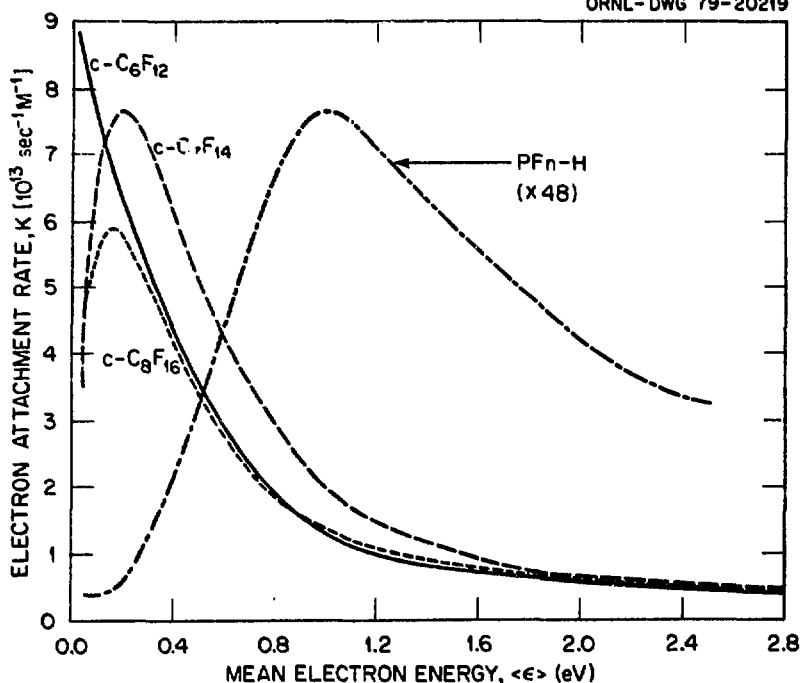
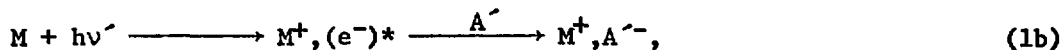
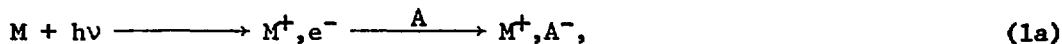


Fig. 3. Electron attachment rates  $k_{\text{cap}}(\epsilon)$  for PFn-H, c-C<sub>7</sub>F<sub>14</sub>, c-C<sub>6</sub>F<sub>12</sub>, and c-C<sub>8</sub>F<sub>16</sub>. Note that the data for PFn-H were multiplied by a factor of 48 for convenience of display. The symbol M = mol dm<sup>-3</sup>.

and Ippen, 1980). The difference between  $\langle \tau_{\text{cap}} \rangle$  and  $\tau_{\text{solv}}$  leads us to conclude that the photoejected electron is captured by A prior to solvation and prior to any possible trapping by the solvent medium.

In light of these observations we proposed (Siomos, 1981) an interaction mechanism shown by reactions (1a,b) and represented schematically in Fig. 4, which accounts for the photoionization behavior of a molecule M in a dielectric liquid in the presence of an efficient A at high concentration, viz.



where  $h\nu' > h\nu$ . On the basis of the preceding and following discussion, the electron-ion pair is formed very fast (at times  $\leq 10^{-14}$  and  $> 10^{-16}$  s) and the  $e^-$  can then be removed via attachment to an A, when it escapes the geminate recombination with thermal energy or via attachment to an A' when the  $e^-$  escapes the geminate recombination as a hot electron,  $(e^-)^*$  (i.e., an electron with kinetic energy in excess of thermal). Thus, the first gives a lower  $I_L^1$  value than the latter. In the latter case the  $I_L^1$  value should be dependent on the position of the maximum of the  $k_{\text{cap}}(\epsilon)$  function of A' (i.e., the photoionization threshold is removed to an apparent higher value depending on the position of the maximum of the attachment cross section of the electron attaching additive). That the electron can be captured by A' as a "hot" electron before it is thermalized by the medium can be shown by the following. The mean scattering cross sections for thermal and near-thermal energy electrons for the alkanes have been measured both in the gaseous (Christophorou, 1976) and in the liquid phase (Sowada, 1977). These studies have shown that the scattering cross sections for liquid alkanes are very close (slightly larger) to the corresponding gaseous values. On the basis of this knowledge then

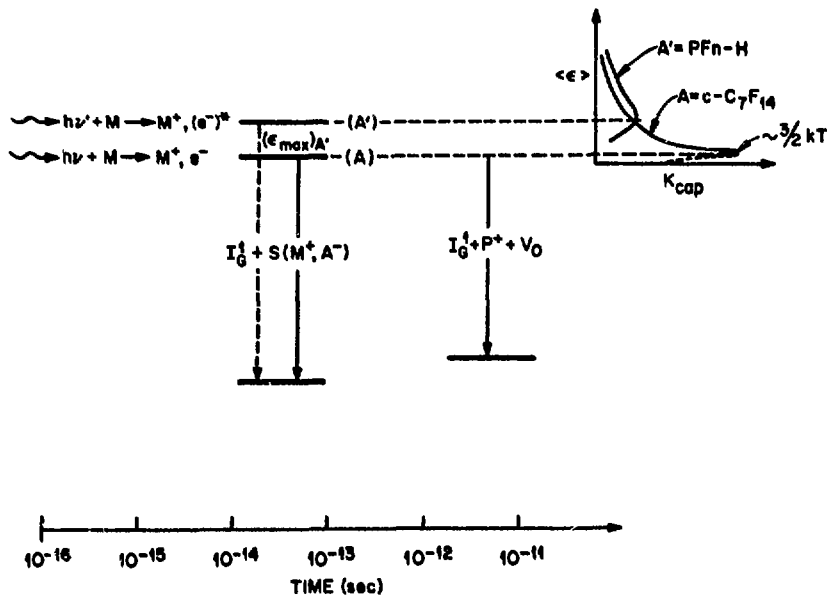


Fig. 4. A schematic illustration of the photoionization and electron attachment processes in the present solutions with efficient electron attaching additives possessing different capture cross section functions (see text for discussion).

we estimate a mean time between collisions for electrons of 0.5 eV energy in the liquid of  $\sim 10^{-14}$  s. Since moreover it has been shown (Christophorou, 1975) that for alkanes the mean fractional energy loss per collision is  $<0.5$ , the time required for thermalization of the "hot" electron is  $>10^{-14}$  s. In both processes (1a) and (1b) the  $e^-$  is captured in a state different from its solvated (or possible trapping) state. This conclusion is consistent with the results obtained by Wiesenfeld and Ippen (1980) using laser picosecond techniques. In view of these findings we indicated in Fig. 4 that  $I_L^1$  is related to  $I_G^1$  via the quantity  $S(M^+, A^-)$  (i.e., the solvation energy of the positive ion-negative ion pair).

In conclusion, the present work--where the photoionization process in liquids is probed with the aid of electron attaching additives--and other photoionization studies in nonpolar and polar liquids utilizing a laser two-photon ionization technique (Siomos, 1980a,b; 1981c) seem to suggest that the photoionization process for a solute molecule in a liquid medium is completed probably at times  $<10^{-14}$  and  $>10^{-16}$  s and its "energetics" are rather independent of the bulk properties of the medium.

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