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Laser Photodetachment Spectra of C₆F₆⁻ in Nonpolar Liquids

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Aromatic anions absorb in the visible region of the spectrum and energetic considerations suggest that in solution photodetachment may be an important process at these wavelengths. This study reports electron photodetachment cross sections for $C_6F_6^-$ for wavelengths between 415 and 700 nm. The anion is generated by electron attachment to solute C_6F_6 during an X-ray pulse. Detachment is observed as a change in conductivity induced by a subsequent light pulse from a tunable dye laser. The threshold values are reported for tetramethylsilane, n-butane, cyclopentane, n-pentane, 2,2,4-trimethylpentane, 2,2-dimethylbutane, and neopentane. The thresholds are consistent with an electron affinity of 1.09 ± 0.04 eV for the C₆F₆ molecule. Comparison of the data to the absorption spectrum of $C_6F_6^-$ shows that for photon energies above threshold the major process is photodetachment. The relationship of photodetachment data to other properties of the excess electrons in these solvents is discussed.

Introduction

The mobility of excess electrons in organic, nonpolar liquids is much larger than that of molecular ions.¹ Therefore photodetachment of electrons from negative ions dissolved in these liquids produces a conductivity change, from which photodetachment cross sections (σ_d) can be determined.^{2,3} In the gas phase the threshold for photodetachment from an anion radical is A_e , the electron affinity of the neutral species. In solution, thresholds are blue shifted due to two additional energy terms:

$$E_{\rm th} = A_{\rm e} + V_0 - P^- \tag{1}$$

where V_0 is the energy of the bottom of the conduction band with respect to vacuum, and P^- is the difference in solvation energy of the anion and the neutral species. A comparison of photodetachment cross sections with molar extinction coefficients (ϵ) permits determination of the quantum yield of electron detachment by

$$\phi_{\rm e} = \sigma_{\rm d} / \sigma_{\rm a} \tag{2}$$

where σ_a is the photon absorption cross section: $\sigma_a = \epsilon \ln \alpha$ $(10)/(6.02 \times 10^{20}).$

In this study photodetachment from the hexafluorobenzene anion is investigated. This anion is unusual in that the lowest unoccupied orbital is known from an ESR study to be a σ^* orbital.⁴ In contrast, the lowest unoccupied orbital in C_6H_6 is a π^* orbital and the spectroscopy of these anions is expected to be quite different. Gas-phase studies indicate there is some uncertainty in the value of $A_{\rm e}$ for C₆F₆, which has been reported to be 1.8 ± 0.3^5 and $1.20 \pm 0.07 \text{ eV.}^6$ The neutral species has a very large cross section for attachment of low energy electrons.⁷ Photodetachment cross sections for C_6F_6 are reported here for several solvents and temperatures for wavelengths in the



Figure 1. Current trace in a solution of C_6F_6 in Si(CH_3)_4 at 255 K; 470 nm and 0.436 mJ.

visible range. The measured thresholds are used to deduce a value for the gas-phase electron affinity. In contrast to a previous study of photodetachment from O_2^- , which is a bound-continuum transition, $C_6F_6^-$ is shown to have excited states which are autoionizing. The absorption spectrum of $C_6F_6^-$, obtained by pulse radiolysis, shows two strong absorption peaks. Comparison of this spectrum with the photodetachment spectra allows an estimate of the importance of autoionization.

Experimental Section

Data Analysis. The experimental procedure, cell, and setup, as described previously,³ make use of the fact that excess electrons have mobilities ranging from 2 to 5 orders of magnitude greater than those for negative ions in the solvents used. Figure 1 shows a current trace obtained in a typical experiment. A square X-ray pulse of $2-10 \ \mu s$ from a 2-MeV Van de Graaff electron accelerator irradiates the cell and creates positive and negative charge carriers of equal concentration. During the pulse the electrons produce a large conductivity signal which rapidly decays after the end of the X-ray pulse because attachment to solute C_6F_6 molecules occurs. The current level observed then is due to ionic motion. After a delay time, which for the present study is usually about 70 μ s, a light pulse of about 150-ns duration from a flashlamp pumped tunable dye laser (Candela model SLL-66) causes detachment of electrons from some of the negative ions, and an increased conductivity spike is observed. The current trace, as shown in Figure 1, is recorded by a transient recorder (Inter Computer Electronics Model PTR 9200) which is remotely controlled by a computer (PDP 11/34).

The cross section for photodetachment is determined from eq 3, where N_e/N_- is the ratio of the number of

$$\sigma_{\rm d} = \frac{N_{\rm e}}{N_{\rm -}} \frac{V}{N_{\rm p}l} = \frac{a_1 A_0}{a_0 A_1} \frac{V}{N_{\rm p}l} \tag{3}$$

electrons that are photodetached to the number of anions present. This ratio can be replaced by a_1A_0/a_0A_1 where a_1 is the amplitude of the photocurrent signal (see Figure 1) following an X-ray pulse of dose A_1 , and a_0 is the amplitude of the X-ray induced current of a calibration pulse with dose A_0 and length of 150 ns. N_p is the number of photons per light pulse which is calculated from the energy that is detected by a pyroelectric probe (Laser Precision Corp. Model RkP335) in connection with a digital display (Laser Precision Corp. Model Rk3230); V is the sensitive volume of the cell and l the optical path length. Equation 3 is valid if all electrons generated by the X rays are converted to one type of negative ion, and if the detachment fraction, N_e/N_- , is <0.1. That this is not entirely correct for high light-pulse energies is shown in Figure 2,



Figure 2. Dependence of the detachment fraction on light pulse energy in a solution of C_6F_6 in 2,2,4-trimethylpentane at 296 K and 470 nm; see text.

where the observed detachment fraction is plotted vs. the light-pulse energy; the corresponding photon number (N_p) is shown at the top of the diagram. At low light-pulse energies the detachment fraction rises linearly with photon number and eq 3 can be used to calculate cross sections. The dashed line corresponds to $\sigma_d = 1.05 \times 10^{-17}$ cm². At pulse energies above 1.5 mJ, the photodetachment fraction rises less than proportional, as evidenced by the experimental points below the dashed line. This is a result of depletion of anions; that is, N_- does not remain constant during the light pulse. In this case the detachment fraction should vary as a function of photon intensity; for weak absorption N_e/N_- is given by

$$N_{\rm e}/N_{\rm -} = 1 - \exp(-N_{\rm p}\sigma_{\rm d}l/V) \tag{4}$$

The solid line is calculated from eq 4 by using $\sigma = 1.05 \times 10^{-17}$ cm². It can be seen that the use of eq 3 to calculate cross sections is justified if the light pulse energy is below 0.5 mJ in regions of the spectrum where the cross section is around 10^{-17} cm². Since photodepletion depends on the product $N_p\sigma_d$, this effect will be less important when the cross section is smaller. The deviation of the experimental points from the solid line in Figure 2 at higher light energies is attributed to inhomogeneous irradiation of the sensitive volume.

Chemicals. Hexafluorobenzene (Aldrich 99%) was used after distillation and degassing. The tetramethylsilane was from PCR (NMR grade) and the hydrocarbons from Phillips (Research grade), except for 2,2,4,4-tetramethylpentane which was from Chemical Samples Co. (99%). After purification of the solvents by the methods described previously,³ the excess electron lifetime, with respect to reaction with trace impurities, was between 10 μ s in Me₄Si and 200 μ s in *n*-pentane. The dyes used for the various wavelength regions were as listed elsewhere;³ one additional dye, coumarin 6, was used from 525 to 545 nm.

Results

Photodetachment spectra of $C_6F_6^-$ in tetramethylsilane at 200 and 296 K and in *n*-butane, *n*-pentane, 2,2,4-trimethylpentane, and 2,2-dimethylpropane, all at 296 K, are shown in Figure 3A–C. Typically, the C_6F_6 concentration was between 0.02 and 0.5 μ M. Spectra were also obtained in cyclopentane at 296 K, in *n*-butane at 273 K, and in 2,2-dimethylbutane at 296 K which are similar to the spectra shown. With the exception of the data obtained in tetramethylsilane at 200 K, all spectra show a decreasing cross section with decreasing photon energy between 3.0



Figure 3. Photodetachment cross section vs. photon energy for the solvents: (A) Si(CH₃)₄ (O) 296 K, (O) 200 K; (B) (O) C(CH₃)₄, (O) 2,2,4-trimethylpentane, both at 296 K; (C) (O) *n*-pentane at 296 K, (O) *n*-butane at 296 K.

and 2.8 eV, then a maximum or shoulder around 2.6 eV, and a continuously decreasing cross section below 2.5 eV. The cross sections are comparable in magnitude at 2.6 eV, ranging from 1.05×10^{-17} cm² in 2,2,4-trimethylpentane to 0.75×10^{-17} cm² in *n*-pentane. However, very large differences are observed in the spectra at photon energies around 2.0 eV; for example, $\sigma_d = 1.8 \times 10^{-18}$ cm² in tetramethylsilane and about 1×10^{-19} in *n*-pentane. The photodetachment cross section in tetramethylsilane at 2.6 eV is 30% higher at 200 K than at 295 K (see Figure 3A). In butane the cross section at this photon energy changed



Figure 4. Pulse radiolysis spectrum obtained in a solution of C_6F_6 in 2,2,4,4-tetramethylpentane at 297 K.

little between 295 and 273 K but increased to 1.3×10^{-17} cm² on further cooling to 261 K.

The similarities of the cross sections at higher photon energies is considered a justification for the assumption that the photon absorption process is only weakly dependent on solvent for these organic liquids. Therefore for the pulse radiolysis experiment a hydrocarbon solvent was chosen that gives a high yield of free electrons and has a low vapor pressure at room temperature and thus could be used in the usual way in a pulse radiolysis experiment.⁸ Such a solvent is 2,2,4,4-tetramethylpentane for which $G_{\rm fi}$ = 0.83 at 295 K.⁹ Standard ferrous sulfate dosimetry was used and corrections were applied for electron density. The extinction coefficient was obtained from the absorbance at the end of a $2-\mu s$ pulse of 2-MeV electrons. Figure 4 shows the absorption spectrum obtained for a 0.5 mM solution of C_6F_6 and attributed to C_6F_6 . The spectrum is very similar to that reported for C_6F_6 in 3 MP at 77 K.¹⁰ The extinction coefficients correspond to the photon absorption cross sections (σ_a) indicated on the right ordinate of the figure. The pure solvent shows no X-ray induced absorption in the visible and near-UV. Two broad peaks at 2.6 and 3.1 eV are apparent and the one at lower energy coincides with the one found in the photodetachment spectra (Figure 3A-C). The peak at 3.1 eV was not observed in the photodetachment experiments because it is outside the range of the dye laser with those dyes used. However, the minimum at 2.8 eV and the increase of cross sections at higher photon energies are observed in both the absorption spectrum and the photodetachment spectra.

Discussion

Thresholds. In an earlier study³ of photodetachment from O_2^- in solution, the cross sections were found empirically to increase above threshold according to the 3/2's power law:

$$\sigma_{\rm d}(E) = BE(E - E_{\rm th})^{3/2}$$
 (5)

where E is the photon energy and B is a constant. In the gas phase, theory¹⁰ indicates that eq 5 should be valid for photodetachment from O_2^- and this has been experimentally confirmed.¹¹ There is no a priori way of predicting threshold laws for polyatomic species in solution. However, in all the cross-section spectra reported here the slope decreases with decreasing photon energy near threshold, which suggests eq 5 may be applicable. This equation predicts that a plot of $(\sigma/E)^{2/3}$ vs. E should be linear, and the threshold is then given by the intercept of such a line on the energy axis. Figure 5 shows the data for cyclopentane and *n*-pentane plotted in this manner. All other spectra were analyzed in a similar way to obtain values of $E_{\rm th}$ and B. These parameters were then used to calculate

solvent	<i>T</i> / K	$E_{\mathrm{th}}/\mathrm{eV}$	$V_{\rm o}/{ m eV^a}$	P^{-}/eV	$A_{ m e}/ m eV$	quantum yields (ϕ_{e})	
						at 2.6 eV	at 3.0 eV
tetramethyl-	296	(1.61)	-0.51	-0.92	(1.21)	0.53	0.64
silane	200	(1.72)	-0.47	-1.02	(1.17)	0.68	0.52
<i>n</i> -butane	296	`1.82 ´	-0.13^{b}	-0.87	· · ·	0.50	0.59
	273	1.92	-0.06^{b}	-0.90		0.50	0.55
<i>n</i> -pentane	296	1.97	0.0	-0.92	1.05	0.39	0.68
neopentane	296	(1.67)	-0.43	-0.88	(1.22)	0.44	0.64
cyclopentane	296	1.88	-0.23	-0.99	1.12	0.47	0.62
neohexane	296	(1.72)	-0.23	-0.94	(1.01)	0.45	0.55
2,2,4-trimethyl-	296	`1.90´	0.17	-0.97	<u>`1.10´</u>	0.55	0.64
pentane					1.13 ± 0.08		
					1.09 ± 0.04		

TABLE I: Thresholds and Quantum Yields

^a Reference 12. ^b These values are calculated from eq 1.



Figure 5. Plot of $(\sigma/E)^{2/3}$ vs. photon energy for the solvents (O) cyclopentane at 296 K and (\bullet) *n*-pentane at 296 K.

the solid lines through the points at low energies in Figure 3A-C. Only the cross section data for low photon energies (below $\sim 2.3 \text{ eV}$) were used for threshold determination. The open points in Figure 5 for cyclopentane deviate from a straight line at the lowest photon energies; that is, some photodetachment was detected at photon energies below the threshold of 1.88 eV. This effect, which was not observed in *n*-pentane, is attributed to residual impurities in the solvent which attach electrons and form anions from which photodetachment can also occur. The excess electrons in *n*-pentane had lifetimes of $\sim 200 \ \mu s$ prior to addition of C_6F_6 ; after addition the electron lifetime was only 1.0 μ s; thus 99.5% of the excess electrons reacted with C₆F₆ and only 0.5% reacted with impurities. The formation of impurity anions with low energy photodetachment thresholds is a difficulty in this type of work but the effect can be minimized by careful and extensive purification of solvents. Where photodetachment due to impurity anions was encountered, as in cyclopentane, the threshold was determined by extrapolation to the impurity level rather than to the energy axis. Threshold data are summarized in Table I.

Thresholds for photodetachment from $C_6F_6^-$ are solvent dependent and exhibit a dependence on both V_0 and $P^$ as required by eq 1. Thus, for example, the threshold is observed to shift to the blue by 0.11 eV on cooling tetramethylsilane from room temperature to 200 K. This is due primarily to the change in magnitude of the polarization energy of the anion which increases by 0.10 eV on cooling. The polarization energy is calculated from Born's equation by using an effective radius of 3.59 Å derived from the molar volume¹⁴ and a measured density of 1.59 g/cm³. On the other hand, the threshold in *n*-pentane is 0.36 eV greater than in tetramethylsilane and these liquids have the same polarization energy. This shift is attributed to a higher conduction band energy (V_0) in *n*-pentane.

The electron affinity of C_6F_6 can be calculated from the threshold values by using eq 1 and known values of V_0 . The values of A_e so derived are shown in the sixth column of Table I for all cases except *n*-butane, for which no work function data on V_0 are available. The overall average gives A_e (for C_6F_6) = 1.13 ± 0.08. Several of the threshold values (those in parentheses) are uncertain because the thresholds are in the infrared, somewhat beyond the low energy limit of the laser. If these values are omitted, a somewhat more accurate value of $A_e = 1.09 \pm 0.04$ eV is obtained. In either case the results are in agreement with the magnetron value of the electron affinity.⁶ Since photodetachment occurs from the ground state of C_6F_6 , this value of A_e is the adiabatic electron affinity of C_6F_6 to form the ground state ion. The π -electron affinity of C_6F_6 is reported to be much less.¹⁵

Up to this point we have considered photodetachment from $C_{6}F_{6}^{-}$ to be a bound-continuum transition, where the electron final state is in the conduction band. In many of the solvents used the conduction band is the lowest energy level of the excess electron. However, in n-pentane and *n*-butane the localized or trapped electron level is lower in energy and a transition to this state is possible, as has been suggested for biphenyl anion in ether solvents.¹⁶ Although we cannot rule out this possibility, the following arguments support our original assumption: first the energetics as given in Table I are consistent with a transition to the conduction band; for example, the threshold for pentane should have been lower if a transition to a trapped state were important. Second, photodetachment cross sections are proportional to the density of states available for the electron and the large cross sections ($\sim 10^{-17}$ cm²) observed here are inconsistent with the expected low concentration of unoccupied trapping sites.

Autoionization. The photodetachment spectra all show either a peak or a shoulder at photon energies of 2.6 eV. The position of this feature is independent of threshold. The absorption spectrum of $C_6F_6^-$ in 2,2,4,4-tetramethylpentane also shows a peak at 2.6 eV and one at 3.1 eV. These bands correspond to excited states of the anion and are thus transitions from the ground state σ orbital⁴ to upper valence orbitals. These states are, however, above the ionization threshold and the results show they are autoionizing.

A comparison of the photodetachment spectra with the absorption spectrum of C_6F_6 provides data on the quantum yields of autoionization. The absorption spectrum

(Figure 4) was obtained in 2,2,4,4,-tetramethylpentane and it is reasonable to assume the spectrum would be very similar in the other nonpolar solvents used. If this assumption is valid, eq 2 can be employed to calculate quantum yields. At the first absorption maximum at 470 nm (2.6 eV), the absorption cross section (σ_{e}) is 1.8×10^{-17} cm². The ratio of the photodetachment cross sections at 2.6 eV to this value gives values of the electron quantum yields. These values are listed in the penultimate column of Table I and range from 0.39 to 0.68 electron/quantum.

Photodetachment is even more efficient in the second absorption band. Experimental limitations precluded detachment measurements in the region of the peak at 3.1 eV but the photodetachment spectra generally show that $\sigma_{\rm d}$ is the largest at the shortest wavelengths employed. At 296 K the quantum yields (ϕ_e) at 3.0 eV, given in the last column of Table I, are consistently higher than the values at 2.6 eV. The average value is $\phi_e = 0.62$, indicating detachment is a major process. A very similar behavior was found for the anthracene anion in THF;17 the reported photoemission spectra show the same spectral structure as the absorption spectra and the yield of photoemission is greatest in the high energy band.

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High Mobility Excess Electrons in the Electron-Attaching Liquid Hexafluorobenzene

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Hexafluorobenzene (C_6F_6) has been found to have an electron affinity between 1 and 2 $eV^{1,2}$ and to undergo rapid attachment of thermal electrons in the gas phase.³ We have found that this compound is also a very efficient scavenger of excess electrons in nonattaching molecular liquids (rate constant $1.2 \times 10^{14} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in tetramethylsilane). On the basis of this it can be concluded with considerable certainty that excess electrons formed in pure liquid C_6F_6 will very rapidly form a bound negative ion state with solvent molecules. Despite this, the negative charge carrier in irradiated liquid C_6F_6 is found to have a mobility more than an order of magnitude greater than would be expected for a molecular ion in this medium, the evidence for which will be discussed below.

In the present experiments, the liquid was ionized by pulsed irradiation with 3-MeV electrons from a Van de Graaff accelerator and the conductivity change was measured by using the microwave absorption method.⁴ The product of the yield of ions per 100 eV absorbed and the sum of the ion mobilities, $G\mu$ cm² V⁻¹ s⁻¹ (100 eV)⁻¹, was determined from the conductivity change and the known dosimetry.

The transient conductivity resulting from pulse irradiation of pure C_6F_6 is considerably greater than that which would be expected on the basis of the formation of ions, the motion of which is dependent on molecular displacements alone. This is illustrated in Figure 1 by comparison of the C_6F_6 data with conductivity transients observed in benzene containing 10^{-2} mol dm⁻³ of SF₆ as an electron scavenger and in the (dissociative) electron-attaching liquid

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CCl₄.

The decay rate of the conductivity signal in C_6F_6 is increased by the addition of small amounts (<10⁻² mol dm⁻³) of the electron acceptors O₂, CCl₄, CBr₄, and tetracyanoethylene but is unaffected by benzene which has a lower ionization potential than C_6F_6 . For a concentration of 10^{-2} mol dm⁻³ CBr₄ in C₆F₆ the conductivity signal observed is similar to that found in the benzene + SF_6 solution or in pure CCl_4 as is shown in Figure 1.

In view of the above, we conclude that the species mainly responsible for the conductivity observed, for several hundred nanoseconds following the pulse in pure hexafluorobenzene, is a highly mobile negative charge carrier. The fact that this carrier is not simply an excess electron partially localized at relatively shallow potential fluctuations in the medium is evidenced by the fact that no effect of SF_6 on the conductivity signal even up to a concentration of 10^{-2} mol dm⁻³ has been found (see Figure 1). This can be understood if excess electrons are, as expected, bound to C_6F_6 molecules since the measured values of the electron affinity of C_6F_6 (1.2¹ and 1.8 eV²) are considerably larger than those found for SF₆ (ca. 0.6 eV^{2,5-7}). In the case of O_2 , the gain in solvation energy resulting from formation of the smaller O_2^- ion is apparently sufficient to overcome the considerable difference in electron affinities involved in this case ($EA_{O_2} = 0.44 \text{ eV}^{8,9}$). This will be more fully discussed in a separate publication.

By comparing the data in pure C_6F_6 with that in C_6F_6 containing a high concentration of negative ion scavenger $(10^{-2} \text{ mol dm}^{-3} \text{ CBr}_4)$, one finds it possible to estimate the ratio of the mobility of the negative charge carrier $\mu(-)$, to the average mobility of a "normal" molecular ion, $\mu(S^+,S^-)/2$. The kinetics of the decay of the charged