Photoionization of C_{60} and C_{70} in Liquid Alkanes

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Z. Naturforsch. **49a,** 793–796 (1994); received May 2, 1994

Single photon ionization of C_{60} in 2,2-dimethylpropane (neopentane, NP), 2,2,4,4-tetramethylpentane (TMP), 2,2-dimethylbutane (neohexane, DMB), and 2,2,4-trimethylpentane (isooctane, iso-OCT), and of C_{70} in TMP was studied by photoconductivity measurement. Threshold energies of the photoconductivity were determined. From these results, the polarization energies and the ionic radii of the cations were obtained by application of Born's formula. The ionic radii turned out to be smaller than the van der Waals radii of the molecules.

Introduction

Photoconductivity measurements on solutions of aromatic solutes in liquid alkanes have been performed by several authors in order to study the influence of an inert dielectric medium on the process of photoionization [1–3]. It was found that the photoconductivity threshold, $I(\text{sol})$, was changed on account of the electron affinity of the liquid alkane, V_0, and of the polarization energy of the cation, P_+,

$$I(\text{sol}) = I(\text{gas}) + V_0 + P_+\,, \tag{1}$$

where $I(\text{gas})$ denotes the ionization potential of the solute molecule in the gas phase. P_+ is always negative while V_0 can be positive or negative depending on the type of alkane [4]. Born expressed the polarization energy of an ion in terms of the dielectric constant of the solvent, ε_r, and the apparent radius of the ion, $R_\pm$, [5]:

$$P_+ = \frac{e_0^2}{8\pi\,\varepsilon_0 R_\pm}\left[1 - \frac{1}{\varepsilon_r}\right]. \tag{2}$$

e_0 denotes the electronic charge and ε_0 is the permittivity of the vacuum. From the value of P_+ obtained from photoconductivity measurements, $R_\pm$ was extracted and compared to the van der Waals radius, R_{vdW}, of the solute molecule. In the case of small aromatic molecules in alkane solvents,

$$R_\pm \approx R_{\text{vdW}} \tag{3}$$

was found to be valid [6]. It seemed to be interesting to study the photoconductivity of solutions of molecules with well known ionization potentials and van der Waals radii. The fullerenes C_{60} and C_{70} are well characterized and, here, we wish to report photoconductivity threshold energies obtained for fullerene solutions of several alkanes.

Experimental

A deuterium discharge lamp with an MgF_2 window (Hamamatsu, L 1835) followed by a vacuum ultraviolet monochromator (Acton, VM 502) was used as light source. The wavelength resolution of the system was 1 nm. The relative intensity distribution of the light source was determined by using sodium salicylate [7], the fluorescence of which was detected with a photomultiplier (Hamamatsu, R 928). The photoconductivity cell was the same as in a previous study [1]. Exciting light entered the cell through the front electrode, which consisted of a thin film of gold (thickness: 7 nm) deposited on a MgF_2 plate. The back electrode was separated by a teflon spacer (thickness: 4 to 5 mm) from the front electrode. Bias voltages between +500 and +1000 V were applied to the front electrode. The corresponding electric field strengths (1 kV/cm to 2 kV/cm) are sufficient to collect all charge carriers without loss due to volume recombination. The photocurrents were measured with a pico-ammeter (Keithley, Model 617). They were in the range of 0.1 to 1 pA. Wavelength change and photocurrent reading were controlled and recorded by a Macintosh™ computer, model IIsi. The whole set-up is shown in Figure 1.

The hydrocarbon solvents were 2,2-dimethylpropane (neopentane, NP) and 2,2-dimethylbutane (neohexane, DMB) from Phillips Petroleum Co., 2,2,4,4-tetramethylpentane (TMP) from Wiley Organics, and

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Table 1. Concentrations of fullerene-solutions employed in the present work.

	Concentration [mol/l]
C_{60}/neopentane	1×10^{-5}
C_{60}/2,2,4,4-tetramethylpentane	9×10^{-5}
C_{60}/neohexane	5×10^{-5}
C_{60}/isooctane	5×10^{-5}
C_{70}/2,2,4,4-tetramethylpentane	5×10^{-5}

2,2,4-trimethylpentane (isooctane, iso-OCT) from Merck. They were purified by percolation through activated silica gel and molecular sieves (pore size, 0.4 nm). C_{60} (Fluka) and C_{70} (Fluka) were used as obtained. The fullerenes exhibit a rather small solubility in these hydrocarbons. The concentrations of the solutions are listed in Table 1.

Results and Discussion

The Figs. 2 and 3 show action spectra of the photoconductivity of C_{60} in various solvents and of C_{70} in TMP, respectively. The rather small photocurrents are superimposed by fluctuations of the dark conductivity of the solution and by the noise of the input stage of the electrometer amplifier. However, the reproducibility of the photocurrents was quite good. For the estimation of the threshold energy, the average of several such traces was taken. In the spectral range of the photoconductivity threshold no direct ionization of the solvent takes place (see also Table 2, where the thresholds of the pure liquids, I_{liq}, are included).

To estimate the threshold energy of photoionization from the photoconductivity action spectrum a power function was used [6],

$$Y = A[h\nu - I(\mathrm{sol})]^n . \tag{4}$$

Y is the apparent efficiency of photoionization, A is a constant and $h\nu$ is the photon energy of the exciting light. In the case of alkane solutions, an exponent of $n = 2.5$ yields good agreement of the data with (4). The values of $I(\mathrm{sol})$ reported in Table 2 and indicated by arrows in Figs. 2 and 3 were determined in this way.

Above the threshold (arrows in the Figs. 2 and 3), the photocurrent increases gradually with photon energy. At higher photon energies the photocurrent decreases steeply due to absorption by the solvent itself.

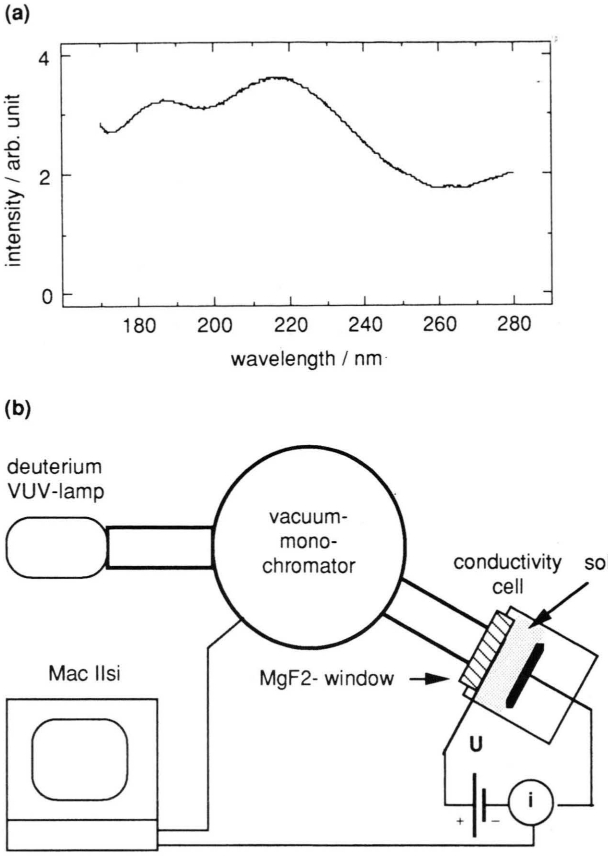

Fig. 1. Photoconductivity measurement set-up; (a) relative spectral distribution of the light entering the solution; (b) schematic diagram of the experimental set-up.

The photoconductivity spectrum reflects the relative ionization efficiency as a function of the photon energy when the exciting light is absorbed completely between the electrodes. In the case of NP, the shape of the spectrum is affected by the absorption coefficient since the concentration of the saturated solution is not sufficient.

In the case of C_{70} (Fig. 3) the exciting light is absorbed completely. The photoconductivity spectrum exhibits a shoulder at 6.3 eV. This may be due to auto-ionization of a highly excited state.

Since the V_0-values of the solvents used in this work and the photoionization energies, $I(\mathrm{gas})$, of C_{60} and C_{70} are known, values of P_+ and R_+ can be obtained. They are included in Table 2. On the other hand, the van der Waals radii of the fullerenes are available from [8, 9]. Comparison of R_+ and R_{vdW} (see Table 2) shows that the ionic radii obtained, here, are much

Table 2. Ionization potential of fullerene in the gas phase I(gas); ionization energy of the pure solvent I(liq); conduction band energy of solvent, V_0; threshold energy of photoconduction of fullerene solution, I(sol); n refractive index; polarization energy $P_{+\mathrm{exp}}$; ionic radius, R_{exp}, derived from $P_{+\mathrm{exp}}$; polarization energy $P_{+\mathrm{vdW}}$, estimated from the van der Waals radius, R_{vdW}.

Solute	Solvent	I(liq) (eV)	I(gas) (eV)	V_0 (eV)	I(sol) (eV)	$\varepsilon_r = n^2$	$P_{+\mathrm{exp}}$ (eV)	R_{exp} (nm)	$P_{+\mathrm{vdW}}$ (eV)	R_{vdW} (nm)
C_{60}	NP	8.7[d]	7.54[a]	−0.43[b]	6.17	1.816	−0.94	0.34	−0.63	0.51
C_{60}	TMP	8.2[d]	7.54[a]	−0.33[b]	6.25	1.979	−0.96	0.37	−0.70	0.51
C_{60}	DMB	8.6[d]	7.54[a]	−0.20[b]	6.3	1.874	−1.0	0.35	−0.66	0.51
C_{60}	iso-OCT	8.3[d]	7.54[a]	−0.24[c]	6.4	1.936	−0.9	0.4	−0.68	0.51
C_{70}	TMP	8.2[d]	7.3[a]	−0.33[b]	5.8	1.979	−1.2	0.30	−0.67	0.53

[a] [12]; [b] [4]; [c] [13]; [d] [14].

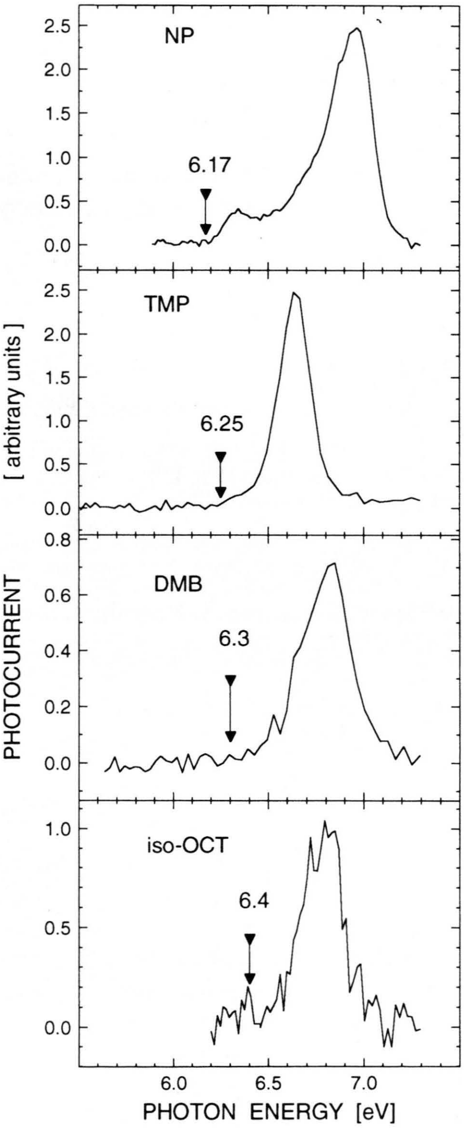

Fig. 2. Action spectra of the photoconductivity of C_{60} in various solvents at room temperature; threshold energies in eV are indicated by arrows; NP: C_{60}-neopentane; TMP: C_{60}-2,2,4,4-tetramethylpentane; DMB: C_{60}-neohexane; iso-OCT: C_{60}-iso-octane.

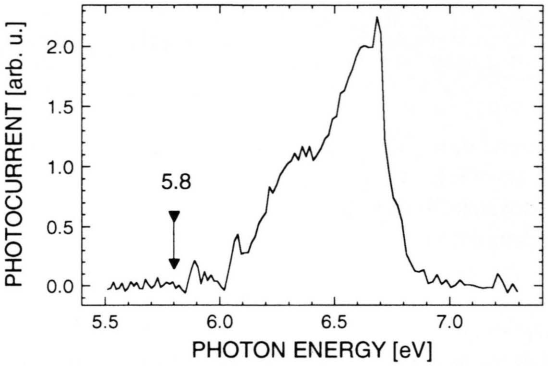

Fig. 3. Action spectrum of the photoconductivity of C_{70} in 2,2,4,4-tetramethylpentane; the threshold energy in eV is indicated by an arrow.

smaller than the van der Waals radii. A priori, we would have expected that the positive charge would be distributed evenly over the whole molecule and that the apparent radius of the charge would be the van der Waals radius. In the case of solutions of aromatic compounds in non-polar liquids, the ionic radii (from Born's equation) and the van der Waals radii agree in magnitude [6].

A smaller ionic radius may be indicative of a localization of the positive charge on a subsection of the $C_{60/70}$ molecule. The photoionization is a fast process which can only be influenced by the electronic polarization. The positive hole created at the surface of the

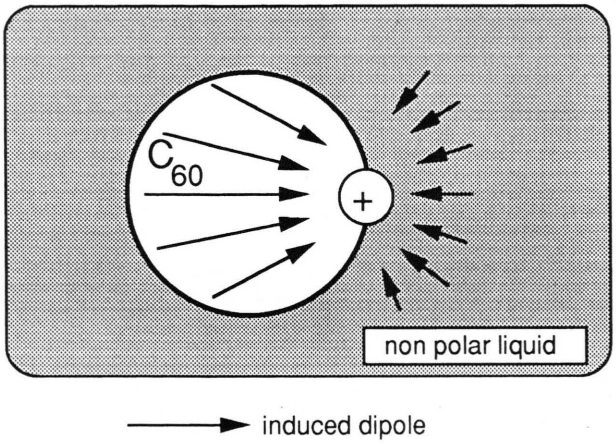

Fig. 4. Schematic representation of positive charge stabilization on a fullerene molecule in solution.

fullerene molecule is immediately stabilized by polarization of the adjacent solvent molecules and possibly by polarization of the fullerene itself (see Figure 4). An anomalously high polarizability of the fullerenes C_{60}/C_{70} (of the order of 10^{-21} cm^3) was reported by Maltsev et al. [10]. Born's equation is based on a dielectric continuum. The influence of steplike changes of the polarizability are not incorporated. Therefore, it is possible that the ionic radii estimated are too small because the influence of the high polarizability of the fullerenes is not taken into account.

Another possibility is a mechanism by which the charge carrier separation occurs in two steps. First an electron-hole pair or an exciton is produced on a fullerene molecule by optical transition, and second, thermal dissociation of this complex takes place. Recently, Schlag and Levine proposed such a model for the photoionization of large molecules and clusters [11].

Acknowledgement

Financial support by the Nishina Memorial Foundation for an one year stay of RK at HMI is gratefully acknowledged.

[1] E. H. Böttcher and W. F. Schmidt, J. Chem. Phys. **80,** 1353 (1984).
[2] R. A. Holroyd, J. M. Preses, E. H. Böttcher, and W. F. Schmidt, J. Phys. Chem. **88,** 744 (1984).
[3] D. W. Tweeten and S. Lipsky, J. Phys. Chem. **93,** 2683 (1989).
[4] A. O. Allen, Drift Mobility and Conduction Band Energies of Excess Electrons in Dielectric Liquids, NSRDS-NBS-58, US Natl. Bur. Stand., 1976.
[5] M. Born, Z. Physik **1,** 45 (1920).
[6] R. A. Holroyd, J. M. Preses, and N. Zevos, J. Chem. Phys. **79,** 483 (1983).
[7] J. A. R. Samson, Technique of Vacuum Ultraviolet Spectroscopy, Wiley, New York 1967.
[8] V. P. Dravid, X. Lin, H. Zhang, S. Liu, and M. M. Kappes, J. Mater. Res. **7,** 2440 (1992).
[9] T. Kato, K. Kikuchi, and Y. Achiba, J. Phys. Chem. **97,** 10251 (1993).
[10] V. A. Maltsev, O. A. Nerushev, S. A. Novopashin, and B. A. Selivanov, Chem. Phys. Lett. **212,** 480 (1993).
[11] E. W. Schlag and R. D. Levine, J. Phys. Chem. **96,** 10608 (1992).
[12] I. V. Hertel, H. Steger, J. de Vries, B. Weisser, C. Menzel, B. Kamke, and W. Kamke, Phys. Rev. Lett. **68,** 784 (1992).
[13] R. A. Holroyd, S. Tames, and A. Kennedy, J. Chem. Phys. **79,** 2857 (1975).
[14] W. F. Schmidt, IEEE Trans. Electr. Insul. **19,** 389 (1984).