Photoconductivity of an Anthracene / 2,2,4,4-Tetramethylpentane Solution: Pressure Effect on the Photoionization of Solute and Solvent

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The photoconductivity spectrum of a solution of anthracene (AN) in 2,2,4,4-tetramethylpentane (TMP) was measured as a function of pressure up to 2 kbar. The threshold energies of photoionization of the solute (AN) and of the solvent (TMP) increase with pressure. The relative quantum yield for charge carrier generation decreased with increasing pressure. The concomitant reduction of the initial separation distance of the geminate charge carrier pairs may be due to an increase of the number of inelastic collisions caused by the increased density of the liquid within the sphere of Coulomb attraction of the positive ion.

1. Introduction

The process of photoionization of a molecule in the gas phase is well understood. When the molecule is embedded in condensed matter, the photoionization process yielding an electron is affected by the various interactions with the surrounding molecules. In principle, one can distinguish two cases: (a) The electrons remain in the liquid and photoconductivity is observed; (b) the electrons are emitted into the vapor phase and the emission current is measured. In this paper, we are concerned with the photoionization process leading to photoconductivity.

The photoionization process in liquid alkanes and solutions has been studied by several authors [1 - 10]. These studies yielded the following results: (i) a decrease of the threshold energy for photoionization compared to the gas phase ionization potential, (ii) a small quantum yield for the ionization process (10^{-2} - 10^{-3}), (iii) the existence of various types of photoionization processes, and (iv) a strong influence of the electron mobility in the solvent on the structure of the solute photoconductivity spectrum.

The decrease of the threshold energy for photoionization is due to the stabilization of the cation generated by polarization of the surrounding molecules, P_+, and due to the potential energy of the emitted electron in the liquid, the so called V_0-value (bottom of the conduction band in terms of solid state physics),

$$I_{\text{liq}} = I_{\text{gas}} + P_+ + V_0. \tag{1}$$

I_{liq} denotes the photoionization threshold in the liquid phase (measured as the threshold energy for photoconductivity) and I_{gas} denotes the ionization potential in the gas phase. P_+, the polarization energy of the positive ion is negative since the energy of the vacuum level is set to be $E_{\text{vac}} = 0$. I_{liq} may refer to the ionization threshold of a solute molecule or to the molecules comprising the liquid itself. V_0 is a property of the pure liquid.

When a very high pressure is applied to a liquid, its electronic properties change [11]. For solid and liquid insulators, it was demonstrated that at sufficiently high pressures of 500 kbar to 1.4 Mbar, valence and conduction band start to overlap leading to a dramatic decrease of the electrical resistance [12 - 14]. Pressures of a few kbar lead to an increase of the energy gap between conduction and valence band [15]. Measurements of the energy V_0 of the conduction band showed that in liquid hydrocarbons the energy level is shifted upwards with increasing pressure [16]. The effect on the polarization energy can be estimated by means of Born's equation [17]

$$P_+ = -\frac{e_0^2}{8\pi\varepsilon_0 R_+}\left[1 - \frac{1}{\varepsilon_{\text{r}}}\right]. \tag{2}$$

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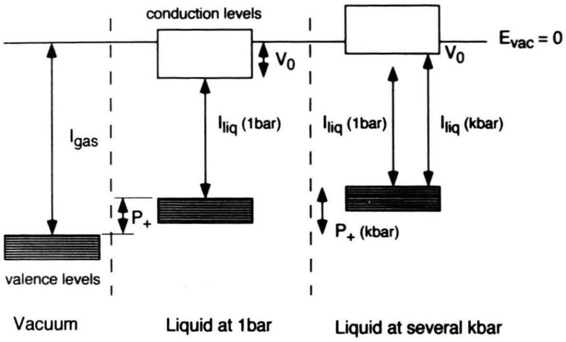

Fig. 1. Energy levels.

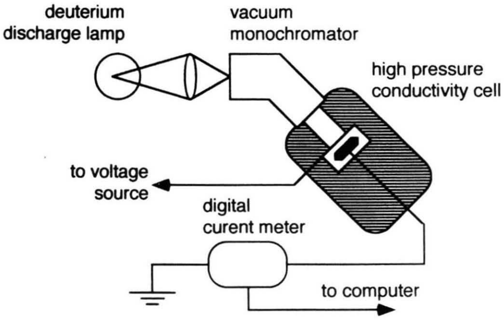

Fig. 2. Experimental set-up.

Here, R_+ denotes the radius of the positive ion and ε_r is the relative dielectric constant of the liquid. The other symbols have the usual meaning. The relative dielectric constant of non-polar liquids increases with pressure due to the increase in density. Therefore the energy level of the positive ion is shifted upwards, too. The increase of I_{liq} with increasing pressure is due to the larger shift of V_0. These conditions are shown schematically in Figure 1.

Here, we present the experimental results of the effect of high pressure on the photoionization of the solute molecule anthracene $C_6H_4 : (CH)_2 : C_6H_4$ (AN) and on the solvent molecule 2,2,4,4-tetramethylpentane (TMP).

2. Experimental

The photoconductivity measurements were made with the same apparatus as in the previous study [15]. Briefly, VUV-light from a deuterium discharge lamp was passed through a vacuum-monochromator and directed to the conductivity cell. The extension of the circular plane electrodes was perpendicular to the direction of the beam. The electrodes consisted of the MgF_2-entrance window, which was coated with 5nm of gold, and of the back electrode separated from the window electrode by about 1mm. The photocurrent was measured by a digital pico-ammeter, and the data were fed into a personal computer. The high pressure

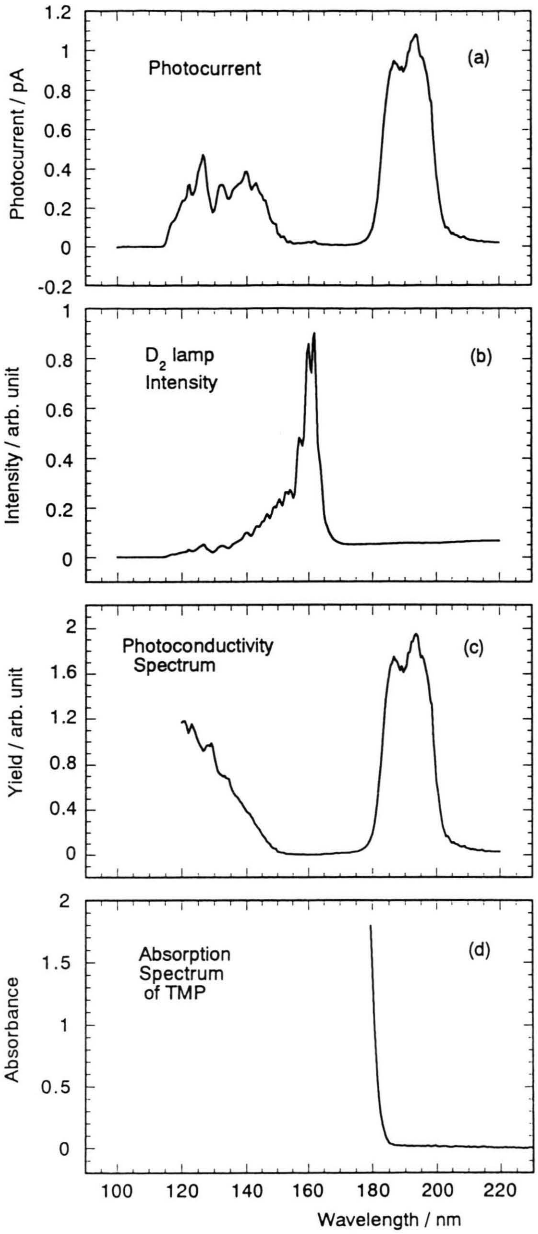

Fig. 3. (a) photocurrent spectrum; (b) relative spectral shape of exciting light intensity; (c) photoconductivity spectrum. The photoconductivity spectrum is obtained from the photocurrent spectrum (a) normalized by the exciting light intensity (b); (d) absorption spectrum of solvent.

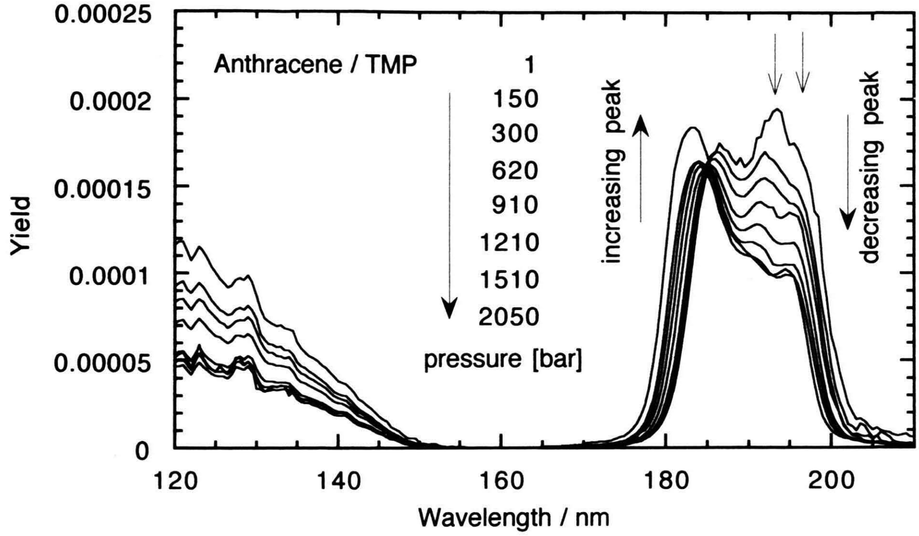

Fig. 4. Photoconductivity spectra of anthracene in liquid TMP as a function of pressure.

was generated by a screw-type hand pump. It was measured with an electric strain gauge-type manometer. A scheme of the experimental set-up is shown in Figure 2. The liquid alkane 2,2,4,4-tetramethylpentane (Wiley Organics, Columbus, Ohio) was purified by percolation through a column of activated silicagel and molecular sieve (pore size: 0.4 nm). Anthracene (Merck, Darmstadt) was used as received. The concentration of the solution was approximately 10^{-3} mol l^{-1}.

3. Results

Figure 3a shows a photocurrent spectrum recorded as a function of wavelength. In Fig. 3b the relative spectral distribution of the exciting light source is given. The normalized photoconductivity spectrum obtained from (a) and (b) is then displayed in Figure 3c. Under the present experimental condition, all photons entering the conductivity cell are absorbed in the measurement volume so that the normalized photoconductivity spectrum also reflects the relative photoionization quantum yield. The photoconductivity yield (Fig. 3c) increases below the photoionization threshold of about 210 nm. It exhibits two shoulders at around 197 nm (shoulder 1: 6.29 eV) and at around 193 nm (shoulder 2: 6.42 eV). Below 180 nm the absorption of solvent itself sets in (Fig. 3d), and as a result, the photocurrent decreases. Below 150 nm, the photocurrent increases again due to the photoionization of the solvent itself. The fine structures observed in this energy range may be an artifact due to the low signal to noise ratio (1:1).

Figure 4 shows the variation of the photoconductivity spectrum as a function of pressure. Both threshold energies for the photoionization of the solute, I_{liq}(AN), and of the solvent, I_{liq}(TMP), shift towards higher energies with increasing pressure. The two shoulders in the photoconductivity spectrum of AN shift in the same direction with pressure as I_{liq}(AN). The apparent quantum yield of the photoionization of AN and of TMP decreases with increasing pressure.

4. Discussion

In order to determine the threshold energy of photoionization, I_{liq}, a power law was applied. Near the threshold energy, the photoionization yield, Φ, varies with photon energy, $h\nu$, as

$$\Phi = A\left[h\nu - I_{liq}\right]^n , \quad (3)$$

where A is a constant. We used $n = 2.5$ since for aromatic molecules in alkane liquids good linear fits to the data were obtained with this exponent [18].

Figure 5 shows the shift of the photoionization threshold energies of the solute AN and the solvent TMP with respect to the value at 1 bar. It is interesting that the shift of the threshold energies of the solute and of the solvent are almost the same. This indicates that solute-solvent interaction is not important

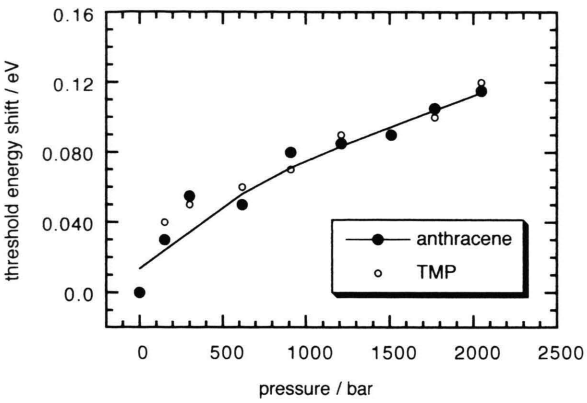

Fig. 5. Threshold energy of photoionization in solute (AN: closed circle) and in solvent (TMP: open circle).

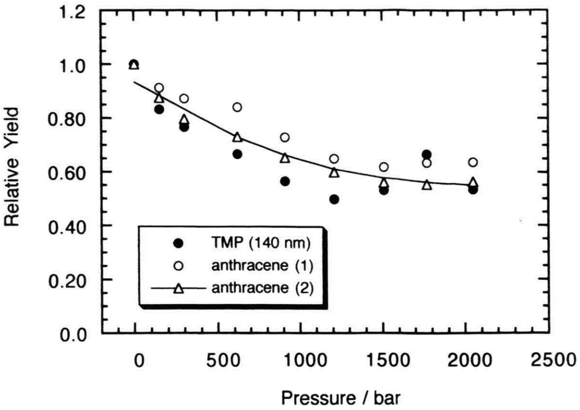

Fig. 6. Relative photocurrent at the 1st and 2nd shoulders and at 140 nm as a function of pressure.

and that the radii of the cations (R_+ of (2)) are very similar. The effect of pressure on I_{liq} is determined by the variation of V_0 and P_+. The V_0-value of TMP increases with pressure [16]. The absolute value of the polarization energy, $|P_+|$, increases with pressure due to the increase of the dielectric constant. The shift of I_{liq} with pressure is given by $P_+ + V_0$. If we assume that the radius R_+ of the cation does not change with pressure, the increase of I_{liq} with pressure is caused by the stronger variation of V_0 with pressure compared to that of P_+.

In a previous study of single photon ionization of anthracene [5] it was found that in neopentane (electron mobility μ_{el} 70 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) the photoconductivity spectrum of AN exhibited a structure with pronounced shoulders around 190 nm and 195 nm. The same shoulders are observed in the spectrum of AN/2,2,4,4 TMP. At room temperature, the electron mobility in 2,2,4,4-TMP is 29 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Figure 6 shows the photoionization yield of AN at the first shoulder (at 197 nm), at the second shoulder (at 193 nm) and of the solvent itself (at 140 nm) as a function of pressure normalized to its value at 1 bar. In all cases the relative photoionization yield decreases with increasing pressure.

The interpretation of the photoconductivity spectrum (see Fig. 4) between 175 nm and 185 nm is complicated by the fact that by the application of the high pressure a blue shift of the absorption edge of the solvent (TMP) occurs. At 1 bar, the light is absorbed completely in a thin liquid layer behind the entrance window for wave lengths smaller 175 nm. At 2 kbar, complete absorption by the solvent sets in below 170 nm, allowing additional photoionization of the anthracene as compared to the low pressure.

In liquid hydrocarbons, the apparent charge carrier quantum yield is much smaller than 1 [1]. Most of the photoelectrons lose their excess energy in the vicinity of their positive parent ion and recombine (geminate recombination). Increase of the pressure increases the liquid density and consequently the number of molecules with which the photoelectron interacts. The mean separation distance is thus reduced. Support for this idea comes from measurements of the free ion yield induced by γ-radiation in *n*-hexane as a function of pressure up to 3 kbar [19]. The free ion yield decreased with increasing pressure. Holroyd inferred that the initial separation of the geminate electron/cation pairs becomes shorter due to more efficient inelastic collisions induced by the increasing density.

For many different γ-irradiated non-polar liquids a correlation was found between the free ion-yield, G_{fi}, and the electron mobility μ_{el} [20]. G_{fi} increases with μ_{el} roughly as

$$G_{\text{fi}} = 0.21(\mu_{\text{el}})^{0.31}. \tag{4}$$

A similar dependence on μ_{el} would be expected also for the apparent photoionization quantum yield Φ. Indeed, it was found by Sethi *et al.* that the photoionization yield of TMPD (N,N,N',N'-tetramethyl-p-phenylenediamine) in various hydrocarbons increased with electron mobility [9]. The present measurements indicate that Φ(AN) decreases with increasing pressure. The electron mobility in TMP,

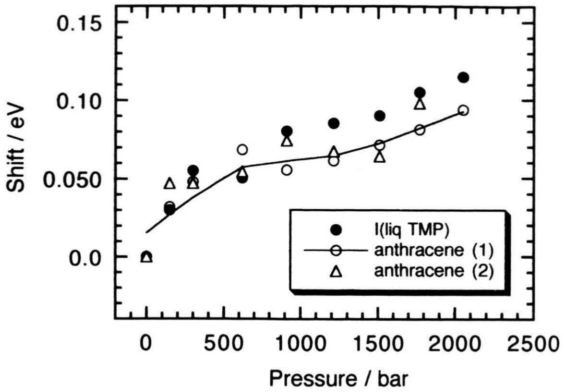

Fig. 7. The shift of the position of the 1st and 2nd shoulders with respect to their positions at 1 bar as a function of pressure. The threshold energy of photoionization of anthracene I_{AN}(liq) is also shown.

however, increases with pressure [16]. We are led to conclude that the effect of high pressure on the transport of superthermal electrons (which determine Φ) is different from that on thermal electrons. A similar conclusion was reached by R. A. Holroyd, P. Chen et al. [21] , who found that the radiation induced ion yield in various liquids decreased with increasing pressure.

Figure 7 shows the energy-shift of the position of the shoulders in the photoconductivity spectrum of the anthracene with respect to that at 1 bar. The tendency of variation is almost the same as for the threshold energy of photoionization. This leads us to speculate that the process of photoionization of anthracene proceeds via an excited state, AN**, as

$$AN \underset{h\nu}{\rightarrow} AN^{**} \rightarrow AN^{+} + e^{-}. \qquad (5)$$

This excited state, obviously, has partial ionic character since it responds to the pressure in the same way as the photoionization threshold, for which a direct process is assumed. In the case of anthracene, the nature of the excited state has been discussed by several authors. Holroyd et al. explained it as Rydberg state [5], while Tweeten and Lipsky interpreted the shoulders as being due to the vibrational structure of the cation [22].

In our previous study of TMPD in neohexane [15], two pronounced peaks were observed. These peaks did not shift under pressure, so that we concluded that the precursor state of the photoionization of TMPD is a neutral.

The foregoing discussion of the conductivity data is based on the assumption of photoionization of the anthracene molecule. In principle, photoinduced ion pair formation could also lead to an increase of conductivity. In the gas phase, photo-induced ion pair formation has been observed, especially with molecules containing strongly electronegative groups. Compared to direct photoionization, this process exhibits much lower cross sections [23]. Anthracene has a small electron affinity, only. Furthermore, electron mobility measurements in various hydrocarbons were made on electrons liberated by light from anthracene dissolved in the hydrocarbon [24]. Consequently, the process of ion pair formation in the photoconductivity of AN/TMP can be excluded.

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[1] E. H. Böttcher and W. F. Schmidt, J. Chem. Phys. **80,** 1353 (1984).
[2] K. Buschick and W. F. Schmidt, IEEE Trans. Electr. Insul. **24,** 353 (1989).
[3] J. Casanovas, R. Grob, J. P. Guelfucci, and R. Laou Sio Hoi, Radiat. Phys. Chem. **23,** 117 (1984).
[4] J. Casanovas, J. P. Guelfucci, and M. Terrisol, Radiat. Phys. Chem. **32,** 361 (1988).
[5] R. A. Holroyd, J. M. Preses, E. H. Böttcher, and W. F. Schmidt, J. Phys. Chem. **88,** 744 (1984).
[6] R. Katoh, K. Lacmann, and W. F. Schmidt, Z. Naturforsch. **49a,** 793 (1994).
[7] K. Lee and S. Lipsky, J. Phys. Chem. **86,** 1985 (1982).
[8] L. V. Lukin, A. V. Tolmachev, and B. S. Yakovlev, Khimicheskaya Fizika **4,** 367 (1985).
[9] D. S. Sethi, H. T. Choi, and C. L. Braun, Chem. Phys. Lett. **74,** 223 (1980).
[10] B. S. Yakovlev and L. V. Lukin, "Photoionization in non-polar liquids" in: Photodissociation and Photoionization. P. K. Lawley ed., John Wiley & Sons, New York 1985.
[11] W. J. Nellis, D. C. Hamilton, R. J. Trainor, H. B. Radousky, A. C. Mitchell, and N. C. Holmes, Physica **139&140B,** 565 (1986).
[12] K. J. Dunn and F. P. Bundy, J. Chem. Phys. **67,** 5048 (1977).

[13] D. A. Nelson and A. L. Ruoff, Phys. Rev. Lett. **42,** 383 (1979).
[14] S. T. Weir, A. C. Mitchel, and W. J. Nellis, Phys. Rev. Lett. **76,** 1860 (1996).
[15] R. Katoh, K. Lacmann, and W. F. Schmidt, Chemical Physics **195,** 457 (1995).
[16] R. A. Holroyd, M. Nishikawa, K. Nakagawa, and N. Kato, Phys. Rev. **B45,** 3215 (1992).
[17] M. Born, Z. Physik **1,** 45 (1920).
[18] R. A. Holroyd, J. M. Preses, and N. Zevos, J. Chem. Phys. **79,** 483 (1983).
[19] R. A. Holroyd, "High energy ionization in liquids: The free ion yield" in: Linking the gaseous and condensed phases of matter: The behavior of slow electrons. L. G. Christophorou, E. Illenberger, and W. F. Schmidt ed., Plenum Press, New York 1994.
[20] J. Jay-Gerrin, T. Goulet, and I. Billard, Can. J. Chem. **71,** 287 (1993).
[21] R. A.Holroyd, P. Chen, E. Stradowska, and K. Itoh, Radiat. Phys. Chem. **48,** 635 (1996).
[22] D. W. Tweeten and S. Lipsky, J. Phys. Chem. **93,** 2683 (1989).
[23] U. Rockland, H. Baumgärtel, E. Rühl, O. Lusking, H. S. P. Möller, and H. Willner, Ber. Bunsenges. Phys. Chem. **99**, 969 (1995).
[24] G. Beck and J. K. Thomas, J. Chem. Phys. **57,** 3649 (1972).