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PHOTO CONDUCTIVITY OF LIQUID TETRAMETHYLSILANE

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W. F. Schmidt and W. Döldissen

Hahn-Meitner-Institut für Kernforschung Berlin GmbH,
Bereich Strahlenchemie
D-1000 Berlin 39

U. Hahn and E. E. Koch

Deutsches Elektronen-Synchrotron DESY, Hamburg

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W.F. Schmidt and W. Döldissen

Hahn-Meitner-Institut für Kernforschung Berlin GmbH,

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and

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D-2000 Hamburg 52

Abstract

Intrinsic photo conductivity of liquid tetramethylsilane was observed in the wave length region from 1100 to 1500 Å. The photo ionization threshold E_I has been determined to be E_I = 8.1 eV.

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Very few investigations have been carried out so far on the direct photo ionization of non-polar liquids. Experiments by Vermeil et al.[1] detected an increase of conductivity in some liquid hydrocarbons when subjected to the light of rare gas resonance lamps. Recently similar experiments were performed by Casanovas and co-workers at the University of Toulouse[2,3]. It was estimated that the ionization threshold energy of the molecules in the gas phase is reduced for the different liquids by 0.5 eV to 1 eV upon condensation.

Direct measurements of the ionization threshold energy for liquid xenon were reported by Roberts and Wilson[4], Asaf and Steinberger[5] and Spear and LeComber[6]. While Roberts and Wilson found a strong increase of the photo current with photon energy above 8.9 eV, Asaf and Steinberger determined the threshold energy to 9.2 eV, which agrees with the value reported by Spear and LeComber.

The photo ionization threshold in the liquid phase E_L should be given by

$$E_L = E_G + V_o + P_+ \qquad (1)$$

with E_G, gas phase energy; P_+, polarization energy of the positive ion and V_o, electron affinity of the liquid.

The electron affinity or the energy of the electronic conduction level has been determined for many hydrocarbons and liquefied rare gases by means of the photoelectric effect on a metal electrode[7-9]. The polarization energy of the positive ion can then be obtained if E_L is measured. On the other hand, P_+ can be estimated from Born's equation[10] which yields for an ion of radius r

$$P = -\frac{e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \qquad (2)$$

with ε the relative dielectric constant of the liquid and e the elementary charge.

Here we wish to report the results of photoconductivity experiments in liquid tetramethylsilane ($(CH_3)_4Si$) at 22°C. The liquid was contained in a parallel plate conductivity cell with 2 mm plate separation. One electrode consisted of a thin gold layer (thickness approximately 150 Å) evaporated on to a LiF plate which served as the entrance window for the radiation. The counter electrode was made of gold plated brass, the cell body was of stainless steel. Synchrotron radiation from the storage ring DORIS was monochromatized by a high intensity monochromator[11]. The resolution was adjusted to approximately 0.1 eV. With DORIS operating in the single bunch mode (10 - 20 mA current of circulating electrons) an intensity of about 10^{10} photons/sec was available at the entrance window of the conductivity cell. In the multi bunch mode (200 - 400 mA current) the intensity would be increased at least by a factor of 10. DC-voltages up to 3 kV were applied across the liquid gap and the photocurrents were measured with a Keithley Mod 602 electrometer. At a particular voltage the wavelength of the radiation was scanned from 1100 Å to 1600 Å and the photo current was recorded. Depending on the applied voltage the photo currents exceeded the dark durrents by a factor of up to 4. The dark currents were subtracted from the currents under illumination in order to obtain the photo currents. Figure 1a shows a typical photo conductivity spectrum obtained. Data were recorded for different polarities and voltages. The spectral dependence of the incident intensity, the transmission of the cell window and the gold electrode was determined by observing the luminescence intensity of sodium

salicylate placed behind the gold film (fig.1b). In fig. 1c the corrected photo current as a function of wavelength is shown. The current begins to rise below 1500 Å and a second steep rise is observed below 1150 Å.

Since the intensity of the synchrotron radiation decreased with time photo conductivity spectra taken at different times were normalized according to the magnitude of the electron current in the storage ring.

In order to determine the threshold E_L, the photo conductivity σ in arbitrary units as a function of photon energy was plotted and a power function was fitted to the points. A surprisingly good fit was obtained with

$$\sigma \propto (E - E_L)^{3/2} \qquad (3)$$

and E_L = 8.1 eV (fig. 2). For the gas phase ionization energy Jonas et al.[12] reported E_G = 9.79 eV. V_o was determined by Holroyd et al. and the mean of the values reported by them is V_o = - 0.57 eV[7,8,13]. From eq. 1 P_+ = - 1.12 eV is obtained which yields an ionic radius of r = 2.95 Å comparable to the hard core radius of the molecule.

The second threshold observed in liquid tetramethylsilane at around 10.75 eV may be compared with the rise in the photo electron spectrum from the gas at 12.2 eV. The difference is 1.45 eV as compared to 1.65 eV for the first threshold. This discrepancy may be due to the fact that the second threshold in the liquid could not be determined from the data in the same way as the first threshold. The photo current due to the second ionization process still contains a considerable contribution due to the first ionization, which impedes the exact determination of this threshold.

References

[1] C. Vermeil, M. Matheson, S. Leach and F. Muller
J. Chim. Physique 61, 596 (1964)

[2] G. Brunet, "Etude de Lampes à Résonance de Gaz Rares pour la Photoionisation d' Alcanes Liquides", Thêse, Université Paul Sabatier de Toulouse, 1977

[3] J. Casanovas, R. Grob, G. Brunet, R. Sabattier,, J.P. Guelfucci and D. Blanc, Sixth Symposium on Microdosimetry, May 1978, Brussels Belgium

[4] I. Roberts and E.G. Wilson, J. Phys. C.: Solid State Phys. 6, 2169 (1973)

[5] U. Asaf and I.T. Steinberger, Phys. Rev. B10, 4464 (1974)

[6] W.E. Spear and P.G LeComber, chapter 18 in "Rare Gas Solids" M.L. Klein and J.A. Venables (Editors), Academic Press, London 1977 Vol II, p 1119

[7] R.A. Holroyd and M. Allen, J. Chem. Phys. 54, 5014 (1971)

[8] R.A. Holroyd, S. Tames and A. Kennedy, J. Phys. Chem. 79, 2857 (1975)

[9] W. Tauchert, H. Jungblut and W.F. Schmidt, Can. J. Chem. 55, 1860 (1977)

[10] M. Born, Z. Physik 1, 45 (1920)

[11] U. Hahn, N. Schwentner and G. Zimmerer, Nucl. Instr. Methods 152, 261 (1978)

[12] A.E. Jonas, G.K. Schweitzer, F.A. Grimm, and T.A. Carlson, J. Electron.Spectrosc. 1, 29 (1972/73)

[13] A.O. Allen, "Drift Mobilities and Conduction Band Energies of Excess Electrons in Dielectric Liquids", NSRDS-NBS58 (1976)

Figure Legends

Fig.1 a) Observed photo current as a function of wave length for liquid Tetramethylsilane; applied voltage - 1300 V, i_D = 5.5 pA, maximum photo current i_{max} = 19.5 pA.

b) Efficiency of the monochromator and transmission of LiF-window and gold layer measured as the photo current of a photomultiplier produced by the luminescence of sodium salicylate.

c) Photo current per incident photon, corrected data of fig. 1a (see text).

Fig.2 Computer averaged dependence of photo conductivity on photon energy for liquid Tetramethylsilane (this plot contains 11 photo conductivitiy spectra for different voltages and intensities); The points have been calculated according to eq.3. In the insert a schematic energy level diagramm for gaseous and liquid Tetramethylsilane is shown.

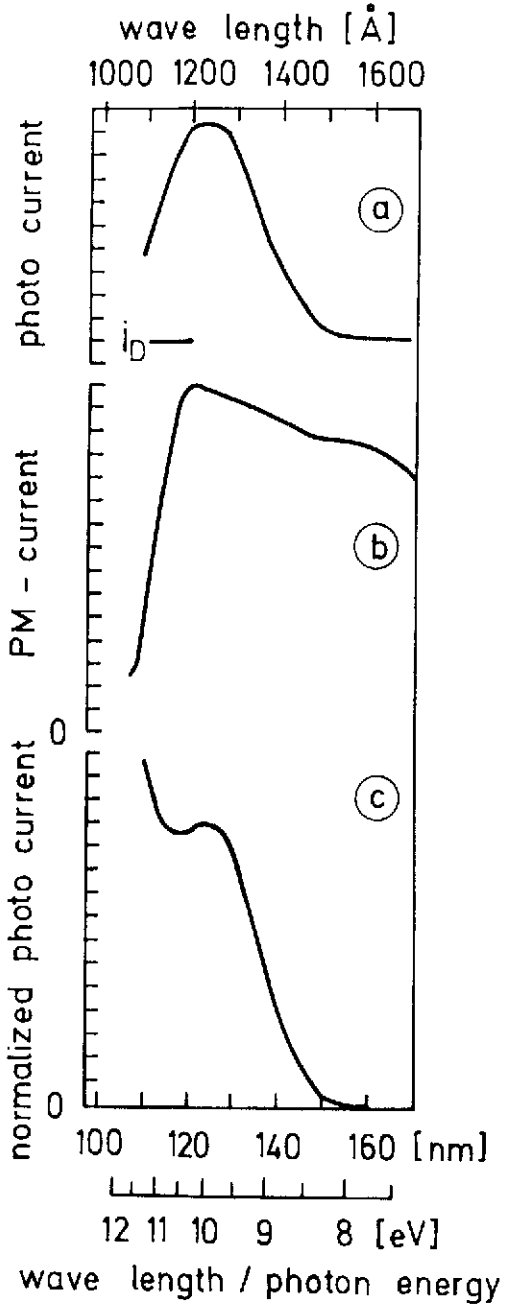
wave length [Å]
1000 1200 1400 1600
photo current
a
i_D
PM - current
b
0
normalized photo current
c
0
100 120 140 160 [nm]
12 11 10 9 8 [eV]
wave length / photon energy

Fig. 1

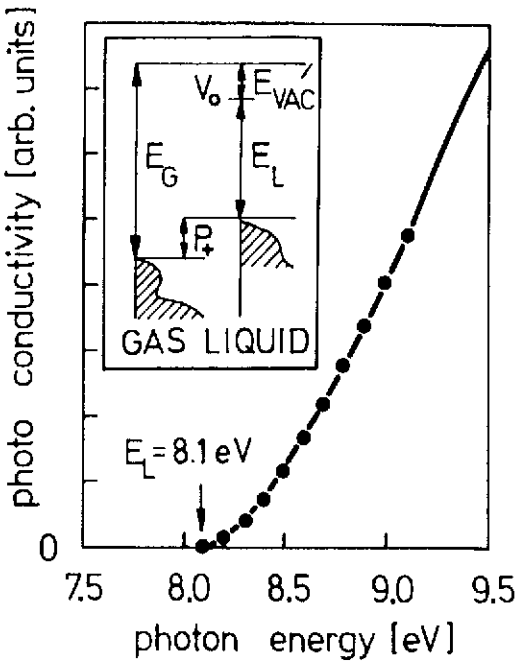
photo conductivity [arb. units]
V_o
E_{VAC}
E_G
E_L
P
GAS LIQUID
E_L=8.1 eV
0
7.5 8.0 8.5 9.0 9.5
photon energy [eV]

Fig. 2