Energy of the Quasi-free Electron State in Liquid Argon, Krypton, and Xenon

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The energy of the conduction state in liquid argon, krypton, and xenon was measured by means of the photo-effect. The data are used to calculate the scattering lengths. The relation between scattering length and electron mobility is discussed.

The energy V_0 of the conduction state of quasi-free electrons in liquefied rare gases has attracted considerable interest during the last decade since it is of great importance for the theory of electron transport in these liquids [1–5]. It was demonstrated that the energy is determined by a delicate balance between a short range repulsive force and a long range screened polarization force.

Although many calculations on V_0 and its relation to the scattering length have been published, the experimental values of V_0 are rather few yet. A direct determination of V_0 can be made by measuring the work function of a metal in a vacuum Φ_{vac} and in the pertinent liquid Φ_{liq}. V_0 is then obtained by

$$V_0 = \Phi_{\text{liq}} - \Phi_{\text{vac}}. \qquad (1)$$

So far only one experiment has been reported in which V_0 was determined in liquid argon [6]. Several measurements were published for liquid helium [7, 8]. V_0-values for liquid Ne, Kr, and Xe were estimated from spectroscopic data involving Wannier impurity states [9–12]. Critical inspection of the published data on argon [6] revealed that V_0 could not have been determined with great precision since the photo response in the liquid showed a knick and no evaluation with the Fowler theory [13] was performed.

Here we report direct measurements of V_0 in liquid Ar, Kr, and Xe and its dependence on temperature in the liquid region up to 1 atmosphere.

The measurements were carried out with an experimental set-up similar to that described by Holroyd and Allen [14]. The gases were obtained from Messer-Griesheim GmbH with a stated purity of 99.99 vol.%. They were passed through columns of activated charcoal and molecular sieve (3 Å), maintained at dry ice temperature and then condensed into the photoelectric cell which had been evacuated to a pressure $<10^{-5}$ torr and which was kept at the proper temperature in a cryostate from Leybold. Details of the experiments are reported in Reference [15].

The photo response as a function of the frequency of the incident light was measured in the liquid and in the vacuum before and after the liquid filling. Figure 1 shows the normalized current of a zinc electrode as a function of $h\nu/k_B T$ for the three liquids and vacuum. In Table 1 the results are compiled and the scattering lengths $\tilde{a}$ as obtained with the Springett-Jortner-Cohen-theory [1] are given. The scattering lengths are positive in contrast to the negative values observed in the gas phase [16]. In scattering theories usually negative values correspond to quasi-free states while a positive scattering length is characteristic for a bound state.

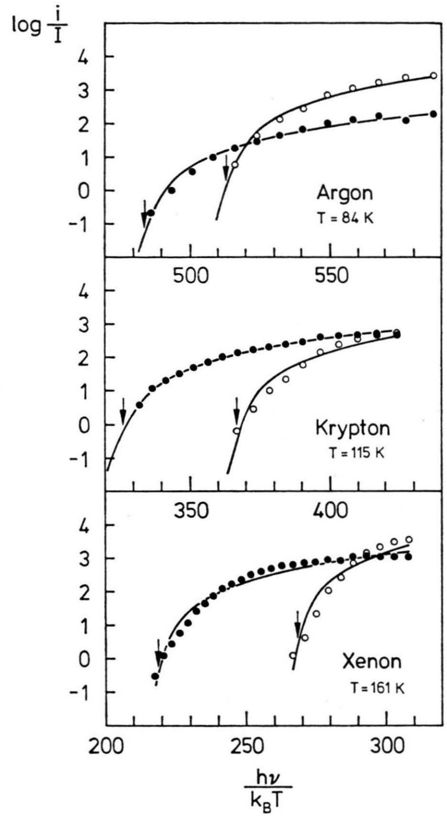

Fig. 1. Fowler plots of photo currents in liquid argon, krypton, and xenon (the arrows denote the work function), ○ vacuum, ● liquid; i photo current, I relative measure of the light intensity.

The electron mobilities measured in liquid argon, krypton, and xenon are, however, large [17] indicating that the quasi-free electron state is stable in these liquids. The scattering length $\tilde{a}$ is connected with the mean free path for energy loss Λ_0 in the Lekner theory of the electron mobility [3] by

$$\Lambda_0^{-1} = 4\pi\tilde{a}\,n \qquad (2)$$

with n the number density of atoms. Λ_0-values thus obtained are also given in Table 1.

Table 1. Energy of the Quasi-free Electron State.

Liquid	T [K]	V_0 [eV]	$\tilde{a}$ [Å]	Λ_0 [Å]	χ [dyne^{-1} cm^2]	$S^*(0)$	Λ_0/Λ_1
Ar	84	-0.20 ± 0.02	0.92	4.4	1.92×10^{-10}	0.048	0.029
	87.5	-0.21 ± 0.02	0.92	4.4			
Kr	115	-0.40 ± 0.05	1.07	4.0	1.53×10^{-10}	0.043	0.0049
	123	-0.45 ± 0.05	1.06	4.1			
Xe	161	-0.67 ± 0.05	1.26	3.6	1.1×10^{-10}	0.034	0.0036
	165	-0.61 ± 0.05	1.26	3.6			

The electron mobility is given by

$$\mu_{el} = \frac{2}{3} \left(\frac{2}{\pi m k_B T} \right)^{1/2} e \Lambda_1 \tag{3}$$

where Λ_1 is the mean free path for momentum transfer, m the electron mass, k_B the Boltzmann constant, e the electronic charge and T the absolute temperature. While Λ_0 is independent of the liquid structure Λ_1 does depend on the structure of the liquid by the structure factor $S(k)$.

In the limit of low electron energies Λ_1 and Λ_0 are connected via

$$\Lambda_0/\Lambda_1 = S(0) . \tag{4}$$

It has been suggested that $S(0)$ is given by the isothermal compressibility χ_{th} of the liquid as

$$S^*(0) = n k_B T \chi_{th} . \tag{5}$$

The values for Λ_1 obtained from the measured mobilities [17] and the ratio Λ_0/Λ_1 are compared with the $S(0)$ values of Equation (5). The compressibilities were calculated in the hard sphere approximation as published by Yosim [18]. The deviations between $S(0)$ and $S^*(0)$ are quite large for liquid krypton and xenon. Jahnke, Holzwarth, and Rice [19] pointed out already that the Lekner theory [3,4] inadequately describes the observations in liquid argon. The present data confirm the necessity of a fresh analysis of the problem.

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