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 photoeffect. 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

$$V_0 = \Phi_{\text{liq}} - \Phi_{\text{vac}}. \tag{1}$$

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.

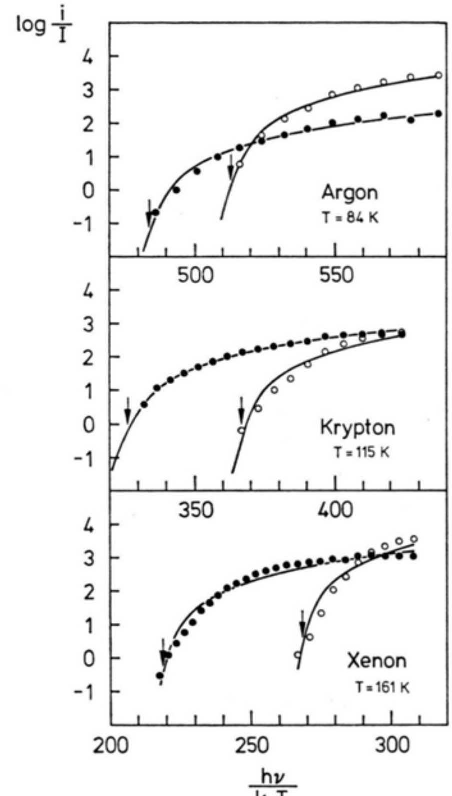

Fig. 1. Fowler plots of photo currents in liquid argon, krypton, and xenon (the arrows denote the work function), ○ vacuum, ● liquid; i photo current, I relative measure of the light intensity.

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

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

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

$$\mu_{\text{el}} = \tfrac{2}{3} \left(\frac{2}{\pi\, m\, k_{\text{B}}\, T} \right)^{1/2} e\, \Lambda_1 \qquad (3)$$

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

$$\Lambda_0/\Lambda_1 = S(0)\ . \qquad (4)$$

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

$$S^*(0) = n\, k_{\text{B}}\, T\, \chi_{\text{th}}\ . \qquad (5)$$

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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