Energy of the Excess Electron State in Liquid Methane

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The energy of the electron conduction state in liquiud methane ($T = 95$ °K) was measured to be $V_0 = 0.0$ eV.

The physical properties of excess electrons in liquid hydrocarbons have been studied rather extensively during recent years. Measurements of the drift mobility have been performed [1–7] and the energy of the conducting statte has been determined [8–10]. The drift mobility was found to depend strongly on the molecular structure of the hydrocarbon, the values ranging from 0.1 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ for n-hexane to 70 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ for neopentane at room temperature or even 400 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ for liquid methane at $T = 111$ °K. The energy of the conducting state V_0 exhibited a similar dependence on molecular structure and varied from $V_0 \approx 0$ eV in n-hexane to $V_0 = -0.45$ eV in neopentane.

Positive V_0 values mean that energy is necessary to bring an electron from the vacuum into the liquid, negative V_0 values correspond to energy being released during this process. The correlation between drift mobilities and V_0-values was rationalized by Fueki [11], who calculated the drift mobility in liquid methane by use of the Cohen-Lehner theory [12, 13] and estimated a V_0 value of $V_0 = -0.74$ eV by applying the Wigner-Seitz model [14].

Quite recently, however, Noda and Kevan [15] measured $V_0 \approx 0$ eV for liquid methane at $T = 111$ °K. Since we had already built up the experimental apparatus for V_0 measurements we repeated their measurement. The principle of the V_0 measurement consists in measuring the work function of a metal electrode in vacuum Φ_{V} and in the liquid Φ_{L}. V_0 is then given by

$$V_0 = \Phi_{\text{L}} - \Phi_{\text{V}} .$$

The experimental set-up was similar to that of Holdoyd [8]. We used a plane zink cathode and a wire mesh anode with an electrode distance of $d = 2$ mm. Monochromatic light was obtained from a high pressure xenon lamp in connection with a Bausch and Lomb high intensity monochromator and proper filters. The light intensity was monitored with a photomultiplier (current I). The photocell in a cuvette with quartz window was placed in a cryostat with suprasil windows (Leybold). The temperature was determined with a thermistor. Liquid methane was purified as described previously [5] and condensed into the cell. The experiment consisted in measuring the photo current i in the cell and the light intensity I as a function of the wave length of the light. The dependence of the photocurrent i on the frequency ν of the incident light is given by the Fowler equation. The experimental values of i/I and ν were fitted to this equation by means of a least squares computer program and values of Φ_{L} and Φ_{V} were obtained. The vacuum work functions before and after filling the cell with methane were identical $\Phi_{\text{V}}(\text{Zn}) = 3.55$ eV and the work function in liquid methane was obtained to $\Phi_{\text{L}}(\text{Zn}) = 3.52$ eV from which

$$V_0 = -0.03 \text{ eV} \approx 0.0 \text{ eV}$$

is obtained in agreement with Noda and Kevan.

Although this lack of correlation between mobility and V_0 seems to be surprising we have to point out that only in liquid methane the drift mobility can be taken as the mobility in the conduction state. In all other hydrocarbons the drift mobility is thermally activated indicating the influence of trapping effects, and although attempts have been made to calculate the mobility in the conduction state, no consistent results have been obtained [7, 16, 17].

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