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Photocurrent thresholds and angular momenta for electrons solvated in some glassy solids

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Solvated electrons can be produced in glassy insulators by ionizing radiation. If after irradiation, these glasses are illuminated in the visible and near infrared, weak photocurrents can be detected.

Photocurrent spectra have been recorded in a number of glassy amines, alcohols, and aqueous solid solutions.¹⁻⁸ Kato *et al.* have fitted the photocurrents observed near threshold in some amines and alcohols to the empirical equation $(I/E)^{2/(2l+1)} = B(E - E_0)$, where B is a constant, E is the photon energy, and E_0 is the photocurrent threshold energy.¹

In support of this concept, we have shown theoretically that the photocurrent measured just above threshold must obey the general equation

$$(I/E)^{2/(2l+1)} = B(E - E_0), \quad (1)$$

where E_0 is the binding energy of the solvated electron, and l is an integer.⁹ In Table I, we give the selection rules connecting the index l with the solvated electron's orbital angular momentum quantum number l' and azimuthal quantum number m' . The selection rules allow or forbid only certain substates m' of l' . The affected values of m' are shown in parentheses next to the values of l' . For $l' = 0$ and $l' = 1$, the rules encompass all substates. However, for $l' \geq 2$, substates $-l' \leq m' \leq -2$ and $2 \leq m' \leq l'$ play no role in the photoconductivity and are neither forbidden nor allowed.⁹

In this note, we report the numerical reduction of some photocurrent spectra²⁻⁸ using Eq. (1). Choosing a value for l by trial and error, we have fitted Eq. (1) to the threshold region of these spectra using linear regression with B and E_0 treated as parameters. In no case did we find a satisfactory fit with $l = 0$. For $l > 0$, however, good fits could always be obtained, but in the case of many of the glasses, it was difficult to choose between $l = 1$ and $l = 2$. Consequently, we have followed Kato *et al.* and have set $l = 1$ for every glass considered. The binding energies E_0 derived thereby are summarized in Table II. The correlation coefficient is given by C while the absolute temperature of the glass is T . For the sake of completeness, we have also included in the table the results of Kato *et al.*

In the case of aqueous 5 M K_2CO_3 , evidence for a solvat-

ed electron excited state was reported.⁴ Assuming $l = 1$, we have analyzed the photocurrent assigned to this state and have found a threshold of 1.38 eV. This state lies 0.48 eV above the ground state whose binding energy we find to be 1.86 eV.

According to Table I, our conclusion that the best fit to the data occurs for $l = 1$ implies that the solvated electron energy eigenstate in all the glasses must contain s character or d character or a mixture of both. The presence of p character is forbidden. The existence of d character does not seem very likely however, when we consider that the geometric shape of the solvated electron orbital is dictated by the molecular symmetry of the binding site. Pure s character would be consistent not only with our results but also with the average isotropy of all glasses. Other theoretical studies^{10,11} have also suggested that the ground state might be a pure s state.

On the other hand, the binding energy E_0 should vary with the polarity of the glass. In Table II, the glasses are listed from the top of the page to the bottom in order of decreasing polarity based upon the dipole moment of the molecule or the dielectric constant of the liquid.^{12,13} For some substances, polarity data was missing, in which case the position of the glass in the table was estimated. In general, the table shows that the binding energy decreases with decreasing polarity. Out of place in this sequence is 10 M LiCl in D_2O at 4.2 K. At this low temperature, however, the molecular rotation is thought to be so slight that the D_2O molecules do not orient to accommodate the presence of the electron. As a consequence, the binding energy remains artificially small.³

TABLE II. Photocurrent thresholds and correlation coefficients for the electron solvated in various glasses

Glass	E_0 (eV)	C	T (K)	Ref.
5% H_2O in methanol	2.0		77	1
5 M K_2CO_3 in H_2O				
(ground state)	1.86	0.999	77	4
(excited state)	1.38	0.997	77	4
10 M LiCl in H_2O	1.37	0.999	85	2
10 M LiCl in D_2O	0.54	0.985	4.2	3
<i>d</i> -glucose	1.67	0.975	77	4
ethanol	1.6		77	1
1-propanol	1.6		77	1
1-butanol	1.6		77	1
2-propanol	1.2		77	1
methyltetrahydrofuran	1.25	0.991	77	6
<i>s</i> -butylamine	1.02	0.996	77	5
1,2-propanediamine	0.91		77	1
triethylamine	0.68	0.977	77	5
di-isopropylamine	0.62		77	1
3-methylhexane	0.93	0.985	77	8
3-methylpentane	0.23	0.996	77	7

TABLE I. Angular momentum selection rules.

l	Allowed states $l'(m')$	Forbidden states $l'(m')$
0	1(0, ± 1)	none
1	0(0), 2(0, ± 1)	1(0, ± 1)
2	3(0, ± 1)	0(0), 1(0, ± 1), 2(0, ± 1)
\vdots	\vdots	\vdots
l	$l + 1(0, \pm 1)$	0(0), 1(0, ± 1), ..., $l - 1(0, \pm 1)$

Also out of place in the order of polarity is the E_0 value for 3-methylhexane glass. This may be due to the fact that, because the photocurrent data in the threshold region was sparse, E_0 was not determined very accurately. In fact, of the data we have analyzed, only that of Kato *et al.*¹ was taken with the determination of the threshold in mind. Consequently, more extensive experimental study of the threshold region is recommended.

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The function $E(N, Z)$ in the Thomas–Fermi approximation as the solution of March equation

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The dependence of the binding energy of atoms and atomic ions on the atomic number Z and the number of electrons N shows substantial regularities, which enables investigation of the binding energy E as a continuous, smooth function of N and Z .^{1–10} The relation of the atomic energy on the number of particles N is particularly important in relation to the definition of the chemical potential of atoms^{11,12} introduced on the ground of density functional theory.^{12,13} Within the framework of Thomas–Fermi method, the following relation between the partial derivatives of the chemical potential μ of an atom has been derived by March:¹⁴

$$N \frac{\partial \mu}{\partial N} + Z \frac{\partial \mu}{\partial Z} = p\mu. \quad (1)$$

Theoretical value of p is $4/3$, but the numerical tests shows dependence of this value on the atom and the method of calculation of μ .¹⁵ There are arguments indicating, that the same relation is valid as an approximation for the Hartree–Fock atom.^{15,16}

It will be shown that Eq. (1) leads to the particular form of function $E(N, Z)$. Treating Z and N as the arguments of function $\mu(N, Z)$ as well as $E(N, Z)$ and introducing into Eq. (1) the definition of μ , we obtain Eq. (2) equivalent to Eq. (1).

$$N \frac{\partial^2 E}{\partial N^2} + Z \frac{\partial^2 E}{\partial N \partial Z} - p \frac{\partial E}{\partial N} = 0. \quad (2)$$

This is the second-order partial differential equation of the hyperbolic type. It is expected that the solution of Eq. (2) gives the function $E(N, Z)$. The transformation of the “natural” coordinates Z, N into the new set of coordinates: $\xi = Z$ and $\eta = \ln(Z/N)$ ($\eta > 0$), brings Eq. (2) into canonical form:

$$\xi \frac{\partial^2 E}{\partial \eta \partial \xi} = (p+1) \frac{\partial E}{\partial \eta}. \quad (3)$$

The solution of this equation may be searched as the product

of two functions, each of them dependent on one coordinate only; then:

$$E(\eta, \xi) = F(\eta) \cdot G(\xi).$$

After substitution into Eq. (3) the equation is obtained:

$$\xi \frac{\partial G}{\partial \xi} = (p+1)G, \quad (4)$$

which depends on ξ only. The solution of Eq. (4) is $G = a_1 \xi^{p+1}$. The shape of Eq. (4) indicates that Eq. (3) is satisfied for any function $F(\eta)$. Particular form of this function depends on the choice of boundary (initial) conditions. For the sake of simplicity the assumption may be made: $E(\xi, 0) = 0$ and thus $\partial E(\xi, 0)/\partial \eta = 0$. The simplest condition relating derivatives of energy, which may be expected to be valid in the hypothetical limit $Z \rightarrow 0$, and, as an approximation, for hydrogen^{16,17} is $\partial E(N, Z)/\partial Z = \partial E(N, Z)/\partial N$. This leads to the Cauchy-type boundary condition:

$$(e^\eta - 1) \frac{\partial E}{\partial \eta} = \xi \frac{\partial E}{\partial \xi}. \quad (5)$$

Substituting solution of Eq. (4) into Eq. (5) the auxiliary equation for $F(\eta)$ is obtained.

$$(p+1)F = (e^\eta - 1) \frac{\partial F}{\partial \eta}. \quad (6)$$

Integration of Eq. (6) gives $F(\eta) = a_2(1 - e^{-\eta})^{p+1}$. Finally,

$$E(\eta, \xi) = a[\xi(1 - e^{-\eta})]^{p+1}, \quad (7)$$

where $a = a_1 a_2$ is a constant which depends on limiting properties of $E(\eta, \xi)$. In the natural coordinates Z, N Eq. (7) assumes the simple shape

$$E(Z, N) = a(Z - N)^{p+1}. \quad (8)$$

According to the chosen boundary conditions, the relation of atomic energy on the atomic number is: $E(\xi, \infty)$