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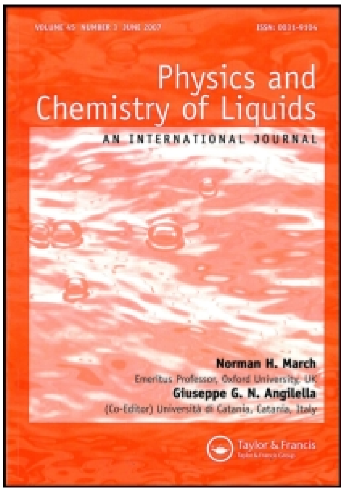

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Proposed Universal form for Position in Energy of Maximum of the Optical Absorption of Solvated Electrons in a Variety of Dipolar Solvents

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PROPOSED UNIVERSAL FORM FOR POSITION IN ENERGY OF MAXIMUM OF THE OPTICAL ABSORPTION OF SOLVATED ELECTRONS IN A VARIETY OF DIPOLAR SOLVENTS

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A universal form is proposed for the position in energy of the maximum $E_{A\mathrm{max}}$ of the optical absorption of solvated electrons in a wide range of dipolar solvents. Following earlier work of one of us (GRF), the independent variable F in $E_{A\mathrm{max}}(F)$ depends solely on solvent properties and involves the product of two dimensionless factors $\{(k_B T/\mu^2)(\frac{\varepsilon\Omega}{6\pi} - \alpha_\infty)\}^{3/2}$and $(\varepsilon n_e \alpha_p)^{1/2}$. Here μ is the molecular dipole moment, Ω is the average volume occupied by a molecule at temperature T, and α_∞ and α_P are the optical polarizabilities of the molecule and the polar end group, respectively. Finally, ε is the dielectric constant, while n_e is the total number of electrons per unit volume.

It is also shown from existing experimental data that there is a correlation between $E_{A\mathrm{max}}$ and the width of the optical absorption spectrum, which depends on compound type.

Keywords: Optical spectra; solvated electrons; liquid structure

INTRODUCTION

There has been a great deal of interest in experiment and theory characterizing the nature of the solvated electron in simple solvents like H_2O, NH_3, alcohols and amines. The model that has emerged from a combination of experiment and simulation studies is that of a cavity in the fluid structure, tenanted by the excess electron, and in which this is surrounded by favourably oriented molecules of the

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solvent (see, for example, Schnitker and Rossky [1] and numerous earlier references cited there).

The aim of this Letter is to propose a universal form for the position in energy, say $E_{A\max}$, of the optical absorption spectrum of the solvated electron in a wide variety of dipolar solvents. Table I collects (a) the energy $E_{A\max}$ corresponding to the maximum in the absorption $A(E)$ as a function of energy $E=\hbar\omega$, (b) the band width $W_r (r \equiv \text{red})$ on the low energy side of $E_{A\max}$ and (c) the ratio $E_{A\max}/W_r$.

From Table I, it is evident that $E_{A\max}$ is correlated with W_r, the ratio $E_{A\max}/W_r$ being 5 for water and ammonia, 4 for alcohols and amines, and 2 for ethers.

One of us (Freeman [2]) has shown in earlier work that $E_{A\max}$ correlates also with a factor involving the Kirkwood structural parameter g_k [3]. This is defined through the equation

$$\left(\frac{2\varepsilon}{9}\right)\Omega = \frac{4\pi}{3}\left[\alpha_\infty + \frac{g_k\mu^2}{3k_BT}\right] \tag{1}$$

where Ω denotes the average volume per molecule of liquid at temperature T, ε is the static dielectric constant of the liquid at T, μ is the molecular dipole moment, and α_∞ is the molecular optical

TABLE I Properties of Liquids and Solvated Electrons

Liquid	$T(K)$	ε	$E_{A\max}$(eV)	W_r(eV)	$\frac{E_{A\max}}{W_r}$	*Ref.*
H_2O	298	78	1.725	0.355	4.9	5
D_2O	298	78	1.755	0.349	5.0	5
NH_3	200	25	0.904	0.170	5.3	6
ND_3	200	25	0.945	0.170	5.6	6
CH_3OH	299	33	1.95	0.47	4.1	7
C_2H_5OH	299	24	1.79	0.46	3.9	7
1-C_3H_7OH	299	20	1.93	0.56	3.4	7
2-C_3H_7OH	299	18	1.52	0.40	3.8	7
1-C_4H_9OH	299	17	1.94	0.53	3.7	7
i-C_4H_9OH	298	18	1.97	0.57	3.5	8
2-C_4H_9OH	298	15	1.59	0.47	3.4	8
t-C_4H_9OH	299	11	0.97	0.315	3.1	9
1-$C_8H_{17}OH$	299	10	1.98	0.55	3.6	7
1-$C_3H_7NH_2$	200		1.03	0.28	3.7	10
$(C_2H_5)_2O$	143		0.73	0.32	2.3	11
THF, C_4H_8O	174		0.78	0.32	2.4	11
$(1\text{-}C_3H_7)_2O$	123		0.75	0.32	2.3	11

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polarizability. In writing eqn. (1), it has been assumed that one can neglect unity with respect to ε.

Then, the independent variable used in Figure 1B of Freeman [2] is replaced by the variable F defined precisely by

$$F = (\varepsilon n_e \alpha_p)^{1/2} \left\{ \frac{k_B T}{\mu^2} \left(\frac{\varepsilon \Omega}{6\pi} - \alpha_\infty \right) \right\}^{3/2} \tag{2}$$

Here, in contrast to polarizability α_∞ defined above, α_p denotes polarizability of the polar end group in the solvent molecules, while n_e is the number of molecular electrons per unit volume.

We have redrawn Figure 1B of Freeman [2] in terms of the above dimensionless variable. At small F, $E_{A\max}$ is found to have the form, in eV,

$$E_{A\max} = 0.4 + 0.33\,F \tag{3}$$

However, the curve of $E_{A\max}$ rapidly falls below the small F limit of eqn. (3) and more parabolic behaviour is in evidence. Though we have not attempted a detailed fit, a possible form giving the correct small and large F behaviours is

$$E_{A\max} = \frac{a + bF + cF^2}{d + fF + hF^2}. \tag{4}$$

Of the six parameters entering eqn. (4), Freeman [2] noted in earlier work that for sufficiently large F the limiting value of $E_{A\max}$ was $\sim$2.5 eV, which then requires that c/h $\approx$ 2.5 eV.

To regain eqn. (3), we note the small F expansion of eqn. (4) as

$$E_{A\max} = \frac{a}{d} + \left(\frac{b}{d} - \frac{af}{d^2} \right) F \tag{5}$$

yielding the further relations $(a/d) = 0.4$ eV and $(\frac{b}{d} - \frac{af}{d^2}) = 0.33$ eV to accord with eqn. (3). This leaves 3 free parameters in the form (4), but because of its presently abitrary nature, beyond reproducing the small F form (3), we shall not go into further details.

However, we think it may be highly relevant that in the quantum simulation studies of the hydrated electron [1] referred to above,

$E_{A\max}$ was found to be 2.7 eV. While the model used has, of course, considerable merit, it is tempting to conclude that the value of F yielded by such a model is considerably greater than the empirical value of F for water at the appropriate thermodynamic state. Put another way, the model used in ref [1] may well be a first-principle calculation of the limit of $E_{A\max}$ for large F in the above formulation.

In summary, a firm conclusion from the above, building on the earlier work of Freeman, is that $E_{A\max}$ has a universal form in terms of the independent variable F defined in eqn. (2). The quantities entering F are observables for the pure solvent, on which F entirely depends, except for the polarizability α_p which can be estimated with sufficient accuracy [4]. As to future work, it is obviously important for the model of ref [1] to be used in condition where it predicts realistic values of ε, n_e and viscosity from its starting assumptions. More investigations using quantum computer simulation, provided they address basic solvent properties quantitatively, should prove of great value in estabilishing the universal curve of $E_{A\max}$ *vs* F in eqn. (2).

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