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A Molecular Orbital Study of a Dimer Model for the Hydrated and the Ammoniated Electron

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Some dimer models are proposed for the hydrated and ammoniated electron. These combine features of both the cavity and polaron formulations. By way of an extended Hückel calculation the size of the cavities in water and ammonia is ascertained. A population analysis shows that whereas in water the charge spreads out almost uniformly over the system, in ammonia the electron remains within the cavity.

Einige dimere Modelle, die Züge der Loch- und Polaronenvorstellungen vereinigen, werden für das hydratisierte und ammonisierte Elektron vorgeschlagen. Mit Hilfe der erweiterten Hückel-Theorie wird die Größe der Löcher in Wasser und Ammoniak bestimmt. Dabei zeigt sich, daß die Ladung im Wasser fast gleichmäßig über das System verteilt ist, während im Ammoniak das Elektron innerhalb des Loches bleibt.

On propose des modèles de dimères pour l'électron hydraté et ammoniaqué. Ces modèles combinent les caractéristiques des formulations de cavité et de polaron. A l'aide d'un calcul Hückel étendu, on fixe la taille des cavités dans l'eau et l'ammoniaque. L'analyse de population montre que dans l'ammoniaque l'électron reste dans la cavité, tandis que dans l'eau la charge s'étend presque uniformément sur le système.

Introduction

From studies of reactions involving radiolysed water it gradually emerged that there was a reducing species present of fascinating simplicity. A single electron in a solvent sheath. By recording its transient absorption spectrum, Boag and Hart placed the hydrated electron amongst the most exciting chemical discoveries of recent times [1].

A wealth of experimental data surrounds another elusive entity, the ammoniated electron [2]. The efficacy of sodium in ammonia, as the agent in the Birsch reduction, is well known. One may also recall that when an alkali metal is added to liquid ammonia an expansion in volume occurs. This has been attributed to the formation of cavities within the solvent. It has become natural therefore to envisage the ammoniated electron as a negatively charged particle trapped in a solvent hole.

Theoretical treatments based upon a cavity model reproduce certain properties of metal ammonia solutions to a notable degree. In contrast, such success has not been forthcoming for the hydrated electron. It may be as Weiss amongst others has suggested, that the hydrated electron should be thought of rather as a polaron; the electron trapped in the medium by a process of self polarisation, belonging collectively to a number of water molecules [3].

These and other theories have been reviewed by Jortner, Rice, and Kestner [4]. It is the purpose of this paper to investigate the potentialities of a molecular orbital description for an electron in a polar solvent, adopting for simplicity, a dimer model.

Some Dimer Models

The presence in water of dimers is not a new idea, though there is no experimental evidence to support a belief in dihydrol. It serves however as a useful starting point from which to consider the structure of the hydrated electron.

Raff and Pohl have studied a situation where the electron is thought to be located between two water molecules, orientated as shown in Fig. 1 [5]. They proceed by reducing the problem to that of the hydrogen molecule ion H_2^+ perturbed by two hydroxyl ions. Incredibly, this drastic oversimplification produces a value for the optical transition energy not too disparate from that observed. One model employed here preserves this dimer skeleton.

Apart from this dimer, two alternative models are also considered, one for the hydrated electron and one for the ammoniated electron respectively. The model apposite to the hydrated electron is based upon the Wurtzite structure for ice. A dimer fragment of the Wurtzite lastice is taken as illustrated in Fig. 2. This differs from the planar dimer previously mentioned, in that non planar configurations are permitted, whilst the hydrogen and oxygen atoms of two distinct molecules are now adjacent. Our purpose is to ascertain if there is a prefered orientation of the two water molecules.

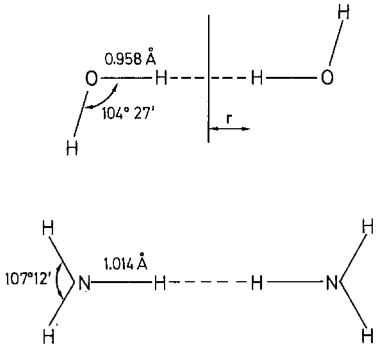

Fig. 1. A planar dimer model for the hydrated and ammoniated electron

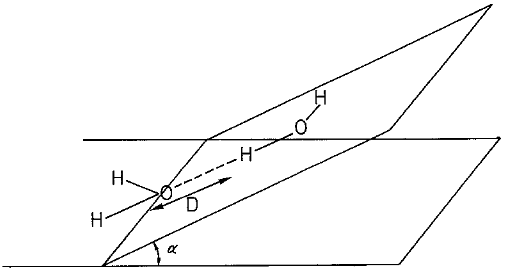

Fig. 2. A Wurtzite type dimer model for the hydrated electron

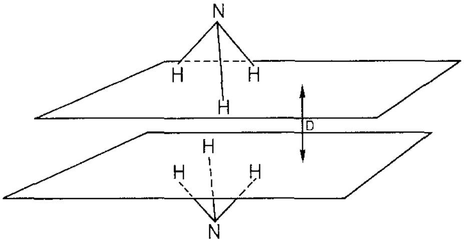

Fig. 3. A pyramidal dimer model for the ammoniated electron

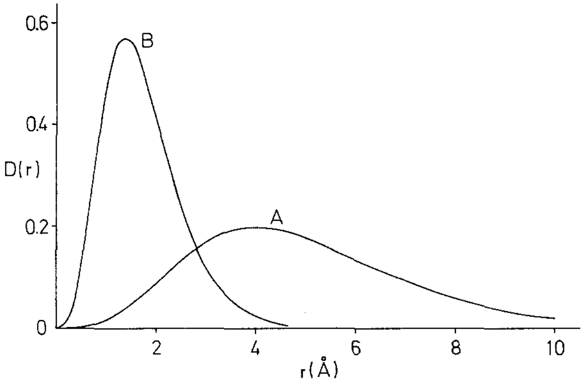

Fig. 4. The radial distribution function $D(r)$ for a hydrogen $2p$ orbital: curve A relates to the free atom whilst curve B is a shrunken orbital with an effective nuclear charge of 2.9

An alternative model for the ammoniated electron consists simply of two pyramidal ammonia molecules juxtaposed as depicted in Fig. 3. The two planes containing the hydrogen atoms of each molecule lie a distance D (Å) apart.

In all of the models an attempt has been made to combine features of both the cavity and polaron formulations. This is accomplished in the following manner. The electron is allowed to choose between two possibilities. Either it may remain in the hole of radius r, noted in Fig. 1, or it may spread over the entire system via $2p$ orbitals upon the hydrogen and oxygen atoms.

The hydrogen orbitals employed are not those of the free atom. They are shrunken orbitals characteristic of the atom in the molecule. This important distinction is portrayed in Fig. 4 which shows the radial distribution function $D(r)$ for the $2p$ orbital: $D(r) = r^2 R^2(r)$ where

$$R(r) = [(Z_{\text{eff}})^5/24]^{1/2} \cdot r \cdot \exp(-Z_{\text{eff}}/2 \cdot r).$$

Curve A is for the free atom, for which of course the effective nuclear charge Z_{eff} is unity. The shrunken orbital, curve B, has an effective nuclear charge of 2.9. This is the value obtained by Dickinson in his calculation on H_2^+ [6]. Accordingly the shrunken orbital is near to one third of the size of the free atom orbital, the maxima in $D(r)$ lying at 0.73 Å and 2.12 Å respectively. Similarly the $1s$ orbital used is also slightly shrunken, having an effective nuclear charge of 1.25.

The Method of Calculation

If one is able to tolerate the assumptions attendant to the extended molecular orbital method, introduced by Longuet-Higgins and Roberts [7] and popularised by Hoffman [8], then it has a certain appeal in providing a tractable approach to the larger molecular problems. Although aware of its deficiencies, it is adopted here in order to test without excessive computation, the dimer models which have been proposed.

A central feature of any semi-empirical calculation is the choice of the values to be assigned to the parameters involved. This is now to be considered, for the formalism of Extended Hückel Theory has been delineated many times elsewhere [8, 9].

May it suffice to say that for the hydrated electron, neglecting the 1s electrons of the oxygen atoms, there are twenty four atomic orbitals ϕ_i from which to compound an equal number of molecular orbitals ψ_i.

$$\psi_i = \sum_{i=1}^{24} c_i \phi_i$$

where $\phi_i \in \mathrm{O}(2s, 2p_x, 2p_y, 2p_z)$; $\mathrm{H}(1s, 2p_x, 2p_y, 2p_z)$. In solving the secular determinant $|H_{ij} - e_i S_{ij}|$ to obtain the set of energy levels e_i, the off diagonal elements $H_{ij} = \int \phi_i H \phi_j \, dt$ have been approximated in a conventional manner, by the formula:

$$H_{ij} = 1.75\, S_{ij}[H_{ii} + H_{jj}]/2$$

where S_{ij} is the overlap integral $\int \phi_i \phi_j \, dt$.

The lowest nine molecular orbitals accommodate the seventeen electrons of the dimer, the ninth orbital being singly occupied. It is the energy gap ΔE between this orbital and the next unoccupied orbital, which it is hoped may be related to the first optical excitation energy of the species.

By evaluating ΔE as a function of r, or in the case of the pyramidal ammonia model D, an estimate of the relative sizes of the cavities in water and ammonia is obtainable from the observed excitation energies. Further, by performing a population analysis it should be possible to see if the charge prefers to remain within the cavity or to spread out over the system.

The radial portions $R(r)$ of the atomic wave functions ϕ_i which comprise the basis set, as has been seen are represented by single exponential functions. The orbital exponents $Z_{\mathrm{eff}}/2$ have been selected from the compilation of Clementi, excepting the hydrogen atom which has already been discussed [10]. For the

Table 1. *The values of the parameters* Z_{eff} *and* H_{ii} *(eV)*

	2s, H(1s)		2p	
	Z_{eff}	$-H_{ii}$	Z_{eff}	$-H_{ii}$
H	1.25	21.22	2.89	28.29
N	3.85	25.84	3.83	15.77
O	4.49	33.73	4.45	17.14

diagonal elements H_{ii} the appropriate one electron orbital energies have been taken. This is the simplest choice in a field overgrown with speculation. Table 1 lists these effective nuclear charges and diagonal elements.

Results and Discussion

a) The Planar Dimer

Excitation energies ΔE (eV) at particular hole radii r (Å) for the planar dimer model are displayed in Table 2. Fig. 5 illustrates the variation of ΔE with r for the hydrated and ammoniated electron. The experimental excitation energies for these two species are 1.72 eV and 0.80 eV respectively [1, 11]. These values are so seen to correspond with holes of radii 0.75 Å in water and 1.76 Å in ammonia; they are highlighted in the figure by arrows.

Volume expansion measurements suggest that the radius of the cavity in ammonia is of the order of 1.5–1.7 Å. They lend a little credence to the present results.

Striking differences may be observed between the two species at separations near to their optimum cavity radii. With the water dimer, ΔE is increasing as the

Table 2. *Excitation energies ΔE (eV) for the planar dimer and pyramidal models*

$(H_2O)_2 \cdot e$		$(NH_3)_2 \cdot e$ [Planar]		$(NH_3)_2 \cdot e$ [Pyr]	
r (Å)	ΔE	r (Å)	ΔE	D (Å)	ΔE
0.70	1.18	1.40	2.44	1.20	1.55
0.80	2.13	1.60	1.34	1.40	1.17
0.90	2.48	1.80	0.68	1.50	0.62
1.0	2.69	2.0	0.33	1.60	0.28

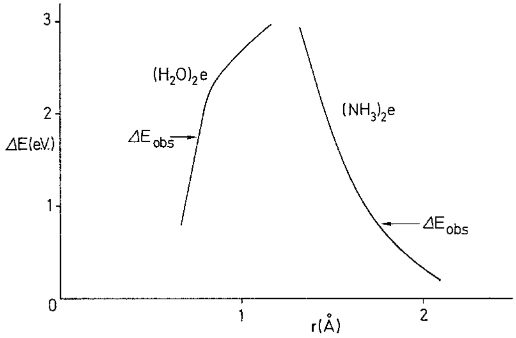

Fig. 5. The variation of the excitation energy ΔE (eV) with r(Å), the hole radius for the hydrated and ammoniated electron

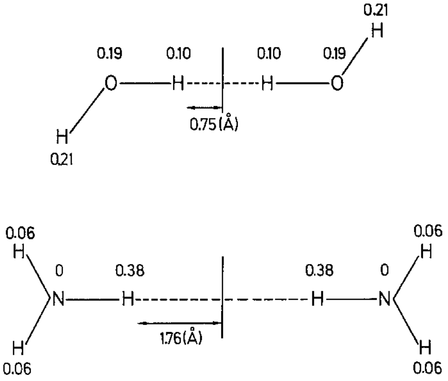

Fig. 6. The charge distribution of the hydrated and ammoniated electron at the optimum cavity radius

hole expands whilst for the ammonia dimer the excitation energy is decreasing as the two molecules move apart. Further the charge is distributed quite differently in each case, as may be seen in Fig. 6. For the hydrated electron the charge spreads out almost evenly over the two water molecules. In ammonia the electron remains almost entirely within the hole. This perhaps is the reason as to why the cavity model may be applied with some success to the ammoniated electron but does not seem to be appropriate to the hydrated electron.

b) The Wurtzite Type Dimer Model for the Hydrated Electron

Some engaging results for this model are to be seen in Table 3. The excitation energy ΔE is tabulated over a range of values of R the oxygen-hydrogen separation, for different choices of the interplane angle α. Fig. 7 illustrates this variation of ΔE with R and α.

Only when α is in the region of 90° is the experimental assignment to ΔE even approached. This is the position when the hydrogen atoms of the two molecules are at their closest distance of approach. It would so appear that the preferred orientation of the two water molecules is such as to permit the maximum delocalisation of the charge. The population analysis, performed at the optimum values for R and $\alpha = 90°$, shown in Fig. 8 supports such a surmise.

Table 3. *Excitation energies ΔE (eV) for the Wurtzite dimer model at various oxygen-hydrogen separations R (Å) and interplane angles α*

R (Å)	ΔE (eV) $\alpha = 0°$	30°	60°	90°
0.70	1.36	1.33	1.45	1.83
0.80	1.43	1.40	1.39	1.86
0.90	1.49	1.43	1.27	1.71
1.0	1.50	1.41	1.17	1.45

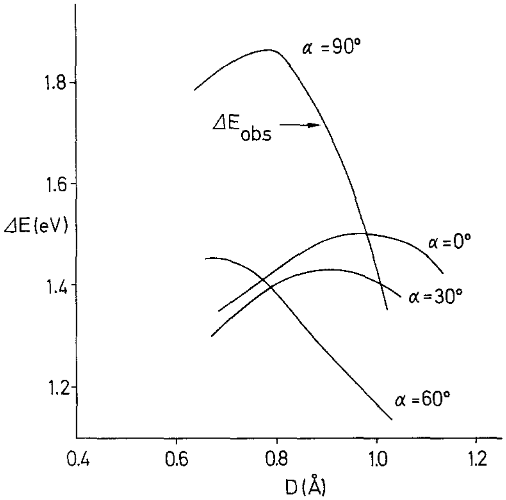

Fig. 7. The variation of the excitation energy ΔE (eV) with R (Å), the O–H separation and α the interplane angle for the Wurtzite model of the hydrated electron

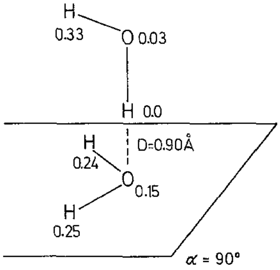

Fig. 8. The charge distribution of the hydrated electron in the Wurtzite model

c) *A Pyramidal Ammonia Dimer Model*

The results obtained from a pyramidal model for the ammoniated electron do not differ markedly from those for the planar model. Excitation energies at different interplane separations D are collated in Table 2. The observed excitation energy of 0.80 eV is reproduced when D equals 1.47 Å which corresponds to a H–H separation of 1.75 Å. At this distance nearly all of the charge is located between the hydrogen atoms.

Conclusion

Despite its blatant artificiality the dimer model for the hydrated and ammoniated electron as treated by the extended molecular orbital method, does provide a realistic estimate of the relative sizes of the cavities within the two solvents. One is also led to think rather tentatively that an electron in water is by no means a similar entity to an electron in ammonia.

The key note to the present study is the use of shrunken orbitals upon the hydrogen atoms, a choice which is tantamount to the inclusion of an angularly dependant effective nuclear charge for the hydrogen atomic orbital. Apart from this, it is unlikely that the use of other methods for approximating the off diagonal elements or allowing the diagonal elements to be charge dependant, would greatly alter the trends already observed.

It is not intended that the models presented here should in any way be placed in the imagination as representing the structure of the solvated electron. This is a highly complex problem in which the dimer model is but a primaeval probe. Further studies are in progress.

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