Long Range Interaction between Hydrated Electrons

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The pulse radiolysis technique has made it possible to observe directly the formation and reactivity of the hydrated electron in liquid water. The bimolecular reaction of the hydrated electron has been found to be a fast reaction[1] and a subject for discussion, since it is the reaction of two negative species in which only a repulsive interaction would be expected from a simple classical consideration.

In order to understand this reaction, it is necessary to consider the interaction between hydrated electrons on a theoretical basis. We have, therefore, made a calculation, using the polaron model, of the long range interaction between hydrated electrons.

The interaction energies between two hydrated electrons in the electronic ground state are expressed as follows:

$$E\begin{Bmatrix} {}^1\Sigma_g{}^+ \\ {}^3\Sigma_u{}^+ \end{Bmatrix} = \frac{1}{1\pm S^2}\Bigg[-2\beta e^2\bigg\{\frac{1}{r_0}\int_{r_{b1}\leq r_0}\psi_a{}^2(1)\mathrm{d}v_1 + \int_{r_{b1}\geq r_0}\frac{\psi_a{}^2(1)}{r_{b1}}\mathrm{d}v_1 \pm S\bigg(\frac{1}{r_0}\int_{r_{b1}\leq r_0}\psi_a(1)\psi_b(1)\mathrm{d}v_1 + \int_{r_{b1}\geq r_0}\frac{\psi_a(1)\psi_b(1)}{r_{b1}}\mathrm{d}v_1\bigg)\bigg\} + \frac{e^2}{D}\bigg\{\iint\frac{\psi_a{}^2(1)\psi_b{}^2(2)}{r_{12}}\mathrm{d}v_1\mathrm{d}v_2 \pm \int\frac{\psi_a(1)\psi_b(2)\psi_a(2)\psi_b(1)}{r_{12}}\mathrm{d}v_1\mathrm{d}v_2\bigg\}\Bigg]$$

where the upper and lower signs on the right-hand side correspond to the $^1\Sigma_g{}^+$ and $^3\Sigma_u{}^+$ states respectively; a and b represent the cavities which are formed by each electron; r_0 is the cavity radius; ψ_a and ψ_b are the wave function of the hydrated electron in the cavities a and b respectively; r_{b1} is the distance between the center of the b cavity and the 1 electron; r_{12} is the distance between the electrons; S is the overlap integral between ψ_a and ψ_b, and $\beta=(1/D_{op})-(1/D_s)$, D_{op} and D_s being the optical and static dielectric constants of water respectively.

The wave function of the hydrated electron is obtained by the SCF dielectric treatment,[2] while the effective dielectric constant, D, has been estimated in the following way:

$D=D_s$ for $R\gtrsim 12$Å
$D=f(R)$ for $12\text{Å}\gtrsim R\gtrsim 6\text{Å}$
$D=D_{op}$[3] for $6\text{Å}\gtrsim R$

where $f(R)$ is a cubic function with srepect to the distance, R, between the cavities and is connected smoothly with D_{op} at $R=6$Å and with D_s at $R=12$ Å.

Figure 1 shows the interaction energy, E, calculated as a function of R for the different cavity radii, $r_0=0$ and 1.8 Å. The interaction potentials for both the $^1\Sigma_g{}^+$ and $^3\Sigma_u{}^+$ states are attractive rather than repulsive except at short distances. The potential curve for the ground state ($^1\Sigma_g{}^+$) has a minimum at 7.5 Å. The increase in the cavity radius lowers the $^1\Sigma_g{}^+$ state slightly and raises the $^3\Sigma_u{}^+$ state to the same extent.

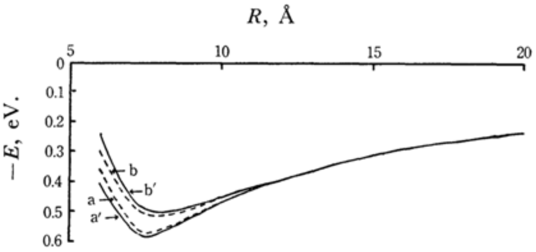

Fig. 1. The interaction energy between hydrated electrons.
a: $^1\Sigma_g{}^+$, $r_0=0$; a′: $^1\Sigma_g{}^+$, $r_0=1.8$Å
b: $^3\Sigma_u{}^+$, $r_0=0$; b′: $^3\Sigma_u{}^+$, $r_0=1.8$Å

The present results suggest that the activation energy for the bimolecular reaction of the hydrated electron arises from a short range interaction when the activation energy for diffusion is properly taken into account, and that it is not justifiable to use a simple electrostatic interaction between hydrated electrons in applying the Debye equation to the second-order rate constant.

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[1] S. Gordon, E. J. Hart, M. S. Matheson and J. Rabani, *Discussions Faraday Soc.*, No. **36**, 193 (1963).

[2] J. Jortner, *Radiation Res.*, *Suppl.* **4**, 24 (1964).

[3] The high frequency limiting value of the dielectric constant, 5.5, has been used for D_{op}. J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).