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*SHORT COMMUNICATION*

# The Binding Energy of an Electron Transferred to a Solvent from Halide Ions

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It is well known that halide ions (the best example is the iodide ion) in aqueous solution show strong absorption bands in the ultraviolet region. These bands are considered to be due to transfer of an electron from the anion to the solvent. The peak frequency of the band depends on electron affinity of the ion, the binding energy B of the electron in its excited state and other terms associated with heats of solvation and electronic polarization.[1,4] In the theory of Franck and Platzman[1] the binding energy B of the electron in its excited state is calculated on the assumption that the electron is subjected to the potential

$$\begin{aligned} V(r) &= -e^2 (D_{op}^{-1} - D_s^{-1})/r \\ &= -e^2 Z_{eff}/r, \end{aligned} \tag{1}$$

where $D_{op}$, $D_s$ are the optical and static dielectric constants of the solvent. The expression (1) gives the potential a dipolar medium arranged round a negative ion would have at small distances.[2] It is essentially a coulomb i.e. potential with a renormalized charge,

$$eZ_{eff} = e\,(D_{op}^{-1} - D_s^{-1}),$$

and the binding energy of the electron is given by

$$B = -mZ_{eff}^2\, e^4/2n^2n^2, \tag{2}$$

where *m* is the electron mass and *n* is an integer. Franck and Platzman[1] assumed that for halides the transferred electron is in a 2S state, so that the binding energy is approximately 1eV. The binding energy in the ground state (1S state) is so high ( ~ 4eV) that it even exceeds the electron affinity of the halogen atom. Franck and Platzman[1] give no satisfactory reason as to why the electron should not be in the 2S excited state. The more recent theory of Stein and Treinin[4] which is partly successful in explaining the variation of peak frequency with temperature and the nature of the medium also makes the same assumption. For halides, they assume that B is given by (2) with $n = 2$. The theory completely fails if the electron is allowed to occupy the 1S state. In this work we present a more realistic calculation of B taking into account the short distance behaviour of the potential to which the electron is subjected. It is shown that the electron could be transferred to the ground state and that binding energy in this state is not impossibly high as in the previous theories.

We assume that the dipolar molecules of the solvent are oriented around the negative ion giving rise to the potential (1). However, at short distances this macroscopic description becomes inaccurate and the effect of individual dipoles has to be taken into account. Since the electric field due to a dipole vary as $1/r^3$, only few oriented dipoles interact with the electron and the potential experienced by the electron due to this field is approximately $\mu e/r^2$, where $\mu$ is a parameter comparable to the dipole moment of a single molecule. As the positive ends of the dipoles are pointed towards the anion the above force is repulsive. The net potential seen by the electron is

$$V(r) = \mu e/r^2 - Z_{eff}e^2/r. \qquad (3)$$

$V(r)$ is repulsive when $r < r_o = \mu/Z_{eff}e$ and becomes minimum when $r = 2r_o$, the minimum value being $V = V_o = -Z^2_{eff}/4\mu$. Setting $\mu = 1.87$ De (dipole moment of the water molecule) we obtain $r_o = 3.2$ A°, which is not unreasonable. The Schrodinger equation is exactly solvable for the potential (3) and the energy eigenvalues are given by the expression,[3]

$$E = -2mZ^2_{eff}\, e^4/n^2 \left[ (2n + 1) + \{ (21 + 1)^2 + B\mu me/n^2 \}^{\frac{1}{2}} \right]^{-2} \qquad (4)$$

where $n$ = zero or an integer and 1 is the orbital angular momentum quantum number. The eigenfunctions can be expressed in terms of confluent hypergeometric functions.[3] For the ground state ($n = 0$, $1 = 0$), the above expression yields $B = -E \simeq .5$ eV(excited states will have much less energy). Thus our calculations show that the major difficulty of the previous theories disappear when the short distance behaviour of the force experienced by the electron transferred to the solvent is taken into account.

## References

1. FRANCK, J., & PLATZMAN, R. L., (1954) Z. *Phys.* **138** : 411.
2. LANDAU, L. D., (1933) *Sowiet Physik*, **3**: 664.
3. LANDAU, L. D., & LIFSHITZ, E. M., (1965) *Quantum Mechanics*, 2nd Edition, Pergamon Press.
4. STEIN, G., & TREININ, A. (1958) *Trans. Faraday Soc.*, **54**: 338.