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Author(s)	KHAN, Shahed U. M. ; BOCKRIS, John O'M.
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MODELS OF ACTIVATION IN THE THEORY OF ELECTROCHEMICAL KINETICS

By

Shahed U. M. KHAN*¹⁾ and John O'M. BOCKRIS*²⁾

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Abstract

The present state applicability of the Continuum Solvent Reorganization (CSR) model of activation is analyzed. It is found that the theoretical predictions and the fluctuational view of the model are too poor to conform to experiment.

Introduction

There exist only two models of activation for the electron transfer reactions in solution and at electrode. The bond activation and stretching (BAS) model of activation was originated from Gurney¹⁾ and developed by Butler²⁾ and others.³⁻¹⁸⁾ The BAS model suggests that the activation of ions in solution arises due to thermal (collisional) interaction with the surrounding solvent translators, and thus, in the process of activation, the inner ion solvent in ligand bonds undergoes enhanced stretching. In the Continuum Solvent Reorganization (CSR) model of activation, it is considered that the ions in solution become activated due to prior fluctuation of the energy of the ions for their electrostatic interaction with the librating solvent dipoles in the solvent continuum outside the inner sphere of reacting ions. The inner sphere is considered to be frozen in room temperature and is not activated and stretched since the energy of ion-solvent bonds is given by $h\nu \gg kT$, since, in CSR view, there is not enough contact with high energy translators from solution to maintain the Boltzmann distribution for higher states. The CSR model was originated from Libby¹⁹⁾ and developed by Marcus²⁰⁾ and others.²¹⁻³³⁾

In this paper, we give a brief analysis of the present state applicability of the CSR model of activation of ions in solution.

Fluctuational View in CSR Model

In the original CSR view of Marcus²⁰⁾ the free energy of activation of

*) Department of Chemistry, Texas A & M University, College Station, Texas 77843, USA.

ions, due to Continuum Solvent Reorganization, was calculated by considering the *post* electron transfer situation (*i. e.*, the Franck Condon Barrier). The preassumption is that the reorganization of the solvent molecules around the reacting ions occurred *prior* to the electronic jump process. However, Marcus's treatment²⁰ did not explain *how* the ions become activated, due to reorganization prior to electron transfer, and did not mention the mechanism by which energy is transferred from the continuum solvent to the central ion containing frozen inner sphere. The original contribution of Levich²¹ lies in the rationalization of the CSR model of activation in terms of solvent polarization fluctuation and the polaron concept in polar solvent. It is considered that each solvent librator can transmit their energy, $h\nu \simeq 0.001$ eV, to the central ion in the form of a polaron. The librator energy is not sufficient to activate the ion, and hence, Levich²¹ specifically introduced the concept of the occasional fluctuation of the solvent polarization energy to supply the central ion the required free energy of activation. This idea seems qualitatively quite reasonable to explain the CSR model of activation prior to electronic jump process. However, a quantitative determination of the probability of this solvent polarization fluctuation is needed to realize the feasibility of the CSR view. The physicists, who subsequently joined this field and worked on the CSR view for more than a decade, made no attempt to determine the probability of this assumed fluctuation. It seems to us that if the fluctuation of solvent polarization occurs with sufficient frequency, everything regarding CSR model perhaps goes well, and the ingenious idea of Levich regarding fluctuation becomes fruitful.

A Proposition

The fluctuational viewpoint was introduced into the CSR model for the reason that in this model, the vibrational-rotational level of the ion-solvent bond, *e. g.*, $\text{H}_2\text{O}-\text{H}^+$ bond in solution, is considered discrete, and activation of these bonds to higher vibrational-rotational level is neglected, since, for these bonds, $h\nu \gg kT$, where ν is the frequency of vibration of the ion-solvent bond. The continuous distribution of vibrational-rotational levels of such bonds in solution was not considered, and the collisional activation is rejected on the assumption that there are no translators (which would have a continuum of energy states) in solution.

We propose here that there is virtually no need for fluctuational activation. The activation is, in fact, all thermal and collisional. There is sufficient spectroscopic evidences^{34,35} that there exists a reasonable amount of translator in solution, so that the vibrational-rotational states in solution become con-

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tinuous.^{35,37)}

Furthermore, it can be shown that the activation and stretching of the bond, for which $h\nu \gg kT$ is sufficiently probable to conform to the observed rate of reaction. For example, the activation energy for the proton transfer reaction on Hg electrode is $E_a = 20$ kcal/mole. Hence, the probability that the $\text{H}_2\text{O}-\text{H}^+$ bond of H_3O^+ goes to activated state is $P_1 = e^{-E_a/kT} = 5.3 \times 10^{-16}$. The activated state of $\text{H}_2\text{O}-\text{H}^+$ bond for which condition $h\nu \gg kT$ is satisfied corresponds to second vibrational level. The energy of $\text{H}_2\text{O}-\text{H}^+$ bond, is $h\nu = 0.447$ eV. The probability that this bond will be in second vibrational level due to thermal interaction is $P_2 = e^{-2h\nu/kT} = 6.7 \times 10^{-16}$. Since $P_2 > P_1$, it is quite possible that the $\text{H}_2\text{O}-\text{H}^+$ bond can be activated to higher vibrational state and become stretched to conform to the observed rate of reaction. This situation is much more probable for the case of redox ions for which the ion-solvent or ligand bond vibrational energy [for example, for $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ ion each ion-solvent bond vibrational energy is 0.06 eV for $\nu_0 = 1.4 \times 10^{13} \text{ sec}^{-1}$] is comparable to kT . The probability that $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ to be in the activated state is $P_1 = e^{-E_a/kT} = 3.6 \times 10^{-7}$ for activation energy of 0.38 eV. Since the redox ion involves six bonds, each bond needs to be only in the first vibration state for activation, and the probability that each $\text{Fe}^{3+}-\text{H}_2\text{O}$ bond will be in the first vibrational state is $P_2 = e^{-h\nu/kT} = 0.09$. Here, P_2 is much higher than P_1 and conforms to the BAS model.

CSR Model and Experiment

Tafel Plots for Redox Reaction

The plot of $\log i$ versus overpotential, η , from the CSR theory expression,^{21,22) i. e.}

$$i = C \exp \left[- \frac{(E_s + \Delta F^\circ + e_0 \eta)^2}{4E_s kT} \right] \quad (1)$$

where C is a constant, E_s is the Continuum Solvent Reorganization energy, and ΔF° is the free energy of reaction at reversible condition, does not give linear Tafel lines and is in disagreement with the recently reported³⁸⁻⁴⁴⁾ experimentally obtained linear Tafel lines for redox reaction at electrodes (Fig. 1). The similar type of disagreement is also observed for the proton transfer reaction at electrode. These observations indicate that the activation process both in redox and proton transfer reaction is not fluctuational and is in disagreement with the attitude that the activation in redox reaction is mostly fluctuational.⁴⁵⁾

A remarkable aspect of Equation (1) is that with the increase of negative

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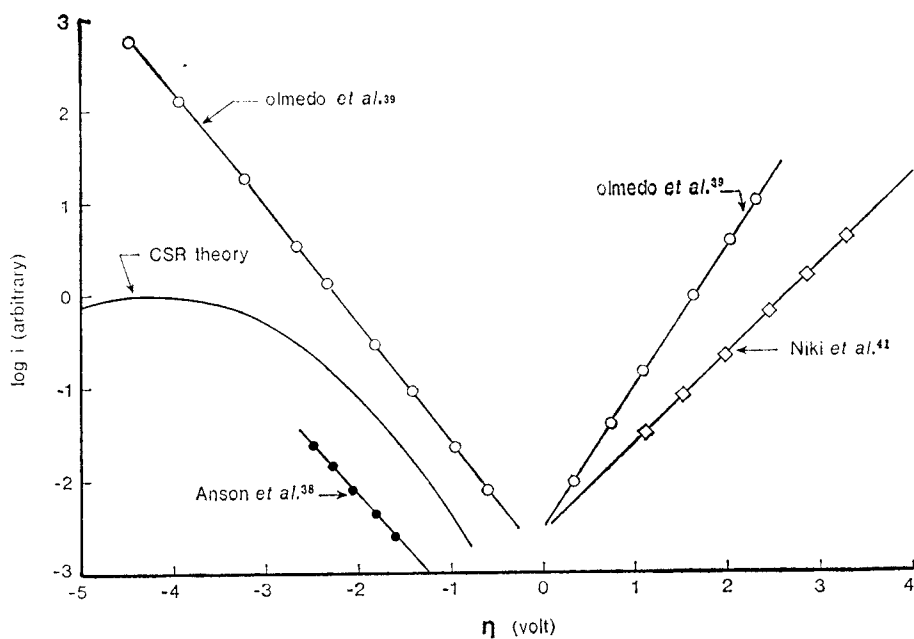


Fig. 1. Logarithm of current density versus overpotential plots, comparing experiment with predictions of the CRS theory for redox reaction.

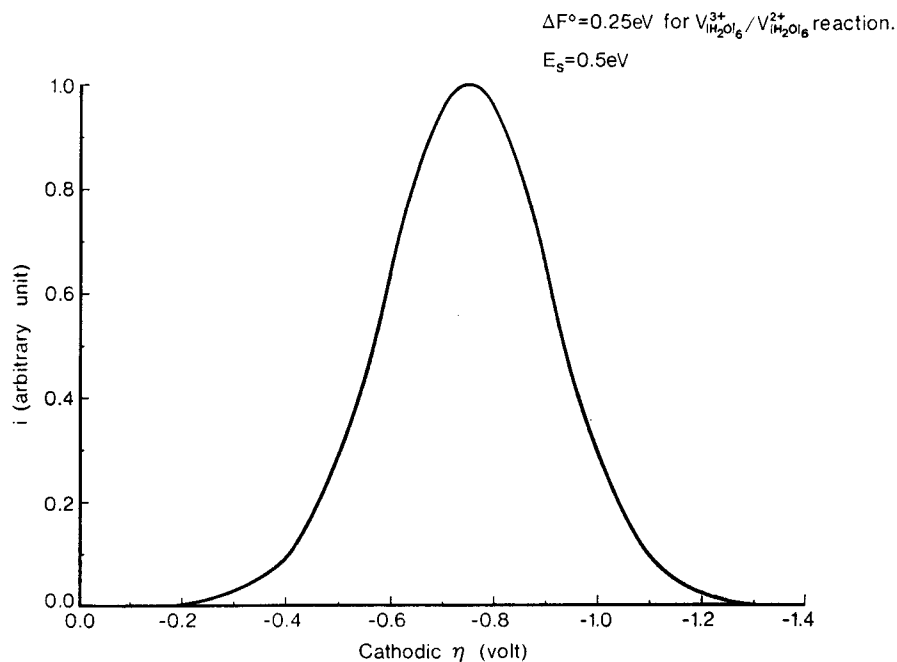


Fig. 2. The plot of current density as a function of η to indicate maximum of current at η_{max} .

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overpotential, the cathodic current starts decreasing in the normal manner until $e_0\eta$ is more than E_s , and the cathodic current starts to fall again (Fig. 2). Hence, one obtains $\eta_{\max} = -(\Delta F^\circ/e_0 + E_s/e_0)$. This η_{\max} should be observed experimentally for the positive ΔF° or $|\Delta F^\circ| < E_s$. However, such a behavior is in complete contrast to experiment.

Free Energy of Activation for the Electrochemical Inorganic and Organic Redox Reaction

The free energy of activation, ΔF^\ddagger (CSR) expression of CSR model²⁰ is

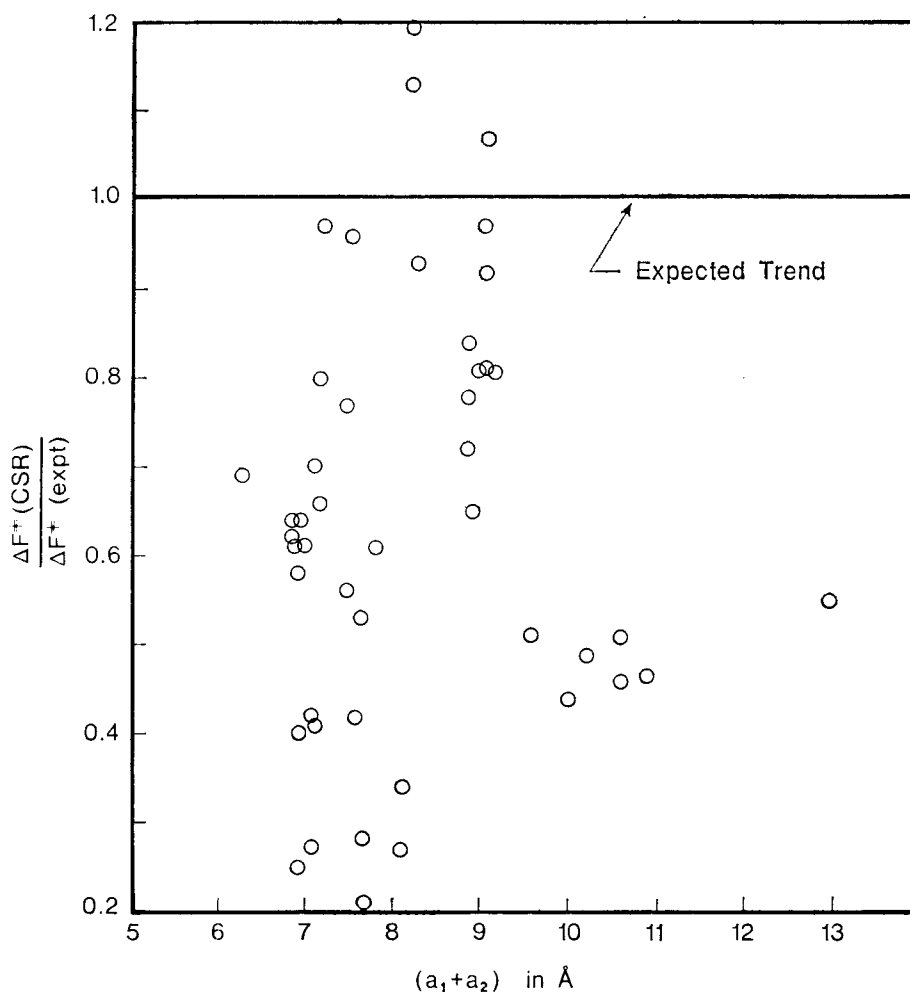


Fig. 3. The plot of $\Delta F^\ddagger(\text{CSR})/\Delta F^\ddagger(\text{expt})$ as a function of the sum of the radii of the ions.

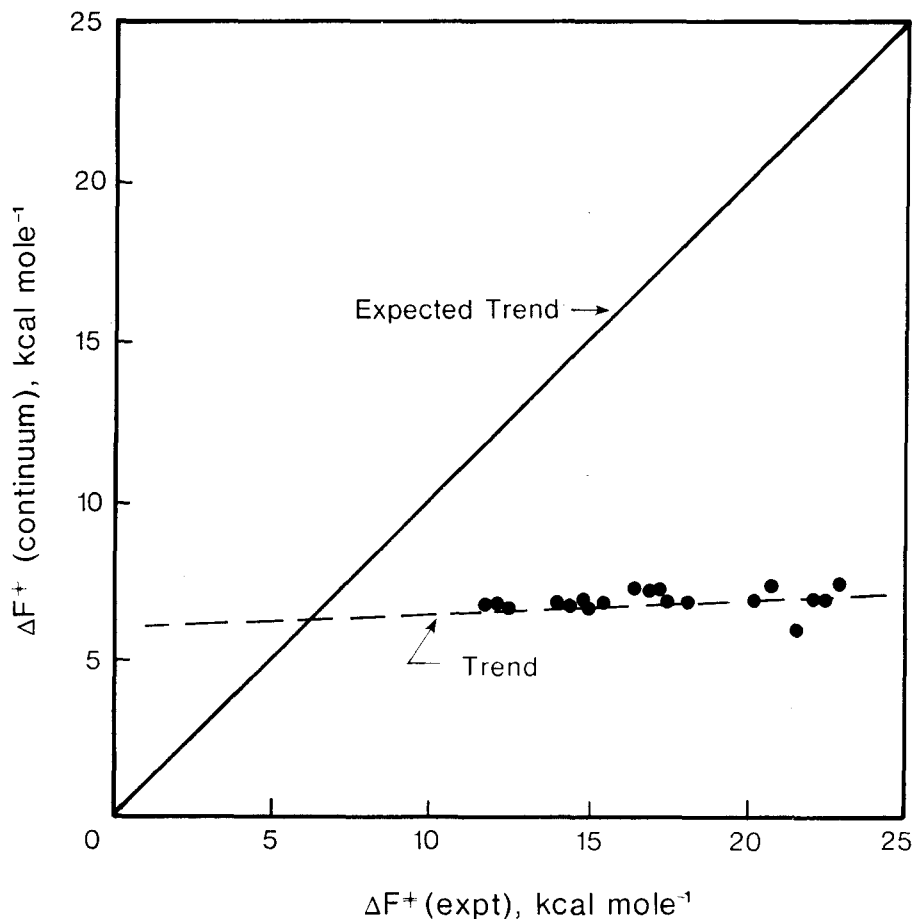


Fig. 4. Plot of $\Delta F^\ddagger(\text{CSR})$ against $\Delta F^\ddagger(\text{expt})$ for electrochemical redox reactions.

dependent on the radii of redox ions and the dielectric constants of the solvent medium. The plot of $\Delta F^\ddagger(\text{CSR})/\Delta F^\ddagger(\text{expt})$ versus the sum of the radii of the ions does not show any tendency to converge to the value of unity, even with the increase of the size of the ion (Fig. 3).

The plot of $\Delta F^\ddagger(\text{expt})$ versus $\Delta F^\ddagger(\text{CSR})$ exhibits no correlation, but rather indicates reverse trends (Fig. 4). If, however, excellent parallelism is noticed between $\Delta F^\ddagger(\text{expt})$ and $\Delta F^\ddagger(\text{BAS})$ calculated using bond activation and stretching expression⁹ (Fig. 5). The agreement between $\Delta F^\ddagger(\text{expt})$ and $\Delta F^\ddagger(\text{BAS})$ would be much better if the proper value of ϵ rather than unity would be used for the estimation of $\Delta F^\ddagger(\text{expt})$ from rate constant data.

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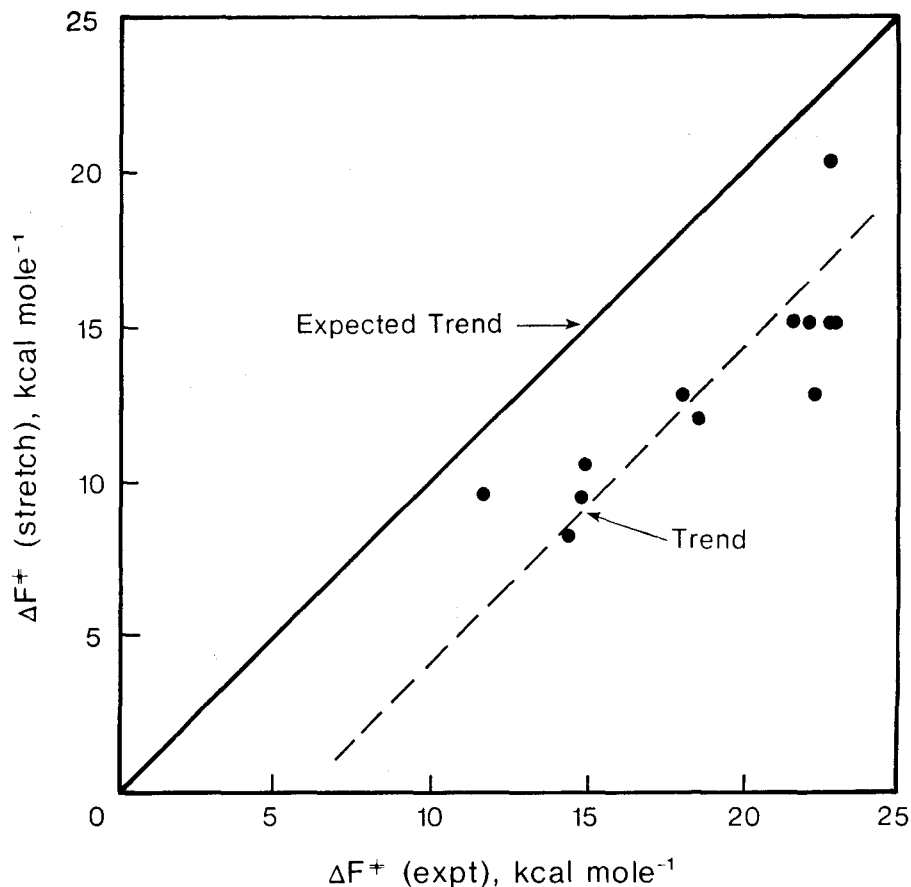


Fig. 5. Plot of ΔF^\ddagger (BAS) against ΔF^\ddagger (expt) for electrochemical redox reactions.

The dependence of ΔF^\ddagger (CSR) on the dielectric constants of different solvent mediums can be verified with ΔF^\ddagger (expt) for an organic redox reaction in different solvent having different dielectric constants. One such plot of ΔF^\ddagger (CSR) versus $(1/\epsilon_{op} - 1/\epsilon_s)$ for benzonitrile reduction at electrode is given in Figure 6, and the experimental data points are put in it for comparison. The theoretical line exhibits opposite trends and indicated no correlation. Bard, *et al.*,^{46,48)} reported poor agreement between ΔF^\ddagger (CSR) and ΔF^\ddagger (expt) for different redox reactions at electrode.

The Solvent Polarization Fluctuation Probability

The statistical theory of fluctuation^{49,50)} in an ensemble enables one to

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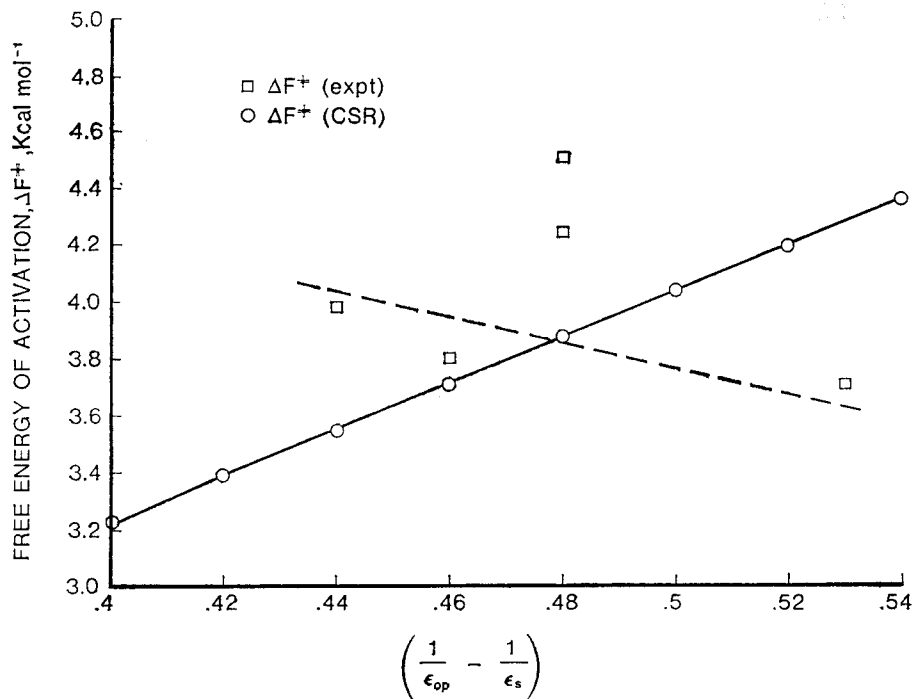


Fig. 6. The plot of ΔF^\ddagger (CSR) versus $(1/\epsilon_{op} - 1/\epsilon_s)$.

compute the probability of fluctuation in the solvent polarization energy during their interaction with the reference ion to supply it sufficient energy to promote it to activated state. To find this probability of fluctuation, it is necessary to know the average energy $\langle u \rangle$ of the ion in the field of the surrounding solvent dipoles. The interaction is computed from the solvent dipoles outside the first solvation shell. Then, we compute $\langle u^2 \rangle$. We do not give the detail calculation as it was done in the original publication.⁵⁰ We give the final results after more correct recalculation. The average energy comes out to be :

$$\langle u \rangle = \frac{e_0^2 \mu_{\text{eff}}^2}{\epsilon_s^2 r_w^3 r_1 k T} \quad (2)$$

and

$$\langle u^2 \rangle = \frac{e_0^2 \mu_{\text{eff}}^2}{\epsilon_s^2 r_w^3 r_1} \quad (3)$$

where μ_{eff} is the effective dipole moment of water dipole in liquid water, r_w is the radius of water molecule, and r_1 is the radius of ion with first

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solvation shell. From the statistical fluctuation theory the probability of fluctuation takes the form of Gaussian type of distribution and considering up to second order term the probability of fluctuation becomes :

$$P = P_{\langle u \rangle} \exp \left[- \frac{(u - \langle u \rangle)^2}{2(\langle u^2 \rangle - \langle u \rangle^2)} \right] \quad (4)$$

where $P_{\langle u \rangle}$ is unity at $u = \langle u \rangle$. To give rise to energy, $u - \langle u \rangle = 0.9 \text{ eV}$, corresponding to activation of proton, the probability of fluctuation became $P = 10^{-2000}$. Thus, fluctuational probability is extremely an unlikely event, and hence, activation due to fluctuation in CSR model is not a probable and acceptable hypothesis.

It may be, therefore, that this pre-rearrangement of molecules and fluctuation around the ion to the extent of activating it to the degree required is the Achilles Heel of the CSR model and is the origin of the incorrect agreement with experiment, which is now so manifestly shown.

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