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Desolvation effects on the dissociation energy of diatomic molecules: *Ab initio* study of the dissociation of Li-F in polar media*

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Summary. The potential curve of the ground state dissociation of Li-F in water has been studied by a combination of a standard *ab initio* Hartree–Fock procedure and a perturbative reaction field approach. The electrostatic solute-solvent interaction is accounted for by the generalized Born formalism introduced through a perturbation approach. The calculations were carried out at a 6-311 + G* basis set level. Diffuse functions of *s* symmetry were included to model a desolvation potential. A double well potential curve was obtained for the dissociation of this molecule in the presence of a highly polarizable medium. The first minimum, corresponding to an ion pair, electrostatically bound, is found at a $R(\text{Li-F}) < 6.0$ Å distance. As the two ions come together, a desolvation barrier of about 30 kcal/mol is to be overcome before the formation of the neutral Li-F at 1.56 Å. The barrier to ionization towards the ion pair is calculated to be about 14 kcal/mol. The dissociation of the ion pair towards the free ions is discussed in terms of the electrostatic solvation entropy changes.

Key words: Dissociation of Li-F in water – Solvation and desolvation effects – *Ab initio* potential curve of Li-F

1. Introduction

Solvent effect is an important factor in chemical reactivity. In many cases solute-solvent interactions lead to changes in electronic and molecular properties that strongly modify the reactivity pattern of a given substrate, with respect to the gas phase process. Many attempts to evaluate such medium effects have been made in the last decades [1–3]. Most of them are based on the Onsager reaction field theory [4] and usually implemented within semiempirical methods of calculation [5–7]. Most reliable attempts to evaluate medium effects within microscopic models have been reported by Warshel and coworkers [8]. We are interested in performing a type of calculation that, retaining the simplicity of the reaction field theory, be able to overcome the problem of describing the gas

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phase properties as a reference state to solvation effects calculations. The progress in this field has been possible with the aid of the methods of quantum chemistry along with the disposability of large computing facilities.

In this paper we present an electrostatic model of solvation which accounts for the interaction of charged solute particles with their surroundings and its application to the study of dissociation of Li-F in solution, as a model system. The main contribution of the present approach consists in using diffuse *s* type atomic orbitals, centered on each atomic center, to distribute the polarization charge density induced in the solvent. In this way, the problem of superimposing the source and polarization charge densities that was present in previous approach [9, 10], is avoided within the present formalism.

2. Theory

2.1 The reaction field theory including desolvation potential

Within the continuum approach of solvent effects representation, the total free energy of the solute in the field of the solvent is expressed as a function parametrically depending on the macroscopic dielectric constant of the medium E as follows:

$$G(\varepsilon) = E(1) + \delta G_s(\varepsilon) \tag{1}$$

where $E(1)$ is the total energy of the isolated solute and $\delta G_s(\varepsilon)$, is the free energy of solvation. A simple approximation to calculate the quantity $\delta G_s(\varepsilon)$ consists in using the generalized Born formula: the free energy of solvation of a molecular solute is built up from atomic contribution of each partially charged atomic center of the molecule plus an interatomic interaction term. The polarized medium is represented within this approach, by a set of virtual charge (polarization charge) distribution, related to the source atomic charges $Q_A(P)$ in the molecule as:

$$Q_A^{pol}(\varepsilon, P) = -[1 - 1/\varepsilon]Q_A(P) \tag{2}$$

We now introduce a "pseudo molecular orbital" $|\Phi\rangle$ as:

$$|\Phi^*\rangle = [2]^{-1/2}(|X_A^*\rangle \pm |X_B^*\rangle) \tag{3}$$

where $|X_A^*\rangle$ and $|X_B^*\rangle$ are diffuse orbitals of *s* symmetry. This "pseudo molecular orbital" is then used to build up the polarization charge density $\Gamma^*(r)$ as follows:

$$\Gamma^*(r) = |\Phi^*\rangle\langle\Phi^*| \tag{4}$$

satisfying the boundary condition:

$$\int \Gamma^*(r)\, dr = Q^{pol} \tag{5}$$

Since these diffuse functions are also added to the basis set for the calculation of the solute total energy, a necessary and sufficient condition to avoid superimposition of a fraction of the source charge density and the polarization charge distribution, is to take the "antibonding" form of $|\Phi^*\rangle$.

Having Eqs. (2)–(5) in mind, the polarization charge may be redefined as:

$$Q'^{pol}(\varepsilon, P) = [1 - S_{AB}^*]Q^{pol} \tag{6}$$

Equation (6) entails the following definition of the reaction field potential

(RFP) on the atomic center A [11]:

$$[V_R(\varepsilon, P)]_A = -[1 - 1/\varepsilon]Q_A(P)/r_A + [1 - 1/\varepsilon]S^*_{AB}Q_B(P)/R_{AB} \tag{7}$$

where r_A and R_{AB} are the atomic radius and the interatomic distances, respectively and S^*_{AB}, the overlap integral between the solvation cospheres:

$$S^*_{AB} = \langle X^*_A | X^*_B \rangle \tag{8}$$

The second term of Eq. (6) represents a destabilizing contribution to the RFP as the two ions plus their cosphere of solvation become within an overlapping distance. It has been shown that it may represent a desolvation potential continuously varying with the interatomic R_{AB} distance through S_{AB} [9].

The solvation free energy is then obtained from [9, 11]:

$$\delta G_S(\varepsilon, P) = -\tfrac{1}{2}\sum_A [V_R(\varepsilon, P)]_A Q_A \tag{9}$$

The application of this model may be understood in the following way: we may consider, according to a previous model [11], that the formation of an ion pair in solution occurs in three elementary steps. First, the free ions separated by a large R_{AB} distance may be as strongly solvated (depending on the q/r ratio). We may further assume that each ion carries at least, a first solvation shell with a finite number of solvent molecules bound to it. In such a case, we have a weak electrostatic interaction as the driving force governing the ionic association. As the two ions approach each other along the trajectory defined by R_{AB}, some solvent molecules should be "squeezed out", allowing for the direct interaction between the counterions. This desolvation process is expected to be critical within the overlapping distance of the cosphere formed by the ion plus their solvation shells. The overlap integral $\langle 6S^*_A | 6S^*_B \rangle$ is used to account for this critical distance. As a result, the total free energy of the solute-solvent system is increased, creating a first minimum in the curve. This minimum should correspond to an ion pair complex, mainly bound by electrostatic interactions. Eventually, the partially desolvated ions may go further in their approach. In such a case, covalent forces may become relevant causing a second minimum in the free energy curve, corresponding to a neutral species.

A graphical representation of this model is illustrated in Fig. 1.

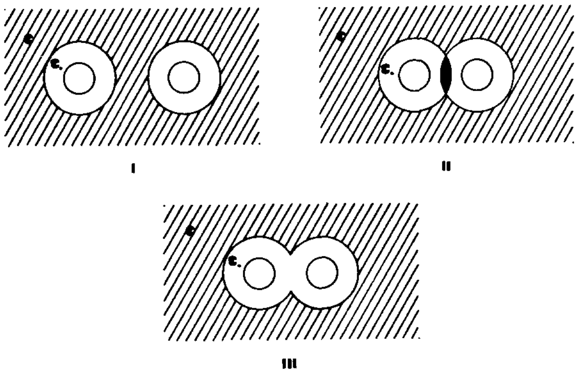

Fig. 1. Solvation model for Li-F including desolvation

3. Results and discussion

The *ab initio* calculations were carried out at 6-311 + G* basis set level, using the MONTERGAUSS package [12]. This basis set was augmented by one diffuse 6*s* orbital on Li and F atoms, with exponents of 0.08. The diffuse atomic functions play the twofold purpose of improving the description of the F^- ion, and defining the cosphere where the polarization charge density is distributed.

Figure 2 shows two curves of dissociation for the ground state in the gas phase of LiF. Curve ***a*** is the dissociation at the SCF level. The computed dipole moment at the equilibrium distance ($r = 1.56$ Å) is 6.246 D in excellent agreement with the experimental value (8) of 6.284. Curve ***b*** includes electronic correlation CI. It can be noted that for distances larger than 6.5 Å this curve behaves abnormally. Kahn et al. [13] studied the potential curve of LiF by *ab initio* configuration methods. They found that in order to have a good description of the dissociation, it is necessary to account for the variation of electronic structure. When including solvent effects, according to Eqs. (1) and (7), a double well free energy curve is obtained. It is shown in Fig. 3. It may be seen that at a separation of about 6 Å a first minimum, corresponding to an ion pair is obtained. A desolvation barrier of about 30 kcal/mol must be overcome before the formation of the neutral molecule at about 1.56 Å. In the opposite direction, a dissociation barrier of about 14 kcal/mol has been estimated.

The discussion of the ionic region of the free energy curve beyond 7 Å may not be discussed with great detail because variation of electronic structure, which according to Kahn is required in this case [13], were not included in the present calculation. The *cut off* criterion was established according to the distance at which the overlap between the 6*S* diffuse orbitals vanishes (i.e. $R_{AB} > 6.5$ Å). Figure 4 displays the variation of the overlap integral with respect to the

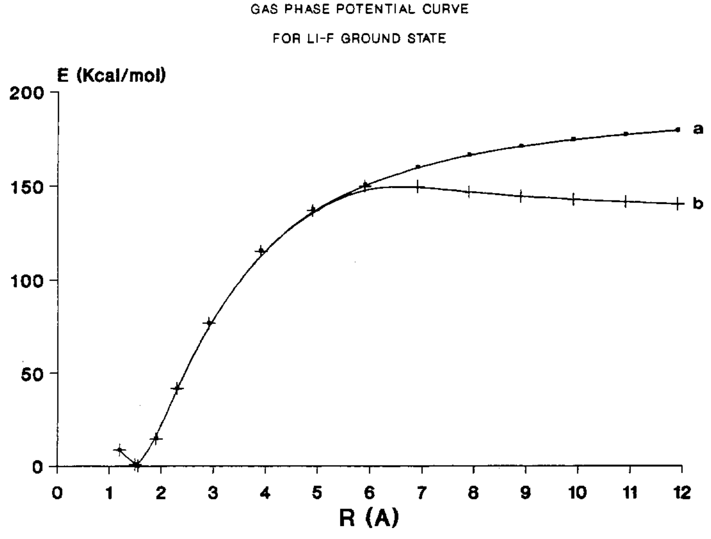

Fig. 2. Gas phase total energy curves for the dissociation of Li-F. SCF (curve A) and SCF + CI (curve B)

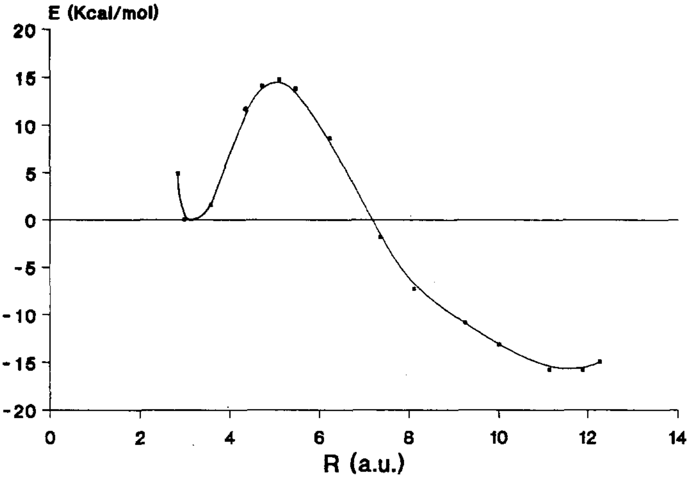

Fig. 3. Free energy curve, including solvent effects, for the dissociation of Li-F

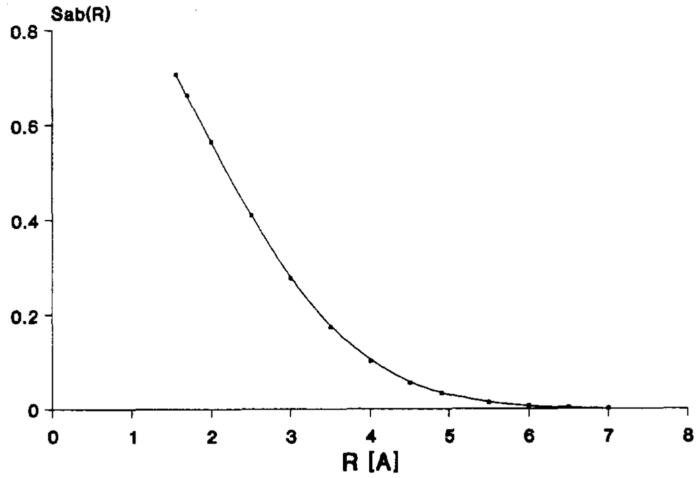

Fig. 4. Variation of the Overlap between diffuse orbitals with respect to the interatomic distance

interatomic distance. It is found that this overlap function behaves as:

$$S(R_{AB}) = \exp[-\alpha R_{AB}^2] \tag{10}$$

with $\alpha = 0.1432$.

Also, it is interesting to characterize the variation of the net charge with respect to the overlap integral. Through a polynomial fit of the calculated points, we have found the following analytic expression:

$$Q(S) = 0.941 - 0.644S + 0.427S^2 \quad (1.56 < r < 6.0) \tag{11}$$

that adequately represents the function $Q(S)$, as can be seen in Fig. 5. Combination of Eqs. (10) and (11) may be used to get a simple analytic expression to

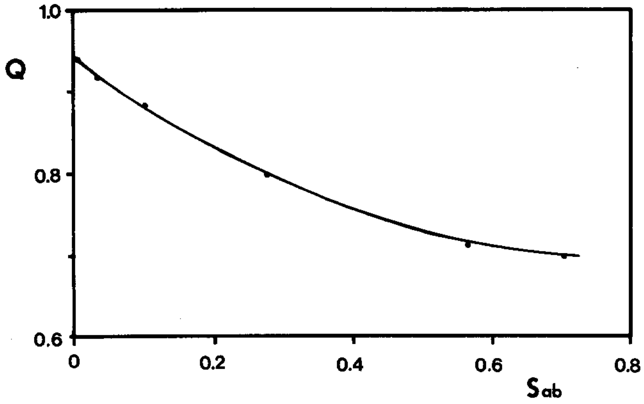

Fig. 5. Net charge variation with the overlap between diffuse 6*s* atomic orbitals

describe the net charges as a function of R_{AB}, leading to a direct characterization of the polarization charge along the reaction coordinate.

After our results, it seems that the dissociation of Li-F in a strongly polarizable medium occurs in two elementary steps. The first one (ionization) consists in the formation of an ion pair at a distance of about 6 Å. An ionization barrier of about 14 kcal/mol was estimated. The second one corresponds to the dissociation of the ion pair into the free F^- and Li^+ ions. The present calculation does not permit further discussion about this last step, due to the poor description of the free energy curve in the dissociative region (i.e. beyond 6.5 Å). However, some qualitative discussion, in terms of the electrostatic entropy changes, may be drawn for the dissociation process. Starting from Eqs. (5) and (7), and using the classical thermodynamic relationship:

$$DS = -[dD\,G/dT]_V \tag{12}$$

where V is the volume of the dielectric, we obtain:

$$TDS^{el}(\varepsilon, P) = -\frac{1}{2}\frac{T\,dL\,n\varepsilon(T)}{dT}\sum_A [V_R(\varepsilon, P)_A Q_A(P)] \tag{13}$$

Calculations of the electrostatic entropy of solvation were done using Eq. (10) for the neutral Li-F ($R_{AB} = 1.56$ Å), the undissociated ion pair ($R_{AB} < 6$ Å) and the free ions ($R_{AB} \to \infty$). The intrinsic dissociation entropy was neglected. The following values for the TDS^{el} were obtained: 1.8 kcal/mol, 4.6 kcal/mol and 5.6 kcal/mol for the neutral molecule, ion pair and free ions, respectively. This gives an ionization entropy change of 2.8 kcal/mol and a dissociation entropy change of 1.0 kcal/mol. This result may indicate that the undissociated ion pair appears to behave as a more powerful solvent structure breaker than the neutral molecule. On the other hand, as expected, the free ions behave as more powerful promoters of solvent structure. In other words, a zone of disorder analogous to that proposed to exist around a structure-breaking ion must thus result in passing from the neutral to the undissociated ion pair forms of Li-F [14]. This entropic contribution, although modest, could be relevant to discuss a probable barrier separating the undissociated ion pair and the free ions (i.e. the dissociation barrier). It is clear that a definitive answer to ths question requires the complete calculation of the free energy curve, including long range interactions. Work along this line is actually on course in our group.

4. Concluding remarks

We have presented a perturbative reaction field model of continuum solvent effects representation that includes a desolvation potential. This desolvation potential appears after separating the source and polarization charge distribution using a "pseudo molecular orbital" representation for the polarization charges. As a result, the desolvation potential behaves as a continuous function of the internuclear distance through the overlap integral between the diffuse atomic orbitals. The Li-F system has been used as a model to illustrate the reliability and usefulness of the proposed formulation. A double well potential for the dissociation of Li-F has been obtained. Barriers to ionization towards an ion pair complex and dissociation have also been obtained. In contrast with previous work reported by Klopman and Andreozzi [15], the present methodology includes the macroscopic dielectric constant ε as the unique parameter of the calculation.

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