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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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(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