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Effect of Hydration on the FH . . . NH_3 Proton Transfer Reaction: Comparison of Some Quantum Chemical Approximations

János Ángyán and Gábor Náray-Szabó
CHINOIN Pharmaceutical and Chemical Works, P.O.B. 110, H-1325 Budapest, Hungary

The proton transfer energy curve for the hydrogen fluoride—ammonia system was studied by semi-empirical methods *in vacuo* and in a hydrated form. It was found that the simple point-charge approximation cannot be used to estimate the Coulombic interaction term rather the molecular electrostatic potential has to be considered. Furthermore, even inclusion of the mutual polarization term is insufficient if quantitative agreement with CNDO/2 supermolecule results is desired since charge transfer plays an important role.

Key words: Proton transfer—Effect of hydration on proton transfer—Semi-empirical treatment of proton transfer.

Proton transfer plays an important role in several chemical and biochemical events [1] therefore its quantum chemical study is of considerable importance [2-3]. In the following we report on quantitative estimation of hydration effects which are often decisive. We treated the FH...NH_3 system and the first hydration shell was modelled by six water molecules (Fig. 1). Reference calculations on the supermolecule were done at the CNDO/2 level of approximation [3-4] keeping all atomic positions, but that of the transferring proton, fixed. Though the CNDO/2 method overestimates interatction energies of hydrogen-bonded complexes it may be used for comparative purposes.

Our goal is to compare some simple methods which are thought to reproduce trends in the variation of hydration energies in the course of proton transfer. One is the point-charge (PC) approximation where empirical or quantum mechanical atomic charges are used to calculate the Coulombic interaction energy (see e.g. Ref. [5]). Another possibility is to replace atomic charges in the hydration

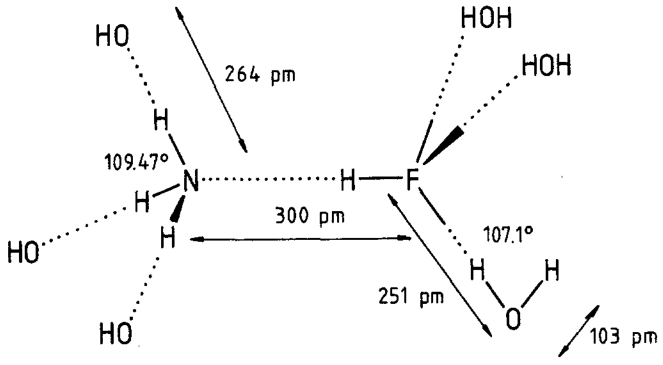

Fig. 1. Geometrical model of the hydrated FH...NH_3 system

shell by the electrostatic potential. Thus the interaction becomes

$$E^{\mathrm{VPC}} = \sum_{a} q_a V_s(\boldsymbol{r}_a) \qquad (1)$$

where q_a is the CNDO/2 net charge on atom a of the solute while $V_s(\boldsymbol{r}_a)$ stands for the solvent electrostatic potential at the same atom. We calculated this by our bond-increment method [6–7]. For the point-charge approximation $V_s(\boldsymbol{r}_a) = \sum q_b r_{ab}^{-1}$. Finally, we applied the inhomogeneous self-consistent reaction-field (INSCRF) method of Tapia [8–9] which considers, besides Coulombic terms, mutual polarization between solute and solvent, too.

Results are summarized in Table 1 and in Fig. 2. It is seen that the INSCRF method alone is able to reproduce the double-minimum character of the potential curve obtained for the supermolecule. However, owing to the neglect of charge transfer which is overestimated by the CNDO/2 method, the agreement is not quantitative. Interaction energy differences for proton positions $R_{\mathrm{H...F}} = 180$ and 100 pm are 339 and 231 kJ/mol (68%) for the supermolecule and INSCRF models, respectively. Eq. (1) yields 181 kJ/mol (53%) and 89 kJ/mol (26%) is obtained using the point-charge approximation. The low extra stabilization energy for the ion-pair form makes that the E_{PC} curve in Fig. 2 is almost equivalent to E_{VAC} depicting the energy change upon proton transfer *in vacuo*. From this we conclude that it is not advisable to use the point-charge approximation to consider hydration effects on proton transfer reactions.

Despite larger sophistication, the INSCRF method yields no considerably better stabilization energy for the ion-pair form than the VPC model does. Fig. 2 indicates the very pronounced shoulder on the E_{VPC} curve which is close to reflect the double-minimum character. Since the INSCRF method works at present only at the CNDO/2 level of approximation several types of solute rearrangements are beyond its scope. No such problem arises for the VPC approximation of Eq. (1) since the solute may be treated by any desired quantum chemical method. It is this feature which makes it a severe competitor to the INSCRF method.

Table 1. Energy change (in kJ/mol) in the free and hydrated FH...NH_3 system as the function of the proton position ($R_{H...F}$ in pm). From each entry 110,000 kJ/mol is substracted. The total CNDO/2 energy of the hydration shell $E(6H_2O)$ is −312,671 kJ/mol

$R_{H...F}$	$-E_{VAC}$	$-E_{PC}$	$-E_{VPC}$	$-E_{INSCRF}$	$-E_{SUPER}$ $+E(6H_2O)$
200	414	568	723	891	953
190	523	660	799	953	1006
180	582	701	822	965	1000
170	625	727	830	961	975
160	672	758	843	962	959
150	734	805	875	985	967
140	817	875	932	1033	1004
130	917	964	1011	1105	1067
120	1021	1060	1099	1188	1144
110	1107	1141	1174	1260	1210
100	1138	1168	1197	1290	1227
90	1058	1083	1110	1203	1134

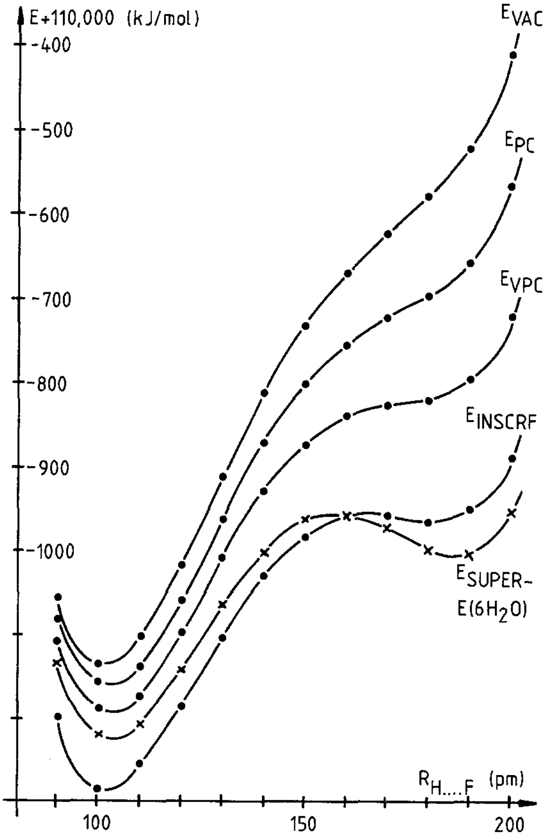

Fig. 2. Potential curves for the proton transfer reaction as obtained by various approximations. Subscripts refer to the notations given in the text

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