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Original Investigations

Solvatons. II. Aqueous Dissociation of Hydrides in the MINDOS Approximation

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A simple electrostatic model of solvation is presented which allows the interaction with solvent to be included systematically within semiempirical SCF calculations. Solvent effects are incorporated into the Hamiltonian for a solute molecule through a series of imaginary particles, solvatons, which represent the oriented solvent distribution around the solute.

The proposed model is based on an algorithm for approximating the enthalpy of solvation of each atomic center from its charge in the molecular system and the experimental hydration enthalpies of its various ions. The calculated atomic solvation energy of one center is then modified to include the interaction with other charged atomic centers in the molecule. The method, developed here for the MINDO/3 approximation, has been applied to the calculation of the aqueous dissociation of a series of hydrides. In general, it leads to fairly accurate solvation enthalpies and pK_a values when applied to systems with fixed molecular geometries. A general discussion of the problems associated with the development of a solvation model within a semiempirical framework is also presented.

Key Words: Heat of solvation – Hydrides, aqueous dissociation of ~

Within the last decade, quantum mechanical techniques have become sufficiently sophisticated to handle the calculation of the molecular properties of large molecules quite reliably. The methods have gained widespread acceptance and have become invaluable tools for many fields of chemistry. Application of the techniques has been limited, however, to calculations of molecular properties in the gas phase. Since the majority of processes of interest to chemists occur in solution and solvents are known to affect the structures and energies of solutes, the representation of the solvation phenomena within quantum chemical computations is a very active area of current research. The traditional approach to the problem, the super molecule method, although promising, suffers from the very practical considerations of computation time and economic feasibility. At present then, no generally applicable methodology for the inclusion of solvent effects within normal SCF calculations is available.

In this paper, we wish to report some preliminary results obtained from a simple electrostatic model which allows the interaction with solvent to be included systematically within SCF MO theory, developed here for the MINDO/3 [1] approximation. The method is based on an application of our solvation theory [2], a procedure in which the solvent distribution around a solute is represented by situating fractional charges at the atomic centers of a given molecular system. The rules that govern the interactions between the "solvatons" and atoms have been derived so as to match both the Born equation and the laws of electrostatics in solution. As a result of the presence of these solvent clusters, the Hamiltonian expression for a solute is modified to include solvation Hamiltonian terms – a refinement over classical electrostatic approaches [3, 4] in which solvent effects are merely tacked on to the already minimized quantum mechanical results. Several extensions [5, 6] of our original theory have already been implemented in the literature, and, in at least one case [7], have proved extremely successful in predicting the effect of solvent on molecular properties such as total energy, electronic transition energies and spin densities of radical anions and molecules.

In our present model, the enthalpy of solvation is approximated by an expression of the form,

$$S=-\sum_{\mathrm{A}}[(aQ_{\mathrm{A}}+bQ_{\mathrm{A}}^{2})(\sum Q_{\mathrm{X}}L_{\mathrm{X}})D_{\mathrm{A}}]\left(1-\frac{1}{\varepsilon}\left(1+T\frac{\partial \ln \varepsilon}{\partial T}\right)\right)$$

which is conveniently broken down into a series of one- and two-center terms. The one-center term has the form $aQ_{\mathrm{A}}^2+bQ_{\mathrm{A}}^3$ and represents the solvation of each atomic center in the molecular system, where Q_{A} is the charge on atom A and a and b are parameters characteristic of the atom and determined from the experimental hydration enthalpies and radii of the ions (parameter selection discussed in detail below). The two-center terms are of the form $(aQ_{\mathrm{A}}+bQ_{\mathrm{A}}^2)(\sum_{\mathrm{X}\neq\mathrm{A}} Q_{\mathrm{X}}L_{\mathrm{X}})D_{\mathrm{A}}$ and represent the effect of neighboring atoms on the solvation of atomic center A. Here, $\sum_{\mathrm{X}\neq\mathrm{A}}Q_{\mathrm{X}}L_{\mathrm{X}}$ is included to represent the effect of neighboring charges on the solvation of atomic center A and D_{A} to represent the accompanying change in the atomic radius of A due to the presence of other atoms. L_{X} and D_{A} are functionals dependent on both the nature of atom A and atom X, whose precise forms will be discussed in detail shortly. For the dielectric constant ε, we use the bulk macroscopic value although the actual dielectric constant of a solvent in the vicinity of an ion is known to be a function of distance from the ion's center [8].

Considering $Q_{\mathrm{A}}=Z_{\mathrm{A}}-2\sum_i c_i^2$ (where Z_{A} is the core nuclear charge on atom A and $2\sum_i c_i^2$ is its total valence shell electron density), the diagonal terms of the

MINDO/3 core and F matrix elements for a solute molecule are now given by:

$$H_{ii}^{A,A} = H_0 + \Big[(a_A + 2Z_A b_A) D_A \sum_X Z_X L_X + \sum_X Z_X (a_X + Z_X b_X) L_X D_X \Big] \left(1 - \frac{1}{\varepsilon}\left(1 + T\frac{\partial \ln \varepsilon}{\partial T}\right)\right)$$

$$F_{ii}^{A,A} = H_{ii}^{A,A} + F_0 - \Big[4 \sum_i c_i^2 b_A D_A \sum_X Z_X L_X + 2 \sum_X \sum_j c_j^2 (a_X + 2Z_X b_X) L_X D_X + 2(a_A + 2Z_A b_A) D_A \sum_X \sum_j c_j^2 L_X + F_i^A \Big] \left(1 - \frac{1}{\varepsilon}\left(1 + T\frac{\partial \ln \varepsilon}{\partial T}\right)\right)$$

where H_0 and F_0 are the gas phase core and F matrix elements respectively and

$$F_i^A = \Big[4 \sum_X \sum_j c_j^2 \sum_j c_j^2 b_X L_X D_X + 8 \sum_i c_i^2 b_A D_A \sum_X \sum_j c_j^2 L_X \Big] \left(1 - \frac{1}{\varepsilon}\left(1 + T\frac{\partial \ln \varepsilon}{\partial T}\right)\right).$$

The total electronic energy of the system is now given by:

$$E_{\text{electronic}} = \sum_i c_i^2 [H_{ii} + F_{ii} - (F_i/3)]$$

and the total intercore repulsion energy is defined as:

$$E_{\text{core}} = \sum_A \sum_X CR_{AX} - \sum_A Z_A (a_A + Z_A b_A) D_A \sum_X Z_X L_X \left(1 - \frac{1}{\varepsilon}\left(1 + T\frac{\partial \ln \varepsilon}{\partial T}\right)\right)$$

where CR_{AX} is the potential energy of repulsion between the cores of atoms A and X as defined for the gas phase interactions.

Before proceeding with a discussion of our methods of parameterization, mention should be made of the difficulties which appear when trying to compare theoretical estimates of solvation energies with experimental results. Judging from the recent literature, the development of a solvation model and the method for fitting parameters to experimental data is a subject open to debate. One possible approach (Method 1) is to try to fit the heats of formation of molecules in solution with their experimental values. In this procedure, the errors inherent to the gas phase calculation method are compensated by solvation terms. Unfortunately for ions, gas phase calculations are very erratic and as a result, the solvation term loses its meaning and known trends disappear from it. On the other hand, one may fit the differences in energy between the stabilities of the solvated and gas phase species to the corresponding experimental values (Method 2). Although at first sight, this seems to be a better procedure, the results one obtains for dissociating molecules into ions in solution rapidly loses its meaning. This dilemma is illustrated below (Table 1) for the case $NH_4^{\oplus} \rightleftharpoons NH_3 + H^{\oplus}$ dissociating in water ($\varepsilon = 78.3$) at 25°C.

The difference in energy between $NH_4^{\oplus}$ and $NH_3 + H^{\oplus}$ is experimentally known to be 12.48 kcal in favor of $NH_4^{\oplus}$. By definition, this is found to be the correct value in Method 1, but the price we had to pay for this is to modify the experimental

Table 1. Comparison of methods for developing a solvation model from experimental data[a]

	ΔH_f (Gas, kcal/mole)		Heat of Solvation (kcal/mole)				ΔH_f (Solution, kcal/mole)			
Species	Exp	MINDO/3	Exp	Method 1	Method 2	Method 3	Exp	Method 1	Method 2	Method 3
NH_4^+	150.0	153.9	82.35	86.25	$\underline{82.35}$	84.50	$\underline{67.65}$	67.65	71.46	69.40
NH_3	−11.04	−9.29	7.29	9.04	$\underline{7.29}$	$\underline{7.29}$	−18.33	$-\underline{18.33}$	−16.58	−16.58
H^+	365.76	340.40	267.30	241.94	$\underline{267.30}$	241.30	98.46	$\underline{98.46}$	73.10	$\underline{98.46}$
				$[\Delta H_f(NH_4^+) - \Delta H_f(NH_3 + H^+)]$			−12.48	−12.48	14.94	$-\underline{12.48}$

[a] The underlined values are those fitted to experiment.

solvation energies by a random amount dictated by the error one makes using MINDO/3 to calculate gas phase stabilities. If on the other hand, we choose to fit the solvation energies as in Method 2, then, due to the large errors that MINDO/3 generates on calculating ions, the very sensitive dissociation energies lose their meaning. In this case, we find that $NH_4^{\oplus}$ is the least stable entity by 15 kcal. Such parameterization precludes any possible geometry minimization and should be restricted, if used, to the calculation of solvation energies *per se.*

There is an alternative approach to the choice of a solvation model which, in a sense, represents a compromise between Methods 1 and 2. This procedure makes use of the fact that the large errors in the dissociation energies with Method 2 can be attributed directly to the spurious results for the calculation of gas phase ions alone. If the error in the ions is compensated for by corrected solvation energies, the experimental solvation energy may still be fitted for the neutral molecule (Method 3) and the experimental dissociation energy may still be reproduced. For the case discussed above, the solvation energy of NH_3 is first fitted to its experimental value of 7.29 kcal, and the experimental dissociation energy, 12.48 kcal, is then used to calculate the heat of formation of $NH_4^{\oplus}$ in solution, 69.4 kcal/mole.

According to our algorithm for approximating the enthalpy of solvation, two variables, a and b, are used to characterize the solvation of each atomic center and two two-center terms, $\sum Q_X L_X$ and D_A, account for changes in this solvation energy due to its presence in a molecular system. For each atom, a and b are found by solving a set of n equations (corresponding to n valence states of the atom) of the form:

$$S_{(\mathrm{X}^{\pm Q})} = aQ_{\mathrm{A}}^2 + bQ_{\mathrm{A}}^3$$

where S is the experimental hydration enthalpy of the ion at 25°C (for which $\varepsilon = 78.3$ and $(\partial \ln \varepsilon)/(\partial \ln T)_p = -1.357$) or an approximated hydration energy calculated from the Born–Bjerrum equation and an effective ionic radius. For the quasi-molecular term $\sum Q_X L_X$, L_X was chosen as P_{AX}/R only after a careful analysis of many functional forms. ($\lim_{R \to 0} L_X = 1$ and $\lim_{R \to \infty} L_X = 1/R$). Here, P_{AX} is a two-center term which is fitted from the experimental solvation energies of a series of compounds containing the atom–atom interaction in question, e.g. the value of the (O, H) and (H, O) parameters is obtained from a fit to the solution energies and dissociation behavior of a series of compounds such as $OH^{\ominus}$, H_2O, $H_3O^{\oplus}$, etc. The other molecular-type term, D_A, is a functional to account for the change in radius of atomic center A due to the presence of neighboring atoms. It is, in effect, a steric inhibition to solvation representing the decrease in the solvation term as two ions approach each other within bonding distance. A number of functions generating S-type curves for the bonding region and beyond have been tried in our formalism, but inclusion of this steric factor is negligible in terms of the calculation of the heats of formation of species in solution or their dissociation behavior. (In the test cases presented below, D_A is neglected.) Values of the atomic parameters, a and b, and the P_{AX} two-center terms for a selected series of atom–atom interactions are summarized in Table 2.

Table 2. *a*, *b*, parameter values for atoms and P_{AX} values for selected atom–atom interactions

Atom	*a*	*b*	A/X	P_{AX} H	C	N	O	F	Cl
H	7.5285	2.9655	H	0.57943	0.62520	0.77081	0.96980	0.8668	0.9900
C	4.1287	0.34153	C	0.9100					
N	5.3810	0.42027	N	0.32252					
O	6.1110	0.27938	O	0.26299					
F	6.8853	0.14973	F	0.74300					
Cl	4.8459	0.24857	Cl	1.0					

Our solvation model has been extensively tested on the hydration behavior of the first-row hydrides including H_2, H_2O, $OH^\ominus$, $H_3O^\oplus$, HF, HCl, CH_4, $CH_3^\oplus$, $CH_5^\oplus$, $NH_4^\oplus$, NH_3, $NH_2^\ominus$. Although the new method is not successful in handling geometry optimization, it does lead to fairly accurate solvation enthalpies for systems with fixed molecular geometries. The calculated heats of formation for the hydrides in the gas phase and in water at 25°C are given in Table 3 along with the corresponding experimental gas phase and hydration enthalpies. Note that the largest errors are found for the ions, particularly for highly protonated species such as $CH_5^\oplus$ and $NH_4^\oplus$. (In fact $CH_5^\oplus$ is calculated to be nearly 33 kcal/mole more stable than dissociated $CH_4 + H^\oplus$ in aqueous solution.) This particular problem is presently under analysis and will hopefully be corrected in later versions of the program.

The real test of the model is, of course, its ability to provide an accurate dissociation picture in solution. We have, in fact, obtained a number of interesting curves for the dissociation of the hydrides in water and several other solvents. Graphical representations of the change in enthalpy as the X–H internuclear distance is varied, are presented for a few representative compounds in Figs. 1–4.

Table 3. Gas phase and hydration ($\varepsilon = 78.3$, $T = 25°C$) heats of formation of selected hydrides

Molecule	Heat of formation, gas (kcal/mole) Experimental	 MINDO/3	Heat of formation, solution Experimental	 MINDO/3
H_2	0.0	0.16	0.0	0.17
H_2O	−57.79	−53.56	−68.30	−68.29
OH^-	−34.1	−6.68	−153.60	−150.75
H_3O^+	139	145.26	30.34	29.17
HF	−64.80	−64.03	−74.82	−74.04
HCl	−22.10	−21.54	−26.28	−26.77
CH_4	−17.90	−6.18	−17.90	−6.18
CH_3^+	260	260.31	~180	162.89
CH_5^+		219.50		58.49
NH_4^+	150.0	153.94	67.83	59.35
NH_3	−11.04	−9.29	−18.33	−16.50
NH_2^-	24.0	56.47		−56.46

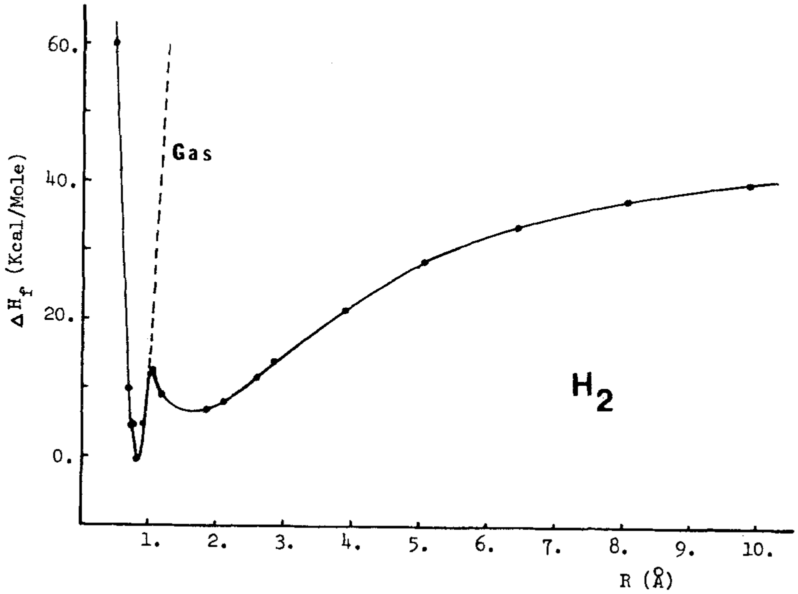

Fig. 1. Dissociation of hydrogen in water

Before proceeding with the detailed analysis of our calculations, a few general comments are offered about them. In order to produce a reasonable dissociation picture in solution, it is essential to understand and to try to describe as accurately as possible the various forces that exist between the interacting ions. At infinite separation, the calculated energy of the isolated ions corresponds to the calculated

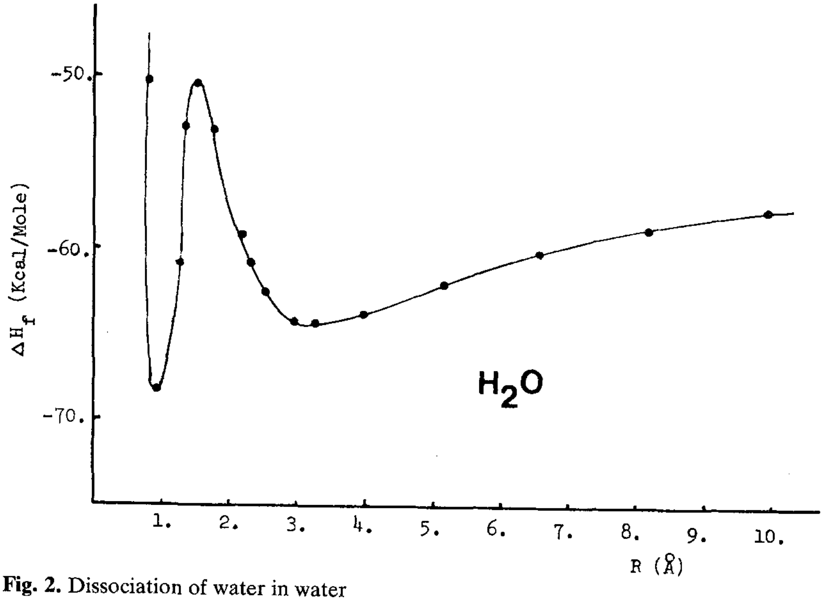

Fig. 2. Dissociation of water in water

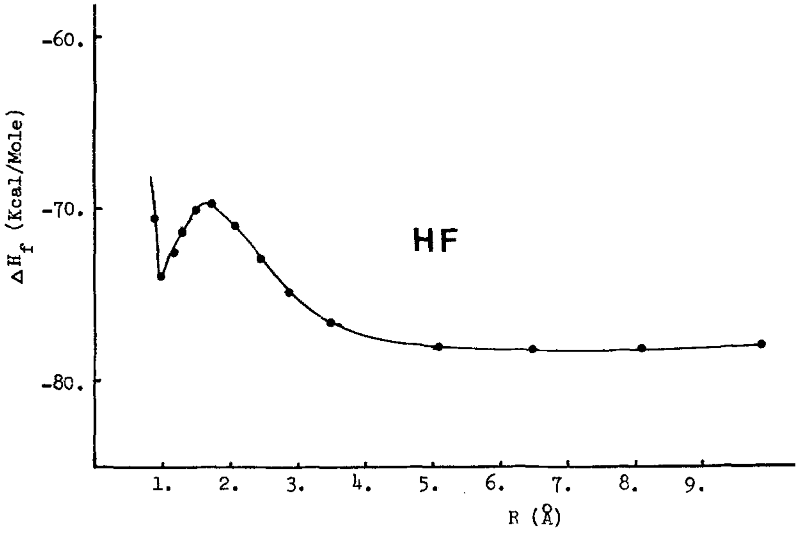

Fig. 3. Dissociation of hydrofluoric acid in water

value of the energy of the ions plus their solvation energy. As the two ions come into closer proximity, however, they are progressively desolvated as solvent molecules are expelled and bond formation begins. Thus, recombination of the ions during bond formation may require passage through an activation state

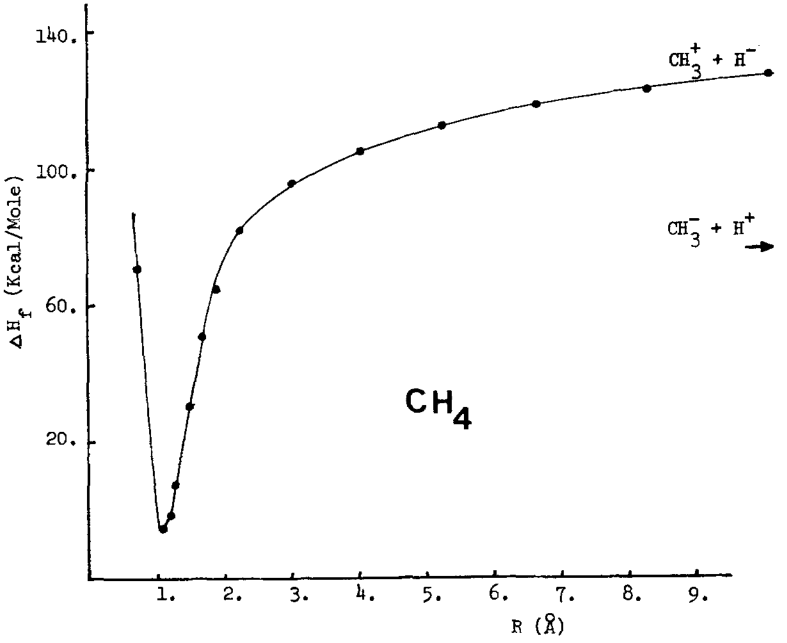

Fig. 4. Dissociation of methane in water (the CH_3 fragment's coordinates are not optimized once the dissociation has started)

before the solvated molecule is formed. Somewhere along this pathway of desolvation and bond formation the curve representing the change in energy with respect to distance tends to merge into the corresponding curve obtained in the gas phase. Depending upon the specific potential used to describe the desolvation at intermediate distances, the two curves merge at larger or shorter distances generating a high or low activation energy. As previously mentioned each of our two center interaction terms, P_{AX}/R_{AX}, is obtained from a fit to the solution energies and dissociation behavior of a series of compounds. Hopefully in this way we have chosen suitable desolvation potentials for each atom–atom interaction.

H_2. The dissociation of H_2 in aqueous solution parallels the gas phase behavior up to approximately 0.95 Å. A small dip of 5.35 kcal (representing the barrier to desolvation of the ions) is then followed by a smooth dissociation to $H^{\oplus} + H^{\ominus}$. The calculated enthalpy of dissociation is 53 kcal/mole.

H_2O. The dissociation of water is characterized by the initial formation of an $H^+ \cdots OH^-$ complex followed by its breakdown to the solvated ions. The activation barrier to dissociation is calculated to be 17.87 kcal and the overall barrier to recombination is nearly 2.0 kcal. The corresponding experimental values [9] for the dissociation of water and the recombination of the ions are 20.2 kcal and 3.5 kcal, respectively. Complex formation is apparent when the O–H internuclear distance is between 2.8–3.4 Å. The overall enthalpy of dissociation is calculated to be 16.21 kcal/mole. Deviation from the experimental value of 13.34 kcal can be directly attributed to the error made in the calculation of aqueous OH^-. From a calculation of the curve for the free energy of dissociation, we find the pK_a of water to be 16.63. An improved estimate of the pK_a, 16.10, can be obtained by using the calculated enthalpy value, 16.21 kcal, with the experimental entropy of -19.31 entropy units.

HF. Figure 3 depicts the dissociation of HF in water. It shows the formation of an ion pair at distances greater than 3 Å followed by an activation state during which solvent is expelled and finally the formation of an HF molecule at 1.05 Å (0.912 Å in gas phase). The barrier to dissociation is calculated to be 4.28 kcal. The calculated overall enthalpy of dissociation is -3.06 kcal/mole in excellent agreement with the experimental value of -3.18 kcal/mole. Based on the calculated enthalpy and an experimental entropy of dissociation of -25.2 entropy units, the pK_a of HF is found to be 3.23 compared with the experimental value of 3.17.

HCl. We calculate the enthalpy of solution of HCl gas in water at 25°C to be -18.64 kcal compared with the experimental value of -17.88 kcal. Formation of the HCl ion pair from molecular HCl (1.33 Å compared with 1.23 Å in the gas phase) occurs at distances greater than 2.8 Å and costs approximately 6.63 kcal/mole. The overall enthalpy of dissociation is found to be 12.95 kcal/mole. Based on the experimental dissociation entropy of -13.4 entropy units, this yields a pK_a for HCl of -6.56, also in excellent agreement with the experimental pK_a of -7.

CH_4. The aqueous dissociation of methane yields the carbenium ion $CH_3^\oplus$ and the hydride ion, although hydrated $CH_3^\ominus + H^\oplus$ is over 65 kcal lower in energy. The dissociation curve is characterized by a steady increase in the energy from molecular methane to the solvated ions. Without geometry optimization, we are, of course, dissociating methane to a tetrahedral carbenium ion rather than the most stable planar configuration. It is roughly 25 kcal less stable than the trigonal ion in both the gas phase and solution.

NH_3. The enthalpy of hydration of NH_3 gas at 25°C is calculated to be 7.21 kcal compared with the experimental estimate of 7.29 kcal/mole. Our calculated dissociation curve shows a steady increase in energy as the molecule dissociates and the solvated ion pair forms. The overall enthalpy of dissociation is calculated to be about 58 kcal/mole. From an estimate of the free energy of dissociation, the pK_a of NH_3 is found to be approximately 47.

NH_4^+. The ammonium ion is one of the cases in which the stabilization due to solvation is overestimated by a fairly large amount, approximately 10 kcal. The enthalpy of dissociation to $NH_3 + H^\oplus$ is thus in error by that amount, 22.79 kcal vs. the experimental value of 12.48 kcal/mole.

In spite of some uncertainties attached to specific energy values discussed above, we believe that the overall results are extremely encouraging and illustrative of what can be obtained with the proposed model. As previously indicated, we are currently examining and testing slightly modified algorithms to correct some of the "problem" cases discussed above. Furthermore, we are concentrating on the question of geometry optimization and the structure of a molecule engaged in a dissociation process will soon be the primary area of investigation.

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References

1. Bingham, R. C., Dewar, M. J. S., Lo, D. H.: J. Am. Chem. Soc. **97**, 1285 (1975)
2. Klopman, G.: Chem. Phys. Letters **1**, 200 (1967)
3. Chalvet, O., Huron, M. J., Peradijordi, F.: Compt. Rend. **259**, 1631 (1964); Chalvet, O., Jano, I.: Compt. Rend. **259**, 1867 (1964); Jano, I.: Compt. Rend. **261**, 103 (1965)
4. Botrel, A., Guirellot, C. R.: J. Chim. Phys. **71**, 974 (1974)
5. Germer, H. A.: Theoret. Chim. Acta (Berl.) **34**, 145 (1974); **35**, 273 (1974)
6. Constanciel, R., and Tapia, O.: Theoret. Chim. Acta (Berl.) **48**, 75 (1978)
7. Miertus, S., Kysel, O.: Chem. Phys. **21**, 27, 33, 47 (1977)
8. Noyes, R. M.: J. Am. Chem. Soc. **84**, 513 (1962)
9. Ertl, V. G., Gerischer, H.: Z. Elektrochem. **66**, 560 (1962)

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