

absolute values of the quantum yields are not required since eq 11 contains the ratio  $\Phi_P^0/\Phi_P$ . It is therefore felt that the present mean  $k_3/k_E$  value of about 25 is more reliable than the previous<sup>2</sup> estimate. For this reason the earlier value<sup>2</sup> is not listed in Table VII.

The activation energy for addition of O(<sup>3</sup>P) atoms to ethylene has been discussed by DeMore in a very recent paper.<sup>8</sup> Using DeMore's method of calculation, we also obtain about 0.5 kcal/mol as an activation energy difference ( $\Delta E$ ) between the O + C<sub>2</sub>H<sub>4</sub> reaction and O + C<sub>3</sub>H<sub>6</sub> or O + 1-C<sub>4</sub>H<sub>8</sub> reaction. Similar  $\Delta E$  values can be also obtained by comparing the ratios of rate constants at 77 and 87.5°K listed in Table VII. On the other hand, comparison of the relative rates at cryogenic temperatures with the gas phase values at 298°K gives  $\Delta E$  of about 0.3 to 0.35 kcal/mol for the above reactions and it also gives for isobutene an activation energy approximately equal to that of ethylene but a 25 times larger *A* factor. This last result would be particularly difficult to accept but would be readily understandable assuming, as discussed earlier, that O(<sup>3</sup>P) reactions with C<sub>3</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>8</sub>, and O<sub>2</sub> are diffusion controlled in liquid nitrogen solution at 77°K (and perhaps also in liquid argon at 87.5°K). Under these conditions the above calculations give only the *lower limits* for  $\Delta E$ . At the same time, the fact that the reactions studied here occur readily at cryogenic temperatures and that some of them are fast enough to be diffusion controlled in liquid nitrogen solution at 77°K places some constraints on the upper limits of the  $\Delta E$  values and of the indi-

vidual activation energies. It may therefore be concluded that the latter must be relatively small, as has been known for some time,<sup>3c, 20, 21</sup> although this conclusion retains here a largely qualitative character. The quantitative aspect of the competitive cryogenic results may be influenced by such factors as the finer details of the diffusion-controlled processes in liquid nitrogen solution at 77°K and the possibility<sup>3c, 21</sup> that  $\pi$ -complex formation between O(<sup>3</sup>P) and olefins may precede the addition reaction under the experimental conditions employed in this study and thus effectively prolong the duration of the "encounters" and speed up the slower of these reactions.

**Formation of Minor Products.** As mentioned earlier, formation of certain minor products (acetaldehyde and formaldehyde in the case of propylene, propanal and formaldehyde in the case of 1-butene, and acetone in the case of isobutene) was observed in the course of the reactions studied. Formaldehyde was also observed as a minor product in the previous study of the O(<sup>3</sup>P) reaction with ethylene in liquid N<sub>2</sub> solution.<sup>2</sup> These minor products are perhaps due to an unavoidable minor thermal attack of ozone on these olefins under the experimental conditions employed, since these products are the major products in the thermal reaction of ozone with the same olefins in the gas phase.<sup>22</sup>

(20) D. D. Davis, R. E. Huie, J. T. Herron, M. J. Kurylo, and W. Braun, *J. Chem. Phys.*, **56**, 4868 (1972).

(21) R. Atkinson and R. J. Cvetanović, *J. Chem. Phys.*, **56**, 432 (1972).

(22) T. Vrbaski and R. J. Cvetanović, *Can. J. Chem.*, **38**, 1063 (1960).

## Stabilization of the Local Water Structure due to Oxygen or Nitrogen Molecules

Germund Höjer\* and Jaime Keller

*Contribution from the División de Estudios Superiores de la Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México 20, D.F. Received September 7, 1973*

**Abstract:** A CNDO study of the influence of oxygen, nitrogen, and water molecules on a model for the local water structure indicates that it is quite possible that air in water would have a stabilizing effect on the water structure. The calculated effect is about 0.5 kcal/mol per hydrogen bond in the particular water model chosen, which should be compared with an experimental value of 0.1 kcal/mol per hydrogen bond for such a stabilizing effect due to air obtained in surface tension experiments.

During the past years a great number of qualitative and quantitative theories<sup>1-7</sup> have been proposed to explain the properties of water and water solutions and to elucidate their structures. Most of these theories

(1) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, 1969, general survey of experimental and theoretical work on water.

(2) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(3) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

(4) O. Ya. Samoilov, "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions," Consultants Bureau, New York, N. Y., 1965.

(5) J. A. Pople, *Proc. Roy. Soc., Ser. A*, **205**, 163 (1951).

(6) J. D. Bernal, *Proc. Roy. Soc., Ser. A*, **280**, 299 (1964).

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

include considerations of water polymers with long lifetimes compared to the dielectric relaxation time, around 10<sup>-11</sup> seconds at room temperature. Among the configurations which have been considered for these hydrogen-bonded water polymers, ice-like cage structures have always played a central role in the description of the local geometry of water in the bulk of the liquid and in the surface or the interface. This is just natural if the hydrogen bonds in water are thought to be similar to those in ice in any of its many polytypes. In an early study of the X-ray diffraction pattern of water, Bernal and Fowler<sup>2</sup> suggested that liquid water had an extensive four-coordinated struc-

ture similar to ice I or the silicon atoms in quartz. This ordering breaks down with rising temperature. However, it is clear, from a detailed analysis of the diffraction pattern, that a simple tetrahedral structure of the water molecules does not completely explain the experimental results. Later more detailed models for liquid water have been able to account for the experimental X-ray diffraction curve with a high degree of accuracy. The merit of any particular model must be judged on its ability to explain other experimental data. All these models contain the concept of hydrogen-bonded water molecules.

Nemethy and Scheraga<sup>3</sup> suggested that the local structure of water is made up of a mixture of tetrahedrally coordinated hydrogen-bonded molecules and nonbonded molecules. The hydrogen-bonded clusters form and break up continuously and all the water molecules have on the average the same environment. The concentration of nonhydrogen-bonded molecules increases with the temperature. In the model proposed by Samoilov<sup>4</sup> the hydrogen-bonded molecules form ice I-like frameworks while the non-hydrogen-bonded molecules are placed inside the cavities of the framework. The melting of ice I is then interpreted as the breaking of some of the hydrogen bonds with the result that a few water molecules go interstitial. In that way the increase in density when ice melts could be explained. Pople<sup>5</sup> suggested that liquid water is made up of extensive regular hydrogen-bonded networks, where, however, the bonds are distorted. This model does not completely account for the observed X-ray diffraction pattern. This problem is solved in Bernal's<sup>6</sup> extension of the distorted hydrogen bond model. Here the water molecules form irregular networks of rings. Each molecule is four coordinated by hydrogen bonds. These bonds may be distorted. In the clathrate model proposed by Pauling<sup>7</sup> 20 hydrogen-bonded molecules form a cluster. Here it is also reasonable to assume interstitial molecules. But this model gives a low density (0.98 g/cm<sup>3</sup>) and a too low heat capacity for water.

The dynamical method for the measurement of the water to air surface tension<sup>8</sup> and the recent studies by Sobol, *et al.*,<sup>9</sup> on the aging of the water-air interface show large changes in the surface tension with the time elapsed since the formation of the interface and with the concentration of air in the liquid previous to the creation of the interface. The behavior observed by Sobol indicates a large change in the structure of the interface with time when foreign molecules are present.

Our problem has been to investigate the possible influence of oxygen, nitrogen, or water molecules on a water structure. To do this it is necessary to have a model for water. At present there is no clear reason to prefer any one of the above mentioned models to the others. However, they all assume that the structure of water depends on hydrogen bonding and that each water molecule is essentially "tetrahedral." It seems to us then quite reasonable to assume an ice-like cage as a first approximation for a local structure in liquid water. We chose a cage made up of ten water molecules arranged as in ice Ic. Once the oxygens are fixed it is possible to choose the positions of the hydrogens

(8) W. Drost-Hansen, *Ind. Eng. Chem.*, **57**, 19 (1965).

(9) H. Sobol, J. Garfias, and J. Keller, "The Effect on the Water/Air Surface Tension of Air Diffusion and Interface Structuring," submitted for publication.

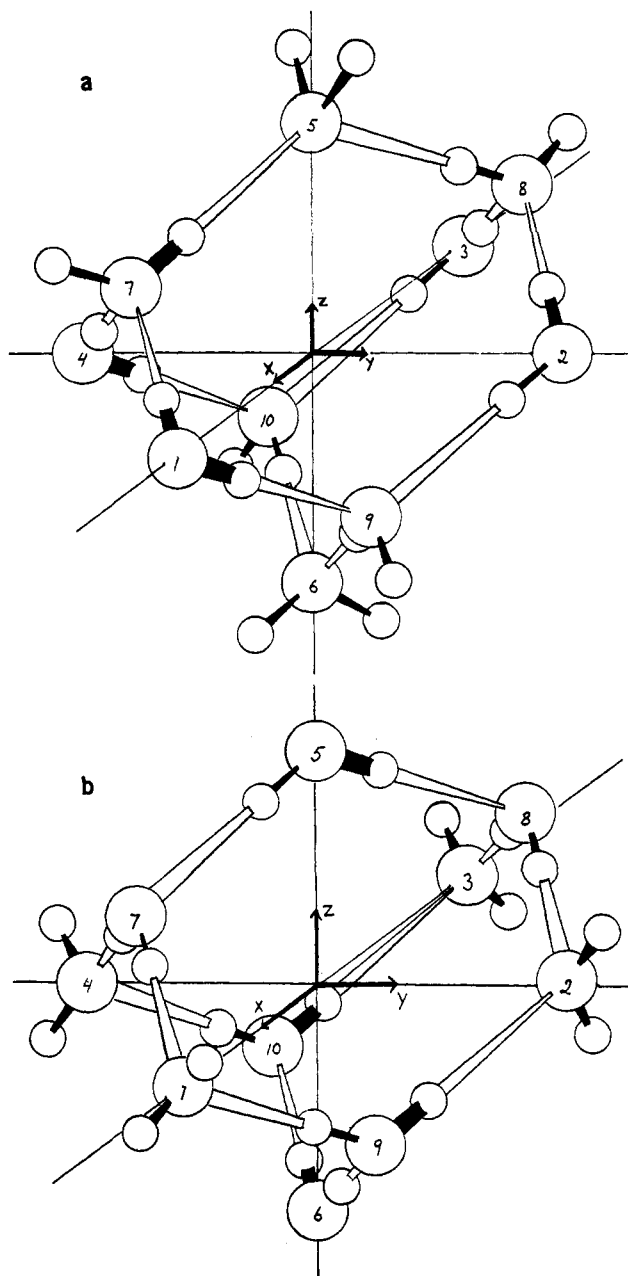


Figure 1.

in two different ways to obtain a cage without a resulting dipole moment. These two cages have the symmetry  $D_{2d}$ ; see Figure 1. These symmetric cages simplify the choice of positions for the interacting foreign molecules. Furthermore these ten-membered cages are big enough to trap a water or an oxygen molecule. These cages are only meant to represent the first layer of water molecules around an oxygen or a nitrogen molecule trapped in the liquid. The surrounding water will interact with both the cage and the interstitial molecule but the main part of the effect we want to study is supposed to be in the interaction between the foreign molecule and the nearest water molecules. Our model in this paper is not meant to suggest that liquid water consists of independent clusters. Some further remarks on this model will be reported elsewhere.<sup>10</sup>

(10) G. Höjer and J. Keller, *Int. J. Quantum Chem.*, accepted for publication in the Sanibel Proceedings issue.

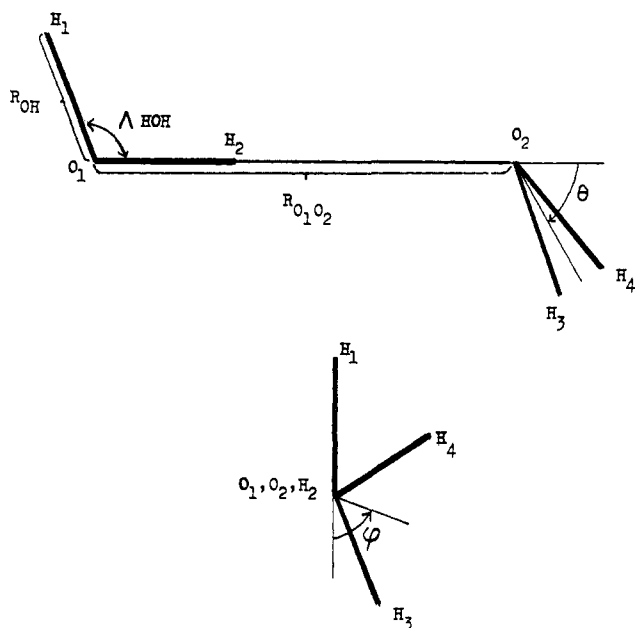


Figure 2.

### Calculation of the Electronic Structures of the Cages

The stabilities and the charge distributions of the cages were studied by means of a CNDO program<sup>11</sup> written by one of us.

The energies involved in hydrogen bonding are very small and the effect, if any, of a foreign molecule like O<sub>2</sub> on a hydrogen-bonded water structure even smaller. To study these problems accurately would require extended basis *ab initio* calculations. However, the size of the problem from a computational point of view excludes such an approach. We have to settle for a less accurate semiempirical method like CNDO. It is then necessary to estimate the validity of the method in this particular problem. To do that we compared our calculations on some water dimers and trimers with accurate extended basis *ab initio* calculations made by Hankins, Moskowitz, and Stillinger.<sup>12</sup> The results are collected in Tables I–III and in Figure 2.

Table I. Isolated Molecules

| Molecule                      | Binding energy, eV |       | Ionization potential, eV |       | Dipole moment, D |      |
|-------------------------------|--------------------|-------|--------------------------|-------|------------------|------|
|                               | Calcd              | Obsd  | Calcd                    | Obsd  | Calcd            | Obsd |
| O <sub>2</sub>                | 13.259             | 5.21  | 11.48                    | 12.08 |                  |      |
| N <sub>2</sub>                | 14.536             | 9.90  | 14.29                    | 15.58 |                  |      |
| H <sub>2</sub> O <sup>a</sup> | 8.975              | 10.06 | 13.40                    | 12.61 | 2.10             | 1.87 |
| H <sub>2</sub> O <sup>b</sup> | 8.973              |       |                          |       |                  |      |

<sup>a</sup> Experimental geometry. <sup>b</sup> Experimental bond length, tetrahedral angle.

In Table I our results for the oxygen, nitrogen, and water molecules are reported. There it can be seen that the stabilities of the isolated O<sub>2</sub> and N<sub>2</sub> molecules are greatly overestimated while the binding energy of water is close to the experimental value. Furthermore the ionization potentials of the three molecules and the dipole moment of water are in good agreement with

(11) G. Höjer and S. Meza, *Acta Chem. Scand.*, **26**, 3723 (1972).

(12) D. Hankins, J. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **53**, 12 (1970).

Table II. Energy Analysis for Some Dimers and Trimers (Energies in kcal/mol and Distances in Å)

| Dimer                         | R <sub>O<sub>1</sub>O<sub>2</sub></sub> | R <sub>OH</sub> | θ, <sup>a</sup><br>deg | φ, <sup>a</sup><br>deg | E(1,2)<br>–ΣE | V <sup>2</sup> (1,2) |                      |                      |                        |
|-------------------------------|---|-----------------|------------------------|------------------------|---------------|----------------------|----------------------|----------------------|------------------------|
| 1,9 1a <sup>b</sup>           | 2.75                                    | 0.9572          | 54.7                   | 60                     | –3.13         | –3.13                |                      |                      |                        |
| 7,5 1a <sup>b</sup>           | 2.75                                    | 0.9572          | 54.7                   | 180                    | –2.95         | –2.95                |                      |                      |                        |
|                               | 2.76                                    | 0.9572          | 40                     | 0                      | –3.34         | –3.34                |                      |                      |                        |
| <i>Ab initio</i> <sup>c</sup> | 2.76                                    | 0.945           | 40                     | 0                      | –3.97         | –3.97                |                      |                      |                        |
| <i>Ab initio</i> <sup>c</sup> | 2.76                                    | 0.945           | 54.7                   | 180                    | –2.40         | –2.40                |                      |                      |                        |
| Trimer <sup>d</sup>           | E(1,2,3)<br>–ΣE                         |                 |                        |                        |               | V <sup>2</sup> (1,2) | V <sup>2</sup> (2,3) | V <sup>2</sup> (1,3) | V <sup>3</sup> (1,2,3) |
| Sequential                    |   |                 |                        |                        |               |                      |                      |                      |                        |
| 6,9,1 1a <sup>b</sup>         |   |                 |                        |                        | –6.49         | –2.95                | –3.13                | –0.16                | –0.25                  |
| 5,8,2 1b <sup>b</sup>         |   |                 |                        |                        | –6.51         | –2.95                | –3.13                | –0.16                | –0.27                  |
| <i>Ab initio</i> <sup>e</sup> |   |                 |                        |                        | –6.77         | –2.40                | –2.40                | –0.61                | –1.36                  |
| Double acceptor               |   |                 |                        |                        |               |                      |                      |                      |                        |
| 2,8,3 1a <sup>b</sup>         |   |                 |                        |                        | –5.92         | –3.13                | –3.13                | +0.15                | +0.19                  |
| 7,5,8 1a <sup>b</sup>         |   |                 |                        |                        | –5.52         | –2.95                | –2.95                | +0.14                | +0.24                  |
| 10,4,7 1b <sup>b</sup>        |   |                 |                        |                        | –6.00         | –3.13                | –3.13                | +0.06                | +0.20                  |
| <i>Ab initio</i> <sup>e</sup> |   |                 |                        |                        | –3.14         | –2.40                | –2.40                | +1.31                | +0.35                  |
| Double donor                  |   |                 |                        |                        |               |                      |                      |                      |                        |
| 10,3,8 1a <sup>b</sup>        |   |                 |                        |                        | –5.90         | –3.13                | –3.13                | +0.06                | +0.30                  |
| 2,8,3 1b <sup>b</sup>         |   |                 |                        |                        | –5.79         | –3.13                | –3.13                | +0.15                | +0.32                  |
| 7,5,8 1b <sup>b</sup>         |   |                 |                        |                        | –5.37         | –2.95                | –2.95                | +0.11                | +0.42                  |
| <i>Ab initio</i> <sup>e</sup> |   |                 |                        |                        | –2.97         | –2.40                | –2.40                | +0.95                | +0.87                  |

<sup>a</sup> Angles defined in Figure 2. <sup>b</sup> Notation refers to the numbering of the oxygen atoms in Figures 1a and 1b. <sup>c</sup> Reference 12, Table IV. <sup>d</sup> Oxygen–oxygen distances are equal to 2.75–2.76 Å. The angles vary; see Figures 1a and 1b in this work and Figures 4–6 in ref 12. <sup>e</sup> Reference 12, Table VIII.

experimental data too. As the water molecules are supposed to have tetrahedral angles in the cages, we calculated water with both the experimental and the tetrahedral bond angle. The OH distance is in both cases the experimental distance. For several reasons we are going to use “the tetrahedral water” as reference in the following. First we are only interested in the changes in a molecule or a cluster of molecules due to other molecules, and second we assumed linear hydrogen bonds for simplicity though the question of nonlinearity has not been solved yet.

The homonuclear diatomics were not included in the parametrization of our method, which could explain their binding energies. However, the oxygen and nitrogen molecules are not expected to form bonds with the water and thus they will not change their properties significantly when they go interstitial. The calculations on the water cages with trapped oxygen or nitrogen molecules show also that they almost retain their identities. We expect therefore the errors in the stabilities of oxygen and nitrogen largely to be canceled when we calculate the extra stability of a water cage due to an interstitial molecule.

With respect to Tables II and III, where the comparisons with the *ab initio* calculations are made, it should be remembered that the calculations do not refer generally to exactly the same geometries. We have used the dimers and trimers which occur in our cages. These differences do not change the conclusions we can draw from these comparisons.

Hankins, *et al.*,<sup>12</sup> found that an extended basis including oxygen 3d and hydrogen 2p functions was essential for an accurate description of intramolecular energies. The CNDO method is in a sense an approximation to minimal basis *ab initio* calculations, but

Table III. Net Valence Electron Densities for CNDO and Gross Atomic Densities (Valence Part) for Reference *ab Initio* Calculation

| Monomer                       | Geometry     |                    |                 | Electron density |        |        |        |        |
|-------------------------------|--------------|--------------------|-----------------|------------------|--------|--------|--------|--------|
|                               | $R_{OH}$     | $\angle HOH$ , deg | $O_1$           | $H_1$            | $H_2$  | $O_2$  | $H_3$  | $H_4$  |
| CNDO                          | 0.9572       | 109.47             | 6.3001          | 0.8499           | 0.8499 |        |        |        |
| <i>Ab initio</i>              | 0.945        | 106                | 6.6465          | 0.6768           | 0.6768 |        |        |        |
| Dimer                         | $R_{O_1O_2}$ | $\theta$ , deg     | $\varphi$ , deg |                  |        |        |        |        |
| 1,9 1a                        | 2.75         | 54.74              | 60              | 6.3243           | 0.8595 | 0.8291 | 6.3041 | 0.8403 |
| 7,5 1a                        | 2.75         | 54.74              | 180             | 6.3223           | 0.8618 | 0.8288 | 6.3024 | 0.8424 |
|                               | 2.75         | 40                 | 0               | 6.3245           | 0.8592 | 0.8284 | 6.3053 | 0.8413 |
| <i>Ab initio</i> <sup>a</sup> | 3.0          | 40                 | 0               | 6.6843           | 0.6864 | 0.6407 | 6.6686 | 0.6600 |

<sup>a</sup> Reference 12, Table VII.

its semiempirical character may in many cases greatly improve its usefulness.

Using the notations of Hankins, *et al.*, with  $V^n(n_1 \dots n_n)$  meaning the contribution to the total energy due to the  $n$ -molecular interaction between the molecules  $n_1 \dots n_n$ , Table II suggests that  $V^2$  is reasonably well described by our CNDO method in the case of two water molecules connected by a hydrogen bond while  $V^2$  for nonnearest neighbors and the  $V^3$  terms are underestimated though they seem to predict attraction or repulsion correctly. Counting all the possible trimers, which occur in our cages, it is found that the three main types, sequential, double donor, and double acceptor, come in equal proportions. If terms like  $V^4$ ,  $V^5$ , etc., are much smaller than the  $V^2$  and  $V^3$  terms, we expect the nonadditive contributions to the stabilities of our cages largely to be canceled. On the other hand, in an infinite cubic ice structure, where the three types of trimers occur in the proportions 4:1:1, the *ab initio* calculations suggest a strong cooperative effect in the hydrogen bonding, which would be underestimated by our method.

Besides studying how the different energy terms are described by our method, it is interesting to study the changes in the charge distributions upon going from monomers to dimers and trimers. Table III and Figure 2 show the changes in the net atomic valence electron populations in the CNDO case and in the gross atomic populations for the *ab initio* calculation in dimers compared to the free monomers. Both calculations show the same trends with the proton donor water molecule gaining electrons, a large redistribution within both water molecules, the oxygen atoms in both water molecules gaining electrons, and a building up of electrons on the back hydrogen in the proton donor. The study of the charge densities in the trimers (the densities are not reported) seems to indicate that these trends are true in the trimers too. It seems also to be true that if the charge on the oxygens increases, the trimer is more stable than the two hydrogen bonds making it up. The reverse is also true, but it is important that all the oxygens increase their charges in such a way that the charge gains are greater than the gains resulting from just adding the two dimers.

Our conclusion is that our CNDO calculations give a reasonable description of the changes in the charge distribution upon cage formation and also of the energies of the local hydrogen bonds. The limitations in the method for the effects related with long range and multimolecular interactions are not serious as these effects seem to be qualitatively correct though the energies involved are too small.

## Results

The results are collected in Tables IV and V. First

Table IV. Stabilization Energies (Cage Type I; See Figure 1a)<sup>a</sup>

|   | Binding energy, eV | Stabilization <sup>b</sup> |
|---|--------------------|----------------------------|
| Reference cage                                      | 91.2914            | 1.5614 eV = 35.9 kcal/mol  |
| Cage with interstitial molecule oriented along axis |                    |                            |
| $N_2$ $x$   | 106.0895           | 1.8239 eV = 42.0 kcal/mol  |
| $N_2$ $z$   | 106.1338           | 1.8682 eV = 43.0 kcal/mol  |
| $O_2$ $x$   | 104.7125           | 1.7231 eV = 39.7 kcal/mol  |
| $O_2$ $z$   | 104.8475           | 1.8581 eV = 42.7 kcal/mol  |

<sup>a</sup>  $\Sigma H_{\text{bond}} = 4 \times 2.95 + 8 \times 3.13 = 36.84$  kcal/mol. Nonadditivity:  $-0.96$  kcal/mol. <sup>b</sup> Relative free "tetrahedral" water molecules.

Table V. Stabilization Energies (Cage Type II; See Figure 1b)<sup>a</sup>

|   | Binding energy, eV | Stabilization <sup>b</sup> |
|---|--------------------|----------------------------|
| Reference cage                                      | 91.2857            | 1.5557 eV = 35.7 kcal/mol  |
| Cage with interstitial molecule oriented along axis |                    |                            |
| $N_2$ $x$   | 106.0599           | 1.7943 eV = 41.3 kcal/mol  |
| $N_2$ $z$   | 106.0196           | 1.7540 eV = 40.4 kcal/mol  |
| $O_2$ $x$   | 104.6766           | 1.6872 eV = 38.9 kcal/mol  |
| $O_2$ $z$   | 104.8309           | 1.8415 eV = 42.4 kcal/mol  |

<sup>a</sup>  $\Sigma H_{\text{bond}} = 8 \times 3.13 + 4 \times 2.95 = 36.84$  kcal/mol. Nonadditivity:  $-1.14$  kcal/mol. <sup>b</sup> Relative free "tetrahedral" water molecules.

each one of the two cages was calculated separately. As mentioned in the introductory section they have the symmetry  $D_{2d}$ . In each cage there are two obvious positions for the interstitial molecule leading to highly symmetric cages without resulting dipole moments. If the foreign molecule is placed along the  $x$  axis (see Figure 1), the over-all symmetry is lowered to  $D_2$ . This has an important consequence in the case of oxygen. The ground state of oxygen is a triplet state. In  $D_2$  there are no degenerate representations which means that the oxygen molecule will have to be promoted to a singlet state in this case and this cage will be less stable than the one with the oxygen along the  $z$  axis, where the oxygen can stay in its slightly perturbed ground state. This problem does not occur with the nitrogen.

As could be expected from the discussion of the method the stabilities of the two pure water cages are very close to the sums of the local hydrogen bonds in-

volved. If anything the calculations show a very small destabilization of about 1 kcal/mol. When an oxygen or nitrogen molecule is put inside a cage the charge in the cage is changed in such a way that the oxygens gain electrons. The charge migration is very small and the resulting stabilization is in the range 4 to 7 kcal/mol in these ten-membered cages with 12 hydrogen bonds. Sobol, *et al.*,<sup>9</sup> estimate from their experiments the effect of an oxygen or a nitrogen molecule to be 0.1 kcal/mol per hydrogen bond (stabilizing effect) in unspecified structured water. The agreement is quite good.

It is reasonable to connect the stabilization effect with charge polarization as dipole interaction is supposed to be the leading term in what we call hydrogen bonding. The question is then why oxygen or nitrogen would have this effect on a water structure while a non-hydrogen-bonded water molecule would not have it or at least to a lesser extent. That is at least a possible interpretation of the experiments by Sobol, *et al.* These experiments revealed a direct relation between the air content in the water and the surface tension. For the discussion of the possible effect of a "free" water molecule to be meaningful, one has to assume a model for water similar to those proposed by Némethy and Scheraga<sup>3</sup> and Samoilov<sup>4</sup> mentioned in the introductory section. To study this possibility we put a water molecule inside the cage described in Figure 1b. The molecule was placed in a plane bisecting the angle between the *xz* and *yz* planes. The resulting sym-

metry is  $C_{2v}$ . The position along the *z* axis and the orientation of the bond angle with respect to the positive *z* direction were varied. It was found that the water molecule had no stabilizing effect on the cage. In these cases we had a resulting dipole moment in the cage. The charge redistribution in the cage itself was smaller than the changes due to oxygen or nitrogen molecules. The main changes were in the two cage water molecules on the *z* axis. The interstitial molecule has attractive interaction with one of them and repulsive interaction with the other one. To diminish this repulsion the polarity of the latter cage molecule is weakened and thus its contribution to the stability of the cage too. In the opposite cage molecule the trend is reversed. The over-all effect seems to be a cancellation of these different contributions to the total energy of the system.

### Conclusion

Our theoretical method shows that it is quite possible that an oxygen or a nitrogen molecule would have a small but measurable stabilizing effect on a local water structure. This stabilization is due to a slightly increased polarization of the water molecules. The advantage of an oxygen or a nitrogen molecule over a non-hydrogen-bonded water molecule could be that this polarization can take place without any repulsive electrostatic interaction between the interstitial molecule and the surrounding water structure.

## Substituent Effects on Proton Affinities of Simple Molecules

Allan Johansson,<sup>1a</sup> Peter A. Kollman,<sup>1b</sup> Joel F. Liebman,<sup>\*1c</sup> and Stephen Rothenberg<sup>1d</sup>

*Contribution from the Department of Inorganic Chemistry, Helsinki University of Technology, Otaniemi, Helsinki, Finland, the School of Pharmacy, Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143, the Department of Chemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228, and Information Systems Design, Oakland, California 94601. Received December 3, 1973*

**Abstract:** Molecular orbital studies of proton affinities of amino, hydroxyl, and fluoro groups predict that the proton affinity of these groups is in the expected order  $\text{NH}_2 > \text{OH} > \text{F}$ . In addition, methyl and amino groups bonded to the proton acceptor group increase its proton affinity; hydroxyl and fluoro decrease the proton affinity relative to the simple hydrides  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ . The agreement with experiment is good in those cases where the proton affinity has been measured; some of the proton affinities presented here are predictions. Application to organic chemical rearrangements is also made.

With the advent of techniques such as chemical ionization mass spectrometry<sup>2</sup> and ion-cyclotron resonance,<sup>3</sup> interest in the proton affinities of various molecules has increased. In addition to interest in the values of proton affinities *per se*, the magnitude of substituent effects on the proton affinities is of interest when compared to these substituent effects on the stability

of carbonium ions<sup>4</sup> and strength of hydrogen bonds.<sup>5</sup> The role of adjacent lone pairs (the "α effect") on the reactivity of nucleophiles<sup>6</sup> has been of some interest so that quantitation of the inherent basicities, *i.e.*, proton affinities, is of relevance. The site of protonation in substituted hydroxylamines and fluoro amines

(1) (a) Helsinki University of Technology; (b) University of California; (c) University of Maryland Baltimore County; (d) Information Systems Design.

(2) See F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1967); *J. Amer. Chem. Soc.*, **92**, 2672 (1970), and references therein.

(3) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(4) P. A. Kollman, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Amer. Chem. Soc.*, **95**, 5460 (1973).

(5) J. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973); **57**, 1899 (1972); *J. Amer. Chem. Soc.*, **95**, 5460 (1973).

(6) See, for example, J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962); N. J. Fina and J. O. Edwards, *Int. J. Chem. Kinet.*, **5**, 1 (1973); J. F. Liebman and R. M. Pollack, *J. Org. Chem.*, **38**, 3444 (1973).