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Theoretical Study of the Ionization of the H_2O–H_2O, NH_3–H_2O, and FH–H_2O Hydrogen-Bonded Molecules

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Abstract: The first two vertical ionization energies of H_2O–H_2O, NH_3–H_2O, and FH–H_2O hydrogen-bonded complexes and the rearrangement processes in their ionized states have been studied by ab initio calculations that include correlation energy. In all cases, the two lowest ionic states are the $^2A'$ and $^2A''$ states depending on whether the ionization is located in the proton acceptor or in the proton donor molecule, respectively. If the ionization is produced in the proton donor, the $^2A''$ state, the dimer evolves to a proton-transfer complex. However, if the ionization is produced in the proton acceptor, the $^2A'$ state, the dimer rearranges to a non-proton-transfer hydrogen-bonded structure in which the role of the two monomers is just the inverse of that of the original neutral dimer. For the water–water and water–ammonia dimers, relaxation of the $^2A'$ state can also lead to three-electron hemibond complexes.

Introduction

Because of the important role that hydrogen bonding plays in numerous biological and chemical processes, the study of hydrogen-bonded clusters has been the subject of a great amount of research. One of the fundamental reactions that can occur in these clusters is ionization. The generated radical cations exhibit a very rich and varied chemistry, since in the ionized state they can evolve via different chemical reactions such as electron transfer, proton trnasfer, or molecular rearrangements. Because of that, the study of the reactivity of clusters upon ionization is currently a very active area of research.[1–5]

While the neutral hydrogen-bonded complexes,[6–18] and in particular the water dimer,[6–13] have been extensively studied theoretically, less work has been done on the electronic and molecular structures of the corresponding radical cations. Studies on the water dimer cation[19–22] have shown that geometry relaxation of the first ionic state leads to a proton-transfer $OH^{\bullet}$–H_3O^+ complex. However, there are some discrepancies in the nature and evolution of the second ionic electronic state. Moreover, Gill and Radom[23] have shown that inclusion of electron correlation is necessary to correctly describe three-electron-bond structures which, as will be shown later, can be involved in the geometrical relaxation of the second ionic state of the water dimer cation. These three-electron-bond structures have a bond order of $^1/_2$ and are called hemibond. Such structures have also been determined in a very recent theoretical study on the methanol–water dimer cation.[24]

Other studies on hydrogen-bonded derived radical cations include the ionization of $(NH_3)_2$ and $(HF)_2$ dimers.[20,25] As in the case of the water dimer cation, relaxation of $(NH_3)_2^+$ and $(HF)_2^+$ in the first ionic state leads to the proton-transfer NH_4^+–NH_2 and FH_2^+–F complexes. Clark has reported also calculations on a series of radical cations within the context of a study of three-electron-bond structures.[26] Burgers et al.[27] studied the H_2CO–H_3N radical cation, and Ventura et al.[28] have recently reported the structure and reactivity of H_2CO–H_2O^+ and related radical cations. For both systems the most stable structure corresponds to the HCO–NH_4^+ and HCO–OH_3^+ proton-transfer complexes. We are not aware of any theoretical study on the potential energy surface of the ionized NH_3–H_2O and HF–H_2O hydrogen-bonded complexes.

In this paper we present a theoretical study of the molecular and electronic structures of the radical cations derived from the ionization of the following hydrogen-bonded molecules: H_2O–H_2O, H_2O–NH_3, and H_2O–HF, at different levels of calculation. Basically, there are two different ionic states depending on whether the ionization is produced in the proton donor or in the proton acceptor molecule. In the first case, one must expect an increase of the acidity of the donor. In the second case, the increase of acidity takes place in the acceptor molecule which drives the dimer to rearrange in such a way that the originally acceptor monomer can act as a proton donor. The study of these three systems will allow us not only to compare and discuss the observed

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[1] Bernstein, E. R. *J. Phys. Chem.* **1992,** *96,* 10105.

[2] Brutschy, B. *Chem. Rev.* **1992,** *92,* 1567.

[3] (a) Wei, S.; Tzeng, W. B.; Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1991,** *113,* 1960. (b) Morgan, S.; Castleman, A. W., Jr. *J. Phys. Chem.* **1989,** *93,* 4544.

[4] (a) Syage, J. A. *Ultrafast Spectroscopy in Chemical Systems;* Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992. (b) Syage, J. A. *Chem. Phys. Lett.* **1993,** *202,* 227. (c) Syage, J. A.; Steadman, J. *J. Phys. Chem.* **1992,** *96,* 9606.

[5] Shinohara, H.; Sato, H.; Misaizu, F.; Ohashi, K.; Nishi, N. *Atoms, Molecules and Clusters* **1991,** *20,* 197.

[6] Saebø, S.; Tong, W.; Pulay, P. *J. Chem. Phys.* **1993,** *98,* 2170.

[7] Chakravorty, S. J.; Davidson, E. R. *J. Phys. Chem.* **1993,** *97,* 6373.

[8] Feller, D. *J. Chem. Phys.* **1992,** *96,* 6104.

[9] van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Chem. Phys.* **1992,** *97,* 5019.

[10] Kim, K. S.; Mhin, B. J.; Choi, U.; Lee, K. *J. Chem. Phys.* **1992,** *97,* 6649.

[11] Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991,** *95,* 6576.

[12] Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988,** *89,* 3662.

[13] Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986,** *84,* 2279.

[14] Del Bene, J. E. *J. Phys. Chem.* **1988,** *92,* 2874.

[15] Olszewski, K. A.; Gutowski, M.; Piela, L. *J. Phys. Chem.* **1990,** *94,* 5710.

[16] Yeo, G. A.; Ford, T. A. *Can. J. Chem.* **1991,** *69,* 632.

[17] Latajka, Z.; Scheiner, S. *J. Phys. Chem.* **1990,** *94,* 217.

[18] Røeggen, I. *Mol. Phys.* **1990,** *70,* 353.

[19] (a) Tomoda, S.; Achiba, Y.; Kimura, K. *Chem. Phys. Lett.* **1982,** *87,* 197. (b) Sato, K.; Tomoda, S.; Kimura, K. *Chem. Phys. Lett.* **1983,** *95,* 579. (c) Tomoda, S.; Kimura, K. *Chem. Phys.* **1983,** *82,* 215. (d) Tomoda, S.; Kimura, K. *Chem. Phys. Lett.* **1984,** *111,* 434.

[20] Tomoda, S. *Faraday Discuss. Chem. Soc.* **1988,** *85,* 53.

[21] Curtiss, L. A. *Chem. Phys. Lett.* **1983,** *96,* 442.

[22] Sosa, R. M.; Irving, K.; Ventura, O. N. *THEOCHEM* **1992,** *254,* 453.

[23] Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988,** *110,* 4931.

[24] Burcl, R.; Hobza, P. *Theor. Chim. Acta* **1993,** *87,* 97.

[25] Tomoda, S.; Kimura, K. *Chem. Phys. Lett.* **1985,** *121,* 159.

[26] Clark, T. *J. Am. Chem. Soc.* **1988,** *110,* 1672.

[27] Burgers, P. C.; Lifshitz, C.; Ruttink, P. J. A.; Schaftenaar, G.; Terlouw, J. K. *Org. Mass Spectrom.* **1989,** *24,* 579.

[28] Coitiño, E. L.; Lledós, A.; Serra, R.; Bertran, J.; Ventura, O. N. *J. Am. Chem. Soc.* **1993,** *115,* 9121.

0002-7863/94/1516-8249$04.50/0

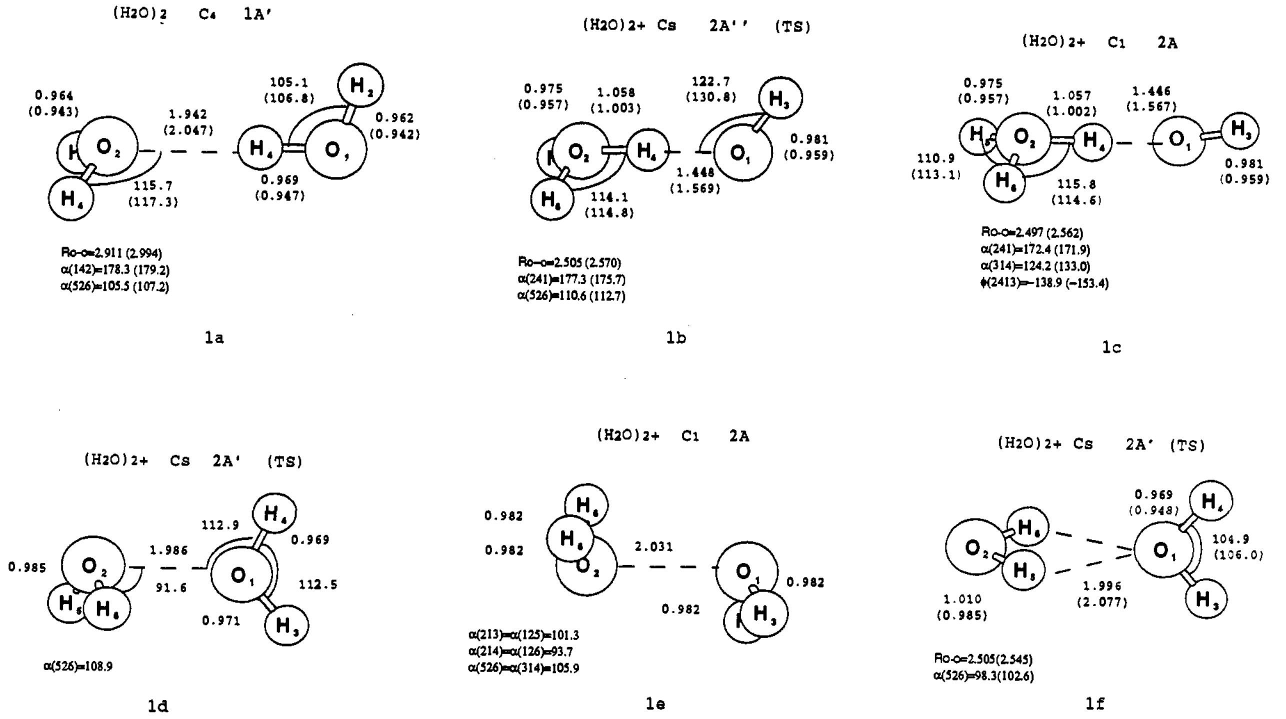

Figure 1. MP2(SCF)-optimized geometries for the neutral $(H_2O)_2$ dimer and its derived radical cations: H_2O, $R(O–H) = 0.963(0.942)$ Å, $\angle HOH = 105.1(106.9)°$; H_2O^+, $R(O–H) = 1.002(0.982)$ Å, $\angle HOH = 110.0(112.0)°$; OH, $R(O–H) = 0.973(0.953)$ Å; H_3O^+, $R(O–H) = 0.981(0.962)$ Å, $\angle HOH = 112.5(114.3)°$.

differences but to get a deeper insight into the nature of the ionic states and its role in the geometrical relaxation. Differences between the present work and the previous theoretical studies will also be discussed.

Methods

Two different approaches are used in the present study. In the first approach, the geometries are optimized and the frequencies determined at the self-consistent-field, SCF, level of theory. Electron correlation is included using the essentially size-extensive modified-coupled-pair functional (MCPF)[29] method at the SCF equilibrium geometries. In these MCPF calculations we correlate all of the electrons of H_2O, NH_3, and HF except the 1s-like electrons of the O, N, and F atoms. In the second approach the geometry optimizations and the frequency calculations are performed including correlation energy at the MP2[30] level. Single-point calculations at the MCPF level are also carried out at the MP2 geometries.

The basis sets used for the geometry optimizations are of triple-ζ plus polarization quality. The O, N, and F basis sets are the (10s 6p)/[5s 3p] sets of Dunning[31] with a d polarization function added ($\alpha_N = 0.80$, $\alpha_O = 0.85$, and $\alpha_F = 0.90$). The H basis set is the (5s)/[3s] set of Dunning with a p ($\alpha = 1.0$) polarization function added. Larger basis sets are used when the correlation energy is included at the MCPF level. These larger basis sets are the previously TZ basis of Dunning plus two sets of polarization functions and one set of diffuse valence functions, TZ2P++. The two d polarization functions are $\alpha = 1.5$ and 0.5 for nitrogen, $\alpha = 1.6$ and 0.6 for oxygen, and $\alpha = 1.7$ and 0.7 for fluorine. The diffuse functions have the following orbital exponents: $\alpha_s = 0.06$ and $\alpha_p = 0.04$ for nitrogen, $\alpha_s = 0.08$ and $\alpha_p = 0.05$ for oxygen, and $\alpha_s = 0.1$ and $\alpha_p = 0.06$ for fluorine. For the hydrogen atom the polarization functions are $\alpha = 1.25$ and 0.45 and the diffuse function is $\alpha_s = 0.03$.

The water dimer molecule has also been optimized using the larger TZ2P++ basis set. While there are small variations in the optimized geometrical parameters, the MCPF dissociation energies of the water dimer using the TZ2P++ basis set agree to better than 0.1 kcal/mol regardless of whether the equilibrium structures are obtained with the TZP or TZ2P++ basis set. Thus, we don't expect significant differences by using the smaller basis set in the optimization process.

The SCF and MCPF calculations were performed using SIRIUS-ABACUS[32] and MOLECULE-SWEDEN[33] program systems, respectively. For the open-shell systems these calculations were based on a spin-restricted treatment. The MP2 calculations were performed using Gaussian92,[34] and the open-shell calculations were based on a spin-unrestricted SCF wave function. In all UHF calculations spin contamination was found to be small.

Results and Discussion

In this section we will first present the results obtained for each one of the three studied hydrogen-bonded complexes and its radical cations. Finally, we will compare and discuss the trends.

A. $(H_2O)_2$ and $(H_2O)_2^+$. In Figure 1 we present the MP2- and SCF-optimized geometrical parameters for the neutral $(H_2O)_2$ and for the different stationary points found after ionization. It has been both theoretically[6–13,35] and experimentally[36] established that the global minimum of the water dimer has C_s symmetry with an almost linear hydrogen bond, see Figure 1a. At the MP2-correlated level the OH distances are larger and the HOH angles of each monomer are smaller than those computed at the SCF level. These changes in the geometrical parameters of the two

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(29) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606. See also Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890.

(30) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(31) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(32) SIRIUS is an MCSCF program written by H. J. Jensen, H. Agren, and J. Olsen; ABACUS is an MCSCF energy derivatives program written by T. Helgaker, H. J. Jensen, P. Jørensen, J. Olsen, and P. R. Taylor.

(33) MOLECULE-SWEDEN is an electronic structure program written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-A. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.

(34) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1992.

(35) (a) Morokuma, K.; Pedersen, L. *J. Chem. Phys.* **1968**, *48*, 3275. (b) Morokuma, K.; Winick, J. R. *J. Chem. Phys.* **1970**, *52*, 1301.

(36) (a) Dyke, T. R. *J. Chem. Phys.* **1977**, *66*, 492. (b) Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J. Chem. Phys.* **1977**, *66*, 498. (c) Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062. (d) Coudert, L. H.; Lovas, F. J.; Suenram, R. D.; Hougen, J. T. *J. Chem. Phys.* **1987**, *87*, 6290. (e) Odutola, J. A.; Hu, T. A.; Prinslow, D.; O'dell, S. E.; Dyke, T. R. *J. Chem. Phys.* **1988**, *88*, 5352.

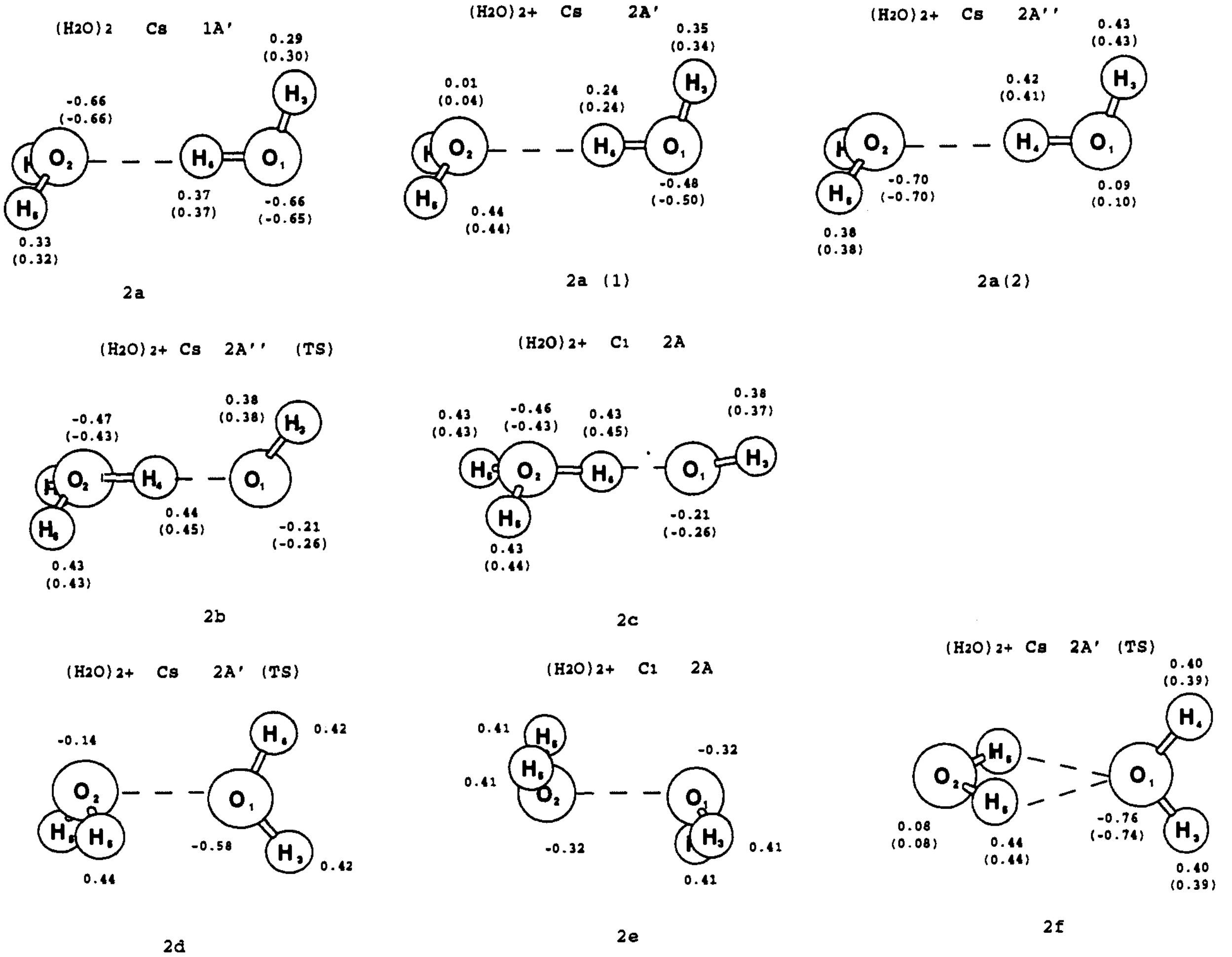

Figure 2. MCPF atomic charges using MP2(SCF) geometries for the neutral $(H_2O)_2$ dimer, the vertical ionized $^2A'$ and $^2A''$ states, and their derived radical cations.

water molecules with the inclusion of correlation energy parallel the changes in the free water monomer. The increase in the H_4–O_1 distance because of the formation of the hydrogen bond is 0.006 Å at the MP2 level and 0.005 Å at the SCF level of calculation. The hydrogen bond is predicted to be almost linear with both methods, in good agreement with the experimental data. Also, the R_{O-O} distance is in reasonably good agreement with the 2.977 Å value determined experimentally.[36]

The computed binding energy of the water dimer, without including the zero point correction, at the MCPF level using the TZ2P++ basis set is 4.97(5.01) kcal/mol depending on whether the geometries are taken from the MP2(SCF) calculations. Thus, even though there are small differences between the SCF and MP2 values of the optimized geometrical parameters, the effect in the binding energy is very small. Increasing the basis set is expected to reduce somewhat the binding energy, because the error due to basis set superposition will be smaller. Overall, the 5.0 kcal/mol value that we get at the MCPF(TZ2P++) is in reasonably good agreement with recent accurate calculations[6-13] and with the experimental measurements of 5.4 ± 0.7 kcal/mol.[37]

We will now consider the ionization process on the water dimer. The electronic configuration of the water monomer in its C_{2v} symmetry ground state is $1a_1{}^2 2a_1{}^2 1b_2{}^2 3a_1{}^2 1b_1{}^2$. The water dimer has C_s symmetry with a $1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 7a'^2 8a'^2 2a''^2$ configuration. The first ionic state is a $^2A''$ state derived from ionizing from the 2a″ orbital, which corresponds to the $1b_1$ orbital of the proton donor water molecule. The second ionic state is a $^2A'$ state that arises from removing the electron from the 8a′ orbital. This 8a′ orbital is a mixture of the $1b_1$ orbital of the proton acceptor water molecule and the $3a_1$ orbital of the hydrogen donor molecule. However, in the ionized $^2A'$ state the open-shell (8a′) orbital mainly corresponds to the $1b_1$ orbital of the acceptor molecule. Analysis of the wave function shows that there is some mixing with the $1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 7a'^1 8a'^2 2a''^2$ configuration, in which the 7a′ orbital, mainly the $3a_1$ orbital of the proton donor monomer, is monoccupied. The coefficient of this configuration in the wave function is 0.19. To get further insight into the nature of these ionic states, we present in Figure 2 the MCPF atomic charges for the neutral dimer, for the vertical ionized dimer in both states, and for all the stationary points found. It can be observed that while in the $^2A''$ electronic state the positive charge is almost entirely on the proton donor molecule, in the $^2A'$ state the charge is in the proton acceptor monomer. Because the H_4–O_1 distance is larger at the correlated level, the coefficient value of the second configuration in the $^2A'$ wave function increases to 0.22 when we use the MP2 geometry of the neutral water dimer. However, the MCPF atomic charge distribution does not change significantly whether we use the SCF or MP2 geometry, see Figure 2a(1).

The MCPF vertical ionization energies computed using the MP2(SCF) geometry of the neutral water dimer are 11.5(11.6) and 12.9(13.0) eV for the $^2A''$ and $^2A'$ states, respectively. These values are in reasonably good agreement with the 12.1 ± 0.1 and 13.2 ± 0.2 eV values determined experimentally.[19] The vertical ionization energies may be compared to the ionization energy of free water, which at the same level of calculation, using both the MP2 or SCF geometries, is 12.3 eV. Thus, ionization of the hydrogen donor water molecule ($^2A''$ state) requires less energy than ionizing free water, while removing an electron from the hydrogen acceptor monomer is more costly energetically. As it

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(37) (a) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703. (b) Reimers, J.; Watts, R.; Klein, M. *Chem. Phys.* **1982**, *64*, 95.

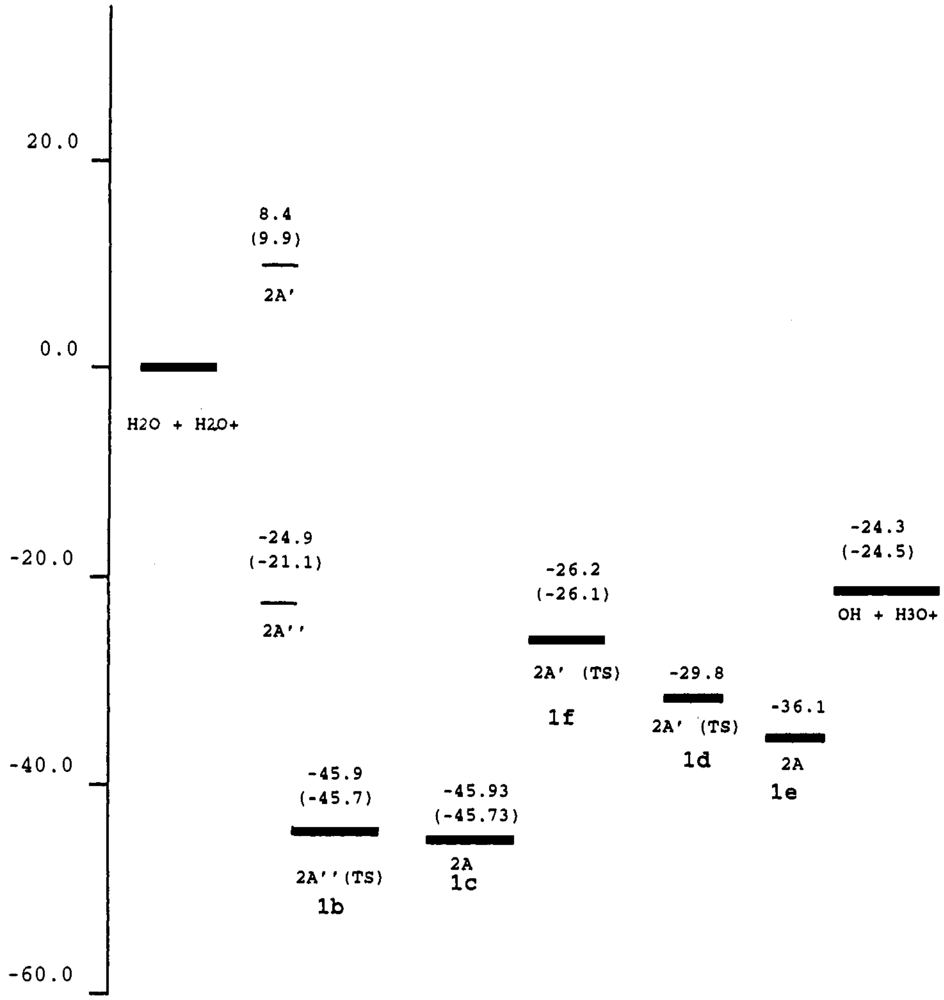

Figure 3. MCPF relative energies (kcal/mol) with respect to the isolated H_2O^+ and H_2O molecules for the $(H_2O)_2$-derived radical cations using MP2(SCF) geometries.

has already been pointed out by Tomoda,[20] the decrease in the first vertical ionization energy of the dimer compared to the ionization potential (IP) of free water is due to the fact that hydrogen bonding causes a destabilization of the HOMO orbital of the proton donor molecule. In contrast, the hydrogen bonding stabilizes the HOMO orbital of the proton acceptor monomer, leading to a second vertical ionization energy that is larger than the IP of free water.

Geometrical relaxation of the $^2A''$ ionic state leads to a structure in which the hydrogen atom involved in the hydrogen bonding has been transferred to the water acceptor molecule, see Figure 1b. The open-shell orbital mainly corresponds to the out-of-plane (a″) hydroxyl orbital. Because the positive charge lies on the H_3O^+ fragment and the unpaired electron on the OH, this structure corresponds to that of a distonic radical cation.[38] There are no significant differences between the SCF and MP2 geometrical parameters, the changes with inclusion of correlation energy being similar to those observed for free H_3O^+ and OH. Both at the SCF and MP2 levels of calculations, this C_s symmetry structure is found to be a transition state. The imaginary frequency corresponds to the symmetry-breaking mode associated to OH rotation. Following this mode we get the minimum presented in Figure 1c, which has very similar parameters but with the OH rotated out of the plane. The energy difference between structures 1b and 1c is very small, in agreement with the very small frequency associated with the H_3O^+–OH twist mode.

While both the SCF and MP2 methods predict the same kind of structures after geometrical relaxation of the $^2A''$ state, important differences appear when we optimize the $^2A'$ state. At the MP2-correlated level the optimization of the $^2A'$ state with C_s constraints leads to the structure displayed in Figure 1d. That is, the water dimer rearranges in such a way that it maximizes the overlap between the monoccupied ($1b_1$) orbital of the originally acceptor monomer and the $3a_1$ orbital of the other water molecule. As a result of this three-electron interaction, the positive charge is more delocalized in the two monomers. Note that in the vertically ionized $^2A'$ state the charges on the acceptor and donor monomers are 0.89 and 0.11, respectively, while in the hemibonded structure the charges are 0.74 and 0.26, see Figure 2. The frequency calculation shows that this structure is a transition state. Releasing the symmetry constraints and following the imaginary mode, we get the minimum three-electron hemibond complex depicted in Figure 1e. Now the covalent bond arises from the interaction between the $1b_1$ orbitals of the two monomers, which leads to a complete delocalization of the positive charge (0.5 in each monomer). No such structures are found when we optimize the $^2A'$ state at the SCF level. Instead, we get the bifurcated structure presented in Figure 1f, which, both at the SCF and MP2 levels of calculations, is found to be a transition state. In this structure the role of the two water monomers has been inverted. That is, the originally acceptor molecule is acting as the proton donor while the other monomer is acting as the proton acceptor. Removing symmetry constraints, the complexes evolve to the same proton-transfer OH–H_3O^+ molecule obtained after relaxation of the $^2A''$ state, structure 1c.

In Figure 3 we present the MCPF relative energies computed with respect to isolated H_2O and H_2O^+ for all the stationary points found using the MP2(SCF) geometries. Given that

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[38] Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

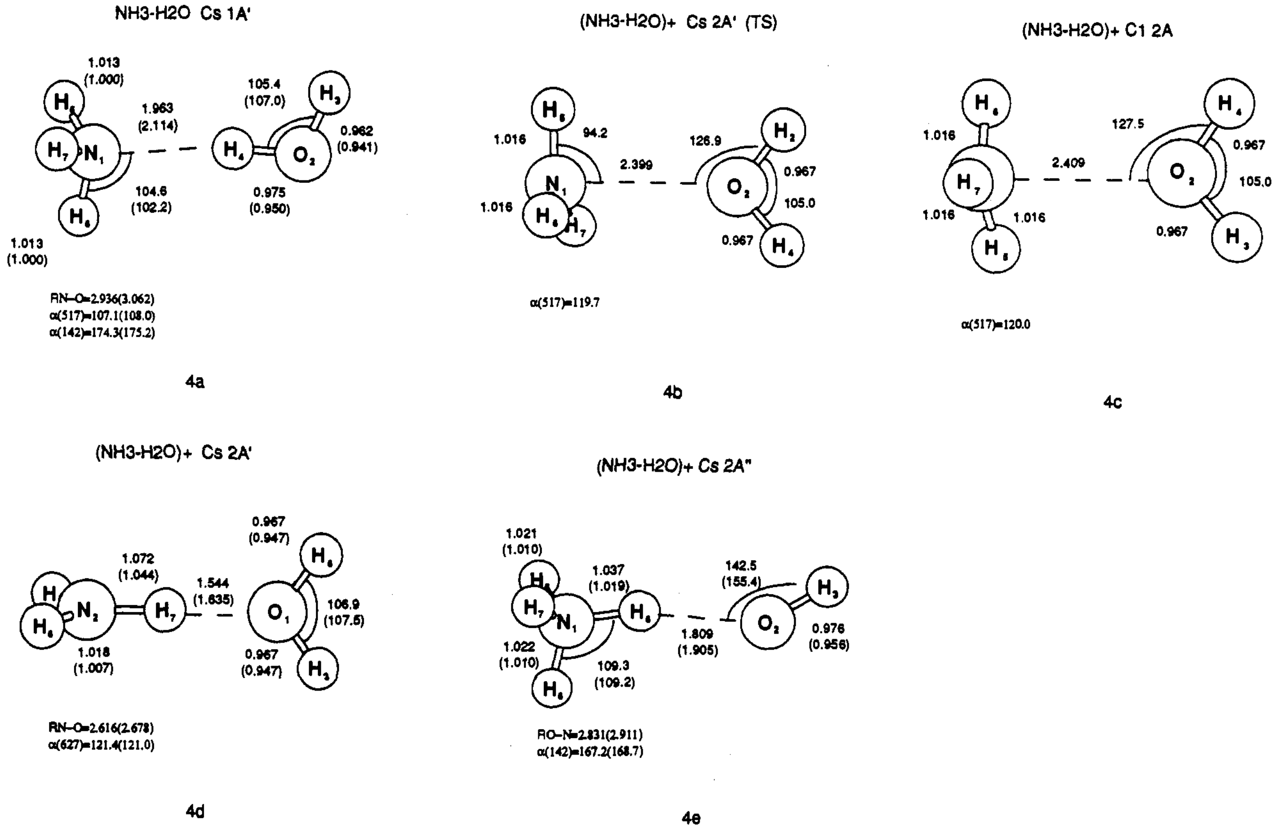

Figure 4. MP2(SCF)-optimized geometries for the neutral NH_3–H_2O dimer and its derived radical cations: NH_3, R(N–H) = 1.011(0.999) Å, ∠HNH = 107.7(108.6)°; NH_3^+, R(N–H) = 1.021(1.010) Å; NH_4^+, R(N–H) = 1.023(1.011) Å.

structures 1d and 1e are only determined when optimizing at the MP2 level and that the MCPF relative energies do not differ significantly whether we use the SCF or the MP2 geometries, we will discuss the results obtained from the MP2 optimizations. We have also included the relative positions of the first and second vertical ionization energies. Because the first vertical ionization energy, IP_v, is smaller than the IP of free water and the formation of the hydrogen bond in the neutral dimer is a stabilizing interaction, the energy of the $^2A''$ state is smaller than that of the isolated H_2O^+ and H_2O molecules. Relaxation of this state leads to the global minimum on the potential energy surface, structure 1c, which corresponds to the proton-transfer H_3O^+–OH complex. The energy difference between this global minimum and the vertical ionized $^2A''$ state is 21.0 kcal/mol (0.9 eV). This large difference between the vertical and adiabatic ionization energies for water dimer is in contrast with that of free water, which is only 0.02 eV,[19] and is due to the large change in the equilibrium geometry between the neutral and the ionic states of water dimer. The computed value for the adiabatic ionization energy of water dimer is 10.6 eV. This value is 0.5 eV smaller than the experimental threshold ionization energy (11.1 eV),[19,39] which could be regarded as the first adiabatic ionization energy. Given that the geometries of the water dimer cation and the neutral dimer are very different and, so, Frank Condon factors may be negligibly small, Tomoda[19] pointed out that the threshold ionization energy of 11.1 may be better taken as an upper bound to the adiabatic ionization energy. However, this 0.5-eV difference is about the same as the one we found for the computed vertical ionization energy when we compared it to experiment, and so, if we consider that the error in the vertical IP remains constant along the relaxation process, our results would suggest that this upper bound is quite close to the real adiabatic ionization energy.

As expected because of electrostatic interactions the proton-transfer complex H_3O^+–OH (1c) is more stable than the isolated OH($^2\Pi$) and H_3O^+ molecules. The energy of these isolated molecules is smaller than that of the isolated H_2O and H_2O^+ molecules and similar to the energy of the vertical ionized $^2A''$ state. Thus, the resulting products of the first ionic state of water dimer will more probably be the equilibrium proton-transfer cation, 1c, or the dissociated pair H_3O^+–OH than the dissociated $H_2O + H_2O^+$ pair. The second vertical ionic state lies higher in energy than the isolated H_2O and H_2O^+ molecules. Relaxation of the second ionic $^2A'$ state leads to the hemibond structure 1e, which is 9.8 kcal/mol less stable than the global minimum. The dissociation energy with respect to the H_2O and H_2O^+ asymptote is 36.1 kcal/mol. This structure may be stable enough to be detected in a sufficiently small time scale experiment.

B. NH_3–H_2O and $(NH_3$–$H_2O)^+$. The NH_3–H_2O hydrogen-bonded complex has C_s symmetry with an almost linear hydrogen bond, see Figure 4a. In this structure the water monomer is acting as the proton donor and the ammonia as the acceptor. An attempt to optimize a structure with the NH_3 molecule acting as the donor caused collapse to structure 4a. The changes in the geometrical parameters of each monomer with inclusion of correlation energy follow the variations in the isolated NH_3 and H_2O. The computed N–O distance is smaller at the MP2 level than at the SCF level, the MP2 value being in quite good agreement with the value of 2.98 Å determined experimentally.[40] Also, the stretching of the H_4–O_2 distance, because of the formation of the hydrogen bond, is larger at the correlated level (0.012 Å) than at the SCF level (0.008 Å). Similar results have been obtained by Scheiner et al.[17] The MCPF binding energy of the NH_3–H_2O complex using the MP2(SCF) geometries is 6.43(6.36) kcal/mol. Thus, as for the water dimer, if a consistent set of geometries is used, the MCPF binding energy varies less than 0.1 kcal/mol regardless of whether the geometries are taken

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(39) A value of 11.21 ± 0.09 eV has also been reported. Ng, C. Y.; Trevor, D. J.; Tiedemann, P. W.; Ceyer, S. T.; Kronebusch, P. L.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1977**, *67*, 4235.

(40) Herbine, P.; Dyke, T. R. *J. Chem. Phys.* **1985**, *83*, 3768.

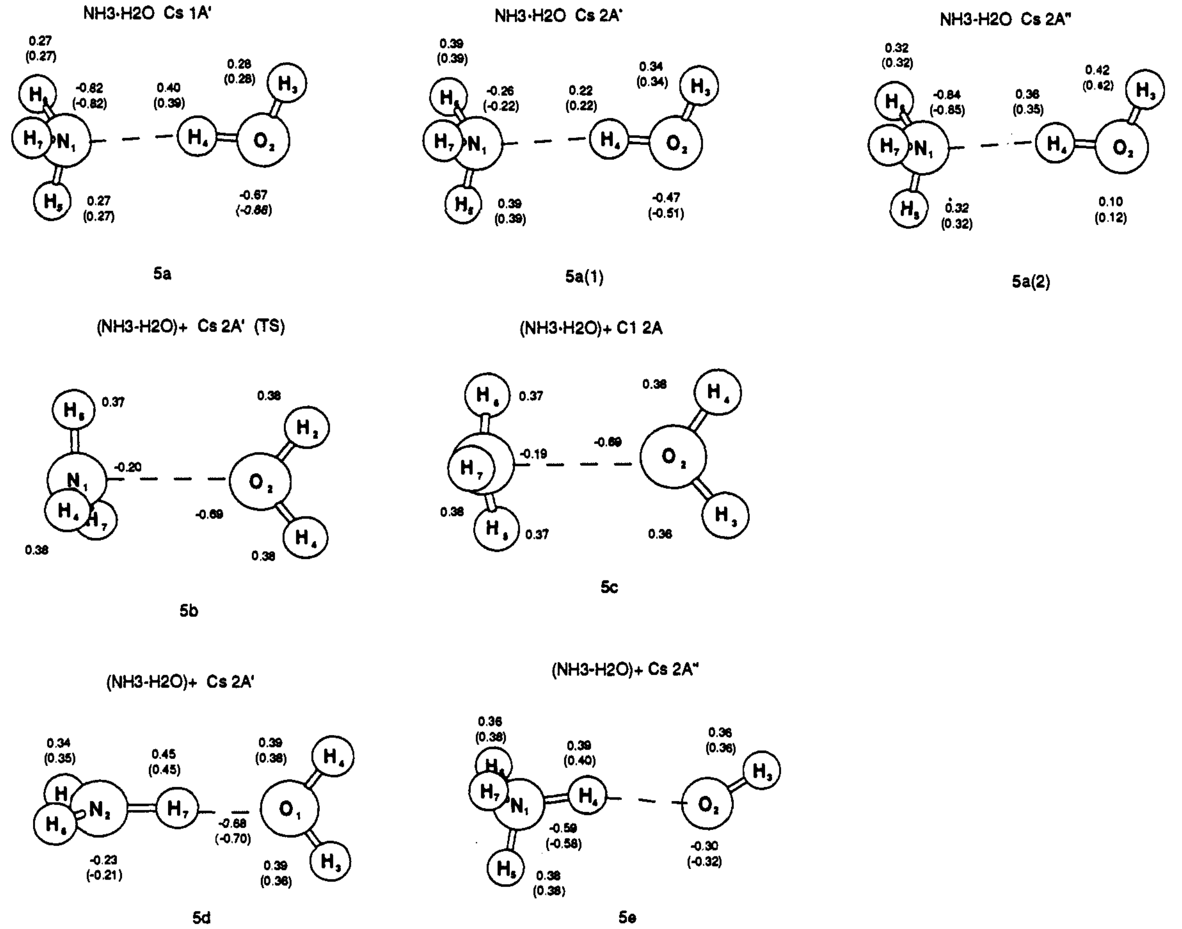

Figure 5. MCPF atomic charges using MP2(SCF) geometries for the neutral NH_3–H_2O dimer, the vertical ionized $^2A'$ and $^2A''$ states, and their derived radical cations.

from an MP2 or an SCF calculation. Our obtained value for the binding energy is very close to the value of 6.5 kcal/mol reported by Del Bene[14] at the MP4/6-311+G(2d,2p) level and 0.7 kcal/mol larger than the estimated value of Scheiner et al.[17] from an MP2 calculation using a smaller basis set and after correcting for basis set superposition error.

The electronic configuration of NH_3–H_2O is $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 2a''^2 8a'^2$. The two lowest vertical ionic states are the $^2A'$ and $^2A''$ states derived from ionizing from the 8a' and 2a'' orbitals, respectively. The 8a' orbital mainly corresponds to the $3a_1$ orbital of ammonia, and the 2a'' orbital, to the $1b_1$ orbital of water. Consistently the MCPF atomic charges show that in the $^2A'$ state the positive charge is almost entirely in the ammonia monomer while in the $^2A''$ state it is in the water monomer, see Figure 5a(1) and a(2).

The MCPF vertical ionization energies to the $^2A'$ and $^2A''$ states, calculated using the MP2(SCF) geometry of the neutral dimer, are 11.2(11.2) and 11.1(11.4) eV, respectively. As expected, ionizing the acceptor molecule (NH_3) in the dimer requires more energy than ionizing free ammonia (9.9 eV), while the ionization of the donor molecule (H_2O) requires less energy than that needed for free water (12.3 eV). The increase of the ionization energy of ammonia and the decrease of the ionization energy of water because of the hydrogen bond interaction leads to two ionic states in the dimer which are almost degenerate. If one uses the SCF geometry of the neutral dimer, the most stable ionic state is the $^2A'$ state. That is, the hydrogen-bonding interaction is not strong enough to make ionization in water more favorable. However, when one uses the MP2 geometry of the neutral dimer, the vertical ionization to the $^2A''$ state decreases by 0.3 eV, this $^2A''$ state becoming then the first ionic state. This is a consequence of the changes in the geometrical parameters with inclusion of correlation energy. Note that the O–N distance is smaller and the H_4–O_2 stretching is larger at the MP2 level than at the SCF level, which leads to a larger destabilization of the HOMO orbital of water and, so, to a smaller ionization potential of the water monomer. Thus, our calculations appear to indicate that the first vertical ionic state of NH_3–H_2O corresponds to the $^2A''$ state. However, given that the two vertical ionization energies are very close and that the relative ordering of these ionic states depends on the geometry of the neutral dimer, optimizations with larger basis sets and improved treatments of correlation energy would be necessary in order to make conclusive assignments.

The optimization of the $^2A'$ state at the MP2 level leads to structure 4b, which maximizes the overlap between the $3a_1$ orbital of NH_3^+ and the $3a_1$ orbital of H_2O. Thus, it resembles the three-electron-hemibond structure that we found for the water dimer. However, the mixing between the $3a_1$ orbital of NH_3^+ and the $3a_1$ orbital of H_2O is very small, and so, the positive charge still remains almost completely on the ammonia monomer, see Figure 5b. This structure 4b with one NH bond eclipsed with the OH bonds of water is a transition state. The imaginary frequency corresponds to the symmetry-breaking mode associated with NH_3 rotation. Releasing symmetry constraints, we get the minimum 4c, which has the NH bonds and OH bonds in an alternate conformation. These structures are not found when we optimize the $^2A'$ state at the SCF level. Instead, we get structure 4d, which has one of the hydrogen atoms of NH_3^+ pointing to the oxygen atom of water. Although the optimization has been carried out with C_s symmetry constraints, this structure has C_{2v} symmetry. Because now the $3a_1$ orbital of NH_3^+ and the $3a_1$ orbital of H_2O lie in different axes, the overlap is zero and the bonding is mainly electrostatic. For the $^2A''$ state the geometrical optimization

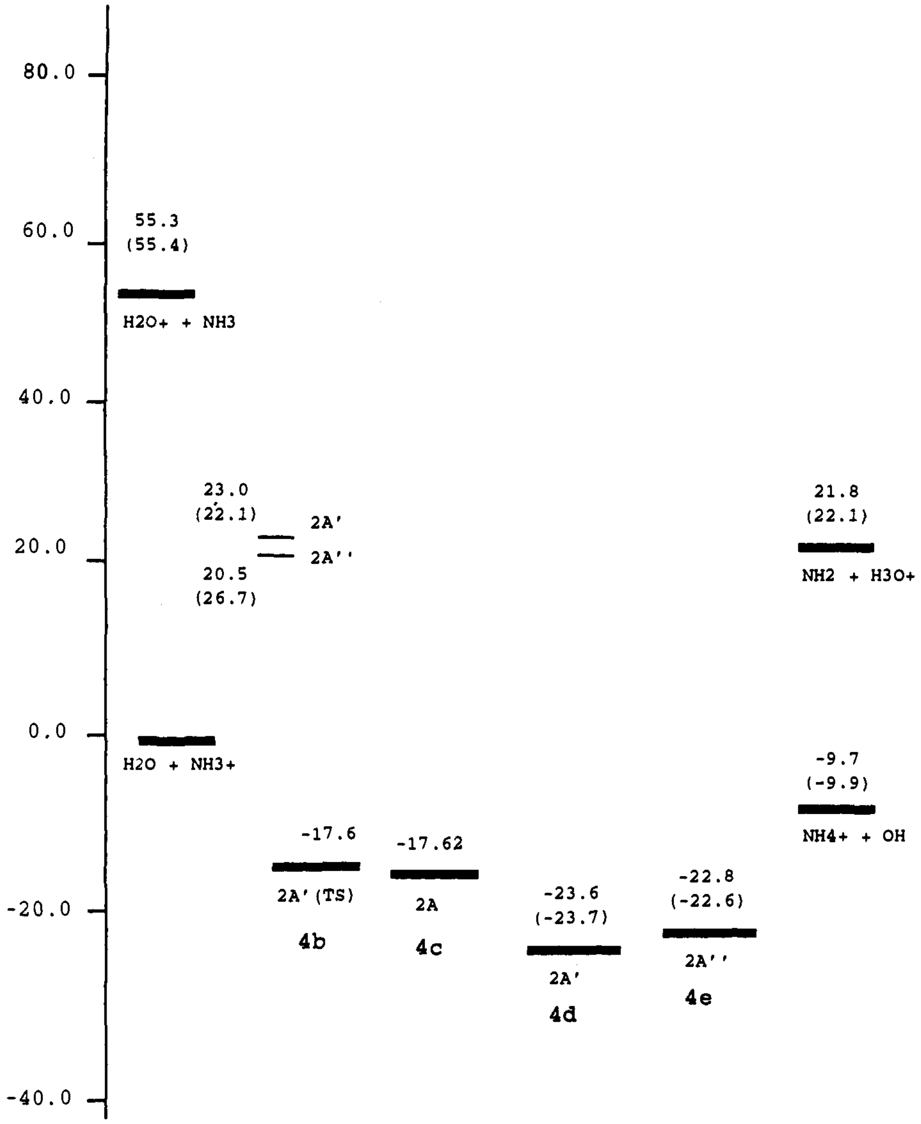

Figure 6. MCPF relative energies (kcal/mol) with respect to the isolated NH_3^+ and H_2O molecules for the NH_3-H_2O-derived radical cations, using MP2(SCF) geometries.

leads, both at the SCF and MP2 levels, to the proton-transfer NH_4^+–OH complex, see Figure 4e. Similar rearrangements have been reported for excited states of NH_3–H_2O.[41]

In Figure 6 we present the MCPF relative energies with respect to the $NH_3^+ + H_2O$ asymptote for all the stationary points found. The relative energies of the vertical ionic $^2A'$ and $^2A''$ states have also been included. As it can be observed, the $^2A'$ and $^2A''$ states are very close in energy and lie within the $NH_3^+ + H_2O$ and $NH_3 + H_2O^+$ asymptotes. This is due to the decrease of the ionization energy of water and the increase of the ionization energy of ammonia in the dimer. The NH_3^+–H_2O complex, structure 4c, that results from the geometrical relaxation of the $^2A'$ state is 17.6 kcal/mol more stable than the isolated NH_3^+ and H_2O molecules. The covalent contribution to the bonding in this structure is small, and therefore, electrostatic interactions favor structure 4d, which is about 6 kcal/mol more stable than structure 4c and corresponds to the global minimum of the potential energy surface. Even though the NH_3^+ is more acidic than H_2O, we have not found the proton-transfer structure NH_2–H_3O^+. Any attempt to optimize such a structure caused collapse to structure 4d. This is not surprising if one considers how high in energy lies the $NH_2 + H_3O^+$ asymptote with respect to the NH_3^+–H_2O global minimum. However, given that the $NH_2 + H_3O^+$ asymptote has a similar energy to the $^2A'$ state, the possibility of obtaining $NH_2 + H_3O^+$ molecules in the ionization process should not be disregarded. Only 0.8 kcal/mol higher than the global minimum lies the proton-transfer NH_4^+–OH complex 4e derived from the relaxation of the $^2A''$ state. This structure has a binding energy with respect to the $NH_4^+ + (^2\Pi)$OH asymptote of 13.1 kcal/mol. Therefore, the products resulting from the ionization of NH_3–H_2O would be either the proton-transfer NH_4^+–OH complex and the dissociated NH_4^+ + OH pair or the non-proton-transfer complex NH_3^+–H_2O and its dissociated $NH_3^+ + H_2O$ molecules, depending on which monomer has been ionized.

C. FH–H_2O and (FH–H_2O)$^+$. The equilibrium structure of the neutral FH–H_2O complex has C_s symmetry with the FH acting as proton donor, see Figure 7a. No minimum was found in an attempt to optimize a structure with H_2O acting as the donor. Similar to the case of the $(H_2O)_2$ and (NH_3–H_2O) dimers, the hydrogen bond in FH–H_2O is almost linear. The optimization at the MP2 level leads to a shorter F–O distance than at the SCF level. Also, the lengthening of the F_1–H_2 distance relative to that in free FH is larger at the correlated level (0.017 Å) than at the SCF level (0.011 Å). The MCPF binding energy is 8.74(8.63) kcal/mol using the MP2(SCF) geometries. Again the effect of the variation of the geometrical parameters on the MCPF binding energy is very small. Our computed value of 8.7 kcal/mol is very similar to the value of 8.8 kcal/mol reported by Del Bene[14] at the MP4/6-311+G(2d,2p) level.

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(41) Köhler, G.; Janoschek, R. *J. Phys. Chem.* **1987**, *91*, 2051.

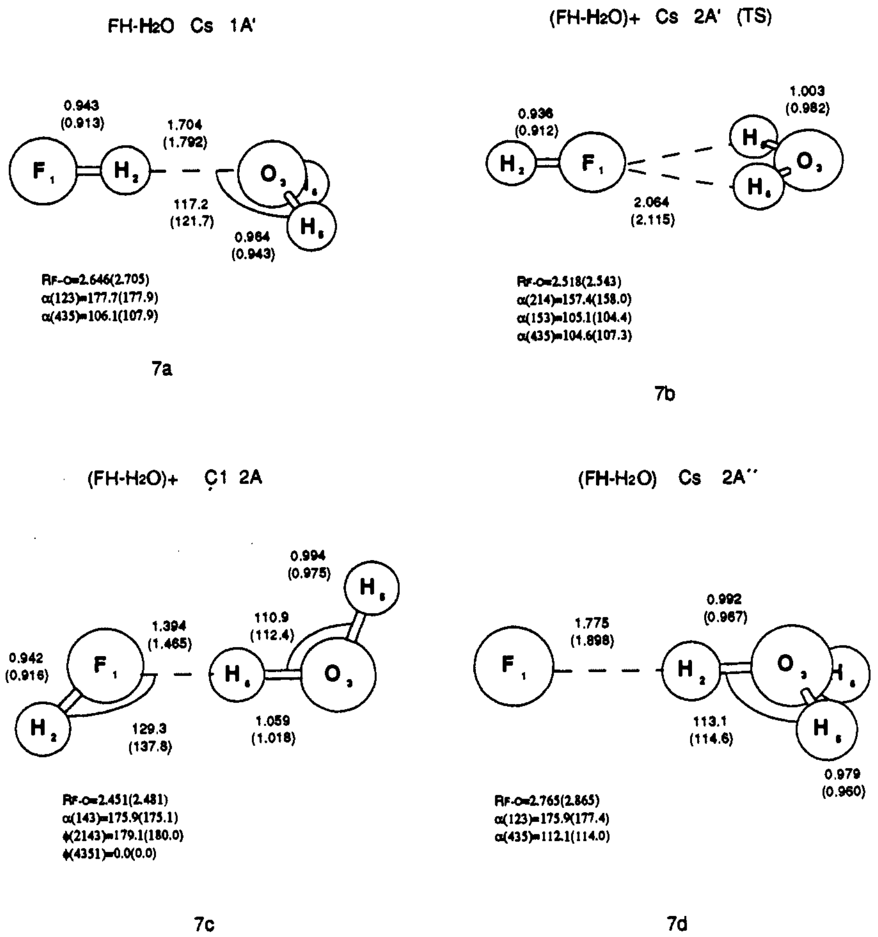

Figure 7. MP2(SCF)-optimized geometries for the neutral FH–H$_2$O dimer and its derived radical cations: FH, R(F–H) = 0.926(0.902) Å; FH$^+$, R(F–H) = 1.007(0.985) Å.

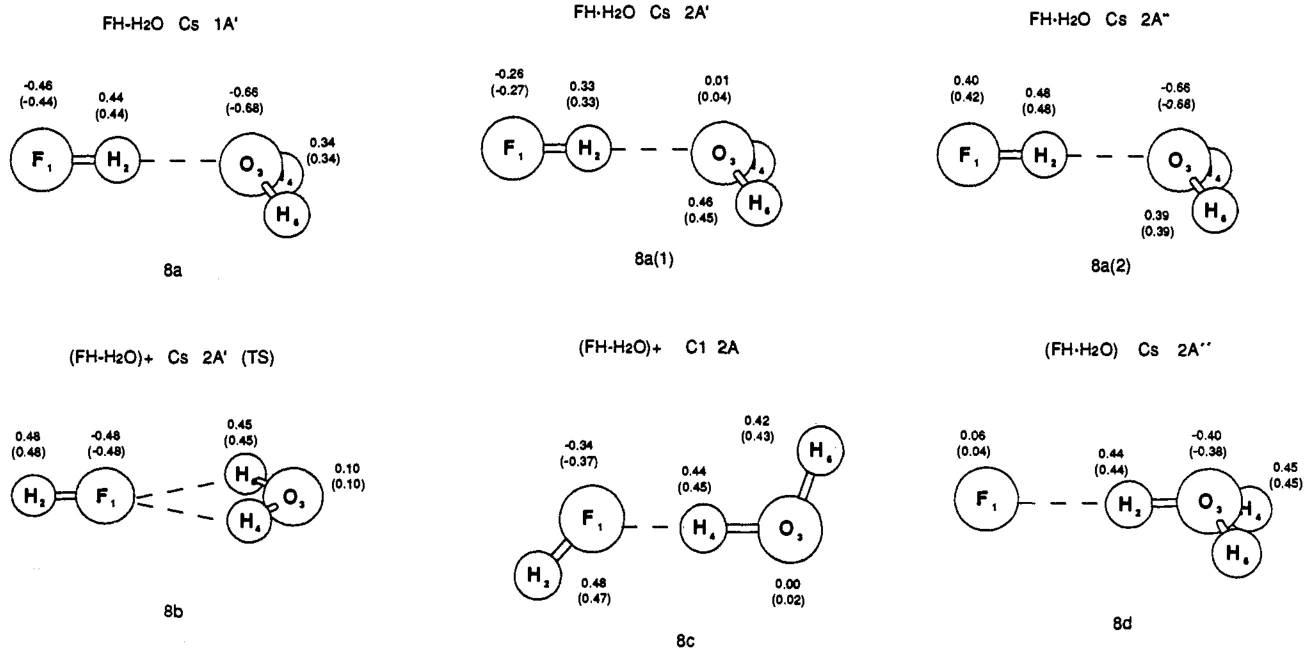

Figure 8. MCPF atomic charges using MP2(SCF) geometries for the neutral FH–H$_2$O dimer, the vertical ionized $^2A'$ and $^2A''$ states, and their derived radical cations.

The electronic configuration of FH–H$_2$O is $1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 7a'^2 2a''^2 8a'^2$. The first vertical ionic state is a $^2A'$ state derived from removing an electron from the 8a′ orbital, which mainly corresponds to the $1b_1$ orbital of water. The second ionic state, $^2A''$, arises from ionizing from the 2a″ orbital, which corresponds to the out-of-plane pπ orbital of FH. The MCPF atomic charges depicted in Figure 8 show that in the $^2A'$ state the charge is almost entirely in the water monomer, while in the $^2A''$ state it is in the hydrogen fluoride. The vertical ionization energies of the $^2A'$ and $^2A''$ states, using the MP2(SCF) geometry

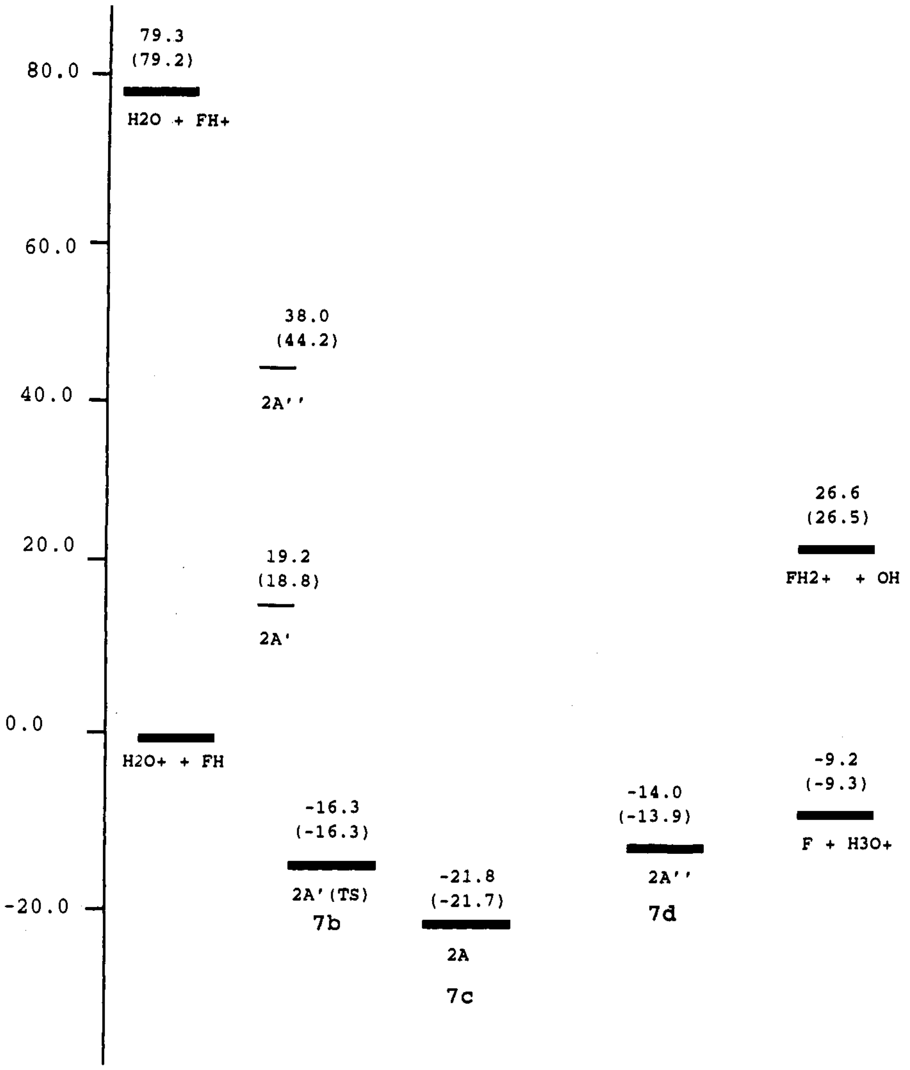

Figure 9. MCPF relative energies (kcal/mol) with respect to the isolated FH and H_2O^+ molecules for the FH-H_2O-derived radical cations, using MP2(SCF) geometries.

of the neutral dimer, are 13.5(13.5) and 14.3(14.6) eV, respectively. Again the formation of the hydrogen bond decreases the ionization energy of the donor (FH) compared to that of free hydrogen fluoride (15.8 eV) and increases the ionization energy of the acceptor (H_2O) relative to free water (12.3 eV). However, given that the difference between the IP of free water and free hydrogen fluoride is large, the ionization of water still remains the most favorable process, even after the formation of the hydrogen bond. This is in contrast to the H_2O–H_2O and NH_3–H_2O dimers, for which the first vertical ionic state corresponds to the ionization of the donor molecule.

Given that removing an electron from water increases its acidity, the $^2A'$ cationic dimer relaxes to a structure with H_2O acting as proton donor and HF acting as proton acceptor, see Figure 7b. Both at the SCF and MP2 levels of calculation this structure is found to be a transition state which, after releasing the symmetry constraints, evolves to structure 7c. In these two stationary points, 7b and 7c, the MCPF atomic charges show that the positive charge remains in the H_2O molecule, see Figure 8b and c. No three-electron-hemibond structures were found in the optimization process of the $^2A'$ state. As expected, the optimization of the second ionic state, $^2A''$, leads to the proton-transfer F–H_3O^+ complex, structure 7d.

In Figure 9 we present the MCPF relative energies, with respect to the H_2O^+ + FH asymptote, of all the stationary points found, as well as the relative position of the two vertical ionic $^2A'$ and $^2A''$ states. These two states lie within the H_2O^+ + FH and H_2O + FH^+ asymptotes, the most stable one being the $^2A'$ state. It can be observed that the global minimum of the potential energy surface corresponds to structure 7c derived from the relaxation of the $^2A'$ state. Significantly higher lies the F–OH_3^+ proton-transfer complex, structure 7d, obtained in the optimization of the $^2A''$ state. Thus, these results show that ionization of FH–H_2O will mainly lead to an hydrogen-bonded complex HF–H_2O^+ in which the HF and H_2O monomers act just inversely than in the neutral parent and not to a proton-transfer complex as in the previous dimers.

Table 1. MP2 Main Geometrical Parameters (in Å) and MCPF(TZ2P++) Binding Energies (in kcal/mol) for H_2O–H_2O, NH_3–H_2O, and H_2O–HF

	r(X–O)	Δ_{XH}	D_e[a]
H_3N–H_2O	2.936	0.012	6.4
H_2O–H_2O	2.911	0.006	5.0
H_2O–HF	2.646	0.017	8.7

[a] The binding energy is computed using the MP2 geometries.

D. Trends. In order to discuss the trends in these hydrogen-bonded complexes, we summarize the most important results of the neutral complexes and their derived radical cations in Tables 1 and 2, respectively. First of all, it is worth noting that the most stable structure of the neutral dimer results as a consequence of the relative acidity/basicity of the two monomers. That is, the monomer with larger basicity acts as proton acceptor and the one with larger acidity acts as proton donor. Because of that, water

Table 2. MCPF Adiabatic, IP_{ad}, and Vertical, IP_v, ionization energies (in eV)[a]

			IP_v		IP_{ad}	
	IP_{ad}		$^2A'$	$^2A''$	npt[b]	pt[c]
NH_3	9.9 (10.2)[d]	NH_3–H_2O	11.2	11.1	9.2	9.2
H_2O	12.3 (12.6)[d]	H_2O–H_2O	12.9 (13.2)[e]	11.5 (12.1)[e]		10.6 (11.1)[e] (11.21)[f]
FH	15.8 (15.9)[d]	H_2O–HF	13.5	14.3	11.7	12.1

[a] Geometries are taken from the MP2 calculations. Experimental values in parentheses. [b] Non-proton-transfer complexes, structures 4d and 7c. [c] Proton-transfer complexes, structures 1c, 4e, and 7d. [d] Reference 20. [e] Reference 19. [f] Reference 39.

is the proton donor when it interacts with ammonia and the proton acceptor when it interacts with hydrogen fluoride. For the three hydrogen-bonded complexes the most stable structure has C_s symmetry with an almost linear hydrogen bond. It can be observed, in Table 1, that the binding energy of the dimer follows the order $(H_2O)_2 < H_3N$–$H_2O <$ FH–OH_2, as expected from electrostatic interactions. Consequently, the lengthening of the HX bond distance due to the formation of the hydrogen bond follows the same order.

Let us now consider the ionization process. In Table 2 we present the MCPF adiabatic ionization potentials of the isolated H_2O, NH_3, and FH molecules and the vertical and adiabatic ionization potentials of the three dimers. As expected the ionization potential of the monomers increases with the atomic number of the heavy atom. Our MCPF values agree reasonably well with the experimental ones. In all cases the two lowest states obtained from ionization of the dimer are the $^2A'$ and $^2A''$ states, depending on whether the ionization is located in the proton acceptor molecule or in the proton donor one. It can also be observed that the formation of the hydrogen bond increases/decreases the energy required to ionize the acceptor/donor monomer. Thus, for the symmetrical $(H_2O)_2$ dimer it is clear that ionizing the donor molecule, the $^2A''$ state, is the most favorable process. For the unsymmetrical (H_3N–H_2O) dimer the hydrogen-bonding interaction leads to two ionic states, $^2A'$ and $^2A''$, that are almost degenerate, the $^2A''$ state being the most stable one at the highest level of calculation. Finally, for the (FH–OH_2) complex the most stable ionic state corresponds to the $^2A'$ state derived from ionizing the acceptor (H_2O) molecule.

For all three hydrogen-bonded dimers the $^2A''$ state evolves to the proton-transfer complex without any barrier due to the increase of acidity of the donor molecule when it is ionized. In contrast, in the $^2A'$ state the increase of acidity is produced in the acceptor molecule and because of that the dimer rearranges in such a way that the role of the two monomers is inverted with respect to the original neutral dimer. For the ammonia–water dimer, the non-proton-transfer (NH_3^+–OH_2) structure is almost degenerate with the proton-transfer (NH_4^+–OH) one. However, for the hydrogen fluoride–water dimer the non-proton-transfer (HF–H_2O^+) complex is clearly more stable than the proton-transfer F–OH_3^+ one. Three-electron-hemibond structures have also been found in the relaxation process of the $^2A'$ state of $(H_2O$–$H_2O)^+$ and $(NH_3$–$H_2O)^+$. However these structures easily evolve to the NH_3^+–H_2O and H_3O^+–OH complexes.

Finally it is worth mentioning the differences between the two approaches of calculation used in the present work. The most important difference is that the three-electron structures are not well described at the SCF level and, so, they don't even exist as minima in the potential energy surface calculated at this level. However, because none of these structures correspond to a global minimum, the main conclusions of this work would not change. The structures that are found at both the SCF and MP2 levels of calculation have similar geometrical parameters, and the relative MCPF energies do not differ significantly whether we use the SCF or the correlated MP2 geometries. Thus, studying the potential energy surface at the SCF level and computing single-point calculations at the correlated MCPF level seems to be a reasonable approach to study these systems. Clearly some caution must be taken when three-electron-bond structures can be involved in the ionization process, especially when these structures are more stable than the proton-transfer complexes, as it happens for the second row AH_n species.[23]

The results obtained in the present work show that, depending on the properties of the monomers that we combine, we can favor the proton-transfer process or the formation of a non-proton-transfer hydrogen-bonded complex in which the role of the two monomers has been inverted with respect to the neutral parent dimer. The proton-transfer process will be favored in those cases where the two monomers have similar IPs while the non-proton-transfer process is expected to be more favorable when the IP of the acceptor molecule is significantly smaller than that of the proton donor molecule. The second process is especially interesting because the monomer that was initially acting as a base is behaving as an acid in the final product. This is the case of the hydrogen fluoride–water dimer and should also be the case of the hydrogen fluoride–ammonia dimer. It would be interesting to test these theoretical previsions by experimental techniques, such as the resonant-enhanced multiphoton ionization (REMPI) techniques, which allow one to study the ionized clusters formed in the supersonic beams.

Conclusions

The vertical ionization of the H_2O–H_2O, NH_3–H_2O, and FH–H_2O hydrogen-bonded dimers and the rearrangement processes in their ionic states have been theoretically studied using a triple-ζ plus two polarization and one diffuse functions basis set and including correlation energy at the MCPF level. Optimizations were carried out at both the SCF and MP2 levels of calculation. The two lowest ionic states are $^2A'$ and $^2A''$ states, depending on whether the ionization is produced in the proton acceptor or in the proton donor molecule. If the ionization is located in the proton donor, the dimer evolves to a proton-transfer complex while, if the ionization is produced in the proton acceptor, it rearranges to a non-proton-transfer hydrogen-bonded structure in which the original acceptor molecule becomes the proton donor. For the water–water and water–ammonia dimers, relaxation of the $^2A'$ state can also lead to three-electron-hemibond complexes. Inclusion of correlation energy is necessary to obtain such structures in the optimization process. For the water dimer cation the most stable structure corresponds to the proton-transfer H_3O^+–OH complex. For the water–ammonia cation the non-proton-transfer complex NH_3^+–H_2O is almost degenerate with the proton-transfer NH_4^+–OH one, and for the hydrogen fluoride–water cation the global minimum corresponds to the hydrogen-bonded HF–H_2O^+ non-proton-transfer complex. The relative energies of these structures can be interpreted in terms of the properties of the monomers and their variation when the hydrogen bond is formed.

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