Ground State of the $(H_2O)_2^+$ Radical Cation: DFT versus Post-Hartree–Fock Methods

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Correlated calculations show the proton-transferred OH–H_3O^+ isomer to be the ground-state structure of the $(H_2O)_2^+$ dimer ion, with the C_{2h} hemibond structure being ca. 8 kcal/mol less stable. Modern density functionals however favor the hemibond structure, overestimating the strength of the three-electron bond by ca. 17 kcal/mol. The wrong prediction of the relative stability of the two isomers is attributed to overestimation by the exchange functionals of the self-interaction part of the exchange energy in the hemibond ion due to its delocalized electron hole. It is cautioned that this erroneous behavior of the density functionals for exchange, if unrecognized, may lead to wrong predictions for ground-state structures of systems with a three-electron bond.

I. Introduction

Ionized hydrogen-bonded clusters are known to play a very important role in atmospheric chemistry or in biological systems. These systems exhibit a very rich chemistry since the ionized clusters can readily experience proton-transfer reactions or molecular rearrangements in which hemibonded species with three-electron bonds are formed.[1–3] The determination of the structure and stability of the derived radical cations is thus important for understanding the reactivity of these clusters upon ionization.

For the most simple $(H_2O)_2^+$ system, previous theoretical studies, using post Hartree–Fock methods,[4,5] have shown that the proton-transferred OH–H_3O^+ isomer is the ground-state structure of the ionized water dimer. Calculations with triple-ζ quality basis sets estimated the hemibonded $(H_2O–H_2O)^+$ isomer to lie 8.9 kcal/mol higher at the MP4 level of theory.[4] The results obtained with the modified coupled pair functional (MCPF) method, which extensively includes electron correlation, provided a similar value; that is, the proton-transferred structure was found to be 9.8 kcal/mol more stable than the hemibonded three-electron one.[5] However, recent density functional calculations with exchange correlation gradient corrections predict the three-electron bond isomer to be the ground-state structure, the computed energy difference between the two structures being 0.22 eV (5.1 kcal/mol).[6]

The previous post Hartree–Fock results are expected to be quite accurate. On the other hand, present functionals have been shown to behave successfully for many systems.[7–9] Thus, at first glance, the discrepancy observed between post-Hartree–Fock methods and density functional calculations in determining the ground-state structure of this system is surprising. We have therefore been motivated to analyze in the present study the performance of different functionals for describing the proton-transferred and hemibonded structures of $(H_2O)_2^+$. Calculations are performed with increasing basis sets to determine the basis set dependence of the DFT functionals, and the DFT results are compared with those obtained at the MP2 level and with

the highly correlated CCSD(T) method. It will be shown that while for the proton-transferred structure all tested functionals provide similar structures and energies, for the three-electron hemibond structure, the dissociation energy and structure are very sensitive to the degree of mixing of the exact HF and DF exchange functional, which leads to a different stability of the two isomers depending on the exchange functional. The different behavior of the tested functionals for the hemibond structure is due to the overestimation of the self-interaction part of the exchange energy, which is not taken into account well in delocalized situations. This is illustrated for the simplest H_2^+ system, for which Bally and Sastry[10] also recently found that it exhibited an anomalous too low energy at long distances.

II. Methods of Calculation

Different density functional approaches have been tested in the present work. In all cases, we have used gradient corrected functionals. For the correlation functional, both the Perdew (P)[11] and the Lee, Yang, and Parr (LYP)[12] functional have been tested along with the exchange functional of Becke (B).[13] Moreover, two different nonlocal hybrid exchange functionals, the Becke's three parameter (B3)[14] and the Beckes's half and half (BH)[15] functionals, have been combined with the LYP correlation functional.

Correlation energy has also been introduced using post Hartree–Fock methods. In particular, calculations have been carried out with the MP2 method and with the most accurate coupled cluster singles and doubles approach including the effect of triple excitations by perturbation theory CCSD(T).[16] In these calculations, all electrons except the 1s-like ones of O have been correlated.
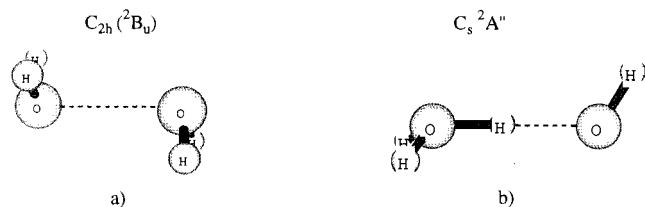
The correlation-consistent polarized valence basis sets, cc-pVxZ, of Dunning et al.[17a] and their extensions to include more diffuse functions, aug-cc-pVxZ,[17b] have been used with all functionals. For the two kinds of basis sets, we have performed calculations with the double-ζ (DZ), triple-ζ (TZ), and quadruple-ζ (QZ) sets.

Calculations have been done imposing C_{2h} symmetry for the hemibonded three-electron $(H_2O–H_2O)^+$ system and C_s sym-

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Ground State of the $(H_2O)_2{}^+$ Radical Cation

J. Phys. Chem. A, Vol. 103, No. 1, 1999 **167**

SCHEME 1

metry for the proton-transfer H_3O^+-OH isomer. Frequency calculations with basis sets larger than double-ζ indicate that these two structures have an imaginary frequency. For H_3O^+-OH, the imaginary frequency corresponds to a symmetry-breaking mode associated to OH rotation. The geometrical parameters of the C_1 minimum obtained following this mode are very similar to the C_s ones and the energy lowering is very small; that is, at the MP2 level with the cc-pVTZ basis set, the energy difference between the C_s and C_1 structures is less than 0.1 kcal/mol. For the hemibond structure, the imaginary frequency corresponds to an out-of-plane twisting mode of the two H_2O monomers. The energy difference between the C_{2h} structure and the C_1 minimum is also very small in this case. Because of that and for computational reasons, we have maintained symmetry in all the reported calculations.

Density functional and MP2 calculations have been performed with the Gaussian 94[18] package and are spin unrestricted. CCSD-(T) calculations have been done with the MOLPRO96[19] programs system and are spin restricted.

III. Results and Discussion

Scheme 1 shows the two molecular structures of $(H_2O)_2{}^+$ that can be obtained after the ionization of the water dimer: (a) the hemibond and (b) the proton-transferred isomers.

The lowest electronic state of the three-electron structure is a ^2B_u state. The singly occupied orbital is the antibonding combination of the two $1b_1$ orbitals of the two monomers, which leads to a complete delocalization of the positive charge (0.5 in each monomer). The lowest electronic state of the proton-transferred structure is a $^2A''$ state. In this case, the open shell mainly corresponds to the out-of-plane a'' orbital of hydroxyl. As a consequence, the positive charge is mainly on the H_3O^+ fragment and the unpaired electron on OH. Because the positive charge and the unpaired electron are on different fragments, this structure corresponds to that of a distonic radical cation.

The variation of the interaction energies of the hemibond and proton-transferred structures computed with respect to the H_2O + H_2O^+ asymptote, with different methods and basis sets, is shown in Figure 1. Except for the CCSD(T) method with the larger aug-cc-pVTZ and QZ basis sets, the interaction energies with each method have been computed using their corresponding optimized geometries. Optimizations at the CCSD(T) level with the larger basis sets have not been possible for computational reasons. In these cases, we have used the optimized MP2 geometries since the results obtained with the smaller basis sets indicate that both methods provide very similar geometrical parameters. Table 1 shows the distances between the two heavy atoms and the energy difference between the two structures obtained with the different theoretical methods used and with the aug-cc-pVxZ basis sets.

First, it can be observed in Figure 1 that, for both structures, the interaction energies decrease when increasing the basis sets due to the diminution of the basis set superposition error. The variation is less pronounced when diffuse functions are added to the basis set: the interaction energies converging quite

rapidly. Correcting for the basis set superposition error by the counterpoise method[20] at the BHLYP level provides binding energies that change less with the basis set and approach the convergence limit. We expect a similar behavior for the other functionals. However, the counterpoise corrections at the MP2 level are larger, with the corrected interaction energies being sometimes too small, compared to the converged value when the diffuse functions basis sets are used, as found in a previous study for the $(H_2O)_2$ neutral system.[21] Thus, Figure 1 only shows the uncorrected values.

Let us first focus on the H_3O^+-OH structure. Figure 1 shows that all functionals provide similar interaction energies. The computed values are only about 2−3 kcal/mol larger than the ones obtained with the conventional correlated MP2 and CCSD-(T) methods. In particular, with the larger augmented basis sets density functional methods provide interaction energies for H_3O^+-OH that lie between 48 and 49 kcal/mol, while the MP2 and CCSD(T) methods provide values of about 46−47 kcal/mol. Moreover, the computed distance between the two heavy atoms is very similar with all methods, with the largest difference being 0.03 Å (see Table 1).

In contrast, for the hemibond structure, the density functional methods tested in this work provide very different interaction energies that range from 57 kcal/mol, for the BP86 and BLYP functionals, to 40 kcal/mol for the BHLYP functional with the larger basis sets. It is worth noting that while changing the correlation functional from P86 to LYP produces only very small variations, the interaction energies differ dramatically when exact HF exchange is introduced in the functional. In particular, it can be observed that the larger is the percentage of exact-exchange mixing the smaller is the interaction energy. The MP2 and CCSD(T) methods with the larger basis sets provide a value of 39−40 kcal/mol. The density functional approach that compares best with the post-Hartree−Fock MP2 and CCSD(T) methods is the BHLYP one, in which the exact-exchange mixing is 50%.

Table 1 also shows that the changes in the computed d_{O-O} distance are more important in the hemibond isomer than in the proton-transferred one; that is, the largest difference is 0.18 Å. It is also interesting to note that the BP86 and BLYP functionals provide similar distances. However, hybrid functionals provide smaller values; the larger the amount of exact exchange introduced in the functional the smaller the obtained distance. As observed for the interaction energies, the functional that better compares with MP2 and CCSD(T) methods is the BH-LYP. Therefore, there is a parallelism between the interaction energies and the d_{O-O} bond length; the larger the bond distances, the larger the interaction energy.

It can be observed in Table 1 that BLYP and BP86 provide the hemibond isomer to be the ground-state structure of $(H_2O)_2{}^+$ due to an overestimation of the three-electron interaction by these functionals. This is in contrast to what is obtained with the post-Hartree−Fock MP2 and CCSD(T) methods, which clearly determine the H_3O^+-OH proton-transfer isomer to be the ground state. Calculations at the CCSD(T) level with the largest aug-cc-pVQZ basis set have not been possible for computational reasons. However, if we assume that the difference between MP2 and CCSD(T) values will be the same as that obtained with the aug-cc-pVTZ set, our best estimate for the energy difference is 7.7 kcal/mol.

The results obtained indicate that for the hemibond structure the density functionals overestimate the interaction energy. The error apparently is related to the functional for exchange, with the overestimation diminishing the more the exchange func-
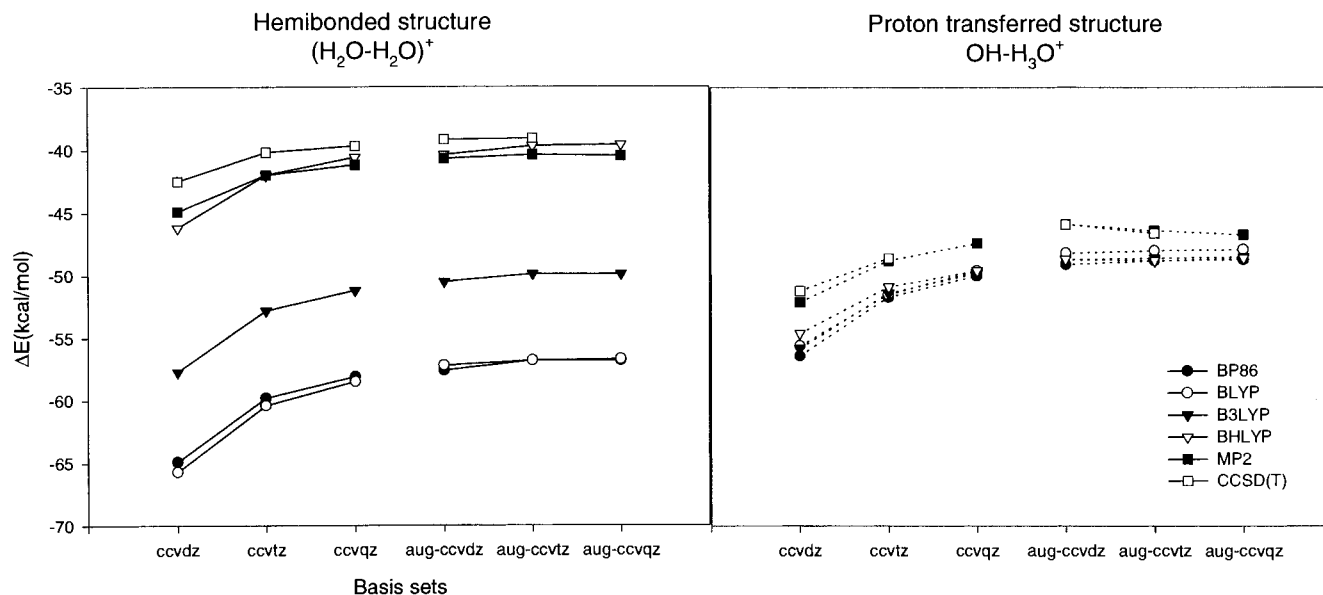
Figure 1. Relative energies with respect to the isolated $H_2O + H_2O^+$ molecules.

TABLE 1. Computed O–O Distances and Relative Energy $\Delta E = E_{hb} - E_{pt}$ with the aug-cc-pVxZ Basis Sets

basis	hemibonded $d_{O–O}$ (Å)			proton transferred $d_{O–O}$ (Å)			ΔE (kcal/mol)		
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
B-P86	2.169	2.170	2.170	2.514	2.511	2.510	−8.5	−8.0	−8.1
B-LYP	2.195	2.204	2.203	2.535	2.535	2.534	−9.0	−8.7	−8.8
B3-LYP	2.120	2.122	2.121	2.517	2.516	2.514	−1.8	−1.3	−1.4
BH-LYP	2.050	2.048	2.047	2.511	2.507	2.508	8.3	9.1	9.0
MP2	2.039	2.024	2.019	2.528	2.502	2.503	5.2	6.0	6.2
CCSD(T)	2.048			2.538			6.6	7.5[a]	7.7[b]

[a] Computed using the MP2 geometries. [b] Estimated from the CCSD(T) and MP2 values computed with the TZ basis set and the MP2 value with the QZ set.

tionals are replaced by exact exchange. An explanation for the failure of the density functionals for exchange in this type of system has been given by Noodleman et al.[22] These authors discussed the simple LDA exchange functional (Xα), but the gradient corrections are not large as a percentage of the calculated exchange energy and the argument holds for the gradient-corrected exchange functionals as well. The largest part of the exchange energy is the cancellation of the self-interaction (SI) included in the Coulomb energy. Noodleman et al. pointed out that the $E_x[\rho]$ functionals overestimate the (negative) SI correction for delocalized states but not for localized states (they can be parametrized, and often are, to have exact SI correction in the localized case). They focused on the problem of ionization from symmetry-equivalent core orbitals or (sub)valence shells (lone pairs, lower ligand orbitals in transition metal complexes). The SI error caused delocalized description of the hole to give a too low energy for the ion. Localized description of the ionization on the other hand, while being variationally the wrong solution in that the computed energy of the ion was higher, usually gave good agreement with experiment, as it avoided the spurious SI error. In addition, the localized ionization provided a better estimate of orbital relaxation upon creation of the hole. The SI error of $E_x[\rho]$ was shown to increase when the delocalization increases, i.e., if the number of sites increases, and when the interaction (overlap between orbitals at the sites) decreases.

The problem has been rediscovered recently by Bally and Sastry[10] who noted that GGA functionals unduly favor delo-

calized solutions in radical ions consisting of two identical dimers, such as the acetylene dimer cation. This could be very clearly demonstrated for the simplest example of ionization from two equivalent shells, the He_2^+ system, where the DFT calculations gave wrong dissociation behavior; at long distance, delocalized solutions are obtained at a too low energy, with the error increasing with increasing distance, i.e., decreasing overlap. A detailed treatment of exactly this problem has been provided by Noodleman et al.,[22] who also stressed the essential difference with the Hartree–Fock method, where the self-interaction is always accounted for exactly, both in the localized and the delocalized case. Bally and Sastry[10] also noted that the H_2^+ ion exhibited similar anomalous low energy in the dissociation limit. Rather than going to the (LDA or GGA) energy of a hydrogen atom (and a proton at large distance), the energy at a distance of 5 Å proved to be ca. 50 kcal/mol too low. Bally and Sastry worried about the delocalized solution also obtained in this case, but as a matter of fact, the simple delocalized single electron wave function

$$\psi_g = (1/\sqrt{2}) \, (1s_a + 1s_b) \tag{1}$$

is in this case the correct solution (if the distance is large enough we may ignore the polarization of the 1s AO by the proton field). Equation 1 stands for the HF and Kohn–Sham solutions as well. A symmetry unrestricted HF calculation may yield the broken symmetry solution with the electron completely localized in a 1s orbital at one H and a proton H^+. Since that solution will be virtually degenerate with the symmetrical solution (which is the proper eigenstate of the $D_{\infty h}$ Hamiltonian), it will also give the right dissociation energy.

This simple H_2^+ case, however, illustrates the problem with the density functionals. If we take the energy of the hydrogen atom

$$E(H) = \left\langle 1s \left| -\frac{1}{2}\nabla^2 + v \right| 1s \right\rangle + \frac{1}{2}J(1s,1s) + E_{xc} \tag{2}$$

written with the Coulomb term (only self-repulsion in this case) and the E_{xc} energy (only SI correction in this case) explicitly, we note that the simple exchange-only LDA, which has α = 2/3, will approximately provide the SI correction, while with α = 0.77725 the SI correction is virtually exact:

Ground State of the (H₂O)₂⁺ Radical Cation

J. Phys. Chem. A, Vol. 103, No. 1, 1999 **169**

$$E_{xc}[1s^2] = -\frac{9\alpha}{2}\left(\frac{3}{4\pi}\right)^{1/3}\int [1s(\mathbf{r})^2]^{4/3}\,d\mathbf{r} = -\frac{1}{2}J(1s,1s) \quad (3)$$

More sophisiticated exchange-correlation functionals also provide good SI correction in the exchange part for the H atom and nearly zero correlation energy, as required. However, in the case of H_2^+, with the wave function of eq 1, the energy can be easily seen to be

$$E = \langle\psi|\bar{h}|\psi\rangle + E_{nuc} = E(H) + \frac{1}{2}\int 1s_a(\mathbf{r})^2 v_b(\mathbf{r})\,d\mathbf{r} +$$
$$\frac{1}{2}\int 1s_b(\mathbf{r})^2 v_a(\mathbf{r})\,d\mathbf{r} + E_{nuc} \quad (4)$$

where we have neglected the slight polarizations of the a atom $1s_a$ wave function by the nuclear potential v_b of the proton at site b and vice versa. Since at large distance the nuclear repulsion $E_{nuc} = +1/R$ will cancel the proton−electron attraction of the second and third terms, the energy of course will approach that of a hydrogen atom. In the DFT case, we write

$$E = \langle\psi|\hat{h}|\psi\rangle + \frac{1}{2}J(\psi,\psi) + E_{xc} + E_{nuc} \quad (5)$$

where again the Coulomb term $(1/2)J(\psi,\psi)$ and the exchange-correlation energy are written explicitly. They will be evaluated in a standard DFT calculation but should of course cancel, representing just self-interaction. The Coulomb term $(1/2)J(\psi,\psi)$ drops for the delocalized ψ of eq 1 to about 50% of what it is in the case of a single H atom,

$$\frac{1}{2}J(\psi,\psi) = \frac{1}{4}J(1s,1s) + \frac{1}{4R} \quad (6)$$

at least at large distances where $1/4R$ is negligible. However, the exhange-correlation energy with the present approximate functionals that employ a $-C[\rho]^{4/3}\,d\mathbf{r}$ form is only reduced by a factor $2(1/2)^{4/3} = 0.794$ if $\rho = (1/2)[1s_a]^2 + (1/2)[1s_b]^2$ and $1s_a$ and $1s_b$ are completely nonoverlapping.

$$E_{xc}\left[\frac{1}{2}1s_a{}^2 + \frac{1}{2}1s_b{}^2\right] = 2E_{xc}\left[\frac{1}{2}1s^2\right] = -2\left(\frac{1}{2}\right)^{4/3}\frac{1}{2}J(1s,1s) \quad (7)$$

So the sum of the Coulomb energy and exchange-correlation energy is no longer zero but becomes $(0.5 - 0.794)J(1s,1s)/2 \approx -57$ kcal/mol, which accounts for the too low energy of this order found in ref 10 at large distances. (At distances of 5 Å, as considered in ref 10 the $1/4R$ factor in eq 6, which has been neglected here, still changes this estimate significantly.)

The H_2^+ molecular ion has been known to be a particularly difficult case for the construction of functionals. Its exchange-correlation hole consists of only an exchange hole that is fully delocalized over the two centers (just $-|\psi(\mathbf{r})|^2$). Since the LDA and GGA model functionals implicitly employ a localized hole, the completely delocalized hole in H_2^+ would require in a hybrid DFT/HF method 100% HF exchange. On the other hand, the H_2 molecule is an example of the extreme opposite; the exact exchange contribution has to go to zero in the dissociation limit.[23] It is obvious that functionals that work only with the local density and density gradient fail to recognize such extreme conditions. It is particularly difficult to devise functionals for these few-electron systems in weak-interaction (dissociation) situations.

The same analysis may be done for the delocalized ionization from two equivalent sites (lone pairs, etc.); see ref 22. Noodleman et al. concentrated on the limit of completely nonoverlapping shells from which the ionization occurred,

similar to the He_2^+ case at large distance. In such cases, DFT calculations with localized ionization usually provide accurate answers. In fact, the quality is the same as in cases where ionization automatically is localized as, for instance, in the unsymmetrical radical cations quoted by Bally and Sastry.[10] Nevertheless, the exact wave function and density for a system like He_2^+ are symmetrical. If one starts from a localized hole, some stabilization would result from the resymmetrizing interaction with the VB structure with the hole localized on the other center. The Kohn−Sham system of independent electrons also ought to yield a symmetrical density, i.e., a delocalized hole. At the same time, the relaxation of the electron density should at each site be as for a local hole. The fact that Kohn−Sham calculations tend to yield delocalized descriptions is not wrong,[10] but the energy of such solutions will suffer from two deficiencies: the error in the self-interaction makes the energy of these delocalized holes too low, while on the other hand, the relaxation of the "passive" orbitals may be underestimated. The relaxation should, like in a solution consisting of two VB structures with local holes, be similar to the one around a local (full) hole. This relaxation is more easily achieved and the SI error avoided by a calculation in which the symmetry is broken and the hole is actually localized, even if such solutions do not have the right symmetry. The energy of such a broken-symmetry solution will however only be reliable if the interaction with the VB structure having the hole on the other site is negligible.

The effect of using delocalized or localized Hartree−Fock orbitals in the correlated post-Hartree−Fock calculations has been checked at the CCSD(T) level. At long distances, the CCSD(T) energy, obtained using delocalized Hartree−Fock orbitals, differs by less than 0.5 kcal/mol from the one computed using localized orbitals.

The three-electron bond, like in the hemibonded $(H_2O)_2^+$ structure, is a particularly difficult case for the existing density functionals. The repulsion coming from the antibonding electron makes the distance between the monomers relatively large. This leads to the SI error for delocalized electrons described above. On the other hand, the interaction is too strong and the distance is too short for application of localized ionization or application of the simple correction formula applied successfully by Noodleman et al.[22] in the case of delocalized core hole ionization.

It is interesting to compare to the second-row analogue $H_2S^+-H_2S$.[24] In this case, the lone pair is softer and the delocalization effect accordingly smaller. The hemibond structure, which is in this case energetically favored over hydrogen-bonded structures, with a bonding energy of ca. 30 kcal/mol[3,24] with respect to H_2S^+ and H_2S, is now calculated to be some 10 kcal/mol too strongly bound at the BP86 level[25] to be compared to the overestimation of 17 kcal/mol found here for the $H_2O^+-H_2O$ system.

IV. Conclusions

The LDA or GGA functionals have a clear tendency to overestimate the energy of the three-electron bond. This is attributed to an overestimation of the self-interaction part by the exchange functionals due to its delocalized electron hole. As a consequence, the hemibond isomer is wrongly predicted to be the ground-state structure of $(H_2O)_2^+$ with the BP86 and BLYP functionals. The admixture of "exact exchange", which rigorously corrects for self-interaction, reduces this error. It is shown that a 50% mixing (in BHLYP) seems to be the hybrid method that provides a better agreement with the MP2 and CCSD(T) calculations, which clearly determine the H_3O^+-OH

proton-transferred isomer to be the ground-state structure. Our best estimate for the energy difference between the two isomers is 7.7 kcal/mol. The obtained results confirm the previous post-Hartree−Fock results and differ from those reported recently by density functional calculations, which predicted the ground-state structure to be the hemibond one. Therefore, density functional calculations for delocalized three-electrons systems should be taken with caution, since they may lead to wrong predictions of the ground-state structures of these systems.

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