Møller–Plesset treatment of electron correlation effects in (HOHOH)⁻

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The effects of electron correlation on the calculated properties of the (HOHOH)⁻ anion are studied using Møller–Plesset (MP) perturbation theory. With this technique, inclusion of corrections up to third order are shown to provide results quite similar to those obtained with an extensive CI approach when equivalent basis sets are used. Barriers to proton transfer between the two oxygen atoms at a fixed $R(OO)$ distance are computed with a number of basis sets ranging from split-valence 4–31G to triple-valence with polarization functions on all atoms, 6–311G**. Each successive enlargement of the basis set leads to a greater barrier. The second-order correction to the energy reduces the Hartree–Fock barrier dramatically while subsequent inclusion of the third-order energy results in an increase over the MP2 barriers. MP3 formalism is found capable of accurately reproducing CI results for both the barrier height and functional dependence of the correlation energy upon the proton position. The potential energy surface is calculated as a function of both the $R(OO)$ distance and the position of the central proton. At the Hartree–Fock level, all basis sets yield a surface with two minima separated by a saddle point, representing the transition state for adiabatic proton transfer. The surface is flattened a great deal by inclusion of second- and third-order corrections such that the barrier to proton transfer is considerably below the estimated zero vibrational level for protonic motion. Electron correlation effects are also responsible for an increase of about 3 kcal/mol in the hydrogen-bond energy of the (HOHOH)⁻ complex.

I. INTRODUCTION

Although capable of supplying useful information, the Hartree–Fock (HF) procedure, when applied to the interactions between closed-shell systems, has been demonstrated to provide poor results in a large number of cases. For example, the HF method fails to corroborate the experimentally established attractive interaction between rare gas atoms.[1] In strong hydrogen-bonded systems of the type (AHA)⁻ or (BHB)⁺, this approximation overestimates the anisotropy of the potential energy surface (PES), leading to a qualitatively incorrect description of the equilibrium region.[2] Generally, the discrepancies between the HF and more exact treatments become more pronounced as one progresses further from the equilibrium region of the PES. Therefore, if one is interested in accurate description of the entire surface, as is necessary in dynamical treatments of reaction, calculation of corrections to the Hartree–Fock PES is essential.

Recent work in this laboratory has centered on studies of proton transfers in hydrogen-bonded systems.[3-5] These calculations, as well as those reported by other workers,[2,6,7] have indicated that inclusion of electron correlation corrections to the HF results are required for accurate treatment of proton transfers. All previous treatments of electron correlation in these systems have utilized either coupled electron pair approach (CEPA) or configuration interaction (CI) techniques. These methods, while capable of providing accurate results, are rather cumbersome and require excessive amounts of computer time and resources. Truncated CI methods are size-inconsistent and approximate relationships are necessary to help correct this deficiency.[8,9]

A second approach to elucidating the effect of electron correlation makes use of Rayleigh–Schrödinger perturbation theory. Møller–Plesset (MP) partitioning of the Hamiltonian[10] offers the advantage of rather simple expressions for correlation energy to second and third orders and partially avoids the full transformation of integrals.[11,12] Also, the time-consuming step of construction and diagonalization of CI matrices is replaced by simple summation. With its greatly reduced demands of computer time, the MP method provides an opportunity to study systems containing larger numbers of electrons than is now feasible with CI approaches. One of the most essential features of this method is its size consistency due to its treatment of linked diagrams only. Like the CI and CEPA approaches,[13-15] the MP method is not entirely free of artifacts such as basis set superposition error (BSSE), particularly when applied to evaluation of interaction energies.

Despite its potential value, previous applications of Rayleigh–Schrödinger perturbation theory to study of intermolecular interactions are few in number and involve van der Waals systems[16,17] and donor-acceptor complexes.[18] We address ourselves in the present communication to the applicability of Møller–Plesset perturbation theory to proton transfer processes and to hydrogen-bonding interactions. As our model system, we choose (HOHOH)⁻ for the following reasons. The simplicity of the system allows us to focus our attention on the fundamental properties of interest without competing effects which might be encountered with more complicated systems. The small size makes possible use of very large basis sets, necessary to eliminate artifacts caused by basis set truncation. A large enough number of points on the potential energy surface may be sampled to reliably extract both general features and specific details of the PES. Of great importance also is the fact that results of a very sophisticated theoretical treatment of this system have been reported previously[7] and may be used to gauge the accuracy of the

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present calculations.

This paper is divided into the following sections: The computational techniques are discussed in Sec. II; the subsequent section is concerned with energetics of proton transfer for a fixed interoxygen separation of 2.65 Å; the characteristics of the two-dimensional potential energy surface which allows for variations in the $R(OO)$ distance are presented in Sec. IV; and in Sec. V, we discuss the binding energy of the (HOHOH)$^-$ complex with respect to dissociation to HOH and OH$^-$.

II. METHODS

All calculations were carried out using the GAUSSIAN 80 computer code.[19] Møller–Plesset perturbation theory to second and third order, respectively denoted as MP2 and MP3,[20] was applied to obtain corrections to the Hartree–Fock energies.[11,12] Where possible, electron correlation effects were computed also using a CI method including all double substitutions (CID). In order to correct the dependence of the CID method upon the number of electron pairs of the system, a size-consistency correction proposed by Pople et al.[9] was applied to the results. All calculations were carried out leaving the oxygen inner-shell orbitals uncorrelated (frozen core approximation).

A number of different basis sets were used in the calculations. The smallest, 4-31G, is of split-valence type.[22] The 6-31G* basis is similar but contains also polarization functions of d type upon the oxygen centers.[23] A triple-valence set, augmented by polarization functions upon the hydrogens (p type) as well as the oxygens, is denoted as 6-311G**.[24] Several basis sets of intermediate size were also used in the calculations. A modification of the 6-31G* basis in which a set of p functions is added to the central hydrogen only is termed 6-31G*(*). The (*) has a similar meaning for the 6-311G*(*) which differs from 6-311G** in that it eliminates the p orbitals from the noncentral hydrogens.

Since we are using the calculated results[7] of Roos, Kraemer, and Diercksen (RKD) as a yardstick by which to measure the accuracy of our own results, molecular geometries were taken from RKD. Specifically, the H bond was assumed linear; i.e., the central proton was restricted to the OO bond axis. The other two hydrogens were maintained at fixed positions relative to the oxygens: $r(OH) = 0.957$ Å; $\theta(HOO) = 104.5°$. These two hydrogens were positioned trans to one another; i.e., $\phi(HOOH) = 180°$.

TABLE I. Energy barriers[a] to proton transfer for $R(OO) = 2.646$ Å.

Basis set	HF	MP2	MP3	HF + $E[2/1]$[b]	CI
4–31G	3.9	0.9	1.6	1.6	1.5[c]
6–31G*	6.2	1.9	3.0	2.7	2.9[c]
6–31G*(*)	6.3	2.1	3.2	3.2	⋯
6–311G*(*)	6.9	3.0	4.3	4.3	⋯
6–311G**	7.5	3.1	4.4	4.4	⋯
[541/31][d]	7.8	⋯	⋯	⋯	4.8

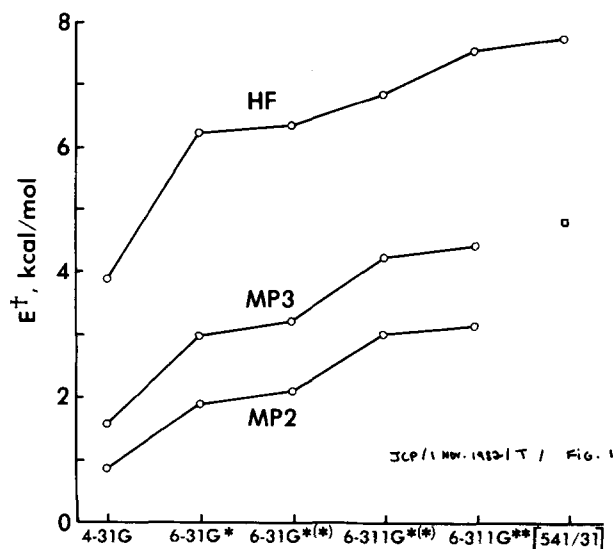[a]In kcal/mol.   [c]CID method.
[b]Padé approximant.   [d]From Ref. 7.

FIG. 1. Calculated barriers $E^\dagger$, for proton transfer in (HOHOH)$^-$ for $R(OO) = 2.646$ Å. [541/31] refers to the basis set of Roos et al. (Ref. 7). The square symbol denotes their result with extensive CI included.

III. PROTON TRANSFER POTENTIALS

Roos, Kraemer, and Diercksen (RKD)[7] have computed the energetics of transfer of the central hydrogen between the two O atoms in (HOHOH)$^-$ at a fixed interoxygen separation of 2.646 Å (5.0 a.u.). The basis set used contained $(11s, 7p, 1d/6s, 1p)$ primitive Gaussians contracted to $[5s, 4p, 1d/3s, 1p]$. Their CI expansion included all single and double excitations, encompassing a total of over 50 000 configurations. At an OO distance of 5 a.u., the potential for proton transfer was found to be of symmetric double-well form with a barrier of 7.8 kcal/mol separating the two minima at the Hartree–Fock level. This barrier was reduced to 4.8 kcal/mol when electron correlation was included via their CI technique.

The results obtained here are summarized in Table I which contains the calculated barrier to proton transfer using the method indicated. All the approaches yield double-well potentials, in agreement with RKD. Proton transfer barriers are defined as the difference in energy between the bottom of the well and the structure in which the proton is midway between the two oxygens. The variations in the calculated barriers reveal some interesting trends. For example, at the Hartree–Fock level, the entries in the first column of the table indicate that increases of the barrier result from progressive enlargements of the basis set. This same pattern is evident also in the MP2 and MP3 barriers in the next two columns.

Besides illustrating the above trend, Fig. 1 also provides more detailed information about the manner in which specific orbital additions influence the transfer barrier. On going from 4-31G to 6-31G*, the principal change is the addition of a set of d orbitals on each oxygen center. As may be noted from Fig. 1, these orbitals produce a rather substantial increase in the transfer barrier at the HF, MP2, and MP3 levels. A much

more modest rise results from further increase of basis set size by incorporation of p polarization functions on the central proton; i.e., 6-31G* to 6-31G*(*). The next increment involves adding a complete set of valence orbitals to each atom. In thus going from a double to a triple-valence basis set [6-31G*(*) to 6-311G*(*)], a fairly large increase in the barrier is noted, particularly at the MP2 and MP3 levels. The last change involves adding p functions to the noncentral hydrogens, giving all protons a polarized basis set. This step from 6-311G*(*) to 6-311G** leads to very small increases for MP2 and MP3 and a slightly larger one for HF. The right terminus of Fig. 1 refers to the [541/31] basis set of RKD. For purposes of comparison, it is noted that 6-311G** would be represented as [431/31] in the same notation. An increase in basis set size from the latter 6-311G** to the RKD set produces a barrier increase of 0.3 kcal/mol at the Hartree–Fock level (see Table I). An increase of a similar amount would bring the MP3 result up quite close to the RKD CI value, indicated by the square in Fig. 1. It therefore appears that third-order Møller–Plesset theory, when applied to a sufficiently large basis set, may reproduce much more time-consuming extensive CI results for proton transfer potentials.

From inspection of Fig. 1, it is clear that second-order MP corrections lead to a rather drastic reduction in the HF barriers with each basis set used. Subsequent inclusion of third-order terms increases the barriers somewhat although the MP3 barriers are still substantially lower than the HF values. The last column of Table I indicates that CI barriers are quite close to those calculated at the MP3 level.

Padé approximants furnish a useful alternative representation of the energy which may be obtained from the perturbation series.[25-27] We use the [2/1] Padé approximant often referred to as a "geometric approximation"

$$E[2/1] = E^{(2)}/(1 - E^{(3)}/E^{(2)}) , \qquad (1)$$

to estimate the infinite sum of higher-order contributions due to double excitations in the HF determinant. Barriers calculated with this approximation, listed in the fourth column of Table I, are identical to the MP3 results (with the exception of 6-31G*). This similarity should be treated with some caution. For example, it has been shown for H_2O that the contribution from double-excitation diagrams to fourth order is larger than that to third order.[26] Whereas inclusion of fourth-order terms seems necessary for absolute energies,

TABLE II. MP perturbation corrections[a] for the midpoint of the proton transfer; $R(OO) = 2.646$ Å.

Basis set	E_{HF}	$E^{(2)}$	$E^{(3)}$	$E^{(2)} + E^{(3)}$
4–31G	−151.194 291	−0.266 043	+0.002 985	−0.263 059
6–31G*	−151.381 582	−0.389 715	−0.004 667	−0.394 382
6–31G*(*)	−151.384 991	−0.390 811	−0.005 523	−0.396 334
6–311G*(*)	−151.434 056	−0.430 060	−0.000 558	−0.430 618
6–311G**	−151.449 070	−0.447 098	−0.000 530	−0.447 628

[a]In hartrees.

TABLE III. Corrections[a] to HF energy of HOH.

Basis set	E_{HF}	$E^{(2)}$	$E^{(3)}$	$E^{(2)} + E^{(3)}$
4–31G	−75.907 385	−0.128 309	−0.001 776	−0.130 085
6–31G*	−76.010 537	−0.186 531	−0.003 880	−0.190 411
6–311G**	−76.046 462	−0.217 407	−0.004 484	−0.221 891
6–311G** +p^b	−76.052 881	−0.221 713	−0.002 702	−0.224 414

[a]In hartrees.
[b]Including an additional set of p functions (exponent 0.072) on O center.

some cancellation of $E^{(4)}$ and higher-order terms is expected when studying energy differences.[17(b),28]

It is worthwhile to compare the magnitudes of the second- and third-order corrections to the Hartree–Fock results. $E^{(2)}$ and $E^{(3)}$ are listed in Table II for each of the basis sets. The entries correspond to the correlation energies of a single geometry; that in which the proton is exactly midway between the two oxygens. From the second column of the table, it may be seen that all second-order terms are of negative sign and are in the general range of 0.3–0.4 hartree. It is particularly interesting that the magnitude of $E^{(2)}$ obeys the same general pattern as the transfer barriers described above. Each successive enlargement of the basis set leads to an increase in $E^{(2)}$ which is directly related to the number of unoccupied orbitals; i.e., the largest increases are noted for the 4-31G to 6-31G* step and the 6-31G*(*) to 6-311G*(*) step.

The third-order corrections are much smaller than $E^{(2)}$, especially for the larger basis sets. The ratio $E^{(3)}/E^{(2)}$ is approximately 0.01 for basis sets up to 6-31G*(*) and only 0.001 for the triple-valence sets. The latter small values demonstrate that second-order perturbation theory yields a much larger fraction of the total correlation energy with larger basis sets. The behavior of $E^{(3)}$ is much more erratic than the second-order term. For example, at the 4-31G level, $E^{(3)}$ is positive while negative terms are obtained with all the other basis sets.

The last column of Table II shows that the total correlation energy included by Møller–Plesset perturbation theory to third order increases with basis set size. As a point of comparison, the E_{corr} obtained by RKD with their CI approach was −0.4208 hartree which is less than $E^{(2)} + E^{(3)}$ obtained with the 6-311G*(*) basis set. This difference is due to the fact that the CI energy includes contributions arising from unlinked diagrams whereas MP3 does not.

Second- and third-order corrections to the Hartree–Fock energy of the HOH monomer are listed in Table III for several of our basis sets. Both terms are negative; $E^{(2)}$ shows an increasing trend with larger basis sets. The ratio $E^{(3)}/E^{(2)}$ lies in the range 0.01 to 0.02. The last row in Table III corresponds to the 6-311G** basis set, augmented by an additional set of p functions on oxygen. The resulting [441/31] basis is nearly equivalent to that used by RKD, who computed a total correlation energy of −0.214 48 a.u., estimated to be 70% of the valence shell correlation energy.[13] The $E^{(2)} + E^{(3)}$
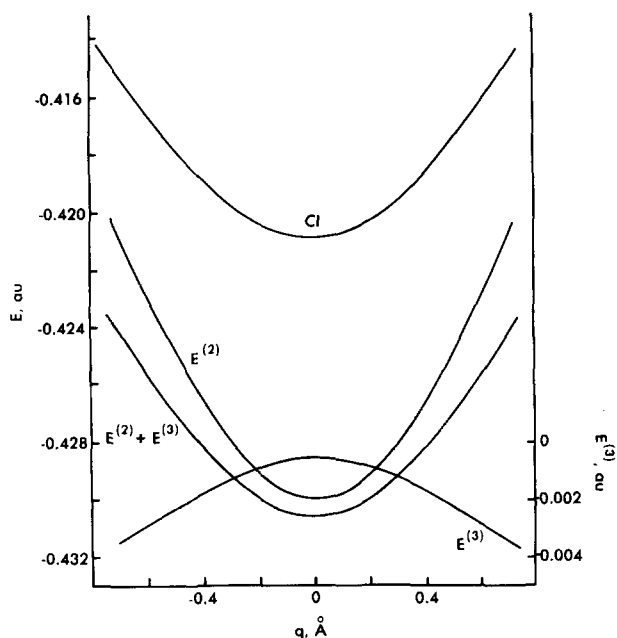
FIG. 2. Contributions to the correlation energy of (HOHOH)⁻ as a function of the motion of the proton between the two oxygen nuclei. $q = r(O_1H) - r(O_2H)$ and is zero when the proton is midway between the two oxygens. The righthand scale refers to $E^{(3)}$; all other properties are referenced against the left scale. $E^{(2)}$ and $E^{(3)}$ were calculated with the 6–311G*(*) basis set. The CI curve refers to the [541/31] basis set of Ref. 7.

correction obtained with our 6-311G** + p basis set, − 0.224 41 a.u., is greater than that noted by RKD. A similar effect was noted by Bartlett for water[21] where MP3 yields 95.2% of the full CI result whereas CI limited to double substitutions leads to only 94.7%. Although it is in principle possible for the truncated perturbation series to yield more than 100% of the full CI value, this was not found to be the case for water[21] nor is it expected for $(O_2H_3)^-$.

As described above, the MP2 barriers to proton transfer are much smaller than the HF values while the MP3 barriers are slightly greater than MP2. In order to analyze the roots of these differences, we have plotted the second- and third-order corrections as a function of the proton position in Fig. 2. The horizontal axis corresponds to $q = r(O_1H) - r(O_2H)$ which is equal to zero when the proton is at the midpoint of the OO axis. $E^{(2)}$ and the sum $E^{(2)} + E^{(3)}$ are measured along the lefthand vertical scale and $E^{(3)}$ on the right axis. The results presented in Fig. 2 were obtained with the 6-311G*(*) basis set for which the second-order correction is three orders of magnitude greater than $E^{(3)}$. However, the influence of these terms upon the barrier depends not upon their relative magnitudes but rather upon the manner in which these terms change as the proton moves along the O–O axis. $E^{(2)}$ is a steep function of the proton position and reaches its maximum negative value when the proton is in the center of the hydrogen bond ($q = 0$). This preferential stabilization of the midpoint results in a greatly reduced barrier to proton transfer for MP2 as compared to HF. $E^{(3)}$, on the other hand, has its *smallest* stabilizing effect when the proton is in the center. Third-order perturbation

corrections therefore destabilize the midpoint and lead to higher barriers than MP2. The greater curvature of the $E^{(2)}$ function than of $E^{(3)}$, and not the greater absolute magnitude of $E^{(2)}$, is responsible for the fact that second-order terms have a greater influence upon the barrier height than do third-order terms. This fact is apparent also from the basic similarity between the $E^{(2)}$ curve in Fig. 2 and that representing the combined effect of $E^{(2)} + E^{(3)}$. Plots of second- and third-order corrections for basis sets other than 6-311G*(*) are quite similar to Fig. 2 with respect to the conclusions outlined above.

The uppermost curve in Fig. 2 corresponds to the correlation energy calculated by the CI approach of RKD with their [541/31] basis set. The close similarity in shape between this curve and that labeled $E^{(2)} + E^{(3)}$ is immediately apparent. The latter curve, if displaced upwards by some 0.01 a.u., may be superimposed almost exactly upon the CI curve. In fact, this relationship is true not only for the 6-311G*(*) basis set to which the curves in Fig. 2 correspond. Curves representing the sum of second- and third-order perturbation energies for each basis set investigated here are quite similar in shape to the CI curve in Fig. 2. It is therefore concluded that third-order Møller–Plesset perturbation theory is capable of accurately reproducing the functional dependence of the CI correlation energy upon the position of the proton, even with relatively small basis sets.

As a point of comparison, the MP3 calculations carried out here with the 4-31G and 6-31G* basis sets required one third the time needed for the CID calculations including double substitutions. The relative efficiency of MP3 is expected to improve further with use of progressively larger basis sets. MP2, on the other hand, which requires essentially the same amount of computer time as Hartree–Fock treatment, is insufficient for accurate determination of proton transfer potentials.

As a final point, we investigated the possible effects on the results of the basis set superposition error (BSSE). In the context of our proton transfer, it might be expected that the magnitude of the BSSE will undergo some change as the proton, with its orbitals, more closely approaches the OH⁻ unit. However, the BSSE was found to be nearly constant as the proton is transferred. Application of the counterpoise method[29] to the 4-31G basis set resulted in very little alteration (by less than 0.1 kcal/mol) of the energetics of the transfer at the SCF level. It is reasonable to assume that the BSSE, an artifact of use of small basis sets, will be of even lesser magnitude for the larger basis sets considered in this paper.

IV. POTENTIAL ENERGY SURFACE

In the previous section, the proton transfer was carried out for a fixed interoxygen distance of 5 a.u. In the absence of extramolecular constraints maintaining these oxygen atoms at a constant distance, it is expected that variations of the $r(OH)$ distance will be dependent upon the values of $R(OO)$ and vice versa. Hence, the in-

TABLE IV. Characteristics of potential energy surface and stationary point $(q = 0)$.

	4–31G				6–31G*				6–311G*(*)			[541/31][a]	
	HF	MP2	MP3	CID	HF	MP2	MP3	CID	HF	MP2	MP3	HF	CI
Number of minima in PES	2	1	2	2	2	1	2	1	2	1	2	2	2
$R(OO)$, Å	2.43	2.50	2.48	2.49	2.42	2.46	2.45	2.45	2.40	2.42	2.41	2.41	2.42
$-\Delta E^b$, kcal/mol	41.2	47.0	44.4	44.3	34.0	42.3	45.2	39.3	34.1	42.7	40.4	23.1	28.0

[a]From Ref. 7.   [b]Relative to isolated HOH+OH⁻.

vestigation of the proton transfer process in two dimensions is necessary. For this purpose the coordinates defining the two-dimensional PES were chosen as follows. The first is simply the interoxygen distance R, equal to $r(O_1H) + r(O_2H)$. We define as our second parameter the difference between these two OH distances: $q = r(O_1H) - r(O_2H)$. q therefore represents twice the distance of the central proton from the midpoint of the OO axis.

The PES for the symmetric (HOHOH)⁻ system may take one of two general shapes. The surface may contain a single minimum in which the proton is located midway between the two oxygen atoms (O–H–O). An alternate shape of the PES contains two equivalent minima, in each of which the proton is more closely associated with one oxygen or the other. These two minima may be denoted (OH–O) and O–HO). It is a straightforward matter to distinguish between these two cases. An optimization of $R(OO)$ with q held at zero $(r(O_1H) = r(O_2H))$ leads to a stationary point on the surface. If at this point the second derivative matrix of the energy with respect to R and q has two positive eigenvalues, the stationary point represents a minimum and we have case (1). If the surface is of type (2), on the other hand, one eigenvalue will be negative and we are sitting at a saddle point, representing the transition state for the proton transfer between the two minima.

The type of surface calculated by each of several theoretical approaches is supplied in the first row of Table IV which contains the number of minima in the PES. At the Hartree–Fock level, all basis sets lead to a double-well PES. MP3 surfaces also contain two minima as does the PES of RKD computed at the CI level. One feature which distinguishes these surfaces from one another is their degree of flatness. Those surfaces computed at the MP3 level are extremely flat; i.e., the curvature of the surface in the vicinity of the saddle point is quite small, of the order of -0.01 mdyn/Å or less. The curvature of the HF surfaces, on the other hand, are several times larger and show an increasing trend as the basis set is enlarged. The greater curvature of the HF surfaces indicate better defined transition states and minima, a feature consistent with the higher barriers to proton transfer at fixed R described in the previous section. All MP2 surfaces contain a single minimum, again in accord with the very low transfer barriers found above for MP2.

The optimized values of $R(OO)$ of the stationary point in Table IV provide another source of comparison. At HF, MP2, and MP3 levels, enlargements of basis set lead to reduced interoxygen separations. Within the framework of a given basis set, R is increased from the HF value by introduction of second-order effects while a small reduction arises from inclusion of third-order terms. With increasing basis set size comes a decreased sensitivity of R to electron correlation. For example, introduction of MP2 to the HF calculation increases R by 0.07 Å for 4-31G but by only 0.02 Å at 6-311G*(*). Møller–Plesset and CI approaches yield quite similar values of R, as evidenced by the agreement between MP3 and CID values for the first two basis sets. It is noted that the 6-311G*(*) values of R are quite similar to the results of RKD. Further agreement is noted in that at the Hartree–Fock level both basis sets yield double-well surfaces. Inclusion of electron correlation via MP3 for 6-311G*(*) and via CI for [541/31] leads also to double-well surfaces but substantially flatter ones.

As noted above, the Hartree–Fock surface contains two minima for each basis set studied here. The positions of these minima were accurately located by simultaneous optimization of both $R(OO)$ and q, and are described in Table V. Enlargement of basis set leads generally to increases in R of the equilibrium structure, a trend opposite to that noted in Table IV for the saddle points in the HF surfaces. This feature is consistent with greater curvature of the PES for larger basis sets and hence higher barriers to proton transfer. Table V also reveals that the equilibrium OH distance gets progressively shorter as the basis set is enlarged. This trend indicates successively weaker interactions between

TABLE V. Characteristics of minima in the Hartree–Fock PES.

	Basis set				
	4–31G	6–31G*(*)	6–311G*(*)	6–311G**	[541/31][a]
$R(OO)$, Å	2.469	2.515	2.509	2.509[b]	2.546
$r(OH)$, Å	1.098	1.046	1.033	1.033[b]	1.022
$E^{\dagger}$, kcal/mol	0.2	0.8	0.6	1.0	1.4
E_{HB}, kcal/mol	41.4	34.8	34.7	34.2	24.5

[a]From Ref. 7. [b]Geometry taken from 6–311G*(*) optimization.

the OH⁻ and HOH units, a property to be discussed further in the next section.

The difference in energy between the minima in Table V and the optimized saddle points in Table IV represents the barrier $E^\dagger$, for proton transfer between the two oxygen atoms along the potential energy surface. The entries in the third row of Table V therefore refer to the barrier to "adiabatic" transfer in which the proton moves sufficiently slowly for the other nuclei to adjust their positions at each stage of transfer. These adiabatic transfer barriers, like the barriers computed in Sec. III for rapid transfers with fixed R, show a generally increasing trend with successive enlargements of the basis set.

The barriers in Table V were all computed at the Hartree–Fock level. It would be useful to calculate these barriers also for approaches incorporating electron correlation. However such evaluation requires accurate location of the minima on the PES. While feasible at the Hartree–Fock level, the necessary optimizations were not possible with the more time-consuming MP techniques. One possible approach at this point might be to simply apply the MP methods to those minima and saddle points already located on the HF surfaces. However, this approach leads to erroneous results since the geometries of the HF and MP minima are not identical. For example, RKD found that the HF and CI minima differ by about 0.1 Å in R and 0.07 Å in r(OH). A small barrier of 0.15 kcal/mol separates the two minima on their CI surface. However, after inclusion of correlation the minima in the HF surface are *higher* in energy than the saddle point, leading to the erroneous conclusion of a single-well potential. Analogous treatment of our 6-311G** results leads to a similar false conclusion; application of MP3 to the HF minima and saddle point indicates a single-well potential while accurate location of the MP3 stationary point shows it to be a saddle point and that the MP3 surface actually is of double-well type.

It is perhaps interesting to note that Hartree–Fock treatment of the 4-31G basis set reproduces surprisingly well most of the properties obtained with much larger basis sets and including electron correlation. The HF/4-31G adiabatic transfer barrier of 0.2 kcal/mol is quite close to the RKD CI/[541/31] value of 0.15. The geometry of the 4-31G minimum is $R = 2.47$ Å, r(OH) $= 1.10$ Å; RKD get 2.465 Å and 1.09 Å. R(OO) in the saddle point for HF/4-31G and CI/[541/31] are 2.43 Å and 2.42 Å, respectively. The transfer barriers obtained in the previous section for fixed R also are in good accord: 3.9 and 4.8 kcal/mol. This close agreement between the two approaches appears to result from a fortuitous cancellation of errors. Enlargement of the basis set beyond 4-31G leads to greater barriers at the Hartree–Fock level while subsequent inclusion of electron correlation produces an opposite effect. Similar arguments pertain to the geometrical parameters.

V. HYDROGEN-BOND ENERGY

In this section we consider the energy of the (HOHOH)⁻ complex relative to the isolated OH⁻ and HOH species

(with geometries as specified in Sec. II). This hydrogen-bond energy, computed at the Hartree–Fock level, is provided in the last row of Table V. The 4-31G H-bond energy is 41.4 kcal/mol while that calculated with the polarized basis sets is between 34.2 and 34.8 kcal/mol. (After correcting the 4-31G value for BSSE, the H-bond energy obtained, 34.7 kcal/mol, resembles closely the latter ones.) The greater interaction energy of 4-31G is reflected also in its shorter interoxygen separation of 2.47 Å as compared to 2.51 Å with the other basis sets. It is notable that the basis sets being applied here lead to substantially greater hydrogen-bond energies than does the [541/31] basis of RKD. Their Hartree–Fock result of 24.5 kcal/mol is nearly eight less than that calculated with the [431/31] basis set denoted 6-311G**. The RKD interoxygen distance is also somewhat longer than for the other basis sets.

Inclusion of electron correlation has in the past been demonstrated to produce H-bond energies in most cases greater than those calculated at the Hartree–Fock level. Indeed, RKD have verified this fact for (HOHOH)⁻ as their CI H-bond energy was 3.6 kcal/mol greater than their HF value of 24.5 kcal/mol. Before comparing the effect of our MP treatment of electron correlation, we reemphasize that evaluation of this quantity requires accurate location of the minima on the PES. Due to computational limitations, we were able to pinpoint the minima with each basis set only on the Hartree–Fock surface. Direct application of perturbation theory to these points may lead to erroneous results for the H-bond energy, as was shown above for the adiabatic barriers to proton transfer. This problem may be circumvented, however, by taking advantage of the flatness of the MP surfaces. Due to this flatness, the energy of the minima differ very little from that of the saddle point. We may therefore approximate the H-bond energy as that of the saddle point and thereby introduce only a small error. To get an estimate of the magnitude of this error, we note that the greatest difference between the saddle point and minimum in a Hartree–Fock PES is 1.0 kcal/mol (see Table V). Since, the MP surfaces are much flatter than each HF PES, we may expect our errors to be substantially smaller than this amount. In the case of a single-well surface, as obtained with MP2, the stationary point is in fact the minimum and is a true representation of the hydrogen-bond energy.

The energies of the stationary points on each PES, relative to isolated OH⁻ and HOH, are presented in the last row of Table IV. It may first be noted that Møller–Plesset treatment of electron correlation, like CI methods, leads to an increased interaction energy. This increase is variable, lying in the range 3.2–11.2 kcal/mol. With the largest basis set, 6-311G*(*), the increase in the HF hydrogen-bond energy produced by MP3 is 6.3 kcal/mol, comparing favorably with the increase of 4.9 kcal/mol obtained by the CI treatment of RKD for the saddle point.

These correlation-induced strengthenings of the H bond may be attributed to the fact that correlation effects tend to build up additional electron density in the region located between the two molecules.[2] This same

charge accumulation is probably responsible also for the fact that inclusion of correlation reduces barriers to proton transfer. The extra charge between the transferring proton and the accepting group may facilitate the motion of the proton towards that group.

A significant discrepancy between the results reported here and those of RKD is the much smaller H-bond energy found by the latter authors. At the Hartree−Fock level, our largest basis set yields a value of 34 kcal/mol while RKD obtain 24.5. Electron correlation increases both values by approximately equal amounts and the discrepancy remains. A similar overestimation of the CI H-bond energy was obtained in an earlier treatment[2] of $(H_3O_2)^-$. It should be stressed that our largest basis set, 6-311G**, was obtained by minimization of the UMP2 rather than HF energies for atoms.[24] This prescription may be expected to lead to rather compact atomic orbitals which can provide an unsatisfactory description of the interaction energy, especially in the case of negative ions. For this reason, 6-311G** was augmented by a set of very diffuse p functions (with exponent 0.072). HF and MP3 calculations with this basis set, applied to the corresponding minima located by RKD in the HF and CI PES led to hydrogen-bond energies of 23.9 and 27.1 kcal/mol, respectively.

The theoretical estimates of the hydrogen-bond energy of (HOHOH)⁻ may be compared with experimental values in the literature. Early work by Friedman et al.[30] led to an energy of 34.5 kcal/mol while more recent mass spectrometric data yielded the smaller value[31] of 25. It must be remembered, however, that these experimental energies refer to $\Delta H°$ measured at approximately 300 K whereas the theoretical values correspond to the electronic contribution to $\Delta E°$. Comparison of the two first requires introduction of zero-point vibrational energies which we estimate to be between 2.4 and 2.9 kcal/mol based in part on empirical correlations with H-bond spectroscopic data described by Novak.[32] Including also the changes in rotational and translational degrees of freedom and ΔPV, we estimate a correction of $+1.0$ kcal/mol in the theoretical H-bond energy for comparison with the experimental value. If we accept the lower experimental value of 25 as probably the more accurate, our calculations with our largest (augmented 6-311G**) basis set agree quite favorably with experiment. The remaining discrepancy between the experimental value and our MP3 hydrogen-bond energy is expected to be reduced by further enlargement of the basis set.

VI. CONCLUSIONS

Møller−Plesset perturbation theory offers an efficient and accurate means of studying the effects of electron correlation in hydrogen-bonded systems. Collection of terms up to third order provides results of comparable accuracy to extensive CI calculations in a fraction of the computer time.

At the Hartree−Fock level, enlargements of the basis set lead to greater barriers to proton transfer. The largest increases arise from introduction of additional orbitals on the oxygen centers. Introduction of electron correlation reduces the Hartree−Fock barriers substantially. Two-electron correlations included in second-order are the chief cause of this lowering as they preferentially stabilize the midpoint of the transfer. An opposite but smaller effect results from inclusion of third-order corrections. The combination of the two correction terms via MP3 leads to close agreement with the extensive CI calculations of Roos et al.[7]

Møller−Plesset and CI approaches also lead to similar potential energy surfaces involving as coordinates $R(OO)$ and $r(OH)$. Hartree−Fock treatment yields double-well surfaces with a saddle point separating the two minima. Electron-correlated surfaces also contain two minima but are extremely flat with a barrier for adiabatic proton transfer of much less than 1 kcal/mol. Since the OH stretching frequency for O−H−O H bonds with bondlength 2.46 Å is of the order[32] of 800−1000 cm⁻¹ it is anticipated that the barrier height mentioned will be far below the ground vibrational level for proton motion.

Electron correlation effects tend to strengthen the interaction between the OH⁻ and HOH units. The increase in the hydrogen-bond energy, obtained with both CI and MP3, is approximately 3 kcal/mol. The magnitude of the interaction energy, like the proton transfer barrier, is quite sensitive to the choice of basis set. The largest basis set used here, 6-311G**, smaller than the [541/31] basis used by RKD, yielded a hydrogen-bond energy higher by some 10 kcal/mol at the Hartree−Fock level. However, when this basis set is supplemented by a set of diffuse p functions on oxygen, the calculated hydrogen-bond energy is in excellent agreement with the results of RKD and with experiment.

Although the magnitude of $E^{(3)}$ is much smaller than the second-order term, it may have a very substantial effect upon properties calculated as energy differences, e.g., transfer barriers and interaction energies.

ACKNOWLEDGMENTS

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