SCF-CI Studies of the Equilibrium Structure and the Proton Transfer Barrier $H_3O_2^-$

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Large-scale configuration interaction (CI) calculations have been performed in order to study the effect of the correlation energy on the equilibrium geometrical structure, the stability, and on the energy barrier of the proton transfer reaction in the hydrogen bonded system $HO^- \cdot HOH$. An extended Gaussian basis set including polarization functions on each nuclear centre has been employed to approximate the molecular orbitals. All possible single and double replacements resulting from a single determinant Hartree-Fock reference state have been taken into account in the CI wavefunction. Compared to the SCF results the equilibrium oxygen/oxygen distance has been obtained from the CI calculations to be smaller by about 0.08 Å and the correlation energy has been found to stabilize the composed system by 3.6 kcal/mole. An almost symmetric equilibrium structure with the hydrogen bonding H-atom midway between the two oxygen centres has been obtained in the CI treatment, whereas SCF calculations yield an asymmetric geometrical configuration with a small energy barrier of 1.4 kcal/mole for the proton transfer process.

1. Introduction

It is a well-known fact that the single determinant Hartree-Fock SCF model is incapable to describe correctly molecular dissociation processes in which a covalent chemical bond is broken. This incorrect behaviour of the Hartree-Fock approximation affects also those molecular properties which depend only on the shape of the energy hypersurface close to the energy minimum. Thus, for example, bond distances usually become too short and stretching force constants too large. The errors in the bond distances, however, happen to be relatively small in most cases (in general not more than a few hundredths of an Ångstrøm), which justifies the use of Hartree-Fock calculations to determine equilibrium geometrical structures and various equilibrium properties.

The deficiencies of the Hartree-Fock model may be expected to show up even for processes where chemical bonds are simply stretched without any bond dissociation. This can already happen during the formation of strong hydrogen bonds as they are found for example in hydrated negative ions. Particularly, the correlation energy contribution, neglected in the Hartree-Fock approach, will play an important rôle if proton transfer reactions are studied

in such systems. Corresponding effects have been discussed for the special case of the monohydrated hydronium ion, $H_3O^+ \cdot H_2O$ [1], which has frequently been used as a model system to investigate the proton mobility in acid solutions by theoretical methods. The same effect has recently been studied for the systems FHF^- and $HO^- \cdot HOH$ within the configuration interaction approach employing only limited Gaussian basis sets to approximate the molecular orbitals [2].

In the present paper results from a more extended SCF and configuration interaction study of the hydrogen bonded system $HO^- \cdot HOH$ are presented. This system has previously been studied [3] within the Hartree-Fock SCF level of approximation using the same Gaussian basis set as in this work. A slightly asymmetric hydrogen bond has been obtained there with a small energy barrier of about 1 kcal/mole for the proton transfer reaction. The corresponding SCF result for the hydration energy of 24.3 kcal/mole appears to be somewhat too small compared to the experimental value of 24.0 kcal/mole, since the theoretical value has still to be corrected for the zero vibrational energy level. On the other hand, an SCF hydration energy of 40 kcal/mole, as has been computed recently [2], is certainly much too large due to the inflexibility of the limited Gaussian basis set used in that particular study.

The main purpose of this investigation was to calculate the effect of the correlation energy on the hydration energy and on the proton transfer barrier in a most accurate way utilizing advanced computer programs presently available. Within the same accuracy correlation energy calculations have been performed for the monohydrated system $H^+ \cdot H_2O$, $Li^+ \cdot H_2O$, $F^- \cdot H_2O$ as well as for the water dimer [5]. In the case of the $F^- \cdot H_2O$ the correlation energy contribution to the binding energy (hydration energy) has been calculated to be about 2.0 kcal/mole. It can be expected that the correlation effect on the binding will be larger for $HO^- \cdot HOH$ since the OH bond in the attached water molecule will be considerably stretched during the hydrogen bond formation.

2. Computational Details

The investigations were performed using a combination of the MUNICH [6] and the MOLECULE [7] program systems. The calculation of the basic integrals, the self-consistent field (SCF) iterations and the transformation of the basic integrals from the atomic to the molecular orbital basis [8] were carried out by the MUNICH programs. For the calculation of the correlation energy contributions a version of the MOLECULE CI program (CIMI method) [9, 10] interfaced to the MUNICH programs was employed.

The molecular orbitals were approximated as linear combinations of contracted Gaussian functions located at the atomic centres. The basis sets used consisted of $(11s\ 7p\ 1d)$ functions at the oxygen centres [11] and of $(6s\ 1p)$ functions at the hydrogens [12]. These functions were contracted to $[5s\ 4p\ 1d]$ and $[3s\ 1p]$ at the oxygens and the hydrogens, respectively, to reduce the number of linear parameters in the SCF iterations and hence the number of configurations in the CI expansion. The exponents of the polarization functions had previously been optimized in SCF calculations for the water molecule [13]. The basis sets presently employed yield an SCF energy for water of -76.05198 hartree. The best value found in the literature is -76.06587 hartree [14].

All single and double excitations arising within the molecular orbital basis, generated in the SCF step, were included in the CI wavefunction. Only the oxygen 1s orbitals were left uncorrelated (frozen). The CI expansion thus comprised a total of 50 280 configura-
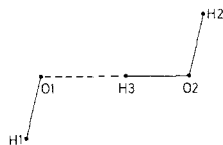
Fig. 1. Geometry of the system $HO^- \cdot HOH$ with a linear hydrogen bond (d(O1H1) = d(O2H2) = 0.957 A; angle (H1O1H3) = angle (H2O2H3) = 104.5°)

tions. In the case of the single water molecule at its experimental equilibrium geometry this type of CI wavefunction gives a total energy of -76.26645 hartree which corresponds to a correlation energy of -0.21448 hartree or 70% of the estimated valence shell correlation energy [5]. As has been shown in a previous study [5], the geometry parameters and force constants obtained on this level of accuracy are all in close agreement with the corresponding experimental data.

The present calculations on the system $HO^- \cdot HOH$ were restricted to a linear structure as shown in Fig. 1. Only the oxygen/oxygen distance and the position of the central hydrogen bonding proton were varied. The outer OH distances as well as the two HOH angles were kept fixed at their values for the isolated water molecule 0.957 Å and 104.5°, respectively. Calculations were performed for four different oxygen/oxygen distances (d(OO) = 2.38 Å, 2.49 Å, 2.51 Å, 2.65 Å), and for each of these distances the position of the central H-atom was varied. The binding energy (hydration energy) of the composed system was determined relative to the energy limit obtained at d(OO) = $100.0a_0$ (52.92 Å).

3. Results and Discussion

In previous studies using the single determinant Hartree-Fock SCF approximation the equilibrium geometry of the system $HO^- \cdot HOH$ has been obtained with a linear, slightly asymmetric hydrogen bond between the two subsystems [2, 3, 15]. Kraemer and Diercksen [3] calculated the equilibrium bond distances for this structure to be d(OO) = 2.51 Å and d(OH) = 1.16 Å, and a value of ΔE = 0.5 kcal/mole was estimated from this SCF energy hypersurface for the proton transfer barrier. In a more extensive geometry variation using, however, a less flexible basis set Newton and Ehrenson [15] obtained also a linear H-bond with d(OO) = 2.45 Å and d(OH) = 1.11 Å, but only a very small value of ΔE = 0.1 kcal/mole for the energy barrier.

Experimental data and theoretical experience show that asymmetric hydrogen bonds occur only in those systems where the hydrogen bond length (the oxygen/oxygen distance in the present case) is larger than about 2.5 Å [16, 17]. Since the calculated oxygen/oxygen distance in $HO^- \cdot HOH$ is very close to this limiting value, it is not possible to decide without further calculations whether the hydrogen bond in $HO^- \cdot HOH$ has a single or a double minimum. Actually, previous configuration interaction calculations [2] yielded a symmetric, single minimum H-bond, but they appeared to be not quite reliable using a rather limited basis set and hence overestimating for example the binding energy of the system (40 kcal/mole).

More accurate SCF and CI total energy values obtained in the present study are compiled in Table 1. The calculated potentials for the hydrogen bonding H-centre are displayed in Fig. 2 for four different d(OO) values. The energy data of Table 1 were used to fit a polynomial expression which was taken up through the third order in D and $\delta(H)^2$, where D is the oxygen/oxygen distance and $\delta(H)$ an asymmetry parameter measuring the displacement of the central proton from the symmetric position midway between the two oxygens.

Table 1. SCF and CI energies for the system $H_3O_2^-$ in different geometrical configurations

$d(OO)$ (a_0)	$\delta(H)^a$ (a_0)	E^{SCF} (Hartree)	$E^{corr.}$ (Hartree)	E^{CI} (Hartree)
4.50	0.000	−151.495226	−0.419317	−151.914543
	0.075	−151.495310	−0.419205	−151.914515
	0.147	−151.495476	−0.418889	−151.914365
	0.200	−151.495558	−0.418535	−151.914093
	0.294	−151.495223	−0.417678	−151.912901
	0.441	−151.491359	−0.415879	−151.907238
4.70	0.000	−151.494166	−0.419855	−151.914021
	0.200	−151.495646	−0.419117	−151.924763
	0.250	−151.496291	−0.418717	−151.915008
	0.300	−151.496893	−0.418244	−151.915137
	0.350	−151.497337	−0.417704	−151.915041
	0.400	−151.497485	−0.417105	−151.914590
4.75	0.000	−151.493173	−0.420002	−151.913175
	0.189	−151.494711	−0.419353	−151.914064
	0.280	−151.496140	−0.418609	−151.914749
	0.340	−151.497006	−0.417991	−151.914997
	0.377	−151.497410	−0.417562	−151.914972
	0.420	−151.497651	−0.417037	−151.914688
	0.500	−151.497118	−0.415963	−151.913081
	0.566	−151.495207	−0.415010	−151.910217
5.00	0.000	−151.484904	−0.420797	−151.905701
	0.230	−151.488226	−0.419905	−151.908131
	0.461	−151.495149	−0.417513	−151.912662
	0.500	−151.496099	−0.417001	−151.913100
	0.550	−151.496965	−0.416316	−151.913281
	0.600	−151.497288	−0.415603	−151.912891
	0.650	−151.496875	−0.414869	−151.911744
	0.691	−151.495825	−0.414253	−151.910078
100.00	−	−151.458642	−0.411679	−151.870321

[a] Displacement of the hydrogen bonding proton from the symmetric position midway between the two oxygens.

This polynomial function was used to determine the equilibrium property values listed in Table 2. The slight differences of the present SCF results to those reported previously by Kraemer and Diercksen [3] are due to a larger number of points, which have been calculated on the energy hypersurface in this study, enabling a more accurate determination of the equilibrium geometry.

Compared to the $d(OH)$ value of the single water molecule the OH distance of the H-atom in the hydrogen bond in $HO^- \cdot HOH$ is increased by 0.135 Å in the CI treatment, but only by 0.065 Å in SCF. This indicates that the process of strong hydrogen bond formation in the present system is connected with a considerable correlation energy effect, as has already been expected. In agreement with this result there is also a big change in the oxygen/oxygen distance due to inclusion of correlation energy. With respect to the corresponding SCF value the $d(OO)$ distance is decreased by 3% (0.081 Å). According to these changes in the bond distances the asymmetry parameter becomes very small $\delta(H) = 0.14$ Å compared to its SCF value of $\delta(H) = 0.25$ Å, i.e. the hydrogen bond becomes almost symmetric (single minimum) after inclusion of the correlation energy. It can be expected that the remaining small
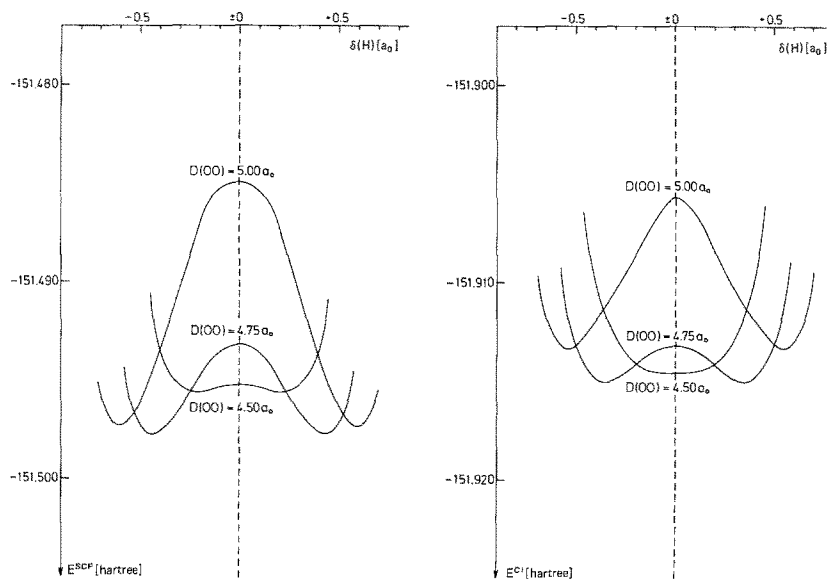
Fig. 2. Potential curves for the hydrogen bonding proton in $HO^- \cdot HOH$ at different oxygen/oxygen distances, on the SCF and the CI level of approximation

asymmetry of the hydrogen bond in the CI treatment will disappear entirely after a complete optimization of the molecular geometry including the outer $d(OH)$ distances and the (HOH) angles.

The correlation energy contribution to the total binding energy is 3.6 kcal/mole (about 15%). As has been expected this value is somewhat larger than in the case of the $F^- \cdot H_2O$ [3]. The SCF value of 24.5 kcal/mole is thus increased to 28.2 kcal/mole. This number has still to be corrected for the zero vibrational energy level in order to be able to compare with experimental data. Due to the very limited geometry variation of this study it was, however, not possible to determine this vibrational correction from the data available. For the related system $F^- \cdot H_2O$ the corresponding correction had recently been evaluated to be about -3 kcal/mole [3]. It seems to be justified to use this value for $HO^- \cdot HOH$ as

Table 2. Calculated equilibrium properties for the system $H_3O_2^-$

	SCF	CI
Total energy (Hartree)[a]	-151.497742	-151.915175
Correlation energy (Hartree)[a]		-0.417433
$d(OO)$ (Å)	2.546	2.465
$d(OH)$ (Å)[b]	1.022	1.092
Binding energy (kcal/mole)[c]	24.54	28.15
Saddle point geometry: $d(OO)$ (Å)	2.411	2.422
ΔE (kcal/mole)[d]	1.44	0.15

[a] At the calculated equilibrium geometry (interpolated values).
[b] Shortest OH distance for the hydrogen bonded proton.
[c] $\Delta E = E(H_2O) + E(OH^-) - E(H_3O_2^-)$. The energies given do not include vibrational corrections.
[d] Energy barrier for proton transfer along the minimum energy path (simultaneous variations of the $d(OH)$ and $d(OO)$).

well, since the hydration energies are similar in both cases. The binding energy is thus finally obtained to be 25 ± 1 kcal/mole, where the error limits are primarily due to the uncertainty in the vibrational energy correction. This value for the hydration energy is in reasonable agreement with the most recent experimental result of 24.0 kcal/mole published by Kebarle *et al.* [4]. It certainly rules out the much higher value of 34.5 kcal/mole reported by Friedman *et al.* [18] as well as the earlier measurement of 22.5 kcal/mole by Kerbarle *et al.* [19].

It can be concluded from the results of this study that the accuracy achieved, using basis sets of the present size and CI expansions including all single and double excitations, appears to be sufficient to calculate reliable molecular geometries and binding energies. Further truncations of the basis set will, however, increase the uncertainty of the calculated results as has been realized from the previous SCF-CI study of $HO^- \cdot HOH$ [2]. It has further been demonstrated that accurate *ab initio* studies of strongly interacting molecular systems have to take into account the correlation energy effects since these effects have apparently a considerable influence on the computed equilibrium structures and binding energies.

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