Physical Chemistry

Interaction of O^+ ion with water molecules: a quantum-chemical study

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The interaction of O^+ ion with several (from one to four) water molecules was studied by the *ab initio* (UMP4/4-31G*) and semiempirical (AM1) quantum-chemical methods. It was found that the energy of binding the O^+ ion to the first water molecule is appreciably higher than those of binding to the subsequent water molecules. In the complex with a water molecule, whose structure corresponds to that of water oxide, the O^+ ion retains high reactivity. The barrier to the transfer of O^+ ion to another water molecule is much lower than the barrier to analogous transfer of O atom from the molecule of water oxide, despite the lower dissociation energy of the H_2O—O bond. Consideration of subsequent interactions with water molecules leads to an increase in the barrier to the transfer of O^+ ion. The doublet and quadruplet excited states of the $O^+ + 2\,H_2O$ system were also studied. In these cases, the formation energies are well described by the ion-dipole model.

Key words: oxygen radical cation, water, transfer reaction, quantum-chemical calculations.

Oxygen transfer plays an important role in many biological and chemical oxidative processes.[1] The mechanism of three-electron oxidation of substrate involving the transfer of O^+ ion:

$$LO^+ + B \longrightarrow BO^+ + L,$$

where L and B are bases, seems to be selective[2] and is of particular interest. This mechanism was proposed to explain unusual selectivity of the oxidation of hydrocarbons in several chemical systems.[2—6] Later, it has been confirmed experimentally.[7]

Previously,[8] we have discussed the problem of the transfer of O^+ cation in our *ab initio* quantum-chemical study of its interaction with methane.[8] Because of high exothermicity of the reactions between O^+ and CH_4, they appeared to be virtually barrierless. If an O^+ cation is bound to a solvate molecule L, its transfer requires overcoming of an energy barrier and is accompanied by cleavage of the L—O^+ bond.

In this work, we studied the thermoneutral reaction

$$H_2O—O^{\cdot +} + H_2O \longrightarrow H_2O + H_2OO^+, \qquad (1)$$

since in this case the energy barrier to transfer of O^+ ion can be assumed to be the upper bound for exothermic oxidation processes. In order to simulate the effects of the medium, we studied the interaction of the reactants and activated complex with one and two extra water molecules. Information on the coordination of O^+ cation to several water molecules is also of importance for an understanding of the mechanisms of not only the reactions under study, but also possible stabilization of O^+ cation in the course of its interaction with ligands.

Calculation procedure

Ab initio calculations were carried out in the unrestricted Hartree—Fock (UHF) approximation with inclusion of correlation effects in the framework of the Møller—Plesset (MP) perturbation theory with the 4-31G* and 6-31G** basis sets using the GAUSSIAN-92 program package.[9] Correlation effects calculated at the MP2—MP4 levels of theory were taken into account. In some instances, the effect of augmentation of the basis set was also studied. The equilibrium geometries and relative energies of the systems under consideration were obtained from UMP2/4-31G* and UMP4SDTQ/4-31G*//UMP2/4-31G* calculations, respectively. Excited states were calculated by the UCIS/4-31G* or UMP2/4-31G* methods, unless otherwise specified.

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The inclusion of correlation effects appreciably affects the energy profile of reaction (1), the geometry of the system in the transition state, and the mutual position of the energy levels. Calculations of electron correlation corrections at higher levels of theory decrease the barrier to this reaction from 18.8 to 1.7 kcal mol^{-1}. This also leads to qualitative changes in the potential energy surface. For instance, if the transition state (TS) energy obtained from the Hartree—Fock calculations is 5 kcal mol^{-1} higher than the energies of the initial reagents, it appears to be 14 kcal mol^{-1} lower than that of the initial level after inclusion of correlation effects. The corresponding changes in the geometry are insignificant.

The interaction of O^+ cation with three or four water molecules was studied by the semiempirical AM1 method,[10] which was chosen after comparing the numerical values of the interaction energies calculated in different approximations (Table 1). Some qualitative differences between the results obtained using the semiempirical and *ab initio* approaches should be pointed out. According to AM1 calculations, one of the TS of the transfer of O^+ ion from the $H_2O—O^+$ system to the water molecule is characterized by positive frequencies of normal vibrations and one of the minima of the $H_2O—O^+ + H_2O$ system is not located. The energy characteristics calculated by the AM1 method agree satisfactorily with those obtained in the UHF approximation. Somewhat worse was the agreement between the results of AM1 calculations and those of calculations performed with inclusion of correlation effects. The structures optimized using the AM1 and *ab initio* approaches have close geometries. The largest differences are 0.15 Å for the O—O bond lengths and 13° for the O—O—H bond angles.

The aforesaid suggests that the AM1 method can be used for qualitative description of the reactions of O^+ cation with several water molecules. One can expect that it satisfactorily reproduces the geometry of stationary states and the affinity of the O^+ ion toward several water molecules. Though the barriers to the transfer of O^+ ion are distinctly overestimated in the AM1 approximation, it is likely that this method can correctly describe changes in their values observed with increasing the number of H_2O solvate molecules.

Results and Discussion

System $O^+ + H_2O$

The interaction of O^+ ion with one water molecule results in a pyramidal complex (**1A**) (Figs. 1 and 2, Table 2):

$$O^{\cdot+}(^4S) + H_2O \longrightarrow H_2O—O^{\cdot+}\ (\mathbf{1A}) + 75.6\ \text{kcal mol}^{-1},$$

in which the O—O bond length is 1.38 Å. This bond is shorter and stronger than the O—O bond (r(O—O) = 1.52 Å) in the water oxide molecule:

$$H_2O—O^{\cdot+} \longrightarrow H_2O + O - 19.9\ \text{kcal mol}^{-1},$$

which is explained by detachment of an electron from the antibonding orbital. Analogous correspondence is also observed for the O_2 and O_2^+ systems: r(O—O) = 1.604 Å, r(O—O^+) = 1.34 Å, D(O—O) = 118.0 kcal mol^{-1}, and D(O—O^+) = 153.5 kcal mol^{-1} [11] (here, D is the dissociation energy of the corresponding bond).

In the $H_2OO^{\cdot+}$ complex, the electron density is appreciably shifted to the O^+ ion (0.78 e), so that the positive charge is localized on the H atoms (each H atom carries a charge of 0.60 e). Therefore the $H_2OO^{\cdot+}$

Table 1. Relative energies (kcal mol^{-1}) of the $H_2OO^{\cdot+}$ + $H_2O \rightarrow H_2OO^{\cdot+}—H_2O$ (**2C**) + ΔE_I and $H_2OO^{\cdot+} + H_2O \rightarrow O^+—2H_2O$ (**2E**) + ΔE_{II} interactions

Method of calculation	ΔE_I	ΔE_{II}
UHF/6-31G**	−23.5	6.7
UMP2/6-31G** //UHF/6-31G**	−25.8	−7.5
UMP3/6-31G**//UHF/6-31G**	−25.2	−2.5
AM1	−27.9	11.2
MNDO	−11.3	37.3
PM3	−28.0	−27.3

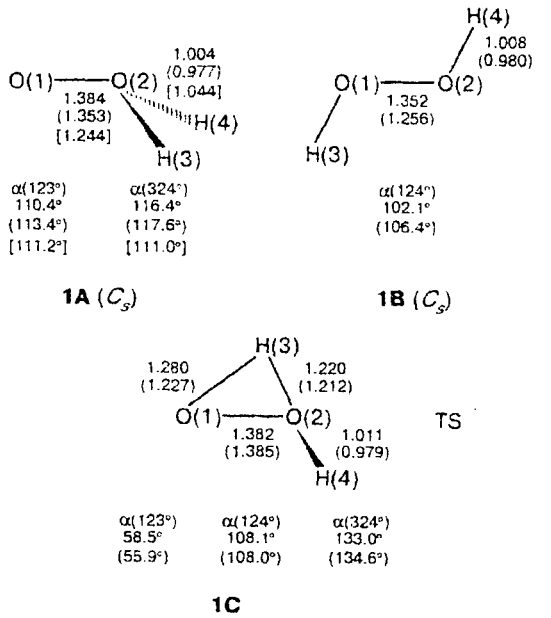


Fig. 1. Geometric characteristics of the structures in the $O^+ + H_2O$ system optimized in the UMP2/4-31G*, UHF/4-31G* (figures in parentheses), and AM1 (figures in square brackets) approximations. For H_2O, r_{OH} = 0.969 (0.948) [0.961] Å and α_{HOH} = 103.8° (105.3°) [103.5°].

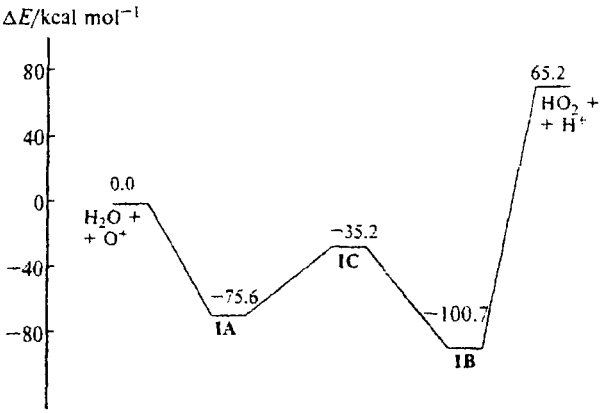


Fig. 2. Relative energies (E) of isomers in the $H_2O_2^+$ system calculated in the UMP4(SDTQ)/4-31G*//UMP2/4-31G* approximation.

Table 2. Energies of the $H_2O_2^+$ and H_2O structures (au) calculated in different approximations

Method of calculation	1A	1B	1C	H_2O
UHF/4-31G*	−150.2618	−150.2716	−150.1668	−75.5860
UMP2/4-31G*//UHF/4-31G*	−150.5783	−150.6185	−150.5147	−75.7069
UMP3/4-31G*//UHF/4-31G*	−150.5906	−150.6231	−150.5182	−75.7101
UHF/6-31G**	−150.4157			−76.0236
UMP2/6-31G**//UHF/6-31G**	−150.7369			−76.2191
UMP3/6-31G**//UHF/6-31G**	−150.7500			−76.2256
UMP2/4-31G*	−150.5800	−150.6269	−150.5155	−76.1251
UMP3/4-31G*//UMP2/4-31G*	−150.5919	−150.6261	−150.5186	−76.1311
UMP4/4-31G*//UMP2/4-31G*	−150.6067	−150.6467	−150.5423	−76.1357
UHF/4-31G*(*ZPE*/kcal mol^{-1})[a]	17.6		13.1	14.4

[a] *ZPE* is the zero-point vibrational energy.

system can also be considered as a complex between the H^+ cation and the $HO_2^{\cdot}$ radical:

$$H^+ + HO_2^{\cdot} \longrightarrow H_2OO^{\cdot+} + 140.83 \text{ kcal mol}^{-1}.$$

However, the protonated radical $HO_2^{\cdot}$ can adopt the energetically more favorable peroxide form **1B**:

$$H^+ + HO_2^{\cdot} \longrightarrow HOO{-}H^{\cdot+} + 165.93 \text{ kcal mol}^{-1}.$$

Interconversion between structures **1A** and **1B** proceeds *via* TS **1C**. However, the barriers to both the forward (**1A** → **1C** → **1B**) and reverse reactions are rather high (40.4 and 65.5 kcal mol^{-1}, respectively). According to MP4/6-31G*//MP2/6-31G* calculations, analogous isomerization of water oxide into hydrogen peroxide is characterized by barriers of 6.3 and 56.0 kcal mol^{-1} to the forward and reverse reaction, respectively.[12] This indicates that ionization of water oxide leads to greater stabilization of the nonclassical structure **1A** as compared to the classical structure **1B**.

System $O^+ + 2H_2O$

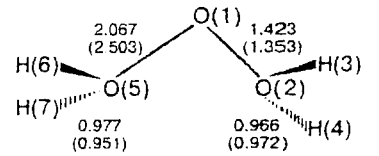
Because of the small size of O^+ cation and its high affinity toward the water molecule, one can expect that it is capable of binding to several H_2O molecules. The interaction of the cation with two water molecules can follow at least three directions.

Complexation. According to our calculations, the interaction of H_2O with $H_2OO^{\cdot+}$ (**1A**) results in the barrierless formation of the equilibrium structure **2A** (Figs. 3 and 4, Table 3):

$$H_2O{-}O^{\cdot+}\ (\mathbf{1A}) + H_2O \longrightarrow H_2OO^{\cdot+}{-}OH_2\ (\mathbf{2A}) + 17.6 \text{ kcal mol}^{-1}.$$

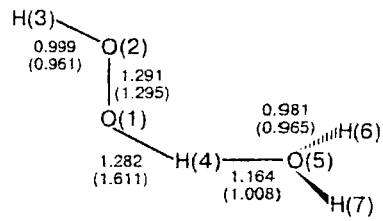
Since this leaves the geometry and charge distribution in the $H_2O{-}O^{\cdot+}$ fragment virtually unchanged (the $O{-}O^+$ bond is lengthened by 0.04 Å only and the atomic charges change by at most 0.01 e), structure **2A** can be considered as a complex between the O^+ ion and two water molecules. One of these molecules is a constituent of the inner coordination sphere whereas the other is a constituent of the outer coordination sphere of the O^+ ion.

H^+ Transfer. Hydrogen atoms in the H_2OO^+ system carry a large positive charge. Hence it should be expected that if a water molecule interacts with H_2OO^+, the water dipole is oriented to a H atom rather than to the O atom and it is the negative pole of the dipole that



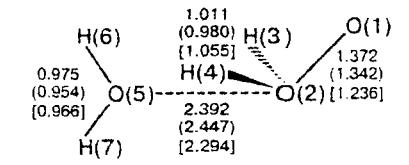
α(215°) α(123°) α(156°) α(324°) α(657°)
95.7° 107.4° 106.4° 107.4° 105.0°
(85.4°) (113.8°) (122.5°) (118.0°) (104.8°)

2A (C_s)



α(123°) α(214°) α(145°) α(456°) α(657°)
105.1° 104.7° 178.1° 114.1° 108.6°
(106.2°) (103.8°) (177.2°) (113.6°) (112.0°)

2B (C_s)



α(125°) α(123°) α(324°) α(256°) α(257°)
140.7° 113.7° 104.8° 117.4° 137.8°
(146.2°) (115.1°) (108.9°) (123.2°) (131.3°)
[117.9°] [111.6°] [109.7°] [125.2°] [129.4°]

2C (C_s)

Fig. 3. Geometric characteristics of structures in the $O^+ + 2H_2O$ system optimized in the UMP2/4-31G*, UHF/4-31G* (figures in parentheses), and AM1 (figures in square brackets) approximations.

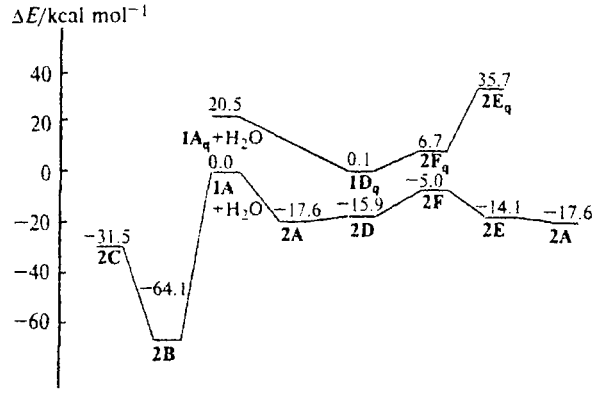


Fig. 4. Relative energies (E) of stationary states in the $O^+ + 2H_2O$ system calculated in the UMP4(SDTQ)/4-31G*//UMP2/4-31G* approximation. The energies of quadruplet states were obtained by the UMP2/4-31G*//UMP2/4-31G* method.

is directed at the H atom. However, this is accompanied by a barrierless proton abstraction from H_2OO^+ and by the formation of structure **2B** (see Figs. 3 and 4), which can be considered as a complex of the H^+ cation with the H_2O molecule and $HO_2^{\cdot}$ radical:

$$H_2OO^{\cdot +} + H_2O \longrightarrow HO_2^{\cdot}\text{—}H_3O^+ \ (\mathbf{2B}) + 64.1 \text{ kcal mol}^{-1}.$$

Unlike the structurally similar radical cation of water dimer[13] with bonds of different length ($r(H_2O\text{—}H)$ = 1.053 Å and $r(H\text{—}OH)$ = 1.524 Å), complex **2B** has a strong hydrogen bond.

Symmetrical interaction of H_2OO^+ with the water molecule results in the formation of structure **2C** with two strongly polarized O—H bonds. This structure corresponds to a transition state through which the exchange of H atoms in complex **2B** can occur rather than to a minimum on the potential energy surface (PES):

$$HO_2^{\cdot}\text{—}H^*H_2O^+ \ (\mathbf{2B}) \longrightarrow \mathbf{2C} \longrightarrow H^*O_2^{\cdot}\text{—}H_3O^+ \ (\mathbf{2B}),$$
$$\Delta E^{\#} = 32.6 \text{ kcal mol}^{-1}.$$

O^+ Transfer from $H_2OO^{\cdot +}$ to H_2O. Our search for the TS of the reaction of transfer of O^+ cation from H_2OO^+ to the other water molecule revealed two saddle points on the PES corresponding to structures **2D** and **2E** with C_{2v} and C_{2h} symmetry, respectively (Fig. 5, Table 3). These structures differ only in tilt of the water molecule; the bond lengths and bond angles in them are rather close. Structures **2E** and **2D** have close energies (E(**2E**) − E(**2D**) = 1.8 kcal mol^{-1}) (see Fig. 4) and the imaginary frequencies of normal vibrations are 653i and 668i cm^{-1}, respectively. These saddle points are separated by a barrier corresponding to a planar structure **2F** with D_{2h} symmetry (E(**2F**) − E(**2D**) = 10.5 kcal mol^{-1}). The O—O bond in the transition state is lengthened to 1.75 Å for both structures. The positive charge on the central O atom increases to 0.4 e. The unpaired electron is also mainly localized on this atom (the spin density is 1.09). Transfer of O^+ cation **2A** → **2D** (**2E**) → **2A** is accompanied by overcoming of a low activation barrier (1.7 kcal mol^{-1} for **2D** and 3.5 kcal mol^{-1} for **2E**). The energies of structures **2D** and **2E** are lower than those of the initial reactants by 15.9 and 14.1 kcal mol^{-1}, respectively.

It is of interest to compare the results obtained in this work with the data on the transfer of O atoms in the $H_2OO + H_2O$ system.[12] According to MP4/6-31G*//MP2/6-31G* calculations, the O—O bond length in both the $H_2O\text{—}O\text{—}OH_2$ transition state with C_{2h} symmetry and structure **2E** is ~1.7 Å, whereas the energy barriers relative to the noninteracting $H_2OO + H_2O$

Table 3. Energies of stationary states in the $O^+ + 2H_2O$ system (au) calculated in different approximations

Method of calculation	$H_2OO^+ + H_2O$	**2A**	**2B**	**2C**	$HO_2 + H_3O^+$	**2D**	**2E**	**2F**
UHF/4-31G*	−226.2008	−226.2229	−226.2816	−226.2453	−226.2487	−226.1919	−226.1928	−226.1883
UMP2/4-31G*// UHF/4-31G*	−226.7026	−226.7270		−226.7531	−226.7610	−226.7157	−226.7163	−226.7050
UMP3/4-31G*// UHF/4-31G*	−226.7210	−226.7450		−226.7700	−226.7766	−226.7261	−226.7268	−226.7170
UHF/6-31G**	−226.4393			−226.4825	−226.4870	−226.4279	−226.4286	−226.4255
UMP2/6-31G**// UHF/6-31G**	−226.9560	−226.9834[a]		−227.0042	−227.0126	−226.9665	−226.9680	−226.9581
UMP3/6-31G**// UHF/6-31G**	−226.9756	−226.7322		−227.0225	−227.0294	−226.9783	−226.9795	−226.9711
UMP2/4-31G*	−226.7051	−226.7322	−226.8115	−226.7562	−226.7633	−226.7254	−226.7230	−226.7087
UMP3/4-31G*// UMP2/4-31G*	−226.7230	−226.7475	−226.8207	−226.7722	−226.7784	−226.7315	−226.7312	−226.7190
UMP4/4-31G*// UMP2/4-31G*	−226.7424	−226.7704	−226.8446	−226.7926	−226.7997	−226.7678	−226.7648	−226.7505
UHF/4-31G* (ZPE/kcal mol^{-1})	32.0	33.7	34.8	34.5	32.8	33.4	32.3[b]	31.6

[a] Calculated by the UMP2/6-31G**//UMP2/6-31G** method.
[b] Calculated by the UMP2/4-31G* method.

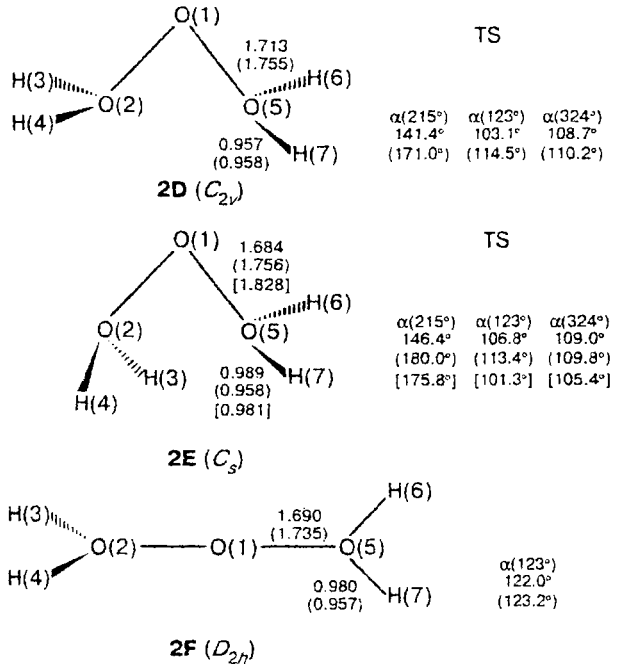


Fig. 5. Geometric characteristics of transition states of the reaction of the transfer of the O^+ cation in the $O^+ + 2H_2O$ system optimized in the UMP2/4-31G*, UHF/4-31G* (figures in parentheses), and AM1 (figures in square brackets) approximations.

system and the $H_2OO—H_2O$ complex are 2.8 and 24.4 kcal mol^{-1}, respectively. Thus the activation energies for the transfer of O atoms and O^+ cation, as well as the energies of binding between these species and the water molecule, change in opposite directions, which indicates that the stabilized O^+ cation retains its high reactivity.

Excited states of the $O^+ + H_2O$ and $O^+ + 2H_2O$ systems

Characteristic of the $H_2OO^{\cdot+}$ associate is a doublet ground state with A' symmetry, which correlates with the triply degenerate doublet ^2P term of the O^+ ion. Hence the interaction of $O^+(^2P)$ with a water molecule leads to the appearance of low-lying excited states caused by splitting of the degenerate atom P term. In terms of the molecular orbital (MO) theory, these excitations correspond to the transfer of an electron between π-MOs of the O—O bond, differing in orientation with respect to the symmetry plane of the $H_2OO^{\cdot+}$ cation, as well as to the electron transfer from the σ-MO to the π-MO.

We studied the lowest A'' and A' excited states of the $H_2OO^{\cdot+}$ associate and the corresponding B_1 and B_2 states of the $H_2O—O—H_2O^+$ (**2D**) system (Table 4, Fig. 6). The first excited state of the H_2OO^+ associate (**1A***) has an A'' symmetry and its energy is 15.6 kcal mol^{-1} higher than that of the ground state. The energy difference between structures **2D** and **2D*** with B_1 symmetry is close to this value (11.2 kcal mol^{-1}). However, form **2D*** is not a TS since it is transformed into the $HO_2^{\cdot}—H_3O^+$ complex owing to proton transfer after removal of symmetry restrictions and further optimization.

The second A' excited state appears after the transfer of an electron from the σ-MO to π-MO of the O—O bond. Optimization yields a planar structure **1A**** with C_{2v} symmetry and substantially lengthened (up to 3.5 Å) O—O bond. This structure is a polarization complex between the an O atom and the $H_2O^{\cdot+}$ ion (E(**1A****) − E(**1A**) = 6.6 kcal mol^{-1}). The energy of the corresponding structure **2D**** with B_2 symmetry, which is also a polarization complex between an O atom and the cation comprising two bound water molecules, is 17.2 kcal mol^{-1} lower than that of structure **2D**.

Thus, the transfer of an electron between the π-MOs of the O—O bond involves a shift of the states of the $H_2O—O^{\cdot+} + H_2O$ system toward higher energies relative to the ground state (**1A** − **2D** → **1A*** − **2D***), whereas the σ→π excitation appreciably changes the PES profile due to the formation of a low-lying structure **2D**** in which the electron is transferred from the water molecule to the O^+ ion. The existence of symmetric complexes of the $O—(H_2O—H_2O)^{\cdot+}$ type can be suggested; however, our attempts to locate them failed.

Table 4. Energies (au) of excited states in the H_2OO^+ and $H_2O—O—H_2O^+$ systems

Method of calculation	Structure			
	1A*	**1A****	**2D***	**2D****
UCIS/4-31G*	−150.2370	−150.2512	−226.1741	−226.2194
UMP2/4-31G*	−150.5621		−226.7108	

Quadruplet states of the $O^+ + H_2O$ and $O^+ + 2H_2O$ systems

Characteristic of the O^+ ion is a quadruplet ground state (^4S). Therefore, it is appropriate to consider "quadruplet" products of the interaction of O^+ cation with one or two water molecules in addition to "doublet" products. Compared to form **1A**, the $H_2OO^{\cdot+}$ ion in the $\mathbf{1A_q}$ quadruplet state (Fig. 7, Table 5) is characterized by the O—O bond being lengthened by 0.57 Å, as well as by a large positive charge (0.52 e) and spin density on the terminal O atom. The formation energy of complex $\mathbf{1A_q}$ is 55.1 kcal mol^{-1}.

The interaction of $H_2OO^{\cdot+}$ ($\mathbf{1A_q}$) with one water molecule leads to changes in the distribution of stationary points on the PES. No complex of the type **2A** is located since it is transformed into a form similar to **2B** due to the transfer of H^+ cation (this structure was not studied in detail). However, despite the polarized nature of complex $\mathbf{1A_q}$, calculations of the interaction with an extra water molecule performed assuming equivalence of

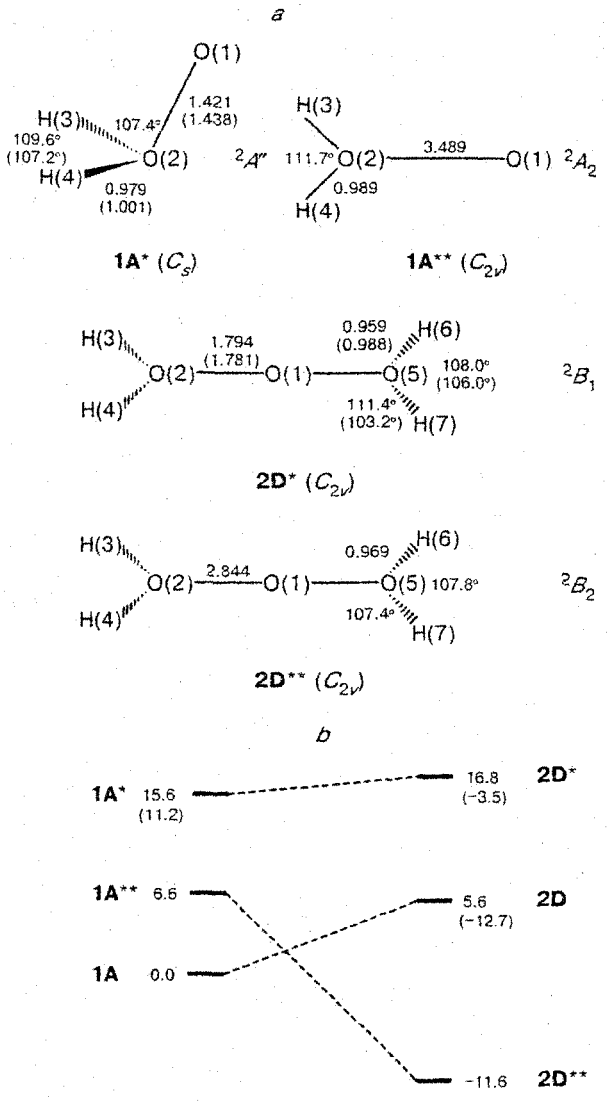


Fig. 6. Geometric characteristics of structures (*a*) and relative energies (*b*) of excited states in the $H_2OO^{\cdot+}$ and $H_2O{-}O{-}H_2O^+$ systems calculated in the UCIS/4-31G* and UMP2/4-31G*//UMP2/4-31G* (figures in parentheses) approximations.

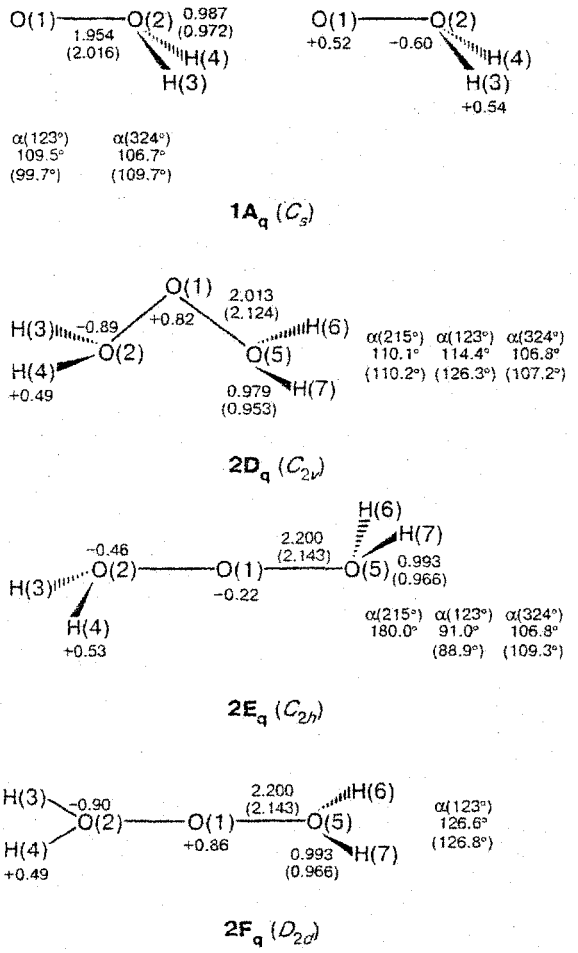


Fig. 7. Geometric parameters and charge distributions in the structures of stationary "quadruplet" states in the H_2OO^+ and $H_2OO^+ + H_2O$ systems calculated in the UMP2/4-31G*// UMP2/4-31G* and UHF/4-31G* (figures in parentheses) approximations.

the O—O bonds lead to unstable structures $\mathbf{2D_q}$ and $\mathbf{2E_q}$ corresponding to the third- and fourth-order saddle points (Fig. 7). The geometries of these structures are similar to those of systems **2E** and **2D**. No planar structure similar to **2F** was found; at the same time, if calculations are performed assuming a D_{2d} symmetry of the system, the corresponding second-order saddle point ($\mathbf{2F_q}$) was located. In all of these structures, the O—O distance (2.0—2.2 Å) is appreciably longer than that in structure $\mathbf{1A_q}$. Systems $\mathbf{2D_q}$ and $\mathbf{2F_q}$ are more stable relative to the initial reagents, H_2OO^+ ($\mathbf{1A_q}$) and H_2O, as compared to the corresponding doublet states. Considering these structures as a "rigid" O^+ ion and

Table 5. Energies of quadruplet states in the $H_2OO^{\cdot+} + H_2O$ system (au)

Method of calculation	Structure			
	$H_2OO^{\cdot+} + H_2O$	$\mathbf{2D_q}$	$\mathbf{2E_q}$	$\mathbf{2F_q}$
UHF/4-31G*	−226.2132	−226.2427	−226.1662	−226.2406
UMP2/4-31G*//UMP2/4-31G*	−226.6705	−226.7030	−226.6462	−226.6925
UMP3/4-31G*//UMP2/4-31G*	−226.6951	−226.7239		
UMP4/4-31G*//UMP2/4-31G*	−226.7098	−226.7419		
UHF/4-31G*(*ZPE*/kcal mol^{-1})	30.1	31.0	31.7	31.4

polarizable water dipoles, it is possible to find the energies of their formation

$$O^+ (^4S) + 2\,H_2O \longrightarrow H_2O{-}O^{\cdot+}{-}H_2O\ (\mathbf{2D_q},\ \mathbf{2F_q},\ \mathbf{2E_q}).$$

Taking into account the Coulomb and polarization contributions, we get 65.5, 65.8, and 38.8 kcal mol^{-1} for $\mathbf{2D_q}$, $\mathbf{2F_q}$, and $\mathbf{2E_q}$, respectively. These values are in good agreement with the results of *ab initio* calculations (73.7, 67.1, and 38.0 kcal mol^{-1}, respectively), except for structure $\mathbf{2D_q}$, for which the contribution of chemical (exchange) interactions seems to be larger than for other structures.

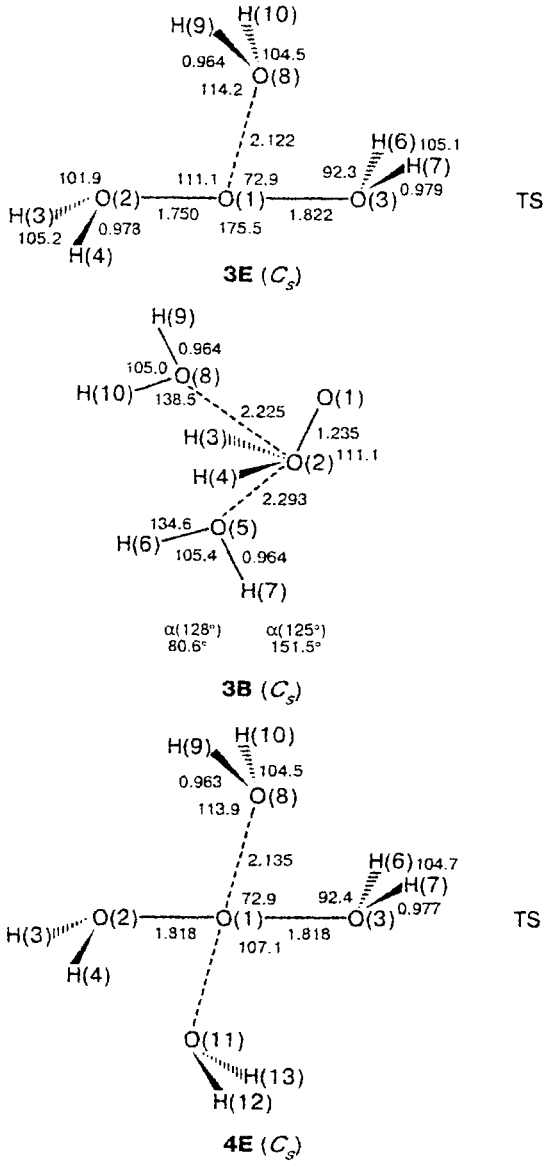


Fig. 8. Geometric structures of the $O^+ + 3H_2O$ and $O^+ + 4H_2O$ systems optimized in the AM1 approximation ("TS" denotes transition states).

Though the "quadruplet" PES of the $H_2OO^{\cdot+} + H_2O$ system was studied in less detail than the "doublet" PES, the results obtained suggest a less selective (more "rigid") interaction. Only proton transfer resulting in the formation of the $HO_2{-}H_3O^+$ adduct is observed instead of the formation of the $H_2OO^{\cdot+}{-}H_2O$ complex and the transfer of O^+ cation from one to the other water molecule in the case of the doublet state of the system.

Systems $O^+ + 3H_2O$ and $O^+ + 4H_2O$

The interactions of O^+ cation with three and four water molecules were studied by the semiempirical AM1 method. In the first case, a $H_2OO^{\cdot+}{-}2H_2O$ structure (**3B**) is formed (Fig. 8), comprising a virtually undistorted $H_2OO^{\cdot+}$ radical ion and two water molecules lying in the symmetry plane of the H_2OO^+ fragment and formally constituting the outer coordination sphere of the O^+ ion.

$$O^+ (^4S) + H_2O \longrightarrow H_2OO^{\cdot+}\ (\mathbf{1A}) + 57.2\ \text{kcal mol}^{-1}\ (\text{AM1}),$$

$$H_2OO^{\cdot+} + H_2O \longrightarrow H_2OO^{\cdot+}{-}H_2O\ (\mathbf{2C}) + 27.9\ \text{kcal mol}^{-1},$$

$$H_2OO^{\cdot+}{-}H_2O + H_2O \longrightarrow H_2OO^{\cdot+}{-}2\,H_2O\ (\mathbf{3B}) + 22.5\ \text{kcal mol}^{-1}.$$

Close values of binding energies of the outer-sphere water molecules and their coordination to H atoms in the $H_2OO^{\cdot+}$ fragment, carrying the largest positive charges, indicate a polarized nature of the complex (Table 5). On the contrary, TS **2E** is characterized by concentration of a rather large positive charge on the central O atom. Therefore it can be suggested that the concentration of charge on the transferred O^+ ion will cause strengthening of the interaction of this TS with the

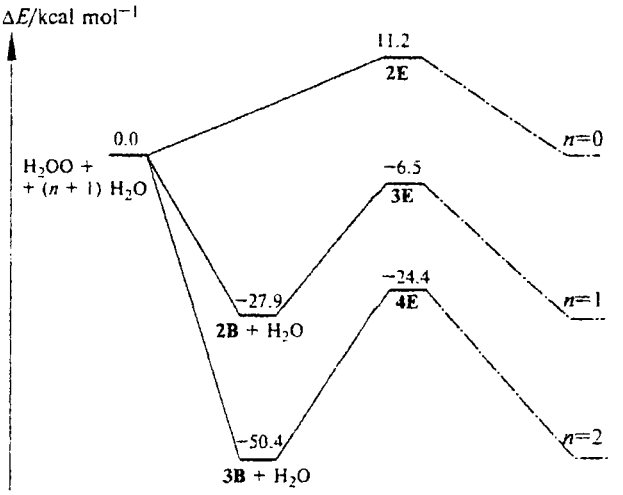


Fig. 9. Relative energies (E) of complexes and transition states of the reaction of the transfer of the O^+ cation in the $H_2OO^{\cdot+} + (n + 1)H_2O$ (n = 0, 1, 2) systems calculated by the AM1 method.

Table 6. Energies (E/au) and charges (e) on the O and H atoms calculated by the AM1 method (for H_2O, $E = -0.0944$ au)

Structure	E /au	ZPE /kcal mol^{-1}	q/e				
			O(1) (H(3,4))	O(2) (H(6,7))	O(5) (H(9,10))	O(8) (H(12,13))	O(11)
1A	0.3784		0.11	−0.05 (0.47)			
2E	0.3018	30.7	0.15	−0.26 (0.32)	−0.19 (0.33)		
2B	0.2395	31.3	0.07	−0.05 (0.47)	−0.6 (0.32)		
3E	0.1791	46.1	0.19	−0.25 (0.33)	−0.28 (0.32)	−0.54 (0.29)	
3B	0.1092	46.7	0.04	−0.02 (0.46)	−0.57 (0.30)	−0.57 (0.30)	
4E	0.0562	61.6	0.26	−0.29 (0.32)	−0.29 (0.32)	−0.54 (0.28)	−0.54 (0.28)

medium and, as a consequence, a decrease in the activation barrier.

Our calculations of the interaction of TS **2E** with extra water molecules show that the latter are grouped around the central O atom to form structures **3E** and **4E** (Fig. 8) and that the charge on this atom is nearly doubled on going from **2E** to **4E**. However, the activation barriers to transfer of O^+ cation

$$H_2OO^{\cdot+}—nH_2O + H_2O \longrightarrow H_2O—O^{\cdot+}—OH_2—nH_2O$$

increase as n increases, namely, $\Delta E^{\neq} = 11.2$, 21.4, and 26.0 kcal mol^{-1} for $n = 0$, 1, and 2, respectively (Fig. 9). This is eventually due to a lower polarity of the $O—O^+$ bonds compared to that of the O—H bonds even in the transition state. Hence this suggests that the reaction of transfer of O^+ cation:

$$LO^+—nB + L \longrightarrow L—O^+—L—nB \longrightarrow LO^+ + L—nB,$$

where L and B are bases (in particular, $L = B = H_2O$), is characterized by an increase both in the stability of the $LO^+—nB$ complex and in the reaction barrier with increasing n. This means that stable asymmetric complexes of O^+ ion of the $(LO^+)—nB$ type with one coordination bond can be formed under appropriate conditions.

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