

A QUANTUM-CHEMICAL STUDY OF STRUCTURE OF H_3O^+ IN ELECTRONICALLY EXCITED STATES

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The CNDO/2-CI method has been used for full optimization of geometry of the H_3O^+ ion in all its electronically excited singlet states and for calculation of electron distribution. The electronic structure shows that H_3O^+ in almost all states exhibits lower tendency to split off the proton than it does in the ground state. For the first excited state the geometries and electron distributions of the isoelectronic set H_3O^+ , NH_3 , CH_3^- have been calculated by the INDO-CI method in the triplet state, too. The particles only have slightly different geometry and electronic distribution from those of the first singlet state.

The significance of H_3O^+ ion in both chemistry and physiology initiated studies of its structure in the ground state by spectroscopic methods¹⁻⁴ as well as by quantum-chemical *ab initio* methods with high-quality bases and with involvement of the correlation energy⁵⁻⁷. The H_3O^+ ion is also supposed to exist in interstellar space⁸, and it is believed to play an important role in the dynamic processes taking place in cometary nuclei and trains^{9,10}. The mechanism of formation of the excited H_3O^+ ions in gas phase was experimentally studied at laboratory conditions¹¹. As far as we know, however, no quantum-chemical studies of structure of H_3O^+ ion in electronically excited states have been carried out so far (except for electronic vertical absorption spectra¹²). Therefore, we have carried out calculations of the equilibrium geometry and electron distribution of the H_3O^+ ion in all the excited states which correspond to the levels involving all monoexcited configurations in the configuration interaction. This was carried out with regard to the possible occurrence of higher states of H_3O^+ in the interstellar space and especially in the cometary trains, because there the particles exist practically isolated, which prevents the energy exchange with the environment. We applied the CNDO/2-CI method¹³ which has proved useful in calculations of molecular geometries in electronically excited states.

RESULTS AND DISCUSSION

According to the calculations the H_3O^+ ion in the S_0 ground state has the electron configuration $(1 a_1)^2 (1 e)^4 (2 a_1)^2 (3 a_1)^0 (2 e)^0$. The optimum geometry is pyramidal

(Fig. 3) with the HOH angle equal to 111.0° , which agrees well with the value 111.3° obtained from the ^{17}O NMR spectral measurements² and with the values 111.6° , 113.1° , 111.6° obtained from the *ab initio* calculations with a large basis involving the correlation energy (refs⁵⁻⁷, resp.). The O—H bond length 0.105 nm calculated by us is somewhat greater than the *ab initio* values 0.097 and 0.098 nm (refs^{5,7}, resp.).

From the character of orbitals of the H_3O^+ ion it follows that the energy needed for excitation of an electron into one of the unoccupied levels will be comparatively high. It can also be expected that the lowest transitions will also include the Rydberg transitions to $3s$ and $3p$ orbitals of the central atom, as it is the case with ammonia¹⁴. The method used, however, does not make it possible to include the Rydberg states, and the calculation is limited to the valence excited states only.

The dependences of the overall energies of the various states on the changes of HOH angle in the pyramidal (Fig. 1) and planar geometry (Fig. 2) indicate clearly the preference of a certain geometry in the respective excited state. From the correlation diagram (Fig. 1) it can be seen that the excited states S_1 , S_2 , S_3 , and S_{12} have lower energy in the planar geometry, whereas S_6 , S_7 , S_8 , and S_9 have lower energy in the pyramidal geometry.

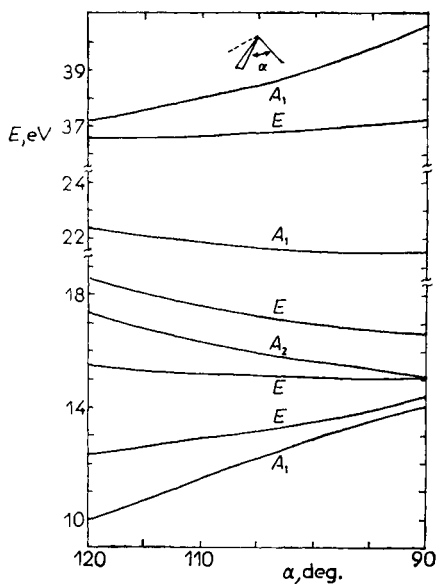


FIG. 1

Dependence of energy of individual states of pyramidal form on bond angle. The energies are related to the ground state energy

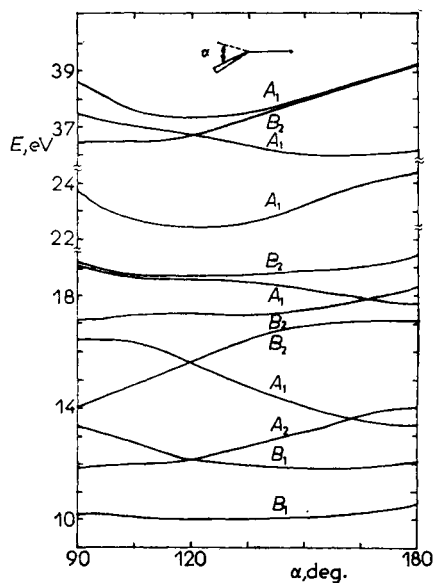


FIG. 2

Dependence of energy of individual states of planar form on bond angle. The energies are related to the ground state energy

For S_4 , S_5 , S_{10} , and S_{11} the diagram shows small energy differences between the planar and pyramidal geometries. The preference of a certain geometry in a given state will be shown by the full optimization. The correlation diagrams in Fig. 2 are much more complex. The potential curves representing simplified energy hypersurfaces are mutually intersected and exhibit minima. As the natural sequence of levels is controlled by increasing energy, in the intersection points the levels have their maxima or minima (in the hypersurfaces they are mutually opposed cones touching by their peaks¹⁵). The crossing of hypersurfaces also causes a change in character of the given state after the crossing point. The first, third, fifth, eighth, ninth, eleventh, and twelfth curves show the minimum at $\approx 120^\circ$; the second, fourth, sixth, seventh, and tenth ones at higher angles. This means that about these angles the H_3O^+ ion should have the planar geometry in the respective excited states. The equilibrium planar forms of H_3O^+ really exist in all these states. But according to Fig. 3 the optimum geometry is pyramidal in the states S_5 , S_6 , S_7 , S_8 , S_9 , and S_{11} . The corresponding planar forms possess somewhat higher energies in these states.

According to the given results we have chosen the starting geometries for the optimization in the individual excited states. In the S_1 , S_3 , and S_{12} states H_3O^+ has

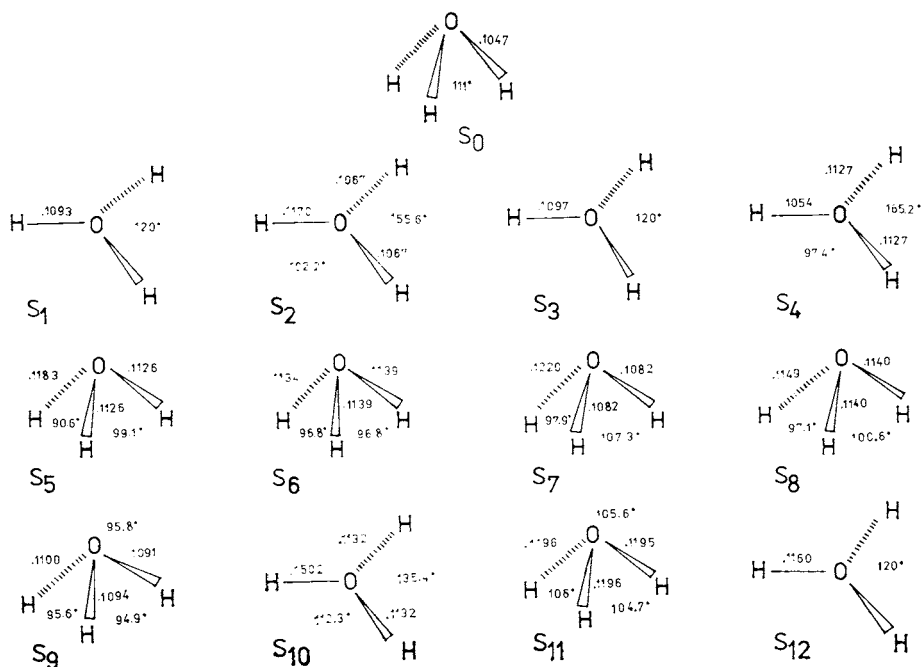


FIG. 3

Equilibrium geometries of the H_3O^+ ion in the ground and the excited states

the optimum geometry (Fig. 3) of the D_{3h} symmetry, which corresponds precisely to the minima at the potential curves (Fig. 2) for these states at \sphericalangle HOH 120° . Two equilibrium geometries of C_{2v} symmetry with various HOH angles are obtained for the S_2 state. The geometry with \sphericalangle HOH 92° has a higher energy by 0.16 eV than the optimum geometry with \sphericalangle HOH 155.6° . Similarly two equilibrium geometries of C_{2v} symmetry are also obtained for S_4 (with \sphericalangle HOH 86.6° it is higher by 0.15 eV than the optimum with \sphericalangle HOH 165.2°) and S_{10} (with \sphericalangle HOH 97.1° it is higher by 0.26 eV than the optimum with \sphericalangle HOH 135.4°). In these states, too, the local minima correspond to the course of the respective curves in Fig. 2. In the S_3 , S_4 , S_{10} , and S_{12} states there are also local minima with the geometry of C_s symmetry and with energies higher by 0.01, 1.16, 0.36, and 0.20 eV, resp. In the excited states S_5 through S_8 , H_3O^+ has the optimum pyramidal geometry of C_s symmetry. In contrast to the first four states (each of them has one predominant configuration), structure of these states is determined by 2–3 configurations with equivalent weights. The S_9 state has the geometry of non-symmetrical pyramide (C_1), the differences in bond lengths and angles being but negligible and ascribable to the calculation inaccuracy. It is noteworthy, however, that the form of C_{3v} geometry with the bond angles and lengths equal to the average of the little differing bond lengths and angles has its energy higher by as much as about 1 eV. The structure of S_9 state is determined by five configurations of equal weights. The structure of S_{10} state is noteworthy with respect to extremely high length of one O—H bond (about 0.150 nm). An only little unsymmetrical geometry (C_1 very near to C_{3v}) is also found with the S_{11} state. Its structure is determined by a single configuration. Comparison of the optimum geometries with prediction according to Fig. 2 shows that the crossing of hypersurfaces of the S_2 , S_3 ; S_4 , S_5 ; S_{10} , S_{11} at \sphericalangle 120° leads to the optimum geometry of higher symmetry (D_{3h}) with a defined character of the state, whereas the crossing of S_3 , S_4 and S_6 , S_7 states near \sphericalangle 165° retains the C_{2v} symmetry, but the character of the state is uncertain (Table I). The local minima of the states S_5 and S_8 having the geometry of C_{2v} symmetry and the S_6 , S_7 , S_9 , and S_{11} states with D_{3h} symmetry have the energies higher by 0.57, 1.73, 1.46, 1.95, 1.75, and 0.17 eV than the optimum states. The S_1 through S_3 states are pure $n \rightarrow \sigma^*$ transitions. The other transitions are of $\sigma \rightarrow \sigma^*$ type. The optimum geometries of H_3O^+ ion in all the excited states considered are given in Fig. 3. Characters of the states are given in Table I along with the adiabatic, vertical emission and absorption transition energies.

The calculated net charges at the atoms (Table II) show that the excitation to all the states is connected with electron shift from oxygen to hydrogens so that oxygen carries positive charge in all the states, the positive charge being the highest in the S_1 through S_3 states. On the contrary, positive charge of hydrogens is lower in the majority of states compared with the ground state, in several states one of the hydrogens even being negatively charged. In the S_5 and S_{10} states the charge distribution among the hydrogens is most unequal, two of the H atoms having a higher positive

TABLE I
Data on structure and transition energies of the H_3O^+ ion in electronically excited states

State	Symmetry	Character of state		Transition energies, eV		
		adiabat.	vert. abs.	adiabat.	vert. emis.	vert. abs.
S_0	C_{3v}		A_1			
S_1	D_{3h}	A_2''	A_1	9.75	9.26	11.41
S_2	C_{2v}	B_1	E	11.34	9.98	12.76
S_3	D_{3h}	E''	E	11.89	11.34	12.78
S_4	C_{2v}	a	E	13.00	11.49	15.41
S_5	C_s	A'	E	14.23	12.66	15.41
S_6	C_s^b	A''	A_1	14.90	13.69	16.47
S_7	C_s	a	E	15.54	14.28	17.75
S_8	C_s	A''	E	16.16	14.87	17.75
S_9	C_1^b	$(E)^c$	A_2	20.17	19.55	22.00
S_{10}	C_{2v}	A_1	E	33.61	28.13	36.55
S_{11}	C_1^b	$(E)^c$	E	34.29	31.81	36.57
S_{12}	D_{3h}	A_1'	A_1	35.95	34.23	37.75

^a The energy minimum is at the point of intersection of the levels and its character is indefinite;
^b very close to C_{3v} ; ^c character of the state in the C_{3v} geometry.

TABLE II
Net charges at individual atoms of the H_3O^+ ion in the electronically excited states (the order of the hydrogens $\text{H}_1\text{H}_2\text{H}_3$ in Fig. 3 is from the left to the right anti-clockwise)

State	Net charge at the atom			
	O	H_1	H_2	H_3
S_0	-0.118	0.373	0.373	0.373
S_1	0.590	0.137	0.137	0.137
S_2	0.514	-0.139	0.312	0.312
S_3	0.471	-0.043	0.289	0.282
S_4	0.329	0.549	0.061	0.061
S_5	0.303	-0.111	0.404	0.404
S_6	0.326	0.192	0.241	0.241
S_7	0.314	0.108	0.289	0.289
S_8	0.314	0.373	0.156	0.156
S_9	0.378	0.210	0.207	0.204
S_{10}	0.297	-0.143	0.423	0.423
S_{11}	0.352	-0.003	0.288	0.363
S_{12}	0.360	0.213	0.213	0.213

TABLE III
Data on geometry, net charges, and transition energies of the H_3O^+ , NH_3 , and CH_3^- molecules in the S_1 , T_1 states (the INDO-CI calculation)

Molecule	State	Symmetry	State character	Geometry parameters			Charge densities			Transition energies, eV		
				X-H nm	$\angle\text{HXH}$ deg	X	H	H	adiabat.	vert. emis.	vert. abs.	
H_3O^+	S_0	C_{3v}	$1A_1$	·1045	117·5	—·143	·381					
	S_1	D_{3h}	$1A_2''$	·1100	120	·609	·130	9·97	9·54	10·53		
	T_1	D_{3h}	$3A_2''$	·1091	120	·609	·130	8·24	7·93	8·76		
NH_3	S_0	C_{3v}	$1A_1$	·1069	106·4	—·233	·078					
	S_1	D_{3h}	$1A_2''$	·1106	120	·363	—·121	7·03	6·32	8·14		
	T_1	D_{3h}	$3A_2''$	·1106	120	·363	—·121	4·92	4·21	6·95		
CH_3^-	S_0	C_{3v}	$1A_1$	·1139	104·1	—·533	—·156					
	S_1	D_{3h}	$1A_2''$	·1175	120	—·047	—·318	5·52	4·49	6·63		
	T_1	D_{3h}	$3A_2''$	·1173	120	—·050	—·317	3·30	2·31	5·86		

charge than in the ground state and the third H carrying a strong negative charge.

Comparison of the CNDO/2 vertical absorption energies (Table I) with the data of *ab initio* calculations¹² (with involvement of all mono- and biexcited configurations of the reference configurations in CI) shows a very good agreement. So the CNDO/2 values (in eV) A_1 11.41, A_1 16.47, A_2 22.00 and six *E* states from 12.76 to 17.75 correspond to the *ab initio* values A_1 12.00, A_1 17.12, A_2 20.53, A_2 23.11, *E* 14.64, *E* 17.24.

The H_3O^+ ion is isoelectronic with NH_3 molecule and CH_3^- ion. To compare the structural changes due to electronic excitation in this isoelectronic set, we optimized the geometry in both the first singlet and triplet states by the INDO-CI method. For both H_3O^+ and NH_3 this method gives practically the same geometry in the S_1 state (Table III) as compared with that of the CNDO-CI method. But for H_3O^+ in the S_0 state it gives a higher value of $\angle HOH$. The CH_3^- ion in the S_1 state has the same symmetry (D_{3h}) as H_3O^+ and NH_3 ; only different (somewhat longer) is the bond length CH. In the T_1 state all three isoelectronic molecules have but slightly different geometry from the S_1 state. The same is true for the net charges at the atoms and of the transition energies.

The results given can serve as useful information for studies of photochemical reactions of H_3O^+ ion at cosmic conditions. The electron distribution shows that the H_3O^+ ion has a lower tendency to split off the proton in all the electronically excited states than it does in the ground state; in some of the states the O—H bond is even specially strengthened by interaction of negative charge at hydrogen with positive charge at oxygen. Therefore, even in the S_{10} state the extremely long OH bond (about 0.150 nm) does not indicate weakness of this bond, because splitting off of hydride anion from the positive H_3O^+ ion is little probable. But in spite of that, homolyses and heterolyses of O—H bonds are likely in higher electronically and, at the same time, vibronically excited states. With respect to semiempirical character of the calculations the results, especially the order of levels, must be accepted somewhat carefully.

Another aim of this paper consisted in further testing of the gradient optimization method¹³. In all the calculations the gradient procedure converged relatively rapidly. Certain difficulties only were encountered near the minimum, especially so in the higher states, which is obviously due to neglecting the terms $(\partial E/\partial c)(\partial c/\partial q_x)$.

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