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Hydrogen Trioxide Anion: A Possible Atmospheric Intermediate and Path to Oxygen-Rich Molecules

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The structure of the HO_3^- anion has been studied theoretically using many theoretical methods. We found two metastable isomers for HO_3^-. The most stable isomer has a structure reminiscent to its neutral HOOO and cationic $HOOO^+$ relatives. However, the central O−O bond in the anion was found to be unusually long (1.79 Å) compared to the same bond in the cation (1.40 Å) and in the neutral molecule (1.56 Å). Careful analysis reveals that the long O−O bond in the anion is a true chemical bond, but the bond order is only 0.75, which is the reason for its extreme length. We believe that the HO_3^- anion may play a role in atmospheric processes and its unusual long bond can expand our view of chemical bonding in oxygen-rich molecules.

1. Introduction

Hydrogen trioxide radical (HOOO), hydrogen trioxide cation ($HOOO^+$) and hydrogen trioxide (HOOOH) all have received substantial attention from experimentalists[1−5] and theoreticians.[6−10] This is not only because these species have been postulated to be important atmospheric molecules but also because they represent the next step in the search for oxygen-rich molecules. And yet much less is known about hydrogen trioxide anion ($HOOO^-$). Recently, Cacace and co-workers[1] reported capturing a mass-spectroscopic signal of $HOOO^-$ without any further analysis. We believe that the hydrogen trioxide anion may also play a role in atmospheric processes as well as being a method of using anions in the search for oxygen-rich molecules.

Here, we provide theoretical evidence for the existence of the HO_3^- anion on the bases of high-level ab initio calculations. We then predict its photoelectron spectrum, which will help to characterize the anion experimentally.

2. Theoretical Method

We optimized geometries and calculated frequencies of HO_3^- using a viriety of theoretical methods: B3LYP,[11−13] RHF,[14,] MP2(full),[15,16] MP2,[15,16] MP3,[15,16] MP4(SDQ),[15,16] MP4,[15,17] CISD,[18] CCSD,[19−21] CCSD(T),[19−21] CASSCF(10,9)-MRCI,[22,23] and the 6-311++G** basis sets.[24,25] The energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311++G(2df,2pd) basis sets. The vertical electron detachment energies were calculated using the outer valence Green Function method [OVGF/6-311++G-(2df,2pd)].[26−28] Core electrons were kept frozen in treating the electron correlation at all post Hatree-Fock levels of theory except the MP2(full)/6-311++G** level of theory, where all electron were included in correlation. All calculations were performed using the Gaussian 98 program,[29] except CASSCF-(10,9)-MRCISD/6-311++G** calculations, which have been performed using the MOLPRO-1999 program.[30]

3. Theoretical Results

We initially optimized geometries for two structures **I** and **II** (Figure 1) at the B3LYP/6-311++G** level of theory

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assuming singlet and triplet state for each structure. We found that the triplet structures are lower in energy, but they are weakly bound van der Waals minima on the potential energy surface and will not be considered here further. In our calculations we identified two singlet local minimum structures **I** and **II**. We further refined geometries and frequencies of both singlet structures using the CCSD(T)/6-311++G* level of theory and the geometric parameters at this level of theory are presented in Figure 1.

Structure **I** was found to be the most stable, and is similar to the most stable structures of the HO_3^+ and HO_3 species. The main difference between $HOOO^+$, HOOO and $HOOO^-$ is the presence of a long O_2-O_3 bond (1.883 Å) at the center of the anion, as compared to the same bond length in the cation (1.403 Å)[8] and in the neutral molecule (1.558).[7]

Such long O_2-O_3 bond is very unusual and require further investigation. We perform geometry optimization and frequency calculations using a variety of theoretical methods, and the results of these calculations are presented in Tables 1 and 2. Optimized geometry and harmonic frequencies were found to be in a rather good agreement at two most popular theoretical methods: B3LYP/6-311++G** and CCSD(T)/6-311++G** (Table 1). However, Tables 1 and 2 reveal a remarkable dependence of geometric parameters and harmonic frequencies on a theoretical method. The most affected geometric parameter is the central O_2-O_3 bond length. It changes from 1.41 Å at RHF, to 1.99 Å at MP2, to 1.48 Å at MP3 and to 2.11 at MP4. Such enormous alteration of the bond length is a sign of the multiconfigurational character of the wave function. The CCSD-(T) method can deal better with the muticonfigurational character of the wave function then the perturbation methods, but we found that the central bond changes from 1.52 Å at CCSD to 1.88 Å at CCSD(T). To clarify the multiconfigurational issue, we further performed geometry optimization for structure **I** using the CASSCF(10,9)-MRCISD method (4,030,390 total contracted functions in the MRCISD expansion). Suprisingly, we found that the optimal O_2-O_3 bond value was almost exactly between the CCSD and CCSD(T) values (Table 1). The $HOOO^-$ anion is certainly a challenge for quantum chemistry and obtaining its accurate spectroscopic parameters will require very large basis sets and very large CASSCF-MRCI expansions. Such calculations are beyond our current computational facilities.
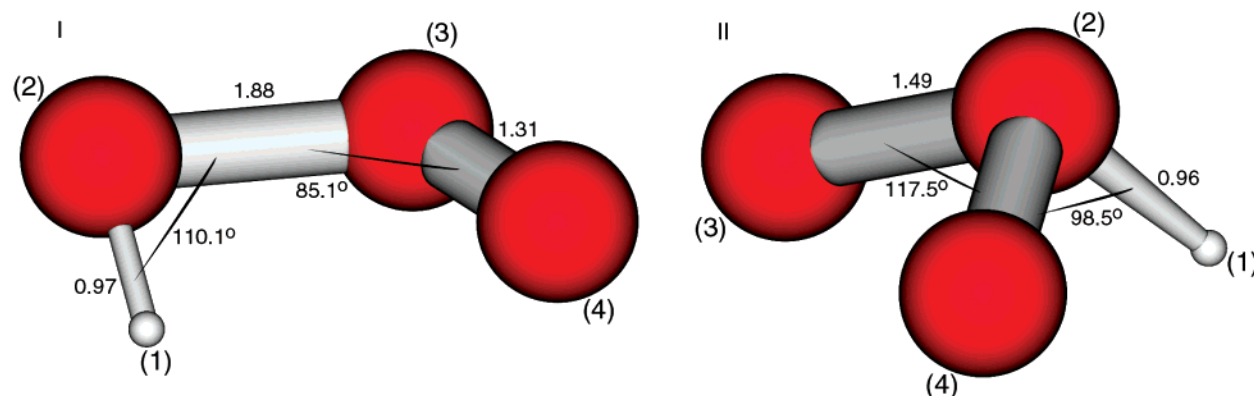
Figure 1. Optimized structures of HO_3^- (at the CCSD(T)/6-311++G** level of theory). Bond lengths are given in angstroms and angles in degrees.

TABLE 1: Optimized Geometries and Harmonic Frequencies for the Structure I of HO_3^-

molecular parameter	B3LYP/ 6-311++G**	CISD/ 6-311++G**	CCSD/ 6-311++G**	CCSD(T)/ 6-311++G**	CASSCF-MRCISD/ 6-311++G**
E_{tot}, au	−226.19358	−225.57469	−225.65105	−225.68260	−225.62795
$R(H_1-O_2)$, Å	0.965	0.960	0.969	0.966	0.958
$R(O_2-O_3)$, Å	1.840	1.454	1.520	1.880	1.761
$R(O_3-O_4)$, Å	1.300	1.395	1.401	1.316	1.341
$\angle H_1O_2O_3$, deg	90.5	94.4	92.2	85.1	88.5
$\angle O_2O_3O_4$, deg	112.0	104.4	104.6	110.1	108.8
$\angle H_1O_2O_3O_4$, deg	54.6	0	0	43.1	a
ω_1, cm^{-1}	3804	3863	3741	3801	a
ω_2, cm^{-1}	1176	1415	1332	1114	a
ω_3, cm^{-1}	861	967	899	855	a
ω_4, cm^{-1}	456	832	629	419	a
ω_5, cm^{-1}	275	493	390	280	a
ω_6, cm^{-1}	128	235	171	147	a

^{a} Geometry optimized assuming the planar cis structure. Frequencies have not been calculated at this level of theory.

TABLE 2: Optimized Geometries and Harmonic Frequencies for the Structure I of HO_3^-

molecular parameter	RHF/ 6-311++G**	MP2/ 6-311++G**	MP2(full)/ 6-311++G**	MP3/ 6-311++G**	MP4(SDQ)/ 6-311++G**	MP4/ 6-311++G**
E_{tot}, a.u.	−225.01823	−225.65868	−225.71498	−225.63431	−225.64562	−225.69948
$R(H_1-O_2)$, Å	0.947	0.967	0.967	0.966	0.970	0.974
$R(O_2-O_3)$, Å	1.408	1.986	1.983	1.475	1.526	2.108
$R(O_3-O_4)$, Å	1.394	1.287	1.286	1.399	1.394	1.327
$H_1O_2O_3$, deg	98.4	79.4	79.5	92.9	91.7	72.2
$\angle O_2O_3O_4$, deg	105.4	111.4	111.4	103.8	104.6	110.2
$\angle H_1O_2O_3O_4$, deg	0.	61.8	62.3	0.	0.	44.7
ω_1, cm^{-1}	4066	3822	3827	3773	3719	3684
ω_2, cm^{-1}	1515	1568	1568	1384	1332	1330
ω_3, cm^{-1}	1037	741	741	953	912	735
ω_4, cm^{-1}	976	418	419	759	604	319
ω_5, cm^{-1}	547	300	301	468	355	243
ω_6, cm^{-1}	254	158	157	257	195	116

While we were not able to obtain very accurate O_2-O_3 bond length, it is certainly expected to be unusually long and this length requires some explanation. We believe that despite the long O_2-O_3 bond length, the $HOOO^-$ anion is a chemically bound species and it is not a van der Waals complex between OH^- and O_2. To prove this we performed a natural bond order analysis[31] on $HOOO^-$, which usually yields a classical bonding picture. For example in a water molecule this analysis yields two two-electron two-center O−H bonds and two lone pairs located at the oxygen atom. When performed on $HOOO^-$ we obtained one H_1-O_2 bond, two-electron two-center O_2-O_3 and O_3-O_4 bonds, two lone pairs at O_2 and O_3, and three lone pairs at O_4. However, one lone pair at O_4 has the occupation number 1.5 instead of 2.0. The missing 0.5 electron is occupying the antibonding O_2-O_3 bond. Therefore, the resulting O_2-O_3 bond order is 0.75, which is responsible for a long O_2-O_3 bond. In addition, the calculated effective atomic charges (at the NPA

using the QCISD/6-311++G** density), which yielded $Q(H_1) = +0.38e$, $Q(O_2) = -0.79e$, $Q(O_3) = -0.14e$, and $Q(O_4) = -0.45e$, show a substantial charge transfer from HO^- to O_2 supporting our conclusion about chemical bonding between OH^- and O_2. Indeed, such long O−O bonds are known for other oxygen-rich anions such as O_4^- (1.998 Å).[20]

Structure **II** was found to be 34 kcal/mol less stable than the structure **I** and will not be discussed here in any details.

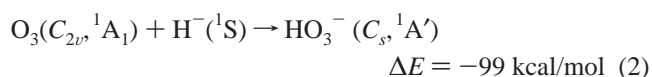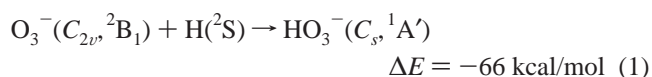How, then, can this anion be formed? We believe that there are two reactions 1 and 2
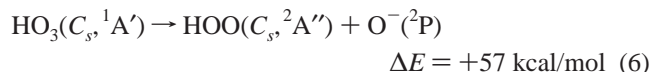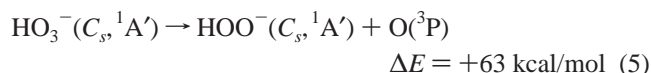
$$O_3^- (C_{2v}, {}^2B_1) + H({}^2S) \rightarrow HO_3^- (C_s, {}^1A')$$
$$\Delta E = -66 \text{ kcal/mol} \quad (1)$$

$$O_3(C_{2v}, {}^1A_1) + H^-({}^1S) \rightarrow HO_3^- (C_s, {}^1A')$$
$$\Delta E = -99 \text{ kcal/mol} \quad (2)$$

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TABLE 3: Theoretical Vertical Electron Detachment Energies in eV for HO$_3^-$

structure I, MO	VDE^a	structure II, MO	VDE^a
10a	2.34 (0.87)	6a′	3.53 (0.90)
9a	3.53 (0.86)	4a″	3.86 (0.90)
8a	5.14 (0.88)	5a′	4.25 (0.90)
7a	8.30 (0.81)	3a″	4.45 (0.90)
6a	8.42 (0.77)	4a′	9.77 (0.89)

^{a} The VDEs were calculated at the ROVGF/6-311++G(2df,2pd) level of theory. The numbers in the parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture.

involving the ozone molecule or ozone anion which are able to produce HO$_3^-$ anion (all data at CCSD(T)/6-311++G-(2df,2pd)+ZPE corrections at CCSD(T)/6-311++G**). Ozone molecules and ozone anions can be produced, together with hydrogen atoms or hydrogen ions, by lightning or by solar radiation from molecular oxygen and water. The calculated energies of both reactions were found to be highly exothermic. It is known that HO$_3$ radical is barely stable or it is merely a transient species with the short lifetime. The question of the HO$_3$ stability is not yet completely resolved.[32] We looked at all possible dissociation channels for the HO$_3^-$ anion. The two reverse reactions of (1) and (2) are certainly highly endothermic and cannot contribute to the instability of the anion. Next we calculated dissociation energies for four other dissociate reactions 3−6

$$HO_3^-(C_s, {}^1A') \rightarrow HO^-(C_{\infty v}, {}^1\Sigma^+) + O_2(D_{\infty h}, {}^3\Sigma_g^-)$$
$$\Delta E = -5 \text{ kcal/mol} \quad (3)$$

$$HO_3(C_s, {}^1A') \rightarrow HO(C_{\infty v}, {}^2\Pi) + O_2^-(D_{\infty h}, {}^2\Pi_g)$$
$$\Delta E = +25 \text{ kcal/mol} \quad (4)$$

$$HO_3^-(C_s, {}^1A') \rightarrow HOO^-(C_s, {}^1A') + O({}^3P)$$
$$\Delta E = +63 \text{ kcal/mol} \quad (5)$$

$$HO_3(C_s, {}^1A') \rightarrow HOO(C_s, {}^2A'') + O^-({}^2P)$$
$$\Delta E = +57 \text{ kcal/mol} \quad (6)$$
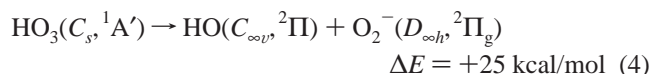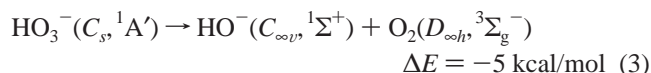
and found that the three reactions 4−6 are clearly endothermic (at the same level of theory as above), but reaction 3 is exothermic; the exothermicity of the reaction 3 is rather small. We would like to stress the lowest dissociation channel does not lie on one potential energy surface, because HO$_3^-$ is singlet and one of the products (O$_2$) is triplet. Therefore a nonadiabatic transition must occur from the singlet energy surface into a triplet potential energy surface and such transitions have a very low probability. This will enhance a lifetime of HO$_3^-$, which was experimentally observed by Cacace and co-workers. [1]

One way to experimentally test our predictions for the structure of HO$_3^-$ would be to take its photoelectron spectrum. In our previous works we proved that the photoelectron spectrum could be used as a fingerprint in the identification of new molecules.[33] In Table 3 we presented theoretical photoelectron spectra of two HO$_3^-$ isomers calculated by the restricted outer valence Green function method (ROVGF). It has been shown that the ROVGF method is capable to give a reasonable agreement for small molecules.[28,33] The experimental photoelectron spectrum of HO$_3^-$ is expected to have rather broad peaks due to a photodissociation of HO$_3^-$ upon electron detachment. An example of such spectrum would be the photoelectron spectrum of O$_4^-$ recorded recently by Hanold,

Garner, and Continenti.[34] However, we expect that tops of the peaks could be used to fit into our theoretical spectra.

4. Conclusions

The structure of the HO$_3^-$ anion has been studied theoretically using many theoretical methods. We found that geometry and frequencies are very sensitive to the theoretical method and require muticonfigurational treatment. We found two metastable isomers for HO$_3^-$. The most stable isomer has a structure reminiscent to its neutral HOOO and cationic HOOO$^+$ relatives. However, the central O−O bond in the anion was found to be unusually long compared to the same bond in the cation and in the neutral molecule. Still, the HOOO$^-$ anion is a chemically bound species and it is not a van der Waals complex between OH$^-$ and O$_2$. Careful analysis reveals that the long O−O bond in the anion is a true chemical bond, but the bond order is only 0.75, which is the reason for its extreme length. The HO$_3^-$ anion can be produced in atmosphere through the reactions of O$_3^-$ with H or O$_3$ with H$^-$. Ozone molecules and ozone anions can be produced, together with hydrogen atoms or hydrogen ions, by lightning or by solar radiation from molecular oxygen and water. The calculated energies of both reactions were found to be highly exothermic.

We hope that our work will stimulate further experimental and theoretical studies of the HO$_3^-$ anion and that it will help to find the right place for it in environmental and atmospheric chemistry, as well as extend our view of chemical bonding in oxygen-rich molecules.

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