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Structures and Vibrational Frequencies of NaO_3 and NaO_3^+: The Ionization Energy of NaO_3

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We use high-level ab initio, up to RCCSD(T), and the density functional theory (DFT) method, B3LYP, to obtain the geometry, vibrational frequencies, and heats of formation of $NaO_3(\tilde{X}^2B_1)$ and $NaO_3^+(\tilde{X}^1A_1)$. In both cases, a C_{2v} diamond structure is deduced. These values allow us also to derive the adiabatic ionization energy. We obtain the following values: $\Delta H_f[NaO_3,0K] = -13 \pm 2$ kcal mol^{-1}, $\Delta H_f[NaO_3^+,0K] = 167 \pm 2$ kcal mol^{-1}, and AIE(NaO_3) = 7.80 ± 0.05 eV. In addition, it was found that the B3LYP functional performs very well for the O_3^- species: both geometry and vibrational frequencies. For O_3, the method performed well for the geometry, but not so well for the vibrational frequencies. Comparison is made where appropriate to experimental data and to previous calculations. Finally, ΔH_r is calculated for a range of reactions that may contribute to the formation of NaO_3 or NaO_3^+ in the atmosphere.

Introduction

The reactions of Na with O_3 are important in the upper reaches of the Earth's atmosphere[1,2] and a detailed understanding of the kinetics of these reactions[3,4] and photolysis[5] of the species formed in such reactions are important for being able to model the chemistry accurately.[1,2] The main reactions occurring are

$$Na + O_3 \rightarrow NaO + O_2 \tag{1}$$

and

$$NaO + O \rightarrow Na(^2P_J;\ ^2S) + O_2 \tag{2}$$

and the decay

$$Na(^2P_J) \rightarrow Na(^2S)$$

which gives rise to the sodium D line. The above is essentially the Chapman mechanism for the production of airglow[6] and the longevity of some meteor trails.[7]

If [NaO] and [O_3] are high enough, then it is possible for a secondary reaction to occur:

$$NaO + O_3 \rightarrow NaO_2 + O_2 \tag{3}$$

The sodium ozonide molecule, NaO_3, could potentially form via a number of routes:

$$NaO_2 + O_3 \rightarrow NaO_3 + O_2 \tag{4}$$

$$Na + O_3 \xrightarrow{M} NaO_3 \tag{5}$$

$$NaO + O_2 \xrightarrow{M} NaO_3 \tag{6}$$

$$NaO_2 + O \xrightarrow{M} NaO_3 \tag{7}$$

with reactions 5−7 only being feasible in high-pressure regions, and generally M = N_2. Consequently, the properties of the NaO_3 molecule are of some importance if the whole system of Na/O_3 reactions is to be elucidated.

NaO_3 has been studied by a number of means. Spectroscopically, it has been studied in inert gas matrices[8−12] and in ammonia,[13] employing electronic, ESR, infrared, and Raman spectroscopies. In some of these studies, the main aim has been to identify the spectroscopy of the ozone anion, O_3^-, employing Na^+ (and other alkali metal cations) as the counterion. In addition, a limited number of ab initio studies have been employed. Plane et al.[3] employed UHF/6-31+G calculations on NaO_3, obtaining a diamond-shaped C_{2v} structure, where the Na atom bonds to the two terminal O atoms. Another geometry has been investigated: the C_{2v} structure where the Na atom interacts with the central O atom, but on the opposite side to the two terminal O atoms[3], but has been found to lie ~20 kcal mol^{-1} higher in energy. Nonplanar structures were found to converge to planar structures in ref 3. Vibrational frequencies were also calculated in ref 3, but the conclusive establishment of the C_{2v} structure as a minimum was obfuscated by the presence of an imaginary b_2 vibration, and this was attributed to symmetry breaking therein. More recently, Bruna and Grein[14] performed UMP2/6-31+G* and UMP2/6-311+G* calculations, and again obtained both a C_{2v} diamond structure and one imaginary b_2 vibrational frequency, once again attributed to a symmetry-breaking effect. The planar C_{2v} geometry for NaO_3 is supported by infrared studies in an inert gas matrix,[10] where

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an O−O−O angle in the range (106 ± 1)−(116 ± 1)° was obtained for NaO_3 from isotopic studies; and the midvalue of 111° led to $\angle$O−Na−O = 41°. The conclusion from the ESR study[12] that the anisotropic part of the hyperfine splitting tensor was only consistent with a nonplanar NaO_3 structure has generally been dismissed[3,14] and attributed to the significant error margins in that work.

For NaO_3^+ there appears to be no information in the literature, but it is likely that small concentrations of NaO_3^+ are present in the atmosphere either from the direct photoionization of NaO_3

$$NaO_3 + h\nu \rightarrow NaO_3^+ + e^- \qquad (8)$$

or from ion−molecule reactions, such as

$$NaO_2^+ + O_3 \rightarrow NaO_3^+ + O_2 \qquad (9)$$

$$NaO^+ + O_2 \xrightarrow{M} NaO_3^+ \qquad (10)$$

$$NaO_2^+ + O \xrightarrow{M} NaO_3^+ \qquad (11)$$

$$Na^+ + O_3 \xrightarrow{M} NaO_3^+ \qquad (12)$$

with reactions 10−12 only being feasible in high-pressure regions, and generally M = N_2. There is also the possibility of forming the neutral NaO_3 species by associative neutralization of $Na^+ + O_3^-$, which may involve a third body for stabilization and/or chemiluminescence:

$$Na^+ + O_3^- \xrightarrow{M} NaO_3\ (+\ h\nu) \qquad (13)$$

The ionization energy of NaO_3 is expected to be low, since the sodium oxide species, NaO_n, tend to be highly ionic, and the ionization occurs from the O_n^- moiety—this is the case for two of the species we have studied previously, NaO[15,16] and NaO_2.[17]

In the present work we tackle both NaO_3 and NaO_3^+ at high levels of theory to confirm the equilibrium geometry of the neutral, and to establish a geometry for the cation. We also aim to obtain reliable vibrational frequencies and thermodynamic quantities, such as heats of formation, and the ionization energy of NaO_3.

Calculational Details

In the following, all geometry optimizations and vibrational frequency calculations using the B3LYP, MP2, and QCISD methods were performed with the Gaussian suite of programs.[18] RCCSD(T) calculations were performed with MOLPRO.[19] Basis sets used were standard, except for the aug-cc-pV*X*Z basis sets for Na^+, where our own versions of these were employed (they are detailed in ref 20). In all calculations, the 2s and 2p electrons of sodium are active, since in Na^+ these are the valence electrons; sometimes the 1s electrons of sodium and oxygen are frozen, and sometimes all electrons are correlated, which is specified below. Except for the RCCSD(T) calculations, unrestricted wave functions were employed. For most structures $\langle S^2 \rangle$ was 0.78 or less, indicating that spin-contamination was not an issue; however, for the C_{3v} species (vide infra) $\langle S^2 \rangle$ was slightly greater than 0.9, suggesting spin contamination was more of a serious problem. When energies are cited, the projected energies are employed for MP2 calculations, but for the QCISD and B3LYP calculations, unprojected calculations are cited, since the projected ones are not available.

Results

NaO_3. NaO_3 is expected to be a largely ionic species, and is consequently expected to consist of an interaction between Na^+ and O_3^-. This immediately leads to caution being required since O_3^- [21] (and indeed O_3 itself[22]) are well-known species where symmetry breaking occurs, leading to an incorrect wave function along coordinates which move the molecular geometry away from the equilibrium symmetry. This can lead, for example, to the incorrect calculation of nontotally symmetric vibrational frequencies. One way to address this problem is to perform calculations with multireference approaches, such as CASSCF, with dynamical correlation effects accounted for either by employing MRCI methods or by using the CASPT2 approach. Such methods have been shown to allow a balanced wave function to be obtained, and produce good values for the geometry and all vibrational frequencies of O_3 and O_3^- (refs 21 and 22). The LiO_2 [23] and NaO_2 [24] species also suffer from symmetry breaking, and this phenomenon has been studied for these species in great depth, with again good values for the geometries and vibrational frequencies being obtained when employing multireference approaches. It has also been shown that the CCSD(T) method, despite being based on a single-reference wave function, can be capable of providing reasonable values for the geometry and all vibrational frequencies.[22,25] Note that generally the calculated geometric parameters of the symmetric structures are reliable when symmetry breaking occurs.

Recently we showed that the B3LYP method was capable of describing the NaO_2 [17] and KO_2 [26,27] species with values obtained for all of the vibrational frequencies being in good agreement with both experiment and sophisticated multireference approaches. Although the B3LYP method (and other DFT methods) can be rather “hit and miss” for weakly bound species, on the whole they have been proven to perform to a very high standard for strongly bound species. We thus employed the B3LYP method, with the results being shown in Table 1, compared to other recent results, as well as to experimental gas-phase experiments[28−32] on the isolated moiety. As may be seen, the B3LYP results, especially the ones performed as part of the present work, with large basis sets, agree extremely well with the CASPT2 and the best CCSD(T) results, and indicate that this method is capable of dealing with this tricky species. We therefore anticipate that both the geometry and the vibrational frequencies obtained with the B3LYP method for the largely ionic NaO_3 species will also be reliable. The bond length obtained for O_3^- is in good agreement with experiment (see Table 1); however, the bond angle is consistently calculated to be larger than the experimental value, being just outside the higher range. We therefore concur with the conclusion of the authors of ref 25 that the experimental bond angle seems to be on the low side.

Initially, we performed optimizations on a range of structures for NaO_3 to ascertain the configuration of the global minimum. Table 2 shows the results of optimizations of the main structures for NaO_3 employing both B3LYP and MP2(full) levels of theory, with the 6-311+G(3df) basis set. Essentially our results agree with the conclusions of previous workers. The C_{2v} structure with the Na bonded to the central atom, NaO(O_2), lies significantly higher in energy than the C_{2v} diamond structure at both levels of theory, where the Na atom interacts with the two terminal O atoms. This conclusion makes sense when one

TABLE 1: Calculated Geometry and Vibrational Frequencies of O_3^- [a]

method	r_e	θ_e	ω_1 a_1	ω_2 a_1	ω_3 b_2	ref
CASPT2	1.361	115.4	992	572	879	21
CCSD(T)/cc-pVTZ	1.358	115.3	1044	587	911	21
CCSD(T)/aug-cc-pVTZ	1.357	115.0	1028	584	863	21, 25
B3LYP/6-311+G(3df)	1.346	115.4	1069	603	896	this work
B3LYP/aug-cc-pVTZ	1.350	115.4	1057	596	878	this work
B3LYP/aug-cc-pVQZ	1.347	115.5	1063	600	885	this work
B3LYP/aug-cc-pV5Z	1.346	115.4				this work
experiment	1.36 ± 0.02	111.8 ± 2.0	975 ± 50	550 ± 50	880 ± 50	32
experiment			975 ± 10	590 ± 10		29
experiment			982 ± 30	550 ± 50		28
experiment	1.34 ± 0.03	112.6 ± 2.0				29
experiment[b]			790 ± 50 or 928 ± 50	419 ± 20 or 403 ± 2		30

[a] Units: r_e in Å; θ in cm^{-1}; ω in cm^{-1}. [b] Two assignments offered.

TABLE 2: Optimized Geometries and Vibrational Frequencies of Various Structures of NaO_3[a]

description	bond angles	bond lengths	vib freq	total energy/E_h	rel energy
		B3LYP/6-311+G(3df)			
NaO_3 C_{3v}	ONaO = 43.2	NaO = 2.211	1278.9i(e); 263.2(e); 383.2(a_1); 870.4(a_1)	−387.78833	60.5
NaO(O′$_2$) C_{2v} $^2B_1$	NaOO′ = 120.2	NaO = 2.069 O′O′ = 1.341	178i(b_2);159i(b_1); 324(a_1); 595(a_1); 946(b_2); 1097(a_1)	−387.86285	31.1
trans-NaOO′O″ C_s $^2A''$	NaOO′ = 78.3 OO′O″ = 115.5	NaO = 2.104 OO′ = 1.422 O′O″ = 1.288	27i(a″); 119(a′); 399(a′); 592(a′); 817(a′); 1180(a′)	−387.88482	17.3
trans-NaOO′O″ C_s $^2A'$	structure dissociated.				
Na(O_2)O′ C_{2v} $^2B_1$	OO′O = 114.1 NaOO′ = 91.8	NaO = 2.184 NaO′ = 2.601 OO′ = 1.346	167(b_1); 303(b_2); 332(a_1); 665(a_1); 893(b_2); 1081(a_1)	−387.91239	0.0
		MP2(full)/6-311+G(3df)			
NaO_3 C_{3v}	ONaO = 42.5	NaO = 2.218	278(e); 385.6(a_1); 884(a_1); 5488(e)	−387.16902	72.2
NaO(O′$_2$) C_{2v} $^2B_1$	NaOO′ = 121.0	NaO = 2.186 O′O′ = 1.336	170i(b_1); 154i(b_2); 327(a_1); 666(a_1); 1243(a_1); 5494(b_2)	−387.24004	27.6
trans-NaOO′O″ C_s $^2A''$	NaOO′ = 83.5 OO′O″ = 115.6	NaO = 2.103 OO′ = 1.396 O′O″ = 1.252	29i(a″); 83(a′); 400(a′); 657(a′); 847(a′); 1491(a′)	−387.24673	23.4
trans-NaOO′O″ C_s $^2A'$	NaOO′ = 78.2 OO′O″ = 114.6	NaO = 4.800 OO′ = 1.273 O′O″ = 1.273	9(a′); 16(a′); 18(a″); 717(a′); 1079(a′); 1153(a′)	−387.14011	90.3
Na(O_2)O′ C_{2v} $^2B_1$	OO′O = 114.0 NaOO′ = 93.0	NaO = 2.198 NaO′ = 2.618 OO′ = 1.314	158(b_1); 163(b_2); 333(a_1); 731(a_1); 931(b_2); 1352(a_1)	−387.28402	0.0

[a] Units: bond angles in deg; bond lengths in Å; vib freq in cm^{-1}; rel energy in kcal mol^{-1}; total energy in hartrees.

looks at the charge distribution. NaO_3 is largely ionic, being approximately $Na^{+0.9}(O_3)^{-0.9}$ as calculated from a Mulliken analysis in the present work. The charge on O_3 is almost exclusively on the terminal O atoms, giving rise to the strongest interaction when Na^+ is interacting with them. One might also wonder whether asymmetric structures would be possible where the Na^+ interacts with a single terminal O atom in a trans configuration. The results in Table 2 show that the $^2A''$ state with this orientation is a minimum, lying ca. 20 kcal mol^{-1} above the C_{2v} diamond structure at both levels of theory. At the MP2 level the $^2A'$ state was also a minimum, but lay significantly higher in energy and had the Na atom positioned quite far away (this structure dissociated with B3LYP). We also performed calculations on a nonplanar C_{3v} structure, which was a saddle point at the B3LYP level of theory, but was calculated to be a minimum at the MP2(full) level of theory. This structure was, however, significantly higher in energy than the C_{2v} diamond structure, and so was not considered further; in addition, it had a very high *e* vibrational frequency, suggesting that symmetry breaking may be an issue. Other calculations starting with nonplanar geometries converged to planar ones, again suggesting that the conclusions of a nonplanar geometry from the ESR study[12] are incorrect—this conclusion agrees with that reached in refs 3 and 14.

We therefore only continued calculations on the C_{2v} diamond structure at B3LYP, QCISD, and RCCSD(T) levels of theory and the results of these calculations are given in Table 3. In the QCISD calculations, we explored whether freezing the four 1s orbitals (one on Na, and three on the O atoms) made any significant difference to the calculated geometry—as may be seen, there is very little difference. The RCCSD(T) optimizations were performed with the four 1s orbitals frozen. Comparing the B3LYP, MP2, QCISD, and RCCSD(T) optimized geometries, we can see that there is very good agreement between

TABLE 3: Calculated Geometric Paramaters and Vibrational Frequencies for the C_{2v} Diamond Structure of NaO_3[a,b]

level of theory	∠OO′O	∠NaOO′	R_{NaO}	$R_{NaO'}$	$R_{OO'}$	ω_1 a_1	ω_2 a_1	ω_3 a_1	ω_4 b_2	ω_5 b_2	ω_6 b_1	energy/E_h
MP2(full)/6-311+G(3df)	114.0	93.0	2.198	2.618	1.314	1352	731	333	931	163	158	−387.28402
QCISD(full)/6-311+G(3df)	113.9	92.2	2.186	2.606	1.337							−387.28875
QCISD(1s frozen[c])/6-311+G(3df)	113.9	92.2	2.188	2.609	1.340	1081	666	335	810	304	162	−387.20750
						1.5	*8.1*	*47.4*	*467.0*	*0.3*	*22.0*	
RCCSD(T,1s frozen[c])/aug-cc-pVTZ	114.0	93.0	2.198	2.618	1.314							−387.34054
B3LYP/6-311+G(3df)	114.1	91.8	2.184	2.601	1.346	1081	665	332	893	303	167	−387.91239
B3LYP/aug-cc-pVTZ			2.194	2.613	1.350	1070	658	328	880	304	167	−387.92820
						0.0	*6.3*	*44.6*	*370.1*	*1.6*	*20.8*	
O_3^- B3LYP/aug-cc-pVTZ						1057	596		878			
expt (ammonia)[13] NaO_3						1034	605		852			
expt (matrix)[10,11] NaO_3						1011	599		804−807			
expt (gas phase)[32] O_3^-	111.8 ± 2				1.36 ± 0.02	975 ± 50	550 ± 50		880 ± 50			

[a] Units: angles in deg; R in Å; ω in deg; energy in hartrees. [b] Infrared Intensities (km mol^{-1}) are given in some cases in italics. [c] 1s orbitals on sodium and oxygen frozen.

the results obtained. In addition, the B3LYP calculations indicate that only small differences occur between the 6-311+G(3df) and the aug-cc-pVTZ basis sets. Our best structure is in good agreement with that obtained by Plane et al.[3] and similarly with the structure reported by Bruna and Grein.[14]

An imaginary b_2 frequency was obtained in both refs 3 and 14 and attributed to symmetry breaking in both cases. Although we do not obtain an imaginary frequency, we do find that the lowest frequency b_2 vibrational frequency at the MP2(full)/6-311+G(3df) level of theory is far removed from the value obtained at the B3LYP and QCISD levels. Both of the latter levels of theory yield similar values for the vibrational frequencies. Recent infrared and Raman values obtained for NaO_3 in ammonia[13] yielded values for the frequencies of the O_3^- vibrations as 1034 (Raman), 605 (IR) and 852 cm^{-1} (IR), corresponding to the symmetric stretch, bend, and asymmetric stretches, respectively. These may be seen to be in reasonable agreement with the B3LYP/aug-cc-pVTZ values obtained herein of 1070, 658, and 880 cm^{-1}. Matrix studies yield values of 1010 cm^{-1} for the symmetric stretch[11] (Raman), 599 cm^{-1} for the bending mode[11] (Raman), and 804−807 cm^{-1} for the asymmetric bend[10] (IR) and are also in reasonable agreement. We also calculated IR intensities at the QCISD/6-311+G(3df) and B3LYP/aug-cc-pVTZ levels of theory (Table 3), and it is clear that the most intense absorption by a significant margin should be the asymmetric stretch, ν_4, which is in line with observations in matrix studies,[10] where a very intense doublet was observed at 807.0/804.2 cm^{-1}, with the splitting being attributed to different matrix sites. The symmetric stretch at 1010 cm^{-1} was not observed in the IR study, which is consistent with its calculated IR intensity being over 2 orders of magnitude less that that of the ν_4 feature (although it was seen for other MO_3 species). Interestingly, there is a low-frequency a_1 vibration at 335 cm^{-1}, which is calculated to have an intensity an order of magnitude below that of the ν_2 vibration, but ought to have been observable; however, although a vibration was observed at 334.8 cm^{-1} in the IR study it was not assigned to NaO_3, but to NaO_2; thus an absorption of the NaO_3 ω_3 vibraton may have been obscured by this feature. Returning to the 599 cm^{-1} absorption observed in the Raman study,[11] the agreement between the calculated harmonic frequency and the observed fundamental is reasonable, but not good. It is unlikely that anharmonicity can play such a huge role, although the influence of the matrix atoms will shift the absorption somewhat. It should also be noted that the assignment of this vibration was not wholly conclusive, and it was noted[11] that the ν_1/ν_2 intensity ratio was anomalous for some isotopomers. It would be interesting to reinvestigate this spectrum again.

TABLE 4: RCCSD(T)/aug-cc-pVQZ//RCCSD(T)/aug-cc-pVTZ Calculations on the X^2B_1 State of the C_{2v} Diamond Structure of NaO_3 [a]

	RCCSD	RCCSD(T)
E_e, hartrees		
NaO_3	−387.370598	−387.414696
$Na^+(O_3)_G$	−161.896029	−161.898739
$O_3(Na)_G$	−225.245128	−225.287257
ΔE_e(CP)/kcal·mol^{-1}	143.98	143.51
BSSE(Na^+)/cm^{-1}	198.7	202.0
BSSE(O_3)/cm^{-1}	100.4	105.9
BSSE$_{total}$/cm^{-1}	299.1	307.9

[a] Where the subscript G represents a ghost center.

We note that ω_2 in particular changes dramatically between O_3^- and NaO_3—this is to be expected as this requires the two terminal O atoms to pull away from the Na^+ during the vibration. The Mulliken charges indicate that most of the negative charge of the O_3^- moiety is located on these two terminal atoms, thus there is a fair amount of electrostatic force influencing this vibration. Consequently, the force constant is expected to be higher in NaO_3 than in O_3^-, and thus the corresponding vibrational frequency is higher.

Finally, we performed RCCSD(T)/aug-cc-pVQZ//RCCSD(T)/aug-cc-pVTZ calculations, including full counterpoise corrections, to calculate the $Na^+\cdots O_3^-$ binding energy. In these calculations, the geometric parameters of the monomer were kept fixed at the optimized values in the complex, which were very similar to the experimental ones. The results are given in Table 4. As may be seen, the results at the RCCSD and RCCSD(T) levels gave very similar CP-corrected binding energies, and a final value of $D_e(Na^+\cdots O_3^-) = 143.5 \pm 1.5$ kcal mol^{-1} is

TABLE 5: Optimized Geometries and Vibrational Frequencies of Various Structures of NaO_3^+ [a]

geometry	bond angles	bond lengths	vib freq	total energy/E_h	rel energy
		MP2(full)/6-311+G(3df)			
C_s *trans*-planar NaOO′O″	OO′O″ = 116.1 NaOO = 130.4	NaO = 2.374 OO′ = 1.258 O′O″ = 1.293	66(a′); 84(a″); 176(a′); 755(a′); 1116(a′); 2090(a′)	−387.01371	3.6
C_{2v} diamond NaO_2O'	OO′O = 115.9 NaOO′ = 97.2	NaO = 3.000 OO′ = 1.273	118(b_2); 173(a_1); 237(b_1); 784(a_1); 1197(b_2); 2181(a_1)	−387.01948	0.0
		QCISD(full)/6-311+G(3df)			
C_s *trans*-planar NaOO′O″	OO′O″ = 116.4 NaOO = 133.0	NaO = 2.293 OO′ = 1.205 O′O″ = 1.309	77(a′); 84(a″); 206(a′); 745(a′); 806(a′);1458(a′)	−386.99389	0.5
C_{2v} diamond NaO_2O'	OO′O = 116.7 NaOO′ = 80.9	NaO = 2.965 OO′ = 1.246	78(b_2); 175(a_1); 240(b_1); 795(a_1); 1015(b_2); 1283(a_1)	−386.99470	0.0
		B3LYP/6-311+G(3df)			
C_s *trans*-planar NaOO′O″	OO′O″ = 117.3 NaOO = 133.2	NaO = 2.305 OO′ = 1.220 O′O″ = 1.285	74(a′); 84(a″); 196(a′); 765(a′); 1120(a′);1356(a′)	−387.60335	1.5
C_{2v} diamond NaO_2O'	OO′O = 117.0 NaOO′ = 96.9	NaO = 2.980 OO′ = 1.252	81(b_2); 163(a_1); 242(b_1); 788(a_1); 1204(b_2); 1267(a_1)	−387.60572	0.0
		RCCSD(T, frozen 1*s* orbs)/aug-cc-pVTZ			
C_s *trans*-Planar NaOO′O″	OO′O″ = 116.1 NaOO = 129.0	NaO = 2.326 OO′ = 1.246 O′O″ = 1.306		−387.05231	1.8
C_{2v} diamond NaO_2O'	OO′O = 115.9 NaOO′ = 97.0	NaO = 2.989 OO′ = 1.276		−387.05526	0.0

[a] Units: bond angles in deg; bond lengths in Å; vib freq in cm^{-1}; rel energy in kcal mol^{-1}.

TABLE 6: Calculated Geometry and Vibrational Frequencies of O_3 [a]

method	r_e	θ_e	ω_1 a_1	ω_2 a_1	ω_3 b_2	ref
B3LYP/ aug-cc-pVTZ	1.255	118.3	1249	746	1189	this work
B3LYP/ aug-cc-pV5Z	1.252	118.3	1260	751	1206	this work
MRCI-2	1.274	116.5	1149	698	1075	22
MRCI-4	1.264	116.7	1186	735	1211	22
MRCI-10	1.288	116.7	1096	685	898	22
MRCI-27	1.283	116.4	1112	709	1062	22
CASPT2(18,12)/ cc-pV∞Z [b]	1.2781	116.72	1111	703	1031	35
CASPT2(12,9)/ c-pwCV∞Z [b]	1.2708	116.84	1127	714	1056	35
expt	1.2717 [c]	116.8 [c]	1135 [c]	716 [d]	1089 [d]	

[a] Units: r_e in Å; θ in deg; ω in cm^{-1}. [b] Extrapolated to the corresponding infinite basis set limit. [c] From ref 33. [d] From force field of ref 34.

obtained, with the error being estimated to cover the BSSE value, as well as residual errors from higher correlation and incomplete basis set effects. RCCSD(T)/aug-cc-pV5Z calculations on NaO_3^+ (vide infra) indicate that in fact the aug-cc-pVQZ basis set is close to being saturated.

NaO_3^+. For NaO_3^+, we concentrated on the two lowest energy structures: the *trans*-planar structure and the C_{2v} diamond structure. The results of geometry optimizations and vibrational frequency calculations are given in Table 5. As may be seen, at all levels of theory, the C_{2v} diamond structure is the lowest energy structure, but the difference in energy is rather small. Of note is that the B3LYP/6-311+G(3df) and the RCCSD(T)/aug-cc-pVTZ geometries are very similar to each other.

Regarding the vibrational frequencies, the three highest vibrational frequencies in NaO_3^+ are expected to be similar to those of O_3 itself, since the ionization of NaO_3 is expected to be predominantly the removal of an electron from O_3^-, and this expectation is confirmed by the Mulliken population analysis. We therefore carried out B3LYP calculations on O_3 to ascertain whether this method would be as successful as it was in describing the O_3^- species. The results are given in Table 6, and are compared with experimental values of the geometry[33] and the vibrational frequencies,[34] as well as previous multireference calculations from refs 22 and 35. It is immediately clear that the B3LYP method is not performing as well in this case, although there is not an obvious symmetry-breaking problem. We note that two other sets of workers[36,37] have recently published B3LYP studies of O_3, but that neither calculated vibrational frequencies. We conclude that the more multireference nature of O_3 relative to O_3^- (refs 21 and 22) leads to the B3LYP method not performing as well for the former as the latter, for the vibrational frequencies.

Going back to the NaO_3^+ calculations, we note that the three highest O_3 vibrational frequencies are very close to the experimental ones at the QCISD level. Since the negative charge on the O_3 moiety has been removed, the perturbation of the force constants for the vibrational modes should be much less for NaO_3^+ than they are for NaO_3 itself, and so the three highest NaO_3^+ vibrational frequencies correspond closely to those of free O_3. Consequently we conclude that the QCISD method appears to be able to reproduce the vibrational frequencies more accurately than the B3LYP method in the case of NaO_3^+.

Since the energy difference between the two NaO_3^+ structures was so small we also performed single-point RCCSD(T)/aug-cc-pVQZ//RCCSD(T)/aug-cc-pVTZ calculations on both the C_s and C_{2v} structures, including full counterpoise corrections. The results are given in Table 7. As may be seen from this table, the C_{2v} structure still lies lower in energy, by 0.54 and 1.23 kcal mol^{-1} at the RCCSD and RCCSD(T) levels, respectively. The results of corresponding calculations from the aug-cc-pV5Z basis set, Table 7, for the C_{2v} structure indicate that the aug-cc-pVQZ basis set is close to complete. Our best binding energy of $Na^+\cdots O_3$ is therefore 12 ± 1 kcal mol^{-1}, where the error has been estimated on the basis of the BSSE and considering there will be some higher order correlation effects.

No experimental data appear to be available to which to compare these values.

TABLE 7: RCCSD(T)/aug-cc-pV*X*Z//RCCSD(T)/aug-cc-pVTZ Calculations on the C_{2v} and C_s Structures of NaO_3^+ ($X = Q, 5$)[a]

	RCCSD/ aug-cc-pVQZ	RCCSD(T)/ aug-cc-pVQZ	RCCSD/ aug-cc-pV5Z	RCCSD(T)/ aug-cc-pV5Z
C_s				
NaO_3	−387.071380	−387.125437		
$Na^+(O_3)_G$	−161.895627	−161.898331		
$O_3(Na)_G$	−225.157482	−225.210064		
ΔE_e(CP)/kcal·mol^{-1}	11.47	10.69		
BSSE(Na^+)/cm^{-1}	110.4	112.5		
BSSE(O_3)/cm^{-1}	51.4	54.8		
BSSE$_{total}$/cm^{-1}	161.8	167.3		
C_{2v}				
NaO_3	−387.073342	−387.128297	−387.101587	−387.157694
$Na^+(O_3)_G$	−161.895679	−161.898384	−161.906298	−161.909104
$O_3(Na)_G$	−225.158518	−225.210918	−225.176045	−225.229492
ΔE_e(CP)/kcal·mol^{-1}	12.01	11.92	12.08	11.99
BSSE(Na^+)/cm^{-1}	121.9	124.0		
BSSE(O_3)/cm^{-1}	60.4	53.1		
BSSE$_{total}$/cm^{-1}	182.3	177.1		

[a] Where the subscript G represents a ghost center.

Ionization Energy of NaO_3. From the above data, it is straightforward to calculate the ionization energy of NaO_3, with a value of 7.79 eV being obtained at the RCCSD(T)/aug-cc-pVQZ level of theory. This value is uncorrected for zero-point vibrational energy. To correct the latter, we take the vibrational frequencies for NaO_3 from Table 3 and those for NaO_3^+ from Table 5: we obtain AIE(NaO_3) = 7.81 eV.

To estimate the error in the ionization energy we calculated the adiabatic electron affinity of O_3 to compare to the experimental value. We employed the experimental geometry of O_3 from ref 33, and the experimental geometry of O_3^- as derived in ref 32. We obtained a value of 2.05 eV before correction for zero-point vibrational energy, and 2.08 eV afterward. This value compares very well with the experimental value of 2.10 eV, and suggests an error of 0.02 eV. We cite a value of 7.80 ± 0.05 eV for AIE(NaO_3) to cover other residual errors. Although the products of the reactions of Na with O_3 have been studied by photoelectron spectroscopy,[38] no features were assigned to NaO_3 in that work, with the spectrum being dominated by NaO and NaO_2 bands.

ΔH_f(0K) of NaO_3 and NaO_3^+. Using the above data, together with known values for the heats of formation of Na and O_3, the ionization energy of Na (all from ref 39), and the electron affinity of O_3, from refs 28 and 32, gives $\Delta H_f(0\ K) = -13 \pm 2$ kcal mol^{-1} NaO_3, where the error is an estimate based on our error for the binding energy of $Na^+\cdots O_3^-$ and other residual errors. Similarly, ΔH_f(0K) for NaO_3^+ may then be derived as 167 ± 2 kcal mol^{-1}.

TABLE 8: Heats of Formation and Sources for Relevant Species[a]

species	ΔH_f(0K)	ref
Na	25.9	39
Na^+	144.2	39
NaO	22 ± 2	15, 44[b]
NaO^+	196 ± 1.5	15, 44[b]
NaO_2	−12 ± 3	17[b]
NaO_2^+	140 ± 2	17[b]
NaO_3	−13 ± 2	this work
NaO_3^+	167 ± 2	this work
O_3	34.7	39
O_3^-	−13.8	*c*
O_2	0	by definition
O	59.0	39

[a] Where no error is cited, the error is less than 1 kcal mol^{-1}. [b] Values adjusted to 0 K from values therein. [c] Value for O_3 from ref 39 combined with adiabatic electron affinity from refs 28 and 32.

TABLE 9: Calculated Heats of Reaction[a]

reaction	ΔH_r(0K)	reaction	ΔH_r(0K)	reaction	ΔH_r(0K)
1	−39 ± 2	6	−35 ± 3	10	−29 ± 3
2	−55 ± 2[b]	7	−60 ± 4	11	−32 ± 3
3	−69 ± 4	8	180 ± 1	12	−12 ± 2
4	−36 ± 4	9	−8 ± 3	13	−143 ± 2
5	−73 ± 2				

[a] Unit: ΔH_r in kcal mol^{-1}. For reactions that involve O atoms, the averaged heat of formation is taken; clearly, there is the possibility of spin−orbit contributions being nonstatistical. [b] Producing Na(^{2}S).

Comments on Atmospheric Chemistry

From the present and previous work, we now have all of the data required to calculate ΔH_r for reactions 1−12. The data required are summarized in Table 8, and the ΔH_r values are summarized in Table 9. We give values at 0 K, and the small adjustments required for atmospheric temperatures may be obtained by the use of standard statistical mechanical formulas. Reactions 1 and 2 are clearly exothermic, which comes as no surprise since they have been discussed for many years with regard to the Chapman mechanism of airglow: in particular, the branching ratio of reaction 2 to form the electronically excited Na(^2P_J)—a good summary of this has recently been given by Plane,[2] and revolves around the production of electronically excited NaO in reaction 1. The kinetics of reaction 3 have been studied by Plane et al.[3] The five suggested reactions for the formation of NaO_3, reactions 4−7 and 13, may all be seen to be exothermic to varying extents. Reaction 4 was suggested by Plane et al. in ref 3 and seems a likely route for the formation of NaO_3 if [Na] and [O_3] are high enough. [NaO_3] from reaction 4 is not likely to be very high, as one of the reactants is NaO_2, which itself is formed from two successive ozonolyses: reactions 1 and 3. Reactions 5−7 all require a third body, and indeed so may reaction 13; consequently, these reactions are only going to have any importance lower down in the upper atmosphere where the pressure is high enough to raise the reaction probability. That said, reaction 5 would only then require reasonable concentrations of [Na] and [O_3] to occur, possibly by the harpoon mechanism, if the pressure were sufficient; but there is competition with other reaction channels, forming NaO + O_2 and NaO_2 + O. It is worth noting in passing that the reaction

$$NaO_2 + O \rightarrow NaO + O_2 \qquad (14)$$

has been studied kinetically by Helmer and Plane.[4] Clearly, formation of NaO_3 is a possible side reaction, being exothermic by 60 kcal mol^{-1}, compared to the exothermicity of reaction 14 of 25 kcal mol^{-1}. We also note that reaction 6 was included in a kinetic model in ref 4, and had been studied previously by Ager and Howard.[40] Reaction 13 is an associative neutralization, where the considerable excess energy may potentially be dissipated by chemiluminescence if suitable NaO_3* states exists, or simply by collisional means.

Reactions 9 through 12 are suggestions for the formation of NaO_3^+, other than the direct photoionization process, (8). These are all exothermic, although reactions 9 and 12 are not very exothermic. In addition, it may be deduced from Table 8 that the following reaction is close to thermoneutral:

$$NaO^+ + O_3 \rightarrow NaO_3^+ + O \qquad (15)$$

with $\Delta H_r = -5 \pm 5$ kcal mol^{-1}. That said, reactions 9 and 15 are perhaps the most likely to occur, as they do not require a third body for stabilization, whereas the other three reactions do. Whether these reactions have any great importance in the sodium ion chemistry of the upper atmosphere remains to be seen. It is worth noting in passing that the sodium ion chemistry has attained a greater significance recently since its implication in the formation of *neutral* sodium sporadic layers.[2,41−43]

Conclusions

High-level calculations, up to the RCCSD(T) level, employing large basis sets have been employed to calculate the geometry and vibrational frequencies of NaO_3 and NaO_3^+. In both cases, a C_{2v} diamond structure has been deduced which, for the neutral, is in agreement with that obtained by previous workers. Data from these calculations allowed reliable values for the ionization energy to be derived, as well as heats of formation for both the neutral and the cation.

In addition, related to the work on NaO_3 and NaO_3^+, some investigation of the B3LYP method's performance on O_3 and O_3^- was undertaken. It was found that the method works very well for the anion for obtaining both a reliable geometry and reliable frequencies, despite the known symmetry-breaking problem in O_3^-. Comparisons were made to both experimental gas-phase and rare-gas matrix values and to those obtained by other workers using multireference methods. For the neutral, again a reliable geometry was obtained, but vibrational frequencies were in poorer agreement.

Finally, the likely formation mechanisms for NaO_3 and NaO_3^+ in the upper atmosphere were discussed.

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