S_3O and S_3O^+ in the gas phase: ring and open-chain structures

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Ring and open-chain S_3O sulfur oxides are detected by neutralization–reionization experiments.

S_3O is the most recently discovered sulfur oxide.[1,2] It was detected in the gas phase by reduction of the S_3O^+ ion in neutralization–reionization (NR) experiments. Very recently high-level theoretical calculations[3] predicted that ring structures are the most stable minima on the singlet S_3O and doublet S_3O^+ surfaces (Fig. 1).

It remains a matter of great interest to assess the structure of the experimentally detected S_3O oxide, because in NR experiments both the precursor ion and the neutral species are not supposed to be the most stable species on their surfaces.[9,10] For this very reason, NR mass spectrometry often succeeds in detecting species inaccessible to other techniques. This feature relies on the vertical nature of the NR processes, which allows detection of neutrals provided that ions of closely related structure are prepared. As a consequence, the definite identification of the precursor ion is crucial to the assignment of the neutral structure. We here report a simple experiment aimed at identifying the structure of the S_3O^+ precursor ion and the S_3O oxide.

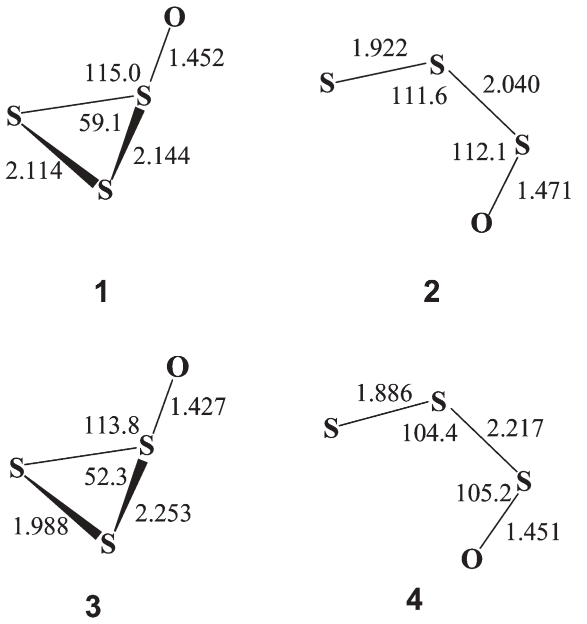

Fig. 1 B3LYP optimized geometries of the ring (**1** and **3**) and *cis* open-chain (**2** and **4**) S_3O (top) and S_3O^+ (bottom) species. See ref. 4–8.

S_3O^+ is effectively generated by reaction of S_2O^+ and SCO.[1,11]

$$S_2O^+ + SCO \rightarrow S_3O^+ + CO \quad (1)$$

In the previous experiments, the S_2O^+ reactant ion was in turn produced by a two-reaction sequence involving SCO.[12] Therefore, the S_3O^+ ion eventually formed contained indistinguishable sulfur atoms, all coming from SCO. We have now succeeded in the preparation of S_3O^+ ions containing distinguishable, structurally diagnostic sulfur atoms.

To this end, labelled $^{34}S_2O^+$ reactant ions (*m*/*z* 84) were prepared by chemical ionization (CI) of O_2 and elemental sulfur ^{34}S.[13] As shown in Fig. 2, O_2^+ (*m*/*z* 32) is the most abundant ion in the CI spectrum. A conceivable route to $^{34}S_2O^+$ is eqn (2), though disulfur is a minor fraction in the vapor produced by heating elemental sulfur.[14]

$$O_2^+ + {}^{34}S_2 \rightarrow {}^{34}S_2O^+ + O \quad (2)$$

Reactions with $^{34}S_n$ species ($n > 2$) cannot be excluded, whereas $^{34}S_n^+$ ions are unreactive towards O_2.[15]

By addition of SCO (*m*/*z* 60) to the gaseous mixture, a peak at *m*/*z* 116 ($S^{34}S_2O^+$) was readily observed (see the inset of Fig. 2).

$${}^{34}S_2O^+ + SCO \rightarrow [O^{34}S^{34}SSCO]^+ \rightarrow S^{34}S_2O^+ + CO \quad (3)$$

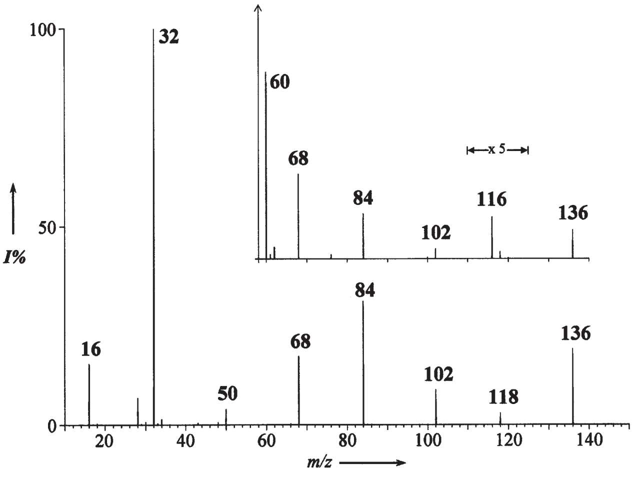

Fig. 2 CI spectrum of O_2 and elemental ^{34}S. The peak at *m*/*z* 32 (O_2^+) displays no contribution from $^{32}S^+$. Other peaks: *m*/*z* 50 ($^{34}SO^+$), *m*/*z* 68 ($^{34}S_2^+$), *m*/*z* 84 ($^{34}S_2O^+$), *m*/*z* 102 ($^{34}S_3^+$), *m*/*z* 118 ($^{34}S_3O^+$), *m*/*z* 136 ($^{34}S_4^+$). The peak at *m*/*z* 118 indicates a route to S_3O^+ only involving $^{34}S_2$ and O_2. The inset shows the appearance of the peak at *m*/*z* 116 ($S^{34}S_2O^+$) after introduction of SCO (*m*/*z* 60).

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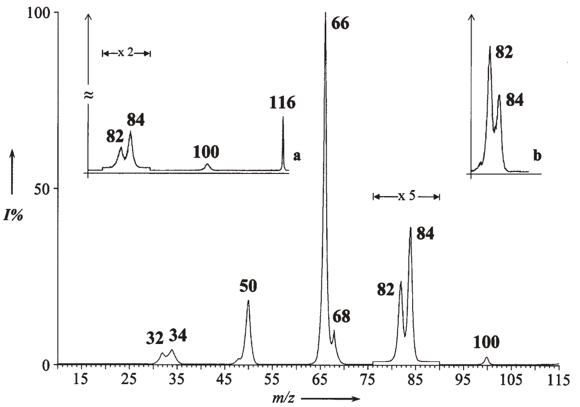
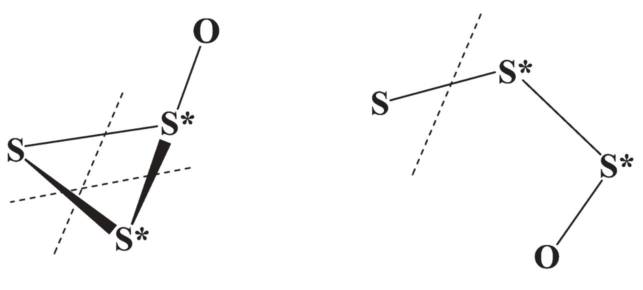


Fig. 3 CAD spectrum of $S^{34}S_2O^+$ ion at *m/z* 116. The inset (a) shows the peaks at *m/z* 82 and 84 in the NR spectrum of $S^{34}S_2O^+$. The inset (b) shows the peaks at *m/z* 82 and 84 in the CAD of the natural *m/z* 116 isotopomer of S_3O^+.

Accordingly, only one sulfur atom of the S_3O^+ ion comes from SCO, namely the S atom added to the $^{34}S_2O$ moiety. Accurate mass measurements were performed under high resolution conditions, to conclusively assign the elemental composition and rule out any isobaric contaminations.[13]

The *m/z* 116 ions, generated in the high-pressure source of the mass spectrometer, were mass selected and analyzed by CAD (collisionally activated dissociation) *ca.* 5×10^{-5} seconds after their formation.[16] The CAD spectrum of $S^{34}S_2O^+$ is reported in Fig. 3. In addition to the peaks at *m/z* 100 ($S^{34}S_2^+$), *m/z* 68 ($^{34}S_2^+$), *m/z* 66 ($S^{34}S^+$) and *m/z* 50 ($^{34}SO^+$), diagnostic peaks are found at *m/z* 82 ($S^{34}SO^+$) and *m/z* 84 ($^{34}S_2O^+$).[17]

The striking feature of the CAD spectrum is the $S^{34}SO^+$: $^{34}S_2O^+$ ratio, in that $S^{34}SO^+$ (*m/z* 82) is 65% of $^{34}S_2O^+$(*m/z* 84). This finding suggests that the ionic population does not exclusively contain the ring structure **3**, which is expected to equally decompose into $S^{34}SO^+$ and $^{34}S_2O^+$ (see Scheme 1). On the other hand, any scrambling occurring within the source would have the effect of statistically enhancing the *m/z* 82 peak. As a confirmation, the CAD spectrum of the *m/z* 116 peak obtained by S_2/O_2/SCO CI was recorded (see the inset (b) of Fig. 3). Here the only source of the S_3O^+ ion containing two ^{34}S atoms is the naturally occurring isotopomer of S_3O^+ at *m/z* 112. The CAD spectrum of this *m/z* 116 ion shows an almost reversed 84 : 82 ratio (*m/z* 84 is about 70% of *m/z* 82), which also rules out any possible isotope effects.



3 **4**

Scheme 1 Fragmentation ways conducive to S loss from S_3O^+ ions: both the $S^{34}SO^+$ and $^{34}S_2O^+$ ions are formed by dissociation of the symmetric ring **3**, whereas only $^{34}S_2O^+$ is formed from the open-chain structure **4**.

Table 1 Energy changes and barrier heights (kcal mol^{-1}, 298 K) computed for selected processes of S_3O^+ and S_3O

Process	ΔH°	
	B3LYP[a]	CCSD(T)[b]
1 → **2**	0.7	3.0
1 → S_2 + SO	18.5	23.5
TS **1** → **2**	27.7	25.2
3 → **4**	6.6	10.1
TS **3** → **4**	19.5	21.1
3 → S_2^+ + SO	34.7	33.7
S_2O^+ + SCO → **3** + CO	−9.9	−14.3
S_2O^+ + SCO → **4** + CO	−3.3	−4.2
	ΔG°	
S_2O^+ + SCO → **3** + CO	−9.8	−14.2
S_2O^+ + SCO → **4** + CO	−3.8	−4.7
3 → **4**	6.0	9.5

[a] 6-311 + G(3df) [b] aug-cc-pVTZ

Thus, the 84 : 82 ratio recorded in the CAD of Fig. 3 indicates the presence of an open-chain structure $S^{34}S^{34}SO^+$, that has memory of its formation process and can decompose only into $^{34}S_2O^+$.[18] Notably, the same ratio was found in the NR spectrum of $S^{34}S_2O^+$ (inset (a) of Fig. 3).

The theoretical analysis is in good agreement with the experimental evidence.[4–8] As shown in Table 1, the computed ΔG° of eqn (1) with respect to the S_3O^+ ions **3** and **4** is −14.2 and −4.7 kcal mol^{-1}, respectively. The **3** → **4** stability difference was found to be ΔH° = 10.1 kcal mol^{-1} and ΔG° = 9.5 kcal mol^{-1}. The ΔH° value fairly compares to that computed by Wong and Steudel (13.9 kcal mol^{-1}).[3,19] Formation of both the ring and open-chain S_3O^+ ions by eqn (1) is thus thermodynamically allowed, the open-chain isomer being possibly kinetically favored. Moreover, the open-chain ions are mainly generated below the isomerization barrier and are not expected to completely isomerize to the ring form, consistent with the experimental evidence. With this regard it must be noted that the reaction of formation of the S_2O^+ reactant ion from SO^+ and SCO is slightly exothermic (ΔH° = −1.4 kcal mol^{-1}).[1,20]

Nonetheless, even considering excited S_2O^+ reactant ions, high-energy S_3O^+ isomers could not account for the obtained result. Further exploration of the S_3O^+ surface allowed identification of the $SOSS^+$ ion, which is less stable than ion **3** by 30.6 kcal mol^{-1} and easily isomerizes to an electrostatic (S_2^+–SO) complex (through a very small barrier of 0.4 kcal mol^{-1}). This complex, less stable than **3** by 26.5 kcal mol^{-1}, is expected to decompose only into S_2^+ and SO. In addition, ions having C_{2v} trigonal and C_{2v} quasi-square structures were located higher in energy than ion **3** by 35.9 and 17.4 kcal mol^{-1}, respectively.[21] These ions are however expected to decompose like the ring ion **3**.

In conclusion, ring and open-chain S_3O^+ ions are submitted to the NR process as stable, distinct species in the gaseous isolated state. The NR spectrum shows that both the S_3O oxides are formed by neutralization and survive for a time period of at least 1 microsecond. Consistently, theory predicts that ring and open-chain S_3O^+ and S_3O species are generated below their isomerization and dissociation energies. The neutralization is indeed characterized by highly favorable Franck–Condon factors (Fig. 1), the computed vertical excitation energies of the neutral species **1** and **2** amounting to 7.0 and 2.4 kcal mol^{-1}, respectively.

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4 Structures were fully optimized with B3LYP/6-311 + G(3df).[5] Single point energies were calculated using the coupled-cluster single and double excitation method with a perturbational estimate of the triple excitation [CCSD(T)] approach,[6] and the correlation-consistent valence-polarized set aug-cc-pVTZ.[7] Zero-point energy corrections (B3LYP/6-311 + G(3df)) were added to CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational and vibrational contributions. All calculations were performed using Gaussian 03.[8] The absolute entropies were calculated by standard statistical-mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311 + G(3df) optimized geometries.

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12 $SCO^+ + O_3 \rightarrow SO^+ + O_2 + CO$ and $SO^+ + SCO \rightarrow S_2O^+ + CO$.

13 The experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration (E and B, electric and magnetic sectors, oa-TOF, orthogonal time-of-flight mass spectrometer). High-resolution mass spectra were recorded at 15000 FWHM. Accurate mass measurements were performed by standard calibration procedures (±10 ppm maximum deviation). The CAD spectra were recorded with fully open source and energy slits, using He as the collision gas (85% T) in the second collision cell located in the second field free region of the instrument. The NR experiments were performed at 8 keV, the neutralizing and reionizing gas were Xe and O_2 (80% T). All chemicals were research-grade products with a stated purity in excess of 99.95 mol%. Elemental sulfur ^{34}S (Aldrich, 99.5 mol%) was introduced through a direct insertion probe and heated in vacuo at temperatures not exceeding 400 K.

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17 The $^{34}S^+ : {}^{32}S^+$ ratio is not expected to reflect the isotopic abundance, as it is heavily affected by further dissociations of daughter ions, as for example the most abundant ion $^{34}S^{32}S^+$ (*m*/*z* 66).

18 Post-collisional isomerization is minimized at 8 keV under single-collision conditions, see H. I. Kenttamaa and R. G. Cooks, *J. Am. Chem. Soc.*, 1985, **107**, 1881. If any, this process could cause overestimation of the ring structure, since both **3** → **4** and **4** → **3** isomerizations would enhance the *m*/*z* 82 fragment.

19 The ΔG° value is very different, probably due to a misprint in ref. 3 (Table 1) where the reported $\Delta H^\circ - \Delta G^\circ$ difference (12.5 kcal mol^{-1}) appears very high.

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21 The least endothermic reaction ($\Delta H^\circ \approx 3$ kcal mol^{-1}) possibly accounts for the negligible peak at *m*/*z* 48.