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Ion structures

Discovery and characterization of atmospherically relevant inorganic species by structurally diagnostic mass spectrometric techniques

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Abstract

The role of structurally diagnostic techniques such as Mass-analyzed Kinetic Energy (MIKE), Collisionally Activated Dissociation (CAD), Neutralization Reionization (NR) and Fourier-Trena form Ion Cyclotram Reionization (FT-ICR) mass spectrometry, complemented by theoretical calculations, in atmospheric chemistry is illustrated by representative examples. The results outlined include the recent experimental discovery of the $(\text{H}_2\text{O}^+\text{O}_2^-)$ charge-transfer complex, long postulated as the key agent in atmospheric photonucleation theory. Next, the successful application of NR mass spectrometry to the detection of hydrogen trioxide, HOOO, as a gaseous species with a lifetime in excess of $1 \mu\text{s}$ at 298 K is discussed. The radical, whose role in the stratospheric ozone depletion and in the formation of the excited OH radicals responsible for night sky afterglow had long been postulated, defied all previous efforts of experimental detection. A new ionic route to tropospheric N_2O from electrical discharges associated with thunderstorms and power-line coronas has been reported, involving the intermediacy of isomeric $[\text{N}_2\text{O}_3]^+$ complexes. Finally, the new OSOSO sulfur oxide and its cation have been detected and characterized, and their presence in the atmosphere of Io, consisting of SO_2 and SO, is briefly discussed. (Int J Mass Spectrom 212 (2001) 403–411) © 2001 Elsevier Science B.V.

Keywords: Atmospheric chemistry; Kinetic energy; Collisionally activated dissociation; Neutralization reionization; Mass spectrometry

1. Introduction

All the areas of atmospheric chemistry, from the study of terrestrial and planetary composition to the

evolution of atmospheres on geological timescales, their short-term natural and anthropogenic changes, the global chemical and biochemical cycles, the climatic effects of trace pollutants, the development of new observational techniques, and so forth, are the focus of great current interest [1]. A recurring theme is the recognition of the atmospheric role of simple inorganic species as intermediates, sinks, catalysts, and reservoirs in key atmospheric reactions, which

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Dedicated to Professor R.G. Cooks for his outstanding contributions to mass spectrometry and gas phase ion chemistry and physics.

accounts for the active interest in their detection and characterization.

As most of the species involved are neutral, it would appear that, in this research area, mass spectrometry plays an ancillary, if very useful role, restricted to the detection and quantification of the neutrals of interest: for example, using specialized spectrometers aboard balloons, aircrafts, and rockets [2].

Recently, however, the situation has undergone a significant change, as atmospheric research calls for a more fundamental use of mass spectrometry; in particular, as concerns its structurally diagnostic techniques. This shift of emphasis reflects the growing recognition of the role of ionic reactions in atmospheric chemistry [3] and, especially, the recent demonstration of the usefulness of Neutralization Reionization (NR) mass spectrometry as a tool for the experimental preparation and detection of transient neutral species of particular atmospheric relevance [4].

Because the neutralization step of NR mass spectrometry is a vertical process, structural characterization of the uncharged species formed depends on the structural analysis of their ionic precursors, which in turn, requires the use of appropriate diagnostic techniques, such as reactive probing, isotopic labeling, and especially, Mass-analyzed Kinetic Energy (MIKE) and Collisionally Activated Dissociation (CAD) mass spectrometry.

In this article, a concise illustration will be given of recent representative examples of mass spectrometric results relevant to terrestrial and planetary atmospheric chemistry.

2. The $\text{H}_2\text{O}^+\text{O}_2^-$ charge-transfer complex: the key agent of photonucleation theory

Formation of water droplets on the event of UV irradiation of supersaturated air was observed as early as in 1899, and the role of oxygen in the phenomenon, later named photonucleation, was rapidly recognized [5]. Although the atmospheric relevance of photonucleation became immediately apparent, its mecha-

nism remained obscure and controversial in spite of extensive experimental and modeling studies [6]—until Byers Brown developed a theory based on the UV excitation of a transient van der Waals complex, $(\text{H}_2\text{O} \cdot \text{O}_2)$, to a charge-transfer complex, $(\text{H}_2\text{O}^+\text{O}_2^-)$, characterized by a large dipole moment and, hence, acting as an effective nucleation center [7]. The charge-transfer complex must be sufficiently long lived to organize a certain number of polar H_2O molecules into a microscopic droplet. Whereas a sound foundation to the Byers Brown theory was provided by numerous ab initio and modeling studies [8], it suffered from the complete lack of experimental evidence for the very existence of its pivotal agent, the neutral $(\text{H}_2\text{O}^+\text{O}_2^-)$ charge-transfer complex, which in view of its postulated lifetime, should have been detectable.

Because of the obvious atmospheric relevance of the problem, we have undertaken an experimental study aimed at demonstrating the occurrence of the $(\text{H}_2\text{O}^+\text{O}_2^-)$ charge-transfer complex as a gaseous species with a lifetime sufficiently long ($\geq 1 \mu\text{s}$) to perform its role of nucleating agent. The starting point of the investigation was based on the different binding energy of the monomers in the $(\text{H}_2\text{O} \cdot \text{O}_2)$ van der Waals complex and in the $(\text{H}_2\text{O}^+\text{O}_2^-)$ charge-transfer complex, whose energy separation is computed to be 5.75 eV, corresponding to an excitation wavelength of 215.6 nm [8]. The interaction between O_2 and H_2O in the van der Waals complex is essentially repulsive at short separations, with an extremely shallow energy well at the equilibrium distance, whereas in the charge-transfer complex, the equilibrium $\text{H}_2\text{O}^+-\text{O}_2^-$ separation is short, and their binding energy is large. On the basis of the above considerations, our approach [9] was based on NR mass spectrometry, an established technique capable of discriminating between strongly bound neutral species, such as the charge-transfer complex, and weakly bound species, such as the van der Waals complex, where the binding energy of the monomers is several orders of magnitude below the threshold ($\sim 10 \text{ kcal mol}^{-1}$) necessary to survive the neutralization step and, hence, be detectable by NR spectrometry [10].

Well-defined ion–molecule clustering reactions

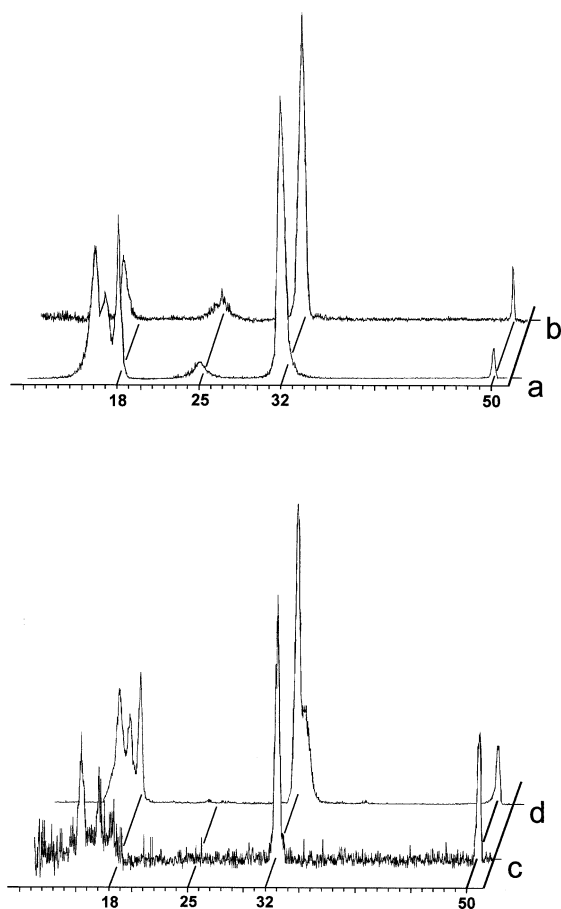


Fig. 1. $^+NR^+$ spectrum (a), $^+NR^-$ spectrum (b), $^-NR^-$ spectrum (c), and $^-NR^+$ spectrum (d) of the $(H_2O \cdot O_2)^+$ cation and of the $(H_2O \cdot O_2)^-$ anion, $m/z = 50$. Note the “recovery” peak at the same m/z ratio from all the sequences. (Reproduced by permission of *Angew. Chem. Int. Ed. Engl.*).

were used in the Chemical Ionization (CI) source of a multisector mass spectrometer of the Electrostatic-Magnetic-Electrostatic-orthogonal Time of Flight (EBE o-TOF) configuration to obtain $(H_2 \cdot O_2)^+$ or $(H_2 \cdot O_2)^-$ adducts, each of which was mass selected and assayed by NR^+ and NR^- mass spectrometry. The four spectra illustrated in Fig. 1 display significant recovery peaks of $m/z = 50$, denoting the existence of a neutral species containing the H_2O and O_2 monomers, whose binding energy is on the order of 10 kcal mol^{-1} . The lifetime of the adduct was found to exceed 0.7μ , that is, the minimum flight time from

the neutralization to the reionization cell of the NR spectrometer for a 50-Da molecule traveling at a speed corresponding to a kinetic energy of 4 keV.

The results of the NR experiments provide strong evidence for the $(H_2O^+O_2^-)$ charge-transfer complex, whose binding energy is sufficiently large to survive the neutralization step, in contrast with the weakly bound van der Waals complex. However, to make the assignment irrefutable, it was necessary to dispose of another conceivable candidate, the covalently bound HOOH molecule, isobaric with the $(H_2O^+O_2^-)$ charge-transfer complex. Formation of $(HOOH)^+$ from the clustering of O_2^+ ions with water in the CI source was regarded as quite unlikely, yet the point deserved further consideration. Accordingly, both the unlabeled $(H_2O \cdot O_2)^+$ ions and its $(H_2^{16}O \cdot ^{18}O_2)^+$ and $(H_2^{18}O \cdot ^{16}O_2)^+$ isotopomers from the reionization step of NR experiments were probed by CAD mass spectrometry, using the TOF sector of the instrument. The $(H_2O \cdot O_2)^+$ ion of $m/z = 50$ gave only the O_2^+ and H_2O^+ fragments ($m/z = 32$ and 18, respectively) without detectable formation of any OH fragments. The CAD spectra of the labeled species, illustrated in Fig. 2, show that the monomers contained in the $(H_2O \cdot O_2)^+$ ion and, hence, in its neutral precursor, retain their discrete identity without isotopic O mixing and without the formation of any HO fragments, which would be expected from a precursor of H–O–O–O–H connectivity. The summary of the experimental results is that a neutral species containing strongly bound H_2O and O_2 units does exist in the isolate state, with a lifetime exceeding 0.7μ s. The results point to the $(H_2O^+O_2^-)$ charge-transfer complex, already identified by a detailed theoretical analysis of the H_2O/O_2 system, as the only plausible candidate, ruling out other species such as the van der Waals complex and the HOOH molecule. The charge-transfer complex, located 5.75 eV above the ground-state van der Waals collision complex, although stable against dissociation into its charged monomers, can be liable to dissociation into neutral H_2O and O_2 following intramolecular processes such as fluorescence or inter-system crossing.

In any case, the lifetime of the charge-transfer complex deduced from the NR experiments is suffi-

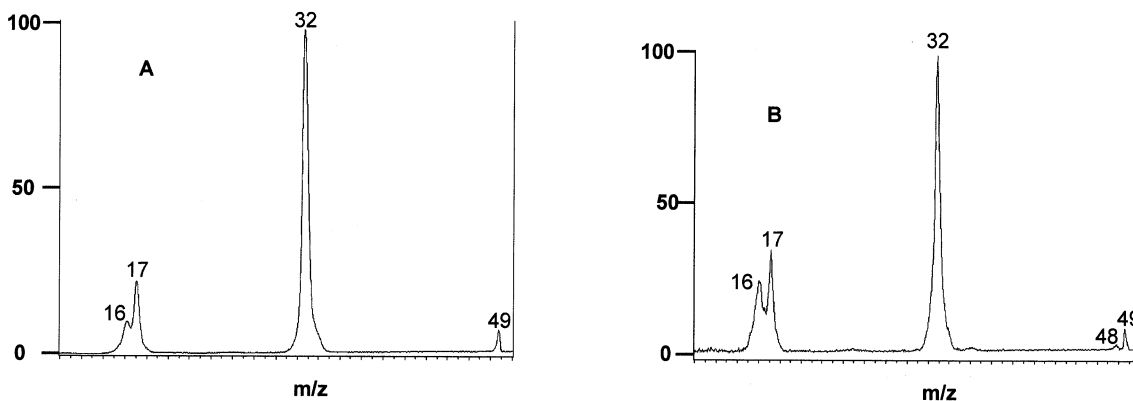


Fig. 2. $^+NR^+$ spectrum of the $(H_2O \cdot ^{18}O_2)^+$ ion, $m/z = 54$ (a) and of the $(H_2^{18}O \cdot O_2)^+$ ion, $m/z = 52$ (b), both displaying “recovery” peaks at the expected m/z ratios. (Reproduced by permission of *Angew. Chem. Int. Ed. Engl.*).

ciently long to support its atmospheric role as an effective nucleation center.

3. HO_3 , a stratospheric reservoir of OH radicals

Hydrogen trioxide, HO_3 , was long postulated to be an important sink of OH radicals in atmospheric chemistry [11]. In addition, it is a key intermediate in the photochemical formation of excited OH radicals, whose typical emission spectrum has long been recorded in atmospheric research. The fact that the emission persists, causing the night-sky afterglow well after the sunset that marks the end of photochemical excitation, points to the existence of a relatively long-lived reservoir molecule, most likely HO_3 , whose dissociation is known to yield excited OH radicals [12–15]. The atmospheric relevance of HO_3 stimulated an impressive theoretical effort aimed at evaluating the thermodynamic stability of the radical to ascertain whether it could be experimentally observable. The results, which critically depend on the theoretical approach followed, provided contradictory answers regarding the stability of HO_3 . At variance with previous conclusions, the most recent theoretical results predict that HO_3 is unstable, or marginally stable, and hence, should not be detectable at 298 K [16]. It should be further pointed out that neither the

theoretical results nor those of thermochemical cycles [17] exclude the possibility that, even if thermodynamically unstable, HO_3 can be sufficiently long lived to allow its detection because of a sizeable kinetic barrier to its dissociation. Under the circumstances, the question could only be solved by the actual experimental detection of the hitherto unknown HOOO radical and, again, NR mass spectrometry appeared to be a viable approach [18]. Our starting reagent was protonated ozone, HO_3^+ , whose preparation and characterization we had reported previously [19]. The CAD spectrum of the cation is consistent with a H–O–O–O connectivity, and its NR^+ and NR^- spectra, as well as those of the DO_3^+ isotopomer, illustrated in Figs. 3 and 4, display significant recovery peaks of $m/z = 49$ and 50, respectively. Further evidence was provided by the CAD spectra recorded, using the TOF sector of the instrument.

The cation of $m/z = 49$ from the reionization of the HO_3 gives $O_2^+ \cdot$, OH^+ , and $O^+ \cdot$ fragments, all consistent with the H–O–O–O connectivity. More important, the spectrum is indistinguishable from that of HO_3^+ ions from the protonation of ozone, recorded under the same conditions (Fig. 5). These conclusive results end the long search for the elusive HO_3 radical and show that the species is stable, or metastable, with a lifetime $>1 \mu s$ at 298 K.

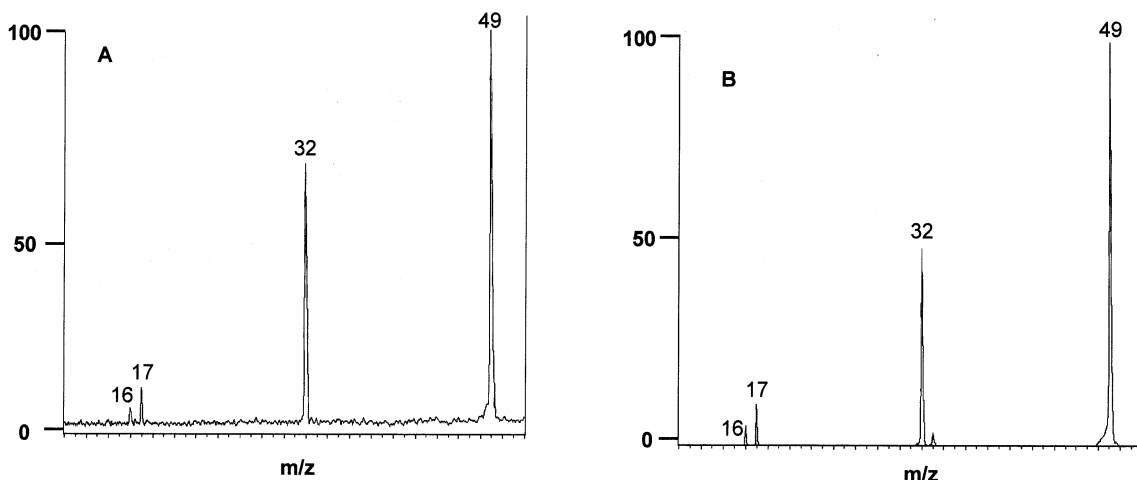
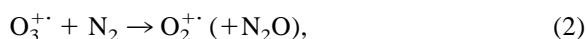
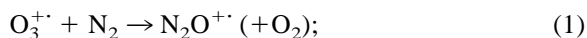


Fig. 3. (A) NR^+ spectrum of HO_3^+ ions, $m/z = 49$, kinetic energy 4 keV. Neutralizing and reionizing gas Xe and O_2 , respectively. (B) NR^- spectrum of HO_3^+ ions, kinetic energy 8 keV, neutralizing and reionizing gas CH_4 . (Reproduced by permission of *Science*).

4. Thunderstorms and power lines: a tropospheric source of N_2O via isomeric N_2O_3^+ complexes

Nitrous oxide is a harmful, long-lived greenhouse gas responsible for ozone depletion in the stratosphere [20–22], which accounts for the active search of its tropospheric sources in addition to microbiological soil denitrification [23]. We have recently identified a new route to N_2O , involving ionization of N_2/O_3

mixtures [24]. Preliminary FT-ICR experiments demonstrated the occurrence of the exothermic reactions



whose rate constants were approximately estimated to be $k_1 \approx 1.4 \cdot 10^{-11}$ and $k_2 \approx 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ mole}^{-1}$. Next, CI of N_2 containing $\sim 5 \text{ mol}\%$ O_3 was performed at 373 K, 0.01–0.1 torr, using both $^{14}\text{N}_2$ and $^{15}\text{N}_2$. Labeled nitrogen was used to simplify the interpretation of the spectra and to exclude possible interferences from isobaric contaminants. The CI

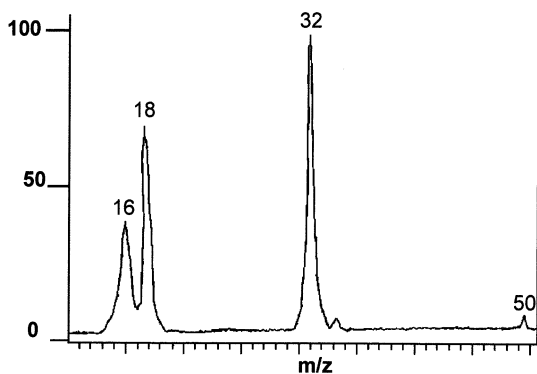
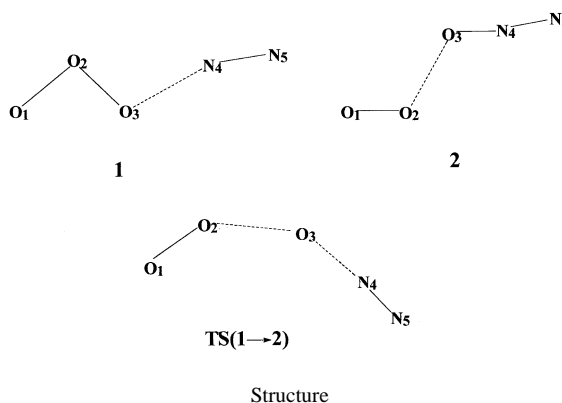


Fig. 4. NR^+ spectrum of DO_3^+ ions, $m/z = 50$, kinetic energy 8 keV, neutralizing and reionizing gas Xe and O_2 , respectively. (Reproduced by permission of *Science*).



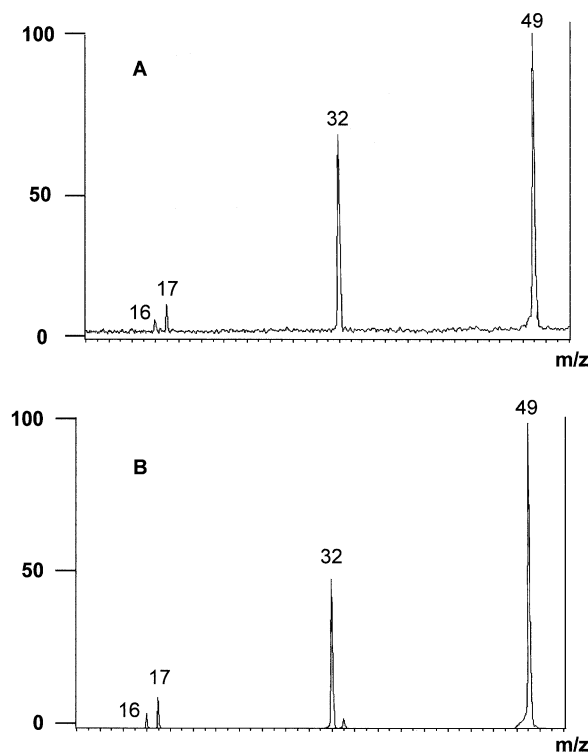


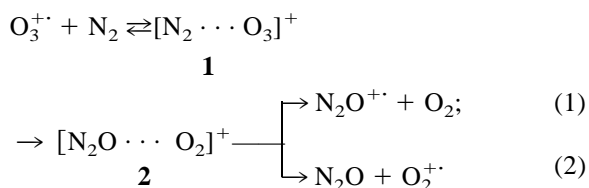
Fig. 5. (A) CAD spectrum of $m/z = 49$ ions (kinetic energy 0.8 keV, target gas He), obtained by neutralization and consequent reionization of HO_3^+ ions. (B) CAD spectrum of HO_3^+ ions from the protonation of ozone, recorded under the same conditions as in (A). (Reproduced by permission of *Science*).

spectra denote the formation of a N_2O^+ cation, identified by comparison of its CAD and MIKE spectra (in particular the kinetic energy release of the metastable loss of N) as the molecular ion of nitrous oxide, with the corresponding features of the model ion from N_2O . A clue to the process responsible for the formation of N_2O^+ is provided by the presence in the N_2/O_3 CI spectrum of a $[\text{N}_2\text{O}_3]^+$ adduct of $m/z = 76$, which shifts to 80 when $^{15}\text{N}_2$ is used. The CAD spectrum of the adduct displays two major fragments of $m/z = 32$ and 44, identified by comparison of their MS/MS spectra with those of the corresponding model ions from oxygen and nitrous oxide as O_2^+ and N_2O^+ . Interestingly, such a fragmentation pattern denotes a $[\text{N}-\text{N}-\text{N} \cdots \text{O}-\text{O}]^+$ connectivity, rather from the $[\text{N}-\text{N} \cdots \text{O}-\text{O}-\text{O}]^+$ connectivity typical of the initial association of the monomers. This obser-

vation is confirmed by the identity of the CAD spectrum of the adduct from the N_2/O_3 CI with that of the model $[\text{N}_2\text{O} \cdots \text{O}_2]^+$ adduct obtained in the CI of $\text{N}_2\text{O}/\text{O}_2$ mixtures.

The theoretical analysis of the system was performed using the B3LYP density functional theory [25] with a 6-311 + G (3d) basis set [26] and the method of Schlegel and coworkers [27] to locate the transition states. The complexes **1** and **2** were localized as minima on the doublet potential energy surface of the $[\text{N}_2, \text{O}_3]^+$ system.

Complex **1**, whose formation on addition of O_3^{++} to N_2 is computed to be exothermic by $11.0 \text{ kcal mol}^{-1}$, overcoming a barrier of $10.6 \text{ kcal mol}^{-1}$ ($\text{TS } \mathbf{1} \rightarrow \mathbf{2}$) evolves into the complex **2**, more stable by $47.2 \text{ kcal mol}^{-1}$, which eventually dissociates into O_2 and N_2O . By combining the experimental and the computational results, one obtains a consistent picture: adduct **1** can evolve into **2** or undergo back dissociation, two processes of comparable energetic requirements

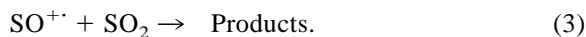


However, back dissociation is entropically favored, which accounts for the low combined efficiency ($\sim 10\%$) of reactions (1) and (2) as well as for the failure to detect $(\text{N}_2\text{O}_3)^+$ adducts at the low pressures typical of FT-ICR experiments. At the higher pressures of CI experiments, a larger fraction of **1** escapes back dissociation and evolves into **2**, which in turn, experiences partial collisional stabilization that not only allows detection but is expected to shift the branching ratio of processes (1) and (2) in favor of the latter. It should be noted that both processes, when occurring in the atmosphere, are a source of neutral N_2O , in that any N_2O^+ ions from process (1) are expected to be neutralized by fast charge exchange with O_2 [28]. In summary, we have shown that ionization of N_2/O_3 mixtures yields N_2O via a sequence of ionic reaction characterized by the intermediacy of isomeric $[\text{N}_2\text{O}_3]^+$ complexes.

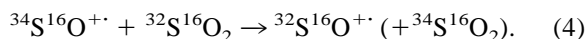
One can wonder whether, and to what an extent, the above results bear on atmospheric chemistry. The answer depends on the identification of a specific environment where ionization of ozone and nitrogen, both present in significant concentrations, occurs on a large scale. Such an environment is to be found in air subjected to disruptive (lightning) and/or corona discharges (thunderstorms, high-voltage power lines) that produce high local concentrations of ozone. These phenomena are by no means negligible on a global scale, for example, they are known to contribute by 10%–15% to the overall production of tropospheric NO_x oxides by natural or anthropogenic sources [29]. It has also been shown that the production of ozone by the electric discharges occurring in lightning and coronas actually exceeds that of NO_x oxides [30]. In this framework, the ionization of air containing a high local concentration of ozone is very likely to represent one of the long-sought tropospheric sources of N_2O .

5. Ion chemistry in the Io atmosphere: a new sulfur oxide, OSOSO, and its cation

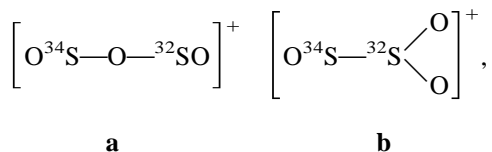
According to the recently released results of the orbiter Galileo, the atmosphere of Io, Jupiter's innermost moon, can be regarded as a huge natural laboratory where gas phase ion chemistry of sulfur oxides occurs on a large scale. The atmosphere, consisting mainly of SO_2 with 5 mol%–10 mol% SO , is ionized by intense (10^9 W) electron beams [31], forming a plasma cloud that contains sulfur oxides and their molecular cations [32,33]. The plasma around Io is depleted of ions at an estimated rate of 10^3 Kg s^{-1} , corresponding to a current of 2×10^9 Å [34]. Given its planetary relevance, we set out to examine the major features of the ion chemistry of sulfur oxides under conditions comparable to, and using the same reagents present in, Io's atmosphere [35,36]. The major charged species is SO^+ , detected by its ion cyclotron waves, and because SO_2 is the bulk atmospheric gas, we focused attention on the process



When low-resolution techniques are used, the study is complicated by the fact that two ^{16}O atoms are isobaric with one of ^{32}S , which calls for labeled reagents. This, of course, does not apply to a high-resolution technique, FT-ICR, used at pressures from 10^{-8} to 10^{-7} torr. In this low-pressure range, no adducts were detectable, yet formation of some transient complex was suggested by the occurrence of the fast ($k = 6.0 \pm 1.5 \times 10^{-10}$ $\text{cm}^3 \text{ s}^{-1} \text{ mole}^{-1}$) isotope exchange



Furthermore, the high efficiency of the process suggests that if, indeed, a transient complex is involved, it should be characterized by connectivity **a** where two preformed, easily exchangeable SO units are present, rather than by connectivity **b**, where the isotope exchange would require fission of one of the strong S-O bonds in the SO_2 unit.



Formation of a S_2O_3^+ complex was directly observed in CI experiments performed at much higher pressures (up to 0.1 torr) using neat SO_2 . The CAD spectra of various isotopomers, reported in Table 1, are consistent with the assignment of connectivity **a** to the S_2O_3^+ adduct, in that formation of all charged fragments can be accounted for by the fission of one or two bonds of that species.

The NR spectra of S_2O_3^+ demonstrated the presence of significant recovery peaks. This shows that OSOSO, a new sulfur oxide, exists in the isolated state with a lifetime >1 μs .

The S_2O_3^+ and S_2O_3 systems were also examined by computational methods, using the B3LYP functional [25] and the 6-311++G (2d) basis set [26]. Single-point energy calculations at the optimized geometries were performed according to the CCSD(T) approach [35], whereas transition states were located according to the method of Schlegel and coworkers [27].

Consistent with the experimental evidence, the

Table 1
Collisionally activated dissociation spectra of different $S_2O_3^+$ isotopomers

$^{32}S^{16}O_3^+$		$^{34}S^{32}S^{16}O_3^+$		$^{32}S_2^{18}O_3^+$		$^{34}S^{32}S^{18}O_3^+$		Assignments ^a
<i>m/z</i>	I (%Σ) ^b	<i>m/z</i>	I (%Σ)	<i>m/z</i>	I (%E)	<i>m/z</i>	I (%E)	
96	2.0	98	2.1	100	1.6	102	1.8	$S_2O_2^+$ [$^{32}S_2^{16}O_2^+$, $^{34}S^{32}S^{16}O_2^+$, $^{32}S_2^{18}O_2^+$, $^{34}S^{32}S^{18}O_2^+$]
80	0.3	82	0.5	82	0.3	84	0.3	S_2O^+ [$^{32}S_2^{16}O^+$, $^{34}S^{32}S^{16}O^+$, $^{32}S_2^{18}O^+$, $^{34}S^{32}S^{18}O^+$]
64	33.8	66	17.5	68	35.7	70	18.7	SO_2^{+c} [$^{32}S^{16}O_2^+$, $^{34}S^{16}O_2^+$, $^{32}S^{18}O_2^+$, $^{34}S^{18}O_2^+$]
		64	15.0			68	17.1	SO_2^{+c} [$^{32}S^{16}O_2^+$, $^{32}S^{18}O_2^+$]
48	62.2	50	31.7	50	60.9	52	30.3	SO^{+c} [$^{32}S^{16}O^+$, $^{34}S^{16}O^+$, $^{32}S^{18}O^+$, $^{34}S^{18}O^+$]
		48	31.5			50	30.0	SO^{+c} [$^{32}S^{16}O^+$, $^{32}S^{18}O^+$]
32	1.7	34	0.8	32	1.5	34	0.9	S^+ [$^{32}S^+$, $^{34}S^+$]
		32	0.9			32	0.9	S^+ [$^{32}S^+$]

^aIn parentheses the isotopomers of the CAD fragments

^bPercentage of the fragments intensity with respect to the total fragments intensities, standard deviation $\pm 10\%$.

^cThese fragments are also present in the MIKE spectra.

lowest minimum identified on the $[S_2, O_3]^+$ surface is a planar species of connectivity **a**, that is, O–S–O–S–O, which can be seen as an electrostatic complex between SO^+ and SO_2 and is stable at 298 K with respect to dissociation into SO_2 and SO^+ by 25.3 kcal mol⁻¹ at the CCSD(T) level of theory. The species of connectivity **b**, that is, O–S–S $\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$, planar, is less stable by 23.4 kcal mol⁻¹ (298 K) at the CCSD(T) level of theory. As to neutral S_2O_3 , the most stable species is a triplet of O–S–O–S–O connectivity, unstable with respect to dissociation into SO_2 and SO ($X^3\Sigma^-$) by 16.8 kcal mol⁻¹ (298 K) at the CCSD(T) level. However, its dissociation requires overcoming a barrier of 6.1 kcal mol⁻¹, which accounts for the detection of the radical by NR mass spectrometry.

The experimental and computational evidence concur in showing that the $S_2O_3^+$ cation of O–S–O–S–O connectivity is a product of the association of SO^+ with SO_2 and is stable with respect to dissociation into the monomers. Its neutralization gives neutral OSOSO, a new sulfur oxide, theoretically characterized as a metastable triplet. The barrier to its dissociation, albeit relatively low according to the computational results, is nevertheless sufficient to allow detection as an isolated gaseous species at 298 K by NR mass spectrometry.

As to the relevance of the above findings to planetary science, the $S_2O_3^+$ inventory in Io's atmosphere depends on two factors, namely, the abundance

of its charged precursor, SO^+ , and the density of SO_2 in the regions where reaction (5) takes place. As to the first factor, whereas the average concentration of ions in Io's atmosphere is low (J. Moses, personal communication), intense ionic beams from the exosphere, where SO^+ is the major ion, impinge on the frozen SO_2 surface layer, causing sublimation and, hence, large local concentrations, of sulfur dioxide [37]. As to the second factor, Io's atmosphere is not uniform, owing to the presence of large, high-pressure "patches," where the SO_2 columnar density reaches 10^{19} mole cm⁻² [38].

On the basis of the above consideration, the presence of $S_2O_3^+$ in Io's atmosphere seems very likely, and the cation might well be detected in future observational studies. The presence of significant amounts of neutral OSOSO is far more uncertain, although one can envisage plausible formation routes involving charge exchange of $S_2O_3^+$ with gaseous SO , or neutralization of $S_2O_3^+$ in the solid phase, following adsorption on the frozen SO_2 surface layer.

6. Conclusion

The representative examples outlined in the previous sections show that techniques such as MIKE, CAD, NR, and FT-ICR mass spectrometry are of considerable interest to the chemistry of atmospheres,

both terrestrial and planetary, allowing experimental detection and structural characterization of exotic and/or transient species that play an important role in atmospheric processes. Furthermore, the studies illustrated underline the highly synergic role of mass spectrometric and theoretical methods. Finally, the interdisciplinary relevance of the results should not obscure their interest to fundamental research, especially as regards the inorganic chemistry of main-group elements of the first rows of the Periodic Table.

Acknowledgements

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