

Mass Spectrometric Contributions to Problems Related to the Chemistry of Atmospheres

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ABSTRACT

Recent mass spectrometric studies of species and processes relevant to the chemistry of atmospheres are reported. New species have been detected, including HO₃; a stratospheric reservoir of OH radicals; the [H₂O⁺O₂⁻] charge transfer complex, central to the atmospheric photonucleation theory; and the OSOSO oxide and its cation, likely present in the Io's atmosphere. As to ionic processes, a new route to tropospheric N₂O in air ionized by lightning and coronas is reported, as well as the complex chemistry promoted by ionization of ozone/freon and ozone/carbonyl sulfide mixtures and the formation of O₅⁺, relevant to the problem of ¹⁸O excess in stratospheric ozone.

Introduction

The current interest in atmospheric sciences^{1–5} has given renewed impetus to the development of a wide research area that pertains to the fundamental chemistry of gaseous, transient species such as ions, radicals, metastable molecules, and clusters that play key roles in important atmospheric processes. The study of charged species is long peculiar to mass spectrometry (MS), due to their well-recognized role in the terrestrial and planetary atmospheres.^{6–18} By contrast, the potentiality of the technique for the study of neutral species, undoubtedly most relevant to atmospheric chemistry, is less generally perceived. Neutralization reionization mass spectrometry (NRMS), a purely mass spectrometric approach to the detection and characterization of transient neutrals, has proved in recent years to be an extremely successful tool for the study of atmospherically relevant species.

Studies in my laboratory have focused on problems related to the existence, the lifetime, the structure, and the reactivity of simple, mostly inorganic, gaseous species, both charged and neutral, regarded as particularly relevant

Giulia de Petris, born in 1958, obtained her basic academic degree at the Rome University "La Sapienza", where she became a permanent staff member in 1986. In 1992 she became an associate professor, first at the University della Tuscia (Viterbo), and then at the University "La Sapienza". She is now a full professor, and holds a chair of general and inorganic chemistry at the University "La Sapienza". Her research interests focus on gas-phase ion chemistry and atmospheric chemistry, investigated with experimental approaches ranging from high-pressure radiolysis to mass spectrometry, including FT-ICR, MIKE, CAD, NR, MSⁿ, and ESI techniques. The research is aimed, in general, at establishing the existence of new neutral and charged species of atmospheric interest and characterizing their lifetime, structure, stability, and reactivity. A pet research area is the construction of extended thermochemical scales correlating the binding energies of a large number of molecules toward different gaseous cations (H⁺, NO⁺, NO₂⁺).

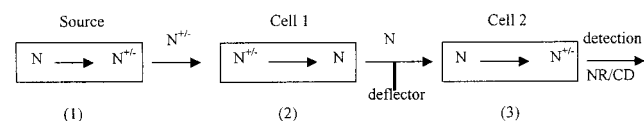
to the chemistry of the atmospheres. In all cases, MS in its various forms was utilized as the one and only experimental tool, complemented, when required, by theoretical methods.

Consistent with the above outlined distinction between the two areas of application of MS, this Account is organized in two sections, showing representative results in the domain of neutral and ionic chemistry.

New Inorganic Neutral Species

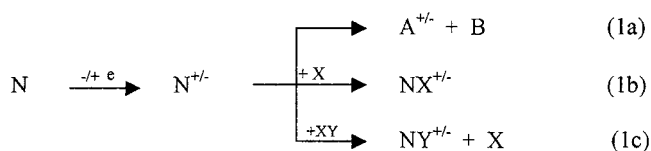
Methodology. The basic experimental approach utilized, NRMS, is a well-established technique that has previously demonstrated its value as a route to otherwise inaccessible species of considerable fundamental interest and has been repeatedly reviewed.^{19–24} Nevertheless, a very concise illustration of its principles may prove useful to the nonspecialist readers.

MS of neutral species stems from the idea that formation of ions from neutral molecules, in the source of a mass spectrometer (1), can be usefully mirrored by formation of neutrals from mass-selected ions (2), in a cell located along the flight path. Like only ions, acceler-



ated by the high voltage, are extracted from the source, so only neutrals are allowed to proceed after cell 1, since any ions that survive the neutralization process (2) are removed from the beam by a charged deflector electrode. Due to the inherent requirements of MS, by which only ions can be revealed, the beam of fast moving neutrals has to be reionized in a second cell in order to be detected (3), the last steps 2 and 3 representing the sequential events of NRMS. Note that the ion from process 1 can be either positive or negative and correspondingly reionization 3 can be either a reduction or an oxidation; hence, four processes can be carried out, denoted ⁺NR^{+/-} and ⁻NR^{-/+}.

Despite some similarities in processes 1–3, distinct features characterize them, which gives NRMS its unique ability to detect highly reactive and/or metastable neutral species. As to process 1, the charged parent, henceforth denoted the precursor ion, can be obtained by a variety of processes, e.g., dissociative ionization (1a), formation of adducts (1b), and ligand exchange (1c), capable of generating species not accessible from direct ionization of stable molecules.



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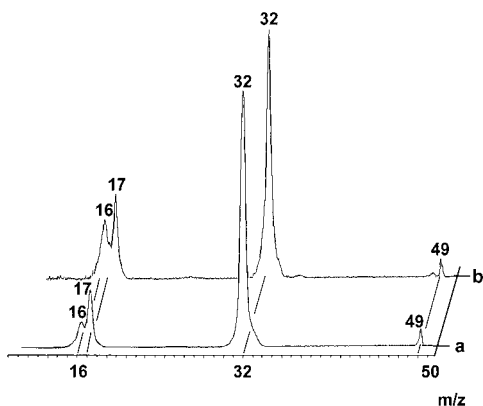
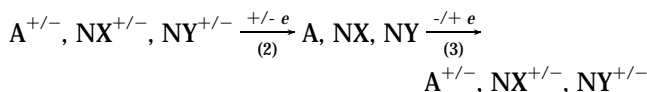


FIGURE 1. $^+NR^+$ (a) and $^+NR^-$ (b) spectra of HO_3^+ ion from protonation of ozone (m/z 49). (a) The kinetic energy is 4 kV, Xe is the neutralizing gas, and O_2 is the reionizing gas. (b) The kinetic energy is 8 kV, and CH_4 is the neutralizing and reionizing gas.

Conversely, processes 2 and 3, accomplished by collision with appropriate target gases, whose atoms or molecules act as electron exchangers, are vertical processes occurring without appreciable changes of geometry. The connectivity and the geometrical features of the precursor ion are “frozen” and preserved in the whole process, whose efficiency strictly depends on the Franck–Condon factors involved.

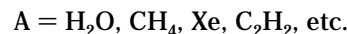
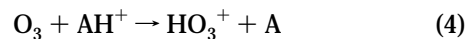


Accordingly, the structure of a neutral species detected by NRMS reproduces that of the precursor ion, which can be independently characterized by structurally diagnostic MS methods, such as mass-analyzed ion kinetic energy (MIKE), collisionally activated dissociation (CAD), and multistage tandem mass spectrometry (MS^3).^{25,26} The features of the NRMS technique can be summarized as follows: (i) formation of ions by processes other than ionization of stable neutrals can be exploited to investigate the existence of elusive or reactive neutral species; (ii) neutrals having the same connectivity of the precursor ion can be formed, provided that favorable Franck–Condon factors characterize processes 2 and 3 and their dissociation requires overcoming a barrier of the order of 10 kcal mol⁻¹; (iii) only the neutrals that survive longer than the flight time from the neutralization to the reionization cell are detected, which allows the lower limit of their lifetime to be evaluated.²⁴

As previously noted, we have found NRMS to be an extremely powerful tool for the study of simple, inorganic species relevant to atmospheric chemistry. This procedure was generally followed: the precursor ion was produced by chemical ionization (CI), its structure and connectivity were assigned by CAD and MS^3 , and its NR spectrum was recorded. Simply detecting a “recovery” peak, characterized by the same m/z ratio of the original ion, proves the existence of a neutral species which, based on the considerations above, has the connectivity of its precursor ion. Moreover, if there is a sufficiently high intensity, a

direct structural assay can be performed, by further mass selection and CAD of the recovery peak (NR/CD).

Hydrogen Trioxide. The atmospheric relevance of hydrogen trioxide, HO_3 , descends from the importance of the excited hydroxyl radicals, OH, formed from the photochemical reaction between H and O_3 , responsible, inter alia, for airglow emission.²⁷ Due to the photochemical daytime generation of the OH radicals, nightglow cannot likewise be explained, which accounts for the interest attached to the existence of a sufficiently long-lived reservoir molecule whose dissociation generates excited OH radicals at night. Hydrogen trioxide, HO_3 , long postulated as the key intermediate of the reaction between H and O_3 , has been extensively studied by computational methods at various levels of theory.^{28–30} A long debate as to the detectability of HO_3 proved rather inconclusive, since the theoretical results and thermochemical considerations characterize the radical as unstable or only marginally stable. Furthermore, purely thermochemical data would be in any case insufficient, since HO_3 , although thermodynamically unstable, could be detectable as a long-lived metastable species, due to a conceivable kinetic barrier to its dissociation. We utilized as the precursor the HO_3^+ ion from the protonation of ozone by gaseous Brønsted acids.³¹



HO_3^+ was structurally characterized as a species of H–O–O–O connectivity, whose positive and negative NR spectra show significant recovery peaks at m/z 49 (Figure 1).³² The HO_3 radical detected was accordingly assigned the H–O–O–O connectivity, further confirmed by the CAD spectrum of the HO_3^+ ion from its reionization process. The cation, reselected and structurally probed by NR/CD, gave, indeed, a spectrum indistinguishable from that of the HO_3^+ ions directly formed upon protonation of ozone in the CI source. The results of the NRMS experiments conclusively demonstrate that indeed HO_3 does exist as an isolated species; its lifetime exceeds 1 μs , and a sizable barrier (of thermochemical and/or kinetic nature) characterizes its dissociation. All these findings support the role of HO_3 as a reservoir of OH radicals and identify an additional, important member of the HO_x “odd hydrogen” family so relevant to atmospheric chemistry.

$H_2O^+O_2^-$ Charge-Transfer Complex. Detection of this complex represents a particularly significant demonstration of the usefulness to atmospherically relevant problems of NRMS, whose utilization has brought to an end the long search for a species essential to the theory of an important atmospheric phenomenon. Photonucleation was discovered at the turn of the century by C. T. R. Wilson, the inventor of the cloud chamber.³³ It can be described as the formation of water droplets upon UV irradiation of supersaturated air, in the presence of oxygen. Although considered to be of great interest for atmospheric chemistry, the photonucleation mechanism had never been cleared up, until Byers Brown proposed

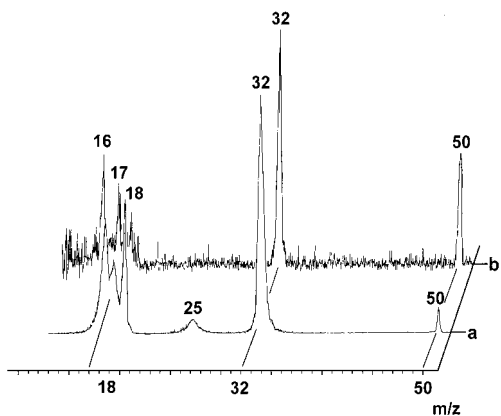
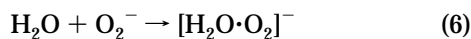
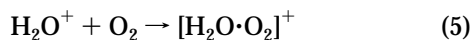


FIGURE 2. $^+NR^+$ (a) and $^-NR^-$ (b) spectra of $[H_2O \cdot O_2]^+$ cation and $[H_2O \cdot O_2]^-$ anion. The kinetic energy is 4 kV; Xe or CH_4 are used as neutralizing gases, and O_2 is used as the reionizing gas. Doubly charged species appear at m/z 25.

a theory that postulates the initial formation of a van der Waals (vdW) complex, $[H_2O \cdot O_2]$.³⁴ Its conversion into a charge-transfer (CT) complex, $[H_2O^+ \cdot O_2^-]$, upon UV irradiation, would provide an effective nucleation center, whose large dipole moment can actually favor the aggregation of a number of H_2O polar molecules into a cluster. The theory and the supporting high-level theoretical calculations predicted a sufficient stability and a relatively long lifetime of the neutral CT complex, $[H_2O^+ \cdot O_2^-]$,³⁵ yet no experimental evidence for the existence of this key species had been obtained. The possible detection of such a neutral by the NRMS technique is based on the large difference between the binding energy of the H_2O/O_2 pair in a vdW complex and that of the H_2O^+/O_2^- pair in a CT complex. Whereas the vdW collision complex is characterized by a large separation, 3.484 Å, of the monomers, with an essentially repulsive interaction at short separations, the CT complex is characterized by a short distance, 2.344 Å, between the two constituents,³⁶ and it can be reasonably considered a strongly bound neutral species. In this case³⁷ suitable precursor ions were obtained from the reactions



accomplished by positive and negative CI of gaseous water/oxygen mixtures. Both adducts have to be regarded as ion–molecule complexes, as demonstrated by their CAD spectra. E.g., the spectrum of $[H_2O \cdot O_2]^+$ displays only the O_2^+ and H_2O^+ fragments, and the $[H_2^{16}O \cdot ^{18}O_2]^+$ and $[H_2^{18}O \cdot ^{16}O_2]^+$ isotopomers give fragments corresponding to the O_2 and H_2O moieties, retaining their identity without any isotopic scrambling. The NR spectra of ions from reactions 5 and 6 show significant recovery peaks (Figure 2), pointing to the existence of a metastable neutral species containing strongly bound O_2 and H_2O units, the best candidate being indeed the CT complex, $[H_2O^+ \cdot O_2^-]$, whose role in atmospheric chemistry as a nucleation center according to the Byers Brown theory thus finds crucial support.

Tetraoxygen. The role of excited electronic states of oxygen O_2 is well-recognized in a number of processes relevant to atmospheric chemistry. As an example, the long-sought O_4 molecule was suggested to exist as a metastable long-lived complex between a ground-state O_2 molecule and a $c^1\Sigma_u^-$ excited electronic state of an O_2 molecule.³⁸ Strong, if indirect, evidence for metastable O_4 was previously obtained by experiments involving electron transfer from Cs to O_4^+ ³⁹ and photoionization of O_2 excited by a DC discharge.^{38,40} We have eventually succeeded in positively detecting intact O_4 by NR spectrometry, thus providing conclusive proof of the existence of the long-lived metastable O_4 .⁴¹ The charged precursor, O_4^+ , was obtained from the association reaction



undergone by O_2^+ primary ions generated both in the ground state and in electronically excited states by ionization of O_2 . First the O_4^+ product ions were mass selected and structurally assayed by CAD spectrometry, giving O_2^+ as the only charged fragment. The CAD spectra of $^{16}O_2^{18}O_2^+$ ions, generated by using $^{16}O_2/^{18}O_2$ mixtures, showed only the $^{16}O_2^+$ and $^{18}O_2^+$ fragments, the lack of isotopic scrambling pointing to a structure of O_4^+ that contains two discrete O_2 units. In the NR experiments, the O_4^+ ions were mass selected and neutralized obtaining, after reionization, an O_4^+ recovery peak. This result indicates that a fraction of neutral O_4 , derived from the neutralization process, has survived at least for a time exceeding the flight time from the neutralization to the reionization cell. In addition, the NRMS of the $^{16}O_2^{18}O_2^+$ ion shows no isotopically scrambled fragments, suggesting, as expected, that the structure of the neutral species is strictly related to that of the ion. Whereas, on this basis, it is difficult to assign a precise structure to the neutral, it is possible to rule out the covalently bound O_4 molecules so far theoretically characterized, whose structural features are not consistent with the observed lack of isotopic scrambling. Some O_4 complex, and in particular that between a ground-state O_2 molecule and one in the excited $c^1\Sigma_u^-$ state,^{38,39} proves more compatible with our obtained results.

New Sulfur Oxide S_2O_3 . So far, we have examined species relevant to the chemistry of the terrestrial atmosphere. Now we provide an example of studies aimed at the identification of species whose existence in planetary atmospheres is suggested by observational results that reveal features not traceable to known chemical species. A large body of data on the surface and the atmosphere of Io, the innermost moon of Jupiter, has been gathered both by Earth-based instruments and by planetary probes. The atmosphere of Io mainly consists of SO_2 with 5–10 mol % of SO, and it is strongly ionized by electron beams, forming a plasma cloud containing, in addition, the SO_2^+ and SO^+ cations.⁴² The surface reflectivity, the millimeter band, and the ion cyclotron wave spectra measured by the orbiter Galileo point to the presence of unknown molecules whose identification and characterization would

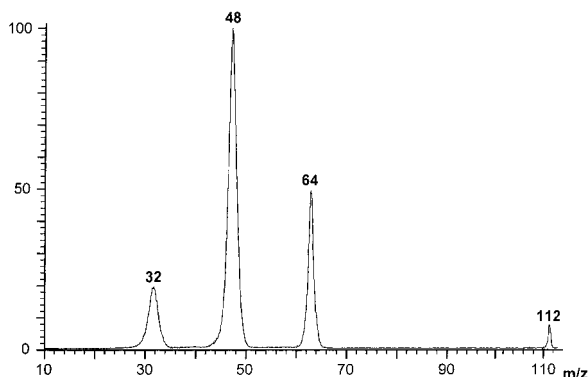
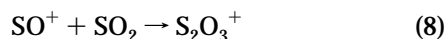


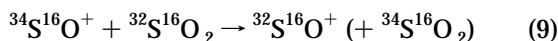
FIGURE 3. $^+NR^+$ spectrum of $S_2O_3^+$ ion. The kinetic energy is 4 kV, Xe is the neutralizing gas, and O_2 is the reionizing gas.

lead to a better understanding and a correct modeling of Io's planetary environment.⁴³ We have therefore attempted to reproduce the sulfur oxide ion chemistry occurring in Io's atmosphere, starting with the reaction between SO^+ and SO_2 , its main charged and neutral components.⁴⁴ Although the average concentration of SO^+ in Io's atmosphere is low, SO^+ is the major ion in the ionic beams from the exosphere. It is formed by direct ionization of SO, favored by the lower ionization potential with respect to SO_2 (10.32 and 12.32 eV, respectively), or by dissociation of SO_2^+ . SO_2 is by far the major neutral species, and, albeit not uniformly dense, it reaches high local concentrations in high-pressure "patches" from volcanic emissions.

In our experiments the reactions promoted by CI of neat SO_2 , where SO^+ is the most abundant ion, were investigated. Formation of the $S_2O_3^+$ adduct was observed, likely from the reaction



The structural assay of $S_2O_3^+$ by CAD spectrometry of the $^{34}S^{32}S^{16}O_3^+$, $^{32}S^{18}O_3^+$, and $^{34}S^{32}S^{18}O_3^+$ isotopomers, allowed the assignment of the O–S–O–S–O connectivity. The occurrence of reaction 8 and the structure of the product ion were confirmed by Fourier transform ion cyclotron resonance (FT-ICR) experiments, performed by selecting the $^{34}S^{16}O^+$ isotopomer and monitoring its reaction with SO_2 of natural isotopic composition.

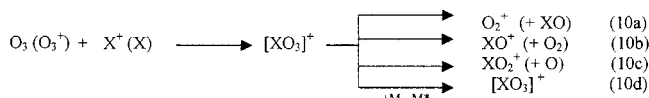


The observed isotopic exchange ($k_8 = (6.0 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) points to the existence of a transient $S_2O_3^+$ adduct that cannot be stabilized at the low pressures (10^{-8} to 10^{-7} Torr) typical of FT-ICR experiments. Moreover, it positively supports the O–S–O–S–O connectivity assigned, since the isotopic exchange can only occur if the transient complex contains two preformed, indistinguishable and interchangeable SO units. This further explains why SO^+ was long considered unreactive toward SO_2 . Having established its structural features, the $S_2O_3^+$ ion was assayed by NR mass spectrometry (Figure 3), whose results clearly demonstrate the existence of a new S_2O_3 sulfur oxide of O–S–O–S–O connectivity. The structure and the stability of $S_2O_3^+$ and S_2O_3 were also

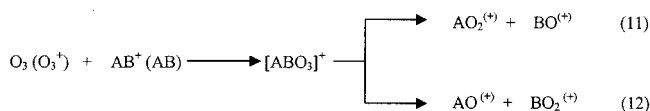
theoretically studied using the B3LYP⁴⁵ functional with the 6-311++G(2d) basis set and performing single point energy calculations at the optimized geometries using the CCSD(T) approach.⁴⁶ The potential energy surface of $S_2O_3^+$ displays, in agreement with the experimental results, a planar species of O–S–O–S–O connectivity as the lowest minimum. Although partially electrostatic, the bonding between SO^+ and SO_2 is probably enhanced by covalent interaction, as witnessed by the large BE, $25.3 \text{ kcal mol}^{-1}$ at 298 K. The most stable S_2O_3 neutral is a triplet of the same connectivity whose dissociation into SO_2 and SO ($X^3\Sigma^-$), albeit exothermic by $16.8 \text{ kcal mol}^{-1}$ at 298 K, requires overcoming a $6.1 \text{ kcal mol}^{-1}$ barrier, sufficient to allow its detection by NRMS. Whereas the presence of $S_2O_3^+$ is very likely in Io's atmosphere and its computed spectroscopic properties will probably allow its detection in future observational studies, the possible existence of S_2O_3 , from charge exchange processes or neutralization of $S_2O_3^+$ in the solid phase, appears more uncertain.

Study of Ionic Processes

Ionization of the lower atmosphere is caused by emanation from radioactive rocks, galactic cosmic rays, lightning, and thunderstorms, etc., as well as by anthropogenic sources, e.g., corona discharges along power lines, whereas ionization by solar radiation and particles is most effective in the upper atmosphere. Atmospheric ions and their chemistry play several significant roles: they affect the composition of neutral species that are destroyed or produced by ionic reactions; they affect the propagation of radio waves with a strong impact in the field of communications; finally they establish the vicious sequence by which ionic reactions can yield species that contribute to ozone depletion. Due to its 2-fold role of tropospheric pollutant and stratospheric protective molecule, ozone has a special role in this play, and some of its ionic reactions occurring in the troposphere can indeed be responsible for its depletion in the stratosphere. A general theme of our research is therefore the study of the processes occurring in ionized mixtures of ozone with traces or bulk components of the low atmosphere. The general reactivity pattern outlined by these studies is illustrated in the scheme of eqs 10,



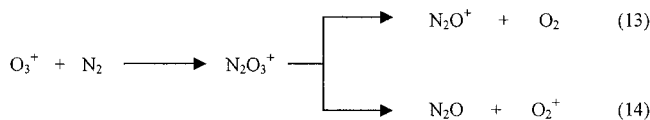
where X denotes the atmospheric species of interest. The results underline the O- and O_2 -donor character of O_3 and/or its cation,⁴⁷ whereas the specific course of the reaction is influenced by factors such as the ionization potential (IP) of the species involved and the stability of the primary adduct. In some cases dissociative oxidation is observed, as the O and/or O_2 transfer promotes the breaking of bonds between atoms or groups of atoms of the species involved, as summarized in the scheme of eqs 11 and 12,



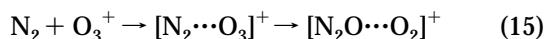
where AB denotes a generic polyatomic molecule. Some examples of these processes will be described in the following.

Ionization of Ozone/Nitrogen Mixtures. The reaction of O_3^+ with N_2 is an excellent example of how ionic reactions can affect on a global scale the composition of neutrals in the troposphere and contribute to the formation of species responsible for stratospheric ozone depletion. Our results have identified a new route to atmospheric N_2O , a greenhouse gas produced from a variety of natural, mostly biological sources, and by anthropogenic sources, including agricultural, industrial, and waste management activities.⁴⁸ Although N_2O emissions are much smaller than CO_2 emissions, N_2O is approximately 310 times more effective than CO_2 as a greenhouse gas. In addition, N_2O is long-lived in the troposphere and diffuses into the stratosphere, being the main source of the stratospheric NO_x oxides responsible for ozone depletion.⁵

FT-ICR experiments and high-pressure CI of N_2/O_3 mixtures (5 mol % O_3) have shown that O_3^+ acts toward N_2 exclusively as an O-donor (eqs 13 and 14).⁴⁹



The CAD spectrum of the N_2O_3^+ adduct from the O_3/N_2 CI displays two major peaks at m/z 44 and 32, assigned by MS^3 experiments as N_2O^+ and O_2^+ , respectively. This fragmentation denotes a $\text{N}-\text{N}-\text{O}\cdots\text{OO}$, rather than a $\text{N}-\text{N}\cdots\text{O}-\text{O}-\text{O}$ connectivity, pointing to a complete isomerization of the initially formed population, before its structural assay.



This inference was further confirmed by the observation that the N_2O_3^+ adduct formed in $\text{N}_2\text{O}/\text{O}_2$ CI gives CAD and MS^3 spectra identical to those of N_2O_3^+ from sequence 15. In addition, the $[\text{N}_2\text{O}\cdots\text{O}_2]^+$ complex was theoretically computed at the B3LYP/6-311+G(3d)⁴⁵ level to be more stable than the $[\text{N}_2\cdots\text{O}_3]^+$ one by 47.2 kcal mol⁻¹. Nevertheless, although detection of N_2O^+ from (13) and of O_2^+ from (14) suggests the intermediacy of a $[\text{N}_2\text{O}\cdots\text{O}_2]^+$ complex, and thus indicates O-transfer to N_2 , the actual formation of N_2O as the neutral counterpart of O_2^+ needed positive evidence. We therefore resorted to the neutral fragment reionization (N_fR) technique, which allows characterization of the neutral counterparts of fragment ions from a CAD experiment. The spectrum obtained (Figure 4) shows a peak at m/z 44, demonstrating that at least a fraction of the dissociation events undergone by N_2O_3^+ leads to a N_2O molecule. This evidence is limited to the *direct* formation of N_2O from reaction 14. However the

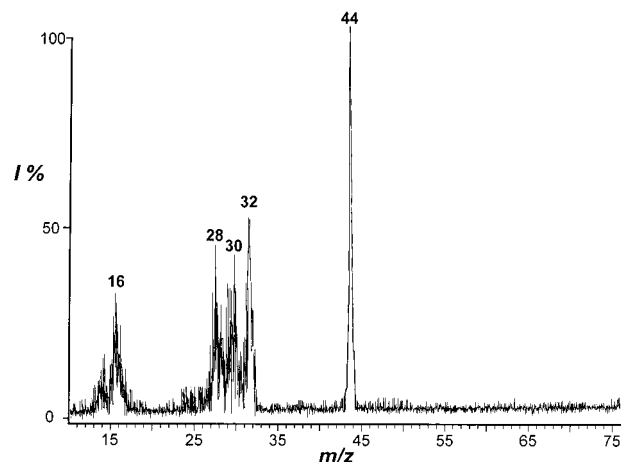
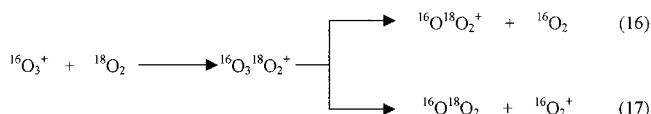


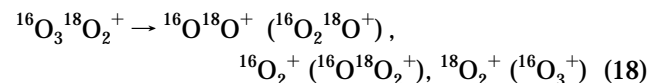
FIGURE 4. N_fR spectrum of neutral species from the CAD of the N_2O_3^+ ion. Reprinted with permission from ref 49. Copyright 2001 Wiley-VCH.

atmospheric process (13) as well is a likely source of N_2O , due to the expected fast ($k = 2.7 \times 10^{-10}$ cm² s⁻¹ molecule⁻¹) charge exchange of N_2O^+ with O_2 . The reaction studied requires conditions, e.g., a relatively high local concentration of ozone, that exist and affect atmospheric chemistry on a global scale in the air ionized by lightning, and corona discharges in and around thunderstorms, and high-voltage power lines. E.g., NO_x oxides from natural and anthropogenic electric phenomena are estimated to account for 10%, or more, of the global emissions. The above outlined study suggests that such phenomena can contribute as well to the formation of N_2O , which is much more effective in the stratospheric ozone depletion than the NO_x oxides.

Ionization of Ozone/Oxygen Mixtures. As in the previous case, O_3^+ acts toward O_2 exclusively as an O-donor.⁵⁰ FT-ICR experiments have shown that the O-transfer processes (eqs 16 and 17) are relatively efficient, e.g., the

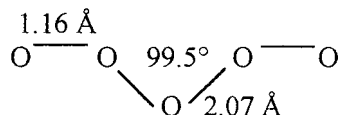


collisional efficiency of reaction 16 is about 10%, and the k_{16}/k_{17} branching ratio amounts to 1:5, consistent with the lower ionization potential of O_2 than O_3 . The most relevant result, however, concerns the O_3^+ ion, actually detected by high-pressure CI of O_2/O_3 mixtures. Whereas its CAD spectrum displays only the O_2^+ fragment, extensive isotopic scrambling is observed from $^{16}\text{O}_3^{18}\text{O}_2^+$, the abundances of the $^{16}\text{O}_2^+$, $^{18}\text{O}_2^+$, and $^{16}\text{O}^{18}\text{O}^+$ fragments being very close to the statistical distribution.

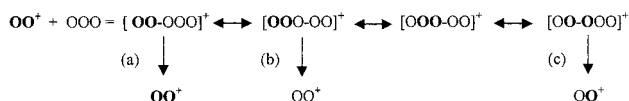


This result is relevant to the problem of the different isotopic enrichment of ozone in the stratosphere and in the troposphere.^{51,52} Whereas the ^{18}O enrichment in stratospheric ozone has not yet been fully understood, occurrence of the ionic processes 16 and 17 would act in

the direction of reducing the observable ^{18}O excess of ozone, which is important for modeling the phenomenon, in view of the presence of O_n^+ clusters in the atmosphere. We performed calculations at the CCSD(T)//B3LYP/6-311G(d) level of theory on O_5^+ , the intermediate of the isotopic exchange, finding that the most stable species has a symmetrical structure, with two longer bonds between the central O atom and two O_2 units. Comparison with



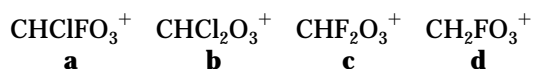
the adduct of O_3^+ with N_2 , where the computed bond lengths in the most stable $[\text{N}-\text{N}-\text{O}\cdots\text{O}_2]^+$ ion are $\text{N}-\text{O} = 1.20 \text{ \AA}$ and $\text{O}-\text{O}_2 = 2.24 \text{ \AA}$, shows that in both cases the central O atom has lost the memory of its original bonding in ozone, yet in O_5^+ it has the peculiarity of being bound to two indistinguishable O_2 units. Hence, in FT-ICR conditions only the central O atom is exchanged, whereas, in the CI experiments, where collisional stabilization allows detection of long-lived species, repeated association–dissociation and rotation processes can occur within the complex, which eventually decomposes into completely randomized O_2^+ fragments. Some of these



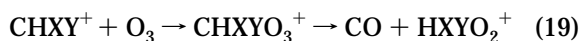
processes (for example c) are examples of the previously described dissociative oxidation, as the original bond between the two O atoms of O_2^+ is broken, and the O and O_2 units of ozone are bound to each of them (cf. reactions 11 and 12). An example of much more profound molecular reorganization is illustrated in the next section.

Ionization of Ozone/Chlorofluorocarbons Mixtures.

We investigated for the first time the effects of the interactions of ozone and halocarbons in ionized mixtures.⁵³ Hydrogenated halocarbons have been chosen that are known to show a lower ozone depletion potential with respect to non-hydrogenated halocarbons, due to their high reactivity in the troposphere. Different mixtures containing $\text{O}_3/\text{CHClF}_2$, $\text{O}_3/\text{CHCl}_2\text{F}$, O_3/CHF_3 , and $\text{O}_3/\text{CH}_3\text{F}$ were investigated by high-pressure CI/CAD experiments. The major ionic species observed were



a from $\text{O}_3/\text{CHClF}_2$ and $\text{O}_3/\text{CHCl}_2\text{F}$, **b** from $\text{O}_3/\text{CHCl}_2\text{F}$, **c** from $\text{O}_3/\text{CHClF}_2$ and O_3/CHF_3 , and **d** from $\text{O}_3/\text{CH}_3\text{F}$ ionized mixtures. Remarkably, irrespective of their source and formation process, all these ions undergo metastable loss of a CO molecule



This represents a typical dissociative oxidation process, whereby O- and/or O_2 -transfer from ozone occurs to

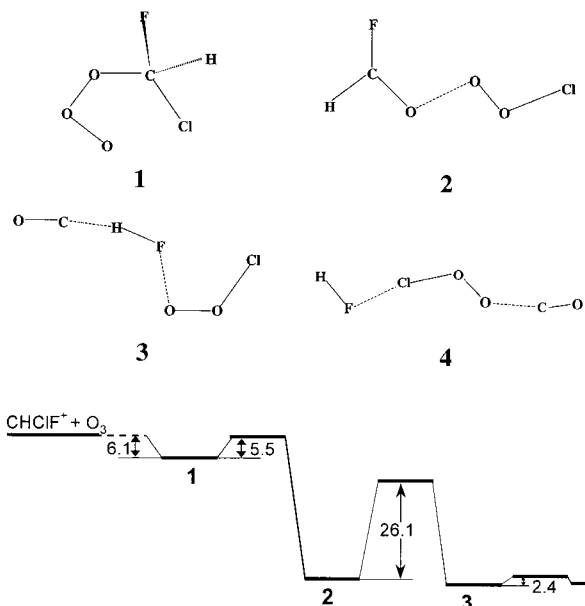
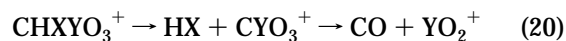


FIGURE 5. Structures of relevant minima and energy profile for the CHClFO_3^+ system.

atoms, or groups of atoms, separated from each other upon breaking of their original bonds. This is the most extensive molecular reorganization observed, in that not only does it involve the fission of all the C–H, C–X, and C–Y bonds, but also the H, X, and Y atoms are then required to be bound together in the HXYO_2^+ ion. MS³ experiments allowed establishment of a fragmentation sequence leading to the loss of CO, following that of HX, another peculiar feature of those systems.



Likewise, HXYO_2^+ ion from reaction 19 further loses HX



Therefore YO_2^+ is always obtained as the final product, suggesting the existence of a $[\text{YO}_2, \text{CO}, \text{HX}]^+$ complex that may evolve into a YO_2^+ ion solvated by either CO (CYO_3^+) or by HX (HXYO_2^+). Theoretical calculations performed at the B3LYP//CCSD(T)/6-311G(d,p) level support this view. Investigation of the potential energy surfaces of ions **a–d** shows, despite some differences, a common pathway from CHXYO_3^+ to CO, involving four relevant minima **1–4**. As an example, Figure 5 reports structures **1–4** relevant to the CHClFO_3^+ ($\text{X} = \text{F}$, $\text{Y} = \text{Cl}$) system and the corresponding energy profile. As illustrated, **1** → **2** isomerization involves preliminary breaking of the C–Y bond of CHXYO_3^+ , leading to the YOOOCHX^+ ion **2**, essentially a YO_2^+ ion solvated by a formyl halide molecule. In the following **2** → **3** and **3** → **4** steps the other C–H, C–X, and O–O bonds are broken, leading to ions **3** and **4**, which can reasonably be regarded as electrostatic complexes containing different arrangements of the HX, CO, and YO_2 moieties, all liable to CO loss. As a final remark, it is noteworthy to stress the key role played by the hydrogen atom, capable of forming the HX molecule, which is

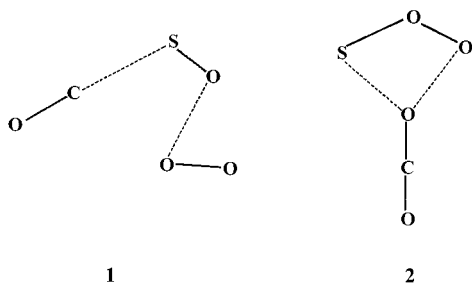


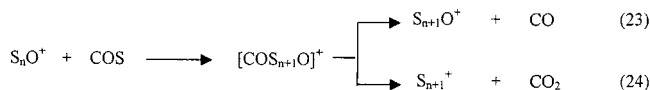
FIGURE 6. Structures of relevant minima in the COS^+/O_3 system.

essential in stabilizing the complex and providing the driving force for the whole process.

Ionization of Ozone/Carbonyl Sulfide Mixtures. Unlike other sulfur compounds, COS has a low reactivity and hence a sufficiently long lifetime in the troposphere to diffuse to the stratosphere, where it represents the main source of sulfur. By contrast, investigation of the reactions occurring in ionized mixtures containing O_3 and COS reveals a highly reactive interaction.⁵⁴ Indeed O-transfer to COS causes a prompt dissociation, likely due to the presence of a *preformed* good leaving group such as CO, so that no $[\text{COS}-\text{O}_3]^+$ adduct is detected.



The experimental pattern reveals an ionic chemistry essentially promoted by the SO^+ ion,⁵⁵ and indeed this system proves a very effective route to SO^+ . Theoretical calculations performed at the B3LYP//CCSD(T)/6-311+G-(2d) level have identified the two most stable minima in the COS^+/O_3 system (Figure 6): **1**, prone to dissociation into SO^+ , CO, and O_2 , and **2**, prone to dissociation into SOO^+ and CO_2 . Both decomposition channels confirm the 2-fold reactivity of ozone and represent efficient routes to SO^+ , owing to the instability of SOO^+ , prone to exothermic ($2.1 \text{ kcal mol}^{-1}$) dissociation into SO^+ , which subsequently promotes the oligomerization sequence in eqs 23 and 24, leading to S_{n+1}O^+ and S_{n+1}^+ ($n = 1-4$) ions.



Therefore, the reaction between COS^+ and O_3 is a route to species, such as the S_nO^+ cations, of higher sulfur content than the products from the oxidation of neutral COS, and moreover some of them, e.g., S_nO^+ ($n = 3-5$), have been detected for the first time, including the hitherto unknown S_3O oxide. Once again, these results show that an ionic reaction can affect the concentration of trace neutrals diffusing to the stratosphere; in particular, it points to the ionic COS/O_3 system as the source of SO^+ ion, since all other conceivable sources, SO_2 and other sulfur-containing compounds, are rapidly converted to aerosols in the troposphere.⁵

Conclusions

The examples illustrated are sufficiently representative of the role of mass spectrometry, often complemented by

theoretical methods, in the fundamental study of species and processes relevant to the chemistry of the atmospheres. The species involved are very simple inorganic molecules and radicals, containing atoms of the most abundant atmospheric gases (N_2 , O_2 , H_2O) and inorganic pollutants. Hopefully, their relevance to the science of the atmospheres will enhance the interest in the fundamental “inorganic” of main group elements. The interdisciplinary impact of this research area is bound to increase in the future, since its results are required for the modeling of the terrestrial and planetary atmospheres. Furthermore, the experimental and theoretical definition of the properties of species, hitherto unknown in the terrestrial environment, may help planning future missions of dedicated planetary orbiters.

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References

- (1) Graedel, T. E.; Crutzen, S. J. *Atmospheric Changes: An Earth System Perspective*; Freeman: New York, 1993.
- (2) Seinfeld, S. H.; Pandis S. N. *Atmospheric Chemistry and Physics*; Wiley: Chichester, U.K., 1998.
- (3) Hobbs, P. V. *Introduction to Atmospheric Chemistry*; Cambridge University Press: Cambridge, U.K., 1999.
- (4) Jakosky, B. M. Atmospheres of Terrestrial Planets. In *The New Solar System*; Betty, J. K., Petersen, C. C., Chaickin, A., Eds.; Cambridge University Press: Cambridge, U.K., 1999.
- (5) Wayne, R. P. *Chemistry of Atmospheres*, 3rd ed.; Clarendon Press: Oxford, U.K., 2000.
- (6) Smith, D.; Adams, N. G. Elementary Plasma Reactions of Environmental Interest. *Top. Curr. Chem.* **1980**, *89*, 1–43.
- (7) Smith, D.; Spanel P. Ions in the Terrestrial Atmosphere and in Interstellar Clouds. *Mass Spectrom. Rev.* **1998**, *14*, 255–278.
- (8) Ferguson, E. E.; Fehsenfeld, F. C.; Albritton, D. L. In *Gas-Phase Ion Chemistry*; Bowers M. T., Ed.; Academic Press: New York, 1979.
- (9) Thomas L. Modeling of Ion Composition in the Middle Atmosphere. *Ann. Geophys.* **1983**, *1*, 61–73.
- (10) Squires, R. R. Atmospheric Chemistry and the Flowing Afterglow Technique. *J. Mass Spectrom.* **1997**, *32*, 1271–1272.
- (11) Kull, A.; Kopp, E.; Gramer, C.; Brasseur, G. Ions and Electrons at the Lower-Latitude D Region. *J. Geophys. Res.* **1997**, *102*, 9705–9716.
- (12) Angel, L.; Stace, A. J. Reappraisal of the Contribution from $[\text{O}_2(\text{H}_2\text{O})_n]^+$ Cluster Ions to the Chemistry of Ionosphere. *J. Phys. Chem. A* **1999**, *103*, 2999–3005.
- (13) Beig, G.; Brasseur, G. Anthropogenic Perturbations of Tropospheric Ion Composition. *Geophys. Res. Lett.* **1999**, *210*, 1303–1306.
- (14) Turco, R. P.; Zhao, J. X.; Yu, F. A New Source of Tropospheric Aerosols Ion-Ion Recombination. *Geophys. Res. Lett.* **1998**, *25*, 635–638.
- (15) Lewis, J. S. *Physics and Chemistry of the Solar System*, 2nd ed.; Academic Press: San Diego, 1999.
- (16) Schunk, R. W.; Nagy, A. F. Ionospheres of the Terrestrial Planets. *Rev. Geophys. Space Phys.* **1980**, *18*, 813–852.
- (17) Kim, Y. H.; Fox, J. L. The Chemistry of Hydrocarbon Ions in the Jovian Ionosphere. *Icarus* **1994**, *112*, 310–325.
- (18) Huang, T. S.; Ho, C. W.; Alexander C. J. The Plasmasphere of Neptune. *J. Geophys. Res.* **1998**, *103*, 20267–20278.
- (19) Wesdemiotis, C.; McLafferty, F. W. Neutralization-Reionization Mass Spectrometry (NRMS). *Chem. Rev.* **1987**, *87*, 485–500.
- (20) Terlouw, J. K.; Schwarz H. The Generation and Characterization of Molecules by Neutralization-Reionization Mass Spectrometry (NRMS). *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805–938.
- (21) McLafferty, F. W. Study of Unusual Simple Molecules by Neutralization-Reionization Mass Spectrometry. *Science* **1990**, *247*, 925–929.
- (22) McLafferty, F. W. Neutralization-Reionization Mass Spectrometry. *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 221–235.

- (23) Goldberg, N.; Schwarz, H. Neutralization–Reionization Mass Spectrometry: A Powerful “Laboratory” To Generate and Probe Elusive Neutral Molecules. *Acc. Chem. Res.* **1994**, *27*, 347–352.
- (24) Schalley, C. A.; Hornung, G.; Schröder, D.; Schwarz, H. Mass Spectrometric Approaches to the Reactivity of Transient Neutrals. *Chem. Soc. Rev.* **1998**, *27*, 91–104.
- (25) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.
- (26) Cooks, R. G. *Collision Spectroscopy*; Plenum Press: New York, 1978.
- (27) Hargraves, J. K. *The Solar Terrestrial Environment*; Cambridge University Press: Cambridge, U.K., 1992.
- (28) Szichman, H.; Baer, M.; Varandas, A. J. C. Quantum Dynamical Rate Constant for the $H + O_3$ Reaction Using a Six-Dimensional Double Many-Body Expansion Potential Energy Surface. *J. Phys. Chem. A* **1997**, *101*, 8817–8821, and references therein.
- (29) Dupuis, M.; Fitzgerald, G.; Hammond, B.; Lester, W. A., Jr.; Schaefer, H. F., III. Theoretical Study of the $H + O_3 \leftrightarrow OH + O_2 \leftrightarrow O + HO_2$ System. *J. Chem. Phys.* **1986**, *84*, 2691–2697, and references therein.
- (30) Jungkamp, T. P. W.; Seifeld, J. H. The Enthalpy of Formation of Trioxy Radicals ROOO (R = H, CH₃, C₂H₅). An ab Initio Study. *Chem. Phys. Lett.* **1996**, *257*, 15–22.
- (31) Cacace, F.; Speranza, M. Protonated Ozone: Experimental Detection of O₃H⁺ and Evaluation of the Proton Affinity of Ozone. *Science* **1994**, *255*, 208–209.
- (32) Cacace, F.; de Petris, G.; Pepi, F.; Troiani, A. Experimental Detection of Hydrogen Trioxide. *Science* **1999**, *285*, 81–82.
- (33) Wilson, C. T. R. On the Condensation Nuclei Produced in Gases by the Action of Rontgen Rays, Uranium Rays, Ultraviolet Light, and Other Agents. *Philos. Trans. R. Soc. London, Ser. A* **1899**, *192*, 403–453.
- (34) Byers Brown, W. Photonucleation of Water Vapor in the Presence of Oxygen. *Chem. Phys. Lett.* **1995**, *235*, 94–98.
- (35) Dos Santos, D. M. V.; Vaughn, S. A. J.; Akhmat-Skaya, E. V.; Vincent, M. A.; Masters, A. J. Computer Simulation of Water Clusters Containing an H₂O–O₂ Charge-Transfer Complex. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2781–2785.
- (36) Palmer, I. J.; Byers Brown, W.; Hillier, I. H. Simulation of the Charge Transfer Absorption of the H₂O/O₂ van der Waals Complex using High Level ab Initio Calculations. *J. Chem. Phys.* **1996**, *104*, 3198–3204.
- (37) Cacace, F.; de Petris, G.; Pepi, F.; Troiani, A. Direct Experimental Evidence for the H₂O⁺O₂⁻ Charge-Transfer Complex: Crucial Support to Atmospheric Photonucleation Theory. *Angew. Chem., Int. Ed.* **2000**, *39*, 367–369.
- (38) Peterka, D. S.; Ahmed, M.; Suits, A. G.; Wilson, K. J.; Korkin, A.; Nooijen, M.; Bartlett, R. J. Unravelling the Mysteries of Metastable O₄^{*}. *J. Chem. Phys.* **1999**, *110*, 6095–6098.
- (39) Helm, H.; Walter, C. W. Observation of Electronically Excited States of Tetraoxygen. *J. Chem. Phys.* **1993**, *98*, 5444–5449.
- (40) Bevssek, H. M.; Ahmed, M.; Peterka, D. S.; Cortney Sailes, F.; Suits, A. G. Direct Detection and Spectroscopy of O₄^{*}. *Faraday Discuss.* **1998**, *108*, 131–138.
- (41) Cacace, F.; de Petris, G.; Troiani, A. Experimental Detection of Tetraoxygen. *Angew. Chem., Int. Ed.* **2001**, *40*, 4062–4065.
- (42) Russel, C. T.; Kivelson, M. G. Detection of SO in Io's Exosphere. *Science* **2000**, *287*, 1998–1999.
- (43) Galileo project: <http://galileo.jpl.nasa.gov/moons/io.html>.
- (44) Cacace, F.; Cipollini, R.; de Petris, G.; Rosi, M.; Troiani, A. New Sulfur Oxide, OSOSO, and Its Cation, Likely Present in the Io's Atmosphere: Detection and Characterization by Mass Spectrometric and Theoretical Methods. *J. Am. Chem. Soc.* **2001**, *123*, 478–484.
- (45) Bauschlicher, C. W.; Ruda, A.; Partridge, H.; Langhoff, S. R. In *Recent Advances in Density Functional Theory*; Chong, D. P., Ed.; World Scientific: Singapore, 1997.
- (46) Bartlett, R. J. Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359–401.
- (47) O-atom transfer ability of neutral ozone to gaseous cation has been reported by: Mendes, M. A.; Moraes, L. A. B.; Sparrapan, R.; Eberlin, M. N.; Kostianen, R.; Kotihao, T. Oxygen Atom Transfer to Positive Ions: A Novel Reaction of Ozone in the Gas-Phase. *J. Am. Chem. Soc.* **1998**, *120*, 7869–7874.
- (48) Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Ojima, D. S.; Kulmala, A. E.; Phongpan, S. General Model for N₂O and N₂ Gas Emissions from Soils due to Denitrification. *Global Biogeochem. Cycles* **2000**, *4*, 1045–1060.
- (49) Cacace, F.; de Petris, G.; Rosi, M.; Troiani, A. Ionization of O₃ in Excess N₂. A New Route to N₂O via Intermediate [N₂O₃]⁺ Complexes. *Angew. Chem., Int. Ed.* **2001**, *40*, 1938–1941.
- (50) Cacace, F.; Cipollini, R.; de Petris, G.; Pepi, F.; Rosi, M.; Sgamellotti, A. Isotope Exchange in Ionized O₃/O₂ Mixtures: The Role of O₅⁺, a Unique O_n⁺ Complex. *Inorg. Chem.* **1998**, *37*, 1398–1400.
- (51) Gellene, G. I. An Explanation for Symmetry-Induced Isotopic Fractionation in Ozone. *Science* **1996**, *274*, 1344–1346.
- (52) Mauersberger, K.; Erbacher, B.; Krankowsky, D.; Gunther, J.; Nickel, R. Ozone Isotope Enrichment: Isotopomer-Specific Rate Coefficients. *Science* **1999**, *283*, 370–372.
- (53) Cacace, F.; de Petris, G.; Pepi, F.; Rosi, M.; Troiani, A. Ionization of Ozone/Chlorofluorocarbon Mixtures in Atmospheric Gases. Formation and Remarkable Dissociation of [CHXYO₃]⁺ (X = H, Cl, F; Y = Cl, F) Complexes. *Chem.—Eur. J.* **2000**, *6*, 2572–2581.
- (54) Cacace, F.; de Petris, G.; Rosi, M.; Troiani, A. Ionization of Atmospheric Gases Containing Ozone and Carbonyl Sulphide. Formation and Reactivity of SO⁺ Ions. *J. Phys. Chem. A* **2001**, *105*, 1144–1149.
- (55) Decker, B. K.; Adams, N. G.; Babcock, L. M. Gas-Phase Reactivity of SO⁺: A Selected Ion Flow Tube Study. *Int. J. Mass Spectrom.* **2000**, *195*, 185–201.

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