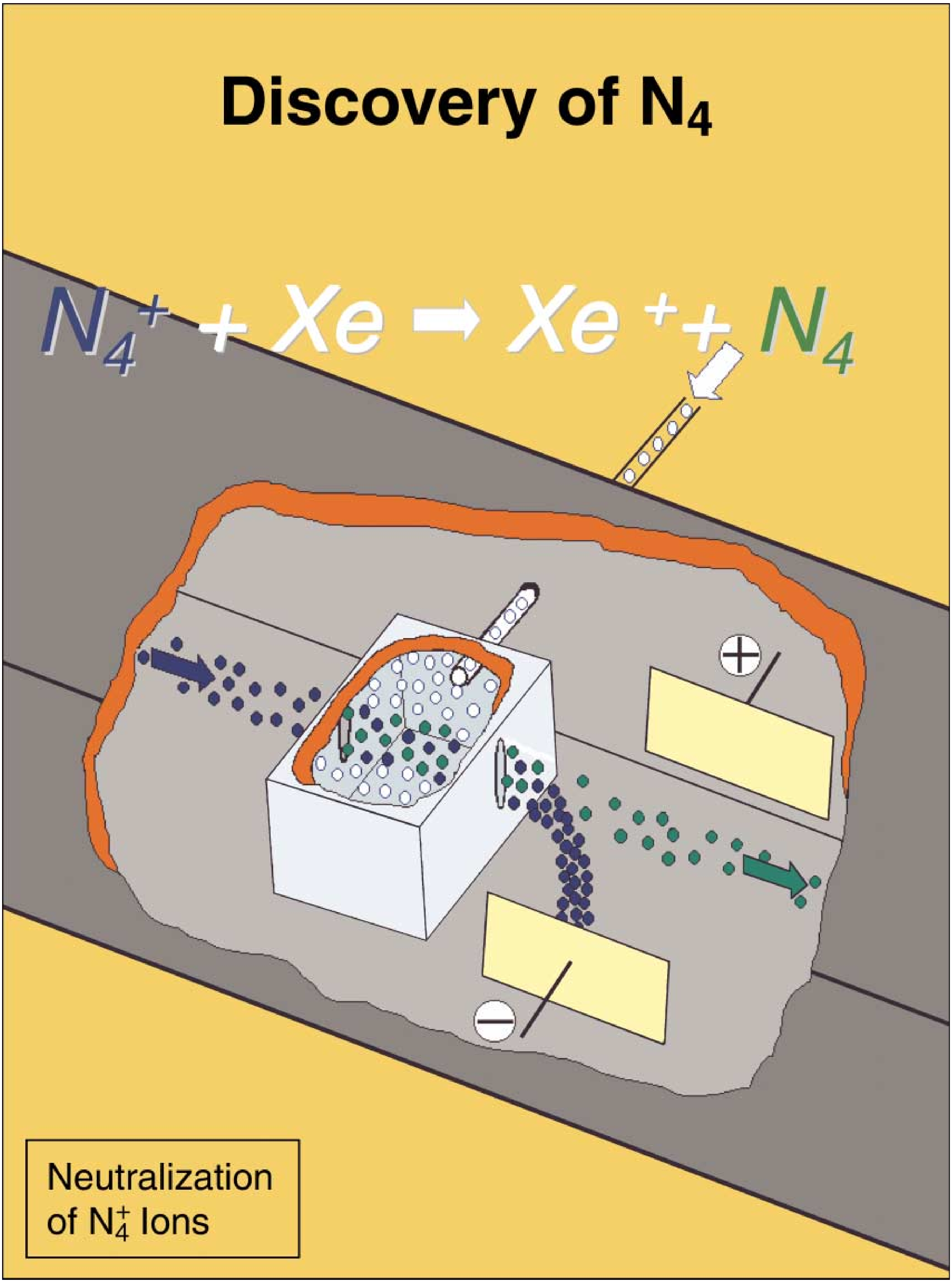
Discovery of N$_4$
$N_4^+ + Xe \rightarrow Xe^+ + N_4$
+
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Neutralization of N_4^+ Ions

From N_2 and O_2 to N_4 and O_4: Pneumatic Chemistry in the 21st Century

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Abstract: A brief account is given of the theoretical and experimental endeavors that span the last decade and eventually led to the discovery of N_4 and O_4, which have been actively sought for their fundamental interest and their relevance to atmospheric sciences and the development of high energy density materials (HEDM). The discovery and characterization of N_4 and O_4 as metastable species with lifetimes exceeding 1 µs in the isolated gas state have finally been achieved utilizing neutralization–reionization mass spectrometry (NRMS), a powerful technique based on collisional redox processes. The principles of NRMS, experimental outline, main features, and limitations are succinctly examined in comparison with other current approaches to the detection of metastable, short-lived neutral species.

Keywords: atmospheric chemistry · mass spectrometry · nitrogen · oxygen · theoretical chemistry

Introduction

The historians of science attribute pneumatic chemistry to the glorious period in the second half of the 18th century that witnessed the extension of chemical research from solid and liquid substances to gaseous substances, which were previously elusive and considered as best avoided, unwholesome effluvia. Since its very beginning, pneumatic chemistry was closely associated with the chemistry of the atmosphere. Indeed, its most celebrated triumphs were the discoveries of the two major components of air, N_2, discovered more or less independently by J. Priestley, D. Rutherford, C. W. Scheele, and H. Cavendish around 1772, and O_2, discovered by J. Priestley and C. W. Scheele around 1774.[1]

Nowadays, the tremendous upsurge of interest in atmospheric sciences has given new impetus to the specific research theme that represented the distinctive feature of early pneumatic chemistry, namely the discovery and the study of very simple gaseous molecules, in particular the ones formed of N and O, the most abundant elements of the atmosphere.

A striking parallel between pneumatic chemistry in its golden infancy and the present gas-phase chemistry is provided by the recent discovery of N_4[2] and O_4,[3] that mirrors that of the corresponding diatomic molecules in the 18th century. Such a singularly precise and symmetrical historical recurrence points to the fundamental continuity of the chemical progress, which is not entirely obscured by the enormous changes undergone in over two centuries by the specific targets, the theoretical grounds, and the experimental tools of the research.

In the following sections we shall briefly illustrate the principles and the experimental features of neutralization–reionization mass spectrometry, the most effective technique currently available for the preparation and positive detection of otherwise inaccessible molecules in the isolated gas state. Next, we shall recount in some detail the development of the research lines that, through the constructive interaction of theoretical and experimental studies, eventually led to the discovery of the title molecules.

Methods

The search for new gaseous, inorganic molecules is currently focused on short-lived, metastable, and highly reactive species that can hardly be studied by conventional techniques in condensed phases. In certain cases, such transient species have been prepared and trapped in cryogenic rare-gas matrices and examined by spectroscopic techniques. However, the most successful approach is based on the combination of high-level theoretical methods with a powerful experimental technique, neutralization–reionization mass spectrometry (NRMS). The latter can legitimately be regarded as the modern counterpart of the “pneumatic trough”, the experimental device that first allowed the collection and the study of gaseous substances, and hence the birth of pneumatic chemistry. Indeed, NRMS allows a wide range of exotic, metastable, often short-lived molecules and radicals, inaccessible by other preparative approaches, to be generated and structurally characterized in the isolated gas state, unperturbed by the constraints of a solid lattice. More important, NRMS provides *positive*, direct proof

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0947-6539/02/0817-3839 $ 20.00+.50/0

of the existence of the species of interest by measuring its molecular mass and elemental composition, whereas in matrix-isolation studies the assignment is based on the comparison of the observed spectral features with those theoretically computed or predicted on the basis of structural models. According to the time-honored, but undoubtedly still sound, aphorism that "he alone discovers who proves",[4] NRMS is to be regarded as the most effective tool available to the 21st century pneumatic chemists for the rigorous demonstration of the existence of a new molecule.

Principles and experimental outline of NRMS: Given the central role of the technique, a summary account of its principles, instruments, and experimental aspects is in order. For a more complete treatment, interested readers are directed to the excellent reviews available.[5] In essence, a NR experiment is a sequence of two separate, consecutive redox reactions, promoted in the gas phase by a single collision of the reagents. Consider, as an example, the search for an unknown species that, for the sake of simplicity, is assumed to be a diatomic molecule, XY. The first step is the preparation of a charged precursor, for example, the cation XY^+, which can be achieved by the dissociative ionization of some available precursor or from a suitable ion–molecule reaction in the ion source 1 of a multisector mass spectrometer (Figure 1). The XY^+ ion, accelerated by a voltage of several kV, is mass selected by the magnet 2, and enters cell 3, containing a suitable target gas, N, the pressure of which is adjusted to ensure that the projectile ion interacts with the target molecules under essentially single collision conditions. Here, a small fraction of the XY^+ ions undergoes one-electron reduction to the corresponding neutral molecule [Eq. (1)].

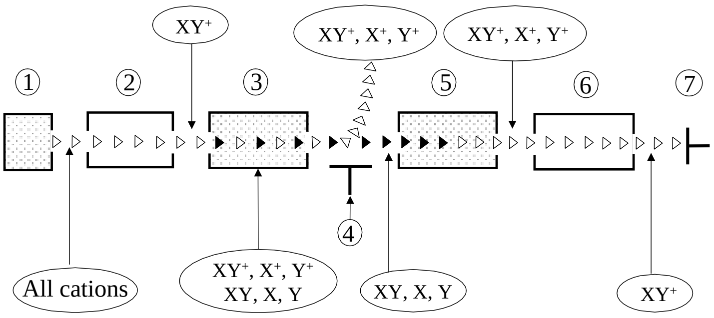

Figure 1. Schematic outline of a NR mass spectrometer, see text: (△) indicates ions, (▲) neutral species.

$$XY^+ + N \longrightarrow XY + N^+ \tag{1}$$

The collision also causes the fragmentation of the ion [Eq. (2)], and dissociation of the XY molecule can contribute as well to the formation of neutral X and Y fragments.

$$XY^+ \xrightarrow{N} X^+ + Y,\ \text{or}\ X + Y^+ \tag{2}$$

In summary, the beam leaving cell 3 consists largely of the original XY^+ ions that escaped collision, the fragment ions X^+ and Y^+, and the neutral XY, X, and Y species. All ions are deflected away by the high-voltage electrode 4, and this leaves a beam of fast neutrals that enter cell 5 containing a suitable target gas (M_1, M_2, or M_3), in which they undergo a single collision that causes one-electron oxidation and hence reionization back to the original cation [Eqs. (3 a) and (3 b)].

$$XY + M_1 \longrightarrow XY^+ + M_1 + e \tag{3a}$$

$$XY + M_2 \longrightarrow XY^+ + M_2^- \tag{3b}$$

With a proper choice of the target gas, one can perform an one-electron reduction of the neutral by collisional electron transfer, and in this case reionization yields anions [Eq. (3 c)].

$$XY + M_3 \longrightarrow XY^- + M_3^+ \tag{3c}$$

The ion beam will now contain chiefly the reionized species and/or fragment ions from its collisional dissociation. The resulting mass spectrum is recorded in the usual way by means of the magnetic, or electrostatic, analyzer 6 and the detector 7. Detection of a "recovery" peak, that is, of an ion having the same mass, or more accurately the same mass to charge ratio m/z, as that of the original XY^+ ion, proves that the neutral XY molecule does exist, and its lifetime exceeds the time interval between the neutralization and the reionization events, namely the time required to travel from cell 3 to cell 5. Given the typical intercell distance, of the order of 10 cm, the kinetic energy of the molecules, of the order of several keV, and their mass, ≤ 100 Da, the travel time, and hence the minimum lifetime, fall in the μs range. Limited variations of the flight time, and hence of the lower lifetime limit, are allowed by a change of the intercell distance (moveable cells) and/or of the kinetic energy of the molecules (different accelerating voltages).

Several NR spectrometers allow the reionized species to be further probed by utilizing additional gas collision cells, followed by a mass analyzer. This is a useful design, in that it provides additional structural insight and further confirmation of the elemental composition of the species of interest.

So far, we have restricted the discussion to experiments, in which the charged precursor is a cation. However, one can also utilize an anion as the precursor, for example, obtained by negative chemical ionization (CI). Depending on the sign of the charge of the precursor and of the reionized species, four types of experiments are possible, denoted as $^+NR^+$, $^+NR^-$, $^-NR^+$, and $^-NR^-$. Finally, it should be noted that the reionization process is not necessarily collisional, in that ionization of the fast neutral species has been achieved by electron ionization (EI), field ionization (FI), and photoionization (PI) as well.[5]

Collisional redox reactions: The one-electron transfer promoted by the collision of a fast-moving projectile ion with a target molecule deserves a brief discussion because its efficiency greatly affects the outcome of the NR experiment. The energy balance of the process is the difference between the ionization energy (IE) of the target molecule and the vertical neutralization energy (NE) of the cation. The process

[Eq. (1)] is very efficient when the reaction is thermoneutral (resonant electron transfer), a condition rarely attainable in practice. Use as the stationary target of metal atoms, the IE of which is generally low, ensures that electron transfer [Eq. (1)] to most projectile ions is exothermic. However, in addition to the problems associated with handling metal vapors, the exothermic character of its formation process yields a highly excited neutral, prone to dissociation before it can be detected. This has led to the widespread use of target molecules of high IE, such as Xe, the electron transfer from which [Eq. (1)] to many projectile ions is endothermic, which does not impair the efficiency of the reaction, since the energy deficit is easily made up by the large translational energy of the projectile ion.

The reionization process, [Eq. (3a)], that occurs when a "hard" M_1 target, such as He, is used, causes a more extensive fragmentation than the reaction involving a "soft" M_2 target, such as O_2 [Eq. (3b)]. Hence, O_2 is the target of choice when a high yield of intact reionized molecules is desired, whereas He is used to obtain a high yield of structurally informative fragment ions.

Requisites for detection by NRMS: The interaction of small ions having translational energies of several keV with a stationary target molecule occurs in a time frame of the order of 10^{-15} s. The electron transfer [Eq. (1)] is therefore a vertical process, as illustrated in Figure 2, in which again the case of a diatomic molecule is considered for the sake of simplicity. If the geometries of the XY^+ precursor and of the XY neutral are similar, the latter is formed in a low vibrational level and is likely to survive dissociation, provided that it resides in a sufficiently deep potential energy well (Figure 2a). On the other hand, if the geometries of the ion and of the neutral are appreciably different, the Franck–Condon factor of the vertical transition is low, and the molecule is formed, if at all, in a high vibrational level and undergoes dissociation before it can be detected (Figure 2b). In summary, a successful NR experiment requires that the barrier to dissociation is sufficiently high, and that the geometries of the charged and of the neutral species are similar. From a quantitative standpoint, a survey of the numerous experimental results so far reported suggests that the size of the barrier must exceed 30 to 50 kJ mol^{-1} to allow detection of the neutral molecule from the neutralization process [Eq. (1)].[5o] It is more difficult to quantify the degree of structural similarity required. At the very least, the connectivity of the neutral species must be the same as that of its ionic precursor. This limitation is actually a blessing in disguise, since it allows one to derive the connectivity of the neutral species detected from that of its charged precursor, which can be probed utilizing a number of structurally diagnostic techniques, for example, mass analyzed ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) mass spectrometry. Insight can be obtained recording the CAD spectrum of the reionized species that, based on the above considerations, is also expected to maintain the same connectivity as that of the neutral molecule.

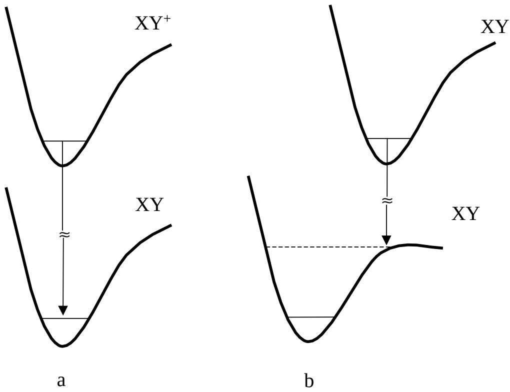

Figure 2. Vertical neutralization and ionization processes of a XY molecule and a XY^+ cation, having: a) similar geometries; b) different geometries.

The Discovery of N_4

Ordinary nitrogen consists of diatomic molecules, which are very stable (bond dissociation energy 954 kJ mol^{-1}), remarkably unreactive and reluctant, in particular, to bind to other N atoms to give N_n species with $n > 2$. Polynitrogen species are inherently metastable, since invariably their dissociation into N_2 is highly exothermic, which accounts in part for the experimental difficulties encountered in their preparation. As a matter of fact, until very recently, the only neutral polynitrogen species known beyond N_2 was the $N_3^{\bullet}$ radical, the discovery of which occurred 184 years after the discovery of N_2, a significantly long period of time.[6]

Recently there has been a vigorous upsurge of interest in homoatomic polynitrogen molecules that, in addition to their relevance to fundamental inorganic chemistry, are excellent models of, and promising candidates for, environmentally benign high energy density materials (HEDM), the next generation of green propellants, and explosives.[7]

Quite naturally, a great deal of attention has been devoted to the next polynitrogen species beyond $N_3^{\bullet}$, namely tetranitrogen, that has been the focus of an extraordinarily intense theoretical effort, steadily growing during the last decade.[8–19] Among the theoretically predicted species illustrated in Figure 3, the most thoroughly investigated one is the T_4 singlet **1**, tetraazatetrahedrane, a metastable species, the dissociation of which into N_2 is predicted to overcome a barrier of at least 54 kJ mol^{-1} and to release as much as 800 kJ mol^{-1}.[8–11] At high theoretical levels, the lowest energy N_4 isomer identified is the acyclic C_{2h} triplet **2**, the dissociation of which into N_2 is computed to release about 505 kJ mol^{-1} at the B3LYP/6–311 + G (3df) level and according to the G2 theory.[14] However, a study performed at the MP4SDTQ// MBTP(2)/6-31G* level shows that **2** is instead a transition state, and the most stable isomer is the acyclic C_s triplet **3**, predicted to be experimentally detectable.[13] Another minimum identified at the B3LYP/6-311 + G(3df) level of theory is the rectangular D_{2h} singlet **4**, which is also metastable, and its dissociation into N_2 is computed to release 766 kJ mol^{-1}.[13, 14] The above summary account reveals the richness of the N_4

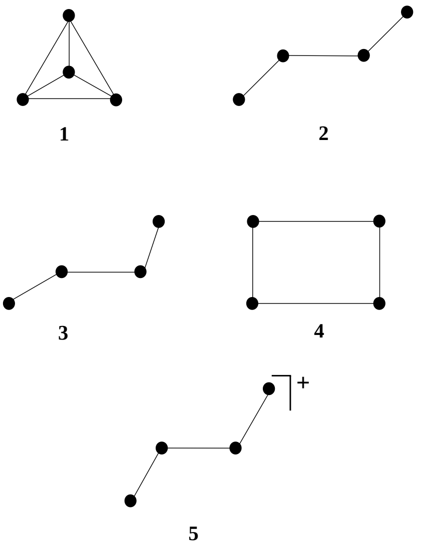

Figure 3. Connectivity of theoretically predicted N_4 molecules and of the N_4^+ cation.

energy surfaces and hints at the possible existence of experimentally detectable species. However, one should be aware that accurate evaluation of the barriers to the exoergic dissociation of the metastable N_4 species into N_2, the height of which is the crucial factor that determines their experimental detectability, remains a difficult task, even when utilizing state-of-the-art theoretical approaches.

In striking contrast to the wealth of theoretical results, experimental information on chemically bound tetranitrogen is almost inexistent. The only well-known and thoroughly characterized N_4 species is the $(N_2)_2$ gaseous cluster, in which the constituent molecules are held together by weak intermolecular forces, and hence it is regarded as a mere van der Waals complex, consistent with its dissociation energy, which is as low as 1 kJ mol^{-1}.[20] As to chemically bound species, none of the suggested routes to N_4, including the combination of N and N_3 radicals, the addition of an activated N_2* molecule to N_2, nor the "extrusion" from (still unknown) larger N_n molecules,[21] proved viable. The only small piece of evidence for N_4 is a weak IR transition observed in a solid matrix obtained from the deposition of microwave-irradiated N_2 gas on a cold (6.2 to 35 K) spectroscopic window.[21] The wavelength of the transition is close to one of those computed by an ab initio study[15] of tetraazatetrahedrane **1**, one of the theoretically predicted N_4 isomers. However, the evidence is weakened by the failure to detect other theoretically predicted transitions and especially by the discrepancy between the experimentally measured isotopic shift of the transition and the theoretically computed value.

The successful preparation, positive detection, and characterization of N_4 by NRMS stemmed from the availability of a suitable precursor, the N_4^+ cation, long known and well characterized as a result of mass-spectrometric,[22, 23] matrix-isolation,[24, 25] spectroscopic,[26, 27] and theoretical studies.[24, 28–33] Its use was motivated by the cation's role in N_2 plasmas and in stratospheric chemistry. Ground-state and excited N_4^+ ions are conveniently obtained by electron impact ionization of N_2 in a low-pressure CI source. Their connectivity has been probed by CAD mass spectrometry, and the assignment of the polyatomic fragments confirmed by examining their further dissociation according to the technique known as tandem mass spectrometry (MS/MS).[2] The CAD spectrum of ${}^{14}N_4^+$ (Figure 4) displays the ${}^{14}N^+$, ${}^{14}N_2^+$, and ${}^{14}N_3^+$ fragments, and that of ${}^{15}N_4^+$, the ${}^{15}N^+$, ${}^{15}N_2^+$, and ${}^{15}N_3^+$ fragments. The CAD spectrum of ${}^{14}N_2{}^{15}N_2^+$ displays ${}^{14}N^+$ and ${}^{15}N^+$, ${}^{14}N_2^+$ and ${}^{15}N_2^+$, and ${}^{14}N_2{}^{15}N^+$ and ${}^{14}N^{15}N_2^+$ fragments. The nature and relative abundances of the fragments are consistent with the connectivity assigned to N_4^+ in its ${}^2\Sigma_u^+$ ground state by experimental and theoretical studies,[22–33] the results of which characterize the cation as the acyclic species **5** with two closely bound N_2 units joined by a longer, weaker bond (Figure 3). Based on the observed formation of the N_3^+ ion in the CI source, and as a fragment in the CAD spectra of N_4^+, it cannot be excluded that excited species, in particular N_4^+ in the first-quartet state (${}^4A'$), are present in the N_4^+ population. However, this complication has little bearing on the present discussion, because recent theoretical calculations show that N_4^+ (${}^4A'$) has the same connectivity as ground-state N_4^+, which is also characterized by two closely bound N_2 units joined by a longer, weaker bond.[34] The N_4^+ ions, generated as described above and mass selected, were accelerated to kinetic energies from 6 to 8 kV and neutralized according to [Eq. (1)]; this process utilized several target gases, for example, Xe and CH_4. In all experiments, the reionization

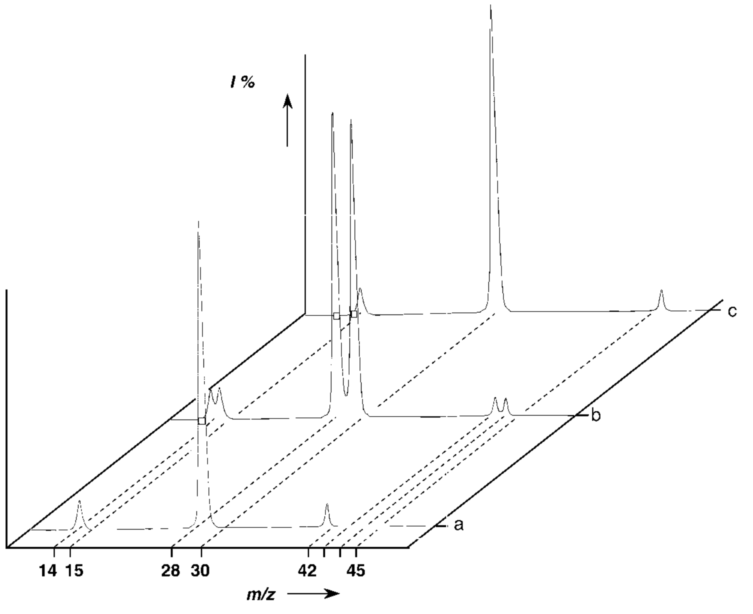

Figure 4. CAD spectra of N_4^+ isotopomers: a) ${}^{14}N_4^+$; b) ${}^{14}N_2{}^{15}N_2^+$; c) ${}^{15}N_4^+$ (reprinted by permission of *Science*).

process was performed utilizing O_2 as the stationary target. The results were rewarding, in that a significant "recovery" peak was displayed by the NR spectra, irrespective of the gas utilized in the neutralization process, although CH_4 was the most efficient target (Figure 5). In order to prove beyond doubt that the species detected was indeed N_4, it is necessary to rule out the conceivable, if highly unlikely, interference from isobaric adventitious contaminants. To this end, $^{14}N_2$ was replaced in the ion source by a $^{14}N_2/^{15}N_2$ mixture, and the $^{14}N_4^+$, $^{14}N_2{}^{15}N_2^+$, and $^{15}N_4^+$ isotopomers of *m/z* 56, 58, and 60, respectively, were obtained, the individual NR spectra of which were recorded. As apparent from Figure 5, the "recovery" peaks are characterized in all the spectra by a *m/z* ratio corresponding to that of the specific N_4^+ isotopomer utilized as the precursor, which positively identifies the neutral species detected as N_4.

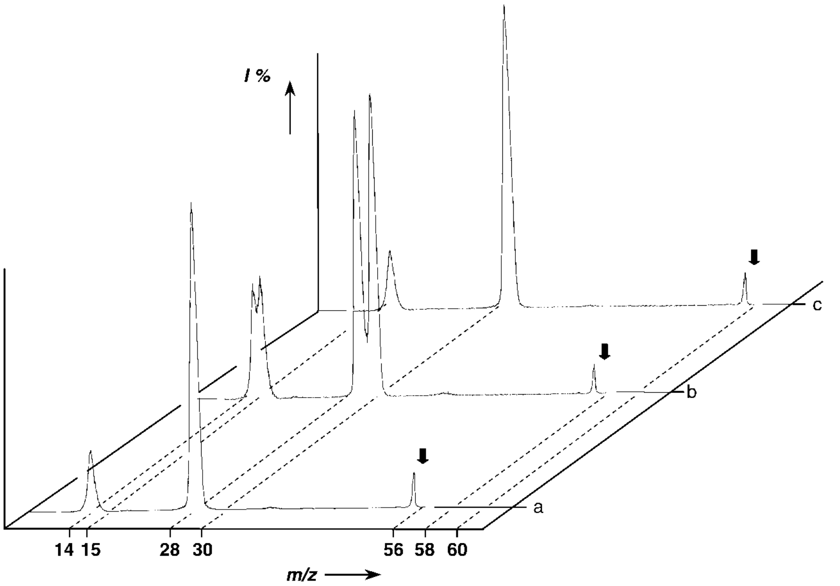

Figure 5. $^+NR^+$ spectra of N_4^+ isotopomers: a) $^{14}N_4^+$; b) $^{14}N_2{}^{15}N_2^+$; c) $^{15}N_4^+$ (reprinted by permission of *Science*).

In conclusion, the NRMS experiments demonstrate that tetranitrogen does exist in the gas phase as an isolated molecule, the lifetime of which exceeds 1 μs at 298 K. This may appear to be a rather short time, however, it should be noted that 1 μs is only the *lower limit* of the N_4 life span, which is likely to be much longer in the dilute gas state at, or below, 298 K. Even more important, as aptly noted by Schröder, a lifetime of 1 μs is very long, almost an eternity on the molecular timescale, since the entire rovibrational manifold of a small molecule like N_4 can exhaustively be explored in that period.[35]

The general criteria outlined in the previous paragraph provide useful guidelines for examining the nature and the structure of the N_4 molecule detected. It can be excluded that it is a $(N_2)_2$ van der Waals cluster, the dissociation energy of which, as mentioned above, is far too low to allow survival following the neutralization event. It follows that N_4 must be a chemically bound species, the structure of which, or more correctly, connectivity,[36] can be derived from that of the charged precursor, and this also takes into account the results of the isotopic labeling experiments.

The theoretically computed geometry of N_4^+, both in the $^2\Sigma_u^+$ ground state and in the excited $^4A'$ state, which is fully consistent with the mass-spectrometric evidence from this study, rules out the possibility that the N_4 molecule detected is tetraazatetrahedrane **1**, the connectivity of which is entirely different from that of the precursor, and the N atoms of which are all indistinguishable. The latter feature of **1** requires that its $^{14}N_2{}^{15}N_2$ isotopomer must give an abundant $^{14}N^{15}N^+$ fragment in the reionization-induced dissociation, whereas only $^{14}N_2^+$ and $^{15}N_2^+$ fragments are experimentally detected (Figure 5). The rectangular D_{2h} singlet **4**, that contains two distinct N_2 units, has a connectivity compatible with the fragmentation pattern of the $^{14}N_2{}^{15}N_2$ isotopomer. However, the geometry of **4** would be considerably different from that of the N_4^+ precursor, the vertical neutralization of which to **4** is characterized by a highly unfavorable Franck–Condon factor. The acyclic triplets **2** and **3** appear to be the best candidates among the theoretically characterized N_4 isomers, in particular the C_s triplet **3** has been predicted to be experimentally detectable.[13] This conclusion does not exclude the existence, nor the possible experimental detectability, of other N_4 isomers, for example, tetraazatetrahedrane **1**, which, however, is not the species detected by NRMS. Further theoretical work is clearly required for a full, accurate description of the deceptively simple N_4 system, and it is hoped that the experimental discovery of a metastable N_4 molecule will encourage a computational effort in this direction.

Even more importantly, the discovery of long-sought N_4, predicted on theoretical grounds, will hopefully encourage experimental studies aimed at the preparation, detection, and characterization of larger homoatomic polynitrogen molecules, and interest in these as HEDM has stimulated, in the past two years, an impressive theoretical effort, focused on N_5,[37] N_6,[37–40] N_8,[41] N_9,[42] N_{10},[43, 44] and N_{11}.[45]

Should the experimental preparation of one such species prove feasible, it could provide an alternative route to N_4, based on its "extrusion" from a larger N_n molecule.

The Discovery of O_4

The search for a covalent O_4 molecule that dates back to a seminal study by Lewis in 1924[46] has undergone a brisk acceleration in the last decade. The motivations are manifold, including the relevance of polyoxygen species to fundamental inorganic chemistry,[47] their potential utilization as HEDM,[48, 49] their suggested role in the operation of O_2–halogen lasers,[50] the evidence for O_4 units in metallic ("red") oxygen under very high pressures,[51] and especially the current upsurge of interest in excited states of O_2 and related metastable molecules relevant to atmospheric chemistry and to the terrestrial and Venusian nightglow.[52]

The interest in O_4 has stimulated numerous computational studies performed at various levels of theory, the rather scattered results of which reflect the unusual difficulties encountered even by the most robust theoretical methods. The troublesome features peculiar to the O_4 system are the multireference character of the wavefunction, the critical impact of electron correlation, and the vexing symmetry breaking problem. Furthermore, realistic evaluation of the kinetic barrier to dissociation into O_2, necessary to assess the experimental detectability of the intrinsically metastable O_4 molecule, requires inclusion of spin-orbit coupling effects.

Subject to the above limitations, the theoretical studies have predicted the existence of **6**, a covalent species with a quasisquare D_{2d} geometry,[53–57] or of **7**, with a "pinwheel" D_{3h} geometry,[58, 59] as illustrated in Figure 6. A third metastable species has been predicted, that is, a relatively stable and long-lived $[O_2{*}O_2]$ complex formed by an excited $O_2{*}$ molecule associated with a ground-state one.[60, 61]

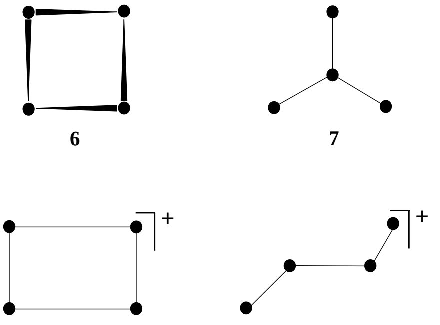

Figure 6. Connectivity of theoretically predicted O_4 molecules and of the O_4^+ charged precursors.

From an experimental standpoint, only the $(O_2)_2$ cluster, formed by the association of monomers by weak intermolecular forces, is long known and well characterized.[62] Consistent with the large separation of the constituent O_2 molecules and their low binding energy (below 5 kJ mol^{-1}), the dimer is regarded as a mere van der Waals complex.

Two different techniques have been utilized in the search for chemically bound, gaseous O_4 molecules. An interesting experiment, reported in 1993, involved the neutralization of the O_4^+ cation from the low-pressure CI of oxygen by electron transfer from O_2, NO, or better Cs atoms in a gas collision cell. The molecular beam emerging from the cell was analyzed by coincident measurement of the translational energies of the pairs of O_2 fragments from the same neutralization-induced, dissociation event.[60] Whereas the experiment could not allow detection of *intact* O_4, the kinetic energy spectrum of the O_2 fragments displayed features that provided indirect evidence for the existence of a metastable tetraoxygen molecule, the lifetime of which was estimated to range from 10^{-13} s to a few tenths of a µs.[60]

The results obtained by Suits and co-workers utilizing a different experimental technique represent a significant stride towards the positive identification of tetraoxygen in the gas phase. The experiment consisted of passing an O_2 molecular beam though a 3–5 kV dc discharge and recording its photoionization and photoelectron spectra in a chamber, in which the beam was crossed by photons of a wavelength tunable around 300 nm from a Nd-YAG pumped dye laser. The charged species from the photoionization chamber were analyzed by a time of flight mass spectrometer.[61, 63] The only significant ion detected was O_4^+, m/z 64, which provides strong evidence for the presence of a metastable O_4 species in the beam excited by the dc discharge. Furthermore, photoionization had a threshold of about 8 eV, considerably lower than the ionization potential of a complex formed by two ground-state O_2 molecules and of those computed for **6** and **7**, the two covalent molecules predicted by theory. This has led Suits and co-workers to identify the metastable O_4 species detected in their experiment, and in that of Helm and Walter,[60] as a complex between a ground-state O_2 molecule and one in the $c^1\Sigma_u^-$ electronically excited state.

Albeit higher in energy than the $(O_2)_2$ dimer formed by ground-state molecules, the $[O_2(c^1\Sigma_u^-)O_2(X^3\Sigma_g^-)]$ metastable complex is characterized by a larger binding energy of the monomers, consistent with the enhanced clustering ability of electronically excited O_2 molecules with respect to ground-state ones noted in earlier studies.[64] Whereas the above results provide strong evidence for the existence of O_4, in order to make the assignment airtight one must exclude the conceivable, if unlikely, possibility that the observed O_4^+ arises, rather than from O_4, from the dissociative photoionization of some higher oxygen polymers present in the mass-unresolved molecular beam.[63]

Once again, conclusive proof was obtained by NRMS[3] by utilizing as the precursor O_4^+, produced by CI of oxygen. The primary O_2^+ ions, formed in the ground-state and in long-lived electronically excited states,[64, 65] are known to associate with O_2 to yield ground-state and excited O_4^+ ions, in relative amounts depending on the source pressure.[66] The structure of O_4^+ in cryogenic Ne matrices has been probed by photoionization and Penning ionization spectroscopy,[67] ESR,[68] IR, and photoelectron spectroscopy.[69, 70] The O_4^+ has been characterized as having an acyclic, *trans*-planar geometry, although an isomer of rectangular geometry could also be present.

The theoretical studies, which suffer from the same problems encountered in the description of O_4,[71] have identified the rectangular D_{2h} species **8** and the *trans*-planar C_{2h} species **9** (illustrated in Figure 6), located 46 and 48 kJ mol^{-1}, respectively, below separated O_2^+ and O_2;[72] these results are in fair agreement with the experimental binding energy.[66]

The CAD spectra of the O_4^+ isotopomers (Figure 7) are structurally informative, in that the $^{16}O_2{}^{18}O_2^+$ ion from a $^{16}O_2$/$^{18}O_2$ mixture displays only $^{16}O_2^+$ and $^{18}O_2^+$ fragments, without isotopically mixed $^{16}O^{18}O^+$, which is suggestive of the presence of two distinct O_2 units in the O_4^+ cation.[3]

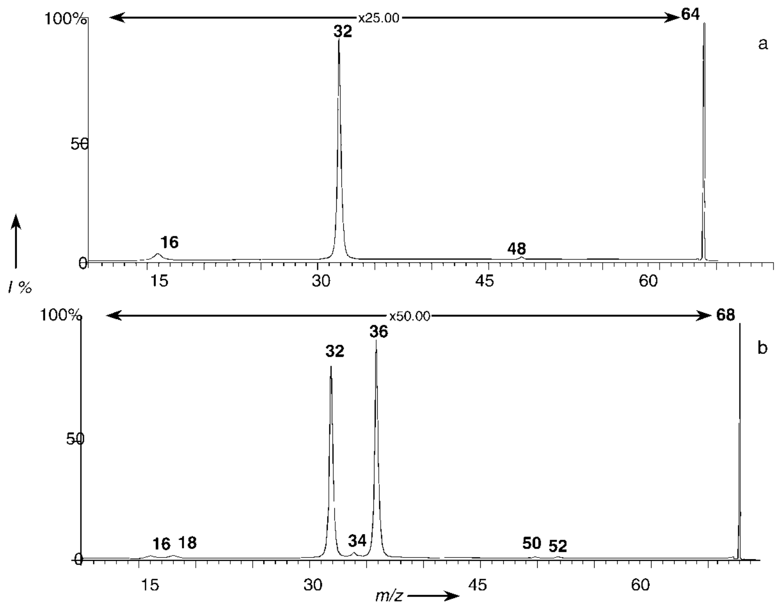

Figure 7. CAD spectra of O_4^+ isotopomers: a) $^{16}O_4^+$; b) $^{16}O_2{}^{18}O_2^+$ (reprinted by permission of *Angew. Chem.*).

The NR spectra display significant "recovery" peaks (Figure 8), which provide the long-sought, conclusive proof that neutral tetraoxygen does exist as an isolated gaseous species, the lifetime of which has a *lower limit* of 0.95 ± 0.15 μs. Experiments utilizing $^{16}O_2{}^{18}O_2^+$ ions show that neutral O_4, as its charged precursor, contains two distinct O_2 units that do not exchange their constituent atoms when O_4 dissociates.[3] Structural assignment of the experimentally observed species on theoretical grounds is clearly difficult in view of the above-mentioned problems that plague the computational study of both O_4^+ and O_4. It appears that neither **6** nor **7** have a geometry sufficiently close to that of the **8** and **9** precursors to account for their detection by NRMS, in view of the unfavorable Frank–Condon factors that would characterize vertical neutralization. Furthermore, the fragmentation pattern displayed by the NR spectra of $^{16}O_2{}^{18}O_2^+$ is hardly consistent with those expected for either of the covalent **6** and **7** molecules. The quasisquare D_{2h} isomer **6**, containing four indistinguishable atoms, should give, in addition to $^{16}O_2$ and $^{18}O_2$, the isotopically mixed $^{16}O^{18}O$ fragment, not displayed by the spectra. Furthermore, owing to the presence of three equivalent atoms in the hypothetical isomer **7** of D_{3h} geometry, isotopically mixed $^{16}O^{18}O$ should be formed together with $^{16}O_2$ and $^{18}O_2$ fragments from the $^{16}O_2{}^{18}O_2$ isotopomer, and this runs contrary to the experimental results.

In summary, neither of the covalent molecules so far theoretically predicted satisfactorily accounts for the experimental evidence for a structure reminiscent of that of the parent cation **9**, which contains two distinct, strongly bound O_2 units joined by a longer, weaker bond.

As a definitive structural assignment is not possible, awaiting further computational analyses of this theoretically troublesome system, it appears that the most likely candidate is to be tentatively identified at present time as the metastable $[O_2{}^*O_2]$ complex between a O_2 $(X^3\Sigma_g^-)$ ground-state molecule and one in the $c^1\Sigma_u^-$ excited state, predicted by Suits and coworkers.[61]

As in the case of N_4, the discovery of tetraoxygen is expected to provide further impetus to the theoretical and experimental study of new O_n allotropes of oxygen.

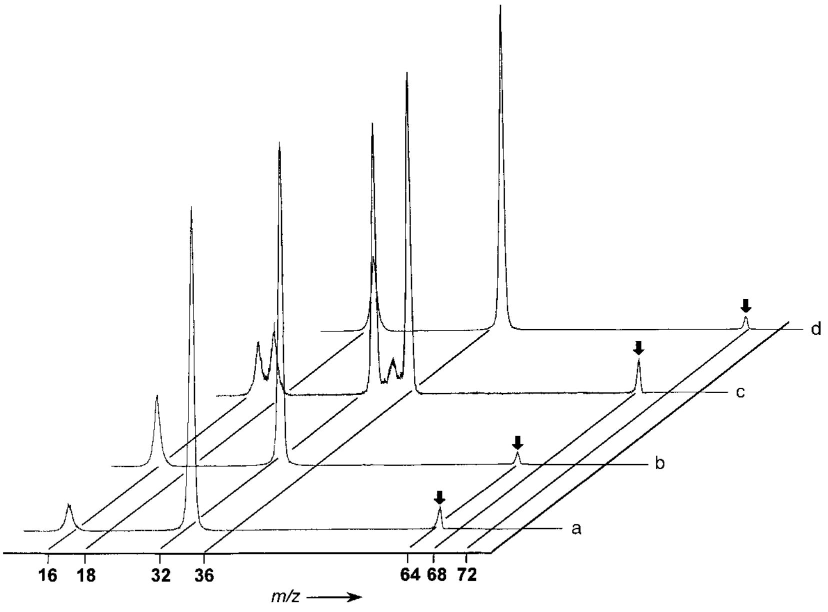

Figure 8. $^+NR^+$ spectra of O_4^+ isotopomers: a) $^{16}O_4^+$; b) $^{18}O_4^+$; c) $^{16}O_2{}^{18}O_2^+$, recorded at a kinetic energy of 6 keV; d) $^{16}O_4^+$, recorded at a kinetic energy of 4 keV. The arrows indicate the "recovery" peaks, which are all of the expected m/z ratios (reprinted by permission of *Angew. Chem.*).

Conclusion and Outlook

The recent discovery of the title molecules, and of other neutral species such as water oxide,[73] hydrogen trioxide,[74] ammonia oxide,[75] gaseous carbonic acid,[76] and so on, which all contain the most abundant atmospheric elements, shows that the research field initiated by the pneumatic chemists of the 18th century is currently very active and fruitful. The combination of theory with powerful spectrometric techniques has allowed the discovery and characterization of new, metastable species relevant to atmospheric chemistry and to the development of HEDM.

Among the available experimental tools, NRMS has demonstrated its pivotal role because, albeit unable to produce the new molecules in bulk amounts, it represents a much needed link between theoretical and preparative chemistry. Indeed, the most exciting development anticipated in the near future is the utilization of the information on new gaseous molecules gathered by the joint application of computational and spectroscopic methods, in particular NRMS, in inorganic preparative chemistry.

Acknowledgments

Financial support from the Rome University “La Sapienza”, the Italian National Research Council (CNR), and the Ministero dell'Istruzione, Università e Ricerca (MIUR) is acknowledged.

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