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Discovery of two high-energy N_2O_2 isomers

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Two N_2O_2 isomers containing N_2/O_2 and NO/NO subunits, respectively, were detected by neutralization-reionization mass spectrometry (NRMS) as metastable species with lifetimes exceeding 1 μs.

Since N_2O_2 was suggested as a possible intermediate in the detonation of nitric oxide,[1] its potential role as a high-energy density material (HEDM) and its relevance to important research areas have stimulated much theoretical and experimental work. First, theoretical studies predicted several high-energy N_2O_2 isomers, that are thermodynamically unstable with respect to the dissociation, and kinetically stable due to the existence of sizable barriers, both to dissociation and to isomerization to more stable isomers.[2] These covalently bound, metastable N_2O_2 isomers release up to 400 kJ mol^{-1} upon dissociation, and are viable candidates for HEDM. Secondly, N_2O_2 bears on the important issue of the missing sources of NO_x in the odd-nitrogen budget of the Earth's lower atmosphere. Laboratory studies revealed indeed an unexpected route to NO_x from the O_2/N_2 photolysis, suggesting N_2O_2 as the key intermediate of excited states reactions.[3] Third, N_2O_2 is relevant to the study of the reverse reaction, the NO reduction to N_2 and O_2, a useful model for the understanding of selective catalytic processes of environmental significance.[4] These seemingly different issues center on the existence and role of high-energy species in the endothermic reaction (1), also characterized by a large reverse activation energy.[5]

$$N_2 + O_2 \rightarrow [N_2, O_2] \rightarrow NO + NO \quad (1)$$

Interesting studies of energy transfer in excited NO molecules[6] and photoelectron spectroscopy of the $N_2O_2^-$ anion[7] suggest that transient energetic N_2O_2 species can be formed in the gas phase. However, whereas the above theoretical and experimental results unravel a rich high-energy chemistry of N_2O_2, thus far no direct evidence has been reported for the existence of metastable species sufficiently long-lived to be detected.

We now report the proof of existence of two N_2O_2 isomers, namely their positive detection as gaseous species obtained from $N_2O_2^+$ ions by NRMS.[8] The $N_2O_2^+$ precursor ions were generated in the chemical ionization (CI) source of a ZABSpec-oa TOF mass spectrometer, utilizing two preparation routes, namely the CI of N_2/O_2 and of NO/Ar mixtures.

$$O_2{}^{(+/0)} + N_2{}^{(0/+)} \rightarrow N_2O_2^+ \quad (2)$$

$$NO^+ + NO \rightarrow (NO)_2^+ \quad (3)$$

The O_2^+, N_2^+ and NO^+ primary ions are known to be formed both in the ground and in excited states upon 50–70 eV electron impact on the reactant gases.[9] Accordingly, in addition to the weakly bound $N_2O_2^+$ (ref. 10) and $(NO)_2^+$ complexes,[11] formed from ground-state reactants, different products were likely formed from excited-state reactants, through reaction pathways inaccessible to ground-state reagents. The ions were thus structurally analyzed by collisionally activated dissociation (CAD) mass spectrometry. The CAD spectrum of the ions from reaction (2) displays exclusively the O_2^+ and N_2^+ fragments, and that of the ions from reaction (3) shows the NO^+ fragment, which points to distinct species containing the N_2/O_2 and the NO/NO subunits, respectively. Experiments performed with isotopically labelled ions, from $^{15}N_2/O_2$, $N_2/^{18}O_2$, $^{15}N_2/^{18}O_2$, and $^{15}N^{18}O$/Ar mixtures, confirmed the assignments.

The isomeric precursor ions, henceforth denoted $N_2O_2^+$ and $(NO)_2^+$, accelerated to 6–8 kV and mass selected, underwent neutralization by collision with a target gas in a first cell located along the beam path. After deflection of any surviving ions by a high-voltage electrode, a beam consisting only of fast neutrals was re-ionized in a second cell by collision with O_2, giving again cations (NR$^+$). The detected NR$^+$ spectra of $N_2O_2^+$, $^{15}N_2O_2^+$, $^{15}N_2{}^{18}O_2^+$, (Fig. 1), and of $(NO)_2^+$ and $(^{15}N^{18}O)_2^+$ (Fig. 2) show intense "recovery" peaks, namely peaks at the same *m*/*z* ratio as the precursor ions, proving that a neutral species is formed and has survived at least the flight from the first to the second cell, *ca*. 1 μs.

No weakly bound species, *e.g.* van der Waals complexes, survive neutralization, and only covalently bound species, characterized by a barrier to their dissociation of at least 40 kJ mol^{-1}, can be detected.[8] Moreover, given the vertical character of the NR

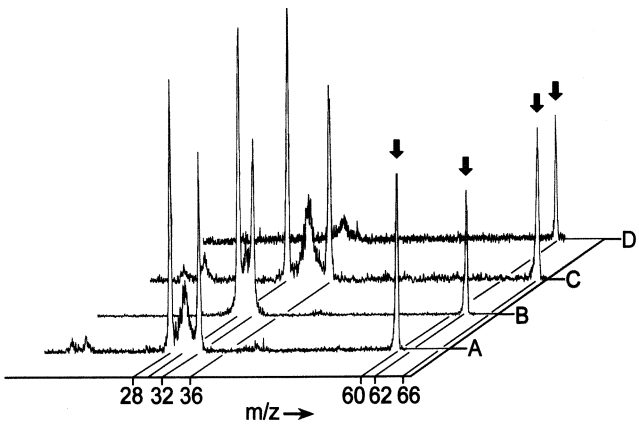

Fig. 1 NR$^+$ spectra of $^{14}N_2{}^{16}O_2^+$, *m*/*z* 60 (**A**), $^{15}N_2{}^{16}O_2^+$, *m*/*z* 62 (**B**) and $^{15}N_2{}^{18}O_2^+$, *m*/*z* 66 (**C**) ions, and NR$^-$ spectrum of $^{14}N_2{}^{16}O_2^+$, *m*/*z* 60 (**D**) ion. Neutralizing and re-ionizing gases were CH_4/O_2 (NR$^+$) and O_2/O_2 (NR$^-$). The recovery peaks are indicated by arrows. Doubly charged ions are found at *m*/*z* 30 (**A**), 31 (**B**) and 33 (**C**).

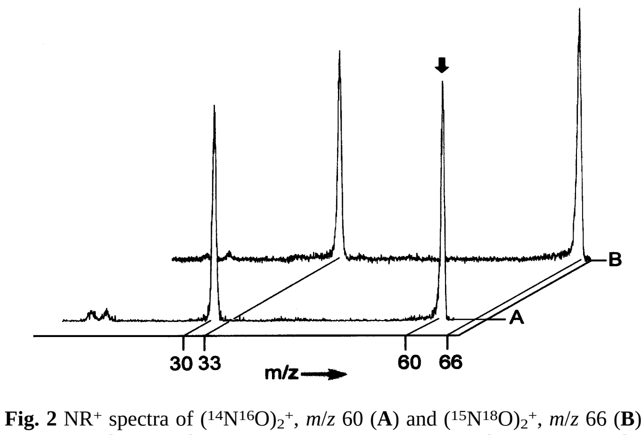

Fig. 2 NR$^+$ spectra of $(^{14}N^{16}O)_2^+$, *m*/*z* 60 (**A**) and $(^{15}N^{18}O)_2^+$, *m*/*z* 66 (**B**) ions. Neutralizing and re-ionizing gases were CH_4/O_2. The recovery peaks are indicated by arrows.

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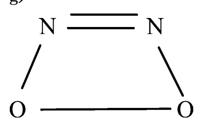
processes, governed by Franck–Condon factors, only neutrals having a geometry similar to that of the precursor ions can be formed. Thus based on the different connectivity of the precursor ions utilized, the NR experiments demonstrate that N_2O_2 and $(NO)_2$ do exist in the gas phase as distinct species. The actual detection of *two* isomers is conclusively proved by NR^- experiments, where the re-ionization process yields anions by electron attachment to the neutral. Such a process requires in addition adequate Franck–Condon overlap in the transition from the neutral to the anion. The result is particularly telling, as the NR^- spectrum of $N_2O_2^+$ displays an intense "recovery" peak at *m*/*z* 60 (Fig. 1D), whereas no recovery signal is detected from $(NO)_2^+$.[12]

As to the structures of the neutral species detected, and their identification with the theoretically predicted [N_2, O_2] high-energy species,[2] useful criteria are provided by the above mentioned constraints imposed by NRMS, namely the existence of sizable barriers to dissociation of the neutral, and its close structural similarity to the precursor ion. Having excluded weakly bound N_2O_2 dimers and high-energy species predicted experimentally undetectable or characterized by very low barriers to their dissociation, we suggest that the best candidate for N_2O_2 is 1,2-diaza-3,4-dioxacyclobut-1-ene,[2] a four-membered trapezoid ring, the nitrogen-oxygen analogue of cyclobutene, whose dissociation into N_2 and $O_2(^1\Delta_g)$ would release about 400 kJ mol^{-1}.



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Theory predicts that **1** is separated from its dissociation products and from its lower energy isomers by significant barriers, ranging from 80 to 190 kJ mol^{-1}, and that the lowest triplet state lies higher in energy along all the singlet dissociation path, which prevents singlet–triplet crossing. Most important, bound states of the *cis*-$ONNO^-$ anion were identified, whose geometrical parameters are sufficiently close to those of **1**.[13] Finally, a precursor ion having the structure of **1** can be conceivably formed from reaction (2) involving excited-state reactants, considering that molecules often have binding energies to excited ions that are higher than to ground-state ions. Reactions traceable to $O_2^+(a^4\Pi_u)$ were already described under our experimental conditions,[14] and the O–O length in O_2^+ $(a^4\Pi_u)$ fairly compares to the computed O–O length of **1** (1.47 Å). Unfortunately we don't find a suitable candidate for $(NO)_2$ among the theoretically predicted isomers, and further theoretical work along this line is currently under way in our group. Moreover the present result encourages theoretical analysis that would benefit from the clear-cut constraints provided by this work. As an example, experiments performed using $NO/^{15}N^{18}O/Ar$ mixtures show exclusively the NO^+ and $^{15}N^{18}O^+$ fragments in the CAD and NR spectra of the ions obtained, ruling out a symmetric cyclic structure, and suggesting an asymmetric cyclic or acyclic structure for $(NO)_2$.

In conclusion the proof of the existence of two distinct, long-lived N_2O_2 and $(NO)_2$ species, whose lifetime exceeds 1 μs at 298 K, is, *per se*, most relevant from a fundamental standpoint, and answers the point at issue. First, N_2O_2 and $(NO)_2$, taken as the species viable to decompose either into N_2 and O_2 or into NO, respectively, can be reasonably considered the high-energy intermediates of the reaction (1). In our experiments the energy content of the neutrals, formed by a vertical process, is well below the barrier to the isomerization, which allows their detection as distinct species.[12] By contrast, in atmospheric environments, long-lived excited states of N_2 $(A^3\Sigma_u^+)$ and O_2 $(c^1\Sigma_u^-, B^3\Sigma_u^-)$, formed by photochemical processes, can produce N_2O_2 molecules with sufficient vibrational energy excess to overcome the barriers existing between the N_2O_2 and $(NO)_2$ systems.[3] In this connection, species **1** is particularly suitable for the role of intermediate of the four-center reaction (1). From a different standpoint, the N_2O_2 molecules detected are good candidates for HEDM, being both high-energy species, whose dissociation is expected to release large amounts of energy, as specifically **1**, which is predicted to release as much as 400 kJ mol^{-1} upon dissociation into the environmentally benign molecules N_2 and O_2. Whereas the very tiny amount obtained from NR prevents of course their direct utilization, the finding that they survive in the isolated state for a sufficiently long lifetime to allow detection gives the preparative inorganic chemists an attainable target.

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