Metastable Molecules

Experimental Detection of Theoretically Predicted N_2CO**

Giulia de Petris,* Fulvio Cacace, Romano Cipollini, Antonella Cartoni, Marzio Rosi, and Anna Troiani

In memory of Fulvio Cacace

"Metastability" has drawn special attention as a means of energy storage, and much theoretical and experimental effort has been devoted to the study of the isoelectronic N_4, N_2CO, and C_2O_2 molecules.[1–3] The largest amounts of energy released per mass unit by dissociation of tetraazatetrahedrane N_4 (T_d; 200 kcal mol^{-1}), diazirinone N_2CO (100 kcal mol^{-1}), ethylenedione C_2O_2 (70 kcal mol^{-1}), and other theoretically predicted isomers prompted intense scrutiny of these 28-electron molecules as leading candidates for high-energy-density materials (HEDM). A renewed upsurge in interest springs from current missions to planetary atmospheres, where detection of reactive, even minor, species is one of the most attractive targets. After the recent experimental discovery of the open-chain N_4 molecule[4] and the ultimate answer to the long-standing challenge of synthesizing C_2O_2,[5] the question remains whether bound, high-energy N_2CO species can be experimentally observed.[6] Ab initio calculations at different levels of theory predict that three N_2CO species are potentially observable: the singlet C_{2v} diazirinone, which is the most stable N_2CO isomer, the triplet open-chain NNCO, and a strained tetrahedrane-like structure, whose "accumulated" energy (about 220 kcal mol^{-1}) would be higher than that of N_4 (T_d).[2] Despite the promising predictions, N_2CO has so far eluded experimental detection and defied all attempts at its characterization as a bound species.

Herein we report the preparation, positive detection, and characterization of N_2CO by the one-electron reduction of the N_2CO^+ cation, a result achieved by neutralization–reionization mass spectrometry (NRMS).[7] We have already utilized this approach for the detection of other metastable, elusive molecules[8] and for the detection of the related 28-electron molecule N_4,[4] which was recently extensively studied by the same technique with various pressure regimes and neutralizing target gases.[9]

The N_2CO^+ ion was formed by chemical ionization (CI) of a CO/N_2 mixture according to Equation (1).

$$CO^{(+/0)} + N_2^{(0/+)} \rightarrow N_2CO^+ \qquad (1)$$

The interfering isobaric N_4^+ and $C_2O_2^+$ ions were separated by using ^{15}N-, ^{13}C-, and ^{18}O-labeled reagents. The remarkably high binding energy of the $(CO)_2^+$ ion[3c,10] required that CO and N_2 were introduced at a 1:20 pressure ratio, which typically ensures the $N_4^+/N_2CO^+/C_2O_2^+$ ratio displayed in the CI spectrum reported in Figure 1. Under such conditions the abundance of the N_2CO^+ species was appreciable, yet the intensity of the N_4^+ ion was far larger. To prevent any possible contamination from N_4^+ isotopomers, which are liable to neutralization, mixtures containing the following combinations of labeled reagents were examined: $N_2/C^{18}O$, $N_2/^{13}C^{18}O$, $^{15}N_2/CO$, $^{15}N_2/^{13}CO$, and $^{15}N_2/^{13}C^{18}O$.

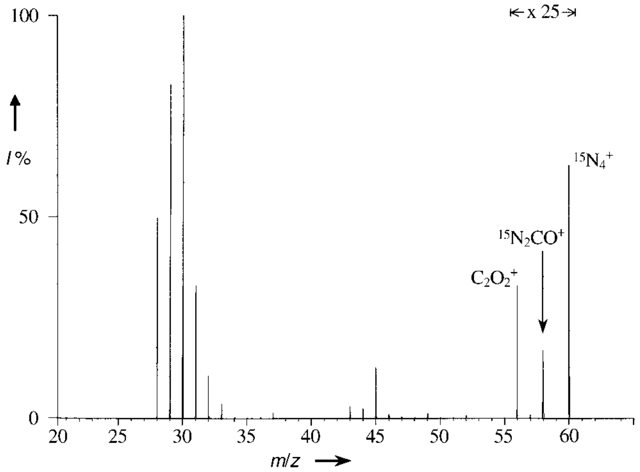

Figure 1. CI mass spectrum of the $^{15}N_2/CO$ mixture showing, in addition to the indicated adducts, peaks at m/z 28 = CO, m/z 29 = COH^+, m/z 30 = $^{15}N_2^+$, m/z 31 = $^{15}N_2H^+$, m/z 32 = O_2^+, m/z 43 = $^{15}NCO^+$, m/z 44 = CO_2^+, and m/z 45 = $^{15}N_3^+$.

The neutralization of the N_2CO^+ ions was accomplished by a one-electron redox sequence utilizing CH_4 (or Xe) and O_2 as neutralizing and reionizing gases, respectively [Eq. (2)].

$$N_2CO^+ \xrightarrow[CH_4,\ \text{1st cell}]{+e} N_2CO \xrightarrow[O_2,\ \text{2nd cell}]{-e} N_2CO^+ \qquad (2)$$

The NR mass spectra of all the examined N_2CO^+ ions display significant recovery peaks at the same m/z value as that of the precursor ion (Figure 2). This result positively proves the existence of a neutral N_2CO species, which has survived at least for the time necessary to travel from the first cell, where it is generated, to the second cell, where it is reionized and detected. This time, which corresponds to the maximum "observation" time window available to the experi-

---

[*] Prof. Dr. G. de Petris, Prof. Dr. F. Cacace, Prof. Dr. R. Cipollini, Dr. A. Cartoni, Dr. A. Troiani
Dipartimento di Studi di Chimica e Tecnologia
delle Sostanze Biologicamente Attive
Università "La Sapienza"
P.le Aldo Moro 5, 00185 Roma (Italy)
Fax: (+39) 06-4991-3602
E-mail: giulia.depetris@uniroma1.it
Prof. Dr. M. Rosi
Dipartimento di Ingegneria Civile ed Ambientale
Sezione Tecnologie Chimiche e Materiali per l'Ingegneria
Università di Perugia
Via Duranti, 06131 Perugia (Italy)

[**] Financial support from the Italian Government (COFIN 2003), Rome University "La Sapienza", and the CNR-MIUR (Legge 16-10-2000 Fondo FISR) is gratefully acknowledged. This work was completed after Prof. Fulvio Cacace's death (deceased December 1, 2003).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460310

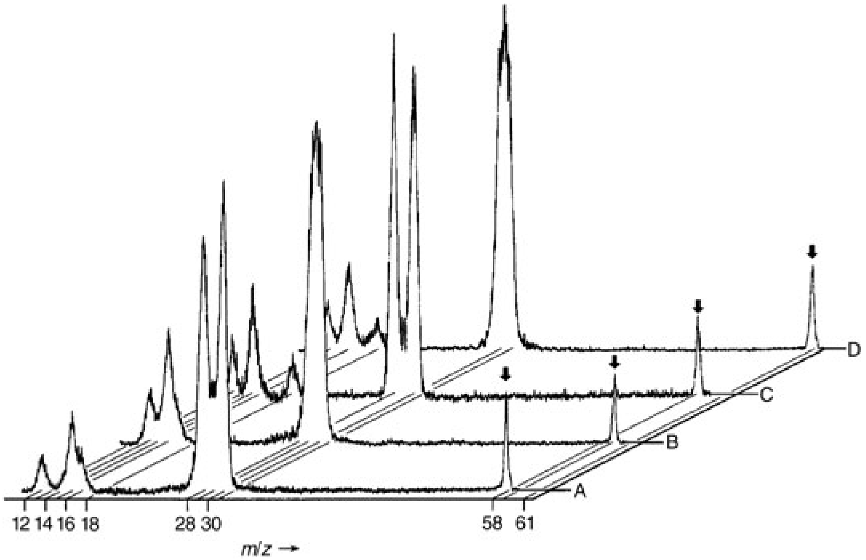

Figure 2. NR mass spectrum of N_2CO^+ ions from different mixtures: A) $^{15}N_2CO^+$ ions (*m/z* 58) from $^{15}N_2/CO$; B) $^{15}N_2{}^{13}CO^+$ ions (*m/z* 59) from $^{15}N_2/^{13}CO$; C) $N_2C^{18}O^+$ ions (*m/z* 58) from $N_2/C^{18}O$; and D) $^{15}N_2{}^{13}C^{18}O^+$ ions (*m/z* 61) from $^{15}N_2/^{13}C^{18}O$. Peaks at *m/z* 30 and 29 (trace B) and *m/z* 30 and 31 (trace D) are not resolved. The recovery peaks are indicated by arrows.

ment, marks the lower limit of the lifetime of the neutral species. The lifetime of N_2CO molecules having masses ranging from 56 to 61 Da and traveling with a kinetic energy of 4–6 keV is $\geq 0.8\,\mu s$. The successful detection of the neutral molecule hinges on the vertical character of the process, that is, the neutral species survives only if its geometry is not significantly different from that of the charged precursor. Such a constraint demands an accurate structural analysis of the parent ion.

The N_2CO^+ ions are seemingly formed by Equation (1) from both the CO^+ and N_2^+ reactant ions. In fact, as with many exothermic charge-transfer processes, the N_2^+/CO charge exchange is not very efficient ($k = 7.3 \times 10^{-11}\,cm^3\,s^{-1}$),[11] and the primary N_2^+ ions, largely supplied by the high N_2 pressure, are not totally depleted. Additional routes to N_2CO^+ ions can be envisaged from long-lived excited state reactants, such as N_2^+ ($A^2\Pi_u$) and N_2^+ ($a^4\Sigma_u^+$), acknowledged to be responsible for the formation of N_3^+,[12] which is indeed appreciably abundant under our experimental conditions. The population of the ionic N_2CO^+ species was probed by collisionally activated dissociation (CAD) and multistage mass spectrometry (MS^3) techniques. The CAD spectra (Figure 3) show CO^+ and N_2^+ as the major fragments, and minor peaks corresponding to the NCO^+ and CNN^+ fragments. The MS^3 spectra of all the daughter ions confirmed the isotopic assignments and the absence of any isobaric contamination.[13]

The fragmentation pattern clearly denotes an N–N–C–O connectivity and, on the basis of the absence of the N_2O^+ fragment among the dissociation products, one can exclude the tetrahedrane-like structure as a candidate for the detected neutral N_2CO species. Therefore, one is left with the singlet C_{2v} diazirinone and the triplet open-chain N_2CO, which both display the N–N–C–O connectivity. Previous experimental and theoretical studies identified only one N_2CO^+ stable ion, the open-chain transplanar N_2CO^+ ion ($X^2\Sigma_u^+$).[14] This would suggest the triplet open-chain N_2CO; however, its formation ($R_{N-C} = 1.234$ Å)[2] from N_2CO^+ ($R_{N-C} = 1.914$ Å)[14c] could be arguable because of an unfavorable Franck–Condon overlap.[15] The N_2CO^+ ($X^2\Sigma_u^+$) cluster ion is likely to prevail within the ionic N_2CO^+ population, yet formation of different ionic species cannot be excluded, especially from diatomic ions in long-lived electronically excited states, which are often conducive to formation of molecule-like ions rather than cluster ions. Although an extensive theoretical analysis was beyond the scope of this work, the results pictured by our NRMS experiments prompted us to make a theoretical study of the N_2CO^+ ion, with the study restricted to the open-chain and T-shaped geometries of the theoretically predicted N_2CO species.

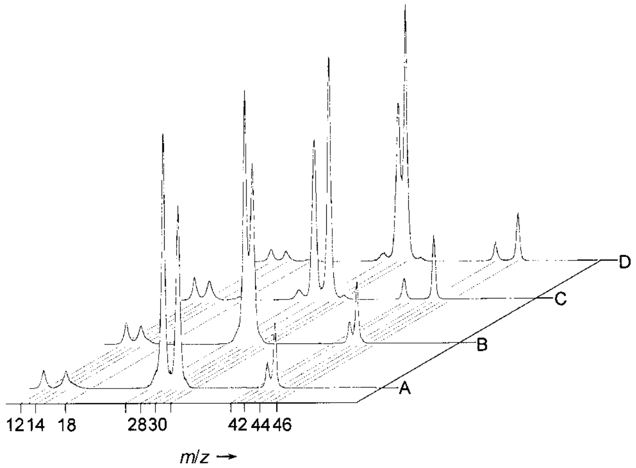

Figure 3. CAD spectra of N_2CO^+ ions from different mixtures: A) $^{15}N_2CO^+$ ions (*m/z* 58) from $^{15}N_2/CO$; B) $^{15}N_2{}^{13}CO^+$ ions (*m/z* 59) from $^{15}N_2/^{13}CO$; C) $N_2C^{18}O^+$ ions (*m/z* 58) from $N_2/C^{18}O$; D) $^{15}N_2{}^{13}C^{18}O^+$ ions (*m/z* 61) from $^{15}N_2/^{13}C^{18}O$.

Figure 4 illustrates the geometries and energies of the N_2CO^+ and N_2CO species identified. According to previous results, the only minimum found on the doublet surface of N_2CO^+ ions was the transplanar ion **1**. We were unable to find any stable T-shaped minimum on the doublet and quartet surfaces, since the doublet ion **2** is unstable toward dissociation once the zero-point energy correction is included. On the quartet surface we found the ions **3** and **4** of C_s symmetry, where the two diatoms are joined at a short distance. They are higher in energy than ion **1** by 97.3 and 106.8 kcal mol^{-1}, respectively, at the CCSD(T) level of theory. The known dissociation energy of the most stable N_2CO^+ ion (0.97 eV,[14b] 1.0 eV,[14c] 0.7 eV,[16]), and the difference between the ground state (CO^+ ($^2\Sigma^+$) and N_2 ($^1\Sigma_g^+$)) and the lowest spin-allowed

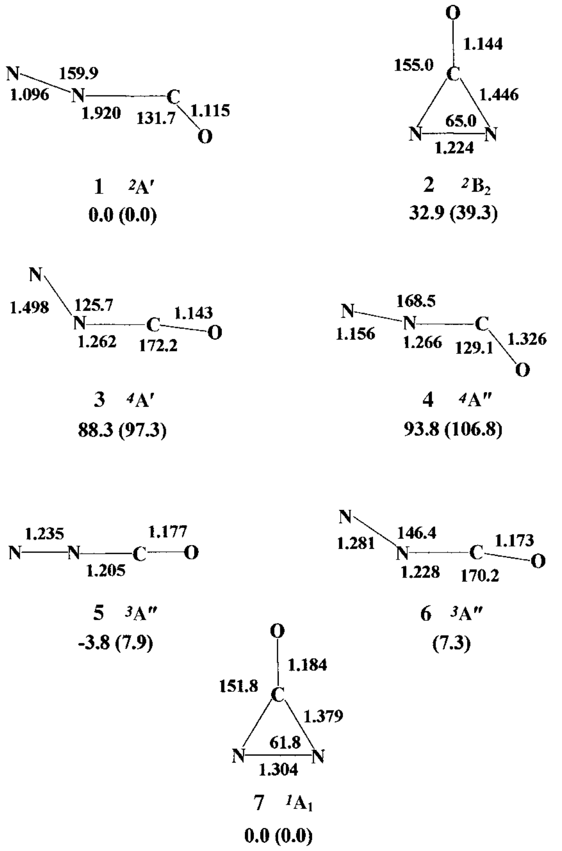

Figure 4. Optimized geometries of the stationary points localized on the potential energy surface of N_2CO^+ ions and N_2CO, at the B3LYP (**1**–**5**, **7**) and CCSD(T) (**6**) levels of theory. B3LYP (CCSD(T)) relative energies at 298 K are shown; bond lengths are in Å, angles in degrees, and energies in kcal mol^{-1}.

asymptotes,[17] allow one to evaluate that both the **3** and **4** quartet ions are stable with respect to dissociation. Since no T-shaped minima were found on either the doublet or quartet surfaces, one can reasonably exclude the diazirinone and assign the open-chain structure to the detected neutral species.

Geometry optimization of the triplet open-chain N_2CO led to the linear D_{2h} ($^3A''$) species **5** and to the bent C_s ($^3A''$) species **6**, which is consistent with previous results. Each is stable at only one level of theory—**5** at the B3LYP level and **6** at the MP2 level. However, their CCSD(T) energies only differ by 0.2 kcal mol^{-1}, and they are less stable by about 7 kcal mol^{-1} than singlet C_{2v} diazirinone **7**, which was identified as the most stable neutral N_2CO species. To settle the question, we resorted to the CCSD(T) geometry optimization, and found that the linear structure **5** is not a true minimum. To evaluate the internal energy excess of the neutral N_2CO C_s ($^3A''$) species **6** formed from ions **1**, **3**, and **4** we computed the CCSD(T) Franck–Condon energies of the vertical processes leading to **6**. The neutral N_2CO species **6** would be formed from the ground-state N_2CO^+ ion **1** with an energy excess of 46.1 kcal mol^{-1},[18] which is not unexpectedly above the dissociation threshold of 35 kcal mol^{-1}.[2] Conversely, species **6** is formed from **3** and **4** far below this limit, with an energy excess of 11.3 and 21.2 kcal mol^{-1}, respectively. It is clear that the bent N_2CO C_s ($^3A''$) species **6** is the most suitable candidate for the detected neutral species,[19] which could be formed with the least energy content from the $^4A'$ ion **3**, which is the most probable precursor ion of strictly related structure, even if a possible role of ion **4** cannot be ruled out.

As to the formation of quartet states of N_2CO^+ ions, the N_4^+ ion is germane to the issue. It was recently confirmed[9] that the N_4^+ quartet ion is the most likely precursor of the N_4 ion detected by NRMS experiments, which is consistent with the effective clustering ability of diatomic reactant ions in long-lived electronically excited states. As a matter of fact, one of the advantages of the NRMS technique is the favorable access to elusive neutral species from nonthermalized or excited ionic species. A more advanced theoretical analysis would be required to ascertain the upper limit of the N_2CO lifetime, but the present result dictates that the kinetic stability of N_2CO is sufficient for observation within 1 μs, and provides the missing link in the family of open-chain N_4, N_2CO, and C_2O_2 molecules.

Experimental Section

The experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration (E and B, electric and magnetic sectors; TOF, orthogonal time-of-flight mass spectrometer). Typical operating conditions of the CI source were: source temperature, 403 K; repeller voltage, 0 V; emission current, 1 mA; nominal electron energy, 50 eV; accelerating voltage, 4–8 kV. Helium was used as the collision gas in the CAD experiments, at such a pressure to achieve a 70 % transmittance. In the NRMS experiments, CH_4 or Xe was used as the neutralizing gas and O_2 as the reionizing gas, admitted into the first and second cell, respectively, at such a pressure to achieve a beam transmittance of 80 %. All ions were removed at the exit of the first cell by a pair of high-voltage (± 0.8 kV) deflecting electrodes, and the beam of fast neutral species entered the second cell. The NR mass spectra were averaged over 100 acquisitions to improve the signal-to-noise ratio. N_2 and CO were research-grade products with a stated purity in excess of 99.95 mol %. The MS/MS experiments were performed by admitting He into a cell located in the TOF sector, and recording the CAD spectra of the mass-selected daughter ion. The $C^{18}O$ (98.8 ^{18}O atom %), $^{13}C^{18}O$ (99.9 ^{13}C atom %, 96.6 ^{18}O atom %), ^{13}CO (99.0 ^{13}C atom %), and $^{15}N_2$ (99.0 ^{15}N atom %) samples were obtained from Ikon Stable Isotopes, Inc.

Computational methods: Density functional theory, using the hybrid B3LYP functional,[20] was used to optimize the geometry of relevant species and evaluate their vibrational frequencies. Single-point energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation method with a perturbational estimate of the triple excitation (CCSD(T)) approach.[21] Selected states were also optimized at the CCSD(T) level. Transition states were located using the synchronous transit-guided quasi-Newton method of Schlegel and co-workers.[22] The 6-311 + G(3d) basis set was used.[23] Zero-point energy corrections evaluated at the B3LYP/6-311 + G(3d) level were added to CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational, and vibrational contributions. The absolute entropies were calculated by standard statistical–mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311 + G(3d) optimized geometries. All calculations were performed using Gaussian 03.[24] The Franck–Condon CCSD(T) energies were computed considering the CCSD(T) optimized geometry of the neutral species and the B3LYP optimized geometries of the ions.

Received: April 13, 2004
Revised: September 21, 2004

Keywords: atmospheric chemistry · cations · mass spectrometry · nitrogen · reactive intermediates

---

[1] a) T. J. Lee, J. E. Rice, *J. Chem. Phys.* **1991**, *94*, 1215; b) M. N. Glukhovtsev, H. Jiao, P. von R. Schleyer, *Inorg. Chem.* **1996**, *35*, 7124; c) M. Bittererová, T. Brinck, H. Östmark, *J. Phys. Chem. A* **2000**, *104*, 11999; d) M. Bittererová, H. Östmark, T. Brinck, *Chem. Phys. Lett.* **2001**, *347*, 220.

[2] a) A. A. Korkin, P. von R. Schleyer, R. J. Boyd, *Chem. Phys. Lett.* **1994**, *227*, 312; b) A. A. Korkin, A. Balkova, R. J. Bartlett, R. J. Boyd, P. von R. Schleyer, *J. Phys. Chem.* **1996**, *100*, 5702.

[3] a) G. P. Raine, H. F. Schaefer III, R. C. Haddon, *J. Am. Chem. Soc.* **1983**, *105*, 194; b) H. Chen, J. L. Holmes, *Int. J. Mass Spectrom. Ion Processes* **1994**, *133*, 111; c) D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, 183; d) D. Dawson, H. Chen, J. L. Holmes, *Eur. J. Mass Spectrom.* **1996**, *2*, 373.

[4] F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480.

[5] D. Schröder, C. Heinemann, H. Schwarz, J. N. Harvey, S. Dua, S. J. Blanksby, J. H. Bowie, *Chem. Eur. J.* **1998**, *4*, 2550.

[6] The known nitrosyl cyanide NCNO is a stable compound synthesized in 1971: P. Horsewood, G. W. Kirby, *Chem. Commun.* **1971**, 1139; see also: G. Maier, H. P. Reisenauer, J. Eckwert, M. Naumann, M. De Marco, *Angew. Chem.* **1997**, *109*, 1785; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1707.

[7] a) G. I. Gellene, R. F. Porter, *Acc. Chem. Res.* **1983**, *16*, 200; b) J. K. Terlouw, H. Schwarz, *Angew. Chem.* **1987**, *99*, 829; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 805; c) C. Wesdemiotis, F. W. McLafferty, *Chem. Rev.* **1987**, *87*, 485; d) J. L. Holmes, *Mass Spectrom. Rev.* **1989**, *8*, 513; e) C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Chem. Soc. Rev.* **1998**, *27*, 91.

[8] a) G. de Petris, *Acc. Chem. Res.* **2002**, *35*, 305; b) F. Cacace, G. de Petris, M. Rosi, A. Troiani, *Angew. Chem.* **2003**, *115*, 3093; *Angew. Chem. Int. Ed.* **2003**, *42*, 2985; d) G. de Petris, F. Cacace, A. Troiani, *Chem. Commun.* **2004**, *3*, 326.

[9] E. E. Rennie, P. M. Mayer, *J. Chem. Phys.* **2004**, *120*, 10561.

[10] K.-M. Weitzel, J. Mähnert, *Int. J. Mass Spectrom. Ion Processes* **2002**, *214*, 175.

[11] V. G. Anicich, *J. Phys. Chem. Ref. Data* **1993**, *22*, 1469.

[12] a) M. T. Bowers, P. R. Kemper, J. B. Laudenslager, *J. Chem. Phys.* **1974**, *61*, 4394; b) P. Tosi, W. Lu, D. Bassi, R. Tarroni, *J. Chem. Phys.* **2001**, *114*, 2149.

[13] For the consecutive dissociations leading to NO^+ and CN^+ ions and the accurate analysis of the elemental composition, see the Supporting Information.

[14] a) L. B. Knight, Jr., J. Steadman, P. K. Miller, J. A. Cleveland, Jr., *J. Chem. Phys.* **1988**, *88*, 2226; b) J. Baker, A. D. Buckingham, *J. Chem. Soc. Faraday Trans. 2* **1987**, *83*, 1609; c) M. Hochlaf, C. Léonard, E. E. Ferguson, P. Rosmus, E.-A. Reinsch, S. Carter, N. C. Handy, *J. Chem. Phys.* **1999**, *111*, 4948.

[15] N_2CO exists as a mere van der Waals complex, characterized by a long intermolecular distance of 4.025 Å, and bound with an energy of only 1.3 kJ mol^{-1}: a) Y. Kawashima, K. Nishizawa, *Chem. Phys. Lett.* **1996**, *249*, 87; b) C. Xia, A. R. W. McKellar, Y. Xu, *J. Chem. Phys.* **2000**, *113*, 525. Based on the available literature, such a binding energy value appears too low to ensure detection by NRMS. (The lowest value reported for a tetraatomic molecule is 6 kcal mol^{-1}: D. Schröder, C. A. Schalley, N. Goldberg, J. Hrusák, H. Schwarz, *Chem. Eur. J.* **1996**, *2*, 1235.) Formation of the strictly related $(N_2)_2$ van der Waals dimer by NR was rigorously excluded in ref. [9].

[16] J. Glosík, G. Bánó, E. E. Ferguson, W. Lindinger, *Int. J. Mass Spectrom. Ion Processes* **1998**, *176*, 177.

[17] a) K. P. Huber, G. Herzberg, *Molecular spectra and molecular structure. IV. Constants of diatomic molecules.* Van Nostrand Reinhold, New York, **1978**; b) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data* **1988**, *17*, suppl. 1.

[18] The computed single-point energies indicate that formation of the ground-state triplet **6** from ion **1** would require an energy excess of 29.0 kcal mol^{-1}, which exceeds the dissociation limit of **1**.

[19] Isomerizations to [N_2, C, O] species of different connectivity, from either the N_2CO^+ precursor ion (within the source) or from N_2CO (in the time interval between the neutralization and reionization), were excluded on the basis of the following CCSD(T)/B3LYP calculations. Doublet $NCNO^+$ and $CNON^+$ ions are located 50–60 kcal mol^{-1} above the ground-state N_2CO^+ ion, whose binding energy is only 16–20 kcal mol^{-1} (see refs. [14] and [16]). On the quartet surface the $NCNO^+$ ion is located 25 kcal mol^{-1} above the quartet N_2CO^+ ion **3**. However, the latter has to overcome a barrier of ≈ 87 kcal mol^{-1} to isomerize to $NCNO^+$ (via a cyclic intermediate), that is some 40 kcal mol^{-1} above the lowest dissociation limit of **3**. As for the neutral species, the triplet CNNO is located 64 kcal mol^{-1} above the N_2CO species **6**, which is far above the barrierless dissociation limit of **6** (35 kcal mol^{-1}), whereas the triplet NCNO is located 22 kcal mol^{-1} above **6**. However, a large barrier, far exceeding the dissociation threshold, is expected for such an isomerization. The process requires a very extensive rearrangement involving the breaking of both the N–N and C–O bonds and, also consistent with the above, it is likely to proceed through the intermediacy of high-energy cyclic isomers (species of N–N–C–O and N–C–N–O connectivity on the singlet surface are connected by cyclic structures located 140 kcal mol^{-1} above the most stable diazirinone, see ref. [2]).

[20] a) A. D. Becke, *J. Phys. Chem.* **1993**, *97*, 5648; b) P. J. Stephens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[21] a) R. J. Bartlett, *Annu. Rev. Phys. Chem.* **1981**, *32*, 359; b) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

[22] a) C. Peng, H. B. Schlegel, *Isr. J. Chem.* **1993**, *33*, 449; b) C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.* **1996**, *17*, 49.

[23] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639; c) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294; d) M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.

[24] Gaussian 03 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.