velocity measurements and C. R. Bentley and R. Bindschadler for ice-thickness profile data. K. Jezek provided the RADARSAT image mosaic. The RAMP DEM and the ground-based and LandSAT feature-tracked measurements of velocity were provided by the National Snow and Ice Data Center. Comments by T. Scambos and C. R. Bentley improved the revised manuscript. I.J. performed this work at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. S.T was funded by NSF–Office of Polar Program grants 9873593 and 0096302.

5 October 2001; accepted 14 December 2001

Experimental Detection of Tetranitrogen

F. Cacace,* G. de Petris, A. Troiani

Tetranitrogen (N_4), which has been the subject of great theoretical interest, has been prepared from the N_4^+ cation and positively detected as a gaseous metastable molecule with a lifetime exceeding 1 microsecond in experiments based on neutralization-reionization mass spectrometry. An examination of the geometry of N_4^+ and the fragmentation pattern of the $^{14}N_2{}^{15}N_2$ neutral molecule has revealed that the latter is characterized by an open-chain geometry with two distinct, closely bound N_2 units joined by a longer weaker bond.

During the last decade, the neutral N_4 molecule has been the subject of intense and sustained theoretical scrutiny, aimed at evaluating the structure, stability, and properties of this experimentally unknown species (*1–13*). Apart from the molecule's fundamental significance, such unusual interest is motivated by the potential of N_4 as a "pure" high-energy density material. Theory predicts that, whereas certain N_4 isomers, such as tetraazatetrahedrane, are metastable and long lived, their dissociation into two environmentally benign N_2 molecules is very exothermic, releasing about 800 kJ mol^{-1} (*7*, *10–12*).

Despite the considerable help provided by the theoretical identification and characterization of the target species, preparing and detecting N_4 has posed a formidable challenge to experimentalists. None of the suggested routes, involving the combination of a nitrogen atom with an $N_3^{\cdot}$ radical, binding of two excited N_2 ($A^3\Sigma_u^+$) molecules, and N_4 extrusion from larger, polycyclic molecules, proved viable (*14*).

Here, we report the preparation, positive detection, and characterization as a long-lived gaseous species of an N_4 molecule obtained by a different approach—the one-electron reduction of the gaseous N_4^+ cation by neutralization-reionization (NR)–mass spectrometry (*15–17*). We have used this technique effectively for the preparation and detection of other elusive species, including HO_3 (*18*), the $[H_2O^+ \ O_2^-]$ charge-transfer complex (*19*), and O_4 (*20*).

The charged precursor chosen, N_4^+, is long known and thoroughly characterized as a result of mass spectrometric (*21*, *22*), matrix isolation (*23*, *24*), spectroscopic (*25*, *26*), and theoretical studies (*23*, *27–31*), motivated by its role in N_2 plasmas and in stratospheric chemistry. Ground-state and excited N_4^+ ions are conveniently obtained by electron bombardment of N_2 (*32*). Our experimental approach was as follows. The N_4^+ ions formed in the chemical ionization (CI) source of a multisector mass spectrometer of EBE-TOF configuration (where E stands for electrostatic, B for magnetic sectors, and TOF for an orthogonal time-of-flight analyzer) were accelerated to 4 to 8 kV and mass selected. The N_4^+ ions underwent two consecutive collision events in the two separate cells located along the beam path, each containing a suitable target gas. In the first cell, a fraction of the ions was neutralized by electron transfer from the molecules of the first target gas, A, yielding N_4

$$N_4^+ \xrightarrow[-A^+]{+A} N_4 \qquad (1)$$

together with neutral and charged fragments. The parent ions surviving neutralization and any charged fragments were removed by a high-voltage deflecting electrode, so that only a fast beam of neutral species entered the second cell, where reionization occurred upon collision with the molecules of the second targed gas, B, giving cations.

$$N_4 \xrightarrow[-e]{+B} N_4^+ \qquad (2)$$

Detection of a "recovery" peak, that is of a charged species with the same mass-to-charge (*m/z*) ratio as the original N_4^+ ions, in the NR spectra (Fig. 1A) of $^{14}N_4^+$, $^{14}N_2{}^{15}N_2^+$, and $^{15}N_4^+$ ions at $m/z = 56, 58$, and 60, respectively, positively demonstrates the occurrence of the reaction sequence in equations 1 and 2 and hence the existence of a neutral N_4 species with a lifetime in excess of the flight time from the neutralization to the reionization cell, i.e, ~1 μs.

Structural insight is provided by the isotopic composition of the N_2^+ fragments displayed by the NR spectra that can originate only from the uncharged species formed in the neutralization and/or in the reionization process. As expected, $^{14}N_4$ gives only $^{14}N_2^+$, and $^{15}N_4$ gives only $^{15}N_2^+$, but $^{14}N_2{}^{15}N_2$ gives equal amounts of $^{14}N_2^+$ and $^{15}N_2^+$, without detectable formation of the isotopically mixed $^{14}N^{15}N^+$ fragment. This pattern strongly suggests that the N_4 molecule contains two distinct N_2 units that maintain their identity without exchanging their constituent atoms and that the four N atoms of N_4 are inequivalent.

As to the structure of the N_4 species detected, and its identification with one of the theoretically predicted isomers, useful criteria are provided by the intrinsic features of NR spectrometry. Detection of a neutral species can occur only if its dissociation requires overcoming a sizeable barrier, on the order of 40 kJ mol^{-1} (*15–17*), and the vertical character of the neutralization process allows survival of the neutral molecule only if its geometry is not significantly different from that of the parent ion (the transition displays adequate Franck-Condon factors).

In view of the latter requirement, the connectivity of the N_4^+ ions used in the NR experiments has been probed by collisionally activated dissociation (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). The CAD spectrum of $^{14}N_4^+$ (Fig. 1B) displays the $^{14}N^+$, $^{14}N_2^+$, and $^{14}N_3^+$ fragments; and the CAD spectrum of $^{15}N_4^+$ displays the $^{15}N^+$, $^{15}N_2^+$, and $^{15}N_3^+$ fragments. The CAD spectrum of the $^{14}N_2{}^{15}N_2^+$ ion 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 $^2\Sigma_m^+$ ground state by experimental and theoretical studies (*21–31*), whose results characterize the cation as an open-chain species with two closely bound N_2 units joined by a longer, weaker bond. 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 the $N_4^+(^4A')$ in the first-quartet state, are present in the N_4^+ population.

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma "La Sapienza," Piazzale Aldo Moro, 5–00185 Roma, Italy.

*To whom correspondence should be addressed. E-mail: fulvio.cacace@uniroma1.it

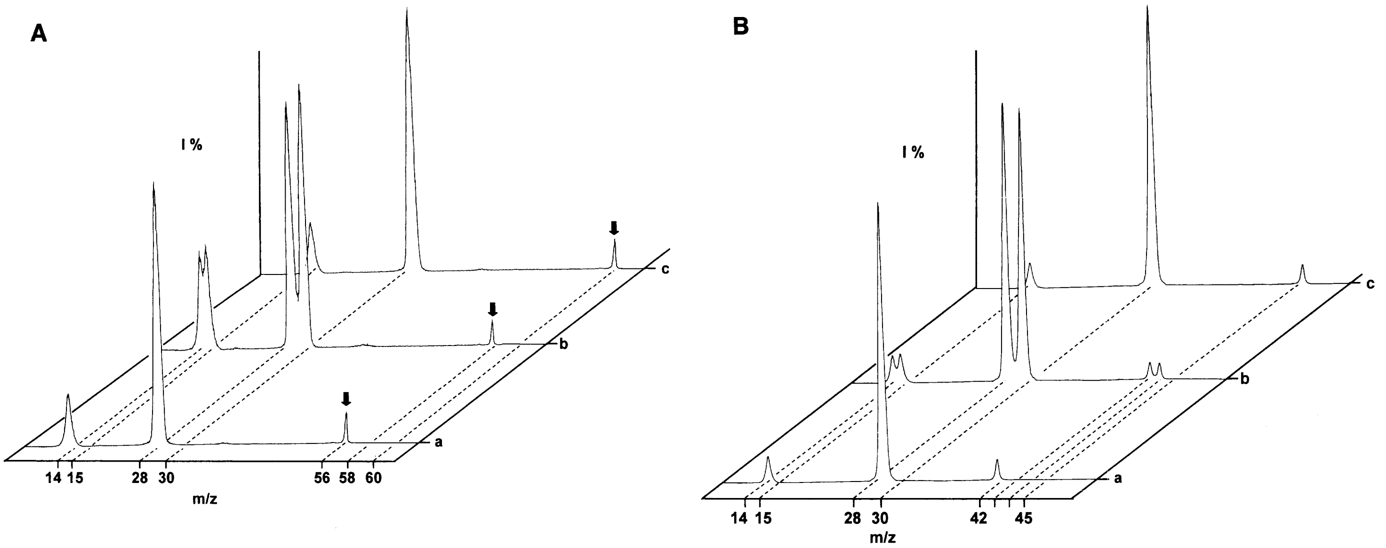

Fig. 1. (**A**) $^+NR^+$ spectra of $^{14}N_4^+$ (a), $^{14}N_2{}^{15}N_2^+$ (b), and $^{15}N_4^+$ ions (c). Neutralizing gas was CH_4, reionization gas, O_2, kinetic energy 6 kV (a and c), 8 kV (b). The "recovery" peaks are indicated by the arrows. (**B**) CAD spectra of $^{14}N_4^+$ (a), $^{14}N_2{}^{15}N_2^+$ (b), and $^{15}N_4^+$ (c) ions. Collisions took place in He gas at a kinetic energy of 8 kV.

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^+ and is also characterized by two closely bound N_2 units joined by a longer, weaker bond (*32*).

Based on the above criteria, we can exclude the idea that the N_4 molecule detected is a $(N_2)_2$ van der Waals complex, whose barrier to dissociation is far too low (*33*), or that it is tetraazatetrahedrane, N_4 (T_d), a singlet containing equivalent N atoms (*7*, *10*–*12*). The fragmentation of the N_4 (T_4) $^{14}N_2{}^{15}N_2$ isotopomer would be expected to give an abundant $^{14}N^{15}N^+$ peak, which was not detected in the NR spectrum. By contrast, the rectangular N_4 (D_{2h}) singlet contains two distinct N_2 units (*7*, *10*–*12*), consistent with the fragmentation pattern observed in the NR spectrum of $^{14}N_2{}^{15}N_2$. However, the N_4 (D_{2h}) geometry is too different from that of the N_4^+ parent, and its formation by neutralization of the cation would be prevented by unfavorable Franck-Condon factors. Among the theoretically identified isomers, the open-chain N_4 ($^3A''$) triplet of C_s symmetry, predicted to be experimentally detectable under certain conditions (*7*, *10*–*12*), appears to be the most likely candidate, with regard to both its structural relationship with the parent cation and the fragmentation pattern displayed by the NR spectra. However, such a tentative assignment does not exclude the existence of other isomers, such as tetraazatetrahedrane, that cannot be prepared by the NR technique because of the different geometry of the available charged precursors. Moreover, the accurate evaluation of the stability of the N_4 isomers, and especially of the barriers to their dissociation, proved a difficult task even using state-of-the-art computational methods. We hope the present study, which shows that an N_4 species is kinetically sufficiently stable for experimental observation, will encourage further theoretical analysis of the system.

We have positively demonstrated the existence of the tetranitrogen molecule, N_4, as a metastable species whose lifetime, in the isolated gas state, exceeds 1 μs at 298 K. The identification of N_4 represents the first addition in nearly half a century to the family of polynitrogen molecules, which now includes just three members, namely N_2 (by Priestley), $N_3^\cdot$ (by Thrush), and N_4 (detailed in this report), discovered in 1772, 1956, and 2001, respectively (*34*, *35*). Such slow progress is a testament to the great experimental difficulties encountered in extending the N_n series beyond N_2 and also to the value of the NR technique for the positive identification of otherwise inaccessible species.

References and Notes

1. M. M. Frankel, J. P. Chesick, *J. Phys. Chem.* **94**, 526 (1990).
2. T. J. Lee, J. E. Rice, *J. Chem. Phys.* **94**, 125 (1991).
3. W. J. Lauderdale, J. F. Stanton, R. J. Bartlett, *J. Phys. Chem.* **96**, 1173 (1992).
4. D. R. Yarkony, *J. Am. Chem. Soc.* **114**, 5406 (1992).
5. K. M. Dunn, K. Morokuma, *J. Chem. Phys.* **102**, 4904 (1995).
6. M. N. Glukhovtsev, S. Laiter, *J. Phys. Chem.* **100**, 1569 (1996).
7. A. A. Korkin, A. Balková, R. J. Bartlett, R. J. Boyd, P. v. R. Schleyer, *J. Phys. Chem.* **100**, 5702 (1996).
8. M. N. Glukhovtsev, H. Jiao, P. v. R. Schleyer, *Inorg. Chem.* **35**, 7124 (1996).
9. S. A. Perera, R. J. Bartlett, *Chem. Phys. Lett.* **314**, 381 (1999).
10. M. Bitterová, T. Brinck, H. Östmark, *J. Phys. Chem. A* **104**, 11999 (2000).
11. ———, *Chem. Phys. Lett.* **340**, 597 (2001).
12. ———, *Chem. Phys. Lett.* **347**, 220 (2001).
13. T. J. Lee, C. E. Dateo, *Chem. Phys. Lett.* **345**, 295 (2001).
14. J. P. Zheng, J. Waluk, J. Spanget-Larsen, D. M. Blake, J. G. Radziszewski, *Chem. Phys. Lett.* **328**, 227 (2000), reported the only faint experimental evidence for N_4. A weak IR transition was observed in an N_2 plasma condensed on a solid matrix at a wavelength close to that of one of the transitions computed in a theoretical study of tetraazatetrahedrane. The evidence is weakened by the observed isotopic shift, which conflicts with the computed value, and by the failure to detect other theoretically predicted transitions.
15. C. Wesdemiotis, F. McLafferty, *Chem. Rev.* **87**, 485 (1987).
16. J. L. Holmes, *Mass Spectrom. Rev.* **8**, 513 (1989).
17. C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Chem. Soc. Rev.* **27**, 91 (1998), and references therein.
18. F. Cacace, G. de Petris, F. Pepi, A. Troiani, *Science* **285**, 81 (1999).
19. ———, *Angew. Chem. Int. Ed.* **39**, 367 (2000).
20. F. Cacace, G. de Petris, A. Troiani, *Angew. Chem. Int. Ed.* **40**, 4062 (2001).
21. W. Lindinger, I. Dotan, D. L. Albritton, F. C. Fehsenfeld, *J. Chem. Phys.* **68**, 2607 (1978).
22. H. Bohringer, F. Arnold, D. Smith, N. G. Adams, *Int. J. Mass Spectrom. Ion Phys.* **52**, 85 (1983).
23. L. B. Knight Jr., *et al.*, *J. Chem. Phys.* **87**, 885 (1987).
24. W. E. Thompson, M. E. Jacox, *J. Chem. Phys.* **93**, 3856 (1990).
25. M. F. Jarrold, A. J. Illies, M. T. Bowers, *J. Chem. Phys.* **81**, 214 (1984).
26. T. Ruchti, *et al.*, *J. Chem. Phys.* **105**, 2591 (1996).
27. S. C. de Castro, H. F. Schaefer III, R. M. Pitzer, *J. Chem. Phys.* **74**, 550 (1981).
28. G. Kenister, J. B. Pell, *Org. Mass Spectrom.* **28**, 311 (1993).
29. J. H. Langenberg, I. B. Bucur, P. Archirel, *Chem. Phys.* **221**, 225 (1997).
30. K. Sohlberg, *J. Mol. Struct. Theochem* **339**, 195 (1995).
31. C. Leonard, P. Rosmus, S. Carter, N. C. Handy, *J. Phys. Chem. A* **103**, 1846 (1999).
32. A. Tosi, W. Lu, D. Bassi, R. Tarroni, *J. Chem. Phys.* **114**, 2149 (2001), and references therein.
33. V. Aquilanti, M. Bartolomei, D. Cappelletti, E. Carmona-Novillo, F. Pirani, *Phys. Chem. Chem. Phys.* **3**, 3891 (2001).
34. J. Priestley, *Phil. Trans.* **62**, 164 (1772).
35. B. A. Thrush, *Proc. R. Soc. London Ser. A* **235**, 143 (1956).

36. Support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), the Italian National Research Council (CNR), and Rome University "La Sapienza" is gratefully acknowledged.

2 November 2001; accepted 4 December 2001