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Azido-Nitrene Is Probably the N_4 Molecule Observed in Mass Spectrometric Experiments

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Ab initio calculations determining structures and stabilities of the tetranitrogen $N_4^{\bullet+}/N_4$ system and mass spectrometric experiments were carried out in an attempt to understand the processes occurring in a recent neutralization−reionization mass spectrometric (NRMS) experiment starting from a linear $N_4^{\bullet+}$ radical cation (Cacace et al. *Science*, **2002**, *295*, 480). Calculations were performed using RCCSD(T) and MRCISD+Q methods with the 6-311+G(3df) basis set. The most stable bound tetranitrogen molecule is an *azidonitrene* (N_3-N) featuring a triplet $^3A''$ ground state and being 56 kJ/mol below the singlet tetrahedral T_d isomer. The singlet azidonitrene has an open-shell $^1A''$ state and the corresponding singlet−triplet energy gap amounts to 69 kJ/mol. In both states, fragmentation giving two N_2 moieties needs to overcome a barrier height of about 55 kJ/mol. A remarkable difference between N_4 isomers is that ionization of triplet azidonitrene leads to the linear $^2\Sigma$ ground-state radical cation, whereas removal of an electron from singlet tetrahedrane (N_4, T_d) gives rise to a cyclic three-membered ring belonging to a Π-type excited state. The standard heats of formation are evaluated as follows: ΔH_f°(triplet azidonitrene) = 714 ± 20 kJ/mol, ΔH_f°(singlet azidonitrene) = 783 ± 20 kJ/mol, ΔH_f° (N_4, T_d) = 770 ± 20 kJ/mol, and ΔH_f° ($N_4^{\bullet+}$) = 1398 ± 20 kJ/mol. The adiabatic ionization energies are estimated as IE_a (triplet azidonitrene) = 7.3 ± 0.3 eV and IE_a (N_4, T_d) = 10.4 ± 0.3 eV. When repeating the NRMS experiments using our tandem mass spectrometer and operating conditions, the collisional activation (CA) spectrum of $N_4^{\bullet+}$ could be recorded, whereas *we could not reproduce the neutralization−reionization spectrum reported by Cacace et al.* These results suggest that although azido-nitrene was apparently generated in NRMS experiments, only a very small fraction of the N_4 neutral could effectively be reionized, and the resulting spectra could not be reproduced easily, when changing even slightly the experimental conditions.

1. Introduction

Nitrogen-rich compounds continue to intrigue chemists due not only to their unusual molecular shape and fascinating chemical properties but also to the difficulties with which they can be prepared in the laboratories. In the past decade, the intense search for efficient, safe, and environment-friendly high energy density materials (HEDM) has revitalized the interest in this field, especially in the polynitrogen compounds (N_n)[1] in view of the ubiquitous presence of nitrogen in the atmosphere and in biological systems (known as the "nitrogen cycle"). In a cluster of nitrogen atoms, a transfer of the strong triple N≡N bond of molecular nitrogen into the much weaker double N=N and single N−N bonds whose strengths are about 50 and 30%, respectively, of the corresponding triple bond, makes the resulting nitrogen cluster a chemical entity with highly energetic content. A complete decomposition of a nitrogen cluster is thus expected to release a large amount of excess energy. For example, dissociation of the tetrahedrane N_4 species is exothermic by up to 770 kJ/mol with respect to $2N_2$, whereas the cubic N_8 form could produce up to 1700 kJ/mol following generation of $4N_2$.[2] As polynitrogen compounds could be made from an unlimited natural source and generate no environmentally harmful byproducts and/or wastes, they become interesting candidates for potential alternative HEDMs. Nevertheless, there still is a long way from attaining such a target in view of the inherent difficulties encountered in the preparation of stable nitrogen clusters. The number of synthetic routes that might lead to N_n is at the present time quite limited.

Besides the natural molecular nitrogen, known stable polynitrogen species are scarce. While the azide anion, N_3^-, was first synthesized in 1890 by Curtius,[3] the stable pentanitrogen cation, N_5^+, was only prepared in 1999 by Christe and co-workers.[4,5] Until recently, the other known N_n species including the $N_3^\bullet$ radical and N_3^+ cation,[6−8] the $N_4^{\bullet+}$ radical cation,[9−20] and the $N_6^{\bullet-}$ radical anion,[21] are reactive species that have been detected and characterized by a variety of spectroscopic techniques. More recently, the long-sought pentazole N_5^- anion has been detected by mass spectrometric techniques[22a] and shown to have a longer lifetime ($t_{1/2}$ > 2 days) in solution.[22b] In this context, much effort has been devoted to search for a way of making a bound tetranitrogen N_4 molecule, the missing but perhaps a key member of the N_n family. The abundant literature[23] points out that both the ionized $N_4^{\bullet+}$ (refs 24−32) and neutral N_4 (refs 33−61) forms are the subject of intense theoretical and computational scrutiny. A recent experimental paper[62] reported on the experimental detection of N_4, but its structural identity is not established yet. Thus, it seems appropriate to briefly summarize the available results on the tetranitrogen system. For a more complete list of relevant theoretical papers, we would

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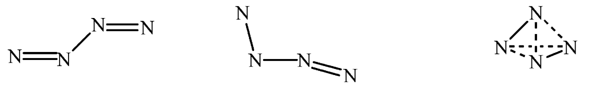
CHART 1

(**A**) Singlet N_4 (T_d)

(also referred to as **N2**)

(**B**) Singlet N_4 (D_{2h})



(**C**) Triplet N_4 (C_{2h})

(**D**) Triplet N_4 (C_s)

(also referred to as **N1**)

(**E**) Triplet N_4 (D_{2d})

refer to the compilation of ab initio articles, namely, the Quantum Chemistry Library Data Base (QCLDB).[23]

2. Brief Summary of Previous Theoretical and Experimental Results

In a cluster of molecular nitrogen $(N_2)_n$, the lowest-energy N_4 entity is usually a van der Waals complex between two nitrogen molecules.[57−61] The resulting dimer which has either a T-shaped, linear, or rectangular form, is extremely weak, with a complexation energy of about 1 kJ/mol. The most recent and accurate theoretical study using CCSD(T)/aug-cc-pVQZ plus BSSE corrections resulted in a complexation energy of 98 cm^{-1} (1.2 kJ/mol).[61] A large majority of previous theoretical studies on N_4 species rather focused on their closed-shell singlet electronic state, including the tetrahedral (Chart 1, tetraaza-tetrahedrane **A**, T_d) and rectangular (Chart 1, tetrazete **B**, D_{2h}) forms. Both have rather comparable relative energies even though the absolute energy difference largely depends on the theoretical methods employed.[44,45] Of the two, the tetrahedrane **A** is found to be much more kinetically stable than the tetrazete **B** with respect to unimolecular decomposition. In fact, the energy barriers for the cycloreversion of **A** and **B** giving two N_2 molecules amount to about 255−315 and 37−60 kJ/mol, respectively.[37,38,42,44,45,54] The interconversion between **A** and **B**, which is also formally forbidden by symmetry and thus difficult to achieve, is characterized by an energy barrier of about 290 kJ/mol[44,54] relative to **A**, bearing again in mind that the energetic values actually vary with the level of quantum chemical theory.

The higher kinetic stability of **A** made it an obvious candidate for experimental observation. Possible production of N_4 from a highly excited state of N_2 generated by laser irradiation, ion bombardment, r.f. excitation, or in a hollow-cathode discharge, has regularly been proposed.[37,55] It has been suggested that, for example, a prolonged irradiation of liquid nitrogen with radiation of wavelength less than 140 nm might yield evidence for N_4 formation.[37] A general but simple approach to make this metastable molecule is to create a high energy plasma and then to quench any possible N_4 that may be formed. For its eventual detection, mass and vibrational IR and Raman absorption spectrometric techniques with appropriate apparatus setups appear to be the more convenient choices.

Nevertheless, there is so far no report on experimental detection of a N_4 species, other than a $(N_2)_2$ dimer, in the last century. In a recent experiment in which the nitrogen plasma, generated by microwave or electrical discharge in gaseous N_2, was quenched and the resulting matrix was monitored by IR and UV−Vis spectrometries, Zheng and co-workers[52] observed a peculiar IR feature and suggested that the tetrahedrane **A** was actually formed. However, the claim was rapidly disproved as the key information for the assignment, namely, the isotopic (^{15}N) shift observed on the IR spectrum, was not supported by theoretical studies[50,53,55,56] (see also ref 75). A route for generating **A** involving a combination of two marginally bound quintet states of N_2 was suggested.[56] However, these excited states are quite high-lying, being more than 10 eV above the ground state of either N_2[56] or N_4[53,54,56] (the ionization energy IE_a of N_2 being 15.58 eV), and such a route does not appear synthetically realisable.

The singlet tetrahedrane **A** is however not the lowest-energy covalently bound N_4 isomer. Numerous studies[41,44,45,51] demonstrated that an *open-chain structure having a triplet electronic state is the more stable N_4 isomer*. Nevertheless, these studies disagreed with each other on the actual shape of the triplet species and its kinetic stability. In their 1993 paper, Glukhovtsev and Schleyer[41] found that the planar trans form **C** characterized by a C_{2h} symmetry (^3B_u, Chart 1) and a central N−N distance of 1.465 Å is the lower-lying minimum being 101 and 88 kJ/mol below **A** and **B**, respectively, but still 659 kJ/mol above two $N_2(^1\Sigma_g^+)$ molecules (values obtained at the QCISD(T)/6-311+G(d) level). In a subsequent paper by the same group,[44] the triplet **C** was calculated at the G2 level to be only 46 and 60 kJ/mol below **A** and **B**, respectively. In addition, the form **C** could be regarded as a short-lived exciplex in the sense that the single-point singlet energy performed at the optimized triplet geometry turns out to be lower than the energy of the ^3B_u minimum.[44]

Another triplet structure **D** having a reduced symmetry (C_s, Chart 1) was also found[44] containing shorter nitrogen−nitrogen distances. The form **D** is about 36 and 88 kJ/mol higher in energy than the form **C** and the $N_2(S_0) + N_2(T_1)$ dissociation limit, respectively (UMP4/6-31G(d) results), and exhibits a large singlet−triplet energy gap of 66 kJ/mol. Although no transition structures for fragmentation have been considered for the triplet entities, Korkin et al.[44] stated that **D** *"might be observed experimentally, as a long-lived intermediate, under certain conditions"*.

In a 2000 theoretical study, Bittererova and co-workers[51] investigated in more detail the triplet N_4 potential energy surface using the coupled-cluster method and confirmed that even though there are several triplet equilibrium structures, only the two forms **C** and **D** are actually more stable than the singlet tetrahedrane **A** by 88 and 54 kJ/mol, respectively (CCSD(T)/cc-pVTZ values). Nevertheless, when using multireference wave functions at the CASSCF(12,12)/cc-pVTZ level, these authors could not locate a C_{2h} triplet minimum **C**; all geometry optimizations led to dissociation. In addition, at the latter level, the triplet **D** was found to be about 13 kJ/mol higher in energy than the singlet **A**, in contrast with the CCSD(T) results mentioned above, presumably due to an insufficient treatment of dynamic electron correlation.

Again, it is puzzling that no transition structure was considered or reported in ref 51 to establish the kinetic stability of the triplet form **D** with respect to various dissociative processes, whereas other portions of the energy surface were explored in detail. On the basis of electronic distribution from which localized unpaired electrons are more reactive with respect to bimolecular processes, the authors stated that **D** *"is expected to have a very short lifetime under normal conditions"*. Other triplet equilibrium structures have been located including the highly symmetrical form **E** (D_{2d}) displayed in Chart 1. The latter was calculated to be about 84 kJ/mol above the singlet **A**, and protected by a rather shallow potential well of 33 kJ/mol against a fragmentation giving $N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^+)$ (CCSD(T)/cc-

TABLE 1: Calculated Harmonic Vibrational Frequencies (in cm^{-1}) of the Tetranitrogen System Considered Using the CASSCF(11 or 12,12)/6-311+G(d) Method[a]

I1$^{\bullet+}$ ($D_{\infty h}$, $^2\Sigma_u^+$)	**I2**$^{\bullet+}$ (C_{2v}, $^2A_1$)	**I3**$^{\bullet+}$ (C_{2v}, $^2B_2$)	**I4**$^{\bullet+}$ (C_{2v}, $^2B_2$)	**N1** (C_s, $^3A''$)	**N2** (T_d, $^1A_1$)	**N3** (C_s, $^1A''$)	**TS1** (C_s, $^3A''$)	**TS2** (C_s, $^1A''$)	**TS3** (C_s, $^1A'$)	**TS3** (C_1, ^1A)	**TS4** (C_s, $^2A''$)
98 (Π_u)	359i (B_2)	340 (B_1)	321 (A_2)	215 (A')	725 (E)	169 (A')	653i (A')	732i (A')	1025i (A”)	2628i (A)	629i (A')
98 (Π_u)	160 (B_2)	366 (B_2)	548 (B_2)	374 (A'')	725 (E)	614 (A'')	152 (A')	188 (A')	2140i (A')	379 (A)	283 (A'')
141 (Π_g)	175 (B_1)	859 (A_1)	652 (B_2)	629 (A')	937 (T_2)	614 (A')	501 (A')	242 (A'')	398 (A'')	457 (A)	298 (A')
141 (Π_g)	358 (A_1)	1260 (B_2)	747 (A_1)	937 (A')	937 (T_2)	824 (A')	568 (A'')	421 (A')	630 (A')	691 (A)	507 (A')
405 (Σ_g)	2030 (A_1)	1552 (A_1)	1468 (A_1)	1065 (A')	937 (T_2)	1281 (A')	1124 (A')	1241 (A')	985 (A')	1007 (A)	1648 (A')
2377 (Σ_u)	2425 (A_1)	1683 (A_1)	1841 (A_1)	2246 (A')	1302 (A_1)	1987 (A')	2086 (A')	1881 (A')	1282 (A')	1263 (A)	2737 (A')
2433 (Σ_g)											

[a] i stands for an imaginary frequency.

pVTZ values). Along with the fact that unpaired electrons are more delocalized (less reactive in biomolecular reactions) in E than in D, this result allowed Bittererova and co-workers[51] to conclude that the triplet form ***E*** *"is the most likely candidate to be observed experimentally"*.

In summary, theory suggested the existence of at least two distinct N_4 entities: the first has a singlet electronic state and the second belongs to the triplet manifold. While the singlet tetrahedrane **A** is compellingly predicted to have a comfortable kinetical stabililty with respect to fragmentation, the stability and observability of the triplet counterpart, either **C**, **D**, or **E**, is not convincingly proven yet.

In this context, the recent report by Cacace, de Petris, and Troiani[62] (referred to hereafter as CPT) on a positive experimental detection of N_4 using the neutralization−reionization mass spectrometric (NRMS) technique constituted, if it is confirmed, an important step in the search for polynitrogen compounds and attracted our particular attention. As expected, the mass spectrometric technique is not able to reveal the shape and electronic state of the neutral species it generated and identified. Therefore, the crucial question on the identity of the detected neutral N_4 species remains open after CPT's study. A rapid comparison of the NMRS and available theoretical results summarized above indicates that the N_4 entity generated in a cell of the mass spectrometer is likely to have an initial triplet state. As a matter of fact, on the basis of the known linear geometry of the $N_4^{\bullet+}$ radical cation and the fragmentation pattern of the isotope $^{14}N_2{}^{15}N_2$ neutral molecule, CPT concluded that *the neutral N_4 is characterized by an open-chain geometry with two distinct, closely bound N_2 units jointed by a longer weaker bond*.

It is clear that none of the structures shown in Chart 1 fully correspond to this description. The cyclic singlet **A** and **B** and triplet **E** forms could be ruled out. Apparently, the triplet **C** looks like a good candidate, even though the two N_2 entities in **C** are equivalent. The most troublesome fact is that **C** is not found to be an equilibrium form. The triplet form **D** does not satisfy the suggested geometry either, as it does not contain two N_2 units. According to available theoretical results mentioned above, such a triplet species were not sufficiently stable to survive under MS collisional conditions and undergo a reionization in the subsequent step of a NRMS experiment. The inherent lifetime of the cations and neutrals involved is usually estimated on the order of microsecond.[62,63] It should be stressed once more that CPT's statement was a suggestion among others, rather than a clear-cut evidence (cf. above).

Regarding CPT's results, the reported NR spectra[62] seem to be sound and the presence of survivor ions for isotopic combinations ($^{14}N_4^+$ and $^{14}N_2{}^{15}N_2^+$) practically suggests no artifacts. For example, hydrocarbon ion contaminants at *m*/*z* 56 and 58 would give some loss of hydrogen atoms or alkyl groups, that were absent in the reported NR mass spectra. However, a very weak *m*/*z* 42 ($^{14}N_3^+$) peak was present in the CA spectrum but not in the NR spectrum.

This unclear situation on both theoretical and experimental sides led us to ask a legitimate question: What is the identity of the tetranitrogen molecule observed in CPT's experiment? In an attempt to provide us with an answer, we set out to carry out in the present work not only quantum chemical computations using reliable levels, but also similar NRMS experiments.

3. Computational Methods

All calculations were performed using the Gaussian 98,[64] Molpro 2000,[65] and Dalton[66] sets of programs. Geometrical parameters of the structures considered on the doublet ionized $N_4^{\bullet+}$ and singlet and triplet neutral N_4 potential energy surfaces were initially optimized and subsequently characterized by vibrational analyses using the Hartree−Fock method in conjunction with the 6-311+G(d) basis set. The unrestricted formalism (UHF) was used to approach open-shell structures. The relevant structures were then reoptimized using the multi-configurational CASSCF method and the same basis set. In the construction of CASSCF wave functions, the active spaces including either 11 electrons (ion) or 12 electrons (neutral) in 12 orbitals have been selected. While all the 16 electrons from eight 1s(N) and 2s(N) orbitals were kept frozen, the twelve 2p-electrons resulting in six highest-occupied orbitals were included in the active spaces. We were aware that correlation of 2s-electrons involved in σ bonds might be important, but CASSCF computations using a full (20) valence space are simply beyond our computational capacities. The harmonic vibrational frequencies and the resulting zero-point energy corrections (ZPE) to relative energies were also obtained at the CAS(12,12)/6-311+G(d) level. To evaluate more reliable relative energies, single point electronic energies were calculated for the stationary points considered using the larger 6-311+G(3df) basis set and three different methods of molecular orbital theory for including dynamic correlation energies, namely, the restricted coupled-cluster theory RCCSD(T), and the multireference configuration interaction calculations MRCISD+Q(8,8) using also CASSCF(8,8) references and including all the single and double excitations and the corrections for quadruple substitutions. The multireference methods were necessary in determining the energies of open-shell singlet states. However, the MRCI computations using the larger (12,12) active spaces were again not realizable simply due to our limited computer resources.

4. Results and Discussion

Figure 1 displays the selected geometrical parameters of the relevant (N_4) stationary points. For the purpose of simplicity, geometries of the fragments are omitted. Table 1 lists their

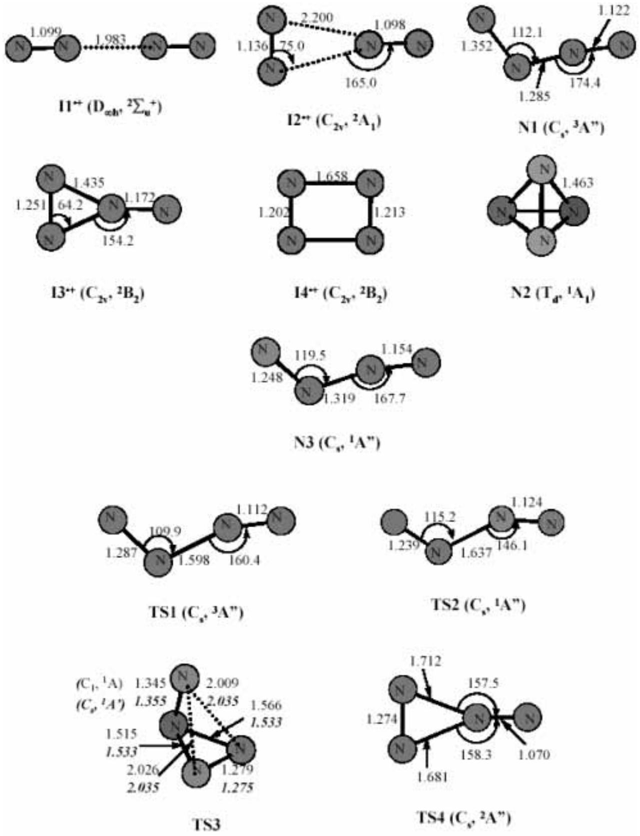


Figure 1. Selected CASSCF(12,12)/6-311+G(d) optimized geometries of the ionized **Ix**$^{\bullet+}$, neutral **Ny** equilibrium structures, and transtition structures **TSz** of the tetranitrogen system considered. Bond lengths are given in angstroms and bond angles in degrees.

harmonic vibrational frequencies computed using CASSCF-(12,12)/6-311+G(d) wave functions. Figure 2 shows the schematic potential energy profiles illustrating the relative energies between the different points of interest and the interconnections between various processes involved in the NRMS experiment. The notations employed in both figures are defined as follows: **Ix**$^{\bullet+}$ (**x** ranging from 1 to 4) stands for a radical cation $N_4^{\bullet+}$ stationary structure, **Ny** (**y** from 1 to 3) designates a neutral N_4 equilibrium form, **TSz** indicates a transition structure on either neutral (**TS1**, **TS2**, and **TS3**) or ionized (**TS4**) potential energy surface. Finally, **Nx**$^{\bullet+}$ describes an ion at the corresponding neutral geometry and conversely, **Iy** refers to a neutral (vertically) calculated at the ion geometry. It is obvious that the equilibrium structures **A** and **D** of Chart 1 correspond to the **N2** and **N1**, respectively, of Figures 1 and 2. The notation **Nx** and **Ix**$^{\bullet+}$ will conveniently be used hereafter in the discussion (not all the structure in Chart 1 will be considered). Although Figure 2 displays not only the relevant doublet $N_4^{\bullet+}$ radical cations but also the singlet and triplet N_4 neutrals, many structures considered in Figure 1 are not included.

Finally, Figure 3 shows a reaction pathway starting from the triplet structure **N1** and follows a breaking of its central nitrogen−nitrogen bond. Throughout this section, bond distances are given in angstroms, bond angles in degrees, and relative energies in kJ/mol. Whenever a comparison is possible, the relative energies obtained using two different methods RCCSD(T) and MRCISD+Q are consistent with each other having quite small fluctuations. Therefore, for the sake of consistency and uniformity, we have chosen the values derived from MRCISD+Q/6-311+G(3df)+ZPE for the open-shell singlet species and from RCCSD(T)/6-311+G(3df)+ZPE calculations for the rest.

A. Structure of the $N_4^{\bullet+}$ Radical Cation. The main purpose of a NRMS experiment is the production and characterization of a neutral species from a stable cation having the same molecular skeleton. Due to the inherent differences in stability and shape of the ion and neutral counterparts, unimolecular rearrangements of the initially generated neutrals often occur and thereby render their identification a difficult exercise with equivocal interpretation. At the NRMS starting point, the selected charged entity should be generated by ionization of appropriate precursors. In the manipulations of CPT,[62] the $N_4^{\bullet+}$ radical cations were thus produced using the classical electron bombardment of molecular nitrogen (N_2).[19] In view of the pivotal role of the resulting gaseous $N_4^{\bullet+}$ ions, it is important to begin the discussion of our results in briefly examining their geometry, shape and stability.

As in seen Figure 2, the linear centro-symmetrical form **I1**$^{\bullet+}$ is, in its $^2\Sigma_u^+$ electronic ground state, confirmed to be the lowest-lying isomer. The central N−N distance of 1.983 Å is rather long but comparable to the value of 2.005 Å obtained using the RCCSD(T) method with a large basis set.[32] All the vibrational frequencies related to the intermolecular motions are indeed small ranging from 405 to 98 cm^{-1} (Table 1). The N_2−N_2^+ bond strength of the ion **I1**$^{\bullet+}$, as measured by the central bond breaking, is calculated to be 115 kJ/mol with respect to the $N_2(^1\Sigma_g^+)$ + N_2^+ $(^2\Sigma_g^+)$ dissociation limit, and thus consistent with an earlier experimental evaluation of 105 ± 6 kJ/mol using MS techniques.[15]

The three-membered cyclic form **I2**$^{\bullet+}$ exhibiting long intermolecular distances of 2.200 Å is characterized as a transition structure (TS) for scrambling of one N_2 moiety in **I1**$^{\bullet+}$ between the two ends of the other moiety. While the associated imaginary frequency of b_2 symmetry amounts to 359*i* cm^{-1} (Table 1), the energy barrier to migration is calculated at 56 kJ/mol relative to **I1**$^{\bullet+}$.

The second cyclic form **I3**$^{\bullet+}$ featuring a real three-membered cycle with shorter distances, is determined by vibrational frequencies as an equilibrium structure. It has a rather high energy content lying 358 kJ/mol above **I1**$^{\bullet+}$ and 133 kJ/mol above its $N_2(^1\Sigma^+_g)$ + N_2^+ $(^2\Pi)$ asymptote. Note that this ion is connected to an excited $^2\Pi$ state of the ion system. The cycle **I3**$^{\bullet+}$ is found to be quite stable with respect to cyclo-reversion, which is associated with a barrier height of 231 kJ/mol via the **TS4** (cf. Figure 2). For its part, the rectangular form **I4**$^{\bullet+}$ is also a high-energy local minimum being 410 kJ/mol above the global linear minimum **I1**$^{\bullet+}$ and also connects to the excited $^2\Pi$ state. It appears to us that the extent to which the excited ions **I3**$^{\bullet+}$ and **I4**$^{\bullet+}$ could be formed following ionization of nitrogen clusters remains an open question.

We wish to take this opportunity to look back at the results reported in an earlier experimental study. Carnovale and coworkers[13a] were successful in obtaining the photoelectron spectrum (PES) of gas-phase molecular nitrogen dimer from a pulsed molecular beam. The first PES band which was identified to be broad and centered at 15.2 ± 0.1 eV could be assigned to the ground state **I1**$^{\bullet+}$ of $(N_2)_2^+$. This value is markedly larger than that of 14.69 ± 0.05 eV obtained earlier by Lin et al.[13b] Our calculated relative energy between the two separated N_2 molecules and the ion **I1**$^{\bullet+}$ amounts to 1379 kJ/mol or 14.3 eV (cf. Figure 2), which is closer to the latter value. The expected underestimation of 0.4 eV arises from on one hand an underestimation of about 0.1 eV on the IE of N_2, and on the other hand a deviation from the bond dissociation energy of **I1**$^{\bullet+}$. In their earlier work, Lin et al.[13b] evaluated this bond energy at 0.9 eV, which is smaller than the present value of 1.2

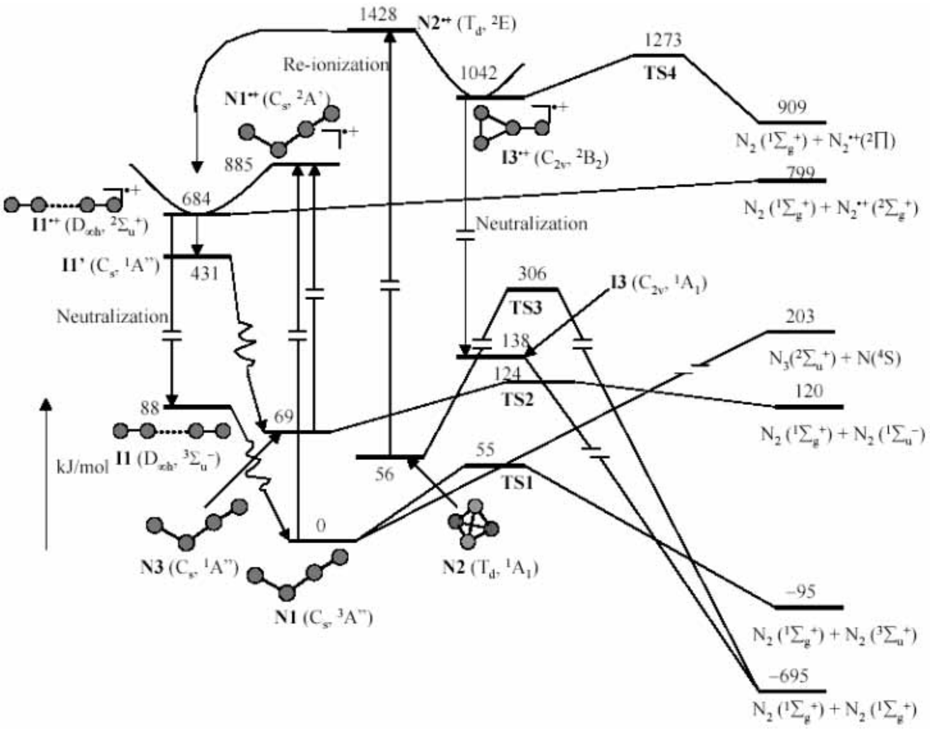


Figure 2. Schematic potential energy profiles showing the interconnections between various processes occurring on the ionized, singlet, and triplet energy surfaces on the N_4 system. **Nx**$^{\bullet+}$ stands for a vertical radical cation at the corresponding neutral geometry. Relative energies given in kJ/mol were obtained, unless otherwise noted, from RCCSD(T)/6-311+G(3df)//CASSCF(12,12)/6-311+G(d) + ZPE computations. The values related to the pathway connecting **N3**−**TS2** fragments were obtained using MRCISD+Q/6-311+G(3df)//CASSCF(12,12)/6-311+G(d). The vertical open-shell singlet neutral from **I1′** (431 kJ/mol) has a linear geometry, but the MRCISD+Q wave function was computed using C_s symmetry to obtain the $^1A''$ state. The energy scale is arbitrary.

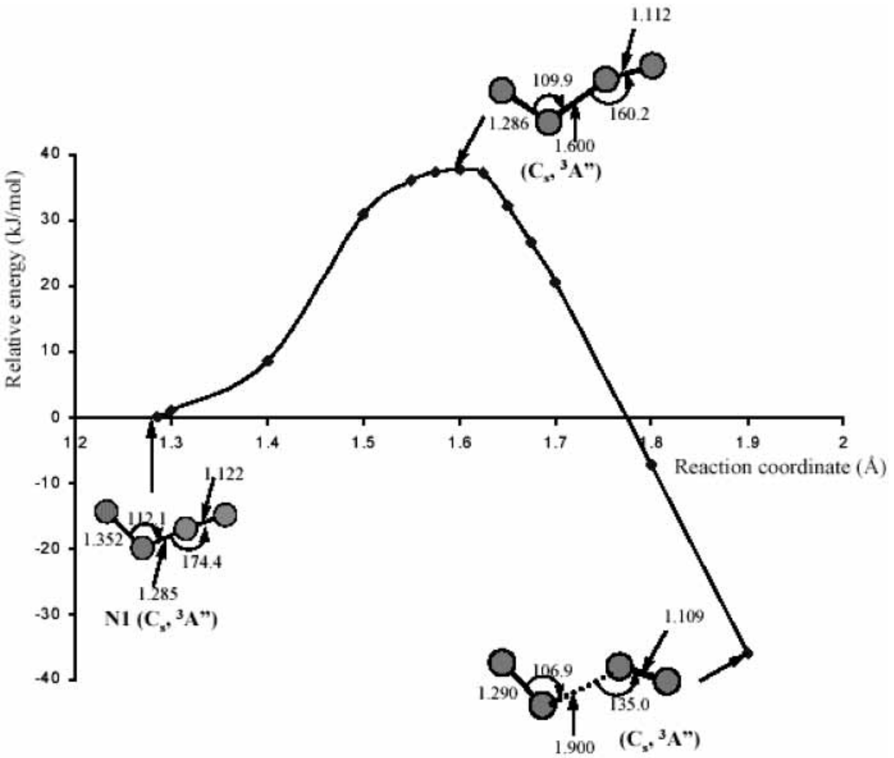


Figure 3. A potential energy profile along a reaction pathway showing the decomposition of the triplet form **N1** (or **D** in Chart 1) giving two N_2 entities. At each value of the central nitrogen−nitrogen distance which was selected as a simple but obvious reaction coordinate, all other geometrical parameters were optimized maintaining the $^3A''$ symmetry of the wave functions. Relative energies given in kJ/mol were obtained from CASSCF-(12,12)/6-311+G(d) calculations. The point of highest energy corresponds to the transition structure **TS1**.

eV (115 kJ/mol) mentioned above. It is thus important noting that in the simulation of their PE spectrum, Carnovale et al. (see Figure 3 in ref 13a) used $D_e = 0.9$ eV for the dimer cation, and assumed equilibrium distances between two N_2 entities as

3.8 Å for the neutral and 3.0 Å for the cation. Now we know that the equilibrium distances amount 4.056 Å for $(N_2)_2$ and 1.983 A for **I1**$^{\bullet+}$. How the simulated PE spectra would be changed and what would be the D_e value corresponding to their best fit remain an open question. In any case, it appears that the deviation on the IE of the dimer is not greater than 0.3 eV. By the way, we note that earlier[67] CCSD(T) calculations with the cc-pVTZ basis set, which is comparable to the present 6-311+G(3df), underestimated the experimental bond energy of N_2 by 0.51 eV, and the error is mostly (0.44 eV) due to the basis set incompleteness.

More interesting is perhaps the experimental result in which the second PES band is even broader than the first and has a maximum at 16.7 eV. Carnovale et al.[13a] proposed that this second band involved a stable dimer ion being formed from the excited $^2\Pi$ state of the N_2^+ cation. In regarding the orbital shape, this dimer ion could associate either with the triangular form **I3**$^{\bullet+}$ having a $^2B_2$ electronic state, or the rectangular geometry **I4**$^{\bullet+}$ with a $^2B_{2u}$ electronic state. In both cases, the resulting SOMO (b_2 or b_{2u}) simply arises from a destabilizing interaction between both π_u orbitals of both monomers. Nevertheless, the calculated energy differences of 3.71 eV (358 kJ/mol) between **I1**$^{\bullet+}$ and **I3**$^{\bullet+}$ and 4.25 eV (410 kJ/mol) between **I1**$^{\bullet+}$ and **I4**$^{\bullet+}$ do not match at all with the PES value of just 1.2 eV[13a] (see also ref 27). It is tempting to suggest that this second band was simply due to the $^2\Pi$ state of N_2^+ cation which corresponds to a second ionization energy of 16.66 eV of N_2 and a $^2\Pi \leftarrow {}^2\Sigma$ excitation energy of 1.14 eV of the N_2^+ cation. In fact, the PE spectrum needs not to be recorded from stable or bound N_4^+ cation.

B. Structure of the N_4 Species and Their Ionization. As mentioned above, there has been a wealth of theoretical studies carried out on the neutral N_4 species. Therefore, it is not our intention here to investigate again the entire energy surface(s), but rather we attempt to understand the ionization processes that happened in the NRMS experiment.

In their recent paper, Bittererova and co-workers[51] reported that when using the multi-configurational CASSCF(12,12) wave functions, they were not able to locate any triplet minimum having the trans form **C** shown in Chart 1. Our results concurred with this finding. All attempts to optimize a C_{2h} geometry at this level invariably led to separated entities. When relaxing the molecular symmetry from C_{2h} to C_s, we obtained the **N1** (**D**) structure. Thus, we could confirm the existence of **N1** (**D**) as an equilibrium structure at the multireference level. The question as to whether **C** exists as an equilibrium structure when larger amount of nondynamic and dynamic electron correlation could be accounted for remains largely open. For the time being, we will no longer consider **C** in following discussion. Overall, we have considered the ionization of two lowest-lying N_4 isomers in two distinct electronic states, namely, the triplet bent **N1** (**D**) and the singlet tetrahedral **N2** (**A**).

The triplet **N1** species features an open-chain skeleton and its optimized short distances and slight bending characterize an azide moiety, $N{\equiv}N{=}N^-$. Analysis of the spin density indicates that all the excess spin in **N1** is concentrated on its terminal fourth atom; this fact confers to the molecule a nitrene character. Formal replacement of the H atom in the parent NH nitrene by an azido group (N_3) simply leads to **N1**. In other words, the triplet **N1** molecule can effectively be named *azido nitrene.* This result reinforces our view[68−70] that the azido N_3 group constitutes a basic group in shaping the structure of polynitrogen N_n compounds.

At this stage, crucial information concerns the kinetic stability relative to fragmentations. The reaction (a) is found to be an endothermic process with reaction energy of 203 kJ/mol.

$$\mathbf{N1} \rightarrow N_3(^2\Sigma^+_u) + N(^4S) \qquad (a)$$

This nitrogen atom elimination corresponds to a simple bond cleavage without a transition structure. When proceeding in the opposite direction, reaction of azide radical and nitrogen atom eventually yields azidonitrene in an exothermic reaction.

$$\mathbf{N1} \rightarrow N_2(^1\Sigma^+_g) + N_2\,(^3\Sigma^+_u) \qquad (b)$$

The reaction (b) is an exothermic process with reaction energy of −95 kJ/mol. The variation of the total energy of **N1** with respect to its central bond stretching taken as the reaction coordinate, as illustrated in Figure 3, demonstrates that there is effectively a transition structure linking **N1** to the two N_2 monomers. A full geometry optimization at the CASSCF(12,12) level ended up yielding **TS1** which also holds a $^3A''$ electronic state and is characterized as a first-order saddle point by a sole imaginary frequency of 653*i* cm^{-1} (Table 1). The structure **TS1** bears a trans bent conformation with a central bond distance of about 1.6 Å. The energy barrier associated with the process **N1** → **TS1** amounts to 55 kJ/mol obtained from MRCI computations (Figure 2). Note that the energy barrier given in Figure 3 slightly differs from the latter value because the electronic energies displayed in Figure 3 were obtained using CASSCF calculations.

Let us now examine ionization of **N1** whose relevant results are described in Figure 2. Removal of an electron from triplet azidonitrene gives rise to the cation **N1**$^{\bullet+}$ in its lower-lying $^2A'$ state. The corresponding vertical ionization energy amounts to 9.17 eV (885 kJ/mol, Figure 2). Geometry relaxation from the bent vertical ion **N1**$^{\bullet+}$ invariably leads to the equilibrium linear ion **I1**$^{\bullet+}$. The large stabilization energy of 201 kJ/mol gained in going down hill from **N1**$^{\bullet+}$ to **I1**$^{\bullet+}$ arises no doubt from the breaking of the central bond which is formally an azide double bond in the former but only a long one-electron bond in the latter. In this context, the adiabatic ionization energy of azidonitrene is equal to the energy difference between **N1** and **I1**$^{\bullet+}$. A separate examination[70] of the performance of the coupled-cluster theory using similar basis sets indicates that the ionization energy of small molecules computed at this level is systematically underestimated by an average amount of 0.2 eV. Taking this empirical correction into account, the adiabatic ionization energy could be suggested as IE_a(azidonitrene) = 7.3 with a probable error of ±0.3 eV.

Regarding the singlet tetrahedrane **N2**(T_d), our calculations concurred with earlier findings[38,39,42] demonstrating that it is quite resistant against monomerization; the corresponding barrier height via **TS3** amounts to 250 kJ/mol, a value comparable to earlier results.[38,42] Its vertical radical cation **N2**$^{\bullet+}$(^2E) lies extremely high in energy, namely, 14.2 eV (1372 kJ/mol). The SOMO of **N2**$^{\bullet+}$ is doubly degenerate, and as a consequence a Jahn−Teller effect is expected to take place removing the high-symmetry tetrahedral form. Following geometry relaxation from **N2**$^{\bullet+}$, the bonds break and the rings effectively open giving the cation **I3**$^{\bullet+}$ and the resulting energy gain amounts to 4.07 eV (386 kJ/mol). The corresponding adiabatic ionization energy, being the energy difference between **N2** and **I3**$^{\bullet+}$, could thus be evaluated to be $IE_a(N_4, T_d) = 10.4 \pm 0.3$ eV, including an empirical correction of 0.2 eV mentioned above.

This certainly constitutes the main and remarkable difference between the behavior of triplet azidonitrene **N1** and singlet tetrahedrane **N2**: ionization of the former gives rise to a linear ground $^2\Sigma$ state ion **I1**$^{\bullet+}$, whereas ionization of the latter yields a cyclic excited state **I3**$^{\bullet+}$ ($^2B_2$). Due to the huge excess energy of 7.7 eV (744 kJ/mol) contained in the vertical ion **N2**$^{\bullet+}$ relative to the linear **I1**$^{\bullet+}$, it is expected that the ionic products dissociate promptly unless efficient collisional deactivation occurs. In other words, it could not be ruled out that the ion supersystem might, by collisional deactivation, directly go down to its global minimum. That is the sense of the arrow seen in Figure 2 going from **N2**$^{\bullet+}$ to **I1**$^{\bullet+}$. However, the problems arise from a possible competition between collisional deactivation and spontaneous dissociation of vibrationally excited species, which requires a different type of treatments and is not considered here.

We have also been able to locate a singlet neutral structure **N3** (Figure 1), which basically corresponds to an excited state of azidonitrene. The singlet **N3** is characterized by its open-shell electronic state, $^1A''$, having the same orbital configuration as the triplet **N1** ($^3A''$). The singlet−triplet separation of azidonitrene, which is equal to the **N1**−**N3** gap, is calculated as ΔE_{ST}(azidonitrene) = 69 kJ/mol using the MRCISD+Q in conjunction with the 6-311+G(3df) basis set and CASSCF(12,12) geometries. Separate second-order perturbation CASPT2(8,8) computations using the same basis set and geometry gave a value of 70 kJ/mol for this singlet−triplet gap.

Decomposition of **N3** occurs through the **TS2** characterized by an imaginary frequency of 732*i* cm^{-1}. This route is also inhibited by a barrier height of 55 kJ/mol obtained using MRCISD+Q calculations. The bond breaking of **N3** is endothermic by 51 kJ/mol and leads to the $N_2(^1\Sigma^+_g)$ + N_2 ($^1\Sigma^-_u$) asymptote involving thus a lower-lying open-shell singlet of molecular nitrogen. Again it is of interest to note that when operating in the opposite direction, interaction of the $N_2(^1\Sigma^+_g)$ and N_2 ($^1\Sigma^-_u$) fragments is exothermic and could easily be achieved through a small energy barrier producing an excited N_4 entity. **N3** is very close in energy to **N2** (by 13 kJ/mol) but belongs to another electronic state. In a sense, **N3** needs also to be considered as a potentially "observable" N_4 entity. However, its ionization also leads to the linear **I1**$^{\bullet+}$, and could therefore not be distinguished from **N1**.

Overall, the following points emerge so far from the calculated results: (i) both the lower-lying neutral N_4 isomers, either the triplet azidonitrene **N1** or the singlet tetrahedrane **N2**, are reasonably stable and detectable species; (ii) they exhibit completely different patterns of decomposition and ionisation; (iii) in each case, the strong difference in shape between both neutral and ionized forms gives rise to a large excess energy between the vertical and adiabatic states of the ionized or neutralized system, and thereby the process is not quite favored by the Franck−Condon effect, irrespective of the forward direction.

C. Processes in the Neutralization Reionization Mass Spectrometric Experiment. Having established the identity of neutral species and their ionization processes, we now attempt to understand the results of the NRMS experiment carried out by CPT[62] to generate the neutral N_4. The following discussion is based on the results schematically displayed in Figure 2.

Let us assume that the starting radical cation produced by electron bombardment of N_2 was the most stable linear ion **I1**$^{\bullet+}$. In the first cell of the mass spectrometer, a fraction of the ions was neutralized by electron transfer from the collision target, which is usually a noble gas (Xe) or methane gas. The latter possess moderate ionization energies (being around 12 eV) and are, in particular, good collision targets in the sense that they do not break too many neutrals being produced into fragments. When using one of these gases, the vertical neutralized species could not reach the dimer $(N_2)_2$ in its closed-shell singlet state, because the neutralization energy needed to generate the dimer (>15 eV) largely exceeds the target ionization energy (<12 eV). On the contrary, the vertical singlet open-shell state at the point **I1′** being 431 kJ/mol above **N1** could easily be reached due to its high energy content (only 253 kJ/mol of transfer energy was required, cf. Figure 2). Following geometry relaxation, the vertical neutral **I1′** is expected to attain the singlet azidonitrene **N3.** In view of the fact that this vertical entity possesses a large internal energy overwhelmingly exceeding that of the transition structure **TS2** (at 124 kJ/mol above **N1**), the nitrene **N3** does not have much chance to survive and subsequently be subjected to a reionization. In the case that a certain portion of **N3** could be formed and undergo a reionization in the second step of the NRMS experiment, the starting linear ion **I1**$^{\bullet+}$ could thus be regenerated.

For its part, the vertical triplet linear neutral form **I1** is made upon neutralization of **I1**$^{\bullet+}$ by an energy transfer of 6.2 eV from the target gas and actually at only 88 kJ/mol (0.91 eV) above its adiabatic triplet azidonitrene **N1.** It is important to note that the vertical position **I1** is about 33 kJ/mol (0.34 eV) above the transition structure **TS1** at its vibrational ground state. With such an amount of excess internal energy, the vertical **I1** does in principle possess enough energy to directly undergo a bond breaking producing $N_2(^1\Sigma^+_g)$ + N_2 ($^3\Sigma^+_u$) (reaction b), even though the energy barrier through the transition structure **TS1** amounts to about 55 kJ/mol. Using a simple RRKM treatment, the rate constants and thereby the lifetimes of singlet **N3** and triplet **N1** nitrene, starting from their vertical positions, are estimated to be in the order of femtosecond and picosecond magnitudes, respectively. Nevertheless, in view of the smaller energy difference **I1**−**N1** (88 kJ/mol) which seems to suggest more favorable Franck−Condon factors, and if the target used in the MS experiment were good collision gas (such as Xe), a small portion of the neutral equilibrium azidonitrene **N1** could be stabilized upon collision into their equilibrium form.

It is also worth mentioning that, according to CPT,[62] detection of neutral species in NRMS experiments could occur if their dissociation requires overcoming a sizable barrier, on the order of 40 kJ/mol. The **N1**, or even the **N3,** does satisfy this criterion when reacting from their equilibrium structure. It is possible that after a collision leading to the ion neutralization, some fraction of internal energy of the appearing neutral is dissipated into translational energy (and/or into internal energy of the collisional counterpart if it is a polyatomic molecule). In such a case, the internal energy of the neutral molecule formed can be below the barrier height and it could survive at the end of the neutralization step. These "survivors" could then further be selected and subjected to a reionization (using another target gas). In any case, ionization of the latter is expected to reproduce the linear radical cation **I1**$^{\bullet+}$ characterized by the "recovery" peaks of the NR spectrum.

To obtain some useful thermochemical parameters, we have computed the standard heats of formation of N_4 species. Using the G3 approach, we obtained for the tetrahedrane **N2** the value ΔH°_f (N_4, T_d) = 770 kJ/mol. This value differs significantly with the G2 value of 733 kJ/mol reported in ref 45, or 751 kJ/mol from Figure 2, but is closer to the W2-value of 762 kJ/mol.[75] This confirms the difficulty to obtain consistent and reliable results for, in particular, multiple bond nitrogen systems. Using the energy differences obtained by RCCSD(T) and MRCISD+Q calculations given in Figure 2, we could derive the following values: ΔH°_f(triplet azidonitrene) = 714 kJ/mol,

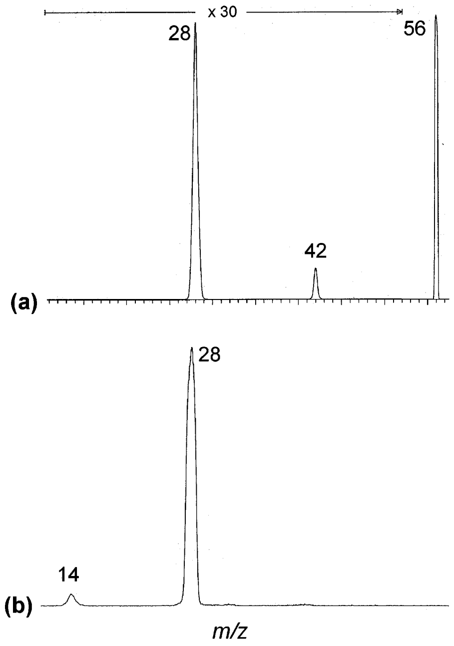


Figure 4. (a) CA spectrum (oxygen collision gas) of N_4 radical cations generated by chemical ionization of nitrogen and (b) NR spectrum of the same ions using methane as the neutralization gas and oxygen as the reionization gas. Identical NR spectra are obtained if methane is replaced by xenon or ammonia.

ΔH_f°(singlet azidonitrene) = 783 kJ/mol and $\Delta H_f^\circ(N_4^{\bullet+})$ = 1398 kJ/mol, with a probable error of ±20 kJ/mol.

D. Repeating the Neutralization Reionization Mass Spectrometric Experiment. In an attempt to reproduce the results reported by CPT,[62] we have repeated the MS experiments using our tandem mass spectrometer.[72,73] Different checks on the instrument setup were done before carrying out the manipulations. The $N_4^{\bullet+}$ radical cations were prepared in a chemical ionization source pressurized with nitrogen. Conditions were 70 eV electron energy, 2 mA emission current, 8 kV accelerating voltage, and 200 °C ion source temperature. Under these conditions, the relative abundances of the *m*/*z* 28, 42, and 56 ions formed in the ion source were 100/0.8/0.6, respectively.

The collisional activation (CA) spectrum shown in Figure 4a features two peaks at *m*/*z* 42 and 28 corresponding to the $N_3^{\bullet+}$ and $N_2^{\bullet+}$ ions. A peak at *m*/*z* 14 is also present but of lower intensity than the signal reported by CPT;[62] this is probably due to an instrumental discrimination by the off-axis photomultiplier detector in our instrument. Replacement of oxygen collision gas by helium does not modify the CA spectrum.

The NR spectra shown in Figure 4b, were recorded using three different neutralization gases, namely, methane ($IE_a = 12.5$ eV), xenon ($IE_a = 12.1$ eV), and ammonia ($IE_a = 10.1$ eV) (cf. ref 76). The ionization energies of these gases are much larger than that of triplet azidonitrene **N1** in such a way that the endothermicity of the neutralization should be supplied by the translational energy of the projectile ion. *A recovery signal corresponding to survivor ions at m*/*z* 56, was not observed at all, and the same for ions at *m*/*z* 42. It thus appears that, under our experimental conditions, the neutral tetranitrogen did not survive the neutralization step and underwent dissociation into two nitrogen molecules within a fraction of a microsecond, the calculated time-of-flight between both neutralization and reionization cells. It is worth noting again that the signal *m*/*z* 42 was absent in CPT's NR spectrum which was presumably extremely weak. The CA spectra of the survivor ions might provide some additional clues, but this was not realisable for sensitivity reasons.

It appears to us that due to a large difference between geometries of ionized and neutral structures, implying a small Franck−Condon overlap, only a very small fraction of N_4 neutrals was likely produced and characterized by CPT,[62] but this is not reproducible under slightly different experimental conditions. Another possible factor was that a neutral N_4 might be formed and then reionized in a high energy excited state, for example, a Rydberg state. Formation of metastable excited states was often invoked to explain the observation of unstable neutral in NRMS experiments.[74] In such a state, the electron is bound to the cation at long distances, but the neutral has a radiative lifetime compatible with the observed metastability, and a low probability for transition to a dissociative ground state.[74] In the absence of detailed information on the N_4 excited states, these are merely speculative interpretations of the subtleties of experimental observations.

5. Concluding Remarks

In the theoretical part of this study, we have determined the structures, stabilities, ionization, and neutralization of the tetranitrogen system related to the entire pathway occurring in a neutralization−reionization mass spectrometric procedure, starting from a linear $N_4^{\bullet+}$ radical cation. The neutral N_4 species is demonstrated to be an *azidonitrene* ($N_3{-}N$) featuring a triplet ground state and a singlet−triplet ($^1A''-{}^3A''$) energy gap of 69 kJ/mol. The singlet state corresponds to an open-shell electronic configuration. In both states, the fragmentation giving two N_2 moieties needs to overcome a barrier height of about 55 kJ/mol. The most remarkable difference between both isomers is that while ionization of the triplet azidonitrene leads to the linear radical cation in its $^2\Sigma$ ground state, removal of an electron from the singlet tetranitrogen tetrahedrane gives rise to a cyclic three-membered ring belonging to a Π-type excited state.

Neutralization−reionization mass spectrometric experiments were also performed to reproduce CPT's results. Although the CA spectrum of the $N_4^{\bullet+}$ radical cation could easily be confirmed, we could not observe a recovery signal in the NR spectrum under our experimental conditions. It is normal that when using different conditions, two MS experiments may give rise to two distinct results. However, this indicates that only a very small fraction of neutral N_4 was generated. In this context, production of the singlet tetrahedrane (N_4, T_d) upon ionization of the starting ion $\mathbf{I3}^{\bullet+}$ whose geometry differ markedly from the neutral **N2** counterpart could be regarded as a difficult task. Finally, the question on the existence of a symmetrical structure **C** needs to be clearly resolved.

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