Mass Spectroscopic Observation of [N$_3$O]$^+$

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We have observed a cation with atomic composition [N$_3$O]$^+$ via time-of-flight mass spectroscopy. This cation was observed in the reaction products of detonated liquid nitromethane. The same 58 amu species was observed when protonated, deuterated, and ^{13}C-labeled nitromethane were detonated; therefore, the only possible atomic composition of the cation is [N$_3$O]$^+$. The existence of a metastable form of [N$_3$O]$^+$ has current interest since this cation is isoelectronic with electrically neutral N$_4$. There is interest in the metastability of N$_4$ structures because such species would have very high energy content and would be very powerful explosives and propellants. We present evidence that the [N$_3$O]$^+$ structure we observe is chemically bound. The results of ab initio quantum chemical calculations at various levels of theory are presented for three [N$_3$O]$^+$ structures. These calculations indicate that two of the structures are metastable and have high energy content; calculated vibrational frequencies are presented for these two forms. A lower bound on the lifetime of the observed cation is 0.52 μs. Our results strengthen the idea that very high energy metastable forms of N$_4$ can exist.

I. Introduction

We have observed a cation with atomic composition [N$_3$O]$^+$ via time-of-flight (TOF) mass spectroscopy. The observed stability of this ion is interesting in its own right and because it is isoelectronic with N$_4$ structures. The observation of [N$_3$O]$^+$ suggests that there may exist analogous electrically neutral fairly long-lived metastable N$_4$ structures. The possible metastability of N$_4$ molecular forms is of current interest because recent theoretical work indicates that such entities, if chemically bound, would be very powerful propellants and explosives.[1] There are a number of experimental efforts in progress whose object is to synthesize chemically bound N$_4$ molecules.[2] Two such structures of interest are T_d-symmetric azatetrahedrane and the aza analogue of cyclobutadiene (i.e., D_{2h}-symmetric tetraazete). Quantum chemical calculations predict that the decomposition of either of these structures to two N$_2$ molecules would yield energies of ca. 175 kcal/mol (see ref 1e). In light of these comments, the observation of a metastable molecule isoelectronic with N$_4$ has some current interest.

An interesting piece of work, related to the current subject, is the recent observation of the N$_5$$^+$ cation by Christe and co-workers.[3] These workers were able to synthesize up to 1/2 g quantities of an AsF$_6$$^-N_5$$^+$ salt and to study its properties mass spectrometrically.

II. Results

Our observations of [N$_3$O]$^+$ were made with the LANL Detonation Chemistry Apparatus; this apparatus has been described in detail elsewhere.[4] Briefly, this apparatus is a TOF mass spectrometer with sufficient size and differential pumping to directly sample the gaseous products of detonation of small samples of explosive without any wall collisions between the expansion of the detonation products and the entry into the mass spectrometer. Our observations were made in the reaction products of detonated liquid nitromethane (NM) [i.e., CH$_3$NO$_2$]. The experimental details associated with the NM experiments can be found in ref 5. For the purposes of this paper, what is important is that a cation with mass 58 amu was observed when protonated NM was detonated and *also* when the same experiment was performed with the ^{13}CH$_3$NO$_2$ and CD$_3$NO$_2$ isotopomers of NM. These results show that no hydrogen or carbon atoms are present in the cation. There are no mass peaks within 3 amu lower than 58 amu in the unlabeled NM that could have been shifted to 58 amu in the labeled experiments. Therefore, one cannot avoid the conclusion that the only possible atomic composition of the cation is [N$_3$O]$^+$.

There have been earlier observations of a weakly bound form of [N$_3$O]$^+$;[6] the measured binding energy of this entity is 4.6 $\pm$ 0.3 kcal/mol.[6d] Clearly, this binding energy is much smaller than that for a chemically bound structure. This weakly bound entity was observed in low-pressure discharges and also at high altitude (in the ionosphere). Because we are seeing [N$_3$O]$^+$ under high-mass-density and high-temperature conditions, it is probable that our form is not a weakly bound cluster; we present further arguments in this vein below.

Since there are, at least, two qualitatively distinct structural forms of [N$_3$O]$^+$ (i.e., a chemically bound molecule or a weakly bound cluster), it is important to try to determine which type of structure is being observed in our experiments.

We believe there are three possibilities for where and how the species is produced in our instrument. These are: (1) the observed species is chemically bound and it is either the parent ion of a neutral molecule of the same stoichiometry or a fragment ion from a more massive (neutral) molecule formed in the very high-pressure reaction zone of detonating NM; (2) it is a weakly bound (neutral) cluster of N$_2$ and NO and is formed during the early stages of the expansion of the detonated material into the vacuum and then is later ionized in the electron beam ionizer of the mass spectrometer; (3) it is a bound complex and is formed from NO$^+$ or N$_2$$^+$ collisions with other neutral molecules in the ionization region of the spectrometer. Note that only electrically neutral species can reach the ionization region of our instrument which is charged to +3800 V with respect to the chamber walls.[4]

**TABLE 1: Absolute Energies (Hartree) For [N₃O]⁺ and Related Structures[a]**

molecular structure	6-31G*[b]		6-31+G(d)[b]			
	(U)RHF	(U)MP3	(U)RHF	(U)MP2	(U)MP3	(U)MP4(DQ)
"tetrahedral" [N₃O]⁺	−0.4869841	−1.1716550	−0.4929633	−1.2140022	−1.1806298	−1.1839922
"linear" [NNNO]⁺	−0.697236	−1.2880356	−0.7016875	*c*	−1.2959334	−1.3014861
[NO]⁺	−0.9096528	−1.2235802	−0.9124881	−1.2469778	−1.2277423	−1.2375574
N₂	−0.9439495	−1.2477530	−0.9470241	−1.2619292	−1.2532484	−1.2588260

[a] Unrestricted methods (e.g., UHF) were used for the "linear" [N₃O]⁺ form and restricted methods (e.g., RHF) for the other structures. [b] To obtain the absolute energies for the "tetrahedral" and "linear" structures, subtract 237. For NO⁺ and N₂, subtract 128 and 108, respectively. [c] We were unable to find an optimum geometry at this level of theory.

TABLE 2: Energies[a] (kcal/mol) of [N₃O]⁺ Relative to N₂ + NO⁺

basis/method	"tetrahedral" [N₃O]⁺	"linear" [NNNO]⁺
6-31G*		
(U)RHF	230.1	98.4
(U)MP3	188.1	115.0
6-31+G(d)		
(U)RHF	230.0	99.0
(U)MP2	185.1	*b*
(U)MP3	188.4	116.0
(U)MP4(DQ)	196.0	122.3

[a] Unrestricted methods (e.g., UHF) were used for the "linear" [NNNO]⁺ form and restricted methods (e.g., RHF) for the "tetrahedral" [N₃O]⁺ structure. [b] We were unable to find an optimum geometry at this level of theory.
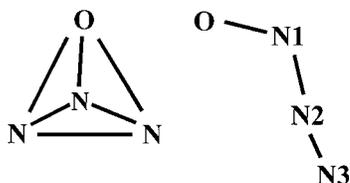
Figure 1. "Tetrahedral" (left) and "linear" (right) forms of [N₃O]⁺.

We discuss the relative likelihood of these three possibilities in order. Evidence for the structure being chemically bound is as follows. It is known that the very high pressures generated by strong shocks or detonation waves (ca. 150 kbar in the case of detonating liquid NM) can cause condensation reactions that result in chemically bound structures with significantly higher internal energies than that of the molecules originally present. An example of this is the formation of dimerized anthracene when crystalline anthracene is shocked to pressures greater that ca. 176 kbar.[7] At this shock strength, the internal energy of the anthracene is increased by ca. 4.3 eV/molecule (8.6 eV per two molecules; i.e., 198 kcal/mol); hence, it is possible to produce high-energy metastable molecular species via shockloading.

To strengthen the idea that the [N₃O]⁺ structure we are observing is a chemically bound structure, we have done ab initio quantum chemical calculations at six levels of theory to examine whether such structures are stable and to obtain estimates of their energetics. The energies that result from these calculations are summarized in Tables 1 and 2. The calculations were done with the Gaussian-98 computer code on a PC.[8] Two chemically bound stable forms of [N₃O]⁺ were found; i.e., a "linear" C_s-symmetric molecule and a C_{3v}-symmetric ("tetrahedral-like") one (see Figure 1). Note that, in the C_s-symmetric "linear" structure, the constituent atoms do not actually all lie on a line. The geometric parameters of the structures are presented in Table 3, and the harmonic vibrational frequencies are presented in Tables 4 and 5. It is worth noting how close the C_{3v} [N₃O]⁺ structure is to tetrahedral (see Table 3). For example, the N−N and N−O bond lengths in the structure differ by only 0.038 Å, and the ∠N−N−O angle differs by only 0.9° from 60° at the highest level of theory used (i.e., MP4(DQ)/6-31+G(d)). Thus, the isoelectronic nature of [N₃O]⁺ and N₄ produces "tetrahedral" structures with very similar geometries.

A point of interest in relation to the level of theory used is the lack of significant changes in the geometric parameters of the molecules when diffuse functions are added to the basis set. The largest change in any bond length (e.g., in going from a (U)MP3/6-31G* calculation to a (U)MP3/6-31+G(d) one) is 0.002 Å, and the largest change in bond angle is 0.5° (see Table 3). A similar statement applies to the computed relative energies (see Table 2), where increasing the complexity of the basis set results in a change in relative energies of, at most, 3 kcal/mol. Upgrading the level of perturbation theory produces larger changes in both the geometries and the relative energies.

A computational search was also made for a metastable form of the N₃O⁺ analogue of azabutadiene. No evidence was found for the metastability of such a structure. When started from reasonable initial geometry guesses, the G98 geometry optimization algorithm followed paths leading to N₂ and NO⁺, rather than to a ring structure.

If the structure we are observing in the mass spectrometer is chemically bound, then based on energy considerations alone, it is likely to be the "linear" C_s-symmetric form, since its energy

TABLE 3: Geometries[a] of [N₃O]⁺ Structures Obtained from Various Levels of Theory

molecular structure	6-31G*[b]		6-31+G(d)[b]			
	(U)RHF	(U)MP3	(U)RHF	(U)MP2	(U)MP3	(U)MP4(DQ)
"tetrahedral" [N₃O]⁺						
R_1 (N−O)	1.444	1.475	1.443	1.522	1.475	1.483
R_2 (N−N)	1.372	1.450	1.372	1.494	1.450	1.445
A_1 (∠NNO)	61.6	60.6	61.6	60.6	60.6	60.9
"linear" [NNNO]⁺						
R_1 (O−N₁)	1.249	1.231	1.250	*c*	1.233	1.234
R_2 (N₁−N₂)	1.331	1.352	1.332		1.354	1.379
R_3 (N₂−N₃)	1.085	1.092	1.085		1.092	1.093
A_1 (∠ON₁N₂)	111.2	114.4	110.9		113.9	112.9
A_2 (∠N₁N₂N₃)	170.5	172.2	170.5		172.1	172.9

[a] Bond lengths are in Å and angles in degrees. [b] Unrestricted methods (e.g., UHF) were used for the "linear" [N₃O]⁺ form and restricted methods (e.g., RHF) for the "tetrahedral" structure. [c] We were unable to find an optimum geometry at this level of theory.

TABLE 4: "Tetrahedral" (C_{3v}) [N3O]+ Vibrational Frequencies (cm^{-1})

basis/method mode symmetry	mode 1 E	mode 2 E	mode 3 A1	mode 4 E	mode 5 E	mode 6 A1
6-31G*						
RHF	742	742	971	1107	1107	1624
MP3	764	764	980	986	986	1352
6-31+G(d)						
RHF	741	741	972	1109	1109	1626
MP2	677	677	881	923	923	1112
MP3	760	760	978	986	986	1353
MP4(DQ)	736	736	966	973	973	1354

TABLE 5: "Linear" (C_s) [NNNO]+ Vibrational Frequencies (cm^{-1})

basis/method mode symmetry	mode 1 A′	mode 2 A″	mode 3 A′	mode 4 A′	mode 5 A′	mode 6 A′
6-31G*						
UHF	273	400	655	754	1404	2343
UMP3	278	459	525	700	1424	3224[b]
6-31+G(d)[a]						
UHF	269	405	657	756	1397	2340
UMP3	272	447	521	696	1410	3244[b]
UMP4(DQ)	271	442	500	580	1382	3453[b]

[a] We were unable find to an optimum geometry for this molecular structure at the (U)MP2 level of theory; therefore, no frequencies were computed. [b] Note the very high frequency of mode 6 when computed with correlated methods. MP4(DQ)/6-31G+(d) frequencies for N_2 and NO^+ are 2405 and 2421 cm^{-1}, respectively; these results are higher than the experimental values by less than 50 cm^{-1}. The normal mode motion corresponding to mode 6 of the linear form resembles an N–N stretch with small motions of the other two nuclei.

relative to $NO^+ + N_2$ (ca. 118 kcal/mol; see Table 2) is significantly less than the same relative energy for the C_{3v} form (ca. 192 kcal/mol). However, we emphasize that energy considerations may not be the dominant factor, as indicated by the anthracene results noted above.

The reader should note that we cannot experimentally distinguish whether the ion we observe is from a direct ionization of a neutral molecule with the same stoichiometry as the observed ion or whether it arises as a fragment ion of a dissociative ionization product of a more massive molecule. We support the latter mechanism as the probable source of the ion, since such processes are known to occur frequently during electron impact in mass spectroscopy. We have also observed other ions from the reaction zone of NM that have masses considerably greater than $m = 58$ but which cannot definitively be correlated with the $m = 58$ ion.[5]

Evidence against a weakly bound electrically neutral [N3O] complex being formed in the early stages of the expansion (i.e., case 2 of the three possible modes of formation outlined above) is as follows. The temperatures present in the detonating liquid NM and in the early stages of expansion of the reacting material are high. In the reaction zone of detonating liquid NM, temperatures are of the order of 2500 K.[9] Such temperatures do not favor the formation of weakly bound electrically neutral complexes. Furthermore, during the multiple mass spectral scans taken during observations of the species resulting from the detonation, the observed intensity of [N3O]+ does not correlate well with the observed intensities of NO^+ and N_2^+. Also, the presence of the [N3O]+ peak is unique, in our experience, to when liquid NM is detonated. In observations on eight other condensed-phase high explosives that contain nitrogen and oxygen atoms within the explosive molecules, we have never seen a peak at 58 amu. This argues against a weakly bound species being formed in the expansion since NO and N_2 are

present in all eight cases. It argues for a chemically bound electrically neutral species formed in the detonation reaction zone of NM, which is unique to NM's reaction zone chemistry.

The possibility of the formation of a [N3O]+ complex during the ionization process in the spectrometer (i.e., case 3 of those outlined above) can be argued against based on the molecular number densities in the ionization region and on the typical rates for ionic association reactions. Typical ion–molecule reactions[10] have rate coefficients of 10^{-9} molecules cm^3/s and lead to time-independent rates of formation of products, if the concentration of reactants remains constant. Using the maximum estimated total number density of molecules in the ionizer[4] of 10^{14} molecules/cm^3 and the ca. 1 μs duration of the ionization pulse, we calculate the production of new ions (such as a weakly bound complex) in the ionizer to be too small to explain our observations. For example, a likely reaction would be N_2^+ with unreacted NM, but this would mean that the $m = 58$ signal would be less than 1% of the observed N_2^+ signal, while the $m = 58$ ion signal is actually larger than the N_2^+ signal. Various other candidate reactions in the ionizer have also been considered and lead to the same conclusion. Also, as already mentioned, we do not see the molecular species at 58 amu in the detonation of eight other condensed-phase explosives that contain N and O atoms. If an ion–molecule reaction were the source of the signal at 58 amu, one would expect to see the 58 amu peak in these other explosives also, and we do not.

Therefore, of the three possible modes of formation of [N3O]+, the above discussion points to a chemically bound parent molecule that is formed in the very high pressure reaction zone chemistry of detonating NM.

We can put bounds on the lifetimes of the neutral precursor molecule and the 58 amu ion as follows. The neutral parent has a lifetime greater than the scan number (minus 1) at which the ion is observed multiplied by the time between scans; i.e., 13×12 μs $= 156$ μs. The mass 58 cation has a lifetime at least as great as the time the ion spends in the acceleration region of the spectrometer after ionization takes place; this value is calculated to be 0.52 μs.

III. Conclusions

The above results are evidence for a chemically bound cation with molecular structure [N3O]+. The lifetime of this cation is at least 0.52 μs. [N3O]+ is isoelectronic with electrically neutral N_4. Consequently, the existence of a chemically bound metastable form of [N3O]+ cation points to the likelihood of the existence of an analogous form of N_4. Chemically bound N_4 structures are of significant interest due to their very high energy content; there are several groups that are, at present, attempting to synthesize such molecules. Our observation of a metastable form of [N3O]+ suggests that these efforts have a possibility of success.

Ab initio calculations up to the MP4(DQ)/6-31+G(d) level of theory were used to determine the stability, geometry, and energetics of two distinct geometrical forms of chemically bound [N3O]+; a triplet biradical "linear" C_s-symmetric form and a singlet tetrahedral-like C_{3v}-symmetric structure. The C_{3v} structure contains ca. 74 kcal/mol more energy than does the C_s structure. On the basis of this, we maybe observing the "linear" C_s form in our experiments, although energy considerations alone are not sufficient to decide the issue. The lowest calculated vibrational frequencies for the two [N3O]+ structures indicate that the tetrahedral-like structure is much more rigidly defined by its energy hypersurface than is the "linear" biradical structure, with the lowest vibrational frequencies in the two cases being

736 and 271 cm^{-1}, respectively, at the highest level of theory used (see Tables 4 and 5). Similar calculations on a third structure (i.e., the $[N_3O]^+$ analogue of azabutadiene) produced no evidence for the metastability of such a molecule.

We speculate that the source of the electrically neutral parent molecule of the observed $[N_3O]^+$ structure is the result of a condensation reaction or reactions in the reaction zone of detonating NM, since such reactions will be strongly enhanced by the very high pressure (ca. 130 kbar) in that region.

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