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# Metastable Dissociation Study of Nitric Oxide Clusters

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Mass spectra of neat $(NO)_n^+$ clusters and mixed $(N_2O)_m(NO)_n^+$ and $(NO_2)_m(NO)_n^+$ clusters are obtained and investigated by nonresonant multiphoton ionization with a femtosecond laser. Intensity alternations observed in the mass spectra of neat NO clusters are explainable in terms of the pairing of the number of total valence electrons in the cluster. A series of $(N_2O)(NO)_n^+$ ($n \geq 3$), which is also observed when pure NO sample gas is used, is suggested to be the product of intracluster reactions of pure NO clusters occurring after ionization. For the series of $(NO)_nN_2O^+$ clusters a polymerized core ion structure is proposed to account for its intensity distribution and the observed metastable decay pathways.

## Introduction

Oxides of nitrogen are chemical compounds of the two most abundant elements in earth's atmosphere: oxygen and nitrogen. The simplest thermally stable form of an oxide of nitrogen is nitric oxide, NO, of which the electronic structure and reaction chemistry have been extensively studied since its discovery 200 years ago. The important role of NO, together with its cousins $NO_x$, in atmospheric pollution puts the NO molecule into the focus of environmental chemistry research.[1,2] In the late 1980s, studies of the free radical NO have been expanded into the fields of biochemistry and physiology ushering into NO being named "Molecule of the year" by *Science* magazine[3,4] in 1992.

Nitric oxide, NO, is an unusual molecule which has the character of a free radical with one unpaired electron, giving it some tendency to dimerize; but unlike nitrogen dioxide, it dimerizes only when it is cooled to very low temperatures. On dimerization a N−N $\sigma$-bond is formed which is unexpectedly long and weak.[5] However, this weak tendency of dimerization and electron pairing is strong enough to cause the intensity alternation in mass spectra of nitric oxide clusters.[6−8] Regarding the origin of alternations of cluster ion distributions, there is still a debate with differing opinions as to whether the alternation reflects the distribution of neutral clusters or is the result of redistribution after ionization caused by different stabilities of the formed product ions.

In this work, both pure nitric oxide NO clusters and its mixed clusters with nitrous oxide $N_2O$ and nitrogen dioxide $NO_2$ are studied. Intracluster reactions during the ionization of neat nitric oxide clusters are observed and discussed. Metastable dissociation studies give insight into the origins of intensity alternations, binding strength, and cluster structures.

## Experimental Section

The laser-based reflectron time-of-flight mass spectrometer used in our studies has been described in detail in previous puplications.[9,10] Briefly, neutral clusters are formed by supersonic expansion through a pulsed nozzle (150 $\mu$m diameter), and then ionized by a focused ($f = 50$ cm) laser beam. The laser system is a mode-locked Ti:sapphire femtosecond laser which has an oscillator (Spectra Physics, Tsunami 3955) pumped by a 10 W $Ar^+$ laser (Spectra Physics, Beam Lock 2060) and a regenerative amplifier (Positive Light) pumped by a 10 Hz Nd:YAG laser (Spectra Physics, GCR 150-10). Following frequency doubling, the final output is typically 1 mJ/pulse at 400 nm with a pulse duration around 100 fs. To reduce the pump oil background, the ionization region is differentially pumped by a turbomolecular pump. The ionic clusters are accelerated by a double-stage electric field and focused with a group of ion lenses before entering a 145 cm long field-free region which terminates at a reflectron. Following the reflector, the ions travel 100 cm backwards where they are detected by a chevron microchannel plate (MCP) and recorded using a 100 MHz transient recorder.

Nitric oxide sample gas with 99% min purity was purchased from Matheson and for some experiments used without further purification. In selected experiments the sample gas was purified according to the following procedure. The commercial nitric oxide was first frozen out in a cooling trap maintained at liquid nitrogen temperature. Then the temperature was raised to 147 K using a slush bath of pentane and liquid nitrogen. The temperature of this slush bath is slightly above the boiling point of NO (bp 121.3 K) but far below those of $N_2O$ (bp 184.6 K) and $NO_2$ (bp 251.6 K); therefore only NO is released from the cooling trap. The experimental results show that most impurities such as $N_2O$, $NO_2$, and $H_2O$ etc. can be removed by this purification process.

## Results and Discussions

Investigation of the ions formed from ionization of a supersonic jet of NO shows two distinct series of cluster ions. A series of pure $(NO)_n^+$ cluster ions, which is discussed in the first section of this chapter, and a series of $N_2O(NO)^+$ cluster ions treated in the second section. The final section describes findings from metastable dissociation studies on these clusters and results from calculations used to explain the experimental observations.

**Pure NO Cluster Series.** To obtain pure nitric oxide cluster ions, it is critical to choose proper experimental conditions regarding both ionization of the neutral clusters and the preparation of these neutrals by controlling the supersonic expansion conditions. Although the ionization potential for NO is low (9.25 eV), in previous experimental attempts with nanosecond multiphoton ionization, using 532 and 355 nm light, only the $NO^+$ monomer could be observed. This is assumed to be due to predissociation on the one- or two-photon level, as has been found for the NO dimer.[11] Using the high photon

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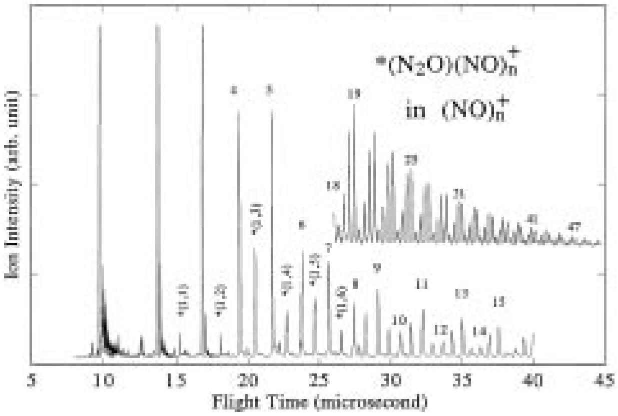

**Figure 1.** TOF mass spectrum of NO cluster ions obtained with purified nitric oxide sample gas. It shows the pure $(NO)_x$ and the mixed $(N_2O)(NO)_m$ series.

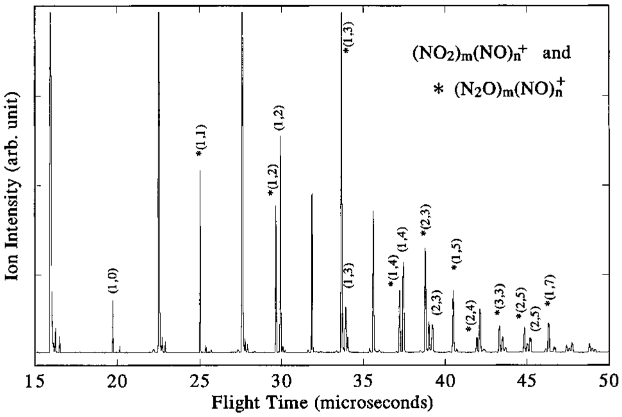

**Figure 2.** Mixed cluster series obtained with unpurified NO sample gases.

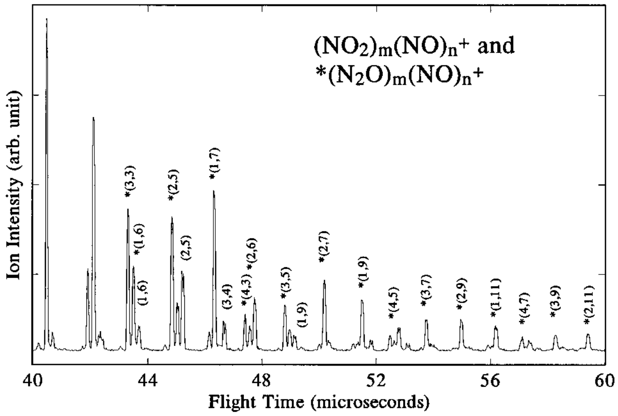

**Figure 3.** TOF mass spectrum of cluster ions using unpurified NO gas: multiple $N_2O$ and $NO_2$ are found in mixed clusters.

flux of a femtosecond laser as the multiphoton ionization source, predissociation of clusters is greatly suppressed and therefore NO cluster ions are produced. However, the signal intensity of NO clusters depends strongly on the carrier gas and mixing ratio used in the supersonic expansion. Our experimental results show that to obtain appreciable signals of neat NO clusters, argon is the best carrier gas and the best NO/Ar mixing ratio is 5−10% at a total backing pressure of approximately 3 bar. When the mixing ratio is below 5%, mixed clusters of $Ar_m(NO)_n^+$ start to become dominant[12] over those corresponding to pure $(NO)_n^+$. On the other hand, a high percentage of NO in the expansion mixture does not facilitate obtaining larger clusters, but rather in some situations it can even cause decreasing signals of the large clusters. However, high total pressure obviously helps to cool the clusters.

Figure 1 shows a time-of-flight mass spectrum of NO clusters where an odd−even alternation can easily be seen as the overall distribution displays a decrease with cluster size. The phenomenon of odd-$n$ $(NO)_n^+$ being more abundant than even-$n$ has been reported earlier by other groups.[5−8] In our experiment, both odd- and even-$n$ series for $(NO)_n^+$ are observed up to $n = 50$, while only odd-$n$ clusters are detected for $n > 21$ by Desai et al.[8] Each series follows a different decrease in intensity with increasing cluster size, with the decreasing rate for the odd-$n$ series being faster than that of the even-$n$ series. Hence, the intensity difference between the two series gradually decreases and finally disappears as the cluster size increases.

Since nitric oxide is a free radical which has an unpaired electron, forming pairs could increase the stability of NO clusters. Therefore, there are two factors that may lead to the abundance of odd-$n$ cluster ions: one is more stable neutral even-$n$ clusters with paired electrons, which are harder to ionize than odd-$n$ neutral clusters; the other is more stable odd-$n$ cluster ions with an even number of total valence electrons, which are favored during dissociation/redistribution after photoionization.

One-photon photoionization threshold studies of $(NO)_n$ clusters found that the ionization potentials of $(NO)_n$ clusters did not alternate, at least within the experimental limit.[13] Furthermore, the multiphoton ionization method used in our experiment is a nonresonant "hard" ionization so that even possible ionization potential alternations should not make much difference in ionization cross sections of these clusters. On the other hand, based on our studies of other cluster systems, we concluded that small differences in the stability of ionic clusters can play an important role in the dissociation of clusters after ionization, as has been found previously for protonated water clusters[9] and $Xe_n^+$ clusters.[14] The observed abundance alternations in the final ion distributions is therefore explainable by simple electron-counting rules. Cluster ions with an even number of NO moieties have one unpaired electron, whereas odd NO cluster ions have an even electron count. In this simple approach the latter series should be more stable than the even NO clusters. Further evidence that the predominant abundance of odd $(NO)_n^+$ clusters ions is not the result of hard-to-be-ionized neutral NO pairs is provided by our metastable dissociation studies which show that, although there is a two NO molecule loss channel for large clusters, the major dissociation channel open for all clusters is NO monomer loss. This implies that the binding of a NO pair is not very strong, even though pairing should be favored.

**$N_2O$/NO Cluster Series.** In mass spectra obtained with unpurified NO sample gas in which $NO_2$ and $N_2O$ are also present as impurities, as well as with premixed NO/$N_2O$ gas samples, mixed composition $NO_2$/NO and $N_2O$/NO cluster ions can be observed additional to $(NO)_n^+$; see Figures 2 and 4, respectively. Interestingly, these mixed cluster series follow different odd−even intensity alternation patterns giving further evidence that the intensity alternation is caused by the electron count of the formed cluster ions.

$(NO_2)_m(NO)_n^+$ mixed cluster ions with $p = m + n$ show pronounced intensity when the total number of molecules $p$ is odd, similar to pure NO cluster ions. Since $NO_2$ has an odd number of valence electrons, electron pairing remains the same without regard to the substitution of NO by $NO_2$. $N_2O$ on the other hand has an even valence electron count. Therefore, an odd number of $N_2O$ molecules in $(N_2O)_q(NO)_r^+$ clusters changes the electron pairing pattern with regard to the total number of molecules $s = q + r$, while an even number of $N_2O$ molecules will keep the same odd−even alternations. It can be seen in Figures 2 and 4 that clusters with an even total number of

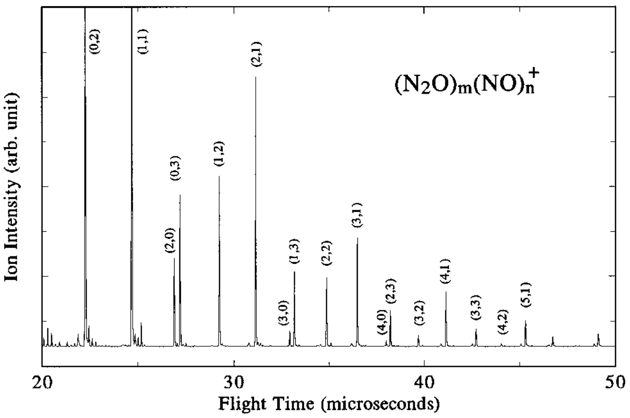

**Figure 4.** TOF mass spectrum of premixed $N_2O$/NO sample: mixing ratio 1:4.

molecules $s$ are more abundant when $q = 1, 3, 5, ...$, whereas for $q = 2, 4, ...$, higher intensity is observed when $s$ is odd. Obviously this simple electron-counting rule is not only applicable for neat NO clusters but also holds true for mixed clusters. Hence, we conclude that the odd−even alternations of the final distributions of neat NO cluster ions and mixed $N_2O$/NO and $NO_2$/NO cluster ions are due to the pairing of total valence electrons in the cluster.

In contrast to the mixed $(NO_2)(NO)_n^+$ series which is observable only when unpurified sample gas is used, $(N_2O)_m(NO)_n^+$ cluster ions are found in mass spectra of both unpurified and purified samples, irrespective of how carefully the sample gas is purified. Figure 1 shows a mass spectrum recorded with nitric oxide sample gas purified according to the procedure described in the experimental part. Signals assigned to $(N_2O)(NO)_n^+$ have been found to be independent of the NO/Ar mixing ratio. Moreover, the intensities of $(N_2O)(NO)_n^+$ clusters are comparable with the intensities of neat $(NO)_n^+$ clusters for larger size clusters. It is well-known that $N_2O$ and $NO_2$ impurities are produced under the high-pressure conditions existing inside a gas cylinder by the reaction $3NO \leftrightarrow N_2O + NO_2$. Accordingly, commercial nitric oxide cylinders usually contain a certain amount of $N_2O$ and $NO_2$ impurities.[15]

Therefore, the observation of mixed cluster ions in the mass spectra of unpurified NO sample gas can be attributed to the existence of impurities inside the nitric oxide cylinders. The experimental finding that $(N_2O)(NO)_n^+$ cluster ions are also formed in the expansion of neat nitric oxide raises a question as to whether this gas is not completely purified or if cluster ions of this composition are formed from pure NO clusters during or shortly after the ionization process. Strikingly, the intensity distribution of $(N_2O)(NO)_n^+$ cluster ions observed for purified NO samples is different from that found for the unpurified samples. The mass spectra of the purified samples display intensities of $(N_2O)(NO)^+$ and $(N_2O)(NO)_2^+$ which are very small compared to $(N_2O)(NO)_3^+$ (see Figure 1), whereas in case of the unpurified samples, $(N_2O)(NO)^+$ and $(N_2O)(NO)_2^+$ signals are observed which have about half the intensity of $(N_2O)(NO)_3^+$ (see Figure 2) and more strikingly both $N_2O$/NO and $NO_2$/NO mixed clusters are observed in unpurified sample experiments, while for clusters formed from purified samples, the only mixed series is one comprised of $N_2O$/NO. Furthermore it is found that clusters containing more than one $N_2O$ or $NO_2$ are only obtained with unpurified samples (Figure 3) but not with purified ones.

According to the disproportionation reaction of NO, the same amount of $NO_2$ and $N_2O$ should be generated inside a high-pressure cylinder. Melia's[15] infrared analysis showed the impurities in a commercial cylinder to be about 1% $NO_2$ and 1% $N_2O$. Assuming that the ionization cross sections of mixed clusters are essentially independent of composition, simple statistical calculations show that both $N_2O$/NO and $NO_2$/NO mixed cluster series should be present starting with the monomer peaks $N_2O^+$ and $NO_2^+$ and for larger size clusters mixed ions $(N_2O)_m(NO)_n^+$ and $(NO_2)_m(NO)_n^+$ with $m > 1$ should be observable even if the impurities are less than 1%. The mass spectra recorded using unpurified samples show exactly the expected cluster ions with the proper intensity distribution, except for the missing peak of $N_2O^+$. Failure to observe this species is attributable to its high ionization potential of 12.89 eV, which makes it impossible to ionize $N_2O$ with the present laser system. Further studies with premixed $N_2O$/NO samples showed that mixed $(N_2O)_m(NO)_n^+$ cluster ion signals can be greatly enhanced in all combinations (Figure 4). Hence, it may be concluded that the $N_2O(NO)_n^+$ series in purified NO experiments is caused by other factors rather than the presence of preexisting impurities.

It is well-known that NO easily disproportionates at elevated pressures according to $3NO \leftrightarrow N_2O + NO_2$. Neutral clusters of NO can be considered as a very high-pressure gas system in view of the intermolecular distances given in the cluster. When the neutral clusters are ionized by multiphoton ionization, excess energies provide cluster ions with a high-temperature environment. Therefore, the $(N_2O)(NO)_n^+$ ($n \geq 3$) cluster series in neat NO experiments could be interpreted as the result of intracluster reactions following ionization, although based on the above the possibility of disproportionation reactions in the formed neutral cluster cannot be excluded. A possible reaction channel leading to this cluster series could be

$$(NO)_n^+ \Rightarrow (NO)^+(N_2O)(NO)_{n-4} + NO_2$$

The preferred formation of clusters containing exactly one $N_2O$ molecule indicates that formation of a molecular unit rather than just dipole interactions is operative in producing these clusters, especially as $N_2O$ with the lower dipole moment ($\mu = 0.166$ D) should be more likely to leave the cluster than $NO_2$ ($\mu = 0.316$ D).

Experiments by Desai et al.[8] showed that in mixtures of 1% $N_2O$/5% NO/95% Ar clusters of the stoichiometry $(NO)_3(N_2O)_n^+$ are the dominant series, indicating a special stability of the NO trimer unit with one or more $N_2O$ attached to it. Jones et al.[16] have performed calculations on both open-chain and cyclic polymeric neutrals and ions of NO. Although in neither case has a special stability been found, a cyclic structure seems to be reasonable for the trimer. However, these calculations indicate that formation of both the neutral and ionic trimer ring is endothermic, whereas addition of a further $N_2O$ molecule to a preformed $(NO)_3^+$ ring is exothermic. Although according to these calculations $(NO)_3N_2O^+$ is unstable toward dissociation into $2NO + N_2O + NO^+$, our experiments show that the $(NO)_3^+$ ion does not appear to be of pronounced stability in the pure NO cluster series, whereas $(NO)_3N_2O^+$ is the first ion in the $N_2O(NO)_x^+$ cluster series to appear with high intensity. Unlike the calculations by Jones and Desai's experiments with premixed samples, in our experiments no evidence for formation of clusters containing more than one $N_2O$ moiety could be found. This supports our suggestion that $N_2O$ is formed during the ionization process and not via neutral disproportionation reactions during expansion or inside the sample gas tank

**Metastable Dissociation Study.** To obtain further structural information on NO and its mixed cluster ions with $N_2O$, metastable dissociation studies were carried out to determine the dissociation channels of these clusters after they have entered

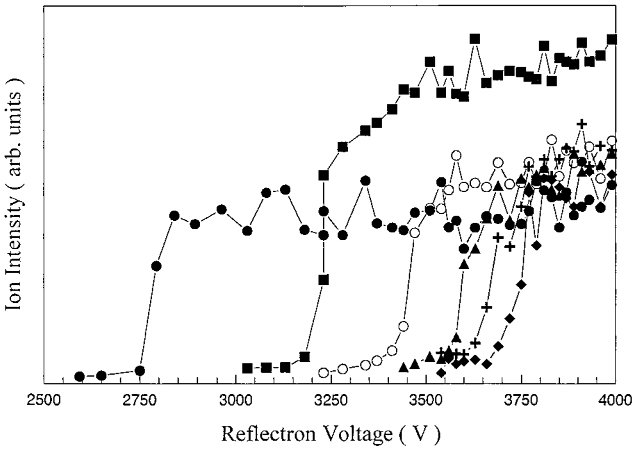

**Figure 5.** Cutoff study of $(N_2O)(NO)_n^+$ clusters. The diagram shows the measured intensities versus the reflectron voltage for $(N_2O)(NO)_3^+$ (●), $(N_2O)(NO)_4^+$ (○), $(N_2O)(NO)_5^+$ (■), $(N_2O)(NO)_6^+$ (▲), $(N_2O)(NO)_7^+$ (+), $(N_2O)(NO)_8^+$ (♦).

**TABLE 1: Metastable Decomposition Channels for $(NO)_n^+$ and $(N_2O)(NO)_n^+$ Clusters**

| clusters | major channel | minor channel |
|---|---|---|
| $(NO)_n^+$ | $-NO$ | $-(NO)_2$ (seen for large *n*) |
| $(N_2O)(NO)_n^+$ ($n = 4$, $n \geq 6$) | $-NO$ | $-(NO)_2$ (seen for large *n*) |
| $(N_2O)(NO)_n^+$ ($n = 3, 5$) | $-N_2O$ | |

the drift region of the time-of-flight instrument (Table 1). Details of this method have been described in previous publications.[14,17]

Pure $(NO)_n^+$ clusters show a major NO monomer loss channel for all investigated cluster sizes, while there is a much smaller secondary channel corresponding to the loss of two NO molecules, probably as $(NO)_2$; this is observed for clusters larger than the pentamer. This result reflects the fact that the NO pair is not strongly bonded since single NO loss is still the preferred channel even for odd-*n* cluster ions where formation of NO dimers can be assumed.

Interesting results have been found in our metastable studies for $(N_2O)(NO)_n^+$ cluster ions which give hints regarding structures and bonding. Measured intensities versus the reflectron voltage are plotted in Figure 5. All larger $(N_2O)(NO)_n^+$ clusters show a loss of NO which occurs during their transit through the field-free drift region in a manner similar to that found for neat NO clusters. However, there are two exceptions to this rule in the small cluster size region. The first cluster, $(N_2O)(NO)_3^+$, and the third cluster, $(N_2O)(NO)_5^+$, of the series have a major $N_2O$ loss instead of an NO loss channel. Since the ionization potential for NO is much lower than that of $N_2O$ (9.25 vs 12.89 eV), it is reasonable to assume that the charge is located on one NO molecule to form the charge center. Assuming that only dipole interactions are active in these clusters, one would expect that all $(N_2O)(NO)_n^+$ clusters would be equally likely to lose either NO or $N_2O$. The formation of a ring-like ion for $(N_2O)(NO)_3^+$ can again easily explain the loss of $N_2O$. During the metastable decay, loss of the dangling $N_2O$ molecule is the preferred process possibly accompanied by a rearrangement of the then formed $(NO)_3^+$ trimer ring. The next cluster in this series $N_2O(NO)_4^+$ has one additional NO molecule bound to the core ion which can be easily removed during metastable decay as it is neither bound to the ring nor does it form a stabilized NO dimer.

The observed loss of a $N_2O$ moiety during decay of the next member of this series $N_2O(NO)_5^+$ series cannot be explained using the model of a $(N_2O)(NO)_3^+$ core ion. Even formation of a NO dimer which is known to have a $C_{2v}$ symmetry,[18,19] with a dipole moment[20] of 0.214 D, and therefore a species which would bind stronger to the positive charge of the cluster than a single NO molecule, cannot explain the loss of $N_2O$.

To provide a theoretical explanation of these findings, we performed semiempirical and ab initio calculations on $(NO)_nN_2O^+$ cations employing MNDO and STO-3G and 3-21G(*) Hamiltonians. The SPARTAN Version 3.1 molecular orbital calculation program was used. For estimating semiempirical enthalpies of formation, the MNDO/RHF model was used; in the ab initio calculations the UHF model was used. All calculations are for fully optimized species without imposing symmetry constraints.

Calculations on the $(NO)_3^+$ trimer ring and the $(NO)_3N_2O^+$ ion resemble closely the results found by Jones et al.[16] and are summarized in Table 2 together with the enthalpy for addition of $N_2O$ to this $(NO)_3^+$ ring.

Attaching another NO molecule to $(NO)_3N_2O^+$ leads, during geometry optimizations on the MNDO level, to very long ($d >$ 5 Å) NO ring bonds, indicating that this molecule is not stable toward dissociation into $(NO)_3N_2O^+ + NO$. The same can be observed when two NO molecules are attached to the cation ring at different sides of the ring. On the other hand when a structure involving two NO molecules forming a bridge between two nitrogen atoms of the ring is optimized on the MNDO level, convergence occures into a structure similar to the one shown in Figure 6 but with a more flat ring geometry. The structure shown in Figure 6 is the result from a geometry optimization using a 3-21G(*)/UHF/TRIPLET Hamiltonian. Enthalpies of formation for this bicyclic NO pentamer cation and its addition product with $N_2O$ are given in Table 2.

As it is found for $(NO)_3ONN^+$ the formation of the $(NO)_5^+$ bicyclic is endothermic but addition of $N_2O$ to a preformed ring is exothermic. Although further calculations will be necessary to convincingly propose a bicyclic structure for $(NO)_5N_2O^+$, this suggestion is attractive as it can account for the observed metastable decay channels. For $(NO)_3N_2O^+$ and $(NO)_5N_2O^+$ the preferred pathway is loss of the dangling $N_2O$, whereas for all other $(NO)_nN_2O^+$ ions it is easier to remove a van der Waals bonded NO molecule.

It should be emphasized that neither Jones' nor our calculation found a special stability for any size cluster toward dissociation into the molecular subunits $NO^+$, NO, and $N_2O$. But the

**TABLE 2: Energies of the Polymerized Trimer and Pentamer Cations and Their $N_2O$ Addition Products**

| ion | Hamiltonian | $\Delta H_f$ | geometry |
|---|---|---|---|
| $(NO)_3^+$ | MNDO/RHF/TRIPLET | 321.81 kcal/mol | $C_{2v}$ |
| $(NO)_3NNO^+$ | MNDO/RHF/TRIPLET | 348.18 kcal/mol | $C_s$, chair ring |
| $(NO)_3ONN^+$ | MNDO/RHF/TRIPLET | 346.27 kcal/mol | $C_s$, chair ring |
| | STO−3G/UHF/TRIPLET | −563.553323 au | $C_s$, chair ring |
| $(NO)_3^+ + N_2O \rightarrow (NO)_3ONN^+$ | MNDO/RHF/TRIPLET | $\Delta H_r = -6.58$ kcal/mol | |
| $(NO)_5^+$ | MNDO/RHF/TRIPLET | 386.03 kcal/mol | $C_{2v}$ |
| $(NO)_5ONN^+$ | MNDO/RHF/TRIPLET | 390.76 kcal/mol | $C_s$, chair ring |
| | 3-21G(*)/UHF/TRIPLET | −824.496 au | $C_s$, chair ring |
| $(NO)_5^+ + N_2O \rightarrow (NO)_3ONN^+$ | MNDO/RHF/TRIPLET | $\Delta H_r = -26.31$ kcal/mol | |

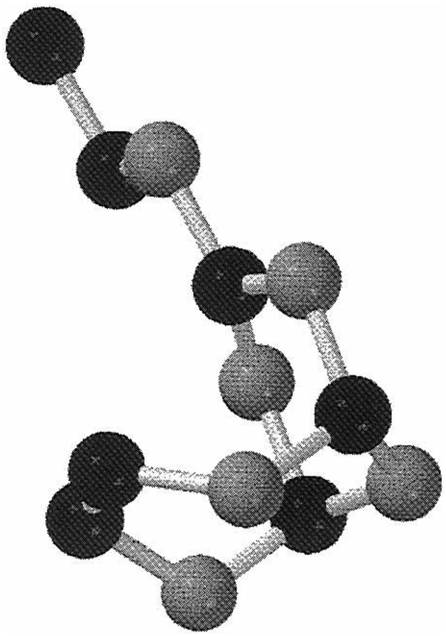

**Figure 6.** Plot of $(NO)_5ONN^+$ calculated on the 3-21G(*)/UHF/TRIPLET level. The MNDO result is essentially similar but tends to flatten the ring.

exothermicity for addition of $N_2O$ onto the trimer and pentamer cation ring indicates a special stability of these binary species.

In fact, sequential condensation of NO monomer units with $NO^+$ does not readily lead to formation of a cationic NO trimer or pentamer core. Perhaps the binary ion $(NON_2O)^+$, which has been detected previously as a photodissociation product of $(N_2O)_2^+$ ions,[21] is a direct product of the disproportionation reaction described in the foregoing section and a necessary intermediate in the formation of $(NO)_3N_2O^+$. Direct formation of $(NON_2O)^+$ and further reaction of this ion forming $(NO)_3N_2O^+$ would also account for the high selectivity toward formation of $N_2O$/NO cluster ions in the purified samples compared to the unpurified samples which show both $N_2O$/NO and $NO_2$/NO cluster series. It might be also speculated that during the ionization process, due to the high photon flux in the femtosecond laser pulse, part of the $NO^+$ ions are generated in a triplet state $(AP(NO^+(^3\Sigma+)) = 15.667$ eV). Starting from this higher energetic level, the formation of polymerized cations would be energetically downhill.

## Conclusion

By studying both pure NO clusters and mixed clusters such as $NO_2$/NO, $N_2O$/NO systems, evidence is acquired suggesting that the $(N_2O)(NO)_n^+$ $(n \geq 3)$ cluster series which appear in pure NO cluster mass spectra are the results of intracluster reactions occurring within $(NO)_n^+$ cluster ions. Whereas the odd−even alternations in neat NO clusters follow a simple electron counting rule and can be explained by the pairing of valence electrons, formation of the $(N_2O)(NO)_n^+$ cluster series and its onset at $(N_2O)(NO)_3^+$ can be explained assuming a polymerized core cation. Calculations on the MNDO and ab initio level indicate that a ring like $(NO_3)N_2O^+$ and a bicyclic $(NO_5)N_2O^+$ cation might be of special stability. The proposed structures not only account for the cluster distribution found, they can also explain the observed switching of decay pathways found in the metastable decay of these binary clusters.

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