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Fast Atom and Fast Ion Bombardment of Solid Nitrogen Oxides: An FT-IR Study

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In secondary ion (SIMS) and fast atom bombardment (FAB) mass spectrometry kilovolt-energy primary ions or atoms, respectively, impact a solid and eject neutral and charged secondary particles; the latter are detected in a mass spectrometer.[1] Upon impact on many simple molecular solids held at 15–20 K, heavy primary ions such as Ar^+ eject large secondary cluster ions of unexpected composition.[2-4] We now report direct evidence in favor of the mechanism proposed[2-4] and emphasize the potential of FAB for the generation of reactive matrix-isolated species.

SIMS of solid nitrogen oxides is particularly interesting.[3,4] The positive SIMS of NO is dominated by the cluster series $(N_{2n+1}O_{3n+1})^+$, with excess nitrogen apparently disposed of in unidentified neutral byproducts. The positive SIMS of N_2O_3, N_2O, and N_2O_4 is dominated by the cluster series $[N_{2(n+m)+1}O_{3n+4m+1}]^+$. The relative oxygen content in the clusters increases in the above order in the oxide series. The originally purely speculative formulation of these clusters in terms of a central ion surrounded by distinct N_2O_3 and N_2O_4 units, $NO^+(N_2O_3)_n\,(N_2O_4)_m$, has recently received direct support from collision-activated dissociation studies.[5]

The proposed mechanism for cluster formation from insulating low-temperature solids[2] postulates (i) excitation of nuclear motion by momentum transfer, (ii) conversion of its energy into electronic excitation, including ionization (primary uncharged and charged damage center formation in the solid), and randomization of the nuclear motion, (iii) chemical conversion of primary to secondary damage centers, (iv) explosion of the thermal spike region into vacuum, and (v) cooling of metastable aggregates into final stable clusters by expansion and by loss of the least firmly held constituent molecules.

In an effort to observe directly those secondary damage centers that have not been ejected but rather remained in the solid, we have deposited N_2O, NO, and N_2O_4–NO_2, both neat (flow ~0.3 mmol in 6 h) and in 1:100 dilution with argon (~3 mmol in 14 h), on a CsI plate held at 14 K (Air Products Displex closed-cycle refrigerator) while bombarding the plate either with the full output of a Capillaritron argon-ion and argon-atom gun (4 kV, 40 μA, Ar flow 0.7 mmol/h) or with its argon-atom-only output obtained by applying an appropriate voltage on the ion-deflection plates.[6,7] FT-IR spectra of the deposits (Figure 1) were the same in both cases. Table I summarizes the neutral species that were unambiguously identified by comparison with the known[8,9] IR spectra and by the use of isotopically labeled nitric oxide.

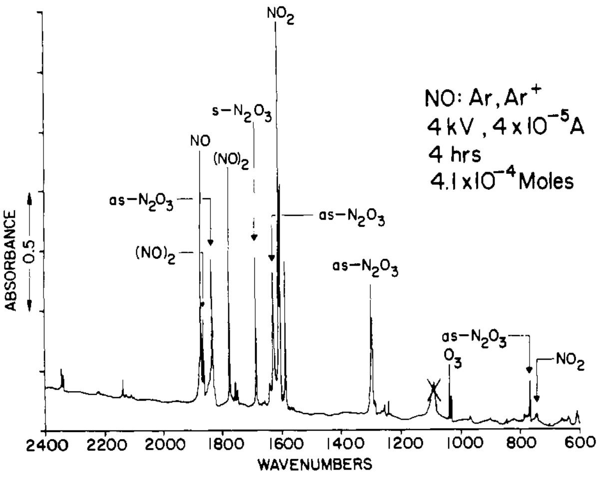

Figure 1. FT-IR spectrum of NO bombarded with 4 keV Ar^+ ions and Ar neutrals during deposition (14 K). The weak peaks near 2340 and 2138 cm^{-1} are due to CO_2 and CO impurities, respectively.

Table I. Matrix-Isolated Products from Fast Atom and Fast Ion Bombardment of Solid Nitrogen Oxides

	substrate[a]		
product	N_2O	NO–N_2O_2	NO_2–N_2O_4
N_2O	vs	–	–
NO	m	s	s
$(NO)_2$	m	vs	m
s-N_2O_3	w	m	m
as-N_2O_3	w	m	m
NO_2	s	s	vs
i-N_2O_4	–	–	w
O_3	m	w	m
H_2O	vvw	vvw	vvw
CO_2	vvw	vvw	vvw
unidentified	vw	vw	vw

[a] IR band intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, – = undetectable.

The results support the proposal[2-4] that the primary damage centers are those expected from the gas-phase radiation chemistry[10] of nitrogen oxides, i.e., ionized and/or electronically excited starting molecules and their neutral or ionized fragments. The proportion of charged species in the matrices is clearly very low, suggesting that most of the primary damage centers are neutral, there is extensive charge neutralization, or most likely both.

Neutral primary fragments are in themselves sufficient to account for the observed products (it is quite possible that analogous ion–molecule reactions play a similar role): $N + N_2O \rightarrow N_2 + NO$; $O + N_2O \rightarrow N_2 + O_2$; $O + N_2O \rightarrow 2NO$; $N + NO \rightarrow N_2 + O$; $N + N_2O_2 \rightarrow N_2 + NO_2$; $N + O_2 \rightarrow NO + O$; $O + NO \rightarrow NO_2$; $O + N_2O_2 \rightarrow N_2O_3$; $O + O_2 \rightarrow O_3$; $NO + NO_2 \rightarrow N_2O_3$; $NO_2 + NO_2 \rightarrow N_2O_4$.

These are just the secondary processes which we proposed in our initial attempt to interpret the SIMS of nitrogen oxides.[3,4] The present experiment apparently produces a snapshot of the composition of the solid half-way through the overall process of cluster formation. Much monomeric NO_2 is observed while very little of it is seen in the charged clusters by SIMS. Presumably, it reacts further as a cluster is ejected, yielding N_2O_3 in an NO matrix and N_2O_4 or N_2O_3 in an N_2O or N_2O_4 matrix. This notion is supported by our matrix annealing experiments, in which N_2O_3 or N_2O_4 peaks grow at the expense of NO_2 peaks.

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(6) Ideally, the bombardment should follow the initial deposition of a nitrogen oxide layer in order to exclude the possibility that some of the products originate in gas-phase reactions. Control experiments showed that our results are not significantly distorted by fast ion or atom impact on gas-phase species.

(7) Matrix deposition with simultaneous proton bombardment was used previously to generate various matrix-isolated ions from materials such as the haloforms: Allen, R. O.; Grzybowski, J. M.; Andrews, L. *J. Phys. Chem.* **1975**, *79*, 898. To our knowledge, no matrix isolation experiments using fast atom bombardment have been described in the literature so far. Such experiments now also are in course in the laboratory of Professor Lon Knight at Furman University, to whom we are grateful for communication of unpublished results.

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The elucidation of the chemical nature of the neutral products by the present technique is particularly important since SIMS only provided information on the charged products. For instance, it was quite possible that the previously unobserved nitrogen-rich neutral byproduct from the bombardment of NO, whose formation needs to be postulated in order to account for the observed cluster ion stoichiometry, is N_2O rather than N_2 (thermal decomposition of solid NO yields N_2O and N_2O_4[11]). Yet, in IR spectra, we observe no N_2O formation upon bombardment of solid NO. The reactions triggered in solid NO by fast ion or atom impact are quite different from those triggered by macroscopic heating or explosion.

In summary, the present results lend credence to the mechanistic proposal for SIMS of solid nitrogen oxides[3,4] and, by extrapolation, of low-temperature solids in general.[2] They also establish fast atom bombardment as a viable tool for the production of reactive matrix-isolated species. Its effects are similar to those of ion bombardment, but it is not subject to the same sample charging difficulty.

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Registry No. Ar, 7440-37-1; Ar^+, 14791-69-6; N_2O, 10024-97-2; NO, 10102-43-9; N_2O_2, 16824-89-8; NO_2, 10102-44-0; N_2O_4, 10544-72-6.

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(12) **Note Added in Proof**: Prof. Knight's results with FAB matrix isolation have now appeared in print: Knight, L. B., Jr.; Steadman, J.; Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700.

Triple-Quadrupole Secondary Ion Mass Spectrometry of Low-Temperature Solids: Collision-Activated Dissociation of Large Cluster Ions

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In secondary ion mass spectrometry (SIMS), primary ions with energies in the kilovolt region impact a solid and cause the ejection of neutral and charged secondary particles; the latter are detected in a mass spectrometer.[1] The method and its variant in which the primary particles are uncharged (FAB) are acquiring rapidly growing importance in analytical chemistry of nonvolatile insulating solids and solutions, but the mechanism of secondary ion formation is still poorly understood. In several of the mechanistic studies the samples were kept at low temperatures.[2] We have investigated simple molecular solids held at 15-30 K and found that the impact of heavy primary ions such as Ar^+ produces secondary cluster ions of large size and often unexpected compositions.[3-9] Now we wish to report the results of a triple-quadrupole collision-activated dissociation (CAD) study of the internal structure of these clusters, which offers some of the first direct evidence in favor of the mechanistic hypothesis proposed[5-9] to account for their formation and composition.

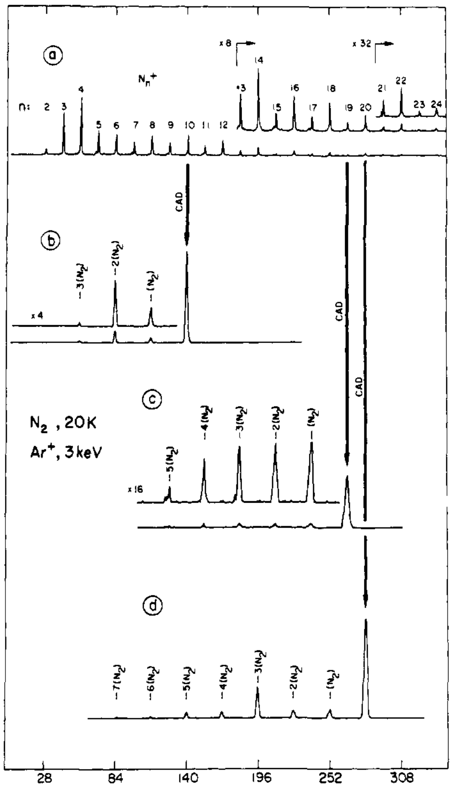

Figure 1. (a) Positive SIMS spectrum of solid N_2 obtained with a 3-keV Ar^+ beam. (b–d) Daughter ion spectra obtained by dissociating N_{10}^+, N_{19}^+, and N_{20}^+ ion with Ar under single-collision conditions.

The measurements were performed on an instrument described earlier,[3] modified by replacing the quadrupole mass filter by a triple quadrupole assembled from components purchased from Extranuclear Laboratories, Inc. The collision gas was argon in the low 10^{-5}-torr range so that only a small fraction of the clusters undergo more than a single reactive collision. The energy transferred to the cluster per collision was estimated to be on the order of at most a few electron volts from the known binding energies of protonated water clusters.[10]

The positive SIMS of solid nitrogen obtained with Ar^+ bombardment[3] contains the cluster series N_n^+, which extends through the range of our mass spectrometer (1000 amu). The most intense peaks are N_3^+ and N_4^+, and the intensities decay approximately exponentially as n increases. In the range $n = 7-46$ the peak intensities of the even and odd n series alternate, with those of even n being more intense. Only losses of nitrogen molecules are observed in the CAD spectra of N_n^+ clusters with $n = 1-30$ (Figure 1), indicating that the fundamental solvating unit is N_2. The CAD spectra of the even and odd cluster series differ in their intensity distributions.

The odd series preferentially loses a single N_2 molecule and the chance of losing several N_2 molecules decreases monotonically with their number, albeit only slowly at first. The same pattern is shown by the even series, but in addition a single very intense loss peak is present for each parent cluster. In small even clusters up to N_8^+, this is the loss of N_2, in the range N_{10}^+-N_{18}^+, this is the loss of $2N_2$, and for N_{20}^+-N_{30}^+, it is the loss of $3N_2$. Unlike

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