

behavior observed in the excitation and emission dependence of the anisotropy decay emphasizes the importance of vibronic coupling between the  ${}^1L_a$  and  ${}^1L_b$  electronic manifolds. These results indicate that the use of time-resolved fluorescence depolarization measurements to obtain information on picosecond and subpicosecond librational motions of tryptophan side chains in proteins may be severely complicated by contributions to the anisotropy from electronic and vibronic relaxation processes. Caution must be taken even when long wavelength excitation ( $>300$  nm) is used. For measurements probing motions on time scales longer than about 5–10 ps, however, a time scale separation between electronic and motional depolarization can be assumed. Under these conditions, an "effective" initial anisotropy can be

defined and the purely motional behavior of the chromophore analyzed.

As noted earlier by Cross et al.<sup>29</sup> and Chen et al.,<sup>42</sup> the complexity associated with fluorescence anisotropy can be avoided by the use of absorption anisotropy. For measurements of tryptophan motion on a time scale  $<5$  ps absorption anisotropy is clearly the method of choice.

**Acknowledgment.** This work was supported by grants from the National Science Foundation. We thank Susan Hudson and Joe Beecham for the global analysis programs used in this work and Harry Guttman for his help in their implementation.

Registry No. H-Trp-OH, 73-22-3.

## Protonated Nitric Acid. Structure and Relative Stability of Isomeric $H_2NO_3^+$ Ions in the Gas Phase

Fulvio Cacace,<sup>\*,†</sup> Marina Attinà,<sup>†</sup> Giulia de Petris,<sup>†</sup> and Maurizio Speranza<sup>‡</sup>

Contribution from the Università di Roma "La Sapienza", p.le Aldo Moro 5, 00185 Rome, Italy, and Università della Tuscia, via S.C.de Lellis, 01100 Viterbo, Italy. Received May 31, 1989

**Abstract:** Gaseous  $H_2NO_3^+$  ions have been obtained from direct protonation of nitric acid by  $H_3^+$ ,  $CH_5^+$ , and  $H_3O^+$  as well as from the protonation of  $C_2H_5ONO_2$  followed by  $C_2H_4$  loss. The proton affinity of nitric acid has been estimated to be  $168 \pm 3$  kcal mol<sup>-1</sup> from the results of bracketing experiments carried out by FT-ICR and CI mass spectrometry. Structural analysis by MIKE and CID spectrometry of  $H_2NO_3^+$  ions and of their  ${}^{18}O$ -labeled isotopomers obtained from the exchange with  $H_2{}^{18}O$  provides strong evidence for the existence of two isomers, characterized by the  $(HO)_2NO^+$  and the  $H_2O \cdot NO_2^+$  structure, and for the higher stability of the latter. The results are consistent with those of independent MO SCF calculations, pointing to the higher stability of the  $H_2O \cdot NO_2^+$  structure.

In a previous communication we have reported preliminary evidence for the existence of two isomeric  $H_2NO_3^+$  ions, obtained from the gas-phase protonation of nitric acid and from the protonation-induced loss of ethylene from ethyl nitrate.<sup>1</sup>

We present here a more complete and detailed account of the converging lines of evidence for the existence of isomeric  $H_2NO_3^+$  ions in the gas-phase. The experimental techniques employed include the following: (i) chemical ionization (CI) and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, (ii) metastable ion kinetic energy (MIKE) and collisionally induced dissociation (CID) spectrometry, (iii) isotopic exchange of gaseous  $H_2NO_3^+$  ions with  $H_2{}^{18}O$  and structural characterization of the  $H_2NO_2{}^{18}O^+$  species formed.

In the following sections we shall examine the reactions employed for the preparation of  $H_2NO_3^+$  ions and their energetics, the closely related problem concerning the proton affinity of gaseous nitric acid, the structural analysis of the  $H_2NO_3^+$  ions by MIKE and CID spectrometry, and the relevant aspects of isotopic labeling experiments.

### Experimental Section

**Materials.** He,  $H_2$ ,  $CH_4$ , and  $C_2H_6$  were research purity gases (99.95 mol % minimum purity) from Matheson Gas Products Inc. Deuterium gas, with a stated isotopic purity of 99.7 mol %, was obtained from BOC Spectral Gases Ltd., while  ${}^{18}O$ -water (98% isotopic purity) was purchased from Cambridge Isotope Laboratories, Inc. The other chemicals were commercially available or were prepared according to established procedures.

**Mass Spectrometric Measurements.** The CI spectra of  $HNO_3$  and of  $EtNO_3$  were recorded with a Hewlett-Packard 5892A quadrupole in-

strument, measuring the pressure in the CI ion source with a Bourdon-type mechanical gauge.

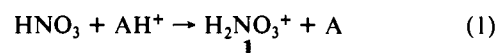
The measurements were repeated with use of a ZAB-2F magnetic spectrometer (VG Micromass Ltd.), whose CI source was fitted with a MKS Baratron Model 221A capacitance manometer. Typical operating conditions were as follows: electron current 0.5–1.0 mA, electron energy 50 eV, repeller voltage 0 V, source temperature 180 °C, accelerating voltage 8 kV, source inlet temperature 30 °C, and total pressure in the ion source 0.2–0.3 Torr. The ZAB-2F instrument was used as well to record MIKE spectra, at a typical mass resolving power of  $2 \times 10^3$  and energy resolution of  $4 \times 10^3$ .

The CID spectra of the  $H_2NO_3^+$  and  $HDNO_3^+$  ions were taken by admitting He into the collision cell of the ZAB-2F spectrometer and increasing the pressure to ca.  $10^{-6}$  Torr, which caused a 30% reduction of the main beam.

The PA of  $HNO_3$  was measured with the "bracketing" technique, in a pressure range of  $1-5 \times 10^{-7}$  Torr, at 30 °C, in a Nicolet FT-MS 1000 ICR mass spectrometer equipped with a 2-T superconducting magnet and a 2.54 cm<sup>3</sup> cell.

### Results

**Preparation of Gaseous  $H_2NO_3^+$  Ions.** The gas-phase reaction



has previously been observed in a particular case,  $A = H_2O$ , in flowing-afterglow studies.<sup>2,3</sup> We have unequivocally established the occurrence of proton transfer (1) from various Brønsted acids by triple-resonance experiments carried out at room temperature, at pressures in the range of  $10^{-7}$  Torr, by FT-ICR spectrometry. The results show that ions **1**, irrespective of the protonating agent

(2) Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1973**, *59*, 6272.

(3) Fehsenfeld, F. C.; Howard, C. J.; Schmeltekopf, A. L. *J. Chem. Phys.* **1975**, *63*, 2835.

(1) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. *J. Am. Chem. Soc.* **1989**, *111*, 5481.

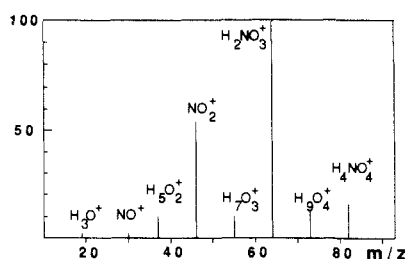


Figure 1. Typical  $\text{CH}_4/\text{CI}$  spectrum of aqueous  $\text{HNO}_3$  (68% w/w) recorded at 1 Torr, at a source temperature of 40 °C.

used, tend to dissociate into  $\text{NO}_2^+$  and  $\text{H}_2\text{O}$  under the conditions prevailing in the ICR spectrometer.

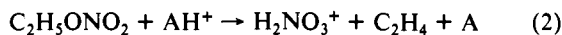
Protonation of nitric acid can also be accomplished under CI conditions; e.g., the CI spectra of 68% aqueous nitric acid, recorded in  $\text{CH}_4$  at 1 Torr at a source temperature of 40 °C, display **1** as the base peak, together with  $\text{H}_2\text{NO}_3^+$ ,  $\text{NO}^+$ , and  $\text{NO}_2^+$  (Figure 1). Formation of  $\text{H}_4\text{NO}_4^+$  ions has previously been observed in a flowing-afterglow,<sup>3</sup> while cluster ions of the general formula  $\text{D}^+(\text{DNO}_3)\cdot(\text{D}_2\text{O})_n$ , with  $n$  values up to 13, have been detected utilizing a free-jet expansion technique.<sup>4</sup>

Calculation of the energetics of process 1, of obvious interest to the present study, requires knowledge of the proton affinity (PA) of gaseous nitric acid, whose only available estimate<sup>3</sup> is affected by an uncertainty of some 40 kcal mol<sup>-1</sup>, being reported as intermediate between those of water, 166.5 kcal mol<sup>-1</sup>, and of ammonia, 204 kcal mol<sup>-1</sup>.<sup>5</sup>

The gas-phase basicity of  $\text{HNO}_3$  cannot be measured by using the method based on proton-transfer equilibrium constants, owing to the decomposition of  $\text{H}_2\text{NO}_3^+$  into  $\text{NO}_2^+$  and  $\text{H}_2\text{O}$ , which occurs under ICR conditions. Consequently, we have resorted to the less accurate "bracketing" technique, in experiments performed on isolated ions by FT-ICR spectrometry as well as at higher pressures by CI mass spectrometry. The PA of  $\text{HNO}_3$  has been found to be intermediate between those of  $\text{H}_2\text{O}$ , 166.5 kcal mol<sup>-1</sup>,<sup>5</sup> and of  $\text{CF}_3\text{CH}_2\text{OH}$ , 169 kcal mol<sup>-1</sup>,<sup>6</sup> leading to an estimated  $\text{PA}(\text{HNO}_3) = 168 \pm 3$  kcal mol<sup>-1</sup>, hence to a heat of formation of  $\text{H}_2\text{NO}_3^+$  of  $166 \pm 3$  kcal mol<sup>-1</sup>.<sup>7</sup>

These values allow calculation of the energetics of proton transfer (**1**) from the Brønsted acids employed in the present study, i.e.  $\Delta H^\circ_1 = -67$  (A =  $\text{H}_2$ ),  $-36$  (A =  $\text{CH}_4$ ),  $-5$  (A =  $\text{C}_2\text{H}_4$ ), and  $-1$  (A =  $\text{H}_2\text{O}$ ) kcal mol<sup>-1</sup>.<sup>5</sup> It should be noted that, since aqueous nitric acid has been employed in the CI experiments, the exothermicity of process 1, hence the excess internal energy of ions **1**, depends on whether they are formed by direct proton transfer from  $\text{AH}^+$  or from the  $\text{H}_3\text{O}^+$  ions arising from the preliminary protonation of water. In other words, a fraction of the  $\text{H}_2\text{NO}_3^+$  ions is invariably formed with little or no excess of internal energy via the nearly thermoneutral, yet very efficient ( $k = 1.6 \times 10^9$  cm<sup>3</sup> s<sup>-1</sup>),<sup>3</sup> proton transfer to  $\text{HNO}_3$  from  $\text{H}_3\text{O}^+$ . An experimental way to alleviate such a problem, based on the use of  $\text{D}_3^+$  as the Brønsted acid, will be discussed in the next section.

Another convenient route to **1** is the reaction



long established by ICR spectrometry<sup>8</sup> and characterized by a  $\Delta H^\circ$  value of  $-50$  (A =  $\text{H}_2$ ) and  $-18$  (A =  $\text{CH}_4$ ) kcal mol<sup>-1</sup>.<sup>9</sup>

(4) Kay, B. D.; Hermann, V.; Castelman, A. W., Jr. *Chem. Phys. Lett.* **1981**, *80*, 469.

(5) Unless stated otherwise, all thermochemical data are taken from the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1.

(6) Pedley, J. B.; Rylander, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: 1977.

(7) This result is consistent with the 6-31G\*\*//44-31G SCF calculations by Nguyen and Hegarty (Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2*, **1984**, 2043) showing that the PA of  $\text{HNO}_3$  exceeds that of  $\text{H}_2\text{O}$  by ca. 1 kcal mol<sup>-1</sup>.

(8) Nixon, W. B.; Bursley, M. M. *Tetrahedron* **1970**, *50*, 4389.

(9) On the basis of the thermochemical data of Kriemler, P.; Buttrill, S. E. *J. Am. Chem. Soc.* **1970**, *92*, 1123.

**Differentiation of Isomeric  $\text{H}_2\text{NO}_3^+$  Ions.** The results obtained from the analysis of the populations of ions **1**, prepared in different ways, with structurally diagnostic techniques, such as MIKE and CID spectrometry, backed by the structural information from isotopic labeling experiments, provide strong evidence for the existence of two isomers. In general, the MIKE and CID spectral features of a given population of ions **1** were found to depend on its internal energy distribution, which reflects the operation of several factors, including (i) any excess energy of the protonating ions, (ii) the fraction of the energy released in the protonation step which is deposited into the  $\text{H}_2\text{NO}_3^+$  ions, and (iii) the efficiency of the collisional deactivation of the latter. These factors depend on the nature and the pressure of the reactant gas in the CI ion source.

Two limiting patterns have been identified in the MIKE and CID spectra. The one typical of the species, henceforth referred to as isomer I, characterizes ions **1** obtained from reactions of low exothermicity, i.e. process 1, A =  $\text{H}_2\text{O}$ , and 2, A =  $\text{CH}_4$ , occurring at the highest pressure attainable in the CI ion source, ca. 0.5 Torr.

The other limiting pattern, taken as the signature of isomer II, is found in the spectra of ions **1** from highly exothermic processes, e.g., reaction 1, A =  $\text{H}_2$ , under conditions of inefficient collisional deactivation, i.e., at source pressures <0.2 Torr.<sup>10</sup>

The evidence for the existence of two isomeric  $\text{H}_2\text{NO}_3^+$  ions derived from different diagnostic techniques is illustrated in the following paragraphs.

**MIKE Spectra.** The only metastable transition observed is the decomposition of **1** into  $\text{NO}_2^+$  and  $\text{H}_2\text{O}$ . The MIKE spectra of the two isomers are markedly different, as regards both the shape of the peaks and the extent of kinetic energy release. Metastable decomposition of II is characterized by a remarkably large release,  $747 \pm 10$  meV measured at half height, and by the typical, dish-topped peak shown in Figure 2A, while isomer I decomposes with a substantially lower kinetic energy release, giving the non-Gaussian metastable peak illustrated in Figure 2B. Such a difference is particularly significant, in that large kinetic energy releases, like the one from isomer II, are generally indicative of high reverse activation energies, typical of those fragmentation processes that require preliminary rearrangement of the decomposing ions, while simple bond cleavages have little or no reverse activation energies.<sup>11,12</sup> Thus, the MIKE spectra provide structurally significant information, namely that isomer II must undergo rearrangement prior to  $\text{H}_2\text{O}$  loss, which is not the case of isomer I.

Worthy to note is also that the populations of ions **1** prepared under intermediate conditions as regards the exothermicity of the formation process and/or the pressure reactant gas display MIKE spectra characterized by a superimposition of the features typical of isomers I and II, as illustrated in Figure 2 (parts C and D), which refer, respectively, to ions **1** from process 1, A =  $\text{C}_2\text{H}_4$ , at a pressure of ca. 0.4 Torr and from process 2, A =  $\text{H}_2$ , at a pressure of ca. 0.2 Torr.

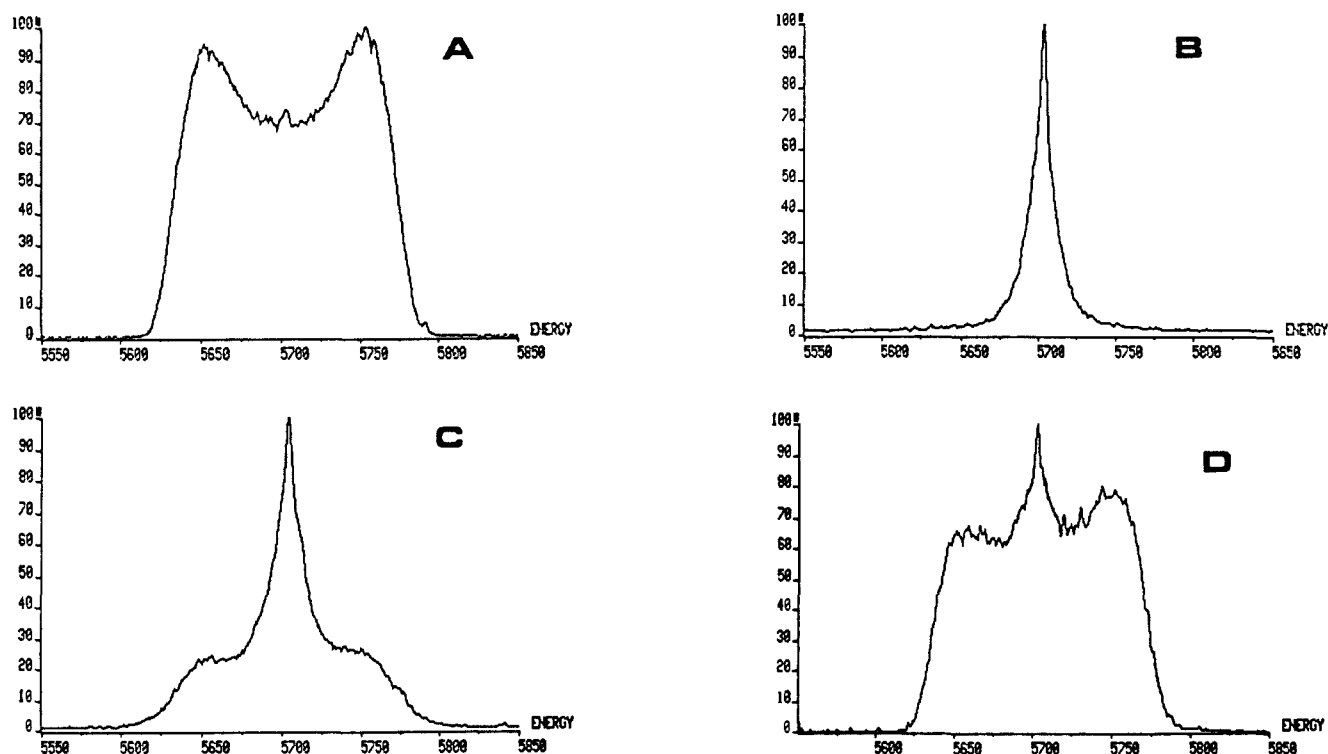
As previously mentioned, aqueous nitric acid has been used in the present study to generate ions **1** via process 1. This has the disadvantage that a mixed population is formed, characterized by two largely different distributions of internal energy, depending on whether proton transfer to  $\text{HNO}_3$  occurs directly from the  $\text{AH}^+$  acid or from the  $\text{H}_3\text{O}^+$  ions arising from the preliminary protonation of water.

The problem has been addressed by using  $\text{D}_3^+$  ion as the Brønsted acid and recording the MIKE spectra of the  $\text{HDNO}_3^+$  ions formed. In a CI plasma containing  $\text{D}_3^+$  and  $\text{H}_2\text{DO}^+$  ions in approximately equal concentrations,  $\text{HDNO}_3^+$  is likely to arise

(10) These results do not imply of course that II is the only or even the most abundant isomer formed but simply that only when prepared under the specified set of conditions its distinctive features become detectable by MIKE and CID spectrometry. Both techniques do not sample the isomeric composition of **1** in the ion source, detecting only the fraction of ions **1** that undergoes metastable, or collisionally induced fragmentation in the appropriate region of the mass spectrometer.

(11) Holmes, J. L.; Terlouw, J. K. *Org. Mass Spectrom.* **1980**, *15*, 393.

(12) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.



**Figure 2.** Metastable peaks due to the loss of H<sub>2</sub>O from ion 1 prepared in different ways. Spectrum A refers to isomer II from process 1 (A = H<sub>2</sub>) in H<sub>2</sub> at low pressure; spectrum B to isomer I from process 2 (A = CH<sub>4</sub>) in CH<sub>4</sub> at high pressure; spectrum C to the mixture of isomers from process 1 (A = C<sub>2</sub>H<sub>4</sub>) in C<sub>2</sub>H<sub>6</sub> at high pressure; and spectrum D to the mixture of isomers from process 2 (A = H<sub>2</sub>) at low pressure.

**Table I.** CID Spectra of Isomeric H<sub>2</sub>NO<sub>3</sub><sup>+</sup> Ions

<i>m/z</i>	charged fragment	relative abundances <sup>a</sup>	
		isomer I <sup>b</sup>	isomer II
18	H <sub>2</sub> O <sup>+</sup>	9	
30	NO <sup>+</sup>	12	97
46	NO <sub>2</sub> <sup>+</sup>	100	100

<sup>a</sup> Referred to the intensity of the most abundant fragment taken = 100 and corrected as described in the text. Standard deviation ca. 10%. <sup>b</sup> Prepared as described in the text.

predominantly from D<sub>3</sub><sup>+</sup>. In fact, the direct deuteration process can be expected to be considerably faster than the two-step sequence involving preliminary deuteration of water, yielding H<sub>2</sub>DO<sup>+</sup>, followed by the almost thermoneutral reaction of the latter with HNO<sub>3</sub>. Furthermore, a 2:1 statistical factor favors H<sup>+</sup> over D<sup>+</sup> transfer from H<sub>2</sub>DO<sup>+</sup>, a bias enhanced by operation of an isotope effect, expected to be particularly large in a nearly thermoneutral process.

In view of the above considerations, it is particularly worthy to note that the MIKE spectra of the HDNO<sub>3</sub><sup>+</sup> ions from the D<sub>2</sub> CI of aqueous nitric acid are identical as to the shape and to the kinetic energy release (746 ± 10 meV) with those of ions II from the protonation of HNO<sub>3</sub> with H<sub>3</sub><sup>+</sup>, while the *unlabeled* H<sub>2</sub>NO<sub>3</sub><sup>+</sup> ions display a MIKE spectrum corresponding to that of ions I.

**CID Spectra.** The abundances of the H<sub>2</sub>O<sup>+</sup>, NO<sup>+</sup>, and NO<sub>2</sub><sup>+</sup> ions, the only charged fragments from the collisionally induced dissociation of the isomeric H<sub>2</sub>NO<sub>3</sub><sup>+</sup> ions, are given in Table I.

Only the NO<sub>2</sub><sup>+</sup> peak can be expected to contain a significant unimolecular component, being the only charged species formed from the metastable decomposition of 1, as discussed in the previous paragraph. Such contribution has approximately been estimated by applying a 1-kV voltage to the collision cell, which allows discrimination against all fragmentation processes occurring outside the cell. The residual contribution from the ions that decompose unimolecularly within the collision cell has been estimated by recording MIKE spectra under exactly the same conditions prevailing in the CID experiments (except for the absence of the collision gas) and applying a 1-kV potential to the cell, which causes the metastable peak to divide into two peaks

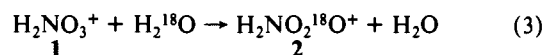
of the same shape but of widely different intensity. Measuring the relative intensity of the minor peak, which is displaced along the energy coordinate since it arises from unimolecular fragmentation processes occurring within the collision cell, one can approximately estimate their contribution. The abundances of the CID peaks corrected according to the above procedures are sufficiently accurate for comparison purposes, especially since the CID spectra of isomers I and II happen to be remarkably different, as regards both the nature of the charged fragments and their relative abundances.

It is worthy to note that, depending on the formation process and on the conditions prevailing in the ion source, with regards to the nature and the pressure of the reactant gas, the CID spectral features of the populations of ions 1 undergo a gradual transition from those typical of isomer I to those typical of isomer II which closely reflects the changes observed in the MIKE spectra.

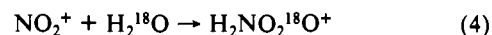
This is particularly evident when the CID spectra are recorded by applying a 1-kV potential to the collision cell, which allows simultaneous detection of the ionic fragments formed by purely metastable processes outside the cell and those arising from collisionally induced dissociation *plus* metastable decomposition within the cell. The results, which are particularly telling, are illustrated in Figure 3.

Finally, the CID spectra of HDNO<sub>3</sub><sup>+</sup> ions from the reaction of D<sub>3</sub><sup>+</sup> with aqueous nitric acid closely match those of the H<sub>2</sub>NO<sub>3</sub><sup>+</sup> isotopomers obtained from H<sub>3</sub><sup>+</sup> under the same conditions, exactly as in the case of the MIKE spectra discussed in the previous section.

**Structural Evidence from Isotopic Labeling Experiments.** When reactions 1 and 2 occur in the presence of H<sub>2</sub><sup>18</sup>O, labeled ions are formed via the exchange process



The conceivable formation of 2 by hydration of the NO<sub>2</sub><sup>+</sup> ions present in the CI source, e.g., in the spectrum illustrated in Figure 1, has been ruled out by control experiments, showing that NO<sub>2</sub><sup>+</sup>



prepared by ionization of nitrogen dioxide does not associate with

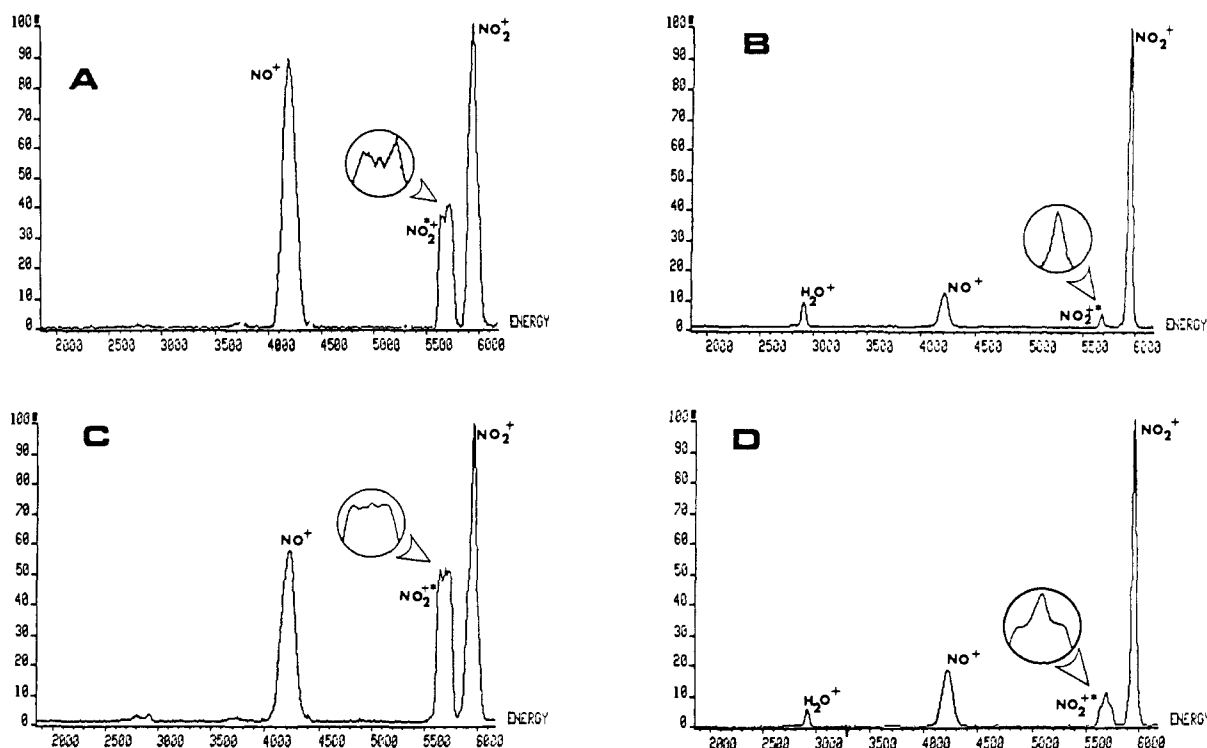
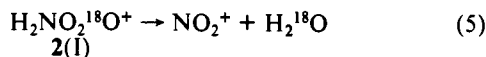


Figure 3. CID spectra of ions **1** from low-pressure  $\text{H}_2/\text{CI}$  of  $\text{HNO}_3$  (spectrum A) and from the  $\text{CH}_4/\text{CI}$  of  $\text{C}_2\text{H}_5\text{ONO}_2$  (spectrum B). Spectra C and D refer to ions **1** from the  $\text{H}_2/\text{CI}$  of  $\text{HNO}_3$  at increasingly higher  $\text{H}_2$  pressures. Asterisks denote purely metastable fragments formed outside the cell (see text), enlarged in the inserts to allow better visual comparison.

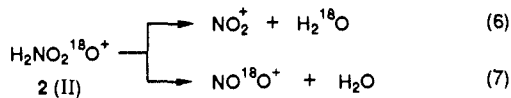
water to any detectable extent under the conditions typical of the exchange 3.

MIKE spectrometry of ions **2** has provided highly significant results that can be summarized as follows. (i) Ions **2** formed respectively from isomer I and II retain the spectral features (shape, kinetic energy release) typical of the corresponding unlabeled precursor, as shown in Figure 4. It follows that isotopic exchange of ions **1** with  $\text{H}_2^{18}\text{O}$  does not promote their complete rearrangement into a single structure. (ii) Ions **2** from isomer I undergo exclusively metastable loss of *labeled* water without



detectable loss of  $\text{H}_2\text{O}$ . Such observation is structurally informative, since the lack of isotopic mixing between the  $\text{NO}_2$  and the  $\text{H}_2\text{O}$  moieties points to the existence of water as a discrete entity in isomer I, hence to a structure akin to a hydrated nitronium ion. (iii) Metastable decompositions of ions **2** from the exchange of  $\text{H}_2^{18}\text{O}$  with isomer II involves the loss of *both* labeled and unlabeled water molecules.

The kinetic energy release from transition 6, i.e.,  $755 \pm 10$  meV, is practically the same as from transition 7, i.e.,  $753 \pm 10$  meV, both values corresponding to the release,  $747 \pm 10$  meV, from the metastable decomposition of the unlabeled isomer II.



The ratio of the abundances of  $\text{NO}_2^+$  and  $\text{NO}^{18}\text{O}^+$  ions from the competing processes 6 and 7 is  $0.42 \pm 0.03$ , close to the statistical ratio of 0.5, which indicates extensive isotopic scrambling of the oxygen atoms within the decomposing ion.

The contrast between the *nearly statistical* loss of  $\text{H}_2\text{O}$  and of  $\text{H}_2^{18}\text{O}$  from labeled isomer II and the *selective* loss of  $\text{H}_2^{18}\text{O}$  from labeled isomer I is a significant piece of evidence for the structural discrimination of the two species.

### Discussion

**Structure of Isomeric  $\text{H}_2\text{NO}_3^+$  Ions.** The results outlined in the previous sections not only allow positive discrimination between

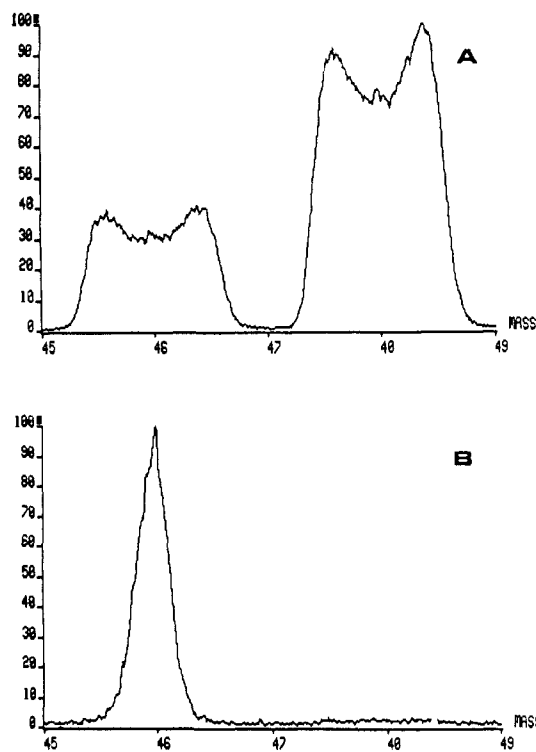
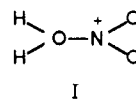


Figure 4. Metastable peaks due to the loss of water from the  $\text{H}_2\text{NO}_2^{18}\text{O}^+$  ions from the exchange of ions II (spectrum A) and ions I (spectrum B) with  $\text{H}_2^{18}\text{O}$ .

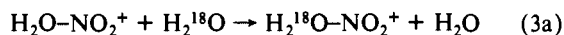
the isomers of protonated nitric acid but also provide, in addition, sufficient elements for their structural characterization.<sup>1,3</sup>

Isomer I can be assigned the hydrated nitronium ion structure



containing a discrete  $\text{H}_2\text{O}$  moiety, whose presence is consistently

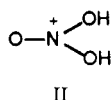
suggested by all diagnostic techniques. Within this framework, the exchange of ions I with  $\text{H}_2^{18}\text{O}$  can be interpreted as a mere ligand substitution in the hydrated nitronium ion occurring without



rearrangement and without affecting the  $\text{NO}_2$  group. This accounts for the lack of  $^{18}\text{O}$  randomization in the labeled ion I, testified by the exclusive loss of  $\text{H}_2^{18}\text{O}$  in its metastable decomposition, whose relatively modest kinetic energy release is justified by its occurrence via a simple bond cleavage, without preliminary reorganization.

Independent support of the suggested structure can be found in the CID spectrum of I, which displays an  $\text{H}_2\text{O}^+$  fragment, providing additional evidence for the presence of a discrete  $\text{H}_2\text{O}$  moiety in the ion.

As to isomer II, the results from all structurally diagnostic techniques concur into excluding that both H atoms are bound to the same O atom, pointing instead to the presence of the two OH groups.

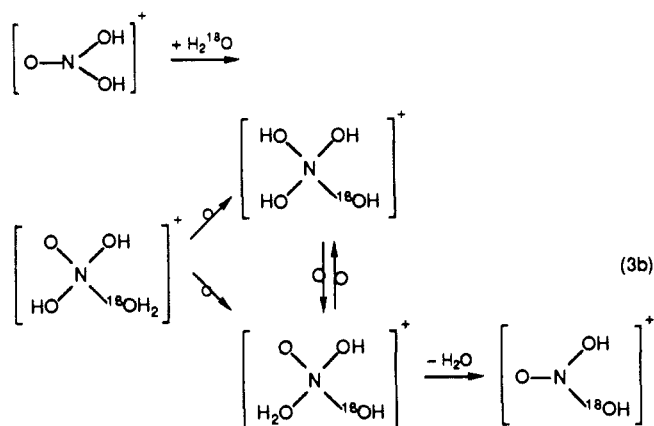


Such an assignment is consistent, in the first place, with the large kinetic energy release, suggestive of molecular reorganization, that characterizes metastable decomposition of the isomer into  $\text{NO}_2^+$  and  $\text{H}_2\text{O}$ , since the loss of water from the proposed structure requires preliminary H migration.

Further evidence is provided by the mixed isotopic composition of water from the metastable decomposition of  $^{18}\text{O}$ -labeled ions II, indicative of a nearly complete  $^{18}\text{O}$  randomization, hence of extensive molecular rearrangement. This accords well with the fact that the suggested structure II does not contain a preexistent  $\text{H}_2\text{O}$  group, whose loss would occur preferentially, as from isomer I, via a simple bond cleavage without preliminary rearrangement.

An interesting problem, related to the structure of isomer II, concerns the mechanism of isotopic exchange leading to formation of the  $^{18}\text{O}$ -labeled isotopomer.

A reasonable interpretation envisages occurrence of proton shifts within a hydrated intermediate, e.g.



Such a process would satisfy the essential requirements imposed by the experimental observations, namely that the isotopic exchange must occur without promoting complete  $\text{II} \rightarrow \text{I}$  isomerization and that the reaction must cause  $^{18}\text{O}$  randomization within the labeled ion II.

The suggested exchange mechanism is indirectly supported by the actual observation of an  $\text{H}_4\text{NO}_4^+$  ion, whose  $m/z$  ratio corresponds to that of the intermediates postulated in eq 3b, in the CI spectra of aqueous nitric acid (Figure 1) and by the reported existence of stable cations containing electronegative groups, such as  $\text{NF}_4^+$ , tetrahedrally coordinated to nitrogen.<sup>14</sup>

**Relative Stability of Isomeric  $\text{H}_2\text{NO}_3^+$  Ions.** The experimental results point to the higher stability of I, the only isomer whose formation from reactions of low exothermicity, in particular from the nearly thermoneutral protonation of  $\text{HNO}_3$  by  $\text{H}_3\text{O}^+$ , can be detected by MIKE and CID spectrometry. On the other hand, only when ions I are formed by highly exothermic reactions do their MIKE and CID spectra display the typical features of isomer II, which suggest an inherently lower stability of the latter than of I. On the basis of such a consideration, isomer I can be assigned the heat of formation,  $166 \pm 3 \text{ kcal mol}^{-1}$ , derived from the PA of  $\text{HNO}_3$  which refers, of course, to the most stable protomer.

While the results from this study do not allow estimation of the heat of formation of II, the large kinetic energy release that characterizes its metastable decomposition is suggestive of a large ( $>20 \text{ kcal mol}^{-1}$ ) activation energy for the reverse reaction i.e., formation of isomer II from the addition of  $\text{H}_2\text{O}$  to  $\text{NO}_2^+$ .

The observation that the only metastable decomposition pathway of II involves  $\text{H}_2\text{O}$  loss, exactly as from I, occurring however with a much larger release of kinetic energy, dictates that the barrier for intramolecular  $\text{II} \rightarrow \text{I}$  isomerization is high, probably in excess of  $20 \text{ kcal mol}^{-1}$ .

It is of interest to compare the present results with those of related studies, in particular of SCF 6-31G\*\*//44-31G calculations on the relative stability of isomeric  $\text{H}_2\text{NO}_3^+$  ions. The most stable species has been found to be a hydrated nitronium ion corresponding to isomer I, while the ions containing two OH groups, akin to isomer II, are less stable by ca.  $8 \text{ kcal mol}^{-1}$ .<sup>7</sup>

The PA of  $\text{HNO}_3$  calculated at the 6-31G\*\*//4-31G level amounts of  $180 \text{ kcal mol}^{-1}$ , considerably higher than our experimental value. However, such discrepancy is only apparent, in that the PA of  $\text{H}_2\text{O}$ , calculated at the same level,  $179 \text{ kcal mol}^{-1}$ ,<sup>7</sup> is correspondingly higher than the well-established experimental value of  $166.5 \text{ kcal mol}^{-1}$ .<sup>5</sup> Apparently, the computational approach tends to systematically overestimate the *absolute* basicities of molecules like  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  by nearly  $13 \text{ kcal mol}^{-1}$ . However, the internal consistency of the results is satisfactory, since not only do they correctly predict the preferred protonation site in  $\text{HNO}_3$ , but the calculated PA *difference* between  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  corresponds to our experimental estimate, ca.  $1 \text{ kcal mol}^{-1}$ .

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(13) The term "structure" is used here simply to denote connectivity rather than detailed geometry, bond lengths and angles, charge location, etc.

(14) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E. *Inorg. Chem.* 1967, 6, 1156.