

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231397624>

# A Discharge Flow–Photoionization Mass Spectrometric Study of the $\text{NO}_3(2A_2')$ Radical: Photoionization Spectrum, Adiabatic Ionization Energy, and Ground State Symmetry

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · OCTOBER 1994

Impact Factor: 2.78 · DOI: 10.1021/j100091a013

---

CITATIONS

23

---

READS

11

6 AUTHORS, INCLUDING:



Paul S. Monks

University of Leicester

294 PUBLICATIONS 5,488 CITATIONS

SEE PROFILE



Zhiqing Philippe Zhang

Laboratoire de l'accélérateur linéaire

26 PUBLICATIONS 415 CITATIONS

SEE PROFILE

# A Discharge Flow–Photoionization Mass Spectrometric Study of the $\text{NO}_3(^2\text{A}_2')$ Radical: Photoionization Spectrum, Adiabatic Ionization Energy, and Ground State Symmetry

P. S. Monks<sup>†</sup> and L. J. Stief<sup>\*</sup>

Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

M. Krauss

Center for Advanced Research in Biotechnology, 9600 Gudelsky Drive, Rockville, Maryland 20850

S. C. Kuo, Z. Zhang, and R. B. Klemm

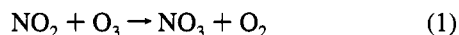
Department of Applied Science/Building 815, Brookhaven National Laboratory, P.O. Box 5000, Upton, New York 11973-5000

Received: May 20, 1994; In Final Form: July 25, 1994<sup>®</sup>

The photoion efficiency spectrum of the nitrate radical ( $\text{NO}_3$ ) was measured over the region  $\lambda = 90\text{--}104\text{ nm}$  by using a discharge flow–photoionization mass spectrometer apparatus coupled to a synchrotron radiation source.  $\text{NO}_3$  was generated by the reaction of fluorine atoms with nitric acid. A value of  $12.57 \pm 0.03\text{ eV}$  was obtained for the adiabatic ionization energy (IE) of  $\text{NO}_3$  from photoion thresholds, corresponding to the  $\text{NO}_3^+(^1\text{A}_1') \leftarrow \text{NO}_3(^2\text{A}_2')$  transition. These direct ionization measurements are the first to be reported for the  $\text{NO}_3$  radical. Relative energetics and optimized geometries for ground state  $\text{NO}_3$  and several states of  $\text{NO}_3^+$  were determined in both  $D_{3h}$  and  $C_{2v}$  symmetries using multiconfiguration self-consistent-field calculations. The results of the present study strongly suggest that the neutral ground state of  $\text{NO}_3$  has  $D_{3h}$  symmetry. This conclusion is based on the following observations: (1) the experimental photoion threshold exhibits a large, steep initial step with no evidence of significant structure, indicating that the neutral and cation must share the same symmetry, and (2) the theoretical evidence is unambiguous that the cation symmetry is  $D_{3h}$ . A value of  $\Delta_f H^\circ_{298}(\text{NO}_3^+)$  and the proton affinity of  $\text{NO}_3$  are also derived. A brief comparison is made of the ionization energies of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_3$ , and some new results on the dissociative ionization of  $\text{HNO}_3$  are discussed.

## Introduction

The nitrate radical ( $\text{NO}_3$ ) is now widely recognized as an important nighttime tropospheric oxidant.<sup>1</sup> The role of  $\text{NO}_3$  chemistry in the stratosphere is less significant because of rapid photolysis during the daylight hours and, as in the troposphere, a relatively low reactivity toward closed-shell species. In the nighttime atmosphere  $\text{NO}_3$  is formed mainly by the reaction



$$k_1(T=298\text{ K}) = 3.2 \times 10^{-17}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \quad (\text{ref } 1)$$

During the daylight hours the  $\text{NO}_3$  radical has a  $1/e$  lifetime on the order of  $5\text{ s}$ .<sup>2</sup> Photolysis of  $\text{NO}_3$  occurs at  $\lambda < 630\text{ nm}$  to produce either  $\text{NO}$  or  $\text{NO}_2$ . The significance of  $\text{NO}_3$  in atmospheric chemistry has produced numerous spectroscopic, kinetic, and theoretical studies.<sup>1</sup>

There is a great deal of conflicting evidence both experimental and theoretical as to the ground electronic state and geometry of  $\text{NO}_3$ .<sup>1</sup> The electronic ground state of  $\text{NO}_3$  is most likely  $^2\text{A}_2'$ , indicative of planar geometry with a 3-fold axis of symmetry ( $D_{3h}$ ).<sup>3</sup> This premise is supported by a recent set of calculations undertaken at a high level of electron correlation,<sup>4</sup> where the energy difference between the  $D_{3h}$  and  $C_{2v}$  equilibrium

geometries was shown to be small at  $0.33\text{ eV}$ <sup>4</sup> but reported only for the smallest basis set used in the calculation. Other treatments at a high level of electron correlation<sup>5</sup> similarly conclude that the  $D_{3h}$  symmetry is preferred, but the energy surface is very flat with energy differences between the two symmetries of much less than  $0.1\text{ eV}$ . Various spectroscopic experimental measurements and analyses also conclude that the preferred structure is  $D_{3h}$ .<sup>3,6</sup> However, there are a number of other theoretical studies which favor a  $C_{2v}$  structure with one long and two short bonds to be lowest in energy.<sup>7</sup> Since the energy surfaces are very flat, there is an obvious need to provide additional experimental evidence to resolve this dispute.

Assuming a  $^2\text{A}_2'$  ground state, the molecular orbitals would be in the following order of increasing energy

$$(s_1s_2s_3)^6(1a_1')^2(1a_2'')^2(3e')^4(4e')^4(1e'')^4(1a_2')^1$$

and ionization using vacuum-ultraviolet light might be expected to originate from the  $(1a_2')^1$  orbital, corresponding to the  $\text{NO}_3^+(^1\text{A}_1') \leftarrow \text{NO}_3(^2\text{A}_2')$  transition. In this work we report the first direct determination of the  $\text{NO}_3$  photoionization efficiency (PIE) spectrum and photoionization threshold from which the ionization energy (IE) was derived. Direct photoionization was accomplished with dispersed synchrotron radiation and detection of the mass-selected ion. The magnitude of the derived IE is discussed in terms of the experimental IEs for the  $\text{NO}_x$  series, where  $x = 1\text{--}3$ . The shape of the derived PIE curve is determined for  $1.21\text{ eV}$  above the threshold. Using the experimental data, coupled to theoretical analysis of the equi-

<sup>†</sup> NAS/NRC Resident Research Associate. Present address: School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, England.

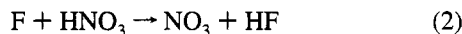
<sup>\*</sup> To whom correspondence should be addressed.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1994.

librium geometries of the neutral and cationic species, further support is provided for the premise of  $D_{3h}$  symmetry for the neutral ground state.

### Experimental Section

Experiments were performed by employing a discharge flow-photoionization mass spectrometer (DF-PIMS) apparatus coupled to the beam line U-11 at the National Synchrotron Light Source (NSLS).<sup>8-11</sup> Briefly,  $\text{NO}_3$  was produced *in situ* by the reaction



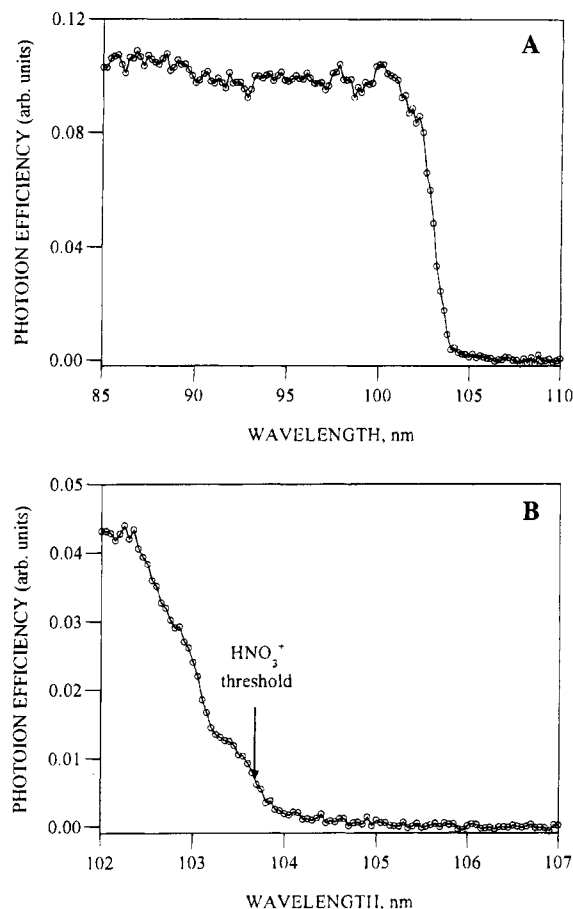
$$k_2(T=298 \text{ K}) = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{ref } 12)$$

in a Teflon-lined flow reactor. Fluorine atoms were produced by passing dilute mixtures of  $\text{F}_2$  ( $\approx 2\%$  in He) through a microwave discharge ( $< 70 \text{ W}$ ,  $2450 \text{ MHz}$ ).  $\text{HNO}_3$  ( $\approx 2\%$  in He) was introduced through the tip of the sliding injector at a distance of about  $15 \text{ cm}$  from the nozzle. The nitric acid concentration ( $(2-6) \times 10^{13} \text{ molecules cm}^{-3}$ ) was always at least in a slight excess over that of  $\text{F}_2$  ( $(0.4-2) \times 10^{13} \text{ molecules cm}^{-3}$ ). The experiments were conducted at ambient temperatures ( $T = 298 \pm 2 \text{ K}$ ). For experiments involving direct ionization and dissociative ionization of  $\text{HNO}_3$ , flow velocities were about  $600-700 \text{ cm s}^{-1}$  and the flow reactor pressure was maintained at about  $5 \text{ Torr}$ . For measurements of  $\text{IE}(\text{NO}_3)$ , flow velocities were usually  $1100-1300 \text{ cm s}^{-1}$  and flow reactor pressures were varied from  $\approx 2$  to  $\approx 4 \text{ Torr}$ . The reaction appeared to be  $95\%$  complete in about  $5 \text{ ms}$  under nominal conditions. The gaseous mixture in the flow reactor was sampled as a pseudomolecular beam into the source chamber and subsequently into the detection chamber of the mass spectrometer.<sup>10</sup> Ions were detected with a channeltron multiplier mounted at the end of an axially aligned quadrupole mass filter. Measurements of PIE spectra were made using tunable vacuum-ultraviolet (VUV) radiation at the NSLS. A monochromator with a normal incidence grating ( $1200 \text{ lines/mm}$ ) was used to disperse the VUV light. Corrections were made for second-order light by scanning the spectral range at one-half the wavelength range and one-half the wavelength step size. These short-wavelength scans were renormalized to reflect the intensity of second-order radiation on the regular scan and subtracted from the raw data.<sup>13</sup> The monochromator slit width was  $400-800 \mu\text{m}$  giving a spectral bandwidth (fwhm) of  $0.14-0.23 \text{ nm}$ . No corrections were made to the measured PIE spectra for the slit function of the monochromator. Ionization thresholds were determined from the peaks of  $d(\text{PIE})/dE$  plots.

The nitric acid vapor was taken at room temperature from  $2:1$  mixtures of sulfuric acid (Mallinkroft, ARG) and fuming nitric acid ( $90\% \text{ HNO}_3$ , Mallinkroft, ARG). Trace amounts of  $\text{NO}_2$  in the  $\text{HNO}_3$  were determined quantitatively from a calibration of  $\text{NO}_2$  (mass scans at  $\lambda = 110.0 \text{ nm}$ ). Typically, the concentration of  $\text{NO}_2$  in the  $\text{HNO}_3$  samples was  $0.2-0.3\%$ . Nitrogen dioxide (CP grade,  $97\%$ , MG Industries) was purified by allowing the sample to stand with  $\text{O}_2$  followed by outgassing at  $77 \text{ K}$  and bulb-to-bulb distillation. Purified  $\text{NO}_2$  and  $\text{NO}_2/\text{He}$  mixtures were kept in blackened bulbs to avoid photolysis. Helium ( $99.9999\%$ , MG Industries) and fluorine ( $99.9\%$ ,  $2\%$  in He, MG Industries) were used as supplied.

### Results

As an example and wavelength calibration of the PIMS experiment, the PIE spectrum of  $\text{HNO}_3$  is shown in Figure 1A. The ionization threshold, indicated in Figure 1B, was obtained at  $\lambda = 103.68 \text{ nm}$ , corresponding to an  $\text{IE}$  of  $11.96 \pm 0.02 \text{ eV}$ .



**Figure 1.** (A) Photoionization efficiency spectrum of  $\text{HNO}_3$  between  $\lambda = 85.0$  and  $110.0 \text{ nm}$  at a nominal resolution of  $0.23 \text{ nm}$ . Photoion efficiency is ion counts at  $m/z = 63$  divided by the light intensity in arbitrary units. (B) Photoionization efficiency spectrum of  $\text{HNO}_3$  at threshold ( $\lambda = 102.0-107.0 \text{ nm}$ ) obtained at a nominal resolution of  $0.12 \text{ nm}$  and with  $0.05 \text{ nm}$  steps. The onset of the ionization occurs at  $\lambda = 103.68 \text{ nm}$  ( $\text{IE} = 11.958 \pm 0.020 \text{ eV}$ ). The uncertainty in the  $\text{IE}$  value is based on combined uncertainties in the resolution ( $0.12 \text{ nm}$ ,  $\pm 0.014 \text{ eV}$ ) and the wavelength calibration ( $0.05 \text{ nm}$ ,  $\pm 0.006 \text{ eV}$ ). The second step, with a threshold at about  $103.08 \text{ nm}$  ( $12.028 \text{ eV}$ ), represents the  $1 \rightarrow 0$  transition. This gives a vibrational frequency of  $0.07 \text{ eV} \equiv 565 \text{ cm}^{-1}$ , which is in excellent agreement with the PES study of Frost *et al.*<sup>15b</sup>

The present result is in good agreement with the recommended value of  $\text{IE}(\text{HNO}_3) = 11.95 \pm 0.01 \text{ eV}$ ,<sup>14</sup> which is based on photoelectron spectroscopic studies.<sup>15</sup> The level of agreement may be indicative of extensive rotational cooling that might be achieved in the nozzle expansion,<sup>13</sup> and thus the threshold is not perturbed within the experimental uncertainty ( $\pm 0.02 \text{ eV}$ ) by thermal effects.

The possibility of producing  $\text{NO}_3^+$  via dissociative ionization of  $\text{HNO}_3$  was investigated by performing experiments to observe fragment ions from  $\text{HNO}_3$ . Other than a small parent ion signal at  $m/z = 63$ , the only significant signal detected was at  $m/z = 46$  ( $\text{NO}_2^+$ ). Neither  $\text{NO}^+$  nor  $\text{NO}_3^+$  fragment ions were observed in the present study at  $\lambda \geq 85 \text{ nm}$  ( $\leq 14.6 \text{ eV}$ ). A small signal for  $\text{NO}^+$  was observed with an onset at  $\lambda \approx 96 \text{ nm}$  ( $12.9 \text{ eV}$ ), but this was due entirely to traces of  $\text{NO}_2$  in the samples. The  $\text{NO}_2^+$  product was presumably formed from the following, thermodynamically allowed, dissociative ionization process

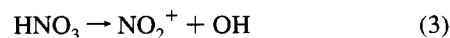
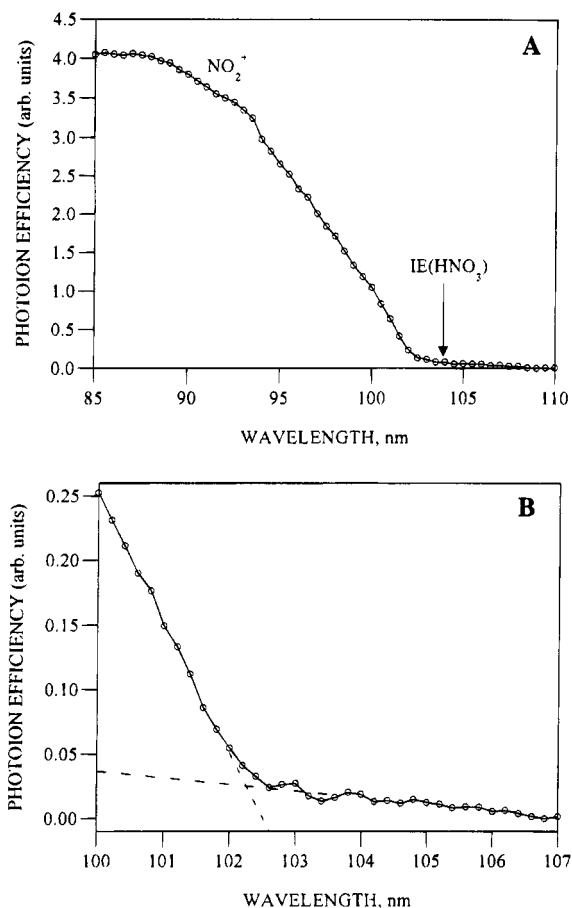
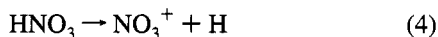


Figure 2A shows the photoion efficiency curve from the



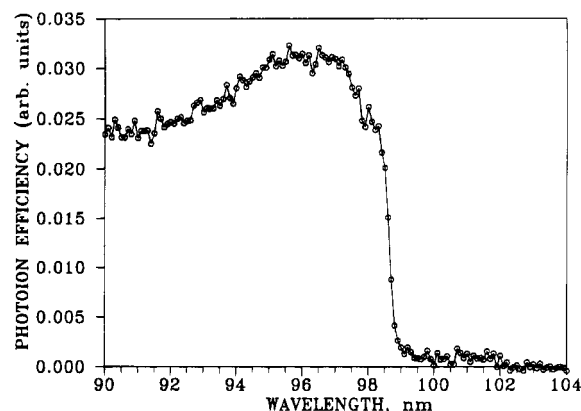
**Figure 2.** (A) Photoionization efficiency curves for the fragment ion,  $\text{NO}_2^+$ , of  $\text{HNO}_3$  from dissociative ionization of the neutral between  $\lambda = 85.0$  and  $110.0$  nm. Photoion efficiency is ion counts at  $m/z = 46$  divided by the light intensity in arbitrary units. The arrow indicates the onset of ionization for  $\text{HNO}_3$ . (B) Photoionization efficiency spectrum of  $\text{NO}_2^+$  fragment ion at threshold. The intersection of the two dashed lines gives an onset at  $\lambda = 102.26$  nm ( $12.12_5$  eV).

dissociative ionization of  $\text{HNO}_3$ . The strong threshold at  $\lambda = 102.26$  nm shown in Figure 2B corresponds to an appearance energy of  $12.12_5$  eV. This value for  $\text{AE}(\text{NO}_2^+, \text{HNO}_3)$  is somewhat larger than that reported recently by Jochims *et al.*<sup>16</sup> However, as also seen in Figure 2B, the  $\text{NO}_2^+$  signal tails off well beyond the strong threshold, toward longer wavelengths. This phenomenon was examined very carefully, and a “weak” threshold was obtained at  $109 \pm 1$  nm from very weak  $\text{NO}_2^+$  signals in experiments performed over the  $\lambda = 105$ – $112$  nm range where a LiF window was employed to exclude second-order light. Using the calculated enthalpy of formation for ( $\text{NO}_3^+$ ) (see Discussion), the process

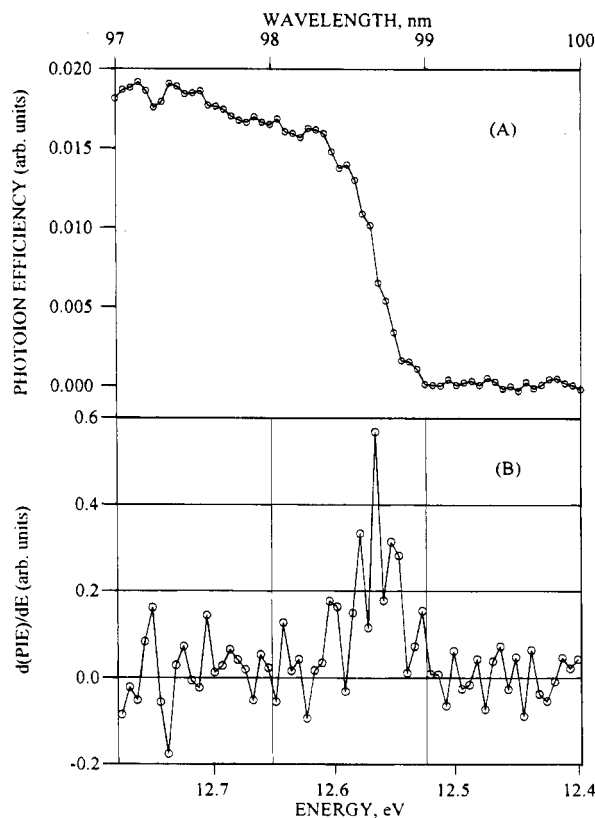


would be expected to occur at ionization energies close to 17 eV. This prediction was confirmed by observation of a weak signal for  $\text{NO}_3^+$  (from  $\text{HNO}_3$ ) with an onset at *ca.* 71 nm ( $\approx 17.5$  eV).

The photoionization for  $\text{NO}_3$  at  $m/z = 62$  in the wavelength region  $\lambda = 90.0$ – $104.0$  nm at  $0.1$  nm intervals has no detectable structure, as shown in Figure 3, from either autoionizing Rydberg states or cation vibrational levels above  $v = 0$ . In order to determine the ionization energy, a detailed examination near the threshold was carried out. The statistics were enhanced by collection of a large number of wavelength scans. Figure 4A shows the spectrum for  $\text{NO}_3$  obtained in the



**Figure 3.** Photoionization efficiency spectrum of  $\text{NO}_3$  between  $\lambda = 90.0$  and  $104.0$  nm obtained at a nominal resolution of  $0.23$  nm and with  $0.1$  nm steps. The photoion efficiency is the ion counts at  $m/z = 62$  divided by the light intensity in arbitrary units.



**Figure 4.** (A) Photoionization threshold region of  $\text{NO}_3$  between  $\lambda = 97.0$  and  $100.0$  nm obtained at a nominal resolution of  $0.14$  nm and with  $0.05$  nm steps. The photoion efficiency is the ion counts at  $m/z = 62$  divided by the light intensity in arbitrary units. (B) The energy derivative of the photoion efficiency spectrum on  $\text{NO}_3$  between  $\lambda = 97.0$  and  $100.0$  nm. The maximum in the derivative is at  $\lambda = 98.67_5$  nm ( $\text{IE} = 12.56_5$  eV).

wavelength region  $\lambda = 97.0$ – $100.0$  nm at  $0.05$  nm intervals at a nominal resolution of  $0.14$  nm. A background spectrum for  $\text{NO}_3$ , obtained with all the reagent flows on and the microwave discharge off, showed no appreciable signal above that due to instrumental noise. The threshold was analyzed by plotting the energy derivative of the  $\text{NO}_3$  PIE curve. This is an approximation of the photoelectron spectrum (see Figure 4B), and the ionization energy was determined as the maximum of this derivative. From Figure 4B, a threshold wavelength of  $\lambda = 98.67_5 \pm 0.14_0$  nm is obtained and therefore an IE of  $12.56_5 \pm 0.02_0$  eV. The IE values for  $\text{NO}_3$  at different nominal wavelength resolutions are listed in Table 1. The results from

**TABLE 1: Wavelength Thresholds and Ionization Energies for NO<sub>3</sub>**

nominal $\lambda$ resolution <sup>a</sup> (nm)	threshold <sup>b</sup> (nm)	IE (eV)
0.14	98.67 <sub>5</sub> ± 0.14	12.56 <sub>5</sub> ± 0.02
0.23	98.67 <sub>5</sub> ± 0.23	12.56 ± 0.03
0.23	98.65 ± 0.23	12.57 ± 0.03
0.23	98.63 ± 0.23	12.57 ± 0.03
0.23	98.60 ± 0.23	12.57 ± 0.03
0.23	98.65 ± 0.23	12.57 ± 0.03
0.23	98.60 ± 0.23	12.57 ± 0.03
0.23	98.65 ± 0.23	12.57 ± 0.03

<sup>a</sup> See Experimental Section. <sup>b</sup> Determined by maxima of d(PIE)/dE of the PIE spectrum: For consideration of uncertainty limits see results.

**TABLE 2: Comparison of IEs and EAs for NO, NO<sub>2</sub>, and NO<sub>3</sub>**

compd	IE/eV	ref	transition	EA/eV	ref
NO	9.26436 ± 0.00006	14	( <sup>1</sup> Σ <sup>+</sup> ) ← ( <sup>2</sup> Π <sub>r</sub> )	0.1 ± 0.1	14
NO <sub>2</sub>	9.60 ± 0.03	18, 21, 22	( <sup>1</sup> A <sub>2</sub> ) ← ( <sup>2</sup> A <sub>1</sub> )	2.3 ± 0.1	14
NO <sub>3</sub>	12.57 ± 0.03	this work	( <sup>1</sup> A <sub>1</sub> ') ← ( <sup>2</sup> A <sub>2</sub> ') <sup>a</sup>	3.937 ± 0.014	3

<sup>a</sup> Assuming D<sub>3h</sub> symmetry in the ground electronic state; see text.

eight measurements are in excellent agreement and lead to a simple average value of 12.57 ± 0.03 eV for the adiabatic ionization energy of NO<sub>3</sub>. The threshold values were obtained without correcting for the slit function of the monochromator as this effect should be included in the combined experimental/analytical uncertainty. The quoted uncertainties are taken as the instrumental resolution (fwhm) since the standard deviation of the mean was small (2σ = 0.009 eV). The spectra should be free of perturbations caused by vibrational hot bands as collisional deactivation of NO<sub>3</sub> radicals could be expected to occur with a time constant of about 1 ms under the experimental conditions, assuming a deactivation efficiency of *ca.* 1 in 10<sup>3</sup> collisions.<sup>9,10</sup>

## Discussion

**Dissociative Ionization of HNO<sub>3</sub>.** The appearance energy for formation of NO<sub>2</sub><sup>+</sup>, *via* reaction 3, can be calculated following standard methods.<sup>17</sup>

$$\begin{aligned} \text{AE}(\text{NO}_2^+, \text{HNO}_3) &= \Delta_f H_{298}^\circ(\text{NO}_2^+) + \Delta_f H_{298}^\circ(\text{OH}) - \\ &\Delta_f H_{298}^\circ(\text{HNO}_3) - (H_{298} - H_0)_{\text{NO}_2^+} - (H_{298} - H_0)_{\text{OH}} + \\ &5RT/2 \quad (5) \end{aligned}$$

The enthalpy of NO<sub>2</sub><sup>+</sup> at *T* = 298 K was computed from known values of the ionization energy of NO<sub>2</sub> (IE = 9.568 eV),<sup>18</sup> the enthalpy of NO<sub>2</sub> (33.045 kJ mol<sup>-1</sup>),<sup>19</sup> and the integrated heat capacities;<sup>19,20</sup> a value for Δ<sub>f</sub>H<sub>298</sub><sup>°</sup>(NO<sub>2</sub><sup>+</sup>) of 957.2 kJ mol<sup>-1</sup> was obtained.<sup>20</sup> Taking this value for Δ<sub>f</sub>H<sub>298</sub><sup>°</sup>(NO<sub>2</sub><sup>+</sup>), eq 5 yields AE(NO<sub>2</sub><sup>+</sup>, HNO<sub>3</sub>) = 11.584 eV. The calculated value for the NO<sub>2</sub><sup>+</sup> appearance energy corresponds to an onset at λ = 107.0 nm and thus is reasonably consistent with the observed, weak threshold at about 109 nm. The strong threshold, observed at λ = 102.26 nm (12.12<sub>5</sub> eV), is more than 0.5 eV larger than the calculated, thermodynamic one. Although it may be coincidental, it is interesting to note that the "excess" energy of 0.54<sub>1</sub> eV is nearly equal to one vibrational quantum in the OH (neutral) fragment, 3735 cm<sup>-1</sup> (or 0.46 eV).

**Comparison of the Ionization Energies of NO, NO<sub>2</sub>, and NO<sub>3</sub>.** Table 2 shows the IE and EA (electron affinity) of the nitrogen oxides, NO, NO<sub>2</sub>, and NO<sub>3</sub>. It is apparent that NO<sub>3</sub> has a significantly larger IE than would be expected from this

simple, linear progression. The photoabsorption and photoionization spectroscopy of NO(<sup>2</sup>Π) has been extensively studied.<sup>21</sup> In general, an electron is easily removed from a singly occupied essentially antibonding 2π orbital. This ease of removal of an electron is reflected in the relatively low values of both the ionization energy and the electron affinity. It should be noted that some uncertainties exist as to the magnitude of the IE for NO<sub>2</sub>.<sup>14,18,22</sup> Accurate measurement of IE(NO<sub>2</sub>) has long eluded experimentalists. The adiabatic ionization transition is difficult to directly access because of the change in geometry from bent in the neutral ground state to linear in the cation ground state, leading to vanishingly small Franck–Condon factors.<sup>18,22</sup> It is not apparent from inspection of Table 2 why NO<sub>3</sub> should have a larger IE than NO<sub>2</sub>. Hartree–Fock (HF) and complete active space, multiconfiguration self-consistent-field (CAS–MCSCF) calculations<sup>4</sup> of the optimized geometries and total energies for neutral and ionic NO<sub>2</sub> and NO<sub>3</sub> have shown that the open-shell electron of NO<sub>3</sub> is localized on the O<sub>3</sub> ring around the N atom and that this is stabilizing in nature. This makes the radical more polar and the electron more difficult to remove. In contrast, the open-shell electron of NO<sub>2</sub> is less localized on oxygen.

Boehm and Lohr<sup>4</sup> calculated the ionization energies and electron affinities for NO, NO<sub>2</sub>, and NO<sub>3</sub> at the fourth-order Moller–Plesset (MP4) level. Hartree–Fock optimized geometries and two levels of basis sets were used. There is a substantial reduction in the calculated ionization energies in going to the largest basis which includes diffuse functions. Ionization energies calculated with the smaller polarization basis actually agree better with experimental values. For the smaller basis, the calculated NO<sub>3</sub> ionization energy is 11.95 eV, which is, of course, also closer to the experimental value obtained in this work. The substantial effects of the basis variation are indicative of the MP perturbation being far from convergence. Nonetheless, the calculation supports the large increase in the ionization energy for NO<sub>3</sub> over that for NO and NO<sub>2</sub>.

**Geometry of NO<sub>3</sub><sup>+</sup> and NO<sub>3</sub>.** The PIE spectrum of NO<sub>3</sub> is characterized by a very sharp transition at the onset. It is also worth noting that there was no observable structure within 8.63 nm (1.21 eV) of the threshold. There has only been one set of calculations on the symmetries and energies of the NO<sub>3</sub> cation.<sup>4</sup> In contrast to the neutral ground state, there is a large energy difference (0.94 eV) between the D<sub>3h</sub> <sup>1</sup>A<sub>1</sub>' and C<sub>2v</sub> <sup>1</sup>A<sub>1</sub> (closed Y) states of the cation.<sup>4</sup> The calculations of Boehm and Lohr<sup>4</sup> at the MP4 level unambiguously show the cationic symmetry to be D<sub>3h</sub>. The calculations on the neutral ground state<sup>4,5</sup> support the D<sub>3h</sub> symmetry, but the energy difference below the equilibrium C<sub>2v</sub> geometry is not sufficient to be conclusive. One of the problems in the analysis of the experimental spectroscopy of neutral NO<sub>3</sub> has been the apparent complexity due to the mixing of the states of both low-lying symmetries.<sup>1,3</sup> In order to ascertain the shift in geometry from the D<sub>3h</sub> to C<sub>2v</sub> symmetries more accurately, calculations were performed to optimize equilibrium geometries at the CAS–MCSCF level. All calculations used the GAMESS suite of electronic structure codes.<sup>23</sup> The valence electrons were placed into 13 active orbitals for both the neutral and cation molecules. Effective core potentials<sup>24</sup> were used to eliminate the K shell of all atoms, and concomitant basis sets were used with one d-polarization function added to nitrogen and two to oxygen to account for the larger polarization there. Optimization was also done at the restricted HF level to demonstrate that there are substantial differences from the correlated geometries. The relative energies and the geometries are shown in Table 3. The HF geometries calculated here are in reasonable agreement with the values

**TABLE 3: Optimized Geometries and Relative Energies for NO<sub>3</sub> and NO<sub>3</sub><sup>+</sup> in D<sub>3h</sub> and C<sub>2v</sub> Symmetries**

molecule	calculation <sup>a</sup>	D <sub>3h</sub>		C <sub>2v</sub>	
		-E/au <sup>b</sup>	r <sub>e</sub> /nm	-E/au <sup>b</sup>	r <sub>e</sub> /nm <sup>c</sup>
NO <sub>3</sub> <sup>+</sup> ( <sup>1</sup> A <sub>1</sub> ') RHF	RHF	55.954 58	0.1193	56.065 36	0.1124
					0.1287
					0.1234
NO <sub>3</sub> <sup>+</sup> ( <sup>3</sup> A <sub>2</sub> ') MCSCF	MCSCF	56.205 69	0.1235	56.164 29	0.1411
					0.1234
					0.1234
NO <sub>3</sub> <sup>+</sup> ( <sup>3</sup> A <sub>2</sub> ') MCSCF	MCSCF	56.192 20	0.1268		
NO <sub>3</sub> <sup>+</sup> ( <sup>1</sup> E') MCSCF	MCSCF	56.191 44	0.1240		
NO <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> ') ROHF	ROHF	56.492 28	0.1210	56.535 30	0.1389
					0.1189
					0.1359
NO <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> ') MCSCF	MCSCF	56.595 32	0.1231	56.588 66	0.1211

<sup>a</sup> R(O)HF = restricted (open-shell) Hartree-Fock; MCSCF = multiconfiguration self-consistent field. <sup>b</sup> 1 au = 27.211 eV. <sup>c</sup> First distance represents single bond along the symmetry axis.

reported by Boehm and Lohr.<sup>4</sup> But the MCSCF values indicate that the equilibrium geometries of the neutral and cation are extremely close (see Table 3). The calculated equilibrium geometry for the radical is also in good agreement with that deduced experimentally.<sup>3,6</sup> In sharp contrast, the C<sub>2v</sub> equilibrium geometry of the neutral shows a difference of at least 0.015 nm in one bond length relative to D<sub>3h</sub>. This change in bond length is quite large, as an example, it exceeds that for the ionization of NO. For NO, the well-known Franck-Condon envelope includes at least four observable transitions.<sup>25</sup> By comparison, the polyatomic Franck-Condon factors for NO<sub>3</sub> would be expected to produce at least as complicated a spectrum if there were a change in symmetry during ionization. Even a shift of 0.003 nm between anion and neutral is sufficient to yield two comparable vibrational transitions in the photodetachment curve.<sup>3</sup> The photoionization efficiency curve (Figure 3) exhibits a single, large, and very sharp initial step with no evidence of additional steps. Since the experimental PIE spectrum shows no evidence of such a Franck-Condon progression and the theoretical evidence is strong that the cation symmetry is D<sub>3h</sub>, one may conclude that the neutral symmetry is also D<sub>3h</sub>. For the very flat neutral surface with a low barrier to distortion from D<sub>3h</sub> to C<sub>2v</sub> symmetry, Mayer *et al.*<sup>5b</sup> have shown that the ground nuclear vibronic wave function has the highest probability at the D<sub>3h</sub> configuration. Therefore, either the barrier is high relative to *kT* and the ground state is in the D<sub>3h</sub> well or the barrier is low relative to *kT* but the molecule is in the ground vibronic state which is effectively D<sub>3h</sub> in character.

The lowest triplet and first excited states of the cation were also calculated by MCSCF with the same number of active orbitals as used previously. The triplet state geometry was optimized. The excited singlet was obtained in an averaged density MCSCF calculation. The symmetry was restricted to D<sub>3h</sub>. A degenerate <sup>1</sup>E' state and <sup>3</sup>A<sub>2</sub>' state are shown in Table 3 to be close in energy and substantially lower than suggested by Boehm and Lohr.<sup>4</sup> These states must be studied at a higher level of correlation to substantiate these predictions. There is no clear evidence for these states in the experimental PIE curve although a small amount of structure is obtained in this region and attributed to instrumental noise.

**Thermochemical Data.** A value for Δ<sub>f</sub>H°<sub>0</sub>(NO<sub>3</sub><sup>+</sup>) may be obtained directly from the enthalpy of formation of NO<sub>3</sub> and the ionization energy of NO<sub>3</sub> (assuming the stationary electron convention<sup>14</sup>):

$$\Delta_f H^\circ_0(\text{NO}_3^+) = \text{IE}(\text{NO}_3) + \Delta_f H^\circ_0(\text{NO}_3) \quad (6)$$

Taking Δ<sub>f</sub>H°<sub>0</sub>(NO<sub>3</sub>) = 79.6 kJ mol<sup>-1</sup> (refs 3, 19, 26, and 27) and IE(NO<sub>3</sub>) = 12.57 eV ≡ 1212.8 kJ mol<sup>-1</sup>, the value for

Δ<sub>f</sub>H°<sub>0</sub>(NO<sub>3</sub><sup>+</sup>) is 1292.4 kJ mol<sup>-1</sup> with an estimated uncertainty of ±5.0 kJ mol<sup>-1</sup>. The enthalpy of formation of NO<sub>3</sub><sup>+</sup> at *T* = 298 K may be computed similarly with the additional correction for integrated heat capacities:

$$\Delta H_1 = \text{IE}(\text{NO}_3) + (H^\circ_{298} - H^\circ_0)_{\text{NO}_3^+} - (H^\circ_{298} - H^\circ_0)_{\text{NO}_3} \quad (7)$$

$$\Delta_f H^\circ_{298}(\text{NO}_3^+) = \Delta H_1 + \Delta_f H^\circ_{298}(\text{NO}_3) \quad (8)$$

where ΔH<sub>1</sub> is the enthalpy of ionization at *T* = 298 K and the (H°<sub>298</sub> - H°<sub>0</sub>) terms are the relevant integrated heat capacities. However, the integrated heat capacities are difficult to determine accurately because of large uncertainties in the vibrational frequencies.<sup>28</sup> Although the integrated heat capacity of the cation might be smaller than that of the neutral (perhaps by 1–2 kJ mol<sup>-1</sup>),<sup>29</sup> we prefer to assume that the integrated heat capacities cancel for the present computation. Thus taking 73.2 kJ mol<sup>-1</sup> (ref 27) as the value for Δ<sub>f</sub>H°<sub>298</sub>(NO<sub>3</sub>) and zero as the value for (H°<sub>298</sub> - H°<sub>0</sub>)<sub>NO<sub>3</sub><sup>+</sup></sub> - (H°<sub>298</sub> - H°<sub>0</sub>)<sub>NO<sub>3</sub></sub>, ΔH<sub>1</sub> = IE(NO<sub>3</sub>) and eq 8 yields a value for Δ<sub>f</sub>H°<sub>298</sub>(NO<sub>3</sub><sup>+</sup>) of 1285.0 kJ mol<sup>-1</sup> with an estimated uncertainty of about ±7.0 kJ mol<sup>-1</sup>.

Finally, the value for Δ<sub>f</sub>H(HNO<sub>3</sub><sup>+</sup>) can be used to derive an estimate for the proton affinity (PA) of NO<sub>3</sub>

$$\text{PA}(\text{NO}_3) = \Delta_f H^\circ_{298}(\text{NO}_3) + \Delta_f H^\circ_{298}(\text{H}^+) - \Delta_f H^\circ_{298}(\text{HNO}_3^+) \quad (9)$$

Estimating Δ<sub>f</sub>H°<sub>298</sub>(HNO<sub>3</sub><sup>+</sup>),<sup>30</sup> as above for NO<sub>3</sub><sup>+</sup>, to be 1018.9 kJ mol<sup>-1</sup> and taking the enthalpies of formation of NO<sub>3</sub> (ref 27) and H<sup>+</sup> (ref 14) at *T* = 298 K to be 73.2 and 1530 kJ mol<sup>-1</sup>, the value for PA(NO<sub>3</sub>) of 584.3 kJ mol<sup>-1</sup> is obtained with an estimated uncertainty of about ±4.5 kJ mol<sup>-1</sup>. Given the difficulty of calculating or measuring directly the proton affinities of open-shell molecules,<sup>31</sup> there is no literature value with which this value for PA(NO<sub>3</sub>) may be compared.

## Conclusion

The PIE spectrum for NO<sub>3</sub> was measured between λ = 90 and 104 nm using dispersed VUV synchrotron radiation. The experimental ionization threshold displays sharp, step function behavior from which an adiabatic IE of 12.57 ± 0.03 eV was derived. The shape of the derived PIE curve was determined for 87 nm (1.21 eV or almost 10 000 cm<sup>-1</sup>) above threshold. The curve does not show any strong features that can be attributed to vibrational structure resulting from a transition from C<sub>2v</sub> in the neutral ground state to D<sub>3h</sub> symmetry in the cation. Equilibrium geometries of the neutral and cationic species are calculated to be sufficiently close in D<sub>3h</sub> symmetry to yield one dominant vibrational transition as observed. Thus, both the PIE curve and theoretical calculations show that it is unlikely that NO<sub>3</sub> undergoes any significant geometry changes upon ionization. From this it may be concluded that the ground state neutral geometry for NO<sub>3</sub> is D<sub>3h</sub>.

**Acknowledgment.** The work at BNL was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC02-76CH00016. The work at GSFC was supported by the NASA Upper Atmosphere Research Program. Paul Monks thanks the NAS/NRC for the award of a Research Associateship.

## References and Notes

- Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J. E.; Le Bras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, *25A*, 1 and references therein.

- (2) Logan, J. A. *J. Geophys. Res.* **1983**, *88*, 10785.
- (3) Weaver, A.; Arnold, D. W.; Bradforth, S. E.; Neumark, D. M. *J. Chem. Phys.* **1991**, *94*, 1740.
- (4) Boehm, R. C.; Lohr, L. L. *J. Comput. Chem.* **1991**, *12*, 119.
- (5) (a) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 5554. (b) Mayer, M.; Cederbaum, L. S.; Köppel, H. *J. Chem. Phys.* **1994**, *100*, 899.
- (6) (a) Ishiwata, T.; Tanaka, I.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 2196. (b) Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1987**, *91*, 2721.
- (7) (a) Siegbahn, P. E. M. *J. Comput. Chem.* **1985**, *6*, 182. (b) Davy, R. D.; Schaefer III, H. F. *J. Chem. Phys.* **1989**, *91*, 4410. (c) Eriksson, L. A.; Wang, J.; Boyd, R. J.; Lunell, S. *J. Phys. Chem.* **1994**, *98*, 792.
- (8) Nesbitt, F. L.; Marston, G.; Stief, L. J.; Wickramaarachchi, M. A.; Tao, W.; Klemm, R. B. *J. Phys. Chem.* **1991**, *95*, 7613 and references therein.
- (9) Tao, W.; Klemm, R. B.; Nesbitt, F. L.; Stief, L. J. *J. Phys. Chem.* **1992**, *96*, 104 and references therein.
- (10) Monks, P. S.; Stief, L. J.; Krauss, M.; Kuo, S. C.; Klemm, R. B. *Chem. Phys. Lett.* **1993**, *211*, 416.
- (11) Kuo, S. C.; Zhang, Z.; Klemm, R. B.; Liebman, J. F.; Nesbitt, F. L.; Stief, L. J. *J. Phys. Chem.* **1994**, *98*, 4026.
- (12) Rahman, M. M.; Becker, E.; Benter, Th.; Schindler, R. N. *Ber. Bunsen.-Ges. Phys. Chem.* **1988**, *92*, 91.
- (13) Grover, J. R.; Walters, E. A.; Newman, J. K.; White, M. C. J. *J. Am. Chem. Soc.* **1985**, *107*, 7329 and references therein.
- (14) Lias, S. G.; Bartmess, J. G.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. No. 1), 1.
- (15) (a) Lloyd, D. R.; Roberts, P. J.; Hillier, J. H. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 496. (b) Frost, D. C.; Lee, S. T.; McDowell, C. A.; Westwood, N. P. C. *J. Electron Spectrosc.* **1975**, *7*, 331.
- (16) Jochims, H.-W.; Denzer, W.; Baumgärtel, H.; Löscking, O.; Willner, H. *Ber. Bunsen.-Ges. Phys. Chem.* **1992**, *96*, 573.
- (17) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.
- (18) Haber, K. S.; Zwanziger, J. W.; Campos, F. X.; Wiedmann, R. T.; Grant, E. R. *Chem. Phys. Lett.* **1988**, *144*, 58.
- (19) Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syvenud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. No. 1).
- (20) The heat of formation of  $\text{NO}_2^+$  at  $T = 298$  K is computed from the equation  $\Delta_f H^\circ_{298}(\text{NO}_2^+) = \text{IE}(\text{NO}_2) + (H_{298} - H_0)_{\text{NO}_2^+} - (H_{298} - H_0)_{\text{NO}_2} + \Delta_f H^\circ_{298}(\text{NO}_2)$ . Using the values listed in the text and estimating  $(H_{298} - H_0)_{\text{NO}_2^+} = 9.7$  kJ mol<sup>-1</sup>, we obtain  $\Delta_f H^\circ_{298}(\text{NO}_2^+) = 957.4$  kJ mol<sup>-1</sup>.
- (21) Berkowitz, J. *Photoabsorption, Photoionization and Photoelectron Spectroscopy*; Academic Press: New York, 1979.
- (22) Clemmer, D. E.; Armentout, P. B. *J. Chem. Phys.* **1992**, *97*, 2451.
- (23) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Jensen, J. H.; Koeski, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE* **1990**, *10*, 52.
- (24) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.
- (25) Wacks, M. E.; Krauss, M. *J. Chem. Phys.* **1961**, *35*, 1902.
- (26) Davis, H. F.; Kim, B.; Johnston, H. S.; Lee, Y. T. *J. Phys. Chem.* **1993**, *97*, 2172.
- (27) The value selected for  $\Delta_f H^\circ_{298}(\text{NO}_3)$ , 73.2 kJ mol<sup>-1</sup>, is a simple mean of values reported in refs 3, 19, and 26. A value for  $\Delta_f H^\circ_0(\text{NO}_3)$ , 79.6 kJ mol<sup>-1</sup>, was estimated by scaling the 0 K value reported in ref 19 (77.5 kJ mol<sup>-1</sup>) by the difference between the 298 K value reported there (71.1 kJ mol<sup>-1</sup>) and the selected value, 73.2 kJ mol<sup>-1</sup>.
- (28) For example, Weaver et al.<sup>3</sup> discuss the difficulty of making accurate assignments for  $\text{NO}_3$  neutral due to strong coupling between the two lowest energy states.
- (29) If the lowest frequency modes in the  $\text{NO}_3$  neutral are absent in the cation ground state, then the integrated heat capacity of the cation would be expected to be smaller than that of the neutral.
- (30) The values used were  $\text{IE}(\text{HNO}_3) = 11.96$  eV (ref 15b and this work);  $(H_{298} - H_0)_{\text{HNO}_3} = 11.8$  kJ mol<sup>-1</sup> (ref 19),  $(H_{298} - H_0)_{\text{HNO}_3^+} = 11.0$  kJ mol<sup>-1</sup> (estimated), and  $\Delta_f H^\circ_{298}(\text{HNO}_3) = 134.3$  kJ mol<sup>-1</sup> (ref 19).
- (31) Monks, P. S.; Stief, L. J.; Krauss, M.; Kuo, S. C.; Klemm, R. B. *J. Chem. Phys.* **1994**, *100*, 1902.