Negative Ion Electron Photodetachment from a Near-Blackbody Photon Source

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We have observed the rapid loss of nitroxide anion ($^3NO^-$) in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). The loss arises from two effects: a pressure-dependent component consistent with collisional electron detachment from $^3NO^-$, and a pressure-independent loss that we attribute to direct (bound-free) photodetachment induced by light emission from a heated filament inside the cell.

Introduction

Ion loss in ion traps generally occurs via collisional mechanisms, although recent experiments have shown that blackbody radiation and direct radiation from a filament can provide a competitive or dominant path for ion dissociation.[1−9] Cross sections for absorption within the spectrum of radiant emission indicate that the process of photochemical activation occurs primarily through vibrational excitation. We report here another mechanism for ion loss: direct electron photodetachment induced by radiation from a heated filament mounted inside the ion trap.

Typically, electron photodetachment from negative ions under ion cyclotron resonance (ICR) experimental conditions requires a bright light source such as an arc lamp or a laser.[10,11] Electron photodetachment can also be induced by infrared laser irradiation, resulting in successive absorption of IR photons giving a "hot" ion whose internal energy is sufficient to produce electron detachment.[12−15] For most negative ions, the ambient flux of photons from other sources, including the cell walls and the filament used in ion generation, is too small to be significant. Very unstable ions such as NO^-, however, can possess significant photodetachment cross sections at much longer wavelengths.

NO^- has a triplet ground state.[16] The electron affinity of NO is extremely low, only 0.026 eV (0.60 kcal/mol).[16−18] The $v = 1$ level of $^3NO^-$ is unbound with respect to electron detachment,[19] and collisional detachment from the ground state occurs at ambient temperatures.[20−24]

$$^3NO^- + M \rightarrow NO + M + e^- \quad (1)$$

While studying the reactivity of $^3NO^-$,[25,26] we observed a rapid nonreactive decrease in the $^3NO^-$ ion signal. The loss rate displayed both pressure-dependent (collisional) and pressure-independent (noncollisional) effects. The collisional loss we observed is consistent with collisional detachment according to eq 1. We suggest that noncollisional ion loss results from thermal radiation from the heated filament used for ion generation. We show here that the filament provides sufficient flux to induce measurable optical (bound-free) electron detachment from $^3NO^-$.

Experimental Section

The ICR cell used in these experiments[27] has a rhenium filament mounted just outside a 1 cm diameter hole in one of the $(5\ cm)^2$ trapping plates. A continuous current of 2.6 A resistively heats the filament, which is held at a large positive voltage relative to the trapping potential. When the filament voltage is pulsed negative, electrons from the heated filament are temporarily accelerated toward the adjacent trapping plate and into the cell, producing negative ions via dissociative attachment with neutral molecules. The filament is then returned to a positive potential for the remainder of the FT-ICR duty cycle.

In our apparatus, light from the glowing filament can be seen illuminating the cell. To demonstrate the contribution of this radiation to $^3NO^-$ ion loss, the electronics were modified to allow the filament current to be turned off immediately after ion generation.[28] The filament current remains off until after detection, when it is turned on for several milliseconds prior to next duty cycle.

$^3NO^-$ was formed from reaction of N_2O with O^-, which was formed by electron impact on N_2O:

$$N_2O + e^- \rightarrow O^- + NO$$

$$O^- + N_2O \rightarrow {}^3NO^- + NO \quad (2)$$

$^3NO^-$ was then isolated and monitored as a function of time under both continuous and pulsed filament conditions.[29]

Results

The observed rate constant for $^3NO^-$ loss as a function of N_2O pressure, obtained with a constant filament current of 2.6 A, is shown in Figure 1. The rate constant consists of collisional and noncollisional components,

$$k_{obs} = k_{CD}\bar{N}_{N_2O} + k_{NCD} \quad (3)$$

where k_{CD} is the collisional detachment rate constant ($cm^3\ s^{-1}$), $\bar{N}_{N_2O}$ is the number density of the collider gas (molecules cm^{-3}), and k_{NCD} is the noncollisional detachment rate constant (s^{-1}).

The best fit line to these data yields a slope, k_{CD}, of $4 \pm 1 \times 10^{-11}\ cm^3\ s^{-1}$ and a y intercept, k_{NCD}, of $7.4 \pm 1\ s^{-1}$. The value obtained for k_{CD} agrees quantitatively with collisional detachment rate constants reported by Ferguson[21] and Viggiano.[24,30]

With the pulsed filament modification, the $^3NO^-$ loss rate at 10^{-6} Torr was reduced from 8.5 to 5.5 s^{-1}, a decrease of about 35%. Within the uncertainty in our data, a single exponential was sufficient to describe the time decay in the $^3NO^-$ signal.

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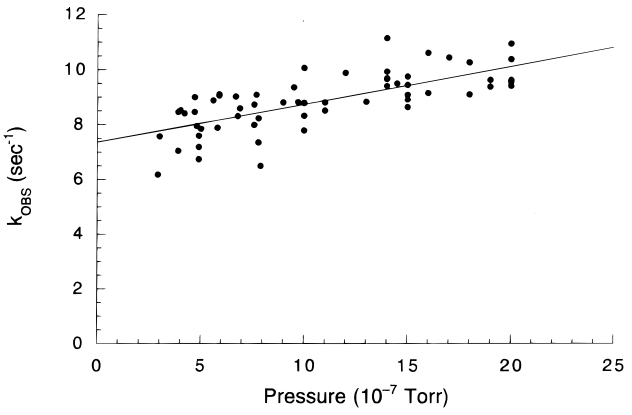

Figure 1. Observed $^3NO^-$ loss rate vs N_2O pressure.

Discussion

The results in Figure 1 show a collisional and a noncollisional effect. The noncollisional component was an order of magnitude larger than the collisional component at 10^{-6} Torr. Such a rapid noncollisional $^3NO^-$ loss rate has not been reported previously. The noncollisional ion loss in our experiments appears to be caused by radiation from the heated filament.

Radiation-induced ion loss can proceed by direct photodetachment,

$$^3NO^- + h\nu \xrightarrow{k_{pd}} NO + e^- \quad (4a)$$

and vibrational detachment,

$$^3NO^-(v=0) + h\nu \xrightarrow{k_{vd}} [^3NO^-(v=1)] \rightarrow NO + e^- \quad (4b)$$

The rate constant for $^3NO^-$ loss due to filament radiation, $k_{filament}$ (s^{-1}), depends on the overlap of the filament emission with cross sections for $^3NO^-$ photodetachment:[31]

$$k_{filament} = k_{pd} + k_{vd} \quad (5a)$$

$$k_{pd} = \int_0^\infty f(\lambda)\, \sigma_{pd}(\lambda)\, \rho(\lambda)\, d\lambda \quad (5b)$$

$$k_{vd} = \int_0^\infty f(\lambda)\, \sigma_{vd}(\lambda)\, \rho(\lambda)\, d\lambda \quad (5c)$$

$\rho(\lambda)\, d\lambda$ is the photon flux from the filament in the wavelength range λ to $\lambda + d\lambda$, $\sigma_{pd}(\lambda)$ is the cross section for direct photodetachment, $\sigma_{vd}(\lambda)$ is the cross section for vibrational absorption, and $f(\lambda)$ is a dimensionless geometric overlap factor.[32]

Filament Emission. The nature of thermal radiation has been extensively discussed in recent blackbody dissociation experiments. Several studies have shown[1-7] that heating the ICR cell walls produces sufficient blackbody radiation to photodissociate trapped ions. Other photon sources recently incorporated inside the ICR vacuum system include a halogen lamp,[33] a hot wire,[34,35] and a heated filament.[8,9]

As in these latter examples, the filament in our instrument can be modeled as a graybody emitter.[36,37] The spectral emittance of the filament, the value of $\rho(\lambda)\, d\lambda$ at the filament surface, is given by

$$\rho(\lambda)\, d\lambda = \frac{\epsilon 2\pi c}{\lambda^4}\left\{\frac{1}{e^{hc/(\lambda kT)} - 1}\right\} d\lambda \quad (6)$$

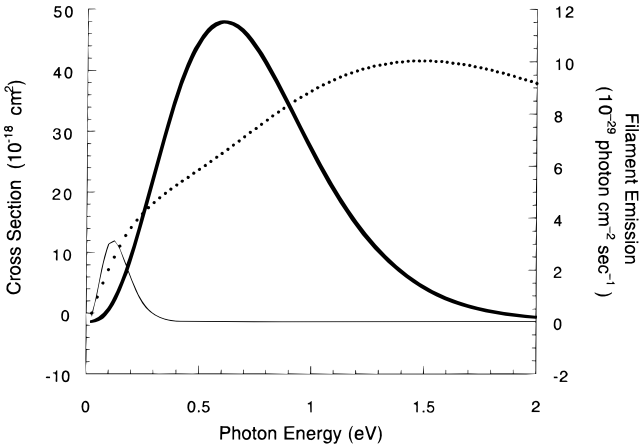

Figure 2. Overlay of filament emission (solid line) and calculated cross section (dotted line) for direct photodetachment of $^3NO^-$. The (0−0) vibrational transition is located near 0.16 eV (not shown). For comparison, thermal Planck emission from the cell walls at 350 K is also shown at 10× magnification (narrow line).

This equation differs from the ideal blackbody spectral emittance by the emissivity ϵ, which has a value of about 0.5 for a rhenium filament.[36]

To calculate $\rho(\lambda)\, d\lambda$, the temperature T must be known. This temperature can be estimated from the power dissipated by the filament once it has reached steady state. With a continuous current of 2.6 A and a measured voltage across the filament of 2.4 V, the power dissipated by the filament is estimated to be (2.6 A)(2.4 V) = 6.2 W. The filament temperature is related to the total radiated power according to the Stefan−Boltzmann equation

$$T = \left(\frac{P}{\sigma A \epsilon}\right)^{1/4} \quad (7)$$

where σ is the Stefan−Boltzmann constant and A is the surface area of the filament (~40 mm^2).

From these values, we estimate the temperature of the filament to be about 1820 K.[38] This temperature estimate agrees well with that found by Riveros,[8] who obtained a value of 1900 K for a similar filament dissipating 6.24 W. The calculated photon flux $\rho(\lambda)\, d\lambda$ at the filament surface is shown in Figure 2.[39] For comparison, the blackbody emittance of the cell walls, estimated to be at 350 K,[40] is also shown.

The photon flux inside the ICR cell is related to the flux at the filament surface by the geometric overlap factor, $f(\lambda)$. This coefficient accounts for the fraction of filament photoemission that passes into the cell and the wavelength-dependent reflectivity of the cell walls. This factor would not be expected to significantly diminish the flux estimated above, and this same overlap factor contributes equally to both direct and vibrational detachment.

Direct Photodetachment. For a given photon flux at wavelength λ, the probability of direct photodetachment is determined by the photodetachment cross section, $\sigma_{PD}(\lambda)$. Relative cross sections for $^3NO^-$ photodetachment have been reported at some photon energies by Farley[41] (0.37−0.52 eV) and Maricq[19] (0.14−0.19 eV). These wavelength regions are small compared to the spectrum of filament photoemission (Figure 2), and for purposes of this discussion, a more general description of the cross section curve is desired.

The shape of the cross section curve can be estimated using partially orthogonalized plane wave (POPW) theory.[42] In this model, the wave function of the detached electron is ap-

proximated as a plane wave that has been orthogonalized to the highest occupied molecular orbital of the anion. As seen in Figure 2, the resulting calculated cross sections are similar in magnitude to known absolute cross sections, falling in the range $10^{-19}-10^{-18}$ cm^2.[43]

The cross section for $^3NO^-$ is large across the range of filament emission. The combination of a large photon flux with a significant cross section for photodetachment at those wavelengths indicates that direct photodetachment of $^3NO^-$ by filament radiation must be significant. Our integral of the calculated cross section with the photon flux is about 100 times larger than the measured value. The photon flux, however, may be considerably smaller than our estimate, owing to the geometry of the cell and the small hole in the cell plates through which the radiation must pass.

Vibrational Autodetachment. The $v = 1$ level of $^3NO^-$ is unbound with respect to autodetachment and is expected to have a very short lifetime.[19] As a result, vibrational detachment of $^3NO^-$ requires only a single photon. This process was reported by Farley and co-workers,[41] who observed a modest decrease in total cross section with increasing energy over the range 3000−4150 cm^{-1}. They argued that this decrease was part of the broad $^3NO^-$ (2−0) overtone transition, which they estimated to occur around 2940 cm^{-1}.

Maricq et al.[19] reported a vibrational detachment resonance at 1284 cm^{-1}, which was assigned to the $^3NO^-$ (1−0) transition. At maximum, the vibrational detachment cross section is about 20 times the direct photodetachment cross section on which it is superimposed. Even with this larger cross section, vibrational detachment, a resonant process, occurs over small wavelength intervals compared to direct photodetachment. Vibrational autodetachment is consequently expected to account for a relatively small fraction of $^3NO^-$ loss.

Pulsed Current. The spectral emittance of the filament can be varied by changing the filament current. The range, however, is limited by the function of filament in ion generation. With a continuous filament current below 2.4 A, too few ions were generated for a rate constant to be reliably measured. Above 2.8 A, fluctuations in the ion signal led to much larger noise in the rate data. Within the range 2.4−2.8 A filament current, the $^3NO^-$ loss rate was indistinguishable within experimental error.

The pulsed filament modification allows the filament current to be varied independent of its use in ion generation. When the filament current is turned off after the electron beam pulse, the filament is allowed to cool and the resulting Planck emission shifts to lower energy and lower total spectral emittance. Although the resulting kinetics of ion loss are complex, the significantly decreased loss rate relative to continuous current conditions strongly suggests that photon emission from the filament contributes to $^3NO^-$ loss via direct bound-free electron photodetachment.

Conclusion

We have observed collisional and significant noncollisional ion loss of $^3NO^-$ in an FT-ICR spectrometer. Collisional loss is consistent with collisional detachment reported by other investigators. Noncollisional ion loss is attributed to optical processes induced by near-blackbody radiation from a heated filament in the ICR cell, with direct photodetachment as the dominant ion loss mechanism.

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(28) This modification was built using schematics kindly provided by Jose Riveros.
(29) No reactions between $^3NO^-$ and N_2O were observed. Electron transfer to form N_2O^- and elimination of N_2 to form NO_2^- have previously been reported (ref 23) with rate constants on the order of 10^{-14} cm^3 s^{-1}, too small for us to observe under these conditions.
(30) The $^3NO^-$ loss rate was also measured against isobutylene, a larger and "softer" collider than N_2O, and found to be identical within experimental error. This observation is consistent with Viggiano's measured $^3NO^-$ collisional detachment rate with propane.
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(39) The power typically required for photodetachment experiments ranges from 50 to 500 mW. The filament dissipates considerably more power with lower energy photons, and the estimated flux at these wavelengths is consequently expected to be very large.

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