

# Laser photoelectron spectrometry of $\text{NH}^-$ : Electron affinity and intercombination energy difference in $\text{NH}^-$ \*

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While spectroscopic measurements can determine molecular constants to high precision, spin conservation selection rules make observation of intercombination transitions difficult, especially when large steady state populations cannot be maintained, as is generally the case for radicals and short lived reactive species. In contrast, intercombination energy differences can often be readily obtained<sup>1-3</sup> from photoelectron spectroscopy of negative ions. In this Note, we report such studies on  $\text{NH}^-$ , resulting in an improved electron affinity for  $\text{NH}$ , and a measurement of the  $\text{NH}^-$  ( $^1\Delta - ^3\Sigma^-$ ) energy difference, confirming the spectroscopic observations<sup>4,5</sup> attributing a 4707 Å band system to  $\text{NH}^-$  ( $^1\Sigma^+ - ^3\Sigma^-$ ).

The experimental apparatus has been described in detail previously.<sup>6</sup> Briefly, a 680 eV mass analyzed negative ion beam is crossed by the focused intracavity beam of a 4880 Å Ar II laser. Electrons photodetached into a small solid angle are energy analyzed (resolution ~ 60 meV) and counted to obtain a photoelectron spectrum. In earlier work, a very small  $\text{NH}^-$  beam was produced from a discharge in  $\text{NH}_3$ ; low intensities precluded definitive identification of the ion, accurate energy determinations, and observations of transitions to the  $\text{NH}^-$   $^1\Delta$  state. These difficulties were largely overcome by substitution of hydrogen azide<sup>7</sup> ( $\text{HN}_3$ ) for the source gas and the installation of a higher power laser.

The absolute electron energy scale is determined by simultaneous photodetachment of the ion of interest and an ion whose E. A. is known. In this case the reference ion is  $\text{O}^-$  and we have

$$\text{E. A.}(\text{NH}) = \text{E. A.}(\text{O}) + \gamma \{ \Omega(\text{O}) - \Omega(\text{NH}) \} + mW \left\{ \frac{1}{M_{\text{O}}} - \frac{1}{M_{\text{NH}}} \right\},$$

where E. A. (O) is the "effective" oxygen electron affinity,<sup>8</sup> 1.465 eV,  $\Omega(\text{X})$  is the measured kinetic energy of electrons from  $\text{X}^-$ , and the last term is a kinematic correction involving the beam energy  $W$ , the ion masses  $M_x$ , and the electron mass  $m$ . The quantity  $\gamma$  is a measured correction for a non-linearity in our electron analyzer; in these studies  $\gamma$  was  $1.022 \pm 0.010$ . In the most favorable cases, where  $\Delta\Omega$  is small, electron affinities and energy differences can be determined to about  $\pm 0.003$  eV. In the data reported here  $\Delta\Omega$  was not small and the uncertainty in  $\gamma$  was a major factor in the error limits for  $\text{NH}$ .

From the  $\text{NH}^-$  ( $2p\pi$ )<sup>3</sup>  $X^2\Pi$  state, transitions to the  $\text{NH}^-$  ( $2p\pi$ )<sup>2</sup>  $X^3\Sigma^-$  and  $a^1\Delta$  states should be accessible with the 2.54 eV Ar II laser source. Since the extra electron in  $\text{NH}^-$  is nonbonding, we expect all geometries to be very similar and the photoelectron spectrum to be dominated by diagonal ( $\Delta V = 0$ ) transitions. The observed  $\text{NH}^-$  photoelectron spectrum (Fig. 1) is in accord with these ex-

expectations; only  $\Delta V = 0$  transitions are observed for both the  $^1\Delta$  and  $^3\Sigma$  states. From these data we conclude the ratio of relative vibrational intensities,  $f(1,0)/f(0,0)$ , is less than 0.005 for  $X^3\Sigma$ . Since  $r_e$  is known<sup>9</sup> for the  $X^3\Sigma$   $\text{NH}$  state we can utilize a harmonic oscillator Franck-Condon factor analysis to obtain bounds for  $r_e'$ ,  $\text{NH}^- X^2\Pi$ . From the  $^3\Sigma^-$  transition,  $r_e' = (1.047 \pm 0.002)$  Å.

Further corrections are necessary to obtain the appropriate detachment energies. Since the geometries of the ion and neutrals are so similar, rotational corrections<sup>10</sup> are  $< 0.0005$  eV. A larger error arises from the unresolved fine structure in the  $^2\Pi$   $\text{NH}^-$ . We estimate the spin-orbit constant  $A$  by an isoelectronic extrapolation,<sup>10</sup>

$$\frac{A(\text{NH}^- X^2\Pi)}{A(\text{NH} A^3\Pi)} \approx \frac{A(\text{OH} X^2\Pi)}{A(\text{OH} A^3\Pi)}.$$

Using known values,<sup>11,12</sup> this expression yields  $A(\text{NH}^- X^2\Pi) = -63 \text{ cm}^{-1}$ . The ion source temperature is  $(1000 \pm 500)$  K, and the resulting spin-orbit correction to the E. A.'s is  $1/2 A$  or  $(4 \pm 2)$  meV. Peak centers are located with a statistical uncertainty of  $\pm 0.003$  eV. By far the largest uncertainty comes from the nonlinearity correction  $\gamma$ , and the fact that the reference ion does not have peaks close to the  $\text{NH}$  ones; this error amounts to  $\pm 0.010$  eV for  $^3\Sigma$  and  $\pm 0.005$  for  $^1\Delta$ . The results so obtained are

$$\text{E. A.}(\text{NH} X^3\Sigma) = (0.381 \pm 0.014) \text{ eV},$$

$$\text{E. A.}(\text{NH} a^1\Delta) = (1.960 \pm 0.010) \text{ eV}.$$

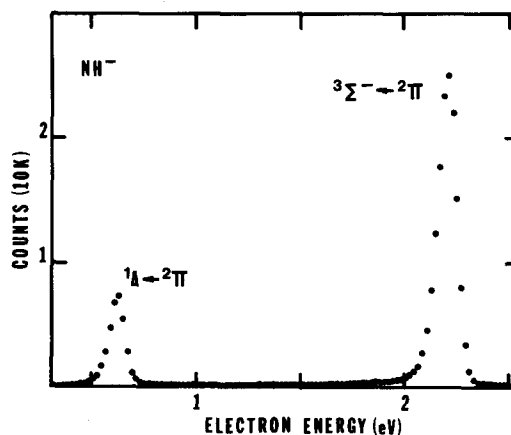


FIG. 1. The  $\text{NH}^-$  photodetachment spectrum collected in 20 mV bins shows the  $\text{NH}^-$   $^1\Delta$  and  $^3\Sigma^-$  peaks resulting from  $(0,0)$  transitions from  $^2\Pi$   $\text{NH}^-$ . No  $(1,0)$  transitions can be seen in this or other, higher resolution spectra. Peak width is primarily instrumental.

The first quantity compares well with the previously determined value<sup>13</sup> of  $(0.38 \pm 0.03)$  eV. The intercombination separation we obtain is  $(1.579 \pm 0.017)$  eV, in agreement with and confirming the more precise spectroscopic value<sup>5</sup> of 1.562 eV. In the course of this work we also observed large quantities of azide ion,  $N_3^-$ , which did not detach with the photon energy (2.54 eV) currently available to us. Further studies with an ultraviolet laser source will provide an accurate E. A. for this species.

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<sup>7</sup>The well documented explosive properties of this compound are accurate; it is shock sensitive. After one detonation of neat  $HN_3$ , we utilized a slurry of  $KN_3/H_2SO_4$  to produce the  $HN_3$  vapor with much less hazard.

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## Vibrational relaxation of nitric oxide by iodine atoms

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The vibrational relaxation of  $NO(X^2\Pi)$  in collisions with the reactive atoms  $O(^3P)$  and  $Cl(^2P)$  has recently been shown<sup>1</sup> to be very efficient, with relaxation rates of the order of the respective high pressure recombination rates. The results suggest that the fast vibrational energy exchange is due to a "complex mechanism," characterized by formation of intermediate collision complexes  $(ONO)^*$  and  $(ClNO)^*$  in bound states. A similar mechanism seems to be possible for  $NO(X^2\Pi)$  vibrational relaxation in collisions with the considerably heavier  $I(^2P)$  atom, i. e.,



with  $(INO)^*$  as the intermediate complex. Since the I-NO bond dissociation energy ( $\Delta H_0^0 = 17.3$  kcal/mol<sup>2</sup>) is much smaller than the one for the O-NO or Cl-NO bond, one may at first argue that in NO-I inelastic scattering the statistical complex formation and decay mechanism cannot be considered as dominant as in the NO-O or NO-Cl case. However, a more quantitative condition for statistical behavior of a bound intermediate complex has been derived in Ref. 3; the latter will occur if

$$\Delta E \gg 1/\rho(E, J),$$

where  $\Delta E$  is the experimental resolution for translational energy in the center of mass system, and  $\rho(E, J)$  is the density of rovibrational states of the complex at

the total energy  $E$  and angular momentum  $J$ .  $\rho(E, J)$  for  $(INO)^*$  can easily be estimated from the INO molecular properties.<sup>2,4</sup> In our experiments, with  $\Delta E \approx kT$ , for all the relevant  $J$  values the condition is quite well fulfilled [e. g.,  $\rho(E, J=10) \cdot kT \approx 400$ ]. This shows that the very efficient energy transfer via the complex mechanism can be expected also in NO-I collisions.

In the present note we report a measurement of the effect of iodine atoms on the vibrational relaxation of NO. The same shock wave technique that has been used in previous investigations<sup>1</sup> was applied. The experimental conditions behind the reflected shock waves were temperatures near to 2050 or 2550 K, and total gas concentrations of  $[M] = (2.5-3.3) \times 10^{-5}$  mol cm<sup>-3</sup>. The reaction mixtures contained NO (mole fractions  $X_{NO} = 4.2 \times 10^{-3}$  or  $1 \times 10^{-2}$ ) and  $I_2[X_{I_2} = (0.9-12.1) \times 10^{-4}]$  diluted in Ar. The actual concentration of  $I_2$  was determined *in situ* from the light absorption at  $\lambda = 487$  nm behind the incident shock wave ( $T \approx 1050$  or  $\approx 1250$  K), using the  $I_2$  absorption coefficient and its temperature dependence from Ref. 5. Behind the reflected shock wave  $I_2$  dissociates rapidly to give 2I; the dissociation rate  $k_{diss}(I_2)/[Ar] = 9.8 \times 10^{13} \exp(-30.4 \text{ kcal mol}^{-1}/RT)$  cm<sup>3</sup> mol<sup>-1</sup> · s<sup>-1</sup><sup>6</sup> exceeds the vibrational relaxation rate of NO by approximately a factor of 10. The population change of the first vibrational level NO(1) was monitored via absorption at the  $\gamma(0,1)$  transition near 236 nm ( $\Delta\lambda$ ,