NEW ELECTRONIC STATES OF NH AND ND OBSERVED BY RESONANCE ENHANCED MULTIPHOTON IONIZATION SPECTROSCOPY

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ABSTRACT

We report Resonance Enhanced MultiPhoton Ionization (REMPI) spectra of NH and ND, which reveal four new electronic states. Transitions from NH $a\ ^1\Delta$ to 3s and 3p Rydberg states in both NH and ND have been observed and rotationally analyzed. The transitions were observed in the wavelength range of 258 to 288 nm. The state assignments are : $e\ ^1\Pi\ (3s\sigma)$ at 82857 cm^{-1}, $f\ ^1\Pi\ (3p\sigma)$ at 86378 cm^{-1}, $g\ ^1\Delta\ (3p\pi)$ at 88141 cm^{-1}, and $h\ ^1\Sigma\ (3p\pi)$ at 89151 cm^{-1}.

INTRODUCTION

REMPI (Resonance Enhanced MultiPhoton Ionization) spectroscopy has proven to be a useful laboratory tool in obtaining new electronic spectra of many transient species.[1] NH in the metastable $a\ ^1\Delta$ state was the first transient to be observed by REMPI.[2] During a search for the REMPI spectra of N_3 we observed spectra of NH produced from the photolysis of HN_3. Six bands which are produced by excitations from the a $^1\Delta$ state to vibrational levels of four new electronic states have been analyzed.

APPARATUS AND METHODS

The apparatus has been described in detail elsewhere.[3] Briefly the NH $a\ ^1\Delta$ was produced by the photolysis of HN_3 (10% in helium) in a vacuum chamber at 10^{-4} Torr. The NH $a\ ^1\Delta$ then absorbed two photons to prepare a Rydberg state, which subsequently absorbed one more photon to ionize. The ions are extracted into a time-of-flight mass spectrometer and detected. A

spectrum consists of the ion current of the mass of interest versus the laser wavelength. The rotational constants ν_0', B', D', B", D" were obtained by using a least-squares procedure to fit the observed lines. ν_0'' was set to the value for the $a\ ^1\Delta$ state, after the lower state was determined to be the $a\ ^1\Delta$ state by minimum J values and rotational constants. The formula used for the rotational fitting was:

$$F(J) = \nu_0 + B[J(J+1)-\Lambda^2] - D[J(J+1)-\Lambda^2]^2 \qquad (1)$$

The values of ν_0 for the $a\ ^1\Delta$ state were obtained from Herzberg[4].

RESULTS

Spectra were observed from 258 to 288 nm. A typical band is shown in Figure 1. Six bands were observed and assigned. The assignments and least-squares fits to the data of the rotational constants are shown in Table I.

Table I. Rotational Assignments of NH and ND bands observed from 258 to 288 nm. All transitions are from the $a\ ^1\Delta$ state.

Species and Transition	Band Origin, (cm^{-1})	B (cm^{-1})	D (10^3 cm^{-1})	quantum defect
NH e $^1\Pi(3s\sigma)$ (0-0)	82 856.76(15)	14.0831(66)	1.680(30)	0.94
ND e $^1\Pi(3s\sigma)$ (0-0)	82 927.60(12)	7.5704(42)	0.479(10)	
NH e $^1\Pi(3s\sigma)$ (1-0)	85 343.38(16)	13.4451(73)	1.597(33)	
ND e $^1\Pi(3s\sigma)$ (1-0)	84 805.43(19)	7.3099(75)	0.413(19)	
NH f $^1\Pi(3p\sigma)$ (0-0)	86 378.13(13)	14.2281(65)	1.629(33)	0.79
ND f $^1\Pi(3p\sigma)$ (0-0)	86 456.89(13)	7.7268(45)	0.494(13)	
NH g $^1\Delta(3p\pi)$ (1-1)	87 419.75(15)	13.7490(240)	4.188(486)	
ND g $^1\Delta(3p\pi)$ (1-1)	87 746.75(17)	7.6469(61)	0.852(40)	
NH g $^1\Delta(3p\pi)$ (0-0)	88 140.54(25)	14.9496(146)	2.236(109)	0.70
ND g $^1\Delta(3p\pi)$ (0-0)	88 228.76(32)	7.8096(249)	1.403(134)	
NH h $^1\Sigma(3p\pi)$ (0-0)	89 531.25(23)	15.2584(210)	2.077(212)	0.61
ND h $^1\Sigma(3p\pi)$ (0-0)	89 568.70(22)	8.1510(116)	0.343(77)	

The symmetry assignments come from tracing the branches to their minimum J values.[4] In most cases this uniquely determines the electronic symmetry of the upper and lower states involved in the transition. The Rydberg

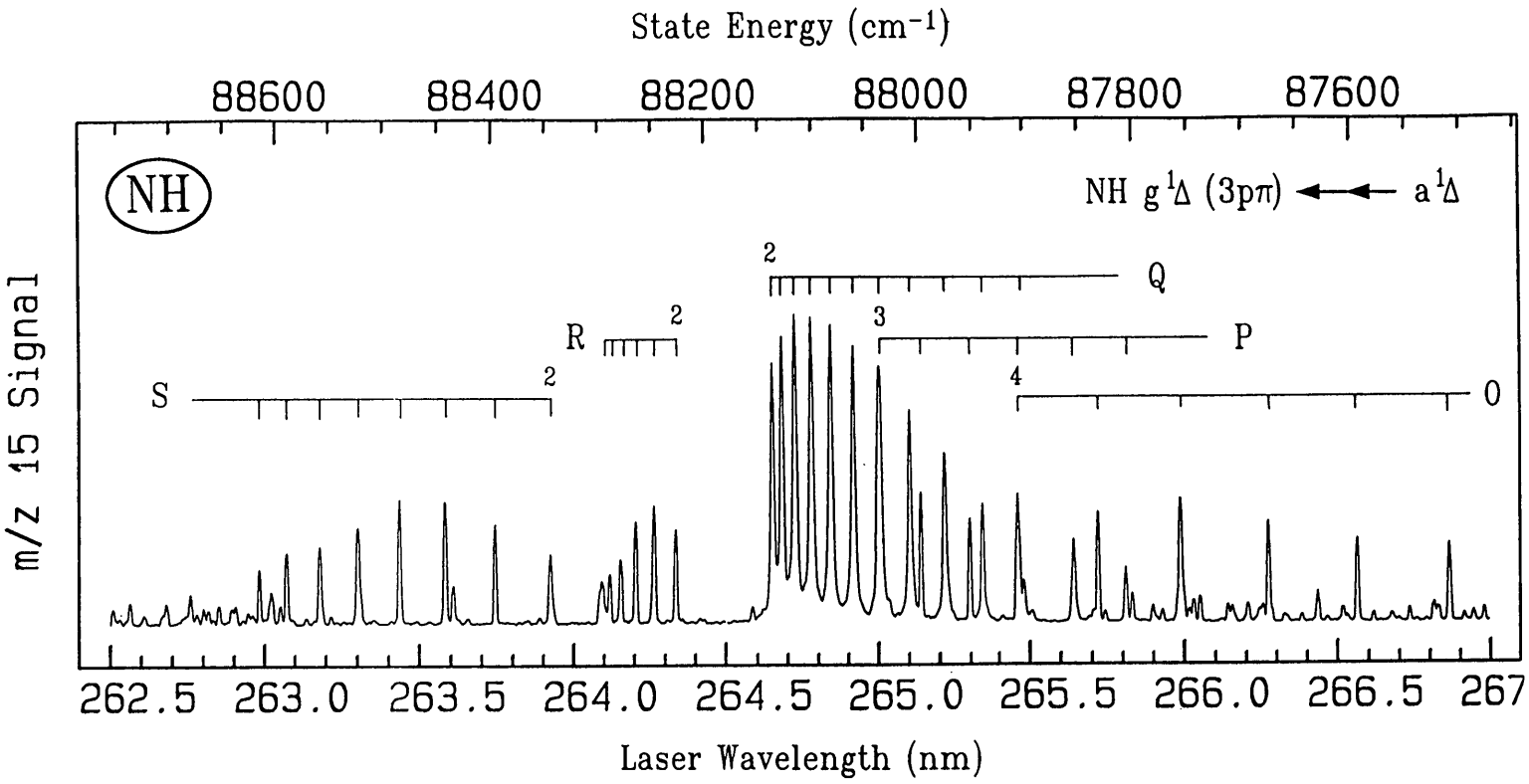

Figure 1. REMPI spectrum of NH from 262.5 to 267 nm. The transition is g $^1\Delta(3p\pi) \leftarrow a\ ^1\Delta$. Five rotational branches are observed, with a strong Q branch as expected for a two-photon transition with $\Delta\Lambda = 0$. The branches and minimum J values are indicated with festoons.

assignments come from calculating the quantum defect, δ, using the Rydberg formula:

$$\nu_{00} = IP - R/(n-\delta)^2 \qquad (2)$$

where ν_{00} is the state origin, IP is the ionization potential (108800 cm^{-1} for NH)[5], R is the Rydberg constant (109737 cm^{-1}), and n is the principal quantum number (3 in this case). For Rydberg states built on nitrogen appropriate quantum defects are: ns 0.95 to 1.1, np 0.6 to 0.8, nd -0.05 to 0.15.[6]

The symmetry assignments are consistent with the possible electronic states given the Rydberg configurations: For an electron in the 3sσ Rydberg orbital the electronic configuration is $\sigma\pi$, which gives rise to $^1\Pi$ and $^3\Pi$ states, of which only the $^1\Pi$ state is accessible through allowed transitions from the a $^1\Delta$ state. Similarly a $^1\Pi$ state is formed from the 3pσ orbital configuration. For the 3pπ orbital the configuration is $\pi\pi$, which gives rise to $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ states, as well as triplet states. All of the possible states which are accessible through allowed transitions have been observed except one of the Σ states. The data do not allow differentiation between the $^1\Sigma^+$ and $^1\Sigma^-$ states. The other Σ state may reside at an energy above the region surveyed.

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