Color-center laser kinetic spectroscopy: observation of the $a^1\Delta$ NH vibrational fundamental

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The vibrational fundamental of $a^1\Delta$ NH formed by 193-nm excimer-laser photolysis of gaseous HN$_3$ has been observed using a color-center laser. The high degree of rotational excitation resulting from the photolysis, corresponding to a temperature of ~10 000 K, allows high-order centrifugal distortion constants to be determined. The frequencies of the 35 observed lines and the centrifugal distortion constants determined from them are reported.

INTRODUCTION

The photolysis of gaseous hydrazoic acid has been a subject of ongoing interest from the points of view both of the primary photolysis step and of the measurement of reaction rates of the many chemical reactions that are postulated to ensue.[1–8] Although the UV absorption spectrum of HN$_3$ has been observed at all wavelengths above 115 nm,[3,5] photochemistry studies have largely been confined either to wavelengths above 248 nm, where it has become established that the photolysis leads to the production of $a^1\Delta$ NH in its ground vibrational state with a quantum yield of at least 98%,[1–4] or to vacuum-UV wavelengths, where $c^1\Pi$ NH is the predominant species formed.[5]

The $a^1\Delta$ NH produced at the longer wavelengths has been observed both by laser-induced fluorescence and by absorption in the visible region (the $c^1\Pi–a^1\Delta$ system, well known for many years[9–11]). Much interest in this reactive biradical, which is isolectronic with both O(^1D) and CH$_2$($^1A_1$), arises from the possibility of its undergoing addition reactions with various hydrocarbons to form amines.[12–15] In the HN$_3$ photolysis system it is established that $^1\Delta$ NH reacts with its precursor on almost every collision, although there remains a discrepancy as to the exact value of the rate constant.[1,2,6]

This work describes the first reported observation of the vibrational fundamental of $^1\Delta$ NH in the infrared region and gives line positions of many of the observed lines. The $^1\Delta$ NH is produced by 193-nm excimer-laser flash photolysis of HN$_3$, and the IR absorption is probed by a color-center laser.

The development of kinetic spectroscopy in the infrared has been slow because of the lack of suitable IR probe sources and array detectors. Before the invention of lasers, Pimentel *et al.*[16] developed a rapid-scanning monochromator using a blackbody source that could scan a significant portion of the IR within a short time after the photolysis pulse. Since the advent of lasers, research activity in IR kinetic spectroscopy has expanded. Sorokin and co-workers[17] tackled the problems of generation and detection of IR radiation by using stimulated Raman scattering of a broadband dye laser to produce the IR continuum and then upconverting this to the visible (after modulation by the sample) by a four-wave mixing process in an alkali-metal vapor, thereby permitting use of a photographic plate. The availability of narrow-band, broadly tunable IR lasers has provided a further improvement in sensitivity as well as the capability of doing high-resolution work, and present investigators are using these sources in combination with UV lasers. References 18–20 cite the achievements of other investigators in this field; Ref. 21 gives an overview of the technique and describes our own preliminary results in this area.

EXPERIMENT

The experimental layout is shown in Fig. 1. The UV beam (approximately 1.5 cm^2 in area) from a Lambda Physik EMG-101 excimer laser operating on the ArF transition at 193 nm was used as a photolysis source. The laser is rated at 200 mJ per pulse at 193 nm for slow repetition rates, degrading slightly at our chosen operating condition of 15 Hz. The UV-laser discharge produces IR emission. The shot-to-shot power fluctuations of this IR emission are a significant noise source. Therefore the UV and the IR beams were arranged to propagate collinearly but in opposite directions through the cell to avoid detecting this weak, broadband IR emission. In addition, to eliminate this interference completely, it was found
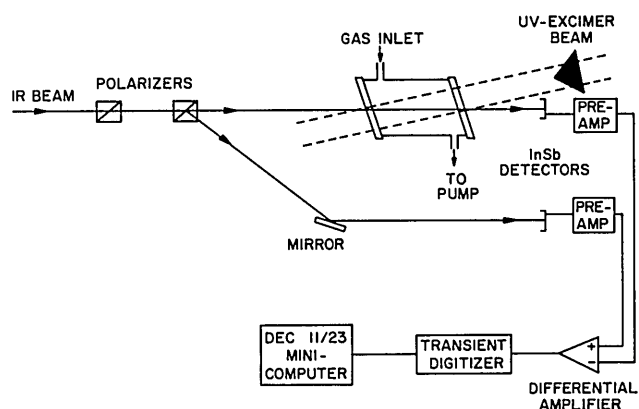
Fig. 1. Experimental layout. The balance between the two beams can be adjusted by rotating the first polarizer.

necessary to tilt the CaF_2 cell windows with respect to the UV beam to avoid reflections into the IR detector.

A balanced detector method was used to reduce the significant source noise of the Burleigh FCL-20 color-center laser used in this work. A Rochon-type polarizer placed before the photolysis cell allowed part of the IR beam to be directed to a liquid-N_2-cooled InSb detector, matched with a similar detector placed beyond the cell. A second polarizer closer to the laser could then be rotated to adjust detector balance. The difference signal between the detectors was amplified and fed into a Lecroy 20-MHz transient digitizer (Model 2256AS), which was triggered by the photolysis pulse and interfaced to the PDP 11/23 DEC minicomputer, which served to scan the color-center laser. (Reference 22 describes our computer-controlled color-center laser in detail.) Appropriate software allowed up to four digitizer channels to be stored for each photolysis pulse, and in the present experiment six traces at each frequency interval were averaged together. In this way we were able to detect a 0.5% absorption of the IR power with a signal-to-noise ratio (S/N) of ~10.

The hydrazoic acid used as the photolysis precursor was synthesized by heating an excess of stearic acid with NaN_3 to 110°C under vacuum and collecting the gas in a 3-liter storage bulb at pressures of no more than 80 Torr to avoid possible explosion.[23] The NaN_3–stearic acid mixture was pumped on overnight to remove H_2O and other volatile impurities, but no other steps were taken to purify the gas further. The major impurity, based on a gas chromatography/mass spectrometry run and interferences in our spectra, appeared to be small amounts of NH_3.

The initial search for the $^1\Delta$ NH lines arising from photolysis of HN_3 was greatly facilitated by the $v = 0$ and $v = 1$ constants for $^1\Delta$ NH obtained[24] from the known frequencies of both (0, 0) (Refs. 9–11) and (0, 1) (Ref. 24) transitions in the $(c^1\Pi–a^1\Delta)$ NH system. These constants are far more refined than those given in an earlier exhaustive account prepared by Lents in 1971 of the molecular constants and transition probabilities of all the NH electronic states.[25] After the NH signals were found initially, experimental conditions could be optimized. The signal strengths were fairly sensitive to both pressure and flow rate. Our best conditions corresponded to a pressure of 1 Torr of HN_3 flowing through the photolysis cell. An increase flow rate at the same pressure resulted in an intense fluorescence at the front of the cell, almost certainly from the excited electronic state of NH_2.

The $^1\Delta$ NH transient signals are quite short lived, and it became necessary to modify the detector preamps in order to estimate the signal lifetime. Without excessively sacrificing sensitivity we were able to shorten our preamplifier time constant (initially ~30 μsec) so that the overall apparatus time constant was reduced to 4 μsec. The NH signal decayed in 6 μsec. Figure 2 displays the comparison between instrument response and NH-signal decay. The presence of an induction period before the NH signal is seen, is not understood.

In wavelength scans we typically acquired a channel 50 nsec before the photolysis pulse and a second channel 2 μsec later, by which time the signal had reached its maximum height. Differencing of these posttrigger and pretrigger channels significantly improved the S/N over that of the raw signal because the laser noise is correlated over such a time scale. (The balancing of the two detectors essentially reduces only low-frequency noise since the time constants of the two de-
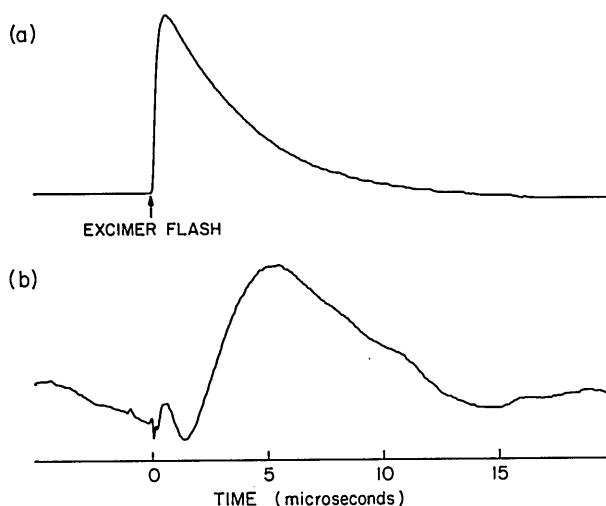

Fig. 2. (a) Detector time-response function as obtained by using the highly attenuated red F atom excimer-laser line (laser pulse length is ~3 nsec) as a delta-function source. $1/e$ time = 4.0 μsec. (b) Decay of the NH $^1\Delta$ transient absorption ($P = 1$ Torr). $1/e$ time = 5.5 μsec. Various slightly different conditions give $1/e$ times ranging from 4.5 to 8.3 μsec.
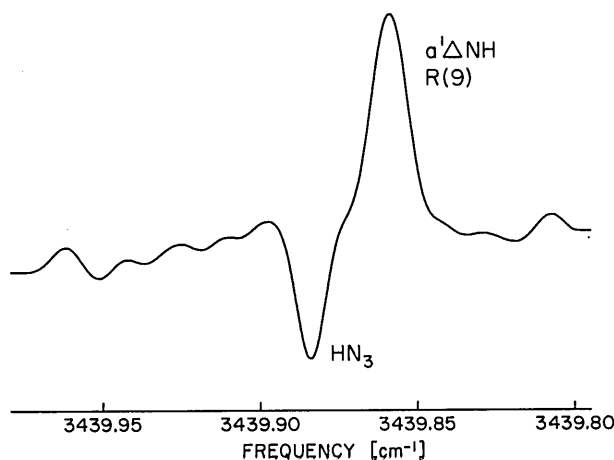

Fig. 3. Typical wavelength scan over a NH $^1\Delta$ transient absorption and HN_3 transient decrease in absorption. The signal is acquired 1.5 μsec after the photolysis flash.

tector/preamp combinations are not matched well enough to reduce high-frequency noise effectively. However, it still appears advantageous to use balanced detectors or at least a high-pass filter to avoid saturating the amplifiers with low-frequency noise.)

For calibration purposes both a reference gas-absorption signal and a marker cavity signal were acquired at the same time as the data, the marker free spectral range being accurately determined from earlier measurements. Line positions were then calculated by extrapolation from known frequencies of NH_3 (Ref. 26) and HN_3 (Ref. 27) reference lines using the marker trace. A typical such scan is shown in Fig. 3. The Doppler width of the observed lines (460 MHz) limits the accuracy to which their frequencies may be determined to 0.003 cm^{-1}. The scarcity of calibration lines in combination with difficulties with the laser meant that comparatively few of the observed NH lines were measured to this accuracy, the rest being determined at lower resolution from survey scans.

RESULTS

A list of the $^1\Delta$ NH lines observed, along with the uncertainties in the measurements, is given in Table 1. The lowermost rotational line positions can be fairly accurately predicted using the constants given in Ramsay and Sarre's paper,[24] but as expected the agreement between prediction and observation becomes progressively worse at higher J values, warranting the inclusion of a higher-order centrifugal distortion term. The rotational energy levels were thus fitted to a formula of the form

$$F_v(J) = B_v[J(J+1) - \Lambda^2] - D_v[J(J+1) - \Lambda^2]^2 + H_v[J(J+1) - \Lambda^2]^3 + L_v[J(J+1) - \Lambda^2]^4.$$

Ramsay and Sarre's measurements of the (0, 1) band of the $c^1\Pi - a^1\Delta$ system were included in the fit but in a manner that eliminated the need to recalculate the $c^1\Pi$ constants. This was achieved by combining their measurements in such a way that the $c^1\Pi$ energy levels do not appear, i.e., by fitting combination differences. The way chosen to handle the combination-difference fitting was to subtract the average of the observed transitions with a common upper-state level from each observed transition. These quantities are all independent of the $c^1\Pi$ constants and are readily incorporated with the IR observations into a standard least-squares routine for the evaluation of the $v = 0$ and $v = 1$ constants for the $a^1\Delta$ state. Table 2 shows the resulting constants in comparison with those of Ramsay and Sarre.

The photolysis wavelength (193 nm) is close to the second UV absorption maximum at 190 nm.[3,5] In contrast to 248-nm photolysis, the nascent state distributions at 193 nm have not been studied. Estimates of the rotational and the translational temperatures can also be obtained from our data, but it should be borne in mind that these do not refer to nascent temperatures since all signals are recorded several microseconds after the flash and at a pressure of 1 Torr (corresponding to 10–100 collisions after formation of the radical). An estimate of the rotational temperature was made based on the scan over $R(14)$ and $R(25)$ shown in Fig. 4 and the assumption that the rotational distribution could be characterized by a

Table 1. Observed Wave Numbers of the Vibrational Fundamental of $a^1\Delta$ NH

J	Observed (cm^{-1})	$(o-c)^a$ (cm^{-1})	$(o-c)^b$ (cm^{-1})	J	Observed (cm^{-1})	$(o-c)^a$ (cm^{-1})	$(o-c)^b$ (cm^{-1})
(a) R-Branch Lines
2	3276.382^c	0.052	0.082	19	3537.097	0.002	0.155
3	3304.035	−0.002	0.029	20	3537.201	−0.006	0.141
4	3330.351	−0.002	0.028	21	3535.518^c	0.016	0.139
5	3355.247	0.003	0.033	22	3531.965^c	−0.005	0.074
6	3378.678	0.002	0.033	23	3526.598	0.001	0.005
7	3400.615	0.001	0.033	24	3519.405^c	0.032	−0.078
8	3421.027	0.000	0.034	25	3510.295	0.006	−0.266
9	3439.885	0.001	0.039	26	3499.331	−0.003	−0.501
10	3457.155^c	0.001	0.044	27	3486.487^c	−0.012	−0.814
11	3472.811	−0.002	0.051	28	3471.774	−0.003	−1.204
12	3486.827^c	−0.004	0.060	29	3455.152^c	−0.005	−1.722
13	3499.184	0.001	0.078	30	3436.638^c	0.007	−2.367
14	3509.840	−0.006	0.086	31	3416.215^c	0.026	−3.172
15	3518.802	0.005	0.112	32	3393.821	−0.001	−4.222
16	3526.050^c	0.033	0.157	33	3369.519	0.003	−5.477
17	3531.486	0.003	0.140	34	3343.258	−0.002	−7.015
18	3535.190^c	0.007	0.156				
(b) Q-Branch Lines
2	3181.564^c	0.023	0.050				
3	3177.871^c	0.036	0.063				

^{a} (Observed − calculated) values using the constants given in Table 2.

^{b} (Observed − calculated) values using the constants of Ramsay and Sarre.[24]

^{c} Not included in least-squares fit. These lines were measured from survey scans and could be as much as 0.030 cm^{-1} in error (corresponding to two laser-cavity modes).

Table 2. Molecular Constants for the Vibrational Fundamental of $a^1\Delta$ NH

	Present Work^a		Ramsay and Sarre	
	$v = 0$	$v = 1$	$v = 0$	$v = 1$
B_v	16.43273(29)^b	15.81475(32)	16.4320	15.8141
$10^3 D_v$	1.6812(36)	1.6502(32)	1.671	1.644
$10^7 H_v$	1.45(10)	1.347(70)	1.207	1.20
$10^{11} L_v$	1.3(16)	1.1(15)	−	−
$\nu_0{}^c$	\multicolumn{2}{c}{3182.7768(37)}	\multicolumn{2}{c}{3182.75}
σ^d	0.0037		

^{a} The constants of the present work were generated using a least-squares procedure incorporating our own IR data and the data of Ramsay and Sarre.[24] The uncertainties in these measurements, used to weight the data, were taken as 0.003 and 0.005 cm^{-1}, respectively.

^{b} The error limits are 1σ and are right justified to the last digit on the line.

^{c} ν_0 corresponds to $\Delta G_{1/2}$.

^{d} Standard deviation of the fit.

Boltzmann temperature. This is the only justifiable way of estimating this quantity from our data because it represents identical conditions (IR-laser power, flow rate, etc.) for both lines. The temperature thus measured was 10 200 ± 800 K. The observed linewidths of the recorded lines yielded an estimate of the translational temperature of 570 ± 60 K.

During the course of our measurements several additional lines were detected near the observed $^1\Delta$ NH lines, which were longer lived than the $^1\Delta$ species. These lines are not at the frequencies of the observed $X\,^3\Sigma^-$ NH transitions[28] or the calculated $b\,^1\Sigma^+$ NH transitions.[29,30] Furthermore, these lines do not belong to ground-state ($\tilde{X}\,^2B_1$) NH$_2$ molecules[31]

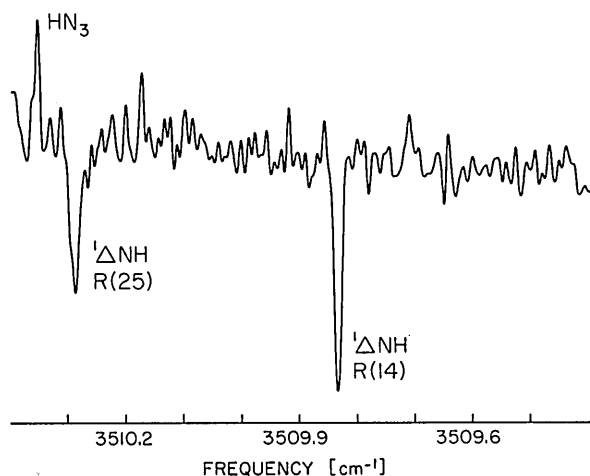Fig. 4. Comparison of intensity of $R(14)$ and $R(25)$ NH $^1\Delta$ transient absorptions used to obtain an estimate of the rotational temperature.

but may have been excited-state ($^2A_1$) NH$_2$ lines since the formation of the excited state is known to be fast on this time scale[1-3,6] (formed from reaction of $^1\Delta$ NH with HN$_3$). It is known[32] that photolysis at 193 nm produces $b\ ^1\Sigma^+$ NH, and searches were undertaken to identify positively some of the R-branch $b\ ^1\Sigma^+$ lines but without success. The frequencies of the unknown lines also precluded them from being $v = 2 \leftarrow v = 1\ ^1\Delta$ NH rotational components.

The NH $^1\Delta$ ($1 \leftarrow 0$) Q-branch lines seen were in a portion (3180 cm^{-1}) of our color-center laser's operating region in which power is decreasing rapidly with increasing wavelength. This precluded the detection of Q-branch lines with J values greater than 4. However, the $J = 2$ line was shown to be magnetic, as expected, in contrast to the almost nonmagnetic R-branch lines (where the magnetic rotation from the various M components cancels identically in first order[33]).

SUMMARY

The vibrational fundamental of the $a\ ^1\Delta$ NH radical formed by 193-nm excimer-laser photolysis of HN$_3$ has been directly observed in the IR region. The present work yields higher-order centrifugal distortion constants for the $a\ ^1\Delta$ state of NH than those of Ramsay and Sarre, owing to the high degree of rotational excitation of the NH produced from HN$_3$ by photolysis at this wavelength.

The measured translational temperature is much smaller than the nascent temperature measured by McDonald *et al.*[2,3] following photolysis above 248 nm, indicating a very fast relaxation process. This is in sharp contrast to the very high degree of rotational excitation still present even after a few microseconds, presumably because of the large rotational constant of this species, which makes relaxation processes slower. Our measurements do not exclude the possibility that higher vibrational states were excited on or after the photolysis, although the work of McDonald *et al.* suggests that this in unlikely. Future experiments are expected to incorporate both lower precursor pressures (as a result of increased UV absorption pathlengths) and faster detector–preamp combinations so that nascent distributions will become accessible.

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