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# **TECHNICAL REPORT BRL-TR-2805**

# KR+ LASER EXCITATION OF NH2 IN ATMOSPHERIC PRESSURE FLAMES

# WILLIAM R. ANDERSON, JOHN A. VANDERHOFF ANTHONY J. KOTLAR, KOON N. WONG

APRIL 13, 1987

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US ARMY BALLISTIC RESEARCH LABORATORY ABERDEEN PROVING GROUND, MARYLAND

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### GENERAL INFORMATION

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### I. INTRODUCTION

The amidogen (NH<sub>2</sub>) radical has been a subject of extensive experimental and theoretical investigations since the discovery of its emission spectrum more than a century ago.<sup>1</sup> The two electronic states involved in the visible transition,  $\tilde{A}^{2}A_{1}$  and  $\tilde{X}^{2}B_{1}$ , result from the Renner-Teller interaction;<sup>2</sup> that is, these two electronic states correlate with the doubly degenerate  $2\pi$  state of the molecule in its linear configuration. Because the molecule is bent the  $\pi$  degeneracy is lifted, giving rise to the widely separated states  $^{2}A_{1}$  and  $^{2}B_{1}$  of  $C_{2v}$  symmetry. The ground state  $^{2}B_{1}$  is bent with an equilibrium bond angle of ~103° and the upper state  $^{2}A_{1}$  is quasi-linear with a bond angle of about 145°. Aside from the interest in effects of the Renner-Teller interaction on the molecular structure, there is a great deal of interest in NH<sub>2</sub> because it plays an important role in atmospheric and combustion chemistry.<sup>4-6</sup> NH<sub>3</sub> is also believed to play a central role in the "thermal de-NO<sub>x</sub>" process<sup>7-9</sup> wherein NH<sub>3</sub> is added to combustion effluents to remove NO from exhaust gases.

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The absorption spectrum of  $NH_2$  was first observed in the wavelength region 3900-8300A during the flash photolysis of ammonia<sup>10</sup> and hydrazine.<sup>11</sup> Dressler and Ramsay<sup>2</sup> later performed a detailed rotational and vibrational analysis of the absorption spectra of  $NH_2$  and  $ND_2$  arising from the  $\widetilde{A}-\widetilde{X}$  transition in this region. Johns, Ramsay and Ross<sup>12</sup> have extended the analysis to the long wavelength end of the spectrum and have identified all the low-lying bending vibronic levels of the excited state up to  $v_2^{+}=8$ . Because of the complexity of the emission spectrum, no detailed analysis has been performed. Laser induced fluorescence (LIF) has been used to simplify the complex emission spectrum. In 1975, Kroll<sup>13</sup> used this technique to obtain approximate molecular constants for the (0,0,0), (0,1,0), (0,2,0), (1,0,0), (1,1,0), and (0,4,0) vibrational levels of the ground state. In addition, collisional dynamics of the excited state were studied. Vervloet and Merienne-Lafore<sup>14</sup> and Vervloet, Merienne-Lafore and Ramsay<sup>15</sup> also used LIF to aid in the analysis of the complex emission spectrum. LIF has also been used for the measurement of radiative lifetimes of several of the excited state vibrational levels. 16-18 Xiang, et al., have used LIF on NH<sub>2</sub> to study its reaction with NO<sub>2</sub> and vibrational deactivation by CH<sub>3</sub>NH<sub>2</sub> and NH<sub>3</sub>. Besides these techniques, NH<sub>2</sub> has been studied by infrared matrix isolation spectroscopy,<sup>20</sup> microwave-optical double resonance,<sup>21</sup> difference frequency laser spectroscopy,<sup>22</sup> infrared-optical double resonance<sup>23</sup> and coherent antistokes Raman spectroscopy.<sup>24</sup> Combined analyses of all the available da Combined analyses of all the available data from the optical to the microwave region has resulted in very accurate molecular parameters 25,26 molecular parameters.

As mentioned previously, LIF is useful in that it simplifies the analysis of the complex emission spectrum. This technique is also a very powerful method for the detection of trace species in combustion systems because of its high sensitivity and selectivity.<sup>27</sup> Usually, tunable dye lasers have been used to excite the fluorescence. However, in recent work in this laboratory it has been shown that a number of radicals can be detected by LIF using the convenient and simpler Ar<sup>+</sup> or Kr<sup>+</sup> ion lasers. In addition, Raman spectroscopy can be used simultaneously to obtain majority species concentration and temperature.<sup>28</sup> Coincidences of the ion laser lines with molecular transitions have been discovered and used to study LIF of C<sub>2</sub> and CN,<sup>29</sup> NCO,<sup>30</sup> and OH and NH<sup>28</sup> in N<sub>2</sub>O supported flames. NH<sub>2</sub> has previously been detected in ammonia flames both by absorption<sup>31,32</sup> and by LIF<sup>33</sup> using tunable dye laser sources. In this paper, we report the excitation of NH2 fluorescence using the 6471Å line of a Kr<sup>+</sup> laser. The radical is present in all N<sub>2</sub>O supported flames which we have studied, namely flames of  $H_2$ ,  $CH_4$ , and  $NH_3$ . Not surprisingly, the LIF intensities indicate the concentration of NH2 is highest in the ammonia flame. These flames are of interest because No0 is currently believed to be of importance in the combustion of nitramine and double base propellants. The H<sub>2</sub> flame is of most interest in this regard because all of the hydrogen reactions in this flame are expected to occur in combustion of the propellants, whereas reactions of  $CH_{\lambda}$  and  $NH_{3}$  are probably not significant. This paper will center around two major issues. First, the identification of the pump transition is obtained using spectra from the NH<sub>2</sub> flame. The second issue is the determination of NH2 density in a flame from the fluorescence signal obtained using the ion laser. For purposes of demonstration, an accurate relative density profile through the reaction zone of a rich  $H_2/N_2O/N_2$  flame and an estimate of the absolute NH<sub>2</sub> density in the flame will be presented. (Profiles for several other species in  $H_2/N_2O$  flames ranging from lean to stoichiometric mixture ratios are given in Ref. 28b).

### II. EXPERIMENTAL

The experiment has been described in detail previously<sup>30</sup> and will only be briefly discussed here. Slightly rich premixed flames of fuel gases and nitrous oxide were supported on an open channel curved knife-edge burner.<sup>36</sup> The burner was placed at the intracavity focus of a krypton ion laser. Movement of this burner allows easy access to the entire flame zone. Since heat losses by the flame to this burner are small, the adiabatic flame temperature is generally reached. Radical concentrations for the burner are therefore, in general, higher than for other types of burner. This type of burner has thus been found to be extremely useful for spectroscopic studies of radicals, as well as determination of flame profiles, both in this laboratory and elsewhere.<sup>33</sup>

A nominal 3W (all lines) Kr<sup>+</sup> ion laser was used as the excitation source. The laser cavity was extended using two highly reflective mirrors with radii of curvature 1.0 and 0.3 m. The circulating intracavity laser power was about 50 watts. This power level is well below that required to observe effects of optical saturation, even with focusing. For the identification of the NH<sub>2</sub> pumping transition, the scattered light was focused onto the vertical slit of a 1 m monochromator. The monochromator was operated in the first order of a 1200 groove/mm grating blazed at 7500Å. Since the burner and laser beam have their long axes horizontal, a glass dove prism was placed in front of the slit to rotate the image 90°. The detected light comes from a volume approximately 100 microns in diameter and 3 mm in length. A silicon-intensified vidicon tube (OMA II) was used to detect the dispersed light. Approximately 50A of the spectrum could be observed at one time with this system. The spectrum was recorded into 500 memory channels of the OMA II. The resolution was about 0.7A. For the measurement of density and temperature profiles a 25 cm monochromator was used. Although the resolution of this system is lower, use of the smaller monochromator allows for the observation of about 400Å of the spectrum at a time. This larger observation range is useful because it allows simultaneous recording of the spontaneous Raman anti-Stokes signal from  $N_2$  (used to monitor flame temperature) together

with the fluorescence from the strongest region of the NH<sub>2</sub> spectrum. A computer was used for data accumulation and processing. For a typical run, the LIF + flame emission spectrum was first obtained (laser on) and then a spectrum consisting only of the flame emission was obtained (laser off). The LIF spectrum was obtained by differencing these spectra. For the spectral investigations, an NH<sub>3</sub>/N<sub>2</sub>O/N<sub>2</sub> flame of equivalence ratio  $\phi \simeq 1.6$  was used. The dilution with N<sub>2</sub> was about 40%. For the measurement of density and temperature profiles in a H<sub>2</sub>/N<sub>2</sub>O/N<sub>2</sub> flame, the flows were measured with a wet test meter. The conditions were  $\phi = 1.97$  with 44% dilution by N<sub>2</sub>. adalah kasaraté kadalah Janahaté kasaraté kasaraté kasaraté kasaraté kasaraté kasaraté kasaraté kas

### III. RESULTS AND DISCUSSION

### A. Interpretation of the Fluorescence Spectra

Some general information regarding the A-X transition of NH<sub>2</sub> may prove useful to this discussion. In the ground state,  $NH_2$  is a bent, highly asymmetric top molecule; however, in high vibrational levels of the excited state, the molecule is quasi-linear and behaves like it has 2m symmetry. Owing to the large change in the equilibrium bond angle in the two states, the absorption spectrum shows a long progression in the bending vibration,  $v_2(a_1)$ . Most of the features in the absorption spectrum arise from the main progression  $(0,v_{2}',0)+(0,0,0)$ . The strongest bands are those at about  $v_{2}'=9$ . In addition, a subsidiary progression,  $(1,v_2',0) \leftarrow (0,0,0)$ , has also been observed. Dressler and Ramsay showed that the absorption spectrum consists of type C bands for which the rotational selection rules are  $\Delta N=0$ ,  $\pm 1$ ,  $\Delta K_{a}=\pm 1$ ,  $\pm 3$ , ... and  $\Delta K_c=0$ ,  $\pm 2$ , ... where N is the total angular momentum excluding spin. The transition  $\widetilde{A}^2 A_1 - \widetilde{X}^2 B_1$  is allowed by dipole selection rules. Therefore in this transition the non-totally symmetric vibration  $v_{3}(b_{2})$  must change by an even number of quanta, but the totally symmetric vibrations  $v_1(a_1)$  and  $v_2(a_1)$  can change by any number of quanta. Another important feature of the spectrum is that successive rotational lines show an alternation in the intensities because of the nuclear spin symmetry properties of  $NH_2$ . Since the H nuclei have spin 1/2, the line intensities show a 1:3 alternation similar to that observed for H2.

In the excited state,  $K_a'$  is a good quantum number given by the vector sum of the orbital angular momentum and the vibrational angular momentum, i.e.,  $K_a' = |\pm \Lambda \pm \pm |$ . In this case  $\Lambda = 1$ , since the state correlates to a  $2\pi$  state, and  $\pounds$  is given by v', v'-2, v'-4, ..., 1 or 0 depending on whether v' is even or odd. Thus, for odd v',  $K_a'=0, 2, 4, \ldots, v'-1$  and, for even v',  $K_a'=1, 3, 5, \ldots, v'-1$ . ( $K_a' = v'+1$  levels are not observed in the excited state because, as demonstrated in Ref. 2, these levels from the "original"  $2\pi$  state of linear NH<sub>2</sub> correlate to levels in the  $X^2B_1$  state when the molecule becomes bent.) Large vibronic splittings of the  $K_a'$  levels are observed due to the Renner-Teller effect. The bands with  $K_a'=0, 1, 2, 3, 4, \ldots$  are referred to as  $\Sigma, \pi, \Lambda, \Phi, \Gamma, \ldots$  vibronic subbands, respectively. In the following, we will show that the 6471A line of the krypton ion laser pumps to the  $(0,11,0)\Sigma$ vibronic level of the excited state.

Several years ago in this laboratory, low resolution Raman spectra (~4Å FWHM) of majority species in  $CH_4/N_2O/N_2$  flames were being studied.<sup>38</sup> During the course of these studies, an intense, unidentified fluorescence spectrum was observed in the region of 5430Å using the 6471Å line of the

krypton ion laser.<sup>39</sup> Under low resolution, the spectrum appears to consist of a simple P and R branch structure. Therefore, it was originally thought that the fluorescence might be due to a  $\Delta\Lambda=0$  transition of some linear molecule. More recently, however, spectra have been taken at higher resolution using the l m monochromator. The higher resolution spectrum in the 5430A region is much more complicated than originally believed. It consists of a series of lines of highly irregular intensities (see Figure 1) whose interpretation was not immediately obvious. In addition, the sensitivity was increased by averaging up to ~1000 OMA scans. It was thus found that, although the 5430A region contains the most intense fluorescence (uncorrected for detector system response), the spectrum extends to at least 8050Å. It should be noted that the region of the laser line was not scanned because of intense interference from laser scatter. Also, at wavelengths longer than 8000Å the OMA sensitivity becomes too small to allow detection of all but the strongest signals.





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At first, it was not known for certain that  $NH_2$  was responsible for the observed spectrum. A preliminary attempt to search the entire spectrum for patterns of lines similar to that in the 5430Å region, thus helping to

identify vibrational spacings, failed. Definite evidence that the spectrum arises from NH2 was obtained from the observation of some easily recognized Q heads of the  ${}^{2}A_{1} - {}^{2}B_{1}$  transition in both the flame emission and LIF spectra. They occur at  $5708^{1}((0,10,0))$ ,  $5977^{1}((0,9,0))$ ,  $6302^{1}((0,8,0))$ , and  $6620^{1}$ [(0,7,0)]. (Here the notation refers to the excited state vibrational level. This notation is intended to indicate that (0,0,0) is the ground state level.) Thereafter, efforts were concentrated upon the task of assigning the pumping transition and, especially, the intense features in the 5430Å region. The key to the assignment was in making the assumption that the 6471Å laser line pumps a vibrational hot band whose excited state then emits to the (0,0,0) level of  $\tilde{X}^2B_1$ . The shortest wavelength fluorescence of appreciable intensity, i.e., that of the 5430Å region, would thus be ascribable to the laser excited state. Upon comparison of the line positions with those in Ref. 2, it was found that all but one of the lines in this region coincide with rotational transitions of the  $(0,11,0)-(0,0,0)\Sigma$  vibronic subband of NH<sub>2</sub>, thus firmly identifying the emitter. The assignments of the lines are given in Figure 1. This band is rather simple in comparison to others for two reasons.<sup>2</sup> First, since it is a  $\Sigma$  subband, it consists of only three strong branches,  $P_{1,N-1}$ ,  $P_{1,N}$ , and  $R_{1,N-1}$ .\* Second, spin splitting of lines in this subband is so small that only single lines are observed, even at a resolution of a few tenths of a cm<sup>-1</sup>.

Upon first inspection of Figure 1, it appears that  $2_{02}$  may be the only upper state rotational level pumped by the laser because the  $2_{02}-3_{12}$ transition is much more intense than others in the  $P_{1,N-1}$  branch. Collisionally induced rotational energy transfer would then give rise to the other less intense peaks. However, if both the  $1_{01}$  and  $3_{03}$  states are populated solely by rotational energy transfer, it is difficult to explain the much higher intensity of the  $3_{03}-4_{13}$  as compared to the  $1_{01}-2_{11}$  transition. In addition,  $1_{01}$  and  $3_{03}$  are ortho levels while  $2_{02}$  is a para level. Kroll<sup>13</sup> and Halpern, et al., have shown that energy transfer between ortho and para states is extremely slow, much as it is for H2. These observations suggest that both the  $2_{02}$  and  $3_{03}$  excited state levels are being pumped simultaneously by the 6471Å laser line. This conclusion is supported by the following calculations. It is a simple matter to determine that the 6471Å line is in the region of the  $(0,11,0)-(0,2,0)\Sigma$  vibronic transition. Table 1 shows calculations of some rotational transitions of this band. (These transitions were calculated in the following manner. Excited state term values were obtained by adding the appropriate ground state term values to the transition frequencies of the  $(0,11,0)-(0,0,0)\Sigma$  band of Ref. 2. Overlapped lines from Ref. 2 were not used. In this note, term values calculated in this way will be referred to as "measured" term values. These "measured" term values were fitted to the equation  $F = T_0 + BN(N+1) - DN^2(N+1)^2 + HN^3(N+1)^3$  to check for possible deviations. The "measured" term value calculated using the  $2_{02}$ - $l_{10}$ transition was rejected since it differed significantly from the fitted value. Multiple determinations of the same excited state "measured" term value were then averaged. The unobserved  $(0,11,0)-(0,2,0)\Sigma$  transitions were calculated from the appropriate (0,2,0) value and from these averaged

\*Here, the notation follows that of Ref. 2 and refers to  ${}^{4}K_{a} = {}^{4}N_{K_{a}}K_{c}$ .

upper state term values, without spin-splitting, were calculated using the constants of Ref. 26. Note that for the excited vibrational level, four parameters in the term value equation are fitted. The remaining higher order centrifugal distortion constants are not well determined. In Ref. 2 only the first three terms were used. For the  $(0,11,0)\Sigma$  level we found: T = 18430.195  $\pm$  0.026 cm<sup>-1</sup>, B = 8.9686  $\pm$  0.0047 cm<sup>-1</sup>, D = -8.08  $\pm$  0.21 x 10<sup>-3</sup> cm<sup>-1</sup> and H = -4.68  $\pm$  0.24 x 10<sup>-5</sup> cm<sup>-1</sup>.) These computations show that one could reasonably assume that the laser line pumps both the  $2_{02}-2_{12}$  and  $3_{03}-3_{13}$ transitions simultaneously since the Doppler broadening at the flame temperature (vide infra) is about 0.12 cm<sup>-1</sup>. Since the results in Table 1 predict that the laser line overlaps the former transition much better than the latter, they are qualitatively in good agreement with the intensity distribution of the fluorescence spectrum of Figure 1. For example, in the absorption spectrum of Dressler and Ramsay,<sup>2</sup> the  $2_{02}-3_{12}$  is ~2 times weaker than the  $3_{03}-4_{13}$  transition and the  $2_{02}-1_{10}$  is 3-4 times weaker than the  $3_{03}-2_{11}$  transition. In the fluorescence spectrum of Figure 1, the  $2_{02}$ transitions are much more intense relative to the 303 transitions. In the  $P_{Q_{1,N}}$  branch, all of the lines overlap at our resolution, resulting in a single, strong line. The remaining lines in the other two branches must arise from rotational energy transfer that is very slow compared to electronic quenching by flame molecules since only a few, very weak rotational lines. other than those arising from the two levels directly pumped by the laser, are observed. Although there is one rather strong, unidentified line in this region, little doubt can remain regarding the NH2 pumping mechanism. Later in this section, evidence corroborating that the unidentified line arises from NH<sub>o</sub> will be given. In addition, the location of the laser line relative to the two pumping lines will be determined more precisely in the next section.

Table 1. Calculated Frequencies of Some Rotational Lines of the

 $\tilde{A}^{2}A_{1}$  (0,11,0) $\Sigma = \tilde{X}^{2}B_{1}$  (0,2,0) Transition of NH<sub>2</sub>\*

Transition	Frequency (cm <sup>-1</sup> )
<sup>1</sup> 01 <sup>-1</sup> 11	15450.30
<sup>2</sup> 02 <sup>-2</sup> 12	15449.48
<sup>3</sup> 03 <sup>-3</sup> 13	15449.30
<sup>4</sup> 04 <sup>-4</sup> 14	15450.93
<sup>5</sup> 05 <sup>-5</sup> 15	15455.29

\*The 6471Å laser line corresponds to an energy of 15449.56  $\pm$  0.12 cm<sup>-1</sup>.40

It was desirable to identify more bands that result from emission of the  $\overline{A}^{2}A$ ,  $(0,11,0)\Sigma$  level to the ground state levels. Two of these bands are located in the regions of 5910Å and 6580Å. They are the (0,11,0)-(0,1,0) and (0,11,0)-(1,0,0) bands, respectively (see Figures 2 and 3). There are many more unknown lines in these bands, which explains the initial difficulty encountered in attempts to identify similar patterns of the various vibrational bands in the spectrum. However, if these unidentified lines are neglected, the similarity of these bands to the (0,11,0)-(0,0,0) band is easily recognized. Fluorescence from the (0,11,0) excited state to the (0,3,0), (1,1,0) and (0,4,0) ground state levels was also observed. These bands (not shown) were weak, however, and in some cases only the central Q head was observed. In comparison to the other bands, the (0,11,0)-(0,0,0)band is much less complicated. This band has a very high S/N ratio, enabling us to identify even the weakest features, i.e., the  $4_{04}$ - $5_{14}$  and  $4_{04}$ - $3_{12}$ transitions, unambiguously. The weak lines from  $l_{01}$  and  $4_{04}$  indicate that rotational transfer in the flame environment is slow in comparison to electronic quenching.

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(0, 11, 0) - (0, 1, 0)PQ I.N Non-NIN PR1, N-1 <sup>Р</sup>Р<sub>1, N</sub>-1 303 - 211 202 - 110 - 1<sup>10</sup> - 3, - 211 000 - 110  $3_{03} - 4_{1}$ 2 02 õ MM 5900 5910 5920 5930 5940 5950 5880 5890 WAVELENGTH (Å)

Figure 2. The  $(0,11,0)-(0,1,0)\Sigma$  Band of the  $\widetilde{A}-\widetilde{X}$  Transition of NH<sub>2</sub> (as in Figure 1)



Figure 3. The  $(0,11,0)-(1,0,0)\Sigma$  Band of the  $\widetilde{A}-\widetilde{X}$  Transition of NH<sub>2</sub> (as in Figure 1)

To conclude this section, the rest of the spectrum is discussed here. It was previously mentioned that the (0,10,0), (0,9,0), (0,8,0), and (0,7,0) Q heads were identified in the fluorescence spectrum. These probably arise from collisionally induced vibrational energy transfer in the excited state prior to emission, resulting in fluorescence signals of NH, over the entire region from 5300Å to ~8000Å where the detection system sensitivity falls off. These bands are weak in comparison to bands from the directly pumped vibrational level. This result indicates that vibrational transfer is small in comparison to electronic quenching, in agreement with the results of Halpern, et al., who studied NH<sub>2</sub> in the presence of NH<sub>3</sub> and Ar, and of Donnelly, et al., who studied NH, in pure ammonia. Unfortunately, there are many strong and sharp, unidentified lines (see Figures 1-3), most of which lie toward the long wavelength end of the spectrum. Unassigned, poorly understood lines have often been observed in the spectra of NH<sub>2</sub>. Dressler and Ramsay<sup>2</sup> suggested that some of the unidentified lines may belong to bands of other progressions or even to bands of a second electronic transition. Some of these extra lines may be due to perturbations of the upper state by high vibrational levels of the ground state.<sup>18,21</sup> Such perturbations could not be the cause of the unidentified lines shown in Figures 1-3 because, although all

three bands have a common upper vibrational level, none of the unidentified lines appears in the same position in all three bands. There are at least three possible explanations for these lines: (1) More NH, transitions than those already identified are pumped by the laser. Such unknown pumping transitions could easily arise from an excitation of a band in which both  $v_1$ ' and  $v_1$ " and/or  $v_3$ ' and  $v_3$ " are nonzero. This possibility cannot be ruled out because nonzero  $v_1$ " and  $v_3$ " states have appreciable populations at the flame temperature. Transitions such as described have not received much, if any, study. (2) The unidentified lines are due to Fermi type interactions amongst the ground state vibrational levels. The appearance of more of the unidentified lines towards the red end of the spectrum would then appear as the logical result of more Fermi resonances being possible as the ground state vibrational energy and, hence, density of vibrational levels, increases. (3) At least one species besides NH, is being pumped by the laser and gives rise to the unknown lines. If the unidentified line in the 5430Å region (Figure 1) arises from said species, then this species is confined to the flame front and its density is roughly proportional to that of NH2. This would have to be the case because spectra taken at several different positions in the flame front show that the intensity of this unidentified line is proportional to that of the other lines in this region which arise from NH2. The absolute intensity of the NH, lines falls rapidly outside the flame front (vide infra). Along these lines, we should mention that in the  $CH_{L}/N_{2}O/N_{2}$  flame two separate transitions of CN are known to be excited. One of these pumps to v'=6 in the  $A^{2}\pi$  state. Emission from v'=6 and lower levels populated by vibrational downtransfer dominates the spectrum in the methane flame at wavelengths above 6000Å. (The CN excitations will be the subject of future publications).

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### B. NH<sub>2</sub> Density in the $H_2/N_2O/N_2$ Flame

A detailed description of the methods of obtaining temperature and relative concentration profiles has been given earlier.<sup>29a</sup> As stated in the experimental section, use of the 25 cm monochromator system allowed for the simultaneous measurement of the entire  $(0,11,0)-(0,0,0)\Sigma$  subband of NH<sub>2</sub> along with the spontaneous Raman signal from the anti-Stokes vibrational Q branch of N<sub>2</sub>. Plots of these spectra as a function of vertical position in the flame appear in Figure 4. The strong peaks to the left are due to the (0,11,0)- $(0,0,0)\Sigma$  fluorescence of the NH<sub>2</sub>, seen at a resolution of about  $3^{\text{A}}$ . The smaller peaks to the right are the antistokes Raman signal of N2. Observe the Raman signal as one traverses the flame front. In the unburnt gases, the signal starts out as a single band due to the 1+0 vibrational transition of N2. As one moves toward the burnt gas region, the temperature increases and a second vibrational band from the 2+1 transition may be observed to the right of the 1+0 band. A multiparameter least squares program, similar to that used previously for the Stokes signals,<sup>28a</sup> was used to extract the flame temperature as a function of position from these anti-Stokes signals. The relative intensity from the NH<sub>2</sub> signal, integrated over the band shown in Figure 4, may then readily be used to obtain an accurate relative density profile of NH<sub>2</sub> in the flame. To do this one must make two assumptions. The first is that the quenching rate, Q, for excited NH, by the flame molecules is constant as a function of position in the flame. Although the temperature and species concentrations have large gradients in the flame zone, work on  $OH^{41}$ ,<sup>42</sup> and CH<sup>43</sup> in flames has shown that large variations in Q do not occur for these species. Since it may be shown that the majority of the LIF measurements are

made in a region where the composition is mainly that of burnt gases, this result is perhaps not too surprising and is generally applicable to trace species in flames. The second assumption is that the ground state  $NH_2$  is in thermal equilibrium with the flame gases. Upon making these assumptions one finds that in general the relative density profiles closely follow the LIF intensity profiles<sup>29a</sup> so that the latter may be used without corrections. Figure 4 therefore indicates that the  $NH_2$  density rapidly rises to a maximum and then decays somewhat more slowly as one traverses the flame zone. This is seen in Figure 5 where the integrated  $NH_2$  intensity from the  $(0,11,0)-(0,0,0)\Sigma$ band and the temperatures are shown as a function of position in the flame. The adiabatic flame temperature was computed to be 2056 K using the code of Svehla and McBride.<sup>44</sup> Note the agreement of the adiabatic and measured flame temperatures which indicates that there is little heat loss to the burner.



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An estimate of the absolute density of the  $NH_2$  requires knowledge of the overlap of the laser line with the molecular transition. The overlap is very difficult to determine in the case of a single transition. This results because the overlap is extremely sensitive to the exact spacing between the laser line and the molecular transition. (A few hundredths of a cm<sup>-1</sup> can make a large difference - see, for instance, Ref. 29a.) One might at first think that this sensitivity would become even more troublesome when two transitions are simultaneously pumped because of the higher spectral complexity. However, in the present case we have been able to turn this complication to our advantage and determine the relative overlaps of the laser line with the two

Figure 4. Flame Spectra Taken at Various Heights in  $H_2/N_2O/N_2$  Flame



Figure 5. Relative  $NH_2$  Fluorescence Intensity and Temperature as a Function of Position in the  $H_2/N_2O/N_2$  Flame. The relative  $NH_2$  density profile is identical to the intensity profile. An estimate of the peak density is given in the text.

pumping transitions. This in turn has allowed the determination of the relative position of the laser line with respect to the two transitions with a precision of  $\pm 0.01$  cm<sup>-1</sup>. The availability of the resolved fluorescence spectrum, Figure 1, allows this determination to be made. We first note from Figure 1 that there is very little rotational transfer to states other than the pumped levels. In addition, recall that experiments of Kroll<sup>13</sup> and of Halpern, et al.,<sup>16</sup> indicate that there will be very little rotational energy transfer between the two pumped levels because the ortho-para transfer is quite slow. We assume that the quenching rate, Q, for the two directly pumped levels is equal. Under these conditions it is readily shown that the relative emission intensity in the two strong  $P_{1,N}$  branch lines of Figure 1 is given by

$$S_{1}/S_{2} = A_{1}B_{1}\sigma_{1}N_{1}/A_{2}B_{2}\sigma_{2}N_{2}$$
(1)

)

where  $S_1$  and  $S_2$  are fluorescence signals from the  $2_{02}-3_{12}$  and  $3_{03}-4_{13}$ transitions, respectively. (Note that we have also made the tacit assumption that spin-splitting of the  $(0,11,0) + (0,2,0)\Sigma$  pumping transition is negligible. This is true for the  $(0,11,0) - (0,0,0)\Sigma$  band (see Ref. 2). However, no measurements are readily available for splittings in the pumped vibrational band.)  $A_1$  and  $A_2$  are the respective Einstein emission coefficients for these transitions.  $B_1$  and  $B_2$  are the Einstein absorption coefficients for  $2_{02}-2_{12}$  and  $3_{03}-3_{13}$  in the  $(0,11,0)-(0,2,0)\Sigma$  band, respectively, and  $\sigma_1$  and  $\sigma_2$  are the respective overlaps of the pumping transitions with the laser line.  $N_1$  and  $N_2$  are the densities of  $2_{12}$  and  $3_{13}$  in the (0,2,0) ground state level. Making the assumption that the electronic transition moment is unaffected by changes in N or  $K_c$  within a given vibrational band, one finds that the Einstein coefficients are proportional to  $S_{N'N''}/(2N'+1)$ , where  $S_{N'N''}$  is the rotational linestrength, ignoring spinsplitting, for the appropriate transition. It should be noted that Green and Miller<sup>31</sup> using a high resolution laser scan have found that the oscillator strengths of individual lines in a spin-split  $P_{Q_{1,N}}$  doublet from the (0,9,0)- $(0,0,0)\Sigma$  band are identical. This result is probably not serendipitous. Satellite transitions for which  $\Delta J \neq \Delta N$  are very weak even at the lowest N values.<sup>12</sup> When this is the case, one expects to find nearly equal oscillator strengths for the two spin-split lines. Therefore, the assumption that spinsplitting may be ignored in the calculation of main branch linestrengths is justified. The  $S_{N'N''}$  were calculated using the direction cosine matrix elements of Cross, et al.,<sup>45</sup> and the eigenvectors resulting from the diagonalization of a Wang transformed asymmetric top Hamiltonian without spin.  $^{46,47}$  It should be stressed here that the ground and excited state asymmetry parameters,  $\kappa$ , are not assumed to be the same, as in the earlier work,<sup>2,18</sup> but are calculated to be -3.84 and -1, respectively, as determined from the observed spectral parameters.<sup>26</sup> Since the upper state is quasilinear with  $\Sigma$  character, only matrix elements having K'=0 are possible. For the type-c transitions considered here, nonzero direction cosine matrix elements result when  $\Delta K = \pm 1$ . Consequently, the only allowed transitions are for K"=1 levels. For Q branch transitions, for which  $S_{N'N''}/(2N'+1) = \frac{1}{2}$  in the limiting symmetric top case, the calculation reduces to the very simple form

$$\frac{{}^{5}N'N''}{2N''+1} = c_{K=1}'^{2}/2 , \qquad (2)$$

where  $c_{K=1}^{"}$  is the mixing coefficient of the K"=1 level. The necessary linestrengths, normalized to 2N'+1, are given in Table 2. The ratio N<sub>1</sub>/N<sub>2</sub> is given by the appropriate Boltzmann fraction at the measured flame temperature of ~2000 K. Finally, S<sub>1</sub>/S<sub>2</sub> may be obtained from the ratio of the appropriate peak heights in Figure 1. Thus, the value of  $\sigma_1/\sigma_2$  is determined. While the relative position of the laser line with respect to the two pumping transitions is not known very precisely from prior measurements (see Table 1), the splitting between the two NH<sub>2</sub> pumping transitions is known. (The problem of relative spacing of the laser line and pump transitions arises because no one has measured the NH<sub>2</sub> and Kr<sup>+</sup> line positions simultaneously. In fact, the relevant NH<sub>2</sub> lines have never been directly observed. In addition, the Kr<sup>+</sup> line position is only known to ±0.12 cm<sup>-1</sup>. It is therefore difficult to place the pump line relative to the NH<sub>2</sub> transitions to within better than 0.12 cm<sup>-1</sup>.) Therefore by making appropriate assumptions about the lineshapes, one may calculate  $\sigma_1$  and  $\sigma_2$  as a function of the relative laser line position. We assumed that the NH<sub>2</sub> transitions are Doppler broadened at the measured flame temperature of ~2000 K (linewidth ~0.12 cm<sup>-1</sup> FWHM). Note that previous measurements on OH in a flame at atmospheric pressure<sup>48</sup> and on NH<sub>2</sub> at low pressure<sup>31</sup> indicate that collisional broadening is probably a very small correction. The laser line was assumed to be Doppler broadened at 300 K (linewidth ~0.02 cm<sup>-1</sup> FWHM).  $\sigma_1$  and  $\sigma_2$  were rewritten in terms of a single variable,  $\Delta v$ , the spacing between the  $2_{02}$ - $2_{12}$  transition and the laser line. An iterative procedure was then used with Eq. (1) and the observed intensity ratio to obtain  $\Delta v$ . The results were surprisingly insensitive to the laser linewidth (this is a very important point because the laser line could easily be power broadened; a range from 0.01 - 0.10 cm<sup>-1</sup> was tried), temperature within its error limits of ~±50 K, the ratio  $S_1/S_2$  within its error limits and the splitting of 0.18 cm<sup>-1</sup> between the  $2_{02}$ - $2_{12}$  and  $3_{03}$ - $3_{13}$  transitions (see

Table 1). The latter was varied from  $0.16 - 0.20 \text{ cm}^{-1}$ . (This range was chosen based on our estimated uncertainty of  $\pm 0.02 \text{ cm}^{-1}$  in the calculated splitting of the lines.) The laser line position was thus determined to be between the two pumping transitions,  $0.06 \pm 0.01 \text{ cm}^{-1}$  from the  $2_{02}-2_{12}$  transition. In addition, relative values of the pumping rate,  $B_1N_1\sigma_1$  +  $B_2N_2\sigma_2$ , were also determined. Error limits on the input data were such that these relative values only varied by  $\pm 15\%$  from the optimum value.

Table 2. Linestrengths for the Overlap Calculations

Transition

 $S_{N'N''}/(2N'+1)$ 

Absorption [(0,11,0) + (0,2,0)]

2<sub>02</sub>-2<sub>12</sub> 0.5000

3<sub>03</sub>-3<sub>13</sub> 0.4979

Emission [(0,11,0) + (0,0,0)]

 $2_{02} - 3_{12}$  0.3959

3<sub>03</sub>-4<sub>13</sub> 0.3403

Having knowledge of the relative line positions and the overlaps of the two pumping transitions with the laser line, we proceeded to calculate an estimate of the absolute density using the methods discussed in detail in Ref. 29a. Franck-Condon factors (FCFs) for the appropriate vibrational bands were obtained from the work of Jungen, Hallin, and Merer.<sup>49</sup> The FCFs were combined with the transition moment<sup>10</sup> (obtained via LIF lifetimes measurements) to obtain Einstein A coefficients for the vibrational bands of interest. The NH<sub>2</sub> partition function was calculated as in Ref. 31. The quenching rate constant used was that obtained by Halpern, et al.,<sup>10</sup> for pure N<sub>2</sub>. (It is interesting to note that their rate constant is quite close to the expected hard-sphere collisional rate constant). This yields a quenching rate of  $1.47 \times 10^9$  sec<sup>-1</sup> at the flame temperature, assuming the quenching cross section does not vary with temperature. The only major difference in the present determination and that for  $C_2$  and  $CN^{29a}$  and  $NCO^{30}$  is that the NH<sub>2</sub> fluorescence intensity was compared to the N<sub>2</sub> anti-Stokes (rather than Stokes) Q-branch signal which was readily available (see Figure 4). The appropriate equation for the anti-Stokes Raman signal is

$$E_{AS} = (P_o/hv_t)\sigma_t (v_t/v_{AS})N_{N_2} L\Omega \epsilon R$$

where  $E_{AS}$  is the number of anti-Stokes photons detected per unit time,  $P_0$  is the laser power,  $\sigma_1$  is the Raman scattering cross section for  $N_2$ ,  $v_1$  and  $v_{as}$ are the laser and anti-Stokes frequencies, respectively,  $N_2$  is the density of  $N_2$  (known from equilibrium flame calculations), L is the length of the excited region viewed by the collection optics,  $\Omega$  is the collection optic's solid angle, and  $\varepsilon$  is the detector efficiency. Finally, R is given by

$$R = \sum_{v=1}^{\infty} G / \sum_{v=0}^{\infty} G$$
 (4)

where G =  $(v+1)exp(-E_v/kT)$ . Equation (4) accounts for the fact that v=0 is not active in the Raman anti-Stokes branch of N<sub>2</sub>. The sums in Eq. (4) were truncated at y=5. The resulting estimated peak density of NH<sub>2</sub> in the flame was 9.3 x 10<sup>13</sup> cm<sup>-3</sup>.

Before leaving this section, two points should be made concerning the estimated peak density. The first is that if the quenching rate were very well known, the error limits for the absolute density would only be about  $\pm 20\%$ . The major source of this error is in the calculation of overlaps of the laser line with the molecular transitions. However, our assumed quenching rate estimated using the cross sections of Halpern, et al.,  $^{10}$  is probably only good to within a factor of about 2-3. This is the case because all of the surrounding gas was assumed to be  $N_2$ , while in fact only about 60% of it is, the rest being composed mostly of nearly equal parts of H<sub>2</sub> and H<sub>2</sub>O. (The combined concentration of other species is expected to be less than 10% at the point where the measurements were performed and is not considered further.) Also, the quenching rate of  $NH_2$  by  $N_2$  was measured at about 298 K. The measured flame temperature was much higher than this. There is no guarantee that the quenching cross section is constant vs. temperature as was assumed. In addition, the quenching measurement of Halpern, et al., was performed for a different excited state vibrational level than was pumped in the present work. Halpern, et al., have, however, shown that the quenching rate is constant vs. vibrational level pumped for NH3 quencher. Since the measured density is proportional to Q, error limits in the density are also a factor of 2-3. Of course, the relative density profile of Figure 5 has much higher precision than this. The value of Q used is given so that the absolute density may be corrected if better estimates of Q become available. The second point we would like to make is that the Einstein coefficients computed for NH<sub>2</sub> are believed to be quite accurate. To investigate this further, measured and calculated oscillator strengths for two transitions are compared here. In rich NH<sub>3</sub>/O<sub>2</sub> flames, previous work has shown that the reactions

$$\mathbf{NH}_2 + \mathbf{OH} = \mathbf{NH} + \mathbf{H}_2 \mathbf{O} \tag{5}$$

and

(6)

(3)

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are rapidly equilibrated.<sup>32,50,51</sup> If one knows thermodynamic data precisely enough, equilibrium constants for (5) and (6) may be calculated. Thus, by doing appropriate absorption measurements on reactants involved in (5) and (6), one can determine oscillator strengths for the NH<sub>2</sub> transitions. Chou, Dean, and Stern<sup>32a</sup> thus found an oscillator strength of  $2.04\pm0.44\times10^{-4}$  for the  $Q_{1,N}$  7 transition in the (0,9,0)-(0,0,0) band. However, using different data they later 32c found this oscillator strength to be ~6.4x10<sup>-5</sup>. The  $\mathbb{R}_{Q_1}$  A transition in the  $(0,12,0)-(0,0,0)\Sigma$  band similarly has had two very different oscillator strengths reported. Nadler, Wang, and Kaskan<sup>50</sup> found a value of ~4x10<sup>-4</sup> for this oscillator strength. Fisher<sup>51</sup> later performed measurements under very similar conditions and found a value of  $2.4\pm0.8\times10^{-4}$ for this quantity. He attributed his different result primarily to the use of newer thermochemical data. Calculated oscillator strengths for these two transitions were obtained in the following manner. Einstein A coefficients for the  $(0,9,0)-(0,0,0)\Sigma$  and  $(0,12,0)-(0,0,0)\pi$  bands were calculated using the transition moment and calculated FCFs.<sup>9</sup> S<sub>N'N''</sub>/(2N'+1) values of 0.451 and 0.709 were then calculated for the  $Q_{1,N}^{-7}$  line in the former band and the  $Q_{0,N}^{-4}$  line in the latter band, respectively. One finds these values lead to Einstein A coefficients of  $3.65 \pm 0.37 \times 10^{4}$  sec<sup>-1</sup> and  $7.09 \pm 0.71 \times 10^{4}$  sec<sup>-1</sup> and oscillator strengths of  $1.96 \pm 0.20 \times 10^{-4}$  and  $2.84 \pm 0.28 \times 10^{-4}$ , respectively. Error limits here arise from the error limits reported in the fit of experimental data to yield the transition moment.<sup>18</sup> The fact that the two calculated oscillator strengths are nearly identical is coincidental. The measured oscillator strengths are of the correct order of magnitude to agree with our calculated values. However, the measured oscillator strengths are quite sensitive to the exact choice of thermochemical data used, in particular the heats of formation of NH and NH<sub>2</sub>. It would appear that our calculated oscillator strengths are presently the best choices for these quantities and are, in fact, much more accurate than the measured values. We believe this to be the case because the FCF calculations of Jungen, et al., 49 coupled with the ab initio transition moment of Peyerimhoff and Buenker<sup>52</sup> yield lifetimes of various vibrational levels of the  $A_state$  of  $NH_2$  in excellent agreement with experiment. (A calculation of the A-X transition moment in Ref. 53 results in a value somewhat different from that in Refs. 18 and 52, probably because no configuration interaction was included. These calculations were only carried out at the MCSCF level because the primary interest was in mapping out the  $NH_2$ potentials, not in determining the  $\overline{A-X}$  transition moment.) In addition, the transition moment from the fit to experimental data<sup>10</sup> is in very good agreement with the ab initio result. Finally, ab initio calculations of the relative vibrational band intensities<sup>54</sup> are in reasonable agreement with calculated FCFs from the semiempirical fitting procedure.<sup>49</sup> A review of the NH and  $NH_2$  heats of formation and the  $NH_2$  oscillator strengths calculated from the flame measurements is currently underway.

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### IV. CONCLUSIONS

Laser excitation of NH<sub>2</sub> using the 6471A line of a Kr<sup>+</sup> laser has been observed. This line simultaneously pumps two rotational transitions in the  $(0,11,0)-(0,2,0)\Sigma$  vibrational hot band. The fluorescence spectrum was used to extract a precise measurement of the relative placement of the laser line and the two pumping transitions. In addition, a precise relative density profile of NH<sub>2</sub> in an H<sub>2</sub>/N<sub>2</sub>O/N<sub>2</sub> flame was obtained. An estimate of the peak density was also determined.

Use of LIF to determine absolute flame radical densities has historically been hampered by a lack of knowledge of the quenching rates of the excited species by flame molecules.<sup>56</sup> Several methods for circumventing this problem, including measurement of Q in low pressure flames, were reviewed in Ref. 56. Recently Bechtel and coworkers<sup>57</sup> have shown that Q may be directly measured in atmospheric pressure flames, via fluorescence lifetime measurements, using an ion laser pumped, picosecond, doubled dye laser system. Our observation of coincidences of ion laser lines with transitions of several radicals suggests that the direct measurement of Q in atmospheric pressure flames might be accomplished by simply using a picosecond ion laser to pump these radicals. The absolute radical density could then be obtained from (amongst other more well-known parameters) the LIF signal strength, the measured value of Q, and a knowledge of the overlap of the laser line with the molecular transition. Of course, the latter is known precisely only for the NH<sub>2</sub> radical from the present work. Measurement of this parameter could be difficult for other radicals. However, it should be pointed out that OH, which is very important chemically in combustion systems, is one of the radicals which may be pumped with the Kr<sup>+</sup> laser.<sup>28a</sup> Therefore, some research in this direction should prove to be valuable.

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5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided or efficiencies achieved, etc? If so, please elaborate.\_\_\_\_\_

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.)

\_\_\_\_\_

Name

------Organization CURRENT ADDRESS Address \_\_\_\_\_

City, State, Lip

7. If indicating a Change of Address or Address Correction, please provide the New or Correct Address in Block 6 above and the Old or Incorrect address below.

	Name
OLD ADDRESS	Örganization
	Address
	City, State, Zip

(Remove this sheet, fold as indicated, staple or tape closed, and mail.)



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