

SATURATION SPECTROSCOPY OF NH_2 USING A CW DYE LASER *

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Hyperfine structure in the electronic spectrum of NH_2 has been resolved using the technique of intermodulated fluorescence with CW dye laser excitation. From the observed spacings values for the ^{14}N Fermi contact and dipole-dipole coupling terms have been estimated for both the ground state and the $\Pi(0, 10, 0)$ vibrational level of the $\tilde{\text{A}}^2\text{A}_1$ excited electronic state.

There has been considerable interest recently in the study of the NH_2 radical using a variety of laser techniques. Davies et al. [1] observed rotational transitions between hyperfine levels in the ground state using far infrared laser magnetic resonance. Both Hancock et al. [2] and Kroll [3] have studied the laser excited fluorescence of the NH_2 radical following the absorption of CW dye laser radiation. From a kinetic study of NH_2 in a fast flow system Hancock et al. [2] were able to determine the rate constant for the reaction with NO. Kroll [3] resolved the laser excited fluorescence to yield rotational constants and vibrational energies for several excited vibrational levels in the ground electronic state.

The absorption spectrum of NH_2 in the visible region has been extensively studied by Dressler and Ramsay [4]. Much of the spectrum falls conveniently in the tuning range of the rhodamine 6G dye laser (560–620 nm) and thus opens up the possibility of the observation of the hyperfine structure within the Doppler width (~ 1500 MHz) by using laser saturation techniques. We wish to report in this work the observation of the saturation spectrum of NH_2 and the determination of the ^{14}N Fermi contact and dipole-dipole coupling terms in the ground state and an excited vibronic state.

NH_2 radicals were most satisfactorily prepared by the reaction of H atoms with anhydrous hydrazine in a fast flow system. The H atoms were produced by a 2450 MHz microwave discharge of 10–70 W power in a flowing gas mixture of Ar and 0.1% H_2 at a total pressure of 0.5–1.5 torr. Chemiluminescence often accompanied the reaction, especially under hydrogen rich conditions, but was normally minimized by working with a slight excess of hydrazine. Laser excited fluorescence of NH_2 was obtained with a Spectra Physics 580 single mode dye laser. Assignment of the observed lines was easily accomplished by measuring the laser wavelength with a 0.75 m Heath EU 700 monochromator to ± 0.1 nm and comparing with the observed line pattern of Dressler and Ramsay [4].

Saturation spectra of NH_2 were obtained using the technique of intermodulated fluorescence developed by Soren and Schawlow [5] and used successfully by Muirhead et al. [6] in the only other saturation spectrum obtained so far for a triatomic radical (BO_2). Two beams of approximately equal intensity (each 12–20 mW) and chopped at different frequencies, f_1 and f_2 , were passed in opposite directions through the NH_2 cell so as to cross in the center at a small angle (< 5 mR). The total fluorescence was carefully focussed on to a slit in front of a RCA 31090F photomultiplier. The saturation component of the fluorescence was phase sensitive detected at the sum frequency, $f_1 + f_2$ ($f_1 \approx 1000$ Hz, $f_2 \approx 700$ Hz), by a PAR HR 8 lock in amplifier. The output of the lock

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in amplifier was fed to an x - y recorder as was the drive voltage for the dye laser frequency scan. Frequency markers were produced by observing the scan of the laser mode with a 2 GHz FSR spectrum analyser.

Saturation spectra were obtained for many of the lines of the $\Pi(0, 10, 0) \rightarrow \Sigma(0, 0, 0)$ band of the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$ electronic transition [4]. Fig. 1 shows the observed hyperfine structure, caused by the interaction of the magnetic moments produced by the ^{14}N nuclear spin with that due to electron spin, of the $R_{0,1} J: \frac{3}{2} \leftarrow \frac{1}{2}$ spin component at 17577.01 cm^{-1} [4]. The observed linewidth (FWHM) of a single hyperfine component of 32 MHz results primarily from the instability of the free running laser over the 5–10 s scan of this frequency interval since the natural linewidth should be less than 0.1 MHz [2] and the contribution from the finite crossing angle amounts to less than 3 MHz [5]. The standard deviation of the average of the splittings for many separate scans was typically 4–6 MHz limited by dye laser jitter.

Consideration of the nuclear spin statistics for NH_2 [4] shows that ground state rotational levels of symmetry eo or oe have a resultant nuclear spin for the hydrogen atoms equal to zero and thus the observed hyperfine structure in these transitions must be due solely to the ^{14}N nucleus. Because of the frequency instability of the laser the hyperfine structure observed from ee or oo ground state levels ($I_H = 1$) of at

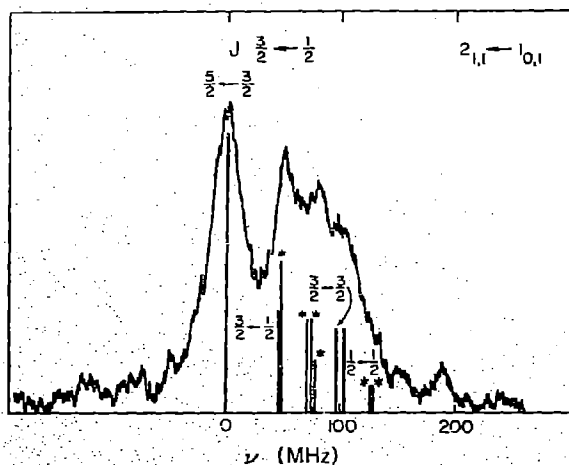


Fig. 1. Intermodulated fluorescence saturation spectrum of NH_2 displaying the hyperfine structure of $2_{11} \leftarrow 1_{01}$, $J: \frac{3}{2} \leftarrow \frac{1}{2}$ at 17577.01 cm^{-1} [4] due to ^{14}N nuclear spin alone.

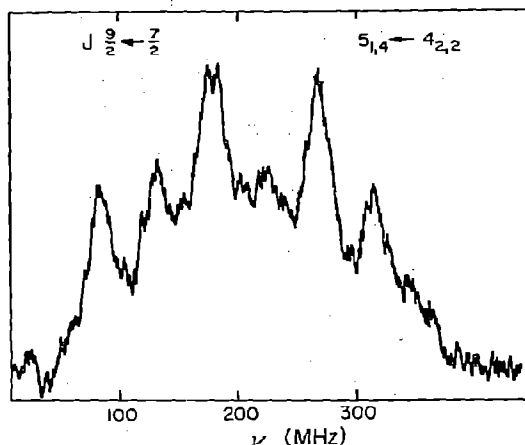


Fig. 2. Complex hyperfine structure of $5_{14} \leftarrow 4_{22}$, $J: \frac{9}{2} \leftarrow \frac{7}{2}$ at 17551.54 cm^{-1} [4] showing the effects of hydrogen and ^{14}N nuclear spins.

least nine components was often only partially resolved (fig. 2) and we thus concentrated on levels with $I_H = 0$.

Figs. 3–6 display the observed hyperfine structure of the $2_{11} \leftarrow 1_{10}$ ($J: \frac{5}{2} \leftarrow \frac{3}{2}$), $4_{13} \leftarrow 3_{03}$ ($J: \frac{9}{2} \leftarrow \frac{7}{2}$ and $J: \frac{7}{2} \leftarrow \frac{5}{2}$) and $6_{15} \leftarrow 5_{23}$ ($J: \frac{13}{2} \leftarrow \frac{11}{2}$) transitions. It is an interesting observation that both spin-rotation splitting "fine structure" components of $R_{0,3}$ and $R_{0,4}$ fall within the Doppler width and are hence not resolved in conventional spectra [4].

Most of the levels of the ground and excited states of NH_2 can be treated adequately with the J coupling scheme [7] (case $b_{\beta J}$),

$$J = N + S$$

and

$$F = J + I.$$

Using the simplest hamiltonian for the hyperfine interaction involving only diagonal elements in the Fermi contact term in both the upper and lower states, with the ground state Fermi contact term set at the solid state ESR value of 30 MHz [8] it is a simple matter to assign most of the observed hyperfine components and obtain an approximate value for the upper state constant of $163 \pm 10 \text{ MHz}$.

As expected a calculation of the relative intensities

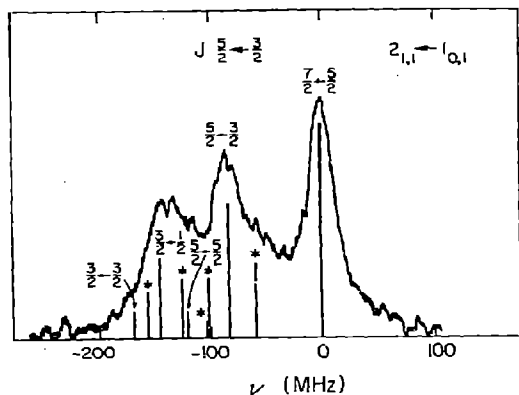


Fig. 3. Hyperfine structure of $2_{1,1} \leftarrow 1_{0,1}$, $J: 5/2 \leftarrow 3/2$ at 17576.70 cm^{-1} [4] obtained with intermodulated fluorescence saturation spectroscopy.

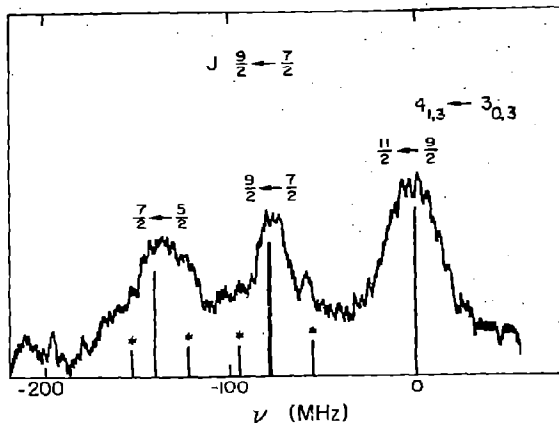


Fig. 4. Hyperfine structure of $4_{1,3} \leftarrow 3_{0,3}$, $J: 9/2 \leftarrow 7/2$ at 17611.76 cm^{-1} [4].

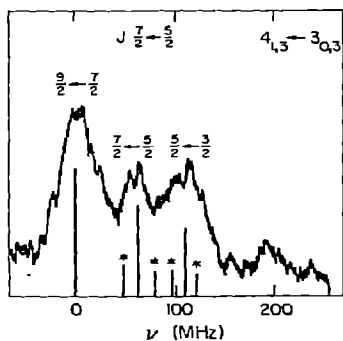


Fig. 5. Hyperfine structure of $4_{1,3} \leftarrow 3_{0,3}$, $J: 7/2 \leftarrow 5/2$. These components are only 800 MHz higher in frequency than the F_1 components of fig. 4 and hence overlap within the Doppler width of 1500 MHz.

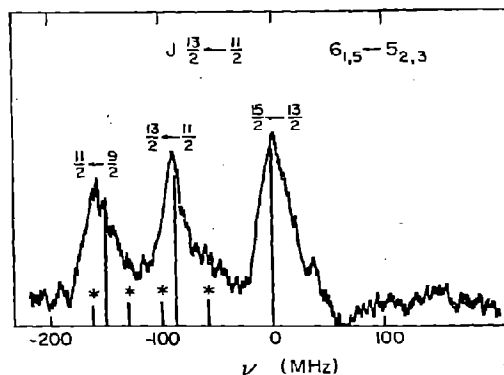


Fig. 6. Hyperfine structure of $6_{1,5} \leftarrow 5_{2,3}$, $J: 13/2 \leftarrow 11/2$ at 17551.34 cm^{-1} (calculated from Dressler and Ramsay [4]).

of the hyperfine structure predicts transitions for which: $\Delta N = \Delta J = \Delta F = \pm 1$ to be strongest but indicates appreciable intensity for lines for which $\Delta N = \Delta J = \pm 1$, $\Delta F = 0$ especially from $N = 1$, $J = 3/2$, $1/2$. However, since these two types of transitions often share common levels, level crossing signals are also possible [9], some with appreciable intensity. Thus up to 16 components contribute to each transition which again, because of the limited resolution, leads to some overlap between closely spaced lines.

Using the matrix elements and terminology of Curl

and Kinsey [7] it is possible to determine, assuming only diagonal elements in N, J, F , explicit expressions for the hyperfine splittings of all the levels. The limited resolution attainable does not allow the determination of the six magnetic coupling terms $[(0)_I]$, $(aa)_I$ and $(cc)_I$ for both the ground and excited states but it is possible by the choice of a suitable model to reduce the number to four. For the ground state the odd electron occupies a pure p orbital along the c axis similar to the ground state of ClO_2 [10] and thus we have assumed by analogy that for the dipole-dipole

Table 1
Hyperfine coupling constants for NH_2 (in MHz) ^{a)}

	$\Pi(0,10,0) \tilde{A}^2 A_1$	Ground state
Fermi contact (0) _I	162.5	39.6
dipole-dipole		
(aa) _I	-16.6	-31.1
(bb) _I	+33.2	-31.1
(cc) _I	-16.6	+62.2

a) The uncertainty in each of these constants is estimated to be 10 MHz.

Table 2
Observed and calculated hyperfine structure in NH_2

$F' \leftarrow F''$	$\Delta\nu$ (MHz) calculated	$\Delta\nu$ (MHz) observed ^{a)}	Calculated relative intensity ^{b)}
$2_{11} \leftarrow 1_{01}$ $J: 3/2 \leftarrow 1/2$			
5/2 \leftarrow 3/2	0	0	1.00
3/2 \leftarrow 1/2	46.8		0.37
* 3/2 5/2 \leftarrow 3/2	48.7	47 (5)	0.54
* 3/2 1/2 \leftarrow 3/2	72.1		0.33
* 1/2 3/2 \leftarrow 1/2	75.8	74 (6)	0.33
* 1/2 5/2 \leftarrow 3/2	77.7		0.19
3/2 \leftarrow 3/2	97.4		0.30
1/2 \leftarrow 1/2	104.7	97 (5)	0.30
$J: 5/2 \leftarrow 3/2$			
7/2 \leftarrow 5/2	0	0	1.60
* 7/2 5/2 \leftarrow 5/2	-60.8	-60 (6)	0.55
5/2 \leftarrow 3/2	-83.0	-83 (5)	1.01
3/2 \leftarrow 1/2	-145.9	-146 (8)	0.60
3/2 \leftarrow 3/2	-168.6	-169 (7)	0.19
$4_{13} \leftarrow 3_{03}$ $J: 7/2 \leftarrow 5/2$			
9/2 \leftarrow 7/2	0	0	1.07
* 7/2 9/2 \leftarrow 7/2	47.3		0.27
7/2 \leftarrow 5/2	62.3	54 (7)	0.79
* 5/2 7/2 \leftarrow 5/2	98.2		0.24
5/2 \leftarrow 3/2	111.1	102 (9)	0.57
$J: 9/2 \leftarrow 7/2$			
11/2 \leftarrow 9/2	0	0	1.33
9/2 \leftarrow 7/2	-78.7	-81 (6)	1.06
7/2 \leftarrow 5/2	-141.7	-138 (7)	0.83
$6_{15} \leftarrow 5_{23}$ $J: 13/2 \leftarrow 11/2$			
15/2 \leftarrow 13/2	0	0	1.23
13/2 \leftarrow 11/2	-87.8	-84 (6)	1.05
11/2 \leftarrow 9/2	-150.3	-159 (8)	0.90

* : Level crossing transitions.

a) The numbers in parentheses are estimated standard deviation.

b) Level crossing transitions have intensities given by the geometric mean of the two transitions sharing the common level [9].

terms, $(aa)_I'' = (bb)_I'' = -\frac{1}{2}(cc)_I''$. Similarly for the upper state the unpaired electron has a configuration similar to that of the NO_2 ground state [11], i.e., $(aa)_I' = -\frac{1}{2}(bb)_I' = (cc)_I'$.

For the $2_{11} \leftarrow 1_{01}$ transitions several combination differences can be obtained which depend solely on the upper or lower state constants and yield values for the four constants.

In order to obtain a better fit to the data terms off-diagonal in J should be included [7] in the hamiltonian. Using the ground state spin-rotational con-

stants of Duxbury [12] $[(0)_s = -3467.63 \text{ MHz}, (aa)_s = -5286.4 \text{ MHz} \text{ and } (cc)_s = 3437.63 \text{ MHz}]$ and upper state constants derived from the observed splittings of Dressler and Ramsay [4] $[(0)_s = -10874.5 \text{ MHz}, (aa)_s = -19857.1 \text{ MHz} \text{ and } (cc)_s = 6940.7 \text{ MHz}]$ accurate hyperfine splittings could be determined for various values of the coupling constants.

Table 1 gives the best set of constants obtained by systematic variation in the constants and comparison with the observed splittings. Table 2 gives these observed frequencies and the calculated splittings determined by the best set of constants. The fit is generally good considering that the observed data has a standard deviation of about 4–6 MHz from the many plots measured. The consistency of the fit is clearly shown in the figs. 1, 3–6 where all the calculated lines of appreciable intensity (> 0.05 of the strongest line) are displayed; in these figures crossing signals are designated with an asterisk, *. The ground state Fermi contact term shown in table 1 falls within the range of the solid state determinations of this constant, representative values for which are 42.6 MHz [13] and 29.1 MHz [8].

The large value for the Fermi contact term in the upper state is worthy of some comments. This corresponds to a $2s_N$ character for the unpaired electron of 11% [11] even though simple molecular orbital considerations would lead to the prediction of pure p character in this near linear state. However, the large vibrational excitation in the bending mode leads to some s–p hybridization of this molecular orbital. It would be interesting to observe the Fermi contact term for other vibrational levels in the series $(0, n, 0)$ and $(1, m, 0)$ so as to see if the s character does in fact increase as n or m increase.

We have demonstrated in this work that saturation spectra can be obtained for transient species using free running dye lasers but that better determination of the hyperfine constants from splittings exhibiting no overlap would require a stability over 1 second of better than 1 MHz.

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