

Infrared diode laser spectroscopy of the fundamental band of NF($a^1\Delta$)

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Thirty-one lines of the fundamental vibration-rotation band of the NF free radical in its $a^1\Delta$ state have been detected in absorption near 8.6 μm using a tunable infrared diode laser. Linewidths were Doppler limited and several transitions were accompanied by resolved hyperfine structure due to fluorine and nitrogen nuclear moments. Wave number calibration using accurately determined N_2O lines yielded $\nu_0 = 1165.952 \pm 0.001 \text{ cm}^{-1}$ for the band center. Rotational and centrifugal distortion constants for both $v=0$ and 1 states have also been determined.

INTRODUCTION

The NF free radical is isoelectronic with O_2 and possesses a $^3\Sigma^-$ ground state along with low lying $^1\Delta$ and $^1\Sigma^+$ excited states. NF $^1\Delta$ can be produced in high yield by the reaction of free atoms with NF_2 radicals¹⁻⁵ and, by analogy with the transfer from O_2 ($a^1\Delta$) to I ($^2P_{3/2}$) in the atomic iodine chemical laser, has aroused interest as a possible chemical pump source for electronic transition lasers.⁶ The reaction of hydrogen atoms with NF_2 is an almost stoichiometric source^{3,4,5} of $^1\Delta$ NF. Both reaction products are formed in excited states and the reaction dynamics and kinetics have been studied by chemiluminescence measurements.⁵

Spectroscopic investigations of NF have been carried out in the visible,^{5,7,8} infrared,^{9,10} and microwave regions.¹¹ Initial studies of emission spectra were made on the $b^1\Sigma^+ - X^3\Sigma^-$ and $a^1\Delta - X^3\Sigma^-$ systems observed in NF_3/Ar discharges.^{7,8} The $^1\Delta$ state has a relatively long (5.6 s) radiative lifetime⁵ and can be generated in sufficient concentrations in the $\text{H} + \text{NF}_2$ reaction for absorption spectroscopy. Curran *et al.*¹¹ measured the electron paramagnetic resonance (EPR) spectrum of the $J=2$ level of $^1\Delta$ NF generated in this way and determined its electric dipole moment and hyperfine coupling constants. More recently, a single rotational transition ($J=7-8$) has been measured by far infrared laser magnetic resonance (LMR)¹² and complements the high resolution EPR investigation for the $v=0$ state.

Although a variety of structural constants for the three lowest electronic states are known, only the 0-0 band of the $a^1\Delta - X^3\Sigma^-$ system was reported in the earliest optical work⁸ giving no information on the vibrational frequency of the $^1\Delta$ state of the molecule. However, very recently Malins and Setser⁵ have measured bands from high levels of $^1\Delta$ NF, and these yielded $\omega_e = 1184$ and $\omega_e X_e = 8.5 \text{ cm}^{-1}$ and hence a band center of $\sim 1167 \text{ cm}^{-1}$. The data were a useful guide in initial searches for the diode laser spectra. Although the infrared spectrum of NF in inert matrices^{9,10} has been known for several years, it arises from the ground electronic state and provides no information in the search for the $^1\Delta$ band. The present study, using a tunable

diode laser, reports the first accurate measurement of the fundamental vibration-rotation spectrum of $^1\Delta$ NF and confirms the position of the band center predicted from optical spectroscopy.

EXPERIMENTAL

Spectra were recorded with a Laser Analytics tunable diode laser spectrometer (LS-3) and 1 m multiple path absorption cell operating with 36 m of pathlength. NF $^1\Delta$ was produced directly in the optical path by reacting H atoms with NF_2 radicals added through diametrically opposed side arms. Hydrogen atoms were generated with a 2450 MHz discharge in hydrogen and NF_2 by the thermal dissociation of N_2F_4 between 150 and 200 $^\circ\text{C}$ using a resistively heated quartz inlet probe. The characteristic orange or green chemiluminescence (depending on conditions) filled the multiple pass cell, and the self-supporting nature of the reaction observed earlier^{2,12} was confirmed. Substitution of deuterium for hydrogen in the microwave discharge yielded the same spectra but with slightly lower intensity.

Approximate calibration was achieved with the 0.5 m monochromator of the LS-3 spectrometer and accurate line positions measured against known N_2O lines.¹³ The NF spectra were recorded with a 15 cm N_2O reference cell in the light path, followed immediately by recording the interference pattern from a 7.6 cm germanium etalon. Repeated measurements demonstrated that negligible errors were introduced by recording the etalon pattern separately. Spectra were also recorded with NF_2 and/or N_2O alone to eliminate absorptions from these species¹⁴ which might also be present in the reaction cell. The laser scan was computer controlled and the digitized spectra were stored on magnetic disc for subsequent analysis. Using rapid scanning techniques, absorption spectra with signal-to-noise ratios $> 500:1$ were achieved in less than 10 s. Further details of the system will be described later.¹⁵

SPECTRA AND RESULTS

The fundamental vibration-rotation band of a molecule with nonzero orbital angular momentum exhibits a Q branch, in addition to P and R branches, with components shifted from the band center by

$$(B_1 - B_0) J(J+1)$$

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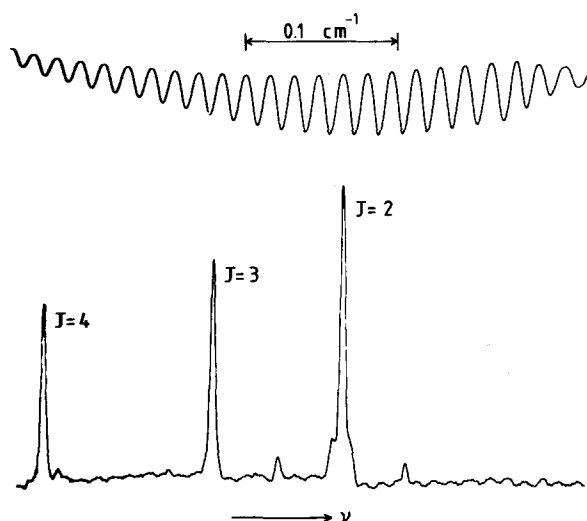


FIG. 1. Diode laser spectrum of the first three members of the Q branch of the fundamental band of NF $a^1\Delta$ near 1166 cm^{-1} . N_2O calibration lines have been omitted for clarity. Absolute positions of the NF lines were measured using the etalon shown at the top of the diagram, and are given in Table I.

with smaller terms due to centrifugal distortion. The linewidths in the diode laser spectrum were Doppler limited and components of the Q branch were easily resolved. This provided the most distinctive feature of the spectrum with several components lying within a single laser mode, usually $\sim 0.5\text{ cm}^{-1}$. Conversely, P- and R-branch components are separated by 2.4 cm^{-1} and no two consecutive lines were simultaneously observable.

Using the optically determined value⁸ of B_0 and estimates of α_e from the data⁷ for $^1\Sigma^+$ and $^3\Sigma^-$ states of NF, the relative positions of the Q-branch components were calculated and readily identified in the region of 1166 cm^{-1} . The first three members of the Q branch formed a recognizable pattern extending to lower wave numbers and are shown in Fig. 1. (The lowest J value permissible for a $^1\Delta$ state is $J=2$.) These yielded $\nu_0 = 1165.95\text{ cm}^{-1}$, and this value of the band center was then used to calculate the expected positions of the P and R components. The intensity of Q-branch lines decreased with increasing J in fair agreement with the intensity formula¹⁶ $I \propto (1/J) \exp[(-BJ(J+1)/kT)]$ and precluded the observation of transitions above $J=9$.

The measured absorption lines are listed in Table I. Although three diodes were used to cover the region of interest, gaps remained in the coverage and several lines were not observed for this reason. The experimental errors quoted arise from uncertainties in the listed positions of the N_2O calibration lines ($\sim 0.002\text{ cm}^{-1}$). Reproducibility of the experimental calibration procedure was estimated to be $\sim 3 \times 10^{-4}\text{ cm}^{-1}$, i.e., about 1/10 the linewidth.

The linewidth of the diode laser spectra was determined by Doppler broadening with a full width half maximum of $\sim 3 \times 10^{-3}\text{ cm}^{-1}$ at 300 K. At this resolution several of the lower J components in all three branches showed resolved hyperfine structure. In the P and R branches

fluorine hyperfine splitting was resolved up to $J=5$ with significant broadening for $J=7$ and 8. The fluorine splittings were calculated from the formula¹⁷

$$W_{\text{hfs}} = a_F \frac{4}{J(J+1)} \left(\frac{F_1(F_1+1) - J(J+1) - I_F(I_F+1)}{2} \right),$$

where F_1 is the resultant of coupling I_F and J . The required magnetic hyperfine constant for fluorine a_F was taken from the work of Curran *et al.*¹¹ and, within the resolution available in this experiment, can be assumed to be unchanged from $v=0$ to 1. The measured splittings were in good agreement with values calculated in this way. Small discrepancies were attributable to additional partially resolved splittings from the nitrogen nucleus, where the corresponding constant is about seven times smaller, and experimental factors such as sloping baselines. Deconvolution of the overlapped lines is a complicated problem due to the nonlinear nature of the diode laser scan and was not considered worthwhile, and, in addition, would not have yielded any improvement in the hyperfine constants determination by EPR.

Generally the most intense hyperfine transitions are

TABLE I. Observed and calculated transitions in the fundamental band of NF $a^1\Delta$.

Assignment	Measured (cm^{-1}) ^a	Calculated-Measured (10^{-3} cm^{-1})
Q(2)	1165.8636	1.4
Q(3)	1165.7774	0.8
Q(4)	1165.6629	-0.5
Q(5)	1165.5194	-1.7
Q(6)	1165.3457	-1.7
Q(8)	1164.9085	1.3
P(5)	1153.4357 ^b	2.5
P(6)	1150.8502	-0.2
P(9)	1142.9177	1.0
P(10)	1140.2157	0.6
P(11)	1137.4891	-0.9
P(12)	1134.7329	-0.5
P(13)	1131.9505	-1.4
P(14)	1129.1372	1.2
P(15)	1126.3015	0.9
P(16)	1123.4372	-2.1
P(17)	1120.5423	0.5
P(18)	1117.6207	2.7
P(19)	1114.6787	-1.5
R(5)	1180.0127 ^b	-1.0
R(6)	1182.2535	-1.7
R(7)	1184.4608	1.3
R(8)	1186.6424	-0.1
R(9)	1188.7918	0.8
R(10)	1190.9109	1.6
R(11)	1193.0027	-0.6
R(14)	1199.0882	-1.0
R(15)	1201.0543	-0.5
R(16)	1202.9897	-0.3
R(17)	1204.8930	0.8
R(18)	1206.7666	0.2

^aEstimated measurement accuracy $\sim 0.002\text{ cm}^{-1}$.

^bValue corrected for resolved asymmetric hyperfine splitting.

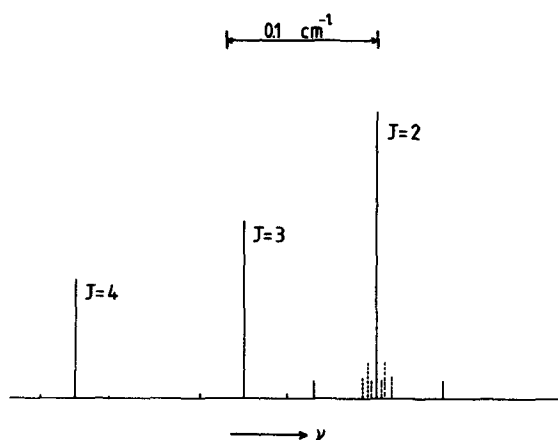


FIG. 2. Calculated spectrum of the Q-branch lines shown in Fig. 1 including hyperfine effects. The most intense peaks correspond to $\Delta J = \Delta F = 0$ transitions. Smaller lines displaced from the main peaks are due to the large fluorine ($I = \frac{1}{2}$) hyperfine splittings. The hyperfine splitting due to the nitrogen ($I = 1$) nucleus is partially resolved for $J = 2$ and is denoted by broken lines.

those with $\Delta F = \Delta J$. The $\Delta F \neq \Delta J$ transitions are calculated to be at least a factor of ten weaker. The predicted fluorine hyperfine pattern in the Q branch is a single strong transition with two weak satellites equally spaced on either side (Figs. 1 and 2), while for P and R branches two strong, closely spaced components are predicted with a much weaker third peak (Fig. 3). The latter lies on the high and low frequency side of the strong doublet for R and P branches, respectively. Figure 2 shows a predicted spectrum for the first three members of the Q branch inclusive of fluorine hyperfine structure, with intensities calculated from standard

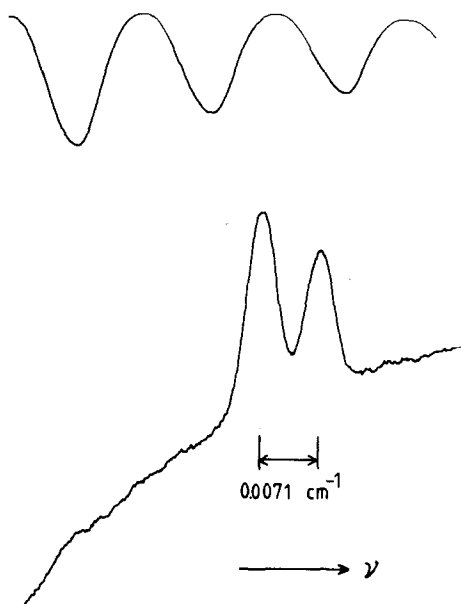


FIG. 3. Fluorine hyperfine structure in the R(3) line of NF $\alpha^1\Delta$. A third much weaker (allowed) component lies at longer wavelengths and does not have measurable intensity.

TABLE II. Spectroscopic parameters for $\alpha^1\Delta$ NF (units are cm^{-1} unless stated otherwise).

	Electronic spectroscopy ^a	Diode laser spectroscopy ^b
ν_0	1167	1165.952(1)
B_0	1.2225(3)	1.22268(6)
D_0	$4.5(3) \times 10^{-6}$	$5.2(1) \times 10^{-6}$
α_e		0.01447(1)
β_e		$5.1(3.7) \times 10^{-8}$
B_e		1.22991(7)
D_e		$5.2(1) \times 10^{-6}$
Magnetic resonance ^c		
a_F (MHz)	+758.06(23)	
a_N (MHz)	+109.92(14)	

^aReferences 5, 7, and 8.

^bUncertainties in the diode laser results are 2 standard deviations in units of the last quoted digit(s) of the parameter.

^cReference 11.

formulas. For the $J = 2$ component the approximate structure due to nitrogen hyperfine is also shown and gives a closely spaced group of six peaks around the center of the transition.

The best estimates of the spectroscopic parameters from a least-squares fit to the data are given in Table II, with quoted uncertainties of two standard deviations. Five parameters were used in the fit: ν_0 , B_0 , D_0 , α_e , and β_e and the vibrational dependence parameters α_e and β_e yielded the equilibrium parameters given in Table II using standard relationships.¹⁶ The differences between the measured and calculated wave numbers of the lines using these parameters are given in Table I and are in excellent agreement within estimated experimental uncertainties.

DISCUSSION AND CONCLUSION

The values of B_0 and D_0 measured by Jones⁸ from the electronic spectrum are given in Table II. The value of B_0 determined here is in good agreement with his value but the value of D_0 falls outside the uncertainties quoted. We have used the same rotational term formula (rather than the more precisely defined formulation given by Mizushima¹⁸) so that a direct comparison of the electronic and diode laser spectra can be made. Fixing B_0 and D_0 to the optically determined values gave an unacceptable fit to the diode laser data. Furthermore, fixing only B_0 to the optical value resulted in a fit to the diode laser data outside the expected error limits and yielded $D_0 = 4.9 \times 10^{-6} \text{ cm}^{-1}$ which is again outside the uncertainty limits quoted by Jones.

The diode laser result for D_0 is in much closer agreement with the values of 5.39×10^{-6} and $5.28 \times 10^{-6} \text{ cm}^{-1}$ found for the $X^3\Sigma^-$ and $b^1\Sigma^+$ states,⁷ respectively, than the optically determined value. It also agrees well with the value predicted by the approximate relationship

$$D_e \sim \frac{4B_e^3}{\omega_e^2} = 5.3 \times 10^{-6} \text{ cm}^{-1}$$

For these reasons the present results are believed to be

more accurate than the earlier values from optical spectroscopy. The recent LMR measurements¹² on $v=0$ NF $^1\Delta$ unfortunately do not provide independent confirmation of these newer values as only a single rotational transition was measured. In the LMR study it was found that a small increase in B_0 of $6 \times 10^{-5} \text{ cm}^{-1}$ was necessary to fit the spectrum, assuming that D_0 was fixed at the quoted optical uncertainties. The rotational spacing of 19.55172 cm^{-1} measured by LMR is also predicted by the diode laser values of B_0 and D_0 , within the uncertainties quoted in Table II. The intrinsically higher measurement accuracy of the far infrared LMR technique should yield more accurate values for the ground state than those in Table II. Nevertheless, the latter represent an improvement in precision of about a factor of five in B_0 and three in D_0 over the earlier optical values.

Malins and Setser⁵ do not quote an uncertainty for their determination of the vibrational frequency or anharmonic constant. However, combining their value of $\omega_e x_e$ with the value of ω_0 in Table II yields $\omega_e = 1182.95 \text{ cm}^{-1}$. This is considerably larger than the value in the $^3\Sigma^-$ ground state (1141.37 cm^{-1}), as predicted by Douglas and Jones⁷ on the basis of the dissociation products, and relatively closer to the $b^1\Sigma^+$ state ($\omega_e = 1197.49 \text{ cm}^{-1}$) which dissociates to the same states of the separated atoms. The $b^1\Sigma^+$ is produced in a subsequent step in the reaction of H with NF₂. Although kinetic arguments suggest its concentration is somewhat lower than the $a^1\Delta$ state, the large signal-to-noise ratio observed for the latter suggests that its spectra should also be detectable by diode laser spectroscopy.

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