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Far infrared laser magnetic resonance spectrum of NF($a\ ^1\Delta$)

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The NF radical in its $a\ ^1\Delta$ metastable state has been detected by far infrared laser magnetic resonance spectroscopy at 513 μm. The spectrum arises from the $J = 7 \rightarrow 8$ rotational transition, and yields an accurate measurement for this spacing of 19.5517_2 cm^{-1}.

INTRODUCTION

The lowest electronic configuration of the NF radical is $(KK)\,(2s\sigma g)^2\,(2s\sigma u)^2\,(2p\sigma g)^2\,(2p\pi u)^4\,(2p\pi g)^2$, which gives rise to $^3\Sigma^-$, $^1\Sigma^+$, and $^1\Delta$ states in an analogous manner to O_2, with which it is isoelectronic. Emission from the $a\,^1\Delta$ and $b\,^1\Sigma^+$ states, which lie 11 435 and 18 905 cm^{-1}, respectively, above the $^3\Sigma^-$ ground state, has been observed in electric discharges[1,2] and from the reactions of free atoms with NF_2 radicals.[3-6] There has recently been renewed interest in the latter sources of NF because of their potential importance in chemical lasers. In particular, the reaction of hydrogen atoms with NF_2 radicals has been shown to yield NF $^1\Delta$ in more than 90% of reactive collisions,[6] in addition to vibrationally excited HF.

Spectroscopic data on NF in the gas phase were first obtained from analysis of the $a\,^1\Delta - X\,^3\Sigma^-$ and $b\,^1\Sigma^+ - X\,^3\Sigma^-$ band systems[1,2] observed in emission from microwave discharges in NF_3 and Ar. Following the discovery by Clyne and White[3] that the reactions of free atoms with NF_2 were convenient sources of singlet NF, the reaction $H + NF_2$ was used to generate sufficient $^1\Delta$NF for EPR spectroscopy.[7] The X-band EPR spectrum of the radical in its $J = 2$ level was subsequently analyzed by Curran *et al.*[7] to yield, primarily, the hyperfine structure parameters for both nucleii and the electric dipole moment. The observation of $^1\Delta$NF by EPR is qualitative confirmation of the relative stability of this state with respect to emission, as expected from the electronic selection rules, and Malins and Setser[6] have recently determined its radiative lifetime to be 5.6 sec.

Far infrared laser magnetic resonance (LMR) has become a powerful technique for high resolution rotational spectroscopy of free radicals, and several rotational transitions in $O_2\,^1\Delta$ have been measured by LMR.[8] Although these spectra are intrinsically weak with only magnetic dipole intensity, this factor is offset by the stability of $O_2\,^1\Delta$ which has a long radiative lifetime of 45 min and which is relatively inert to chemical and collisional removal. This contrasts with $^1\Delta$NF which is shorter lived but should have much stronger electric dipole rotational transitions. We now report the first measurement of a rotational transition in $^1\Delta$NF by far infrared LMR.

EXPERIMENTAL

The far infrared LMR spectrometer was based on the design of Evenson *et al.*[9] and optically pumped in the transverse mode with an Apollo 550 B CO_2 laser giving up to 45 W on the strongest lines. The optically pumped section was equipped with two adjustable mirrors positioned at either end of parallel, gold-coated, optically flat plates which enabled the pump beam to be accurately aligned and the number of reflections optimized. A small fraction of the far infrared radiation was coupled out either from a 1 mm hole in one laser mirror or from a small mirror inserted with a sliding rod into the laser cavity, and detected with a liquid helium cooled Ge bolometer (Infrared Laboratories). The usual Zeeman modulation (at 135 Hz, the optimum sensitivity for the detector) and phase sensitive detection techniques were used. A full description of the spectrometer is given elsewhere.[10]

NF $^1\Delta$ was generated by reacting H atoms with NF_2 radicals at total pressures between 0.5 and 1 Torr:

$$H\,^2S + NF_2\,^2B_1 = HF\,^1\Sigma + NF\,^1\Delta,\quad \Delta H^\circ = -142\ \mathrm{kJ\,mol^{-1}}.$$

Identical spectra were recorded when hydrogen atoms were replaced by deuterium atoms. NF_2 was produced by the thermal dissociation of tetrafluorohydrazine (Air Products) taken from the cylinder, without further purification, via stainless steel and PTFE vacuum lines to a small resistively heated quartz inlet probe located as close as possible to the laser. At ~200 °C, the weak N–N bond energy (~ 93 kJ mol^{-1}) leads to essentially complete dissociation of the N_2F_4. The reaction is strongly chemiluminescent and emits a yellow/orange or green glow, depending on the relative concentrations of H and NF_2. Under our pressure and flow conditions, the chemiluminescence and $^1\Delta$NF LMR signals remained when the microwave discharge generating H atoms was extinguished. The self-sustaining nature of the reaction flame is confirmation of an earlier conclusion that the overall $H + NF_2$ reaction involves a self propagating chain mechanism.[4]

RESULTS

The rotational Hamiltonian appropriate for a diatomic molecule in $a\,^1\Delta$ state has been described in detail previously.[11,12] In a Hund's case (a) representation in which the total angular momentum J and the projection of the orbital angular momentum along the internuclear axis Λ are good quantum numbers, the zero field rotational

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energy levels are given by

$$W(J) = B_0[J(J+1) - \Lambda^2] - D_0[J(J+1) - \Lambda^2]^2, \qquad (1)$$

with $\Lambda = 2$. [This expression for the rotational energy levels differs from that used in the optical analysis[1] by the inclusion of Λ^2 and, when used in Eq. (1), the optical value of B_0 must be reduced by $8D_0$]. Although each level is split by lambda doubling, it can be shown[13] that this splitting is far too small to be resolved even at the relatively high J levels involved in the LMR transitions.

The Zeeman Hamiltonian $H_Z = \mu_B g_L T^1(\mathbf{B}) \cdot T^1(\mathbf{L})$ has matrix elements

$$\langle \Lambda, J, M_J | H_Z | \Lambda, J, M_J \rangle = \mu_B B g_L \frac{\Lambda^2 M_J}{J(J+1)} \qquad (2)$$

and

$$\langle \Lambda, J, M_J | H_Z | \Lambda, J+1, M_J \rangle = \mu_B B g_L \frac{2[(J+1)^2 - \Lambda^2]^{1/2}[(J+1)^2 - M_J^2]^{1/2}}{(J+1)[(2J+1)(2J+3)]^{1/2}} . \qquad (3)$$

This formulism excludes the much smaller contributions from the rotational (g_r) and nuclear (g_I) Zeeman effects. In their EPR study of $^1\Delta$ NF, Curran *et al.*[7] found g_L essentially unity with $g_r \sim -1 \times 10^{-4}$ and adopting an orbital g factor of unity to analyze the 513 μm LMR spectrum reported here is valid within the present measurement accuracy.

The resolved nitrogen and fluorine hyperfine structure can be qualitatively described by first order formulas for the magnetic hyperfine interactions

$$W_I = a_I M_I M_J \frac{\Lambda^2}{J(J+1)} . \qquad (4)$$

However, as noted in the analysis of the EPR spectra, higher terms must be included for a quantitative description, particularly for the fluorine hyperfine splitting.

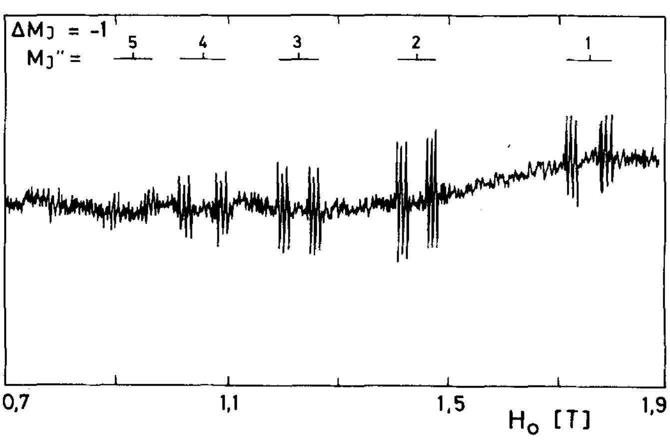

FIG. 1. LMR spectrum of NF a $^1\Delta$ at 513 μm with the electric vector of the laser perpendicular to the magnetic field. Scan rate 18 mT per min with a 1 sec time constant. The intensity of the two lowest field $\Delta M_J = -1$ transitions ($M_{J''} = 6$, 7) is too weak to be observed.

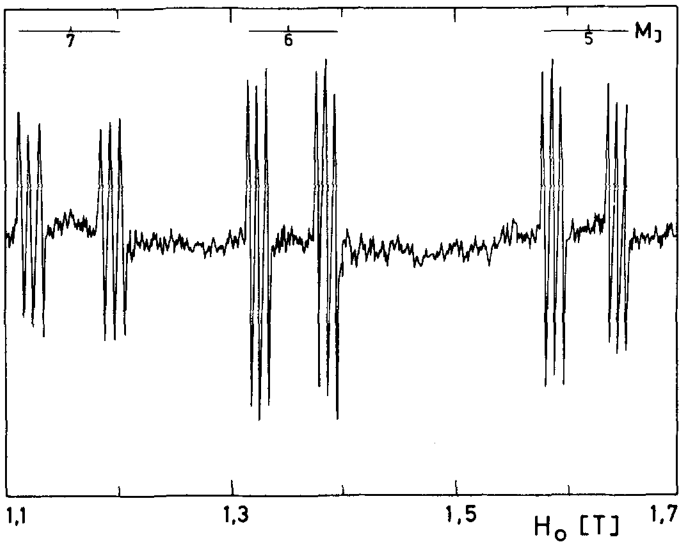

FIG. 2. 513 μm spectrum in parallel polarization up to 1.9 T.

Favorable near coincidences between rotational transitions and strong laser lines were predicted using the optically determined values of B_0 and D_0 in the rotational energy expression of Jones.[1] In particular, the $J = 7 \rightarrow 8$ transition at 19.5508 cm^{-1} lies close to the 513 μm laser line in formic acid[14] at 19.49305 cm^{-1}. The spectra obtained with this laser line in both polarizations are shown in Figs. 1 and 2. Each (M_J)

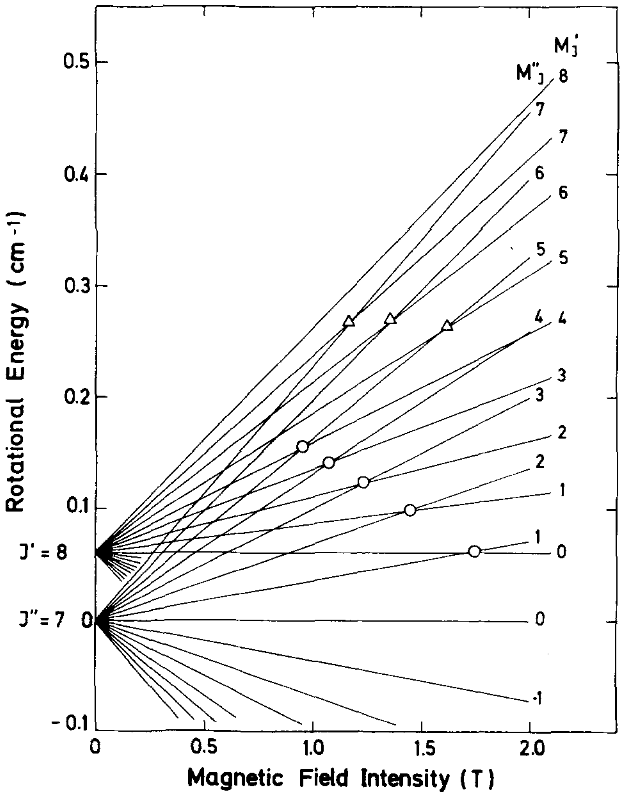

FIG. 3. Zeeman components of the $J = 7$ and 8 rotational levels of $a\,^1\Delta$ NF, $v = 0$, and assignment of the observed perpendicular ○ and parallel △ transitions. The laser frequency has been subtracted from the zero field rotational frequency and the latter adjusted slightly from the value predicted by optical spectroscopy to give the best fit.

transition has six resolved components, a triplet due to the nitrogen-14 ($I=1$) nucleus and a larger doublet splitting from fluorine ($I=1/2$). Using the above laser and transition wave numbers with the first-order Zeeman effect (2) for prediction, the assignment is straightforward, particularly for the parallel (π) spectrum where all three allowed transitions appear with reasonable intensity. Two predicted low field perpendicular transitions were too weak to be detected. The appropriate energy level diagram showing observed transitions is given in Fig. 3.

The magnetic field was calibrated using accurately measured OH spectra. To match the experimental uncertainty of ±1–2 mT, the Zeeman effect was calculated to second order and the rotational interval varied to give the best fit yielding

$$J=7 \rightarrow 8 = 19.5517_2 \pm < 1\times 10^{-4}\,\mathrm{cm}^{-1}.$$

Calculated and experimental field positions are given in Table I.

A higher resolution scan of the $M_J=6$ parallel transition is shown in Fig. 4. The nitrogen hyperfine components are separated by 7.9 ± 0.2 mT compared with a calculated value of 7.92 mT using $a^{14}\mathrm{N}=109$ MHz[7] in the first-order formula (4). There is a small but detectable asymmetry in the spacings within each triplet due to quadrupole and second order magnetic hyperfine effects. The latter are much more noticeable for the fluorine hyperfine spacing which is calculated to be 53.8 mT from Eq. (4) compared with a measured value of 60.8 mT.

DISCUSSION

Although the numerical value of the $J=7\rightarrow 8$ spacing from LMR is little changed from that predicted by the optical constants, the measurement is a factor of 50 more precise. The absolute accuracy of the field measurements will be improved in future experiments, but this is not expected to markedly affect the results quoted here as the transitions involved have small effective g factors and "tune" relatively slowly. Hence, large shifts in resonant fields lead to relatively small changes in zero field transition frequencies. Errors in the former are therefore less serious in determining these frequencies than in examples of more strongly "tuning" LMR transitions, e.g., involving the lower rotational levels of a $^2\pi_{3/2}$ radical. An increase of 28 MHz in the zero field spacing calculated from the optical constants predicts the spectrum within the measurement accuracy. This increment requires a change of only $+6\times 10^{-5}$ cm^{-1} in B_0, to 1.222 56 cm^{-1}, which is well within the quoted[1] uncertainty of ± 0.0003, whereas the uncertainty in D_0 given in Ref. 1 is too small to account for the discrepancy. The value of B_0 appropriate for Eq. (1) then becomes 1.222 52 cm^{-1}.

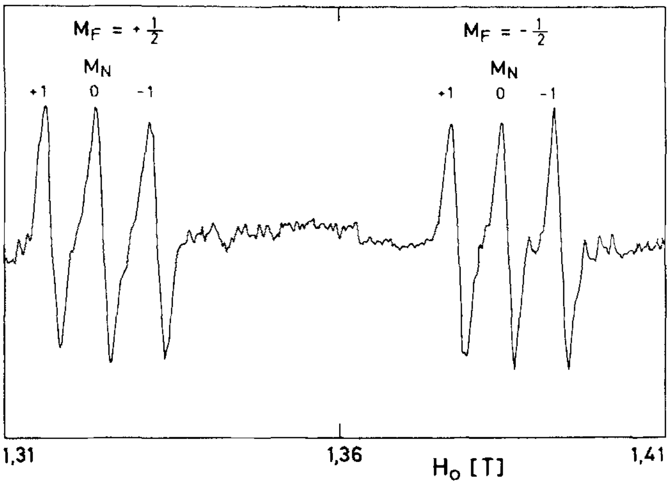

FIG. 4. Hyperfine components of the $M_J=6$ parallel transition at higher resolution.

TABLE I. Experimental and calculated magnetic field positions of transitions in the 513 μm[a] LMR spectrum of a$^1\Delta$NF.

Transition $J=7, M_{J''}\rightarrow J=8, M_{J'}$	Magnetic field intensity (T) Measured[b]	 Calculated[c]
5→4	0.9420	0.9440
4→3	1.0670	1.0680
3→2	1.2270	1.2270
2→1	1.4425	1.4420
1→0	1.7510	1.7515
7→7	1.1640	1.1620
6→6	1.3550	1.3535
5→5	1.6170	1.6185

[a] Laser frequency: 584 386.9 ± 0.7 MHz.

[b] Center of the hyperfine pattern; estimated uncertainty ± 1–2 mT.

[c] Calculated spectrum corresponds to rotational parameters $B_0=1.222\,56$ cm^{-1} and $D_0=4.5\times 10^{-6}$ cm^{-1}, where B_0 and D_0 are defined by Jones[1] (see Discussion section).

Further work is in progress to detect other rotational transitions of $a^1\Delta$NF, and also the $^3\Sigma^-$ ground state. Although the required spectroscopic constants are accurately known,[2] the concentration of the latter species in the H + NF$_2$ system is about a factor of 10 lower.[6] Of particular interest is a comparison of the hyperfine structure in the two electronic states. (For the isoelectronic states of ^{17}O$_2$ the value of $\langle r_I^{-3}\rangle$, where r is the distance from the unpaired electron to the magnetic nucleus I, is essentially the same in both electronic states.)[15] The present study on rotational spectroscopy of $^1\Delta$NF complements other high resolution infrared diode laser experiments in which the fundamental vibration-rotation band is being studied.[16]

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