DETECTION OF THE N_3 FREE RADICAL BY LASER MAGNETIC RESONANCE AT 6.08 μm

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Received 17 March 1988

Lines in the ν_3 (antisymmetric stretch) fundamental band of the N_3 radical in the $\tilde{X}\,^2\Pi_g$ state have been detected by CO laser magnetic resonance. The observations have been assigned to P, Q, and R lines in the fundamental vibration–rotation band and lead to a precise determination of the vibrational interval, the ground-state rotational constant and its dependence on the antisymmetric stretching vibration: $\nu_3 = 1644.67903(24)$ cm^{-1}, $B_0 = 0.431438(16)$ cm^{-1} and $\alpha_3 = 0.004357(18)$ cm^{-1}.

1. Introduction

As Walsh pointed out in his memorable series of papers [1], triatomic molecules of general formula BAC with 16 or fewer valence electrons are expected to be linear in their ground and low-lying states. Several of the possible 15-electron molecules that can be formed from first-row elements have now been identified and characterised. All conform well to Walsh's predictions. The best studied in this group are BO_2 [2], CO_2^+ [3], NCO [4] and N_2O^+ [5]. The molecule N_3 is another example, but there has been comparatively little work so far to determine its structure. It was first identified by Thrush [6], who recorded its electronic spectrum at 270 nm by flash photolysis of hydrazoic acid. The same spectrum was recorded later at higher resolution by Douglas and Jones [7]. They analysed the (0, 0) band of a $^2\Sigma_u^+ - \tilde{X}\,^2\Pi_g$ transition and made the first determination of rotational and spin–orbit parameters for N_3. More recently, the photoelectron spectrum of N_3 has been recorded by Dyke et al. [8], but as usual, this provides information on the positive ion N_3^+ rather than the parent molecule. Nevertheless, the study did show that N_3 can be formed efficiently by a chemical reaction, namely that of F atoms with HN_3.

Direct structural information is hard to come by in the case of N_3. It has no permanent dipole moment in its ground vibrational level (although its equilibrium structure may well be asymmetrical [9]) and consequently no rotational spectrum. However, it should have two strong infrared transitions involving the bending vibration ν_2 (probably in the region of 500 cm^{-1}) and the antisymmetric stretch ν_3. Unfortunately, none of the previous studies involved ν_3 vibrational intervals and there was considerable uncertainty as to its value. We embarked on a search for the ν_3 band several years ago using carbon monoxide laser magnetic resonance (LMR), confident that the band would fall somewhere within the range of the laser (1250–2030 cm^{-1} [10]). The search concentrated on the region near 1900 cm^{-1}, guided by the analogous transition in NCO [11]. These searches were not successful. However, the ν_3 band of N_3 has been detected very recently by FTIR techniques around 1645 cm^{-1} [12]. On searching in this region, we quickly found strong signals. This result highlights the weakness of LMR as a search technique. It is undoubtedly much more tedious to search over tens or even hundreds of CO laser lines than it is to integrate over a broad bandwidth with an interferometer. Unless the search region is fairly well defined by other means, either theoretical or experimental, the LMR spectroscopist is very likely to give up before finding the spectrum.

This paper reports the observation and analysis of preliminary measurements in the (1, 0) band of the N_3 radical by carbon monoxide LMR.

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2. Experimental details and observations

The LMR spectrometer has been described elsewhere [13]. Briefly, it involves a flowing CO laser cooled with liquid nitrogen. A diffraction grating is used to select the laser line and the laser is stabilised by locking to the top of the gain curve. The absorption cell is located inside the laser cavity. Molecular transitions are tuned into coincidence with the laser frequency by application of an external magnetic field which can be varied between 0 and 1.6 T. Zeeman modulation at 5 kHz is applied with a pair of cooled Helmholtz coils, capable of generating a field of up to 12 mT (peak-to-peak). The magnetic flux densities are measured with a proton NMR gaussmeter.

The N_3 radical was generated in the absorption cell by the reaction of F atoms with HN_3, as described by Dyke et al. [8]. Hydrazoic acid was generated in situ by heating a mixture of 10 g of stearic acid with 0.65 g of sodium azide to 90°C. The pressure of HN_3 under these conditions was about 1 Torr (133 Pa). F atoms were generated by passing 5% F_2 in He through a microwave discharge. The total pressure in the reaction cell was about 0.5 Torr (66 Pa).

Signals associated with the ν_3 band of N_3 were detected with four different laser lines. Only spectra in perpendicular polarization have been investigated so far. The spectrum for the $R_1(3/2)$ transition using the $P(16)_{18,17}$ CO laser line at 1647.05403 cm^{-1} is shown in fig. 1. The details of the observed resonances are given in table 1. The laser wavenumbers have been calculated from the Dunham coefficients of Koch, Vanek and Evenson, who have recently measured the frequencies of several CO laser lines directly using heterodyne techniques [14]. It was found to be comparatively easy to produce saturation (or Lamb) dips on most of the lines. Indeed for the $R_1(5/2)$ transition recorded with the $P(9)_{19,18}$ line at 1647.81217 cm^{-1}, almost all the resonances occur at very low fields and are not resolvable with Doppler linewidths. The measurements given in this case all correspond to Lamb dips. It was also possible to resolve ^{14}N hyperfine structure on some lines in the $R_1(3/2)$ spectrum.

One curious characteristic of our observations is that, under certain circumstances, we observed the same spectra in emission rather than absorption. We have not been able to characterise the necessary conditions fully but shall investigate these effects further.

3. Analysis and discussion

The assignments of the LMR spectra were made by comparison of the observed Zeeman patterns with the predictions of a computer program, using the parameters given by Douglas and Jones [7]. The process proved to be quite straightforward. For example the $R_1(3/2)$ spectrum shown in fig. 1 shows the classic Zeeman structure associated with this transition. Details are given in table 1.

As usual with this type of spectrum, our observations have been confined to N_3 in the $^2\Pi_{3/2}$ (F_1) spin component. The measurements depend primarily on the band origin ν_3 (or more strictly the separation between the $^2\Pi_{3/2}$ components) and on the rotational constants for the two vibrational levels involved. There is also a very weak dependence on other parameters for a $^2\Pi$ state such as A (spin–orbit

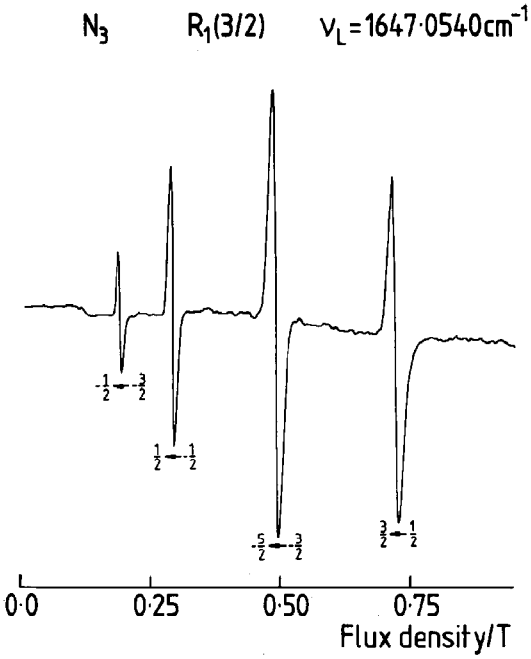

Fig. 1. The LMR spectrum associated with the $R_1(3/2)$ transition of the ν_3 fundamental band of the N_3 radical, observed with the $P(16)_{18,17}$ CO laser line at 1647.05403 cm^{-1} in perpendicular polarisation. The M_J assignments are given below each transition.

Table 1
Observed resonances in the laser magnetic resonance spectrum of the ν_3 band of the N_3 radical

Transition	M_J		Laser frequency (cm^{-1})	Flux density (mT)	10^4(obs−calc) (cm^{-1})	$\partial\nu/\partial B_0$ (MHz/G)
$R_1(5/2)$	1/2	−1/2	1647.81217 [a]	42.5 [b]	0.6	0.387 [c]
	−7/2	−5/2	1647.81217	66.1 [b]	0.4	0.251
	3/2	1/2	1647.81217	93.1 [b]	1.2	0.174
	−5/2	−3/2	1647.81217	444.0 [b]	−2.1	0.043
$R_1(3/2)$	−1/2	−3/2	1647.05403	154.3	−4.9	1.484
	1/2	−1/2	1647.05403	259.2	2.7	0.917
	−5/2	−3/2	1647.05403	473.3	0.6	0.486
	3/2	1/2	1647.05403	716.9	1.6	0.462
$Q_1(3/2)$	1/2	3/2	1644.28899	1430.0	0.8	−1.210
	−1/2	1/2	1644.28899	1569.0	−0.8	−1.008
$P_1(9/2)$	−7/2	−5/2	1640.73237	1090.0	0.5	−0.647
	−5/2	−3/2	1640.73237	1352.0	−0.5	−0.522

[a] Carbon monoxide laser wavenumber, determined from the Dunham coefficients of ref. [14].
[b] Observed as a Lamp dip.
[c] The values quoted for the transition tuning rates are calculated from the parameter values given in table 3.

coupling), γ (spin–rotation coupling) and D (centrifugal distortion). To obtain the best estimates of these quantities, we have refitted the optical data of Douglas and Jones as a $^2\Sigma^+$–$^2\Pi$ transition, using the N^2 formulation of Brown et al. [15] for the $^2\Pi$ state. All lines which were marked by the authors as being assigned to two or more transitions were excluded from the fit. The parameter values obtained are given in table 2. The values for A″ and B″ for the $X\,^2\Pi_g$ state agree reasonably well with those given by Douglas and Jones (−72.26 and 0.43117 cm^{-1}, respectively).

We have used the measurements from the LMR spectrum in table 1 to determine four parameters for N_3 in the $\tilde{X}\,^2\Pi_g$ state: ν_3, B_0, α_3 and g_L. The Hund's case (a) basis set was truncated at $\Delta J=3$ in the calculations and the data were assigned equal weights in the fit. The standard deviation of the fit was 2.3×10^{-4} cm^{-1}. The residuals obtained are given in table 1 and the corresponding set of molecular parameters in table 3. The values obtained for the pa-

Table 2
Molecular parameters (in cm^{-1}) for N_3 obtained from a refit of the (0, 0) band of the $^2\Sigma_u^+$–$\tilde{X}\,^2\Pi_g$ transition [7]

ν_0	36738.751(3) [a]	A''	−71.2675(45)
B'	0.432453(61)	$10^2\gamma''$	−0.227(55)
$10^6D'$	0.203(30)	$10^3p''$	0.95(26)
B''	0.431261(61)	$10^4q''$	−41(15)
$10^6D''$	0.209(30)		

[a] The figures in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

Table 3
Molecular parameters for the N_3 radical in its $\tilde{X}\,^2\Pi_g$ state determined from observations of the ν_3 band by LMR spectroscopy

Parameter [a]	Present work	FTIR study [12]
ν_3	1644.67903(24) [b]	1644.6784
A_0	−71.2675 [c,d]	−71.2722 [d]
α_A	0.3810 [e]	−0.3810
B_0	0.431438(16)	0.43145
$10^2\alpha_3$	0.4357(18)	0.4386
10^6D_0	0.2091 [c]	0.1886
$10^2\gamma_0$	−0.227 [c,d]	−0.074 [d]
g_L	0.98512(86)	–

[a] Value in cm^{-1}, where appropriate.
[b] The figures in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal palce.
[c] Parameter constrained to this value in the fit, obtained from a fit of the optical data of Douglas and Jones [7].
[d] Value for effective parameter, obtained with A_D constrained to zero.
[e] Parameter constrained to this value in the fit, taken from the FTIR results of Brazier et al. [12].

rameters in the FTIR study are also given in table 3 for comparison. There is excellent agreement between the two sets of parameters.

The primary quantity determined by these observations is the antisymmetric stretching frequency ν_3 (1644.6790 cm^{-1}). The value obtained is rather low by comparison with the corresponding frequency for NCO (1920.6 cm^{-1} [11]) but is high when compared with the values for BO_2 (1278.26 cm^{-1} [16]) and for CO_2^+ (1423.08 cm^{-1} [17]). There does not seem to be any simple rationalisation of this set of numbers. The other parameter values given in table 3 are more or less as expected. In particular, the value for the orbital g factor g_L of 0.9851 is significantly less than unity. As has been discussed elsewhere [11,18], this arises in part from Renner–Teller mixing of the bending vibrational levels of the $^2\Pi_g$ state and in part from vibronic mixing of excited $^2\Sigma_u$ and $^2\Delta_u$ states. When the Renner–Teller effect has been better characterised for N_3, it will be possible to separate these two contributions.

Much further work remains to be done on the LMR spectrum of N_3. In addition to characterising the ^{14}N hyperfine interaction from the measurement and analysis of the Lamb dip signals, we hope to be able to detect hot bands involving the bending vibration to learn more about the Renner–Teller coupling. We shall also study the conditions for the observation of the signals in emission in more detail.

Acknowledgement

We are very grateful to Jim Burkholder and his colleagues for communicating the results of their FTIR study of N_3, ref. [12]. Without their help, it might well have been a long time before we looked in the right wavenumber region to observe the spectrum. We also thank Dave Robinson, who was responsible for the construction of the LMR spectrometer and was involved in the early searches for N_3, and Jonathan Towle, who provided valuable back-up services for the present study.

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