

Reinvestigation of the NCN Radical Using Infrared Laser Magnetic Resonance Spectroscopy

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ABSTRACT

The laser magnetic resonance spectroscopic technique has been used to reinvestigate the generation and structure of the carbon-based free radical NCN. In this experiment, a liquid nitrogen-cooled carbon monoxide (CO) laser was used as a source of strong coherent radiation in the 1442 to 1469 cm^{-1} portion of the infrared region. The radicals were brought into resonance with the laser frequency using magnetic fields up to 1.4 T (14 000 Gauss). Using fourteen CO laser emissions, sixty absorption lines were observed, twenty-two of which were observed for the first time. Additionally, detuning experiments were performed on forty-four new and previously observed absorption lines. Analysis of the 3_0^1 fundamental (near 1466.5 cm^{-1}) and $2_1^1 3_0^1$ hot band (near 1455.6 cm^{-1}) in the $^3\Sigma_g^-$ ground electronic state has led to the new assignment of four observed absorption lines as well as the reassignment of a previously assigned absorption line belonging to NCN.

INTRODUCTION

A free radical is a neutral atom or molecule that contains an unpaired electron. All free radicals are characterized by having open valence shell electronic structures and are generally highly reactive, transient species, although stable examples do exist. They are well known intermediates in a number of chemical and biological processes while the upper atmosphere and interstellar space provide near-ideal environments for free radical chemistry. A detailed knowledge of the geometry and energy level structure of a particular free radical is invaluable in the study of the fields in which it may be involved. The instability of the majority of free radicals means that sensitive techniques must be used in their study. Many of these techniques utilize the interaction of the molecular magnetic moment with an external magnetic field, known as magnetic resonance spectroscopy. One particular type of magnetic resonance spectroscopy is laser magnetic resonance (LMR). Since the first LMR observation was made in 1968 [1], this technique has yielded some of the highest resolutions, relative to other types of spectroscopy and it serves as a powerful tool for the investigation of the structure of certain atoms and molecules [2].

In this work, the carbon-based free radical NCN was investigated using the infrared laser magnetic resonance (IR-LMR) system at the University of Oxford. NCN is a linear triatomic molecule with 14 valence electrons and a $^3\Sigma_g^-$ ground state. Jennings and Linnett first observed, but did not identify, the visible and ultraviolet emission spectrum of NCN in 1960 [3]. In 1964, Herzberg and Travis performed the first assignment of the gas-phase electronic spectrum of NCN [4]. Since then, there have been a number of experimental [5-10] and theoretical [11-13] studies on its spectroscopic properties, including the infrared Fourier transform investigation by McNaughton *et al.* [14] and the LMR studies by Brown and co-workers [15-17].

The purpose for reinvestigating NCN is due to a growing interest in linear triatomic molecules containing 13, 14 and 15 valence electrons because of a perplexing variation in the magnitude of their stretching vibrations. At present, the only other 14 valence electron triatomic molecule that has been studied in detail is CCO. Another molecule of interest, having 13 valence electrons, is CNC. As with NCN, CNC is generated by the breakdown of specifically designed stable precursor molecules using discharge techniques, which can simultaneously produce several short-lived radicals. Unfortunately, due to the near coincidence of the antisymmetrical stretch vibrational frequencies between CNC and NCN, the simultaneous production of these molecules complicates the analysis of the observed absorption spectrum. Therefore to investigate CNC, the spectra of NCN must have all of its spectral lines accounted for. Hence, NCN has been reinvestigated in the 1442 to 1469 cm^{-1} spectral region.

EXPERIMENTAL DETAILS

The LMR technique involves identifying a close coincidence between a fixed frequency laser line and a transition in the molecule of interest. A magnetic field is then applied to the sample, employing the Zeeman effect to tune the transitions between the magnetic sub-levels into resonance with the laser line. The IR-LMR system at the University of Oxford, shown in Figure 1, consisted of a liquid nitrogen-cooled CO laser with an intracavity absorption cell that was placed in a variable electromagnet. The CO laser had a 2.4 m gain stabilized cavity and was surrounded by a liquid nitrogen-filled cooling jacket. The ends of the laser cavity were sealed by calcium fluoride (CaF_2) windows positioned at Brewster's angle. The electrical energy source was brought in through two electrodes, across which a d.c. potential of 10 000 V was applied with a total current of approximately 0.014 A supplied to the laser. The laser medium was a flowing gas mixture of helium (He), nitrogen (N_2), CO and air. The ratio of these gases could be altered to optimize particular CO laser lines, however typical ratios were 89% He, 5.4% N_2 , 4.8% CO and 0.8% air at a total pressure of 665 Pa. The end of the laser cavity was an open housing, containing a motorized, computer-controlled grating having 150 lines mm^{-1} .

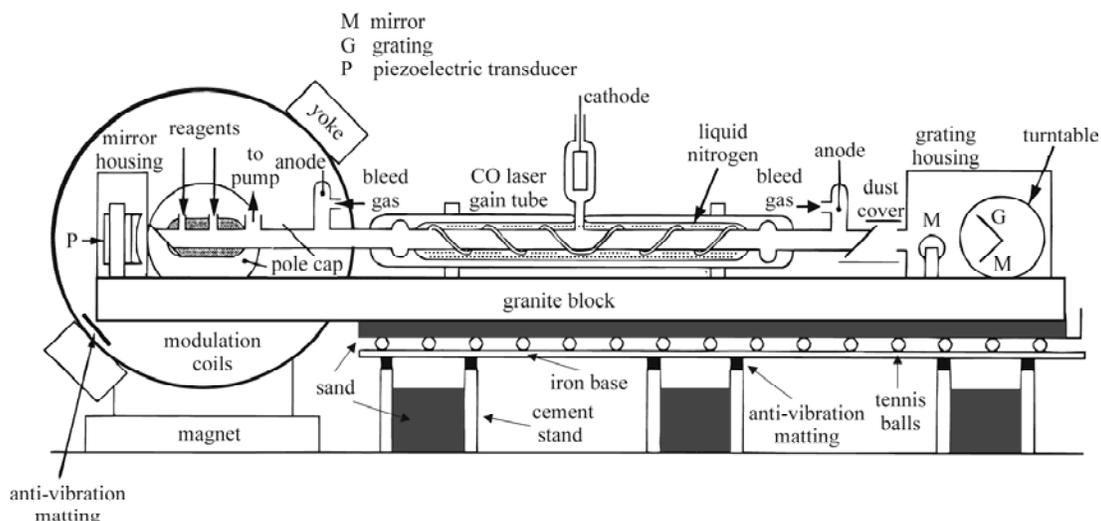


Figure 1. Experimental setup of the Oxford IR-LMR system.

The CO laser typically worked in the vibrational bands from ($v' = 2 \rightarrow v'' = 1$) to ($v' = 37 \rightarrow v'' = 36$) and on the rotational transitions in the P branch ($\Delta J = -1$) from 4 to ≈ 16 . Therefore the CO laser emission $P(15)_{26-25}$ corresponds to an emission from $v' = 26, J' = 14$ to $v'' = 25, J'' = 15$. In this way, laser lines were found about every 2 cm^{-1} in a range between approximately 1190 and 2070 cm^{-1} (from approximately 4.8 to $8.4 \mu\text{m}$). The output power of the CO laser was typically several Watts.

A homogeneous magnetic field up to 1.4 Tesla was created by a 38.1 cm (15 inch) diameter Varian electromagnet having a 10.2 cm (4 inch) pole gap. The magnetic field was monitored by a Brüker digital field controller using a Hall effect probe mounted on one of the pole caps of the magnet. The absorption cell was mounted between these poles, centered on the optical axis of the CO laser. The NCN radicals (as well as other carbon-based radicals) that formed in the discharge tube passed through a Teflon sleeve and the intracavity absorption cell of the LMR spectrometer. Two methods were used in the production of these radicals. The first was a reaction between acetonitrile (CH_3CN at 2 Pa) and atomic fluorine (F at 253 Pa), as produced by a 50 W microwave discharge across the flow of 5% F_2 in He at a total pressure of approximately 279 Pa. The second similar reaction was produced by a 50 W microwave discharge across the flow of carbon tetrafluoride (CF_4 at 2 Pa) with N_2 (at 0.1 Pa) and He (at 147 Pa) at a total pressure of approximately 155 Pa. A liquid nitrogen cooled InSb detector monitored the resonance signals that were then amplified by a lock-in amplifier and recorded on a computer.

Once absorption lines were detected, the spectra were re-recorded while the laser was slightly tuned off the center of its gain curve. The technique of detuning the laser frequency by slightly changing the length of the cavity is called the "Detuning Experiment." This technique is used (i) to determine whether the observed absorption peaks belong to transitions whose frequencies are above or below the laser frequency, and (ii) to separate overlapping peaks.

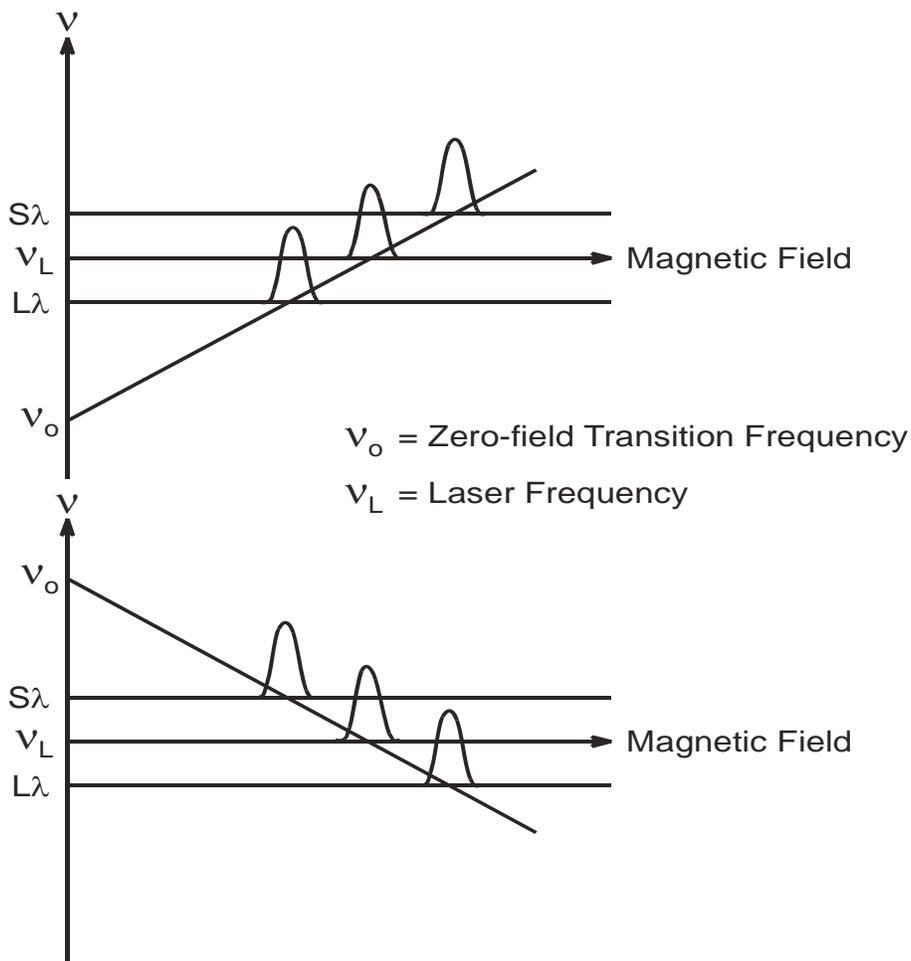


Figure 2. Schematic of the “Detuning Experiment”.

Figure 2 shows the diagram detailing the procedure while Figure 3 shows an actual LMR spectrum where the technique was used. As shown in Figure 2, when the laser was detuned to a slightly higher frequency by shortening the laser cavity, denoted as $S\lambda$, peaks belonging to transitions below (above) the laser frequency will resonate at a slightly higher (lower) magnetic field. On the other hand, if the laser is detuned to a slightly lower frequency by increasing the cavity length, denoted by $L\lambda$, peaks belonging to transitions below (above) the laser frequency will resonate at a slightly lower (higher) magnetic field.

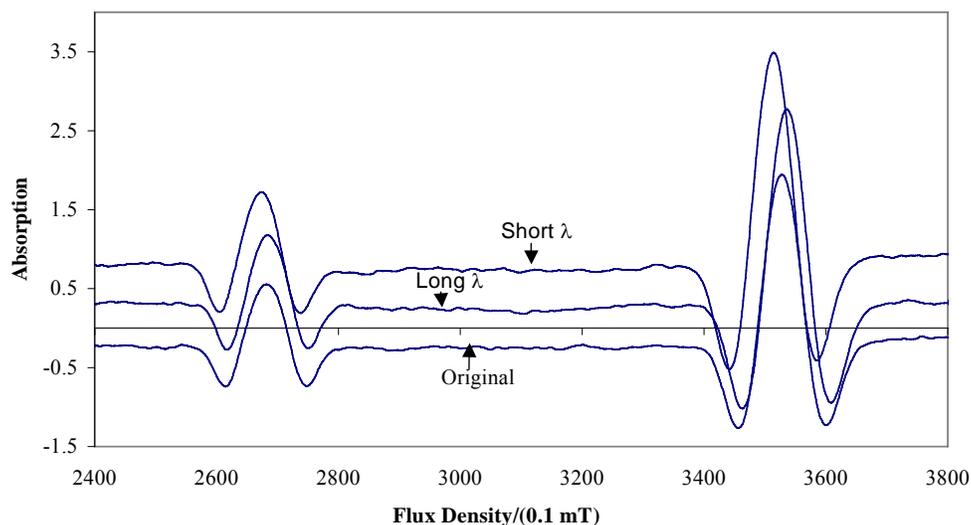


Figure 3. LMR spectrum of NCN recorded using the $P(12)_{26-25}$ line of the CO laser. The spectrum was recorded in the perpendicular polarization with a $150 \text{ lines mm}^{-1}$ grating. The observed absorption peaks were originally fit to transitions above the laser frequency [15], in agreement with the experimental results obtained from the “Detuning Experiment”.

Figure 3 shows the LMR absorption spectra of NCN recorded in the perpendicular polarization with the $P(12)_{26-25}$ line of the CO laser. In the lowest portion of the figure, the laser was tuned to the center of the gain curve. Next the laser cavity was adjusted to $L\lambda$ and later $S\lambda$ and the spectra retaken. From the detuning experiment, the two peaks were verified to belong to transitions that are above the laser frequency, in agreement with their reported spectroscopic assignments [15].

DATA PRESENTATION

The LMR spectra of NCN were recorded in the perpendicular polarization for magnetic fields up to 1.4 T using the $P(5)_{27-26}$ to $P(12)_{27-26}$ lines and the $P(10)_{26-25}$ to $P(15)_{26-25}$ lines of the CO laser. In total, twenty-two resonance signals were observed for the first time in the perpendicular polarization using fourteen different CO laser lines. The average magnetic fields of these absorption signals, along with the CO laser line used and their position with respect to this line, are listed in Table 1. All signals were observed in the perpendicular polarization and the spectra were recorded while the variable magnetic field was increasing and decreasing (typically at rates of 10 mT every 18 seconds). This was done in order to accurately determine the center field position of the resonance, typically to ± 2 mT, minimizing the effect of system response. Detuning experiments were not performed on some of the lines because the signals were either too weak or noisy. The detuning experiment was performed on a number of previously observed absorption signals and the results agreed with their spectroscopic assignments [15, 17].

Table 1. New LMR data for NCN and possibly other carbon-based free radicals using IR-LMR spectroscopy

CO Laser Line	Magnetic Field (mT)	Relative Position
P(11) ₂₆₋₂₅	301.63	above
P(13) ₂₆₋₂₅	871.85	below
P(14) ₂₆₋₂₅	58.35	below
	111.54	below
	153.14	below
P(15) ₂₆₋₂₅	356.69	below
	995.33	
P(6) ₂₇₋₂₆	160.55	above
	171.03	above
	178.64	above
	190.44	above
	202.64	above
	214.09	above
	222.83	above
	233.31	above
	244.81	above
	255.18	above
	271.71	above
	291.26	above
P(11) ₂₇₋₂₆	57.86	
	70.73	
P(12) ₂₇₋₂₆	139.83	

As mentioned, the NCN radical was produced using two different methods. These reactions do not selectively create NCN, rather they generate a variety of small carbon/nitrogen free radicals in the absorption cell (such as CCN [18] and HCCN [19]). The spectra these radicals generated were widely separated in frequency and did not overlap.

RESULTS

Several new absorption lines were observed with detuning experiments performed on new and previously observed absorption lines. Once the IR-LMR spectra of NCN were recorded, the molecular parameters listed in Tables 2 and 3 for the 3_0^1 fundamental and $2_1^1 3_0^1$ hot band in the $^3\Sigma_g^-$ ground electronic state, respectively, were used to predict the theoretical spectrum.

Computer simulations of the spectrum were produced using a standard $^3\Sigma$ Hamiltonian [15, 17, 20], formulated using Hund's case (b) basis functions (for cases where spin-orbit coupling vanishes). The molecular parameters listed in Tables 2 and 3 were determined from a least squares fit of the Fourier transform [14] and LMR [15-17] spectra with a Hund's case (b) basis set truncated at $\Delta N = \pm 3$. Comparison of the predicted spectral lines with the observed absorption spectrum yielded four new spectroscopic assignments listed in Table 4, where N represents the total angular momentum, excluding electron and nuclear spin. The energy order index (E.O.I.) label identifies the energy state corresponding to a particular M_J value¹. M_J denotes the component of the total angular

¹ For a given N, there will be up to three possible energy states that correspond to a particular M_J value. An E.O.I. value of 1 represents the lowest energy state and an E.O.I. value of 3 represents the highest energy state.

momentum along the direction of the external magnetic field (the space-fixed direction) and dv/dB represents the tuning rate of the transition. Table 4 also includes the spectral line reassigned in this work [15].

Table 2. Molecular Parameters for NCN in the ${}^3\Sigma_g^-$ Electronic Ground State [from Ref. 15].

Parameter	Value
ν_3	1466.507530(91) cm^{-1}
B_{000}	0.3972746(62) cm^{-1}
$\alpha_{B,3}$	-0.00430340(60) cm^{-1}
D_{000}	$1.830(28) \times 10^{-7} \text{cm}^{-1}$
$\alpha_{D,3}$	$-0.0209(41) \times 10^{-7} \text{cm}^{-1}$
λ_{000}	0.79420 cm^{-1}
$\alpha_{\lambda,3}$	0.01192(14) cm^{-1}
γ_{000}	-0.001175 cm^{-1}
g_{S_0}	2.01127(50)
g_l^e	0.00126

Table 3. Molecular Parameters for the $2_1^1 3_0^1$ Hot Band of NCN in the ${}^3\Sigma_g^-$ Electronic Ground State [from Ref. 17].

Parameter	Value
ν_0	1455.61085(13) cm^{-1}
B_{010}	0.398621(12) cm^{-1}
$\alpha_{B,3}$	-0.00430111(71) cm^{-1}
D_{010}	$1.619(67) \times 10^{-7} \text{cm}^{-1}$
γ_{010}	-0.001153 cm^{-1}
λ_{010}	0.78081 cm^{-1}
$\alpha_{\lambda,3}$	0.01145(22) cm^{-1}
$o_{G,010}$	-0.01641(34) cm^{-1}
$q_{G,010}$	$-9.95(13) \times 10^{-4} \text{cm}^{-1}$
$\alpha_{q,3}$	$-5.632(86) \times 10^{-5} \text{cm}^{-1}$
g_S	2.0020
$\alpha_{gS,3}$	0.01203(24)
g_l	0.00126

Table 4. LMR data for the 3_0^1 and $2_1^1 3_0^1$ Bands of NCN

N	$E.O.I.$	M_J	N	$E.O.I.$	M_J	B_0 (mT)	$\frac{dv}{dB}$ $\left(\frac{\text{MHz}}{\text{mT}}\right)$
Data for the 3_0^1 Fundamental							
P(14) ₂₆₋₂₅ : 1459.4647 cm ⁻¹							
8	2	-8	9	2	-8	466.8	-18.4
7	1	8	8	2	8	488.6	18.3
P(13) ₂₆₋₂₅ : 1462.8766 cm ⁻¹							
4	2	-4	5	2	-4	547.1 ^a	-12.2
P(11) ₂₆₋₂₅ : 1469.6012 cm ⁻¹							
4	3	-2	3	3	-1	175.6	-1.6
Data for the $2_1^1 3_0^1$ Hot Band							
P(7) ₂₇₋₂₆ : 1458.3706 cm ⁻¹							
3	3	-2	2	2	-2	556.5 ^b	24.0

^aAbsorption line has been reassigned [15].

^bAbsorption line has been assigned a $1 \leftarrow -1$ parity.

CONCLUSIONS

In this work, the IR-LMR spectra were recorded in the perpendicular polarization using fourteen lines of the CO laser. In all, sixty absorption lines were observed, twenty-two of which for the first time. In addition, detuning experiments were performed on forty-four new and previously observed absorption signals. These lines were reproducible using two different methods for creating the radicals, one by mixing CH₃CN with atomic fluorine, as produced by a 50 W microwave discharge across the flow of 5% F₂ in He and a second by a 50 W microwave discharge across the flow of CF₄ with N₂ and He. Although the first procedure produced slightly stronger signals, both methods were successful in generating NCN radicals. Finally, analysis of the spectra has resulted in the assignment of four new absorption lines belonging to NCN along with the reassignment of a previously identified NCN transition. The results of this work can be added to the growing database on vibrational wavenumbers of linear triatomic molecules containing 13, 14 and 15 valence electrons. This is particularly important since there is a perplexing variation in the magnitude of these values, particularly for the stretching vibrations [15].

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REFERENCES

1. K. M. Evenson, H. P. Boida, J. S. Wells, R. J. Mahler and M. Mizushima, *Phys. Rev. Letts.*, **21**, 1038-1040 (1968).
2. C. Bradley Moore, ed., Chemical and Biochemical Applications of Lasers, (Academic Press) (1980).
3. K. R. Jennings and J. W. Linnett, *Trans. Faraday Soc.*, **56**, 1737-1741 (1960).
4. G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658-1675 (1964).
5. D. E. Milligan, M. E. Jacox, J. J. Comeford and D. E. Mann, *J. Chem. Phys.*, **43**, 756-757 (1965).
6. D. E. Milligan, M. E. Jacox and A. M. Bass, *J. Chem. Phys.*, **43**, 3149-3160 (1965).
7. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **45**, 1387-1391 (1966).
8. H. W. Kroto, *J. Chem. Phys.*, **44**, 831-832 (1966).
9. H. W. Kroto, *Can. J. Phys.*, **45**, 1439-1450 (1967).
10. G. P. Smith, R. A. Copeland and D. R. Crosley, *J. Chem. Phys.*, **91**, 1987-1993 (1989).
11. C. W. Murray, G. J. Laming, N. C. Handy and R. D. Amos, *J. Phys. Chem.*, **97**, 1868-1871 (1993).
12. J. M. L. Martin, P. R. Taylor, J. P. François and R. Gijbels, *Chem. Phys. Letts.*, **226**, 475-483 (1994).
13. H. U. Suter, M.-B. Huang and B. Engels, *J. Chem. Phys.*, **101**, 7686-7691 (1994).
14. D. McNaughton, G. F. Metha and R. Tay, *Chem. Phys.*, **198**, 107-117 (1995).
15. K. D. Hensel and J. M. Brown, *J. Mol. Spectrosc.*, **180**, 170-174 (1996).
16. S. A. Beaton and J. M. Brown, *J. Mol. Spectrosc.*, **183**, 347-359 (1997).
17. J. M. Brown, W. Urban and M. Wienkoop, *J. Mol. Spectrosc.*, **185**, 185-186 (1997).
18. M. D. Allen, K. M. Evenson, D. A. Gillett and J. M. Brown, *J. Mol. Spectrosc.*, **201**, 18-29 (2000).
19. M. D. Allen, K. M. Evenson and J. M. Brown, *J. Mol. Spectrosc.*, **209**, 143-164 (2001).
20. J. M. Brown, I. Kopp, C. Malmberg and B. Rydh, *Phys. Scr.*, **17**, 55-67 (1978).