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Millimetre wave spectroscopy of NS ($X^2\Pi$) up to $v = 5$

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Millimetre wave spectra of NS ($X^2\Pi$) have been measured in vibrational levels $v \leq 5$. The results are used to obtain rotational, fine structure and hyperfine parameters, and to investigate their dependence on vibrational state.

1. INTRODUCTION

The NS free radical has been a prototype molecule for developments in microwave and infrared spectroscopy of transients. It was first detected at X-band frequencies via its electron paramagnetic resonance spectrum [1-3]. Although E.P.R. studies were restricted to the lowest rotational transitions of the $X^2\Pi_{3/2}$ manifold they yielded the first determination of hyperfine parameters for the radical and stimulated searches for its microwave spectra at zero field [4]. Several microwave transitions have now been measured in both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ NS, with Λ doubling resolved in the latter state. The most recent microwave study preceding this work, due to Lovas and Suenram [5], reported measurements up to $J = 3.5$ in $v = 0$ $^{14}\text{N}^{32}\text{S}$ and $^{14}\text{N}^{34}\text{S}$ with predictions (1 MHz accuracy) for astrophysical searches extending up to $J = 6.5$.

Data on vibrationally excited states of NS has come from numerous studies of electronic spectra and, more recently, from an analysis of the fundamental band of NS near $8.3 \mu\text{m}$ by diode laser spectroscopy [6]. Much higher J levels were observed in this infrared study than by microwave spectroscopy, and the band origin and $v = 1$ rotational parameters were improved from their values from (less direct) optical spectroscopy. The present millimetre wave study firstly extends the results for $v = 0$ NS to much higher J and secondly reports rotational spectra of NS for $v = 1-5$ for the first time. The analysis of these results provides a more extensive set of parameters for predictive purposes and information on possible variation of the fine and hyperfine parameters with vibrational state.

2. EXPERIMENTAL

The rf excitation (50 MHz) and absorption cell used in this work has been described in detail in other studies of vibrationally excited free radicals and transients [7]. NS was generated inside the absorption cell by first discharging H_2S

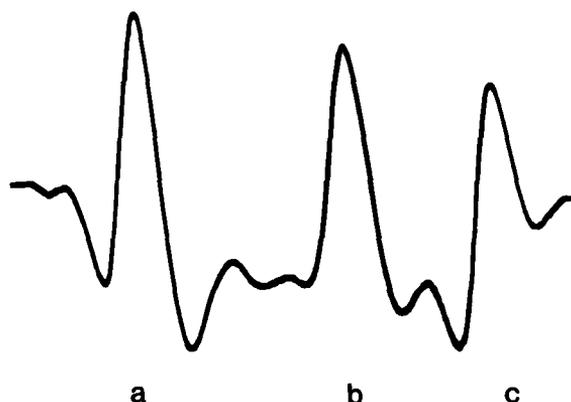


Figure 1. Hyperfine components of the $J = 9/2 \leftarrow 7/2$ transition in $^{14}\text{N}^{32}\text{S}$ in the $v = 2$ $^2\Pi_{3/2}$ state. (a) $F = 11/2 \leftarrow 9/2$, (b) $F = 9/2 \leftarrow 7/2$ and (c) $F = 7/2 \leftarrow 5/2$. The spectrum is an accumulation of 100, one second scans recorded with a 10 ms time constant.

for 10–15 min to deposit elemental sulphur on the cell walls, followed by a discharge in pure N_2 to produce the radical continuously at an optimum pressure of 20 mtorr. Millimetre and sub-millimetre power in the 60 to 350 GHz range was provided by frequency locked klystrons. Above 100 GHz harmonic generation was employed, using a helium cooled InSb detector. Spectra of the ground state were recorded singly or by averaging only a few scans. For the higher vibrational states several hundred scans were accumulated to obtain reasonable signal to noise ratios. Figure 1 shows a spectrum of vibrationally excited ($v = 2$) $^{14}\text{N}^{32}\text{S}$ in the $^2\Pi_{3/2}$ state. $^2\Pi_{3/2}$ transitions were always weaker than the corresponding $^2\Pi_{1/2}$ transitions and could not be observed at the $v = 5$ level of excitation.

3. RESULTS AND ANALYSIS

The measured transitions and their assignments are given in table 1. The present status of the observed rotational spectra of $v = 0$ NS is shown schematically in figure 2.

The least squares analysis followed the procedure given earlier for other Hund's case (a) diatomic molecules [8]. Twelve parameters were used for fitting: the rotational and fine structure parameters B , D , A , A_J ; two lambda doubling parameters p and q ; four hyperfine coupling parameters a , b , c , d and two quadrupole terms eQq_1 and eQq_2 . As shown by Endo *et al.* [8] in their analysis of the analogous molecule SF our parameter B contains a small indeterminate lambda doubling term: $B = B_v + q^*/2$. In addition, the small rotational dependence of A , A_J , must be included since A_J is an effective parameter in this formulation and contains a finite contribution from spin rotation. Although the vibrational dependence of the spin orbit constant cannot be found from these spectra its variation was allowed for using the change in A from $v = 0$ to 1 determined from the fundamental band [6]. The lambda doubling parameters p and q have been defined by Zare *et al.* [10]. In other microwave studies on NS only p has been determined, mainly because of the absence of resolved $^2\Pi_{3/2}$ lambda doubling.

Table 1. Measured transition frequencies (MHz) in $^{14}\text{N}^{32}\text{S}$ ($X^2\Pi$) (precision of the experimental measurements is in the last digits given).

v	$J' \leftarrow J''$	Parity	$F' \leftarrow F''$	Measured frequency	Obs-calc		
0	3/2 \leftarrow 1/2	<i>f</i>	1/2 \leftarrow 3/2	69283.140(50)	-0.064		
			3/2 \leftarrow 3/2	69330.580(50)	0.040		
			5/2 \leftarrow 3/2	69411.890(50)	-0.078		
			1/2 \leftarrow 1/2	69437.840(50)	0.037		
			3/2 \leftarrow 1/2	69485.140(50)	0.001		
			5/2 \leftarrow 3/2	115489.527(80)	0.100		
		5/2 \leftarrow 3/2	<i>f</i>	3/2 \leftarrow 3/2	115524.772(80)	0.109	
				7/2 \leftarrow 5/2	115556.312(80)	0.004	
				5/2 \leftarrow 3/2	115570.762(80)	-0.094	
				3/2 \leftarrow 1/2	115571.930(80)	-0.068	
				7/2 \leftarrow 7/2	161636.541(80)	-0.034	
				5/2 \leftarrow 5/2	161657.845(80)	0.022	
	7/2 \leftarrow 5/2	<i>f</i>	9/2 \leftarrow 7/2	161697.330(80)	0.049		
			7/2 \leftarrow 5/2	161703.500(80)	0.044		
			5/2 \leftarrow 3/2	161704.000(80)	-0.016		
			9/2 \leftarrow 7/2	207777.498(100)	-0.042		
			7/2 \leftarrow 7/2	207792.917(100)	0.006		
			11/2 \leftarrow 9/2	207834.846(100)	-0.016		
	9/2 \leftarrow 7/2	<i>f</i>	9/2 \leftarrow 7/2	207838.348(150)	0.102		
			11/2 \leftarrow 11/2	253913.141(150)	-0.029		
			9/2 \leftarrow 9/2	253925.377(150)	0.065		
			13/2 \leftarrow 11/2	253968.360(150)	-0.014		
			11/2 \leftarrow 9/2	253970.560(200)	0.069		
			15/2 \leftarrow 13/2	300096.867(150)	-0.144		
	13/2 \leftarrow 11/2	<i>f</i>	13/2 \leftarrow 11/2	300098.461(200)	0.015		
			15/2 \leftarrow 13/2	346220.775(250)	-0.178		
			3/2 \leftarrow 1/2	<i>e</i>	5/2 \leftarrow 3/2	69002.990(50)	0.086
					3/2 \leftarrow 1/2	69018.160(50)	0.090
					3/2 \leftarrow 3/2	69037.360(50)	-0.062
					1/2 \leftarrow 1/2	69040.280(50)	-0.146
	1/2 \leftarrow 3/2	69059.870(50)			0.092		
	7/2 \leftarrow 5/2	115153.835(80)			-0.110		
	5/2 \leftarrow 3/2	<i>e</i>	5/2 \leftarrow 3/2	115156.799(80)	0.010		
			3/2 \leftarrow 1/2	115162.955(80)	-0.026		
			3/2 \leftarrow 3/2	115185.394(80)	0.057		
			5/2 \leftarrow 5/2	115191.265(80)	-0.042		
			7/2 \leftarrow 7/2	161297.220(80)	-0.035		
			7/2 \leftarrow 5/2	161298.330(80)	-0.043		
	7/2 \leftarrow 5/2	<i>e</i>	5/2 \leftarrow 3/2	161301.740(80)	-0.013		
			5/2 \leftarrow 5/2	161330.330(80)	0.029		
			7/2 \leftarrow 7/2	161335.646(80)	-0.089		
			9/2 \leftarrow 9/2	207436.238(300)	0.222		
			7/2 \leftarrow 5/2	207438.601(150)	-0.064		
			7/2 \leftarrow 7/2	207470.615(150)	0.022		
	9/2 \leftarrow 7/2	<i>e</i>	9/2 \leftarrow 9/2	207474.999(150)	-0.040		
			11/2 \leftarrow 11/2	253570.457(300)	0.167		
			9/2 \leftarrow 9/2	253606.011(150)	-0.016		
			11/2 \leftarrow 11/2	253609.595(150)	0.001		
13/2 \leftarrow 13/2			299699.803(300)	0.146			
11/2 \leftarrow 11/2							

Table 1 (continued).

v	$J \longleftarrow J''$	Parity	$F' \longleftarrow F''$	Measured frequency	Obs-calc			
1	7/2	5/2	e	${}^2\Pi_{1/2}$		9/2 7/2	159985.394(80)	-0.064
				7/2 5/2	159986.611(80)	0.053		
				5/2 3/2	159989.918(80)	-0.017		
	9/2	7/2	e	11/2 9/2	205749.723(200)	0.248		
				7/2 5/2	205752.173(100)	0.060		
				7/2 7/2	205784.146(100)	-0.026		
				9/2 9/2	205788.643(100)	-0.015		
				9/2 7/2	251509.127(250)	0.125		
	11/2	9/2	e	9/2 7/2	251510.900(150)	0.202		
				13/2 11/2	297263.620(300)	0.144		
	13/2	11/2	e	7/2 7/2	160325.133(80)	-0.004		
				5/2 5/2	160346.388(80)	-0.014		
	7/2	5/2	f	9/2 7/2	160385.978(80)	0.040		
				7/2 5/2	160392.071(80)	-0.036		
				5/2 3/2	160392.706(80)	0.048		
				9/2 9/2	206091.357(100)	0.002		
				7/2 7/2	206106.714(100)	-0.029		
				11/2 9/2	206148.763(100)	-0.011		
				9/2 7/2	206152.277(100)	0.121		
	11/2	9/2	f	13/2 11/2	251907.513(150)	-0.027		
				11/2 9/2	251909.707(250)	0.051		
13/2	11/2	f	15/2 13/2	297661.417(200)	-0.010			
			13/2 11/2	297662.963(200)	0.102			
2	7/2	5/2	e	9/2 7/2	158670.537(80)	-0.048		
				7/2 5/2	158671.733(80)	0.067		
				5/2 3/2	158674.997(80)	-0.044		
	9/2	7/2	e	11/2 9/2	204059.112(200)	0.154		
				7/2 5/2	204061.538(100)	-0.047		
	7/2	5/2	f	9/2 7/2	159071.360(80)	-0.009		
				7/2 5/2	159077.497(80)	-0.036		
				5/2 3/2	159078.041(150)	-0.033		
	9/2	7/2	f	11/2 9/2	204458.513(100)	-0.048		
				9/2 7/2	204462.025(100)	0.085		
	11/2	9/2	f	13/2 11/2	249841.635(150)	-0.046		
				11/2 9/2	249843.886(250)	0.091		
3	7/2	5/2	e	7/2 5/2	157353.216(80)	0.029		
				5/2 3/2	157356.534(80)	-0.025		
	9/2	7/2	e	11/2 9/2	202363.957(200)	0.151		
				7/2 5/2	202366.371(100)	-0.052		
	7/2	5/2	f	9/2 7/2	157753.031(80)	-0.032		
				7/2 5/2	157759.209(80)	-0.012		
				5/2 3/2	157759.777(80)	0.024		
	9/2	7/2	f	11/2 9/2	202763.547(100)	-0.017		
9/2 7/2				202767.068(200)	0.128			
4	7/2	5/2	e	9/2 7/2	156029.482(80)	-0.080		
				7/2 5/2	156030.686(80)	0.079		
				5/2 3/2	156033.949(80)	-0.028		
	9/2	7/2	e	11/2 9/2	200663.557(250)	0.195		
				7/2 5/2	200665.988(100)	0.020		
	7/2	5/2	f	9/2 7/2	156430.526(80)	0.018		
				7/2 5/2	156436.903(200)	0.243		
				11/2 9/2	201063.049(100)	-0.076		
9/2	7/2	f	9/2 7/2	201066.600(200)	0.101			

Table 1 (continued).

v	$J' \leftarrow J''$	Parity	$F' \leftarrow F''$	Measured frequency	Obs-calc
5	9/2 → 7/2	<i>e</i>	$^{2}\pi_{1/2}$ 11/2 → 9/2	198957·111(250)	0·144
			7/2 → 5/2	198959·518(100)	-0·044
		<i>f</i>	11/2 → 9/2	199356·543(100)	-0·043
			9/2 → 7/2	199359·962(100)	0·005
0	5/2 → 3/2	<i>e, f</i>	5/2 → 5/2	116147·270(80)	0·081
			3/2 → 3/2	116179·740(80)	-0·005
			7/2 → 5/2	116181·240(80)	0·048
			5/2 → 3/2	116203·490(80)	0·194
	7/2 → 5/2	<i>e, f</i>	7/2 → 7/2	162634·105(80)	-0·044
			9/2 → 7/2	162658·551(80)	-0·025
			7/2 → 5/2	162668·173(80)	0·022
			5/2 → 3/2	162674·118(80)	0·040
	9/2 → 7/2	<i>e, f</i>	9/2 → 9/2	209111·246(100)	-0·038
			11/2 → 9/2	209130·278(100)	-0·050
			9/2 → 7/2	209135·678(100)	-0·033
			7/2 → 5/2	209139·386(100)	-0·075
	11/2 → 9/2	<i>e, f</i>	13/2 → 11/2	255596·882(150)	-0·062
			11/2 → 9/2	255600·355(150)	-0·061
			9/2 → 7/2	255602·999(150)	-0·035
			13/2 → 11/2	302057·827(150)	-0·128
13/2 → 11/2	<i>e, f</i>	13/2 → 11/2	302060·589(150)	0·195	
		11/2 → 9/2	302062·526(150)	0·181	
		9/2 → 7/2	161327·508(80)	-0·007	
		5/2 → 3/2	161342·990(80)	0·036	
1	7/2 → 5/2	<i>e, f</i>	11/2 → 9/2	207418·912(100)	-0·041
			9/2 → 7/2	207424·261(100)	-0·053
	9/2 → 7/2	<i>e, f</i>	7/2 → 5/2	207427·981(100)	-0·068
			13/2 → 11/2	253505·452(120)	0·188
2	7/2 → 5/2	<i>e, f</i>	11/2 → 9/2	253508·723(120)	0·002
			9/2 → 7/2	253511·242(120)	-0·087
	9/2 → 7/2	<i>e, f</i>	9/2 → 7/2	159993·425(80)	0·043
			7/2 → 5/2	160002·789(80)	-0·088
5/2 → 3/2			160008·753(80)	-0·005	
11/2 → 9/2			205703·596(100)	-0·034	
3	7/2 → 5/2	<i>e, f</i>	9/2 → 7/2	205708·920(100)	-0·049
			7/2 → 5/2	205712·578(100)	-0·110
	9/2 → 7/2	<i>e, f</i>	9/2 → 7/2	158655·726(80)	0·065
			7/2 → 5/2	158665·247(80)	0·131
4	9/2 → 7/2	<i>e, f</i>	11/2 → 9/2	203983·620(100)	-0·073
			9/2 → 7/2	203988·977(100)	-0·032
	7/2 → 5/2	<i>e, f</i>	7/2 → 5/2	203992·624(100)	-0·090
			9/2 → 7/2	202263·976(150)	0·206
7/2 → 5/2	<i>e, f</i>	7/2 → 5/2	202267·488(150)	0·029	

However, at the high J levels investigated in this work mixing of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states occurs and although lambda doubling in the $^2\Pi_{3/2}$ state was unresolved, the finite magnitude of off-diagonal terms in the rotational hamiltonian yielded q (though with large uncertainty). The four hyperfine coupling constants were

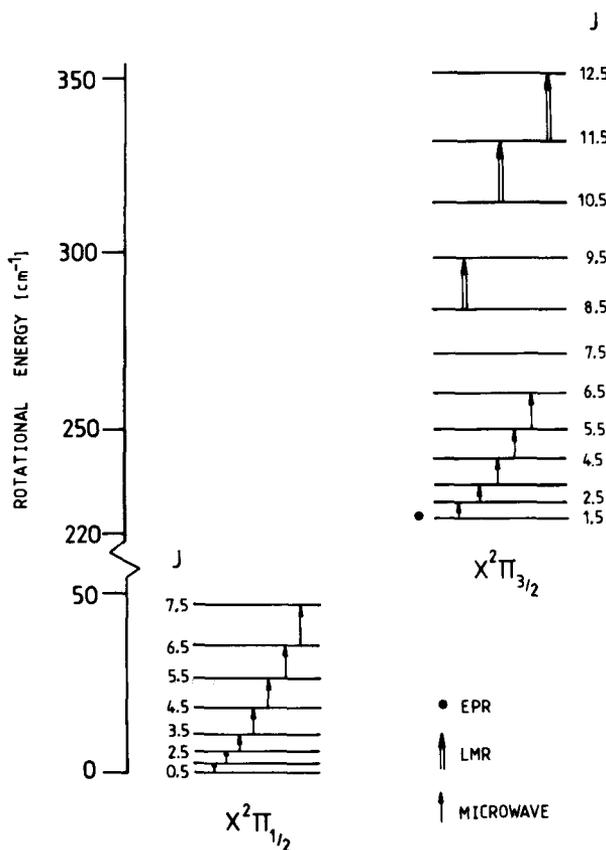


Figure 2. Summary of rotational transitions detected in $v = 0$ $^{14}\text{N}^{32}\text{S}$ ($X^2\Pi$).

Table 2. Vibrational coefficients ($Y^{(n)}$, MHz) of molecular parameters for NS ($X^2\Pi$) (3σ in the last digit(s) are given in brackets).

Parameter	$Y^{(0)}$	$Y^{(1)}$	$Y^{(2)}$	$Y^{(3)}$
B	23249.6573(120)	-188.3874(189)	-0.1671(84)	-0.01226(105)
D	0.037901(153)	0	0	0
A^\dagger	6696434	-5585	—	—
A_J	2.5654(69)	-0.14669(261)	0	0
p	396.56(54)	0.593(129)	-0.0748(256)	0
q	0.366(285)	0	0	0
a	62.356(181)	-0.228(243)	0	0
b_F	23.13(267)	0	0	0
t	-16.97(129)	0	0	0
d	86.837(138)	0.230(204)	0	0
eQq_1	-0.6752(282)	0	0	0
eQq_2	-5.84(228)	0	0	0

† A parameters derived from [4, 6].

Table 3. Parameters (MHz) for $v = 0$ and 1 NS ($X^2\Pi$) (3σ values in the last digit(s) are given in brackets. Spin orbit constant fixed at 223 cm^{-1} for both states [9]).

Parameter	$v = 0$	$v = 1$
B	23155.4226(108) †(23156.00(15))	22966.6514(153) ‡(22967.3(5))
D	0.03794(21) §(0.0387(99))	0.03777(28)
A_J	2.4944(84)	2.3395(93)
p	396.95(72) (397.409(76))	396.77(102) ‡(397.5(39))
q	0.30(39)	0.67(63)
$a + (b + c)/2$	56.872(246) (57.15(20))	56.62(78)
$a - (b + c)/2$	67.645(99) (67.60(12))	67.83(90)
b	39.8(57) (36.3(74))	39.9(87)
d	86.953(81) (86.972(90))	87.142(195)
eQq_1	-0.678(36)	-0.664(57)
eQq_2	-5.8(33)	-6.0(36)

† [4] result quoted by Matsumura *et al.* [6].

‡ [6].

§ D_e value, [6].

|| [5].

fitted in the form a , b_F , t , d where b_F is the Fermi contact term and $t = c/3$. The two quadrupole terms, required if lambda doubling is resolved, have been discussed by Hirota [11].

The parameters (Y) were expanded in Dunham-type series in $(v + 1/2)^n$ up to $n = 3$ (higher terms were found to be unnecessary)

$$Y_v = \sum_{n=0}^3 Y^{(n)}(v + 1/2)^n.$$

In several cases only the first or second coefficients could be determined, while for A values of $A^{(0)}$ and $A^{(1)}$ were derived from other data [4, 6]. A combined fit of all the data up to and including $v = 5$ (145 transitions) yielded the coefficients of the parameters given in table 2. These parameters were obtained after four iterations with a dimensionless reduced standard deviation of 0.686 and yielded the calculated frequencies for table 1. (Lines were weighted in the fits as the inverse square of the measurement precision as given in table 1). For comparison with infrared results on $v = 0$ and $v = 1$ the data for these levels were fitted independently, setting coefficients in $n > 0$ at zero; the results are given in table 3. While these data can be used to obtain equilibrium parameters the associated uncertainties are difficult to calculate accurately. On the other hand the coefficients in $n = 0$, table 2, yield Y_e directly.

4. DISCUSSION

As a test of the fitting program the $v = 0$ data of Lovas and Suenram [5] were fitted alone and also in combination with our results for the vibrational ground

state. Both approaches yielded a marginally better fit than reported in [5]. However, a direct comparison of fitted parameters is not straightforward with the different models used. It is nevertheless clear that an extensive analysis of a large data set is required for accurate predictions up to $J = 6.5$ and beyond [5]. A more direct comparison of parameters can be made with the diode laser results since essentially the same hamiltonian is used although B_0 is derived from early microwave data rather than from Lovas and Suenram. Nevertheless, the B_e value of Matsumura *et al.* [6], 23250.4(3) MHz is satisfactorily close to ours, 23249.657(12) MHz. Similarly, the value of α_e , 188.7(5) MHz, is in good agreement with $-B^{(1)}$, 188.387 MHz (ignoring higher terms in B). There is no detectable dependence of D on v and our result agrees with D_e from the diode laser work: 0.0387(100) MHz.

The present analysis of the lambda doubling parameters is more extensive than previously reported. Our value of p for $v = 0$ is in good agreement with other work and we detect a small vibrational dependence of p up to $(v + 1/2)^2$, although the quadratic coefficient has a large uncertainty (table 2). The much smaller q parameter is not well determined (and there is no vibrational dependence at this level of accuracy). Although analysis of results on the FIR L.M.R. spectra of NS, in which rotational levels up to $J = 12.5$ in the $^2\Pi_{3/2}$ state have been detected (figure 2) [12] and lambda doubling resolved, should yield an improved value for q the L.M.R. results are limited to $v = 0$ and are of lower accuracy than the present zero field measurements. Finally it can be seen in table 2 that within the 3σ limits none of the hyperfine parameters show a variation with v .

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