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# Millimeter-wave spectrum of NCS radical in the ground $^2\Pi$ state

Takayoshi Amano and Takako Amano

*Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada K1A 0R6*

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The rotational transitions of NCS have been observed in the 1 to 3 mm wavelength region in a hollow cathode discharge in a gas mixture of  $\text{CS}_2$  ( $\sim 1$  mTorr) and  $\text{N}_2$  ( $\sim 30$  mTorr). The molecular constants in the ground state are determined by fitting the observed frequencies to the standard Hamiltonian for  $^2\Pi$  states. The accuracy of the molecular constants are greatly improved compared with the values obtained from the optical data. The lines in the excited vibronic states have also been observed. The analysis including those excited state lines is in progress and the results will be published separately.

## I. INTRODUCTION

The emission and absorption spectra of NCS were observed in the 3750–4850 Å region for the first time by Holland and Style in radio-frequency discharge of  $\text{C}_2\text{H}_5\text{NCS}$  and by UV photolysis of the same compound.<sup>1</sup> Dixon and Ramsay<sup>2</sup> presented a detailed rotational analysis of the more extensive spectrum recorded using flash photolysis of  $\text{C}_2\text{H}_5\text{NCS}$  in 1968. Carrington *et al.* observed the electron paramagnetic resonance spectrum of NCS obtained using the hydrogen abstraction reaction of HNCS by F atoms which were generated by microwave discharge in  $\text{CF}_4$ .<sup>3</sup> However, no analysis was carried out.

The NCS radical is isovalent with NCO which is one of the 15 valence electron molecules such as  $\text{BO}_2$ ,  $\text{CO}_2^+$ , and  $\text{N}_2\text{O}^+$ . All of these molecules have  $^2\Pi$  ground states and exhibit a conspicuous Renner-Teller effect.<sup>4</sup> As Dixon and Ramsay's analysis<sup>2</sup> revealed, the Renner-Teller effect is more prominent in NCS due, in part, to the fact that the spin-orbit splitting is comparable to the bending vibrational frequency, which contributes to the very complicated vibronic structure. The observation and analysis of the rotational spectra in these vibronic states will shed light on the details of the Renner-Teller interaction which could not be sorted out solely through the analyses of the electronic spectra.

NCS is probably an important reaction intermediate of various chemical reaction systems such as discharge plasmas and combustion of sulfur containing molecules. It may also be formed in interstellar molecular clouds. Although NCO has not been detected in interstellar space, similar sulfur containing molecules, CCS (Ref. 5) and OCS (Ref. 6), have been found. In particular, CCS is abundant in various molecular clouds, notably in dense molecular clouds.<sup>5</sup> In view of this recent astronomical discovery, it is important to observe the rotational lines of this radical to assist in radio astronomical searches.

Since the analysis by Dixon and Ramsay, however, only a few spectroscopic studies have appeared. Laser induced fluorescence of NCS was observed after the photolysis of  $\text{CH}_3\text{NCS}$  by a 193 nm ArF excimer laser, but the spectrum was recorded primarily for kinetic investigation with low resolution.<sup>7</sup> Tokue and co-workers obtained the low-resolution emission spectrum in the UV region by vacuum ultraviolet photoexcitation<sup>8</sup> and by electron impact excitation.<sup>9</sup> Recently, Northrup and Sears<sup>10,11</sup> observed laser induced

fluorescence signals of NCS in a free jet expansion. They partly reanalyzed the spectra obtained by Dixon and Ramsay<sup>2</sup> together with their own new results and obtained "improved" rotational and vibrational constants.

In this work, the rotational spectrum of NCS has been observed mainly in the 1 to 3 mm wavelength region. The rotational transitions in the ground vibronic state as well as several excited vibronic states have been assigned and analyzed. In this paper, we report the transition frequencies and the spectroscopic parameters in the ground vibronic state. A more detailed analysis including the ground and the excited vibronic states is in progress and the results will be reported in a separate paper.

## II. EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the microwave spectrometer. Klystrons and a Gunn diode are used as radiation sources. The Gunn diode delivers output power of about 30 mW from 80 to 110 GHz and is usable down to 75 GHz with less power. It is powerful enough to drive multipliers, a doubler, and a tripler (Millitech). The doubler covers the frequency range from 140 to 180 GHz, while the tripler delivers the power in the range from 230 to 290 GHz. The tripler was found to provide quite adequate fourth harmonic power. A dichroic filter was utilized to cutoff the third harmonic power when necessary.

The Gunn oscillator or klystrons are phase locked to harmonics of microwave (12.5–18 GHz) generated by a *P*-band backward-wave oscillator (BWO) which in turn is phase-locked to the harmonics of UHF (500–1300 MHz) provided by a frequency synthesizer. The synthesizer frequency is stepped under computer control so that the Gunn or klystron frequency is scanned, usually, with 20 to 40 kHz steps. All the frequency measurements, including intermediate frequencies (IF), were referred to the internal oscillator (10 MHz) of the synthesizer, which was calibrated against the NRC frequency standard. The transmitted microwave is received by an InSb hot electron detector (QMC Instruments) operated at liquid-He temperature (4.2 K).

A commercial phase-lock unit for the Gunn diode was modified to allow the oscillation frequency to be modulated. We employed tone-burst modulation.<sup>12</sup> The tone frequency was set in most cases at about 500 kHz, which was switched at 40 kHz. The modulation depth was monitored by a spec-



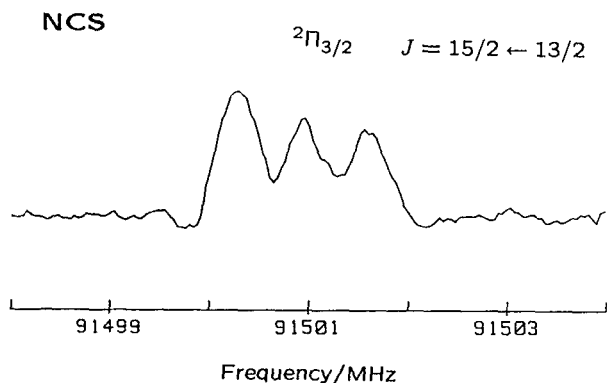


FIG. 3. The hyperfine structures of the  $J = \frac{15}{2} \leftarrow \frac{13}{2}$  transition of NCS in the  $^2\Pi_{3/2}$  state.

effect of every line we observed. A solenoid coil was wound around an aluminum casing which accommodates the hollow-cathode cell. Control of the magnetic field strength was incorporated as a part of the software which controls the instrument and acquires and processes the data. The maximum magnetic field was 70 G which was limited by the power supply. Figure 2(a) shows an example of the lines of NCS in the ground  $^2\Pi_{3/2}$  state. It exhibits a partially resolved  $\Lambda$ -type doubling. Figure 2(b) demonstrates the Zeeman effect of this line. Although the individual  $M$  components are not resolved, the Zeeman shift is as expected for  $J = \frac{41}{2} \leftarrow \frac{39}{2}$  in the  $^2\Pi_{3/2}$  state.<sup>14</sup> Further evidence of the identification of the species was provided by the hyperfine structure resolved for the relatively low- $J$  transitions. Figure 3 is the  $J = \frac{15}{2} \leftarrow \frac{13}{2}$  transition which shows the three hyperfine components of  $\Delta F = \Delta J = 1$ .

Generally, free radicals are very susceptible to metal surfaces. Therefore "free space cells" have been widely used for observations of microwave lines of free radicals. A hollow-cathode discharge cell which in a way is similar to a waveguide cell may not be an ideal cell for free radical detection. Although we have obtained good signals of NCS with a hollow-cathode cell, it was expected at one stage of the experiment that it might be possible to get better signals by using a combination of a free space cell and a glow discharge. We tried glow discharges in a mixture of  $N_2$  and  $CS_2$ ,  $N_2$  and OCS, similar to those used in a hollow cathode discharge, or  $CH_3NCS$  and Ar. All these three discharges yielded much weaker signals. Among these, the discharge in  $CH_3NCS$  provided the best signals, but the parent molecules exhibits an extremely rich spectrum, so the identification of weaker NCS line seemed to be severely hampered. The anode glow of the normal glow discharge emitted pinkish color and the cathode glow was blue emission which is an indication of formation of NCS. In the hollow-cathode discharge plasmas, the blue emission fills the entire cathode volume, which is essential for a strong signal of NCS. Presumably, NCS is predominantly formed in the cathode glow. Therefore, although the metal surface of the cathode may be a disadvantage, the hollow cathode still produces the best signals.

### III. ANALYSIS AND RESULTS

As already stated, in spite of using nonpolar starting molecules, the observed line density was surprisingly high. After extensive scan over several tens of GHz, we noticed several strong doublets which showed characteristic Zeeman effect as shown in Fig. 2. It was concluded that this species contains one nitrogen atom by using a one-to-one mixture of  $^{14}N_2$  and  $^{15}N_2$ . The disappearance of the signal upon substituting normal  $CS_2$  with  $^{13}CS_2$  (95%  $^{13}C$ ) led to a conclusion that this species contains a carbon atom or atoms. In the mean time, it was found that the spacing of the series of lines is about 12.2 GHz, which suggested that the species detected is NCS. Indeed, the series of lines was assigned as the transitions in the ground vibronic state  $^2\Pi_{3/2}$ , and the small splittings (as shown in Fig. 2) are due to the  $\Lambda$  doubling. The assignment of the  $^2\Pi_{1/2}$  lines was more difficult, because of the very small Zeeman effect. However, consideration of the  $\Lambda$ -doubling splittings and the relative intensities eventually led us to the correct assignment.

Table I lists the observed transition frequencies of NCS in the ground vibronic state. The accuracy of the measured frequencies are  $\pm (20\text{--}50)$  kHz except for partially overlapped lines. These line frequencies were fit to the standard Hamiltonian for  $^2\Pi$  states of linear molecules.<sup>15,16</sup> The explicit expression of the matrix elements are given by

$$\begin{aligned} \langle ^2\Pi_{3/2} | H_{\text{eff}} | ^2\Pi_{3/2} \rangle &= (1/2)A - D + (B - D + A_D)(x^2 - 2) \\ &\quad - D(x^2 - 2)^2, \\ \langle ^2\Pi_{1/2} | H_{\text{eff}} | ^2\Pi_{1/2} \rangle &= -(1/2)A + D + (B - D - A_D)x^2 - Dx^4 \\ &\quad \pm (1/2)(\tilde{p} + 2\tilde{p}_D x^2)x, \\ \langle ^2\Pi_{3/2} | H_{\text{eff}} | ^2\Pi_{1/2} \rangle &= [B - (1/2)\gamma - 2D(x^2 - 1)](x^2 - 1)^{1/2} \\ &\quad \pm (1/2)qx(x^2 - 1)^{1/2}, \end{aligned}$$

where  $x$  denotes  $J + \frac{1}{2}$  and the plus sign applies to  $f$  levels and the minus sign to  $e$  levels. The standard magnetic and electric quadrupole hyperfine interaction Hamiltonian was used,<sup>17,18</sup> and the matrix was set up to include the matrix elements of  $|\Delta J|$  up to 2, although only the diagonal terms were found to be significant.

In the fit, the spin-orbit coupling constant  $A$  was fixed at the value obtained from a recent reanalysis by Northrup and Sears.<sup>10,11</sup> It is different from that obtained by Dixon and Ramsay,<sup>2</sup> but the final molecular constants were not affected by this small difference in  $A$ . Table II lists the molecular constants thus determined. The  $\Lambda$  doubling was not resolved previously in the electronic spectra.<sup>2,10,11</sup> This is the first determination of the  $\Lambda$ -doubling constants,  $\tilde{p}$  and  $q$ , for this molecule. Note that the signs of the  $\Lambda$ -doubling constants were assumed as listed in Table II. The effective spin-rotation coupling constant  $\gamma_{\text{eff}}$  was determined by assuming  $A_D = 0$ . In most cases, the spin-rotation coupling constant is of the same order of magnitude as the  $\Lambda$ -type doubling constant  $\tilde{p}$ . As  $|A|/B \sim 1570$ , the assumption  $A_D = 0$  is likely to have resulted in  $\gamma_{\text{eff}}$  which is quite different from the true  $\gamma$ .

TABLE I. Transition frequencies of NCS in the ground  $^2\Pi$  state (in MHz). All the transitions are  $\Delta J = \Delta F = 1$ , and only the quantum numbers of the lower states are indicated.

$J''$	$F''$	$^2\Pi_{3/2}$		$^2\Pi_{1/2}$	
		Obs.	$\Delta^a$	Obs.	$\Delta^a$
5.5	6.5	79 300.536	53		
	5.5	79 301.481	11		
	4.5	79 302.304	21		
6.5	7.5	91 500.074	-42		
	6.5	91 500.837	9		
	5.5	91 501.413	-13		
7.5	8.5	103 699.350	-25		
	7.5	103 699.873	-34		
	6.5	103 700.327	-35		
8.5	9.5	115 898.196	-42		
	8.5	115 898.800	153		
	7.5	115 898.800	-201		
10.5		140 294.909	44		
11.5		152 492.326	19	<i>e</i> 152 672.512	-32
				<i>f</i> 152 949.827	39
12.5		164 689.161	-60	<i>e</i> 164 895.094	9
				<i>f</i> 165 172.057	19
13.5		176 885.577	12	<i>e</i> 177 117.056	-4
				<i>f</i> 177 393.683	-17
14.5		189 081.329	32		
15.5		201 276.268	-106		
16.5		213 470.738	-16		
18.5	<i>e</i>	237 856.813	-10	<i>e</i> 238 216.954	-9
	<i>f</i>	237 857.693	8	<i>f</i> 238 491.679	-22
19.5	<i>e</i>	250 048.818	3	<i>e</i> 250 434.682	32
	<i>f</i>	250 049.767	-1	<i>f</i> 250 708.947	7
20.5	<i>e</i>	262 239.950	12	<i>e</i> 262 651.490	18
	<i>f</i>	262 240.968	-18	<i>f</i> 262 925.280	-12
21.5	<i>e</i>	274 430.151	0	<i>e</i> 274 867.402	14
	<i>f</i>	274 431.292	-6	<i>f</i> 275 140.695	-21
22.5	<i>e</i>	286 619.447	36	<i>e</i> 287 082.358	4
	<i>f</i>	286 620.637	-25	<i>f</i> 287 355.177	9
24.5	<i>e</i>	310 994.894	-12	<i>e</i>	
	<i>f</i>	310 996.374	-4	<i>f</i>	
25.5	<i>e</i>	323 181.000	-56	<i>e</i> 323 721.133	6
	<i>f</i>	323 182.573	-71	<i>f</i> 323 992.256	-8
26.5	<i>e</i>	335 366.128	43	<i>e</i> 335 931.899	32
	<i>f</i>	335 367.836	41	<i>f</i> 336 202.396	-5
27.5	<i>e</i>	347 549.957	8	<i>e</i> 348 141.412	-32
	<i>f</i>	347 551.772	-13	<i>f</i> 348 411.343	-9
28.5	<i>e</i>	359 732.641	32	<i>e</i> 360 349.815	0
	<i>f</i>	359 734.584	9	<i>f</i> 360 619.112	37
29.5	<i>e</i>	371 914.024	5	<i>e</i> 372 556.932	-6
	<i>f</i>	371 916.114	-6	<i>f</i> 372 825.527	-2
30.5	<i>e</i>	384 094.098	-42	<i>e</i> 384 762.743	-26
	<i>f</i>	384 096.437	57	<i>f</i> 385 030.659	-8

<sup>a</sup>(Obs.-calc.)  $\times 10^3$ .TABLE II. Molecular constants of NCS in the ground  $^2\Pi$  state (in MHz).

$A$	-9 820 900 <sup>a</sup>
$A_D$	0.0 <sup>a</sup>
$B$	6106.621 62(25) <sup>b</sup>
$D$	0.001 769 51(17)
$\gamma_{\text{ex}}$	-3632.56(11)
$\bar{p}$	278.994(31)
$q$	-0.358 18(37)
$\bar{p}_D$	-0.001 487 4(87)
$a + (b + c)/2$	26.06(23)
$eqQ$	-3.26(83)

<sup>a</sup>Fixed, see text.<sup>b</sup>The values in parentheses denote one standard error in units of the last quoted digit in the parameter.

The nuclear hyperfine structure due to the  $^{14}\text{N}$  nucleus is resolved for the four lowest rotational transitions in the  $^2\Pi_{3/2}$  state observed in this work. An extensive effort was made to observe the hyperfine structure for  $J = \frac{1}{2} \leftarrow \frac{1}{2}$  and  $J = \frac{3}{2} \leftarrow \frac{1}{2}$  transitions in the  $^2\Pi_{1/2}$  state, but the signals were too weak to warrant reliable measurements. As a result, only two parameters,  $a + (b + c)/2$  and  $eqQ$ , have been determined.

#### IV. DISCUSSION

The rotational constant obtained in this work agrees with that obtained by Dixon and Ramsay<sup>2</sup> within their experimental uncertainty. Northrup and Sears<sup>10,11</sup> revised the rotational constant by reanalyzing the data of Ref. 2 and

TABLE III. Comparison of the rotational constants in the ground  $^2\Pi$  state (in MHz).

Reference	$B$	$D$
Dixon and Ramsay	6104(3)	0.001 86(30)*
Northrup and Sears	6113(3)	
This work	6106.621 62(25)	0.001 769 51(17)

\*From  $^2\Pi_{3/2} - ^2\Pi_{1/2}$  subband.

their new data. Their rotational constant, however, is significantly different from our value, and the accuracy attained in this work is greatly improved as shown in Table III. Other parameters listed in Table II are determined for the first time in this work. Other important molecular constants which are poorly determined or not determined at all are some hyperfine coupling constants and the electric dipole moment (not mentioning various parameters concerning the excited vibronic states). For a more complete determination of the hyperfine constants, observation of low- $J$  transitions is needed. This will not be accomplished very easily, unless an ingenious way to produce more NCS is devised. In addition, the signal is not strong enough to warrant precise Stark effect measurements. Since the dipole moment is very important for the estimation of the radio emission intensity of interstellar NCS, high-level *ab initio* calculations would be very desirable. *Ab initio* calculations of any sort for this radical are surprisingly sparse. To our knowledge only a few have appeared in the last ten years.<sup>19,9</sup>

As the  $^2\Pi_{1/2}$  state is located rather close to the  $\mu^2\Sigma_{1/2}$  state, there is a possibility of interaction between these two states. The analysis was carried out with no interaction explicitly taken into account. The centrifugal distortion term of one of the  $\Lambda$ -type doubling constant  $\tilde{p}_D$  was found to be  $-1.49$  kHz which is much larger in magnitude than expected from the ratio of the centrifugal distortion constant  $D$  to the rotational constant  $B$ . This  $\tilde{p}_D$  value is probably an indication of interaction between the  $^2\Pi_{1/2}$  and  $\mu^2\Sigma_{1/2}$  states. Recently, such perturbation was found in the spectrum of  $C_3H$  and was analyzed by taking the interaction terms explicitly into the Hamiltonian.<sup>20</sup>

The ground electron configuration is  $\cdots(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^3$ . Dixon and Ramsay<sup>2</sup> considered that the  $3\pi$  orbital has a large contribution from the  $3p$  orbital of the S atom because the spin-orbit coupling constant  $A$  is rather similar to that of free S atom. Tokue *et al.* carried out an *ab initio* calculation at the SCF-CISD level and found

that the  $3\pi$  orbital is nonbonding and essentially localized on the S atom with a node near the C atom.<sup>9</sup> The magnetic hyperfine coupling constant,  $a + (b + c)/2$ , obtained in the present work also supports this argument. It is much smaller compared with those for NO,<sup>21,22</sup> NS,<sup>23</sup> or NCO,<sup>24</sup> indicating that the density of the unpaired electrons around the N nucleus in NCS is much less.

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