

MICROWAVE SPECTRUM OF THE NS RADICAL IN THE ${}^2\Pi$, GROUND ELECTRONIC STATE

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ABSTRACT

The microwave spectrum of the NS radical in the ground electronic state has been remeasured in the frequency region of 69 to 350 GHz for the astronomical use. Measurement errors for most of the observed lines were less than 20 kHz so that the observed laboratory frequencies are readily usable for the rest frequencies of NS for astronomical use. The molecular constants including the rotational constant and its centrifugal distortion constant, the Δ -type doubling constants, and the hyperfine coupling constants of the nitrogen nucleus have been determined more precisely, when compared with those reported previously.

Subject headings: ISM: molecules — line: identification — molecular data

1. INTRODUCTION

The NS radical is one of fundamental molecules related to interstellar nitrogen chemistry (Herbst & Leung 1989) and sulfur chemistry (Herbst, DeFrees, & Koch 1989). It was first identified in Sgr B2 (Gottlieb et al. 1975), and is studied mainly in regions of massive star-forming region (McGonagle, Irvine, & Minh 1992). Recently NS has been detected even in cold dark clouds (McGonagle, Irvine, & Ohishi 1994).

The microwave spectrum of the gaseous NS radical was first studied by Amano and his collaborators (Amano et al. 1969) observing the rotational transitions of $N^{32}S$ and $N^{34}S$ in the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ spin sublevels up to 115 GHz. Lovas & Suenram (1982) remeasured most of the lines of NS up to 162 GHz, and redetermined the molecular constants of two main isotopic species of NS. The two earlier studies used the parallel-plate absorption cell with Stark modulation and their frequency measurement errors ranged from 50 to 200 kHz. Anaconda et al. (1986) measured the spectral lines of NS in the vibrational states of $v = 0$ to 5 up to 350 GHz by using a free space cell combined with radio frequency excitation for production. Their measurement errors extend from 50 to 300 kHz. They revised the molecular constants for the ground state and also determined those for the $v = 1$ state. Amano & Amano (1990) extended the millimeter- and submillimeter-wave measurements of NS in highly vibrationally excited states.

Very recently McGonagle and his collaborators (McGonagle et al. 1994) detected the spectral lines of NS in cold dark clouds and reported that the LSR velocities of the $J = \frac{3}{2} - \frac{1}{2}$ parity- f transitions appear slightly low, ~ 100 kHz in frequency, relative to values observed for many molecular lines at L134N and TMC 1, while the corresponding LSR velocities of the $J = \frac{3}{2} - \frac{1}{2}$ parity- e transitions are systematically higher, ~ 200 KHz, toward both positions. We thought that these discrepancies were mainly due to the frequency errors of the laboratory measurements.

In the present study we have remeasured the transition frequencies of the NS radical in the ground electronic state with

higher precision, mainly for astronomical use, and analyzed them to redetermine the molecular constants of NS.

2. EXPERIMENTAL

The observation of the microwave spectra of the NS radical has been carried out using the experimental setup similar to those previously described (Saito & Goto 1993; Lee, Ozeki, & Saito 1994). The millimeter- and submillimeter-wave spectrometer was a 100 kHz source modulation type. Microwave radiation was obtained by a combination of commercial multipliers with several millimeter wave klystrons. The InSb detector operated at the liquid helium temperature was used to measure radiation from the power sources through the cell. The absorption cell 2 m in length and 10 cm in outer diameter, was cooled at about -150 C. The NS radical was generated by hollow-cathode discharge in the gas mixture of either S_2Cl_2 and N_2 or H_2S and N_2 .

The optimum condition for the production of NS was obtained by adjusting the ratio of the gas mixture and the current and by varying the temperature of the cell. The gas mixture of S_2Cl_2 and N_2 has been employed for observation of high J transitions, while the gas mixture of H_2S and N_2 was used for low J transitions. The optimum intensity was obtained at the conditions of S_2Cl_2 of 35 mTorr and N_2 of 10 mTorr, and the current of 300 mA for the observation of high J transitions, and at the conditions of H_2S of 20 mTorr and N_2 of 20 mTorr, and the current of 380 mA for the observation of low J transitions.

Since the present production method gave many spectral lines due to the parent molecules and byproduct molecules over the whole frequency region, we have carefully identified the spectral lines of the NS radical by not only applying a magnetic field but also by switching the discharge current on and off. However, it was difficult to measure precisely several weak but important components of low J transitions. We observed 89 spectral lines of NS in the frequency region of 69 to 350 GHz. The frequency measurement was made by averaging a pair of successive upward and downward scans. The frequency of each line was given as an average of five frequency measurements. The frequencies observed and their one standard frequency measurement errors are listed in Table 1.

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TABLE 1
OBSERVED TRANSITION FREQUENCIES OF $^{14}\text{N}^{32}\text{S}(\chi^2\Pi_r)$ (MHz)

Parity	J'	J''	F'	F''	Observed frequency	(Observed – Calculated)	Weight
$^2\Pi_{1/2}$ State							
<i>e</i>	1.5	0.5	2.5	1.5	69002.890(3) ^a	0.011	1.0
<i>e</i>	1.5	0.5	1.5	0.5	69017.895(3)	-0.150	0.0 ^b
<i>e</i>	1.5	0.5	1.5	1.5	69037.336(10)	-0.139	0.0 ^b
<i>e</i>	1.5	0.5	0.5	0.5	69040.324(1)	0.003	1.0
<i>e</i>	1.5	0.5	0.5	1.5	69059.844(18)	0.093	0.0 ^c
<i>f</i>	1.5	0.5	2.5	1.5	69411.943(2)	0.006	1.0
<i>f</i>	1.5	0.5	1.5	0.5	69485.223(3)	-0.006	1.0
<i>f</i>	1.5	0.5	1.5	1.5	69330.592(3)	0.005	1.0
<i>f</i>	1.5	0.5	0.5	0.5	69437.850(5)	0.021	1.0
<i>f</i>	1.5	0.5	0.5	1.5	69283.195(4)	0.008	1.0
<i>e</i>	2.5	1.5	3.5	2.5	115153.935(6)	0.008	1.0
<i>e</i>	2.5	1.5	2.5	1.5	115156.812(4)	-0.037	1.0
<i>e</i>	2.5	1.5	1.5	0.5	115162.982(6)	-0.008	1.0
<i>e</i>	2.5	1.5	2.5	2.5	115191.288(4)	-0.157	0.0 ^b
<i>e</i>	2.5	1.5	1.5	1.5	115185.411(2)	0.145	0.0 ^b
<i>f</i>	2.5	1.5	1.5	2.5	115556.253(3)	-0.021	1.0
<i>f</i>	2.5	1.5	2.5	1.5	115570.763(5)	-0.005	1.0
<i>f</i>	2.5	1.5	1.5	0.5	115571.954(3)	-0.038	1.0
<i>f</i>	2.5	1.5	2.5	2.5	115489.412(2)	-0.007	1.0
<i>f</i>	2.5	1.5	1.5	1.5	115524.603(7)	0.011	1.0
<i>e</i>	3.5	2.5	4.5	3.5	161297.246(6)	-0.012	1.0
<i>e</i>	3.5	2.5	3.5	2.5	161298.411(5)	-0.024	1.0
<i>e</i>	3.5	2.5	2.5	1.5	161301.747(5)	-0.035	1.0
<i>e</i>	3.5	2.5	3.5	3.5	161335.806(5)	-0.148	0.0 ^d
<i>e</i>	3.5	2.5	2.5	2.5	161330.122(5)	-0.077	0.0 ^d
<i>f</i>	3.5	2.5	4.5	3.5	161697.257(5)	0.004	1.0
<i>f</i>	3.5	2.5	3.5	2.5	161703.404(7)	0.015	1.0
<i>f</i>	3.5	2.5	2.5	1.5	161703.987(5)	-0.017	1.0
<i>f</i>	3.5	2.5	3.5	3.5	161636.517(6)	-0.017	1.0
<i>f</i>	3.5	2.5	2.5	2.5	161657.816(5)	-0.012	1.0
<i>e</i>	4.5	3.5	5.5	4.5	207436.246(4)	0.184	0.0 ^e
<i>e</i>	4.5	3.5	4.5	3.5	207436.246(4)	-0.410	0.0 ^e
<i>e</i>	4.5	3.5	3.5	2.5	207438.692(5)	-0.042	1.0
<i>e</i>	4.5	3.5	4.5	4.5	207475.276(7)	-0.076	0.0 ^d
<i>e</i>	4.5	3.5	3.5	3.5	207470.652(8)	0.153	0.0 ^d
<i>f</i>	4.5	3.5	5.5	4.5	207834.866(4)	0.009	1.0
<i>f</i>	4.5	3.5	4.5	3.5	207838.365(6)	0.004	1.0
<i>f</i>	4.5	3.5	3.5	2.5	207838.365(6)	0.004	1.0
<i>f</i>	4.5	3.5	4.5	4.5	207777.535(3)	0.046	1.0
<i>f</i>	4.5	3.5	3.5	3.5	207792.951(9)	-0.042	1.0
<i>e</i>	5.5	4.5	6.5	5.5	253570.476(8)	0.070	0.0 ^e
<i>e</i>	5.5	4.5	5.5	4.5	253570.476(8)	-0.259	0.0 ^e
<i>e</i>	5.5	4.5	4.5	3.5	253572.148(7)	0.018	1.0
<i>e</i>	5.5	4.5	5.5	5.5	253610.002(3)	-0.023	0.0 ^d
<i>e</i>	5.5	4.5	4.5	4.5	253606.068(6)	0.096	0.0 ^d
<i>f</i>	5.5	4.5	6.5	5.5	253968.393(4)	-0.021	1.0
<i>f</i>	5.5	4.5	5.5	4.5	253970.581(3)	-0.011	1.0 ^e
<i>f</i>	5.5	4.5	4.5	3.5	253970.581(3)	-0.011	1.0 ^e
<i>f</i>	5.5	4.5	5.5	5.5	253913.173(5)	0.040	1.0
<i>f</i>	5.5	4.5	4.5	4.5	253925.462(10)	-0.024	1.0
<i>e</i>	6.5	5.5	7.5	6.5	299699.781(8)	0.045	0.0 ^e
<i>e</i>	6.5	5.5	6.5	5.5	299699.781(8)	-0.141	0.0 ^e
<i>e</i>	6.5	5.5	5.5	4.5	299700.901(10)	-0.005	1.0
<i>e</i>	6.5	5.5	6.5	6.5	299739.525(13)	-0.016	1.0
<i>e</i>	6.5	5.5	5.5	5.5	299736.150(14)	0.008	1.0
<i>f</i>	6.5	5.5	7.5	6.5	300097.098(9)	-0.026	1.0
<i>f</i>	6.5	5.5	6.5	5.5	300098.611(14)	0.028	1.0 ^e
<i>f</i>	6.5	5.5	5.5	4.5	300098.611(14)	0.028	1.0 ^e
<i>f</i>	6.5	5.5	6.5	6.5	300043.582(15)	0.334	0.0 ^d
<i>f</i>	6.5	5.5	5.5	5.5	300053.514(13)	-0.117	0.0 ^d
<i>e</i>	7.5	6.5	8.5	7.5	345823.288(6)	-0.024	0.0 ^e
<i>e</i>	7.5	6.5	7.5	6.5	345823.288(6)	-0.124	0.0 ^e
<i>e</i>	7.5	6.5	6.5	5.5	345824.130(7)	0.000	1.0

TABLE 1—Continued

Parity	J'	J''	F'	F''	Observed frequency	(Observed – Calculated)	Weight
$^2\Pi_{1/2}$ State							
<i>e</i>	7.5	6.5	7.5	7.5	345862.905(6)	–0.313	0.0 ^d
<i>e</i>	7.5	6.5	6.5	6.5	345860.520(8)	0.170	0.0 ^d
<i>f</i>	7.5	6.5	8.5	7.5	346220.137(6)	–0.008	1.0
<i>f</i>	7.5	6.5	7.5	6.5	346221.163(7)	–0.009	1.0 ^e
<i>f</i>	7.5	6.5	6.5	5.5	346221.163(7)	–0.009	1.0 ^e
<i>f</i>	7.5	6.5	7.5	7.5	346167.280(3)	0.013	1.0
<i>f</i>	7.5	6.5	6.5	6.5	346176.298(16)	–0.008	1.0
$^2\Pi_{3/2}$ State							
<i>e,f</i>	2.5	1.5	3.5	2.5	116181.098(14)	–0.007	1.0
<i>e,f</i>	2.5	1.5	2.5	1.5	116203.412(14)	–0.057	1.0
<i>e,f</i>	2.5	1.5	1.5	0.5	116214.820(3)	–0.056	1.0
<i>e,f</i>	3.5	2.5	4.5	3.5	162658.520(6)	0.036	1.0
<i>e,f</i>	3.5	2.5	3.5	2.5	162668.186(8)	–0.007	1.0
<i>e,f</i>	3.5	2.5	2.5	1.5	162674.196(1)	0.026	1.0
<i>e,f</i>	3.5	2.5	3.5	3.5	162633.923(9)	0.007	0.0 ^c
<i>e,f</i>	3.5	2.5	2.5	2.5	162650.100(20)	0.013	1.0
<i>e,f</i>	4.5	3.5	5.5	4.5	209130.298(6)	0.069	1.0
<i>e,f</i>	4.5	3.5	4.5	3.5	209135.713(6)	0.012	1.0
<i>e,f</i>	4.5	3.5	3.5	2.5	209139.484(4)	0.017	1.0
<i>e,f</i>	4.5	3.5	4.5	4.5	209111.199(8)	0.067	0.0 ^d
<i>e,f</i>	4.5	3.5	3.5	3.5	290121.533(9)	0.172	0.0 ^d
<i>e,f</i>	5.5	4.5	6.5	5.5	255596.896(6)	0.062	1.0
<i>e,f</i>	5.5	4.5	5.5	4.5	255600.379(3)	0.005	1.0
<i>e,f</i>	5.5	4.5	4.5	3.5	255602.964(3)	–0.028	1.0
<i>e,f</i>	5.5	4.5	5.5	5.5	255581.379(7)	0.102	0.0 ^d
<i>e,f</i>	5.5	4.5	4.5	4.5	255588.521(5)	–0.131	0.0 ^d
<i>e,f</i>	6.5	5.5	7.5	6.5	302057.835(7)	–0.005	1.0
<i>e,f</i>	6.5	5.5	6.5	5.5	302060.348(9)	0.012	1.0
<i>e,f</i>	6.5	5.5	5.5	4.5	302062.296(7)	0.018	1.0
<i>e,f</i>	6.5	5.5	6.5	6.5	302044.562(20)	–0.217	0.0 ^d
<i>e,f</i>	6.5	5.5	5.5	5.5	302050.565(10)	0.008	1.0
<i>e,f</i>	7.5	6.5	8.5	7.5	348512.506(5)	0.003	1.0
<i>e,f</i>	7.5	6.5	7.5	6.5	348514.362(1)	–0.009	1.0
<i>e,f</i>	7.5	6.5	6.5	5.5	348515.889(4)	0.008	1.0
<i>e,f</i>	7.5	6.5	7.5	7.5	348501.323(2)	0.013	1.0

^a Values in parentheses denote 16 of the frequency measurement and apply to the last digits of the frequencies.

^b Not included in the fit.

^c Not accurately measured due to the bad S/N ratio of the peak.

^d Overlap with nearby line(s) of other species.

^e Overlap of two NS spectral lines.

3. RESULT AND DISCUSSION

A conventional Hamiltonian employed for the analysis of the observed spectral lines is similar to that used previously (Brown et al. 1978; Frosch & Foley 1952). The computer program for the $^2\Pi$ electronic state including the nuclear spin rotation interaction (Saito et al. 1983) was used to analyze the observed spectral lines by the least-squares method.

Of the spectral lines observed, each of the 27 lines which belongs to the $^2\Pi_{3/2}$ state is composed of two nonresolved transition lines with different parity (*e* and *f*) due to the small Λ -type doubling; eight lines are partially overlapped by lines of NS in the $^2\Pi_{1/2}$ state, 15 lines are disturbed by lines arising from the diamagnetic parent molecule or reaction byproducts, and two lines were not precisely measured because of their poor signal-to-noise ratios. For the determination of the molecular constants, the frequencies of the spectral lines which are

TABLE 2
MOLECULAR CONSTANTS OF THE $^{14}\text{N}^{32}\text{S}(^2\Pi)$ RADICAL^a

Parameter	Present Study	Anaconda et al. ^b
B_0	23155.42145(158)	23155.4226(108)
D_0	0.0376587(191)	0.03794(21)
A_J	2.53394(74)	2.4944(84)
p	398.916(62)	396.95(72)
p_D	–0.00814(35)	...
q	–0.684(27)	0.30(39)
$a - (b + c)/2$	67.631(58)	67.645(99)
$a + (b + c)/2$	57.548(52)	56.87(25)
b	37.72(77)	39.8(57)
d	87.012(30)	86.953(81)
eQq_1	–2.515(30)	–0.678(36)
eQq_2	–3.30(151)	–5.8(33)

^a MHz (3 σ).

^b Anaconda et al. 1986.

TABLE 3
SPECTRAL LINE FREQUENCIES OF INTEREST TO ASTRONOMICAL USE

$J'-J''$	$F'-F''$	Parity	Present Study	Anaconda et al. ^b	Lovas & Suenram ^c
$\frac{3}{2}-\frac{1}{2}$	$\frac{3}{2}-\frac{3}{2}$	<i>e</i>	69002.890(3)	69002.990(50)	69002.99(10)
	$\frac{3}{2}-\frac{1}{2}$	<i>f</i>	69411.943(2)	69411.890(50)	69411.89(8)
$\frac{5}{2}-\frac{3}{2}$	$\frac{5}{2}-\frac{5}{2}$	<i>e</i>	115153.935(6)	115153.835(80)	115153.835(80)
	$\frac{5}{2}-\frac{3}{2}$	<i>f</i>	115556.253(3)	115556.312(80)	115556.312(60)
	$\frac{5}{2}-\frac{1}{2}$	<i>e</i>	115156.812(4)	115156.799(80)	115156.799(80)
	$\frac{5}{2}-\frac{3}{2}$	<i>f</i>	115570.763(5)	115570.762(80)	115570.762(80)
	$\frac{5}{2}-\frac{1}{2}$	<i>e</i>	115162.982(6)	115162.955(80)	115162.955(80)
	$\frac{5}{2}-\frac{3}{2}$	<i>f</i>	115571.954(3)	115571.930(80)	115571.93(6)

^a Values in parentheses denote 1σ of the frequency measurement; in megahertz and apply to the last digits of the frequencies.

^b Anaconda et al. 1986.

^c Lovas & Suenram 1982.

free from disturbances and have good line shapes were included into the least-squares fit. For a nonresolved line, the calculated frequency was obtained by averaging the frequencies of the overlapping components which were weighted in proportion to their relative intensities. Thus, 64 spectral lines of NS were subjected to the least-squares analysis. In the fit, we constrained the spin-orbit coupling constant A_{eff} to the value previously given by high-resolution optical spectroscopy (Jenouvrier & Pascat 1973). The nuclear spin-rotation coupling terms of the nitrogen atom were included in an initial analysis, but their contribution to the transition frequencies was found to be smaller than the measurement errors. This is consistent with a prediction that C_1 and C_2 of NS are ~ 6 KHz or less, based on the observed values of NO (Saleck, Yamada, & Winnewisser 1991). The molecular constants determined are listed in Table 2 together with the most recent data for a comparison (Anaconda et al. 1986). The standard deviation of the fit is 23 kHz, which is of the same order of magnitude as the frequency measurement error, as shown in Table 1.

The molecular constants determined in this study agree well with those recently reported (Anaconda et al. 1986), but the precision is improved by 2–10 times. It must be noted that the quadrupole coupling constant determined in the present study, $eQq_1 = -2.5151$ MHz, is consistent with the values reported by the previous studies (Amano et al. 1969; Lovas & Suenram 1982; Uehara & Morino 1969). The present value seems to be more reasonable than that reported by Anaconda et al. (1986),

because several low J transitions were precisely measured in our study.

Finally, the frequencies of the most astronomical interest are compared in Table 3. The $J = \frac{3}{2}-\frac{1}{2}$, $F = 5/2-3/2$, parity-*f* transition of the $^2\Pi_{1/2}$ state shifts to higher frequency by 53 kHz from the previously measured value and the parity-*e* component of the same transition to lower frequency by 100 kHz (Anaconda et al. 1986). The change in the frequencies of these important low J transitions explains half of the scattered LSR velocities derived from the observed frequencies of the interstellar NS in the cold dark clouds (McGonagle, Irvine, & Ohishi 1994). The VLSR values derived by using the newly measured frequencies of the lowest two transitions given in Table 3 are now separated by ~ 0.6 kms $^{-1}$ of ~ 140 kHz for several positions of two dark clouds, TMC 1 and L134N (McGonagle & Irvine 1994).

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