

Infrared Diode Laser Spectroscopy of the NS Radical

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The $v = 1 \leftarrow 0$ vibration–rotation bands of the NS radical in the $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ electronic states were observed by using a tunable diode laser. From the least-squares analysis the band origins were determined to be 1204.2755(12) and 1204.0892(19) cm^{-1} , respectively, for $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$. The rotational and centrifugal distortion constants and the internuclear distance in the $X^2\Pi$ electronic state were obtained as follows: $B_e = 0.775549(10) \text{ cm}^{-1}$, $D_e = 0.00000129(33) \text{ cm}^{-1}$, and $r_e = 1.49403(4) \text{ \AA}$, with three standard deviations indicated in parentheses.

INTRODUCTION

Very few high-resolution infrared studies have been reported on unstable molecules. Because of inherent low intensities of light sources, the sensitivity of a high-resolution infrared spectrometer has been insufficient to detect free radicals and molecular ions of short life. These species have been studied in infrared regions mainly by using low-temperature matrix-isolation techniques. Recently laser magnetic resonance (LMR) spectroscopy was developed in both infrared and far-infrared regions; the use of an intracavity cell has permitted the detection of many short-lived species including molecular ions (*1*). One of the most serious disadvantages of this method is that light sources used are fixed in frequency and are available only in limited regions. Furthermore, many unstable molecules of interest often show Zeeman effects that are not large enough for LMR studies. Recent developments in laser techniques have, however, produced a few kinds of tunable light sources including diode lasers, which cover most of the infrared regions. Typical output of infrared diodes is of the order of 0.1 mW, and therefore use of these sources has considerably increased the sensitivity of high-resolution infrared spectrometers. Todd and Olson (*2*) and Yamada and Hirota (*3*) have independently observed vibration–rotation bands of an unstable molecule CS. Maki and his co-workers (*4*) have succeeded in detecting infrared spectra of SiO which are of astrophysical importance. In the present work we report the fundamental band of NS, as one of our systematic studies on unstable species using diode laser spectroscopy.

The ground electronic state of NS has been known to be $^2\Pi$, with $^2\Pi_{3/2}$ higher than $^2\Pi_{1/2}$ by 223.15 cm^{-1} . Jenouvrier and Pascat (*5*) observed five red-degraded

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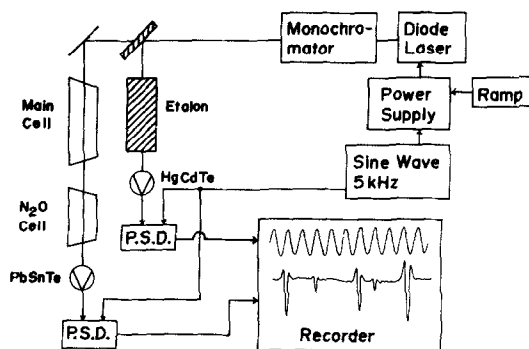


FIG. 1. Block diagram of the diode laser spectrometer.

transitions in the region of 2250–3800 Å, and obtained molecular constants in excited and ground electronic states. Chiu and Silvers (6) observed $C^2\Sigma^+ \rightarrow X^2\Pi_{1/2}$ fluorescence excited by a Ba II 2304-Å line. On the other hand, Carrington and his co-workers (7) and Uehara and Morino (8) detected NS by gas-phase EPR spectroscopy and determined molecular constants of the ground $^2\Pi_{3/2}$ vibronic state. Amano *et al.* (9) derived a more complete and precise set of ground-state constants by analyzing microwave spectra in both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. Recently Lovas (10) has remeasured microwave transitions and improved precisions of some molecular parameters. No vibrational spectra have, however, been reported on NS.

EXPERIMENTAL DETAILS

The NS radicals were produced by passing a mixture of nitrogen and sulfur monochloride through a microwave discharge, which was placed in a side arm attached to an absorption cell 60 cm in length. The optimum partial pressures are 190 and 20 mTorr, respectively, for N_2 and S_2Cl_2 . Under this condition white-blue chemiluminescence emitted from NS was found to be most intense. The spectrometer used is a Laser Analytics LS-3 equipped with a laser diode which covers a region from 1110 to 1368 cm^{-1} with many mode gaps. As shown in Fig. 1, the laser beam is divided into two; one beam passes through the absorption cell and a cell containing N_2O as a wavelength standard and the other passes through a germanium etalon 7.62 cm long as an interpolation device. Because no interference lines appeared in the region we searched, we used source modulation; a 5-kHz sine wave was superimposed on the dc current fed to the diode, and the absorption signal was demodulated by a phase-sensitive detector operated at 10 kHz. The ν_1 and $2\nu_2$ bands of N_2O , as recently calibrated by Olson *et al.* (11), were used as wavenumber references.

OBSERVED SPECTRA AND ANALYSIS

We searched for spectral lines of NS in the region of 1180 to 1240 cm^{-1} . Although continuous coverage was not possible in this region because of mode gaps, we observed 12 and 11 lines, respectively, for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, as listed in

TABLE I
The Fundamental Band of the NS Radical in the ${}^2\Pi_{1/2}$ State

Transition ^a		Obs. (cm ⁻¹)	Weight	(o-c) x 10 ⁴ (cm ⁻¹)	N ₂ O Line ^b
P(11.5)	e	1185.8326	1.0	7	2v ₂ R(19), R(20)
	f	85.8194	1.0	7	
P(9.5)	e	89.1550	1.0	-23	2v ₂ R(23), R(24)
	f	89.1422	1.0	-19	
P(8.5)	e	90.8030	1.0	14	2v ₂ R(24), R(25)
	f	90.7897	1.0	13	
P(6.5)	e	94.0529	1.0	-6	2v ₂ R(28), R(29)
	f	94.0403	1.0	0	
P(3.5)	e	98.8402	1.0	14	2v ₂ R(34), R(35)
	f	98.8270	1.0	14	
P(2.5)	e	1200.4108	1.0	16	2v ₂ R(35), R(36)
	f	00.3971	1.0	12	
P(1.5)	e	01.9661	1.0	-10	2v ₂ R(38), R(39)
	f	01.9521	1.0	-17	
R(3.5)	e	11.0378	1.0	-7	2v ₂ R(48), v ₁ (N ₂ ¹⁸ O)P(42)
	f	11.0515	1.0	-3	
R(6.5)	e	15.4098	1.0	-9	2v ₂ R(53) v ₁ (N ₂ ¹⁸ O)P(37)
	f	15.4232	1.0	-8	
R(17.5)	e	30.4573	0.25	13	v ₁ P(58), P(57)
	f	30.4698	1.0	4	
R(18.5)	e	31.7463	1.0	3	v ₁ P(57), P(58)
	f	31.7579	0.25	-14	
R(23.5)	e	37.9985	1.0	-2	v ₁ P(51), v ₁ +v ₂ -v ₃ (e)P(58)
	f	38.0120	1.0	-1	

Standard deviation 0.0012 cm⁻¹.

a. e and f denote two components of Λ -type doubling.

b. Used as wavenumber standards (11).

Tables I and II. All ${}^2\Pi_{1/2}$ lines were found split by Λ -type doubling, and each component of the doublet was twice as strong as the corresponding transition in the ${}^2\Pi_{3/2}$ state. Figure 2 shows a portion of the observed spectra; $P(2.5)$ and $P(3.5)$ in both ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ appear along with N₂O lines. The upper trace shows fringe patterns produced by a Ge etalon; the fringe separation is about 0.016 cm⁻¹. The last column of Tables I and II lists N₂O lines used as wavenumber standards.

In the least-squares analysis of the observed spectra we assumed the following expressions for energy levels in each vibrational state:

$$E({}^2\Pi_{1/2}; v) = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e x_e - (1/2)A_v + B_{v1}(J + 1/2)^2 - D_{v1}(J + 1/2)^4 - \gamma/2 \pm (1/2)p_v(J + 1/2), \quad (1)$$

$$E({}^2\Pi_{3/2}; v) = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e x_e + (1/2)A_v + B_{v2}[(J + 1/2)^2 - 2] - D_{v2}(J + 1/2)^4 - \gamma/2, \quad (2)$$

where γ denotes the spin-rotation coupling constant. Because for NS the spin-orbit interaction constant A_v (223 cm⁻¹) is much larger than the rotational constant, we may use Eqs. (21) and (22), combined with Eq. (13), of Ref. (12) for the effective rotational constants, B_{v1} and B_{v2} , and Eq. (23) of Ref. (12) for the Λ -doubling

TABLE II
The Fundamental Band of the NS Radical in the $^2\Pi_{3/2}$ State

Transition	Obs. (cm^{-1})	Weight	(o-c) $\times 10^4$ (cm^{-1})	N ₂ O Line ^a
P(11.5)	1185.5156	1.0	9	$2\nu_2$ R(19), R(20)
P(9.5)	88.8640	1.0	-12	$2\nu_2$ R(23), R(24)
P(8.5)	90.5219	1.0	0	$2\nu_2$ R(24), R(25)
P(6.5)	93.7969	1.0	-12	$2\nu_2$ R(28), R(29)
P(3.5)	98.6181	1.0	-9	$2\nu_2$ R(34), R(35)
P(2.5)	1200.2012	1.0	4	$2\nu_2$ R(35), R(36)
R(3.5)	10.9208	1.0	16	$2\nu_2$ R(48), ν_1 (N ₂ ¹⁸ O) P(42)
R(6.5)	15.3217	1.0	6	$2\nu_2$ R(53), ν_1 (N ₂ ¹⁸ O) P(37)
R(17.5)	30.4573	0.5	-18	ν_1 P(58), P(57)
R(18.5)	31.7579	0.5	16	ν_1 P(58), P(57)
R(23.5)	38.0420	1.0	0	ν_1 P(51), $\nu_1 + \nu_2 - \nu_2$ (e) P(58)

Standard deviation 0.0012 cm^{-1} .

a. Used as wavenumber standards (11).

constant p_v . The + and - signs in front of the p_v term in Eq. (1) refer to the f and e components of the Λ doublet, respectively. A least-squares analysis was carried out separately for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. For $^2\Pi_{1/2}$ we fixed B_{01} and p_0 to the microwave values reported in Ref. (9), and adjusted D_{01} , B_{11} , D_{11} , p_1 , and the effective band origin $\tilde{\nu}_0$. Similarly, for the $^2\Pi_{3/2}$ state we treated D_{02} , B_{12} , D_{12} , and $\tilde{\nu}_0$ as adjust-

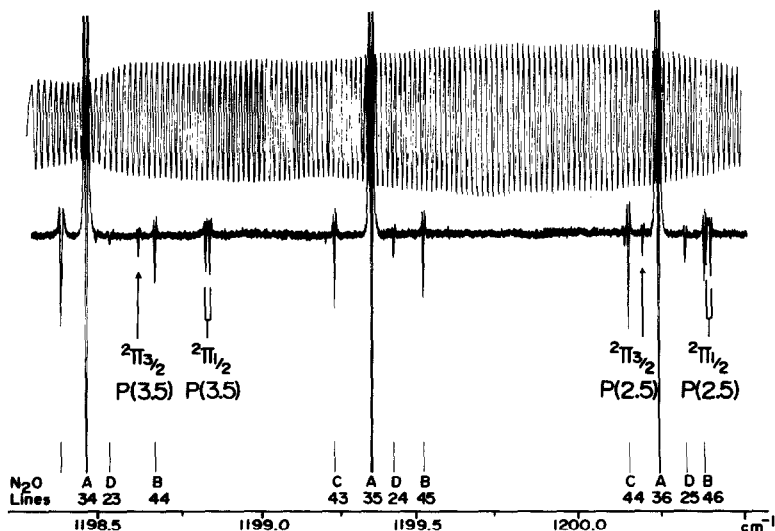


FIG. 2. A portion of the observed spectra. Source modulation was used with $2f$ detection. The $P(2.5)$ and $P(3.5)$ transitions of the NS fundamental band appear along with N₂O lines. The upper trace shows fringes produced by a Ge etalon; the fringe spacing is about 0.016 cm^{-1} . All N₂O lines used as standards are R branches of the following bands: A for $2\nu_2$, B for $3\nu_2$ ($1e \leftarrow \nu_2$ ($1e$), C for $3\nu_2$ ($1f \leftarrow \nu_2$ ($1f$), and D for $2\nu_2$ ($2e$). The numbers attached denote the J values.

TABLE III
Molecular Constants of $^{14}\text{N}^{32}\text{S}$ in $X^2\Pi$, (cm^{-1})^a

Constant	$^2\Pi_{1/2}(i=1)$	$^2\Pi_{3/2}(i=2)$
$B_{v=1,i}$	0.763 351 (17)	0.768 816 (26)
$D_{v=1,i}$	0.000 001 19 (21)	0.000 001 40 (30)
$P_{v=1,i}$	0.013 26 (13)	—
$B_{v=0,i}$	[0.769 602 (4)] ^b	[0.775 157 (6)] ^b
$D_{v=0,i}$	0.000 001 19 (24)	0.000 001 40 (35)
$P_{v=0,i}$	[0.013 253 (13)] ^b	—
$\tilde{\nu}_0$	1204.275 5 (12)	1204.089 2 (19)
Derived parameters		
$\omega_e - 2\omega_e x_e$	1204.182 4 (11)	B_e 0.775 549 (10)
$A_{v=1} - A_{v=0}$	-0.186 3 (22)	α_e 0.006 296 (16)
B_1	0.766 105 (17)	D_e 0.000 001 29 (33)
B_0	[0.772 401 (5)] ^b	r_e (Å) 1.494 03 (4)

a. Values in parentheses denote three standard errors and apply to the last digits of the constants.

b. Ref. (9) fixed.

able parameters, whereas B_{02} was fixed to the microwave value (9). Molecular constants thus obtained are summarized in Table III, where the fixed values are also included. As Tables I and II show, the discrepancies between the observed and calculated wavenumbers are within 0.0023 cm^{-1} , and the standard deviation is 0.0012 cm^{-1} for both spin states, which is nearly equal to the precision of the present measurement. Also note that N_2O line wavenumbers used as standards are accurate to 0.0007 cm^{-1} on the average (11).

DISCUSSION

According to Eqs. (1) and (2) the effective band origins of the two spin states are given by

$$\tilde{\nu}_0(^2\Pi_{1/2}) = \omega_e - 2\omega_e x_e - (1/2)(A_{v=1} - A_{v=0}), \quad (3)$$

$$\tilde{\nu}_0(^2\Pi_{3/2}) = \omega_e - 2\omega_e x_e + (1/2)(A_{v=1} - A_{v=0}). \quad (4)$$

Therefore, the true band origin and the vibrational change of the A constant are calculated to be $\omega_e - 2\omega_e x_e = 1204.1824(11) \text{ cm}^{-1}$ and $A_{v=1} - A_{v=0} = -0.1863(22) \text{ cm}^{-1}$. Our band origin is lower than that of Jenouvrier and Pascat (5) by 0.22 cm^{-1} .

We corrected the effective rotational constants, B_{v1} and B_{v2} , for higher-order terms, by using Eqs. (13), (21), and (22) of Ref. (12). The B_v constants thus

obtained are listed in Table III and are used to derive the equilibrium rotational constant, B_e , and the vibration-rotation constant, α_e . The equilibrium bond length is thus calculated to be $r_e = 1.49403(4)$ Å. Corrections have not been made for electron slipping effects, because the rotational g factor is not available.

Table III shows that both the centrifugal distortion and the Λ -doubling constants remain the same within experimental errors upon vibrational excitation. It may also be noted that, although errors are large, the effective centrifugal distortion constant is slightly larger in $^2\Pi_{3/2}$ than in $^2\Pi_{1/2}$. A simple extension of a perturbation treatment given in Ref. (12) gives

$$D_{v1} = D_v - [4BD/A + B^4/A^3], \quad (5)$$

$$D_{v2} = D_v + [4BD/A + B^4/A^3], \quad (6)$$

and qualitatively explains the observed differences between D_{v1} and D_{v2} . The centrifugal distortion constants, D_1 and D_0 , listed in Table III are thus averages of D_{v1} and D_{v2} . The D_0 constant thus obtained is in better agreement with a more recent microwave value of Lovas (0.00000127 cm $^{-1}$) (10) than with the previous value of Ref. (9). The equilibrium D_e constant we determined agrees very well with the calculated value $D_e = 4B_e^3/\omega_e^2 = 0.00000126$ cm $^{-1}$, where the $\omega_e = 1218.80$ cm $^{-1}$ used is obtained from our values of $\omega_e - 2\omega_e x_e$ and $\omega_e x_e = 7.31$ cm $^{-1}$ of Ref. (5).

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