NOTE

High-Resolution Fourier Transform Infrared Spectroscopy of the NS Radical

High-resolution Fourier transform spectroscopy (FTS) has recently been employed in our laboratory for obtaining infrared absorption spectra of several chemically short-lived species (*1–5*). The precision of the line positions obtained via FTS is comparable to that of other high-resolution infrared techniques such as diode laser, difference frequency laser, and laser magnetic resonance spectroscopy. The FTS technique however, has the advantage of being able to record an entire spectrum simultaneously, thus allowing a consistent set of line positions as well as intensities to be recorded.

In the present work we report high-resolution infrared FTS absorption measurements of the NS ($X^2\Pi$) radical. The NS radical has been previously studied by several groups using diode laser, microwave, millimeter-wave, and UV spectroscopy (*6–12*). The present study extends the measurements for $v = 0$ and $v = 1$ of the $X^2\Pi$ state to higher J, thus allowing a more precise determination of the molecular constants.

Details of the apparatus used in this study have been presented earlier (*1–5, 13*). The NS radical was made in three separate sidearms of the absorption cell. The sidearms were spaced 55 cm apart along the length of the absorption cell with the first sidearm located 10 cm in front of the first multipass mirror. The multipass configuration provided an effective absorption path length of ~100 m. The NS radical was generated by passing a N_2/SCl_2 mixture through a microwave discharge (*6*). The optimum absorption signal was obtained using maximum available pumping speed, with a cell residence time of ~0.08 sec, and at a total pressure of 0.5 Torr. The absorption spectrum, shown in Fig. 1, contains transitions up to $J = 32.5$ for the $^2\Pi_{3/2}$ spin-orbit state and $J = 35.5$ in the $^2\Pi_{1/2}$ spin-orbit state. The observed transitions are listed in Table
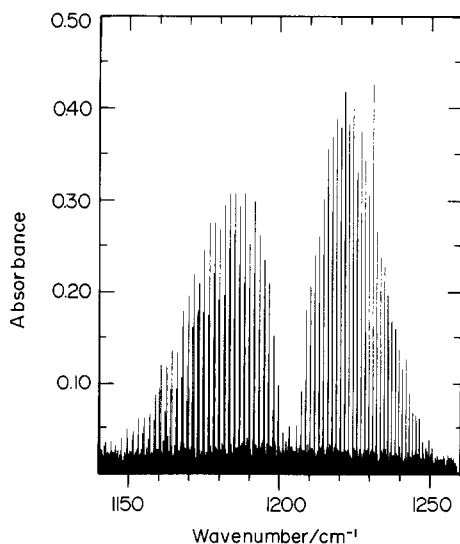

FIG. 1. High-resolution Fourier transform infrared absorption spectrum of the NS radical. The spectrum was recorded at 0.005 cm^{-1} resolution in 61 coadded scans.

TABLE I

Observed Transitions for the $v = 1-0$ Band of $^{14}N^{32}S$ (cm^{-1})

(a) $^2\Pi_{3/2}$ Transitions

J	R(J)	O-C[a]	P(J)	O-C
1.5	1207.92047	-47		
2.5	1209.42681	10	1200.20122	-1
3.5	1210.91965	-4	1198.61898	-36
4.5	1212.40012	28	1197.02519	31
5.5	1213.86661	-52	1195.41769	-18
6.5	1215.32145	-8	1193.79894	60
7.5	1216.76327	26	1192.16673	39
8.5	1218.19166	13	1190.52199	11
9.5	1219.60714	7	1188.86507	6
10.5	1221.00990	32	1187.19563	-11
11.5	1222.39890	-14	1185.51387	-25
12.5	1223.77508	-34	1183.81980	-36
13.5	1225.13869	0	1182.11348	-44
14.5	1226.48882	2	1180.39550	10
15.5	1227.82617	43	1178.66498	33
16.5	-	-	1176.92175	6
17.5	-	-	1175.16640	-15
18.5	-	-	1173.39987	60
19.5	-	-	1171.61985	-3
20.5	1234.31204	47	1169.82820	-20
21.5	1235.56833	-41	1168.02462	-25
22.5	1236.81257	7	1166.20912	-19
23.5	1238.04255	-27	1164.38194	19
24.5	1239.25939	-28	1162.54206	-17
25.5	1240.46288	-13	1160.69064	-13
26.5	1241.65274	-7	1158.82794	53
27.5	1242.82913	10	1156.95185	-32
28.5	1243.99209	44	1155.06519	11
29.5	1245.14032	-31	-	-
30.5	1246.27569	-25	-	-
31.5	1247.39743	-12	-	-

(b) $^2\Pi_{1/2}$ Transitions

J	$R_e(J)$	O-C	$R_f(J)$	O-C	$P_e(J)$	O-C	$P_f(J)$	O-C
0.5	1206.55190	-2	1206.56540	24				
1.5	1208.05998	16	1208.07315	8	1201.96539	-89	1201.95341	31
2.5	1209.55519	5	1209.56822	-18	1200.40849	12	1200.39550	29
3.5	1211.03777	-9	1211.05134	20	1198.83798	-5	1198.82509	19
4.5	1212.50783	-12	1212.52166	42	1197.25515	-14	1197.24219	1
5.5	1213.96514	-24	1213.97862	-6	1195.66018	0	1195.64676	-34
6.5	1215.40997	-16	1215.42377	34	1194.05276	3	1194.03939	-29
7.5	1216.84241	26	1216.85527	-19	1192.43320	24	1192.42005	11
8.5	1218.26117	-25	1218.27511	37	1190.80100	9	1190.78807	15
9.5	1219.66829	37	1219.68118	-6	1189.15639	-21	1189.14365	1
10.5	1221.06189	29	1221.07471	-22	1187.50026	20	1187.48686	-27
11.5	1222.44274	30	1222.45559	-18	1185.83152	21	1185.81829	-13
12.5	1223.81055	14	1223.82388	13	1184.15020	-20	1184.13752	-2
13.5	1225.16555	7	1225.17849	-33	1182.45776	43	1182.44410	-42
14.5	1226.50741	-21	1226.52098	3	1180.75191	-24	1180.73935	-2
15.4	1227.83658	-22	1227.84993	-19	1179.03513	26	1179.02252	38
16.5	1229.15259	-	1229.16593	-37	1177.30576	23	1177.29256	-28
17.5	1230.45664	50	1230.46968	23	1175.56389	-26	1175.55124	-27
18.5	1231.74624	0	-	-	1173.81068	-8	1173.79791	-26
19.5	1233.02293	-32	-	-	1172.04513	-26	1172.03259	-25
20.5	1234.28746	32	1234.30022	-21	1170.26836	30	1170.25585	29
21.5	1235.53800	12	1235.55084	-32	1168.47860	-20	1168.46587	-48
22.5	1236.77579	35	1236.78840	-31	1166.67768	4	1166.66539	15
23.5	1237.99949	-29	1238.01333	29	1164.86492	32	1164.85257	31
24.5	1239.21066	-22	1239.22431	19	1163.04018	46	1163.02765	23
25.5	1240.40858	-12	1240.42160	-32	1161.20311	10	1161.19077	0
26.5	1241.59287	-33	1241.60655	14	1159.35425	-25	1159.34250	18
27.5	1242.76427	-9	1242.77800	44	1157.49417	-5	1157.48163	-47
28.5	1243.92256	41	1243.93525	8	1155.62223	4	1155.61028	15
29.5	1245.06684	31	1245.07928	-40	1153.73843	-2	1153.72708	63
30.5	1246.19790	44	1246.21109	49	1151.84242	-59	1151.83145	37
31.5	1247.31521	29	1247.32805	1	1149.93596	5	1149.92354	-50
32.5	1248.41857	-30	1248.43270	74	-	-	-	-
33.5	1249.50907	-21	1249.52214	-21	-	-	-	-
34.5	1250.58594	-17	1250.59830	-86	-	-	-	-
35.5	1251.64907	-27	1251.66285	49	-	-	-	-

rms standard deviation 0.00026 cm^{-1}

[a] Observed minus Calculated $\times 10^5$.

TABLE II

Molecular Constants for $^{14}N^{32}S$ (cm^{-1})

Constant	v = 0	v = 1
A	[223.15]	222.96490(6)[a]
A_D x10^{-3}	0.1180(12)	0.1085(12)
B	0.7723812(13)	0.7660851(13)
D x10^{-5}	0.12577(10)	0.126156(90)
p	0.013197(70)	0.013215(70)
p_D x10^{-7}	-0.86(43)	[-0.86]
q x10^{-6}	[0.10]	[0.22]
ν_0		1204.18222(4)

Values in brackets were fixed in the fit (see text).
a Values in parentheses are one standard deviation.

1. Absolute frequency calibration was obtained using the infrared spectrum of $N_2O\nu_3$ band as a reference (14).

The observed line positions were fit using the Hamiltonian given by Zare et al. (15). This Hamiltonian, when specialized to $^2\Pi$ systems, takes the form

$$\langle ^2\Pi_{3/2}| H | ^2\Pi_{3/2} \rangle = \tfrac{1}{2}A + \tfrac{1}{2}q - D + (B - D + \tfrac{1}{2}q + \tfrac{1}{2}A_D)(Z^2 - 2) - D(Z^2 - 2)^2 \quad (1)$$

$$\langle ^2\Pi_{1/2}| H | ^2\Pi_{1/2} \rangle = -\tfrac{1}{2}A + D + (B - D - \tfrac{1}{2}A_D)Z^2 - DZ^4$$
$$+ \tfrac{1}{2}(p + \tfrac{1}{2}p_D(Z^2 - \tfrac{1}{4}))(1 \pm Z) + \tfrac{1}{2}q(1 \pm Z)^2 - \gamma \quad (2)$$

$$\langle ^2\Pi_{3/2}| H | ^2\Pi_{1/2} \rangle = -B - \tfrac{1}{4}p - \tfrac{1}{4}p_D(Z^2 - \tfrac{1}{4}) - \tfrac{1}{2}q(1 \pm Z)$$
$$+ 2D(Z^2 - 1)(Z^2 - 1)^{1/2} - (\gamma/2)(Z^2 - 1)^{1/2}, \quad (3)$$

where $Z = J + \tfrac{1}{2}$, A is the spin–orbit interaction parameter, A_D is the centrifugal distortion correction to A, γ is the spin-rotation parameter, p and q are Λ-doubling parameters, p_D is the centrifugal distortion correction to p, and B and D are the rotational and centrifugal distortion parameters, respectively. The $\pm$ signs distinguish between the Λ-doubling components of a given rotational level. When Λ doubling was not resolved, the observed line positions were fitted to the mean of the calculated Λ-doublet splitting. Brown and Watson (16) have shown that γ and A_D are highly correlated and cannot be determined simultaneously. Therefore, we have arbitrarily chosen to set $\gamma = 0$ and allow A_D to vary in the fits.

As observed in previous studies (6, 7), Λ doubling could be resolved only for the $^2\Pi_{1/2}$ spin–orbit state. Consequently, the Λ-doubling parameters p, p_D, and q were not all simultaneously determinable from the fit. In order to circumvent this difficulty, the value of q was fixed to that given in Ref. (10). Preliminary fits showed that the change in the parameter P_D was not statistically significant in going from $v = 0$ to $v = 1$. Thus, $\Delta P_D = P_D (v = 1) - P_D (v = 0)$ was set equal to zero. Since we did not observe any of the extremely weak $^2\Pi_{3/2} \leftrightarrow ^2\Pi_{1/2}$ transitions, the measurements did not allow for an accurate determination of the spin–orbit constant. As a result, the value of the spin–orbit constant $A (v = 0)$, was fixed to the results of the UV measurements of Ref. (12). With $A (v = 0)$ fixed, our analysis provides a determination of ΔA. All transitions included in the fitting were weighted equally.

The quality of the fit, as exhibited by the residuals (obs. − cal.), is shown in Table I and the molecular constants obtained from the fit are given in Table II. The rms standard deviation of the fit is 0.00026 cm^{-1} and is almost a factor of five better than the diode laser study of Matsumura et al. (6). The molecular constants are in good agreement with previous measurements.

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