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Fourier Transform Emission Spectroscopy of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ System of YN

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The electronic emission spectrum of YN has been observed in the 2.3–2.6 μm spectral region using a Fourier transform spectrometer. The bands were excited in a yttrium hollow cathode lamp in the presence of a trace of molecular nitrogen. The observed bands, with origins at 3882.7625(4), 4229.0457(3), 4528.6562(46), 4798.5145(13), 5049.4429(20), and 5281.2129(27) cm^{-1}, have been assigned as the 0–0, 1–1, 2–2, 3–3, 4–4, and 5–5 vibrational bands, respectively, of the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ electronic transition. The principal equilibrium constants for the ground state obtained from this analysis are $B''_e = 0.42815(24)\ cm^{-1}$ and $r''_e = 1.80405(50)$ Å, and the corresponding excited state values are $B'_e = 0.42311(30)\ cm^{-1}$ and $r'_e = 1.81477(64)$ Å. This work represents the first observation of the YN molecule.

INTRODUCTION

Diatomic transition metal nitrides provide the simplest models for the bonding of nitrogen atoms to transition metal surfaces. Their study provides important structural information for the characterization of catalytic processes occurring on transition metal surfaces (*1*). Some of the transition metal elements are known to occur in S-type and M-type stars in the form of metal monoxides (*2*). It is possible that the corresponding transition metal nitrides are also present in stellar atmospheres. Laboratory spectra would be very helpful in identifying any metal nitrides present in the spectra of stars. Solid transition metal nitrides are well-known hard refractory materials that are formed at high temperatures by the reaction of metals with N_2 or NH_3 (*3*).

Although the optical spectra of many gaseous transition metal oxides and hydrides are relatively well characterized, only a few nitrides are known. Since the 1960s when the gas-phase spectra of MoN (*4*) and NbN (*5*) were initially detected, several additional gaseous transition metal nitrides have been characterized experimentally. The other diatomic transition metal nitrides for which gas-phase data are available include ScN (*6*), WN (*7*), TiN (*8, 9*), VN (*10, 11*), and ZrN (*12*). The matrix isolation studies of some of transition metal nitrides are also available, for example for TaN (*13*), ZrN (*14*), MoN (*15, 16*), and NbN (*17*). Mass spectrometric data for several transition metal nitrides obtained by Gingerich (*18*) as well as empirical estimates (*18*) indicate that the early transition metal nitrides have large bond energies ranging from 96 to 145 kcal/mole.

Recently, we have initiated a project aimed at increasing the data available for the transition metal nitrides. We have observed the emission spectra of two new diatomic nitrides ScN (*6*) and WN (*7*) by Fourier transform spectroscopy. In this paper we report the discovery of another gas-phase transition metal nitride, YN.

Until the work described here, no experimental data for YN have been published, although the YNH molecule is known (*19*). The previous work on YN includes the

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work of Gingerich (*18*), who estimated the bond energy of YN as 115 kcal/mole on the basis of empirical correlations. Recently, Shim and Gingerich (*20*) have performed an all-electron CASSCF ab initio calculation on YN. They predict a double bonded $^1\Sigma^+$ ground state for YN with a dissociation energy of 4.59 eV (106 kcal/mole).

YN is isovalent to ScN and, therefore, the electronic states should have the same multiplicity and symmetry. The electronic spectra of YN are also expected to lie in the same spectral region as ScN. An $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of ScN has recently been identified in the 5650–5950 cm^{-1} spectral region (*6*), and the newly observed bands of YN are located in the 3750–5400 cm^{-1} spectral region. We assign this transition of YN as the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition analogous to the infrared transition of ScN (*6*).

EXPERIMENTAL DETAILS

Initially the spectrum of the YN molecule was observed during a search for YH and YD. The YH and YD molecules were made by exciting a mixture of H_2 or D_2 in a yttrium hollow cathode lamp. In these experiments we observed several bands of YH and YD in the near infrared region between 11 000 and 14 700 cm^{-1} (*21*). In addition to YH and YD bands, we also observed several bands in the 3750–5400 cm^{-1} region. These bands were unaffected by the substitution of D_2 for H_2, and a closer inspection of the line spacing in the branches indicated that these bands were not due to YH or YD. None of these bands correspond to the known transitions of YO (*22*) and no transitions of YO are expected to lie in this spectral region. The line spacing pointed to YN as the emitter of these bands. YN is isovalent to ScN and the structure of the newly observed bands closely resembles the structure of the bands in the $A\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition of ScN (*6*).

The next experiment was designed to confirm our identification of YN as the carrier of the new bands by adding a trace of N_2 (about 5 mTorr) to the flow of neon gas in the lamp. (It was observed that at a "high" pressure of N_2 (>10 mTorr), the strong N_2 bands obscure the region of interest.) This time the new bands appeared with twice the intensity. This chemical evidence confirmed that YN was the emitter of the new bands. Most probably there was a trace of N_2 in the system during the first experiment or, more likely, solid YN impurity was sputtered from the cathode surface.

The spectra of YN were recorded using the 1-m Fourier transform spectrometer associated with the McMath Solar Telescope of the National Solar Observatory. The spectra in the 2000–14 800 cm^{-1} region were recorded in two sections. The 2000–9150 cm^{-1} region was recorded using InSb detectors and silicon filters, and with three scans co-added in 20 min of integration. For the 9100–14 800 cm^{-1} spectral region, the spectrometer was operated with a red pass filter and Si-diode detectors. This time a total of 10 scans were co-added in approximately 1 hr of integration. In both cases the spectrometer resolution was set at 0.02 cm^{-1}.

In addition to the YN bands, the final spectra contained several bands belonging to N_2 and N_2^+ as well as Y and Ne atomic lines. The spectra were calibrated using the measurements of the Ne atomic lines made by Palmer and Engleman (*23*). The absolute accuracy of the wavenumber scale is expected to be better than ± 0.001 cm^{-1}. The YN lines have a width of 0.025 cm^{-1} and appear with a maximum signal-to-noise ratio of 15:1, limiting the precision of the measurements of strong and unblended YN lines to ± 0.002 cm^{-1}.

OBSERVATION AND ANALYSIS

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions

were determined by fitting a Voigt lineshape function to each spectral feature using a nonlinear least-squares procedure.

The spectrum of YN has been observed in the 3750–5400 cm^{-1} spectral region. The observed spectrum consists of six bands with origins at 3882.7625(4), 4229.0457(3), 4528.6562(46), 4798.5145(13), 5049.4429(20), and 5281.2129(26) cm^{-1}. The 3882.7624(5) cm^{-1} band is the strongest and has been assigned to the 0–0 vibrational band. The intensity of the other bands decreases with increasing wavenumbers and these bands have been assigned as 1–1, 2–2, 3–3, 4–4, and 5–5, respectively. A compressed plot of the 1–1 band is provided in Fig. 1, showing the typical appearance of the YN bands. Each YN band consists of a single R and P branch, indicating that the bands involve a $\Delta\Lambda = 0$ transition, probably a $^1\Sigma^+$-$^1\Sigma^+$ transition analogous to that of ScN. The lines of the R and P branches have a nearly constant spacing, indicating that the rotational constants in the ground and the excited state are very similar in magnitude. Consistent with the Franck–Condon principle, the off-diagonal bands with $\Delta v \neq 0$ were not observed.

A theoretical study of the isoelectronic ScN molecule by Kunze and Harrison (*24*) suggests that the ground state of ScN is a triply bonded $X^1\Sigma^+$ state, Sc≡N. This state is followed by the low-lying excited $a^3\Sigma^+$, $b^3\Pi$, and $A'^1\Pi$ electronic states located at 2600, 4200, and 4500 cm^{-1}, respectively. Associated with the $a^3\Sigma^+$ state there must be a singlet state of the same nominal configuration lying higher in energy than the $a^3\Sigma^+$ state. Unfortunately, Kunze and Harrison (*24*) did not calculate the location of this $^1\Sigma^+$ state. We attributed the infrared transition of ScN at 6000 cm^{-1} to the $A^1\Sigma^+$-$X^1\Sigma^+$ transition with the $A^1\Sigma^+$ state arising from the same nominal configuration as the $a^3\Sigma^+$ state (*6*).

Recently, Shim and Gingerich (*20*) have performed an all electron CASSCF calculation of the electronic states of YN. They predict a $^1\Sigma^+$ ground state of YN. However, they state that the chemical bond in the ground $^1\Sigma^+$ state is basically a double bond composed of two π bonds. Kunze and Harrison (*24*) also note that the single σ-bond of ScN is very weak in the $X^1\Sigma^+$ state. Shim and Gingerich (*20*) also predict that the low-lying $^3\Sigma^+$, $^3\Pi$, and $^1\Pi$ electronic states are 5177, 9290, and 9915 cm^{-1} above the ground state. Unfortunately, these authors also did not calculate the position of the first excited $^1\Sigma^+$ state with the same nominal configuration as the $^3\Sigma^+$ state. The positions of the low-lying excited states calculated by Shim and Gingerich (*20*) are

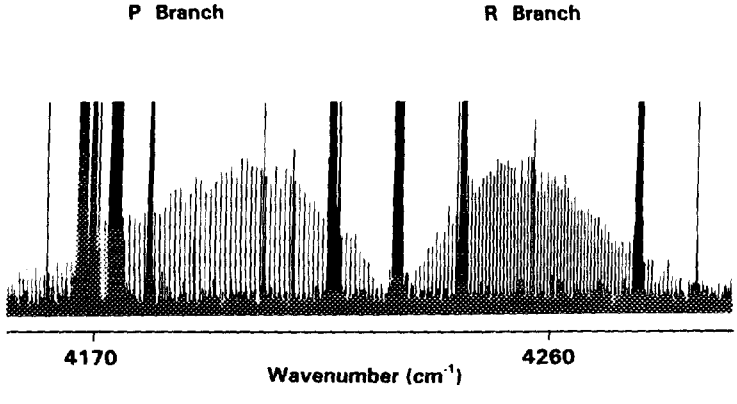

FIG. 1. A compressed view of the 1–1 band of the $A^1\Sigma^+$-$X^1\Sigma^+$ system of YN.

approximately twice the corresponding values obtained for ScN by Kunze and Harrison (*24*). However, we find that the $A^1\Sigma^+$–$X^1\Sigma^+$ transition lies at a lower energy in YN than in ScN. The ground state equilibrium bond length of YN calculated by Shim and Gingerich (*20*) is 1.7886 Å. The discrepancies in the calculated energy positions are presumably due to problems in representing the ground state wavefunction. As in ScN and CaO, the $X^1\Sigma^+$ and $A^1\Sigma^+$ states are not well represented by single electronic configurations.

A part of the spectrum of the 0–0 band is provided in Fig. 2, and several lines belonging to the R branch have been marked. Though this band is the strongest in intensity, part of the band is obscured by strong absorption of H_2O. The lines falling near the H_2O absorption lines could not be reliably measured. Some of the YN lines are also overlapped or blended with strong Ne atomic transitions. The poorly determined transitions were either excluded or they were included with reduced weights in the final fit. The observed line positions were fitted with the customary energy level expression for each vibrational level:

$$F_v(J) = T_v + B_vJ(J+1) - D_v[J(J+1)]^2 + H_v[J(J+1)]^3.$$

For the 0–0 band the absolute J assignment was made from the magnitude of D values since the standard deviation of the fit was not very sensitive to a change in the J numbering by ±1. However the D value was very sensitive to this change. The ground state D values for three possible consecutive J numberings were determined to be 3.106×10^{-7}, 7.092×10^{-7}, and 1.123×10^{-6} cm^{-1}, and the corresponding excited state D values were -8.784×10^{-8}, 3.109×10^{-7}, and 7.092×10^{-7} cm^{-1}, respectively. The first assignment gives a negative sign for D in the excited state while the third assignment gives very large values in both the ground and the excited state. This leaves the second assignment as the correct one. YN is isoelectronic to SrO and the D value for YN should be similar in magnitude to that of SrO. For SrO the D_0'' constant has been determined to be 3.6×10^{-7} cm^{-1} (*22*) consistent with the assignment chosen for YN.

Except for the 0–0 band, all other bands are affected by perturbations in the excited state. Although these perturbations distort the spectroscopic constants, they also confirm the rotational assignments. The perturbations in the 1–1 band seem to be global

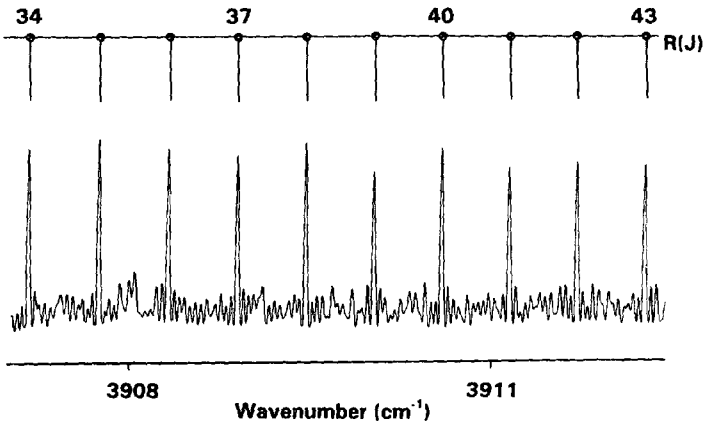

FIG. 2. A part of the spectrum showing the 0–0 band of the $A^1\Sigma^+$–$X^1\Sigma^+$ system of YN.

and an H term is required in the excited state in order to obtain a satisfactory fit. For the 1–1 band, all of the observed lines as well as the lower state combination differences were included in the final fit.

The perturbation in the 2–2 band is more severe. Although a fit of the ground state combination differences results in a reasonable set of lower state constants, an attempt to determine the ground and excited state constants simultaneously from a free fit of all the observed lines was unsuccessful. This is due to the presence of strong perturbations in the excited state which affect all transitions with $J' < 31$. In the final fit of this band we deweighted all transitions with $J' < 31$ and fitted the unperturbed lines together with the ground state combination differences of the perturbed transitions. Even then an H term was needed in the excited state in order to obtain the satisfactory fit. A part of the R branch of this band is presented in Fig. 3.

The 3–3 band, which has an origin at 4798.5145 cm^{-1}, is perturbed for $J' > 45$. Only a few perturbed lines with $J' > 45$ could be identified with certainty because of their weaker intensity and displacement from their predicted positions.

The 4–4 band is perturbed in two ranges of J. The first perturbation is localized at $J' = 37$, 38, and 39. The other perturbation affects all transitions with $J' > 49$. In this band the perturbed lines were excluded from the fit and the lower state combination differences of the perturbed lines were included in the final fit.

The 5–5 band is perturbed for $J' < 15$. These lines were excluded from the final fit. There were some lines found near the expected position of the 6–6 band, but we did not try to assign them because of their weak intensity.

The observed line positions of the vibrational bands of YN are listed in Table I. Since these bands have no common upper or lower vibrational levels, the molecular constants were obtained from a band-by-band fit of the observed transitions in each band. The constants from these fits are provided in Table II. As pointed out earlier, an H term is required for all the excited state vibrational levels (except $v = 0$) in order to obtain a reasonable fit.

DISCUSSION

From the spectroscopic constants of Table II, an attempt was made to estimate the equilibrium molecular constants. It can be seen that the ground state rotational con-

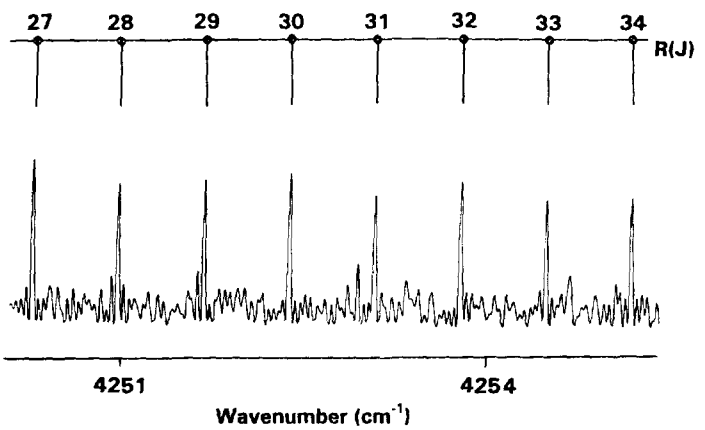

FIG. 3. A part of the spectrum showing the 2–2 band of the $A^1\Sigma^+$–$X^1\Sigma^+$ system of YN.

TABLE I

Observed Transition Wavenumbers (in cm^{-1}) of the $A^1\Sigma^+-X^1\Sigma^+$ System of YN

	0-0 BAND				1-1 BAND				2-2 BAND			
J	R(J)	O-C	P(J)	O-C[a]	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C
2					4231.5500	-13						
3					4232.3770	19					4527.5384	14227 *
4	3886.8881	12	3879.2908	-16	4233.1942	9	4225.6278	28	4534.0596	12768 *	4526.6465	13884 *
5	3887.6839	4	3878.3978	-36	4234.0059	3	4224.7572	15	4534.8042	12122 *	4525.7413	13460 *
6	3888.4683	-24	3877.4985	-26	4234.8125	2	4223.8819	11	4535.5307	11347 *	4524.8056	12783 *
7	3889.2468	-18	3876.5921	5	4235.6149	16	4223.0002	-2	4536.2444	10497 *	4523.8622	12081 *
8	3890.0163	-8	3875.6703	-27	4236.4080	-7	4222.1181	36	4536.9567	9684 *	4522.9100	11343 *
9	3890.7726	-39			4237.1999	14	4221.2235	4	4537.6579	8811 *	4521.9438	10514 *
10					4237.9843	14	4220.3283	19	4538.3578	7975 *	4520.9744	9703 *
11	3892.2703	22	3872.8624	-6	4238.7632	16	4219.4225	-18	4539.0601	7212 *	4519.9938	8828 *
12	3892.9998	-6	3871.9078	-8	4239.5351	2	4218.5159	-11	4539.7552	6425 *	4519.0128	7995 *
13	3893.7240	2	3870.9491	35	4240.3018	-11			4540.4493	5675 *	4518.0306	7198 *
14	3894.4421	35			4241.0653	-2			4541.1453	4991 *	4517.0442	6403 *
15	3895.1448	-0					4215.7612	-32	4541.8405	4342 *	4516.0604	5677 *
16	3895.8434	9	3868.0044	-18			4214.8383	13	4542.5351	3733 *	4515.0736	4964 *
17	3896.5322	2	3867.0100	-1	4243.3203	-19	4213.9032	-15	4543.2322	3190 *	4514.0935	4358 *
18	3897.2133	-0	3866.0045	-16	4244.0649	5	4212.9675	-3	4543.9347	2741 *	4513.1086	3742 *
19	3897.8857	-9			4244.8013	-3	4212.0255	-7	4544.6359	2318 *	4512.1260	3188 *
20	3898.5523	2	3863.9752	0	4245.5337	-2	4211.0795	-6	4545.3357	1921 *	4511.1502	2738 *
21			3862.9495	9	4246.2611	-5	4210.1306	8	4546.0395	1599 *	4510.1718	2295 *
22	3899.8625	20			4246.9845	-2	4209.1750	-2	4546.7416	1293 *	4509.2015	1965 *
23	3900.5042	5	3860.8754	10	4247.7035	2	4208.2171	6	4547.4439	1024 *	4508.2209	1563 *
24	3901.1396	-3	3859.8277	5	4248.4157	-19	4207.2534	-4	4548.1504	828 *	4507.2499	1285 *
25			3858.7722	-14	4249.1271	-5	4206.2874	-0	4548.8546	638 *	4506.2783	1028 *
26	3902.3945	23	3857.7148	10	4249.8321	-14	4205.3161	-11	4549.5585	473 *	4505.3096	825 *
27	3903.0093	5	3856.6483	3	4250.5355	1	4204.3429	-8	4550.2635	345 *	4504.3389	624 *
28	3903.6209	17	3855.5782	17	4251.2332	-4	4203.3654	-14	4550.9680	237 *	4503.3698	460 *
29					4251.9276	-5	4202.3866	0	4551.6738	164 *	4502.4031	338 *
30	3904.8238	9			4252.6186	-5	4201.4038	3	4552.3771	87 *	4501.4353	223 *
31	3905.4211	43			4253.3050	-18	4200.4166	-10	4553.0789	13	4500.4693	139 *
32			3851.2411	11	4253.9901	-11	4199.4291	1	4553.7856	7	4499.5050	85 *
33	3906.5914	14	3850.1441	-5	4254.6733	5	4198.4379	-2	4554.4892	-15	4498.5401	36
34	3907.1707	9	3849.0437	-17	4255.3502	-12	4197.4439	-10	4555.1931	-21	4497.5760	3
35	3907.7472	16	3847.9441	15	4256.0277	2	4196.4508	12	4555.8944	-39	4496.6133	-9
36	3908.3177	0	3846.8377	10	4256.7005	-7	4195.4516	-10	4556.5973	-32	4495.6475	-47
37	3908.8875	11	3845.7288	9	4257.3722	-5	4194.4523	-16	4557.2995	-21	4494.6863	-38
38	3909.4527	6	3844.6175	9	4258.0414	-7	4193.4531	-7	4557.9997	-24		
39	3910.0162	11			4258.7094	-2	4192.4525	-1	4558.6989	-30	4492.7626	-29
40	3910.5759	1	3842.3885	4	4259.3734	-22	4191.4495	-10	4559.3986	-26	4491.8016	-20
41	3911.1348	3			4260.0398	-5	4190.4483	6	4560.1008	7	4490.8421	-1
42	3911.6927	9			4260.7035	-3	4189.4443	-2	4560.7996	9	4489.8810	-3
43	3912.2473	-5	3839.0379	15	4261.3656	-9	4188.4415	4	4561.4989	18	4488.9212	1
44	3912.8036	5			4262.0290	7	4187.4387	10	4562.1981	26	4487.9616	-2
45	3913.3574	-6	3836.8016	9	4262.6900	0	4186.4359	11	4562.8970	31	4487.0067	32
46	3913.9140	10	3835.6839	1	4263.3513	-0	4185.4327	2	4563.5949	25	4486.0497	33
47	3914.4670	-16	3834.5653	-28	4264.0142	13	4184.4312	2	4564.2923	14	4485.0929	24
48	3915.0237	-13	3833.4542	2	4264.6758	10	4183.4312	5	4564.9907	12	4484.1415	56
49	3915.5840	10	3832.3415	-6	4265.3368	-6	4182.4335	16	4565.6933	50	4483.1836	10
50	3916.1363	-65	3831.2339	11	4266.0013	5	4181.4352	3	4566.3880	9	4482.2334	26
51			3830.1272	6	4266.6668	12			4567.0876	15	4481.2816	11
52			3829.0219	-21	4267.3321	2	4179.4489	14	4567.7865	13	4480.3336	19
53	3917.8372	-9	3827.9265	10	4268.0017	17	4178.4599	23	4568.4863	22	4479.3818	-26
54	3918.4076	-25			4268.6717	14	4177.4707	-1	4569.1786	-44	4478.4374	-11
55	3918.9849	-16	3825.7408	-20	4269.3437	7	4176.4869	-4	4569.8798	-19	4477.4907	-33
56	3919.5627	-50	3824.6584	-13	4270.0201	16	4175.5081	4	4570.5754	-46	4476.5497	-12
57			3823.5827	0	4270.6965	-6			4571.2743	-33	4475.6063	-28
58	3920.7474	6	3822.5114	-12	4271.3767	-25			4571.9726	-20	4474.6651	-34
59	3921.3451	-6			4272.0653	3					4473.7258	-29
60	3921.9503	-14			4272.7563	14	4171.6342	15	4573.3597	-56	4472.7862	-37
61	3922.5641	-12			4273.4520	26	4170.6779	11	4574.0563	-21	4471.8521	5
62	3923.1875	6			4274.1513	26			4574.7489	-8	4470.9131	-7
63			3817.2842	9	4274.8518	-15			4575.4403	16	4469.9747	-13
64					4275.5616	-19			4576.1337	86	4469.0378	-4
65			3815.2571	-24	4276.2812	16			4576.8108	24	4468.1023	27
66	3925.7674	4	3814.2622	-23			4165.9903	-28	4577.4909	28	4467.1641	38
67	3926.4396	11	3813.2834	18			4165.0800	16	4578.1652	15	4466.2220	23
68	3927.1228	11	3812.3185	69	4278.4689	8	4164.1736	17	4578.8316	-29	4465.2822	50
69	3927.8100	-75	3811.3572	22	4279.2148	25	4163.2698	-44			4464.3402	77
70	3928.5277	14	3810.4096	-31	4279.9646	2	4162.3850	-5			4463.3783	-67
71	3929.2293	-196	3809.4848	-3	4280.7211	-40	4161.5088	22			4462.4259	-82
72	3929.9883	25	3808.5776	45	4281.4944	-2	4160.6388	11				

Note: [a]Observed minus calculated line positions in units of 10^{-4} cm^{-1}. An asterisk marks perturbed transitions not included in the final fit while "b" marks blended lines. See text for details.

TABLE I—*Continued*

	0-0 BAND				1-1 BAND				2-2 BAND			
J	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C
79	3935.6032	-48			4287.1645	-46	4154.8723	-38				
80	3936.4874	15			4288.0284	19	4154.1014	-34				
81	3937.3922	75					4153.3535	57				
82					4289.7832	17	4152.6144	84				
83	3939.2497	14			4290.6732	-69	4151.8798	2				
84	3940.2060	-85			4291.5937	4	4151.1687	-6				
85	3941.2048	-1			4292.5212	-8						
86												
87					4294.4272	0						
88					4295.4146	95						
89					4296.4093	88						

	3-3 BAND				4-4 BAND				5-5 BAND			
J	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C
3					5052.7506	-196 b			5284.6358	1030 *		
4	4802.6375	29			5053.5940	-77			5285.4702	1050 *		
5	4803.4368	-90	4794.2826	-63	5054.4401	69			5286.2983	998 *		
6	4804.2437	-90	4793.4299	-14	5055.2644	-3			5287.1219	889 *		
7	4805.0475	-76	4792.5662	-33	5056.0957	-5					5275.5348	937 *
8	4805.8474	-57	4791.7011	-25	5056.9235	-41			5288.7682	634 *	5274.7099	889 *
9	4806.6524	57	4790.8317	-17	5057.7583	-8			5289.5941	516 *	5273.8798	778 *
10	4807.4315	-41	4789.9593	3	5058.5865	-43	5041.1058	-162 b			5273.0561	717 *
11	4808.2251	51	4789.0871	66	5059.4249	24	5040.3066	160 b	5291.2613	400 *	5272.2278	598 *
12	4808.9990	-7			5060.2507	-38	5039.4542	-54	5292.0910	285 *	5271.3974	442 *
13	4809.7748	3	4787.3050	-54	5061.0888	21	5038.6304	13	5292.9253	201 *	5270.5765	368 *
14	4810.5480	36	4786.4222	33			5037.8002	10	5293.7678	187 *	5269.7584	304 *
15	4811.3092	-1	4785.5301	73	5062.7439	-83	5036.9673	-25	5294.6049	103	5268.9399	220 *
16	4812.0757	68	4784.6252	30	5063.5895	38	5036.1336	-76	5295.4476	60	5268.1221	126 *
17	4812.8292	62	4783.7183	14	5064.4198	1	5035.3150	18	5296.2902	-2	5267.3107	76
18	4813.5786	72	4782.8068	-1	5065.2585	43	5034.4840	-23	5297.1452	45	5266.5003	17
19	4814.3181	40	4781.8982	64	5066.0975	80	5033.6667	64	5297.9892	-37		
20	4815.0516	12	4780.9730	14			5032.8392	38	5298.8430	-40	5264.8935	-24
21	4815.7799	-3	4780.0464	4			5032.0125	8	5299.7006	-25		
22	4816.5040	8	4779.1157	9	5068.6044	41	5031.1947	54	5300.5562	-51	5263.3009	-14
23	4817.2188	0	4778.1751	-24	5069.4452	61	5030.3724	41	5301.4173	-43	5262.5101	9
24	4817.9253	-12	4777.2341	2	5070.2808	18	5029.5517	29	5302.2791	-52	5261.7162	-27
25	4818.6260	-1	4776.2842	5	5071.1235	34	5028.7324	15	5303.1433	-61	5260.9242	-71
26	4819.3107	-60	4775.3233	-30	5071.9712	87	5027.9166	18	5304.0186	17	5260.1451	-15
27	4819.9979	2	4774.3620	8	5072.8053	-8	5027.1024	20	5304.8792	-79	5259.3607	-42
28	4820.6642	-44	4773.3889	9	5073.6482	-29	5026.2911	30	5305.7580	-19	5258.5856	-8
29	4821.3265	-18	4772.4030	-29			5025.4780	3	5306.6302	-54		
30	4821.9728	-34	4771.4105	-39	5075.3431	-26	5024.6659	-36			5257.0384	-10
31	4822.6055	-57	4770.4073	-53	5076.1962	8	5023.8615	-20	5308.4003	44	5256.2741	29
32	4823.2273	-51	4769.3971	-26	5077.0407	-60	5023.0518	-80	5309.2830	23	5255.5110	44
33	4823.8376	-8	4768.3723	-25			5022.2547	-38	5310.1743	55		
34	4824.4262	-21	4767.3357	-10	5078.7495	-48	5021.4505	-92	5311.0635	32	5253.9914	22
35	4825.0017	11	4766.2837	-9	5079.6000	-107 *	5020.6566	-68	5311.9609	58	5253.2366	1
36	4825.5580	43	4765.2141	-31	5080.4451	-238 *			5312.8519	-16	5252.4924	44
37	4826.0917	53	4764.1332	2	5081.2273	-1016 *	5019.0634	-154 *	5313.7601	45	5251.7446	6
38	4826.6024	58	4763.0316	7	5082.2206	299 *	5018.2628	-278 *	5314.6634	21	5251.0082	39
39	4827.0892	65	4761.9131	41	5083.0634	92	5017.4090	-961 *	5315.5715	6	5250.2701	8
40	4827.5500	73			5083.9271	75	5016.7549	326 *	5316.4825	-20	5249.5411	22
41	4827.9786	41	4759.6074	78	5084.7877	12	5015.9487	63	5317.4029	9	5248.8154	21
42	4828.3727	-31	4758.4106	23	5085.6637	85	5015.1736	84	5318.3246	10	5248.0925	-2
43	4828.7300	-142 *	4757.1894	-5	5086.5307	52	5014.3880	-28			5247.3754	-17
44	4829.0406	-365 *	4755.9442	21	5087.3998	25	5013.6211	18	5320.1817	27	5246.6626	-39
45	4829.3115	-601 *	4754.6470	-155 *	5088.2704	-0	5012.8568	64	5321.1129	-2	5245.9599	-13
46	4829.5252	-997 *	4753.3121	-366 *	5089.1465	16	5012.0865	23	5322.0522	9	5245.2596	-16
47					5090.0119	-87	5011.3227	21	5322.9909	-30		
48					5090.8691	-281 *	5010.5577	-17	5323.9360	-47		
49							5009.7917	-89			5243.1947	13
50							5009.0048	-392 *	5325.8410	-64	5242.5117	-34
51							5008.1986	-909 *	5326.8076	5	5241.8412	-11
52							5007.2896	-2473 *	5327.7740	29	5241.1697	-54
53							5006.5275	-2584 *	5328.7435	42	5240.5165	30
54							5005.7836	-2529 *	5329.7103	-15	5239.8534	-40
55							5005.0786	-2095 *			5239.2111	42
56							5004.3284	-2123 *			5238.5651	32
57							5003.5981	-1957 *				
58							5002.8790	-1682 *				
59							5002.1766	-1237 *				
60							5001.4817	-712 *				
61							5000.7887	-157 *				

TABLE II

Rotational Constants (in cm^{-1}) Obtained for the $A^1\Sigma^+$–$X^1\Sigma^+$ Bands of YN

Constants	0-0 Band	1-1 Band	2-2 Band	3-3 Band	4-4 Band	5-5 Band
$T_{v',v''}$	3882.7625(4)	4229.0457(3)	4528.6563(46)	4798.5145(13)	5049.4429(20)	5281.2129(27)
B_v'	0.4219309(56)	0.4204722(36)	0.4180409(68)	0.416260(14)	0.415986(30)	0.414272(11)
$10^7 \times D_v'$	3.1061(66)	3.6246(44)	1.556(21)	6.37(10)	2.79(13)	2.639(53)
$10^{10} \times H_v'$	--	0.01049(17)	-0.3234(24)	-2.435(32)	-0.338(27)	-0.1991(98)
B_v''	0.42666973(57)	0.4233284(35)	0.4207397(41)	0.418365(12)	0.416036(27)	0.413793(86)
$10^7 \times D_v''$	7.0923(68)	5.9670(37)	5.6440(62)	5.493(44)	5.378(84)	5.206(21)

Note. The numbers in parentheses are one standard deviation in the last digit.

stants do not have a constant successive difference, indicating that a large γ_e is required in the ground state. This is a manifestation of the distant interaction of the $X^1\Sigma^+$ state with the $A^1\Sigma^+$ state (*6*). The ground state centrifugal distortion constants of the different vibrational levels are affected in a similar manner by these interactions.

The excited state rotational constants, however, vary in a more erratic manner than those in the ground state because of the presence of several local and global perturbations. There are at least three excited states, $^3\Sigma^+$, $^3\Pi$, and $^1\Pi$, lying near the $A^1\Sigma^+$ state which could be responsible for these perturbations. From the present work it is impossible to determine the exact nature of the perturbing states.

The equilibrium rotational constants for the ground and excited states estimated from the data listed in Table II are provided in Table III. In the absence of any off-diagonal bands, we have used the ground state vibrational constant reported by Shim

TABLE III

Equilibrium Constants (in cm^{-1}) for the $A^1\Sigma^+$ and $X^1\Sigma^+$ States of YN.

Constants	$A^1\Sigma^+$	$X^1\Sigma^+$
B_e	0.42311(30)	0.42815(24)
α_e	0.00188(17)	0.00333(20)
γ_e	--	0.000134(33)
r_e(Å)	1.81477(64)	1.80405(50)

Note. The numbers in parentheses are one standard deviation in the last digit.

and Gingerich (*20*) in order to estimate the vibrational parameters for the excited state. Shim and Gingerich (*20*) obtained $\omega_e'' = 807$ cm^{-1}. We have determined the ground state anharmonicity constant $\omega_e x_e''$ to be 5.08 cm^{-1} from the Pekeris relation (*25*) using $B_e'' = 0.42815$ cm^{-1} and $\alpha_e'' = 0.00333$ cm^{-1}. From the band origins of 0–0, 1–1, and 2–2 bands we obtain $(\omega_e' - \omega_e'') = 392.963$ cm^{-1} and $\omega_e x_e' - \omega_e x_e'' = 23.34$ cm^{-1}, resulting in $\omega_e' = 1200$ cm^{-1} and $\omega_e x_e' = 28.4$ cm^{-1}.

The vibrational constants in the excited state are considerably larger than those in the ground state although the rotational constants are very similar. Similar results were obtained from the $A^1\Sigma^+$–$X^1\Sigma^+$ infrared transition of the isovalent ScN (*6*). The large magnitude for $\Delta\omega_e$ and $\Delta\omega_e x_e$ result from the strong interactions between the ground and the excited state. As a test we used the B_0 and D_0 constants in the Kratzer relation (*25*) to predict the vibrational constants in these states. The Kratzer relationship predicts $\omega_e'' = 661$ cm^{-1} and $\omega_e' = 983$ cm^{-1}. This provides $(\omega_e' - \omega_e'') = 322$ cm^{-1}, which agrees well with the value of 346.28 cm^{-1} obtained in the present work. In fact the value of $\omega_e'' = 661$ cm^{-1} obtained in this manner is probably more reliable than the 807 cm^{-1} value determined by ab initio calculation (*20*).

The equilibrium constants obtained in this work have been used to calculate the Franck–Condon factors in the $A^1\Sigma^+$–$X^1\Sigma^+$ transition of YN provided in Table IV. The relative intensity of the observed bands agrees reasonably well with the predictions based on the calculated Franck–Condon factors. The Franck–Condon factors for the off-diagonal bands are very small in magnitude and none of the $\Delta v \neq 0$ bands were observed in our spectra.

CONCLUSION

We have observed the $A^1\Sigma^+$–$X^1\Sigma^+$ transition of YN molecule by infrared Fourier transform emission spectroscopy. This transition is analogous to the infrared transition of ScN. The rotational analysis of six bands involving vibrational levels up to $v = 5$ in the ground and excited state provides equilibrium constants for these states. Bands with $v' = 1$–5 are affected by perturbations from unknown electronic states. The ground state bond length of 1.80405(50) Å agrees well with the theoretical value of

TABLE IV

The Franck–Condon Factors for the $A^1\Sigma^+$–$X^1\Sigma^+$ System of YN

v' v''	0	1	2	3	4	5
0	0.9710	0.0095	0.0187	0.0005	0.0001	0.0000
1	0.0125	0.9376	0.0053	0.0436	0.0008	0.0003
2	0.0157	0.0100	0.9036	0.0008	0.0689	0.0006
3	0.0000	0.0402	0.0026	0.8657	0.0004	0.0906
4	0.0006	0.0000	0.0638	0.0004	0.8245	0.0047
5	0.0000	0.0021	0.0013	0.0779	0.0106	0.7806

1.7886 Å obtained by Shim and Gingerich (*20*) and is slightly longer than that of YO (*22*) [$r_e'' = 1.7900$ Å], consistent with multiple bonding. There have been no previous observations of the YN molecule.

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