Fourier transform emission spectroscopy of ScN

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The near-infrared electronic emission spectrum of ScN has been observed in the 1.6–1.8 μm spectral region using a Fourier transform spectrometer. The three bands with origins at 5820.0944(5), 6051.2858(20), and 6266.1290(13) cm^{-1} have been assigned as the 0-0, 1-1, and 2-2 bands of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ electronic transition. The principal equilibrium molecular constants for the ground state obtained from a fit of the observed lines are $B_e'' = 0.554\,609(17)$ cm^{-1}, $r_e'' = 1.687\,23(3)$ Å and the corresponding values for the excited state are $B_e' = 0.549\,277(17)$ cm^{-1}, $r_e' = 1.695\,40(3)$ Å. Although ScN is a well-known refractory solid, our work is the first observation of the gas-phase ScN molecule.

INTRODUCTION

ScN solid is a hard refractory, electrically conducting material with a NaCl-type crystal structure.[1,2] It can be made by the high-temperature reaction of Sc metal with N_2 or NH_3. However, until the work described here, no gas-phase observations of the ScN molecule have been reported.

Although transition-metal-oxide molecules are relatively well characterized,[3] few metal nitrides are known. For example, some analyses for all of the 3d transition metal oxides are available,[4] but the only 3d metal nitrides for which data are published are TiN (Refs. 5–12) and VN (Refs. 13 and 14). Gingerich[15] has studied some metal nitrides by mass spectrometry and predicts, on the basis of empirical correlations, a strong ScN bond of about 112 kcal/mol.

Fortunately there is an excellent *ab initio* calculation by Kunze and Harrison[16] which predicts that ScN has a formal triple bond and an $X\,^1\Sigma^+$ ground state. The previous calculations by Jeung and Koutecky[17] predicted only weak bonding for ScN. This conclusion seems very unlikely since ScN is isoelectronic with the strongly bound CaO (Refs. 18–23) molecule.

We report here on the first spectroscopic detection of the ScN molecule. ScN was made in Sc hollow cathode operated with Ne gas and a trace of N_2. The $A\,^1\Sigma^+ - X\,^1\Sigma^+$ electronic transition was found near 6000 cm^{-1}. The assignment was made by comparison with the analogous transition in the isoelectronic CaO molecule and with the help of the *ab initio* calculation of Kunze and Harrison.[16]

EXPERIMENT

The ScN molecule was made in a hollow cathode lamp. The bands attributed to this species were observed in two separate experiments. In the first experiment two very weak bands were observed in the 1.6–1.8 μm region when the lamp was operated at 250 V, 260 mA current, and 4.0 torr of Ne gas. These bands disappeared when H_2 or D_2 was added to the lamp in an attempt to see the ScH and ScD molecules. None of these bands correspond to the known bands of ScO

(Refs. 23–28) and transitions of ScO are not expected to lie in this spectral region. We suspected ScN as the carrier after the most likely impurities were eliminated as candidates.

In the second experiment the Sc hollow cathode was operated at 220 V and 200 mA current with a pressure of 5.2 torr of Ne and 0.1 torr of added N_2. This time the new bands were observed with approximately five times greater intensity. The chemical evidence thus pointed to ScN as the carrier of the new bands. Presumably there was a trace of N_2 in the system during the first experiment or, more likely, some ScN impurity was sputtered from the cathode surface.

The emission from the hollow cathode was observed with the Fourier transform spectrometer associated with the McMath solar telescope of the National Solar Observatory at Kitt Peak. The InSb detectors and silicon filters restricted the band pass to the 1800–9000 cm^{-1} spectral region. In the second experiment a total of eight scans were coadded in 55 min of integration at an unapodized resolution of 0.02 cm^{-1}.

The spectra were calibrated using Ne atomic lines.[29] The absolute accuracy of the calibration of the wave-number scale is expected to be better than ± 0.001 cm^{-1}. The observed linewidth of 0.025 cm^{-1} for ScN with a maximum
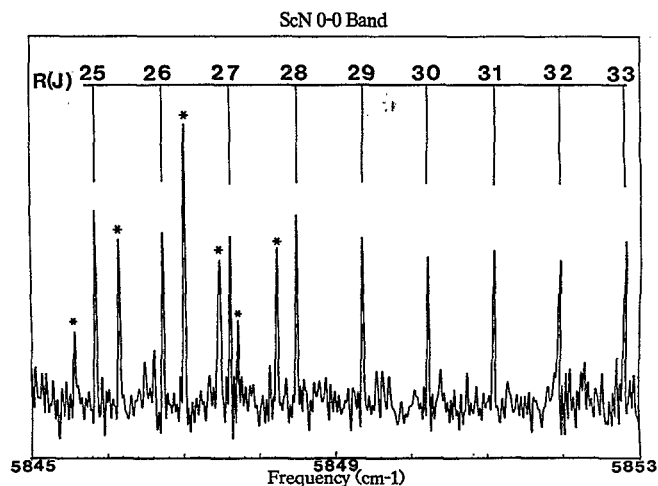

FIG. 1. A portion of the R branch of the 0-0 band of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ transition of ScN. The lines marked by asterisks are due to the N_2 molecule.

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TABLE I. Observed lines of the A-X system of ScN (in cm^{-1})

| J | 0-0 BAND | | | | 1-1 BAND | | | | 2-2 BAND | | | |
	R(J)	O–C	P(J)	O–C	R(J)	O–C	P(J)	O–C	R(J)	O–C	P(J)	O–C
2	5823.3562	−0.0013	5817.8827	0.0082								
3	5824.4311	0.0038	5816.7448	−0.0064								
4												
5	5826.5505	0.0103	5814.4801	0.0018								
6	5827.5849	0.0015	5813.3254	−0.0034	6058.4505	−0.3432			6273.6257	0.0059		
7	5828.6104	−0.0073	5812.1704	−0.0003	6059.5355	−0.3051			6274.6711	0.0024	6258.3808	−0.0007
8	5829.6470	0.0037	5811.0163	0.0122	6060.5991	−0.2821	6041.9688	−0.3541			6257.2522	−0.0022
9	5830.6585	−0.0017	5809.8325	0.0035	6061.6451	−0.2704	6040.8759	−0.2989			6256.1269	0.0045
10	5831.6701	0.0016	5808.6462	0.0006	6062.7127	−0.2308	6039.7358	−0.2850	6277.7870	0.0025	6254.9850	−0.0006
11	5832.6686	0.0003	5807.4544	0.0004	6063.7695	−0.1959	6038.5992	−0.2618	6278.8076	−0.0051		
12	5833.6587	−0.0009	5806.2584	0.0041	6064.7940	−0.1872	6037.4590	−0.2364	6279.8343	−0.0015	6252.7006	0.0029
13	5834.6469	0.0043	5805.0467	0.0001	6065.8247	−0.1662	6036.3211	−0.2031	6280.8530	−0.0011	6251.5501	0.0032
14	5835.6204	0.0031	5803.8303	−0.0008	6066.8497	−0.1450	6035.1689	−0.1787	6281.8548	−0.0124	6250.3789	−0.0128
15	5836.5892	0.0052	5802.6077	−0.0003	6067.8686	−0.1240	6034.0003	−0.1652			6249.2316	−0.0004
16	5837.5468	0.0041	5801.3778	0.0004	6068.8781	−0.1067	6032.8358	−0.1424	6283.8687	−0.0103	6248.0641	−0.0040
17	5838.4948	0.0012	5800.1323	−0.0072	6069.8750	−0.0963	6031.6542	−0.1316			6246.8994	−0.0006
18	5839.4381	0.0013	5798.8946	0.0002	6070.8745	−0.0778	6030.4866	−0.1018	6285.8691	−0.0026	6245.7291	0.0012
19	5840.3714	−0.0011	5797.6430	0.0006	6071.8599	−0.0679	6029.2977	−0.0885	6286.8583	−0.0029	6244.5496	−0.0022
20	5841.2965	−0.0044	5796.3829	−0.0008	6072.8467	−0.0513			6287.8398	−0.0063	6243.3697	−0.0023
21	5842.2202	−0.0020	5795.1176	−0.0009	6073.8222	−0.0409	6026.9004	−0.0676	6288.8236	−0.0032	6242.1879	−0.0007
22	5843.1372	0.0008	5793.8462	−0.0008	6074.7869	−0.0363	6025.6926	−0.0598	6289.8050	0.0019	6240.9959	−0.0057
23	5844.0458	0.0018	5792.5647	−0.0047	6075.7495	−0.0289	6024.4918	−0.0409	6290.7764	0.0010	6239.8081	−0.0033
24	5844.9443	−0.0007	5791.2856	−0.0004	6076.7100	−0.0190	6023.2742	−0.0349	6291.7501	0.0066	6238.6241	0.0062
25	5845.8382	−0.0015	5789.9949	−0.0021	6077.6633	−0.0117	6022.0552	−0.0265	6292.7188	0.0110	6237.4194	−0.0019
26	5846.7273	−0.0011	5788.7026	−0.0001	6078.6029	−0.0137	6020.8356	−0.0153	6293.6743	0.0060	6236.2332	0.0112
27	5847.6092	−0.0020	5787.4052	0.0018	6079.5549	0.0009	6019.6037	−0.0130	6294.6304	0.0052	6235.0207	0.0007
28	5848.4903	0.0019	5786.0974	−0.0020	6080.4882	0.0007	6018.3691	−0.0104	6295.5878	0.0091	6233.8206	0.0051
29	5849.3580	−0.0023	5784.7908	−0.0002	6081.4126	−0.0046	6017.1335	−0.0059	6296.5323	0.0036	6232.6092	0.0006
30	5850.2243	−0.0029	5783.4749	−0.0035	6082.3411	−0.0022	6015.8917	−0.0050	6297.4704	−0.0052	6231.4013	0.0016
31	5851.0887	−0.0006	5782.1615	−0.0004	6083.2690	0.0030	6014.6489	−0.0028	6298.4155	−0.0040	6230.1899	0.0011
32	5851.9445	−0.0025	5780.8445	0.0025	6084.1912	0.0056	6013.4046	0.0000	6299.3364	−0.0241	6228.9622	−0.0141
33	5852.8024	0.0020	5779.5169	−0.0020	6085.1044	0.0021	6012.1585	0.0029	6300.2352	−0.0637	6227.7576	−0.0045
34	5853.6492	−0.0009	5778.1934	0.0005	6086.0167	0.0004	6010.9088	0.0037	6303.3308	0.2311	6226.5256	−0.0211
35	5854.4930	−0.0032	5776.8609	−0.0036	6086.9275	−0.0004	6009.6575	0.0042	6304.1384	0.1091	6225.2705	−0.0598
36	5855.3358	−0.0033	5775.5333	−0.0007	6087.8375	0.0003	6008.4058	0.0054	6304.9952	0.0381	6221.9116	0.2347
37	5856.1774	−0.0018	5774.1989	−0.0029	6088.7473	0.0026	6007.1498	0.0029	6305.8588	−0.0247	6220.5651	0.1066
38	5857.0142	−0.0026	5772.8658	−0.0024	6089.6543	0.0039	6005.9011	0.0082	6306.6622	−0.1464	6219.2765	0.0362
39	5857.8511	−0.0011	5771.5339	0.0003	6090.5551	0.0003	6004.6416	0.0028			6217.9893	−0.0332
40	5858.6840	−0.0019	5770.1975	−0.0010	6091.4552	−0.0029	6003.3836	−0.0014			6216.6654	−0.1399
41	5859.5173	−0.0009	5768.8624	−0.0009	6092.3595	−0.0011	6002.1302	−0.0014				
42	5860.3474	−0.0021	5767.5304	0.0021	6093.2621	−0.0005	6000.8789	−0.0003				
43	5861.1814	0.0011	5766.1917	−0.0023	6094.1695	0.0052	5999.6247	−0.0032				
44	5862.0072	−0.0036	5764.8619	0.0010	6095.0052	−0.0010	5998.3774	−0.0008				
45	5862.8419	0.0002	5763.5261	−0.0034	6095.9669	−0.0016	5997.1262	−0.0042				
46	5863.6775	0.0043	5762.1981	−0.0020	6096.8669	−0.0046	5995.8834	−0.0014				
47	5864.5053	−0.0005	5760.8698	−0.0034	6097.7727	−0.0029	5994.6410	−0.0009				
48	5865.3385	−0.0015	5759.5536	0.0042	6098.6824	0.0013	5993.3974	−0.0046				
49	5866.1742	−0.0021	5758.2329	0.0038	6099.5894	0.0009	5992.1615	−0.0039				
50	5867.0191	0.0040	5756.9187	0.0059	6100.5067	0.0088	5990.9337	0.0010				
51	5867.8586	0.0018	5755.6049	0.0039	6101.4212	0.0113	5989.7045	0.0004				
52	5868.7105	0.0084	5754.2951	0.0007	6102.3253	0.0006	5988.4887	0.0086				
53	5869.5546	0.0032	5752.9952	0.0019	6103.2494	0.0066						
54	5870.4104	0.0053	5751.6979	−0.0004	6104.1652	0.0006	5986.0509	0.0032				
55	5871.2682	0.0043	5750.4178	0.0077	6105.0887	−0.0017	5984.8406	0.0006				
56	5872.1364	0.0082	5749.1279	−0.0012			5983.6381	−0.0005				
57	5872.9993	0.0006	5747.8611	0.0052	6106.9552	−0.0006	5982.4490	0.0050				
58	5873.8808	0.0050	5746.5983	0.0071	6107.8943	−0.0020	5981.2534	−0.0031				
59	5874.7611	0.0010	5745.3388	0.0034	6108.8277	−0.0147	5980.0789	0.0022				
60	5875.6531	0.0010	5744.0923	0.0031			5978.9065	0.0014				
61	5876.5535	0.0009	5742.8566	0.0033			5977.7274	−0.0147				
62	5877.4567	−0.0053	5741.6392	0.0110								
63	5878.3798	−0.0012	5740.4246	0.0101								
64	5879.3080	−0.0022	5739.2080	−0.0050								
65	5880.2481	−0.0020	5738.0185	−0.0058								
66	5881.2034	0.0019	5736.8442	−0.0047								
67	5882.1691	0.0041	5735.6830	−0.0047								
68	5883.1313	−0.0099	5734.5269	−0.0143								
69	5884.1239	−0.0068										

signal-to-noise ratio of 10 means the best unblended lines have a measurement precision of about ± 0.002 cm^{-1}.

RESULTS AND DISCUSSION

The interferograms were transformed to provide the spectrum in the frequency domain. The line frequencies were extracted from the spectrum using a data reduction program called PC-DECOMP. The peak positions were found by fitting a Voigt line-shape function to each feature using a nonlinear least-squares procedure.

Each band assigned to ScN consists of a single R and a single P branch, indicating that the transition has the characteristics of a $\Delta\Lambda = 0$ transition, probably $^1\Sigma^+ - {}^1\Sigma^+$. (See Fig. 1.) The most recent theoretical study of ScN by Kunze and Harrison[16] suggests that the ground state of this molecule is a triply bonded $X\,^1\Sigma^+$ state, Sc≡N. This state of ScN correlates to the excited $4s^13d^2$ (^4F and ^4P) configuration of Sc and the $2p^3$ (^4S) configuration of the N atom. The formal triple bond is made from $4s\sigma$, $3d\pi_x$, and $3d\pi_y$ orbitals on Sc bonding with the $2p\sigma$, $2p_x\pi$, and $2p_y\pi$ orbitals of N. The bonding σ molecular orbital is, in fact, a mixture of $4s\sigma$ and $3d\sigma$ Sc atomic orbitals with mainly $3d\sigma$ character at the short equilibrium internuclear separation of ScN. In fact, the orbitals on Sc are better described as $3d\sigma$, $3d\pi_x$, $3d\pi_y$ in the ground $X\,^1\Sigma^+$ state correlating to the Sc $3d^3$ configuration.[16] The σ orbital is only very weakly bonding so the first excited state, $a\,^3\Sigma^+$, is made unpairing the bonding pair of σ electrons to make a diradical ·Sc=N·. The formal double bond is of the π_x, π_y type with the unpaired electrons in $4s\sigma$ Sc and $2p\sigma$ N orbitals.[16]

The $a\,^3\Sigma^+ - X\,^1\Sigma^+$ separation is predicted to be 2600 cm^{-1}. Associated with the $a\,^3\Sigma^+$ state must be a singlet state of the same nominal configuration but lying higher in energy. This state must be the $A\,^1\Sigma^+$ state observed in our work at $\sim$6000 cm^{-1} but, unfortunately, the location of the $A\,^1\Sigma^+$ state was not calculated by Kunze and Harrison.[16]

In addition to the $A\,^1\Sigma^+$, $a\,^3\Sigma^+$ pair of states, Kunze and Harrison[16] predicted a low-lying $A'\,^1\Pi$ and $b\,^3\Pi$ pair of states located at 4500 and 4200 cm^{-1} above the ground state. These two states are also double bonded ·Sc=N· states but are σ, π bonded rather than π, π bonded. The σ bond is formed from Sc $3d\sigma$ and N $2p\sigma$ while the π bond is from Sc $3d\pi_x$ and N $2p\pi_x$. The two unpaired electrons of the $b\,^3\Pi$ state reside in the nonbonding Sc $4s\sigma$ and N $2p\pi_y$ orbitals.[16]

The low-lying ScN states bear a remarkable resemblance to the corresponding states in the isoelectronic CaO (Refs. 18–23) molecule. For CaO the $A\,^1\Sigma^+$, $b\,^3\Sigma^+$, $A'\,^1\Pi$, and $a\,^3\Pi$ states are located at 11 549, 9472, 8609, and 8276 cm^{-1}, respectively,[20] above the ground $X\,^1\Sigma^+$ state. We, therefore, conclude that we are observing the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ transition in ScN analogous to the corresponding CaO transition. Although the $A\,^1\Sigma^+$ state probably lies above $A'\,^1\Pi$ state, we refrain from renaming the $A\,^1\Sigma^+$ state because of the analogy with CaO and because we have not located the $A'\,^1\Pi$ state yet.

The rotational assignments of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ bands were not straight forward because the first lines were not observed. The strongest of the three bands was assumed

to be the 0-0 vibrational band with the weaker bands assigned as the 1-1 and 2-2 bands. The rotational constants in both upper and lower states were similar in magnitude so vibrational bands with $\Delta v \neq 0$ were not expected (or observed) on the basis of the Franck–Condon principle.

In the 0-0 band there were three possible rotational assignments each producing identically good fits of the line positions using the usual rotational energy-level expression:

$$F(J) = BJ(J+1) - D\,[J(J+1)]^2.$$

The correct assignment was based on the size of the D values in the $X\,^1\Sigma^+$ and $A\,^1\Sigma^+$ states. Comparison of the observed D's with the CaO $D'' = 6.58 \times 10^{-7}$ cm^{-1} and with an estimated $D'' = 9.8 \times 10^{-7}$ cm^{-1} (calculated using the Kratzer relationship, $D = 4B^3/\omega^2$, with ab initio[16] $B = 0.505$ cm^{-1} and $\omega_e = 726$ cm^{-1}) eliminated all of the possibilities but one. The three missing lines were $R(0)$, $R(1)$, and $P(1)$ with $B'' = 0.5528$ cm^{-1} and $D'' = 10.5 \times 10^{-7}$ cm^{-1}. The agreement between experimental and ab initio B values is not as good as we expected but still satisfactory.

The 1-1 band was weaker in intensity than the 0-0 band and even more difficult to assign because of additional missing lines. Moreover, all of the low J transitions ($J' < 27$) were perturbed in the excited state. However, by using the ground-state combination differences and requiring reasonable D and α_e values a unique assignment was achieved. The exact nature of the perturbing state is unclear but in view of the three nearby electronic states there is no shortage of possibilities.

The next band with an origin at 6266.1290(13) cm^{-1} was assigned as the 2-2 band of the same transition. The observed rotational lines were assigned in the same manner as described for the 0-0 and 1-1 bands. This band is also perturbed for $J' \geqslant 33$. The observed ground-state combination differences corresponding to the perturbed transitions were also included in the final fits of the line positions of the 1-1 and 2-2 bands. The line positions of the 0-0, 1-1, and 2-2 bands are provided in Table I while the spectroscopic constants are in Table II.

The difference in the band origins of the 0-0, 1-1, and 2-2 bands indicates that the vibrational constants of the excited state are considerably bigger than in the ground electronic state. From the band origins $\Delta\omega = 247.54$ cm^{-1} and $\Delta\omega_e x_e = 8.17$ cm^{-1} are derived.

The equilibrium molecular constants were derived by

TABLE II. Rotational constants obtained for the A-X bands of ScN (in cm^{-1}). The numbers in parentheses are one standard deviation in the last digit.

Constants	0-0 Band	1-1 Band	2-2 Band
$T_{v',v''}$	5820.0944(5)	6051.2858(20)	6266.1290(13)
B'_v	0.548 306 1(76)	0.545 937 1(88)	0.542 997(21)
$10^7 \times D'_v$	6.361(13)	6.929(19)	7.47(10)
B''_v	0.552 763 1(76)	0.549 145 6(85)	0.545 629(20)
$10^7 \times D''_v$	10.508(13)	10.121(18)	9.983(86)

TABLE III. Equilibrium constants for the $A\,{}^1\Sigma^+$ and $X\,{}^1\Sigma^+$ states of ScN (in cm^{-1}). The numbers in parentheses are one standard deviation in the last digit.

Constants	$A\,{}^1\Sigma^+$	$X\,{}^1\Sigma^+$
B_e	0.549 277(17)	0.554 609(17)
α_e	0.001 798(30)	0.003 718(30)
γ_e	$-$0.000 286(14)	0.000 050(14)
$10^7 \times D_e$	6.078 3(52)	10.685(54)
$10^8 \times \beta_e$	5.661(53)	$-$3.64(54)
r_e (Å)	1.695 40(3)	1.687 23(3)

using the observed parameters for different vibrational levels with the usual expressions:

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \gamma_e (v + \tfrac{1}{2})^2,$$

$$D_v = D_e + \beta_e (v + \tfrac{1}{2}).$$

The constants thus obtained are listed in Table III. The equilibrium internuclear separations were calculated to be 1.687 23 Å in the $X\,{}^1\Sigma^+$ state and 1.695 40 Å in the $A\,{}^1\Sigma^+$ state. The ab initio[16] value of 1.786 Å in the $X\,{}^1\Sigma^+$ state agrees only moderately well with the experimental value. The ab initio[16] value for $\alpha_e = 0.0003$ cm^{-1} for the $X\,{}^1\Sigma^+$ state also deviates from the experimental value of 0.003 72 cm^{-1}. The observed α_e'' value is consistent with the values calculated for the other states in ScN and with the value of 0.003 38 cm^{-1} for CaO.[23]

The Kratzer relationship predicts $\omega_e'' = 795$ cm^{-1} and $\omega_e' = 1045$ cm^{-1} computed from the B_e and D_e values in Table III. The predicted $\Delta\omega = 250$ cm^{-1} agrees well with the observed $\Delta\omega = 248$ cm^{-1} obtained from the band origins.

The $X\,{}^1\Sigma^+$ and $A\,{}^1\Sigma^+$ states have nearly identical bond lengths but rather different vibrational frequencies. As in CaO,[30] it seems likely that the $X\,{}^1\Sigma^+$ and $A\,{}^1\Sigma^+$ are not well represented by single configurations. In fact, because of the equal bond lengths, the $A\,{}^1\Sigma^+$ and $X\,{}^1\Sigma^+$ states are likely to be nearly equal mixtures of two configurations, correlating to Sc $4s^1 3d^2$ and Sc $3d^3$. The rather different ω_e's in the $X\,{}^1\Sigma^+$ and $A\,{}^1\Sigma^+$ states are, therefore, a consequence of the avoided crossing between the two potential curves.

CONCLUSION

We have observed the $A\,{}^1\Sigma^+ - X\,{}^1\Sigma^+$ system of ScN in emission using a Fourier transform spectrometer. Although solid ScN is well known, this work represents the first detection in the gas phase. The rotational analysis of the 0-0, 1-1, and 2-2 bands provide equilibrium molecular constants and bond lengths. The bond distance of 1.687 23 Å in the ground state is slightly longer than the 1.6683 Å found for ScO (Ref. 23) and is consistent with multiple bonding.

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