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 'Σ⁺ – X 'Σ⁺ electronic transition. The principal equilibrium molecular constants for the ground state obtained from a fit of the observed lines are $B_g = 0.554609(17)$ cm⁻¹, $r_g = 1.68723(3)$ Å and the corresponding values for the excited state are $B_e = 0.549277(17)$ cm⁻¹, $r_e = 1.69540(3)$ 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. It can be made by the high-temperature reaction of Sc metal with N₂ or NH₃. 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, few metal nitrides are known. For example, some analyses for all of the 3d transition metal oxides are available, but the only 3d metal nitrides for which data are published are TiN (Refs. 5–12) and VN (Refs. 13 and 14). Gingerich 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 which predicts that ScN has a formal triple bond and an X 'Σ⁺ ground state. The previous calculations by Jeung and Koutecky 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 N₂. The A 'Σ⁺ – X 'Σ⁺ 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.

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 H₂ or D₂ 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 N₂. 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 N₂ 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.

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
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<td>2</td>
<td>5823.3562</td>
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<td>5817.8627</td>
<td>0.0082</td>
<td>6273.6257</td>
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<td>3</td>
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<td>0.0038</td>
<td>5816.7448</td>
<td>0.0064</td>
<td>6277.8870</td>
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TABLE I. Observed lines of the A-X system of ScN (in cm$^{-1}$)
signal-to-noise ratio of 10 means the best unbinned 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-DECIMP. 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 Δν = 0 transition, probably ¹Σ⁺ − ¹Σ⁺. (See Fig. 1.) The most recent theoretical study of ScN by Kunze and Harrison suggests that the ground state of this molecule is a triply bonded X ¹Σ + state, Sc=N=N. This state of ScN correlates to the excited 4s¹3d¹ (4F and 4P) configuration of Sc and the 2p[3/2](4S) configuration of the N atom. The formal triple bond is formed from 4sč, 3d₁č, and 3d₃č orbitals on Sc bonding with 2p₂č, 2p₃č, and 2p₄č orbitals of N. The bonding σ molecular orbital is, in fact, a mixture of 4σ₁, 3d₃, and 3d₄ Sc atomic orbitals with mainly 3dσ character at the short equilibrium internuclear separation of ScN. In fact, the orbitals on Sc are better described as 3dσ, 3d₃č, 3d₄č, in the ground X ¹Σ + state correlating to the Sc 3d³ configuration. The σ orbital is only very weakly bonding so the first excited state, a ³Σ⁺, is made unpairing the bonding pair of σ electrons to make a diradical Sc=⋯N. The formal double bond is of the σ, σ, type with the unpaired electrons in 4σ₁ Sc and 2p₂ N orbitals.

The ¹Σ⁺ − X ¹Σ + separation is predicted to be 2600 cm⁻¹. Associated with the a ¹Σ + state must be a singlet state of the same nominal configuration but lying higher in energy. This state must be the a ¹Σ + state observed in our work at ~6000 cm⁻¹ but, unfortunately, the location of the A ¹Σ + state was not calculated by Kunze and Harrison.

In addition to the A ¹Σ +, a ¹Σ + pair of states, Kunze and Harrison predicted a low-lying A ¹Π + and b ¹Π + pair of states located at 4500 and 4200 cm⁻¹ above the ground state. These two states are also double bonded Sc=N=N states but are σ, π bonded rather than π, π bonded. The σ bond is formed from Sc 3dσ and N 2pσ while the π bond is from Sc 3d₃π and N 2p₃π. The two unpaired electrons of the b ¹Π state reside in the nonbonding Sc 4σ and N 2p₄π orbitals.

The low-lying ScN states bear a remarkable resemblance to the corresponding states in the isoelectronic CaO (Ref. 18-23) molecule. For CaO the A ¹Σ +, b ¹Σ +, A ¹Π +, and a ¹Π states are located at 11549, 9472, 8609, and 8276 cm⁻¹, respectively, above the ground X ¹Σ + state. We, therefore, conclude that we are observing the A ¹Σ + − X ¹Σ + transition in ScN analogous to the corresponding CaO transition. Although the A ¹Σ + state probably lies above A ¹Π, we refrain from renaming the A ¹Σ + state because of the analogy with CaO and because we have not located the A ¹Π state yet.

The rotational assignments of the A ¹Σ + − X ¹Σ + bands were not straightforward 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 Δν≠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.

\[ F(J) = B(J + 1) - D[J(J + 1)]^2. \]

The correct assignment was based on the size of the D values in the X ¹Σ + and A ¹Σ + states. Comparison of the observed D values with the CaO D values was 6.58 x 10⁻⁷ cm⁻¹ and with an estimated D value 9.8 x 10⁻⁷ cm⁻¹ (calculated using the Kratzer relationship, D = 4B²/ω², with ab initio B = 0.505 cm⁻¹ and ω = 726 cm⁻¹) eliminated all of the possibilities but one. The three missing lines were R(0), R(1), and R(2) with B = 0.528 cm⁻¹ and D = 10.5 x 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 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' > 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 larger than in the ground electronic state. From the band origins Δω = 247.54 cm⁻¹ and Δω₁,₂ = 8.17 cm⁻¹ are derived.

The equilibrium molecular constants were derived by

<table>
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<tr>
<th>Constants</th>
<th>0-0 Band</th>
<th>1-1 Band</th>
<th>2-2 Band</th>
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<tr>
<td>T σ⁺⁺⁺⁺</td>
<td>5820.0944(5)</td>
<td>6051.2588(20)</td>
<td>6266.1290(13)</td>
</tr>
<tr>
<td>B σ⁺⁺⁺⁺</td>
<td>0.548 306 1(76)</td>
<td>0.545 937 1(88)</td>
<td>0.542 997(21)</td>
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<tr>
<td>10²σ⁺⁺⁺⁺</td>
<td>6.361(13)</td>
<td>6.929(19)</td>
<td>7.47(10)</td>
</tr>
<tr>
<td>R σ⁺⁺⁺⁺</td>
<td>0.552 763 1(76)</td>
<td>0.549 145 6(85)</td>
<td>0.545 699(70)</td>
</tr>
<tr>
<td>10²R σ⁺⁺⁺⁺</td>
<td>10.508(13)</td>
<td>10.121(18)</td>
<td>9.983(86)</td>
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using the observed parameters for different vibrational levels with the usual expressions:

\[ B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2, \]
\[ D_v = D_e + \beta_e (v + \frac{1}{2}). \]

The constants thus obtained are listed in Table III. The equilibrium internuclear separations were calculated to be 1.687 23 Å in the \( X' \Sigma^+ \) state and 1.695 40 Å in the \( A' \Sigma^+ \) state. The \textit{ab initio}\(^\text{16}\) value of 1.786 Å in the \( X' \Sigma^+ \) state agrees only moderately well with the experimental value. The \textit{ab initio}\(^\text{16}\) value for \( \alpha_e = 0.0003 \text{ cm}^{-1} \) for the \( X' \Sigma^+ \) state also deviates from the experimental value of 0.003 72 cm\(^{-1} \). The observed \( \alpha_e^\text{w} \) 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.\(^\text{23}\)

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

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

**CONCLUSION**

We have observed the \( A' \Sigma^+ - X' \Sigma^+ \) 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.

**ACKNOWLEDGMENTS**

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| TABLE III. Equilibrium constants for the \( A' \Sigma^+ \) and \( X' \Sigma^+ \) states of ScN (in \text{ cm}^{-1} ). The numbers in parentheses are one standard deviation in the last digit. |
|---|---|---|
| Constants | \( A' \Sigma^+ \) | \( X' \Sigma^+ \) |
| \( B_e \) | 0.549 277(17) | 0.554 091(17) |
| \( \alpha_e \) | 0.001 798(30) | 0.003 718(30) |
| \( \gamma_e \) | 0.0000 286(14) | 0.0000 050(14) |
| \( 10^3 \times D_e \) | 6.078 3(52) | 10.685(54) |
| \( 10^4 \times \beta_e \) | 5.661(53) | 3.64(54) |
| \( r_e (\text{Å}) \) | 1.692 40(3) | 1.687 23(3) |

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\(^1\)J. P. Dismukes, W. M. Yim, and V. S. Ban, J. Crystal Growth 13/14, 365 (1972).
\(^22\)D. P. Baldwin, J. B. Norman, R. A. Soltz, A. Sur, and R. W. Field, J. Mol. Spectrosc. 139, 39 (1990), and references therein.