Fourier transform emission spectroscopy of the $B\ ^1\Pi - X\ ^1\Sigma^+$, $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$, and $G\ ^1\Pi - X\ ^1\Sigma^+$ systems of ScH and ScD

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The emission spectra of ScH and ScD have been observed in the 380 nm–2.5 μm spectral region using a Fourier transform spectrometer. The molecules were excited in a scandium hollow cathode lamp operated with neon gas and a trace of hydrogen or deuterium. Three transitions with a common lower state, assigned as the ground $X\ ^1\Sigma^+$ state, have been observed in the near infrared and visible regions. The ScH bands with 0–0 band origins at 5404, 13 574, and 20 547 cm^{-1} have been assigned as the $B\ ^1\Pi - X\ ^1\Sigma^+$, $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$, and $G\ ^1\Pi - X\ ^1\Sigma^+$ transitions, respectively. A rotational analysis of the 0–0, 1–1, 1–0, and 2–1 bands of the $B\ ^1\Pi - X\ ^1\Sigma^+$ system, the 0–0 and 1–1 bands of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ system and the 0–0 band of the $G\ ^1\Pi - X\ ^1\Sigma^+$ system has been obtained. The principal molecular constants for the $X\ ^1\Sigma^+$ state of ScH are $\Delta G(1/2) = 1546.9730(14)$ cm^{-1}, $B_e = 5.425\,432(48)$ cm^{-1}, $\alpha_e = 0.124\,802(84)$ cm^{-1} and $r_e = 1.775\,427(8)$ Å. The corresponding band systems of ScD have also been analyzed. A rotational analysis of the 0–0, 1–1, and 1–0 bands of the $B\ ^1\Pi - X\ ^1\Sigma^+$ system, the 0–0, 1–1, 0–1, and 1–2 bands of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ system and the 0–0 band of the $G\ ^1\Pi - X\ ^1\Sigma^+$ system has been obtained. The equilibrium molecular constants determined for the ground state of ScD are $\omega_e = 1141.2650(31)$ cm^{-1}, $\omega_e x_e = 12.3799(15)$ cm^{-1}, $B_e = 2.787\,432(41)$ cm^{-1}, $\alpha_e = 0.045\,321(73)$ cm^{-1}, and $r_e = 1.771\,219(13)$ Å. The ScH assignments are supported by recent theoretical predictions made by Anglada *et al.* [Mol. Phys. **66**, 541 (1989)] as well as the experimental results available for ScF and the isovalent YH and LaH molecules. Although some unassigned bands have been attributed to ScH and ScD by previous workers, there have been no previous analyses of ScH or ScD spectra. © *1996 American Institute of Physics.* [S0021-9606(96)02631-1]

INTRODUCTION

The electronic spectra of simple transition metal-containing molecules provide the necessary data required to understand the role of d electrons in chemical bond formation. In recent years, there has been an increasing number of theoretical and experimental studies of transition metal-containing diatomics and several review papers have been published on the oxides[1] and the hydrides.[2–5] Prediction of the spectroscopic properties of these molecules has been a challenging job for theoreticians since they possess a large number of closely packed electronic states with large spin multiplicites and large orbital angular momenta. Both relativistic and electron correlation effects need to be taken into account in the *ab initio* studies of these molecules. Several recent high level *ab initio* calculations of transition metal hydride properties, for example, on FeH,[6] CoH,[7] LaH,[8] YH,[9] and HfH,[10] have proved to be very useful in the interpretation of the complex spectra.[11–16]

Transition metal-containing molecules are also of astrophysical importance and several transition metal oxides and hydrides have been observed in the spectra of the sun and other stars. For example, TiH[17] and FeH[18,19] have been iden-

tified in the spectra of M-type stars; NiH[20] and CrH[21] have been seen in the spectra of sunspots.

The heavier members of the group IIIB hydride family, LaH and YH, have been characterized by theoretical[8,9] and experimental[13,14] studies. Recently, we have reported the observation of new transitions of LaH[13] and YH[14] (as well as LaD[13] and YD[15]) in the red and near infrared regions. These observations are consistent with the theoretical predictions of Das and Balasubramanian[8] for LaH and Balasubramanian and Wang[9] for YH and they support the identification of the ground state as a $^1\Sigma^+$ state with a low-lying $^3\Delta$ state.

There are some previous absorption and emission observations of ScH and ScD. In 1973 Smith[3] recorded the absorption spectra of ScH and ScD using a plane grating spectrograph. In this experiment ScO powder was shock heated in hydrogen/argon or deuterium/argon mixtures and absorption spectra were observed using a flash lamp as the continuum source. Smith[3] observed a few complex bands mainly in the visible region of spectrum. Bernard *et al.*[22] also observed ScH and ScD spectra but they used a composite-wall hollow cathode lamp and found some additional bands in the near infrared. The most notable new bands were found at 789.74 and 860.35 nm for ScH and 859.6 nm for ScD. No assignment of the ScH and ScD bands was possible because of limited resolution, poor signal-to-noise ratios and the

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complexity of these bands. The only other experimental information available for ScH is the bond dissociation energy of 205 ± 17 kJ/mol (49 ± 4 kcal/mol).[23]

ScH is the simplest transition metal-containing molecule so it has been the target of many theoretical calculations in the past decade.[24–29] The CI calculations of Bauschlicher and Walsh,[24] Anglada et al.[25] and Bruna et al.[26] all predict the ground state of ScH as a $^1\Sigma^+$ state with a close-lying $^3\Delta$ state. In addition Chong et al.[26] have predicted the dipole moments for many hydrides of the $3d$ and $4d$ transition metals. In a recent paper Anglada et al.[29] have reported the results of their extensive MRD-CI calculations on the electronic states of ScH related to the $3d^14s^2$, $3d^24s^1$, and $3d^14s^14p^1$ configurations of the Sc atom. They have predicted the spectroscopic properties of numerous excited electronic states as well as the transition dipole moments between many of the low-lying states.

Guided by our recent success with YH and LaH we decided to investigate the high resolution spectra of ScH from the visible to the near infrared. We have observed many bands with complex rotational structure throughout the entire region observed. These successful experiments on ScH and ScD were preceded by several failures that resulted in the discovery of ScN.[30] The new observations are consistent with the theoretical predictions of Anglada et al.[29] In this paper we report on the analysis of three relatively strong groups of bands near 5404, 13 574, and 20 547 cm^{-1}, assigned as the $B\,^1\Pi-X\,^1\Sigma^+$, $C\,^1\Sigma^+-X\,^1\Sigma^+$, and $G\,^1\Pi-X\,^1\Sigma^+$ transitions, respectively. Our assignments were made with the help of the *ab initio* calculations and the experimental results for the ScF, YH, and LaH molecules.

EXPERIMENT

The spectra were recorded using the 1 m Fourier transform spectrometer associated with the McMath–Pierce Solar Telescope of the National Solar Observatory. The spectra of ScH and ScD were produced in a scandium hollow cathode lamp. The cathode was prepared by inserting a 0.25 mm thick foil of scandium metal into a hole in a copper block in such a way that there was uniform contact between the scandium foil and the copper walls. The lamp was operated at 400 V with 570 mA current. A slow steady flow of 1.5 Torr Ne and about 40 m Torr of H_2 or D_2 was maintained through the lamp.

The spectra of ScH in the 3500–26 000 cm^{-1} range were recorded in three experiments. The 3500–9150 cm^{-1} region was recorded using InSb detectors, cold green uranium glass filters with ten scans coadded in about one hour of integration. For the 9100–17 000 cm^{-1} region the spectrometer was operated with Si-diode detectors and a red pass filter (OG570) while for the 15 000–26 000 cm^{-1} region a $CuSO_4$ filter was used. Again ten scans were coadded in about 1 h of integration in both of these experiments. The spectrometer resolution was set at 0.02 cm^{-1} for all experiments.

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature.

In addition to the ScH and ScD bands, the spectra also contained ScN bands in the 5700–6500 cm^{-1} region which have been assigned previously to the $A\,^1\Sigma^+-X\,^1\Sigma^+$ transition.[30] The spectra also contained many Sc and Ne atomic lines and the measurements of the Ne atomic lines made by Palmer and Engleman[31] have been used for calibration. The absolute accuracy of the wave number scale is expected to be better than ±0.002 cm^{-1}. However, the measurements of the weaker and blended lines are expected to be less accurate depending on the extent of blending and line broadening, and the signal-to-noise ratio.

OBSERVATION AND ANALYSIS

The spectra of ScH and ScD have been recorded in the 380 nm–2.5 μm spectral region. Numerous bands have been observed and many are very complex in appearance. The most prominent ScH bands have heads at 5463, 11 620, 12 290, 13 620, and 20 550 cm^{-1} with some weaker Q branches at 12 660 and 16 845 cm^{-1}. Some weak ScH/ScD bands near 17 900 cm^{-1} were also observed by Smith[3] in absorption. Smith[3] did not record spectra in the red and infrared regions.

The band at 558 nm (17 900 cm^{-1}) was also observed in emission by Bernard et al.[22] as well as some complex bands in the 780–861 nm region. In this interval the ScH and ScD bands at 860.35 nm (11 620 cm^{-1}) and 859.6 nm (11 630 cm^{-1}), respectively, were the most intense and they appear strongly in our spectra. In our previous studies of YH and LaH we have observed a $^3\Phi-a\,^3\Delta$ transition at 11 500 cm^{-1} for YH and 6238 cm^{-1} for LaH. The appearance of the ScH bands near 11 620 cm^{-1} is very similar to the analogous $^3\Phi-a\,^3\Delta$ transitions of YH and LaH, but more complex because of perturbations and overlapping.

Our previous work showed that the bands involving the $a\,^3\Delta_3$ spin components of YH and LaH show significant hyperfine effects. In fact for the $d\,^3\Phi_4-a\,^3\Delta_3$ subband of LaH the hyperfine structure is well resolved at low J.[13] Similar broadening of the rotational lines has been observed in the bands involving what is presumably the $a\,^3\Delta_3$ spin component of ScH and ScD. This observation is consistent with the $^3\Phi-a\,^3\Delta$ assignment for the ScH and ScD transitions near 11 620 and 11 630 cm^{-1}, respectively. Work on this transition is still in progress.

The bands observed with heads at 5463, 12 290, 13 620, and 20 547 cm^{-1} were not reported by Smith[3] or by Bernard et al.[22] The band with R head at 5463 cm^{-1} (origin at 5404 cm^{-1}) has a strong Q branch and has been assigned as the 0-0 band of the $B\,^1\Pi-X\,^1\Sigma^+$ transition. The rotational structure of the 12 290 cm^{-1} band is complex and most probably triplet states are involved. The structure of the band at 13 620 cm^{-1} of ScH is, in fact, relatively simple but appears to be complex because of perturbations. The corresponding spectrum of ScD is also perturbed but not as extensively. Each band consists of a single R and a single P branch. We have assigned this transition as the $C\,^1\Sigma^+-X\,^1\Sigma^+$ transition
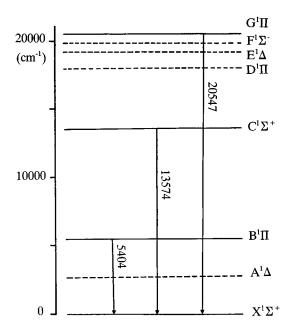
FIG. 1. A schematic energy level diagram of the singlet electronic states of ScH. Dashed lines are predicted energy levels.

FIG. 2. An expanded portion of the spectrum of the 0–0 band of the $B\ ^1\Pi - X\ ^1\Sigma^+$ system of ScH.

on the basis of theoretical calculations and by comparison with YH and ScF.

A schematic energy level diagram of the singlet electronic states of ScH is provided in Fig. 1. The states marked by solid lines represent the observed states discussed in this paper. The positions of the other states have been taken from theoretical calculations.[29] The band with an origin at 20 547 cm^{-1} involves the same lower state as the $B\ ^1\Pi - X\ ^1\Sigma^+$ and $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transitions and is assigned as the $G\ ^1\Pi - X\ ^1\Sigma^+$ on the basis of Anglada et al.'s predictions[29] (Fig. 1).

The $B\ ^1\Pi - X\ ^1\Sigma^+$ transition of ScH

In our recent study of LaH we have observed a $^1\Pi - X\ ^1\Sigma^+$ transition near 4533 cm^{-1} consistent with the theoretical predictions of Das and Balasubramanian.[8] The theoretical work of Anglada et al.[29] predicts an analogous ScH $^1\Pi - X\ ^1\Sigma^+$ transition near 7420 cm^{-1} and we found this transition near 5404 cm^{-1}. Although the calculated transition moment is relatively small (0.2 a.u.) compared to the other transitions discussed here, the intensity of this transition is comparable to the others. The maximum signal-to-noise ratio of the Q-branch lines is about 12:1.

The four bands with origins at 5404, 5220, 6767, and 6536 cm^{-1} have been identified as the 0–0, 1–1, 1–0, and 2–1 bands, respectively, of the $B\ ^1\Pi - X\ ^1\Sigma^+$ transition. Initially the lines of this transition were overlooked because of strong overlapping atomic lines. In fact the 1–0 band head, which is about 50% of the intensity of the 0–0 band, was first identified in our spectra because it has less extensive overlapping by atomic lines. The structure of each band consists of one P, one Q, and one R branch as expected for a $^1\Pi - ^1\Sigma^+$ transition. Part of the 0–0 band is presented in Fig. 2. The lines of this transition have a typical width of 0.031

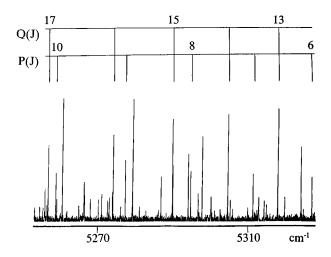± 0.001 cm^{-1} compared to widths of 0.045–0.09 cm^{-1} in the corresponding $A\ ^1\Pi - X\ ^1\Sigma^+$ transition of LaH. The nuclear hyperfine structure is thus observed to be smaller for ScH than for LaH. We have identified rotational lines up to $R(20)$, $P(22)$, and $Q(22)$ in the 0–0 band.

The $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transitionn of ScH

The bands with the origins at 13 574 and 13 396 cm^{-1} have been assigned as the 0–0 and 1–1 bands of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition. The 1–1 band has about 40% of the intensity of the 0–0 band. The low J R and P branch lines of this transition are easily picked out using a color Loomis–Wood program. In the 0–0 band of this transition, there is a strong perturbation at $J' \geq 12$ and the $R(11)$ and $P(13)$ lines are pushed to higher wavenumbers by 80.42 cm^{-1}. The lines corresponding to $J' = 10$ and 11 are also affected by these perturbations. The high-J perturbed lines were picked out using the predicted combination differences derived from the unperturbed low-J R and P lines. The 1–1 band of ScH is perturbed at $J' = 9$. A compressed part of the ScH $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition is provided in Fig. 3 in which the R heads of the 0–0 and 1–1 bands have been marked. The lines observed to higher wave numbers beyond the 0–0 head are the perturbed high J R lines of this band.

The $G\ ^1\Pi - X\ ^1\Sigma^+$ transition of ScH

The band with an origin at 20 547 cm^{-1} consists of a single R, a single P and a single Q branch. The R and P branches are much weaker than the Q branch and no other vibrational bands were observed for this transition. We have assigned this band as the 0–0 band of the $G\ ^1\Pi - X\ ^1\Sigma^+$ transition. This band is also extensively perturbed at both low J' and high J' values for e and f parities. There are several triplet and singlet states predicted to be present in the vicinity of the $G\ ^1\Pi$ state which could be responsible for perturbations. The ground state combination differences from this band match very well with the combination differences from the $B\ ^1\Pi - X\ ^1\Sigma^+$ and $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transi-
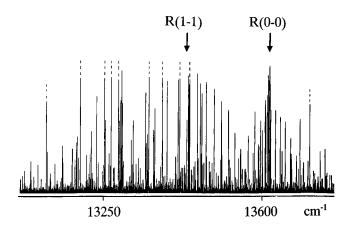
FIG. 3. A portion of the compressed spectrum of the 0–0 band of the $C\ ^1\Sigma^+-X\ ^1\Sigma^+$ system of ScH. The dashed lines are strong atomic lines that are off scale. The arrows mark the 0–0 and 1–1 band heads. Notice that the perturbation has pushed the high J lines to higher wave numbers beyond the R head.
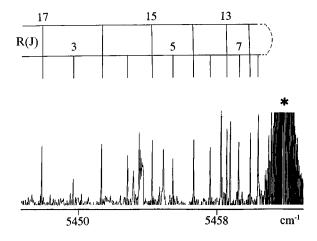

FIG. 4. An expanded portion of the spectrum of the 0–0 band of the $B\ ^1\Pi-X\ ^1\Sigma^+$ system of ScD near the R head. The asterisk marks a strong atomic line near the head.

tions confirming the ground state assignment. Because of perturbations in the excited state, several higher order effective rotational and Λ-doubling constants were required to obtain a satisfactory fit of the observed line positions.

In order to determine the molecular constants, the following customary energy levels expressions for $^1\Pi$ and the $^1\Sigma^+$ states were used

$$F_v(J)=T_v+B_vJ(J+1)-D_v[J(J+1)]^2+H_v[J(J+1)]^3$$
$$\pm 1/2\{qJ(J+1)+q_D[J(J+1)]^2+q_H[J(J+1)]^3$$
$$+q_L[J(J+1)]^4\}, \tag{1}$$

$$F_v(J)=T_v+B_vJ(J+1)-D_v[J(J+1)]^2+H_v[J(J+1)]^3$$
$$+L_v[J(J+1)]^4. \tag{2}$$

The observed line positions were weighted on the basis of the signal-to-noise ratio and the extent of blending. The lines involved in perturbations were excluded from the fit, although the corresponding ground state combination differences were included. As mentioned earlier, the ground state combination differences of the three transitions agree very well with each other to better than ± 0.002 cm^{-1}. The line

positions of the $B\ ^1\Pi-X\ ^1\Sigma^+$, $C\ ^1\Sigma^+-X\ ^1\Sigma^+$, and $G\ ^1\Pi-X\ ^1\Sigma^+$ transitions can be obtained from PAPS[32] or from the authors upon request. The molecular constants for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, $C\ ^1\Sigma^+$, and $G\ ^1\Pi$ states of ScH obtained from a simultaneous fit of the line positions are provided in Table I.

The $B\ ^1\Pi-X\ ^1\Sigma^+$ transition of ScD

Three ScD bands of the $B\ ^1\Pi-X\ ^1\Sigma^+$ system are present in the 5000–6500 cm^{-1} region. The bands with origins at 5432, 5303, and 6419 cm^{-1} have been assigned as the 0–0, 1–1, and 1–0 bands, respectively. Several ScN[30] bands have also been observed in the 5700–6400 cm^{-1} region and the ScN lines frequently overlap the ScD molecular lines. The weaker 2–1 ScD band is, in fact, buried under the dense and relatively strong 2–2 band of ScN and could not be identified.

Part of the 0–0 band of this $B\ ^1\Pi-X\ ^1\Sigma^+$ transition is provided in Fig. 4 and some R lines near the head have been marked. A few R lines near the head are overlapped by a strong atomic line which produces extensive ringing (Fig. 4).

TABLE I. Spectroscopic constants (in cm^{-1}) for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, $C\ ^1\Sigma^+$, and $G\ ^1\Pi$ states of ScH.

Const.[a]	$X\ ^1\Sigma^+$		$B\ ^1\Pi$			$C\ ^1\Sigma^+$		$G\ ^1\Pi$
	$v=0$	$v=1$	$v=0$	$v=1$	$v=2$	$v=0$	$v=1$	$v=0$
T_v	0.0	1546.973 0(14)	5404.185 7(12)	6767.239 1(10)	8083.272 6(25)	13 574.253 7(15)	14 942.691 9(20)	20 546.916 2(35)
B_v	5.363 031(24)	5.238 229(80)	4.915 099(50)	4.772 051(57)	4.631 75(13)	4.797 58(31)	4.601 65(31)	6.431 05(90)
$10^3\times D_v$	0.252 83(12)	0.268 6(14)	0.299 83(43)	0.309 64(71)	0.310 3(20)	0.513(16)	1.227(16)	6.251(45)
$10^5\times H_v$	0.000 952(19)	0.015 09(87)	0.003 27(14)	−0.004 11(34)	−0.007 4(12)	−0.037(27)	−1.206(27)	−2.432(79)
$10^7\times L_v$		−0.004 39(18)	−0.002 635(15)	−0.001 358(53)	−0.000 65(23)	−0.132(15)	0.106(15)	6.024(46)
q_v			0.033 884(47)	0.033 416(30)	0.033 885(66)			1.233 7(16)
$10^2\times q_{Dv}$			−0.001 148(58)	−0.000 443(32)	−0.001 477(97)			−1.952 9(85)
$10^4\times q_{Hv}$			0.000 222(22)	−0.000 5236(78)	−0.000 229(33)			3.572(15)
$10^6\times q_{Lv}$			−0.000 126 4(25)					−2.734 8(90)

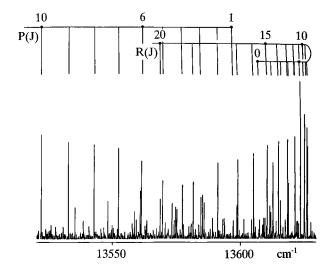[a]Numbers in parentheses are one standard deviation in the last two digits.

FIG. 5. An expanded portion of the spectrum of the 0–0 band of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ system of ScD near the band origin.

FIG. 6. A portion of the Q branch of the $G\ ^1\Pi - X\ ^1\Sigma^+$ system of ScD near the band origin.

The $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition of ScD

The bands of ScD are generally stronger than the corresponding bands of ScH. For the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition of ScD we have identified the 0–0, 1–1, 0–1, and 1–2 bands with origins at 13 603, 13 485, 12 485, and 12 385 cm^{-1}, respectively. The $v' = 0$ vibrational level of the $C\ ^1\Sigma^+$ state is also perturbed, but at a higher J value than in ScH. In the 0–0 band, the effect of perturbations is apparent for lines with $J' \geq 16$. The obs.–calc. deviation changes sign at $J' = 22$ when this deviation jumps from -6.24 (at $J' = 21$) to 75.12 cm^{-1} (at $J' = 22$). The lines of this transition have been identified up to $R(34)$ and $P(35)$. As in ScH, the perturbed lines were not included in the final fit, although the corresponding ground state combination differences up to $J'' = 34$ were included and found to fit with average residuals of ± 0.002 cm^{-1}. Part of the expanded spectrum of the 0–0 band of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition is provided in Fig. 5. The detection of the first lines $[R(0)$ and $P(1)]$ in the strong bands confirms our $^1\Sigma^+ - {}^1\Sigma^+$ assignment.

The $G\ ^1\Pi - X\ ^1\Sigma^+$ transition of ScD

We have observed only the 0–0 band of the ScD $G\ ^1\Pi - X\ ^1\Sigma^+$ transition. The ground state combination differences match very well with those obtained from the $B\ ^1\Pi - X\ ^1\Sigma^+$ and $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transitions. Both e- and f-parity levels of the excited state are involved in perturbations similar to those in ScH. Part of the 0–0 band of this transition is provided in Fig. 6 and some low J Q-branch lines have been marked.

The observed line positions of the ScD $B\ ^1\Pi - X\ ^1\Sigma^+$, $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$, and $G\ ^1\Pi - X\ ^1\Sigma^+$ transitions are available from PAPS[32] or from the authors upon request. The molecular constants for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, $C\ ^1\Sigma^+$, and $G\ ^1\Pi$ states of ScD are provided in Table II.

DISCUSSION
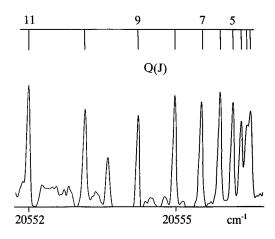
There has been controversy in the past over the nature of the ground electronic state of ScH. A $^3\Delta$ ground state was suggested by Bernard *et al.*[22] on the basis of some primitive calculations carried out by Scott and Richards.[27] However, the observed ground states for the isovalent YH and LaH molecules are $X\ ^1\Sigma^+$. In addition we have noticed a close correspondence between the electronic states of transition metal fluorides (e.g., CoF[33]) and the corresponding hydrides (e.g. CoH[12]). ScF has a $^1\Sigma^+$ ground state, suggesting that ScH also has one. A $^1\Sigma^+$ ground state has also been predicted by several recent *ab initio* calculations including the extensive MRD-CI study by Anglada *et al.*[29] These authors have calculated the spectroscopic properties of a number of singlet and triplet electronic states below 4.0 eV in addition to the transition dipole moments for the most likely transitions. Anglada *et al.*[29] calculate that the ground state of ScH is a $^1\Sigma^+$ state arising from the $6\sigma^2 7\sigma^2$ electron configuration. The first excited state is predicted to be a $^3\Delta$ state arising from the $1\delta 7\sigma^2 8\sigma$ configuration at about 0.33 eV (2700 cm^{-1}) above the ground state. Anglada *et al.*[29] have also predicted the strengths of many allowed transitions terminating on the low-lying $X\ ^1\Sigma^+$, $A\ ^1\Delta$ $B\ ^1\Pi$, $a\ ^3\Delta$, and $b\ ^3\Pi$ electronic states. Allowed transitions connecting to the ground $X\ ^1\Sigma^+$ state are predicted to be the $1\ ^1\Pi - X\ ^1\Sigma^+$, $2\ ^1\Sigma^+ - X\ ^1\Sigma^+$ $2\ ^1\Pi - X\ ^1\Sigma^+$, and $3\ ^1\Pi - X\ ^1\Sigma^+$ at 7420, 15 160, 18 160, and 23 330 cm^{-1} with the transition dipole moments of 0.2, 1.42, 1.58, and 0.77 a.u., respectively. The calculated transition moments provide only a qualitative guide for the observed intensity of these transitions. In our spectra the first three of these transitions have been observed at 5404, 13 574, and 20 547 cm^{-1}, respectively, and have been assigned as the $B\ ^1\Pi - X\ ^1\Sigma^+$, $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$, and $G\ ^1\Pi - X\ ^1\Sigma^+$ transitions. Of these, the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ transition is the most intense and the fourth transition $(3\ ^1\Pi - X\ ^1\Sigma^+)$ has not yet been detected. Anglada *et al.*[29] also predict that several other allowed transitions terminating on the $A\ ^1\Delta$, $B\ ^1\Pi$, and $a\ ^3\Delta$ states will be observed in

TABLE II. Spectroscopic constants (in cm^{-1}) for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, $C\ ^1\Sigma^+$, and $G\ ^1\Pi$ states of ScD.

Const.[a]	$X\ ^1\Sigma^+$			$B\ ^1\Pi$		$C\ ^1\Sigma^+$		$G\ ^1\Pi$
	$v=0$	$v=1$	$v=2$	$v=0$	$v=1$	$v=0$	$v=1$	$v=0$
T_v	0.0	1116.505 3(10)	2208.250 9(25)	5432.350 0(10)	6418.651 5(14)	13 602.680 7(10)	14 592.529 0(21)	20 556.512 4(45)
B_v	2.764 706(15)	2.7188 70(18)	2.672 519(62)	2.5201 44(21)	2.479 456(53)	2.482 467(45)	2.432 185(94)	2.908 67(28)
$10^4 \times D_v$	0.667 50(33)	0.6605 8(47)	0.641 5(31)	0.705 17(61)	0.858 3(60)	0.775 7(45)	1.006(11)	6.575(47)
$10^7 \times H_v$	0.013 19(19)			0.042 52(66)	0.867(22)	−0.882(12)	−2.774(40)	8.32(23)
$10^{11} \times L_v$				−0.072 3(24)	−5.45(19)			
q_v				0.008 8370(80)	0.006 477(50)			0.300 23(17)
$10^4 \times q_{Dv}$				−0.005 60(21)	−0.111 3(78)			−6.775(49)
$10^7 \times q_{Hv}$				0.001 77(13)	0.812(29)			4.93(42)
$10^9 \times q_{Lv}$								4.36(15)

[a]Numbers in parantheses are one standard deviation in the last two digits.

emission. We have observed many additional bands which correspond to these predicted transitions and we will report on them in the future.

The rotational constants for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, and $C\ ^1\Sigma^+$ states of ScH (Table I) and ScD (Table II) have been used to evaluate the equilibrium molecular constants which are provided in Table III. The equilibrium rotational constants for ScH are $B_e = 5.425\ 432(48)$ cm^{-1} and $\alpha_e = 0.124\ 802(84)$ cm^{-1}. When used in the isotopic relationships[34] $B_e^i = \rho^2 B_e$ and $\alpha_e^i = \rho^3 \alpha_e$, the predicted B_e and α_e values of ScD are 2.7742 and 0.0456 cm^{-1}, respectively, compared to the observed values of $B_e = 2.787\ 432(41)$ cm^{-1} and $\alpha_e = 0.045\ 321(73)$ cm^{-1}. The observation of the vibrational intervals $\Delta G(1/2)$ and $\Delta G(3/2)$ for the ground state of ScD provides $\omega_e = 1141.2650(31)$ cm^{-1} and $\omega_e x_e = 12.3799(15)$ cm^{-1}. When used in the isotopic relations[34] $\omega_e^i = \rho \omega_e$ and $\omega_e x_e^i = \rho^2 \omega_e x_e$, the corresponding calculated values for ScH are 1595.9966 and 24.2107 cm^{-1}, respectively, which predict $\Delta G(1/2) = 1547.57$ cm^{-1} [observed $\Delta G(1/2) = 1546.9730(14)$ cm^{-1}]. The equilibrium rotational constants have been used to evaluate the equilibrium bond lengths of the ground and excited states of ScH and ScD which are found to be 1.775 427(8) and 1.771 219(13) Å, respectively. These values can be compared with the theoretical value of 1.80 Å predicted for ScH by Anglada et al.[29] The experimental r_e values for the $B\ ^1\Pi$ and $C\ ^1\Sigma^+$ state of ScH are 1.851 706(31) and 1.869 043(73) Å, to be compared with the predictions of 1.92 and 1.89 Å, respectively.

There are strong similarities between the low-lying electronic states of ScH, YH, and LaH. The ground $X\ ^1\Sigma^+$ states arise from the $1\sigma^2 2\sigma^2$ electron configuration. The observed ground state vibrational interval of ScH [$\Delta G(1/2) = 1547$ cm^{-1}] can be compared with the $\Delta G(1/2) = 1491.6995(15)$ cm^{-1} for YH.[14] For LaH the experimental ground state vibrational interval is not known yet but the theoretical value of Das and Balasubramanian[8] is 1433 cm^{-1}. The ground state r_e values of ScH, YH, and LaH are 1.775 427(8), and 1.922 765(8), and 2.031 969(20) Å, respectively. There is also a very strong correspondence between the states of ScH and ScF and we plan to make a detailed comparison in a future publication.

The observation of the $B\ ^1\Pi - X\ ^1\Sigma^+$ transition of ScH at 5404 cm^{-1} can be compared with the corresponding $A\ ^1\Pi - X\ ^1\Sigma^+$ transition of LaH[13] at 4533 cm^{-1}. This transition has not yet been identified for YH. Similarly the position of the $C\ ^1\Sigma^+$ state at 13 574 cm^{-1} can be compared with the $C\ ^1\Sigma^+$ state of YH at 14 295 cm^{-1}. This transition has not been identified yet for LaH. A $^3\Phi - a\ ^3\Delta$ transition has also been observed for LaH[13] at 6238 cm^{-1} and for YH[14] at 11 500 cm^{-1}. This transition of ScH is located at 11 620 cm^{-1} and its analysis is still in progress.

CONCLUSION

The spectra of ScH and ScD have been investigated in the 2.5 μm–480 nm spectral region using a Fourier transform spectrometer. The bands with 0–0 band origins near

TABLE III. Equilibrium constants (in cm^{-1}) for the $X\ ^1\Sigma^+$, $B\ ^1\Pi$, and $C\ ^1\Sigma^+$ states of ScH and ScD.

Const.[a]	ScH			ScD		
	$X\ ^1\Sigma^+$	$B\ ^1\Pi$	$C\ ^1\Sigma^+$	$X\ ^1\Sigma^+$	$B\ ^1\Pi$	$C\ ^1\Sigma^+$
ω_e	[15 46.973 0(14)][b]	1410.073 3(35)	[1368.4382(25)]	1141.2650(31)	[986.3015(17)]	[989.8483(23)]
$\omega_e x_e$		23.5100(16)		12.3799(15)		
B_e	5.425 432(48)	4.987 65(10)	4.895 55(38)	2.7874 32(41)	2.5404 88(35)	2.507 608(69)
α_e	0.124 802(84)	0.145 80(18)	0.195 93(44)	0.0453 21(73)	0.0406 88(57)	0.050 28(10)
γ_e		0.001 374(81)		−0.000 258(35)		
r_e(Å)	1.775 427(8)	1.851 706(19)	1.869 043(73)	1.771 219(13)	1.855 308(13)	1.867 432(26)

[a]The numbers in parentheses are one standard deviation in the last two digits.
[b]$\Delta G(1/2)$ values.

5404, 13 574, and 20 547 cm^{-1} have been classified into three new electronic transitions: $B\ ^1\Pi - X\ ^1\Sigma^+$, $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$, and $G\ ^1\Pi - X\ ^1\Sigma^+$. These observations are consistent with expectations based on the available data for YH, LaH, and ScF, and confirm the high quality of the theoretical calculations of Anglada *et al.*[29]

In addition to the bands reported here, there are many singlet and triplet bands still to be assigned. The structure of many of these bands is complex because of perturbations, overlapping lines and weak intensity. The analysis of these bands will provide a complete picture of the low-lying electronic states of ScH and ScD.

ACKNOWLEDGMENTS

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