Fourier transform emission spectroscopy of the near infrared transitions of CeS

R.S. Ram,⇑, P.F. Bernath

Abstract

The emission spectra of CeS have been investigated at high resolution with a Fourier transform spectrometer. Several bands observed in the 4000–9000 cm⁻¹ region have been classified into nine transitions having five different lower states, X₂(3), X₂(2), X₁(2), X₁(3) and X₁(0) based on Ω doubling and relative branch intensities.

Out of these, the [7.54] (4) → X₁(3) transition consisting of 0–1, 1–2, 0–0, 1–0 and 2–1 bands is strongest in intensity. A rotational analysis of these bands provides equilibrium spectroscopic constants: \( \omega_e = 461.3947(14) \text{ cm}^{-1} \), \( \omega_x = 1.00095(65) \text{ cm}^{-1} \), \( B_e = 0.118782207(15) \text{ cm}^{-1} \), \( x_e = 0.000341453(14) \text{ cm}^{-1} \) and \( r_e = 2.335399(31) \text{ Å} \) for the lower \( X_2(\Omega = 3) \) state. The [8.78] (3) → X₂(2) transition, for which 0–0 and 0–1 bands were rotationally analyzed, provides \( \Delta G^0 = 458.8741(88) \text{ cm}^{-1} \), \( B_e = 0.1187649(31) \text{ cm}^{-1} \), \( x_e = 0.0003401(37) \text{ cm}^{-1} \) and \( r_e = 2.333399(31) \text{ Å} \) for the \( X_2(\Omega > 2) \) lower state.

1. Introduction

While electronic spectra of many lanthanide-containing diatomic oxides are known, only a few diatomic sulfides such as LaS [1–4], YbS [5,6] and HoS [7] have been investigated in the gas phase. The spectra of lanthanide-containing molecules are very complex with a high density of states resulting from partially filled f-orbitals. The electronic states of these molecules are Hund’s case (c) states in which the spin components are widely separated and only their Ω values remain as good quantum numbers. For most lanthanide sulfides no spectroscopic data are available and in some cases where data are available, knowledge of the low-lying electronic states remains fragmentary.

Among the cerium-containing molecules the electronic spectra of only CeO and CeF have been investigated to date. CeO has been investigated in detail, first by conventional spectrometry [8], and later by laser excitation spectroscopy [9–13] and many low-lying electronic states have been identified. The experimental observations have been supported by several theoretical studies [14–16]. The electronic spectra of CeF have also been investigated in previous experimental studies [17,18].

CeO has been of considerable interest because of its astrophysical importance. This molecule has been identified in the spectra of S-type stars by several workers [19–22] and there is a strong possibility that CeS might also be found. So far no experimental observations have been reported, and no experimental spectroscopic constants are available for CeS. Coppens et al. [23] have provided estimated values of the vibrational constant \( \omega_e = 510 \text{ cm}^{-1} \) and bond length \( r_e = 2.15 \text{ Å} \) based on CeO. They have also reported the dissociation energy \( D_0 = 126 \text{ kcal/mol} \) for CeS. In recent density function calculations on lanthanide monosulfides, Luo et al. [24] have predicted \( \omega_e = 426 \text{ cm}^{-1} \) and \( r_e = 2.36 \text{ Å} \) for CeS while a vibrational frequency of \( \omega_e = 457 \text{ cm}^{-1} \) has been provided [25] by some primitive calculations.

The present work has been motivated by the need to obtain spectroscopic parameters of CeS in the gas phase because of its potential astrophysical importance. In the present paper we report on the identification of a number of transitions of CeS in the near infrared, with their 0–0 bands located near 4374, 4741, 6491, 7541, 7678, 6026, 8428, 8676 and 8781 cm⁻¹. A tentative Ω-assignment of the observed states has been proposed based on the magnitude of the Ω-doubling and the relative intensity of the Q, R and P branches in different bands.

2. Experimental

The spectra of CeS used in the present analysis were recorded by S.P. Davis in thermal emission on 01/17/1989 [spectrum #89011780.002] at Kitt Peak. CeS was produced in a high temperature carbon tube furnace (King furnace) by vaporizing...
CeS$_2$ at a temperature of $\sim$2200 °C in an atmosphere of about 274 Torr of helium. The spectrometer was equipped with a CaF$_2$ beam splitter, Si filter and InSb detectors. The spectra in the 1850–9150 cm$^{-1}$ region were recorded using the 1-m Fourier transform spectrometer of the National Solar Observatory at Kitt Peak by co-adding 8 scans in about 2 h of integration at a resolution of 0.01 cm$^{-1}$. The line positions were extracted using the WSPECTRA program (M. Carleer, Free University of Brussels) by fitting a Voigt line shape function to the individual spectral features. The precision of measurement is expected to be of the order of $\pm 0.003$ cm$^{-1}$ or better for the stronger and unblended lines. However, for rotational lines of weaker bands which are frequently overlapped by lines of stronger bands, the measurement uncertainty is expected to be of the order of $\pm 0.005$ cm$^{-1}$ or higher. Several new bands observed in the near infrared have been attributed to CeS based on a rotational analysis. Prior to this experiment, the furnace was used for the observation of near infrared bands of LaS; therefore, some LaS bands of the A$^2$II-A$^2$A, transition were also present as an impurity. In addition, molecular lines belonging to the $\Delta v = 2$ overtones bands of CO, Balilik–Ramsay system of C$_2$, and $\Delta v = -1$ and $-2$ sequence bands of the A$^2$II$-\chi^2$X$^2$ transition of CN, were also present as impurities. We have used the CN lines [26] to calibrate the wavenumbers of CeS lines. The molecular lines were sorted into branches of different bands using a color Loomis program running on a PC computer and rotational assignment was made by comparing combination differences for common vibrational levels.

3. Description of observed spectra

The spectrum of CeS in general is weak in intensity. In spite of weak intensity, several new bands located near 4374, 4741, 6026, 6491, 7541, 7678, 8428, 8674 and 8781 cm$^{-1}$ have been rotationally analyzed and assigned as 0–0 bands of different transitions. A rotational analysis of some associated higher vibrational bands has also been obtained. The main features of these transitions are summarized in Table 1. Several much weaker bands still remain unanalyzed. Since the spectra were recorded using a furnace, no first lines were identified in any of the observed bands. Spectroscopic constants for the observed states of different transitions were determined by fitting the observed rotational lines using the following simple term energy expressions:

For the $\Omega = 0$ and $\Omega \geq 2$ states without observed $\Omega$-splitting:

$$F_\Omega(J) = T_\Omega + B(J+1)J[J(J+1)] + D(J+1)^2 + H_J[J(J+1)]$$

(1)

For the $\Omega = 1$ and higher states with observed $\Omega$-splitting:

$$F_\Omega(J) = T_\Omega + B(J+1)J[J(J+1)] + D(J+1)^2 + H_J[J(J+1)] + L_J[J(J+1)] + q_{0v}J(J+1)^2$$

(2)

Table 1

Main features of CeS bands in the near infrared.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Main features</th>
</tr>
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<tbody>
<tr>
<td>[4.37] ($\Omega = 3$) $\rightarrow$ $\chi_1(\Omega = 2)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling, no combination defects</td>
</tr>
<tr>
<td>[4.74] ($\Omega &gt; 2$) $\rightarrow$ $\chi_2(\Omega &gt; 3)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; P &gt; R, no doubling, no combination defects</td>
</tr>
<tr>
<td>[6.03] ($\Omega = 1$) $\rightarrow$ $\chi_3(\Omega = 0)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling, combination defects</td>
</tr>
<tr>
<td>[6.49] ($\Omega = 2$) $\rightarrow$ $\chi_4(\Omega = 3)$</td>
<td>2P, 2Q, 2R branches with intensity of Q &gt; R &gt; P, no perturbations</td>
</tr>
<tr>
<td>[7.54] ($\Omega = 4$) $\rightarrow$ $\chi_5(\Omega = 3)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling no combination defects</td>
</tr>
<tr>
<td>[7.68] ($\Omega = 2$) $\rightarrow$ $\chi_6(\Omega = 3)$</td>
<td>2P, 2Q, 2R branches with intensity of Q &gt; R &gt; P, perturbations</td>
</tr>
<tr>
<td>[8.43] ($\Omega = 2$) $\rightarrow$ $\chi_7(\Omega = 3)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling no combination defects</td>
</tr>
<tr>
<td>[8.67] ($\Omega &gt; 3$) $\rightarrow$ $\chi_8(\Omega &gt; 2)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling no combination defects</td>
</tr>
<tr>
<td>[8.78] ($\Omega &gt; 3$) $\rightarrow$ $\chi_9(\Omega &gt; 2)$</td>
<td>1P, 1Q, 1R branches with intensity of Q &gt; R &gt; P, no doubling no combination defects</td>
</tr>
</tbody>
</table>

* See the energy level diagram in Fig. 1, for lower state notations.
lambda doubling constant. 

Two branches of the 0–1 band were easily identified in our spectra. Equilibrium constants (in cm$^{-1}$) must be an argument. A portion of the 0–1 band of this transition was made using the spectroscopic constants for the upper states instead of significant values of $q$. This indicates that upper states of these transitions have $\Omega = 2$. The 0–1 and 1–0 bands of the 6490 cm$^{-1}$ transition were very weak in intensity. In spite of very weak intensity a search for the 0–1 band of this transition was made using the spectroscopic constants for the upper states instead of significant values of $q$. The fact that the quadratic $q_{\Omega}$ doubling term in Eq. (2) is dominant indicates that upper states of these transitions have $\Omega = 2$.

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weights or were de-weighted in the final fits. Rotational lines up to P1(120), P2(124), Q1(154), Q2(151), R1(138) and R2(118) were assigned. A search for the 0–1 and 1–0 bands of this transition was unsuccessful.

For the 0–0 band near 8428 cm\(^{-1}\), we have assigned rotational lines up to P1(148), P2(142), Q1(180), Q2(159), R1(151) and R2(142). No other band associated with this transition has been identified in our spectra.

3.2. Transitions with X2(\(\Omega\) ≥ 2), X3(\(\Omega\) ≥ 2), X4(\(\Omega\) ≥ 3) as lower states

The 8781, 8674 and 4741 cm\(^{-1}\) bands having the lower states X2, X3 and X4, respectively, have single P, Q and R branches. The 8781 and 8674 cm\(^{-1}\) bands (with Q > P > R) involve \(\Delta\Omega = -1\) transitions between higher \(\Omega\) states. The 4741 cm\(^{-1}\) band has intensity Q > P > R indicating that it involves a \(\Delta\Omega = -1\) transition. The three 0–0 bands have been assigned as [8.78] (\(\geq 3\)) \(\rightarrow\) X2(\(\geq 2\)), [8.67] (\(\geq 3\)) \(\rightarrow\) X3(\(\geq 2\)) and [4.74] (\(\geq 2\)) \(\rightarrow\) X4(\(\geq 3\)). Since the case (c) states of CeS may have mixed character, relative intensity of branches especially in high \(\Omega\) transitions may not provide correct information about their \(\Omega\) assignment.

3.2.1. The [8.78] (\(\geq 3\)) \(\rightarrow\) X2(\(\geq 2\)) transition

Two bands with single P, Q, R branches, located at 8781 and 8322 cm\(^{-1}\), have been assigned at the 0–0 and 0–1 bands of the [8.78] (\(\geq 3\)) \(\rightarrow\) X2(\(\geq 2\)). A rotational analysis of these two bands has provided \(\Delta G/2 = 458.87\) cm\(^{-1}\) for the X2(\(\geq 2\)) lower state. This value is very similar to the vibrational interval \(\Delta G/2 = 459.39\) cm\(^{-1}\) of the X1(3) lower state. No other bands having the same lower state have been identified in our spectra.

3.2.2. The [8.67] (\(\geq 3\)) \(\rightarrow\) X3(\(\geq 2\)) transition

Another \(\Delta\Omega = +1\) band with single P, Q, R branches, located at 8674 cm\(^{-1}\), has different lower and upper states than the other transitions. The lower state rotational constants of this transition are \(B_0 = 0.1176391(83), D_0 = 3.131(62) \times 10^{-6}\) cm\(^{-1}\). This transition has been labeled as the [8.67] (\(\geq 3\)) \(\rightarrow\) X3(\(\geq 2\)). A lower wavenumber band located at 8634 cm\(^{-1}\) (with \(B = 0.1172976(76), D = 3.131(34) \times 10^{-6}\) cm\(^{-1}\)) is probably the 1–1 band associated with this transition. This assignment, however, could not be confirmed independently because the 0–1 band was not observed.

3.2.3. The [4.74] (\(\geq 2\)) \(\rightarrow\) X4(\(\geq 3\)) transition

The 4741 cm\(^{-1}\) band having single P, Q, R branches (with Q > P > R), has a different lower state. This observation is consistent with the \(\Delta\Omega = -1\) assignment and this transition has been labeled as [4.74] (\(\geq 2\)) \(\rightarrow\) X4(\(\geq 3\)).

3.3. Transition with X5(0) as the lower state

The 6026 cm\(^{-1}\) transition consists of single P, Q and R branches showing combination defects because of appreciable \(\Omega\)-doubling in the upper state. This transition has the character of a \(^1\Pi \rightarrow ^1\Sigma^+\).
transition and we have labeled it as [6.03] (Ω = 1) → X(Ω = 0) transition. No perturbations have been observed and we have observed rotational lines up to P(151), Q(179) and R(155).

For the isovalent CeO, there are two low-lying Ω = 0 states, V₁ 0⁺ and U₁ 0⁻, and the electronic states of CeO are expected to show a similar pattern. As there is no way to distinguish between 0⁺ and 0⁻ in the present analysis, the lower state has simply been labeled as X(0).

4. Results and discussion

Prior to the present work no experimental observations have been reported on CeS. In a recent theoretical study, density functional calculations have been performed on several lanthanide monosulfide molecules by Luo et al. [24] and spectroscopic properties of the ground state of CeS have been calculated. This calculation provided a ground state vibrational frequency of 426 cm⁻¹; in addition, an estimate of the vibrational frequency of 457 cm⁻¹ was reported based on the experimental value of CeO and some primitive calculations [25]. Contrary to the present observations, Luo et al. [24] predict a Σ ground state for CeS. The electronic structure of CeS is expected to be very similar to that of CeO for which most of the low-lying observed states were identified only by their Ω values. The spectroscopic constants of the X₁ lower state determined from the present work are: \( \omega_0 = 461.3947(14) \), \( \omega_0 \Delta v = 1.00995(65) \) and \( \Delta \omega_v = 0.118782207(15) \) cm⁻¹ and the constants of the X₂ state are: \( \Delta \omega_v = 458.87411(88) \) cm⁻¹ and \( \Delta \omega_v = 0.1187649(31) \) cm⁻¹. The equilibrium rotational constants of the two states provide equilibrium bond lengths of \( r_e = 2.3352875(15) \) Å and 2.335399(31) Å for the two lower states. Our lower state bond lengths agree well with Luo's [24] calculated bond length of \( r_e = 2.36 \) Å.

The electronic structure and spectroscopic properties of CeS are expected to be very similar to that of CeO for which a wealth of information is available from the previous experimental and theoretical studies [9–16]. The ground Ce⁴⁺(4f⁶)O²⁻ configuration produces 16 electronic states, all of which have been characterized experimentally, and are supported by theoretical calculations [15]. The lowest electronic states of CeO have a pattern of \( Ω = 2, 3, 1, 2, 0, 1, 0, 4, 3, 3, 2, 0, 4, 3, 3, 2, 0 \), and a similar pattern is expected for the lowest states of CeS. The CeS lower states observed so far have been labeled as X₁(3), X₂(≥2), X₃(≥2), X₄(≥3) and X₅(0). At this stage we do not have any information on the relative position of the different lower states. We are also unable to decide on the ground state of CeS (although X₂ or X₃ are possible). It is possible that X₁(3) and X₂(≥2) correspond to the X₁(3) and X₂(2) states of CeO, respectively.

A review of the observed low-lying electronic states of lanthanide oxides and sulfides can provide valuable information on the electronic and configurational assignments of CeS. The low-lying states of the lanthanide oxides result from the 4f⁴⁻⁴f⁶ configuration of the lanthanide metal ion, with the exceptions of EuO [27] and YbO [27,28]. The low-lying states of EuO and YbO arise from the 4f⁴² Eu⁺ and 4f⁴² Yb⁺ configurations. Lanthanide oxides with similar ground state configurations have very similar vibrational frequencies because of the shielding properties of the f orbitals. This, therefore, provides a guide to the electron configuration. For the lanthanide oxides, all the ground state frequencies are ~820 cm⁻¹, except for EuO and YbO which have ground state frequencies of ~660 cm⁻¹. A similar situation is expected for the sulfides. Among sulfides, HoS [7] with a ground state vibrational frequency of ~463 cm⁻¹ and YbS [6] with a ground state vibrational frequency of ~366 cm⁻¹ have been observed previously. These two have approximately the same ratio of vibrational frequencies as found for the case of the \( f^{n-1}sf^n \) lanthanide oxides. From this observation we conclude that the ~460 cm⁻¹ vibrational frequency of two of the lower states of CeS arise from the 4f⁶ configuration of the Ce⁴⁺ ion. Since the first lines were not observed in any of the transitions, we would like to emphasize that the proposed electronic assignments are only tentative and further investigations are required for a more definite Ω assignment and energy ordering of the low-lying electronic states of CeS.

5. Conclusions

The emission spectra of CeS have been investigated in the 4000–9000 cm⁻¹ region using a Fourier transform spectrometer. Several bands have been rotationally analyzed and classified into systems having five different lower states. Out of the observed lower states the X₁(3) and X₂(≥2) have very similar Δ\( \omega_v \) vibrational intervals of 459.3283(51) and 458.87411(88) cm⁻¹, respectively. By comparison of lower state vibrational frequencies of CeS with those of the known lanthanide oxides and sulfides, it has been concluded that the lower states arise from the ground configuration, Ce⁴⁺(4f⁶)S²⁻. This work represents the first spectroscopic observation of CeS in the gas phase.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcms.2014.03.003.

References