The spectra of iron in orthopyroxene revisited: the splitting of the ground state

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Abstract

The optical absorption spectra of Fe$^{2+}$ in the M(2) site of orthopyroxene have been reanalyzed, in view of the experimental observation of a mid-infrared band at 2350 cm$^{-1}$ arising from an electronic transition within the split $^4T_{2g}$ ground state of the low-symmetry site. This analysis uses $C_{2v}$ spectroscopic symmetry and a crystal-field potential which includes fourth-order harmonic terms. The order of the energy states is found to depend upon specific bond angles and lengths. The 2350 cm$^{-1}$ band is assigned as a transition to the $^6B_{2}$ state, calculated to lie above the $^4A_{1}$ state. This result indicates that the entire splitting of the $^4T_{2g}$ ground state is 2350 cm$^{-1}$.

Introduction

The electronic absorption spectrum of ferrous iron in the M(2) site of orthopyroxene, (Mg,Fe)SiO$_3$, has been the subject of many investigations aimed at understanding the polarization properties and splittings among the various bands that result from iron in a low-symmetry, coordination environment. White and Keester (1966) assigned a band at 11,000 cm$^{-1}$ in the spectrum of enstatite to Fe$^{2+}$ in octahedral coordination, and assigned a band at about 5400 cm$^{-1}$ to Fe$^{2+}$ in tetrahedral coordination. It was subsequently suggested by Bancroft and Burns (1967) and later accepted by White and Keester (1967) that both bands arise from Fe$^{2+}$ in the distorted, six-coordinate M(2) site. Runciman et al. (1973) pointed out an incorrect classification of $C_{2v}$ states used in the previous studies to explain the polarization properties of these bands. They presented spectra of enstatite and analyzed the results in a crystal-field analysis that was also based upon a $C_{2v}$ model, but with a different classification of states. Because of the large energy splittings and the polarization characteristics exhibited by these bands, the spectra of Fe$^{2+}$ in the M(2) site of orthopyroxene are used as the model for the study of the spectra of iron in a variety of low-symmetry environments.

The degeneracies within the octahedral $^4T_{2g}$ and $^6E_{g}$ states of Fe$^{2+}$ are removed in $C_{2v}$ symmetry, producing five states, among which a maximum of three allowed electric dipole transitions are possible, depending upon the symmetry of the ground state. For this reason, a third absorption band was sought in previous studies. White and Keester (1966) observed a band at 3100 cm$^{-1}$ and attributed it to a vibrational overtone of the silicate lattice. Bancroft and Burns (1967) assigned this band to Fe$^{2+}$ in the M(2) site. Runciman et al. determined the polarization properties of a band at 3100 cm$^{-1}$ and also assigned it to Fe$^{2+}$ in the M(2) site.

It was pointed out by Goldman and Rossman (1976) that the half-width of the 3100 cm$^{-1}$ band is an order of magnitude smaller than the other M(2) Fe$^{2+}$ bands. This suggested a vibrational origin and led them to examine a number of orthopyroxenes to determine the origin of this band. It was found that this band does not arise from M(2) Fe$^{2+}$. In the course of that investigation, they found a band at 2350 cm$^{-1}$ which correlated with M(2) Fe$^{2+}$ content, had the correct polarization properties for the $C_{2v}$ model proposed by Runciman et al., and had a half-width similar to those of the other M(2) Fe$^{2+}$ bands. Thus, the crystal-field analysis of the orthopyroxene spectral data of Runciman et al. is quantitatively incorrect, due to the incorporation of the incorrectly assigned 3100 cm$^{-1}$ band.

Orthopyroxene is the only documented sample in which all three $C_{2v}$ allowed transitions are observed.
In addition, it is the only sample in which a mid-infrared absorption band of Fe\textsuperscript{2+} within the split \(\text{T}_{5/2}\) ground state has been confirmed. Therefore, it is essential to quantitatively understand these data. For this reason, the orthopyroxene spectral data will be reanalyzed with a quantitatively different \(C_6\), point-charge model. It will be shown that this model results in a more acceptable and understandable energy-level scheme while still explaining the observed absorption anisotropy of the various bands.

**Experimental method**

Self-supporting sections of bronzite from Bamble, Norway, were cut parallel and perpendicular to \(c\), using external crystal morphology for orientation. An additional (001) section was set in epoxy on a microscope slide, thinned and polished to about 100 \(\mu\)m for measurement of the intense \(a\) band at 930 nm. The thickness of this section was determined by removing the sample from the epoxy and measuring it directly. Euhedral crystals, tabular along (100), of a hypersthene from Summit Rock, Oregon (Kleck, 1970) were sufficiently thin so that only polishing was necessary prior to obtaining their spectra. The orientation in all cases was confirmed by conoscopic interference figures. All spectra presented herein were obtained at room temperature, although the mid-infrared spectra of the Bamble bronzite were also obtained at 12°K using a Cryogenic Technology, Inc. cryogenic refrigerator. Other experimental details are similar to those presented in Rossman (1975 a,b).

Chemical analyses were obtained with an automated MAC5-SA3 electron microprobe using the technique of Bence and Albee (1968) for data reduction (Table 1).

Each spectrum and its polarized baseline was digitized, using a Calma X-Y digitizer. A plotting program was written for the IBM 370/155 to correct each spectrum for its polarizer baseline, to normalize the intensity to represent a desired crystal thickness, and to plot a smooth curve through all data points using a second-order polynomial interpolation function.

**Crystal structure and optical orientation**

Ghose (1965) analyzed the crystal structure of a hypersthene, \(\text{Mg}_{0.99}\text{Fe}_{1.01}\text{Si}_{3}\text{O}_{8}\), with space-group \(Pbca\): \(a = 18.310, b = 8.927,\) and \(c = 5.226\) Å. The optical orientation is \(\alpha = \beta = a,\) and \(\gamma = c.\) All atoms have \(C_1\) point-group symmetry. (100) and (010) ORTEP (Johnson, 1965) projections of the \(M(2)\) site are presented in Figure 1. The position of the metal ion in Figure 1 represents an \(M(2)\) site that contains 90 percent \(\text{Fe}^{2+}\). The principal distortion of this site from octahedral geometry results from an elongation of the \(M(2)-O(6)\) and \(M(2)-O(3)\) bonds with a reduction in the \(O(6)-M(2)-O(3)\) angle to 72.2°.

**Spectroscopic data**

The room-temperature spectra of the Bamble bronzite are presented in the 15000–4000 cm\(^{-1}\) region in Figure 2 to illustrate the absorption bands due to \(\text{Fe}^{2+}\) in the \(M(2)\) site. Bancroft and Burns (1967) and Burns (1970) reported room-temperature, polarized spectra in the 25000–4000 cm\(^{-1}\) region of a bronzite sample from this locality, and the reader is referred to these studies for the spectroscopic details that occur...
above 15000 cm⁻¹. Mössbauer analysis of that sample (Bancroft et al., 1967) indicated that greater than 90 percent of the total Fe²⁺ is in the M(2) site. In fact, a quadrupole-split doublet due to Fe²⁺ in M(1) was not detected. The spectra in Figure 2 differ from those previously reported in the intensities of the α, β, and γ components of the band at 11,000 cm⁻¹.

The band in the mid-infrared at 2350 cm⁻¹ (Fig. 3) is assigned to Fe²⁺ in the M(2) site. Runciman et al. indicated that a mid-infrared band due to Fe²⁺ in this site must be polarized mostly in γ to conform to a C₄ᵥ point-group, which explains the α and β-polarized bands at 11,000 cm⁻¹ and 5400 cm⁻¹, respectively. The α, β and γ spectra of the Bamble bronzite have been obtained at 12 K to determine the polarization ratios for the 2350 cm⁻¹ band. The low temperature diminishes the overlap of the 2350 cm⁻¹ band with the vibrational overtones that occur below 2200 cm⁻¹ so that more accurate intensity ratios can be obtained. The resulting ratios for the α, β, and γ bands at 2350 cm⁻¹ are 0.28:0.20:0.52. Therefore, this band is predominantly γ-polarized with some α and some β due to the different orientations of the C₄ᵥ crystal-field axes and the principal optical directions, as will be discussed in the next section. Coincidentally, these polarization ratios are nearly identical to the ratios determined for the 3100 cm⁻¹ band by Runciman et al., which were used to compare the theoretical intensities calculated from the selected C₄ᵥ crystal-field axes with the experimental intensities.

### Point group and band assignments

The crystallographic point-group symmetry of the M(2) site is C₁. In this point group, all transitions are allowed in each polarization. However, the 11,000 cm⁻¹, 5400 cm⁻¹, and 2350 cm⁻¹ bands are strongly polarized, indicating that the Fe²⁺ ion experiences an effective electrostatic symmetry higher than C₁. Runciman et al. developed a model based upon C₄ᵥ symmetry, and noted errors made in earlier studies in the assignment of absorption bands to specific transitions of Fe²⁺. This process utilizes the descent-in-symmetry method from D₄h to D₄ to C₄ᵥ. Problems arose because the assignment of experimentally-determined energy values to the specific symmetry states of C₄ᵥ by reducing the overall symmetry from D₄h is not unique and depends upon the type of rhombic distortion. There are four types of rhombic distortions that can arise.
Fig. 4. Four types of $C_{2v}$ polyhedra resulting from rhombic distortions of a $D_{4h}$ polyhedron. Each $C_{2v}$ figure is designated by the only symmetry elements that remain from $D_{4h}$. For each $C_{2v}$ figure, the sections viewed along the former $C_{4}$ axis of $D_{4h}$ and the $X, Y, Z$ axes are also shown where $Z$ corresponds to the two-fold rotation axis.

be applied to a $D_{4h}$ polyhedron, each resulting in a distinct $C_{2v}$ polyhedron whose symmetry elements (a two-fold rotation axis and two mirror planes) are related differently to the original symmetry elements of the $D_{4h}$ polyhedron. Figure 4 illustrates the four $C_{2v}$ types, in which each type is designated by the only symmetry elements that remain from $D_{4h}$ (Wilson et al., 1955). In addition, the section of each $C_{2v}$ type viewed along the former $C_{4}$ axis of $D_{4h}$ is presented to facilitate a comparison of the distortions.

Idealized energy-level schemes for each $C_{2v}$ type have been constructed from the correlation tables in Wilson et al. and are presented in Figure 5, in which the descent-in-symmetry from $O_{h}$ to $C_{2v}$ is given. The polarization properties of the allowed transitions have been determined using the character table for $C_{2v}$ in Cotton (1963).

The appropriate $C_{2v}$ model for the $M(2)$ site is $C_{2}''$, due to the orientation of an approximate two-fold rotation axis between the O(1)–O(4) and O(6)–O(3) oxygen pairs. The $XZ$ plane of $C_{2v}(C_{2}''')$ symmetry (Fig. 4) was approximated in the orthopyroxene $M(2)$ coordination polyhedron by the $M(2)$ metal ion and the O(1), O(3), O(4) and O(6) oxygens (Runciman et al.). Hence, the 11,000 cm$^{-1}$, 5400 cm$^{-1}$, and 2350 cm$^{-1}$ absorption bands are assigned from Figure 5 to the $A_{1} \rightarrow A_{1}$, $A_{1} \rightarrow B_{1}$, and $A_{1} \rightarrow B_{2}$ transitions of Fe$^{2+}$ in the $M(2)$ site. Each of these transitions is allowed in only one of the crystal-field directions. However, the crystal-field directions are not aligned with the principal vibration directions of the indicatrix. Therefore, components of each transition will occur in all vibration directions, but the transitions to $A_{1}$, $B_{1}$, and $B_{2}$ polarized in $Z$, $X$, and $Y$, are expected to occur mostly in $\alpha$, $\beta$, and $\gamma$, respectively.

Runciman et al. (Table 1, set I) calculated theoretical intensity ratios of the $\alpha$, $\beta$, and $\gamma$ components for these transitions of 0.85:0.02:0.14, 0.05:0.67:0.29, and 0.10:0.33:0.58, respectively. Our measured ratios for the Bamble bronzite for these bands are 0.86:0.10:0.04, 0.11:0.70:0.19, and 0.28:0.20:0.52, respectively. The general agreement between the theoretical and experimental intensity ratios for the three $M(2)$ Fe$^{2+}$ bands is certainly suggestive of a $C_{2v}$ spectroscopy. These data could not be explained using either $C_{1}$ or $C_{2}$ point-group symmetry.

Upon considering the orientation of the five $d$ orbitals in each of the $C_{2v}$ polyhedra in Figure 4, a
general ordering scheme of the various states is readily obtained. For instance, by assuming tetragonal compression between $O_6$ and $D_{4h}$ (Fig. 5), $A_{1g}$ is expected to be at higher energy than $B_{1g}$ in $D_{4h}$ symmetry. As a consequence, $A_1$ is expected to be at higher energy than $B_1$ in $C_{2h}(C_{2}^{z})$. In the same manner, the energy level of the two $C_{2g}$ states derived from the $E_g$ state of $D_{4h}$ were obtained for the distortions presented in Figure 4. Generally, the relative energy levels of these states are reversed if (1) the elongation in the $XZ$ plane is along $X$ in $C_{2}$, $\sigma_d$; (2) the dihedral angle about $X$ is greater than $90^\circ$ in $C_{2}$, $\sigma_d$; (3) the elongation in the $XZ$ plane is along $X$ in $C_{2}'$; and (4) the dihedral angle about $Z$ is greater than $90^\circ$ in $C_{2}''$.

The $O(3)-M(2)-O(6)$ and $O(1)-M(2)-O(4)$ angles about the crystal-field $Z$ axis of the $M(2)$ site are both less than $90^\circ$. Therefore, $A_2$ is expected to be at a lower energy than $B_2$ from the arguments presented above. However, Runciman et al. calculated just the reverse. This discrepancy will be examined in the following section.

**Crystal field analysis**

The general crystal-field treatment described by Runciman et al. will be used to analyze the spectra of bronzite presented in this paper in light of the assignment of a third $C_{2v}$ band of Fe$^{2+}$ in the $M(2)$ site at 2350 cm$^{-1}$. However, it will be shown that this method does not result in a satisfactory energy-level scheme, and for this reason, the bronzite data will be reanalyzed using a different crystal-field treatment. First, it is helpful to review the pertinent aspects of the crystal-field method of Runciman et al.

Runciman et al. derived a crystal-field potential using a $C_{2v}(C_{2}^{z})$ model. Fourth and higher order harmonic terms were excluded from the potential, after extracting octahedral terms, because an exact solution for their coefficients would require more data than are available in the spectra. Hence, $\Delta$ and two additional fitting parameters that relate to the coefficients of the $Y_{2u}^{4}$ and $Y_{2e}^{4}$ harmonic terms were fitted. $\Delta(10D_{4g})$ refers to the energy separation between the octahedral $^{5}T_{2g}$ and $^{5}E_g$ states initially needed to produce the observed splittings of the $C_{2v}$ states, and which also accounts for the effect of configuration interaction between the two $A_1$ states. It is important to realize that this method does not incorporate the specific bond-length and bond-angle distortions of the $C_{2v}$ site within the potential, and therefore does not distinguish between sites of different $C_{2v}(C_{2}^{z})$ coordination geometries.

The values of $\Delta$ and of the forbidden $A_1 \rightarrow A_2$ transition have been calculated from the energy expressions given in Runciman et al., using the following bronzite data from Figures 2 and 3: $A_1 \rightarrow A_1 = 10930 \text{ cm}^{-1}$; $A_1 \rightarrow B_1 = 5400 \text{ cm}^{-1}$, and $A_1 \rightarrow B_2 = 2350 \text{ cm}^{-1}$. The energy values of $\Delta$ and of the $A_1 \rightarrow A_2$ transition are calculated to be $4934 \text{ cm}^{-1}$ and $6178 \text{ cm}^{-1}$, respectively. These results indicate that the splitting of the $^{5}T_{2g}(O_{6})$ state is also $6178 \text{ cm}^{-1}$, because $B_2$ is at lower energy than $A_2$. However, from the discussion in the previous section, a dihedral angle about $Z$ of less than $90^\circ$ leads to the prediction that $A_2$ is at lower energy than $B_2$. As will be shown subsequently, $A_2$ transforms as an $XY$ wavefunction in $C_{2h}(C_{2}^{z})$ and $B_2$ transforms as a $YZ$ wavefunction. An acute dihedral angle about $Z$ increases the potential about $YZ$ relative to $XY$, and thus $A_2$ is expected to lie beneath $B_2$. Therefore, the $O(6)-M(2)-O(3)$ angle of $72.2^\circ$ and the $O(1)-M(2)-O(4)$ angle of $83^\circ$ suggest that the energy level scheme resulting from the method of Runciman et al. is incorrect. For this reason, the bronzite data will be reanalyzed, using a crystal-field treatment that incorporates fourth-order contributions of the distortion into the potential and also considers the effect of specific bond lengths and angles.

The bronzite data have been reanalyzed using the operator-equivalent method described in Hutchings (1964) to derive energy expressions for the various $C_{2v}(C_{2}^{z})$ states using the $Z$ axis in Figure 1 as the axis of quantization. Contributions from the $Y_{2u}^{3}$, $Y_{2e}^{3}$, $Y_{4u}^{3}$, $Y_{4e}^{3}$ harmonic terms remain in the potential after subtracting the octahedral terms. The number of fitting parameters in addition to $\Delta$ are reduced to two by deriving the potential in terms of one specified bond length, which in this case is taken to be the average metal–oxygen distance, $\bar{d}$; one fitting parameter is related to the second-order terms and the other is related to the fourth-order terms. The method assumes that each ligand constitutes a point charge. Hence, there are three fitting parameters, and the spectra can be analyzed as before. The potential, written in operator-equivalent notation, consists of an octahedral term, $\Delta$, and

$$M\left[\frac{A}{3} \hat{O}_z^2 + B \hat{O}_z^2\right] + N \left[\frac{C}{8} \hat{O}_z^4 + \frac{5D\hat{O}_z^4}{4} + \frac{3E}{4} \hat{O}_z^4\right]$$

\(^{3}\) A detailed description of the crystal-field method used in this paper can be obtained by ordering Document AM-76-035 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D. C. 20006. Please remit $1.00 in advance for the microfiche.
O₂, O₃, O₄, and O₅ are the operator equivalents of the associated spherical harmonic terms, and A, B, C, D, and E are determined by the bond angles and bond lengths of the site. The M(2) site possesses six unequal metal-oxygen bond lengths, from which three bond lengths must be selected to conform to a C₆v point-group symmetry. Therefore, the averages of the following bond lengths are used: M(2)-O(6), M(2)-O(3), M(2)-O(4), M(2)-O(2), M(2)-O(5).

The energy expressions for the two A states are the eigenvalues of the following configuration interaction matrix:

\[
\begin{align*}
M &= -\frac{g(r^2)}{14a^3} \\
N &= \frac{g(r^6)}{504a^5}
\end{align*}
\]

Table 2 lists the wavefunctions and energies of the other three states.

The solutions for the orthopyroxene data are: \( \Delta = 6522 \text{ cm}^{-1}; A_1 \rightarrow A_2 = 354 \text{ cm}^{-1}; M = -636 \text{ cm}^{-1}, \) and \( N = 9.5 \text{ cm}^{-1}. \) The energy-level scheme based upon these calculations is presented in Figure 6. As predicted from the acute dihedral angles about Z for the M(2) site, the energy level of \( A_2 \) is calculated below \( B_2 \) and the overall splitting of the \( ^5T_{2g}(O_h) \) state, determined by the \( A_1 \rightarrow B_2 \) transition energy, is only 2350 cm⁻¹. This splitting of the \( ^5T_{2g}(O_h) \) state, much smaller than previously calculated, supports the contention by Faye (1972) that the splitting of this state is either small or nearly the same for a large variety of mineral spectra. It is unlikely that Faye's suggestion can be accurately tested below 2000 cm⁻¹, due to the presence of vibrational absorptions in that region. However, the identification of the \( \text{Fe}^{2+} \) band at 2350 cm⁻¹ represents the largest confirmed splitting of the \( ^5T_{2g}(O_h) \) ground state known to us. Also, the magnitude of splitting indicated by this band arises from one of the largest, distorted six-coordinate mineral sites. These observations suggest that the splitting of the \( ^5T_{2g}(O_h) \) state is probably not greater than 2000 cm⁻¹ is most minerals, although further data are needed, especially in the 2000-4000 cm⁻¹ region, to examine this possibility further.

The calculated value of \( \Delta \) for \( \text{Fe}^{2+} \) in the M(2) site is 6522 cm⁻¹. This value is reasonable, considering the dependence of \( \Delta \) on \( 1/\tilde{a}^2 \) (Figgis, 1966). To determine a value of \( \Delta \) for \( \text{Fe}^{2+} \) in a more regular, six-coordinate site so that the \( 1/\tilde{a}^2 \) dependence can be evaluated for the orthopyroxene data, use is made of a study conducted by Faye (1972). Faye indicated that the barycenter energy of the states derived from the splitting of the \( ^5T_{2g}(O_h) \) state is approximately 10,000 cm⁻¹ for many six-coordinate sites (i.e., the M(1) sites in orthopyroxene, etc.) which have \( \tilde{a} \) values of about 2.1 Å. Since the barycenter energy is determined by the transitions from the ground state, any splitting of the \( ^5T_{2g}(O_h) \) states results in a barycenter energy that is larger than \( \Delta \) (see Fig. 6). Therefore, assuming that a \( \Delta \) of 9500 cm⁻¹ is produced from a site with \( \tilde{a} = 2.1 \text{ Å}, a 1/\tilde{a}^2 \) dependence predicts a \( \Delta \) of about 7200 cm⁻¹ for \( \text{Fe}^{2+} \) in the orthopyroxene M(2) site, using 2.22 Å for \( \tilde{a} \) (Ghose, 1965). Although there appears to be general agreement between the values of \( \Delta \) calculated from the spectral data and from the

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**Table 2.** C₆v crystal-field levels

<table>
<thead>
<tr>
<th>State</th>
<th>Wavefunction</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>( \sqrt{3}xz ) ( -M(A3B) - 6N(C10D) + 0.6\Delta )</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>( \sqrt{3}yz ) ( M(3B-A) - 6N(C+10D) - 0.4\Delta )</td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>( \sqrt{3}xy ) ( 2AM + \frac{2}{3}N(C70E) - 0.4\Delta )</td>
<td></td>
</tr>
</tbody>
</table>

\[ M = -\frac{g(r^6)}{14a^3} \qquad N = \frac{g(r^6)}{504a^5} \]

\[ \text{where} \]

FIG. 6. Energy level scheme of \( \text{Fe}^{2+} \) in the M(2) site using a \( C_{6v}(O_6) \) theoretical point-charge model.
dependence, it should be realized that this dependence assumes octahedral geometry. The validity
of calculating a value for $\Delta$ based upon the average of six $M-O$ bond lengths in a distorted coordination
site is subject to question, especially when four $M-O$ bonds are typically 2.1 Å in length, whereas the re-
mainder of the bond lengths are extremely long at greater than 2.4 Å. However, using $\bar{d}$ in these calculations may
be the most appropriate way in which the analysis of the spectral data from distorted coordination sites can be
compared. From the analysis of the bronzite spectra, it is concluded that by incorporating the fourth-order
contributions into the potential and by considering the effect of bond-length and bond-angle distortions
of the $M(2)$ site, a more reasonable $C_{\infty v}$ energy level scheme is obtained which still explains the polarization
properties of the various bands.

Finally, it must be pointed out that the $\beta$ and $\gamma$
components of the bands near 11,000 cm$^{-1}$ and the $\alpha$
and $\gamma$ components of the band near 5400 cm$^{-1}$ do not
occur at the same energy at which the main com-
ponents occur (Fig. 2). These differences may result
from weak spin-orbit coupling interactions. Ham $et
al.$ (1969) in a study of Fe$^{2+}$ doped into octahedrally-
coordinated sites in MgO suggested that spin-orbit
interactions, affected by Jahn-Teller distortions, pro-
duce a splitting of the $5T_{2g}$ state of approximately 100
$\text{cm}^{-1}$. Runciman $et al.$ pointed out that spin-orbit
splittings of Fe$^{2+}$ in the $M(2)$ site are expected to be
small, due to a quenching effect of a low-symmetry
environment. It is therefore conceivable that the
small differences ($\approx 100$ cm$^{-1}$) in the energy locations
of the various components of the band near 11,000
$\text{cm}^{-1}$ and 5400 $\text{cm}^{-1}$ are due to spin-orbit in-
teractions, although more data are required to evaluate
this possibility.

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