

Raman Spectra of CaWO_4 , SrWO_4 , CaMoO_4 , and SrMoO_4

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The first-order Raman spectra of CaWO_4 , CaMoO_4 , SrWO_4 , and SrMoO_4 have been obtained. All theoretically predicted vibrations have been observed, and assignment has been given for the internal vibrations of the tungstate and molybdate ions as well as for the external vibrations involving the rest of the lattice.

INTRODUCTION

EARLIER work^{1,2} in our laboratory has shown that lasers afford an ideal method of measuring the frequencies and symmetries of the Raman-active lattice vibrations of crystals, since each component of the polarizability tensor can be measured individually for each vibrational frequency. Recently the laser Raman technique has been applied to a number of crystals,³ including CaWO_4 ,^{4,5} where somewhat incomplete results have been reported. Raman data on the other Scheelites discussed in the present work have not appeared in the literature previously.

The tungstates and molybdates can be easily doped with rare-earth ions and are available in the form of large single crystals^{6,7}; consequently, they are of interest as laser materials⁸⁻¹⁰ and have therefore been chosen for study. CaWO_4 , CaMoO_4 , SrWO_4 , and SrMoO_4 are all crystals of the Scheelite type, having C_{4h} point-group symmetry and $I4_1/a$ space-group symmetry, with two formula groups per primitive cell.¹¹⁻¹⁴ The Ca or Sr ions are at S_4 sites, as are the W's or Mo's, and the oxygen ions are at C_1 sites. Group-theory calculations show¹⁵ that the $3N=36$ degrees of freedom for the 12 atoms in each primitive cell are divided into 26 vibrations of species $3A_g+5A_u+5B_g+3B_u+5E_g+5E_u$, where the species E vibrations are doubly degenerate. All of the even (g) vibrations are Raman-active, with

the polarizability tensors given below:

$$A_g: \begin{pmatrix} C_1 & 0 & 0 \\ 0 & C_1 & 0 \\ 0 & 0 & C_2 \end{pmatrix} \quad B_g: \begin{pmatrix} C_3 & C_4 & 0 \\ C_4 & -C_3 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$E_g: \begin{pmatrix} 0 & 0 & C_5 \\ 0 & 0 & C_5 \\ C_5 & C_5 & 0 \end{pmatrix}.$$

It can be seen from the form of the polarizability tensors that measurement of the α_{zz} component will yield only type E_g vibrations, measurement of α_{xx} will yield only type A_g vibrations, and measurement of α_{xy} will yield only B_g vibrations. In the present work measurement of each of these three components of the polarizability tensor for each crystal has been made, along with a measurement of α_{xx} , which yields both A_g and B_g vibrations and serves as a check on the other measurements. Throughout the rest of the paper we shall use the shortened notation¹⁶ (ij) to denote α_{ij} , where $i, j=x, y, z$.

Many crystals are known to consist of tightly bound atoms in a molecular group which is loosely bound to the rest of the lattice; the CO_3^{--} ion in calcite^{17,18} is a good example. Experimentally, as will be discussed further in this paper, the vibrational frequencies in CaWO_4 are similar to those of SrWO_4 , CaMoO_4 and SrMoO_4 . This suggests weak coupling between XO_4^{--} ions and the rest of the lattice and that it might be a good approximation to label vibrations as internal or external (as has been done with calcite^{18,19}), where "internal" refers to motion in which the center of mass of the XO_4^{--} ion does not move, and "external" refers to motion of XO_4^{--} ions as rigid units. Barker²⁰ and Russell and Loudon^{4,5} have taken this approach in discussing Scheelites.

Some physical insight is granted by further labeling the internal modes by the designation each would have if the XO_4^{--} ions were free molecules. The T_d symmetry a free tetrahedral XO_4 ion would have is reduced to S_4 in the crystal lattice. The presence of two

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¹⁹ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand, Inc., New York, 1945).

²⁰ A. S. Barker, Jr., *Phys. Rev.* **135**, A742 (1964).

TABLE I. (XO_4^{--}) vibrations in Scheelites ($X=W, Mo$).

Vibrational mode and symmetry	Isolated tetrahedrons	Tetrahedrons in lattice	Observed wave number (cm^{-1})			
			CaWO ₄	SrWO ₄	CaMoO ₄	SrMoO ₄
T_d		C_{4h}				
$\nu_1(2A_1)$		$\nu_1(A_g)$	912 ^a	925	878	887
		$\nu_1(B_u)$		Forbidden		
$\nu_3(2F_2)$		$\nu_3(A_u)$	778 ^b		775	
		$\nu_3(B_g)$	838	839	844	842
		$\nu_3(E_g)$	797	797	797	797
		$\nu_3(E_u)$	793		802	
		$\nu_3(A_u)$	435		425	
$\nu_4(2F_2)$		$\nu_4(B_g)$	401	370	393	367
		$\nu_4(E_g)$	409	378	401	381
		$\nu_4(E_u)$	309		318	
		$\nu_2(B_u)$		Forbidden		
		$\nu_2(A_g)$	336	334	333	327
$\nu_2(2E)$		$\nu_2(B_g)$	336	334	339	327
		$\nu_2(A_u)$	237		245	
		B_u		Forbidden		
Rotation ($2F_1$)		A_g	218	187	205	181
		E_g	275	238	263	231
		E_u	202		208	

^a Uncertainties are approximately $\pm 3 cm^{-1}$.

^b Odd (u) levels of CaWO₄ and CaMoO₄ from Barker (Ref. 20).

XO_4 groups in each primitive cell further alters the symmetry to C_{4h} . These symmetry changes remove some of the degeneracies of the vibrational wave functions which would characterize free XO_4 ions. For example, in the case of two uncoupled XO_4 ions, each vibrating in the totally symmetric mode ν_1 , we can consider the system as a whole to have symmetry $2A_1$. In the crystal lattice this degeneracy is split: $2A_1 \rightarrow A_g + B_u$, since the symmetry of the XO_4 ion is changed from T_d to S_4 . It is useful to designate these two vibrations as $\nu_1(A_g)$ and $\nu_1(B_u)$. Similarly, the notation $\nu_3(B_g)$ refers to a B_g internal vibration which would be sixfold degenerate, $\nu_3(2F_2)$, in the limiting case of two uncoupled XO_4 ions. The other five degrees of freedom occur as an A_g , an E_g and an E_u vibration in the C_{4h} symmetry crystal. This ν_3 mode is diagrammed in Fig. 1. Diagrams of the other XO_4 modes, ν_1 , ν_2 , and ν_4 are given by Herzberg.¹⁹

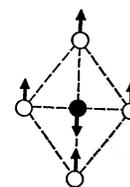
Four Raman-active external vibrations are predicted for Scheelites. They consist²⁰ of $2B_g + 2E_g$ and are assigned in Table II. As in Table I, comparison is

TABLE II. External optical modes in Scheelites (cm^{-1}).

Species	CaWO ₄	SrWO ₄	CaMoO ₄	SrMoO ₄
B_g	84 ^a	75	110	94
E_g	117	101	145	111
E_u	143 ^b		150	
A_u	180		196	
E_g	195	131	189	137
B_g	210		219	157

^a Uncertainties are approximately $\pm 3 cm^{-1}$.

^b Odd (u) levels of CaWO₄ and CaMoO₄ from Barker (Ref. 20).

FIG. 1. The ν_3 vibration of a tetrahedral WO_4 ion of T_d symmetry (Ref. 19).

made with the available infrared data. Of the $2A_u + 2E_u$ predicted external modes, one of each is acoustic; the optical modes are listed in Table II.

EXPERIMENTAL

The Raman spectra were excited with an argon ion laser emitting about 80 mW at either 4880 or 5145 Å. Detection was by means of a Spex 1400 tandem grating spectrograph and a cooled EMI 6256 photomultiplier. Slit width varied from 100 μ to less than 50 μ . This gave a spectral resolution of about 3 cm^{-1} ; the $A_g + B_g$ doublet in CaMoO₄ has a separation of $\sim 6 cm^{-1}$ and is shown resolved in Fig. 2. Signal ampli-

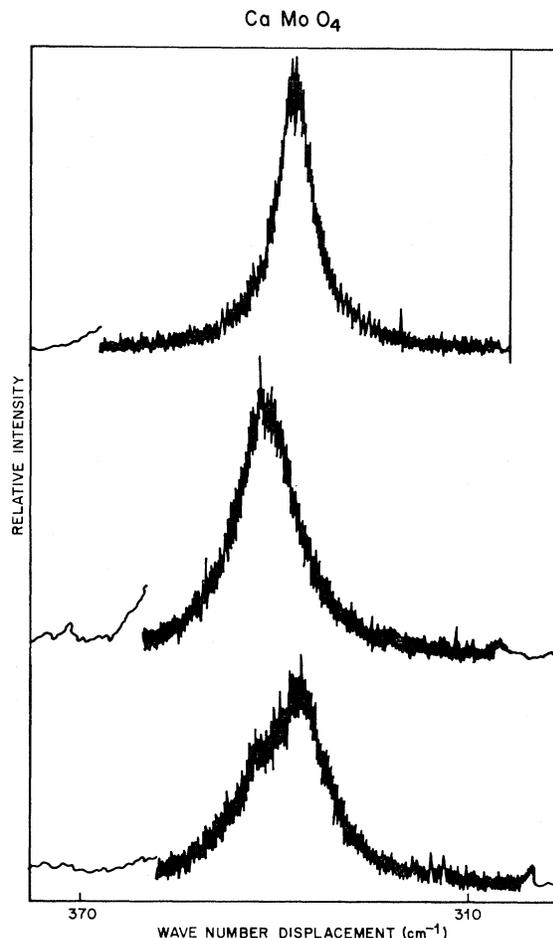


FIG. 2. The $A_g + B_g$ doublet of CaMoO₄ at 336 cm^{-1} . Top to bottom: measurement of α_{zz} , showing A_g mode; measurement of α_{zx} , showing B_g mode; measurement of α_{xy} , showing $A_g + B_g$.

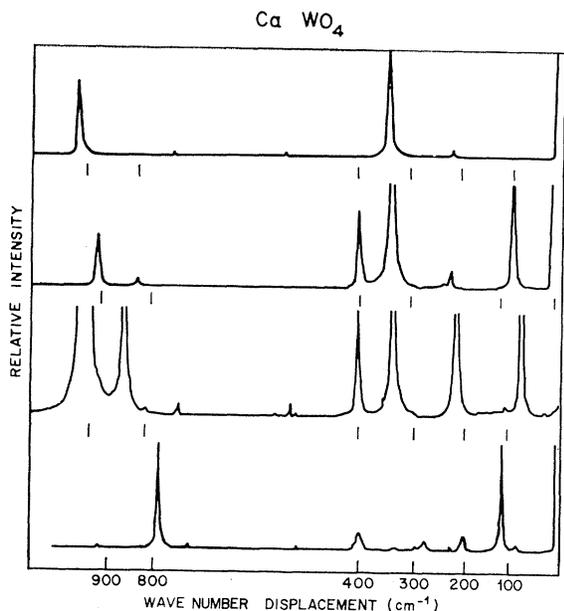


FIG. 3. Raman vibrations of CaWO₄. Top to bottom: $x(zz)y$, $y(xy)z$, $x(yy)z$, and $x(yz)y$.

fication from the photomultiplier was via a Keithley 610BR electrometer. Time constants were about three seconds. The data shown in Figs. 2-6 were taken on a Sanborn 7700 recording voltmeter.

The samples were clear single crystals grown by the Czochralski method^{6,7}; they averaged 4×4×10 mm in size and were oriented by x-ray techniques.

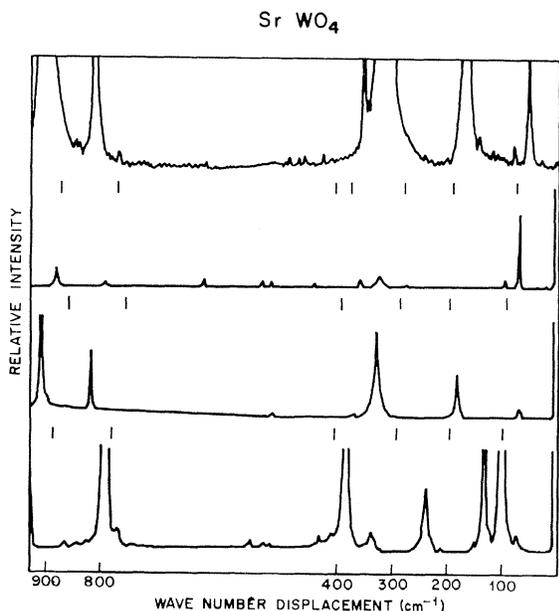


FIG. 4. Raman vibrations of SrWO₄. Top to bottom: $x(zz)y$, $y(xy)z$, $x(yy)z$, and $x(yz)y$.

Plane-polarized radiation from the laser was focused inside the crystal in a direction parallel to one axis. Scattered radiation was collected perpendicular to the laser beam and was focused onto the spectrometer entrance slit. A quarter-wave plate was used to change the direction of the incident polarization, and a polarizer was inserted in front of the entrance slit.

For each crystal four orientations were used, and both Stokes and anti-Stokes lines were measured. An additional calibration check was afforded by the presence of weak argon spontaneous emission lines at 5009 and 5062 Å when the 4880 Å laser line was used.

Figures 3-6 show the data for each crystal. All data were obtained at a temperature of approximately

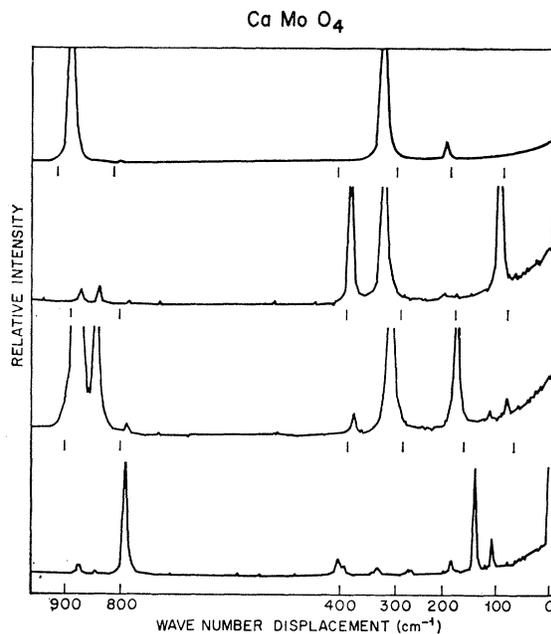


FIG. 5. Raman vibrations of CaMoO₄. Top to bottom: $x(zz)y$, $y(xy)z$, $x(yy)z$, and $x(yz)y$.

300°K. The traces are, top to bottom: $x(zz)y$, $y(xy)z$, $x(yy)z$, and $x(yz)y$. Here the notation¹⁶ $x(yz)y$ denotes incident radiation along the x axis of the crystal, plane-polarized in the y direction, with scattered radiation polarized in the z direction and collected in the y direction: in other words, a measurement of α_{yz} for a phonon propagating in the xy plane. The top trace for each crystal shows three strong Raman emission lines corresponding to the three predicted A_g vibrations, plus weaker lines (B_g and E_g vibrations) which arise from slight misalignment of the crystal in the laser beam and from crystal imperfections. Misorientation lines occur in the other traces also and can easily be identified by comparing intensities of the four traces. The second trace for each crystal shows the five B_g vibrations permitted by the selection rules for α_{xy} .

Note that, in each case, one of the strongest B_g vibrations has nearly the same wave number displacement ($\sim 335 \text{ cm}^{-1}$) as a strong A_g . The third trace is $x(yy)z$ and shows both A_g and B_g vibrations. Figure 2 shows a slower trace of the A_g+B_g pair in CaMoO_4 and resolves the doublet. The fourth trace for each crystal shows the remaining Raman-active vibrations, the five E_g modes.

DISCUSSION

In the lowest order of approximation, assuming the normal modes of isolated XO_4 ions, the frequencies identified as ν_1 and ν_2 in Table I do not depend upon the mass of the central atom and should, therefore, be the same for each crystal if W and Mo are treated as isotopes and hence force constants assumed equal. This is nearly true for ν_2 , but not for ν_1 , which shows a shift in going from WO_4 to MoO_4 .

Since no other Raman work on CaMoO_4 , SrWO_4 or SrMoO_4 has been published, no comparisons can be made. The vibrational frequencies obtained for CaWO_4 in the present work agree fairly well with those published by Russell and Loudon.^{4,5} Some differences are to be noted, however. Firstly, we have observed all the expected vibrations, including three which Russell and Loudon did not report. Secondly, Russell reported appearance of a Raman line at 180 cm^{-1} which he suggested is a Raman-forbidden A_u vibration. We find no line at 180 cm^{-1} in CaWO_4 , and we observe no selection rule breakdown.

Some final comment on the assignment is warranted. The high frequency mode ν_1 is unambiguous. Of the vibrations ν_3 and ν_4 , the latter normally has a frequency approximately half that of the former,¹⁹ as is observed in Table I. ν_2 is, as expected,¹⁹ comparable in frequency to ν_4 . The modes which become free rotation in the limiting case of uncoupled XO_4 ions are expected to be lowest in frequency of all the internal modes and were so assigned. The rotation symmetry, $2F_1$, breaks down to $B_u+A_g+E_g+E_u$ for C_{4h} crystals; since no A_g external modes are predicted, the rotational modes can also be identified by the fact that they include the lowest A_g vibration.

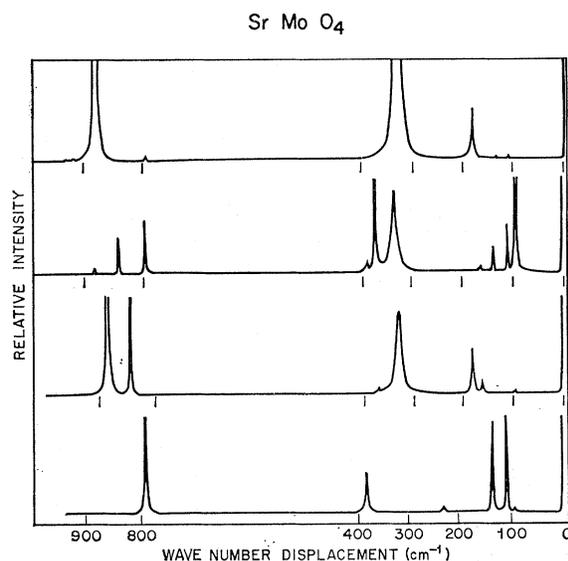


FIG. 6. Raman vibrations of SrMoO_4 . Top to bottom: $x(zz)y$, $y(xy)z$, $x(yy)z$, and $x(yz)y$.

The external modes are assigned as the remaining low-lying levels. External modes are expected to be low in frequency because they involve motion of heavier units (whole XO_4 ions) and also involve weaker coupling.

In actuality, however, the true normal modes are normalized linear combinations of all zero-order modes of the same symmetry, and there might be considerable mixing between, for example, the E_u mode at $125\text{--}150 \text{ cm}^{-1}$ labeled "external" in Table II and the E_u mode at $150\text{--}200 \text{ cm}^{-1}$ associated with rotation in Table I. In summary, the labeling of modes is intended to be physically meaningful and not mathematically rigorous.

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