

# RAMAN SPECTRUM OF $\text{Cs}_2\text{SO}_4$ USING $\text{Ar}^+$ LASER EXCITATION\*

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## ABSTRACT

Raman spectrum of a  $\text{Cs}_2\text{SO}_4$  single crystal has been recorded and measured using an  $\text{Ar}^+$  laser as a source of excitation. The polarization behaviour of the Raman lines under different crystal orientations has been studied. Symmetry co-ordinates of the Raman active lattice modes as worked out from group theoretical concepts are presented.

## INTRODUCTION

SIGNIFICANT new results have been recently obtained from reinvestigations of the Raman effect in single crystals using laser excitation.<sup>1-3</sup> Raman spectra of some of the alkali sulphate single crystals taken with conventional mercury arc sources are reported in the literature.<sup>4-8</sup> Recently, Claus<sup>9</sup> has reported in his Ph.D. thesis the Raman Spectrum of  $\text{K}_2\text{SO}_4$  single crystal using He-Ne Laser. However, no detailed report is available on the polarization data or on the analysis of external or internal oscillations in  $\text{Cs}_2\text{SO}_4$ . Therefore, a single crystal of  $\text{Cs}_2\text{SO}_4$  is grown from solution and its Raman spectrum using argon ion laser excitation is taken in order to have an understanding of the internal and external oscillations in the crystal.

## EXPERIMENTAL

Single crystals of  $\text{Cs}_2\text{SO}_4$  were grown by slow evaporation of a saturated aqueous solution of cesium sulphate. The crystals were clear and trans-

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parent. The one used in the experiment is about  $5 \text{ mm} \times 3 \text{ mm} \times 2 \text{ mm}$  in size. Crystal faces were easily identified by crystal morphology and confirmed by X-ray rotation photographs of other indential looking crystals of  $\text{Cs}_2\text{SO}_4$ . The  $\text{Ar}^{+1}$  lines at  $4880 \text{ \AA}$  and  $5145 \text{ \AA}$  from a Coherent Radiation Laboratory Model 52 Argon ion laser were used for excitation in the Raman studies. For measurements the spectra obtained using  $4880 \text{ \AA}$  excitation were mostly used. A Spex model 1400 double grating monochromator, capable of  $0.1 \text{ \AA}$  resolution in the first order, was used for recording the spectra. Frequency measurements are accurate to better than  $\pm 1 \text{ cm}^{-1}$  with the width of the Raman line as the major contribution to the inaccuracy.

#### CRYSTAL STRUCTURE OF $\text{Cs}_2\text{SO}_4$

Crystal structure of the isomorphous sulphates of potassium, ammonium, rubidium and cesium have been determined by Ogg<sup>10</sup>. These sulphate crystals belong to the space group  $V_h^{16}$  with unit cells containing two reflection planes, four glide planes, twelve dyad screw axes and four centres of symmetry. Figure 1 shows the orthorhombic unit cell of  $\text{Cs}_2\text{SO}_4$  with dimensions  $a=6.218$ ,  $b=10.884$  and  $c=8.198 \text{ \AA}$ . The structure consists of layers of atoms parallel to (100) plane separated by a distance of  $a/2$ . The reflection planes are  $(100)_+$  and  $(100)_-$  if we assume the origin of co-ordinates is at the centre of the unit cell. The unit cell contains four molecules. Depending on the oxygen environment the cesium atoms are classified as  $\alpha$  or  $\beta$  type. As a result there are four cesium ions of  $\alpha$  type and four of  $\beta$  type in a unit cell. The site symmetry of the individual  $\text{SO}_4$  ions and Cs ions is  $C_s$ .

#### OPTICAL PHONONS

Bhagavantam and Venkatarayudu<sup>11-13</sup> developed a useful method for calculating the internal and external oscillations in a crystal. If there are  $p$  atoms in a unit cell ( $p=28$  in  $\text{Cs}_2\text{SO}_4$  unit cell) there will be  $n=3p$  normal modes of vibration in the crystal of which 3 will correspond to acoustic series and the others to the optical series. If the  $p$  atoms are divided into  $s$  groups (in  $\text{Cs}_2\text{SO}_4$ ,  $s=12$  with 8 Cs monatomic groups and four  $\text{SO}_4$  groups) the oscillations between different groups which are called external oscillations will amount to  $T=3s$  out of which  $T_a=3$  will correspond to acoustic phonons while the others  $T_0=T-T_a$  will form part of the optical phonons ( $T_0=33$  in  $\text{Cs}_2\text{SO}_4$ ). If  $v$  corresponds to the number of monatomic groups in  $s$ , the librations or external rotatory normal modes will be given by  $R'=3(s-v)$  or  $2(s-v)$  depending upon the group capable of rotatory motion being non-linear or linear ( $R'=12$  in  $\text{Cs}_2\text{SO}_4$ ). Finally,

the number of internal oscillations will be given by  $n' = n - T - R'$ , the number in  $\text{Cs}_2\text{SO}_4$  being 36. The normal modes of vibration  $n$ ,  $T$ ,  $R'$  or  $n'$  will form basis for reducible representations of the factor group of the unit cell, the order of the representation being  $n$ ,  $T$ ,  $R$  or  $n'$  respectively. The characters for these representations under different symmetry operations ( $R$ ) are easily calculated noting that each atom or a group in the unit cell that remains invariant under the particular operation contributes  $(\pm 1 + 2 \cos \psi)$  to the character  $\chi(R)$  of the reducible representations  $\Gamma(n)$ ,  $\Gamma(n')$ ,  $\Gamma(T)$  or  $\Gamma(T_a)$  where  $\psi$  represents the angle of rotation in a symmetry operation  $R$  and a plus sign is to be taken in an operation involving pure rotation while a minus sign is to be taken in an operation involving rotation-reflection. For a reducible representation  $\Gamma(R')$  corresponding to the rotatory normal modes  $R'$  in a non-linear rotating group, the contribution to  $\Gamma(R)$  by each group that is invariant under the symmetry operation ( $R$ ) will be  $(1 \pm 2 \cos \psi)$  where again the plus sign is to be used for operations involving pure rotation while the minus sign is to be used for a rotation-reflection operation. The character table for the factor group  $V_h^{16}$  and the classification of the

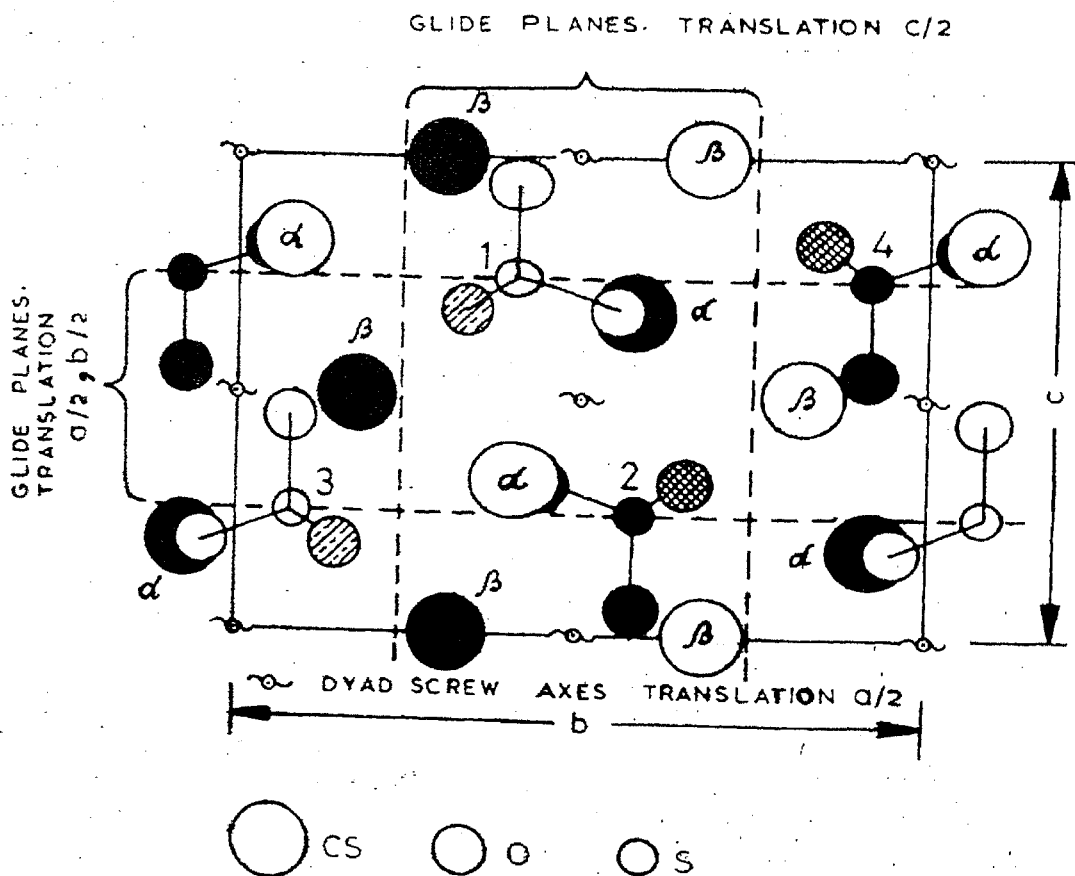


FIG. 1 Projection of the atoms in a unit cell of  $\text{Cs}_2\text{SO}_4$  crystal in the  $bc$  plane.

normal modes  $n$ ,  $n'$ , T,  $T_a$  and  $R'$  are given in Table I for a  $\text{Cs}_2\text{SO}_4$  single crystal. Detailed steps used in obtaining the number and classification of the normal modes are also included in the table.

A clearer idea of the physical nature of the  $n'$  internal oscillations corresponding to the  $\text{SO}_4$  groups can be obtained by considering them to arise from the coupling of the normal modes of free sulphate ions using the site method developed by Halford,<sup>14</sup> Horning<sup>15</sup> and Winston and Halford.<sup>16</sup> To make the picture more complete, detailed steps in the procedure for obtaining the normal modes  $n'$ , T and  $R'$  and their symmetries from the site method are given in Table II. Though the final results obtained in Table II are the same as those obtained in Table I, some of the steps in Table II make use of Table I and the two tables put together give a much clearer picture of the problem than either of the two tables given.

The site symmetry of the  $\text{SO}_4$  group and that of the Cs atom are  $C_s$ . It is sufficient to consider the site group  $C_s$  individually for  $\text{SO}_4$  and Cs ions. The  $\text{SO}_4$  free ion belongs to  $T_d$  point group and has four frequencies  $\nu_1$  ( $A_1$ ),  $\nu_2$  (E),  $\nu_3$  ( $F_2$ ) and  $\nu_4$  ( $F_2$ ) at 981, 451, 1104 and  $613\text{ cm}^{-1}$  respectively.<sup>17</sup> Irreducible representations  $A_1$ , E and  $F_2$  of the point group  $T_d$  get correlated to ( $A'$ ), ( $A' + A''$ ) and ( $2A' + A''$ ) respectively of the point group  $C_s$ . As there are four  $\text{SO}_4$  groups in a unit cell of  $\text{Cs}_2\text{SO}_4$  one has to find out how the sets of ( $4A'$ ), ( $4A' + 4A''$ ) and ( $8A' + 4A''$ ) go over under the factor group  $V_h$ <sup>16</sup> wherein they form bases for reducible representations. The characters for the reducible representations ( $4A'$ ) and ( $4A''$ ) are included in Table I, which in  $V_h$ <sup>16</sup> reduce to ( $A_g + B_{1g} + B_{2u} + B_{3u}$ ) and ( $A_u + B_{1u} + B_{2g} + B_{3g}$ ) respectively. ( $4A' + 4A''$ ) and ( $8A' + 4A''$ ) will thus reduce to ( $A_g + B_{1g} + B_{2u} + B_{3u} + A_u + B_{1u} + B_{2g} + B_{3g}$ ) and ( $2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u} + A_u + B_{1u} + B_{2g} + B_{3g}$ ) respectively. All the external and internal oscillations in  $\text{Cs}_2\text{SO}_4$  obtained in this manner are listed in Table II. It is shown in Table I that the vibrations  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$  are active in the infrared while  $A_g$ ,  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$  are active in the Raman effect. The three acoustic phonons are  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$ . Of the 12 librations the six Raman active ones are  $A_g$ ,  $B_{1g}$ ,  $2B_{2g}$  and  $2B_{3g}$ . Again of the other lattice vibrations  $6A_g$ ,  $6B_{1g}$ ,  $3B_{2g}$  and  $3B_{3g}$  are Raman active. There are 36 internal oscillations of which the eighteen Raman active ones are  $6A_g$ ,  $6B_{1g}$ ,  $3B_{2g}$  and  $3B_{3g}$ . The expected polarization behaviour<sup>18</sup> of the different Raman active vibrations in  $\text{Cs}_2\text{SO}_4$  is indicated in Table III.

TABLE II  
Correlation table for normal modes in  $Cs_2SO_4$

Free $SO_4$ ion		Internal oscillations ( $n'$ )	
Molecular point group	Site group	Modes from site group	Modes in space group
$T_d$	$C_s$	$C_s$	$V_h^{16}$
$\nu_1 (A_1)$	$A'$	$4A'$	$A_g + B_{1g} + B_{2u} + B_{3u}$
$\nu_2 (E)$	$A' + A''$	$\begin{cases} 4A' \\ 4A'' \end{cases}$	$\begin{cases} A_g + B_{1g} + B_{2u} + B_{3u} \\ A_u + B_{1u} + B_{2g} + 2B_{3g} \end{cases}$
$\nu_3 (F_2)$	$2A' + A''$	$\begin{cases} 8A' \\ 4A'' \end{cases}$	$\begin{cases} 2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u} \\ A_u + B_{1u} + B_{2g} + B_{3g} \end{cases}$
$\nu_4 (F_2)$	$2A' + A''$	$\begin{cases} 8A' \\ 4A'' \end{cases}$	$\begin{cases} 2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u} \\ A_u + B_{1u} + B_{2g} + B_{3g} \end{cases}$
Rotations of $SO_4$ in $T_d$ group		Librations ( $R'$ )	
Site group	Modes from site group	Modes in space group	
$C_s$	$C_s$	$V_h^{16}$	
$F_1 (R_x, R_y, R_z)$	$A' (R_z)$ $2A'' (R_x, R_y)$	$4A'$ $8A''$	$A_g + B_{1g} + B_{2u} + B_{3u}$ $2A_u + 2B_{1u} + 2B_{2g} + 2B_{3g}$
Translations of $SO_4$ in $T_d$ group		External oscillations (T)	
Site group	Modes from site group	Modes in space group	
$C_s$	$C_s$	$V_h^{16}$	
$F_2 (T_x, T_y, T_z)$	$2A' (T_x, T_y)$ $A'' (T_z)$	$8A'$ $4A''$	$2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u}$ $A_u + B_{1u} + B_{2g} + B_{3g}$
Translations of $C_s$		Modes in space group	
Site group	Modes from site group	$V_h^{16}$	
$C_s$	$C_s$	$V_h^{16}$	
$2A' (T_x, T_y)$ $A'' (T_z)$	$8A'$ $4A''$	$2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u}$ $A_u + B_{1u} + B_{2g} + B_{3g}$	

TABLE III

*Raman tensors for  $V_h^{16}$  space group*

$A_g$	$B_{1g}$	$B_{2g}$	$B_{3g}$
$\begin{pmatrix} aa & - & - \\ - & bb & - \\ - & - & cc \end{pmatrix}$	$\begin{pmatrix} - & - & - \\ - & - & bc \\ - & cb & - \end{pmatrix}$	$\begin{pmatrix} - & - & ac \\ - & - & - \\ ca & - & - \end{pmatrix}$	$\begin{pmatrix} - & ab & - \\ ba & - & - \\ - & - & - \end{pmatrix}$

## RESULTS AND DISCUSSION

Representative recordings of spectra obtained are shown in Figs. 2 to 4. In the notation  $c(bc)a$ , etc., the first letter  $c$  represents the direction of the incident beam in the crystal while the last letter represents the direction of the scattered light observed. The first letter in parenthesis represents the direction of polarization of the incident beam while the second letter represents the direction of polarization of the observed scattered beam. In the cases when no polarizer is used in the scattered beam the second letter in parenthesis is replaced by a hyphen.  $a$ ,  $b$  and  $c$  represent the sides of the unit cell of the crystal. It can be seen from Figs. 2 to 4 that the fundamental  $\nu_2(E)$  which occurs at  $451\text{ cm}^{-1}$  in the free ion of  $\text{SO}_4^{2-}$  is split into three components in  $\text{Cs}_2\text{SO}_4$  crystal, their positions being at 447, 445 and  $442\text{ cm}^{-1}$  with polarizations ( $B_{2g} + B_{3g}$ ),  $B_{1g}$  and  $A_g$  respectively. The splittings of the other internal oscillations could also be seen in the figures along with the expected polarizations. Superpositions of more than one component in some of these lines are confirmed through their polarization behaviour. Observed details of all the internal oscillations are listed in Table IV.

The frequencies of the observed lattice modes and their symmetries as determined from the polarization experiments are listed in Table V. It is not possible at this stage to identify unambiguously the Raman lines corresponding to librations from those corresponding to the translatory motions in the lattice spectrum. This identification will be postponed till the infrared work in  $\text{Cs}_2\text{SO}_4$  as well as the infrared and Raman spectroscopic work in  $\text{Rb}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are completed.

TABLE IV  
Observed internal oscillations of  $SO_4^-$

Free ion ( $cm^{-1}$ )	$Cs_2SO_4$ crystal ( $cm^{-1}$ )
981 [ $\nu_1$ ( $A_1$ )]	970 [ $A_g + B_{1g}$ (?)]
451 [ $\nu_2$ ( $E$ )]	{ 447 [ $B_{2g} + B_{3g}$ ]
	{ 445 [ $B_{1g}$ ]
	{ 442 [ $A_g$ ]
1104 [ $\nu_3$ ( $F_2$ )]	{ 1118 [ $A_g + B_{1g}$ ]
	{ 1090 [ $B_{1g} + B_{2g} + B_{3g}$ ]
	{ 1082 [ $A_g$ ]
613 [ $\nu_4$ ( $F_2$ )]	{ 617 [ $A_g + B_{1g}$ ]
	{ 614 [ $B_{1g} + B_{2g} + B_{3g}$ ]
	{ 610 [ $A_g$ ]

TABLE V  
Observed lattice modes in  $Cs_2SO_4$  and their symmetries

( $cm^{-1}$ )	Symmetry
119	$B_{1g}$
113	$A_g + B_{2g}$
107	$B_{3g}$
72	$B_{1g}$
65	$A_g + B_{2g}$
62	$B_{3g}$
58	$A_g + B_{1g}$
50	$A_g + B_{2g} + B_{3g}$
40	$A_g$

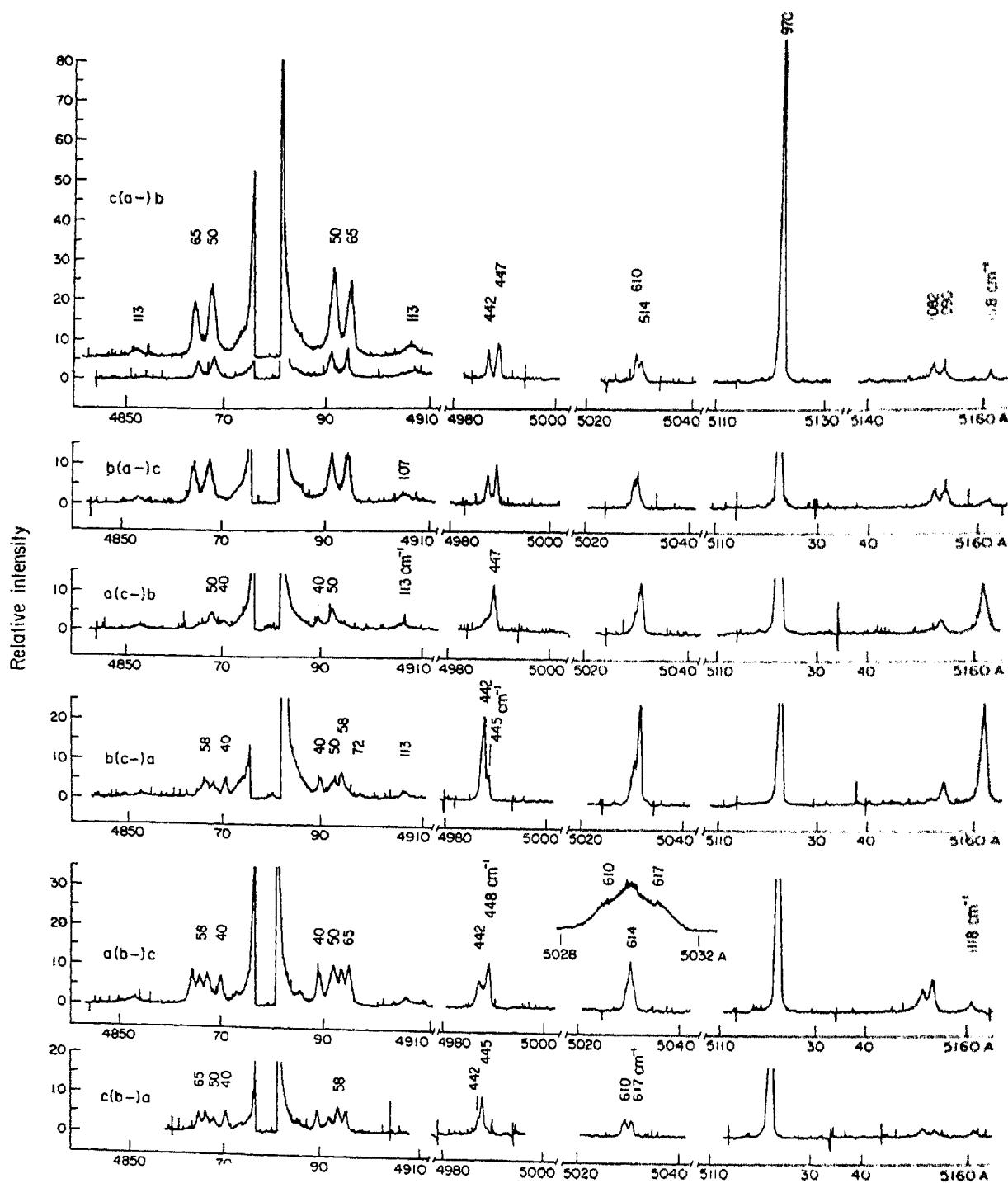


FIG. 2. Raman spectrum of  $\text{Cs}_2\text{SO}_4$  crystal using 4880 Å excitation with different crystal orientations. No polarizer is used in the scattered beam.

### SYMMETRY CO-ORDINATES OF THE NORMAL MODES

Symmetry co-ordinates of the normal modes in  $\text{Cs}_2\text{SO}_4$  single crystal which will be useful in the calculation of their frequencies and intensities



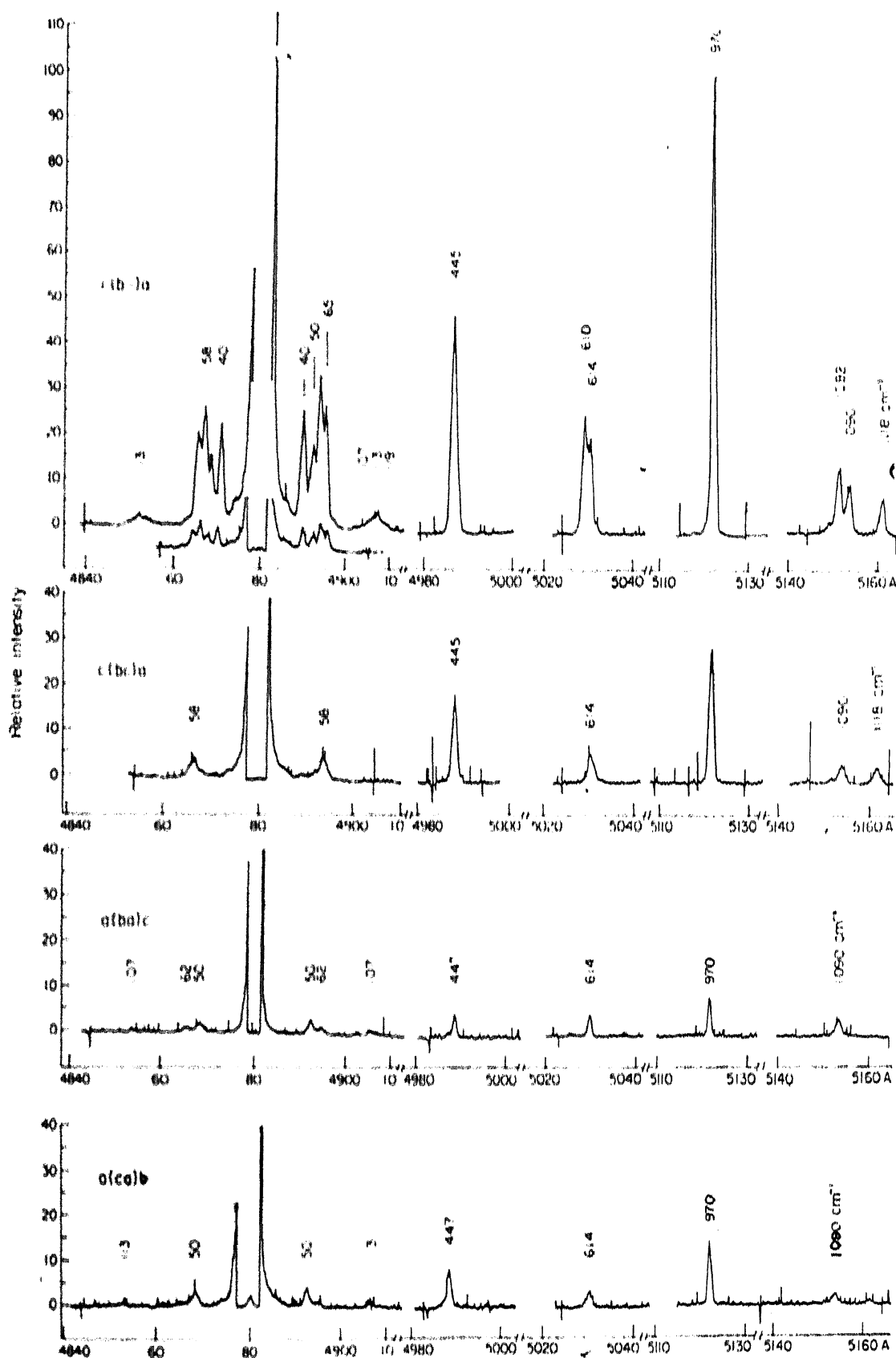


FIG. 3. Raman spectrum of  $\text{Cs}_2\text{SO}_4$  crystal using 4880 Å excitation with different crystal orientations. The direction of polarization of the incident beam is perpendicular to that of the observed scattered beam in the lower three spectra.

are worked out using the procedures used by other workers.<sup>12, 19, 20</sup> Those that correspond to the Raman active librations in the crystal are

$$Q_{A_g} = \frac{1}{2} [l_{z1} + l_{z2} - l_{z3} - l_{z4}]$$

$$Q_{B_{1g}} = \frac{1}{2} [l_{z1} + l_{z2} + l_{z3} + l_{z4}]$$

$$Q_{B_{2g}} = \frac{1}{2} [l_{x1} + l_{x2} - l_{x3} - l_{x4}]$$

$$Q_{B_{3g}} = \frac{1}{2} [l_{x1} + l_{x2} + l_{x3} + l_{x4}]$$

$$Q_{B_{2g}} = \frac{1}{2} [l_{y1} + l_{y2} + l_{y3} + l_{y4}]$$

$$Q_{B_{3g}} = \frac{1}{2} [l_{y1} + l_{y2} - l_{y3} - l_{y4}]$$

where  $\frac{1}{2}$  is a normalizing factor,  $l_{x1}$ ,  $l_{y1}$  and  $l_{z1}$  are the displacement components because of the rotations around  $x_1$ ,  $y_1$  and  $z_1$  axes respectively of the sulphate group marked 1 in Fig. 1 and similarly  $l_{x2}$ ,  $l_{y2}$  and  $l_{z2}$ , etc. The three components of  $l$  are  $l_x = y\delta z - z\delta y$ ,  $l_y = z\delta x - x\delta z$  and  $l_z = x\delta y - y\delta x$  where  $\delta x$ ,  $\delta y$  and  $\delta z$  are the components of the rotation vector.  $x$ ,  $y$  and  $z$  directions are respectively parallel to the crystallographic  $c$ ,  $b$  and  $a$  axes in the crystal.

There are 18 external oscillatory type normal modes which are Raman active. Since the centre of mass of the unit cell is one of the inversion centres and does not move in any of these Raman active vibrations, these oscillations can be separately grouped into three sets with a set of six belonging to the 4  $SO_4$  ions, a second set of six belonging to the 4 Cs ( $\alpha$ ) ions and a third set of six belonging to the 4 Cs ( $\beta$ ) ions. The symmetry co-ordinates of the six Raman active external oscillations under any one of these three sets will be of the type

$$Q_{A_g} = \frac{1}{2} (x_1 - x_2 + x_3 - x_4)$$

$$Q_{A_g} = \frac{1}{2} (y_1 - y_2 + y_3 - y_4)$$

$$Q_{B_{1g}} = \frac{1}{2} (x_1 - x_2 + x_4 - x_3)$$

$$Q_{B_{1g}} = \frac{1}{2} (y_1 - y_2 + y_3 - y_4)$$

$$Q_{B_{2g}} = \frac{1}{2} (z_1 - z_2 + z_3 - z_4)$$

$$Q_{B_{2g}} = \frac{1}{2} (z_1 - z_2 + z_4 - z_3)$$

where  $x_1$ ,  $y_1$ , and  $z_1$  represent respectively displacements of group 1 [ $SO_4$ , Cs ( $\alpha$ ) or Cs ( $\beta$ )] along the crystallographic  $c$ ,  $b$  and  $a$  directions in the unit cell and similarly  $x_2$ ,  $y_2$  and  $z_2$  for group 2, etc.

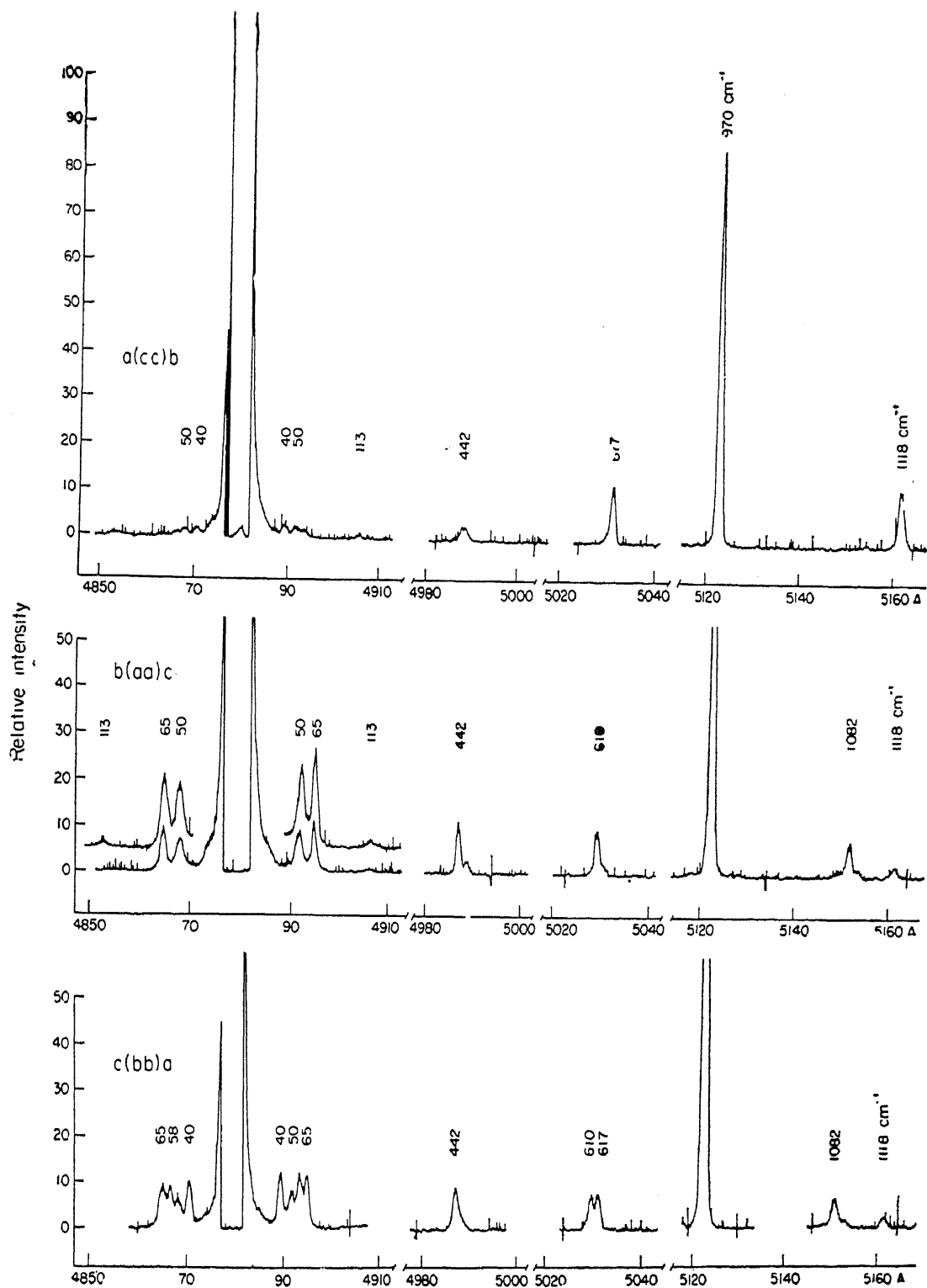


FIG. 4. Raman spectrum of  $\text{Cs}_2\text{SO}_4$  crystal using  $4880 \text{ Å}$  excitation with different crystal orientations. The direction of polarization of the incident beam is parallel to that of the observed scattered beam.

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