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On the basis of the available force fields for the S_8 ring the vibrational Raman intensities of an α-S_8 single crystal and of a randomly oriented polycrystalline sample are interpreted in the frame of the bond polarizability model. The whole set of Raman tensors of the S_8-molecular ring and of the single crystal including relative signs are reported, as well as the polarizability parameters for the S–S bond. These magnitudes and the related Raman scattering coefficients are finally reported in an absolute scale by means of the optical refractivities of the crystal.

I. INTRODUCTION

The molecular crystal of sulphur α-S_8 has been the subject of several previous spectroscopic studies from theoretical and experimental points of view. The available information is thus enough to attempt a detailed interpretation of the vibrational Raman intensities of α-S_8 as observed from oriented single crystals or from polycrystalline samples. This is the aim of the present work.

The structural data used here for the crystal and for the S_8 ring are due to Abrahams.[1] Previous works of Scott *et al.*,[2,3] Cyvin,[4] and very recently of Eysel[5] reporting vibrational force fields for the S_8 ring have been useful since knowledge of the vibrational eigenvectors is a prerequisite for the interpretation of the vibrational intensities. Experimental works by Anderson and Loh,[6] Ozin,[7] Gautier and Debeau,[8] and Rinaldi and Pawley[9] give support for a quite unambiguous assignment of the first order Raman spectra ($k=0$) of the single crystal according to the irreducible representations of the factor group D_{2h}^{24}.

Partial aspects of the Raman intensities of α-S_8 have been considered before. The distribution of relative intensities of bands originating from the crystal field splitting of fundamentals ν_1 and ν_2 of the S_8 ring has been studied by Ozin.[7] The relative intensities of external modes of the crystal have been convincingly analyzed by Arthur and McKenzie[10] and Rinaldi and Pawley.[9]

For our purpose the Volkenstein bond polarizability approach[11] has been assumed for the S_8 ring. Additional working hypotheses were separability of internal and external modes in the crystal and negligibility of electro-optical interactions among S_8 rings of the primitive cell. In view of the results previously reported,[9,10] both hypotheses seem reasonable.

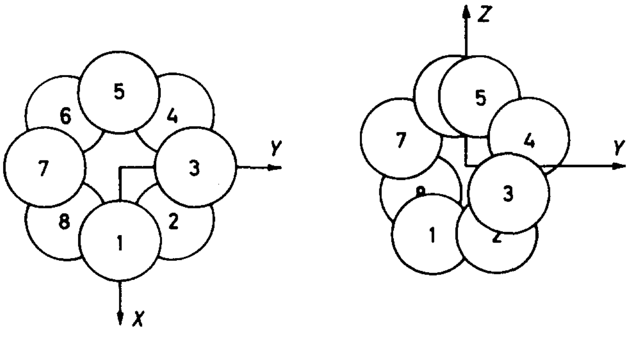
The pattern for the present work is as follows: In Sec. II the Raman intensities characteristic of the "free" S_8 ring with point symmetry D_{4d} are analyzed without including any feature of the crystal. As a result of this analysis a set of nine bond polarizability parameters (referred to as eop's in the following) is obtained. In a second step described in Sec. III B these eop's are transferred to the true geometry of the distorted S_8 ring of local symmetry C_2 in the crystal. This way the Raman tensors of an actual S_8 ring of the crystal are calculated. Combining the Raman tensors of the four S_8 molecules (Sec. III C) of the primitive cell according to the symmetry coordinates of the crystal, the Raman tensors for a primitive cell are obtained. From them, the vibrational intensities of the crystal are easily derived. A critical evaluation of the results is accomplished in Sec. IV and an attempt to give all the calculated values in an absolute scale of intensities is made in Sec. V.

II. THE FREE S_8 RING

We shall consider the free S_8 ring as an isolated molecule of ideal D_{4d} point symmetry (Fig. 1). The study of its vibrational Raman intensities will be accomplished within the frame of the bond polarizability theory[11] by using the compact formulation of Montero and del Rio.[12] In this mathematical approach Wilson's **B** and $\mathbf{G}^{-1}$ matrices as well as the **L** matrix of vibrational eigenvectors are needed. In general, the calculation of **B** and $\mathbf{G}^{-1}$ is nowadays a trivial problem as is the calculation of **L** provided the molecular force field is known. However, the S_8 ring shows some specific difficulties because of the existence of nonzero redundancies. Comments about this point may be valuable for the study of other cyclic molecules.

The expression for the calculation of the derivatives of the molecular polarizability with respect to the symmetry coordinates S_l,[12]

$$\frac{\partial\alpha}{\partial S_l}=\sum_k \mathbf{T}_k^{+}\{\alpha_x', \alpha_y', \alpha_z'\}_k \xi_{kl}\mathbf{T}_k+\sum_k{}' \mathbf{T}_k^{+}\beta_{kl}\mathbf{T}_k , \qquad (1)$$



(a) (b)

FIG. 1. (a) "free" S_8 ring with point symmetry D_{4d}. $r_{S-S}=2.048$ Å, X–S–S–S = 107.9°. (b) Actual S_8 ring in α-S_8 crystal, with point symmetry C_2. Angles and distances as in Ref. 1.

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includes the vectors ξ_{kl}. Such vectors describe in polar coordinates the participation of the bond k in the symmetry coordinate S_l. According to the definition given in Ref. 12, ξ_{kl} are simple functions of the $\mathbf{B}^{+}$ and $\mathbf{G}^{-1}$ matrices. By using a set of 24 internal coordinates (eight stretches r_i, eight bends α_i, and eight torsions τ_i) to describe the distortions of an S_8 ring, it is possible to build up a set of 24 symmetry coordinates[4] transforming as the irreducible representations of the D_{4d} point group. This set includes six nonzero redundancy conditions with symmetry $A_1+B_1+E_1+E_3$. This implies that the ξ_{kl} vectors can not be obtained in the usual way since the G matrix is singular. To overcome this difficulty the G matrix of each species A_1, B_1, E_1, and E_3 was diagonalized by means of the transformation

$$\mathbf{G}_{\text{diag}}=\mathbf{U}^{+}\mathbf{G}\mathbf{U}\,. \tag{2}$$

The six zero eigenvalues of $\mathbf{G}_{\text{diag}}$ were eliminated yielding a new nonsingular G matrix of dimension $24-6=18$, from which it was possible to obtain $\mathbf{G}^{-1}$ and then the ξ_{kl} vectors.

The eigenvectors corresponding to the zero eigenvalues of G represent identically zero redundancies which may now be removed to obtain a nonredundant set of 18 symmetry coordinates with the distribution.

$$2A_1+1B_1+1B_2+2E_1+3E_2+2E_3\,.$$

We disagree with the method reported in Ref. 4, where the nonzero redundancies were directly removed. (Nonredundant U matrix, ξ_{kl} vectors, and $\mathbf{T}_k$ matrices are available upon request.)

Raman intensities are a function of the invariants of the derivatives $\partial\boldsymbol{\alpha}/\partial Q$ of the molecular polarizability tensor with respect to the normal coordinates. The relation between the $\partial\boldsymbol{\alpha}/\partial Q$'s and the $\partial\boldsymbol{\alpha}/\partial S$'s of Eq. (1) is given by

$$\frac{\partial\boldsymbol{\alpha}}{\partial Q}=\mathbf{L}^{+}\frac{\partial\boldsymbol{\alpha}}{\partial S}\,, \tag{3}$$

where $\mathbf{L}$ is the matrix of vibrational eigenvectors expressed in terms of symmetry coordinates. In the present work the L matrices derived from the force fields of Refs. 3 and 5 were used.

Assuming cylindrical symmetry for the polarizability of an S–S bond and for its derivatives with respect to internal coordinates 29 eop's are in principle necessary for describing the Raman intensities of an S_8 ring according to Eq. (1). Three eop's, namely, $\gamma-\alpha$, α', and γ', correspond to the customarily called "zero order approximation" and the other 26 to the complete first order approximation. The nomenclature used for the zero order eop's is as follows:

$$\boldsymbol{\alpha}_{S-S}=\begin{pmatrix}\alpha & & \\ & \alpha & \\ & & \gamma\end{pmatrix},\quad \partial\boldsymbol{\alpha}_{S-S}/\partial r_{S-S}=\begin{pmatrix}\alpha' & & \\ & \alpha' & \\ & & \gamma'\end{pmatrix}, \tag{4}$$

where $\boldsymbol{\alpha}_{S-S}$ is the equilibrium polarizability of an S–S bond and $\partial\boldsymbol{\alpha}_{S-S}/\partial r_{S-S}$ its derivative with respect to the stretching of the same bond. The nomenclature of the first order eop's is summarized in Table I.

TABLE I. Definition of first order electro-optical parameters of the S–S bond in the molecule S_8 assuming D_{4d} symmetry.[a]

$\partial\alpha_k/\partial r_{k+1}=\partial\alpha_k/\partial r_{k-1}=\text{diag}\,(a_2,a_2,c_2)$
$\partial\alpha_k/\partial r_{k+2}=\partial\alpha_k/\partial r_{k-2}=\text{diag}\,(a_3,a_3,c_3)$
$\partial\alpha_k/\partial r_{k+3}=\partial\alpha_k/\partial r_{k-3}=\text{diag}\,(a_4,a_4,c_4)$
$\partial\alpha_k/\partial r_{k+4}=\text{diag}\,(a_5,a_5,c_5)$
$\partial\alpha_k/\partial\alpha_{k,k+1}=\partial\alpha_k/\partial\alpha_{k,k-1}=\text{diag}\,(a_6,a_6,c_6)$
$\partial\alpha_k/\partial\alpha_{k+1,k+2}=\partial\alpha_k/\partial\alpha_{k-1,k-2}=\text{diag}\,(a_7,a_7,c_7)$
$\partial\alpha_k/\partial\alpha_{k+2,k+3}=\partial\alpha_k/\partial\alpha_{k-2,k-3}=\text{diag}\,(a_8,a_8,c_8)$
$\partial\alpha_k/\partial\alpha_{k+3,k+4}=\partial\alpha_k/\partial\alpha_{k-3,k-4}=\text{diag}\,(a_9,a_9,c_9)$
$\partial\alpha_k/\partial\tau_k=\text{diag}\,(a_{10},a_{10},c_{10})$
$\partial\alpha_k/\partial\tau_{k+1}=\partial\alpha_k/\partial\tau_{k-1}=\text{diag}\,(a_{11},a_{11},c_{11})$
$\partial\alpha_k/\partial\tau_{k+2}=\partial\alpha_k/\partial\tau_{k-2}=\text{diag}\,(a_{12},a_{12},c_{12})$
$\partial\alpha_k/\partial\tau_{k+3}=\partial\alpha_k/\partial\tau_{k-3}=\text{diag}\,(a_{13},a_{13},c_{13})$
$\partial\alpha_k/\partial\tau_{k+4}=\text{diag}\,(a_{14},a_{14},c_{14})$

[a] Nomenclature: α_k = polarizability of the bond k, $k=1,\ldots,8$; r_i = stretching of the bond i; $\alpha_{i,j}$ = bending of the angle between the bonds i and j; τ_i = torsion of the bond i, and

$$\text{diag}\,(a_l,a_l,c_l)=\begin{pmatrix}a_l & & \\ & a_l & \\ & & c_l\end{pmatrix}.$$

Using the Fortran program TENS based on the formulation of Ref. 12, it is possible to obtain explicitly linear algebraic equations of $\partial\boldsymbol{\alpha}/\partial S$ as a function of the complete set of eop's. These derivatives with respect to the set of nonredundant symmetry coordinates are given in Table II. It is interesting to realize that the 29 eop's are actually grouped in only 13 linearly independent combinations. Among them two are combinations of traces and the other 11 are combinations of anisotropies.

At this point it is convenient to review the Raman intensity data available for a free S_8 ring. From a solution of S_8 in CS_2 a maximum of nine intensity data with the following distribution might in principle be obtained: from A_1 species the squares of the traces and of the anisotropies of tensors $\partial\boldsymbol{\alpha}/\partial Q_1$ and $\partial\boldsymbol{\alpha}/\partial Q_2$; from E_2 species the squares of the anisotropies of tensors $\partial\boldsymbol{\alpha}/\partial Q_7$, $\partial\boldsymbol{\alpha}/\partial Q_8$, and $\partial\boldsymbol{\alpha}/\partial Q_9$; and from E_3 species the squares of the anisotropies of tensors $\partial\boldsymbol{\alpha}/\partial Q_{10}$ and $\partial\boldsymbol{\alpha}/\partial Q_{11}$. However, in practice, Raman bands of the solvent do partially overlap with those of S_8. Since interactions with the solvent may additionally occur, the Raman intensities measured from a polycrystalline sample are preferred. From a polycrystalline sample only seven intensity data related to the fundamentals Q_1, Q_2, Q_7, Q_8, Q_9, Q_{10}, and Q_{11} can be obtained. Due to multiple reflections and refractions within the polycrystalline sample, depolarization ratios cannot be measured. For the same reason the scattering coefficient is

$$S=(45\bar{\alpha}'^2+10\gamma'^2)g\,, \tag{5}$$

instead of

TABLE II. Derivatives of the molecular polarizability of S_8 (D_{4d} symmetry) with respect to the set of nonredundant symmetry coordinates.[a]

$$A_1:\ \partial\alpha/\partial S_1:\quad 2XX+ZZ=1.188M-3.326N$$
$$ZZ-XX=1.390\,(\gamma-\alpha)-0.177P+0.494Q$$
$$\partial\alpha/\partial S_2:\quad 2XX+ZZ=2.567M+1.539N$$
$$ZZ-XX=-0.643\,(\gamma-\alpha)-0.382P-0.229Q$$
$$E_2:\partial\alpha/\partial S_{1a}:\quad XX=-YY=-0.766\,[(\gamma'-\alpha')-2\,(c_3-a_3)+(c_5-a_5)]$$
$$XY=0$$
$$\partial\alpha/\partial S_{2a}:\quad XX=-YY=-0.993\,(\gamma-\alpha)-$$
$$-1.083\,[(c_6-a_6)-(c_7-a_7)-(c_8-a_8)+(c_9-a_9)]$$
$$XY=0$$
$$\partial\alpha/\partial S_{3a}:\quad XX=-YY=-0.524\,(\gamma-\alpha)$$
$$XY=-0.766\,[(c_{10}-a_{10})-2\,(c_{12}-a_{12})+(c_{14}-a_{14})]$$
$$E_3:\partial\alpha/\partial S_{7a}:\quad YZ=0.118\,(\gamma-\alpha)+0.783\,(\gamma'-\alpha')$$
$$-1.108R-0.783\,(c_5-a_5)-0.180S+0.434T$$
$$\partial\alpha/\partial S_{2a}:\quad YZ=-0.619\,(\gamma-\alpha)+0.322\,(\gamma'-\alpha')$$
$$-0.455R-0.322\,(c_5-a_5)+0.437S-1.055T$$

[a] $M=(2\alpha'+\gamma')+2\,(2a_2+c_2)+2\,(2a_3+c_3)+2\,(2a_4+c_4)+(2a_5+c_5)$, $N=(2a_6+c_6)+(2a_7+c_7)+(2a_8+c_8)+(2a_9+c_9)$, $P=(\gamma'-\alpha')+2(c_2-a_2)+2\,(c_3-a_3)+2\,(c_4-a_4)+(c_5-a_5)$, $Q=(c_6-a_6)+(c_7-a_7)+(c_8-a_8)+(c_9-a_9)$, $R=(c_2-a_2)-(c_4-a_4)$, $S=(c_6-a_6)-(c_9-a_9)$, $T=(c_7-a_7)-(c_8-a_8)$.

$$S=(45\bar{\alpha}'^2+7\gamma'^2)g\ , \qquad (6)$$

which is only valid for gases and liquids.[13] Summarizing, the two depolarization ratios of the A_1 species measured from the solution and the seven scattering coefficients measured from a polycrystalline sample are the whole of intensity data used throughout the present work. Indeed, they are not sufficient to fix the 13 combinations of eop's before mentioned. Some additional hypotheses are necessary to reduce the number of eop's involved. It seems a reasonable one to neglect those eop's related with interactions between bonds n and $n\pm3$ as well as between bonds n and $n\pm4$ of the S_8 ring. In fact, these are the approximations involved in the force field in internal coordinates according to Refs. 3 and 5. In our case these approximations imply the following constraints upon the first order eop's of Table I:

$$2c_i+a_i=0 \quad \text{for } i\neq 6\ ,$$
$$c_i-a_i=0\ , \quad i=4,5,8,9,11,12,13,14\ .$$

The numerical problem of finding the set of eop's which best reproduces the experimental values of Table III was solved for two force fields[3,5] with the aid of the FORTRAN program IRAM. The fitted Raman scattering coefficients and depolarization ratios are given in Table III as well. The calculated eop's and Raman tensors are reported in Tables IV and V, respectively.

From the results of Table III there is no clear reason to prefer *a priori* one or the other set of eop's of Table IV. However, as will be shown later, the calculated Raman spectrum of the single crystal using both sets of eop's without any further refinement permits an objective comparison to be made of both force fields involved in the calculation.

Additionally, it is of interest to note how different are

TABLE IV. Bond polarizability parameters of an S–S bond in the molecule of S_8.

a	b
Trace combinations	Trace combinations
$2\alpha'+\gamma'=18.41\sqrt{k}$ Å^2	$2\alpha'+\gamma'=17.38\sqrt{k}$ Å^2
$2a_6+c_6=4.03\sqrt{k}$ Å^2	$2a_6+c_6=2.81\sqrt{k}$ Å^2
Anisotropy combinations	Anisotropy combinations
$\gamma-\alpha=4.97\sqrt{k}$ Å^3	$\gamma-\alpha=6.63\sqrt{k}$ Å^3
$\gamma'-\alpha'=4.67\sqrt{k}$ Å^2	$\gamma'-\alpha'=3.43\sqrt{k}$ Å^2
$c_2-a_2=0.15\sqrt{k}$ Å^2	$c_2-a_2=-0.57\sqrt{k}$ Å^2
$c_3-a_3=-0.28\sqrt{k}$ Å^2	$c_3-a_3=-0.12\sqrt{k}$ Å^2
$c_6-a_6=1.14\sqrt{k}$ Å^2	$c_6-a_6=-1.82\sqrt{k}$ Å^2
$c_7-a_7=-0.83\sqrt{k}$ Å^2	$c_7-a_7=-2.37\sqrt{k}$ Å^2
$c_{10}-a_{10}=-3.06\sqrt{k}$ Å^2	$c_{10}-a_{10}=-1.69\sqrt{k}$ Å^2
$c_i-a_i=0$ for $i=4, 5, 8, 9, 11, 12, 13, 14$ assumed $2c_i+a_i=0$ for $i\neq6$ assumed	

[a] Using vibrational eigenvectors of the force field of Ref. 3.

[b] Using vibrational eigenvectors of the force field of Ref. 5.

TABLE III. Experimental and calculated Raman scattering coefficients (S) and depolarization ratios (ρ) for a free S_8 molecule of symmetry D_{4d}.

		Experimental		Calculated[d]		Calculated[e]	
Sim	ν[a]	S[b]	ρ[c]	S[b]	ρ[c]	S[b]	ρ[c]
A_1	ν_1 (460–495)	165 ± 17	0.024 ± 0.008	170.3	0.026	181.4	0.046
A_1	ν_2 (205–230)	60	0.12 ± 0.02	68.5	0.145	63.2	0.113
E_2	ν_7 (460–495)	4.2 ± 4.2		4.8		4.0	
E_2	ν_8 (135–175)	37 ± 3.7		33.8		35.5	
E_2	ν_9 (75–100)	7.2 ± 7.2		7.3		7.2	
E_3	ν_{10} (420–450)	29.3 ± 3		29.6		29.1	
E_3	ν_{11} (245–260)	6.6 ± 0.7		6.3		6.5	

[a] Integration interval at 130 °K, in cm^{-1}.

[b] $S=(45\bar{\alpha}'^2+10\gamma'^2)\cdot g$ in units of $10^{-8}k$ (cm^4 g^{-1}); g = degeneracy; k = adimensional scaling factor.

[c] $\rho=3\gamma'^2/(45\bar{\alpha}'^2+4\gamma'^2)$.

[d] Using vibrational eigenvectors of the force field of Ref. 3.

[e] Using vibrational eigenvectors of the force field of Ref. 5.

TABLE V. Calculated Raman tensors of a free molecule of S_8 (symmetry D_{4d}) in units of $10^{-4}\sqrt{k}$ ($cm^2\,g^{-1/2}$).[a]

		b	c
A_1	$\partial\alpha/\partial Q_1$	$XX=YY=1.467$ $ZZ=2.654$	$XX=YY=1.326$ $ZZ=2.929$
	$\partial\alpha/\partial Q_2$	$XX=YY=1.510$ $ZZ=-0.092$	$XX=YY=1.449$ $ZZ=0.059$
E_2	$\partial\alpha/\partial Q_7$	$XX=-YY=-0.166$ $XY=-0.227$	$XX=-YY=0.225$ $XY=-0.124$
	$\partial\alpha/\partial Q_8$	$XX=-YY=-0.744$ $XY=0.101$	$XX=-YY=-0.768$ $XY=0.037$
	$\partial\alpha/\partial Q_9$	$XX=-YY=-0.161$ $XY=0.309$	$XX=-YY=-0.299$ $XY=0.176$
E_3	$\partial\alpha/\partial Q_{10}$	$YZ=0.702$	$YZ=0.697$
	$\partial\alpha/\partial Q_{11}$	$YZ=-0.324$	$YZ=-0.329$

[a] Nonlisted elements of the tensor are zero.
[b] Using the vibrational eigenvectors of the force field of Ref. 3.
[c] Using the vibrational eigenvectors of the force field of Ref. 5.

some of the eop's of Table IV, depending on the force field used.

III. THE SINGLE CRYSTAL OF α-S_8

A. Crystal structure

At temperatures below 95 °C the structure of the α-S_8 crystal may be described according to the symmetry properties of the space group D_{2h}^{24} (F_{ddd}). The primitive cell has four S_8 rings whose centers of mass are at crystallographic positions

$P_1(0, 0, Z)$; $P_2(0, 0, \bar{Z})$; $P_3(1/4, 1/4, 1/4-Z)$;
$P_4(1/4, 1/4, 1/4+Z)$

when referred to the origin 222. A projection of the primitive cell onto XZ and YZ planes is shown in Fig. 2. S_8 rings of the crystal are slightly distorted from the "ideal" D_{4d} symmetry. Actually, they have C_2 symmetry[1] with the binary axis parallel to the Z axis of orthorhombic face centered cell, passing through the center of opposite S–S bonds.

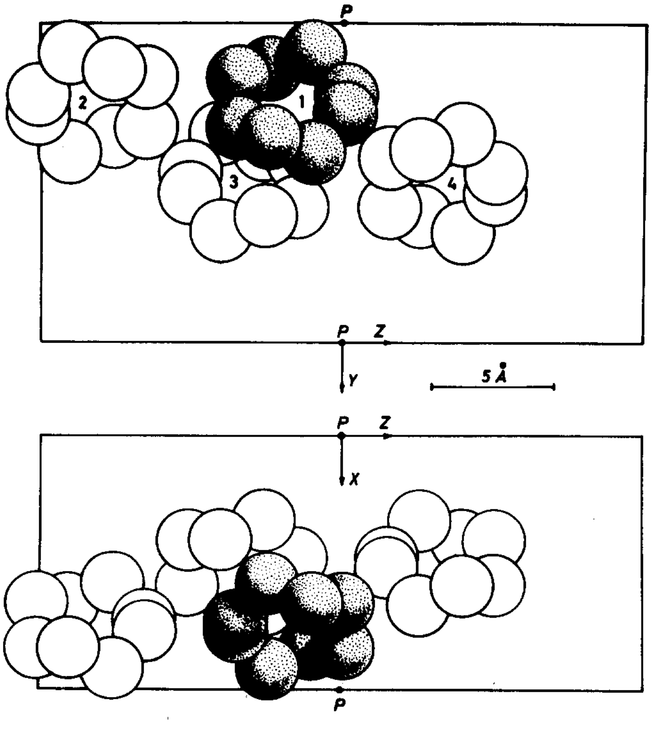

FIG. 2. Projections of the primitive cell of α-S_8.

The symmetry operators of factor group D_{2h}^{24} which are necessary for the construction of symmetry coordinates of the crystal related to internal vibrations of the S_8 ring are reported in Table VI.

B. The S_8 ring of local C_2 symmetry

Because of the C_2 geometry of the molecule in the crystal [Fig. 1(b)] and of the new set of molecular axis (those of the orthorhombic unit cell were chosen), the factors $\mathbf{T}_k$ and ξ_{kl} in Eq. (1) are now different from those used for the free S_8 ring. The new nonredundant $\mathbf{U}$ matrix of symmetry coordinates and the corresponding ξ_{kl} vectors were calculated according to the method described in Sec. II. Using Eq. (1) with the eop's of Table IV without any further refinement, a set of 18 tensors $\partial\alpha/\partial S_l$ of the form

$$\frac{\partial\alpha}{\partial S_A}=\begin{pmatrix} XX & XY & 0 \\ XY & YY & 0 \\ 0 & 0 & ZZ \end{pmatrix}$$

or

$$\frac{\partial\alpha}{\partial S_B}=\begin{pmatrix} 0 & 0 & XZ \\ 0 & 0 & YZ \\ XZ & YZ & 0 \end{pmatrix} \tag{7}$$

were calculated. The new 18×18 $\mathbf{L}$ matrix for the C_2 local symmetry has two blocks of dimension 10×10 (A

TABLE VI. Symmetry operators of the factor group D_{2h}^{24} and its action upon the four S_8 rings of the primitive cell of α-S_8 in the nomenclature of substitutions.[a]

Operator	Transformation
$(E\,\vert\,0)$	(1) (2) (3) (4)
$(C_z\,\vert\,0)$	(1) (2) (3) (4)
$(C_y\,\vert\,0)$	(12) (34)
$(C_x\,\vert\,0)$	(12) (34)
$(i\,\vert\,\tau)$	(13) (24)
$(\sigma_{xy}\,\vert\,\tau)$	(13) (24)
$(\sigma_{xz}\,\vert\,\tau)$	(14) (23)
$(\sigma_{yz}\,\vert\,\tau)$	(14) (23)

[a] The fractional translation $\tau=(3/4, 3/4, 3/4)$ is referred to the axes of the face centered Bravais lattice defined by the primitive translations $\vec{t}_1=(a/2, 0, c/2)$, $\vec{t}_2=(0, -b/2, c/2)$, and $\vec{t}_3=(a/2, -b/2, 0)$. The reference for $(\mathbf{R}\,\vert\,\mathbf{t})$ operators is the point P of Fig. 2. Labeling of molecules is according to Fig. 2.

TABLE VII. Calculated Raman tensors of an S_8 ring (no. 1 in Fig. 2) with its actual C_2 geometry. Units of $10^{-4}\sqrt{k}$ ($\mathrm{cm}^2\mathrm{g}^{-1/2}$), the scaling factor k being the same as in Tables IV, V, and IX. The tensors are referred to the system of axes X, Y, Z of the orthorhombic unit cell of α-S_8.

a D_{4d} Q_j	b C_2 Q_j	c $\Delta\nu$ (cm^{-1})		d C_2 $\partial\alpha/\partial Q_j$	e C_2 $\partial\alpha/\partial Q_j$
$Q_1(A_1)$	$Q_1(A)$	460–495	XX	−1.211	−1.656
			YY	−0.957	−1.381
			ZZ	−1.172	−1.060
			XY	0.537	0.590
$Q_7(E_2)$	$Q_2(A)$	460–495	XX	1.492	1.559
			YY	1.342	1.324
			ZZ	0.747	0.775
			XY	−0.248	−0.502
$Q_5(E_1)$	$Q_3(A)$	460–495	XX	1.030	0.297
			YY	0.994	0.314
			ZZ	0.611	0.206
			XY	−0.225	−0.121
$Q_{10}(E_3)$	$Q_4(A)$	420–450	XX	−0.661	−0.659
			YY	0.679	0.684
			ZZ	0.011	0.009
			XY	−0.149	−0.152
$Q_3(E_2)$	$Q_5(A)$	415–420	XX	0.006	0.000
			YY	0.022	0.030
			ZZ	−0.034	−0.038
			XY	−0.038	−0.014
$Q_{11}(E_3)$	$Q_6(A)$	240–260	XX	0.351	0.369
			YY	−0.343	−0.362
			ZZ	0.020	0.019
			XY	0.085	0.087
$Q_2(A_1)$	$Q_7(A)$	205–230	XX	0.571	0.617
			YY	0.906	0.918
			ZZ	1.508	1.446
			XY	0.798	0.681
$Q_6(E_1)$	$Q_8(A)$	180–200	XX	0.439	0.215
			YY	−0.459	−0.224
			ZZ	−0.019	−0.008
			XY	0.083	0.037
$Q_8(E_2)$	$Q_9(A)$	135–175	XX	−0.265	−0.299
			YY	−0.392	−0.446
			ZZ	0.646	0.742
			XY	−0.312	−0.348
$Q_9(E_2)$	$Q_{10}(A)$	75–100	XX	0.103	0.056
			YY	0.129	0.071
			ZZ	−0.136	−0.127
			XY	0.044	0.054
$Q_7(E_2)$	$Q_{11}(B)$	460–495	XZ	−0.059	0.191
			YZ	−0.029	0.272
$Q_5(E_1)$	$Q_{12}(B)$	460–495	XZ	−0.018	−0.146
			YZ	0.051	−0.044
$Q_{10}(E_3)$	$Q_{13}(B)$	420–450	XZ	−0.553	−0.540
			YZ	0.446	0.440
$Q_{11}(E_3)$	$Q_{14}(B)$	240–260	XZ	−0.211	−0.203
			YZ	0.184	0.117
$Q_4(B_2)$	$Q_{15}(B)$	230–245	XZ	−0.097	−0.094
			YZ	0.002	0.134
$Q_6(E_1)$	$Q_{16}(B)$	180–200	XZ	0.423	0.247
			YZ	−0.339	−0.198
$Q_8(E_2)$	$Q_{17}(B)$	135–175	XZ	0.533	0.509
			YZ	0.660	0.628
$Q_9(E_2)$	$Q_{18}(B)$	75–100	XZ	0.292	0.293
			YZ	0.371	0.376

[a] Label j corresponding to the ideal symmetry D_{4d} of the free S_8 ring.

[b] Label j corresponding to the actual symmetry C_2 of the S_8 ring in α-S_8 crystal.

[c] Wave number interval where splittings $A \rightarrow A_g + B_{1g}$ and $B \rightarrow B_{2g} + B_{3g}$ are observed.

[d] Calculation carried out with the force field of Ref. 3.

[e] Calculation carried out with the force field of Ref. 5.

species) and 8×8 (B species). It was derived from the force fields of Refs. 3 and 5. With these results at hand and with Eq. (3) the 18 Raman tensors $\partial\boldsymbol{\alpha}/\partial Q$ of one molecule of the crystal (molecule 1 of Fig. 2) were calculated. They are reported in Table VII.

C. The Raman tensors for a primitive cell of α-S_8

Due to the relations of phase among the four molecules of the primitive cell of α-S_8, each mode of local symmetry A or B splits, respectively, (in $\mathbf{k}=0$) into $A_g + B_{1g}$ and $B_{2g} + B_{3g}$ components of D_{2h}^{24} space group. Consequently, the Raman tensors split as well as

$$\frac{\partial\boldsymbol{\alpha}}{\partial Q_A} = \begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}, \qquad \frac{\partial\boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{A_g}} = \begin{pmatrix} m & 0 & 0 \\ 0 & n & 0 \\ 0 & 0 & p \end{pmatrix}, \qquad \frac{\partial\boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{B_{1g}}} = \begin{pmatrix} 0 & q & 0 \\ q & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\frac{\partial\boldsymbol{\alpha}}{\partial Q_B} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{pmatrix}, \qquad \frac{\partial\boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{B_{2g}}} = \begin{pmatrix} 0 & 0 & r \\ 0 & 0 & 0 \\ r & 0 & 0 \end{pmatrix}, \qquad \frac{\partial\boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{B_{3g}}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & s \\ 0 & s & 0 \end{pmatrix}. \tag{8}$$

From the point of view of symmetry this result can be easily derived from correlation tables. However, we are looking for the Raman tensors of the primitive cell of α-S_8 with the intention of calculating the Raman intensities of the crystal. Thus, qualitative relations such as those supplied by correlation tables are insufficient.

To obtain the numerical relations the projection operator method was used in the space of Raman tensors. Accordingly, the Raman tensors of the primitive cell of the crystal were generated from the Raman tensors of molecule 1 of Fig. 2 by

$$\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{\mathrm{crystal}}} = N \sum_{(\mathbf{R}|\tau)\in D_{2h}^{24}} \chi^{(p)}(\hat{\mathbf{R}})^* \cdot \tau \cdot \mathbf{R}^+ \left(\frac{\partial \boldsymbol{\alpha}_1}{\partial Q_{j,1}}\right) \mathbf{R} \,, \tag{9}$$

where N stands for the normalization factor. In this equation the projection operator acts upon the derivative of the molecular polarizability of molecule 1 respect to its own $Q_{j,1}$ normal mode as follows: First, the molecular Raman tensor $(\partial\boldsymbol{\alpha}_1/\partial Q_j)$ is transformed by the rotational part $\hat{\mathbf{R}}$ of the factor group operator $(\mathbf{R}|\tau)$ and then the resulting tensor changes its label to that of other molecule of the primitive cell as a result of the nonprimitive translation τ of the factor group operator; the resulting tensor $(\partial\boldsymbol{\alpha}/\partial Q_{j,k})$ $(k=1,2,3,4)$ is afterwards multiplied by $\chi^{(p)}(\hat{\mathbf{R}})^*$, conjugated of the character of the symmetry operator $\hat{\mathbf{R}}$ of D_{2h} point group for the irreducible representation $\Gamma^{(p)}$. The procedure is repeated for the eight operators of the factor group D_{2h}^{24} (given in Table VI) and the results added. For instance, a tensor of species A in the local symmetry group C_2,

$$\frac{\partial \boldsymbol{\alpha}_1}{\partial Q_{j,1}} = \begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}_1 \,, \tag{10}$$

generates the following Raman tensors of the primitive cell:

$$\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{A_g}} = \frac{1}{\sqrt{16}} \left[2\begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}_1 + 2\begin{pmatrix} a & -d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}_2 + 2\begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}_3 + 2\begin{pmatrix} a & -d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}_4 \right] \,, \tag{11}$$

$$\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{B_{1g}}} = \frac{1}{\sqrt{16}} \left[2\begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}_1 - 2\begin{pmatrix} a & -d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}_2 + 2\begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}_3 - 2\begin{pmatrix} a & -d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}_4 \right] \,, \tag{12}$$

$$\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_{\Gamma^{(p)}}} = 0 \,, \quad \text{for } \Gamma^{(p)} \text{ other than } A_g \text{ or } B_{1g}. \tag{13}$$

In the particular case of α-S_8 the numerical values for correlations described by Eqs. (8) are

$$m = 2a \,, \quad n = 2b \,, \quad p = 2c \,, \quad q = 2d \,, \quad r = 2e \,, \quad s = 2f \,. \tag{14}$$

D. Calculated and experimental Raman intensities of α-S_8

The differential Raman scattering cross section per primitive cell associated to the normal mode Q_l of a single crystal with negligible intermolecular interactions is given for the experimental conditions $[M(IJ)N]$ and $\mathbf{k}=0$ by

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}^{[M(IJ)N]} = (2\pi)^4 B \left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{IJ}^2 \,, \quad M,N,I,J = X,Y,Z \,, \quad M\perp N, M\perp I, N\perp J \,, \tag{15}$$

with

$$B = \frac{h}{8\pi^2 \nu_l c} \, \frac{(\nu_0 - \nu_l)^4}{[1 - \exp(-h\nu_l c/kT)]} \,. \tag{16}$$

ν_0 and ν_l are the wavenumbers of the exciting radiation and of the normal mode Q_l, respectively; h, c, k, and T have the usual meaning. $(\partial\boldsymbol{\alpha}^{\mathrm{PC}}/\partial Q_l)_{IJ}$ stands for the IJ element of the Raman tensor of the primitive cell.

According to Ref. 13 the differential cross section per primitive cell of a polycrystalline sample is

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}^{\mathrm{polycrystal}} = (2\pi)^4 \frac{B}{3} \left[\left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{XX}^2 + \left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{YY}^2 + \left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{ZZ}^2 + 2\left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{XY}^2 + 2\left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{XZ}^2 + 2\left(\frac{\partial \boldsymbol{\alpha}^{\mathrm{PC}}}{\partial Q_l}\right)_{YZ}^2 \right] . \tag{17}$$

This equation can be expressed in terms of the invariants of the Raman tensors either of the primitive cell or of one of its molecular units. In the first case we have

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}^{\mathrm{polycrystal}} = (2\pi)^4 B \, \frac{45(\bar{\alpha}_l'^{\mathrm{PC}})^2 + 10(\gamma_l'^{\mathrm{PC}})^2}{45} \cdot g_l \,, \tag{18}$$

where g_l is the degeneracy of the crystal mode Q_l in the space group of the crystal. When expressed in terms of the molecular invariants this experimental magnitude becomes

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}^{\mathrm{polycrystal}} = (2\pi)^4 B \, \frac{45(\bar{\alpha}_j'^{\mathrm{mol}})^2 + 10(\gamma_j'^{\mathrm{mol}})^2}{45} \cdot g_j \cdot N^{\mathrm{PC}} \,. \tag{19}$$

Here N^{PC} is the number of molecular units in the primitive cell (assuming all of them of the same class) and g_j the degeneracy of the molecular mode Q_j related to the crystal mode Q_l; $(\bar{\alpha}_j'^{\mathrm{mol}})^2$ and $(\gamma_j'^{\mathrm{mol}})^2$ are the usual invariants of the molecular Raman tensor $(\partial\boldsymbol{\alpha}^{\mathrm{mol}}/\partial Q_j)$.

It has to be noticed that Eq. (19) may be used either for the symmetry of the free molecule (point group D_{4d} in this case) or for the local symmetry of the molecule in the crystal (here C_2). In the former case the invariants $(\bar{\alpha}_j'^{\mathrm{mol}})^2$ and $(\gamma_j'^{\mathrm{mol}})^2$ involved in Eq. (19) are derived from the tensors of Table V while in the latter they are derived from those of Table VII.

If the approximate symmetry D_{4d} is assumed for the free molecule, Eq. (19) yields only a restricted description of the vibrational intensities. For instance, modes of symmetry B_1, B_2, and E_1 would appear inactive when, in fact, they are observed in the spectrum of α-S_8. It must be pointed out that the sum of cross sections of various modes (in symmetry C_2) related to a common vibration of the free molecule (in symmetry D_{4d}) is according to Eq. (19) very nearly the cross section of the free molecule mode. In fact, Eqs. (18) and (19)

TABLE VIII. Calculated Raman scattering differential cross sections (per primitive cell, $Z=4$) of an oriented single crystal of α-S_8. The reference axes X, Y, Z are those of the nonprimitive face centered orthorhombic cell. Units of $10^{-31}k$ (cm^2 sterad^{-1}).

					$\lambda_0=514.5$ nm, $T=130\,°$K	
a D_{4d}	b C_2	$D_{2h}{}^{24}$	c ν (cm^{-1})	Scattering geometry^f	d $\left(\frac{\partial\sigma}{\partial\Omega}\right)$	e $\left(\frac{\partial\sigma}{\partial\Omega}\right)$
$Q_1(A_1)+Q_5(E_1)+Q_7(E_2)$	$Q_1(A)$	$Q_1(A_g)$	477	$[M(XX)N]$	174.1	325.7
				$[M(YY)N]$	108.6	226.3
				$[M(ZZ)N]$	163.2	133.3
		$Q_1(B_{1g})$	478	$[M(XY)N]$	34.2	41.3
	$Q_2(A)$	$Q_2(A_g)$	474	$[M(XX)N]$	266.3	290.6
				$[M(YY)N]$	215.5	209.5
				$[M(ZZ)N]$	66.8	71.9
		$Q_2(B_{1g})$	473	$[M(XY)N]$	7.3	30.2
	$Q_{11}(B)$	$Q_{11}(B_{2g})$	472	$[M(XZ)N]$	0.4	4.4
		$Q_{11}(B_{3g})$	472	$[M(YZ)N]$	0.10	8.9
	$Q_3(A)$	$Q_3(A_g)$	470	$[M(XX)N]$	128.1	10.6
				$[M(YY)N]$	119.3	11.9
				$[M(ZZ)N]$	45.1	5.1
		$Q_3(B_{1g})$	473	$[M(XY)N]$	6.0	1.8
	$Q_{12}(B)$	$Q_{12}(B_{2g})$	472	$[M(XZ)N]$	0.04	2.6
		$Q_{12}(B_{3g})$	468	$[M(YZ)N]$	0.31	0.23
$Q_{10}(E_3)$	$Q_4(A)$	$Q_4(A_g)$	441	$[M(XX)N]$	56.7	56.4
				$[M(YY)N]$	59.8	60.6
				$[M(ZZ)N]$	0.02	0.01
		$Q_4(B_{1g})$	434	$[M(XY)N]$	2.9	3.0
	$Q_{13}(B)$	$Q_{13}(B_{2g})$	441	$[M(XZ)N]$	39.7	37.8
		$Q_{13}(B_{3g})$	443	$[M(YZ)N]$	25.7	25.0
$Q_3(B_1)$	$Q_5(A)$	$Q_5(A_g)$	419	$[M(XX)N]$	~ 0	0.00
				$[M(YY)N]$	0.07	0.12
				$[M(ZZ)N]$	0.16	0.20
		$Q_5(B_{1g})$	420	$[M(XY)N]$	0.20	0.03
$Q_{11}(E_3)$	$Q_6(A)$	$Q_6(A_g)$	249	$[M(XX)N]$	31.2	34.6
				$[M(YY)N]$	29.8	33.2
				$[M(ZZ)N]$	0.10	0.09
		$Q_6(B_{1g})$	249	$[M(XY)N]$	1.84	1.91
	$Q_{14}(B)$	$Q_{14}(B_{2g})$	253	$[M(XZ)N]$	11.1	10.2
		$Q_{14}(B_{3g})$	253	$[M(YZ)N]$	8.4	3.4
$Q_4(B_2)$	$Q_{15}(B)$	$Q_{15}(B_{2g})$	239	$[M(XZ)N]$	2.5	2.4
		$Q_{15}(B_{3g})$	236	$[M(YZ)N]$	0	4.9
$Q_2(A_1)$	$Q_7(A)$	$Q_7(A_g)$	221	$[M(XX)N]$	95.9	112.2
				$[M(YY)N]$	241.8	248.2
				$[M(ZZ)N]$	669.7	615.6
		$Q_7(B_{1g})$	217	$[M(XY)N]$	192.3	139.9
$Q_6(E_1)$	$Q_8(A)$	$Q_8(A_g)$	199	$[M(XX)N]$	64.9	15.6
				$[M(YY)N]$	71.1	16.9
				$[M(ZZ)N]$	0.12	0.02
		$Q_8(B_{1g})$	188	$[M(XY)N]$	2.5	0.5
	$Q_{16}(B)$	$Q_{16}(B_{2g})$	188	$[M(XZ)N]$	65.1	22.1
		$Q_{16}(B_{3g})$	183	$[M(YZ)N]$	43.3	14.9

TABLE VII (*Continued*)

a D_{4d}	b C_2	$D_{2h}{}^{24}$	c ν (cm^{-1})	Scattering geometry[f]	$\lambda_0=514.5$ nm, $T=130$ °K d $\left(\frac{\partial\sigma}{\partial\Omega}\right)$	e $\left(\frac{\partial\sigma}{\partial\Omega}\right)$
$Q_8(E_2)$	$Q_9(A)$	$Q_9(A_g)$	159	$[M(XX)N]$	32.0	40.9
				$[M(YY)N]$	70.2	91.0
				$[M(ZZ)N]$	190.8	251.9
		$Q_9(B_{1g})$	150	$[M(XY)N]$	48.5	60.0
	$Q_{17}(B)$	$Q_{17}(B_{2g})$	161	$[M(XZ)N]$	127.7	116.6
		$Q_{17}(B_{3g})$	154	$[M(YZ)N]$	208.7	188.5
$Q_9(E_2)$	$Q_{10}(A)$	$Q_{10}(A_g)$	92	$[M(XX)N]$	11.0	3.3
				$[M(YY)N]$	17.3	5.2
				$[M(ZZ)N]$	19.1	16.8
		$Q_{10}(B_{1g})$	79	$[M(XY)N]$	2.5	3.9
	$Q_{18}(B)$	$Q_{18}(B_{2g})$	79	$[M(XZ)N]$	113.3	114.3
		$Q_{18}(B_{3g})$	86	$[M(YZ)N]$	159.6	164.0

[a,b] Since the C_{2z} axis of the molecule of symmetry C_2 is rotated $\pi/8$ with respect to the C_{2x} axis in symmetry D_{4d}, a proper correlation between the groups D_{4d} and C_2 is not possible here. Where possible an approximate (descriptive) correlation has been used. In particular, the modes $Q_1(A_1)+Q_5(E_1)+Q_7(E_2)$ of the group D_{4d} split in the group C_2 into $Q_1(A)+Q_2(A)+Q_3(A)+Q_{11}(B)+Q_{12}(B)$, any further correspondence not being possible.

[c] The wave numbers here reported are those of Ref. 8 at 30 °K. Assignment of crystal modes $Q_1(A_g)$ and $Q_2(A_g)$ and modes $Q_{11}(B_{3g})$ and $Q_{12}(B_{3g})$ is tempting and could probably be reversed.

[d] Calculation carried out with the force field of Ref. 3.

[e] Calculation carried out with the force field of Ref. 5.

[f] Scattering geometry $[M(IJ)N]$ according to Eq. (15).

give a quantitative description of the correlation

$$P_M \to P' \to S$$

between the point groups P_M of the free molecule, P' of its local symmetry, and the factor group S of the crystal.

The Raman scattering cross sections were calculated for different orientations of an α-S_8 single crystal by using Eq. (15). The tensors $(\partial\alpha^{PC}/\partial Q_l)$ therein were deduced from the molecular tensors of Table VII according to the method described in Sec. III C. The results are reported in Table VIII for both force fields of Refs. 3 and 5.

With the tensors of Table VII in connection with Eq. (19) the cross sections for a polycrystalline sample were calculated. The simulated spectrum is shown in Fig. 3 together with the experimental one obtained at 130 °K from a polycrystalline sample. To simulate the spectrum the center and the half-width were taken for each band as empirical data, while the integrated intensity was calculated on the basis of Eq. (19). The shape of the band centered at ν_l was described by the square of a Lorentzian function

$$y(\nu,\nu_l)=\frac{2a}{\pi}\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}[1+a^2(\nu-\nu_l)^2]^{-2}\,, \tag{20}$$

which gives an excellent fitting to the observed band contour and fulfills the condition

$$\int_{-\infty}^{+\infty} y(\nu,\nu_l)d\nu=\left(\frac{\partial\sigma}{\partial\Omega}\right)_{Q_l}\,. \tag{21}$$

Here $(\partial\sigma/\partial\Omega)_{Q_l}$ stands for the differential scattering cross section corresponding to the Q_l mode, and a (above) is related to the half-bandwidth Δ [Δ = bandwidth at $(1/2)y_{\max}$] by

$$a=2(2^{1/2}-1)^{1/2}/\Delta\,. \tag{22}$$

IV. DISCUSSION OF RESULTS

The scattering coefficients S of Table III are given in units of (cm^4 g^{-1}) including the indeterminate dimensionless scaling factor k which takes account of the fact that the scattering coefficients are not absolute. Possible values for k are suggested in Sec. V in order to produce absolute values for the scattering coefficients and for the eop's and Raman tensors as well.

As mentioned in Sec. II, it was possible to find two sets of nine eop's which satisfactorily reproduced the nine experimental intensity observables related to the free S_8 molecule. These two sets correspond to the vibrational eigenvectors produced by the two different force fields of the S_8 ring. These sets of eop's of Table IV are quite different to each other in as far as the first order eop's are concerned. In both cases their values are nonnegligible when compared with the zero order eop's. This might be interpreted as a proof of electro-optical interactions between adjacent bonds and between next-

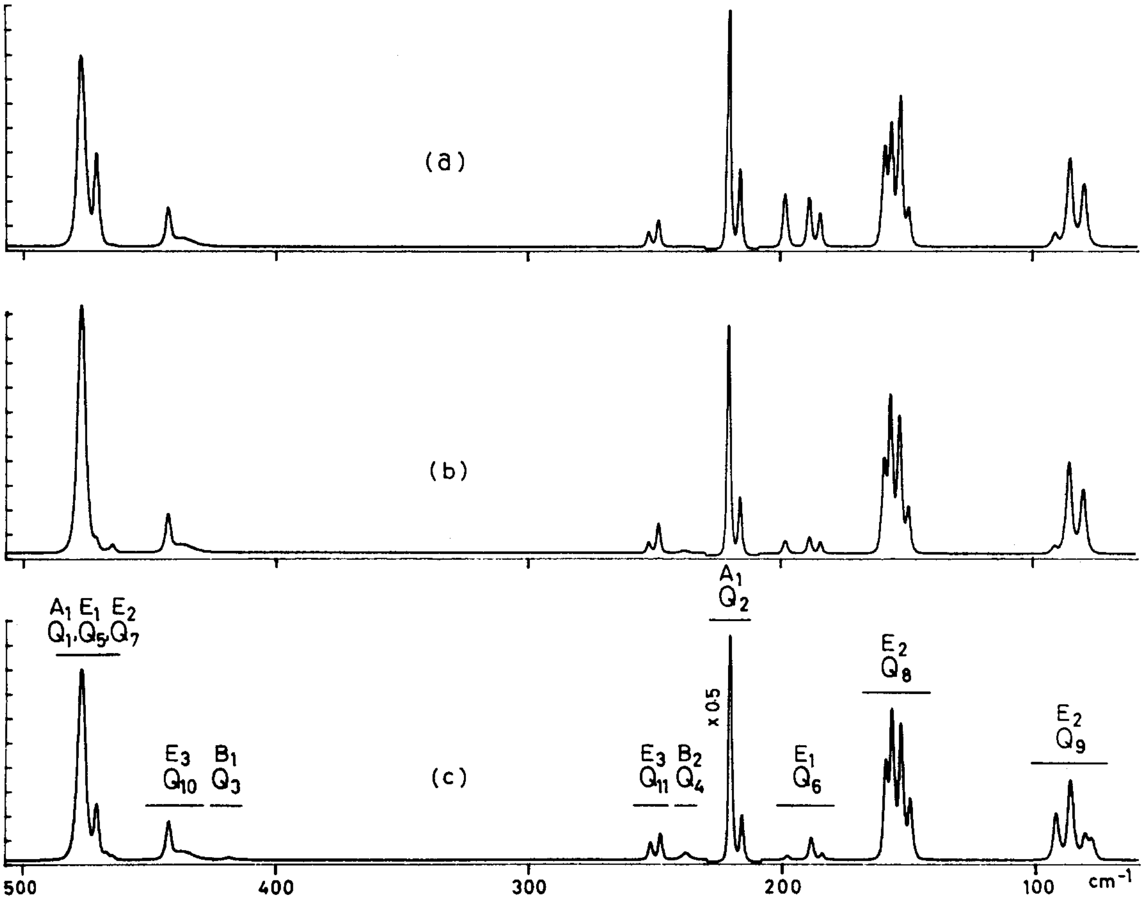

FIG. 3. (a), (b) Calculated cross sections of the vibrational Raman spectrum of polycrystalline α-S_8: (a) using the force field of Ref. 3, (b) with the force field of Ref. 5, and (c) experimental Raman spectrum of polycrystalline α-S_8 at 130 °K and $\lambda_0 = 514.5$ nm.

to-adjacent bonds of the S_8 ring.

There is no *a priori* evidence whether the calculated eop's have any physical meaning or are just the result of a numerical fitting process. Quantum mechanical calculations might prove of some help here; however, no calculation of this nature for S_8 is known to us. Despite this, it is possible to test the corresponding Raman tensors of the free molecule S_8 given in Table V to decide whether the individual elements of the tensors (including relative signs!) are meaningful or only its invariants $\bar{\alpha}'^2$ and γ'^2 are fixed by the experimental intensities. We propose the following arguments in favor of the molecular Raman tensors of Table V: Because of the wide integration interval of the band areas (Table III) all details of the crystal field splitting were added together. This way the information concommitant to the crystal was destroyed and only the information about the free S_8 molecule was retained. The molecular Raman tensors obtained on the basis of the above information were checked by transferring them to the crystal of α-S_8, looking to see whether the generated Raman tensors of the crystal are consistent or not with the ratios of intensities of the various components of the crystal field splitting as observed for different orientations of the single crystal.

The form of the Raman tensors of the crystal as a function of the molecular Raman tensors of Table V was deduced according to the method described in Ref. 14. This information is summarized in Table IX.

By comparison with the results reported in Ref. 7, we found that the Raman tensors of Table IX, once substituting the numerical values for *a*, *b*, *c* etc., do give account of most features of the Raman spectrum of the oriented single crystal. Hence, we conclude that the individual elements of the molecular tensors of Table V are approximately correct and that the eop's of Table IV are appropriate to describe the involved electro-optical properties of S–S bonds in the molecule of S_8.

Because of its complex numerical treatment, a less intuitive although a more accurate proof of the above assertion is the calculation of the Raman spectra of the oriented single crystal and of the polycrystalline sample maintaining the true C_2 local symmetry of the S_8 ring. This was accomplished in Sec. III D with the same set of eop's of Table IV.

Inspection of Table VIII shows that the group of bands between 470 and 480 cm^{-1} has two strong components (unresolved in the spectrum of Fig. 3) of approximately the same intensity, a third band slightly weaker, and seven more very weak bands. The low temperature Raman spectra of the oriented single crystal recently reported by Gauthier and Debeau[8] qualitatively confirm this complex structure. Unfortunately, they do not give

TABLE IX. Raman tensors of a primitive cell of α-S_8 single crystal as a function of the Raman tensors of a free S_8 molecule of symmetry D_{4d}.[a]

Free molecule	Crystal	
$\alpha'(A_1)=\begin{pmatrix} a_i & & \\ & a_i & \\ & & b_i \end{pmatrix}$ $i=1, 2$	$\alpha'(A_{1g})$:	$XX=C_i(s^2b_i+c^2a_i)$ $YY=C_i(c^2b_i+s^2a_i)$ $ZZ=C_ia_i$
	$\alpha'(B_{1g})$:	$XY=C_isc(a_i-b_i)$
$\alpha'(E_2^a)=\begin{pmatrix} m_i & n_i & 0 \\ n_i & -m_i & 0 \\ 0 & 0 & 0 \end{pmatrix}$; $\alpha'(E_2^b)=\begin{pmatrix} n_i & m_i & 0 \\ m_i & -n_i & 0 \\ 0 & 0 & 0 \end{pmatrix}$ $i=7, 8, 9$	$\alpha'(A_{1g})$:	$XX=-C_ic^2(m_i+n_i)$ $YY=-C_is^2(m_i+n_i)$ $ZZ=C_i(m_i+n_i)$
	$\alpha'(B_{1g})$:	$XY=-C_isc(m_i+n_i)$
	$\alpha'(B_{2g})$:	$XZ=C_ic(m_i-n_i)$
	$\alpha'(B_{3g})$:	$YZ=C_is(m_i-n_i)$
$\alpha'(E_3^a)=\begin{pmatrix} 0 & 0 & q_i \\ 0 & 0 & 0 \\ q_i & 0 & 0 \end{pmatrix}$; $\alpha'(E_3^b)=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & q_i \\ 0 & q_i & 0 \end{pmatrix}$ $i=10, 11$	$\alpha'(A_{1g})$:	$XX=2C_iscq_i$ $YY=-XX$ $ZZ=0$
	$\alpha'(B_{1g})$:	$XY=-C_i(c^2-s^2)q_i$
	$\alpha'(B_{2g})$:	$XZ=-C_isq_i$
	$\alpha'(B_{3g})$:	$YZ=C_icq_i$

[a] Nonlisted elements of the crystal tensors are zero. $c=0.78$, $s=0.63$.

quantitative relations for the spectra obtained under different orientations of the crystal. The force field of Ref. 3 apparently provides a slightly better description of the spectrum in this region than that of Ref. 5. However, the possibility of a Fermi resonance between Q_1 (A_1) and the first overtone of Q_4 (B_2) does not allow an unambiguous interpretation of the intensities in this region. Both force fields provide a satisfactory description of the region between 420 and 450 cm^{-1}, corresponding to the mode Q_{10} (E_3) of the free S_8 ring. The disagreement with the single crystal data of Ref. 7 at 438 cm^{-1} is only apparent since this band is very broad and the data of Ref. 7 are reported as peak heights.

Various bands related to Q_{11} (E_3) are found between 245 and 260 cm^{-1}. The spectrum of the polycrystalline sample is very well reproduced in this region with Scott's force field; however, there is no agreement with some of the single crystal values of Ref. 7.

Q_3 (B_1) and Q_4 (B_2) are inactive modes in the free D_{4d} S_8 ring. They were observed as very weak bands in the spectrum of the polycrystalline sample at 418 and 238 cm^{-1}, respectively. The calculated intensity was even lower for both force fields.

Q_2 (A_1) and Q_8 (E_2) present very strong bands that split in the Raman spectrum of the crystal into two components $A_{1g}+B_{1g}$ and into four components $A_g+B_{1g}+B_{2g}+B_{3g}$, respectively. The intensities of both groups of bands are quite accurately predicted with Eysel's force field, not only for the polycrystalline sample but for all the orientations of the single crystal reported in Ref. 7 as well.

The bands between 180 and 200 cm^{-1} correspond to the mode Q_6 (E_1), which is Raman inactive in the free molecule. In the crystal it becomes active. Eysel's force field provides a much better description of these intensities.

The region from 75 to 100 cm^{-1} is related to the torsional mode Q_9 (E_2) of the free molecule. In the crystal it is very close to the lattice vibrations, if not overlapping with them. Its dynamical description hence must be done on the basis of the joint interpretation of internal and of lattice modes assuming nonrigid molecules. This has not been taken into account for the obtention of the force fields used in the present work; thus, a satisfactory explanation of the intensities should not be expected for this region. In particular, the value of the eop $(c_{10}-a_{10})$ is probably an artifact without a concrete physical meaning.

V. ABSOLUTE SCATTERING COEFFICIENTS

As has been mentioned before, the scattering coefficients S, the Raman tensors, and the eop's of the present work are reported as a function of a scaling factor k. If by any means the factor k could be fixed, the results reported in Tables III–V, VII, and VIII would be given in an absolute scale. The procedures for measuring absolute Raman scattering cross sections of solids is at present not so far developed to provide accurate results for k. Thus, we propose a numerical value for k on the basis of other experimental magnitudes.

Urano and Inoue[15] have recently shown the validity of Clausius–Mossotti equation for anisotropic dielectrics under the condition of negligible short range interactions. Such interactions seem to be unimportant in the crystal of α-S_8, as the relative Raman intensities of the lattice modes can be fairly well described in terms of librational contributions[9,10] without taking into account translational contributions arising from short range intermolecular interactions. It is hence justified to relate the effective polarizability tensor $\boldsymbol{\alpha}^{UC}$ of the orthorhombic unit cell with the principal refractive indices n_i by means of equation

$$\alpha_{ii}^{UC}=\frac{3V^{UC}}{4\pi}\left(\frac{n_i^2-1}{n_i^2+2}\right) \quad , \quad i=X, Y, Z \; , \tag{23}$$

where V^{UC} is the volume of the unit cell. On the other hand, it is possible to express the effective polarizability $\boldsymbol{\alpha}^{UC}$ of the unit cell as a function of the effective equilibrium polarizability tensor $\boldsymbol{\alpha}^*$ of an S–S bond. Using the molecular geometry of Ref. 1 in connection with the refractive indices at 508 nm reported in Ref. 16, one obtains

$$\begin{aligned} \alpha_{XX}^{UC} &= 386.73\ \text{Å}^3 = 16(1.1962\alpha^* + 4.4593\beta^* + 2.3445\gamma^*) \; , \\ \alpha_{YY}^{UC} &= 407.87\ \text{Å}^3 = 16(5.4114\ \alpha^* + 2.5886\gamma^*) \; , \\ \alpha_{ZZ}^{UC} &= 458.14\ \text{Å}^3 = 16(1.3924\alpha^* + 3.5407\beta^* + 3.0669\gamma^*) \; , \end{aligned} \tag{24}$$

the solution of the system being

$$\alpha^* = 1.17\ \text{Å}^3, \quad \beta^* = 1.21\ \text{Å}^3 \; , \quad \gamma^* = 7.40\ \text{Å}^3 \; ,$$

which *a posteriori* justifies the assumption of cylindrical symmetry for the bond polarizability. Since the anisotropy $\gamma - \alpha$ is one of the eop's involved in the calculation of the Raman intensities, it can be used to derive a value for the scaling factor k. Setting the values reported for $\gamma - \alpha$ in Table IV into the equation

$$(\gamma-\alpha)\sqrt{k}=\left[\gamma^* - \frac{(\alpha^*+\beta^*)}{2}\right] \quad , \tag{25}$$

one obtains the numerical values

$$k_{\text{Scott}} = 1.56 \quad \text{and} \quad k_{\text{Eysel}} = 0.88 \; ,$$

which should be applied to all the calculated results derived from either force field. The lack of agreement between the two values of k does not permit us to deduce an accurate result for the absolute scattering coefficients of α-S_8.

Eysel's force field seems to provide a better description of the vibrational normal modes with important bending contributions, as for instance Q_8 (135–175 cm^{-1} region). It can hence be expected the value derived for $\gamma - \alpha$ from Eysel's force field to be more reliable than that originating from Scott's force field. In consequence, we would suggest the value

$$k_{\text{Eysel}} = 0.9 \pm 0.5$$

to be more realistic. A reference value for the absolute scattering coefficient $S = (45\bar{\alpha}'^2 + 10\gamma'^2)\cdot g$ of polycrystalline samples would then be

$$S(Q_1, Q_7) = (148 \pm 82)\times 10^{-8}(\text{cm}^4\text{g}^{-1}) \; ,$$

with integration interval 460–495 cm^{-1}, per molecular unit of S_8. Preresonance intensity enhancement cannot be excluded. The above value for S is hence only valid for $\lambda_0 = 514.5$ nm.

VI. CONCLUSIONS

The use of the bond polarizability model has proved to be a suitable procedure for describing parametrically the vibrational Raman intensities of molecules and even of rather more complex structures such as the crystal of α-S_8. The fact that the intensities of both kinds of structures—molecule and crystal—were described with an unique set of eop's derived from the more simple system (the molecule) suggests that the use of the information contained in the Raman intensities may be a powerful method for studying structural problems as, for instance, local symmetries of molecules in crystals and phase transitions or also for quantitative analytical purposes in polycrystalline samples.

Besides that, the joint interpretation of molecule and crystal greatly reduces the important problem of the multiplicity of solutions for the molecular Raman tensors deduced experimentally, since only one among the possible sets of molecular Raman tensors is compatible with the intensities of the crystal.

Additionally, we conclude that the vibrational intensities of molecular crystals give indirect information about the quality of molecular vibrational force fields, since the vibrational eigenvectors are also involved in the interpretation of the intensities.

Finally, we believe that the present results can substantially be improved by lifting the assumption that molecular vibrations of S_8 ring and librational/translational lattice vibrations of α-S_8 are separable. Indeed, this approximation seems to be too severe to enable a good dynamical description of the overlapping region between 70 and 100 cm^{-1}. Further improvements would require a more elaborate force field simultaneously including intra- and intermolecular force constants.

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