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Vibrational Assignment of S_8 from Normal Coordinate Analysis

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Normal modes of crystalline orthorhombic sulfur belonging to the space group D_{2h}-Fddd, have been evaluated by taking the lowest temperature phase in the solid. Normal modes are obtained by the valence force field with modified force constants and a quantitative description of the mode is adjusted by the potential energy distribution. Since the full crystal system of orthorhombic sulfur is so large, we intended to calculate the normal modes simply by constructing the imaginary box made by the infinite mass boundary. And the Raman experiment is done by using the more powerful Ar-Kr gas laser with lowering the temperature to ~10°K.

Introduction

Crystalline orthorhombic sulfur has been shown to contain sixteen molecules in an unit cell, which belongs to the space group D_{2h}-Fddd and each sulfur molecule finds itself at a site of only C_2 symmetry, where the symmetry of the isolated molecule is D_{4d}[1,2] This means that the degenerate modes of the isolated molecule may be split and that all vibrational transitions of a single molecule are allowed. Factor group splitting[3] may introduce further complications. Additional transitions may arise from lattice modes.

Since the first infrared spectrum of crystalline S_8 was taken by Coblentz[4] in 1905, many workers examined the far-infrared[5,6] and Raman spectra[7-10] of cyclo-S_8. And a number of normal coordinate analyses[11-13] has been made for orthorhombic sulfur. In the latest normal coordinate analysis, Scott *et al*[13]. fit the assigned frequencies with a modified Urey-Bradley force field. To calculate the normal frequencies and normal coordinates, the computer program having the valence force field and a very simple input data, was used and some details of the method are given in Ref. 14 to 16.

In this paper, we adjust the assigned frequencies and additionally calculate the lattice modes and predict a crystallographic assignment of each calculated frequencies, and the results are listed in Table 1.

Experiments of Raman spectra near the exciting line were done by the use of polarization analyzer, polarization scrambler, and double grating monochromator to minimize the excessive Rayleigh scattering. In a recent paper, Anderson and Loh[10] presented high resolution Raman results on orthorhombic sulfur by using a argon ion laser. The experiment described here covers the same procedure, but we take the more powerful Ar-Kr gas laser where the sulfur pellet was cooled to~10°K by using a liquid helium. And then we obtain Raman spectra with high resolution as shown in Figure. 1.

TABLE 1: Experimental and Calculated Frequencies (in cm^{-1}) of Orthorhombic Sulfur

Our work		Others		Assignment[c]
Raman (10°K)	Calculated	Raman[a] (100°K)	Calculated[b]	
477 471	479 478 477	477 470	473	$a_1\begin{cases}a_g\\b_{1g}\end{cases}$
	475 474		474	$e_2\begin{cases}b_{1g^+}\\b_{3g}^+\end{cases}$
466 464	471 470 469 468	466 464	474	$e_1\begin{cases}a_g^+\\b_g^+\end{cases}$
441	440	441	436	$e_3\begin{cases}a_gb_{1g}\\b_{2g}b_{3g}\end{cases}$
417	413 412	417	412	b_1 a_gb_{1g}
250 246	262 256 252 249 248	250 246	239	$e_3\begin{cases}a_gb_{1g}\\b_{2g}b_{3g}\end{cases}$
236	243 241 239	236	245	$b_2\begin{cases}b_{2g}\\b_{3g}\end{cases}$
218 214	223 221 217	218 214	216	$a_1\begin{cases}b_{1g}\\a_g\end{cases}$
197 187 182	189 187 186 185 184	197 187 182	192	$e_1\begin{cases}b_{1g}\\a_g\\b_{2g}b_{3g}\end{cases}$
160 156 152 150	166 159 155 154 152	150 156 152 149	161	$e_2\begin{cases}b_{2g}\\a_{1g}\\b_{3g}\\b_{1g}\end{cases}$
91 85 97 77	101 97 97 78	91 85 79 77	88	$e_2\begin{cases}b_{1g}\\a_g\\b_{3g}\\b_{2g}\end{cases}$
63 55 52 50	62 52 47 39	63 55 52 50		$R_xR_y\begin{cases}b_{3g}\\b_{2g}\\b_{1g}\\a_g\end{cases}$
44 39	30 23	44 39		$T_xT_y\begin{cases}b_{1g}b_{2g}b_{3g}\\a_g\end{cases}$
29	19 11	29 28		$R_z\begin{cases}b_{2g}\\b_{3g}\end{cases}$

[a] from Ref. 7 and 10; [b] from Ref. 13; [c] from Ref. 7 and 10.

Experiment

The Ar-Kr gas laser (Spectra Physics 165) was operated at 5145Å with power set at 300 mW. Laser beam was incident on the sample from below, and perpendicularly scattered light was collected by the double grating monochromator (Spex-1302) with all the slit width setting at 200 μm (spectral

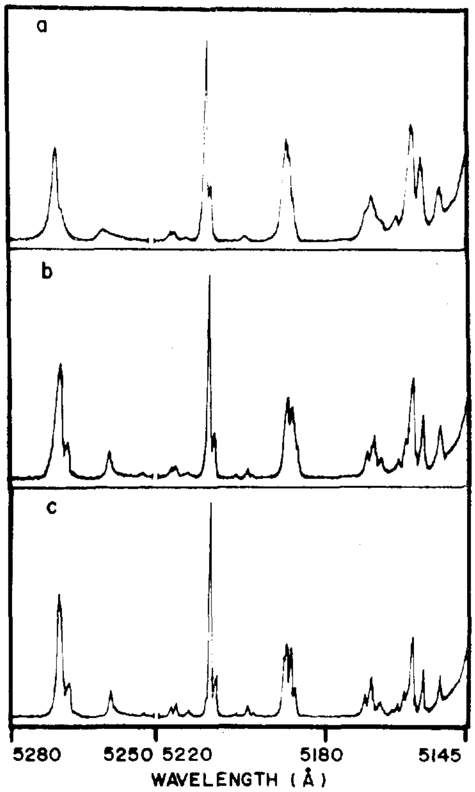

Figure 1. Raman spectra of sulfur excited by 5145Å Ar-Kr line. a : the solid at room tempreature, b : the solid at 100°K, c : the solid at 10°k.

bandpass of $7cm^{-1}$ at 5145Å).

Scattered polarizations are selected by the polarization analyzer, and a polarization scambler is inserted in front of the monochromator to reduce the grating depending on the polarization. The photon counter system with the cooled P.M. tube was used to record the spectral output, and the low temperature(~10°K) Raman spectra are obtained by using the closed cycle Helium refrigerator system (Air Products-Displex).

The sulfur pellet with 1 cm diameter and about 0.5 mm thick, being made by pressing the powdered sulfur (Fisher, U.S.P. grade), was used. By lowering the temperature to ~10°K, we obtained the Raman spectra and these spectra are shown in Figure 1.

Theory

The modified potential[14-16] suitable for both intra- and intermolecular motions is wirtten as follows.

$$2V=K\sum_{i,j}^{N}(\delta r_{ij})^2+H_\alpha\sum_{i,j,k}^{N}(\delta\alpha_{ijk})^2 +H_\tau\sum_{i,j,k,l}^{N}(\delta\tau_{ijkl})^2+\text{Interaction terms} \qquad (1)$$

where K, H_α, and H_τ are stretching, bending, and torsional force constant, respectively. The first term in eq.(1) represents the quadratic potentials between any two bonded atoms i and j. The next two terms describe the more commonly used angular deformation potentials; $\delta\tau_{ijk}$ is the change in a angle between the bonds ij and jk, and $\delta\tau_{ijkl}$ is the change in a bond torsion. And the last interaction terms are the crossterms describing the coupling between the above quadratic force fields, and these terms are obtained by using the same procedure in Ref. 14.

The internal displacement coordinates, $\delta\tau_{ij}$,$\delta\alpha_{ijk}$, and etc. are expanded with Cartesian displacement as follows.

$$\left(\frac{\partial r_{ij}}{\partial x_s}\right)_\circ=\frac{(x_i-x_j)_s}{r_{ij}^0}=\begin{cases}\Phi_{s,ij} \text{ for atom } i\\ -\Phi_{s,ij} \text{ for atom } j\end{cases} \qquad (2)$$

$$\left(\frac{\partial \alpha_{ijk}}{\partial x_s}\right)_\circ=\left\{\frac{\alpha_{ijk}(x_s^0+1/2\varDelta)-\alpha_{ijk}(x_s^0-1/2\varDelta)}{\varDelta}\right\} =\Phi_{s,ijk} \qquad (3)$$

The squares of the first derivatives constitute the force field matrix of the quadratic terms and the force field is represented as follows.

$$K\sum_{i,j}^{N}(\delta r_{ij})^2=K\sum_{i,j}^{N}\sum_{s,t}\pm\Phi_{s,ij}\Phi_{t,ij}\delta x_s\delta x_t \qquad (4)$$

$$H_\alpha\sum_{i,j,k}^{N}(\delta\alpha_{ijk})^2=H_\alpha\sum_{i,jk}^{N}\sum_{s,t}\Phi_{s,ijk}\Phi_{t,ijk}\delta x_s\delta x_t \qquad (5)$$

where s and t are the running index for Cartesian coordinates, x and $\varDelta$ are the Cartesian axis and infinitesimal, respectively, and Φ_{ij} represents the element of directive cosine of the vector γ_{ij}. The explicit explanations and derivations are given in Ref. 14 to 16.

Results and Discussion

The molecular structural constants (S-S bond length; 2.048Å, S-S-S bond angle; 107°54′) are taken from the x-ray crystallographic data[17]. The splittings of vibration in the spectra of orthorhombic sulfur are explained by the crystal field splitting with four molecules in a primitive unit cell. The real crystalline state of orthorhombic sulfur is represented as($\Phi_{n-1,n}^a e^{-i\phi a}+\Phi_{n,n}^a+\Phi_{n,n-1}^a e^{i\phi a}$, where $\phi_a$is a phase factor of a direction), but to simplify the system in a large crystalline state, the operating molecules surrounded by boundaries were considered as if these molecules were located in an imaginary box made from infinite mass boundary such as $\Phi_{n-1,n}^a,(m=\infty)+\Phi_{nn,}^a+\Phi_{n,n-1}^a(m=\infty)$. In calculating the lattice mode and the splitting of a fundamental mode, the full crystal system of orthorhombic sulfur is so large that the above technique is useful to simplify such a large system.

Figure 1 shows the spectra obtained from (a) the solid at room temperature, (b) the solid at 100°K, and (c) the solid at 10°K. In experiment with lowering the temperature to 10°K, we do not find any new peak but obtain the more sensitive and more clear peak than others.

Figure 2 shows a projection being perpendicular to the mean plane of the molecules, which are established by the crystallographic data. There exhibit a four-fold splitting for every fundamental vibrations. To explain these four-fold splitting, we adopt the crystal field splitting with taking the four molecules in the primitive unit cell being included by a dashed box in Figure 2.

In calculating the normal mode of orthorhombic sulfur, we have chosen the simplest form of molecular force field, *i.e.*, *K*;*S-S* stretching constant, *K′*; *S---S* non-bonded stretching constant between the nearest non-bonded *S* atom, *H*;*S-S-S* bending constant, *τ*; *S-S-S-S* torsional constant, and five interaction constants. The interaction constants; f_{KK} between the two stretching constants *K* and *K*, f_{KH} between the non-bonded stretching constand *K′* and bending constant *H*, f_H between the two bending constants *H* and *H*, $f_{H\tau}$ between the bending constant *H* and torsional constant

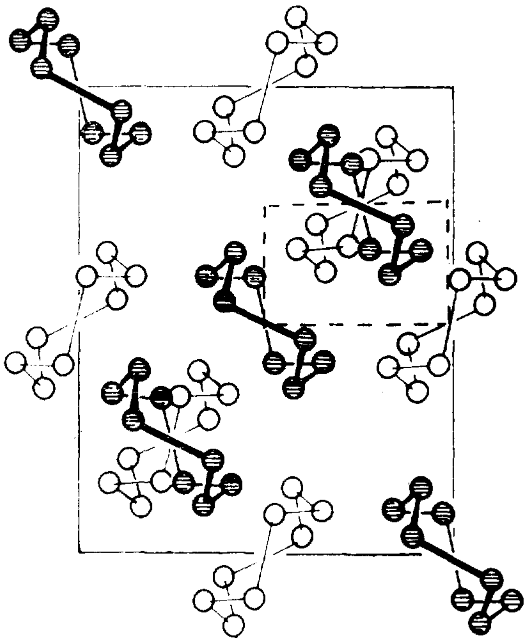

Figure 2. The contents of an unit cell of orthorhombic sulfur between Z=0 and Z=$\frac{1}{2}$, projected down the c-axis and the dashed box represents a ptimitive unit cell.

TABLE 2: Valence Force Constants Used for Calculated Frequencies Listed in Table 1

Force Constant	Coordinate involved	Valuse
K	S–S stretching	1.812(mdyn/Å)
K'	S---S non–bonded stretching	0.35(mdyn/Å)
H	S–S–S bending	0.284(mdynÅ/rad^2)
τ	S–S–S–S torsion	0.138(mdynÅ/rad^2)
f_{KK}	S–S & S–S interaction	0.45(mdyn/Å)
$f_{K'H}$	S---S & S–S–S interaction	–0.12(mdyn/rad)
f_{HH}	S–S–S &S–S–S interaction	–0.1(mdynÅ/rad^2)
$f_{\tau\tau}$	S–S–S–S & S–S–S–S interaction	0.08(mdynÅ/rad^2)
$H_{H\tau}$	S–S–S & S–S–S–S interaction	0.130(mdyn/Årad$_2$)
k_1	nearest intermolecular interaction	0.182(mdyn/Å)
k_2	next nearest intermolecular interaction	0.131(mdyn/Å)

τ, and $f_{\tau\tau}$ between the two torsional constants τ and τ, were significant in all analyses. The initial choice of the force constants was based on Ref. 12 and 13. And then we modified it to adjust the normal frequencies. This set of trial force constants is given in Table 2. The interaction constant f_{KK} splits the higher frequency mode into frequency increasing mode (a_1 and e_1) and frequency decreasing mode (e_3 and b_1). The interaction constant f_{HH} selectively increases the a_1 and b_2 frequency at the lower frequency region, and the interaction constant f_{KH} clearly splits the above two modes into the frequency increasing mode (a_1) and the frequency decreasing mode (b_2) by increasing this constant.

The four molecules in a primitive unit cell are surrounded by the sulfur atom at the boundary and these number of sulfur atoms at the boundaries are 13 atoms, which are replaced by an infinite mass in our calculation. In the operating system, intermolecular force constant of the nearest distance, k_1, is sensitive in the lowest lattice mode, B_{1g} mode of a lowest e_2 fundamental, and the splitting of fundamentals.

In ordinary normal mode analyses including our calculations, it is shown that lattice modes are slightly mixed with the internal mode in the same symmetry species, and such a mixing has an effect on lowering the lattice frequency. This feature may be due to the reason of using the various constants being not orthogonal each other.

The assignments and symmetry identifications of the internal and external vibrations of molecules in a primitive unit cell are listed in Table 1 and compared with others.

Conclusion

Since we do not find any further new peak in the high resolutional Raman experiment of orthorhombic sulfur compared with others, the motions of molecules in the solid are approximately same near the low temperature region below 100°K.

To obtain a crystal field splitting and lattice modes, we take four molecules in a primitive unit cell and construct an imaginary box being made by infinite mass boundary. The full crystal system of orthorhombic sulfur is so large that this boundary condition can simply reduce the complexity in a bulky system, and these crystal field splitting give the four-fold splitting for every fundamentals. A computer program using the valence force field and this boundary condition saves the computing time and gives a very simple program input.

Thus this technique is found to be useful to simplify the large system such as an orthorhombic sulfur.

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