

Normal Coordinate Analysis and Mean Amplitudes of Vibration for Octasulphur

S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, N-7034 Trondheim, Norway

The mean amplitudes of vibration and generalized mean-square amplitudes have been computed for the S_8 molecule. The applied harmonic force field is given in terms of symmetry F matrix blocks based on specified symmetry coordinates.

Several spectroscopic investigations of octasulphur, S_8 , have been performed (for references, see below), and calculated generalized mean-square amplitudes¹ have been published.² That calculation² did not employ the most recent data of vibrational frequencies.^{3,4} Moreover, some strange effects are reported therein, which would imply $l_{14} < l_{13}$ for the mean amplitudes of the $S_1 \cdots S_4$ and $S_1 \cdots S_3$ distances, respectively, despite the fact that $R_{14} > R_{13}$ for the corresponding equilibrium distances. This would be an unexpected anomaly on the basis of previous experience for regular ring structures. For the CC mean amplitudes in benzene as an example it has been found¹ (at 298°K and in Å units) about 0.046, 0.055, and 0.059 with increasing equilibrium values.* The same effect of increasing mean amplitudes is found in nonplanar rings. For instance in cyclohexane the appropriate figures are 0.0482, 0.0702, and 0.0731.⁵

STRUCTURE PARAMETERS AND VIBRATIONAL FREQUENCIES

The values of 2.060 Å and 108.0° for the S-S distance and SSS angle were adopted in this work. They are quoted in a recent work on hexasulphur,⁶ and they correspond to $S_1 \cdots S_3$, $S_1 \cdots S_4$, and $S_1 \cdots S_5$ nonbonded distances of 3.333, 4.467, and 4.714 Å, respectively.

The early assignment of vibrational frequencies for S_8 due to Bernstein and Powling⁷ has been used in previous determinations of force constants,^{8,9} and

* For the nonbonded CH distances on the other hand, the mean amplitudes decrease with increasing equilibrium distances. In benzene at 298°K the figures are¹ (in Å) about 0.100, 0.097, and 0.093 for $C_1 \cdots H_2$, $C_1 \cdots H_3$, and $C_1 \cdots H_4$, respectively.

also in the recent calculations of mean-square amplitudes.² This assignment⁷ has been revised through a series of works by Scott with collaborators^{4,10,11} and others.³ In the present work the most recent assignment of Scott *et al.*⁴ has been adopted, and is shown together with the early assignment in Table 1.

Table 1. Vibrational assignments (frequencies in cm^{-1}) for octasulphur.

		Previous ⁷	Recent ⁴
A_1	1	474	475
	2	218	218
B_1	3	532	411
B_2	4	267	243
E_1	5	471	471
	6	191	191
E_2	7	437	475
	8	184	152
	9	151	86
E_3	10	523	437
	11	248	248

Several discrepancies between these two assignments are seen. The most prominent feature of the new assignment⁴ in contrast to the old one⁷ is the occurrence of an extremely low frequency (86 cm^{-1}) in E_2 .

SYMMETRY COORDINATES

The purpose of this section is to specify a complete set of symmetry coordinates with no redundants for the vibrations of the S_8 molecular model.

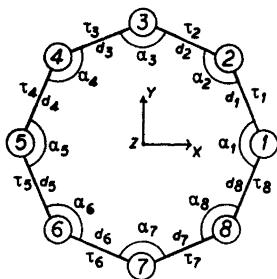


Fig. 1. The S_8 molecular model; symmetry D_{4d} . Atoms 1, 3, 5, and 7 are above the XY plane; 2, 4, 6, and 8 are below. Valence coordinates are indicated, viz. stretchings (d), bendings (α) and torsions (τ). The equilibrium S—S bond distance is denoted by D .

The molecular model is a puckered ring of symmetry D_{4d} (see Fig. 1). The normal modes of vibration are distributed among the appropriate symmetry species according to

$$\Gamma(\text{vib}) = 2A_1 + B_1 + B_2 + 2E_1 + 3E_2 + 2E_3 \quad (1)$$

Eight stretchings (d), eight bendings (α) and eight torsions (τ) may be defined as standard types of valence coordinates (*cf.* Fig. 1). These sets possess the following symmetric structures.

$$\Gamma(d) = A_1 + B_1 + E_1 + E_2 + E_3 \quad (2)$$

$$\Gamma(\alpha) = A_1 + B_2 + E_1 + E_2 + E_3 \quad (3)$$

$$\Gamma(\tau) = A_1 + B_1 + E_1 + E_2 + E_3 \quad (4)$$

Hence there are six redundants among the totality of twenty-four coordinates, distributed according to

$$\Gamma(\text{red}) = A_1 + B_1 + E_1 + E_3 \quad (5)$$

Species A_1

In species A_1 the symmetry coordinates are chosen as

$$S_1(A_1) = 8^{-\frac{1}{2}}(d_1 + d_2 + d_3 + d_4 + d_5 + d_6 + d_7 + d_8) \quad (6)$$

$$S_2(A_1) = 8^{-\frac{1}{2}}D(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8) \quad (7)$$

where D is the equilibrium SS distance. There exists also a combination of the torsions belonging to this species, *viz.*

$$S_r(A_1) = 8^{-\frac{1}{2}}D(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6 + \tau_7 - \tau_8) \quad (8)$$

The inclusion of S_r would introduce a redundant. It would be possible to remove this redundant by means of the zero coordinate, which is a certain combination of $S_2(A_1)$ and $S_r(A_1)$. Here the other alternative has been chosen, namely omitting the coordinate $S_r(A_1)$.

Species B_1

$$S(B_1) = 8^{-\frac{1}{2}}(d_1 - d_2 + d_3 - d_4 + d_5 - d_6 + d_7 - d_8) \quad (9)$$

The combination of torsions,

$$S_r(B_1) = 8^{-\frac{1}{2}}D(\tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_7 + \tau_8) \quad (10)$$

which belongs to the B_1 species and forms a zero coordinate together with $S(B_1)$, has simply been omitted.

Species B_2

$$S(B_2) = 8^{-\frac{1}{2}}D(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8) \quad (11)$$

Species E_1

$$S_{1a}(E_1) = 8^{-\frac{1}{2}}(2 + 2^{\frac{1}{2}})^{-\frac{1}{2}}[(1 + 2^{\frac{1}{2}})(d_1 - d_4 - d_5 + d_8) + d_2 - d_3 - d_6 + d_7] \quad (12)$$

$$S_{2a}(E_1) = 8^{-\frac{1}{2}}D[2^{\frac{1}{2}}(\alpha_1 - \alpha_5) + \alpha_2 - \alpha_4 - \alpha_6 + \alpha_8] \quad (13)$$

$$S_{1b}(E_1) = 8^{-\frac{1}{2}}(2 + 2^{\frac{1}{2}})^{-\frac{1}{2}}[(1 + 2^{\frac{1}{2}})(d_2 + d_3 - d_6 - d_7) + d_1 + d_4 - d_5 - d_8] \quad (14)$$

$$S_{2b}(E_1) = 8^{-\frac{1}{2}}D[2^{\frac{1}{2}}(\alpha_3 - \alpha_7) + \alpha_2 + \alpha_4 - \alpha_6 - \alpha_8] \quad (15)$$

The two omitted combinations of torsions, which belong to the E_1 species, are:

$$S_{ra}(E_1) = 8^{-\frac{1}{2}}(2 + 2^{\frac{1}{2}})^{-\frac{1}{2}}D[(1 + 2^{\frac{1}{2}})(\tau_1 + \tau_4 - \tau_5 - \tau_8) - \tau_2 - \tau_3 + \tau_6 + \tau_7] \quad (16)$$

$$S_{rb}(E_1) = 8^{-\frac{1}{2}}(2 + 2^{\frac{1}{2}})^{-\frac{1}{2}}D[(1 + 2^{\frac{1}{2}})(-\tau_2 + \tau_3 + \tau_6 - \tau_7) + \tau_1 - \tau_4 - \tau_5 + \tau_8] \quad (17)$$

Species E₂

$$S_{1a}(E_2) = 8^{-\frac{1}{2}}(d_1 - d_2 - d_3 + d_4 + d_5 - d_6 - d_7 + d_8) \quad (18)$$

$$S_{2a}(E_2) = \frac{1}{2}D(\alpha_1 - \alpha_3 + \alpha_5 - \alpha_7) \quad (19)$$

$$S_{3a}(E_2) = D\delta_1 \quad (20)$$

$$S_{1b}(E_2) = 8^{-\frac{1}{2}}(d_1 + d_2 - d_3 - d_4 + d_5 + d_6 - d_7 - d_8) \quad (21)$$

$$S_{2b}(E_2) = \frac{1}{2}D(\alpha_2 - \alpha_4 + \alpha_6 - \alpha_8) \quad (22)$$

$$S_{3b}(E_2) = D\delta_2 \quad (23)$$

The two δ coordinates are defined as:

$$\delta_1 = 8^{-\frac{1}{2}}(\tau_1 + \tau_2 - \tau_3 - \tau_4 + \tau_5 + \tau_6 - \tau_7 - \tau_8) \quad (24)$$

$$\delta_2 = 8^{-\frac{1}{2}}(\tau_1 - \tau_2 - \tau_3 + \tau_4 + \tau_5 - \tau_6 - \tau_7 + \tau_8) \quad (25)$$

When introducing the notation of δ for the appropriate combinations of torsions the transformation matrix between symmetry coordinates and valence coordinates becomes formally orthogonal. This statement is true if the δ coordinates are accepted as valence coordinates, although they do not belong to the conventional types.

Species E₃

$$S_{1a}(E_3) = 8^{-\frac{1}{2}}(2 - 2^{\frac{1}{2}})^{-\frac{1}{2}}[(2^{\frac{1}{2}} - 1)(d_2 + d_3 - d_6 - d_7) - d_1 - d_4 + d_5 + d_8] \quad (26)$$

$$S_{2a}(E_3) = 8^{-\frac{1}{2}}D[2^{\frac{1}{2}}(\alpha_3 - \alpha_7) - \alpha_2 - \alpha_4 + \alpha_6 + \alpha_8] \quad (27)$$

$$S_{1b}(E_3) = 8^{-\frac{1}{2}}(2 - 2^{\frac{1}{2}})^{-\frac{1}{2}}[(2^{\frac{1}{2}} - 1)(d_1 - d_4 - d_5 + d_8) - d_2 + d_3 + d_6 - d_7] \quad (28)$$

$$S_{2b}(E_3) = 8^{-\frac{1}{2}}D[2^{\frac{1}{2}}(\alpha_1 - \alpha_5) - \alpha_2 + \alpha_4 + \alpha_6 - \alpha_8] \quad (29)$$

The omitted combinations of torsions:

$$S_{\tau a}(E_3) = 8^{-\frac{1}{2}}(2 - 2^{\frac{1}{2}})^{-\frac{1}{2}}D[(2^{\frac{1}{2}} - 1)(\tau_2 - \tau_3 - \tau_6 + \tau_7) + \tau_1 - \tau_4 - \tau_5 + \tau_8] \quad (30)$$

$$S_{\tau b}(E_3) = 8^{-\frac{1}{2}}(2 - 2^{\frac{1}{2}})^{-\frac{1}{2}}D[(2^{\frac{1}{2}} - 1)(-\tau_1 - \tau_4 + \tau_5 + \tau_8) - \tau_2 - \tau_3 + \tau_6 + \tau_7] \quad (31)$$

The here derived set of symmetry coordinates is believed to be convenient when a final harmonic force field is to be reported, and for further computations with this force field. But it is not advisable to work with these symmetry coordinates from the start when a force field is to be determined. Especially there is no particular reason to believe that a diagonal F matrix in terms of the here constructed symmetry coordinates will give a good approximation.

FORCE FIELD

A harmonic force field was determined, using the six-constant potential function of a modified Urey-Bradley force field from Scott *et al.*⁴ as the starting point. The force constants were converted to a set of symmetry force constants based on the symmetry coordinates specified in the preceding section. Finally these force constants were adjusted to fit exactly the observed frequencies.⁴ The resulting force field in terms of the symmetrized F matrix blocks is given in Table 2.

Table 2. Symmetry force constants (mdyne/Å) for octasulphur.

A_1	3.917 0.449	0.232	B_1 B_2	1.219 0.193	
E_1	3.299 0.407	0.240	E_3	1.506 0.106	0.295
E_2	2.353 0.283 0.024	0.213 0.028			0.039

Table 3. Mean amplitudes of vibration (Å) for octasulphur.

Distance	$T=0$	298°K
S_1-S_2	0.0484	0.0547
$S_1\cdots S_3$	0.0611	0.0857
$S_1\cdots S_4$	0.0676	0.1039
$S_1\cdots S_5$	0.0793	0.1435

Table 4. Generalized mean-square amplitudes (Å²) for octasulphur.

Distance	Temp. (°K)	$\langle \Delta z^2 \rangle$	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$	$\langle \Delta x \Delta y \rangle$	$\langle \Delta y \Delta z \rangle$	$\langle \Delta z \Delta x \rangle$
S_1-S_2	0	0.00235	0.00465	0.00547	0	0.00015	0
	298	0.00299	0.01262	0.01791	0	0.00075	0
$S_1\cdots S_3$	0	0.00374	0.00356	0.00637	-0.00083	0	0
	298	0.00734	0.00818	0.02627	-0.00442	0	0
$S_1\cdots S_4$	0	0.00457	0.00270	0.00385	0	-0.00087	0
	298	0.01079	0.00545	0.01427	0	-0.00429	0
$S_1\cdots S_5$	0	0.00629	0.00217	0.00247	0	0	0
	298	0.02058	0.00440	0.00505	0	0	0

MEAN AMPLITUDES OF VIBRATION

The derived force field was used to calculate the mean amplitudes of vibration with the results at absolute zero and 298°K shown in Table 3. It is seen that the mean amplitudes increase with increasing equilibrium distances. Hence there are no anomalies of the type reported previously² as a result of the present calculations. It is not clear whether the employment of the old assignment⁷ gives the full explanation to the anomalous effect of $l_{13} > l_{14}$, which on the basis of the present work is not believed to be true.

GENERALIZED MEAN-SQUARE AMPLITUDES

Table 4 shows the generalized mean-square amplitudes¹ calculated from the force field of the present work (Table 2). The values are entirely different from those of the previous publication.² All values of the mean-square parallel and perpendicular amplitudes (at room temperature) are higher in the present work. This feature is explained at least in part by the employment of the low frequency of 86 cm⁻¹ (cf. Table 1). The values of the individual mean-square perpendicular amplitudes $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ depend on the choice of the corresponding two directions perpendicular to the connecting line of the atom pair (ij) in question. In the present work the Δx and Δy directions are, respectively, parallel and perpendicular to the O_{ij} plane, where O is the molecule center. However, the sum of the quantities $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ for every atom pair does not depend on the individual orientations of the mutually perpendicular directions of Δx and Δy .

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