Vibrational Assignment and Force Constants of Cyclo Octaselenium, Se_8, and of the Cyclo Tetraselenium(2+) Cation, Se_4^{2+}

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Force constants have been calculated for Se_8 (α-monoclinic selenium) after reassigning the literature values of the fundamental frequencies and using a modified Urey-Bradley force field with six force constants. Very good agreement between observed and calculated frequencies was obtained and valence force constants were calculated. A non-linear relationship holds for SeSe stretching force constants and bond distances. Using the Se_8 force constants the fundamental frequencies of the square-planar Se_4^{2+} were calculated and compared with the observed values.

Introduction

Se_8 crystallizes from carbon disulfide in two different forms, monoclinic α-Se and monoclinic β-Se. The structures of both phases have been investigated several times by X-ray diffraction on single crystals leading to R values of 7.2% for α-Se and 9% for β-Se [1–3]. The most recent results show that the Se_8 molecules are very similar in both phases. The unit cell of α-monoclinic selenium contains four molecules on general positions. However, the approximate symmetry of the crown-shaped molecules is D_{4d}, and the average bond distance, valence angle and dihedral angle are $d = 2.336 \pm 0.006$ Å, $\alpha = 105.7 \pm 1.6°$ and $\tau = 101.4°$ [4]. The space group of α-Se is $P2_1/n$. The shortest intermolecular distances of 3.5Å indicate a somewhat stronger than van der Waals interaction of neighboring molecules (van der Waals distance 4.0 Å).

The infrared and Raman spectra of α-Se were reported by Lucovsky et al. [5–7] and by Mooradian and Wright [8]. Eleven fundamental frequencies are to be expected belonging to the symmetry species a_1, b_1, b_2, e_1, e_2 and e_3. The b_2 and e_1 modes are infrared active and the a_1, e_2 and e_3 vibrations are Raman active. All these fundamentals were observed in the region $45 - 260\ \text{cm}^{-1}$ despite the fact that Se_8 is thermally unstable and light sensitive and undergoes conversion to trigonal selenium. The inactive b_1 fundamental was estimated from the two phonon spectrum to be at $216\ \text{cm}^{-1}$. The Raman spectra of α-Se were recorded at room temperature and at liquid helium temperature and a significant improvement of the spectrum was observed at 4 K. Many lines are resolved from neighboring lines at low temperatures only. The observed frequencies and estimated relative intensities are listed in Table I together with the assignments given by several workers and based mainly on the comparison of the α-Se spectra with those of S_8 in orthorhombic sulfur whose molecules belong to the same point group. To check this assignment and to calculate the force constants of Se_8 we made a normal-coordinate treatment.

Table 1. Infrared and Raman spectra of α-monoclinic selenium and assignment of the 11 fundamentals of Se_8 (s strong, m medium, w weak, v very, sh shoulder).

infrared	Raman		assignment		
	at 4 K	at 300 K			
l.c. [6]	(l. c. [8])	(l.c. [7])	l.c. [8]	l.c. [5, 7]	this work
	38 w				lattice
	47 w	50	e_2	e_2	e_2
	55 w				lattice
	60 vvw				lattice
	74 76 m				
	86 w-m	84	e_2	e_2	e_2
92 97 w	96 vw		e_1	e_1	e_1
	103 vvw				
	113 vs	114	a_1	a_1	a_1
116 sh 122 s	120 w		b_2	b_2	b_2
	128 vw	128	e_3	e_3	e_3
	162 vvw				113+47
	176 vvw				96+86 or 128+47
[216]				b_1	
	240 vw	239	e_3	e_3	e_3
250 sh 254 vs	251 m	249	a_1	a_1	e_1
	256 vs	254	e_2	e_1+e_2	a_1+e_2
	264 w-m		e_1		
	271 w				2·113+47

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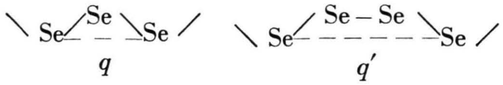
Calculations

The calculations were made using a modified Urey-Bradley force field with six independent force constants as has been applied to S_8 [9]. This force field is

$$\begin{aligned} 2V = {} & \sum^{8} K(\Delta r)^2 + 2\sum^{8} K' r\,\Delta r + \sum^{8} H(r\,\Delta\alpha)^2 + 2\sum^{8} H' r(r\,\Delta\alpha) \\ & + \sum^{8} F(\Delta q)^2 + 2\sum^{8} F'(q\,\Delta q) + \sum^{8} Y(r\,\Delta\tau)^2 + 2\sum^{8} Y' r(r\,\Delta\tau) \\ & + \sum^{8} C(\Delta q')^2 + 2\sum^{8} C'(q'\,\Delta q') + 2\sum^{8} P\,\Delta r\,\Delta r' \end{aligned}$$

with the force constants K (bond stretching), H (valence angle bending), F (next nearest atom repulsion), Y (torsion), C (long range repulsion) and P (bond-bond interaction). The coordinates q and q' are defined



and possess the values 3.72 and 5.01 Å, respectively. r and r' are the distances of neighboring bonds. The constants K', H' and Y' are eliminated in the removal of the redunant coordinates, q and q', and F' and C' were constrained by the conventional assumptions $F' = -0.1\,F$ and $C' = -0.1\,C$. The symmetry coordinates were taken from S_8 [10].

The calculations were performed by a CD 6500 computer using the programs UBZM by Schachtschneider [11] and BGLZ and LSMA by Shimanouchi [12].

Results and Discussion

Because of the structural similarities between Se_8 and S_8 we calculated the first set of frequencies using force constants which were obtained by lowering the corresponding S_8 values [9] by 25% each. The mass of Se was taken as 79 since natural selenium consists of isotopes with masses 74, 76, 77, 78, 80 and 82 and with abundances between 1 and 50% leading to the atomic weight of 78.96. The frequencies thus obtained are listed in Table II and are all very close to certain observed values allowing the assignment of most of the fundamentals. Since only b_2 and e_1 modes are infrared active the assignment $b_2 = 120$ and $e_1 = 253$ and 95 cm^{-1} seems to be reasonable. All three frequencies are split into two components by intermolecular vibrational coupling as has been observed in the case of S_8 too [13]. The vibrations of symmetry a_1, e_2 and e_3 are allowed in the Raman spectrum, and despite the fact that polarization data are not available it follows from the high intensity of the lines at 256 and 113 cm^{-1} that these must be the a_1 modes. From the values in Table 2 it is suggested that the frequencies 240 and 128 cm^{-1} belong to the e_3 modes. The assignment of the remaining e_2 vibrations is more difficult since several alternatives are possible. Therefore we calculated the e_2 frequencies from new force constants which were obtained by adjusting the seven calculated a_1, b_2, e_1 and e_3 frequencies to the observed values by the least squares method varying all six force constants. The e_2 frequencies thus obtained were 253, 89 and 44 cm^{-1}. From these values it follows that the Raman lines at 256, 86 and 47 cm^{-1} must be the e_2 fundamentals assuming an incidental degeneracy of the a_1 and e_2 stretching modes which also has been observed for S_8 [9]. The attempt to assign the lines at 264 and 75 cm^{-1} as e_2 stretching and bending modes, respectively, did not give good agreement between *all* observed and calculated frequencies (maximum difference after adjustment: 7 cm^{-1}) and the force constant H became negative. Therefore the slightly split line at 75 cm^{-1} may be a lattice mode and the 264 cm^{-1} line may be one of the two components of the e_2 stretching vibration if this fundamental should be split by intermolecular interaction. The final assignment is given in column 6 of Table I.

Frequencies [cm^{-1}]	Force Constants [mdyn/Å]
a_1: 265, 118	$K = 1.387$
b_1: 224	$H = 0.029$
b_2: 127	$F = 0.247$
e_1: 264, 104	$Y = 0.014$
e_2: 261, 90, 46	$P = 0.226$
e_3: 238, 130	$C = 0.058$

Table II. Fundamental frequencies of Se_8 calculated with assumed force constants.

To adjust the calculated to the observed frequencies by the least squares method all six force constants were varied simultaneously until the corrections became zero. The frequency of the inactive b_1 mode was not adjusted since this frequency was estimated from the 2nd order infrared spectrum only.

1	2	3	4	5	6	*K*	*H*	*F*	*Y*	*P*	*C*
a_1	ν_1	256	255	1	ν	65	2	9	2	17	5
	ν_2	113	111	2	δ	0	15	60	13	0	11
b_1	ν_3	—	231	—	ν	137	0	−3	0	−36	1
b_2	ν_4	120	120	0	δ	0	15	65	2	0	19
e_1	ν_5	253	255	−2	ν	72	1	10	0	13	3
	ν_6	95	97	−2	δ	1	15	59	26	0	0
e_2	ν_7	256	255	1	ν	88	0	10	1	0	1
	ν_8	86	88	−2	δ	0	10	44	2	0	43
	ν_9	47	46	1	τ	2	5	18	56	0	18
e_3	ν_{10}	240	240	0	ν	119	0	3	0	−22	0
	ν_{11}	128	127	1	δ	0	11	44	7	0	37

Force constants:	$K=1.341$	$H=0.021$	$F=0.214$	$Y=0.015$	$P=0.175$	$C=0.070$
Dispersions:	0.022	0.026	0.063	0.002	0.010	0.007

Table III. Frequencies, assignment, potential energy distribution and Urey-Bradley force constants of Se_8 (column 3: observed frequencies, 4: calculated frequencies, 5: difference between obs. and calc. frequencies, 6: assignment; frequencies in cm^{-1}, force constants and dispersions in mdyn/Å).

The calculated frequencies, force constants, dispersions and potential energy distribution are shown in Table III. The maximum difference between observed and calculated frequencies amounts to 2 cm^{-1}.

Because of the many isotopes of selenium cyclo octaselenium is a very complicated mixture of molecules with masses between 592 and 656, most of them existing in several isomers. The most abundant species is $^{80}Se_6\,^{78}Se_2$ with 28 isomers. In order to determine the isotopic frequency shifts and the splittings of degenerate modes we calculated the frequencies of $^{80}Se_7\,^{78}Se$, 1,2-$^{80}Se_6\,^{78}Se_2$ and 1,5-$^{80}Se_6\,^{78}Se_2$ using the force constants in Table III. Compared with $^{80}Se_8$ the maximum frequency difference was 1.2 cm^{-1} and the maximum splitting of frequencies in the twofold substituted molecules was 0.9 cm^{-1}. Thus the two Raman lines at 264 and 271 cm^{-1} cannot be explained by isotopic substitution. Only line broadening can be expected from the presence of several hundred different molecules Se_8. Table IV lists the valence force constants of Se_8 which were obtained from the symmetrized *F* matrix whose elements are linear combinations of those constants. All values are smaller than the corresponding S_8 values. As has been found for SS bonds the bond-bond interaction constant f_{rr} is very high (20% of f_r) which can be rationalized by electron rearrangement during antisymmetric stretching vibrations:

Table IV. Valence force constants of Se_8 (mdyn/Å; f_r stretching, f_α bending, f_τ torsion; f_{ij} interaction constants between the nearest and f_{ij}' between the next nearest coordinates indicated).

f_r	1.695	f_{rr}	0.394	f_{rr}'	0.037
f_α	0.166	$f_{\alpha\alpha}$	0.019	$f_{r\alpha}'$	0.028
f_τ	0.030	$f_{r\alpha}$	0.138	$f_{r\tau}'$	0.017
		$f_{r\tau}$	−0.023		
		$f_{\alpha\tau}$	−0.020		

$$-\overline{\underline{\mathrm{Se}}}-\overline{\underline{\mathrm{Se}}}-\overline{\underline{\mathrm{Se}}}- \longleftrightarrow -\overset{\oplus}{\underline{\mathrm{Se}}}=\overline{\underline{\mathrm{Se}}}\ |\overset{\ominus}{\overline{\underline{\mathrm{Se}}}}- .$$

For SS bonds in molecules of type S_n the linear relationship $\log f_r = a - b \log r$ has been derived[14] ($a = 2.66$, $b = 7.26$, f_r in mdyn/Å, r in Å). Because of the well known similarities between sulfur and selenium a similar relationship can be expected for SeSe bonds. Unfortunately beside of the stretching force constant of Se_8 only two more f_r values are known. For the diatomic molecule $^{80}Se_2$, present in selenium vapour, in its ground state and one of its electronically excited states the force constants $f_r =$ 3.493 (with $r = 2.165$ Å) and 1.414 mdyn/Å (with $r = 2.442$ Å) can be calculated from the anharmonic vibrational frequencies derived from the uv spectrum[15]. However, these data do not fit any equation $\log f_r = a - b \log r$ or $f_r = a + b\,r$. Only a non-linear relationship between f_r and r can be obtained which is useful, however, to check uncertain f_r values as will be shown later.

Cyclo Tetraselenium(2+) Cation

Several salt-like compounds containing the cation Se_4^{2+} have been prepared and by x-ray structure analysis of $Se_4(HS_2O_7)_2$ it was shown that the cation is a square (symmetry D_{4h})[16]. The infrared and Raman spectra of $Se_4(SO_3F)_2$, $Se_4(HS_2O_7)_2$, $Se_4(S_4O_{13})$ and $Se_4(Sb_2F_{11})_2$ have been investigated by Gillespie and Pez[17] and of the five fundamental frequencies four have been observed and have been assigned as shown in Table V. The totally symmetric stretching frequency is higher than in Se_8 indicating stronger bonds in Se_4^{2+} which also follows from the shorter bond distance ($r = 2.283$ Å)[16]. Using a simple Urey-Bradley force field with constants *K*, *H*

species	symmetry coordinate [20]	IR	Ra	frequency obs. [17]	calc.
ν_1 a_{1g}	$r_1+r_2+r_3+r_4$	—	+	327 p	301
ν_2 b_{1g}	$\alpha_1-\alpha_2+\alpha_3-\alpha_4$	—	+	188 dp	154
ν_3 b_{2g}	$r_1-r_2+r_3-r_4$	—	+	319	202
ν_4 b_{2u}	$\tau_1-\tau_2+\tau_3-\tau_4$	—	—	—	73
ν_5 e_u	$r_1-r_2-r_3+r_4-2(\alpha_1-\alpha_3)$ $r_1+r_2-r_3-r_4-2(\alpha_2-\alpha_4)$	+	—	306	248

Table V. Symmetry coordinates and fundamental frequencies of Se_4^{2+} (cm^{-1}). The calculated values were obtained with the force constants of Se_8.

and F the frequencies could be calculated [17]. However, the force constant $K = 2.2$ mdyn/Å obtained seems to be too high compared with the Se_8 value of 1.34 mdyn/Å. For this reason we repeated the normal-coordinate treatment using the symmetry coordinates given by Cyvin [19] and a force field with the constans K, P, H, F and Y. In the first calculation the force constants were taken from Se_8 and the frequencies listed in column 7 of Table V were obtained. These values support the assignment made by Gillespie and Pez [17] excepting the b_{2g} stretching frequency. The value 319 cm^{-1} observed for $Se_4(SO_3F)_2$ only, seems to be too high and can be explained alternatively as one component of a dublett arising from the interaction of the a_{1g} modes of two or more cations in the unit cell. Attempts to adjust the calculated to the four observed frequencies by varying the force constants K, P, H and F yielded good agreement but the constant P became negative (-0.17 mdyn/Å) which is unacceptable. Therefore we only used the well established frequencies at 327, 188 and 306 cm^{-1} which have been observed for all the above mentioned Se_4^{2+} salts. In the adjustment only K, H and F were varied and complete agreement between observed and calculated frequencies was obtained with $K = 1.88$, $H = 0.135$ and $F = 0.128$ mdyn/Å ($P = 0.175$). With these constants the b_{2g} frequency is calculated as 255 cm^{-1}. Obviously this mode is of low Raman intensity since the volume of the molecule does not change much during vibration and therefore it has not been observed yet.

The valence force constants of Se_4^{2+} can be estimated only. Taking $f'_{rr} = 0.04$ and $f_{\alpha\alpha} = 0.02$ from Se_8 one obtaines from the F matrix of Se_4^{2+}: $f_r = 1.96$, $f_{rr} = 0.15$ and $f_\alpha = 0.25$ mdyn/Å. The stretching constant f_r is in agreement with the value of 1.95 mdyn/Å obtained from the above mentioned non-linear relationship between f_r and bond distance supporting this relation.

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