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VIBRATIONAL SPECTRA OF S_7Se AND A COMMON FORCE FIELD FOR $^{34}S_8$, $^{32}S_8$ AND S_7Se

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ABSTRACT

Raman spectra of solid S_7Se have been recorded both at room temperature and at low temperatures down to ~30 K. Abnormal half-widths of the low-temperature spectra compared with those of S_8 indicate that an ordered phase of S_7Se does not exist. Simultaneous calculations of a valence force field for $^{32}S_8$, $^{34}S_8$ and S_7Se yielded a refined force field for elemental sulphur along with the force constants of SSe bonds and SSeS angle deformations. The observed frequencies are reproduced to within 0.5% for all three molecules.

INTRODUCTION

As early as 1903 Rathke [1] suggested that the sulphur—selenium interchalcogene compounds prepared by reduction of SeO_2 by H_2S or from molten mixtures of the elements consist of eight-membered rings like S_8, Se_4S_4, Se_2S_6 and Se_6S_2. This suggestion was confirmed by mass spectroscopic [2, 3] and X-ray [4, 5] studies. Further information on the structure of the molecules could not be obtained by X-ray methods since the crystals are not only mixed but also orientationally disordered.

Several attempts have been made to prepare chemically pure samples of sulphur—selenium compounds of which the work of Hawes [6] (Se_2S_6, Se_4S_4, $SnI_4 \cdot SeS_7$), Schmidt and Wilhelm [7] (Se_2S_6 and Se_3S_5), Datta and Krishnan [8] (Se_4S_4), and Cooper and Culka [9] (S_7Se) should be mentioned. The product $SnI_4 \cdot 2SeS_7$ seems to be sufficiently well characterized by X-ray study whereas Se_2S_6, Se_4S_4 and Se_3S_5 prepared according to refs. 6 and 7 do not yield stable recrystallization products [3, 10, 11]. From the Raman spectra of these products one can conclude that the compounds do not rearrange in solution provided that the solvent temperatures are lower than ambient [11]. Observed changes in the sample composition are due to the gradual separation of different chemical species within the mixed-crystal system. The spectroscopic evidence of Datta and Krishnan [8] for the isolation of pure Se_4S_4 has been shown to be erroneous [12].

In this paper we demonstrate by means of vibrational spectroscopy and mass spectra that S_7Se prepared carefully after the method of ref. 9 or from repeated fractionation of S_xSe_{8-x} [11] can be obtained as an essentially pure compound. Minor contaminants of S_8 and Se_2S_6 cannot be avoided.

Sulphur—selenium mixed compounds give, like sulphur, very poor IR spectra and there is, to our knowledge, only one such study in the literature [14]. Because of the high polarizability of the compounds, however, very strong Raman spectra are observed [8, 10—12, 15—18]. Assignment of the Raman frequencies to characteristic groups has been achieved by qualitative considerations [8, 15, 17, 18] and by model calculations [16, 19]. The lack of chemically pure samples made it impossible for previous workers in this field to provide experimental proof for their calculated frequencies. Here, we assign all the observed Raman frequencies of S_7Se, give symmetry correlations to the parent molecule S_8 and calculate a general valence force field of 24 force constants based on 17 observed frequencies from S_7Se and 22 frequencies from $^{32}S_8$ and $^{34}S_8$.

EXPERIMENTAL

The compound S_7Se was prepared by the method of Cooper and Culka [9]. A second sample was obtained by the following procedure. A melt of sulphur (85 g) and selenium (15 g) was maintained at 400°C for 5 h in an evacuated Pyrex tube. The benzene-soluble portions of the product were extracted with benzene at 25°C in a Soxhlet apparatus, a process which took 2 weeks of continuous flux for complete extraction. After removal of the solvent, orange crystals (74 g) containing 66.9% selenium are formed (corresponding to an average composition of $Se_{3.9}S_{4.1}$). The product was dissolved in a mixture of benzene (2000 ml) and carbon disulphide (1200 ml). Fractionated crystallization was achieved by alternately removing part of the solvent under reduced pressure, cooling to 4°C for 20 h and isolating the crystalline products. The selenium content of the sixth fraction (solvent volume, 1200 ml) dropped below one selenium per ring, yield 6.2 g, analysis 19.6% Se. Fractionation of this product, as before but with benzene as solvent, gave as the fourth fraction (initial solvent volume, 660 ml; volume at fraction four, 300 ml) yellow needles (1.1 g), containing 26.5% Se (average composition $Se_{1.02}S_{6.98}$).

Spectra

IR spectra were recorded on a Perkin-Elmer 180 IR/FIR spectrometer. The IR sample comprised "S_7Se" (60 mg) and polythene (100 mg) pressed to a disc 25 mm in diameter, but only very poor quality spectra could be obtained even when the samples were cooled to 170 K. Raman spectra were recorded on a Spex 1403 spectrometer with He—Ne laser excitation and photon-counting electronics. A scattering geometry of 90° and a "line focus" was used as described elsewhere [13]. IR and Raman spectra were also measured at low temperatures using a closed-cycle helium device, the CTI

Cryocooler model 21. Mass spectra were kindly supplied by Dr. Krauss, Organic Chemistry Department, University of Heidelberg.

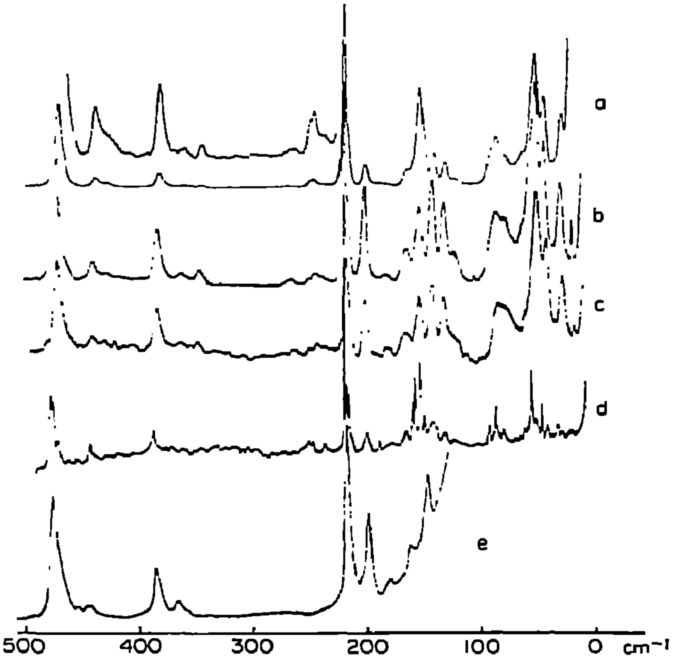
RESULTS AND DISCUSSION

Two samples of S_7Se: sample A, $S_{6.78}Se_{1.22}$, prepared by the method of ref. 9, and sample B, $S_{7.08}Se_{0.92}$, recrystallized from a mixture [6, 11], give very similar Raman spectra, see Figs.1a and 1b. The relative intensities in the 120—220 cm^{-1} region and the intensities of the symmetric SS and SeS stretches indicate varying degrees of S_8 contamination. Fig. 1c was recorded at a sample temperature of approximately 30 K. It is important to notice, that the line width of most of the bands does not decrease significantly on cooling. We conclude, therefore, that the Raman spectral line width of S_7Se is not determined by thermal motion but by orientational disorder. This conclusion is supported by Fig. 1d which represents the low-temperature spectrum of a 1:1 mixture of S_8 and sample A. The broad S_7Se bands are superimposed by the sharp and well resolved bands of the sulphur spectrum. The spectrum of S_7Se in a CS_2 solution, Fig. 1e, is added for completeness. Mass spectra, Fig. 2, of the samples prepared by the two different methods support the spectroscopic assumptions concerning the sample composition.

While for sample A, S_7Se^+ gives the most intense group of peaks, despite the expected higher volatility of S_8, for sample B, the S_8^+ peaks are the more intense. To compensate for the lower selenium concentration more $Se_3S_5^+$ is present in sample B than in sample A. The contamination by small amounts of S_6Se_2 is similar in samples A and B, although the Raman bands for the Se—Se stretch near 260 cm^{-1} [16—19] and for the non adjacent SeS stretch near 360 cm^{-1} [12, 17] indicate a lower proportion of SeSe bonds in sample B. The qualitative pattern of the intensities of fragment peaks is given by the following sequence (in decreasing order of intensities): $S_2 > S_4Se > S_3Se > S_4 > SSe > S_5 > S_5Se > S_6 > SeS_2 > S_7 > S > Se > S_6Se > S_9 + Se_2S_4 > S_{10} > SeS_8$.

Introduction of one selenium atom into an S_8 ring reduces the symmetry from D_{4d} to C_s. This is a very drastic lowering of symmetry, destroying all the symmetry elements except one of the mirror planes, σ_d. The way in which degeneracy is removed together with the selection rules for vibrational spectra predict 18 vibrational modes, both IR and Raman allowed. Table 1 gives the correlation between the molecular vibrations of D_{4d} and C_s symmetry along with the observed vibrational frequencies of the solid. Crystal-field splitting has been neglected, although with high resolution and at low temperatures some of the predicted splittings can be observed [20, 21] in the S_8 spectrum.

As can be seen from Table 1, most of the vibrational bands suffer a slight decrease in their frequencies on going from S_8 to S_7Se. The assignment of the observed vibrational bands for S_7Se was performed by inspection of the eigenvectors of a preliminary normal coordinate treatment and com-



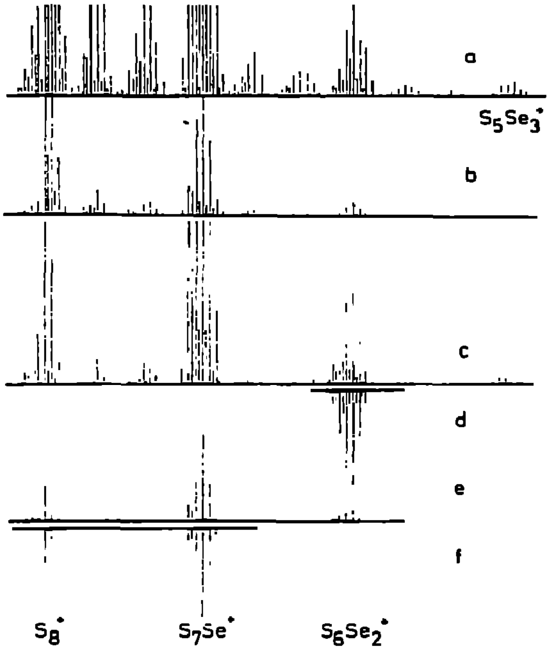


Fig. 1. Raman spectra of S_7Se: (a) prepared by recrystallization of a sulphur—selenium (15%) melt; (b), (c) samples prepared by the method of ref. 9; (d) mixture of S_7Se and α-S_8 (50% v/v); (e) saturated solution of S_7Se in CS_2. Spectra (a) and (b) were recorded at room-temperature, (c) and (d) at ~30 K; spectral slit width, 2 cm^{-1} for all spectra.

Fig. 2. Mass spectra of S_7Se: (a) and (b) prepared by recrystallization of a sulphur—selenium (15%) and sulphur—selenium (35%) melt, respectively; (c) and (e) prepared by the method of ref. 9; (d) and (f), calculated intensity distribution for naturally abundant isotopes. Spectra (a) and (c) have a ten-fold gain over (b) and (e).

TABLE 1

Correlation diagram for vibrational spectra of S_8 and S_7Se[a]

S_8 (Symmetry D_{4d})		S_7Se (Symmetry C_s)		
Raman or IR		Raman		IR
A_1	474, 218.5	A'	466.5, 215	
B_1	411	A''	348	
B_2	243	A'	243	230 s[b]
E_1	468, 187	A'	383, 137	385 w[b]
		A''	(458), 180.5	465 w, 180[b]
E_2	474, 152.5, 82.3	A'	471, 152, 73	
		A''	471, 127, 80	
E_3	440.5, 244	A'	440.5, 197.5	
		A''	423, 243	

[a] Values in cm^{-1}. [b] Strong and broad absorption from 100 to 300 cm^{-1}.

parison with the eigenvectors of S_8. Figure 3 illustrates the numbering of internal coordinates used here, while the internal valence coordinates are listed in Table 2.

The symmetry coordinates can be constructed from the U matrix, given in Table 3 for $^{32}S_8$ as an example. Redundant coordinates were removed by construction of zero motions [22] and subsequent orthogonalization of the U matrix. Rows 3, 5, 9, 12, 21 and 24 represent zero-motion coordinates.

Complete U and G matrices for $^{32}S_8$, $^{34}S_8$ and $^{32}S_7Se$ can be obtained from the author on request.

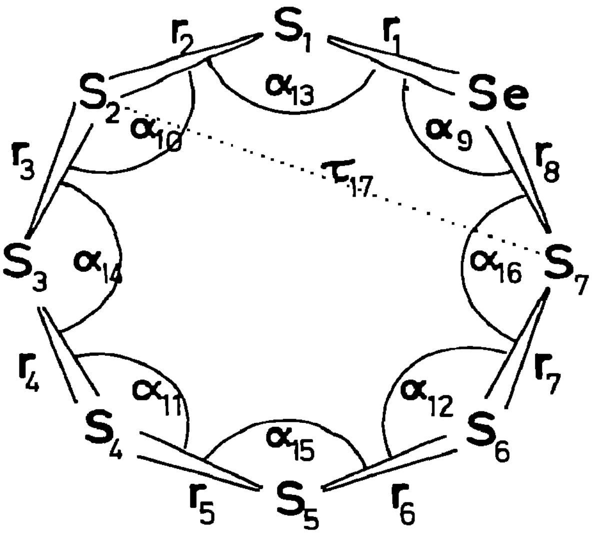


Fig. 3. Internal valence coordinates of S_7Se: R_1—R_8 = Δr_1—Δr_8, r_1 to r_8 stretch, R_9—R_{16} = $\Delta\alpha_9$—$\Delta\alpha_{16}$, α_9 to α_{16} angle deformation; R_{17}—R_{24} = $\Delta\tau_{17}$—$\Delta\tau_{24}$, torsional motions around r_1 to r_8.

TABLE 2

Internal valence coordinates for S_8 and S_7Se

S_8	S_7Se	S_8	S_7Se
$R_1 = \Delta r_1(S_1S_2)$	$R_1 = \Delta r_1$ (SeS)	$R_{13} = \Delta\alpha_5(S_1S_2S_3)$	$R_{13} = \Delta\gamma_1$
$R_2 = \Delta r_2(S_2S_3)$		$R_{14} = \Delta\alpha_6(S_3S_4S_5)$	
$R_3 = \Delta r_3(S_3S_4)$		$R_{15} = \Delta\alpha_7(S_5S_6S_7)$	
$R_4 = \Delta r_4(S_4S_5)$		$R_{16} = \Delta\alpha_8(S_7S_8S_1)$	$R_{16} = \Delta\gamma_2$
$R_5 = \Delta r_5(S_5S_6)$		$R_{17} = \Delta\tau_1(S_8S_1S_2S_3)$	$R_{17} = \Delta\tau_1{}^{\text{end}}$
$R_6 = \Delta r_6(S_6S_7)$		$R_{18} = \Delta\tau_2$	$R_{18} = \Delta\tau_2{}^{\text{centre}}$
$R_7 = \Delta r_7(S_7S_8)$		$R_{19} = \Delta\tau_3$	
$R_8 = \Delta r_8(S_8S_1)$	$R_8 = \Delta r_8$ (SeS)	$R_{20} = \Delta\tau_4$	
$R_9 = \Delta\alpha_1(S_8S_1S_2)$	$R_9 = \Delta\beta$	$R_{21} = \Delta\tau_5$	
$R_{10} = \Delta\alpha_2(S_2S_3S_4)$		$R_{22} = \Delta\tau_6$	
$R_{11} = \Delta\alpha_3(S_4S_5S_6)$		$R_{23} = \Delta\tau_7$	$R_{23} = \Delta\tau_7{}^{\text{end}}$
$R_{12} = \Delta\alpha_4(S_6S_7S_8)$		$R_{24} = \Delta\tau_8$	$R_{24} = \Delta\tau_8{}^{\text{centre}}$

TABLE 3

Non-zero U-matrix elements for S_8, D_{4d} symmetry[a]

1	1	0.354	1	2	0.354	1	3	0.354	1	4	0.354
1	5	0.354	1	6	0.354	1	7	0.354	1	8	0.354
2	9	0.222	2	10	0.222	2	11	0.222	2	12	0.222
2	13	0.222	2	14	0.222	2	15	0.222	2	16	0.222
2	17	−0.275	2	18	−0.275	2	19	−0.275	2	20	−0.275
2	21	−0.275	2	22	−0.275	2	23	−0.275	2	24	−0.275
3	9	0.275	3	10	0.275	3	11	0.275	3	12	0.275
3	13	0.275	3	14	0.275	3	15	0.275	3	16	0.275
3	17	0.222	3	18	0.222	3	19	0.222	3	20	0.222
3	21	0.222	3	22	0.222	3	23	0.222	3	24	0.222
4	1	0.310	4	2	−0.310	4	3	0.310	4	4	−0.310
4	5	0.310	4	6	−0.310	4	7	0.310	4	8	−0.310
4	17	0.170	4	18	−0.170	4	19	0.170	4	20	−0.170
4	21	0.170	4	22	−0.170	4	23	0.170	4	24	−0.170
5	1	0.170	5	2	−0.170	5	3	0.170	5	4	−0.170
5	5	0.170	5	6	−0.170	5	7	0.170	5	8	−0.170
5	17	−0.310	5	18	0.310	5	19	−0.310	5	20	0.310
5	21	−0.310	5	22	0.310	5	23	−0.310	5	24	0.310
6	9	0.354	6	10	0.354	6	11	0.354	6	12	0.354
6	13	−0.354	6	14	−0.354	6	15	−0.354	6	16	−0.354
7	1	0.323	7	2	0.134	7	3	−0.134	7	4	−0.323
7	5	−0.323	7	6	−0.134	7	7	0.134	7	8	0.323
7	9	−0.357	7	11	0.357	7	13	−0.253	7	14	0.253
7	15	0.253	7	16	−0.253	7	17	−0.005	7	18	−0.002
7	19	0.002	7	20	0.005	7	21	0.005	7	22	0.002
7	23	−0.002	7	24	−0.005						
8	1	0.119	8	2	0.049	8	3	−0.049	8	4	−0.119
8	5	−0.119	8	6	−0.049	8	7	0.049	8	8	0.119
8	9	0.133	8	11	−0.133	8	13	0.094	8	14	−0.094
8	15	−0.094	8	16	0.094	8	17	−0.429	8	18	−0.178
8	19	0.178	8	20	0.429	8	21	0.429	8	22	0.178
8	23	−0.178	8	24	−0.429						
9	1	0.308	9	2	0.128	9	3	−0.128	9	4	−0.308
9	5	−0.308	9	6	−0.128	9	7	0.128	9	8	0.308
9	9	0.324	9	11	−0.324	9	13	0.229	9	14	−0.229
9	15	−0.229	9	16	0.229	9	17	0.171	9	18	0.071
9	19	−0.071	9	20	−0.171	9	21	−0.171	9	22	−0.071
9	23	0.071	9	24	0.171						
10	1	0.134	10	2	0.323	10	3	0.323	10	4	0.134
10	5	−0.134	10	6	−0.323	10	7	−0.323	10	8	−0.134
10	10	−0.357	10	12	0.357	10	13	−0.253	10	14	−0.253
10	15	0.253	10	16	0.253	10	17	−0.002	10	18	−0.005
10	19	−0.005	10	20	−0.002	10	21	0.002	10	22	0.005
10	23	0.005	10	24	0.002						
11	1	0.049	11	2	0.119	11	3	0.119	11	4	0.049
11	5	−0.049	11	6	−0.119	11	7	−0.119	11	8	−0.049
11	10	0.133	11	12	−0.133	11	13	0.094	11	14	0.094
11	15	−0.094	11	16	−0.094	11	17	−0.178	11	18	−0.429
11	19	−0.429	11	20	−0.178	11	21	0.178	11	22	0.429
11	23	0.429	11	24	0.178						

TABLE 3 (continued)

12	1	0.128	12	2	0.308	12	3	0.308	12	4	0.128
12	5	−0.128	12	6	−0.308	12	7	−0.308	12	8	−0.128
12	10	0.324	12	12	−0.324	12	13	0.229	12	14	0.229
12	15	−0.229	12	16	−0.229	12	17	0.071	12	18	0.171
12	19	0.171	12	20	0.071	12	21	−0.071	12	22	−0.171
12	23	−0.171	12	24	−0.071						
13	1	0.354	13	2	−0.354	13	3	−0.354	13	4	0.354
13	5	0.354	13	6	−0.354	13	7	−0.354	13	8	0.354
14	9	0.500	14	10	−0.500	14	11	0.500	14	12	−0.500
15	17	−0.354	15	18	0.354	15	19	0.354	15	20	−0.354
15	21	−0.354	15	22	0.354	15	23	0.354	15	24	−0.354
16	1	0.354	16	2	0.354	16	3	−0.354	16	4	−0.354
16	5	0.354	16	6	0.354	16	7	−0.354	16	8	−0.354
17	13	0.500	17	14	−0.500	17	15	0.500	17	16	−0.500
18	17	−0.354	18	18	−0.354	18	19	0.354	18	20	0.354
18	21	−0.354	18	22	−0.354	18	23	0.354	18	24	0.354
19	1	0.191	19	2	−0.462	19	3	0.462	19	4	−0.191
19	5	−0.191	19	6	0.462	19	7	−0.462	19	8	0.191
20	9	0.356	20	11	−0.356	20	13	−0.252	20	14	0.252
20	15	0.252	20	16	−0.252	20	17	0.134	20	18	−0.324
20	19	0.324	20	20	−0.134	20	21	−0.134	20	22	0.324
20	23	−0.324	20	24	0.134						
21	9	0.351	21	11	−0.351	21	13	−0.248	21	14	0.248
21	15	0.248	21	16	−0.248	21	17	−0.136	21	18	0.329
21	19	−0.329	21	20	0.136	21	21	0.136	21	22	−0.329
21	23	0.329	21	24	−0.136						
22	1	−0.462	22	2	0.191	22	3	0.191	22	4	−0.462
22	5	0.462	22	6	−0.191	22	7	−0.191	22	8	0.462
23	10	0.356	23	12	−0.356	23	13	−0.252	23	14	−0.252
23	15	0.252	23	16	0.252	23	17	−0.324	23	18	0.134
23	19	0.134	23	20	−0.324	23	21	0.324	23	22	−0.134
23	23	−0.134	23	24	0.324						
24	10	0.351	24	12	−0.351	24	13	−0.248	24	14	−0.248
24	15	0.248	24	16	0.248	24	17	0.329	24	18	−0.136
24	19	−0.136	24	20	0.329	24	21	−0.329	24	22	0.136
24	23	0.136	24	24	−0.329						

[a] Rows 3, 5, 9, 12, 21 and 24 represent zero-motion coordinates.

An initial set of force constants for S_8 was taken from the force field of Scott et al. [23]. Several new interaction constants had to be included in order to achieve sufficient fit for both $^{34}S_8$ and $^{32}S_8$ frequencies. GVFF force-constant refinement was then performed using Schachtschneider's [25] FPERT program, for which 14 force constants were used to reproduce the 22 frequencies of the two isotopic molecules, within an average error of 0.5%. Ten new force constants were added in order to account for the substitution of one sulphur atom by selenium. Several runs were necessary to achieve a stable minimum for the refinement procedure. The final values of the force field are given in Table 4 and compared with those of Scott et al. [23] and

TABLE 4

Internal valence force field (mdyn·Å^{-1}) for S_7Se and related molecules

Force constant	S_8 + S_7Se[a]	S_8[b]	S_8[c]	S_xSe_{8-x}[d]	Se_8[e]
f_r(SS)	2.061	2.366	2.32	2.312	1.695
f_{rr}(SS,SS)	0.432	0.612	0.55	0.546	0.394
$f_{rr'}$(SS,SS)[f]	0.001	0.041	0.04	0.037	0.037
f_α(SSS)	0.223	0.234	0.23	0.242	0.166
$f_{\alpha\alpha}$	0.013	0.019	0.04	0.017	0.019
$f_{\alpha\alpha'}$[f]	0.0002	—	—	—	—
f_τ	0.030	0.040	0.03	0.034	0.030
$f_{\tau\tau}$	−0.010	—	—	—	—
$f_{r\alpha}$	0.070	0.192	0.19	0.158	0.138
$f_{r\alpha'}$[f]	0.056	0.031	—	0.029	0.028
$f_{r\tau}$	0.034	0.026	0.06	0.024	0.023[g]
$f_{r\tau'}$[f]	0.011	0.018	—	0.016	0.017
$f_{\alpha\tau}$	0.011	0.022	—	—	0.020[g]
$f_{\alpha\tau'}$[f]	−0.007	—	—	—	—
f_R(SeS)	1.850	—	—	2.030	—
f_{RR}(SeS,SeS)	0.391	—	—	0.487	—
f_{Rr}(SeS,SS)	0.302	—	—	0.533	—
f_β(SSeS)	0.207	—	—	0.182	—
f_γ(SeSS)	0.144	—	—	0.233	—
$f_{\tau_{\mathrm{Se,centre}}}$	0.036	—	—	0.032	—
$f_{\tau_{\mathrm{Se,edge}}}$	0.027	—	—	0.034	—
$f_{R\beta}$	0.008	—	—	0.158	—
$f_{\tau\tau_{\mathrm{Se,centre}}}$	−0.012	—	—	—	—
$f_{\gamma\gamma'}$	0.003	—	—	—	—

[a] This work. [b] Ref. 23. [c] Ref. 24. [d] Ref. 19. Calculated by transformation of the UBFF constants. [e] Ref. 26. [f] Next nearest neighbour interactions are denoted by primes. [g] Ref. 26 gives negative values, but they are produced by the alternating sense of rotation for the eight torsional coordinates.

Steudel and Mäusle [24] for S_8, those of Laitinen and Steudel [19] for S_7Se and those of Steudel for Se_8 [26]. Some of the literature data was converted from UBFF into GVFF constants using Schachtschneider's [25] UBZM program. Our final force field differs by more than 10% from those previously published in the principal stretching force constants and in some stretch—stretch and stretch—bend interactions. A comparison of the observed and calculated frequencies is given in Table 5. Raman intensity calculations performed by Domingo and Montero [21] slightly favour our force field as regards the quality of observed intensity reproduction. In spite of the changes in the stretching force constants and the minor changes in the bending constants, the new force field is better able to reproduce the bending motions than the previous force fields without a loss of accuracy in the stretching frequencies and intensities.

TABLE 5

Observed and calculated frequencies (cm^{-1}) for sulphur and S_7Se

S_7Se				$^{32}S_8$			$^{34}S_8$		
Species	Obs.	Calc.	Calc.[a]	Species	Obs.	Calc.	Species	Obs.	Calc.
A'	471	471.3	475	A_1	474	472.1	A_1	459	458.0
	467	470.9	473		218	217.4		212	210.9
	440.5	439.4	446						
	383	383.5	383	B_1	411	413.2	B_1	399.5	400.9
	243	244.6	246						
	215	218.8	215	B_2	243	246.1	B_2	239	238.8
	197.5	198.2	205						
	152	152.3	170	E_1	468	470.0	E_1	454	456.0
	137	134.2	136		187	187.5		181	181.9
	73	73.1	73						
A''	471	470.9	475	E_2	474	473.4	E_2	459	459.3
	465(IR)	458.1	463		152.5	154.0		149.5	149.4
	423	422.6	432		82.3	82.5		80.3	80.5
	348	347.7	339						
	243	238.9	241	E_3	440.5	438.2	E_3	426.5	425.1
	180.5	178.0	190		244	244.3		241	237.1
	127	127.6	153						
	80	80.1	83						

[a] Ref. 19.

It is interesting to compare the principal force constants of the ring molecules with those of sulphur—sulphur chains already reported (see Table 6). For the radical ion, S_2^-, and the diatomic sulphur molecule, extremely high stretching frequencies and force constants are found. With the exception of these two species, for which double-bond contribution can be assumed, the force constant of a sulphur—sulphur bond stretch is about 2.15 ± 0.1 mdyn Å^{-1}. For S_4^{2-} [29], S_8O [34] and S_7NH [35], the presence of two different force constants was attributed to the S—S bonds having slightly different bond lengths. It should be noted, that the introduction of the Se heteroatom

TABLE 6

S—S stretching frequencies and force constants

Compound	BaS_2	BaS_3	Na_2S_4	S_2^-	S_2	S_6	S_8	S_8O	S_7NH	S_7Se
S—S stretching frequency (cm^{-1}) (highest and lowest)	473	480 458	483 445	594	716	471 390	475 411	514 423	495 424	471 423
S—S stretching force constant (mdyn Å^{-1})	2.11	2.18	1.98 2.05	3.33	4.84	2.23	2.061	2.66 1.45	2.23 2.53	2.061
S—S bond length (Å)	2.126	2.076	2.061 2.075		1.89	2.057	2.048	2.003 2.202	2.048 2.062	—
Ref. (spectroscopic data)	27	28	29	30, 31	32	33	This work	34	35	This work

into the S_8 ring does not appear to change the properties of the adjacent S—S bonds significantly. There is only one primary S—S force constant necessary to reproduce the frequencies and only one set of EOPS for S—S bonds [36] required to reproduce the Raman intensities.

With the aid of this force field and additional data which we are deriving from NC—XYX—CN molecules, (X = S or Se, Y = S or Se), we shall be able to predict the frequencies and intensities of the spectra of the complete Se_xS_{8-x} series using Domingo and Montero's [21, 36] electrooptical parameters. By a deconvolution and superposition procedure of observed and calculated spectra we should be able to determine the abundance of particular species in the mixed-crystal system.

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