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Raman Spectra of the Tetraphosphorus Trichalcogenide Cage Molecules P_4S_2Se and P_4SSe_2

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Abstract

Mixtures of the four cage molecules $P_4S_xSe_{3-x}$· ($x = 0$, 1, 2, 3) were prepared from α-P_4S_3 and α-P_4Se_3. The Raman-active bands of the mixed chalcogenide molecules have been identified and used together with the results of a normal coordinate analysis to provide assignments for 14 of the 15 normal modes of vibration of P_4S_2Se and P_4SSe_2.

A decrease in wavenumber observed for the most intense Raman-active band of crystalline P_4SSe_2 with increasing concentration in the mixed solids is attributed to intermolecular Se–Se interactions weakening the intramolecular bonds.

Introduction

Tetraphosphorus trisulphide and tetraphosphorus triselenide are cage-like molecules with C_{3v} symmetry (see Fig. 1). Both occur in the solid state in a number of polymorphic forms which are summarised in Scheme 1. In particular, they have at least one low temperature normal crystalline phase, the α phase, and a high temperature plastically crystalline phase, the β phase. Melting these compounds together produces a mixture of the four separate cage molecules $P_4S_xSe_{3-x}$ ($x = 0, 1, 2, 3$) [1]. The presence of the four separate compounds was established by HPLC which showed that their relative amounts are governed mainly by statistical factors. However, the mixed chalcogenide cage molecules P_4S_2Se and P_4SSe_2 have not previously been isolated in sufficient quantities to enable their vibrational spectra to be recorded and assigned.

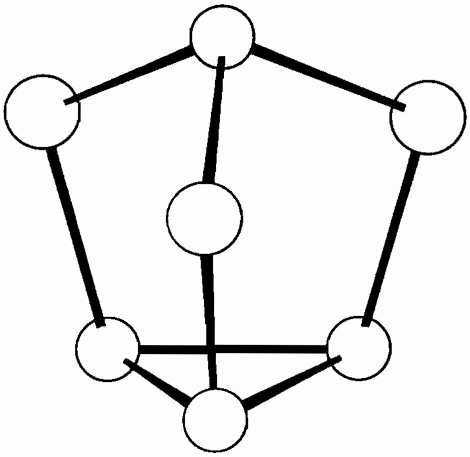

Fig. 1. The C_{3v} cage structure of the group V chalcogenides P_4S_3 and P_4Se_3.

	$\alpha \longrightarrow$	$\alpha' \xrightarrow{T_P}$	$\beta \longrightarrow$	$\gamma \xrightarrow{T_M}$
P_4S_3		314 K		445 K
P_4Se_3		356 K	479 K	522 K

Scheme 1. The polymorphic phase changes of P_4S_3 and P_4Se_3. α, Low temperature crystalline phase; α′, high temperature crystalline phase; β, low temperature plastically crystalline phase; γ, high temperature plastically crystalline phase; T_P, crystalline to plastically crystalline transition temperature; T_M, plastically crystalline to liquid transition temperature.

We have studied the Raman-active phonons of the molecules P_4S_2Se and P_4SSe_2 as mixed crystals containing varying concentrations of the four possible chalcogenide molecules. The phonons attributable to P_4S_2Se and P_4SSe_2 have been observed without isolating the pure compounds by obtaining crystals enriched in one of these two species and using spectral subtraction of the known Raman-active phonons of α-P_4S_3 and α-P_4Se_3 from the Raman spectra of the mixed crystals.

The molecules P_4S_2Se and P_4SSe_2 both belong to the C_s point group and are presumed to have the same D_{2h} space group as the parent C_{3v} cage molecules, α-P_4S_3 [2] and α-P_4Se_3 [3]. The 15 normal modes are both infrared and Raman active. They comprise 9 in-plane (A′) vibrations and 6 out-of-plane (A″) vibrations. Based on the α-P_4S_3 unit cell [4] a

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total of 60 Raman-active $k = 0$ phonons is expected for crystalline P_4S_2Se and P_4SSe_2.

Assignments for the normal modes of the mixed chalcogenide molecules have been made with the aid of a normal coordinate analysis of P_4S_3. The results of that analysis, based on a previously described [5] set of internal valence displacement coordinates, are also reported.

Experimental

A sample of α-P_4Se_3 was prepared from yellow phosphorus and selenium powder [6] and recrystallised from carbon disulphide. Commercial α-P_4S_3 (Fluka AG, pract.) was purified by recrystallisation from carbon disulphide under a nitrogen atmosphere.

Heating an equimolar mixture of α-P_4S_3 and α-P_4Se_3 in an evacuated glass ampoule at 520 K for 12 h produced an orange–yellow solid on cooling. The sample was analysed by HPLC. A 1.5% wt./vol. solution in carbon disulphide was eluted through a Waters Radial Pak C18 column using a 9:1 methanol/water mixture with a flow rate of 1 ml/min. The wavelength detector was set at 254 nm and four carbon disulphide soluble components were identified in the solid mixture.

Attempts to use column and thin layer chromatography with 9:1 methanol/water, carbon disulphide or toluene as solvents to separate the mixture were unsuccessful.

Crystals enriched in either P_4S_2Se (and containing a negligible amount of α-P_4Se_3) or P_4SSe_2 (and containing a negligible amount of α-P_4S_3) were prepared by melting α-P_4S_3 and α-P_4Se_3 in mole ratios of 5:1, 3:1, 1:3 and 1:5. For the 5:1 mixture the proportions based on a statistical distribution of the chalcogens would be 125:75:15:1 for P_4S_3:P_4S_2Se:P_4SSe_2:P_4Se_3

A vacuum sublimation of the finely ground solid 1:1 mixture in a temperature gradient furnace produced small (0.5 × 0.5 × 0.5 mm) crystals enriched in P_4S_3 and P_4S_2Se. The temperature at the hot end was held at 350 K, just below the crystalline to plastically crystalline phase change, T_P, of α-P_4Se_3 (see Scheme 1), while the other end was maintained at 300 K, a temperature just below the equivalent phase change for α-P_4S_3.

Raman spectra were recorded with a Spex Model 1401 double monochromator. The exciting line was the 647.1 nm line from a Spectra Physics Model 164-01 krypton ion laser using power levels of 50 mW at the sample. The scattered light was detected by an air-cooled Thorn EMI 9658 photomultiplier with instrumental slit widths of 150 μm. The wavenumber calibration was achieved using neon emission lines.

Results

The Raman spectra of the molecules P_4S_2Se and P_4SSe_2 are shown in Fig. 2. The spectrum of P_4S_2Se was obtained by subtracting the Raman spectrum of α-P_4S_3 from the Raman spectrum of crystals containing α-P_4S_3, P_4S_2Se and P_4SSe_2, grown by vacuum sublimation of the melt obtained from a 1:1 mole ratio of α-P_4S_3 and α-P_4Se_3. Only the strongest Raman-active band of P_4SSe_2, at 380 cm^{-1}, is apparent in the spectrum and the strongest Raman-active band of α-P_4Se_3, at 365 cm^{-1}, is absent. The Raman spectrum of P_4SSe_2 was derived by subtracting the Raman spectrum of α-P_4Se_3 from the Raman spectrum of the melt obtained from a 1:3 mole ratio of α-P_4S_3 and α-P_4Se_3. Previous studies of the thermal stability of P_4Se_3 [7] would suggest that some P_4Se_4 should result from the peritectoidal decomposition of the P_4Se_3 dominant melt for temperatures above 450 K. However, there is no sign of any Raman-active phonons attributable to P_4Se_4 and in particular the strongly Raman-active phonon at 186 cm^{-1} [8] is absent.

The wavenumber of the strongly Raman-active band of P_4SSe_2 at 380 cm^{-1} is observed to increase as the concentration of P_4SSe_2 in the host crystal decreases. There is an increase of 3 cm^{-1} in going from the 1:5 to the 5:1 mole ratio of α-P_4S_3 to α-P_4Se_3. A smaller but discernable shift is also observed for the band at 345 cm^{-1}. This effect appears

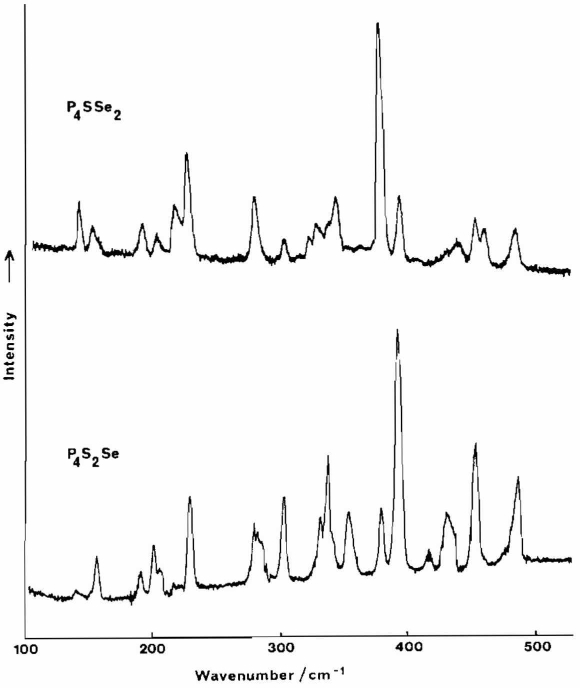

Fig. 2. The Raman spectra of P_4S_2Se and P_4SSe_2 measured under ambient conditions.

to be due to intermolecular Se–Se interactions weakening the intramolecular bonding and causing a softening of selenium based normal modes. A similar effect has already been observed with α-P_4Se_3 where selenium based normal modes harden when α-P_4Se_3 is doped into a α-P_4S_3 crystal [9]. Because of this effect increasing the wavenumbers of bands of both α-P_4Se_3 and P_4SSe_2 in the mixtures, the subtraction of the α-P_4Se_3 spectrum from the spectra of the mixtures was not perfect and there is some remaining intensity at 365, 215 and 135 cm^{-1} attributable to α-P_4Se_3.

In Table 1 we have correlated the fundamental modes of vibration of the molecules P_4S_2Se and P_4SSe_2 with those of the parent molecules α-P_4S_3 and α-P_4Se_3 using the results of a normal coordinate analysis of α-P_4S_3. The unassigned modes for P_4S_2Se and P_4SSe_2 correspond to the E mode of α-P_4S_3 at 440 cm^{-1}.

To perform the normal coordinate analysis we have used a set of internal valence displacement coordinates and symmetry adapted coordinates described previously [5]. The feature of the coordinate set used was the explicit recognition of the intramolecular chalcogen–chalcogen bond. The final *F* matrix and the eigenvector matrix elements for the A_1 and E modes of α-P_4S_3 are given in Table 2. Estimates of the more important off-diagonal terms in the *F* matrix were obtained by cyclically constraining diagonal force constants. The calculated wavenumbers for α-P_4S_3, the mixed species P_4S_2Se and P_4SSe_2 and for α-P_4Se_3 are shown in Table 3. It can be seen that the force field for the A_1 and E species of α-P_4S_3 provides reasonable estimates for the A′ and A″ wavenumbers of the mixed species, P_4S_2Se and P_4SSe_2.

TABLE 1. The assignments (cm^{-1}) of the fundamental modes of vibration of P_4S_3, P_4S_2Se, P_4SSe_2 and P_4Se_3

	P_4S_3	P_4S_2Se	P_4SSe_2	P_4Se_3
A_1	488	486	485	485
	446	395	380	361
	424	356	345	330
	284	228	216	213
A_2	185	158	154	154
E	457	455 432	460 430	405
	440	417	408	365
	343	337 330	327 320	323
	291	305 284	281 226	274
	225	202,206 193	191 142	135

TABLE 2. The final *F* matrix elements and the *L* matrix elements for the A_1 and E modes of α-P_4S_3

Final *F* matrix elements (10^2 Nm^{-1})

A_1 symmetry species

2.64	0	0	−0.84
	1.62	0	0
		1.32	0
			1.15

E symmetry species

2.64	0	0	1.84	−1.89
	1.65	0	0	0
		2.05	0	1.06
			2.23	−1.98
				3.87

L matrix elements for P_4S_3

A_1 symmetry species

−0.040	0.217	−0.057	−0.037
0.169	−0.058	−0.162	−0.074
−0.262	−0.089	−0.141	−0.020
0.026	0.197	−0.191	0.134

E symmetry species

0.162	−0.063	−0.139	−0.134	−0.033
−0.160	−0.185	−0.009	−0.051	0.030
0.080	−0.128	0.150	0.015	−0.054
0.025	−0.010	0.009	0.170	0.131
0.041	−0.048	−0.174	0.089	0.029

TABLE 3. The observed and calculated wavenumbers for the normal modes of the molecules $P_4S_{3-x}Se_x$ (x = 0, 1, 2, 3) based on the symmetry coordinates defined in ref. 5

	Observed	Calculated		Observed	Calculated
P_4S_3	488	492.7	P_4Se_3	485	479
	446	437.8		361	362
	424	413.9		330	326
	284	266.3		213	219
	458	460.7		405	426
	441	435.6		365	370
	344	342.6		323	324
	292	295.7		274	249
	227	188.9		135	143
P_4S_2Se	486	486	P_4SSe_2	485	482
	395	413		380	388
	356	386		345	354
	228	259		216	246
	455 432	449		460 430	437
	417	427		408	419
	337 330	337		327 320	333
	305 284	280		281 226	261
	202,206 193	179		191 142	164

A description of the A_1 normal modes for α-P_4S_3 is relatively straightforward. Q_1 is a symmetric stretch of the basal P–P bonds. A major component of Q_2 is a symmetric stretch of the apical P–S bonds. Q_3 involves the basal P–S bonds, the basal P–P bonds and the chalcogen–chalcogen S...S intramolecular bond and can be described as a deformation of the base of the molecule. Q_4 is relatively well defined as a change in the S–S intramolecular distance.

The normal modes of E symmetry show strong coupling of symmetry coordinates. The main components of Q_6 are the apical P–S and basal P–S stretch coordinates. Q_7 involves a deformation of the base of the molecule, mainly the basal P–S stretch. Q_8 is a combination of several symmetry coordinates, while Q_9 and Q_{10} may be described as involving a significant change in the chalcogen–chalcogen intramolecular bond.

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