Resonance-Raman and Infrared Spectra of the Dimeric Iron–Chalcogenide Complexes $[Fe_2X_2(YR)_4]^{2-}$ (X and Y = S or Se)

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Resonance-Raman spectra are reported for the dimeric iron-chalcogenide complexes $[Fe_2X_2(SR)_4]^{2-}$ [X = S or Se; $(SR)_2 = (SCH_2)_2C_6H_4$-*o* or R = Ph, C_6H_4Me-*p*, or C_6H_4Cl-*p*], $[Fe_2X_2(SePh)_4]^{2-}$ (X = S or Se), $[Fe_2X_2Cl_4]^{2-}$ (X = S or Se), and $[Fe_2S_2Br_4]^{2-}$ down to 100 cm^{-1} or lower using a range of laser excitation wavelengths. Complementary i.r. spectra are also reported. Assignment of iron–chalcogenide stretching modes and some deformation modes is attempted. Iron–sulphur bridge-stretching vibrations are found to be affected little by the nature of the terminal ligands with the Raman-active symmetric mode assigned in the range 375—396 cm^{-1} and the two i.r. asymmetric modes in the ranges 415—420 and 274—328 cm^{-1}. Their frequency shifts on going to selenium bridging are helpful in making these assignments. Frequencies for the totally-symmetric terminal-ligand stretch and its i.r. counterpart are observed to be much higher (381—429 cm^{-1}) for the aromatic thiolates than for the $(SCH_2)_2C_6H_4$-*o* or chloride ligands (321—334 cm^{-1}). The symmetric in-plane ring deformations are assigned in the range 178—256 cm^{-1} for sulphur bridging and show a correlation with crystallographically determined Fe–Fe bond lengths. Electronic spectra of $[Fe_2S_2(SC_6H_4Y\text{-}p)_4]^{2-}$ (Y = H or Cl) in the visible region are deconvoluted into Gaussian bands. Component bands at *ca.* 550—560 nm compare favourably in position and width with crude Raman excitation profiles for intense polarised solution peaks attributable to Fe–(terminal ligand-) vibrations. Comparison of the Raman spectra is made with those previously reported for 2Fe-ferredoxins.

Complexes of the type $[Fe(SR)_4]^-$, $[Fe_2S_2(SR)_4]^{2-}$, and $[Fe_4S_4(SR)_4]^{2-}$,[1] like the iron–sulphur proteins which they model, show intense S→Fe charge-transfer absorption throughout the visible and near-u.v. spectral regions which should selectively promote resonance enhancement of Raman transitions involving Fe–S vibrations. Since the frequencies and intensities of bands in resonance-Raman (r.R.) spectra are highly sensitive to geometric and bonding arrangements amongst the vibrating atoms, comparisons between spectra of inorganic iron–sulphur complexes and of the corresponding proteins could lead to the identification of fine structural differences.

However, despite the potential utility of the r.R. technique in this application, and the availability of suitable model complexes for almost a decade, it is not until quite recently that spectra of adequate quality for detailed analysis have been obtained.[2] As has been pointed out,[2] this slow development has resulted largely from the acute instability of the iron–sulphur complexes under intense irradiation and from their poor r.R. enhancements relative to their large molar extinctions. Improvements in instrumentation and sampling techniques now, however, make possible the recording of spectra with good resolution and high signal to noise ratio. The interpretation of such spectra for the symmetrized analogue inorganic complexes proves to be a vital starting point in reaching a detailed understanding of the spectra for the proteins.[2] In this context we report here r.R. spectra together with complementary i.r. measurements for several $[Fe_2S_2(SR)_4]^{2-}$ [$(SR)_2 = (SCH_2)_2C_6H_4$-*o* or R = Ph, C_6H_4Me-*p*, or C_6H_4Cl-*p*] complexes and their selenide-bridged homologues, for the complexes $[Fe_2X_2(SePh)_4]^{2-}$ (X = S or Se), and for $[Fe_2X_2Cl_4]^{2-}$ (X = S or Se) and $[Fe_2S_2Br_4]^{2-}$. The selenium and halide dimers have been studied primarily with the purpose of aiding the accurate assignment of the $[Fe_2S_2(SR)_4]^{2-}$ ferredoxin analogues.

Experimental

The iron–sulphur complexes were prepared according to published methods: $[NEt_4]_2[Fe_2X_2(SR)_4]$ [X = S or Se; $(SR)_2 = (SCH_2)_2C_6H_4$-*o*,[3,4] R = Ph, C_6H_4Me-*p*, or C_6H_4Cl-*p*[3,5]], $[NEt_4]_2[Fe_2X_2(SePh)_4]$ (X = S or Se),[6] $[NEt_4]_2[Fe_2S_2Y_4]$ (Y = Cl or Br),[7] and $[NEt_4]_2[Fe_2Se_2Cl_4]$ in a similar way to the sulphur-bridged homologue. Samples were handled under a dinitrogen atmosphere.

Resonance-Raman spectra were obtained using a Spex Ramalog V instrument having a cooled RCA gallium–arsenide photomultiplier and DPC-2 photon counter. A CRL-52 krypton-ion laser was employed for excitation and scattered light was collected at 90° to the incident beam. Plasma emission lines from the laser (marked with a P in the Figures) and the spectrum of CCl_4 were used to calibrate the frequency scale of the monochromators; quoted frequencies are accurate to ± 1 cm^{-1} for sharp lines. Solid samples were diluted with KBr or KCl and pressed under vacuum at 10 tonne (*ca.* 10^5 N) into 13-mm diameter discs. These were mounted on a Spex sample rotator and spun at high speed in a dinitrogen atmosphere. Triple monochromation was employed for these samples, enabling the collection of data to within 50 cm^{-1} of the laser line in some instances. Solution samples of 1—2 cm^3 were contained in 2-cm diameter cylindrical quartz cells sealed at the top with a rubber septum. These were mounted vertically on the Spex sample rotator such that the incident laser beam just grazed the inner surface of the cell. Obscuring bands occur in the region of interest for all the solvents employed: acetone (391, 492, and 530 cm^{-1}), acetonitrile (380 cm^{-1}), and dimethyl sulphoxide (307, 334, and 384 cm^{-1}). Intense scattering was found only for bands attributable to totally-symmetric terminal-ligand stretching modes and as a consequence of the poor signal to noise ratio for the other peaks only limited polarisation data can be reported.

Samples for i.r. measurements were diluted in spectroscopic

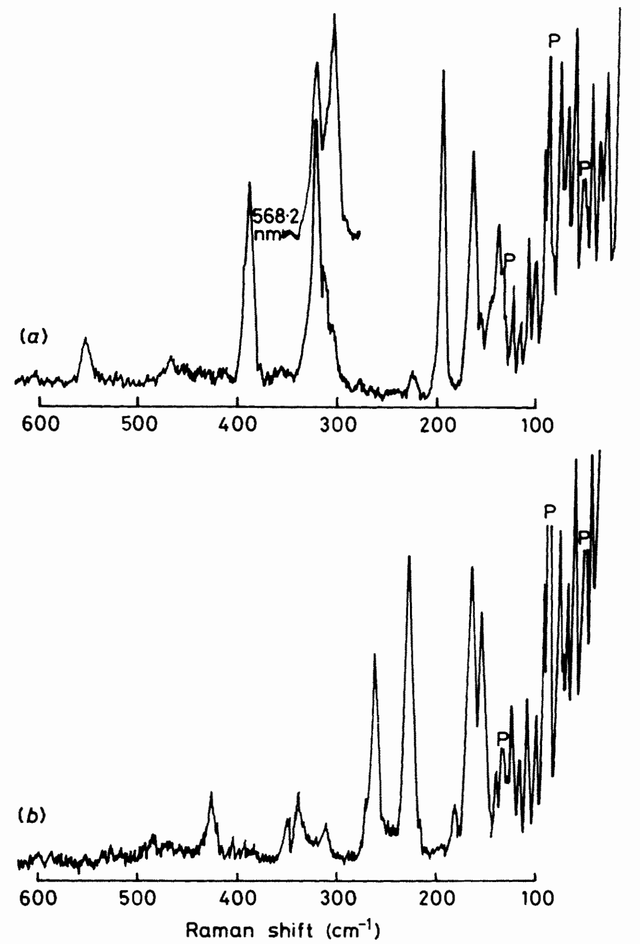

Figure 1. Resonance-Raman spectra of $[NEt_4]_2[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ in KBr: (a) X = S; (b) X = Se. λ_{ex} = 530.9 nm (ca. 140 mW); spectral resolution = 3 cm^{-1}. Inset of (a): λ_{ex} = 568.2 nm (160 mW); spectral resolution = 4 cm^{-1}. Laser plasma emission lines are truncated and marked with a P

polyethylene (Merck 7422) and compressed at 10 tonne under vacuum to give 13-mm diameter discs of ca. 0.1-mm thickness. The i.r. spectra were recorded using Perkin-Elmer 597 and 683 spectrometers.

Electronic absorption spectra were obtained using a Perkin-Elmer 551 spectrophotometer.

Results

Description of Spectra and Vibrational Assignments.—The tentative assignments of r.R. and i.r. bands in the Tables are made for a bridged dimeric molecule, M_2X_6, of point group D_{2h} and are labelled according to a numbering scheme (ν_1—ν_{18})[8,9] originally used by Bell and Longuet-Higgins[10] to describe the vibrations of diborane and aluminium halides. The description of the modes according to symmetry species depends in detail upon the assumption that the x axis lies along the metal–metal vector and the y axis along the line joining the two bridging atoms. In idealized D_{2h} symmetry, nine of the modes are Raman active $[4A_g(\nu_1—\nu_4) + 2B_{1g}(\nu_6$ and $\nu_7) + 2B_{2g}(\nu_{11}$ and $\nu_{12}) + B_{3g}(\nu_{15})]$; eight are i.r. active $[3B_{1u}(\nu_8—\nu_{10}) + 2B_{2u}(\nu_{13}$ and $\nu_{14}) + 3B_{3u}(\nu_{16}—\nu_{18})]$; one is inactive $[A_u(\nu_5)]$. X-Ray structural details are available for five complexes containing $[2Fe\text{–}2S]^{2+}$ cores and in each case there is a crystallographically imposed centre of symmetry.[1] However, since all the Fe–S bands are to be accommodated in a frequency interval of only ca. 400 cm^{-1}, strict adherence to the mutual exclusion of r.R. and i.r. bands is hardly to be expected in the observed spectra; indeed, accidental coincidences or near-coincidences may be anticipated for vibrational modes of similar type.

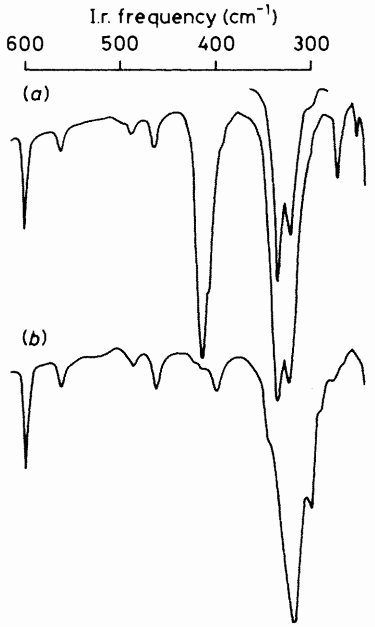

Figure 2. Infrared spectra of $[NEt_4]_2[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ in polyethylene: (a) X = S (inset spectrum shows the double peak for higher dilution); (b) X = Se

$[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ (X = S or Se). Figure 1 shows solid-state r.R. spectra for $[NEt_4]_2[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ (X = S or Se) measured in the range ca. 40—600 cm^{-1} using exciting light of wavelength (λ_{ex}) 530.9 nm. These spectra have been selected from a large number of scans to have maximum resolution (3 cm^{-1}) rather than optimum signal to noise ratio. The frequencies of the observed bands and their intensities for four excitation wavelengths (λ_{ex} = 482.5, 530.9, 568.2, or 647.1 nm) are collected in Table 1. Also reported here are data for the complexes in solution and i.r. absorption bands for the energy region 250—600 cm^{-1} corresponding to the spectra in Figure 2.

Spiro et al.[2] have previously reported a r.R. spectrum of $[NEt_4]_2[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ down to 200 cm^{-1} at a single λ_{ex} of 488.0 nm which has peak positions in substantial agreement with those given in Table 1(a), and we come to broadly the same conclusions on the assignment of these bands and those in the i.r. spectrum. The Fe_2S_2 ring-breathing mode, ν_2, is assigned to the intense r.R. band at 388 cm^{-1} which is absent in the selenium-bridged dimer. The antisymmetric ring stretches ν_{13} and ν_{17} at 415 and 274 cm^{-1} respectively in the i.r. spectrum are also lost on selenium substitution and a new medium strength absorption arises at 302 cm^{-1} assignable to ν_{13}. In the Raman spectrum of $[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ there is a new intense line at 261 cm^{-1} with a polarised solution counterpart at 259 cm^{-1} which we assign to ν_2. This gives a ratio of 0.67 for $\nu_2(Se)/\nu_2(S)$ which is close to that of 0.64[11] for $\nu_2(Br)/\nu_2(Cl)$ in the dimeric gallium halides, where there are comparable atomic weights for the bridging atoms. An alternative assignment for ν_2 is to the comparably intense band at 228 cm^{-1} [$\nu_2(Se)/\nu_2(S)$ = 0.59]. The value of 0.73 for $\nu_{13}(Br)/\nu_{13}(Cl)$ in the gallium halides[11] is the same as that for $\nu_{13}(Se)/\nu_{13}(S)$ in the present complexes assuming the assignments of

Table 1. Resonance-Raman and i.r. data [a] for $[NEt_4]_2[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ (X = S or Se)

(*a*) $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$

Assignment	r.R. band maxima [b]	Intensity [c] *versus* λ_{ex}/nm 482.5	530.9	568.2	647.1	Bands in solution [b,d]	I.r. band maxima [b]	Assignment
	139	P	15	15	25		274m	ν_{17}
ν_3	165	15	25	15	10	160	325vs	ν_{16}
ν_4	196	25	35	60	40	198 (pol)	337vs	ν_8
	224	3	3	P	P		415vs	ν_{13}
	304	w (sh)	w (sh)	50	10	304 (0.3)	464mw	L
ν_6	312 (sh)	w	w	w	w		488w	L
ν_1	321	50	25	40	70	327 (0.35)	~500w,br	L
ν_{11}	348	3	w	w	2		562w	L
ν_2	388	10	20	45	100		600m	L
	415	2						

Other r.R. bands at 28, 35, 44, 52, 60, 67, 75, 83, 91, 100, 108, 116, 124 (all w to m,n); 145w (sh); 278w; 470w,br; 548mw

(*b*) $[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$

Assignment	r.R. band maxima [b]	Intensity [c] *versus* λ_{ex}/nm 482.5	530.9	568.2	647.1	Bands in solution [b,d]	I.r. band maxima [b]	Assignment
ν_4, ν_3	155	6 (sh)	25	40	50	~150 (sh)	~278vw	
	165	12	30	20 (sh)	30	~160 (sh)	~290vw (sh)	
	183		4	3	w		302m	ν_{13}
	228	25	30	20	10	228 (pol)	320vs	ν_8, ν_{16}
ν_2	261	20	20	15	100	259 (0.3)	~345w (sh)	
	311	3	3	3		299 (pol)	400w	
	319	6			8	320	464w	L
ν_1?	339	9	5	6	13		488w	L
ν_{11}?	349	9	3	3	w (sh)		525vw,br	L
	426		5	3	20	427	562w	L
							600m	L

Other r.R. bands at 44, 60, 67, 75, 91, 100, 108, 117, 124, 140 (all w to m,n); 520w

[a] w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad, n = narrow and d = double; L = ligand or cation band; ? = possible assignment. [b] Frequencies of band maxima are in cm^{-1}. [c] Relative intensities for the different λ_{ex} were calculated with reference to the totally symmetric NO_3^- stretch of KNO_3 (1 050 cm^{-1}) incorporated in the sample and are on an arbitrary scale of 0—100. Bands obscured for any λ_{ex} by a plasma emission line are indicated by a P. [d] Depolarisation ratios, or an indication that the band is polarised, are in parentheses.

Table 1. The remaining cluster stretching mode, ν_6, has been suggested by Spiro *et al.*[2] to lie at *ca.* 316—318 cm^{-1} in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ from comparison with $[Fe_2S_2Y_4]^{2-}$ (Y = Cl or Br), although they resolved no band at this frequency. In the high-resolution r.R. spectrum of Figure 1(*a*) a weak band is just resolved at *ca.* 312 cm^{-1} and is a reasonable assignment for the B_{1g} bridge mode.

The terminal stretching modes active in the Raman (ν_1 and ν_{11}) and i.r. (ν_{16} and ν_8) are assigned for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ in the same way as by Spiro *et al.*[2] The band at 321 cm^{-1} due to ν_1 has a polarised solution counterpart at 327 cm^{-1}. Given no drastic structural changes on selenium substitution, this group of vibrations should remain in the same frequency region, so ν_8 and ν_{16} are assigned to the strong asymmetrically shaped absorption at 320 cm^{-1} in the i.r. spectrum of $[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. In the r.R. spectra of this complex, only weakly-enhanced lines are found in the range 300—350 cm^{-1}. Because of the poor resolution of the four bands quoted at 311, 319, 339, and 349 cm^{-1} in Table 1(*b*) and their interplay of relative intensities as λ_{ex} varies, the Raman shifts represent a summary for spectra obtained using different Kr^+ laser lines. It is difficult to make any assignment as to which peaks originate from ν_1 and ν_{11} but those at 339 and 349 cm^{-1} respectively are chosen as they are the most intense; the other features may then result from ν_8 and ν_{16} made active by loss of centrosymmetry in the cluster.

The strong band at 196 cm^{-1} (polarised in solution) in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ is assigned to ν_4, the symmetric in-plane ring deformation. This frequency would imply a medium degree of Fe–Fe interaction, in keeping with the bond length of 2.698 Å.[1] In $[Fe_2(CO)_6(S_2)]$, with a shorter bond length (2.55 Å), a Raman band at 191 [12] or 195 cm^{-1} [13] has been described as principally ν(Fe–Fe). Other iron–iron stretching frequencies in dimers fall in the region 190—280 cm^{-1} depending on the degree of bonding interaction.[14-17] Lower frequencies are observed where there are no bridging atoms [14] or where no metal–metal interaction exists (*e.g.* in Fe_2Cl_6, ν_4 = 108 cm^{-1} [18]). In the selenium-bridged homologue the band at 196 cm^{-1} is absent but new features of comparable intensity are found at 155 and 165 cm^{-1} either of which could be ν_4.

We tentatively assign ν_3, which amongst the deformation modes is expected to be highest in frequency and intensity, to the band at 165 cm^{-1} in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ and at 155 or 165 cm^{-1} in $[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. Of the remaining unassigned bands reported in Table 1 many of the narrow r.R. lines at low energy are assumed to result from lattice modes. The r.R. band of $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ at 304 cm^{-1} only has appreciable intensity for λ_{ex} = 568.2 nm and is possibly a combination band (*e.g.* 139 + 165 cm^{-1}) for which resonance enhancement is very dependent upon the complex interplay of contributions from the large number of overlapping charge-transfer bands in the electronic absorption spectrum.

$[Fe_2X_2(YPh)_4]^{2-}$ (X *and* Y = S *or* Se). Resonance-Raman and i.r. frequencies, together with suggested vibrational assignments, are given for this group of complexes in Table 2 and correspond to the spectra of Figures 3 and 4. The major

Table 2. Resonance-Raman and i.r. data [a] for $[NEt_4]_2[Fe_2X_2(YPh)_4]$ (X and Y = S or Se)

Assignment	r.R. band maxima [b]	Intensity [c] *versus* λ_{ex}/nm				Bands in solution [b,d]	I.r. band maxima [b]	Assignment
		482.5	530.9	568.2	647.1			
(*a*) $[Fe_2S_2(SPh)_4]^{2-}$								
ν_3	160	3	4	3	2		275vw	
	201	1	1	1			305vw (sh)	
	244 (sh)	w	w	w		240 (sh)	315s	ν_{17}
ν_4	256	10	8	9	10	253 (0.3)	356vs,d	ν_8
ν_6	320	1	w	1	3	317	~405w	
ν_{11}	351	8	3	3		354 (pol)	420s	ν_{13}
ν_2	387	4	2	3	8		429m	ν_{16}
	406	1	1	w			478s	L
ν_1	428	10	10	10	8	430 (0.3)		
L	478	1	P	1				
	510	1	w	1				
(*b*) $[Fe_2Se_2(SPh)_4]^{2-}$								
ν_3	140	P	P	2	3		260m	ν_{17}
ν_4	202	10	10	8	10	206	313ms	ν_{13}
ν_2	235	2	3	2	P		359s	ν_8
	255	1	1	1	1	~250	366m (sh)	
ν_6?	284	1	2	2	3	282 (pol)	~400w,br	
	314	w	w	1	2	314	428m	ν_{16}
ν_{11}	363	3	2	1	1		477ms	L
	410	1	w (sh)	w (sh)	w (sh)			
ν_1	428	7	10	10	10	429 (0.3)		
L	475	w	P	1				
(*c*) $[Fe_2S_2(SePh)_4]^{2-}$								
	109	2	1	1	1		273m	ν_8?
ν_3	123	8	6	10	2		307w	ν_{16}?
	180br	1	1	1	w	~180 (sh)	328s	ν_{17}
	214	4	8	P	6	~220	408vw (sh)	
ν_4	242	10	9	5	5	~243 (pol)	416s	ν_{13}
ν_{11}	272	10	8	P	5	~272	465s	L
ν_1	306	8	10	10	10	310 (0.3)		
ν_2	383	6	2	1	2			
Other r.R. bands at ~150w (sh), ~320w (sh), 386w,br (sh), and 504w,br								
(*d*) $[Fe_2Se_2(SePh)_4]^{2-}$								
ν_4	187	10	10	10	10	188	274s	ν_8?
ν_2	217	3	6	P	8	217 (pol)	306mw	ν_{16}?
ν_{11}	276br	w	1	1		274	320m	ν_{13}
	298 (sh)	1	1	w	1	300 (sh)	332w	
ν_1	309	3	6	10	9	309 (0.35)	400mw,br	
							465s	L
Other r.R. bands at 258w,br, ~380w,br, and ~400w,br								

[a,b] See footnotes to Table 1. [c] Relative intensities are on an arbitrary scale of 0—10. Bands obscured for any λ_{ex} by a plasma emission line are indicated by a P. [d] See footnote to Table 1.

difference in the assignments from those for $[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ (X = S or Se) is with respect to the modes ν_1 and ν_{16}. Intense bands of totally symmetric origin at 428 cm^{-1} in the PhS-ligated dimers are assigned to ν_1; these shift to 306 cm^{-1} in $[Fe_2S_2(SePh)_4]^{2-}$ and to 309 cm^{-1} in $[Fe_2Se_2(SePh)_4]^{2-}$. The similar i.r. mode, ν_{16}, is thought to give rise to absorption at 429 cm^{-1} in $[Fe_2S_2(SPh)_4]^{2-}$ and 428 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$. An absorption at 356 cm^{-1} for $[Fe_2S_2(SPh)_4]^{2-}$ correlates with a similar feature in $[Fe_2Se_2(SPh)_4]^{2-}$ and these are tentatively assigned as ν_8. The related Raman mode ν_{11} can then be matched with the relatively intense bands at 351 and 363 cm^{-1} respectively for these sulphur- and selenium-bridged complexes. Such assignments are close to those made for the $(SCH_2)_2C_6H_4$-*o*-ligated complexes. For the PhSe-ligated dimers, ν_{11} is considered to shift to 272 and 276 cm^{-1} respectively for sulphur and selenium bridging; similarly ν_8 in the i.r. shifts to 273 and 274 cm^{-1} respectively. The ν_{16} modes for these complexes could then be assigned close to the comparable ν_1 frequencies, at 307 and 306 cm^{-1}; the bands at these frequencies are, however, not very intense.

The designations $\nu_1 > \nu_{11}$ and $\nu_{16} > \nu_8$ are at variance with vibrational analyses for other M_2X_6 bridged structures.[8] This arises mainly from the assignments of ν_1 which are considered reasonable on the basis of the high intensities and the polarisation of the bands. For the series of tetramer complexes $[Fe_4X_4(YPh)_4]^{2-}$ (X and Y = S or Se) the corresponding totally-symmetric terminal-ligand breathing modes are found at 434 (X = Y = S), 431 (X = Se and Y = S), 309 (X = S and Y = Se) and 311 cm^{-1} (X = Y = Se) (unpublished work of present authors). These frequencies correlate very well with those of the corresponding dimers. With the exception of $[Fe_4S_4(SePh)_4]^{2-}$, the symmetric terminal-ligand breathing

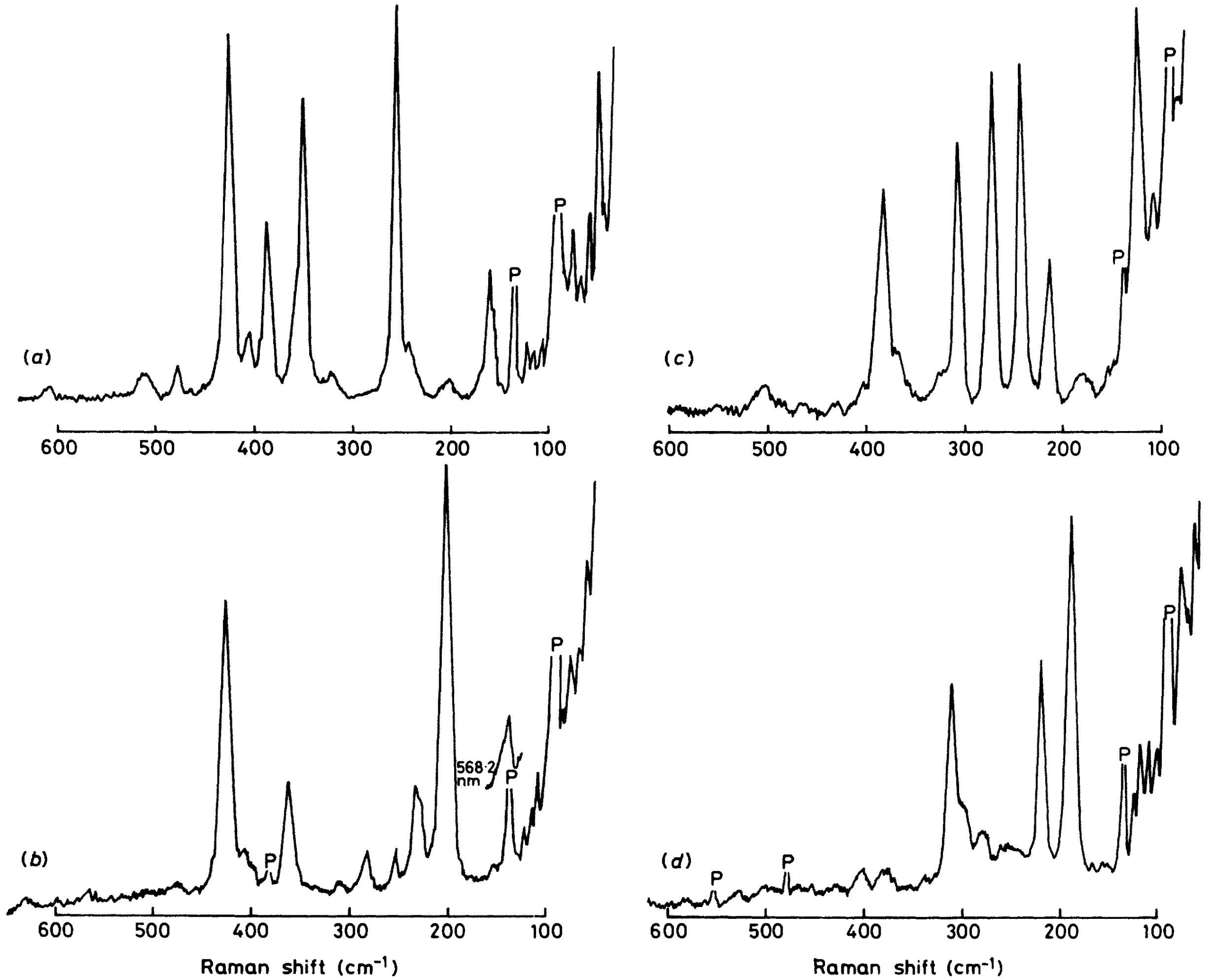

Figure 3. Resonance-Raman spectra of $[NEt_4]_2[Fe_2X_2(YPh)_4]$ in KBr: (*a*) X = Y = S (λ_{ex} = 482.5 nm, laser power = 50 mW, spectral resolution = 3 cm^{-1}); (*b*) X = Se, Y = S (482.5 nm, 50 mW, 5 cm^{-1}); (*c*) X = S, Y = Se (482.5 nm, 50 mW, 5 cm^{-1}); (*d*) X = Y = Se (530.9 nm, 80 mW, 4 cm^{-1})

mode is the highest frequency in the Fe–S stretching region of the 4Fe-clusters. We do not, however, rule out the reversal of our assignments for the pairs of terminal-ligand modes in the dimers.

The symmetric bridge stretch in $[Fe_2S_2(SPh)_4]^{2-}$ is assigned at 387 cm^{-1}, a frequency very close to that for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$, in keeping with the likely similarity of their $[2Fe\text{-}2S]^{2+}$ core dimensions.[1] In $[Fe_2Se_2(SPh)_4]^{2-}$, ν_2 is considered to be shifted to 235 cm^{-1} [$\nu_2(Se)/\nu_2(S)$ = 0.61]; the band at 255 cm^{-1} [$\nu_2(Se)/\nu_2(S)$ = 0.66] is an alternative possibility, but is of rather low intensity. The frequencies of 383 and 217 cm^{-1} for the sulphur-bridged and selenium-bridged PhSe-ligated dimers follow from these. The i.r.-active bridge stretches, ν_{13} and ν_{17}, are assigned to absorptions at 420 and 315 and at 416 and 328 cm^{-1} respectively in $[Fe_2S_2(YPh)_4]^{2-}$ (Y = S or Se) shifted to 313 (ν_{13}) and 260 cm^{-1} (ν_{17}) in $[Fe_2Se_2(SPh)_4]^{2-}$ and to 320 cm^{-1} (ν_{13}) in $[Fe_2Se_2(SePh)_4]^{2-}$.

The remaining intense r.R. band of totally-symmetric origin observed in $[Fe_2S_2(SPh)_4]^{2-}$ at 256 cm^{-1} is thought to be ν_4, shifted considerably to 202 cm^{-1} in $[Fe_2Se_2(SPh)_4]^{2-}$ but less so to 242 cm^{-1} in $[Fe_2S_2(SePh)_4]^{2-}$. For the weak Fe–Fe bonding anticipated in these complexes, 256 cm^{-1} is an unusually high frequency for the ring deformation, some 60 cm^{-1} higher than in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. As judged by the Fe–Fe distance available for $[Fe_2S_2(SC_6H_4Me\text{-}p)_4]^{2-}$ the metallic bonding may well be slightly stronger in the complexes co-ordinated by aromatic thiolates, but ν_4 could only arise at such a large Raman shift by, for example, mixing with some higher frequency vibration.

Tentative assignments of ν_3 and ν_6 for some of the complexes are made in Table 2 which are in keeping with those suggested for the $(SCH_2)_2C_6H_4\text{-}o$-ligated dimers.

$[Fe_2X_2(SC_6H_4Me\text{-}p)_4]^{2-}$ (X = S *or* Se) *and* $[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$. The reasoning behind the assignment of bands for these complexes (Table 3, illustrative spectra in Figures 5 and 6) follows similar lines to those used in the previous section and will not be treated in detail. For each of the three complexes there is a superfluity of observed bands, particularly in the i.r., and ambiguous or conflicting assignments have been resolved to fit as far as possible with those for $[Fe_2X_2(SPh)_4]^{2-}$ (X = S or Se) in Table 2. The interpretation is pre-eminently problematical for spectra of $[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$, and the assignments given are necessarily speculative in view of the redundancy of intense bands. Incorporation of chlorine in the ligand considerably changes the positions and intensities of the Fe–S fundamental modes.

$[Fe_2X_2Cl_4]^{2-}$ (X = S *or* Se) *and* $[Fe_2S_2Br_4]^{2-}$. The vibrational assignments for the chloride-ligated dimers (Table 4) are related to those for $(SCH_2)_2C_6H_4\text{-}o$ terminal ligation (Table 1). Spiro *et al.*[2] have already reported r.R. spectra for $[Fe_2S_2$-

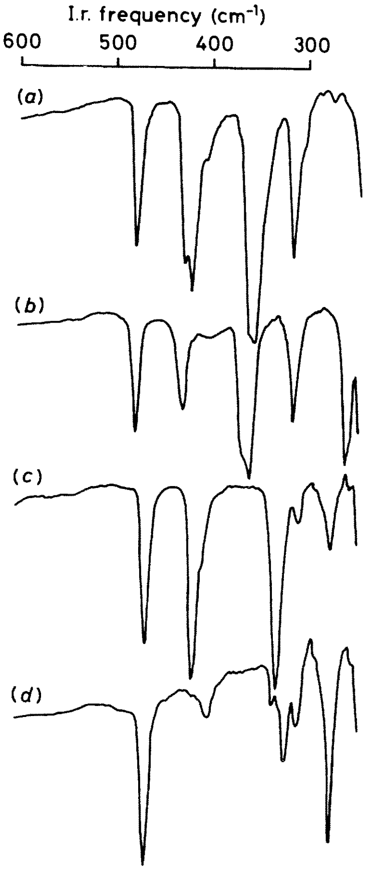

Figure 4. Infrared spectra of $[NEt_4]_2[Fe_2X_2(YPh)_4]$ in polyethylene: (*a*) X = Y = S; (*b*) X = Se, Y = S; (*c*) X = S, Y = Se; (*d*) X = Y = Se

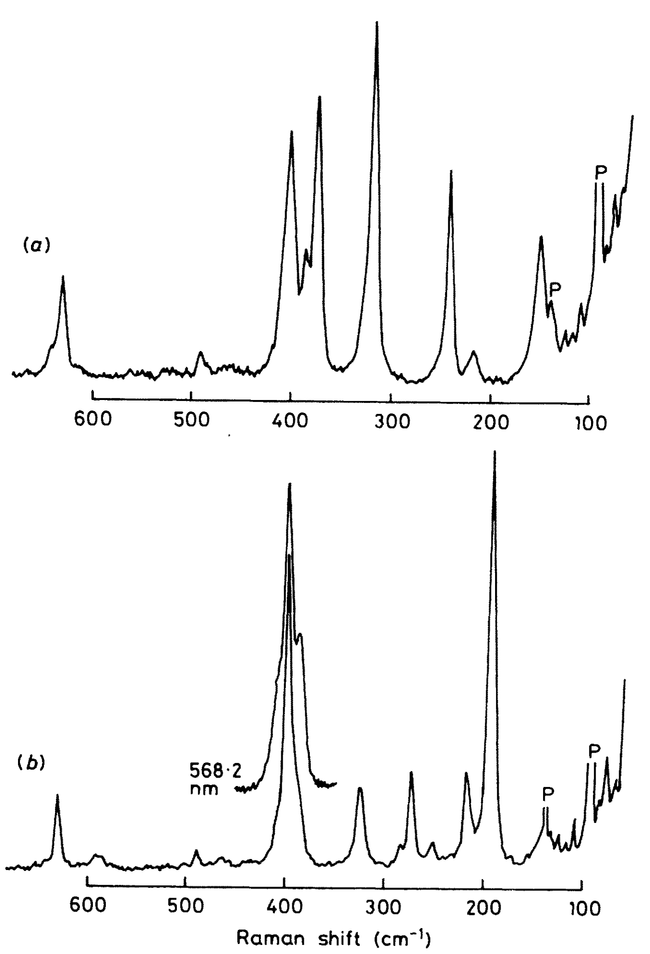

Figure 5. Resonance-Raman spectra of $[NEt_4]_2[Fe_2X_2(SC_6H_4Me\text{-}p)_4]$ in KBr: (*a*) X = S (spectral resolution = 5 cm⁻¹); (*b*) X = Se (3 cm⁻¹). λ_{ex} = 482.5 nm (50 mW). Inset of (*b*): λ_{ex} = 568.2 nm (100 mW)

$Y_4]^{2-}$ (Y = Cl or Br) down to 200 cm⁻¹ with λ_{ex} = 454.5 nm and we agree with their assignments, although finding slightly shifted frequencies for some bands. Our observations extend to lower frequencies and for $[Fe_2S_2Cl_4]^{2-}$ we find two further intense transitions at 178 and 144 cm⁻¹ which we suggest have their origins in the ν_4 and ν_3 fundamentals respectively. Additionally we assign a weak band at 357 cm⁻¹, best observed using λ_{ex} = 530.9 nm, to ν_{11}, in keeping with the analysis for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. The Raman spectra of each of the three complexes are dominated by a band assigned to ν_2, and for $[Fe_2Se_2Cl_4]^{2-}$ and $[Fe_2S_2Br_4]^{2-}$ the remaining weak features are difficult to interpret accurately.

Resonance enhancement. The dependence upon λ_{ex} of the relative intensities (normalised with respect to a KNO_3 internal standard) for the Raman bands of $[NEt_4]_2[Fe_2X_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]$ (X = S or Se) (Table 1) clearly implicates resonance enhancement in the solid-state spectra. The largest peak in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ (388 cm⁻¹ at λ_{ex} = 647.1 nm) is, however, only *ca.* 40 times more intense than the symmetric nitrate stretch, after taking into account differences in surface concentrations. Reflectance spectra of the iron–sulphur dimers diluted in MgO show numerous broad overlapping features throughout the visible region and extending well into the near-i.r.

Allowing for concentration differences, the bands assigned as ν_1 for $[Fe_2X_2(YPh)_4]^{2-}$ (X and Y = S or Se) in acetone solution range, at full resonance, are some 1 300—1 600 times more intense than the symmetric stretch at 787 cm⁻¹ of the solvent (details of the electronic absorption spectra for these and other $[2Fe\text{-}2S]^{2+}$ complexes may be found in references 3, 5, and 6). In Figure 7(*a*) the relative intensities (normalised with respect to the solvent peak at 787 cm⁻¹) of the ν_1 band at 430 cm⁻¹ for $[Fe_2S_2(SPh)_4]^{2-}$ in acetone are plotted against the corresponding wavelengths of the eight emission lines available on a Kr^+ laser. This Raman excitation profile for ν_1 is compared in Figure 7(*a*) with the electronic absorption spectrum of the complex in the same solvent. It is just discernible from the experimental electronic spectrum that there are two or more underlying bands contributing to the envelope of absorption centred around 500 nm. In the spectra of the selenium-substituted complexes this becomes much more pronounced. For the region 400—800 nm the spectrum may be deconvoluted (least-squares fit) into three bands of Gaussian shape centred at 449, 553, and 707 nm, as shown in Figure 7(*a*). The broad feature at low energy included in this analysis is necessary to account for the broad tailing-off into the near-i.r. characteristic of all the iron–chalcogenide complexes. The position of this band is not very reliable as it shows a strong interaction with the width in the iterative fitting procedure; this has, however, very little effect on the parameters for the other two Gaussian bands. A comparable fit to the experimental spectrum may be obtained using only two Lorentzian bands centred at 471 and 551 nm and having very similar widths to their Gaussian counterparts in Figure 7(*a*). However, in the $[2Fe\text{-}2S]^{2+}$ ferredoxins a broad feature is

Table 3. Resonance Raman and i.r. data [a] for $[NEt_4]_2[Fe_2X_2(SC_6H_4Me\text{-}p)_4]$ (X = S or Se) and $[NEt_4]_2[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]$

Assignment	r.R. band maxima [a]	Intensity [c] *versus* λ_{ex}/nm				Bands in solution [b,d]	I.r. band maxima [b]	Assignment
		482.5	530.9	568.2	647.1			
(*a*) $[Fe_2S_2(SC_6H_4Me\text{-}p)_4]^{2-}$								
ν_3	149	4	6	4	1		~300vw,br	
	216	w	2	1	P		325m (sh)	ν_{17}
ν_4	240	6	8	10	10	238 (pol)	333s	ν_8
ν_6, ν_{11}	319	10	10	7	3	323 (0.3)	379w (sh)	
ν_2	375	8	8	7	9		383mw	
L	385	w	3	6	8	384 (sh)	398s	ν_{16}
ν_1	401	7	9	9	4		416ms	ν_{13}
L	490	w	1	1	1		490s	L
(*b*) $[Fe_2Se_2(SC_6H_4Me\text{-}p)_4]^{2-}$								
ν_4	192	10	10	8	10		305ms	
ν_2	217	2	3	P	1		318ms	ν_{13}
	251	w	1	1	1		332m	ν_8
ν_6?	272	2	1	P	4		384vw (sh)	
ν_{11}	324	2	2	1	2		397ms 402ms	ν_{16}?
L	387 (sh)	w	3	5	5			
ν_1	397	8	8	10	7		490s	L
Other r.R. bands are at 283w, 490w and 590w								
(*c*) $[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$								
ν_3	137	P	P	1	2		274w	
	201	2	2	1	1		293ms	ν_{17}?
	221	3	2	2	1	~220 (sh)	323ms	ν_8?
	295	9	6	5	4	286 (0.3)	345mw	L
ν_6?	320	2	1	1	1	320	384s	ν_{16}
ν_{11}?	342	10	10	10	10	342 (0.36)	409w (sh)	
ν_2?	368	8	7	7	6	~370 (sh)	418ms	ν_{13}
ν_1?	381	4	4	1	1		450vw,br	
	401	4	3	3	1		490s	L
	542	3	3	3	3		526w	
							543s	L

[a,b] See footnotes to Table 1. [c] See footnote to Table 2. [d] See footnote to Table 1.

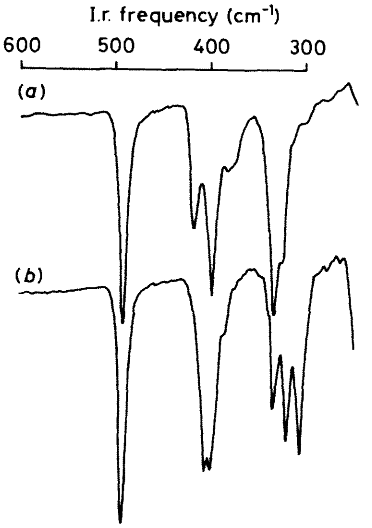

Figure 6. Infrared spectra of $[NEt_4]_2[Fe_2X_2(SC_6H_4Me\text{-}p)_4]$ in polyethylene: (*a*) X = S; (*b*) X = Se

resolved at *ca.* 700 nm.[19,20] Between 400 and 800 nm three bands are resolved for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ [3] and $[Fe_2S_2(SEt)_4]^{2-}$,[21] four are observed for $[Fe_2S_2(btpo)_2]^{2-}$ [btpo = 2,2′-bis(thiophenolate)] [6] whilst for the proteins there are four or more.[19,20,22,23] Undoubtedly superior fits to the spectrum of $[Fe_2S_2(SPh)_4]^{2-}$ could be obtained by employing more components, but the simulation of Figure 7(*a*) is considered adequate to reveal the positions of the main underlying features. Allowing reasonable analytical and experimental uncertainties in the positions and widths of the deconvoluted band at *ca.* 550 nm and of the ν_1 excitation profile there exists quite a good correlation between the two. Thus, the absorption in this part of the visible spectrum probably arises from charge transfer involving the PhS–Fe bonds. A similar analysis for $[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$ in acetone is presented in Figure 7(*b*) involving an excitation profile for the r.R. band at 342 cm⁻¹ tentatively assigned as ν_{11}. Visible absorption Gaussian components are deconvoluted at 454, 558, and 701 nm and the middle one of these again agrees quite well in position and width with the Raman excitation profile.

Discussion

Table 5 lists by order of mode the vibrational assignments made for the twelve dimer complexes studied. Although the small spread in Fe–S frequencies and the likely extensive mixing of internal co-ordinate types for most modes makes their accurate assignment difficult, there is a fair degree of correlation amongst several of the assigned frequencies for the different compounds when comparing Fe–X vibrations for a given X-atom type. A correlation of ν_4 with Fe–Fe distance is observed for the three complexes for which dimensional structure information is available. As the Fe–Fe

Table 4. Resonance-Raman and i.r. data[a] for $[NEt_4]_2[Fe_2X_2Cl_4]$ (X = S or Se) and $[NEt_4]_2[Fe_2S_2Br_4]$

Assignment	r.R. band maxima[b]	Intensity[c] *versus* λ_{ex}/nm			I.r. band maxima[b]	Assignment
		482.5	530.9	568.2		
(*a*) $[Fe_2S_2Cl_4]^{2-}$						
ν_3	144	4	5	2	286ms	ν_{17}
ν_4	178	4	5	1	326w (sh)	
	220	w	1	P	334s	ν_{16}
ν_6	310	2		3	345vs	ν_8
ν_1	333	5	6	1	416s	ν_{13}
ν_{11}	357	w	1			
ν_2	396	10	10	10		
	574	1	2	1		
(*b*) $[Fe_2Se_2Cl_4]^{2-}$						
ν_2	245	10	10	10	~290mw,br	ν_{13}
ν_6?	274	1	w	P	320s	ν_{16}
	337	1	w (sh)	w (sh)	342s	ν_8
	348	1	1	1	405w	
	396	1	1	1	416w	
	406	1	w	w (sh)		
	435	1	w	w		
	492	2	2	w		
Other r.R. bands at 168w, 182w, and ~538w,br						
(*c*) $[Fe_2S_2Br_4]^{2-}$						
ν_3?	122	3	10	10	263ms	ν_8?
	133	P	P	5	327ms	ν_{17}?
ν_1?, ν_{11}?	259br	1	w	w	340w (sh)	
	272	1	4	P	418ms	ν_{13}
ν_6	314	1	1	3	~510w,vbr	
ν_2	391	10	9	8		
	~410br	w (sh)	1	w (sh)		
	~530br	1	1	2		

[a,b] See footnotes to Table 1. [c] See footnote to Table 2.

separation increases from 2.691 Å in $[Fe_2S_2(SC_6H_4Me\text{-}p)_4]^{2-}$, through 2.698 Å in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$, to 2.716 Å in $[Fe_2S_2Cl_4]^{2-}$ the frequency assigned to ν_4 decreases from 240 cm^{-1}, through 196 cm^{-1}, to 178 cm^{-1}. Although this probably does reflect the decreasing bonding interaction to some extent, other factors are also likely to be involved in determining these frequencies, as stated earlier.

The bands observed in adrenal and spinach $[2Fe\text{-}2S]^{2+}$ ferredoxin Raman spectra [2,24-26] compare well in position, but not always in intensity, with corresponding features for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. The assignments of ν_1 and ν_2 at 321 and 388 cm^{-1} respectively for the latter ion correlate with bands at *ca.* 328 and 390–395 cm^{-1} in the proteins. For the analogue complexes having terminal arenethiolate ligands we assign $\nu_1 > \nu_2$ and thus the alkanethiolate-chelated compound seems better to model the protein, in keeping with the cysteine co-ordination of the latter. In this respect it would be of interest to obtain Raman and i.r. data for the complex $[Fe_2S_2(SEt)_4]^{2-}$, the synthesis of which has only recently been described.[21]

The most anomalous feature of the protein spectra is an intense peak at *ca.* 284—290 cm^{-1}. Spiro *et al.*[2] have assigned this as ν_{17}, implying gross loss of centrosymmetry. These authors have reported a corresponding feature in $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ at 279 cm^{-1} having about half the intensity of the ν_2 peak for λ_{ex} = 488.0 nm. We, however, found only very weak Raman scattering around this frequency for λ_{ex} ranging from 482.5 to 647.1 nm [Figure 1(*a*) and Table 1(*a*)], in keeping with the crystallographically-imposed centre of symmetry.[3] In addition to ν_{17}, the ν_{11} bands for the $[2Fe\text{-}2S]^{2+}$ ferredoxins,[2] in particular adrenodoxin, are also of anomalous intensity relative to those for $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$. We have assigned ν_{11} to prominent bands for the complexes ligated by arenethiolates, most notably to the strong band at 319 cm^{-1} in $[Fe_2S_2(SC_6H_4Me\text{-}p)_4]^{2-}$. It would be of interest to obtain r.R. spectra for the proteins at longer excitation wavelengths than have been ubiquitously employed in the past,[2,24-26] since their electronic spectra demonstrate overlapping bands extending out to the low-energy edge of the visible region.[19,20,22,23] Certainly we have observed fairly wide changes in relative intensities amongst the r.R. bands given by a single complex on varying λ_{ex}.

The only selenium-substituted ferredoxin for which Raman data have been reported is adrenodoxin; [24] two bands were observed, at *ca.* 350 and at 263 cm^{-1}. Tang *et al.*[24] considered that the latter band was shifted from 297 cm^{-1} in the native protein and tentatively identified on the band at 350 cm^{-1} a shoulder as the shifted position of the ν_2 vibration. For $[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ ν_2 has been assigned at 261 cm^{-1} [Table 1(*b*)] and we favour the same assignment for the comparable peak at 263 cm^{-1} in selena-adrenodoxin, with the broad band at *ca.* 350 cm^{-1} being accounted for by ν_1 and ν_{11}, unshifted from their positions in native adrenodoxin. Shifts of similar magnitude on going from sulphur to selenium bridging have been found for the other complexes described in this work.

Blum, Adar and co-workers [25,26] have measured Raman spectra for spinach and adrenal ferredoxins out to 3 000 cm^{-1} and have assigned peaks distributed over this range as arising from transitions within the manifold of spin states resulting from the antiferromagnetic exchange coupling of the irons. For $[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$ and $[Fe_2S_2Cl_4]^{2-}$, magnetic

Table 5. Correlation of vibrational assignments *

Compound	ν_1	ν_2	ν_3	ν_4	ν_6	ν_8	ν_{11}	ν_{13}	ν_{16}	ν_{17}
$[Fe_2S_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$	321	388	165	196	312	337	348	415	325	274
$[Fe_2S_2Cl_4]^{2-}$	333	396	144	178	310	345	357	416	334	286
$[Fe_2S_2(SPh)_4]^{2-}$	428	387	160	256	320	356	351	420	429	315
$[Fe_2S_2(SC_6H_4Me\text{-}p)_4]^{2-}$	401	375	149	240	319	333	319	416	398	325
$[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$	381 ?	368 ?	137	—	320 ?	323 ?	342 ?	418	384	293 ?
$[Fe_2Se_2\{(SCH_2)_2C_6H_4\text{-}o\}_2]^{2-}$	339 ?	261	155 ↔	165	—	320	349 ?	302	320	—
$[Fe_2Se_2Cl_4]^{2-}$	—	245	—	—	274 ?	342	—	290	320	—
$[Fe_2Se_2(SPh)_4]^{2-}$	428	235	140	202	284 ?	359	363	313	428	260
$[Fe_2Se_2(SC_6H_4Me\text{-}p)_4]^{2-}$	397	217	—	192	272 ?	332	324	318	~400	—
$[Fe_2S_2(SePh)_4]^{2-}$	306	383	123	242	—	273 ?	272	416	307 ?	328
$[Fe_2S_2Br_4]^{2-}$	259 ?	391	122 ?	—	314	263 ?	272 ?	418	—	327 ?
$[Fe_2Se_2(SePh)_4]^{2-}$	309	217	—	187	—	274 ?	276	320	306 ?	—

* A double-headed arrow indicates interchangeable assignments; ? = possible assignment.

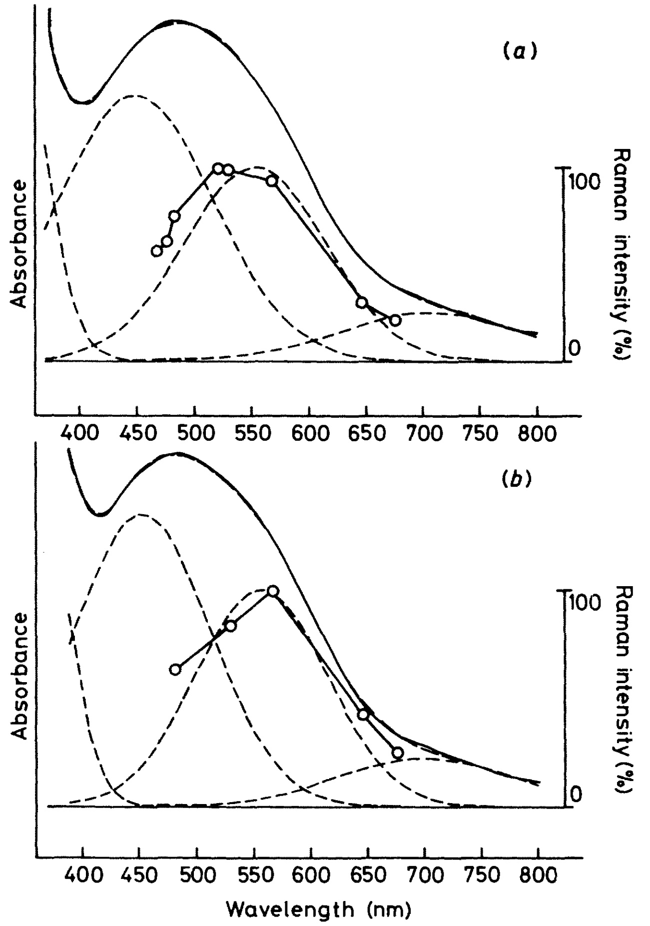

Figure 7. Electronic absorption spectra and excitation profiles for (*a*) $[Fe_2S_2(SPh)_4]^{2-}$ and (*b*) $[Fe_2S_2(SC_6H_4Cl\text{-}p)_4]^{2-}$ in acetone solution: (———) experimental absorption spectrum; (- - - -) component Gaussian bands; (– – –) sum of Gaussian components; and (—○—) relative intensities of the Raman bands at (*a*) 430 and (*b*) 342 cm^{-1} normalised relative to the solvent peak at 787 cm^{-1}

measurements have demonstrated antiferromagnetic behaviour involving exchange interactions having $-J = 149 \pm 8$ and 158 cm^{-1} respectively.[27,7] We have made Raman measurements out to *ca.* 1 700 cm^{-1} for these complexes but have been unable to find any convincing correlation between the bands observed and the expected spin-flip transitions corresponding to these *J* values. It is difficult in seeking such a correlation to eliminate bands originating from vibrations extraneous to the $Fe_2S_2X_4$ moiety. Similar circumspection is probably appropriate in judging the validity of the spin-flip Raman assignments made for the proteins,[25,26] especially in view of the lower signal to noise ratio in their spectra.

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