

## Vibrational spectra of the charge transfer complexes between organic sulfides and iodine

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**Abstract**—I.r. spectra of the charge transfer complexes between nine organic sulfides (as well as diethylselenide) with iodine were recorded between 1500 and 400  $\text{cm}^{-1}$  in  $\text{CS}_2$  and  $\text{CCl}_4$  solutions and in the region 600–50  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{H}_6$  solutions. Raman spectra of the complexes were recorded below 600  $\text{cm}^{-1}$ . For each system, i.r. and Raman bands in the 200–160  $\text{cm}^{-1}$  were assigned to the I–I stretching mode of the complex. Additional i.r. bands below 160  $\text{cm}^{-1}$ , absent in Raman, were ascribed to intermolecular S··I stretching vibrations. The integral intensities of these bands were determined and correlated with the thermodynamic functions. Some Raman active fundamentals of 1,4-dithiane became i.r. active in the iodine complex in accordance with a break down of the  $C_{2h}$  symmetry. A force constant calculation was carried out for the dimethylsulfide–iodine complex and simplified calculations of the three point mass models were made for all the systems.

### INTRODUCTION

Nearly three decades ago, it was first reported that the chlorine [1], iodine [2] and bromine [3] stretching vibrations became i.r. active upon complex formation. Moreover, the i.r. active stretching modes of I–Cl and I–Br were enhanced and displaced in the complexes [3, 4]. With great efforts, certain Raman spectra of the halogens in various basic solvents were observed, using the weak rubidium or helium sources for excitation [5]. When lasers became available for excitation, Raman spectra of the halogen complexes with  $n$ - and  $\pi$ -donors could easily be observed [6] e.g. with helium–neon or krypton lasers.

Later, a large number of spectral studies have been concerned with far i.r. spectra of charge transfer complexes between halogens or interhalogens and  $\pi$ - and  $n$ -donors in the solid state or in solution. The wave numbers, displacements and intensities of the halogen stretching vibrations have been correlated with donor basicity, formation constants and enthalpy of formation of the complexes [7]. While the earlier far i.r. studies were concerned with halogen complexes of benzene [1, 8], the more recent work has predominantly dealt with the stronger  $n$ -donors. Among these, the pyridine systems with  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{ICl}$  and  $\text{IBr}$  have been studied by LAKE and THOMPSON [9], WOOD *et al.* [10] and by YARWOOD *et al.* [11]. Recently, a series of papers on substituted pyridines with bromine and iodine have been published by MAES and ZEEGERS-HUYSKENS employing Raman [12] and far i.r. [13] spectroscopy.

The organic sulfides represent another group of  $n$ -donors which form strong complexes with the halogens. The charge transfer complexes between iodine and alkylsulfides have been studied by u.v. and visible spectroscopy in solution [14–16], in the vapor phase [17] and under pressure [18]. Solution data are also reported for 1,4-dithiane, 1,4-thioxane [19] and dimethylselenide [20]. X-ray crystallographic investigations

have revealed linear S(Se)–I–I arrangements of the donor–acceptor bond in 1,4-dithiane and 1,4-diselenane [21] believed to be the case for all the sulfide–iodine systems.

Far i.r. studies of diethylsulfide [22], certain alkyl and arylsulfides [23] and three cyclic sulfides [24] with iodine have been reported. These investigations were partly done in solution [22, 24], partly in polyethylene matrices [23]. Some of these results were quite surprising since YAMADA *et al.* [24] assigned the intermolecular S–I stretching modes to bands at higher wave numbers than the I–I stretches for three cyclic sulfides. This conclusion was in conflict with those for the alkyl and arylsulfides [22, 24] and the pyridine–iodine systems [9–13], for which the I–I stretch is constantly at higher wave numbers than the S(N)–I stretch.

Since the sulfide–iodine complexes have been thoroughly investigated by u.v. and visible spectroscopy and by X-ray crystallography, we decided to study the vibrational spectra of these systems. Primarily, we wanted to investigate the far i.r. spectra (600–50  $\text{cm}^{-1}$ ) quantitatively in solution. For this purpose we used an evacuable fast scan Fourier transform spectrometer in which the solvent, window and donor absorption could be effectively subtracted. Secondly, Raman spectra of the sulfide–iodine complexes were recorded in the same region. It is well known that the perturbed I–I stretch of the complex appears in Raman whereas the intermolecular S–I mode apparently is too weak to be observed [6, 13]. Finally, we wanted to investigate eventual perturbations of the sulfide spectra in the mid i.r. region upon complex formation to iodine.

### EXPERIMENTAL

#### Chemicals

The sulfides were commercial products from the following suppliers: Koch Light, K & K Laboratories, Fluka and

Aldrich. Pentamethylenesulfide, 1,4-thioxane and 1,4-dithiane had been purified for previous spectral studies in this laboratory and were still of high purity. Dibenzylsulfide and dibenzyldisulfide were recrystallized from benzene. Gas chromatographic analyses revealed that diethylsulfide, trimethylenesulfide, tetramethylenesulfide and diethylselenide had better than 99% purity and they were employed without purification. Iodine, as well as the solvents, carbon tetrachloride, carbon disulfide, benzene and cyclohexane, were all of p.a. quality from Merck.

#### Instrumental

The i.r. spectra in the mid i.r. region  $1600\text{--}400\text{ cm}^{-1}$  were recorded with a Perkin-Elmer model 225 spectrometer. Solutions of the sulfides in known concentrations in carbon disulfide and carbon tetrachloride were investigated in sealed liquid cells of thickness *ca* 0.4 mm having windows of KBr. Corresponding solutions with identical donor concentrations and with iodine concentrations of 0.958 M (in  $\text{CS}_2$ ) and 0.121 M (in  $\text{CCl}_4$ ) were recorded under identical experimental conditions.

Far i.r. spectra in the  $600\text{--}50\text{ cm}^{-1}$  region were recorded with an evacuable, fast scan Fourier transform spectrometer (IFS 114 C) from Bruker, using a TGS detector and beam-splitters of Mylar of thicknesses 3.5, 6 and 12  $\mu\text{m}$ . Vacuum tight liquid cells with amalgamated Pb-spacers and polyethylene windows with thicknesses 1.0, 2.0 and 10 mm were used in this region. When the cells acquired a significant self-absorption, they were opened and fitted with new polyethylene windows. Solutions of the donors and iodine (0.20 M) in cyclohexane and benzene were investigated and background corrections were made with the same donor concentration (without iodine). The ratioed spectra were plotted in percentage transmission and in absorbance values to facilitate a quantitative evaluation of the data.

Raman spectra were obtained, using a Cary 81 spectrometer and a helium-neon laser (Spectra Physics 125 A). The  $180^\circ$  excitation technique (retro Raman) is suitable for strongly coloured iodine solutions [16] and was employed. Cyclohexane has a low background below  $250\text{ cm}^{-1}$ , and was used as solvent for the Raman spectra. Mixed donor and iodine (0.042 M) solutions were recorded below  $600\text{ cm}^{-1}$  and compared with the corresponding donor solutions (without iodine).

## RESULTS

#### Far i.r. region

The observed far i.r. curves for dimethylsulfide are shown in the upper left corner of Fig. 1. Dimethylsulfide (0.4 M) in cyclohexane gave rise to the dotted curve, whereas the sulfide of the same concentration with iodine (0.1 M) gave the dashed curve. When ratioed, the two curves gave the solid line. Since iodine dissolved in cyclohexane has no i.r. active band, the solid curve represents (at least to a very high approximation) the spectrum of the complex. The remaining eight curves of Fig. 1 demonstrate the absorption curves for the other sulfide (selenide) iodine complexes obtained in the same manner. As apparent, two or three absorption bands were observed for each complex. The wave numbers and half intensity widths of these bands (including the unstable trimethylenesulfide-iodine system not shown in Fig. 1) are listed in Table 1.

In the 1,4-dithiane-iodine complex ( $\text{C}_6\text{H}_8$  was chosen as the solvent since 1,4-dithiane has a very low

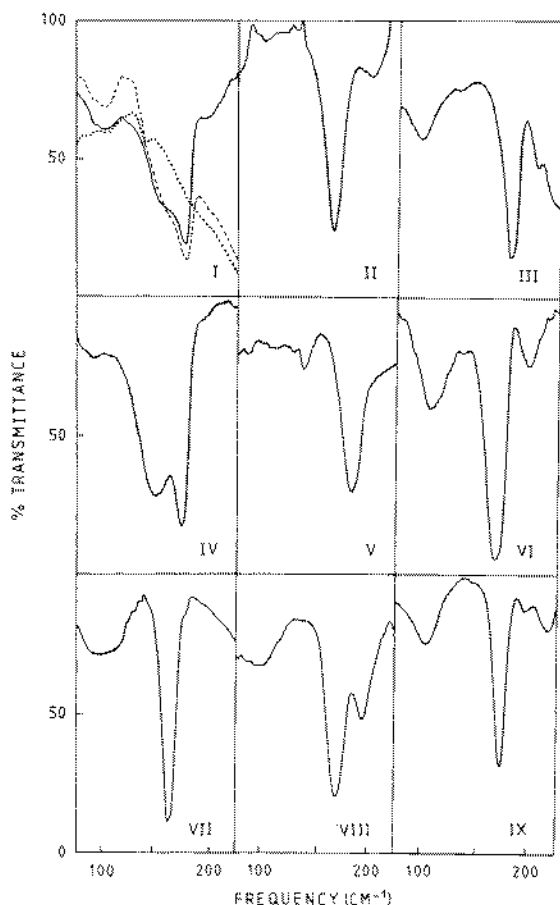


Fig. 1. Far i.r. transmission curves of sulfide (selenide)-iodine solutions in cyclohexane. Curve I, dimethylsulfide (0.4 M) dotted line, dimethylsulfide + iodine (0.1 M) dashed line, ratioed spectra solid line, 1 mm path. Curve II dibenzylsulfide, III 1,4-thioxane, IV diethylsulfide, V dibenzyldisulfide, VI tetramethylenesulfide, VII diethylselenide, VIII 1,4-dithiane (benzene solution) and IX pentamethylenesulfide.

solubility in  $\text{C}_6\text{H}_{12}$ ), significant spectral changes occurred between  $200$  and  $350\text{ cm}^{-1}$ . As shown in Fig. 2, i.r. bands appeared at  $277$  and  $333\text{ cm}^{-1}$  not present in the donor spectrum. To be discussed later, these bands (as well as others in the mid i.r. region) are interpreted as Raman active modes of species  $A_g$  or  $B_g$  which become i.r. activated in the complex.

#### Mid i.r. region

I.r. spectra of sulfides in  $\text{CS}_2$  and  $\text{CCl}_4$  solutions were recorded in the  $1500\text{--}400\text{ cm}^{-1}$  region. Mixed solutions of the same donor concentration with additional iodine (*ca* 0.9 M in  $\text{CS}_2$  and 0.1 M in  $\text{CCl}_4$ ) were subsequently recorded in the same region. As a demonstration the two sets of absorption curves for 1,4-thioxane are shown in Fig. 3. Certain frequency shifts and intensity changes were observed when iodine was added to the donor, but the perturbations were smaller than those observed in the far i.r. region. Generally, the sulfides showed distinct shifts and

Table 1. The far i.r. and Raman ( $250\text{--}50\text{ cm}^{-1}$ ) bands observed for the sulfide (selenide)-iodine complexes in cyclohexane solution

Donor	Infrared						Raman	
	$\nu(\text{I-I})$	$\nu_{\text{I}}$	$\nu(\text{S(Se)-I})$	$\nu_{\text{I}}$	$\nu(\text{others})$	$\nu_{\text{I}}$	$\nu(\text{I-I})$	$\nu_{\text{I}}$
Dibenzyldisulfide	180	10					181	9
1,4-Thioxane	177	9	100	30			177	11
Dimethylsulfide	172	12	155	29	105	40	173	12
Pentamethylenesulfide	171	11	105	28	212	19	168	10
Diethylsulfide	170	12	148	29	94	47	165*	12
Dibenzylsulfide	169	13	100		191	24	166	12
1,4-Dithiane *	166	10	95	50	190	17	166	11
Tetramethylenesulfide	166	13	111	24	196	15	165	12
Diethylselenide	162	13	100	42			155	13
Trimethylenesulfide *	159	18	113		195			

\*Benzene solution.

intensity variations in the  $700\text{--}650\text{ cm}^{-1}$  region (around  $550\text{ cm}^{-1}$  for diethylselenide) as shown for dimethylsulfide in Fig. 4. To be discussed later, the shifts are connected with the C-S-C (C-Se-C) stretching modes of the donor. The observed perturbations (frequency shifts and intensity variations) for the various donors are listed in Table 2. Two of the sulfides, however, (dibenzyldisulfide and trimethylenesulfide) reacted slowly with iodine and no quantitative data were obtained for these complexes.

#### Far i.r. band intensities

The integrated i.r. band intensities were estimated from the far i.r. plots, using a program written in this

laboratory [25] for the Nicolet 1180 computer. Three or four donor-iodine solutions in cyclohexane (benzene was the solvent for 1,4-dithiane) were recorded for each sulfide in cells of various thicknesses. The concentration of the complex was estimated from the formation constants ( $K_c$ ) reported from either the charge transfer band or the blueshifted iodine band [14, 16, 19, 20]. We adopted the values obtained for heptane or  $\text{CCl}_4$  solutions at  $25^\circ\text{C}$  (the vapour complex value for dimethylsulfide-iodine) in our cyclohexane (benzene) solutions at ambient temperature (*ca*  $23^\circ\text{C}$ ) without corrections. The calculated intensities in darks ( $\text{cm mmol}^{-1}$ ) for the  $\nu(\text{I-I})$ ,  $\nu(\text{S-I})$  and eventual other bands are given in Table 3 for five sulfide and a selenide complex with iodine. Dibenzylsulfide has been left out since no formation constant for the iodine complex has been reported. For diethylselenide we employed the formation constant reported for dimethylselenide-iodine [19]. However, with the donor concentrations employed (*ca*  $0.5\text{ M}$ ) practically all the iodine was converted to the complex. Therefore, the exact value of the formation constant

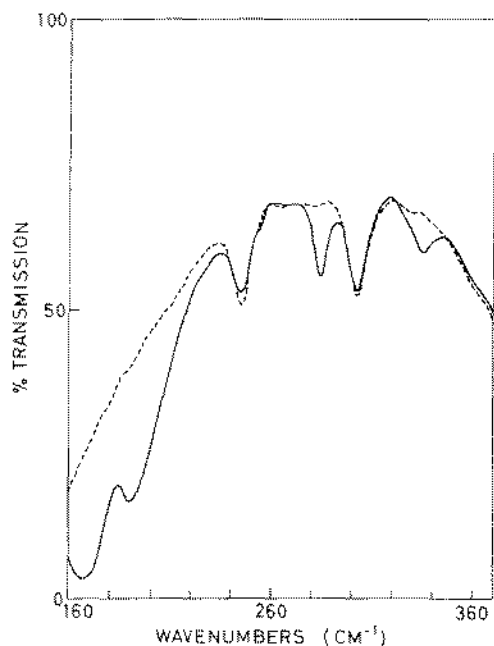


Fig. 2. Far i.r. spectra of 1,4-dithiane (0.48 M) in benzene (dashed curve); 1,4-dithiane + iodine (0.65 M) in benzene (solid curve), 2 mm path.

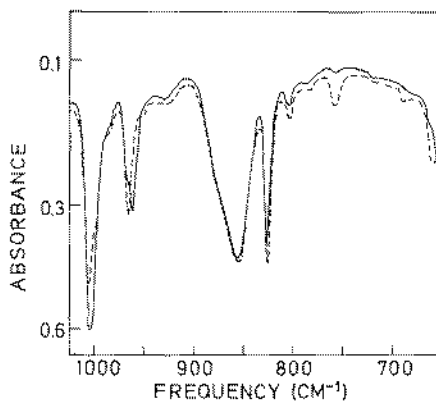


Fig. 3. Mid. i.r. spectra of 1,4-thioxane (0.14 M) in carbon disulfide (dashed curve); 1,4-thioxane + iodine (0.85 M) in carbon disulfide (solid curve), path 0.4 mm.

Table 2. I.r. bands ( $1500\text{--}250\text{ cm}^{-1}$ ) of the sulfides (selenide) perturbed upon complex formation to iodine\*

Dibenzylsulfide				Dibenzylsulfide <sup>§</sup>			
no perturbations observed				Donor	Complex	Interpretation	
1,4-Thioxane <sup>4</sup>				982	977	D,S	
				932	926	S	
				712	705	S	
				664	667	S C-S str	
				469	474	S	
				1,4-Dithiane <sup>7</sup>			
				Donor	Complex	Interpretation	
				1295	A $\nu_4$	A <sub>g</sub>	CH <sub>2</sub> wag
				1202	A $\nu_{23}$	B <sub>g</sub>	CH <sub>2</sub> wag
				1148	E $\nu_{15}$	A <sub>u</sub>	CH <sub>2</sub> twist
				994	S $\nu_{16}$	A <sub>u</sub>	C-C str
				944	A $\nu_9$	A <sub>g</sub>	CH <sub>2</sub> rock
				903	S $\nu_{33}$	B <sub>u</sub>	CH <sub>2</sub> rock
				628	A $\nu_8$	A <sub>g</sub>	C-S str
				480	S $\nu_{25}$	B <sub>g</sub>	ring def
				333	A $\nu_9$	A <sub>g</sub>	ring def
				277	A $\nu_{10}$	A <sub>g</sub>	ring def
				Bimethylsulfide <sup>†</sup>			
				Donor	Complex	Interpretation	
				1331	E,S	A <sub>1</sub>	CH <sub>3</sub> def
				910	S,S		
				735	S	B <sub>1</sub>	C-S str.
				685	E,S	A <sub>1</sub>	C-S str
				Pentamethylensulfide <sup>‡</sup>			
				Donor	Complex	Interpretation	
				1348	1349	E,S	$\nu_{16}$ A' CH <sub>2</sub> wag
				1308	1305	E,S	$\nu_{11}$ A' CH <sub>2</sub> wag
				1237	1239	E,S	$\nu_{12}$ A' CH <sub>2</sub> twist
				1215	1215	E	$\nu_{13}$ A' CH <sub>2</sub> twist
				1059	1059	E	$\nu_{14}$ A' C-C str
				966	964	E,S	$\nu_{15}$ A' C-C str
				688	683	E,S	$\nu_{40}$ A' C-S str
				655	647	S	$\nu_{19}$ A' C-S str
				515	515	E	
				500	504	E,S	$\nu_{20}$ A' ring def
				Diethylsulfide <sup>†</sup>			
				Donor	Complex	Interpretation	
				1376	1376	S	
				1223	1223	D	
				964	964	D	
				760	755	E,S	
				754	754	D	
				740	745	S	
				718	725	S	
				Diethylselenide <sup>§</sup>			
				Donor	Complex	Interpretation	
				664	664	D	
				582	566	E	C-Se str
				556	544	E,S	C-Se str
				Trimethylensulfide			
				unstable			

\*Solvents: CS<sub>2</sub>, CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>.†Interpretation, C<sub>s</sub> symmetry Ref. [30].‡Interpretation, C<sub>2v</sub> symmetry Ref. [29].§Interpretation, C<sub>s</sub> symmetry Ref. [26].

§Interpretation, this work.

\*Interpretation, C<sub>2h</sub> symmetry Refs [30, 31].

++E, Enhanced intensity; D, diminished intensity; S, shifted wave number; A, i.r. activated Raman band.

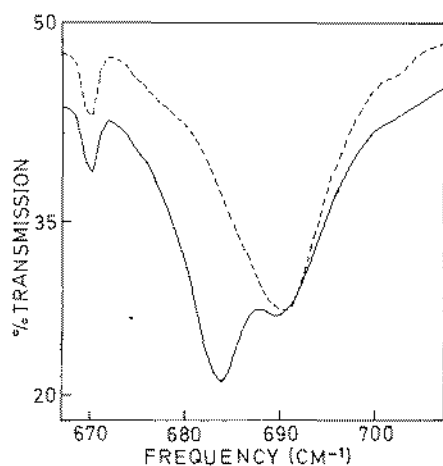


Fig. 4. Mid. i.r. spectra of dimethylsulfide (0.16 M) in carbon disulfide (dashed curve); dimethylsulfide + iodine (0.85 M) in carbon disulfide (solid curve), path 0.4 mm.

( $K_c$ ) at the temperature of measurement was not very critical.

#### Raman spectra

A typical Raman plot of dimethylsulfide (0.9 M) and iodine (0.04 M) in cyclohexane is shown in Fig. 5. A Raman band at  $172\text{ cm}^{-1}$  in the complex (curve A) which was not present in the sulfide or in the solvent spectrum (curve B) is obviously the iodine stretching mode of the complex. These bands, observed between  $180$  and  $160\text{ cm}^{-1}$  for the donors studied, are listed in Table 1. In some systems an additional band at  $105\text{ cm}^{-1}$ , interpreted as the  $\nu_1$  mode of the  $\text{I}_3^-$  ion [16, 13] was detected. Weak Raman bands of the donors (e.g. at  $242$  and  $195\text{ cm}^{-1}$  of pentamethylene-sulfide [26]) were not detected under the present conditions (low sulfide concentrations, coloured solutions, He-Ne laser excitation).

## DISCUSSION

### Far i.r. region

As is apparent from Table 1, the observed Raman band corresponded to the most prominent far i.r. band in all the sulfide-iodine complexes investigated. It was concluded long ago [6] that the Raman band observed in donor-iodine complexes was the perturbed Raman active iodine stretching mode. Later, it has been confirmed [7, 13] that while the halogen stretching mode appears strongly in iodine, bromine and iodine monochloride complexes, no intermolecular stretching or bending modes have been observed in the Raman spectra. Thus, the fairly sharp i.r. and Raman bands observed between  $180$  and  $160\text{ cm}^{-1}$  in the present spectra are undoubtedly the I-I stretching modes of the complexes (Table 1). This mode is situated at  $213\text{ cm}^{-1}$  in the vapor and at  $207\text{ cm}^{-1}$  in  $\text{CCl}_4$  solution. In accordance with the prevailing theory [27] the electron donated goes into an antibonding ( $\sigma^*$ ) orbital of the acceptor, weakening the I-I bond and resulting in a shift to lower wave numbers. The frequency decrease  $\Delta\nu/\nu$  (from the  $\text{CCl}_4$  value) depends upon the donor strength (Lewis basicity) of the sulfides and can be correlated with changes in the force constants and the thermodynamic functions of the complex formation. The half band widths of the i.r. as well as the Raman bands pertaining to I-I stretch seem to increase slightly with stronger interactions, contrary to the results obtained for the pyridine- $\text{I}_2$  systems [13]. Also these bands have a slight asymmetry with larger band widths on the low wave number side. Since approximately 35% of the molecules will be present in excited vibrational levels at ambient temperature, the asymmetry is undoubtedly due to hot bands, assuming a moderate anharmonicity.

In the pyridine-iodine complexes which are of comparable stability to the sulfide-iodine systems, low frequency i.r. bands in the  $120\text{--}70\text{ cm}^{-1}$  range are

Table 3. The i.r. intensities of far i.r. bands of the sulfide (selenide)-iodine complexes in cyclohexane solution

Donor	$\nu(\text{I-I})$ $\text{cm}^{-1}$	$B(\text{I-I})$ darks <sup>+</sup>	$\nu(\text{S-I})$ $\text{cm}^{-1}$	$B(\text{S-I})$ darks <sup>+</sup>	$\nu(\text{other})$ $\text{cm}^{-1}$	$B(\text{other})$ darks <sup>+</sup>	$-\Delta H^*$ $\text{kJ mol}^{-1}$	$-\Delta G^*$ $\text{kJ mol}^{-1}$	$-\Delta S^*$ $\text{J mol}^{-1}\text{K}^{-1}$
1,4-Thioxane	177	480	100	340	220 198	360	21.8	10.1	39.7
Dimethylsulfide	172	1100	155	1600	105	450	31.0 <sup>o</sup>	9.7 <sup>p</sup>	36.9 <sup>o</sup>
Pentamethylene sulfide	171	1260	105	1300	212	550	32.4	12.5	66.9
Diethylsulfide	170	1180	148	1640	94	520	34.8	12.9	73.6
1,4-Dithiane †	166	1130	95	660	190	620	25.9	10.8	53.1
Tetramethylene sulfide ‡	166	1900	111	290	195	105	34.6	13.3	71.5
Diethylselenide §	162	2100	100	1830			36.0	15.4	68.6

\* Values from Ref. [16], obtained in heptane solution at  $25^\circ\text{C}$  from blue-shifted iodine band.

† Darks ( $\text{cm mmol}^{-1}$ ).

<sup>o</sup> Vapor value,  $100^\circ\text{C}$ , Ref. [17].

‡ Solvent, benzene.

§ Thermodynamic functions for dimethyl selenide [20].

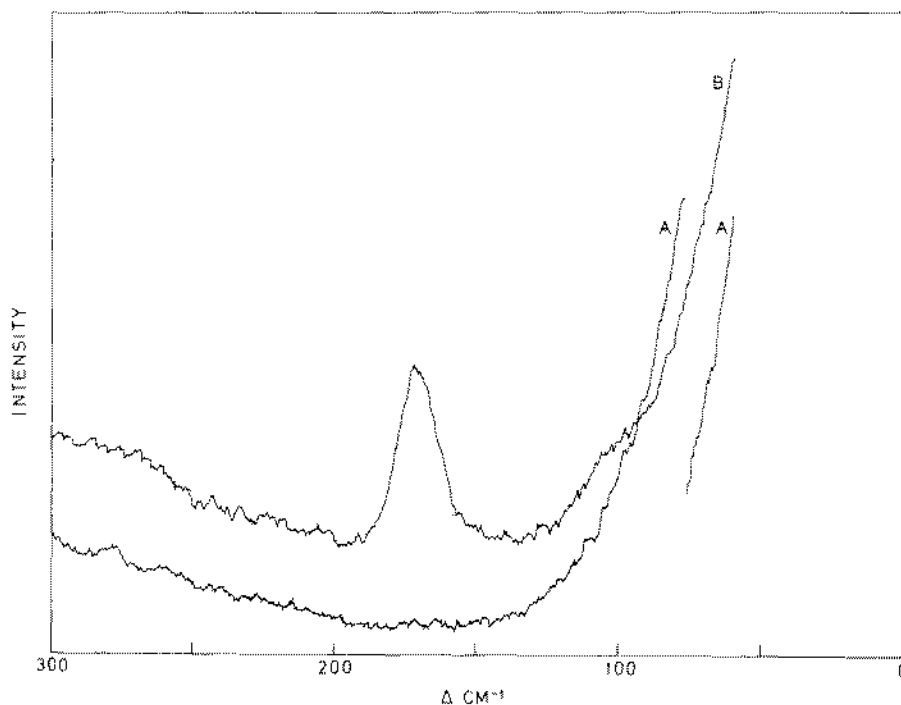


Fig. 5. Raman spectra of dimethylsulfide (0.9 M) in cyclohexane (curve A); dimethylsulfide + iodine (0.04 M) in cyclohexane (curve B), He-Ne laser excitation.

attributed to intermolecular N··I stretching modes [9–13]. Careful recording of the far i.r. spectra of the present sulfide (selenide)-iodine complexes, revealed bands partly at lower, partly at higher wavenumbers than the I–I stretch (Fig. 1, Table 1). This feature led YAMADA *et al.* [24] to assign bands between 200 and 185  $\text{cm}^{-1}$  to the S··I intermolecular mode for three cyclic sulfides (tetramethylenesulfide, pentamethylenesulfide and 1,4-dithiane). For a group of aliphatic sulfides, however, they assigned the S··I modes to bands between 160 and 95  $\text{cm}^{-1}$  (on the low frequency side of the I–I stretch) [23]. We have after careful consideration rejected their interpretation of the cyclic sulfide complex spectra [24] for the following reasons: (1) the force constants  $k_{S-I}$  (see below), would be much higher for the cyclic sulfides than for the others, contrary to expectations; (2) 1,4-thioxan- $\text{I}_2$  does not have any bands in the 200–185  $\text{cm}^{-1}$  region like the other cyclic sulfides investigated (Table 1); (3) the non cyclic dibenzylsulfide- $\text{I}_2$  complex also has a band at 191  $\text{cm}^{-1}$ .

Instead, we have assigned the S··I intermolecular stretching mode to bands situated between 155 and 95  $\text{cm}^{-1}$  for all sulfide (selenide)-iodine complexes investigated. A reasonable correlation between the  $k_{S-I}$  and  $\Delta H$  for the complex formation was achieved (see below). No good explanation can be made for the high wave number bands (215–190  $\text{cm}^{-1}$ ) observed for five of the sulfide-iodine complexes, although they might be due to combination bands between  $\nu(\text{I-I})$  and  $\delta(\text{S-I})$  or they are donor bands enhanced in the complex.

The integrated intensities of the  $\nu(\text{I-I})$  and the  $\nu(\text{S-I})$  bands listed in Table 3 reveal various trends when correlated with the  $\Delta H$  and  $\Delta G$  of the complexes or with the shifts  $\Delta\nu(\text{I-I})$ . First of all the  $B$ -values for  $\nu(\text{I-I})$  found between 480 and 2100  $\text{cm}^{-1}$  are no more than half of the corresponding values for pyridine-iodine [7, 9, 11, 13] although these complexes are of comparable strengths. Secondly, the  $B(\text{I-I})$  values generally increase with the donor strengths for the present sulfides. This trend contradicts the results of MAES [13] obtained for 11 halogen or alkylsubstituted pyridines and iodine. According to FRIEDRICH and PERSON [28] the i.r. intensity of the halogen stretching vibration is determined by the static moment and the vibronic effect of which the later gives the major contribution. Apparently, the change in dipole moment between the sulfide and the iodine with the frequency of the I–I vibration is smaller than in the case of pyridine. The lower electronegativity of the sulfur atom compared to the nitrogen atom as part of the aromatic ring system may be the deciding factor.

As seen from Fig. 1 and the  $\nu_{1/2}$  values of Table 1 the  $\nu(\text{S-I})$  bands are much broader with smaller absorbance values than  $\nu(\text{I-I})$ . However, the  $B(\text{S-I})$  values are of comparable magnitude as  $B(\text{I-I})$ , although the actual values vary erratically through the series. There is apparently no monotonic relation between  $B(\text{S-I})$  and the donor strengths or with the  $\nu(\text{S-I})$  values. Finally the remaining far i.r. bands listed as (other) of Table 3 have  $B$ -values which are generally much lower than the  $B(\text{I-I})$  and  $B(\text{S-I})$ . As discussed above three of

these bands (those for tetramethylenesulfide, pentamethylenesulfide and 1,4-dithiane) were actually assigned as  $\nu(\text{S-I})$  by the earlier authors [24].

#### Force constants

Among the present donors dimethylsulfide [29], pentamethylenesulfide [26], 1,4-thioxane [30] and 1,4-dithiane [30, 31] have all been subject to vibrational analyses, and force fields for these molecules have been derived. Since dimethylsulfide is by far the smallest of these molecules, a force constant calculation for the iodine complex of this molecule was carried out. Based upon the force field for dimethylsulfide [29], the additional force constants  $k_{\text{I-I}}$ ,  $k_{\text{S-I}}$  and the interaction term  $k_{\text{S-I-I}}(k_{12})$  were introduced. No bending force constants were included since the bending modes are supposedly outside the spectral range covered. An iteration program was adopted and the calculated wavenumbers were fitted to the experimental values in dimethylsulfide-iodine at 172 and 155  $\text{cm}^{-1}$  for various values of  $k_{\text{I-I}}$ ,  $k_{\text{S-I}}$  and  $k_{12}$ . The two ellipses giving  $k_{12}$  as a function of  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$  are shown as solid lines in Fig. 6. A simplified calculation treating the donor as a point mass (the linear three point mass approximation) was also adopted, and the two dashed ellipses in Fig. 6 were obtained. As apparent, the force constants for  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$  have somewhat higher values for the same interaction constant  $k_{12}$  in the complete calculation than in the simplified three point mass approximation.

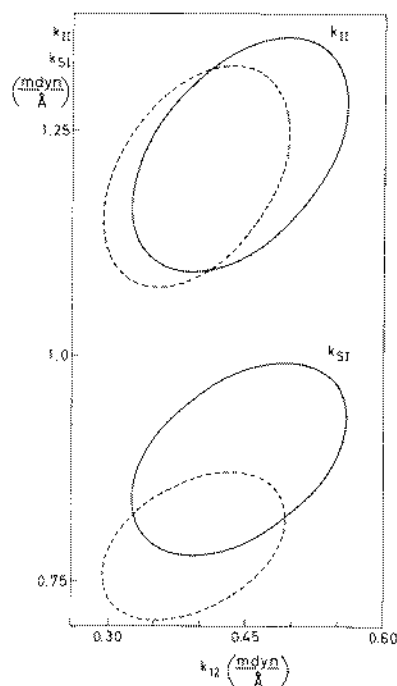


Fig. 6. Force constant ellipses for dimethylsulfide-iodine, using the linear three point mass model (dashed curves) and the complete force constant calculation (solid curves). The force constants  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$  are plotted as a function of  $k_{12}(k_{\text{I-I}}/k_{\text{S-I}})$  interaction term.

As expected the three point mass approximation is more severe for  $k_{\text{S-I}}$  than for  $k_{\text{I-I}}$ . However, the simplified calculations gave a reasonably good agreement with the complete treatment. Therefore, it seems justified to adapt the three point mass approximation to the whole series of donors. The values for  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$  in the various sulfides, obtained for two or three arbitrary values of  $k_{12}$ , are listed in Table 4.

We would expect  $k_{\text{I-I}}$  to be reduced with increased donor strength since the donated electron goes into an antibonding orbital and weakens the I-I bond [27]. The opposite should be true for  $k_{\text{S-I}}$ , since the complex bond should increase with higher donor strength.

Three somewhat arbitrary values of  $k_{\text{I-I}}$ ,  $k_{\text{S-I}}$  and  $k_{12}$  (the lowest and the highest  $k_{12}$  values giving real values of  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$  and the  $k_{12}$  value giving the maximum value of  $k_{\text{I-I}}$ ) are listed in Table 4. As is apparent from Fig. 7 a slight decrease in  $k_{\text{I-I}}$  and increase in  $k_{\text{S-I}}$  (at the  $k_{12}$  value giving the maximum value of  $k_{\text{I-I}}$ ) appear with larger  $-\Delta H$  values of the complexes. However, the present donors ranging from 1,4-thioxane ( $-\Delta H = 21.8 \text{ kJ mol}^{-1}$ ) to diethylselenide ( $-\Delta H = 36.8 \text{ kJ mol}^{-1}$ ) probably represent too small a difference in basicity towards iodine to make this correlation conclusive. The three point mass model and the uncertainty of the  $k_{12}$  values combined with the errors

Table 4. Force constants based upon the three point approximation

Donor	$k_{\text{I-I}}$ , m dyn/A	$k_{\text{S-I}}$ , m dyn/A	$k_{12}$ ** m dyn/A
1,4-Thioxane	0.98	0.52	0.61 †
	1.51	0.64	0.68 ‡
	1.32	1.04	0.93 §
Dimethylsulfide	1.20	0.72	0.30
	1.32	0.73	0.43
	1.28	0.80	0.49
Pentamethylene sulfide	0.80	0.64	0.62
	1.41	0.65	0.63
	1.23	0.89	0.84
Diethylsulfide	1.15	0.91	0.39
	1.36	0.82	0.57
	1.31	1.01	0.64
Dibenzylsulfide <sup>c</sup>			
1,4-Dithiane	0.91	0.55	0.61
	1.36	0.65	0.66
	1.38	1.05	0.89
Tetramethylene sulfide	0.79	0.63	0.66
	1.30	0.59	0.53
Diethylselenide	0.74	0.69	0.66
	1.33	0.75	0.69
	1.16	1.12	0.89
Trimethylene sulfide	0.80	0.51	0.68
	1.16	0.51	0.43
	1.05	0.68	0.56

\*  $k_{12} = k_{\text{I-I}}/k_{\text{S-I}}$  interaction.

† The lowest value for  $k_{12} > 0$ , giving real values for  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$ .

‡ The value for  $k_{12}$  which gives the maximum value for  $k_{\text{I-I}}$ .

§ The highest value for  $k_{12} > 0$ , giving real values for  $k_{\text{I-I}}$  and  $k_{\text{S-I}}$ .

<sup>c</sup> The three point mass approximation is inadequate for this flexible molecule.

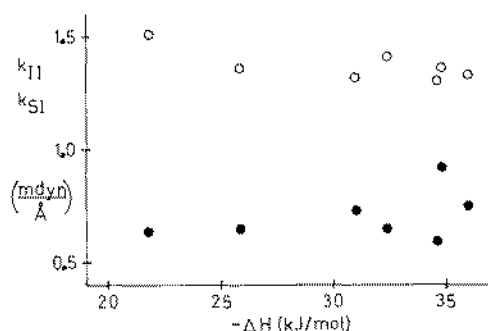


Fig. 7. Plots  $k_{1-1}$  and  $k_{5-1}$  (at the  $k_{1,2}$  values giving the maximum  $k_{1-1}$ , Table 4) vs  $-\Delta H$ .

of the  $\Delta H$  values make these correlations fairly uncertain.

#### Perturbed donor spectra

As apparent from Fig. 3 and Table 2, a number of changes occurred in the i.r. donor spectra when iodine was added. The changes can be classified as: (1) i.r. bands shifted on complex formation, (2) i.r. bands which are subject to intensity changes (enhanced, diminished) and (3) new bands activated on complex formation.

It is well known that in donor molecules with the functional groups C=O, P=O, or S=O, the characteristic X=O stretching band is shifted to lower wavenumbers on complex formation to the halogens [7]. In cyanides, however, the C≡N stretching mode is shifted to higher wave numbers on complex formation [32]. For *n*-donors like the sulfides, ethers or phosphines, the perturbations of the donor spectra are fairly small and not so easily interpreted. The partial donation of lone pair electrons from the sulfide to the iodine and formation of the complex bond will have some obvious consequences for the vibrational spectra of the donor: (1) kinematic or mass effect of the iodine adduct, (2) electronic effects which tend to weaken or strengthen the chemical bonds of the donor, (3) reduced symmetry of the donor which may relax certain selection rules.

The spectral perturbations listed in Table 2 can be interpreted in terms of these effects. Thus, in dimethylsulfide and diethylsulfide the symmetric ( $A_1$ ) and asymmetric ( $B_1$ ) C-S-C stretching modes [29] are both shifted to lower wave numbers on complex formation as expected from effects (1) and (2). An additional number of CH<sub>2</sub> wag, twist and rock of diethylsulfide seem shifted and/or enhanced.

Various i.r. bands of dibenzylsulfide and tetramethylenesulfide in the 1400–400 cm<sup>-1</sup> region were perturbed on complex formation. Among these, the 694 cm<sup>-1</sup> band in the former and 686 cm<sup>-1</sup> band in the latter spectrum are probably connected with C-S stretch and are both shifted to lower wave numbers.

In pentamethylenesulfide all the perturbed bands except 688 cm<sup>-1</sup> (which is the  $A''$  C-S stretch) were of species  $A'$  [26]. Various CH<sub>2</sub> wag and twisting modes as well as the C-C stretch and ring bending modes were

perturbed in addition to the two C-S stretches  $\nu_{40}$  and  $\nu_{19}$  [26]. In 1,4-dithiane only one of the four C-S stretches [30, 31] were perturbed (only one of the sulfur atoms is engaged in complex formation [19, 20]). However, it seems highly significant that a number of i.r. bands (1295, 1202, 944, 628, 333 and 277 cm<sup>-1</sup>) absent in 1,4-dithiane [30, 31] appear in the complex (Fig. 2). All these bands are Raman active fundamentals of species  $A_g$  and  $B_g$  which are activated in the complex. Thus, just as the Raman active stretching mode of the acceptor becomes i.r. active on complex formation (Table 1), several Raman active donor fundamentals become i.r. active. This is expected when the  $C_{2h}$  symmetry of 1,4-dithiane is reduced to  $C_s$  in the complex.

It is expected also that the i.r. active modes should become Raman active on complex formation. The high concentration of iodine necessary to convert a considerable fraction of 1,4-dithiane into the complex would result in a deep red colour which would prevent recording with the He-Ne laser. We plan to apply a low frequency dye-laser to this problem.

In the spectra of 1,4-thioxane various bands present in the donor spectrum are enhanced on complex formation (Fig. 3). As a hybrid between 1,4-dioxane and 1,4-dithiane, 1,4-thioxane has  $C_{2h}$  pseudosymmetry [30], with bands weak either in i.r. or in Raman. It is expected that the pseudosymmetry will be reduced on complex formation from the sulfur atom, leading to enhanced i.r. bands. It is surprising that the 663 cm<sup>-1</sup> band interpreted as the C-S stretch of species  $A'$  is merely enhanced and not shifted on complex formation.

In diethyl selenide the donor-acceptor interaction is stronger than for the sulfides investigated. Various i.r. bands are reduced or enhanced, and some are shifted on complex formation. It seems likely that the bands at 582 and 556 cm<sup>-1</sup> which are close to the corresponding band for pentamethylene selenide [26] are mainly connected with the asymmetric and the symmetric C-Se stretch. As is apparent from Table 2 these bands are shifted 14 and 12 cm<sup>-1</sup>, respectively, to lower wave numbers.

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