4. *Thermochromism of Compounds containing the Thiocarbonyl and Disulphide Functions.*

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The spectra in solution of some thiocarbonyl compounds and disulphides have been measured in the temperature range 20—115°. The visual thermochromism of the thiocarbonyl compounds is associated with the first ($N \longrightarrow A$) electronic absorption band and is due to a redistribution of intensity with temperature, the integrated intensity remaining constant; at high temperature the band broadens and moves slightly (100—150 cm.$^{-1}$) to lower frequencies. The broadening is attributable to the change with temperature of the relative population of the lower vibrational levels of the ground state; the frequency shift is a new effect, explained by a diminution of solvent–solute interaction with rising temperature.

Di-1-thionaphthoyl disulphide obeys Beer's law at 100°, but a slow, irreversible decomposition occurs at this temperature. With di(benzothiazol-2-yl) disulphide, the thermochromism (to 100°) is due to thermal broadening of the spectrum and not to reversible dissociation into benzothiazol-2-ylthio-radicals.

THIOCARBONYL compounds and aryl disulphides are weakly thermochromic; the thermochromism is visually not striking, but the colour of a melt or solution deepens on heating and the normal colour returns on cooling. This study is concerned with the nature of the spectral changes, and the spectra of representative compounds have been measured at normal and high temperatures. The results are probably of wider application, for most coloured substances change their colour on warming and the underlying spectral differences must also arise when absorption is entirely in the ultraviolet region.

Thiocarbonyl Compounds.—Five compounds of this class were examined (Table 1). Among them the visual thermochromism of methyl 1-dithionaphthoate (I) and diphenyl trithiocarbonate (V) has been described by Schönberg, Nickel, and Cernik (*Ber.*, 1932, **65**, 293), and 1-naphthyl phenyl thioketone (II) in solution deepens in colour from blue to blue-green on warming; the thioncarbonates (III) and (IV) do not absorb in the visible region. With all five compounds the spectral changes on heating were the same, but for reasons mentioned later the most satisfactory results were obtained with methyl 1-dithionaphthoate and 1-naphthyl phenyl thioketone.

TABLE 1. *$N \longrightarrow A$ Transitions of thiocarbonyl compounds (solvents are shown in parentheses).*

	Temp.	$\nu_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$(\Delta\varepsilon)_{max.}$	Oscillator strength ($10^4 f$)
			(l. mole^{-1} cm.$^{-1}$)		
1-$C_{10}H_7$·CS·SMe (I)	20°	20,450	115	—	14·1
	60	20,420	113	8	14·2
(Ethyl Oxalate)	101	20,400	112	12	14·3
	115	20,380	111	14	14·4
1-$C_{10}H_7$·CS·Ph (II)	21	16,200	155	—	19·8
(Decalin)	81	16,100	151	14	19·8
$(PhO)_2CS$ (III)	18	30,550	45	—	2·0
(96%-Ethanol)	70	30,500	46	3	—
p-MeO·C_6H_4·O)$_2$CS (IV) ...	17	30,100	75	—	2·8
(Decalin)	81	30,100	73	5	—
$(PhS)_2CS$ (V)	19	21,750	32	—	1·0
(Decalin)	101	21,650	35	7	—

The first absorption band of the dithionaphthoate is reproduced in Fig. 1. The curves of $\Delta\varepsilon$ [$\varepsilon(20°) - \varepsilon(115°)$, etc.] are asymmetrical, being mainly positive on the red side of the absorption maximum and mainly negative on the blue; this is equivalent to a small net transfer of intensity to the red, corresponding to the deepening of colour observed visually. The integrated intensity apparently rises slightly with temperature (Table 1), but the increment can be attributed to the proximity of a much stronger ultraviolet band (cf. Fig. 3); the broadening of the second band in the hot solution contributes some intensity to the area under the envelope of the first band. With 1-naphthyl phenyl thioketone (Fig. 2) the resolution of the first and second absorption bands is sharper and the integrated intensity of the first band is independent of temperature.

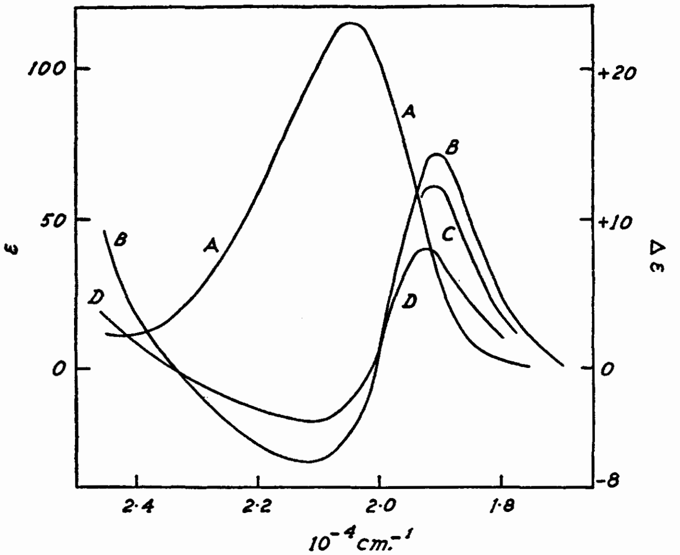

FIG. 1. *Methyl 1-dithionaphthoate in ethyl oxalate.*

A, ε (20°);
B, ε (115°) − ε (20°);
C, ε (101°) − ε (20°);
D, ε (60°) − (20°).

Constancy of $\int \varepsilon d\nu$ means that the number of electrons, and hence the number of molecules, excited in absorption does not vary with temperature. In this case it is almost certain that the spectral changes are not to be attributed to excitation from two (or more) discrete, lower states of unequal energy. Near-lying states of this kind might result from different conformations of the molecule (with 1-naphthyl phenyl thioketone, for example, it is most improbable that the naphthyl, phenyl, and thiocarbonyl chromophores are coplanar at equilibrium, and different rotational conformations with slightly different energies and electronic spectra are conceivable) or, possibly, from a very low-lying excited electronic state. Such an explanation is difficult to rule out, because it is impossible to know in advance what range of temperature will be required to disclose a real change in $\int \varepsilon d\nu$, but there seems to be no evidence to support it; constancy of $\int \varepsilon d\nu$ will therefore be accepted as genuine. Granted this, the spectral changes must be attributed to the change with temperature of the population of the ground-state vibrational levels, or to a relaxation of solvent–solute interaction, or both.

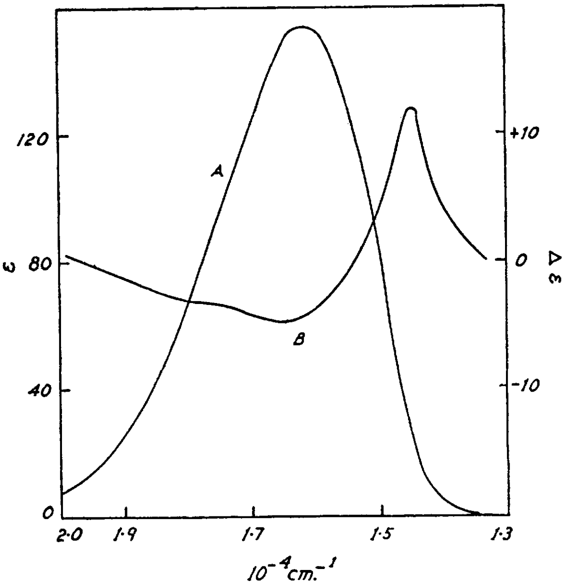

FIG. 2. 1-*Naphthyl phenyl thioketone in decalin.*

A, ε (21°);
B, ε (81°) − ε (21°).

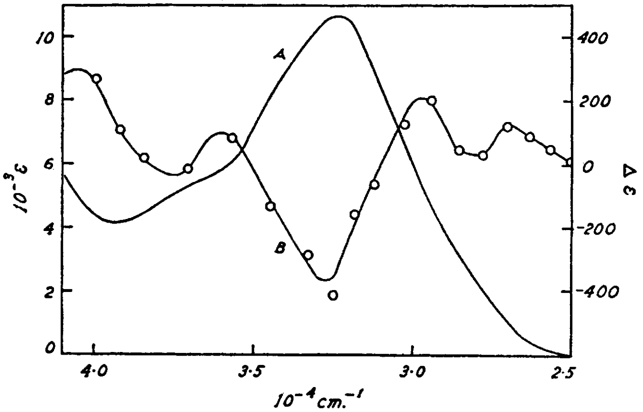

FIG. 3. *Methyl* 1-*dithionaphthoate in ethanol* (2500—4000 Å).

A, ε (19°);
B, ε (71°) − ε (19°).

As a consequence of the Franck–Condon principle a change in the distribution of molecules over the vibrational levels of the gound state leads to a broadening of the absorption band with rise of temperature (Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419). This effect, which we will term *thermal broadening*, has been observed with continuous vapour-phase spectra (Gibson, Rice, and Bayliss, *Phys. Rev.*, 1933, **44**, 193; Almasy and Laemmel, *Helv. Chim. Acta*, 1950, **33**, 2092) and is a property of the isolated molecule: the characteristic Δε curve associated with it has a maximum below each of the extremities of the absorption band, and a central minimum. Curves of this type were obtained in the ultraviolet spectrum of methyl 1-dithionaphthoate (Fig. 3) wherein each band, including the partly submerged bands that appear as an inflection of the spectral envelope, corresponds to a minimum in Δε. (Where two bands are fused, as on each wing of the central 32,500 cm.$^{-1}$ peak, the maxima in the Δε curve are superimposed.) The first absorption band of the ester, however, does not conform to this pattern; compared with the more or less symmetrical $\Delta\varepsilon$ curve in Fig. 3, the highly asymmetrical curves in Fig. 1 suggest that, in addition to thermal broadening, there has been a movement of the whole absorption band towards the red in the hot solution. This second effect we term the *thermal shift.* As the thermal shift is important with the first absorption band only, it is unlikely that the correct explanation will be in terms of the isolated molecule : a more promising correlation is with the well-known frequency shifts observed at room temperature between different solvents. The width of the band is normal and we will assume that there is no major difference in size (or shape) of the molecule after excitation, but because the band is weak it must be inferred that the electronic distribution differs considerably, and consequently that the solvation shell, after excitation, must undergo reorganisation before the excited molecules attain the equilibrium excited state. The energies of the ground state and the equilibrium excited state will rise with temperature, as the (free) energy of solvation falls. In greater detail, the increment in energy will be larger for the ground state, because the electronic transition ($N \longrightarrow A$) is presumably associated with a decrease of (permanent) dipole moment (Bayliss and McRae, *J. Phys. Chem.*, 1954, **54**, 1002); consequently the pure electronic transition will move slightly towards the red in solution as the temperature rises. The experimental $\nu_{max.}$, however, refers to a " vertical " excited state which, because it is destabilised by the unfavourable conformation of the surrounding solvent molecules, will approach the equilibrium excited state as interaction with the solvent is increasingly broken down by thermal motion. These movements are illustrated in Fig. 4; their sum represents an overall loss of height of the " vertical " state, relative to the ground state, at high temperatures. It is shown in the Appendix that the thermal shift corresponds to a movement of the peak frequency towards the red by 100—150 cm.$^{-1}$; most of the shift is attributable to the change in energy of the vertical state, and hence to the peculiarly unfavourable conditions of solvation resulting from the major change in electronic distribution.

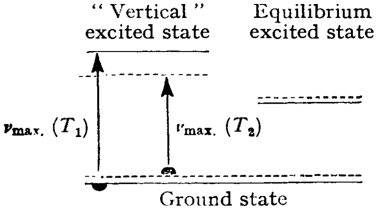

FIG. 4. T_1 ———, T_2 ------- ($T_2 > T_1$)

The results for diphenyl thioncarbonate (III), di-*p*-methoxyphenyl thioncarbonate (IV), and diphenyl trithiocarbonate (V) are summarised in Table 1. With these compounds the influence of temperature on the first absorption band is qualitatively the same as recorded for the thionaphthoate and the thioketone but thermal broadening of the second band tends to obscure the details. For this reason the integrated intensities are only approximate, and a comparison of integrated intensities at different temperatures is not attempted.

Disulphides.—It has frequently been asserted that the thermochromism of disulphides is associated with a *reversible* dissociation equilibrium, the development of colour being assigned to the absorption of the arylthio-radicals (Schönberg *et al.*, *Ber.*, 1932, **65**, 1864; 1935, **68**, 163; *Naturwiss.*, 1933, **21**, 561; *J.*, 1949, 889; Mustafa and Kamal, *Science*, 1953, **118**, 411).* There is evidence, however, that the temperature required for thermal fission is much higher than that needed to observe the thermochromism of disulphides (Bloomfield, *J.*, 1947, 1547; Kharasch, Nudenberg, and Meltzer, *J. Org. Chem.*, 1953, **18**, 1233), and three representative compounds were examined in the present study to determine whether there is any real connection between the phenomena.

Definitive results were obtained with di(benzothiazol-2-yl) disulphide. This compound is thermochromic in solution (Koch, *J.*, 1949, 401) and the spectrum was remeasured in

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* The reversibility of the dissociation follows from the putative correlation with the colour change; insofar as the original colour returns on cooling, the arylthio-radicals cannot disappear except by recombination.

decalin (18° and 80° : Fig. 5) and anisole (18° and 100°). The $\Delta\varepsilon$ curve is accounted for entirely by thermal broadening; of the four minima (*A*—*D*), *B* corresponds to the principal absorption maximum at 36,700 cm.$^{-1}$ and *A*, *C*, and *D* to the partially submerged bands at approximately 41,000, 35,000, and 33,500 cm.$^{-1}$ respectively. The main increment of intensity is at 32,000 cm.$^{-1}$ but a long tail runs into the visible region and is sufficient, in moderately concentrated solutions, to account for the visual thermochromism (in anisole, at 100°, $\Delta\varepsilon = +40$ at 4000 Å). As Beer's law is obeyed in the near ultraviolet region at 100°, it is concluded that the thermochromism, as ordinarily understood, is wholly a property of the undissociated molecule. The results do not prove that no fission occurs at 100° (except on the negative evidence that nothing in the spectrum is attributable to absorption by benzothiazol-2-ylthio-radicals) and, in fact, susceptibility measurements indicate a small degree of dissociation (3%) at this temperature (Cutforth and Selwood, *J. Amer. Chem. Soc.*, 1948, **70**, 278).

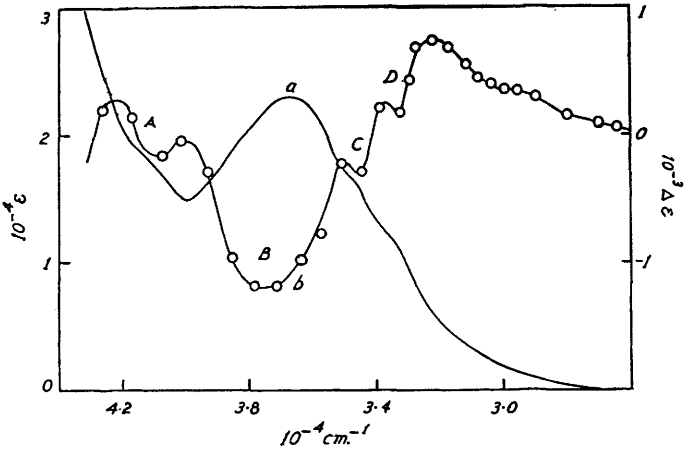

FIG. 5. *Di(benzothiazol-2-yl) disulphide in decalin.*
a, ε (19°);
b, ε (80°) − ε (19°).

Di(benzothiazol-2-yl) disulphide in anisole.

λ (Å)	3800	3750	3700	3650
Concn. (10^{-3} M)		ε, 100°		
2·80	116	162	221	298
0·56	116	161	218	298

Di-1-thionaphthoyl disulphide has been investigated by Schönberg, Rupp, and Gumlich (*Ber.*, 1933, **66**, 1932) who reported failure of Beer's law at 100° and tacitly assigned a peak at 5200 Å to the 1-thionaphthoylthio-radical. Apart from the matter of the assignment (the 5200 Å band almost certainly marks the usual $N \longrightarrow A$ transition of the undissociated molecule), the failure of Beer's law was not confirmed in the present experiments. Results are given below for two wavelengths, one near the peak of the first band and the other on the shoulder of the second band, where, according to Schönberg, deviations from Beer's law are especially large. At 100°, however, the solutions were unstable and the optical density

ε for di-1-*thionaphthoyl disulphide in anisole* (*temp.* 100°).

λ (Å)	5250		4250	
Concn. (10^{-3} M)	This paper	Schönberg *et al.**	This paper	Schönberg *et al.**
5	—	150	—	55
4·64	257	—	363	—
1	—	185	—	140
0·93	254	—	372	—
0·2	—	255	—	—

* Similar behaviour was reported for diphenyl disulphide (*idem*, *loc. cit.*) : this result has also been shown to be erroneous (Lecher, *Science*, 1954, **120**, 220).

slowly decreased; on cooling to room temperature some solutions (those in tetrabromoethane) were visibly turbid. It is clear therefore that irreversible fission occurs in the hot solution, probably analogous to the decomposition of benzoyl peroxide:

$$C_{10}H_7{\cdot}CS{\cdot}S\text{–}S{\cdot}CS{\cdot}C_{10}H_7 = 2C_{10}H_7{\cdot}CS{\cdot}S{\cdot}$$

$$\text{Products} \longleftarrow C_{10}H_7{\cdot}CS{\cdot}S{\cdot} = CS_2 + C_{10}H_7{\cdot} \longrightarrow \text{Products}$$

Di(tetramethylthiuram) disulphide, though not an aryl disulphide, was studied because it is a vulcanisation accelerator and is thermochromic; once again, the thermochromism has been correlated with dissociation (Koch, *loc. cit.*). In support of the dissociation hypothesis it has been claimed that solutions (in ethylene dibromide) do not obey Beer's law at 20° (Bergem, " Contributions to the Theory of Vulcanisation," A/S Askim Gummivarefabrik, Norway, 1948, pp. 136—7). Our measurements do not agree with this, and within rather wide limits of experimental error (the optical density of a freshly prepared solution increases considerably on standing) we were unable to detect significant failure of Beer's law at room temperature. The explanation of Bergem's results may be that the solutions were not examined at the same time, and it is noteworthy that his ε's are all higher than ours. In view of the decomposition at room temperature (probably by initial scission of the central S–S bond) the spectrum of a hot solution was not examined.

Di(tetramethylthiuram) disulphide in ethylene dibromide.

λ (Å)	4050	4200	4340	4500	4630
Concn. (10^{-3} M)		ε (20°) of a fresh solution			
103	11·2	4·38	1·95	0·76	0·37
		ε (20°) of a solution after 24 hr.*			
103	12·4	5·5	2·7	1·1	0·53
50·5	12·6	5·4	2·6	1·1	0·51
10·2	12·2	5·2	2·5	1·1	0·54
		ε (20°) according to Bergem			
50	—	—	4·46	—	1·80
1·5	—	—	14·00	—	4·00

* Validity of Beer's law in the aged solution indicates that the decomposition is of the first order.

Assignments.—The recorded frequencies, intensities, and spectral assignments are summarised in Table 2. In general the assignments are straightforward, except for the

TABLE 2.

Probable assigt.*	$1\text{-}C_{10}H_7{\cdot}CS{\cdot}SMe$		$1\text{-}C_{10}H_7{\cdot}CS{\cdot}Ph$	$C_{10}H_7{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}C_{10}H_7$	
	n-Hexane	95% Ethanol	Decalin	*cyclo*Hexane	Anisole
$N \longrightarrow A$	20,170 (2·048)	20,520 (2·048)	16,150 (2·190)	—	19,230 (2·43)
$N \longrightarrow L_b$	*ca.* 29,400 (*s*)	~28,600 (*s*)	26,700 (3·49)	28,500 (3·96) *sh*	—
$N \longrightarrow L_a$	32,700 (4·03)	32,500 (4·03)	31,500 (4·19)	33,800 (4·21)	—
$N \longrightarrow B$	37,000 (3·74) *sh*	~37,000 (*s*)	39,200 (3·93) *sh*	—	—
$N \longrightarrow B_b$	—	45,500 (4·76)	45,400 (4·76) ‡	45,500 (4·97)	—

	$(PhO_2)CS$	$(p\text{-}MeO{\cdot}C_6H_4O)_2CS$		$(PhS)_2CS$	
	95% Ethanol	Decalin	95% Ethanol	Decalin	95% Ethanol
$N \longrightarrow A$	30,450 (1·65)	30,100 (1·88)	30,770 (1·94)	21,800 (1·50)	21,980 (1·50)
	—	—	—	32,200 (4·01) †	32,500 (4·03) †
	—	—	—	35,500 (4·08) †	36,000 (3·96 †
$N \longrightarrow L_b$	~35,700 (*s*)	35,100 (3·57) *s* 36,000 (3·69) 36,900 (3·69)	35,200 (3·57) *s* 36,360 (3·69) *sh*	—	—
$N \longrightarrow B$	42,500 (3·82) *sh*	—	40,000 (*s*)	39,700 (3·84)	40,000 (*s*)
$N \longrightarrow L_a$	>46,000	—	44,400 (4·33)	—	—

sh = shoulder; *s* = submerged maximum.

Frequencies ($\nu_{max.}$) are in cm.$^{-1}$, usually to three significant figures : values of log $\varepsilon_{max.}$ are given in parentheses.

* L_a, L_b, and B_b are excited states of the (conjugated) aromatic chromophores (Platt, *J. Chem. Phys.*, 1949, **17**, 484).

† Assignment uncertain. ‡ Solution in *cyclo*hexane.

second and third transitions of diphenyl trithiocarbonate where the interpretation is uncertain. The spectra of methyl 1-dithionaphthoate (Fig. 3) and diphenyl trithiocarbonate were measured at high temperature but, with the exception of the $N \longrightarrow A$ transitions, the principal aspect was of thermal broadening.

EXPERIMENTAL

Microanalyses by Mr. J. M. L. Cameron and Miss M. Christie.

Materials.—*Di*-p-*methoxyphenyl thioncarbonate*, obtained by condensation of thiocarbonyl chloride with quinol monomethyl ether in aqueous sodium hydroxide, had m. p. 164·5° (Found : C, 62·1; H, 4·8; S, 11·1. $C_{15}H_{14}O_4S$ requires C, 62·1; H, 4·9; S, 11·1%). The remaining compounds were purified commercial samples or were prepared by standard methods : methyl 1-dithionaphthoate, m. p. 55°; 1-naphthyl phenyl thioketone, m. p. 110°; diphenyl thioncarbonate, m. p. 106°; diphenyl trithiocarbonate, m. p. 98°; di(benzothiazol-2-yl) disulphide, m. p. 180·5°; di-1-thionaphthoyl disulphide, m. p. 167°; di(tetramethylthiuram) disulphide, m. p. 157° (decomp.).

Decalin was distilled from sodium, and passed through a column packed with silical gel previously activated *in vacuo* at 250°.

Spectra.—Extinction coefficients were measured with a Unicam SP 500 Spectrophotometer, fitted with a small electronically controlled (Vodden, *J. Soc. Chem. Ind.*, 1950, **69**, 51) thermostatic cell-compartment regulated to $\pm 0{\cdot}3°$. Water or glycol was used as bath-liquid; the latter gradually lost transparency at 100°, owing to dehydration to acetaldehyde. The solutions were examined in 1 cm. fused-quartz stoppered cells : a sealing agent was unnecessary except with ethanolic solutions, for which phosphoric oxide was used. (Silicone grease was extracted by the hot solution and affected the transmission at $\lambda < 2800$ Å.)

To eliminate the band-width of the spectrophotometer as a source of error the width of the slit was kept constant at a given wavelength, the sensitivity control being used to compensate the change in response of the photocell with temperature. The wavelength calibration of the instrument was affected by the conduction of heat from the thermostat and was standardised against a mercury or helium spectrum at each temperature; the correction at 100° was *ca.* 10 Å at 4359 Å, decreasing at shorter wavelengths. Solute concentrations *at the working temperature* were used to evaluate ε (l. mole^{-1} cm.$^{-1}$) from the readings of optical density. Except with di-1-thionaphthoyl disulphide, the extinction coefficients at room temperature were reproducible after one or more cycles of heating and cooling.

APPENDIX

The thermal shift is treated as a displacement of the whole absorption band (without change of shape) by $\Delta\nu$ along the frequency axis. If the band is approximated by a Gaussian function,

$$\varepsilon = \varepsilon_{\text{max.}} \exp(-x^2/2)\,;\quad x = (\nu_{\text{max.}} - \nu)/a_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the frequency, ν_c, corresponding to $(\Delta\varepsilon)_{\text{max.}}$ is given by the expression,

$$\nu_c = \nu_{\text{max.}} - (a_r + \Delta\nu/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(where $\nu_{\text{max.}}$ refers to the peak frequency of the absorption band before displacement) and the value of $(\Delta\varepsilon)_{\text{max.}}$, if $a_r \gg \Delta\nu$, is

$$(\Delta\varepsilon)_{\text{max.}} = 0{\cdot}6\ \varepsilon_{\text{max.}}\ \Delta\nu/a_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In practice, a different value of the parameter a is required for each wing of the absorption band. The red wing is chosen for comparison because it is influenced less by thermal broadening of the second transition; to emphasise this, the parameter a in equations (1)—(3) is specified by the subscript r. $\Delta\nu$ must be a function of the temperature change and presumably of the solvent also; but with the present measurements it is not possible to sort out these effects, and the values of ν_c and $(\Delta\varepsilon)_{\text{max.}}$ in columns 5 and 6 of Table 3 are evaluated from equations (2) and (3) with $\Delta\nu$ uniformly put equal to 100 cm.$^{-1}$.

Agreement between ν_c and the recorded frequency of $(\Delta\varepsilon)_{\text{max.}}$ (col. 2 of Table 3) is only qualitative, the recorded frequencies being on an average some 300 cm.$^{-1}$ to the red of ν_c.

According to (2), however, ν_c is independent of $\Delta\nu$ (provided a_r is $\gg\Delta\nu$) and therefore of temperature : that this condition is satisfied can be seen from Fig. 1 where the position of $(\Delta\varepsilon)_{\text{max.}}$ is unchanged at 60—115°. The values of $(\Delta\varepsilon)_{\text{max.}}$ calculated from (3) with $\Delta\nu$ = 100 cm.$^{-1}$ are all lower than the experimental, but this is deliberate and agreement would be reached with $\Delta\nu$ = 150 cm.$^{-1}$. The experimental values of $(\Delta\varepsilon)_{\text{max.}}$ include a (positive) contribution from the thermal broadening estimated, by inspection of the curves, at about one-third; the remaining two-thirds is attributed to the thermal red shift, and the preferred value of $\Delta\nu$ is therefore ~100 cm.$^{-1}$ with 150 cm.$^{-1}$ as an upper limit. The experimental peak frequencies do in fact change with temperature (Table 1) and the observed shifts are of this order; but it should be noted that the recorded values of $\nu_{\text{max.}}$ are not certain to within ±40 cm.$^{-1}$ and therefore that the direct observation of $\Delta\nu$ is subject to a considerable error.

TABLE 3.

	$(\Delta\varepsilon)_{\text{max.}}$			$\Delta\nu$ = 100 cm.$^{-1}$	
Compound *	ν (cm.$^{-1}$)	Intensity	a_r (cm.$^{-1}$)	ν_c (cm.$^{-1}$)	$(\Delta\varepsilon)_{\text{max.}}$ (Calc.)
1-$C_{10}H_7$·CS·SMe (I)	19,100	14	900	19,500	8
1-$C_{10}H_7$·CS·Ph (II)	14,500	14	1100	15,050	8
$(PhO)_2CS$ (III)	28,500	3	1600	28,900	2
(*p*-MeO·C_6H_4·O)$_2$CS (IV)	28,600	5	1400	28,650	3
$(PhS)_2CS$ (V)	20,300	7	1100	20,600	2

* The temperature range and the solvent are specified in Table 1.

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