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Structure of Organic Oxygen Compounds of Sulphur

Yu.A.Kolesnik and V.V.Kozlov

The nature of the sulphur-oxygen bond, the geometry of molecules of the types XYSO, $XYSO_2$, XSOOH, and XSO_2OH, and the character of the intramolecular interactions in these compounds are discussed. Apart from the σ-bond between sulphur and oxygen, interaction obviously occurs by means of the $3d$-orbital of sulphur and the $2p$-orbital of oxygen ($2p$-$3d$ hybridisation). The interaction of a sulphinyl group with the substituents X and Y is not conjugation, but has an induction and electron-acceptor character.

In all oxygen compounds of sulphur the sulphonyl group has a tetrahedral structure with the sulphur atom at the centre of the tetrahedron, in good agreement both with the chemical properties and with the assignment of the modes of vibration of sulphur-oxygen bonds in infrared and Raman spectra. The position ν_{SO} of the stretching bands is affected only by change in the character and length of the sulphur-oxygen bond with variation in the electronegativity of the substituents X and Y or on passing from ionised to covalent compounds. These properties of the ν_{SO} absorption bands are explained by the highly specific character of the sulphur-oxygen vibrations. The bibliography contains 139 references.

CONTENTS

I. Introduction 519
II. Groups containing a sulphur-oxygen bond 519
III. Infrared spectra of oxygen compounds of sulphur 523
1. Appearance of sulphur-oxygen bond in infrared spectra 523
2. Factors affecting position of sulphur-oxygen stretching bands 526
3. Relation between sulphur-oxygen stretching frequencies and parameters of the sulphur-oxygen bond 529
4. Intensity of ν_{SO_2} bands 529

I. INTRODUCTION

The sulphonation of organic compounds is widely used in the manufacture of many industrial products. The introduction of a sulpho-group SO_2OH into an organic molecule confers on the resulting compound several specific properties.

The chemical properties of sulpho-derivatives have been investigated in fair detail. Far less work has been done on the structure of the sulphonic acids and their derivatives, in particular on the way in which the SO_2R group interacts intramolecularly with the remainder of the molecule.

Much remains obscure in the structure of the sulpho-group itself, e.g. the character of the bonds formed by the sulphur atom, the part played by the d-orbitals of the sulphur atom in the formation of bonds, the stereochemistry of the sulpho-group, and the interaction between the sulpho-group and the rest of the molecule. There is as yet no generally accepted view on the type of electronic interaction occurring in the XSOY and XSO_2Y systems, where Y represents an organic radical and X = OH, OAlk, OAr, NR′R″, Hal, etc. Is conjugation present between the SO_2R group and the organic (in particular aromatic) radical or is this interaction different in character? Do the character and the intensity of this interaction change on passing to various derivatives of sulphonic acids? All the above questions have recently been attracting increasing attention from research workers. A study of the physicochemical properties of sulpho-compounds should obviously give an answer to these questions.

The present review covers work on the nature of sulphur–oxygen bonds and the infrared spectroscopy of oxygen compounds of sulphur.

II. GROUPS CONTAINING A SULPHUR–OXYGEN BOND

(a) Sulphur–Oxygen Bonds

Organic compounds containing sulphur–oxygen bonds are classified as sulphoxides XSOY, sulphones XSO_2Y, sulphinic acids XSOOH, sulphonic acids XSO_2OH, and also various derivatives thereof (salts, halogeno- and amino-derivatives, esters, etc.). For a long time the nature of the sulphur–oxygen bond in these compounds was a subject of discussion, and this question cannot be regarded as finally settled even at the present time.

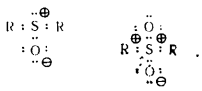
It can probably be supposed that the simple σ-bond between sulphur and oxygen is always supplemented by further interaction[1]. This additional bonding was shown by Cruickshank[2] to consist in interaction between the $2p$-orbital of oxygen and one of the $3d$-orbitals of the sulphur atom. In his view this interaction was universal, and could be considered as π-bonding.

It was assumed[3-5] that the sulphur–oxygen bond was a covalent double bond. The valency of sulphur would then be 4 in sulphoxides, and 6 in sulphones. This would require that the octet rule must be assumed to break down, i.e. that sulphur will be surrounded by 10 electrons in a sulphoxide, and by 12 electrons in a sulphone:

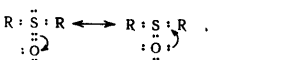


Other authors[5-7] have attributed a polar coordinate single bond to these compounds. They assumed that oxygen

was bound to sulphur only by one pair of electrons, both of which had previously belonged to the sulphur:



It was supposed that complete loss of an electron by the sulphur atom occurred, i.e. that the bond became ionic in character. In other words, the sulphur–oxygen bond was interpreted as a covalent single bond plus an ionic bond, i.e. a so called "semipolar bond". This view was still used by Suter[8] in 1948 in discussing the dipole moments of diphenyl sulphones. Such a view still exists even now[9], with the reservation that the sulphur–oxygen bond is a resonance hybrid of two structures, but nevertheless the true state is closer to a semipolar double bond than to a covalent double bond:



In some experimental papers[4,10] such a concept of the sulphur–oxygen bonds is utilised to demonstrate the chemical properties of the compounds under investigation.

In several recent papers[11–16], however, doubt has been cast on the presence of a semipolar bond. This work has been based on exact measurements of parameters of the sulphinyl group (interatomic distances, bond angles, force constants, spectral data, and certain chemical properties). A summary table of bond lengths, bond orders, force constants, and bond angles has been given in a recent paper[15].

For various compounds the length of the sulphur–oxygen bond, measured by different methods[12,17,18], varies over the range 1.39–1.55 Å. This is shorter than the length of a simple covalent bond (1.70 Å) and in many compounds is shorter than a double bond (1.49 Å), all calculated from the covalent radii for sulphur–oxygen.

For most unionised oxygen compounds of sulphur–aliphatic and aromatic sulphoxides and sulphones, sulphonic acids and their esters, and also compounds such as the halogen derivatives of sulphurous and sulphuric acids—the length of the sulphur–oxygen bond is 1.42–1.47 Å (SO_2Cl_2 1.43,[9] SO_2 1.43,[12] $(CH_3)_2SO$ 1.47,[19] and SO_2F_2 1.405 Å[20,21]). This value increases sharply on passing to ions: thus for the ions $S_2O_6^{2-}$, $S_3O_6^{2-}$, SO_4^{2-}, and $S_2O_5^{2-}$ it varies from 1.46 ($S_2O_5^{2-}$) to 1.50 Å (for the remaining ions)[9,15,20–23]. For the ion HSO_4^- the length of the S–O(H) bond is given as 1.54 Å, and that of the S=O bond as 1.46 Å.[23–25] However, crystallographic measurements for the HSO_4^- ion in $NaHSO_4.H_2O$ gave corresponding values of S–O(H) 2.613 Å and S–O 1.450 Å.[26] The maximum sulphur–oxygen bond length of 1.66 Å has been found in the compound SF_5OOSF_5,[27] and 1.64 Å in SF_5OF.[28] The probable explanation of this is that, under the influence of five fluorine atoms, which interact vigorously with the 3*d*-orbitals of sulphur, the latter take practically no part in π-bonding with the 2*p*-orbitals of oxygen[29].

The shortest sulphur–oxygen bonds are found in the molecules SO_2F_2 (1.404 Å [21]) and SOF_2 (1.412 Å [30]). No attempts were made to explain this fact, but obviously no doubt attaches to the accuracy of these results, for it has subsequently been shown[15] that the shortest sulphur–oxygen distances correspond to the highest sulphur–oxygen stretching vibrations and force constants.

Cruickshank[2] considers that the sp^3d^2 state of sulphur is actually realised in the compound SO_2F_2, where the sulphur has six octahedral σ-orbitals, while the sulphur–oxygen bond is a true double bond. The same paper shows that the order of the sulphur–oxygen bonds always exceeds 1.50 for ions (SO_3^{2-} 1.50, $CH_3SO_3^-$ 1.58, FSO_3^- 1.67). This value increases considerably for unionised compounds (CH_3SO_2OH 1.81, CH_3SO_2F 1.88, CH_3OSO_2F 1.97), which is explained[2] by the lower electronegativity of the alkyl substituents.

Force constants of the sulphur–oxygen bond have been calculated[12,31,32] for several sulphones from the spectra. Subsequent investigations have shown poor agreement between these results and more recent calculations[15]. For example, Hungarian workers[12] obtained force constants of $(14.69–14.99) \times 10^{-5}$ dyn cm^{-1} for sulphones. However, Gillespie, Robinson, et al.[15,33–35] have obtained results giving considerably smaller values (in 10^{-5} dyn cm^{-1}—SO_4^{2-} 7.1, SO_3^{2-} 3.86, HSO_4^- 8.26, H_2SO_4 8.1, 10.29, $(CH_3)_2SO_2$ 9.48, SOF_2 10.95, SO_2F_2 12.05). Values given in several papers[2,9,12,15,36] for the O–S–O bond angle usually exceed the normal tetrahedral angle (109°). The lowest value (96°) is shown by the SO_3^{2-} ion. In other ions this parameter increases ($CH_3SO_3^-$ 106°, $ClSO_3^-$ 114°). In non-ionic compounds the angle approaches 120° and above (FSO_2OH 118°, CH_3OSO_2F 120°, CH_3SO_2F 122°, $(C_6H_5)_2SO_2$ 131°).

From a comparison of numerous experimental data on the lengths, orders, and force constants of sulphur–oxygen bonds, Gillespie and Robinson conclude[15] that a direct relationship exists between bond length and force constant: with increase in the sulphur–oxygen bond length the force constant decreases. The relationship can be expressed by the equation $\lg k_{SO} = -7.41 \lg r_{SO} + 7.15$.

A similar relationship exists between bond order and force constant: with increase in the multiplicity of the bond from 1.5 to 2.0 the force constant doubles.

A non-linear relation was obtained between bond order and bond length. It is not direct[2], but is represented by a curve recalling that for bond multiplicity as a function of bond length (for the carbon–carbon bond[20]).

According to Cruickshank and Robinson[24] the constants characterising the sulphur–oxygen bond are linked by the relations

$$k_{SO} \cdot r_{SO}^{7.4} = 1.41 \times 10^7$$

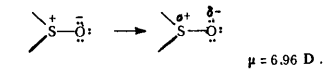
$$n_{SO} = 1.11 \times 10^{-6} \cdot k_{SO} + 0.7$$

$$r_{SO} = 1.70 - \frac{0.30}{1 + 0.46\left[\frac{2-n}{n-1}\right]}$$

$$r_{SO} = 1.69 - 0.40(n_{SO} - 1)$$

where k_{SO} is the force constant of the sulphur–oxygen bond, r_{SO} the interatomic sulphur–oxygen distance, $r_{SO}^{7.4}$ the corresponding distance for a force constant of 7.4, and n_{SO} the order of the sulphur–oxygen bond. Calculations based on these equations show satisfactory agreement with experimental values.

Calculation by means of the equation[9] for a semipolar double bond gives for the dipole moments of sulphur–oxygen bonds the value $\mu = 4.80 \times 1.45 = 6.96$ D (where 4.80×10^{-10} is the electrostatic charge on the electron, and 1.45 the experimental sulphur–oxygen distance in sulphones). This value (6.96 D) should correspond to the charge distribution



$\mu = 6.96$ D.

However, dipole moments of sulphur–oxygen bonds calculated from experimental data for certain sulphones[37] and also calculated by vector analysis[38] are considerably smaller (2.2–2.9 D), which probably indicates that a double bond is present between sulphur and oxygen.

The increase in dipole moments in the sequence

$CH_3SO_2CH_3$	$C_6H_5SO_2CH_3$	$C_6H_5SO_2C_6H_5$	p-$NH_2C_6H_4SO_2CH_3$
4.46D	4.73D	5.1D	6.09D

may constitute evidence that donor–acceptor interaction occurs between the sulphonyl group and the substituent, the sulphur acting as acceptor of electrons[13].

Several papers contain data on the dipole moments of various sulphonyl derivatives—sulphonic acids[39], sulphonyl chlorides[40,41], sulphinic acids[42].

Some workers conclude[2,9,15] that a simple σ-bond between sulphur and oxygen is supplemented by interaction between a $2p$-orbital of the oxygen atom and one of the $3d$-orbitals of the sulphur atom. This $2p-3d$ hybridisation, which is in general extremely weak, always develops, and can be regarded as π-bonding[43]. The bonding may be considerably strengthened if the electron affinity of the sulphur is increased by interaction with a strongly electronegative atom (e.g. fluorine), and also if the sulphur acquires a formal positive charge (as e.g. in a sulphonyl group). It is postulated also that the $3d$-orbitals undergo considerable compression in this type of interaction, which, of course, increases the energy of the bond.

In other words, the sulphur–oxygen bond can be regarded as in considerable measure a double bond with the electron cloud displaced towards the oxygen.

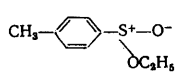
In view of the nature of the $3d$-orbitals, their overlapping with $2p$-orbitals of oxygen does not require exact agreement between the angles, as in $2p-2p$ bonding.

Similar conclusions are reached from molecular-orbital calculations of the molecules SO_2 and SO_3 and the ions SO_3^-, SO_3^{2-}, SO_4^{2-}, and $S_2O_3^{2-}$.[44,45]

(b) Geometry of the Groups XSOY, XSO_2Y, XSOOH, and XSO_2OH

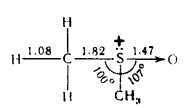
As has been shown above, it can now be regarded as proved that all cases of bond formation by sulphur involve its $3d$-orbitals. The contribution of d-orbital interaction may vary depending on the atom with which the sulphur is combined. If this atom is oxygen, the state of the sulphur atom will be s^2p^3d if surrounded by a decet of electrons, and sp^3d^2 if surrounded by a dodecet[46]. The first of these configurations corresponds to a pyramidal structure, and the second to an octahedral structure[20].

However, only one example—the sulphur hexafluoride molecule—is known of an octahedral configuration of sulphur. Such a configuration has not been found with the oxygen compounds of sulphur. Thus the study of sulphoxides, begun in 1925 by Phillips[47] on aromatic sulphoxides—ethyl toluene-p-sulphinate



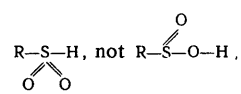
and then the work of Karrer et al.[48] showed the presence of optical isomerism in these compounds. Consequently sulphur in a sulphoxide must have a stable pyramidal structure, and may become a centre of asymmetry if all the substituents are different.

A crystallographic study of dimethyl sulphoxide[49] showed it actually to have a pyramidal structure, with the parameters



It may be supposed that in this case the nature of the bonds linking the sulphur atom will not influence the configuration. Actually, if all three bonds are semipolar σ-bonds, they will have a pyramidal p^3-distribution (the lone pair of electrons remaining in the $3s$-orbital of the sulphur[14]). If, however, the sulphur–oxygen bond is regarded as a covalent double π-bond, the bonds formed by $2p-3d$ interaction will also have a pyramidal arrangement, as Kucsman has shown[50].

Study of the vibrational spectra and of the dipole moments of sulphinic acids[42] led to the conclusion that they had the structure



In an SO_2H group sulphur is surrounded by four atoms, and the structure of the group is tetrahedral.

In sulphones, too, the structure of sulphur is close to a tetrahedron, but with considerable distortion of the bond angles. Thus for diphenyl sulphone Suter[8] gives 90° as the angle between the planes of the rings. Other workers[12,51] constructed a model of diphenyl sulphone by replacing one oxygen atom in an SO_3 group by two benzene rings, and found that one each of the two C–S and S=O bonds lies in the plane of one ring, and the other in that of the other ring. The planes of the rings are perpendicular, and the O–S–O angle is 120°. It is pointed out[12], however, that the angles may vary: for example, the O–S–O angle considerably exceeds the tetrahedral angle owing to the electrostatic repulsion between the oxygen atoms. It is assumed also that the C–S–C angle differs from 90°†. A recent work[9] gives the structure illustrated in Fig. 1 for bis-p-bromophenyl sulphone.

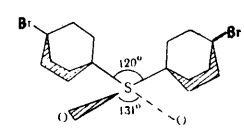
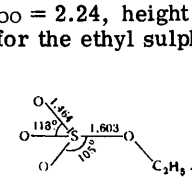


Figure 1. Diagram of molecule of bis-p-bromophenyl sulphone.

The sulpho-group in sulphonic acids and their derivatives has been assumed to have a tetrahedral structure[2,12,39,40,46,53]. However, the parameters of this pyramid are indicated only by Gur'yanova[40] for benzenesulphonyl chloride (interatomic distances), by Babaeva et al.[54] for the ion SO_3^- in Na_2SO_3 ($r_{SO} = 1.39$, $r_{OO} = 2.24$, height of pyramid 0.51 Å), and by Cruickshank[2] for the ethyl sulphate ion in potassium ethyl sulphate



Thus a tetrahedral structure, with the sulphur atom at the centre of the tetrahedron, is now generally accepted for the sulpho-group. With the polarity of the sulphur–oxygen bonds taken into account, such a structure for the

† More detailed information on the bond angles in these compounds will be found in Ref. 52.

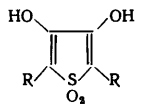
sulpho-group agrees well with the chemical properties[16], and also with the assignment of modes of vibration of sulphur–oxygen bonds in the Raman and infrared spectra[55].

(*c*) Nature of Interaction with Substituents

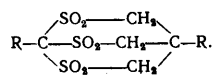
In view of the non-planar structure of the sulpho-group, it is apparently impossible to expect interaction involving conjugation of the sulpho-group with substituents. Nevertheless, it may be supposed that some interaction involving $2p-3d$ orbitals of the sulphur–oxygen bond may occur, provided that they are conveniently disposed in relation to unsaturated bonds of the substituents. There should also be some interaction of substituents transmitted through the sulphur atoms of the sulpho-group, without involving sulphur–oxygen bonds.

Both types of interaction actually occur. Thus Leandri et al.[14] showed, on the basis of the ultraviolet spectra over the range 200–300 nm for a large number of sulphoxides, that the sulphur atom is in this case in the $3sp^3$ state with one lone pair ($3s$). But besides this, weak conjugation is observed between this pair and the π-shell of unsaturated substituents. This interaction is responsible for extremely weak additional π-bonding in the sulphur–carbon(substituent) direction.

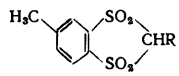
Moffitt showed[11,13] that conjugation along sulphur–oxygen bonds in sulphones is quite strongly developed when not prevented by the geometry of the molecule, e.g. in



This effect appears as a lowering of the sulphonyl frequencies in the infrared spectra and as a bathochromic shift of the bands in the ultraviolet spectra[56]. Such conjugation is also supported by results obtained by Doering[57–59], who studied the stabilising effect of the sulphonyl group on the carbanion derived from a bicyclic trisulphone of the type

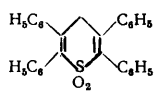


Koch and Moffitt[13] consider also that conjugation can occur in sulphones by means of a $2p$-orbital of a carbon atom (substituent), provided that these orbitals lie in the plane of the carbon–sulphur–carbon bonds. However, this is not consistent with results obtained by Jaffé[60] and Breslow[61], who studied pK_a values for the enolate ions of disulphonyl esters of the type

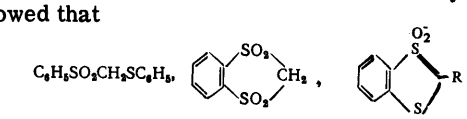


and showed that, owing to the geometrical structure of such compounds, when R = $COOC_2H_5$ [57–59] only conjugation of the type suggested by Moffitt[13] is possible. They established that there is no substantial conjugation between the $2p$-orbitals of the carbon atom and the hybrid orbitals of the sulphone.

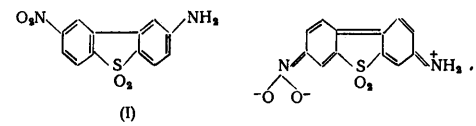
Suld and Price[62] synthesised compounds of the type



in which the "thiabenzene" ring was, in their opinion, conjugated (aromatic). This was not confirmed by Breslow[63], who showed that



have the same acidity, so that the anion is not stabilised by cyclic conjugation: i.e. it is not aromatic. Weak transmission of a conjugation effect through the sulphonyl group is suggested, even if the two rings are coplanar, by a comparison of the ultraviolet spectra of the two sulphones[9]



(I)

In compound (I) the effect of conjugation is transmitted through the sulphonyl group, whereas in the second compound it is transmitted away from this group. The ultraviolet spectrum of the second compound differs very greatly from those of (I) and of the unsubstituted sulphone.

Weak interaction of the sulphonyl group in alkyl phenyl and diphenyl sulphones is indicated also by other work[4,13,36,64–66], in which it was noted that interaction in *para*-substituted aromatic sulphones is strengthened by the introduction of electron-donor substituents. The explanation given was that the formal positive charge on the sulphur was responsible for certain of its electron-acceptor properties. The presence of a positive charge on the sulphur atom in dimethyl sulphoxide is suggested by recent spectroscopic results[67].

An assessment of the strength of interaction of the sulphonyl group from the Hammett σ-parameters[68] showed that this group possessed very little capacity for conjugation.

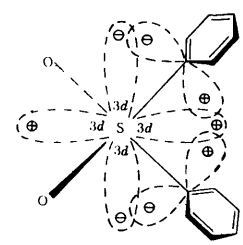


Figure 2. Scheme of electronic interaction due to $3d$-orbitals of the sulphur atom in diphenyl sulphone.

Assessing the possibility of interaction between the phenyl rings in diphenyl sulphone by means of the $3d$-orbitals of sulphur, i.e. without involving the sulphur–oxygen bonds, Price[9] points out that such interaction is quite real (Fig. 2); the two benzene rings may be non-coplanar[69]. As is evident from Fig. 2, the unsaturated orbitals of the two benzene rings—or more precisely the $2p$-orbitals of the carbon atoms—supply electrons to the free $3d$-orbitals of the sulphur, without involving the sulphur–oxygen bonds. The energy of such bonding will be slight.

In studies of the nature and strength of interaction by the sulpho-group in sulphonic acids[10,12] the authors write that "the sulpho-group (SO_2OH) does not interact with

strongly conjugated systems, such as, for example, benzene rings". This conclusion was reached from a study of the ultraviolet spectra of benzesulphonic acid. Comparison of the spectra of this acid with those of nitrobenzene, aniline, and benzoic acid showed that the SO_2OH group produces a far weaker bathochromic effect than do the nitro-, amino-, and carboxy-groups.

The vibrational structure of the absorption band is fairly well preserved in the ultraviolet spectra of substituted benzenesulphonic acids[10,64]. The authors consider that there is no conjugation between the sulpho-group and the ring, but that the sulphur exerts an electron-acceptor effect. This is demonstrated by the enhanced tendency to acylation of the amino-hydrogen atoms in the *p*-aminobenzenesulphonate ion. This occurs because the oxygen atoms of the sulpho-group in this ion carry a greater negative charge, while the positive charge on the sulphur diminishes. As a consequence, the sulphur shows less tendency to draw electrons out of the ring, which in turn weakens the displacement of the lone pair of electrons towards the ring.

To elucidate the character of the interaction between the SO_2R group and an aromatic system much information could be obtained by determining the substituent constants for the SO_2R group[70,71]. Exner[71] gives values of the induction constants σ_{ind} for a *p*-SO_2R group (SO_2O^- 0.25, SO_2NH_2 0.46, $SO_2OC_2H_5$ 0.63, SO_2Cl 0.86). It might be thought, however, that the induction constants do not reflect the actual character of the interaction, since the SO_2O^- and SO_2R groups (R = OAlk, NH_2, Hal) differ not only in the strength but also in the character of the interaction with the π-electron system of an aromatic radical.

From the above discussion it can obviously be assumed that interaction between a sulpho-group and a substituent is inductive and of electron-acceptor character rather than in the nature of conjugation. The strength of this interaction is comparatively slight. On passing to derivatives of sulphonic acids (chlorides, amides, esters) this interaction is considerably strengthened.

III. INFRARED SPECTRA OF OXYGEN COMPOUNDS OF SULPHUR

Study of the vibrational spectra of the oxygen compounds of sulphur was begun comparatively recently[18,72], at the end of the 1940s and the beginning of the 1950s. A considerable number of the papers known at the present time are still descriptive in character, and only during recent years have attempts been made to link the results of absorption spectroscopy with the structure and the properties of the oxygen compounds of sulphur. By no means all work undertaken with this aim was successful, obviously because the authors based their arguments on analogies with the carbonyl group[18]. These analogies (effect of substituents, participation in conjugation, effect of solvent) were unable, of course, to explain peculiarities observed in the infrared spectra of sulphinyl compounds, owing to the fundamental difference between these two groups both in symmetry and in electronic structure. It is now possible to link certain general features of the infrared spectra with the stereochemistry of the sulphinyl group, the nature of the substituent groups, the effect of the solvent, etc.

1. Appearance of Sulphur–Oxygen Bond in Infrared Spectra

Sulphur–oxygen bonds give strong bands in the infrared spectrum, the number of bands depending on the number of oxygen atoms attached to the sulphur. Thus the compounds XSOY give one band due to sulphur–oxygen stretching vibrations, while compounds of the type XSO_2Y give two bands. Furthermore, covalent compounds differ from ionised compounds in the position of the bands. In this way it is possible in principle to distinguish by means of the infrared spectrum the groups $\diagdown\!\!\diagup SO$, $\diagdown\!\!\diagup SO_2$, and SO_3^-. This fact can be easily explained by considering the stereochemistry of the groups XSOY and XSO_2Y from the viewpoint of the possible vibrations of atoms in these groups. The stereochemistry of sulphur and the sulphonyl group has been discussed in the preceding Section. Here we consider only papers in which the authors discuss spatial structure directly from the viewpoint of possible modes of vibration.

The earlier work showed[18,72] that the infrared spectra of sulphoxides contain one strong band, which from its position could be assigned to a sulphur–oxygen stretching vibration (by analogy with sulphur monoxide[73]). It has since been shown[14,74] that the sulphoxide group has a quasi-tetrahedral structure with p^3d or sp^3d hybridisation. As is evident from Fig. 3, the site of one of the sulphur bonds is occupied by the orbital of the lone pair of electrons of the sulphur, and as a consequence the trigonal pyramid is extended to a tetrahedron. Such a structure, containing one oxygen atom, should, of course, have one sulphur–oxygen stretching vibration. O'Loane concluded[75] that the symmetry of the XSOY group should be *C*.

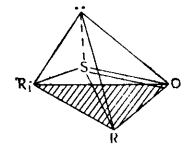


Figure 3. Structure of R_2SO group.

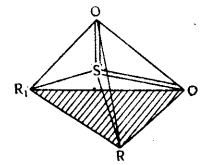
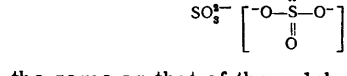
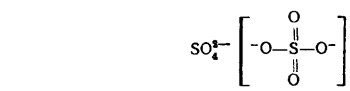


Figure 4. Structure of R_2SO_2 group

Discussion of the structure of the molecules XSO_2Y (see preceding Section) led to the conclusion that the sulphonyl group should be tetrahedral[74,76,77] (Fig. 4) or close thereto[78] both in covalent and in ionic compounds. According to Robinson[34] the spatial structure of the ion



will be the same as that of the sulphate ion



except that the position of one double bond is occupied in the sulphite ion by the lone pair of electrons of the sulphur. Consequently the modes of vibration of such ions will be identical.

These modes of vibration have been examined[79] with SO_2F_2 and the ion $CH_3OSO_2^-$ as examples[50]. The SO_2F_2 molecule has two planes of symmetry[80], one containing the two oxygen atoms, and the other the two fluorine atoms[77] (Fig. 5).

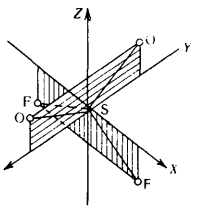


Figure 5. Diagram of SO_2F_2 molecule.

Assignment of all frequencies among types of vibrations has been made also for the simple molecules SO_3,[81] $SO_2(OH)_2$,[82,83] SO_2Cl_2,[78] and also SO_2F_2 and SO_2FCl.[84] An attempt to calculate the molecules SO_2Cl_2 and SO_2F_2 [77] was unsuccessful, for the frequencies calculated for the latter molecule did not agree with experiment. The symmetry of the group XSO_2Y is universally accepted as C_{2v},[79,80,82] and the sulphur–oxygen vibrations in such a molecule should comprise two stretching vibrations (symmetric and antisymmetric) and three deformation vibrations (twisting oscillations of sulphur–oxygen are forbidden in the infrared spectra[79]). In all a molecule having C_{2v} symmetry should describe nine normal vibrations[77], distributed among four types of symmetry:

$$C_{2v} = 4a(\nu_1; \nu_2; \nu_3; \nu_4) + a_2(\nu_5) + 2b_1(\nu_6; \nu_7) + 2b_2(\nu_8; \nu_9).$$

(*a*) Sulphur–oxygen stretching bands. Table 1[85] gives the sulphur–oxygen stretching frequencies in compounds of the type XSOY. The scatter in the results of different workers for each class of compounds does not exceed ±5 cm^{-1} from the value indicated in Table 1. It has been shown above that compounds XSO_2Y are characterised by bands due to antisymmetric and symmetric sulphur–oxygen stretching vibrations. Results for these compounds are listed in Table 2, set out in the same manner[85] as for the compounds XSOY. It is seen from Tables 1 and 2 that reliable experimental data are not available for all compounds, while certain classes of compounds have not been studied at all.

From a study of the effect of the immediate environment of an atom X in the groups $-X\begin{matrix}O\\ \\O\end{matrix}$ on the X=O bonds Bellamy[86] concluded that, by analogy with carbonyl compounds[87], there should be a correlation here between the positions of the absorption bands due to the various bonds forming this group. Although it had been shown somewhat earlier, with nitro-compounds as example[88], that no satisfactory relation of such a kind is observed in these compounds, Bellamy[86] explained this by the presence of interaction between carbon–nitrogen stretching vibrations and ν_{NO_2} symmetric vibrations; furthermore, steric interactions are also possible between a substituent X and an oxygen atom in the nitro-group. Bellamy chose for investigation the compounds RSO_2R' (sulphones) and other compounds XSO_2Y (taken from Refs. 89–91). From these data a graph was plotted of the relative positions of the sulphur–oxygen stretching bands. Fig. 6 shows that the bands due to antisymmetric and symmetric sulphur–oxygen vibrations are arranged in two fairly clustered groups. The slight scatter in the values may be caused by the fact that not all the substances were examined under identical conditions, most of them being in solution, but several in the vapour state.

Table 1. Position of bands due to sulphur–oxygen stretching vibrations in compounds of the type XSOY.

X	Y						
	O–	>C<	Cl	OH	OAlk	OC_6H_5	F
>C<	1020	1050	1150	1090	1130		
Cl	980	1150	1231		1213		
OAlk		1130	1213		1200		
OC_6H_5						1245	
F							1312

Table 2. Position of bands due to sulphur–oxygen stretching vibrations in compounds of the type XSO_2Y.

X	Y							
	O–	>C<	SR	Cl	N	OH	OR	F
C_g^u	1190 1050	1325 1140	1340 1150	1380 1170	1350 1165	1350 1160	1365 1176	1400 1200
Cl		1380 1170		1437 1205				
OR	1200 1050	1365 1175					1400 1200	
CF_3	1270 1030	1360 1120	1422 1235	1439 1239	1380 1200			1475 1240
F		1400 1200						1502 1269

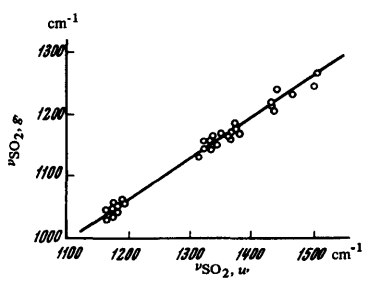


Figure 6. Relative positions of absorption bands due to symmetric and antisymmetric sulphur–oxygen stretching vibrations.

Somewhat later Robinson showed[92] that the positions of $\nu_{SO_2,g}$ and $\nu_{SO_2,u}$ are fully consistent with this relationship in other compounds of the type XSO_2Y, the ions XSO_3^- and SO_4^{2-}, and also in those cases in which the sulphonyl group is located in a ring or a chain. This correlation proved

to be very useful, since, if the position of one band in the infrared spectrum is known, the other can be found without difficulty. For this purpose the formula $\nu_u = 1.470$, $\nu_g = 359$ was proposed[86].

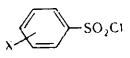
It has since proved possible to work either with the position of only one band[93] or with the half-sum of the bands $\frac{1}{2}(\nu_u + \nu_g)$‡, since this quantity is practically constant for all compounds[27,94]. The constancy of this parameter probably indicates that there is no or only very weak interaction between the sulphur–oxygen bonds in the compounds XSO_2Y.[15]

No systematic investigation was made into the shape or width of the sulphur–oxygen stretching bands. There are merely indications that these bands are usually symmetrical[95,96]. The band due to antisymmetric sulphur–oxygen stretching vibrations in compounds XSO_2Y is almost always broad and is often split into several maxima[97,98]. The band due to symmetric vibrations appears as a single peak (except in the case of $RSO_2NR'R''$ [99]), which is very convenient for the determination of intensities[100].

(*b*) Sulphur–oxygen deformation vibrations. Information on other modes of vibration of sulphur–oxygen bonds is still more scanty than that on the stretching vibrations, and is often less reliable. No systematic searches for these vibrations have been made. As has been shown above, among nine normal vibrations in a molecule X_2SO_2 there should be four deformation vibrations involving the sulphur–oxygen bonds—ν_3 (A_1) scissor, ν_7 (B_1) rocking, ν_9 (B_2) rocking, and ν_5 (A_2) twisting.

Table 3 shows that the majority of compounds investigated are various sulphonyl chlorides; there are far fewer representatives of sulphonic acids and their derivatives or of ions. The frequency ranges are 500–600 cm^{-1} for acid halides, 775–900 cm^{-1} for sulphonic acids and their esters, and 530–670 cm^{-1} for various ions. It is not yet possible to draw any definite conclusions from available data, either on the exact value of δ_{SO} nor, still less, on the influence of various factors on them.

Table 3. Position of bands due to deformation vibrations δ_{SO}.

Compound	Frequency, cm^{-1}	Mode of vibration	Ref.
SOF_4	481	wagging	
	640	wagging	
SO_2Cl_2	586	scissors	80
SO_2F_2	544	deformation	84
	539	rocking	
SO_2FCl	480	deformation	84
	505	rocking	
$SO_2(OH)_2$	563	deformation	84
	563	rocking	
CH_3SO_2OH	480	wagging	101*
	501	rocking	
	534	scissors	
$SO_2(OH)Cl$	482	deformation	84
	513	rocking	
$SO_2(OH)F$	556	wagging	101*
	545	or scissors	
	568	rocking	
	556		
SO_2	519	deformation	
CH_3SO_2Cl	528	ditto	76
CH_3SO_2F	534	»	
$ArSO_2OH$	860	»	102
$C_6H_5SO_2OC_2H_5$	900	»	98
$CH_3C_6H_4SO_2OC_2H_5$	788	»	98
$TolylSO_2OC_2H_5$	778	»	98
$AlkSO_2Cl$	565	»	103
	590	scissors	
	545	rocking	
	532—570	rocking	97**
	565—610	scissors	
	570	deformation	104
$AlkSO_2O^-$	620	deformation	
	530	antisymmetric	
$AlkSO_2O^-$		deformation	
	590	symmetric	104
SO_3^{2-}	615—660	deformation	105
		ditto	
SO_4^{2-}	580—670	»	
HSO_4^-	570—600	»	
		deformation	
SO_3^{2-}	494	symmetric	
	632	deformation	54
$(NH_4)_2SO_4$	616—655	symmetric	106
		deformation	

* Small differences in frequency are observed with liquid and gaseous specimens.

** For compounds of the type $R(SO_2Cl)_2$ the authors indicate that the bands are split into two.

(*c*) Other bands in the spectra of compounds XSOY and XSO_2Y. Published information on the presence of other vibrations involving sulphur–oxygen bonds in the infrared spectra of oxygen compounds of sulphur is extremely scanty, and it all relates to sulphonyl chlorides. Thus for benzenesulphonyl chloride a band has been found at 800 cm^{-1} and assigned to vibrations of the S–OR group[103]. Bands at 407 or 413 cm^{-1} [78] in the $HOSO_2$. .Cl molecule and a band at 412 cm^{-1} in the $HOSO_2OH$ molecule[107] are assigned[107] to the S–OH group.

With compounds XSO_2Y a band of moderate intensity is often observed in the region of 1100 cm^{-1}. The assignment of this band is still a matter for discussion. This band in the ion SO_4^{2-} in aqueous solution and in the solid state (at 1104 and 1108 cm^{-1} respectively) is attributed by Herzberg[73] to one of the main skeletal vibrations of the tetrahedron. In sulphates $MSO_4.nH_2O$ it is located at 1105–1090 cm^{-1}.[108,109]

This band is almost always present in covalent compounds. It has frequencies of 1063–1072 cm^{-1} in propanesulphonic acid and its anhydride[110]. In sulphinic acids Detoni and Hadzi[102] found it at 1000 cm^{-1} and ascribed it to sulphur–oxygen oscillations in the appropriate structures. Their results indicate that this band is more intense in the esters than in the acids themselves. The weakening of intensity and some lowering of its frequency in the free acids are explained by intermolecular hydrogen bonding.

Study of aromatic sulphonyl chlorides showed[76,98,103] the presence of a band of moderate intensity in the range 1095–1099 cm^{-1}. It was regarded as characteristic of an aromatic chlorosulphonyl group ($ArSO_2Cl$). It has been suggested[91,111] that this band may belong either to sulphur–nitrogen vibrations in sulphonamides§ or to the first overtone of sulphonyl deformation vibrations, and it may also be due to planar carbon–hydrogen deformation vibrations.

Detoni and Hadzi[98] showed that a band always appeared at 1060–1100 cm^{-1} in a large number of compounds comprising sulphonic acids (other than ethanesulphonic acid), their esters, chlorides, and amides. This band was therefore regarded as the first overtone of an O–SO deformation vibration, analogous to the overtone of OSO in SO_2Cl.[80]

Bellamy[115], who detected this band in diphenyl sulphoxide at 1096 cm^{-1}, studied its displacements under the influence of the solvent. He assigned this band to vibrations of a phenyl ring, and explained its displacement on passing to polar solvents by the presence of Fermi resonance.

‡ This was first suggested in 1949.[18]

§ In some investigations of the infrared spectra of aromatic sulphonyl chlorides, however, this band was not observed [112,113]. Tosilini[114] assigned the frequency 829–910 cm^{-1} in compounds $RSO_2N:CH.R'$ to vibration of the sulphur–nitrogen bond.

Some part of the polar character of the sulphur–oxygen bonds is then transferred to absorption by an aromatic ring. This is supported by the fact that, in a strongly polar solvent, where the sulphur–oxygen bands undergo the greatest shifts, the intensity of the 1096 cm^{-1} band drops sharply.

Thus it is evidently still premature to draw final conclusions on the assignment of the 1100 cm^{-1} band.

2. Factors affecting Position of Sulphur–Oxygen Stretching Bands

The geometry of the groups enclosing the sulphur–oxygen bonds is of decisive importance among the various factors influencing the position of bands due to stretching vibrations of these bonds. As has been shown above, the stereochemistry of sulphur in various valency states leads to a tetrahedral or nearly tetrahedral structure for both XSOY and XSO_2Y compounds. It can therefore be assumed that the influence of both substituents and other factors on the position of these stretching bands is explained by the same causes in both classes of compounds. We shall therefore discuss all the information on the various factors for the two classes of compounds together. However, it is useful to consider covalent compounds separately from ionic compounds, since the sulphur–oxygen frequencies in the latter are far less sensitive to the various factors.

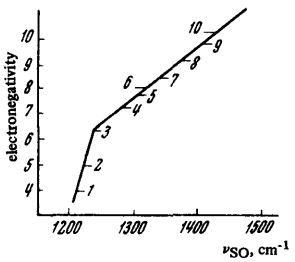


Figure 7. Correlation of electronegativity of substituents with position of sulphur-oxygen stretching bands in compounds R_2SO and R_2SO_2:
1) $(RO)_2SO$; *2*) ROSOCl; *3*) $SOCl_2$; *4*) $(RO)_2SO_2$; *5*) RSO_2OR; *6*) SOF_2; *7*) RSO_2; *8*) RSO_2Cl; *9*) SO_2Cl_2; *10*) RSO_2F.

A. Covalent Compounds

A systematic study of the influence of substituents on the position of sulphur–oxygen stretching bands must probably be regarded as starting with a paper by Bellamy and Williams[86]. On the basis of a few published data[90] and their own experimental work they showed that symmetric and antisymmetric vibrations of sulphur–oxygen bonds in compounds RSO_2R' depend on the nature of the substituent groups.

Below we shall examine the position of sulphur–oxygen stretching bands as a function of various constants of the substituents X and Y, and also the effect of the solvent.

(*a*) Effect of substituents

Electronegativity of substituents. A relation between the position of the ν_{SO_2} frequencies and the electronegativity of the substituents was first shown by Szmant and Emerson[93]. Their results (Fig. 7) indicate that the frequencies of the sulphur–oxygen bonds increase with increase in the electronegativity of the substituent Y in compounds CH_3SOY and CH_3SO_2Y (for compounds containing a sulphonyl group they plotted the antisymmetric bands along the horizontal axis, and the effective electronegativity according to Kagaraise's data[116] along the vertical axis). It is seen from Fig. 7 that the sulphonyl group is far more sensitive to variation in the electronegativity of the substituent than is the sulphoxide group $\diagdown S{-}O \diagup$.

Robinson[92] showed that, in a large number of compounds, increase in the electronegativity of the substituents is accompanied by a shift in the antisymmetric and symmetric sulphur–oxygen bands to higher frequencies (Table 4).

Table 4. Position of ν_{SO_2} bands in compounds XSO_2Y.

Group	Type of compounds	ν_{SO_2}, cm^{-1}	
		symmetric	antisymmetric
C—SO_2—F	sulphonyl fluorides	1203—1210	1401—1412
C—SO_2—Cl	sulphonyl chlorides	1169—1185	1365—1390
C—SO_2—O	sulphonic acids and esters	1165—1185	1360—1375
C—SO_2—N	sulphonamides	1152—1169	1336—1358
C—SO_2—S	thiosulphonates	1144—1154	1331—1342
C—SO_2—C	sulphones	1136—1160	1307—1334
O—SO_2—F; F—SO_2—F etc. HSO_3F		1230—1260	1445—1510
O—SO_2—Cl; $HOSO_2Cl$ etc. $S_2O_5Cl_2$		1205—1225	1408—1452
O—SO_2—O	covalent sulphates	1137—1195	1390—1415
N—SO_2—N	sulphamides	1163	1350

Thus a linear relation exists between these two parameters, the rise in the frequency ν_{SO} corresponding exactly with the increase in the electronegativity of the substituent:

$$F > OF > CF_3 > OR \simeq OH > Cl \simeq \simeq CCl_3 > SR \simeq NH_2 > Ar > R.$$

This sequence reproduces in essentials Pauling's electronegativity series[117]. The highest value of sulphur–oxygen stretching vibrations has probably been found[118] for the compound SF_5OOSF_5.

Aliphatic, aromatic, and conjugated substituents X and Y. The replacement of aliphatic by aromatic substituents in sulphoxides produces a considerable drop in the frequency ν_{SO} in non-polar solvents[96] (cm^{-1}):

CH_3SOCH_3	1069
$C_6H_5CH_2SOCH_2C_6H_5$	1056
$C_6H_5SOCH_2C_6H_5$	1054
$C_6H_5SOCH_3$	1055
$C_6H_5SOC_6H_5$	1052

Contrary to the views of Bellamy[85], the compounds XSO_2Y exhibit several differences in the position of absorption frequencies between diaryl and dialkyl sulphones. This is readily noticeable in the spectra of sulphones, but is far less readily seen in the spectra of other compounds[119] (Table 5). From Table 5 it is seen that, if the sulphonyl group is linked with two alkyl radicals, the symmetric frequencies ν_{SO_2} lie in the range 1136–1145 cm^{-1}, while in the diaryl or alkyl aryl derivatives this band has been displaced to the range 1150–1160 cm^{-1}. The antisymmetric stretching band is less sensitive, lying in both cases in the range 1312–1334 cm^{-1}.

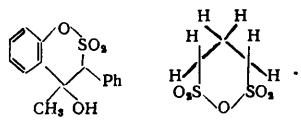
Conjugated substituents somewhat lower the frequencies of both bands (Table 5), although not always; in the compounds $RSO_2N{:}CH.R'$ the frequencies of the sulphonyl group remained practically constant whatever the substituents R and R'.

A study[93] of the cyclic sulphites $[C]_n$$S{=}O$ showed that the position of the bands was almost independent of whether the ring contained five, six, or seven carbon atoms.

Table 5. Effect of nature of substituent on position of ν_{SO_2} bands.

Compounds	ν_{SO_2}, cm^{-1} symmetric	antisymmetric	Ref.
Sulphones			
Ethyl methyl sulphone	1145	1330	72
Methyl phenyl sulphone	1160	1334	18
Diphenyl sulphone	1158	1319	120
Methyl vinyl sulphone	1139	1312	121
Allyl methyl sulphone	1136	1307	121
Sulphonic esters			
$R{-}SO_2{-}OR'$			
Methyl ethanesulphonate	1165	1356	122
Methyl toluene-*p*-sulphonate	1185	1375	72
Phenyl toluene-*p*-sulphonate	1170	1375	123
Sulphonamides			
$R{-}SO_2{-}NH_2$			
Methanesulphonamide	1169	1336	123
Benzenesulphonamide	1167	1358	72
Sulphonyl chlorides			
$R{-}SO_2{-}Cl$			
Methanesulphonyl chloride	1175	1370	76
Benzenesulphonyl chloride	1185	1390	72

Later work has shown that the position of sulphur–oxygen stretching bands is independent of the size of the ring also in the compounds[124,110]



The infrared spectra of alkane-1-sulphonates from C_1 to C_{13} indicated no dependence of the frequency ν_{SO_2} on the length of the carbon chain. Thus the symmetric sulphur–oxygen stretching vibrations were found to be located at 1060, 1055, 1062, and 1063 cm^{-1} for C_1, C_3, C_6, and C_{12}, etc.[125]

In a study of the effect of degree of substitution at the nitrogen atom in the sulphonamide group[114] on the ν_{SO_2} frequencies it was shown that in *N*-alkylated sulphonamides the sulphur–oxygen frequencies are practically constant—ν_g = 1150–1170 cm^{-1} and ν_u = 1310–1350 cm^{-1}—and only in a quaternary sulphonamide group do they rise to 1180 and 1388 cm^{-1} respectively.

In sulphoxide complexes having the composition $[[(CH_3)_2.SO]_2M][MX_4]$ the ν_{SO} frequency was found[114] to be ~ 1000 cm^{-1} independently of the metal.

In the compounds $ArSO_2CR{:}CR'R''$ the band due to the sulphonyl group has been found[126] to depend neither on *cis–trans* isomerism nor on the nature of R, R', or R''.

The infrared spectra of twenty-seven thiosulphones $RSSO_2R'$ have been examined[127]. The properties of the sulphonyl group are unaffected by the substituent: the position of the ν_{SO_2} bands is affected neither by the nature of the radical SR nor by steric hindrance in *ortho*-substituted SAr substituents. The position of the bands due to symmetric and antisymmetric SO_2-stretching vibrations in thiosulphones $RSSO_2R'$ is analogous to that in the corresponding sulphones RSO_2R'.

An attempt has recently been made to express quantitatively the effect of substituents on the position of sulphur–oxygen stretching vibrations[94]. The formula used was

$$\frac{1}{2}(\nu_g + \nu_u) = \nu^0 + x_i \cdot x_j$$

where ν^0 = 907 cm^{-1} is a universal constant and x_i and x_j are empirical constants characterising individual substituents attached to the sulphonyl group, which were determined graphically (Fig. 8). This graph was plotted from published data, and the calculated values of x_i and x_j are given in Table 6.

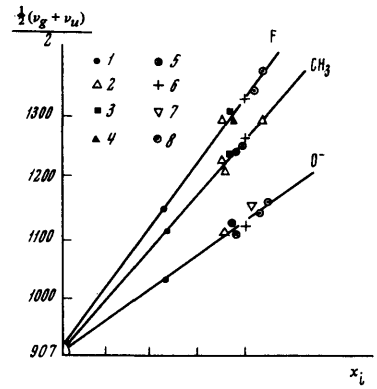


Figure 8. Explanation in text:
1) O^-; *2*) R; *3*) C_6H_5; *4*) NH_2; *5*) OR; *6*) Cl; *7*) CF_3; *8*) F.

Table 6. Values of the constants x_i and x_j for various substituents.

Substituent	x	Substituent	x
F	21.7	C_6H_5, $CH_3C_6H_4$ (*o*, *m*, *p*)	18.5
CF_3	21	Sulphonic esters	18.2
Cl	20.1	cyclo-C_6H_{11}	17.8
OR (Alk)	19.7	$-CH{=}CH_2$	17.8
OH	19.5	$-CH_2CH{=}CH_2$	17.7
NH_2	19.0	O^-	11.4

Exner combined his equation with Bellamy's equation[86], and obtained two equations from which it was possible to calculate values of ν_g and ν_u for vibrations of SO_2: ν_g = 880 + 0.810x_ix_j and ν_u = 934 + 1.190x_ix_j, the empirical constants x in these equations being given in Table 6. He considers that these empirical constants represent mainly the inductive effect of the substituents, and that adequate confirmation of this is provided by the linear relation between the Taft σ-parameter and the values of x for various substituents (Fig. 9).

Exner asserts that the quantity ν^0 = 907 cm^{-1} has a physical meaning, although the nature of this meaning is not yet known. A somewhat unexpected conclusion is that the effect of substituents on the characteristic sulphur–oxygen stretching frequencies is non-additive. Robinson's data

(Table 4 in Ref. 92) indicate strict additivity in the effect of substituents on the frequencies:

$$\begin{array}{lll} & C{-}SO_2{-}C & 1136\ cm^{-1} \\ C{-}SO_2{-}F & 1203\ cm^{-1} & \Delta\nu = 67\ cm^{-1} \\ & & \Delta\nu = 30\ cm^{-1} \\ C{-}SO_2{-}O & 1165\ cm^{-1} & \Sigma\Delta\nu = 97\ cm^{-1} \\ O{-}SO_2{-}F & 1230\ cm^{-1} & (\Delta\nu = 94\ cm^{-1}) \end{array}.$$

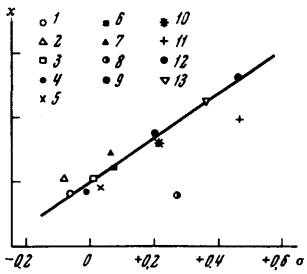


Figure 9. Explanation in text:
1) C_6H_{11}; *2)* R; *3)* $CH_2C_6H_5$; *4)* $CH_2{:}CHCH_2$; *5)* $CH_2{:}CH$; *6)* C_6H_5; *7)* NH_2; *8)* C_6H_5S; *9)* OR; *10)* OH; *11)* Cl; *12)* F; *13)* CF_3.

Table 7. Effect of solvent on the frequency ν_{SO} in dimethyl sulphoxide.

Solvent	ν_{SO}	Solvent	ν_{SO}
Cyclohexane	1083	1,2-Dichloroethane	1061
Tetrachloroethylene	1074	Dibromoethane	1061
Carbon disulphide	1070	Acetonitrile	1058
Carbon tetrachloride	1069	Nitromethane	1057
Benzene	1068	Dichloromethane	1057
Acetone	1064	Methyl chloride	1054
		Di-iodomethane	1051

(*b*) Solvent effect

The influence of solvents on the position of the ν_{SO_2} bands has been studied systematically only for the simple triatomic molecules COS and SO_2.[128] The positions of the absorption bands due to symmetric and antisymmetric stretching vibrations of sulphur dioxide have been examined in fifteen aliphatic and ten aromatic solvents. For $\nu_{SO_2,g}$ the smallest shifts (relative to the gas phase) have been found for solutions in n-hexane and in nitrobenzene (~ 6 cm^{-1}), and the largest shifts in di-iodomethane and in mesitylene (~ 11 cm^{-1}). For $\nu_{SO_2,u}$ the smallest shifts occur in n-hexane (~ 14.5 cm^{-1}) and in fluorobenzene (21 cm^{-1}), and the largest in acetone (28.5 cm^{-1}) and in mesitylene (29.5 cm^{-1}). It was established that in any solvent the shifts in the symmetric bands were always much smaller than those in the antisymmetric bands.

Relatively few data are available for more complicated compounds. As shown by Barnard et al.[18] and also by subsequent work[95,115,126,129,130], sulphoxides exhibit some displacement of the ν_{SO} band to lower frequencies in polar solvents (nitromethane) and in those capable of forming hydrogen bonds (alcohols, chloroform). This is evident in the case of dimethyl sulphoxide[27] (Table 7).

Biscarini[95] has shown that the equilibrium

$$R'R''SO + HX \rightleftarrows R'R''SO \ldots HX$$

is established in solutions of a sulphoxide in a mixture of a polar and a non-polar solvent. The compounds XSO_2Y have not been systematically studied from this point of view. The few results scattered in different papers provide no basis for generalisations: it can only be said that the ν_{SO_2} bands are displaced very slightly to lower frequencies in proton-donor solvents.

Thus the frequencies of sulphur–oxygen stretching vibrations in covalent compounds undergo substantial shifts only under the influence of change in the electronegativity of the substituents. For sulphoxides

$$\begin{array}{ll} C{-}SO{-}C & 1050\ cm^{-1} \\ F{-}SO{-}F & 1312\ cm^{-1} \end{array}$$

for sulphones, sulphonic acids, and their derivatives

$$\begin{array}{ll} C{-}SO_2{-}C & 1140\ cm^{-1} \\ & 1325\ cm^{-1} \\ F{-}SO_2{-}F & 1269\ cm^{-1} \\ & 1502\ cm^{-1} \end{array}.$$

All other factors produce far smaller displacements of the bands.

It must also be noted that the "sensitivity" of sulphonyl compounds is about half that of their carbonyl analogues[93]:

$$\begin{array}{lll} F_2CO & 1928\ cm^{-1} & \Delta\nu_{CO} = 219\ cm^{-1} \\ (RO)_2CO & 1709\ cm^{-1} & \\ F_2SO & 1312\ cm^{-1} & \\ (RO)_2SO & 1202\ cm^{-1} & \Delta\nu_{SO} = 110\ cm^{-1} \end{array}.$$

B. Ionic Compounds

Ionised compounds are characterised by a marked lowering of the sulphur–oxygen stretching frequencies: $\nu_{SO_2,g} = 986$–$1082\ cm^{-1}$ and $\nu_{SO_2,u} = 1090$–$1218\ cm^{-1}$.[92] Organic and inorganic sulphites and sulphates, both in solution and in the solid state, lie within these ranges. Such a drop in frequency is usually explained by a decrease in the "double-bondedness" of the sulphur–oxygen bond. The ion $X{-}SO_2{-}O^-$ is assumed to have a tetrahedral structure[34,54,104,106,108,109,131] of symmetry C_{3v}. There are indications that the tetrahedron is not regular[108].

The influence of various factors (primarily the nature of the substituent) on the sulphur–oxygen vibrational frequency is considerably less marked in ions than in covalent compounds. Thus Haszeldine pointed out[89] that the introduction of fluorine into the anion RSO_2O^- has no effect on the position of the band due to symmetric sulphur–oxygen vibrations, while the bands due to antisymmetric vibrations are slightly raised.

Robinson has shown[92] that increasing the electronegativity of the substituent X in the ion XSO_3^- raises the symmetric bands but has no effect on the antisymmetric bands: $\nu_{SO_2} = 1040$, 1054, 1080 cm^{-1} for HSO_4^-, $ClSO_3^-$, FSO_3^-.

Gamo[108], Ross[109], and Nakamoto[132] have shown that the bands due to stretching vibrations in crystalline hydrates of metal sulphates and in metal complexes containing the sulpho-group ($-SO_2OH$) lie in the ranges $\nu_{SO_2,g} = 1100$–$1090\ cm^{-1}$ (doublet) and $\nu_{SO_2,u} = 1140$–$1145\ cm^{-1}$, being independent both of the metal in the salts and on the composition of the complex.

Ionised organic sulphonates were studied in the form of the cyclohexylamine salts by la Lau and Dahmen[104]. These workers showed that the symmetric and antisymmetric ν_{SO_2} bands lie at 1040–1050 and 1180 cm^{-1} respectively. It was found that the position of the bands did not depend on the

nature of the radical. The antisymmetric band is usually broad, and is often split into several maxima.

With regard to other regions of the infrared spectrum, Miller [105] showed that there were several bands which could be assigned to an ionised sulpho-group: SO_3^{2-} sulphite at 615–660 cm^{-1}, SO_4^{2-} sulphate at 580–670 cm^{-1}, and HSO_4^- hydrogen sulphate at 570–600 cm^{-1}. Although recent papers have been specially devoted to the infrared spectra of sulphuric acid [82,83,133–135], the assignment of bands in these spectra encounters great difficulties, primarily owing to the fact that sulphuric acid and its aqueous solutions are strongly associated. Furthermore, the spectrum of H_3O^+ (the oxonium cation) is superimposed on that of sulphuric acid itself, which also greatly increases the difficulty of assignment.

Conversion of a covalent into an ionic compound substantially lowers the frequencies of stretching vibrations [136]. This indicates that a large negative charge is delocalised on the oxygen atoms and that the sulphur–oxygen bonds are lengthened, becoming at the same time more "single" and simple. The proportion of 3*d*-orbital interaction with the sulphur atom correspondingly diminishes, and transmission of a substituent effect to the sulphur–oxygen bond in the ion is hindered.

3. Relation between Sulphur–Oxygen Stretching Frequencies and Parameters of the Sulphur–Oxygen Bond

The correlation of parameters characterising the sulphur–oxygen bond with the frequencies of sulphur–oxygen stretching vibrations forms the subject of a single paper by Gillespie and Robinson [15], in which practically all the known experimental information is assembled.

(*a*) Bond lengths and angles. These workers found a definite link (Fig. 10) between the sulphur–oxygen bond lengths determined by various methods, both for covalent and for ionic compounds, and the position of the bands due to sulphur–oxygen stretching vibrations. They regard this relation as universal, and it can be used to predict such bond lengths in molecules where direct measurement is not possible. The accuracy of a prediction is ±0.02 Å.

It has been shown also that a linear correlation exists between the O–S–O bond angles and the sulphur–oxygen stretching frequencies (Fig. 11). Gillespie and Robinson showed further that these angles can be evaluated from the equation $\nu_{SO_2,g}/\nu_{SO_2,u} = \frac{1}{2}(1 + \cos^2\alpha)/(1 + \sin^2\alpha)$, if the frequencies are known. Values showing good agreement with experiment are obtained both by calculation and by interpolation (Fig. 8).

(*b*) Force constants of sulphur–oxygen bond. Gillespie and Robinson assume that there is no interaction between the sulphur–oxygen vibrations in the $\diagdown SO_2$ group, as also with other vibrations in the molecule¶. Then the force constant can be deduced from a consideration of the sulphonyl group as a simple triatomic molecule:

$$k_{SO} = \frac{5.889 \cdot \nu_{SO_2} \cdot 10^{-2}}{\left(\frac{1}{m_S} + \frac{1}{m_O}\right)} = 0.6282\,\nu_{SO_2},$$

where m_S and m_O are the atomic weights of sulphur and oxygen. Values of k_{SO} calculated by means of this equation agree well with results obtained by other methods. These workers obtain the same relationship between the frequency ν_{SO} and the bond order as between this frequency and the bond length, since a linear relationship exists between the order and the length of a bond.

¶ However, this is not always true [115].

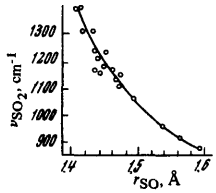


Figure 10. Correlation between position of absorption bands due to sulphur–oxygen stretching vibrations and bond length.

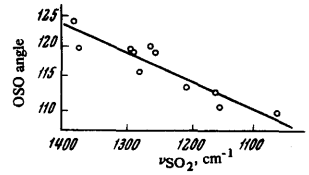


Figure 11. Correlation between sulphur–oxygen stretching frequencies and O–S–O bond angles.

Table 8. Correlation between $\nu_{SO_2,g}$ and acidity constant of sulphonic acid in sulphuric acid.

Acid	$\nu_{SO_2,g}$, cm^{-1}	K_α (25°C), mole kg^{-1}
Disulphuric	1240	0.014
Fluorosulphuric	1230	0.002
Chlorosulphuric	1209	0.001
Sulphuric	1195	—
Benzenesulphonic	1182	base
Toluene-*p*-sulphonic	1170	base

(*c*) Dissociation constants of sulphonic acids. The ν_{SO_2} vibration frequencies have been compared with the strength of the corresponding sulphonic acid, as measured by the dissociation constant of this acid in sulphuric acid [92].

It was shown that the larger is the value of K_α, the higher the frequency of the symmetric stretching vibration (Table 8). Thus the strength sequence of the various sulphonic acids relative to sulphuric acid was assessed from the SO_2-stretching frequencies to be

$$H_2S_2O_7 > FSO_3H > CF_3SO_3H > ClSO_3H < H_2SO_4 < CH_3SO_3H.$$

4. Intensity of ν_{SO_2} Bands

Very little work has been published on the intensities of the ν_{SO_2} bands. In 1961 Ghersetti [96] measured the intensity of ν_{SO} for five sulphoxides, and showed that it depended on the solvent, but did not explain this fact (Table 9). In a

non-polar solvent (carbon tetrachloride) dimethyl sulphoxide forms intermolecular dimers[67], as is shown by the changes in intensity of the 1060-cm^{-1} band. On passing to polar solvents dimethyl sulphoxide showed an increase in intensity ($10^{-4}A$), from cyclohexane 1.62 to carbon tetrachloride 1.87 and acetonitrile 1.90.

Table 9. Intensity of ν_{SO} band in some sulphoxides (dissolved in carbon tetrachloride).

Sulphoxide	ν_{SO}	$10^{-2}\epsilon^a$	$\Delta\nu_{1/2}$	$10^{-4}A$
Dimethyl	1069	7.7	15.5	1.87
Dibenzyl	1056	7.0	14.0	1.60
Benzyl phenyl	1054	8.2	10.2	1.26
Methyl phenyl	1055	7.1	9.5	1.01
Diphenyl	1052	7.8	9.0	1.00

Table 10. Intensity of $\nu_{SO_2, g}$ band in some sulphones.

Sulphone	$10^{-4}A$
Dibutyl	$1.38 \cdot 10^{-4}$
Methyl vinyl	$1.57 \cdot 10^{-4}$
Methyl phenyl	$2.1 \cdot 10^{-4}$
m-Methoxyphenyl methyl	$2.1 \cdot 10^{-4}$
p-Methoxyphenyl methyl	$3.1 \cdot 10^{-4}$

Table 11. Intensity of ν_{SO_2} stretching bands in compounds XSO_2Y.

Compounds	Stretching vibration	$10^{-2}B$	Standard deviation *s*
Sulphones	ν_{SO_2}, *g*	64.5	20.4
C—SO_2—C	ν_{SO_2}, *u*	66.5	10.7
Sulphonamides	ν_{SO_2}, *g*	91.3	18.4
C—SO_2—N	ν_{SO_2}, *u*	92.0	18.0
Sulphonic acids	ν_{SO_2}	238	50.5
C—SO_2—O	ν_{SO_2}	46.0	14.6

Five sulphones were examined by Rogers[137], who showed that the integral intensity of the ν_{SO_2} bands increases on passing to conjugated substituents (Table 10). The integral intensity of the symmetric SO_2-stretching bands can be correlated with the Taft constants (σ_{ind} and σ_R) for various sulphones[138].

Flett[100] has investigated a far larger number of compounds (Table 11). According to his results the bands are usually more intense in aromatic than in aliphatic compounds.

An attempt has been made[139] to determine sulpho-compounds quantitatively by means of the intensities of the ν_{SO_2} bands.

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Hydroxyalkylphosphines and Hydroxyalkylphosphine Oxides

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The paper discusses the condensation of phosphine and of primary and secondary phosphines with aliphatic and aromatic aldehydes and ketones, the reaction mechanisms, and the influence of the structure of the starting materials on the final products.
A detailed account is given of the chemical properties of the hydroxymethylphosphonium halides and of hydroxymethylphosphines and -phosphine oxides. Particular attention is paid to the reactions of tervalent phosphorus—oxidation, addition of sulphur, formation of quaternary phosphonium compounds with alkyl halides, alkene oxides, aldehydes, unsaturated acids, and other compounds—and also reactions at the labile hydrogen atom of the hydroxymethyl groups in hydroxymethylphosphines.
Information is given on methods for preparing organophosphorus polymers from tetrakishydroxymethylphosphonium chloride and its derivatives by the processes of polytransesterification, alcoholysis, phenolysis, and polycondensation with nitrogen-containing compounds. Problems of the practical application of the products are examined. The bibliography contains 162 references.

CONTENTS

I. Introduction 532
II. Condensation of phosphine and of primary and secondary phosphines with aldehydes and ketones 532
III. Chemical properties of hydroxymethylphosphonium halides and of hydroxymethyl-phosphines and -phosphine oxides 537
IV. Preparation of phosphorus-containing polymers based on tetrakishydroxymethylphosphonium chloride and its derivatives 539

I. INTRODUCTION

An important place in the chemistry of organophosphorus compounds is occupied by compounds containing a coordinatively unsaturated phosphorus atom. Among them are phosphites and phosphines, by means of which it is possible to synthesise diverse derivatives containing tervalent and quinquevalent phosphorus. The Michaelis and Arbuzov reactions, which have served as foundation for numerous researches on the chemistry of organic phosphorus compounds, are based on the use of acid and normal phosphites.

The present paper gives information, widely scattered in the literature, on the condensation of phosphine and of primary and secondary phosphines with aldehydes and ketones, the chemical properties of the condensation products, and the use of hydroxymethylphosphonium halides and of hydroxymethyl-phosphines and -phosphine oxides for the synthesis of organophosphorus polymers possessing flame-resistant and ion-exchange properties, and of alkylenediphosphine oxides suitable for use as extractants in the recovery and preparation of valuable elements.

II. CONDENSATION OF PHOSPHINE AND OF PRIMARY AND SECONDARY PHOSPHINES WITH ALDEHYDES AND KETONES

Hoffmann was the first to show that phosphine reacts with formaldehyde in the presence of hydrochloric acid at 80°C in the absence of stirring with the slow formation of tetrakishydroxymethylphosphonium chloride[1,2]:

$$PH_3 + 4CH_2O + HCl \rightarrow [P(CH_2OH)_4]^+\bar{Cl}.$$

It has since been established that the reaction is best conducted with a molar ratio of formaldehyde to hydrochloric acid of 4.2 : 1 at 20°C with vigorous stirring. These conditions ensure good absorption of phosphine and its reaction with formaldehyde. The yield of tetrakishydroxymethylphosphonium chloride reaches 85–90%.[3-7]

Condensation between phosphine and formaldehyde takes place not only under the influence of acids but also in the presence of many metals of Groups II–VII or their salts, as well as in the absence of catalysts. Good results are given by the use of mercury, silver, platinum, or palladium deposited on kieselguhr or pumice[7-9]. The reaction