164. *Infrared Spectra and Polar Effects. Part VI.* Internal and External Spectral Relationships.*

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The asymmetric and symmetric stretching frequencies of the group $R^1R^2SO_2$ are shown to be directly related to each other over a wide range of different molecules. Relationships also exist between carbonyl frequencies and the frequencies of some other double-bonded groups carrying the same substituents. The applications and limitations of these correlations are discussed.

Many data are available showing that the frequency shifts of mass-insensitive vibrations are in general directly controlled by the inductive and mesomeric effects of the substituents.[1-3] However, in certain cases, additional effects which may well be dipolar in character also appear to play an important part.[4, 5] As induction and mesomerism are essentially short-range effects, the number of bonds affected is small and this leads to the idea that in suitable cases the frequency shift shown by one group which has gained electrons will be paralleled by a proportionate shift in the frequency of some other bond from which they have been contributed. There should therefore be some degree of

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* Part V, preceding paper.

[1] Bellamy, *J.*, 1955, 2818.

[2] *Idem, J.*, 1955, 4221.

[3] Bellamy and Williams, *J.*, 1956, 2753.

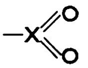
[4] *Idem, ibid.*, p. 3704.

[5] Preceding paper.

interlocking between the precise positions of some bands, which could be useful in structural diagnosis. On the other hand, any such relationship might well fail where dipolar effects occur that involve intramolecular forces in addition to the normal effects along the bonds. The study of possible relationships of this type therefore offers a possible means of exploring the operation of dipolar effects.

We have already suggested tentatively that a relationship exists between the νC=O and δCH frequencies of benzoyl compounds,[2] and have shown that the various methyl-group frequencies of many simple molecules are so closely interlocked that from a knowledge of any one fundamental it is possible to predict the others.[3] Another very clear illustration of this principle is the linear relationship which Jones and Sandorfy [6] have shown to exist between the C=O and C–O stretching frequencies of steroid acetates CH$_3$·CO·OR. In these molecules the carbonyl frequency shifts will be determined almost wholly by the electron-donating or -accepting properties of the group R, and as the C–O bond is maintained in a constant environment which will effectively offset its mass dependence, its frequency will also be dependent upon R and the two therefore are directly related. In this paper other relationships of this kind are discussed, together with some "external relationships" in which the shifts in one type of characteristic group frequency are compared directly with those shown by some other type when subjected to the same changes in environment.

(a) *Internal Relationships.*—One case in which a simple frequency relationship might be expected to arise is between the asymmetric and symmetric stretching modes of compounds containing the group (*A*), as these would be expected to be affected to proportionate extents by changes in the substituents of X. However, Brown [7] has studied this possibility in the case of the nitro-group and has not found any overall relation of this type, although reasonably good correlations occur within limited classes of related nitro-compounds. This could be due to coupling effects between the C–N stretching frequency and the symmetric NO$_2$ mode, but the fact that limited correlations occur within any one class of compound suggests that it is more likely to be connected with dipolar or steric effects, arising from the small size of the nitrogen atom and the consequent proximity of α-substituents to the oxygen atoms.



(*A*)

We have therefore studied the corresponding relationship in compounds of the type R^{1}R^{2}SO$_2$, in which any such effects should be eliminated by the large size of the sulphur atom. Data have recently become available on sulphone frequencies in various environments and include studies on SO$_2$F$_2$, sulphones, thiolsulphonates, sulphonates, and sulphonic acids.[8-10] All these data, together with those on some representative sulphonamides,[11] have been used in the construction of Fig. 1, in which the asymmetric and symmetric SO$_2$ frequencies are plotted directly against each other, and it will be seen that the expected relationship is found. In most cases solution data have been employed but vapour-phase data have been used in a few instances in which only these were available. This probably accounts for some of the scatter shown in Fig. 1, but the errors introduced in this way are small, as the SO$_2$ frequencies are not very sensitive to changes of phase and are probably both affected to proportionate extents. This correlation should find useful applications in structural diagnosis work. Each of the two $>$SO$_2$ stretching frequencies occurs over a fairly wide wavelength range so that, despite their high intensity, the identification of this group is often difficult in unknown compounds. It should, however, be possible to check a tentative identification of one of these frequencies by reference to the reasonably precise position of the other as indicated by Fig. 1.

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[6] Jones and Sandorfy, "Chemical Applications of Spectroscopy," Interscience, New York, 1956, p. 482.

[7] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[8] Haszeldine and Kidd, *J.*, 1955, 2901.

[9] *Idem, J.*, 1954, 4228.

[10] Barnard, Fabian, and Koch, *J.*, 1949, 2442.

[11] Baxter, Cymerman-Craig, and Willis, *J.*, 1955, 669.

(b) *External Relationships.*—In any comparisons between the frequency shifts shown by one mass-insensitive vibration and those of another similarly substituted, it is essential to consider the molecular geometry of the two groups. For example, if only inductive effects are operating it is possible to compare directly the carbonyl frequencies of ketones R^1R^2CO with the S=O stretching frequencies of sulphones $R^1R^2SO_2$ carrying the same substituents. A good relationship can indeed be realised in this way, as any change in the inductive effects of R will affect the C=O and S=O frequencies to proportionate extents in the two cases. However, the tetrahedral structure of the $>SO_2$ group does not allow mesomeric effects to operate upon the S=O bonds to the same extent as in the planar carbonyl group, and for this reason they are virtually insensitive to conjugation effects.[10] No overall relationships of this type can therefore be expected unless the groups under consideration have similar configurations, and for this reason we have confined the following discussion to planar structures.

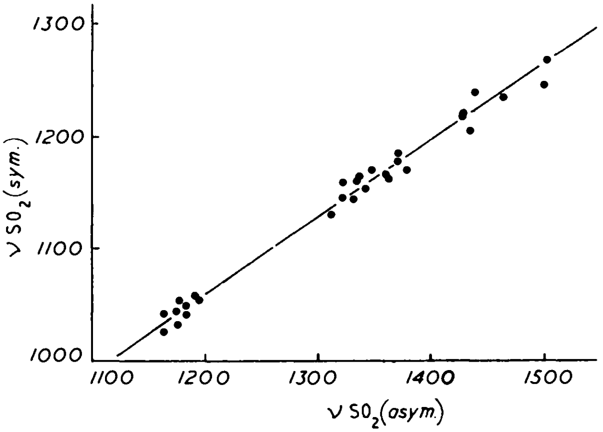

FIG. 1.

(1) $R\cdot CO\cdot CH_3$ *vs.* $R\cdot NO$ *Frequencies.*—The C=O andN =O groups are both planar. If therefore one of the carbonyl substituents is kept constant as a methyl group it should be possible to compare directly the frequencies of these two groups in similarly substituted compounds $R\cdot CO\cdot CH_3$ and $R\cdot NO$. Changes in the group R should bring about proportionate changes in both frequencies which, in the absence of mass or dipolar effects, should therefore be interrelated. Halford [12] has recently studied the influences of mass upon the carbonyl frequency from a theoretical point of view and concluded that the effect is extremely small for all masses between 12 and infinity. It is likely that similar considerations will apply in the case of the −N=O vibration. However, some differences in dipolar effects between the two series may arise in certain cases. This arises from the shorter C−N and N=O distances and the reduced R−N=O angles as compared with the carbonyl group. These factors will bring any α-substituents of R much closer to the oxygen atom in the nitroso-compounds than in the corresponding carbonyl series. This effect is clearly shown in the differing N=O stretching frequencies of *cis*- and *trans*-alkyl nitrites in which the proximity of the oxygen atom to the alkyl group leads to a lowering of the N=O frequency in the *cis*-form. For comparison with carbonyl frequencies therefore the data on *trans*-forms, in which this effect is absent, have been employed in the Table and below.

The −N=O and C=O stretching frequencies of a series of similarly substituted molecules are listed in the Table, and in Fig. 2 these are plotted directly against each other. In comparing different compounds in this way it is less safe to assume that the frequency shifts accompanying changes of state will be the same in both cases, and separate plots have

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[12] Halford, *J. Chem. Phys.*, 1956, **24**, 830.

Vapour phase			Condensed phase or solution		
R	νR·NO (cm.$^{-1}$)	νR·CO·CH_3 (cm.$^{-1}$)	R	νR·NO (cm.$^{-1}$)	νR·CO·CH_3 (cm.$^{-1}$)
Cl	1799 (*a*, *b*)	1822 (*a*, *d*)	Cl	1813 (*a*)	1806 (*a*)
Br	1801 (*a*, *b*)	1827 (*a*)	Br	1807 (*a*)	1814 (*a*)
F	1844 (*c*)	1872 (*a*)	$N(CH_3)_2$	1453 (*e*)	1639 (*k*)
OH	1696 (*d*)	1785 (*h*)	$N(C_2H_5)_2$	1462 (*e*)	1652 (*e*)
OCH_3	1682 (*e*)	1774 (*h*)	$N(C_4H_9)_2$	1460 (*e*)	1647 (*m*)
OC_2H_5	1676 (*e*)	1765 (*h*)	OC_2H_5	1653 (*e*)	1745 (*k*)
OC_4H_9	1675 (*e*)	1768 (*h*)	OC_4H_9	1650 (*e*)	1740 (*n*)
OC_5H_{11}(*iso*) ...	1675 (*e*)	1769 (*h*)	OC_5H_{11}(*iso*) ...	1650 (*e*)	1743 (*o*)
C_6H_5	1520 (*f*)	1707 (*h*)	C_6H_5	1513 (*f*)	1682 (*p*)
CF_3	1596 (*g*)	1780 (*i*)			

(*a*) This laboratory. (*b*) Burns and Bernstein, *J. Chem. Phys.*, 1950, **18**, 1669. (*c*) Woltz, Jones, and Nielsen, *ibid.*, 1952, **20**, 378. (*d*) Jones, Badger, and Moore, *ibid.*, 1951, **19**, 1599. (*e*) Haszeldine and Mattinson, *J.*, 1955, 4172. (*f*) Ref. 14. (*g*) Ref. 15. (*h*) Hartwell, Richards, and Thompson, *J.*, 1948, 1436. (*i*) Whiffen, personal communication. (*k*) Barrow, *J. Chem. Phys.*, 1953, **21**, 2008. (*l*) Cannon, *Mikrochim. Acta*, 1955, 555. (*m*) Letaw and Groop, *J. Chem. Phys.*, 1953, **21**, 1621. (*n*) Thompson and Torkington, *J.*, 1945, 640. (*o*) Hampton and Newall, *Analyt. Chem.*, 1949, **21**, 914. (*p*) Ref. 4.

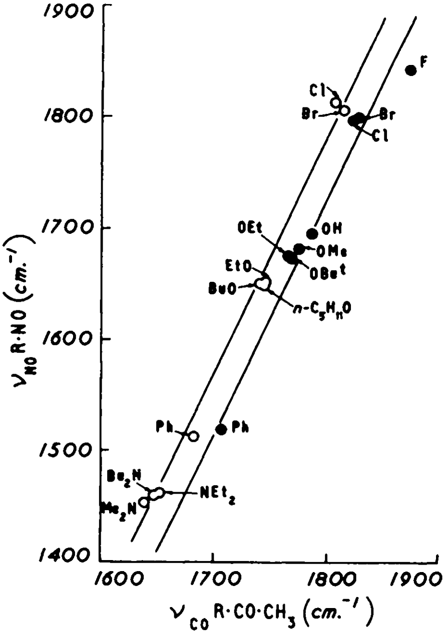

FIG. 2.

been prepared for vapour-phase (●) and condensed-phase (○) data. It will be seen that for the data quoted the agreement is reasonably good and it is clear that some generalised relation of the type predicted does exist. This has one immediately useful application in that it permits the N=O stretching frequency of monomeric alkyl nitroso-compounds to be predicted directly from data on alkyl methyl ketones. The vapour-phase frequency of acetone (1742 cm.$^{-1}$), for example, corresponds to a value of 1600 cm.$^{-1}$ for the N=O stretching frequency of nitrosomethane. The characteristic group frequencies of alkyl nitroso-compounds are difficult to determine owing to the ease with which they dimerise, and various values have been proposed in the literature. Recently Tarte [13, 14] and Jander and Haszeldine [15] have suggested that this group frequency falls near 1600 cm.$^{-1}$, and our value therefore provides a measure of support for their assignment, in contrast to the alternative range of 1400—1300 cm.$^{-1}$ suggested by other workers.[16]

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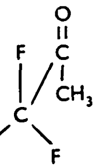
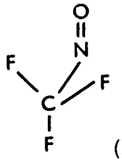
[13] Tarte, *Bull. Soc. chim. Belge*, 1951, **60**, 227, 240.
[14] *Idem, ibid.*, 1954, **63**, 525.
[15] Jander and Haszeldine, *J.*, 1954, 919.
[16] Nakamoto and Rundle, *J. Amer. Chem. Soc.*, 1956, **78**, 1113.

However, the change in the N=O frequency on passing from *cis*- to *trans*-forms, and the failure of the compound CF_3·NO to correspond in Fig. 2 to the frequency of CF_3·CO·CH_3 are clear indications of the need for caution in applying these findings, which can be invalidated by dipolar effects. The case of CF_3·NO is particularly interesting. In α-halogenated ketones it has been shown that the carbonyl frequency rises only when the halogen atom is collinear with the carbonyl group and close to it, as in (I).[4] We envisage this effect as being the induction by the halogen atom of some positive charge in the carbonyl oxygen atom whereby the covalent character of the bond is increased. In the case of CF_3·NO, however, the halogen–oxygen distance will be much reduced owing to the differences in angle and in the C–N and N=O bond lengths. In this case therefore strong van der Waals repulsive forces would be expected to arise which would lead to a configuration similar to that shown in (II). In the case of (II) the O–F distance is increased and coplanarity is lost so that the resultant effect upon the frequency would be small. The nitroso-frequency in this case would correspond to that of acetone rather than with the fluorinated material. The corresponding carbonyl frequency derived from Fig. 2 is 1739 cm.$^{-1}$, in excellent agreement with this hypothesis.


(I)


(II)

One other possible instance of an anomaly in this relationship is found in compounds of the type R·CO·N(NO)·R which give carbonyl frequencies corresponding to esters rather than to amides,[17] but this could equally well be associated with the known ability of such materials to tautomerise to the form R·CO·O·N_2·R.

One other point of interest in the Table is the rise in the N=O stretching frequencies of nitrosyl chloride and nitrosyl bromide on passing from the vapour phase to carbon tetrachloride solution, suggesting an increase in the ionic character of the molecules as the frequencies tend towards that of the NO^+ ion. This effect has been confirmed in a variety of solvents and is an interesting inversion of the usual effects of change of phase which is being further investigated.

(2) *Other External Relationships*.—A number of other possible relationships of the above type have been explored. We have compared the carbonyl frequencies of compounds $R^1R^2C=O$ with the δCH_2 deformation frequencies of similarly substituted ethylenes $R^1R^2C=CH_2$. Similarly the asymmetric NO_2 stretching frequency of nitro-compounds has been compared with the frequencies of R·NO and of R·CO·CH_3 compounds. In each case the same general pattern emerges, of what appears to be a general relationship which, however, breaks down in a few specific instances in which dipolar effects could reasonably be expected to influence one frequency more than another. These cases will not therefore be considered in detail.

Conclusions.—It is clear that the concept that inductive and mesomeric effects alone determine the scale of frequency shifts of mass-insensitive vibrations requires modification to allow for the abnormalities revealed by the intercomparison of group frequencies. Nevertheless, the large measure of agreement found confirms that they are the major basic factors although there are additional effects in some instances. From the nature of the compounds concerned we believe these effects to be dipolar in character.

In compounds such as the sulphones in which any dipolar effects will be small, useful correlations can be obtained from the inter-comparison of group frequencies. This approach is also useful in the assignment of group frequencies such as that of the –C–N=O

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[17] White, *J. Amer. Chem. Soc.*, 1955, **77**, 6008.

compounds, and provided due caution is exercised it may occasionally prove useful in the prediction of some specific frequency of an unknown compound from the known frequency of some related group which has the same substituents.

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