

*Infrared Spectra and Polar Effects. Part II.**

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A number of instances are given in which infrared-frequency shifts of mass-insensitive vibrations can be quantitatively correlated with inductive and mesomeric effects, and it is suggested that in selected cases infrared measurements may provide a reliable measure of these effects and of certain physical properties associated with them.

A NUMBER of workers have recently found empirically that group frequency shifts in the infrared region can be correlated with reactivities and other important physical properties. For example, correlations have been found between infrared-frequency shifts and the Hammett σ values of substituted benzenes (Flett, *Trans. Faraday Soc.*, 1948, **44**, 767; Davison, *J.*, 1951, 2456; Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526; Bellamy, *J.*, 1955, 2818; Scrocco and Liberti, *Ricerca sci.*, 1954, **24**, 1687; Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297). In addition, Goulden (*Spectrochim. Acta*, 1954, **6**, 129) has found a direct relation between the pK_a values of acids and their OH stretching frequencies, and Bell, Heisler, Tannebaum, and Goldenson (*J. Amer. Chem. Soc.*, 1954, **76**, 5185) have shown that the frequency of the phosphoryl absorption band is a direct function of the sum of the Pauling electronegativities of the substituents. It is the purpose of this paper to suggest a unifying basis for some of these observations, supported by some additional findings.

In considering the influence of polar effects on infrared frequencies we have confined ourselves to those group frequencies which are largely independent of mass or combination effects. The majority of such frequencies arise from vibrations of a single or double bond, $-X-Y$, in which Y is attached only to X, and any alteration in the frequency will be due primarily to a change in the electron density at X. This is determined by the inductive and mesomeric effects of the substituents on X, so that the extent of the observed frequency shifts will be a direct measure of one or both of these effects as appropriate. Similar reasoning has been applied by Richards and Thompson (*J.*, 1947, 1248) to explain the qualitative shifts observed in amide-carbonyl frequencies, but the quantitative aspects do not appear to have been explored previously. Mesomeric effects arise only in unsaturated molecules and are subject to the steric restriction that the groups producing the effect must lie in the plane of the double bond. It should therefore be possible to isolate the inductive effect by studies on saturated molecules and on unsaturated ones which are not planar.

Inductive Effects.—In saturated compounds, only the motions of hydrogen atoms are largely independent of mass effects and it is therefore encouraging to find that the H-Halogen stretching frequencies as given by Herzberg ("The Infra-Red Spectra of Diatomic Molecules," Van Nostrand, New York, 1950) are a linear function of the halogen electronegativities. Comparisons with other hydrides are complicated by the occurrence of symmetric and asymmetric vibrations but a very close connection between their frequencies and the electronegativity of the central atom is apparent from the work of Gordy (*J. Chem. Phys.*, 1946, **14**, 305) and of Heath, Linnett, and Wheatley (*Trans. Faraday Soc.*, 1950, **46**, 137).

A more straightforward case is that of the OH stretching frequencies of carboxylic acids. The pK_a values of saturated acids are a recognised quantitative measure of the inductive effect of the carboxyl substituent and Goulden's findings (*loc. cit.*) are therefore in accordance with expectation. In the aromatic series the pK_a values are a measure of both inductive and mesomeric effects so that linearity is again to be expected, but the slope of the line obtained should be different from that given by the aliphatic acids. This is of course the case.

The linear phosphoryl relation due to Bell *et al.* (*loc. cit.*) is also readily predicted on this basis, as the symmetry of the phosphate group is such as to cause the substituent groups to

* Part I, *J.*, 1955, 2818.

lie out of the plane of the P=O vibration. Mesomeric effects are therefore eliminated and the only factor influencing the P=O frequency is the inductive effect which is measured by the sum of the electronegativities of the substituents. The "group electronegativities" derived in this way have little physical meaning except as a measure of the inductive effects of the substituents, and it is reassuring that they follow approximately the scale of pK_a values for acids with similar substituents. In the case of the carbonyl absorption for which Kagarise (*J. Amer. Chem. Soc.*, 1955, **77**, 1377) has reported a similar relation the derived "group electronegativities" are widely different and do not appear to be directly related to the inductive effects. This is presumably because of the planar structure of the carbonyl group.

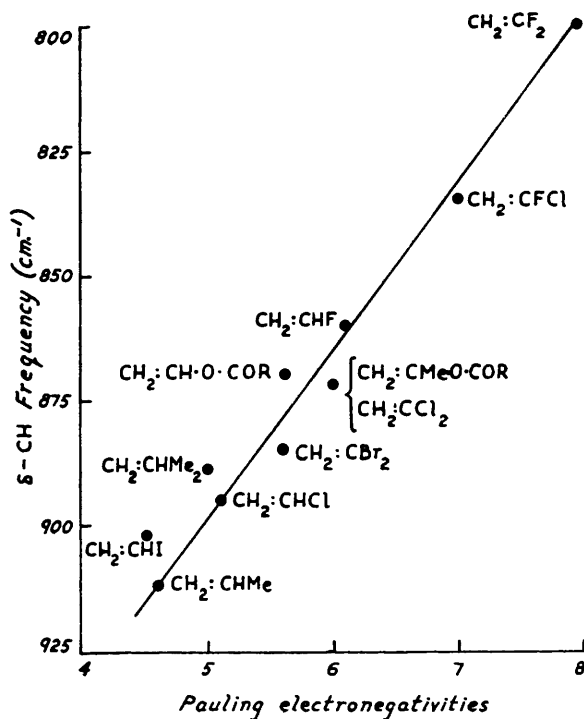
It is to be expected that other non-planar doubly-bonded groups such as >SO , will show a similar linear frequency-dependence upon the electronegativities of their substituents and, although insufficient results are yet available to confirm this, it is interesting that, unlike the carbonyl vibration, the characteristic frequencies of the SO group are very little affected by conjugation whereas they are sensitive to changes in electronegativity. Thus cyclohexyl methyl sulphoxide, methyl phenyl sulphoxide, and diallyl sulphoxide all absorb near 1050 cm^{-1} (Barnard, Fabian, and Koch, *J.*, 1949, 2442) but thionyl chloride absorbs at 1282 cm^{-1} (Schrieber, *Analyt. Chem.*, 1949, **21**, 1168).

This hypothesis can also be checked experimentally for the out-of-plane CH_2 deformations of some vinyl and isopropenyl compounds $\text{CH}_2\text{:CRR}'$. This vibration occurs near 890 cm^{-1} in the hydrocarbons and is virtually insensitive to mass effects. Owing to the planar structure it will be subject to both inductive and mesomeric effects and Torkington (*Proc. Roy. Soc.*, 1951, *A*, **206**, 17) and Sheppard and Sutherland (*ibid.*, 1949, *A*, **196**, 195) have discussed the resultant effect upon the frequency in qualitative terms. However, there are instances in which only the inductive effect plays a significant part. Thus, it is known that in the substituted ethylenes $\text{CH}_2\text{:CHCl}$ and $\text{CH}_2\text{:CFCl}$ the mesomeric effects give rise to only about 4–5% double-bond character (Good, *Phys. Rev.*, 1946, **70**, 213), so that in vinyl and vinylidene halides this frequency should be a direct function of the sum of the electronegativities of the RR' substituents. That this is realised in practise is shown in Fig. 1, in which these electronegativities are plotted directly against the observed frequencies as given by Torkington and Thompson (*Trans. Faraday Soc.*, 1945, **41**, 236; *Proc. Roy. Soc.*, 1945, *A*, **184**, 3, 211). The frequencies of hydrocarbons also fall on this line and are included in Fig. 1 but, in accordance with expectation, none of the oxygenated compounds studied by Davison and Bates (*J.*, 1953, 2607) does so, with two important exceptions. These exceptions are the vinyl and vinylidene esters $\text{CH}_2\text{:CHR}\cdot\text{O}\cdot\text{COR}$, etc. These are included in the plot using Davison and Bates's data and their agreement is particularly satisfying, as in these structures there is an internal cancellation of mesomeric effects so that they are the only oxygenated derivatives which could be expected to follow the linear electronegativity function. The existence of this internal cancellation is clearly shown in the absence of resonance energy in vinyl acetate (Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1954, p. 117) and can also be demonstrated directly from infrared data. The carbonyl frequencies of vinyl esters are abnormally high (vinyl acetate absorbs at 1776 cm^{-1}), indicating a shortening of the C=O bond. Clearly therefore any contribution from a mesomeric form $\text{CH}_2\text{:CR}^+\text{O:CR}\cdot\text{O}^-$, in which the bond would be lengthened, must be extremely small.

Combined Inductive and Mesomeric Effects.—In an unsaturated compound in which the substituents at the double bond lie in the same plane, it is to be expected that any mass-insensitive vibrations involving the double bond will be subject to the resultant of both inductive and mesomeric effects, and the frequency shifts following changes in the substituents should be a quantitative measure of this resultant effect. Unfortunately, in seeking experimental evidence it is difficult to find parameters for this resultant effect which can be accurately measured. Resonance energies, for example, determine only the mesomeric effect, so that they are unlikely to be directly related to infrared frequencies, although there does appear to be a relation with infrared intensities (Barrow, *J. Chem. Phys.*, 1953, **21**, 2008). However, two parameters which appear to offer some possibilities in this respect are atomic refractivity exaltations and, in selected cases, reactivity.

Atomic-refractivity exaltations. The property of the exaltation of the molecular refraction of visible light over the value from the sum of the individual atomic refraction constants is a common property of unsaturated systems and is a measure of the tendency for mesomeric displacement. However, when the atomic exaltation is determined by the usual method of measuring the differences between related aryl and alkyl compounds it contains also an element of electronegativity (Ingold, *op. cit.*, p. 127). This arises from the fact that electronegative groups have a greater influence on the more polarisable aryl group than on the alkyl group. The exaltations of atomic refraction constants measured in this way therefore provide at least a rough guide to the resultant of the *I* and the *M* effect. Ingold (*op. cit.*, p. 129) gives a table of positive and negative exaltations of refraction of a

FIG. 1.



series of carbonyl compounds compared with the ester forms. These values have been plotted in Fig. 2 against typical carbonyl frequencies of the various forms and it will be seen that the agreement is surprisingly good. The frequencies employed were as follows: R·COCl 1800, R·CO₂R 1740, R·CO₂H 1708, R·CO·NR₂ 1645, and R·CO₂⁻ 1560 cm.⁻¹. These were chosen as being typical values for the condensed state in which the refractivities were measured and the 1560 cm.⁻¹ band of ionised acids was chosen in preference to the mean of the asymmetric and the symmetric vibrations on the grounds that the corresponding C=O bond in aluminium halide complexes of ketones, in which only a single oxygen is involved, absorbs near this point (Susz and Cooke, *Helv. Chim. Acta*, 1954, **37**, 1273; Cooke, Susz, and Hershmann, *ibid.*, p. 1280).

A similar plot (Fig. 3) shows atomic refraction exaltations plotted against the CH₂ out-of-plane deformation frequencies of vinyl compounds. In the absence of more precise data we have had to employ exaltations based on comparisons between aromatic and alkyl compounds (Ingold, *op. cit.*, pp. 127, 128, 136) rather than between alkenyl and alkyl compounds, but it will be seen, after allowance for this, that the agreement is reasonable

and that it is now possible to take account of Davison and Bates's data (*loc. cit.*) for those oxygenated compounds which do not follow the electronegativity relation of Fig. 1.

Reactivities. The resultant of the *I* and the *M* effect is also measured directly by reactivities, in selected cases in which electromeric effects are small. For aromatic compounds the series of papers referred to above relating Hammett's σ values to infrared

FIG. 2.

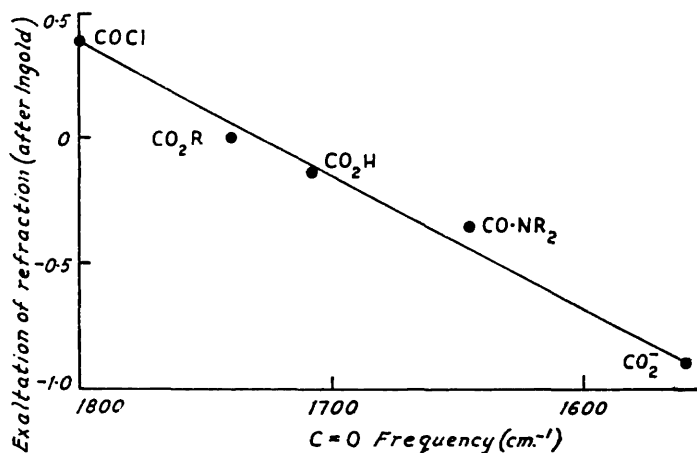
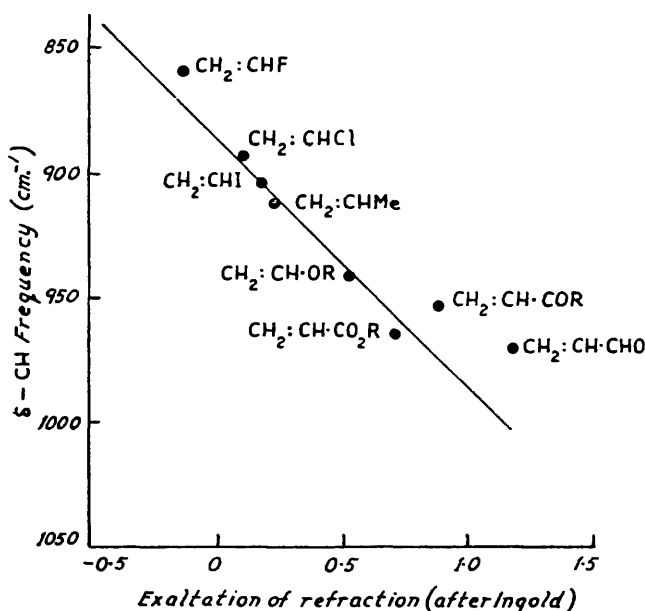


FIG. 3.



frequencies has already established that a relation exists between frequencies and reactivities within this limited series. It is more difficult to establish a similar relation for aliphatic substituents as no comparable kinetic data are available. Taft (*J. Amer. Chem. Soc.*, 1953, 75, 4231) derived a number of constants for alkyl groups which related to reactions in which only inductive effects play a part and it is reassuring to find that we obtain a linear function on plotting these against the OH stretching frequencies of the corresponding alkyl acids

given by Goulden. However no suitable data covering both *I* and *M* effects are available for this series.

For benzoyl compounds the carbonyl frequencies of any series of *m*- or *p*-substituted compounds $X \cdot C_6H_4 \cdot COR$ are a linear function of the Hammett σ values (Josien *et al.*, *loc. cit.*), and a change in the group R gives rise to a similar function which is parallel with the first. This implies that the change in the group R has brought about a constant change which is related to the change in the *I* and the *M* effects which it introduces. As, however, this cannot be demonstrated quantitatively in the absence of suitable kinetic data for alkyl groups, we have explored the possibility of obtaining some further data by a study of the internal relation between the carbonyl and the ring frequencies. If in a series of unsubstituted benzoyl compounds Ph·COR the carbonyl frequency is a function of the *I* and the *M* effect of the R group (the influence of the ring remaining constant), the demands for electrons which the carbonyl group makes upon the ring should vary proportionately in the same way. It is therefore possible that in any single compound of this type a direct relation exists between the carbonyl frequency and the δ -CH vibrations which for monosubstituted aromatic compounds occur near 750 cm.^{-1} . In monosubstituted compounds this vibration is rather complex in its origin, as it is derived from vibrations of a group of hydrogen atoms on carbon atoms of differing electron density, but it was hoped that within a constant series such as the benzoyl series any interactions due to this might be constant and that differences due to mass effects would be small. We have therefore measured the carbonyl frequencies of a variety of carbonyl compounds and the frequencies in the range $850\text{--}650 \text{ cm.}^{-1}$. The results are shown in the Table and Fig. 4. The results for benzo-

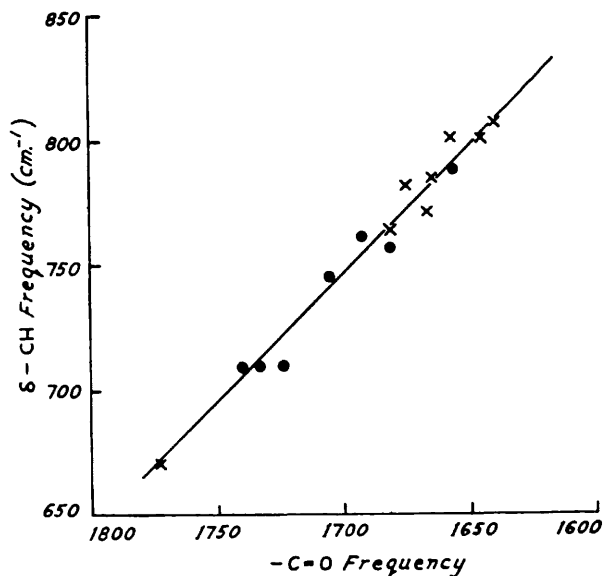
Compound	C=O frequency (cm.^{-1})	Absorption bands at $850\text{--}850 \text{ cm.}^{-1}$
Ph·CO ₂ H	1730 ^a	811 vw, 806 vw, 714 vs, 683 s
Ph·COMe	1692	761 s, 730 w, 690 s
Ph·CHO	1705	826 m, 745 s, 687 s
Ph·CO·NH ₂	1675	810 w, 790 m, 771 ms, 704 s, 684 s
Ph·CO·[CH ₂] ₂ ·COPh	1681	772 s, 735 s, 692 s
Ph·CO·CH:N·OH	1656	788 m, 698 vs, 682 w
Ph·CO·CH:CPh	1664	784 m, 750 s, 688 s
Ph·CO·NMe ₂	1645	800 s, 738 s, 724 s, 698 m
Ph·CO·NH·CH ₂ ·CO ₂ H	1640 ^b	807 m, 722 s, 707 m, 704 m
Ph·CO·CHPh·OH	1681	756 s, 702 s, 694 m, 681 m, 673
Ph·COCl	1773 ^c	772 m, 684 s, 671 vs
Ph·CO·NHMe	1657	804, 801 m, 719 s, 708 s, 694 s
COPh ₂	1664	756 m, 700 s, 694 vw, 681 vw
Ph·CO·COPh	1675	794 m, 724 m, 717 s, 690 m, 680 m
Ph·CO ₂ Me	1724	820 vw, 710 vs, 687 w, 675 w
Ph·CO ₂ Et	1733	809 vw, 710 vs, 685 w, 674 w
Ph·CO·CPh:N·OH	1667	771 w, 730 m, 692 s

^a In CCl₄. ^b In dioxan. ^c In cyclohexane.

phenone and for benzil, in which obvious interaction effects are to be expected, have been omitted from the plot but they are included in the Table and it will be seen that even these show an approximate agreement. The agreement for the remainder is very satisfactory, but these results cannot be regarded as conclusive at present owing to the difficulty in accurately identifying the δ -CH vibration in all cases. Within the range $850\text{--}650 \text{ cm.}^{-1}$ all the compounds studied show at least one additional band (near 690 cm.^{-1}) and sometimes two. The first of these is invariant in position and can be discounted, but the appearance of a second band in many cases makes the identification of the δ -CH mode difficult. In compounds such as benzaldehyde the δ -CH band is readily recognisable by its intensity, but it appears to show a progressive weakening as its frequency rises, so that in ω -hydroxyiminoacetophenone it is of only moderate intensity. In the last case identification is simplified by the absence of other bands and we are therefore encouraged in our identification of bands of similar intensity in other compounds. However, the acceptance of our identifications implies a wider range of both frequency and intensity than is usual for the δ -CH vibration and, to avoid confusion, those points in Fig. 4 for which identification can be made with reasonable certainty have been indicated by black dots and the remainder by crosses. Nevertheless, with so few bands in this region it would be a surprising coincidence

if in each case a random band happened to occur at the right point to correlate with the carbonyl frequency in the way which we have found. Margoshes and Fassel (*Spectrochim. Acta*, 1955, 7, 14) also have pointed out that the carbonyl group, along with the nitro-group, can change very considerably the δ -CH frequency, although we do not agree with their assignments in all cases. The frequencies of all bands in the 850—650 cm^{-1} region are included in the Table, and the particular band which has been employed in the plot is italicised in each case.

FIG. 4.



Conclusions.—There appear to be at least strong grounds for the supposition that the study of infrared shifts of mass-insensitive vibrations can afford a reasonably precise relative measurement of the I and the $(I + M)$ effects of substituent groups. This, coupled with the possibility of the independent measurement of M effects through intensity studies, has important implications in the field of kinetics. In addition, frequency shifts of this type may be expected to be correlated directly with other physical properties which depend upon these effects. The fact that a number of empirical correlations of this type have already been observed, in addition to these already mentioned, lends further support to this idea. Typical physical properties correlated in this way in limited cases include half-wave potentials with carbonyl frequencies (Josien *et al.*, *loc. cit.*), chelate stabilities with carbonyl frequencies (Bellamy and Branch, *J.*, 1954, 4491), bond strengths (Bellamy and Beecher, *ibid.*, p. 4487), and reactivities of alcohols (Taft, *loc. cit.*). In addition, the observed linearity of carbonyl frequencies with Hammett's σ values implies also a direct relation with redox potentials which are themselves a linear function of σ .

Experimental.—The spectra were measured in a Perkin-Elmer 21 double beam spectrometer fitted with a rock-salt prism. Samples were examined in very dilute solution in chloroform (or other nonpolar solvents where indicated), in 0.05 mm. cells. The low-frequency region was studied either in the condensed phase or in solution in cyclohexane or dioxan.

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