INFRARED INTENSITIES AND MOLECULAR STRUCTURE

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Received January 30, 1958

CONTENTS

I. INTRODUCTION

Every distinct absorption band in the infrared is characterized by the frequency at which maximum absorption occurs and by the absorption intensity. The term intensity as used here does not refer to the extinction coefficient at band maximum, but to the integrated absorption coefficient for the entire band envelope. It is this so-called "integrated intensity" which is related in a fundamental way to the electronic properties of the molecule. The integrated intensity is, when used in conjunction with a knowledge of frequency, very useful information. That it is not more commonly measured, and has in fact only recently become at all popular, is due largely to the difficulties and tediousness of the experimental procedures. With the advent of mechanical devices for performing most of the labor (88, 99), a major obstacle to increased use of the technique has been removed.

The aim of this review is to acquaint the reader with the potentialities of intensity measurements in the application of infrared spectroscopy to problems of chemical interest. The present usefulness of infrared spectroscopy in chemical research rests largely upon the empirical and semiempirical correlations of frequency data which have accumulated over the years. The future usefulness of intensity measurements will no doubt follow in the same way. The aim here has been to give literature sources for most of the recorded intensity studies, and to point out their relationship to other aspects of molecular structure.

There are no general reviews of work on infrared intensities in the literature, but some bibliographic and review material of limited scope has appeared (87, 94).

II. THEORY

This review is concerned with the intensity of absorption on the part of molecules when they are vibrating in an infrared-active normal mode. In the classical model, a molecule consisting of a set of point masses connected to one another by a set of elastic forces is considered to undergo vibrational motion in accordance with the laws of mechanics (40, 100). The $3N - 6$ vibrational degrees of freedom ($3N - 5$ for a linear molecule) of an N-atom molecule are termed the normal modes. According to classical electrodynamics any motion of an atomic system that produces a change in dipole moment leads to emission or absorption of radiation. During the vibrational motion connected with a normal vibration the charge distribution undergoes a periodic change; this may or may not result in a change in the molecular dipole moment. If it does, the vibration is said to be infrared-active. Since any vibrational motion of the molecule can be resolved as a superposition of the normal vibrations, it follows that the frequencies at which absorption and emission occur are the normal vibration frequencies. The frequencies of nuclear motion lie in the infrared, and generally it is absorption which is observed.

From a quantum-mechanical point of view the infrared absorption is seen in terms of the transition probability. If ψ_n and ψ_m represent the time-independent factors of the wave function for a molecule in the states n and m, respectively, and $\vec{M}$ is a vector representing the dipole moment, then the transition probability is proportional to the square of the term:

$$[M]^{nm} = \int \psi_n^* \vec{M} \psi_m \, d\tau \tag{1}$$

From considerations of the symmetry properties of the wave functions ψ_n and ψ_m, and of the dipole moment, $\vec{M}$, the selection rules for infrared absorption can be derived. Depending on the symmetry of the molecule, certain of the normal vibrational transitions will be infrared-active and others will be inactive.

The integrated intensity of an infrared band, A, corresponding to the i^{th} fundamental vibrational transition, is expressed as

$$A_i = \frac{N\pi}{3c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2 \tag{2}$$

where N is a number which depends upon the units in which A_i is expressed (see later), c is the velocity of light, μ is the molecular dipole moment, and Q_i is the normal coördinate for the i^{th} vibration. The normal coördinates of an N-atom molecule are not generally easy to visualize in terms of simple motions of isolated parts of the molecule. The requirements which the normal vibrations must satisfy are that they be independent of one another, and that for each the molecule remain fixed with respect to translation or rotation. Thus, Q_i, the normal coördinate for the i^{th} vibrational transition, may be a rather complex mixture of bending and stretching motions of all the atoms with respect to the bond axes. For relatively simple molecules, and for larger molecules which possess sufficient symmetry, it is possible to transform the coördinate system so that the coördinates, Q_i, can be associated with bond distances, r_k, and bond angles, θ_k. In all but the simplest cases this kind of transformation can only be made by virtue of some assumptions, which may be quite drastic, about the form of the forces which exist between the atoms.

Equation 2 is derived without the need of any assumptions which are likely to prove troublesome in practice. Electrical and mechanical anharmonicity are both ignored (25, 77). Although both kinds of anharmonicity are important in determining the intensities of overtone bands, their effect on the intensity of the fundamental is negligible. We may thus consider that, for fundamental bands, equation 2 is the starting point in relating intensities to molecular structure.

The experimentally observed intensity, A, is related to the absorption coefficient, α_ν, by

$$A = \int \alpha_\nu \, d\nu = \frac{1}{cl} \int \log_e \frac{I_0}{I} \, d\nu \qquad (3)$$

where c is a unit of concentration, l is the path length, I_0 is the incident intensity of radiation of frequency ν, and I is the transmitted intensity. The experimental procedures for securing the value of A depend upon the state of the absorbing molecules.

III. EXPERIMENTAL METHODS

A. GAS-PHASE MEASUREMENTS

The molecules of a gas at room temperature are distributed among the various rotational energy levels in accordance with the laws of statistical mechanics. When these molecules are excited to a higher vibrational level, there may be an interaction between the vibrational and rotational energies. There is no need to go into detail here regarding the selection rules which govern the nature of the spectra (40). It is sufficient to say that in addition to a single sharp absorption line corresponding to the simple vibrational transition (the Q branch), there also appears on either side of this central line a series of closely spaced narrow lines (the P and R branches). In some cases the central Q branch is absent. The entire set of lines is termed the vibration-rotation band. In order to obtain the value of the intensity for the vibrational transition it is necessary to integrate over the entire band. The integration poses some experimental difficulties, however, because the individual lines of the band are very narrow. It can be shown (101) that in order to obtain a correct estimate of the intensity of such a set of narrow lines the spectral slit width of the instrument must be small in comparison with the line width. The spectral slit width is a measure of the resolving power of the instrument. When a spectrometer is set to pass a frequency ν_0, the spectral slit width, s, is the interval between the two frequencies on either side of ν_0 which the instrument is allowing to pass with relative intensity one-half that of ν_0. Although the precise nature of the response curve for a spectrometer is rather critically dependent on design and on the condition of the entrance and exit slits, it is roughly a triangular function (98).

For most spectrometers the condition that s be small in comparison with the line width is not met for gas-phase bands. It was discovered quite early, however, that the difficulty could be overcome in large measure by causing the lines to broaden as a result of increased gas pressure (3). The line width is the result of many factors, one of which is the average time between collisions for the absorbing molecules. When the gas pressure increases and the time between collisions becomes sufficiently short, a broadening of the line results. It is thus possible to produce a "smearing out" of the rotational fine structure by introducing a nonabsorbing foreign gas in pressures of 1–50 atm. The spectral slit width of the ordinary spectrometer is narrow in comparison with the resulting wide band widths. In practice the integrated absorption,

$$B = \int \log_e \frac{I_0}{I} \, d\nu$$

is determined for a set of equivalent path lengths, pl, where p is the pressure in atmospheres, and a plot of B vs. pl is extrapolated to $pl \rightarrow 0$. The limiting slope of this plot is A, the absolute integrated intensity, expressed as a rule in units of cm.$^{-1}$/cm. atm. (77). The units of N in equation 2 are then molecules/cm.^{3} While the procedure just described is satisfactory for the P and R branches, it is not possible to broaden the Q branch to more than a few wave numbers at most by introduction of a foreign gas. An instrument of relatively high resolving power is therefore desirable when a perpendicular band possessing a Q branch is under study. Even under the best conditions, however, the intensity of the branch is likely to be underestimated from use of extrapolation techniques. Curve-of-growth methods, which are not subject to an extrapolation error, have been used in a few instances (52, 53, 65). In this method the calculated absorption in terms of pressure, path length, and unknown parameters is compared with experiment. The unknown parameters (e.g., line widths and band intensity) are adjusted to give the best fit with experiment.

With improved instrumentation and techniques the number of gas-phase measurements has steadily increased in recent years.

B. LIQUID-PHASE MEASUREMENTS

From an experimental point of view the measurement of intensity for molecules in solution or as pure liquids is a simpler matter than gas-phase measurements. Because rotational motion is damped out for almost all molecules in the liquid phase, only a single band occurs for a vibrational transition. This single band is relatively wide, however, because of collisional broadening. In the majority of cases the band shape of a single band (one which does not overlap appreciably with adjacent bands) is of the form of a Lorentz curve (68)

$$\text{Log}_e \frac{I_0}{I} = \frac{a}{(\nu - \nu_m)^2 + b^2} \tag{4}$$

where ν_m is the frequency of maximum absorption, and a and b are constants. An absorption curve of the form of equation 4 is shown in figure 1. The half-intensity width, $\Delta\nu_{1/2}$, is defined as the frequency interval separating the points on the curve at which $\log_e (I_0/I)$ has a value one-half the maximum. It is evident from the figure that the absorption approaches zero very slowly. In order to obtain the correct value for the integrated intensity, the absorption would have to be determined for frequencies far removed from ν_m. The common procedure in determining the intensity is to measure the value of $\log (I_0/I)$ at closely spaced intervals, graph these values on a plot which is linear in both frequency and $\log (I_0/I)$, and then determine the area under the curve with the aid of a planimeter. Since the spectrometer is not capable of accurately measuring small absorptions, it is not feasible to make measurements outside a small interval on either side of the band center. This situation is illustrated in figure 1, in which the dotted lines represent the limits of useful measurement. Unless a correction is made for the residual areas lying outside this interval, it will not be possible to obtain the absolute value of the intensity. Ramsay (68) has discussed methods for making this "wing correction" which are based on the assumption that the band shape is that of a Lorentz curve. The magnitude of the correction would not be appreciably different for other, similar band shapes (50). It is easily shown that the percentage correction to the measured intensity is a function of the ratio of integration interval to $\Delta\nu_{1/2}$. When this ratio is 5, for example, the wing correction is about 14 per cent.

It should be emphasized that the wing corrections are important when the absolute values of the intensity are desired. When a band common to a series of molecules is under study, the integration interval can easily be chosen to be a constant multiple of $\Delta\nu_{1/2}$, so that the correction is the same for all the compounds in the series. The relative values can then be compared. The problem of correcting for wing absorptions does not arise in gas-phase measurements, because the integration interval is large in comparison with the width of any one line in the pressure-broadened band.

Although some dependence of the intensity upon concentration may be found, it is seldom very marked when dilute solutions are employed. It is usual to determine the intensity for three or four samples with varying concentration and average these results in the absence of any obvious concentration effect. If a concentration effect is observed, the intensity is graphed vs. $\log (I_0/I)_{\text{max}}$ for a series of concentrations. The set of points is linearly extrapolated to $\log (I_0/I)_{\text{max}\to 0}$, the intercept being taken as the true intensity (68). A is commonly expressed in units of 1×10^4 mole^{-1} liter cm.$^{-2}$ N in equation 2 is then Avogadro's number.

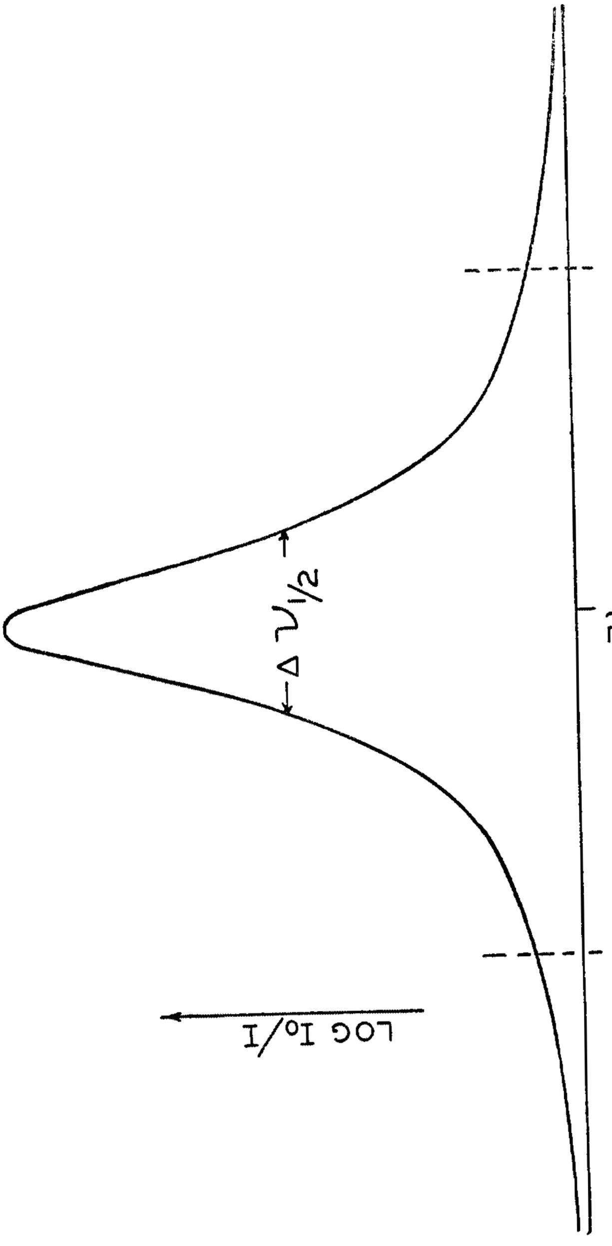

Fig. 1. Typical liquid-phase infrared absorption band

Ramsay (68) has given a formula for estimating the integrated intensity from log $(I_0/I)_{\max}$, the absorption maximum, and $\Delta\nu_{1/2}$. This formula, again based upon the assumption that the band shape is that of a Lorentz curve, has been widely used because of its convenience. If the band does not have this shape however, for one reason or another, the value taken for $\Delta\nu_{1/2}$ is liable to be seriously in error (76). In addition, for many bands $\Delta\nu_{1/2}$ is only 6–7 cm.$^{-1}$, so that an error of only 0.5 cm.$^{-1}$ in estimating this quantity is serious.

C. SOLID-PHASE MEASUREMENTS

Because of the effects of scattering and reflection it is difficult to make reliable measurements of intensity for solids. The work which has been done appears to be largely restricted to determinations of the extinction coefficient at band maximum, α_m, rather than the integrated value. The compound upon which measurements are to be made is commonly dispersed as a finely ground powder in a mineral oil or a perfluorinated oil, or it may be pressed with potassium bromide into a transparent disk (27). The value of α_m is found to depend upon particle size in a complex manner (64). It has been reported that solid solutions of ammonium halides in alkali halides, when ground and pressed into disks, yield reproducible intensity data for the ammonium-ion bands, whereas mechanical mixtures of ammonium and alkali halide crystals do not (29a). It has recently been pointed out that values of $(\partial\mu/\partial r)$, ordinarily obtained from intensity measurements, can be calculated from observations of the shape of the infrared reflection band of a solid (35).

D. A COMPARISON OF GAS-PHASE AND LIQUID-PHASE MEASUREMENTS

The spectrum of a compound measured as a gas generally is quite different from the liquid-phase spectrum, aside from the changes in band shape which have already been mentioned. Frequencies of band maxima may be shifted, new bands may appear, and intensities may change. There is little doubt that the structure of the liquid-phase molecule is markedly perturbed from that for the more or less isolated gaseous molecule. For this reason it is desirable to make use of gas-phase measurements when possible for the determination of absolute intensities. The number of compounds which are sufficiently volatile at room temperature to permit of easy gas-phase measurement is, however, comparatively small. As a result it is inevitable that a large number of compounds must be studied in solution. It is desirable, therefore, that some relationship be found between the intensities measured in solution and those obtained for the gas. In addition, since various solvents are used for solution studies, it is desirable that intensities measured in different solvents be comparable. This is a formidable problem, and a solution to it appears far off. The change in intensity of a vibrational band measured in solution as compared with the gas phase may be ascribed to the following factors:

(*a*) Specific interactions with the solvent molecules. These include hydrogen bonding and dipole-dipole interactions and are certain to be important if the solvent molecules are polar.

(*b*) The dielectric constants of the solvent, ϵ_1, and solute, ϵ_2. The term "solute dielectric constant" refers to the effective value in the cavity in which the solute molecule resides. The oscillating dipole might be thought of as immersed in a cavity of dielectric constant ϵ_2, which is in turn surrounded by a medium of dielectric constant ϵ_1.

(*c*) The geometrical shape of the solute molecule, and the location of the oscillating dipole within it. It is to be expected that the packing of the solvent around the solute molecules will be different for solutes of widely differing molecular shapes. This factor, and the location of the dipole within the soluble molecule, will determine the effective field acting on the dipole.

(*d*) Various other effects of presumably lesser importance, such as the anisotropic character of the polarizabilities of both solvent and solute molecules, short-range intermolecular forces, and the shape of the solvent molecules.

The problem relating to the intensities is closely analogous to that for the static electric moments, and it has been possible to obtain expressions for A_s/A_v, where A_s is the intensity measured in solution and A_v that for the vapor, from those originally relating μ_s and μ_v (16, 48, 67). Comparisons of theory and experiment are rendered difficult, however, by the extreme sensitivity of the intensity to the specific interactions mentioned in paragraph (a). This point is discussed further in Section IV,C.

It will be pointed out in detail later that one of the most fruitful uses of intensity results is in correlating the intensity variations in a band possessed in common by a series of molecules with other molecular properties closely related to structure. For these purposes measurements in solution are quite satisfactory, since it is only the relative intensities which are important. If all of the compounds in the series are of similar shape and size, the solvent effect is likely to be the same for all of them. The series can be studied in several nonpolar solvents to determine whether this is the case.

A word may be in order on the effect of temperature. An increasing temperature results in a change in the distribution of gas-phase molecules among the rotational energy levels, but there is no appreciable population of the vibrationally excited states for temperatures near 300°K. The redistribution among the rotational levels does not result in any significant change in the band intensity, so that the temperature is not an important consideration in gas-phase measurements (25). For solutions, however, it is another matter. It has been shown (45, 80) that the absorption at band maximum decreases with increasing temperature for a number of bands measured in solution. This decrease, with an accompanying increase in $\Delta\nu_{1/2}$, can be explained in terms of changing band shape as a result of collisional processes (11). The rate of collision of the solute molecules with the walls of the solvent cage increases with increasing temperature, and a wider band with decreased value of log $(I_0/I)_{\max}$ results. It is not clear whether the integrated intensity of the band undergoes any change, although it appears that there may be some decrease with increasing temperature (80).

Since the refractive index of the solution, known to be important in determining the intensity, changes with temperature it appears that the intensity ought to be temperature-dependent. Another explanation which has been offered for intensity change is that some vibrational modes are strongly coupled in the liquid state, and this coupling is affected by temperature (80). Although more work is needed to clarify this problem, it can at least be said that wide variations in temperature are to be avoided when measuring intensities for compounds in solution.

IV. THE RELATION OF INTENSITY TO MOLECULAR PROPERTIES

A. CALCULATION OF BOND MOMENTS AND BOND MOMENT DERIVATIVES

The subject matter of this section has been reviewed by Hornig and McKean (42). Accordingly, only the most recent work which has some bearing on the conclusions presented by these authors will be discussed here.

In order to reduce the measured quantities, $(\partial\mu/\partial q)^2$, to something which is characteristic of the individual bonds the following assumptions are needed: (*a*) the potential energy of the molecule in terms of all possible distortions is accurately known; (*b*) when a bond is stretched by an amount dr, a moment $(\partial\mu/\partial r)\,dr$ is produced in the direction of the bond; (*c*) when a bond is bent through an angle $d\theta$, a moment $\mu_0 d\theta$, where μ_0 is the "effective bond moment," is produced in the plane of bending and perpendicular to the direction of the bond; (*d*) when any one bond is bent or stretched, no changes in moments are produced in other bonds.

The fact that the first assumption is difficult to meet satisfactorily has been known for a long time, and work on intensities has not introduced much that is new in this area. The apparent failure of the last three assumptions in many instances has, however, prompted interesting and fruitful reëxamination of the ideas of bond and molecular polarity. The observed molecular dipole is conveniently considered as the sum of individual bond components: the overlap moment, the hybridization moment, and the partial ionic character (22, 81). In addition to these the moment due to the lone electron pairs, if any, must be considered. These four factors are certainly not independent of one another, but the classification is useful for purposes of discussion. The goal of the theoretical chemist is the quantitative assignment of the contribution made by each of these factors to the total change in molecular moment when the molecule is distorted.

When a bond stretches, the principal contribution to $\partial\mu/\partial r$ comes from variation in the overlap moment and in partial ionic character. Particularly large values of $\partial\mu/\partial r$ arise when one or both of the atoms involved forms part of a π-electron system. The charge distribution in such molecules is quite sensitive to bond distances, and large values of $\partial\mu/\partial r$ may result from certain stretching vibrations. Bond moment derivatives determined from different vibrations in the same molecule are frequently very different in magnitude (42, 58). It cannot be said that there is at present any satisfactory quantitative explanation for this. It does appear reasonable that in a molecule such as NH_3 the variation in partial ionic character of the N—H bonds with bond distance should be different for the stretching vibrations of different symmetry, but it is difficult to express such a notion quantitatively.

Bending motions may result in a change in the contribution from all of the factors mentioned above. The extent to which each is operative, however, depends on the form of the overall molecular distortion. In ammonia, for example, the values of μ_{N-H} calculated from the intensities of the A_1 symmetry class vibrations, assuming that the vibrations are accompanied by moment changes only within the bonds, are quite different from those derived from the E_1 class (58). In the A_1 bending vibration, a symmetrical change in the HNH angles, the moment due to the lone pair may change and thus contribute to the total change in molecular moment. If it is assumed that the bonds from nitrogen are directed along the NH axes, the hybridization above the nitrogen, and thus the lone-pair moment, may be calculated as a function of the HNH angle. In a simple treatment the N—H bond moment is assumed fixed during the vibration. Partial orbital following can be introduced as an additional refinement (58). Such a model is only partially successful in that the calculated values of the lone-pair moment do not agree well with those calculated from a fairly complete SCF LCAO[1] treatment of ammonia (41). Accurate molecular wave functions have recently been utilized for calculations of the lone-pair and bond moments (19, 36). In such models it turns out that the bonds are not directed along the lines of nuclear centers except for a single value of bond angle, and as a result the bond moments have transverse components which are strongly dependent on the valency angle. In addition, the longitudinal component of the bond moment and the lone-pair moment vary with bond angle, so that the total change in the molecular dipole is a complex resultant of all these factors.

The intensities of C—H bending vibrations have been the subject of much interesting study. Early in the history of these measurements it was thought that the variations in the effective C—H moment obtained for carbon in different hybridizations represented real variations in the static C—H bond moment. In a single molecule such as ethylene, however, the effective C—H moment varies widely for vibrations of different symmetry (34). Again, it is now clear that the contributions to the intensity are complex and cannot readily be associated with values for the static bond monents. The intensities of some of the vibrations of acetylene, ethylene, and benzene have been calculated quantum-mechanically on the basis of a molecular-orbital-type wave-function (24). The results show that the values of $\partial\mu/\partial Q$ are dependent on the degree of bond following and on the hybridization changes taking place during the vibration. Depending on the symmetry properties of the vibration, certain components of the individual bond moments may or may not contribute to the total molecular dipole change, so that the variations in calculated values of μ_{C-H} in a molecule such as ethylene can be accounted for.

The C—H intensities of solid normal paraffins have recently been treated

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[1] SCF LCAO = self-consistent field, linear combination of atomic orbitals.

theoretically (86). One of the results of this study is a value for the C—H bond moment of 0.085 Debye. This value was obtained by dropping the assumption that the C—H bond moment is fixed during a bending vibration, although it was assumed that the bond moment is directed along the line of nuclear centers.

One of the most interesting, although formidable, problems relating to infrared intensities is the evaluation of the molecular dipole moment as a function of bond distances. In general it is not possible to derive any analytical expression for the dependence of M on internuclear distance from quantum-mechanical considerations alone. Each component of the moment, M_x, M_y, and M_z, can, however, be expressed as a function of the coördinates of the atoms, such as a power series expansion in the normal coördinates (100).

Some of the earliest measurements of intensity were made on the hydrogen halides for the purpose of obtaining expressions for the electric moment as a function of internuclear distance (3, 26, 62). For a diatomic or pseudo-diatomic molecule, the dipole moment is readily expressed in terms of some function ξ of the bond coördinates such as $r - r_e$ or $r - r_e/r_e$:

$$M = \sum_{i=0}^{\infty} M_i \xi^i$$

When this expression for M is inserted in equation 1, the result is

$$[M]^{nm} = \sum_i M_i \int \psi_n^* \xi^i \psi_m \, d\tau$$

The $[M]^{nm}$ are obtained experimentally from the band intensities of the fundamental and overtone bands. The intensities are proportional to the square of this term, however, so that there is an ambiguity in the sign of each term:

$$[M]^{nm} = \pm |M_1| \int \psi_n \xi \psi_m \, d\tau \pm |M_2| \int \psi_n \xi^2 \psi_m \, d\tau \pm \cdots$$

In order to evaluate the integrals in this expression a form for the potential function must be chosen. Morse and anharmonic oscillator (38, 39) and power series (25) functions have been used, and evaluations made for the first few terms. $[M]^{01}$, $[M]^{02}$, etc., determined from the intensity results (except for sign), must then be used to obtain sets of simultaneous equations involving the M_i as unknowns. In some instances a choice of signs for M_1 is possible from structural arguments; this in turn serves to fix the sign of $[M]^{01}$ if the leading term is large. The simultaneous equations in the remaining unknowns are then set up for all possible combinations of signs of $[M]^{nm}$ with the sign of $[M]^{01}$ fixed. The choice of signs for the remaining terms, if it can be made at all, is made on the basis of various criteria, depending on the amount of data available and the potential function in use.

The requisite intensity data are difficult to obtain; for the most part only fundamental and first overtone measurements have been made (8, 59, 66, 75). The most complete set of data obtained to date is that for HCl and DCl (6, 7);

more data were obtained, in fact, than were needed for the calculation of the coefficients M_i, so that the remaining data could be used to test the results. Agreement between calculated and observed intensities is consistently better for a Morse vibrational wave-function than for the anharmonic oscillator.

B. CORRELATION OF INTENSITIES WITH OTHER INTRAMOLECULAR PROPERTIES

It is clear from what has been said in the preceding section that a detailed analysis of band intensities in terms of individual bond properties is a difficult matter. For all but the simplest molecules it is in fact out of the question. A similar situation has existed for years with regard to the determination of accurate bond-force constants from frequency data. Despite the fact that a normal coördinate treatment for almost all molecules of chemical interest is not possible, however, infrared spectroscopy has proven to be a most important physicochemical research tool. The recognition of characteristic group frequencies and the correlation of frequency variations with variations of other physical and chemical properties throughout a series of related molecules have proven particularly valuable. In the same way, the integrated absorption intensity of a band which is identified with a localized vibration in the molecule can be related semiempirically or empirically to other molecular properties. In general such studies are carried out using solutions. The applications of such intensity results to problems of chemical interest are many and varied; for this reason it seems best to discuss the work by consideration of individual functional groups. All of the numerical values of intensity given in the sections which follow are in units of 1×10^4 mole^{-1} liter cm.$^{-2}$

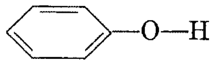
1. The O—H *group*

The form of the normal vibration leading to absorption in the 3600 cm.$^{-1}$ region for O—H compounds can be considered entirely as a change in the hydrogen–oxygen bond distance. The intensity is determined by the change which occurs in the O—H bond moment and by changes in the hybridization of the oxygen orbitals, which will affect lone-pair and overlap moments. Because these contributing factors do not all operate in the same direction, the sign of $\partial\mu/\partial r$ cannot be argued satisfactorily *a priori* (92). Examination of the O—H intensity for a series of simple aliphatic alcohols of the form R—O—H reveals that the intensity is strongly dependent on the electron-withdrawing power of the group R and is greatest when R is most electron-withdrawing (13, 14). The ground electronic state of the alcohols may be described as a mixture of the structures I and II.

$$\underset{\text{I}}{\mathrm{R{-}O{-}H}} \qquad\qquad \underset{\text{II}}{\mathrm{R{-}\overset{-}{O}\ \ \overset{+}{H}}}$$

Structure II, corresponding to a fully charge-separated form, will possess a larger moment for increased oxygen–hydrogen distance. A portion of the intensity arises from the fact that the moment represented by this structure increases with oxygen–hydrogen distance as the bond stretches. If the contribution of the ionic form to the ground state is increased, as it would be by a more electron-withdrawing group R, the change in moment with increasing oxygen–hydrogen distance will be correspondingly larger. In addition, however, the importance of the ionic form may not remain constant as the bond stretches. A small change in the contribution of structure II will result in a rather large change in moment because the dipole represented by this structure is large. It is not possible to say with any certainty how the ionic character depends on the oxygen–hydrogen distance for a free OH group, but it does seem reasonable that for hydrogen-bonded OH, the ionic character should increase with increasing bond distance (2, 44, 92). It may tentatively be concluded from this that if the change in per cent ionic character is important in determining the intensity of the free O—H, it is the result of increased ionicity with increasing oxygen–hydrogen distance. If it were not, the intensity change from this factor would be in the opposite sense from the charge-transfer effect of hydrogen bonding, and a minimum value of intensity should result for some range of hydrogen-bond strength (92).

From the magnitude of the intensity for aliphatic alcohols it is clear that the change in per cent ionic character is not large; in addition, since the O—H stretching does not affect the bond angles, it is unlikely that there occurs any appreciable change in hybridization of the oxygen orbitals. In phenols, however, in which there is an interaction of the lone pairs on the oxygen with the π-electron system of the ring, the charge-separated structure is stabilized by resonance:



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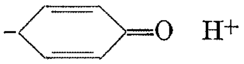


IV

The O—H intensities of phenols are considerably greater than those of aliphatic alcohols (12, 82). Since the phenyl ring is not strongly electron-withdrawing inductively, the increased intensity in the aromatic alcohols must be ascribed to the fact that the per cent ionic character increases with oxygen–hydrogen distance, and the increased charge on the oxygen is stabilized by resonance. The intensities of meta- and para-substituted phenols are strongly dependent on the electronic properties of the substituent; from the preceding discussion it follows that the intensity should be greatest for the most electron-withdrawing groups, since these are best able to absorb the increased electron density on the ring incident to the O—H stretch. Figure 2 shows a plot of the O—H intensities of a series of substituted phenols vs. the Hammett σ constant for the substituent (12). The substituents represented on the line are, in order of decreasing value of σ: *m*-nitro, *m*-chloro, *m*-bromo, *p*-bromo, *p*-chloro, hydrogen, and 3,5-dimethyl. A fairly good linear relationship is found for all the substituents except *p*-methoxy and possibly *p*-butyl. It is interesting to note that the intensity results for these two groups signify more electron withdrawal than is indicated by the σ value. The fact that the σ value for *p*-methoxy is not more positive (the value for *p*-methoxy is -0.268 as compared with $+0.115$ for the meta substituent) is explained in terms of electron release by the oxygen through a resonance interaction with the ring. This resonance, or mesomeric, interaction is in opposition to the electron-withdrawing inductive effect and leads to a more negative value for the σ constant. The extent to which the resonance interaction contributes to the electronic properties of the substituent depends largely on the nature of the process used to study these properties. When the process occurring at the position para to the substituent is strongly electron-releasing to the phenyl ring, it is to be expected that electron release by the substituent will be minimized. That this is the case is shown by the fact that the value of σ for groups such as *p*-methoxy varies with the particular process being studied (47b). Since the O—H stretch is an electron-releasing process with respect to the phenyl ring, it is not surprising that an electron-releasing resonance contribution to the value of σ for a group such as *p*-methoxy is not large. A similar explanation invoking the notion of C—C hyperconjugation as a mode of electron release can be applied (but with considerably less confidence) to the *p-tert*-butyl group (10). A linear relationship has also been claimed between the intensity and log A for phenols (82). While there are not at the present any theoretical grounds on which to choose a suitable function of the intensity for comparison with substituent constants, the writer

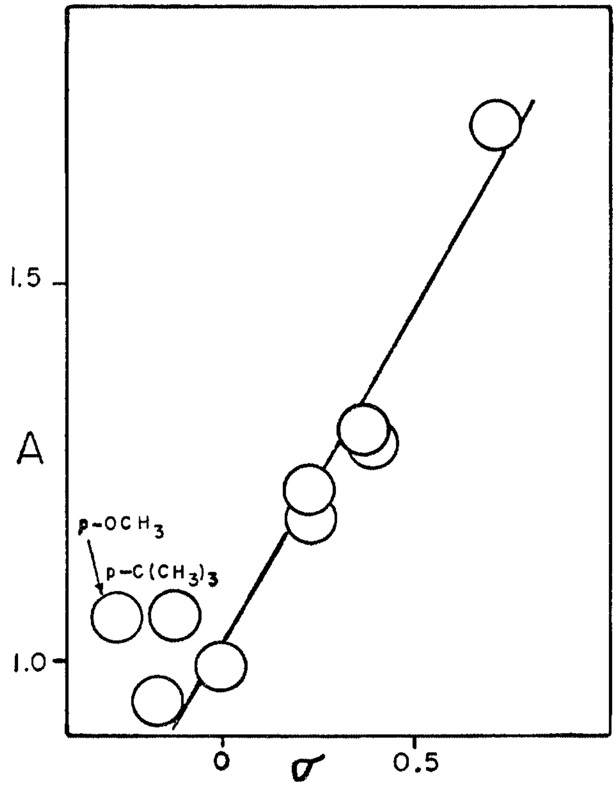


FIG. 2. The O—H intensity of substituted phenols plotted against the Hammett σ constant of the substituent.

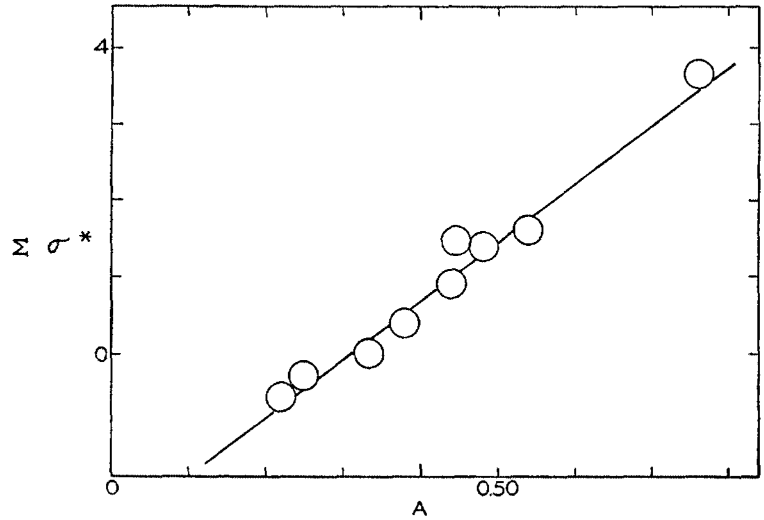


FIG. 3. The O—H intensity of aliphatic alcohols plotted against the sum of the polar substituent constants for the groups attached to the carbinol.

is convinced that the use simply of the intensity results in an interesting and consistent set of comparisons for all types of functional groups.

The relationship between the Hammett σ constant and the O—H intensity in phenols has its analog in the aliphatic series in the form of a linear relationship between the O—H intensity of substituted carbinols and the sum of the Taft polar substituent constants, σ* (83), of the attached groups (37). The relationship is shown in figure 3 for a number of compounds. By use of this graph the σ* value for a group can be determined by measuring the O—H intensity of appropriate alcohols. Values of σ* determined in this way for the HC≡C— and cyclopropyl groups are 1.43 ± 0.15 and 0.15 ± 0.01, respectively.

2. The N—H *group*

Study of the N—H fundamental for a large number of organic molecules has led to the conclusion that the different classes of compounds possess characteristic ranges of intensity (74). The ratio A_{01}/A_{02}, where A_{01} and A_{02} are the intensities of the fundamental and first overtone, respectively, has been determined for a number of N—H compounds (75). Coupled with a knowledge of the frequencies these data permit some evaluation of the importance of electrical anharmonicity in the N—H band. In general it appears that the more ionic bonds exhibit greater electrical anharmonicity. It is difficult to draw detailed conclusions from this type of work, however, because the variation of dipole moment with bond length is the result of so many factors, as pointed out in Section IV,A.

The band intensities of aliphatic N—H compounds are not large; the difficulties of accurate measurement are compounded by the occurrence of overlapping C—H bands (74). Accordingly, there are no data available for testing a relationship between the N—H intensity and the σ^* values of attached groups. In an interesting application of intensity measurements it has been shown, however, that the N—H intensity for piperidine in trans-platinum complexes varies with the charge on the nitrogen (21). When the platinum is most electron-withdrawing as a result of the inductive properties of the trans-coördinated group, the N—H intensity is highest. This is the same sort of behavior observed for the O—H intensity in aliphatic alcohols.

The intensities of both the symmetric and the antisymmetric $—NH_2$ bands in substituted anilines have been observed (20). These data yield some interesting comparisons with the results for phenols. By analogy, it is to be expected that as the N—H bonds stretch, they become more ionic. Electron-withdrawing meta and para groups, by increasing the resonance stabilization of the charge-separated form, should produce higher values of intensity. The intensities of the symmetric stretch bands, which should resemble those of phenols, are graphed in figure 4 vs. the Hammett σ values. It will be noted that there are three compounds which deviate from the linear relationship. As in the case of phenols, the intensity results for these compounds indicate more electron withdrawal than do the σ values. The explanation for the deviation of the p-NH_2 group is the same as that advanced for p-methoxy in the phenol series. In order to understand the deviations of the p-nitro and p-acetyl groups it must be realized that the large positive values of σ for these groups are partly the result of electron withdrawal by resonance interaction with the ring. Again, it is found that the extent of electron withdrawal by this means depends on the nature of the process which is occurring in the position para to the substituent. Thus, a special set of σ values applicable to phenols and anilines is needed for these groups to account for their greater electron-withdrawal properties in these compounds (47b). They are even more effective in electron withdrawal, insofar as their effect on the intensity of the symmetric NH_2 stretching band is concerned, than these σ values would imply, as evidenced by the deviations from the linear relationship in figure 4.

It is interesting to compare the changes in electron distribution which occur in a molecule incident to a stretching vibration with those which occur during a reaction process. For example, many substitution reactions occurring at a side chain attached to the phenyl ring proceed through a transition state which is electron-releasing with respect to the ring. In the same way, the symmetric N—H stretching vibration results in a release of electrons to the ring. A similar comparison can be made between reactions for which the transition state is electron-demanding and vibrations which result in a withdrawal of electron density from the ring (see later). Within these two classifications, however, there is considerable variance in the degree of electron withdrawal or release. From the intensity results it *appears* that the O—H and symmetric $N—H_2$ vibrations in phenols and anilines, respectively, are more electron-releasing in character than most kinetic processes for which the transition state is electron-releasing. This follows from the fact that the deviations discussed above occur when intensi-

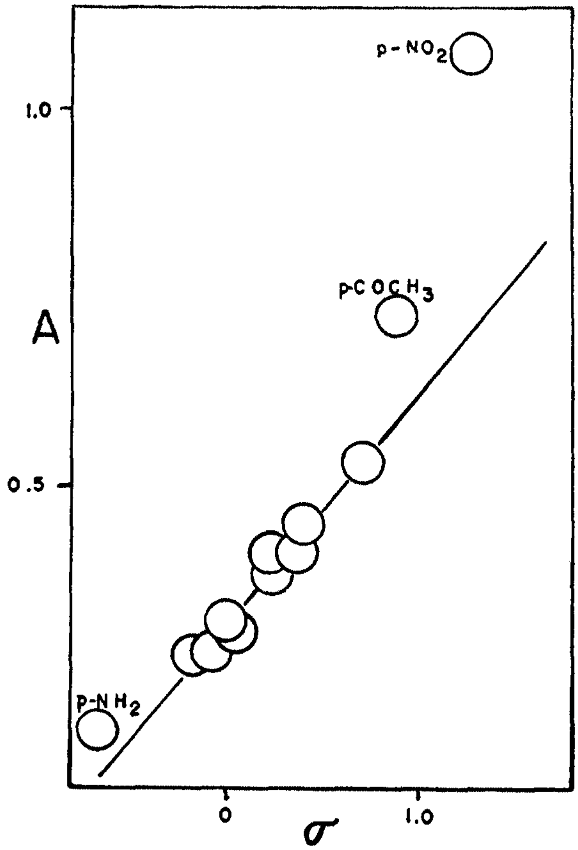


FIG. 4. Intensity of the symmetric —NH_2 band in substituted anilines plotted against the Hammett σ constant of the substituent.

ties are related to the Hammett σ constants, whereas for a very large number of reaction series the Hammett equation is obeyed for all substituent groups studied. The fact that the stretching modes of both phenols and anilines are apparently so strongly electron-releasing in character is of some interest in itself. It possibly arises from the fact that the intensities are determined in nonpolar solvents, whereas the rate processes which are utilized in determining the σ values for substituents are generally studied in polar media. Solvation in the polar media has the effect of reducing the effective charge involved in the transition state, and thus the process appears to be less electron-releasing (47c).

There is no way of predicting what effect the asymmetric N—H stretch will have on the electron density in the ring. In any case it is not likely to be very great, since the change in polarity of one N—H bond produced by stretching is opposed by the simultaneous contraction of the other. The intensity of this band proves to increase with increasing electron withdrawal of the substituent (20). The variation throughout the series is only about a third as large as for the symmetric stretching band, however, and a satisfactorily linear relationship between the intensity and σ values is observed.

The intensity of the N—H bending mode in pyrrole has been measured in a variety of solvents (61). The results are of interest in connection with the effects of hydrogen bonding, a topic which is discussed in Section IV,C.

3. *The* C—H *group*

The determination of the C—H bond moment has provided impetus for much of the work done on C—H band intensities (Section IV,A). In a more empirical vein, the intensity of the in-plane C—H deformation of mono- and para-disubstituted benzenes has been studied (69). The dependence of the intensity on the mass sum of the substituents is an indication that the substituents participate in the vibration. In this instance there is no obvious indication that their electronegativity is important in determining the intensity. The C—H stretching bands in compounds of the type p-$XC_6H_4CH_3$ and $C_6H_5CH_2Y$ are, however, quite sensitive in this respect (31). The complexity of the system studied, and the fact that the overlapping C—H bands were integrated as a whole, make a further analysis of the results very difficult. Francis has studied the C—H band intensities in a number of aliphatic hydrocarbons (33) and found that characteristic values of structural group intensities can be assigned to CH, CH_2, and CH_3 groups. The total carbon–hydrogen intensity of a hydrocarbon can be predicted by this means to within 10 per cent. A summary of the results is shown in table 1.

The additivity of hydrocarbon-group intensities is of interest for analytical purposes and has been studied by various workers (56, 60, 96). The intensities of the group vibrations are markedly different in compounds containing electron-withdrawing functional groups such as ester or carbonyl (32). The intensities of the stretching bands of CH_3 and CH_2 groups adjacent to carbonyl decrease by a factor of 7–9 from the values in table 1. As a further comparison, the C—H stretching intensity in chloroform is 0.04 (4), as compared with 0.28 for the tertiary C—H bond in hydrocarbons (table 1). The deformation bands, on the other hand, show increased intensity. Groups which are once removed from the electron-withdrawing functional group are also affected, but to a much lesser extent. It is interesting to note that whereas the intensities of O—H and N—H stretching bands are increased by the presence of adjacent electronegative groups, the opposite is true of the C—H band, at least in saturated hydrocar-

TABLE 1

Characteristic intensities of carbon–hydrogen group vibrations (33)

Band Frequency	Band Intensity		
	CH_3	CH_2	CH
cm.$^{-1}$			
2900	0.88	0.76	0.28
1460	0.11	0.046	
1370	0.078		

TABLE 2

Comparison of aliphatic and aromatic compounds for some X—H *band intensities measured in carbon tetrachloride*

Compound	Group	ν cm.$^{-1}$	Intensity	Reference
Propargyl alcohol	C≡C—H	3327	0.68	(16)
Phenylacetylene	C≡C—H	3323	1.04	(17)
1-Propanol	O—H	3634	0.45	(13)
Phenol	O—H	3610	0.99	(12)
Diethylamine	N—H	3334	0.01	(74)
N-Ethylaniline	N—H	3422	0.27	(74)
tert-Butyl mercaptan*	S—H	2570	0.039	(5)
Thiophenol*	S—H	2570	0.061	(5)

* Isoöctane as solvent.

bons. At the same time, the increased intensity of the C—H deformation modes is indicative of increasing static bond moment. The C≡C—H group might be expected to behave in a manner similar to the N—H and O—H groups, insofar as the C—H intensity is concerned. Table 2 provides a comparison of intensities which are characteristic of these three groups as well as of the S—H group, in both aliphatic and aromatic systems. The relative intensities for the aliphatic and aromatic compounds indicate in each case the importance of resonance in the aromatic compounds.

An extensive study has been made of overtone C—H and O—H intensities (59), which in combination with frequency data can be used to evaluate terms in an expression relating bond moment to internuclear distance. The model chosen accounts for all of the change in molecular moment as arising in a single bond, so that it can hardly be adequate for the O—H bond in phenol, where resonance effects result in a redistribution of charge throughout the entire molecule. In the simplest cases studied, however, such as the C—H bond in chloroform or trichloroethylene, the assumptions appear more reasonable and the results are more satisfying.

4. The S—H *group*

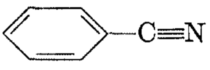
The values for thiophenol and *tert*-butyl mercaptan listed in table 2 represent the only measurements on S—H bands in nonpolar solvents. The S—H intensities of these same two compounds in more polar media are discussed in Section IV,C.

5. The C≡N *group*

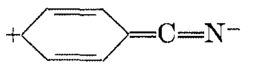
The ground electronic state of a nitrile compound is contributed to by structures V and VI. Structure VI, with a carbon–nitrogen bond order of 2, corresponds

$$\underset{\text{V}}{R{-}C{\equiv}N} \qquad\qquad \underset{\text{VI}}{R{-}\overset{+}{C}{=}N^{-}}$$

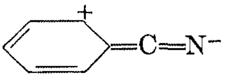
to a larger carbon–nitrogen bond distance than V. Therefore, as the C≡N bond distance increases, structure VI will become more important in determining the ground electronic state. The sign of $\partial\mu/\partial r$ is then positive. In contrast with the O—H and N—H stretchings, which result in an electron release to the attached groups, the $\mathrm{C{\equiv}N}$ stretch is an electron-withdrawing process. A variation in the electronegativity of the group R in $\mathrm{R{-}C{\equiv}N}$ has an effect on the $\mathrm{C{\equiv}N}$ intensity opposite to that which it has on the former two groups. Thus, substitution of one of the hydrogens in acetonitrile by an electron-withdrawing substituent such as a halogen results in a decrease in the intensity (78). The intensities of aliphatic nitriles are comparatively low (5, 78, 89); the values for aromatic nitriles as a group are much higher. This is understandable in terms of resonance interaction of the $\mathrm{C{\equiv}N}$ group with the π-electron system of the ring:



VII



VIII



IX

The effect of ring substituents on the $\mathrm{C{\equiv}N}$ intensity has been investigated by several workers (15, 57, 79). It is to be expected that electron-releasing substituents will increase the intensity, and this is found to be the case. It is not strictly correct to look for a relationship between the $\mathrm{C{\equiv}N}$ intensity and the Hammett σ values, as was found for phenols and anilines, because the $\mathrm{C{\equiv}N}$ stretching is an electron-withdrawing process, and the Hammett constants are applicable to nucleophilic processes (15, 63). Although electrophilic substituent constants are to be found in the literature (63), it appears that the $\mathrm{C{\equiv}N}$ stretching transition is apparently more electron-withdrawing than the rate process from which the constants were determined, so that electron-releasing groups such as *p*-amino and *p*-methoxy show marked deviations from a regular relationship with these constants. On the other hand, it is possible to determine a set of constants from the intensity data which do yield a linear relationship with log rate values for a few electrophilic processes. It is interesting to note that for a fairly wide range of solvent types the variation of intensity throughout the series of compounds is independent of solvent (15, 57). This is shown by the results for a few compounds listed in table 3. There is some question, however, as to whether the relative intensities would remain independent of solvent in highly polar media. It is quite possible that solvation effects would operate to change the relative intensities in such a way that the substituent constants derived from studies of intensity would approach the values obtained in kinetic studies.

TABLE 3

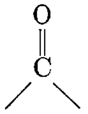
The intensity of the $\mathrm{C{\equiv}N}$ band of some benzonitriles in various solvents (15)

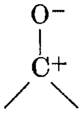
Compound	Solvent			
	Hexane	Tetrachloroethylene	Carbon tetrachloride	Chloroform
p-Aminobenzonitrile			0.82	1.43
p-Methoxybenzonitrile	0.34	0.41	0.44	0.76
p-Methylbenzonitrile	0.21	0.26	0.28	0.48
Benzonitrile	0.15	0.19	0.20	0.35
p-Chlorobenzonitrile	0.14	0.18	0.20	0.36

The intensities for a few ortho-substituted benzonitriles have been observed (89). If a suitable correction for the solvent effect for these compounds could be made (the different shape in the vicinity of the nitrile group probably results in a different solvent effect from that for the meta- or para-substituted compounds), these data are of great potential value for evaluating the internal electron contribution from ortho substituents.

5. The C═O *group*

The carbonyl group has been the most extensively studied of the functional groups with respect to infrared intensities. The electronic ground state of a carbonyl compound is contributed to by structures X and XI. With the same argument employed in the case of the nitrile group it can be said that as the carbonyl bond stretches, the ionic form becomes more important, so that $\partial\mu/\partial r$ is in the direction of increasing C═O bond moment. It follows also that the stretching is an electron-demanding process. The carbonyl intensity in a group of steroids was found to depend on the vicinal substituent in the expected way; it is the lowest for the most electron-withdrawing groups (51). An additional example of the effect of the inductive properties of attached groups in affecting


X


XI

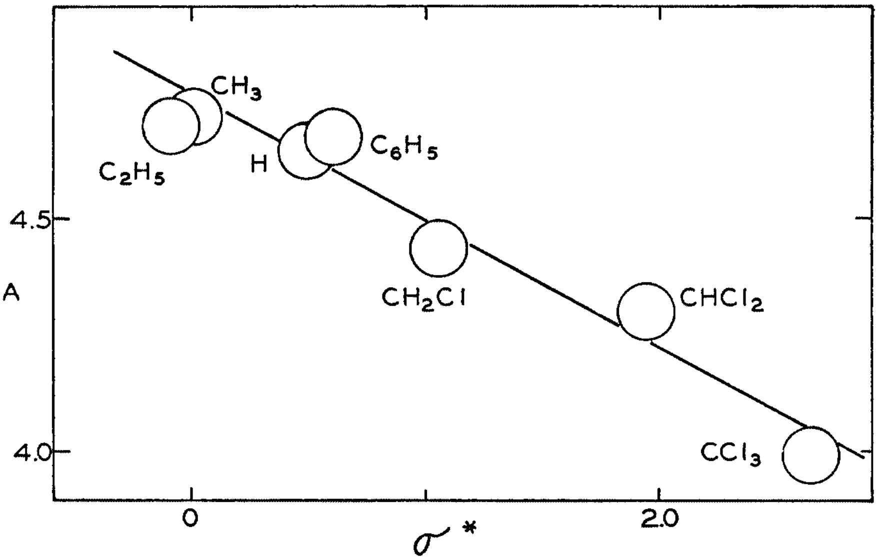


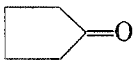
FIG. 5. Intensity of the C═O band in amides of the form $RCONH_2$ plotted against the Taft polar substituent constant for the group R. (Added in proof: More recent work in the writer's laboratory indicates that a large part of the decrease in intensity upon substitution of a halogen or other large group onto the methyl is due to steric effects.)

the intensity is shown in figure 5, in which the carbonyl intensities of a series of amides, $RCONH_2$, are plotted as a function of the σ^* values of the groups R (70). In general these groups do not interact conjugatively with the carbonyl, so that σ^* is determined by inductive properties.

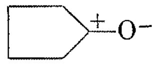
Another factor observed in the steroids was the effect on the intensity of adjacent double bonds. These result in a large increase in the intensity, through resonance interaction with the carbonyl. The importance of resonance in determining the carbonyl intensity is shown by the observation that a more or less linear relationship exists between the resonance energy and the carbonyl intensity (1, 71).

In view of the obvious similarities in the two groups, the variation in intensity in substituted acetophenones might be expected to parallel that in benzonitriles. Two earlier studies of acetophenones do not reveal any apparent relationship between the carbonyl intensity and the substituent constant (49, 84). Graphical integration of the absorption curves was not performed in either study, however, and the accuracy of the reported results is open to question. The carbonyl band frequently falls far short of possessing a Lorentz shape, and in such cases the use of Ramsay's approximation formula is not satisfactory. A more precise study of aromatic carbonyl systems reveals that the carbonyl intensity is dependent on the substituent in a regular way, although the dependence is not very marked (90).

The carbonyl intensity of an interesting series of compounds, the cyclanones, has been studied (18), and it has been found that the intensity decreases with increasing ring size, starting with cyclopentanone, and reaches a more or less constant value with the nine-membered ring. The ground state of a ring compound such as cyclopentanone is represented by structures XII and XIII. In XIII the ring angle is free to change to relieve any internal strain; perhaps more important for some of the ring compounds, unfavorable conformations can be avoided in this structure (9). The additional stabilization resulting from these factors is probably partly responsible for the observed variation in intensity. In any case, the intensity data provide additional evidence bearing on the structure of the compounds.



XII



XIII

It is instructive to examine the range of carbonyl intensities encountered in various classes of compounds. The list shown in table 4, while not exhaustive, gives an indication of the dependence of the intensity on structure. In the interests of uniformity all of the results shown were obtained for the compounds in solvents of low polarity.

7. *The* S=O *group*

By analogy with the carbonyl group, the S=O stretching vibration should be an electron-demanding process. The S=O intensity in some sulfones increases

TABLE 4

Characteristic values of carbonyl intensities

Compound	Intensity	Solvent	References
Unsubstituted aliphatic ketone and aldehyde	1.5–1.8	CCl_4	(1, 33)
Aromatic ketone and aldehyde	1.9–2.4	CCl_4	(1)
Six-membered-ring ketone	2.2–2.7	CCl_4, CS_2	(18, 51)
Acetyl chloride	2.5	CCl_4	(1)
α,β-Unsaturated six-membered-ring ketone	2.9–3.7	CS_2	(51)
Unsubstituted ester	2.5–3.1	CCl_4	(1, 33)
Aliphatic acid	3.6–3.8	CCl_4	(95, 96)
α-Hydroxy aliphatic acid	3.2	CCl_4	(96)
α,β-Unsaturated acid	4.6	CCl_4	(95)
Unsubstituted amide	4.7	$CHCl_3$	(70)
N,*N*-Dimethyl amide	5.7	$CHCl_3$	(1)
α,α-Dichloro amide	4.3	$CHCl_3$	(70)

with increasing electron release of the attached group, in agreement with expectation (72).

8. The NO_2 *group*

The symmetric nitrogen–oxygen stretching vibration of some nitro compounds appears to be quite electron-demanding in nature; the intensity of this band for *p*-methylaminonitrobenzene is about 3.5 times larger than that for *p*-methylnitrobenzene (54). There is, however, essentially no difference in the intensity of the asymmetric stretching band for these two compounds.

9. The C—O—R *group*

The 1200 cm.$^{-1}$ band in esters, identified with a rather complex changing of C—O and O—R bond distances, has been studied in a variety of esters (33, 73). There is little basis in the results for a correlation of intensity with structure.

C. INTENSITIES AND INTERMOLECULAR EFFECTS

The intensities of many of the vibrational bands of functional groups are extremely sensitive to intermolecular effects. Because of this the intensities can be utilized in studies of interactions which are too weak to be observed easily by other means.

Hydrogen bonding (H-bonding), a particularly important type of specific interaction, may affect the intensities of two functional-group vibrations. In the hydrogen-bonded system

$$R—X—H \cdots Y—R'$$

the intensity of the X—H bond is, of course, markedly different from that of the free X—H. But the intensity of the Y—R′ stretching band may also change as a result of hydrogen bonding. Hydrogen bonding of O—H groups to relatively strong (proton) acceptor atoms results in the appearance of a distinctly separate O—H band which possesses an intensity much greater than that of the free O—H (2, 92). Some typical instances of this behavior are shown in table 5, in which

TABLE 5

Effect of hydrogen bonding on the O—H *stretching band*

Donor	Acceptor	Solvent	A_b/A_f	$\Delta\nu_m$	Reference
				cm.$^{-1}$	
Phenol	67% chlorobenzene	CCl_4	1.9	29	(92)
	0.1 *M* acetonitrile	C_7H_{16}	4.3	139	(92)
	0.08 *M* ethyl acetate	C_7H_{16}	7.2	156	(92)
	Ethyl ether	Ethyl ether	7.1–7.9	276	(2, 44)
tert-Butyl alcohol	Ethyl ether	Ethyl ether	6.2	116	(2)
	Triethylamine	Triethylamine	11.0	337	(2)
Methyl alcohol	Ethyl ether	Ethyl ether	7.4–8.1	136	(2, 44)
	Triethylamine	Triethylamine	11.7–15.4	401	(2, 44)

A_b/A_f represents the ratio of the intensity of hydrogen-bonded O—H to that of the free O—H in carbon tetrachloride solution, and $\Delta\nu_m$ the decrease in frequency on hydrogen bonding. The very large increase in intensity which is observed on hydrogen-bond formation cannot be ascribed to an electrostatic effect, or to change in the per cent ionic character, but is due to delocalization of the electrons in the proton-acceptor atom Y (44, 92). Delocalization is in effect a transfer of electrons from the acceptor to the donor system. This idea is represented by structures XIV and XV, which are those giving rise to delocalization energy.

$$\underset{\mathrm{XIV}}{R{-}X{-}H\cdots Y{-}R'} \qquad\qquad \underset{\mathrm{XV}}{R{-}\overset{-}{X}\cdots H{-}\overset{+}{Y}{-}R'}$$

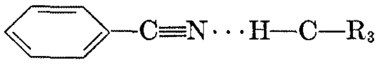
Although the characterization of the O—H bending modes is not complete enough to permit measurement of an O—H bending mode intensity (44, 85), all the indications are that it is not increased appreciably on hydrogen bonding. This observation is further indication that delocalization rather than change in ionic character is largely responsible for the major part of the increase in intensity (44). The argument in this instance is that change in ionic character, resulting in a larger contribution from the structure O^-H^+, would certainly result in a higher bending intensity. Delocalization, on the other hand, since it does not formally change the charge on the hydrogen, would not be expected to have a pronounced effect on the bending intensity. Increasing temperature results in a decrease in the intensity of hydrogen-bonded O—H (30).

The intensity of the N—H stretching band in pyrrole also increases on hydrogen bonding, though the increase is not so large as for O—H (44). The intensity of the bending mode is not appreciably affected, a fact which is consistent with the proposal that the increased intensity of the stretching band is the result of delocalization energy.

The intensity of the S—H band is markedly affected by hydrogen bonding. For *tert*-butyl mercaptan in isoöctane, dioxane, and pyridine the relative intensities are 1:3.18:7.70. For thiophenol in these same three solvents the values are 1:6.15:20.0 (5).

The intensity of the C—D stretching band of chloroform-*d* in a solvent such as ether or triethylamine is greatly increased in comparison with the intensity in carbon tetrachloride (43, 55). The intensity of the bending mode, however, remains essentially unchanged. Except for the most basic solvents, the interaction of C—D with acceptor solvents is not strong enough to result in a separate hydrogen-bond band as distinct from the free band. The numerical value of the intensity change is also much smaller than that observed for N—H or O—H. It is large enough to be measured, however, even for solvents which are not commonly considered to be very basic. The measurements of infrared intensities are thus capable of detecting hydrogen-bonding interactions of very low energy, and they provide experimental data with which to test certain aspects of hydrogen-bond theory.

The intensity of a stretching band involving the acceptor atom is also subject to change upon hydrogen bonding. For example, the intensity of the C≡N band in benzonitriles is about 80 per cent higher in chloroform solution than in carbon tetrachloride (15, 57), presumably because of hydrogen bonding. This behavior is understandable if delocalization energy is important in determining the hydrogen-bond energy. This can be seen by considering structures XVI and XVII, which are those giving rise to delocalization energy. The increased electronic charge on the nitrogen as the C≡N bond stretches is stabilized by increased delocalization energy. A portion of the intensity increase must then be due to increased importance of the ionic form in the vibrationally excited state as compared with the ground state, and a portion must arise from the fact that the length of the dipole in the ionic form is increased as a result of the delocalization.



XVI

XVII

The carbonyl intensity is also affected by hydrogen bonding. For example, the C=O intensity of monomeric aromatic acids is about 3.6 as compared with 4.5 for the dimer (95); the C=O intensity of acetone is also found to increase with increased hydrogen bonding (93).

Aside from hydrogen bonding, infrared intensities provide evidence of other forms of solute–solvent interactions for compounds in solution. The influence of polar solvents on the intensity and band shape of the carbon–halogen bands in a few halogen-containing compounds has been noted (102). The changes in intensity are not large, but for some bands are clearly dependent on solvent polarity. In table 6 the data for the 506 cm.$^{-1}$ band of *cis*-1,4-dibromocyclohexane are

TABLE 6

Dependence of a carbon–halogen band in cis-1,4-dibromocyclohexane on the solvent (102)

Solvent	ν_m	$\Delta\nu_{1/2}$	A	Solvent	ν_m	$\Delta\nu_{1/2}$	A
n-Heptane	506.0	6.6	0.110	Chloroform	502.8	8.2	0.121
Cyclohexane	506.1	6.1	0.106	Ethyl acetate	502.4	8.1	0.116
Carbon tetrachloride	505.1	6.6	0.114	Dioxane	502.4	8.2	0.131
Benzene	502.8	7.1	0.123				

shown. Similar results have been reported for the 760 cm.$^{-1}$ band of chloroform (97).

The appearance of forbidden bands in solution spectra provides an opportunity for interesting studies. The fact that the bands appear at all is evidence of intermolecular forces which act to perturb the absorbing molecule. The intensities of the inactive fundamentals of benzene in solution have recently been studied (29, 91). A marked dependence on solvent is observed; in general, the intensity increases with increasing polarizability of the solvent molecules. From the evidence which is presently available, it is difficult to say whether the lower symmetry of the benzene molecules in solution is the result of the formation of a complex of some sort, or is the result of collisional perturbations. The latter explanation seems the more likely.

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ADDENDUM

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