

Integrated Intensities of Absorption Bands in Infrared Spectroscopy

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An infrared absorption band may be characterized by several parameters, including frequency, intensity, and band half-width. Usually the frequency and absorption coefficient at the band maximum are the data reported in chemical spectroscopy. In recent years the absolute intensity has been a quantity of considerable interest in molecular spectroscopy because of the relationship of this quantity to the polar properties of molecules [1-5]. The absolute intensity is a difficult quantity to obtain experimentally and it is usually the relative integrated intensity that is measured and reported. The integrated intensity has been correlated with other important properties, including chemical reactivities of substituents [6-9], hydrogen bonding [10-11], and presence of functional groups [12-23].

There has been little emphasis on the application of integrated intensity measurements to systematic determination of functional substituents. It was felt that a survey for purposes of tabulation and comparison of published intensity data might be of value to chemists who seek to use intensity as a parameter of analysis, analogous to the way frequency is now employed for qualitative detection of groups. The

emphasis in this review therefore is a comparison of the numbers reported in the literature for organic compounds in the frequency range 5000 to 650 cm^{-1} .

I. PRINCIPLES

The integrated intensity of an infrared absorption band is related to electron charge displacements occurring in chemical bonds over the lifetime of a vibration. A well-known requirement [24] for the appearance of an infrared band is a change in the dipole moment vector with vibrational coordinate, the intensity being related to the change by

$$\text{absolute intensity (i)} = \left(\frac{\nu_i}{\omega} \right) \frac{N\pi}{3c^2} \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \quad (1)$$

where N is the number of molecules per cm^3 , c the speed of light, the quantity in parentheses the rate of change of the dipole moment vector with the i th normal coordinate, ω the frequency of the transition (harmonic frequency), and ν_i the absorption frequency.

The absolute intensity is measured as the integral of the absorption coefficient α_ν over the entire vibration band between frequencies ν_1 and ν_2 :

$$\text{absolute intensity} = \int_{\nu_1}^{\nu_2} \alpha_\nu d\nu \quad (2)$$

In practical work it is customary to refer to the integral as the "integrated intensity," given by

$$\text{integrated intensity} = \int_{\nu_1}^{\nu_2} \epsilon_\nu d\nu \quad (3)$$

where ϵ_ν is the molar absorptivity at frequency ν and is given by

$$\epsilon_\nu = (1/C \ell) \log_{10} (I_0/I)_\nu d\nu \quad (4)$$

where C is the concentration in moles per liter, ℓ the path length in centimeters, ν the frequency in cm^{-1} , and $(I_0/I)_\nu$ the ratio of the intensity of incident and transmitted radiation at frequency ν . Because of the finite slit width required, the radiation at any nominal frequency is not monochromatic and the band contour is to some degree distorted by the slit-width effect. It is the apparent molar absorptivity which is actually obtained, given by

$$\epsilon_\nu^a = (1/C \ell) \log_{10} (T_0/T)_\nu d\nu \quad (5)$$

where $(T_0/T)_\nu$ is the ratio of the intensities of actual incident and transmitted radiation at a nominal frequency ν . The exact value of this ratio depends on the slit function and resolving power of the monochromator. The integrated intensity obtained by measurement is therefore the apparent intensity. Integrated intensities have been frequently obtained by approximation or extrapolation procedures which supposedly correct for the instrumental error. In practice the currently available wide-range "high performance" grating infrared spectrophotometers have sufficient resolving power to yield nearly undistorted spectra for the majority of bands measured in solution (over 5 cm^{-1} in band half-width).

The absorption coefficients can be determined by any experimental procedure capable of yielding the optical constants n and k . These are related by

$$\alpha_\lambda = 4\pi nk/\lambda \quad (6)$$

$$n' = n(1 - ik) \quad (7)$$

where n' is the complex refractive index with n being the real part and k being a quantity called the absorption index. These optical constants have been determined by dispersion methods [25] and by reflection [26, 27]. The classical reflection methods are of low sensitivity. The methods of total attenuated reflection [28-32] appear to have sufficient sensitivity to measure optical constants of intense bands of liquids with accuracies equal to or better than transmission methods.

In chemical spectroscopy the emphasis is on interpretation of the spectra in terms of chemical bonds and groups by means of frequency correlations. In the absence of intensity data it is possible only to make crude qualitative comparisons. Also of importance is the interpretation of frequency shifts related to chemical changes and alteration of bond properties. The question of the effects of such changes on intensities is an important problem in spectroscopy.

To correlate frequencies and intensities with specific groups and the polar properties of chemical (covalent) bonds, it is worthwhile to examine the published data for evidence of trends. Although a great deal of useful frequency data is available and significant frequency correlations are known [33, 34], relatively little intensity data has been published. In some cases there is disagreement between results from different sources. The reliability of much of the intensity data is still an unknown quantity because of the approximation procedures used, or because of failure to specify the precise conditions for measuring and calculating intensities. Various intensity standards have

been proposed as a check on instrumental accuracy [35-38].

Unfortunately much of the earlier data is questionable because measurements were made on prism instruments of inadequate resolving power and uncertain slit-width performance.

The basic problem is to produce the true band shape and intensities, free of the distortions introduced by the measuring apparatus and the finite slit function [39, 40], so as to enable the experimenter to make reliable correlations with chemical properties. The most obvious effect of inadequate resolution is band broadening and lowering of intensity. More insidious is the loss of information about band contour, as shown by spectra of a band scanned at high and low resolving power, reproduced in Fig. 1. The sharper curve was run at slit width/band half-width ratio ($S/\Delta\nu_{1/2}^a$) of 0.1. Weak bands are evident on each shoulder of the band, indicated by arrows. Superimposed is a second scan of the same band at an $S/\Delta\nu_{1/2}^a$ ratio of 0.9, run at the same signal-to-noise ratio. The peak intensity is markedly reduced and the

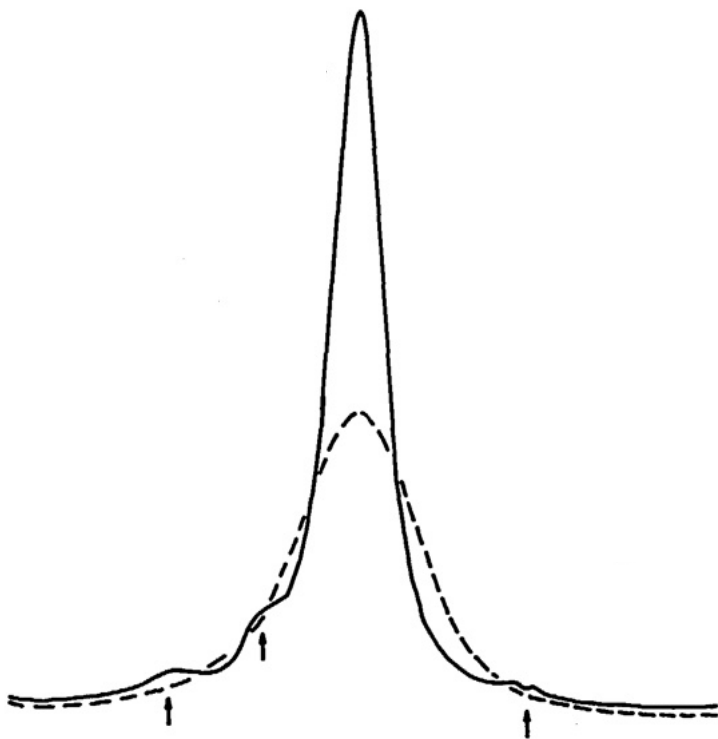


FIG. 1. Infrared absorption band scanned at high resolution (—) and low resolution (---).

band half-width markedly increased at low resolution. Even worse is the loss of information at low resolution, caused by the disappearance of the weak bands evident at high resolving power. There is also a shift of base line, which may be a source of error in intensity measurements unless carefully determined. Of interest is the fact that the product of peak height and band half-width for each of the bands differ by less than 4%, since some spectroscopists have reported intensities as $(\epsilon \times \Delta\nu_{1/2})$ times a "constant" (K). The rationale for this may be based on the assumption that an infrared absorption band can be characterized by a simple shape function involving peak-height and band half-width parameters.

It has been shown by Ramsay [39] that the shape of many infrared bands can be described by a Cauchy (Lorentzian) function under certain conditions:

$$\ln (I_0/I)_\nu = a/[(\nu - \nu_0)^2 + b^2] \quad (8)$$

where $a/b^2 = \ln (I_0/I)_{\max}$ and $2b = \Delta\nu_{1/2}^t$; ν_0 is the frequency at the maximum, $\ln (I_0/I)/2.303$ is the true absorbance at frequency ν , a and b are constants, and $\Delta\nu_{1/2}^t$ is the true band half-width.

Integration of the expression on the right side of Eq. (8) yields a simple expression for the integrated intensity:

$$\begin{aligned} \text{integrated intensity} &= \frac{1}{C\ell} \int_{-\infty}^{+\infty} \frac{a}{(\nu - \nu_0)^2 + b^2} d\nu \\ &= \frac{1}{C\ell} \frac{a}{b} \tan^{-1} \left[\frac{\nu - \nu_0}{b} \right]_{-\infty}^{+\infty} \\ &= \frac{1}{C\ell} \frac{\pi a}{b} \end{aligned} \quad (9)$$

Substituting for the values of a and b from above yields

$$\text{integrated intensity} = \frac{\pi}{2} \frac{1}{C\ell} \ln (I_0/I)_{\max} \times \Delta\nu_{1/2}^t \quad (10)$$

In practice the radiation is not monochromatic and $(I_0/I)_{\max}$ must be replaced by $(T_0/T)_{\max}$. For Lorentzian-shaped bands and a triangular slit function the following expression applies:

$$A = (K/C\ell) \ln (T_0/T)_{\max} \times \Delta\nu_{1/2}^a \quad (11)$$

where $\Delta\nu_{1/2}^a$ is the apparent (observed) slit width and K is a constant with a value between 1.4 and 1.6 (depending on the absorbance and the $S/\Delta\nu_{1/2}$ ratio) over the range of instrumental settings usually employed.

An equivalent form of Eq. (11) is the integrated intensity (practical

units), which has the dimensions of liter/cm²/mole and differs only by a factor of 2.303 (log₁₀ basis instead of log_e):

$$\text{integrated intensity (practical)} = K' \times \epsilon_{\max} \times \Delta\nu_{1/2}^2 \quad (12)$$

Calculation of intensity by Eq. (12) appears attractive because of the simplicity and speed of the procedure, as only two easily measured quantities are required. Calculation of intensity by the method of Eq. (3) is more time-consuming, inherently less precise, and in principle yields lower results, because the area under the wings beyond the practical extrapolation range is not included. Ramsay has calculated a table of wing corrections to add to the measured area [39] for Lorentzian-shaped bands, the addition being of the order of 5 to 10% for typical measurements.

Over a fairly large range of instrumental settings the product of ϵ_{\max} and $\Delta\nu_{1/2}^2$ should vary by less than 10% according to the assumptions implicit in Eq. (12).

II. EXPERIMENTAL PROCEDURES

The application of Eq. (3) (Ramsay method II) and (12) (Ramsay method I) to intensity measurements can be illustrated by an example from the author's files [41], which was selected to show the effect of low-, medium-, and high-resolution conditions of measurement on the various infrared band parameters. The 1745-cm⁻¹ band of the carbonyl stretching mode of methyl n-butyrate was scanned in absorbance at several $S/\Delta\nu_{1/2}$ ratios and the effects on peak height, band half-width, and area were measured. Results of these measurements are presented in Table 1. A typical spectrum, with various band parameters labeled, is reproduced in Fig. 2. The effects of slit width on the integrated intensity (B), ϵ_{\max} and $\epsilon_{\max} \times \Delta\nu_{1/2}^2$, are shown by the plot in Fig. 3 as a percentage of the true value. The true value was assumed to be the average of several readings taken at an $S/\Delta\nu_{1/2}$ of 0.15.

The integration range was ± 80 to 85 cm⁻¹, which is the point at which the wings of the band were merged with the background. Gain and scanning speeds were optimized to yield approximately equal signal-to-noise ratios. The spectra were run at 0.1 M concentration in carbon tetrachloride. At an $S/\Delta\nu_{1/2}$ ratio of 0.15 the precision of scanning was 2.4% for area and 0.8% for peak-height measurements (relative standard deviation). The band half-width could be estimated to 0.1 cm⁻¹.

For this particular system the following observations are relevant

TABLE 1
 Effect of $S/\Delta\nu_{1/2}^t$ on Intensity Parameters of the Carbonyl
 Stretching Mode of Methyl n-Butyrate
 (Solvent: CCl_4)

Effective slit width, cm^{-1}	$\Delta\nu_{1/2}, \text{cm}^{-1}$	$S/\Delta\nu_{1/2}^t$	ϵ	B	B (corr.)	K' (app.)	K (Ramsay)	Ratio K/K'	$\epsilon \times \Delta\nu_{1/2}^a$
1.15	15.55	0.075	555	1.14	1.23	1.40	1.57	1.09	0.86
1.7	15.7	0.11	555	1.13	1.22	1.43	1.56	1.09	0.86
2.3	15.7	0.15	555	1.16	1.24	1.45	1.56	1.08	0.86
4.6	16.25	0.3 (0.3) ^a	529	1.14	1.22	1.42	1.54	1.08	0.86
7.0	17.0	0.45	508	1.10	1.18	1.37	1.50	1.09	0.865
9.3	18.65	0.60	463	1.08	1.16	1.34	1.46	1.09	0.865
14.0	22.5	0.9 (0.6)	392	1.08	1.16	1.31	1.40	1.07	0.885
18.5	26.3	1.20	336	1.045	1.12	1.27	1.33	1.05	0.88
28.0	34.3	1.80	273	1.00	1.08	1.21	1.30	1.07	0.91
37.0	41.3	2.4 (0.9)	222	1.00	1.08	1.17	1.30	1.11	0.92

^aFigures in parentheses are ratios of $S/\Delta\nu_{1/2}^a$.

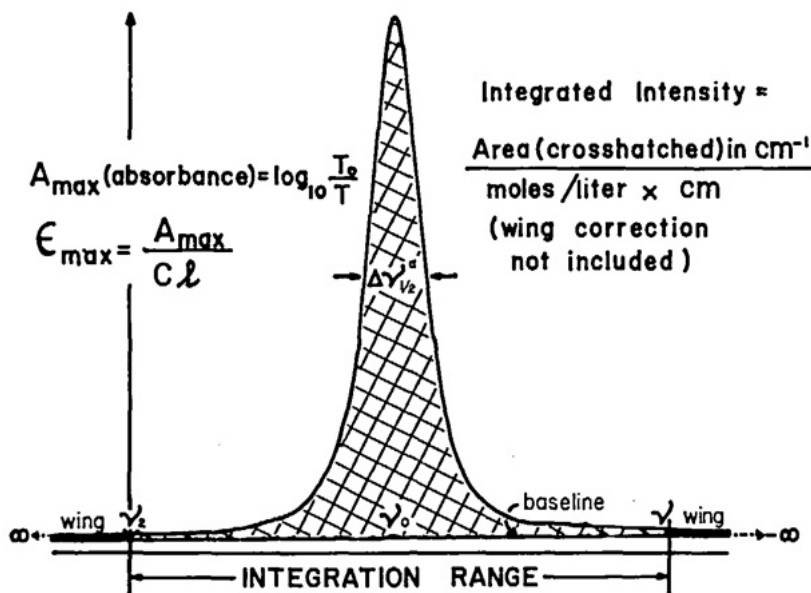


FIG. 2. Infrared band scanned in absorbance mode on linear wavenumber scale for determination of band parameters.

to the problem of intensity measurements and the slit-width effect:

1. At medium-resolution conditions typical of many sodium chloride prism instruments ($S/\Delta\nu_{1/2}$ of about 0.6), the molar absorptivity and integrated intensity error are significant, being of the order of 15 and 6%, respectively.

2. It is necessary to maintain an $S/\Delta\nu_{1/2}^t$ ratio of less than 0.2 to reduce the slit-width error to negligible proportions (below 2%).

3. A fairly constant value of $\epsilon_{\max} \times \Delta\nu_{1/2}^a$ was obtained over a wide range of $S/\Delta\nu_{1/2}^t$, justifying the estimation of intensity from these two parameters for a symmetrical band.

The wing correction was estimated to be $\sim 8\%$. The apparent values of K calculated from the data by means of Eq. (12) for most of the slit-width settings were about 8 to 10% below the corresponding value of K in Ramsay's table [39]. This means that the estimation of integrated intensity by the approximation procedure (Ramsay method I) will be about 10% too high in this case. The calculation of intensity by Eq. (12) does have merit if experience can indicate a probable value of K . Values of K of about 1.2 to 1.3 have been obtained for polar bonds by various investigators [42-46].

If insufficient resolution is available and a knowledge of K is lack-

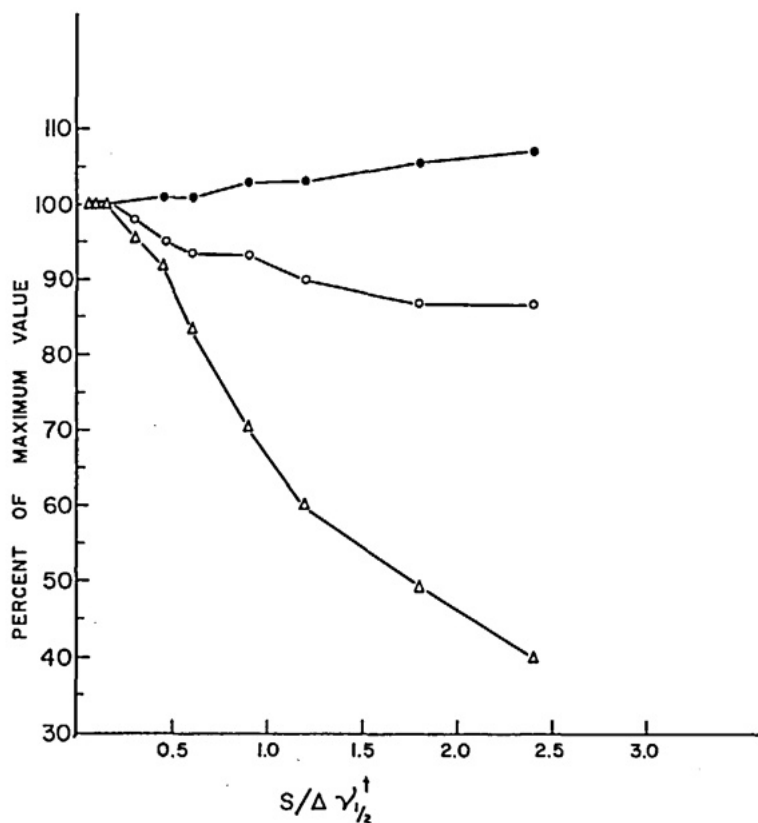


FIG. 3. Infrared band parameters of butyl n-butyrate as a function of $S/\Delta\nu_{1/2}^\dagger$: $\epsilon_{\max} \times \Delta\nu_{1/2}^\dagger$ (●—●—●); integrated intensity B, with wing correction (○—○—○); and ϵ_{\max} (△—△—△).

ing, then some method of extrapolation will be required. Extrapolation procedures have been discussed comprehensively in a review by Seshadri and Jones [40]. It is preferable to vary path length rather than concentration in extrapolation procedures because of the possibility of concentration-dependent interactions such as hydrogen bonding.

The numerical integration procedure by Eq. (12) may be questionable in the case of asymmetrically shaped bands. A related procedure employing several band widths has been suggested by Cabana and Sandorfy [45] for such cases.

III. FACTORS AFFECTING INTENSITY

A. Sources of Error in the Determination of True Band Parameters

Uncertainty in the base line due to drift, cell-window reflection losses, and other causes may be a major source of error in intensity determination [47]. It has been proposed that the base line be established by measurement at very short path lengths of the same solution or sample in a variable path cell used for intensity measurements [48]. Another source of uncertainty is the slit-width function and it has been shown that it may be necessary to work at an $S/\Delta\nu_{1/2}$ not greater than 0.1 to produce accurate band shapes [46]. A technique for estimating the slit function by measurement of narrow bands in the rotation spectra of some small molecules in the vapor state has been described [49].

The question of photometric accuracy is still unsettled. The use of rotating sectors for calibrating the photometric scale has been described [50] but their status is still uncertain, pending further study of the problem by Jones and his collaborators at the National Research Council [51].

Transferability of intensity data to within $\pm 10\%$ between various instruments has been demonstrated [52]. A major part of the difference may have been due to photometric errors. Variation of results within a set of measurements was believed to be due largely to baseline uncertainty.

The use of digital recording techniques [53] and appropriate computer programs [54] makes it feasible to evaluate error and distortion of band profiles [55] and to correct band shapes for the finite-slit-width effect by "pseudo-deconvolution" methods [56, 57]. Computer-aided computations have been of value in the study of the relations between slit-width functions and true band parameters [58] and in the application of numerical methods for correction of apparent band shapes due to finite slit width [59]. The application of computers to digitized spectrophotometric data may speed up the calculation of true band parameters [60].

Suggestions for recording and standardizing spectra which may meet the specifications desired for publishing have been offered by the Coblenz Society [61].

B. Effect of Environmental Variables

1. Temperature

It may be overlooked that the temperature at which a sample is maintained during an infrared scan may be well above the tempera-

ture at which the solution is prepared, resulting in a change in molar concentration due to expansion of the liquid. Temperature can also effect band width and integrated intensity [62, 63]. The effect of temperature on equilibria has been studied for purposes of calculation of the thermodynamics of intramolecular reactions involving isomers [64] and of intermolecular reactions of associated species [65, 66], the principal variable in these instances being the temperature-dependent integrated intensity associated with each species or conformer. A theoretical interpretation of the relationship between temperature and intensity has been published [67].

The effects of temperature on first- and second-order transitions of solid phases, reflecting changes in state of aggregation and internal mobility, are of importance in the study of polymers and these effects are reflected in variations in band shapes, intensities, and dichroic ratios [68, 69].

2. State of Aggregation

Intensities and band shapes are frequently altered on passage from vapor to liquid to solid state, owing to the effects of various intra- and intermolecular forces. In certain cases the change in intensity has been found to fit the Polo-Wilson equation [70, 71], deduced from the Debye theory of dielectric polarization [72]:

$$A_l/A_g = (n^2 + 2)^2/9n$$

where A_l and A_g are the intensities in liquid and gas phases, respectively, and n is the refractive index of the medium. Implicit in this relationship is the assumption of a Lorentz-type effective field as the internal field:

$$E_e = 1/3(\epsilon + 2)E$$

where E_e is the effective field at a molecule, E the macroscopic field in the medium, and ϵ the dielectric constant. The effect of the frequency-dependent internal field on band shape and intensity has been discussed by Illinger [73].

3. Effect of Solvent

The influence of solvent in terms of field and dielectric effects has been the subject of various papers, e.g., La Lau [74]; Buckingham [75], and others [76, 77]. The detailed discussion of these theories is outside the scope of this review, but a few practical pointers are in or-

der. The solvent should be pure, freed of inhibitors and stabilizers which are frequently added, and dried, if necessary, by passage through a molecular sieve or other drying agent. In general the least reactive solvents are paraffinic hydrocarbons such as hexane. Carbon disulfide can react with amines. Carbon tetrachloride is highly toxic and should be handled with great care. Chloroform and methylene chloride can form hydrogen bonds, as can solvents with an OH group. Specific interactions may occur with any polar group in a solvent and the bandshapes and intensities may be altered.

The remainder of this review consists primarily of tables and discussion of intensities of various characteristic chemical groups in organic compounds which have been reported in the literature. In some cases the listed values are given in more significant figures than may be warranted, in view of the experimental difficulties and theoretical uncertainties involved in the estimation of intensities. Hence practically all the results are provisional or tentative, pending the issuance of high-quality spectral data under rigorously standardized conditions. Probably most of the intensity data are within $\pm 20\%$ of the true value, but the possibility of greater variations does exist. These uncertainties do not necessarily vitiate the conclusions drawn concerning the effect of various chemical factors on the relative integrated intensities of a set of related molecules obtained by measurements which are internally consistent.

IV. INTENSITY UNITS

The literature values for integrated intensities vary, owing to the multiplicity of units (sometimes only implicitly reported). The abscissa scale may be in $d\nu$, sec^{-1} , $d\nu$, cm^{-1} , $d \ln \nu$, cm^{-1} or $d\lambda$. The intensity scale may be either on a log 10 or log e basis. The concentration may be on a mole/liter, moles/ cm^3 , atmospheres (gases), or other basis. In this review, data, where necessary, have been converted to the "practical" unit in liter/ cm^2 /mole (log 10) as defined by the Commission on Molecular Structure and Spectroscopy of the I.U.P.A.C. [78]. Various other units and their conversion factors to practical units are given in Table 2. The conversion factors involving ν_0 or ν_0^2 are approximate and can be accurate only if the band half-width is small in comparison with frequency at the band center.

Some uncertainty exists about the symbols to use for intensity. The symbol A is frequently used for integrated intensity in dimensions of either liter/ cm^2 /mole or cm^2 /sec/molecule as well as for the absorbance. In this review the symbol B will be used for the practical unit. For brevity, and to be consistent with the implied significance

TABLE 2
Integrated Intensity Units

Type of unit	Dimensions of the unit	Conversion factor (F)	Multiplier to convert to practical unit
Absolute (Thompson)	cm ² /sec/molecule (molecules/cm ³)	$\frac{2.303 \times 10^3 \times 3 \times 10^{10}}{N}$	8.728 × 10 ⁹
Practical	liter/cm ² /mole (moles/liter)	1	1
Secondary (Mecke-Crawford)	cm ² /molecule (molecules/cm ³)	$\frac{2.303 \times 10^3}{N \times \nu_0}$	2.617 × 10 ²⁰ × ν ₀
(Mecke-Crawford)	cm ² /mole (moles/cm ³)	$\frac{2.303 \times 10^3}{\nu_0}$	4.343 × 10 ⁻⁴ × ν ₀
Ramsay-Jones	liter/cm ² /mole	2.303	0.434
Mecke (λ scale)	cm ³ /mole (moles/cm ³)	$\frac{2.303 \times 10^3}{\nu_0^2}$	4.343 × 10 ⁻⁴ × ν ₀ ²
Gas scale	sec ⁻¹ /cm at NTP	$\frac{3 \times 10^{10} \times 2.303 \times 10^3}{22,415}$	3.24 × 10 ⁻¹⁰

Integrated Intensity = $F \int_{\nu_1}^{\nu_2} \epsilon_\nu d\nu$

of the reported figures, data will usually be abbreviated in intensity units where 1 intensity unit equals 10,000 liter/cm²/mole. Most bands fall in the range 0.01 to 1 intensity unit.

V. INTENSITIES OF THE CH BAND

A. Saturated Hydrocarbons

Integrated intensities of the methyl, methylene, and methyldene groups as structural units in saturated hydrocarbons are listed in Table 3. The discrepancies between the two sets of data from different investigators are due in part to the use of different sets of hydrocarbons, in part to differences in averaging, and in part to difference in background assumptions. Areas in one case were measured directly with an electronic integrator [79], in the other case with a planimeter [19].

TABLE 3
 Integrated Intensities of Structural Units
 in Saturated Hydrocarbons
 (Solvents: CCl₄, 2900 to 1300 cm⁻¹; CS₂, 720 cm⁻¹)

Band, cm ⁻¹	Structural unit values in intensity units					
	Methyl		Methylene		Methylidene	
	a	b	a	b	a	b
2900	0.45	0.39	0.37	0.33	0.16	0.12
1460	0.048	0.048	0.018	0.02	0	0
1380						
normal	0.02	0.02	(0.004) ^c		0	0
branched	0.04	0.04				
721	0.005					

^aRef. [19].

^bRef. [79].

^cRef. [80].

The 1380 cm⁻¹ intensity of an internal pendant methyl has been reported as 0.03 unit by other investigators, or nearly double the value for a terminal methyl group in a normal paraffin [80, 81]. The value for normal methyl in Table 3 apparently was uncorrected for background absorption due to methylene in the 1380-cm⁻¹ region, and a value of 0.017 intensity unit for this group appears to be reasonable.

The integrated intensities of alicyclic methylene 1450-cm⁻¹ and 2900-cm⁻¹ bands display anomalous trends when extrapolated to large rings [82]. Significant absorption is shown by the larger rings in the 1370-cm⁻¹ region, equivalent to one methyl group in cyclooctane and two in cyclododecane. For group-analysis purposes the structural unit intensities of the methylene group in the C-5 to C-8 ring size range is 0.37 ± 0.03 in the 2900-cm⁻¹ region and 0.024 ± 0.01 in the 1450-cm⁻¹ region.

The integrated intensities of crystalline normal paraffin hydrocarbons have been reported by Snyder [83]. The sum of the observed intensities in the 2900-cm⁻¹ region (his values were subdivided into symmetric and asymmetric methyl and methylene modes by arbitrary curve division) were not very different from values reported in solution [19, 79], the differences being about 10 to 15% lower in the solid phase.

Structural unit peak intensities (ϵ) for the methylene and methyl symmetric and asymmetric stretching modes have been reported by Jones [84] (his values are presented in Table 4 along with data for other modes).

TABLE 4
 Molar (Peak) Absorptivities of Structural Units in
 n-Paraffin Hydrocarbons^a
 (Solvents: CCl₄, 3000 to 1300 cm⁻¹; CS₂, 1300 to 700 cm⁻¹)

Band	Position, cm ⁻¹	ε _{max}	Δν _{1/2} est., cm ⁻¹
Methylene			
asym. CH stretch	2927	77	19
sym. CH stretch	2855-2853	46	
scissor	1467	8	14
wag	1307-1304	1.2	
rock	722-719	2.4	13.5
Methyl			
asym. CH stretch	2988-2954	129	16
sym. CH stretch	3872-2869	55	
asym. CH deformation	1458-1467	17.5	17.5
sym. CH deformation	1379	20.5	6

^aRef. [84].

From these data we can draw inferences about the band half-widths which were estimated (by the reviewer) as follows (assuming a Lorentzian profile):

$$\Delta\nu_{1/2} \text{ (estimated)} = \frac{\text{integrated intensity (from Table 3)}}{1.57 \times \epsilon}$$

The estimated values for Δν_{1/2} in Table 4 seem reasonable. Some knowledge of band contour would be required to arrive at reliable values of integrated intensities for the methyl and methylene symmetric and asymmetric stretching modes. Such knowledge might be obtained by study of suitable model substances such as polymethylene and tetramethylethane.

The percentage of hydrogen in the alkyl portion of organic compounds can be estimated from CH stretching integrated intensities, since the intensity per CH group in methyl and methylene is near the value for methyldene, the respective values from Table 3 being 0.15, 0.185, and 0.16 (date of Ref. [19]). The hydrogen content can also be estimated from peak-intensity data, the value per CH group being (77 + 46)/2 = 61.5 for methylene and (124 + 55)/3 = 59.6 for methyl (data in Table 4).

The methyl intensities in the 1380-cm⁻¹ region are of key significance in the analysis of types of methyl in organic compounds because

of the sensitivity of this absorption to branching. There may be some value in attempting curve resolution of overlapped bands which are observed in isopropyl, tert-butyl, gem-dimethyl, and other structures. The frequency and intensity of each band may be related to a different conformation of the methyl group in symmetrical deformation mode.

B. Olefinic Hydrocarbons

The intensity of a CH_2 or CH_3 group attached to an olefinic double bond appears to be decreased in the 2900-cm^{-1} region and increased in the 1460-cm^{-1} region (shifted to 1440 cm^{-1}), compared with the group values for paraffinic hydrocarbons. Strong bands due to out-of-plane deformations of ethylenic groups are observed in the 700- to 1000-cm^{-1} region. Olefinic structural unit intensities are listed in Table 5.

TABLE 5
Integrated Intensities of Structural Units in
Unsaturated Hydrocarbons^a
(Solvents: CCl_4 , 3000 to 1300 cm^{-1} ; CS_2 , 1000 to 650 cm^{-1})

Band, cm^{-1}	Assignment (C—H vibrations)	Intensity
6000	Overtone of $=\text{CH}_2$ stretching	0.015
3000	$\text{C}=\text{CH}$ stretching (vinyl, vinylidene, trans)	0.1
3000	$\text{C}=\text{CH}$ cis stretching	0.2
2900	$\text{C}=\text{C}-\text{CH}_3$ methyl stretching	0.15-0.27
1820	$\text{C}=\text{CH}_2$ vinyl o.p.d. overtone	0.013
1440	$=\text{CH}_2$ methylenic scissors (vinyl, vinylidene)	0.08-0.1
1440	$\text{C}=\text{C}-\text{CH}_3$ asymmetric CH bending (cis, trans)	0.08-0.1
1416	$\text{C}=\text{CH}_2$ in plane ethylenic bending (vinyl)	0.02
1404	$\text{C}=\text{CH}$ in plane ethylenic bending (cis)	0.04
1370	$=\text{C}-\text{CH}_3$ methyl symmetric CH deformation	0.27
993	trans- $=\text{CH}_2$ wag (vinyl)	0.08
965	$\text{C}=\text{CH}$ out-of-plane deformation (trans)	0.21
908	$=\text{CH}_2$ wag (vinyl)	0.20
888	$\text{C}=\text{CH}_2$ out-of-plane deformation (vinylidene)	0.23
700	$\text{C}=\text{CH}$ out-of-plane deformation (cis)	0.19

^aRef. [19].

The effects of olefinic unsaturation on the CH stretching and bending intensities in the 2900- and 1460-cm^{-1} regions are illustrated by the examples of n-pentane and pentene-2, presented in Table 6. The intensity in the 2900-cm^{-1} region in these examples drops twofold as

a result of unsaturation due to the loss of two CH_2 units (the *cis* hydrogen absorption is shifted to above 3000 cm^{-1}) and to the depressing effect of the double bond on adjacent methyl and methylene intensities. Striking changes are observed in the 1460-cm^{-1} region due to the shifting of the methyl vibration to the 1440-cm^{-1} region and the appearance of a *cis* band at 1404 cm^{-1} .

TABLE 6

Comparison of Calculated and Observed CH Intensities of
Normal Pentane and of *cis*-Pentene-2^a
(Solvents: CCl_4 , 3000 cm^{-1} ; C_2Cl_4 , 1400 to 1500 cm^{-1})

Region, cm^{-1}	Structural unit intensities (in intensity units)					Calc.	Obs.
	n-pentane						
2900	0.45	0.37	0.37	0.37	0.45	2.01	2.02
	$\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_3$						
1460	0.048	0.018	0.018	0.018	0.048	0.150	0.150
	<u>cis-pentene-2</u>						
2900 to 3000	0.45	0.22	0.20	0.27		1.14	1.09
	$\text{CH}_3\text{---CH}_2\text{---CH=CH---CH}_3$						
1400 to 1460	0.048	0.018	0.04	0.08		0.186	0.169

^aRef. [19].

The methyl symmetric deformation mode apparently is somewhat intensified when adjacent to double bonds, comparable values being about 0.017 for paraffinic methyl (corrected for background methylene) and 0.027 for methyl adjacent to a double bond as in *cis* and *trans* butene-2 [19].

The olefinic group is most readily characterized by out-of-plane deformations in the $700\text{- to }1000\text{-cm}^{-1}$ region, since each type of ethylenic group (*cis*, *trans*, vinyl, vinylidene) is well separated. The intensity per $=\text{CH}$ oscillator in this region is 0.09 to 0.12 (the vinyl modes at 910 and 990 cm^{-1} being summed). The sum of all the intensities in this region may be related analytically to total olefinic unsaturation in mixtures of hydrocarbons.

The intensity of the *trans* band is about one-third higher in the *trans*-stilbenes, probably because of the effect of conjugation with the aromatic rings (a value of 2.9 intensity units being reported as an average for 12 compounds) [85]. Substitution in the *ortho* position was correlated with band broadening, the effect being interpreted as evidence of steric hindrance and vibration damping. Energy transfer from the olefinic hydrogen out-of-plane deformation vibration to the

vibration of the interfering group was postulated, the result being an increase in the lifetime of a vibration.

C. Acetylenic Hydrocarbons

The acetylenic $\equiv\text{CH}$ stretching vibration is nearly constant in frequency at about 3300 cm^{-1} . The intensity is about 0.3 unit in aliphatic acetylenes, lowered by an adjacent hetero atom such as germanium to 0.2 [86]. The intensity of acetylene itself in the gas phase is about 0.15 per CH oscillator, increased to 0.85 in the solid phase [87]. The large increase in intensity in this case, accompanied by a decrease in frequency, was interpreted as evidence of the effect of hydrogen bonding between the acidic hydrogen of acetylene and the π electron cloud of the triple-bond system which has electron-donor characteristics.

The intensity of the $\equiv\text{CH}$ stretching vibration in phenyl acetylenes is fairly close to 0.4 unit and is only slightly effected by either electron-donor or electron-attracting substituents. The somewhat higher intensity observed in basic solvents [88] is consistent with the supposition that hydrogen bonding can occur between acetylenic hydrogen and an electron-donor group.

D. Aromatic Hydrocarbons

The most useful bands assignable to the aromatic CH intensities in benzene derivatives are the stretching vibrations in the $3000\text{-}3100\text{-cm}^{-1}$ region (several overlapping bands) and the out-of-plane deformations in the $675\text{-}900\text{-cm}^{-1}$ region. The integrated intensity per CH oscillator for both types of vibration is comparable in magnitude, being about 0.05 intensity unit for the stretching [19] and 0.07 intensity unit for the out-of-plane CH deformation [89].

The CH stretching intensity of a methyl group attached to the ring is lowered by a factor of 2 and the intensity of the methyl 1370-cm^{-1} deformation band is similarly lower than the unit value of 0.017 for normal paraffinic methyl. Structural unit intensities for these bands are listed in Table 7.

Both types, the stretching and out-of-plane deformation vibrations of the ring CH, overlap with the corresponding olefinic CH absorption in each region. Since intensities are comparable, the total absorption in either the $3000\text{-}3100\text{-}$ or $700\text{-}900\text{-cm}^{-1}$ region is a measure of total $\equiv\text{CH}$ unsaturation, counting an aromatic double bond as equivalent to an olefinic bond. A compound or a mixture containing both types of unsaturation can be further characterized by catalytic hydrogenation of the olefin unsaturation, leaving only aromatic rings for analysis.

TABLE 7
 Intensities of the CH Group in Aromatic Hydrocarbons
 (Benzene Derivatives)
 (Solvents: CCl_4 ; 3000 to 1300 cm^{-1} ; CS_2 , 900 to 700 cm^{-1})

Band, cm^{-1}	Assignment	Structural unit intensity
3050	Aromatic CH stretching, per CH oscillator	0.05 ^a
2900	Ring methyl CH stretching, per CH_3 group	0.23 ^b
1720-2000	Overtone of out-of-plane deformation	
1370	Ring methyl CH deformation, per CH_3 group	0.01 ^a
700-900	Out-of-plane deformation, per CH oscillator	0.05-0.08 ^c

^a Ref. [19].

^b Ref. [93].

^c Ref. [89].

A constant intensity of 0.099 cm^3/mole (wavelength scale) per CH (D) oscillator stretching vibration in the 3000 (2200 cm^{-1}) region was obtained for benzene and its deuterated derivatives [90]. This constancy on a wavelength scale was interpreted as a special case of the isotope intensity sum rule, or invariance of intensity to isotopic substitution in the case of stretching modes of the same symmetry species [91].

The intensity of the ring CH stretching vibration in benzene derivatives was found to vary with an inductive parameter σ_1 in a manner suggestive of a $\text{C}-\text{H}$ polarity during the stretching process [92]. A monotonic relation was observed between the intensity, and this parameter which was linear over most of the range, the intensity being given by (cm^3/mole):

$$I = 0.77\sigma_1 + 0.54 \quad (\sigma_1 \text{ range, } 0.1 \text{ to } 0.4)$$

The ring CH stretching intensity decreased with increasing σ_1 and electronegativity of the substituent, the range being 0.58 unit (ethyl) to 0.17 (CN), or about threefold. The intensity range was thus found to be $0.4 \pm 0.2 \text{ cm}^3/\text{mole}$. Aniline and fluoro- and nitrobenzene deviated from the linear portion of the plot, possibly because of compensating resonance interaction between these substituents and the ring. The over-all effect then was a diminution of intensity, owing to the effect of electron-withdrawing substituents in reducing the partial moment of the $\text{C}-\text{H}$ bond. The CH stretching intensity in ethylbenzene and in toluene was 0.6 cm^3/mole , which is equivalent to 0.044 per CH oscillator in intensity units, compared with a value of 0.050 obtained with these and other aromatic methyl groups [19].

The intensity of ring CH stretching vibrations in ortho benzene derivatives was found to be correlated with the sum $\sum \sigma_1$ of the inductive parameters [93], the correlation being expressed as

$$\log I_{ar} = -(0.72 \pm 0.13) \sum \sigma_1 - (0.23 \pm 0.06)$$

In the case of toluene derivatives the absorption was divided into two regions, above and below 3000 cm^{-1} , the lower frequency region being attributed to the aliphatic CH vibration. The intensity per methyl ranged from 0.77 in *o*-aminotoluene to 0.40 cm^3/mole in *o*-nitrotoluene. The midpoint value of 0.55 cm^3/mole is equal to 0.185 intensity unit. The intensity of methyl in *o*-xylene was 0.230 intensity unit per methyl, which is low by a factor of nearly 2, similar to the lowered intensity of methyl attached to the olefinic double bond [19].

A linear correlation between the inductive parameter of σ_1 and log of the intensity of the aliphatic methyl CH stretching vibration was also found in *o*-toluene derivatives [93]:

$$\log I_{aliph} = -(0.70 \pm 0.2) \sigma_{1,Y} - (0.04 \pm 0.07)$$

where $\sigma_{1,Y}$ is the value for the substituent ortho to the methyl group. The slope of the correlation plot was nearly the same as the plot for aromatic CH, which was taken as indicating that the polarities are the same, $\dot{C}-\dot{H}$ in both types of vibration (aromatic ring CH and aliphatic ring methyl CH=).

The intensity of benzene ring out-of-plane CH deformations in 51 benzene derivatives ranged from a low of 0.05 intensity unit in penta-substituted compounds to a high of 0.5 in benzene itself in a study of dipole moments of the sp^2 CH bond [89]. The dipole moment was found to be 0.64 D, compared with a value of 0.68 for ethylene [94]. Band widths were usually of the order of 4 to 6 cm^{-1} . Band broadening in monoalkyl benzenes containing a straight chain was attributed to partial steric hindrance of the adjacent ring hydrogens. "Complete" steric hindrance was inferred in *tert*-butylbenzene, which was favorable to narrowing of the band to values found in unhindered conformations. The intensity was somewhat exalted in some of the fluorinated compounds, compared with nonhalogenated derivatives. The intensity per CH oscillator (calculations of the reviewer) fell in the range 0.06 ± 0.02 , obtained by dividing the total intensity by the number of aromatic ring hydrogen atoms. This value is not conclusive because of the possibility of coupling with benzene ring sextant vibrations such as the 700-cm^{-1} vibration in monosubstituted alkylbenzenes. Calculations based on the data of Cole and Michell [89] and Wexler [19] are presented in Table 8.

TABLE 8
 Intensities per CH Oscillator of Out-of-plane Vibrations
 in Benzene Derivatives
 (Solvent: CS₂)

Benzene derivatives	Band, cm ⁻¹	Total intensity	Intensity per CH oscillator	Ref.
Benzene	675	0.5	0.08	89
Monosubstituted	700+760	0.4	0.08	19
Disubstituted	740-800	0.25	0.06	89
Trisubstituted	765-840	0.15-0.20	0.05-0.07	89
Tetrasubstituted	800-880	0.15	0.07	89
Pentasubstituted	860	0.05	0.05	89

In the monosubstituted alkylbenzenes two bands are observed near 700 and 760 cm⁻¹. The intensity sum of these two bands is fairly constant, as shown in Table 9.

The effect of branching next to the benzene ring is to cause the 760-cm⁻¹ band to become narrower and lower in intensity in the mo-

TABLE 9
 Intensities of Out-of-plane Deformations in
 Monosubstituted Alkylbenzenes^a
 (Solvent: CS₂)

Compound	700-cm ⁻¹ band	760-cm ⁻¹ band	Intensity sum	Ratio 760/700
Toluene	0.086	0.314	0.400	3.65
Ethylbenzene	0.196	0.206	0.402	1.05
n-Propylbenzene	0.205	0.227	0.432	1.11
Isopropylbenzene	0.226	0.171	0.397	0.76
n-Butylbenzene	0.199	0.224	0.423	1.12
sec-Butylbenzene	0.210	0.136	0.346	0.65
Isobutylbenzene	0.197	0.208	0.405	1.06
tert-Butylbenzene	0.235	0.148	0.383	0.63
(1,1-Dimethylpropyl) benzene	0.245	0.153	0.398	0.62
Cyclohexylbenzene	0.237	0.205	0.442	0.87
1-Phenyldodecane	0.206	0.213	0.419	1.03
3-Phenyldodecane	0.215	0.160	0.375	0.74

^aRef. [19].

noalkylbenzenes. The intensity ratio of the 760/700-cm⁻¹ bands is near 0.65 to 0.75 in the alpha-branched structures, and near 1.0 to 1.1 in structures without alpha-branching. The value of 0.08 intensity unit per CH oscillator in Table 8 was calculated from the intensity sum of the 700- and 760-cm⁻¹ bands in the monoalkylated benzenes. If individual band intensities are used, the value per CH oscillator drops to 0.04. A value of about 0.08 per oscillator is not far from the value of 0.1 per CH oscillator calculated for the out-of-plane vibrations of olefinic structures.

E. Effect of Change of Phase on Intensities

Hollenberg and Dows [95] formulated a sum rule for the constancy of the sum of all the integrated intensities, irrespective of the state of aggregation for the benzene molecule. Their comparison is shown in Table 10 along with more recent data on intensities in an "inert" solvent.

TABLE 10
Intensity Sums of Infrared Bands of Benzene in
Various States of Aggregation
(Solvents: CCl₄, 3000 to 1400 cm⁻¹; CS₂, 700 cm⁻¹)

Band, cm ⁻¹	Gas ^a	Liquid ^b	Solid ^c	Solution ^d
3060	0.260	0.191	0.087	0.237
1480	0.056	0.083	0.165	0.105
1036	0.038	0.050	0.076	(0.04)
673	0.380	0.415	0.400	0.598
Sum	0.734	0.739	0.728	0.980

^a Ref. [96].

^b Ref. [97].

^c Ref. [95].

^d Ref. [19].

The higher intensity in the solvent case may be due to either a solvent effect or the higher resolution at which this band was measured in solution. Undoubtedly this rule would not hold for cases where band intensity increases due to hydrogen bonding and other interactions, as in the case of acetylene, which undergoes a fivefold increase in CH stretching intensity on passage from the gas to the solid phase [87].

The effect of change of phase on the intensities of the CH stretching vibration of hydrocarbons other than benzene is variable, as shown in Table 11.

TABLE 11
Intensities of CH Stretching Vibration of
Hydrocarbons in Various Phases
(Solvent: CCl_4)

Compound	Gas	Solution	Solid
Methane	0.31 ^a		
Ethane	0.74 ^b		0.63 ^c
Butane			1.1 ^d
Pentane		2.0 ^e	1.9 ^d
Hexane		2.4 ^e	2.1 ^d
Heptane		2.8 ^e	2.5 ^d
Ethylene	0.50 ^f		0.67 ^g
Acetylene	0.31 ^h		1.7 ^c

^aRef. [98].

^bRef. [99].

^cRef. [101].

^dRef. [83].

^eRef. [19].

^fRef. [94].

^gRef. [87].

^hRef. [100].

The CH intensity in partly deuterated methanes is nearly constant, a value of 0.08 per CH unit being obtained for the CH stretching vibration and a value of 0.03 to 0.05 for the CD oscillator [102].

Invariance of intensity with respect to isotopic substitution is obtainable only on a wavelength scale or its equivalent. This invariance may be stated: The sum (Γ/ν or A/ν^2) over the bands of a given symmetry species common to both molecules is an isotopic invariant. The example of benzene and hexadeuterobenzene is illustrative of this constancy expected from the rule [103], as shown in Table 12.

F. Effect of Carbonyl Group on Intensities

The CH_3 and CH_2 stretching intensities are reduced about 7 to 10 times if a carbonyl group is adjacent. The bending intensities are increased several fold in the 1460- and 1370- cm^{-1} regions [104]. The stretching intensities of the CH_3 and CH_2 groups adjacent to the alkoxy

TABLE 12
 Intensities of Infrared Bands of Benzene and
 Hexadeuterobenzene (10^{-6} dark-cm²)^a

Symmetry class	C ₆ H ₆		C ₆ D ₆	
	ν	Intensity	ν	Intensity
a ₂ μ	673	19,400	496	20,200
e ₁ μ	3080	2,054	2287	2,041
	1485		1335	
	1037		814	

^aRef. [103].

group are reduced and the methyl symmetric deformation is shifted to the 1440-cm⁻¹ region. The CH₂ intensities in the 1460- and 1370-cm⁻¹ regions are intensified. The results are tabulated by structure in Table 13. The absorption due to methylene in the 1370-cm⁻¹ region is increased several fold when adjacent to a carbonyl group.

G. Effect of OH Groups on Intensities

The CH stretching intensity of methyl groups adjacent to an OH group is reduced, whereas the bending intensities are only slightly effected [105]. The intensities of the methyl group in the series methanol, ethanol, n-propanol, and higher homologs were 0.14, 0.27, 0.33, and 0.45, respectively. The effect of OH on methylene intensities was not spelled out.

H. Effect of Halogens on Intensities

The CH stretching intensities in the gas phase are noticeably reduced by attached halogens, the reduction being much greater per halogen in polyhalogenated linkages. In solution, strong bonding effects and intensity increases are observed in the case of chloroform, which contains an acidic hydrogen and readily associates with its own kind, and very strongly associates with basic, electron-donor groups [106]. Some intensity data for methane and halogenated methanes in the gas phase are shown in Table 14. The data in this table indicate that the effect of a halogen atom on the CH vibration is complex. The CH stretching intensity variations are explainable in terms of the presence of C— $\overset{+}{H}$ polarity, which is favored by electronegative substituents. With decreasing electronegativity, the intensity may decrease because of reversal of polarity to the $\overset{+}{C}$ — $\overset{-}{H}$ state. The effect

TABLE 13
Effect of Keto and Ester Groups on CH Intensities^a
(Solvent: CCl₄)

Band, cm ⁻¹	Ketone					Ester				Ester			
	CH ₃	CH ₂	CH ₂	$\begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array}$	CH ₃	-CH ₂	$\begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array}$	O	CH ₂ ⁻	CH ₃	$\begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array}$	O	CH ₃
2900	0.4	0.35	0.04	0	0.065	-0.045	0	0	-0.03	0.065	0	0	0.2
1460	0.05	0.025	0.1	0	0.1	0.1	0	0	0.06	0.1	0	0	0.2
1370	0.02	0	0.07	0	0.2	0.25	0	0	0.05	0.2	0	0	0
1720	0	0	0	0.7	0	0	1.2	0	0	0	1.2	0	0
1200	0	0	0	0.2	0	0	0	1.3	0	0	0	1.3	0

^a Ref. [104].

TABLE 14
Intensities of CH Vibrations in Halogenated Methanes^a
(Intensity units per CH oscillator)

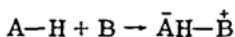
Derivative	Stretching vibrations					Bending vibrations				
	H	F	Cl	Br	I	H	F	Cl	Br	I
CH ₃ X	0.08	0.10	0.04	0.03	0.02	0.04	0.007	0.03	0.03	0.03
CH ₂ X ₂			0.03	0.003	0.006		0.06	0.10	0.18	
CH X ₃		0.15	0.002	0.015			0.42	0.18		
Alkanes	0.16					0.015				

^a Ref. [24, 107-111] (gas-phase data).

of polyhalogenation is to greatly decrease stretching intensities except in the fluoromethanes. Polyhalogenation increases the CH bending intensities.

In the gas phase methylene chloride displays a single band near 3000 cm^{-1} assignable to a CH symmetrical stretching vibration (ν_1). In solution, or in the liquid phase, a second band assignable to a CH asymmetrical stretching vibration is observed. Evans and Lo [112] account for these observations by assuming that the principal dipole-moment-derivative contributions to the stretching intensities are the change in the CCl and CH moments with CH stretching. The derivative $\partial\mu_{\text{CH}}/\partial r_{\text{CH}}$ is considered to be effectively zero in the gas phase and therefore the asymmetrical CH stretching band (ν_6) is absent.

In solution, the $\partial\mu_{\text{CH}}/\partial r_{\text{CH}}$ dipole-moment derivative increases (probably with opposite sign to that of the cross-term derivative), owing to a charge transfer mechanism between the somewhat acidic hydrogen of methylene chloride and acceptor atoms:



This change does not involve alteration of the polarizability of the CH bond, as shown by the fact that both bands are present in the Raman spectra and no changes occur in their intensity ratios on going from the gas to the liquid state. The charge transfer is favored by electron-donor solvents, with resulting changes in intensities in solvents. Therefore the ν_6 band intensity increases in solution. The intensity of the ν_1 band varies, depending on the magnitude of the contributions of each of the dipole-moment derivatives, since the over-all intensity of this vibration is the result of composite effects of terms (of opposite sign?) involving a CH and CCl moment.

VI. INTENSITIES OF C=C STRETCHING VIBRATIONS IN HYDROCARBONS

The intensity of the C=C stretching vibration in the $1500\text{--}1700\text{-cm}^{-1}$ region of hydrocarbons has been reported [19], as shown in Table 15.

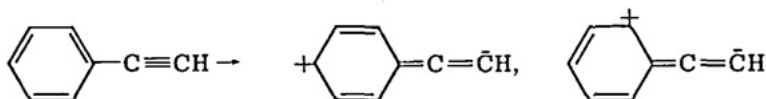
Trans and other ethylenic bands are usually too weak to be detected. The intensity may be raised by conjugation involving multiple double bonds. This vibration can couple with a carbonyl vibration when these are conjugated, as discussed later.

TABLE 15
 Intensities of C=C Stretching Vibrations
 in Hydrocarbons
 (Solvent: CCl₄)

Group	Band, cm ⁻¹	Intensities
Vinyl	1641	0.050
Vinylidene	1645	0.077
cis-Olefin	1657	0.020
Monoalkylbenzenes	1500	0.080
	1600	0.040

VII. INTENSITIES OF C≡C STRETCHING VIBRATIONS IN HYDROCARBONS

This vibration shows very little frequency variation but quite marked intensity change with the effect of substituents. By contrast, the intensity of the ≡CH vibration in phenyl acetylenes is relatively insensitive to substituent effects. Compared with phenylacetylene (intensity 0.02 unit), the intensity of the C≡C band at 2110 cm⁻¹ is lower by a factor of 10 in the p-CF₃ derivative (containing a strong electron-attracting substituent) and higher by a factor of nearly 4 in the p-OCH₃ derivative (containing a strong electron-donor substituent). A linear correlation was obtained between the square root of the integrated intensity and the electrophilic substituent constants in the phenylacetylenes [88]. Most of the intensity increase in the substituted phenylacetylenic C≡C stretching vibration was interpreted as resulting from transfer of the π electronic charge between the ring and the ethynyl group during the vibration with the formation of polar states:



An electron-donor substituent on the ring would favor the polarity, thereby increasing the intensity, whereas an electron-attracting substituent would oppose the polarity, lowering the intensity. The favorable correlation in this case with the Taft electrophilic substituent [113, 114] constant is evidence that the functional group resonance interaction is either aided or opposed by the polar inductive effect of

the substituent in the para position.

A linear correlation with negative slope was also observed between the integrated intensity of the $C\equiv C$ stretching vibration in organo-germanium compounds with the structure $R-Ge-C\equiv C-R'$ and the Taft coefficient for the substituent R' ($\sigma^* = 0.49$ for $R' = H$ and 0.130 for $R' = C_4H_9$) [86]. Some of the $C\equiv C$ integrated intensities for aliphatic and aromatic acetylenes are reported in Table 16.

TABLE 16
Intensities of $C\equiv C$ Stretching Vibrations in Hydrocarbons
(Solvent: CCl_4)

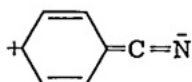
Group	Frequency, cm^{-1}	Intensity	Ref.
$R-C\equiv CH$	2120	0.03	86
$R-Ge-CH_2-C\equiv CH$	2112	0.08	86
$R-Ge-C\equiv CH$	2027	0.04	86
$R-Ge-C\equiv C-R$	2168	0.18	86
Phenylacetylene	2112	0.02	88
<i>p</i> - CH_3 phenylacetylene	2110	0.04	88
<i>m</i> - CH_3 phenylacetylene	2108	0.02	88
<i>p</i> - OCH_3 phenylacetylene	2109	0.075	88
<i>p</i> - CF_3 phenylacetylene	2117	0.002	88

VIII. INTENSITIES OF $C\equiv N$ STRETCHING VIBRATIONS

The frequencies of the $C\equiv N$ stretching vibration fall within the relatively narrow range 2210 to 2270 cm^{-1} , whereas the intensity varies over a several hundred-fold range, the lowest value being that for vinyl cyanide in vapor phase (0.0026 intensity unit) and the highest that for *p*-aminobenzonitrile (0.62 unit) and diethyl cyanamide (1.00 unit) in chloroform. The intensity increases going from gas to "inert" solvent to chloroform. Inductive and resonance as well as solvent effects alter the intensities, with very little effect on frequency. The unperturbed intensity of an isolated CN vibration in a hydrocarbon is about 0.04 to 0.06 . However, the intensity is lowered by an adjacent $C-CN$ or $C-Cl$ group and is lower by a factor of 2 in methyl cyanide than in the higher homologs. The intensity of the CN vibrations in the benzonitriles is 5 to 10 times higher than in aliphatic configurations.

A linear correlation was found between either the log [115, 116] or the square root [88] of the CN stretching intensities in the benzonitriles and the corresponding Taft electrophilic substituent constant.

The slope of the plot of the square root of the intensity of the ethylnic $C\equiv C$ vibration has been found to be nearly the same [88], suggesting a similar electronic process associated with the stretching mode to be occurring. The substituent effect on the intensity is consistent with the contribution of resonance forms such as



contributing to the intensity. Resonance interaction of the electrons of both the ring and the triple bond with lowering of bond order and increase in intensity may be responsible, in the first place, for the higher intensity of aromatic nitriles as compared with aliphatic. Resonance with formation of forms such as $R_2\text{N}=\text{C}=\text{N}^-$ may be responsible for the high intensities observed in the cyanamides. An electron-donating group such as NH_2 in *p*-aminobenzonitrile would contribute to the intensity by favoring the polarizations developed during the stretching process.

The increased intensity in chloroform by a factor of 1.5 to 2 times compared with CCl_4 may be evidence of hydrogen bonding between the acidic hydrogen and the nitrogen lone-pair electrons. The ethylnic $C\equiv C$ stretching vibration by contrast is relatively solvent insensitive. Intensities for the CN group are presented in Table 17.

IX. CARBONYL STRETCHING VIBRATIONS IN ORGANIC COMPOUNDS

The vibrations in multiple-bonded systems which contain atoms differing only slightly in electronegativity, such as the $C=C$ and $C\equiv N$ bonds, are well localized and the force constants do not vary much with structure. In the $C=O$ bond the vibration is still fairly well localized but the electronegativity difference between these two atoms is sufficiently great that the $C=O$ frequency as well as the intensity are affected by substituents.

The stretching process in the carbonyl bond is electron-demanding, and electron-donor substituents can exert both a polar inductive effect and a resonance effect in altering the bond polarity, as in the amides:

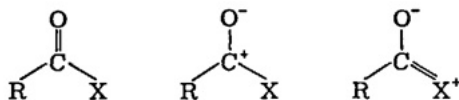


TABLE 17
Intensities of C≡N Stretching Vibrations (2200 cm⁻¹)

	Gas		CCl ₄		CHCl ₃		Ref.
	cm ⁻¹	B	cm ⁻¹	B	cm ⁻¹	B	
CH ₃ CN	2267	0.0072	2255	0.018	2255	0.037	117, 118
iso-C ₅ H ₁₁ CN			2253	0.035	2253	0.059	118
CH ₂ (CN) ₂					2273	0.0074	118
(CH ₂) ₁₀ -(CN) ₂			2249	0.032	2249	0.053	118
Cl-CH ₂ -CN	2266	0.0034	2260	0.0033	2261	0.0039	118
Cl ₃ -C-CN	2256	0.046	3249	0.028	2250	0.021	118
CH ₂ =CH-CN	2241	0.0026	2230	0.021	2231	0.048	118
N(CH ₃) ₂ -CN			2214	0.72	2209	1.00	118
N(C ₂ H ₅) ₂ -CN			2221	0.72	2218	0.95	118
Benzonitrile			2230	0.087	2230	0.15	115, 119
p-Chlorobenzonitrile			2233	0.087	2235	0.16	115, 119
p-Nitrobenzonitrile			2238		2239	0.065	115, 119
p-Methoxybenzonitrile			2226	0.19		0.33	115, 116
p-Aminobenzonitrile				0.36	2221	0.62	115, 119
Polynuclear aromatic nitriles			2223	0.25			120

The amides absorb at lower frequency (below 1700 cm^{-1}) with higher intensity than ketones, aldehydes, acids, and esters because of a strong resonance effect.

Electronegative substituents tend to oppose the polarization and raise the force constant of the carbonyl double bond, with a resulting increase in frequency and decrease in intensity. Resonance effects of the substituent X favor the formation of charge-separated structures with lowering of frequency and increasing of intensity. Steric effects may come into play, resulting in the formation of conformational isomers absorbing at different frequencies when the group X is bulky, especially if field effects which alter the electron density around the oxygen atom can be exerted by the group or atom X. Conjugation with olefinic or aromatic double bonds favors the polarization with a lowering of frequency.

A. Ketone Carbonyl

Intensity and frequency data for the keto carbonyl stretching modes are listed by group in Table 18 into open chain, saturated cyclic, unsaturated cyclic, and aromatic ketones. Within each group steric, inductive, and conjugative effects may be observed which alter the intensity when compared with the parent compound in the series. Steric hindrance around the carbonyl group causes the intensity to decrease, as in pinacolone and 2,2-dimethylcyclohexanone [23].

The effect of a vicinal halogen is to lower the intensity either by an inductive effect, as in the keto steroids [15], or by a field effect, as in the equatorial conformation of α -bromocyclohexanone [23].

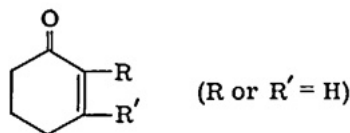
Conjugation with an olefinic or aromatic system decreases the frequency and increases the intensity moderately, except in *cis* conformation of α,β -unsaturated ketones, where a decrease in intensity, attributed to coupling with the double bond, is observed [121-124].

Coupling with ring stretching modes may cause the intensity to be higher in cyclobutanone [125,126]. The intensity in cyclonones steadily decreases, reaching a constant value equivalent to the open-chain value in cyclononanone [125].

The combined effects of unsaturation and ring coupling are observed in α,β -unsaturated keto steroids with intensities of about 1.6 units, or nearly double the open-chain, saturated ketone value. Part of the increase is due to conjugation, part to the six-membered ring effect.

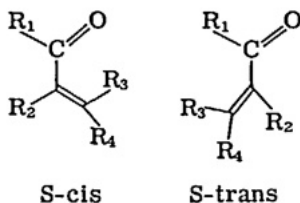
The highest ketone intensity reported was in flavone, with a value of 2.0 units, attributed to a pronounced mesomeric effect [127].

Splitting of the carbonyl band can occur in some α,β -unsaturated cyclic ketones with the structure



provided a hydrogen is present at the double bond [123]. The splitting was attributed to Fermi resonance between the carbonyl vibration and an overtone of an olefinic CH out-of-plane deformation (fundamental at 875 to 900 cm^{-1} ; overtone at 1750 cm^{-1}). The intensities of the carbonyl and olefinic stretching vibrations were about 1.1 to 1.3 and 0.01 to 0.15, respectively. The total intensity is attributable almost entirely to the carbonyl mode, with some "borrowing" of intensity by the normally very weak overtone.

Splitting of the carbonyl band observed in open-chain ketones is due to the presence of cis and trans conformations [122]:



The condition for the presence of both forms in equilibrium is that R_2 , R_3 , and R_4 must be hydrogen atoms (vinyl ketones). If position R_2 only is substituted, the trans form predominates, owing to steric repulsion between R_2 and R_1 . If the position R_3 is substituted with an alkyl group, the cis form predominates, even if R_2 is also substituted. The equilibrium, when present, shifts in the trans direction with lowering of temperature. The trans C=O band is relatively much more intense in the Raman spectrum than the cis C=O. The C=C Raman intensities also are more intense, relative to the C=O intensity, than the corresponding infrared intensities.

As previously noted, the intensity of the C=O stretching mode in α, β -unsaturated ketones is lowered, owing to coupling with the adjacent C=C vibration. The intensity sum of the C=O and C=C bands is approximately constant at about 1.0 [121]. The normally weak C=C band is greatly intensified by coupling, the process being regarded as a transfer of intensity from the C=O vibration to the C=C vibration. The intensity of the trans C=O band is closer to the value expected for open-chain carbonyl, being somewhat intensified in the

TABLE 18

Intensities of Carbonyl Stretching Vibrations in Ketones
(Solvents: chlorinated solvents and CS₂)

Structural type	cm ⁻¹	Inten- sities	Comment	Ref.
Open chain				
Saturated	1715	0.75	Steric hindrance at α -carbon may lower intensity	23
α -Halogenated	1735		Cis and gauche conformations may occur	15
α,β -Unsaturated (trans)	1690	0.8	C=C band near 1660 cm ⁻¹ , intensity about 0.1	121, 124
α,β -Unsaturated (cis)	1680	0.6	Lower value due to coupling with intensified C=C band near 1630 cm ⁻¹ ^a	122
α -Diketones	1720		Normal intensity expected	
α -Diketones (enolized)	1600		Hydrogen-bonded resonance forms may increase intensity	
Cyclic saturated				
Cyclobutanone	1790	1.35	Increased intensity due to coupling with ring vibrations; effect diminishes with increase in ring size	125, 126
Cyclopentanone	1751	1.26		125, 126
Cyclohexanone	1719	1.10		125, 126
2,2-Dimethylcyclohexanone		0.70	Steric effect lowers intensity (nonplanar)	23
α -Bromocyclohexanone (axial)		0.91	Inductive effect of Br atom lowers intensity	23
α -Bromocyclohexanone (equatorial)		0.58	Field effect of Br atom in equatorial position	23
1,4-Cyclohexadione	1728	0.94 ^b	Six-membered ring intensity	23

Unsaturated cyclic				
α,β -Unsaturated (cis)		0.6	See remark of analogous open chain	121, 124, 134
α,β -Unsaturated (trans)	1670	1.2	Higher intensity due to ring strain (five- and six-membered rings)	121, 123, 134
p-Quinones	1650, 1665	0.76 ^b	Fermi resonance causes splitting of the C=O band	127
3-Methylcyclopent-2-enone	1711	1.80	Five-membered ring intensities plus conjugation	134
3,3,5-Trimethylcyclohex-2-enone	1679	1.22	Six-membered ring intensity plus conjugation	134
α,β -Unsaturated ketosteroids	1715	1.6	Intensities increase 0.4 for six-membered ring and 0.4 for conjugation	15
Aromatic				
Alkyl aryl ketone	1690	0.85	Non-Lorentzian; K value about 1.3	43, 129, 130, 135
Diaryl ketone	1670	0.90		
Anthraquinones	1680	0.70 ^b		
Anthrone	1670	1.18	Six-membered ring intensity	127
α -Fluorenone	1722	1.30	Five-membered ring intensity	127
Flavone	1654	2.02	Strong resonance affect lowers frequency, raises intensity	127

^aVinyl ketones may show two bands due to cis,trans isomerism, the cis band being at lower frequency. Equilibrium shifts to trans as temperature decreases. All trans in solid.

^bPer C=O group.

^c α,β -Unsaturated trans cyclic ketones with olefinic hydrogen show splitting due to Fermi resonance.

cyclic structure either by conjugation or coupling with ring vibrations.

The ketone C=O stretching mode intensity is lowest in nonpolar solvents such as hexane, and increases appreciably in polar solvents [128-130]. Band asymmetry and non-Lorentzian contour with a K value of about 1.3 has been reported for the carbonyl band in ketones [43]. Complex formation between the carbonyl stretching vibration and proton donors such as chloroform has been observed [131-133].

The effects of modification of structure or presence of substituents on the C=O stretching intensity in ketones are summarized in Tables 18 and 19.

TABLE 19
Effect of Structural Units on C=O Stretching
Intensity in Ketones
(Solvents: chlorinated solvents and CS₂)

Structural unit	cm ⁻¹	Intensity
Standard ketone, —CH ₂ —CO—CH ₂ —	1720	0.75
Vicinal bromination	+20	-0.3
tert-Butyl group		-0.2
α,β-Unsaturation (cis)	-30	-0.2
α,β-Unsaturation (trans)	-20	+0.4
Ring closure, five-membered	+30	+0.5
Ring closure + α,β-unsaturation	Variable	+1.0
Aryl group	-30	+0.2

B. Ester Carbonyl

The carbonyl stretching mode in esters is near 1740 cm⁻¹, with an intensity of about 1.2 units with few exceptions. The ester C=O stretching frequency is lowered by conjugation of the carbonyl with unsaturation or aromatic rings (α,β-unsaturated; benzoates; phthalates) and is raised in vinyl and phenyl esters without much effect on the intensity, compared with aliphatic esters. The intensity is somewhat higher in formates, and both the intensity and frequency are markedly higher in chloroformates, opposite to the expected trends. The intensity is much higher in certain polynuclear aromatic esters such as the ethyl ester of 4-pyrenecarboxylic acid [120]. Characteristic data by groups for the ester C=O stretching intensity are presented in Table 20.

The intensity of the C=O stretching overtone near 3450 cm⁻¹ is approximately 1/100 of the intensity of the fundamental at 1740 cm⁻¹ [129]. The intensity of the fundamental in benzoate esters is slightly

TABLE 20
Integrated Intensities of Carbonyl Stretching
Vibrations in Esters

	cm ⁻¹	Intensity ^a	Ref.
Formates	1735	1.4	129
Acetates	1740	1.2	129
Propionates	1740	1.2	129
Benzoates	1725	1.3	129,130
Halogenated acetates	1740-1780	1.2	136-138
Chloroformates	1780	1.7	129
Acrylates	1730	1.15	129
Methacrylates	1723	1.15	129
Phenyl esters	1770	1.2	139
Vinyl esters	1750-1770	1.35	139
Polycyclic aromatic acid esters	1720	2.4	120

^aIn carbon tetrachloride.

affected by substituents, being somewhat lowered in the p-amino and p-methoxy derivatives [130]. The slope of the plot of log intensity vs. σ is slightly negative, whereas the frequency vs. σ plot is positive in slope [129]. The intensity of some benzoate esters in potassium bromide dispersion averaged 0.8 unit [18] compared with values of about 1.2 units in carbon tetrachloride solution [130]. Of interest is the variation in intensity of ethyl acetate reported by different investigators ranging from 1.13 [135] to 1.53 [129]. These variations cast some doubt on the reliability of any given value until confirmed in different laboratories. Part of the variation may be due to differences in extrapolation range, background correction, method of integration, concentration effects, and instrumental and sampling errors. The intensity of the acetate group was 1.40 units in acetylated steroids and 1.2 units in the phenyl acetate derivatives [15], in fair agreement with values in Table 20 for each structural type.

The intensity of the ester $\nu_{C=O}$ vibration was found to be 10 to 20% higher in chloroform than in carbon tetrachloride [136, 137], whereas the frequency was about 10 cm⁻¹ lower. The ester carbonyl group associates with chloroform by hydrogen bonding to form a 1:1 complex [140]. Two peaks, or a peak and a shoulder, are observed in the carbonyl stretching band of esters in solvents containing alcohol [141]. The lower frequency peak is probably due to the complex between carbonyl and monomeric hydroxyl of the alcohol, whereas the higher frequency peak is assignable to free carbonyl. The total integrated

intensity may be nearly constant over the entire band structure.

Substituted esters with a halogen atom on the carbon atom adjacent to the carbonyl group, such as ethyl monochloroacetate and difluoroacetate, show splitting of the carbonyl band, attributable to the presence in equilibrium of *cis* and *gauche* conformers [137]. Splitting of the carbonyl band due to formation of rotational isomers in equilibrium has been observed in halogenated ketones [23]. In esters, electrostatic repulsion between the alkoxy oxygen and the α -halogen may be a factor in orientation of the substituent [137]. The total intensity may not vary much between isomers. Bulkiness of the α substituent may be a factor in decreasing the total intensity from 1.48 units in ethyl acetate to 1.10 units in ethyl trichloroacetate [130].

A roughly linear correlation was observed between intensity and $-\log K$ of the corresponding acid in some substituted aliphatic esters, indicating the possibility of a mesomeric electron displacement as affecting the ground state and therefore the intensity of the carbonyl stretching vibration [138]. The mesomeric effect in the chloroformate esters apparently overrides the negative inductive effect with the formation of a polar structure with charge separation which contributes to the ground electronic state:

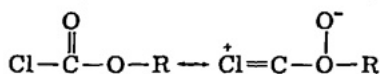


TABLE 21
Ratio of Integrated Intensities of Ester
Carbonyl Stretching Vibrations (1740 cm^{-1}) to
the Alkoxy Absorption (1200 cm^{-1})
(Solvents: chlorinated)

Structural unit	Intensity ratio, ^a C=O/CO	Ref.
Formates	1.0	142
Higher aliphatic esters	0.8	142, 143
Phenyl, vinyl esters	0.6	139
Phthalates	0.7	139
	(1250-cm ⁻¹ region only)	
Phthalates	0.4	139
	(1200-cm ⁻¹ region + 1000 to 1150-cm ⁻¹ region)	
Steroid acetates	0.7	144

^aThese ratios were calculated by the reviewer.

The ratio of the integrated intensity of the ester carbonyl stretching vibration at 1740 cm^{-1} to the alkoxy CO stretching vibration near 1200 cm^{-1} may be of diagnostic significance, as shown by the data in Table 21.

C. Carboxy Carbonyl

The carboxyl group tends to complex either through the carbonyl group with proton donors or through the hydroxyl group with proton acceptors. Either intramolecular (chelated) or intermolecular (dimeric, polymeric) species may exist, in addition to complexes between unlike molecules. The most characteristic infrared band of carboxylic acids is the dimer carbonyl stretching mode which predominates above 0.1 M concentration in inert nonpolar solvents. On dilution the dimer dissociates to yield monomer. Some dimer is still evident even at 10^{-5} M concentration in carbon tetrachloride. Dissociation constants for dimer-monomer equilibria have been determined [145].

The C=O integrated intensities of the dimer and monomer species may not be very different [146], nor may the intensities of the various solvent-complex forms vary much from the values for dimer [147]. Some characteristic data are presented in Table 22. The total integrated intensity is in the range 1.6 to 2.1 units, depending on the solvent. Polar solvents such as methanol and dioxane are necessary to dissolve polyfunctional acids which are difficult to dissolve in chlorinated solvents.

Intensities in potassium bromide dispersions have also been reported [14] for organic acids. A correlation between the C=O bond intensity and the Taft σ^* constant has been observed [146] in halogenated acetic acids. The intensities and σ^* values ranged from 1.95 units ($\sigma^* 0.0$) in acetic acid to 1.47 units ($\sigma^* 2.6$) in trifluoroacetic acid. Band asymmetry in some of the halogenated acids was ascribed to possible presence of rotational isomers. Conformational isomerism has been suggested in the cases of ortho-halogenated acids and their esters [148]. One clue to possible presence of rotational and conformational isomers is in broadening of the band, which is observed in monochloroacetic [146] and isobutyric acid [147]. Extreme broadening of the band is observed in o-chlorobenzoic acid (dimer) with a band half-width of 45 cm^{-1} compared with a group average of about 16 cm^{-1} in meta- and para-substituted benzoic acids. In dilute solution two separate peaks at 1700 and 1755 cm^{-1} are observed, the higher frequency peak being attributed to monomer [149].

TABLE 22
Integrated Intensities of Carboxy Carbonyl Stretching Vibrations

Structural unit	Solvent	Molarity	Cm^{-1}	Inten- sity	Remarks	Ref.
Aliphatic carboxy	CCl_4	10^{-1}	1710	1.9	Over 95% of the absorption is due to - COOH dimer	147
Aromatic carboxy	CCl_4	10^{-1}	1695	2.2	Over 95% of the absorption is due to - COOH dimer	147
α -halogenated Carboxy	CCl_4 CCl_2	10^{-1} - 10^{-2} 2×10^{-4}	1740-1780 a	1.5-1.9 1.8	Several conformations may exist - COOH free and dimeric forms roughly 1:1 ratio	146 147
Carboxy	CCl_4	0.5×10^{-5}	1750-1800	1.7	Over 90% free - COOH absorption	147
Carboxy	CH_2Cl_2	10^{-4}	1730-1780	2.1	Carboxy carbonyl complexed with acidic hydrogen of CH_2Cl_2	147
Carboxy	Methanol	0.2	1690-1780	1.6-1.9	Part - COOH dimer, part complex of carbonyl with methanol OH	147
Carboxy	Dioxane	0.2	1740	1.6	Carboxy hydroxyl complexed with ether oxygen	147
Aliphatic carboxy	KBr			1.2	Data for a few dicarboxylic acids	14
Aromatic carboxy	KBr			1.6	Mainly benzoic acids	14

^a Two peaks spaced about 40 to 50 cm^{-1} apart in the 1700 to 1760- cm^{-1} region; low-frequency peak due to - COOH dimer, other peak to free COOH carbonyl absorption.

D. Ionic Carboxylate Stretching Mode

The strongest band in the spectrum of carboxylic acid salts of moderate equivalent weight is the antisymmetric stretching mode of the ionic carboxylate group near 1550 to 1600 cm^{-1} , with an integrated intensity of 3 to 4 units (Table 23).

TABLE 23
Integrated Intensities of Antisymmetric COO^-
Stretching Mode of Ionic Carboxylates
(1550 to 1600 cm^{-1})

Structural type	Medium	Intensity	Ref.
Aliphatic, monobasic	KBr	3.6	14
Aliphatic, dibasic	KBr	3.7	14
Aliphatic, monobasic	Methanol	2.7-3.0	150
Benzoates	Methanol	3.0-3.6	150

In methanol and other solvents, such as dimethylsulfoxide, the aliphatic carboxylates display one band with an intensity of about 2.9 units. Benzoate salts show a complex pattern of one, two, or three bands depending on the location of substituents with respect to the ring [150]. The total intensity of all the bands in such cases is about 3.2 ± 0.4 units (\pm dispersion of data in standard deviation units for various compounds). A pattern of two peaks is observed if both ortho positions are unsubstituted, as in benzoic acid salt and *p*-substituted benzoates, with bands near 1560 and 1600 cm^{-1} . The 1600- cm^{-1} absorption in benzoic acid is about 0.1 to 0.3 unit and in the salts is greatly intensified. The total absorption in this region appears to be the sum of contributions from the COO^- antisymmetric stretching mode (equal to about 2.9 units in aliphatic salts) and ring stretching modes (equal in most cases to about 0.3 unit in the acid). The intensification of the 1600- cm^{-1} band and the lower intensity of the 1500- cm^{-1} band in benzoates with both ortho positions unsubstituted has been interpreted [150] as evidence of interaction due to coupling of the antisymmetric, COO^- stretching mode and one of the components of the ring doublet stretching frequencies which are of the same symmetry species. The intensity of the 1600- cm^{-1} band is therefore increased at the expense of the intensity of the coupled 1560- cm^{-1} vibration.

E. Amide I and Amide II Bands

Primary, secondary, and tertiary amides display an amide I band due predominantly to $\text{C}=\text{O}$ stretching near 1660 to 1680 cm^{-1} . The

amide II band, owing to a combination of NH bending and CN stretching motions, appears near 1620 cm^{-1} in primary amides and may be overlapped as a weaker band on the side of the usually stronger amide I band. The amide II band is well resolved, appearing near 1550 cm^{-1} in secondary amides. It is absent in tertiary amides. In the solid state, hydrogen bonding in primary amides causes the Amide I and II bands to appear at a lower frequency than the bands displayed in dilute solutions.

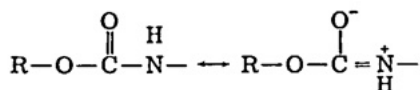
Integrated intensity data for amide I and II band intensities of the various structural types are listed in Table 24. The amide I band of

TABLE 24
Integrated Intensities of Amide I and Amide II Bands

Structural type	Solvent	Primary amides				Ref.
		cm^{-1}	B	ϵ		
Aliphatic amides	CHCl_3	1690	2.0			9
Aliphatic amides	KBr	1670	1.1-1.5	140-280		14
Halogenated amides	KBr	1650-1700	1.5-2.0	300-700		14
Benzamides	KBr	1660-1680	2.0-3.0	300-700		14
o-Cyanobenzamide	KBr	1753	2.76	312		14
Phthalic acid diamide	KBr	1681	1.44	250		14
Fumaramide	KBr	1700	2.65	665		14
		Secondary amides				
		Amide I		Amide II		
	Solvent	cm^{-1}	B	cm^{-1}	B	Ref.
N, N-Dialkyldiamides	KBr	1650	1.0-1.5	1560	0.6-1.0	14
Acetamides	KBr	1670	1.0	1540	0.9	14
Acetamides	CHCl_3	1695	1.3			130
Benzanilides	KBr	1660	1.0	1535	1.2	14
N-Methylbenzamides	CHCl_3	1660	1.5			130
Urethanes	CCl_4	1705	2.3			130
Acetanilides	CHCl_3	1685-1730	0.8-1.3			150a
		Tertiary amides				
	Solvent	cm^{-1}	B	ϵ	Ref.	
N, N-Dialkylformamide	CCl_4	1685	3.0			130
N, N-Dialkylacetamide	CCl_4	1650	1.8			130
N, N-Dialkylacetamide	CHCl_3		2.5			135
N, N-Diethyldiphenyl urea	CCl_4	1654	2.4			130
Tertiary aromatic amides	KBr	1650-1680	1.0-1.3	300-700		14

o-cyanobenzamide is shifted from the 1670-cm⁻¹ region characteristic of the hydrogen-bonded band to 1753 cm⁻¹, because of the interference of the bulky —CN group to intermolecular hydrogen bonding [14]. Halogenation raises the intensity of the primary amide I band, and higher intensity is observed in some of the benzamides.

The intensity of the amide I and amide II bands in secondary amides is approximately 1.0 unit but is increased in urethanes, possibly because of the inductive effect of the alkoxy oxygen plus a mesomeric contribution which increases the electron density at the amide oxygen.



Substitution of amide hydrogens by alkyl groups raises the amide I band intensity in tertiary aliphatic amides but the intensity in secondary amides such as *N*-methylacetamide is lower than in the corresponding primary amides. The intensity may be higher in chloroform than in carbon tetrachloride and lower in potassium bromide dispersions.

In the absence of detailed knowledge of the effect of the mixing, grinding, and dispersing technique on intensities, reservations should be maintained as to the reliability of intensity data for solids. Variable states of aggregation or clustering of molecules and of crystallites can cause both band shapes and intensities to vary in an unpredictable fashion.

F. Isocyanates and Isothiocyanates

Organic isocyanates and isothiocyanates contain a cumulative double-bond system, —N=C=O and —N=C=S, which exhibits an intense absorption due to asymmetric stretching modes in the 2100- to 2300-cm⁻¹ region. The phenyl isocyanates display a relatively narrow band, ϵ , about 2000 [151], with an integrated intensity of about 6.5 units. Splitting of the band in phenyl isocyanates, attributed to Fermi resonance, has been reported [152]. The intensity and frequency are relatively unaffected by substituents on the ring in the phenyl isocyanates [153].

In contrast to the isocyanates the isothiocyanates show a very broad band assignable to the asymmetric stretching mode with complex structure suggestive of Fermi resonance in the phenyl derivatives and of rotational isomerism in the alkyl derivatives [153]. The plot of log *A* vs. σ is roughly linear in the isothiocyanates with a small positive slope, whereas the frequency vs. σ plot has a small negative slope.

TABLE 25
 Integrated Intensities of —SCN, —NCS, and NCO Groups in Organic
 Compounds in the 2100 to 2300-cm⁻¹ Region^a

Structure	Solvent	cm ⁻¹	Intensity	Comment
Phenyl isothiocyanates (—N=C=S)	CCl ₄	2060	7.0	Bands very broad, with multiplet structure; log A/σ slope small, positive
Phenyl thiocyanates (—S—C≡N)	CHCl ₃	2170	0.2	Δν _{1/2} ~ 15 cm ⁻¹ ; log A/σ slope small, negative
Alkyl isothiocyanates (—N=C=S)	CHCl ₃	2100	4.0	Bands very broad, splitting observed; log A/σ slope small, positive
Phenyl isocyanates (—N=C=O)	CCl ₄	2270	6.5	log A/σ plot zero slope

^a Ref. [153].

The data of Caldow and Thompson [153] for these compounds and for phenyl thiocyanates are presented in Table 25. The spectral behavior of the phenyl thiocyanates is much closer in intensity and band shape to the benzonitriles, although displaced to a lower frequency.

G. Intensities and Splitting of Carbonyl Mode

Splitting of the carbonyl band into solvent- and temperature-sensitive peaks at 1750 and 1790 cm^{-1} has been reported in α, β -unsaturated lactones. The splitting has been attributed to Fermi resonance between an overtone of the strong olefinic CH out-of-plane deformation near 850 cm^{-1} and the C=O fundamental near 1740 cm^{-1} [154]. Splitting of the carbonyl band in cyclopentanone [155], Δ^2 -cyclopentenones [156], benzoyl chlorides [154, 157, 158], and in the low-frequency component of the coupled anhydride C=O absorption [154] has been attributed to Fermi resonance or a similar type of intramolecular vibrational effect. Contributions from Fermi resonance, mechanical coupling, rotational isomerism, and the formation of associated species may broaden, distort, or otherwise alter the band shape in the carbonyl stretching region. Careful measurement of the band contour under a variety of conditions of concentration, temperature, solvent, pH, etc., may help to sift out and recognize the various possibilities.

X. INTENSITIES OF HYDROXYL STRETCHING VIBRATION

A. Free Hydroxyl

The OH stretching vibration is complicated by the tendency of the hydroxylic hydrogen to form hydrogen bonds with an acceptor atom (usually an electronegative atom with lone-pair electrons such as O, N, and Cl). In solution, equilibria between free and hydrogen-bonded species may exist, which shift in the direction of association with increase in concentration and decrease in temperature in a nonbonding solvent. Equilibria with proton acceptor molecules may also be observed, association increasing with increasing basicity of the acceptor and increasing acidity of the donor molecules [159]. The observation of a frequency lowering, band broadening, and an increase in integrated intensity of the OH stretching vibration as a result of increase in concentration, lowering of temperature, or addition of basic solvents are spectral criteria of hydrogen-bond formation [160, 161].

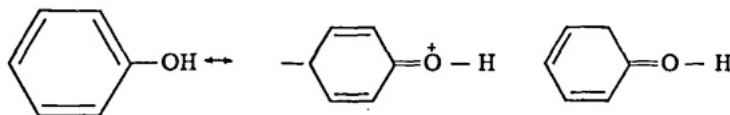
The free OH stretching vibration is characterized by a sharp band near 3600 cm^{-1} with an integrated intensity of about 0.2 unit in alcohols and 0.6 unit in phenols, in dilute solution, in the absence of pro-

ton acceptor atoms. Presence of free hydroxyl can be confirmed by the first overtone absorption near 7100 cm^{-1} , with a molar absorptivity of about 2 in alcohols and 3 in phenols in unbranched nonhindered conformations [162].

Electronegative groups such as in 2,2,2-trichloroethanol increase the intensity [163], whereas electron-donating alkyl groups in highly branched structures such as triisopropyl carbinol lower the intensity [164] of the free hydroxyl stretching mode in alcohols in dilute solution in carbon tetrachloride.

Phenols display a sharper band at a somewhat lower frequency, of intensity 0.5 to 1.0 unit, the higher values being reached in compounds with electronegative substituents in the *m* or *p* positions, as in *p*-nitrophenol [165-167]. A linear correlation between the Hammett σ value of the substituent and the log of the integrated intensity has been reported for phenols [167]. The slope of the plot is positive (the reverse of the slope of the frequency vs. σ plot).

The intensity behavior of the stretching vibration of the OH group in alcohols has been explained as resulting from the increasing ionicity of the OH bond with stretching, with charge separation being favored by the inductive effect of electronegative substituents [164, 168]. The higher intensity in phenols has been explained as resulting from the contribution of conjugatively stabilized charged structures [9, 165] which increase the ionicity of the bond:



A number of workers have reported integrated intensities of the free hydroxyl stretching vibration by the method of numerical integration (Ramsay) using a factor of $\pi/2$. There is some doubt about the validity of this calculation for phenols since the calculated value of K has been found to be between 1.2 and 1.3 [167]. An uncertainty of perhaps 20 to 30% applies to many of the data summarized in Table 26 and elsewhere because of slit-width errors, uncertainty as to wing correction, and overlapping absorption.

B. Polymeric Hydroxyl

The intensity of the self-associated hydroxyl stretching mode is illustrated by the typical curves in Fig. 4. The polymeric band is not detectable below 0.01 M concentration. At 0.1 M several associated species including dimer, which absorbs near 3500 cm^{-1} , are evident.

TABLE 26
 Integrated Intensities and Frequencies of Free and Bonded
 Hydroxyl Group Stretching Mode in Organic Compounds
 (Solvent: CCl₄)

	ν , cm ⁻¹	$\Delta\nu^{1/2}$, cm ⁻¹	B	Type of compound	Ref.
Compounds without internal hydrogen bonding					
Aliphatic alcohols					
(monomer)	3635	30-35	0.2-0.25	Ethanol	163, 166, 168
(dimer)	3500	75-90	0.6		174
(polymer)	3330	160-200	2.0-2.5		174
Alcohols with electronegative groups					
(monomer)		30-35	0.25-0.3	2,2,2-Trichloroethanol	163
Highly branched alcohols					
(monomer)	3620	20-25	0.1-0.15	Triisopropyl carbinol	164
Oximes—C=N—OH (monomer)	3600	25	0.55-0.65		166
 H					
O OH —C—O—X—C (monomer)	3615	45	0.2-0.25	Ethylene glycol monoacetate	166
Phenols ($\sigma < 0.5$)					
(monomer)	3610	15-20	0.5-0.7	Phenol	166, 167
(dimer)	3480	130	1.5		159
(polymer)	3350	190	3		171
Phenols ($\sigma < 0.5$) (monomer)	3595	15-20	0.8-1.0	p-Nitrophenol	166, 167

Compounds with internal
hydrogen bonding

di-o-Substituted phenols	3470-3610	20-30	0.4-0.8	di-o-Bromophenol	47
o-Substituted phenols	3550-3600	20	0.6-0.75	o-Chlorophenol	166
Chelated phenols	3200	120-150	0.8-1.5	Salicylaldehyde	175
HO(CH ₂) ₂ NR ₂	3300	230	2.0	3-Diethylaminopropan-1-ol	166
HO(CH ₂) ₃ NR ₂	3500	140	0.5	2-di-n-Propylaminoethanol	166
HO(CH ₂) ₄ O CH ₃ ^a	3465	90	1.4	4-Methoxybutanol	176
HO(CH ₂) ₃ O CH ₃ ^a	3560	60	0.6	3-Methoxypropanol	176
HO(CH ₂) ₂ O CH ₃ ^a	3615	30	0.3	Methoxyethanol	176
$\begin{array}{c} \text{O} \quad \text{OH} \\ \parallel \quad \\ \text{—C—X—C—} \end{array}$	3550	40-90	0.3-0.5	Hydracetyl acetone	166
Acetic acid (monomer)	3529		0.087		159
Acetic acid (dimer)	3020	380	3.2		159

^aDisplay a free OH band at 3645 cm⁻¹

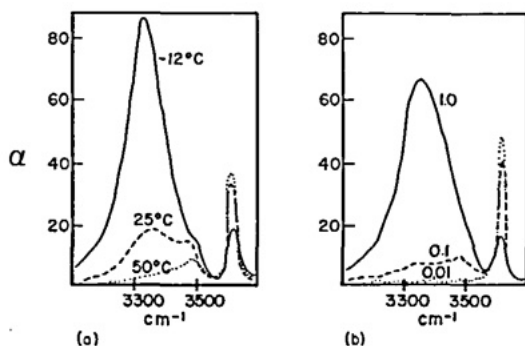


FIG. 4. Absorption of an aliphatic alcohol in the 3100- to 3700- cm^{-1} region: (a) as a function of temperature at 0.2 M concentration, and (b) as a function of concentration at 25°C. (Data of Ref. [174].)

Highly branched alcohols tend not to associate, forming dimers in preference to higher polymers if association does occur [169, 170]. Above 1 M the polymeric species with a maximum at 3330 cm^{-1} predominates in unhindered phenols and alcohols. The following are characteristic of the polymeric band compared with the monomeric hydroxyl absorption:

	Monomer	Polymer	Increase in polymer
Band half-width $\nu_{1/2}$	15-30	150-250	7- to 10-fold
Frequency	3610	3330	$\Delta\nu = 250-300$
Integrated intensity alcohols	0.25	2.5	10-fold
Integrated intensity phenols	0.7	3.0	4-fold

Equilibria between monomeric and associated hydroxyl bonds have been studied by numerous investigators for the purposes of obtaining association constants, evidence of hydrogen-bond formation, and other thermodynamic data [160, 161]. The increase in both frequency and integrated intensity of the OH stretching vibration due to bonded hydroxy of alcohols were found to be inversely proportional to the absolute temperature [171]. The intensity increase was about 60% for a decrease from 300 to 200°K. The frequency increase over this temperature decrease was of the order of 30 to 50 cm^{-1} .

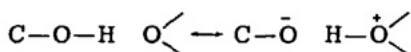
The intensity of the polymeric OH stretching vibration of isopropanol was nearly the same (about 2.3 units) in CCl_4 , ethanol, and triethylamine over the range 2 to 12 M concentration [171]. Francis reported a concentration dependency for a similar band in n-propanol in CCl_4 with values of 2.54 at 0.5 M and 2.90 at 1.0 M [172]. This was

said to be in marked contrast to the results of Luttke and Mecke [173] for similar bands in phenol, the integrated intensity for pure phenol being approximately one-half as great as for a very dilute solution of phenol in CCl_4 . These observations cast doubt on the implied constancy of the integrated intensities of hydrogen-bonded OH stretching vibrations, unless carefully measured over a range of both concentration and temperature in a suitable solvent. Complex formation with acceptor molecules involves still another concentration parameter.

Integrated intensities for the absorption at 3500 cm^{-1} assigned to dimers [169, 170] have been reported for methanol and phenol [159] and for methanol, ethanol, and tert-butanol [174]. Liddell and Becker obtained much higher values of $\Delta\nu/\Delta t$ for polymeric OH than were obtained by Finch and Lippincott [171], possibly due to the difference in concentration range (0.005 to 0.2 M in CCl_4 compared with undiluted alcohols or above 2 M. H-bond energies of the dimer were in the range 5 to 9 kcal/mole [174].

Dimer formation is also favored in carboxylic acids, owing to resonance stabilization, and association constants have been reported based on intensity data [145].

The marked increase in integrated intensity of polymeric OH stretching vibrations with decrease in temperature has been explained as due to the formation of charge transfer complexes [171]



caused by transfer of unpaired electrons from the acceptor atom to the hydrogen atom to form a dative, weakly covalent bond. The transfer is accompanied by a shortening of the O—O distance and an increase in the C—H distance. These changes, favored at low temperature, also account for the markedly higher intensity of the hydrogen-bonded vibration compared with the unbonded values according to several other investigators [159, 175].

C. Internally Bonded

An internal hydrogen bond can form between the hydroxyl hydrogen (also between the NH bond and the acidic CH bond in chloroform and similar molecules) and any acceptor atom within the molecule such as N, O, and Cl. Very strong bonds are formed in closed ring structures between a carbonyl oxygen and a phenolic hydroxyl as in salicyl aldehyde, methyl salicylate, and o-hydroxy acetophenone. Such compounds show no monomeric absorption even in extremely dilute solution, and the internally bonded OH vibration can be recognized only

by a very broad band below 3550 cm^{-1} . Some values in Table 26 for such chelated structures have been reported by Tsubomura [175].

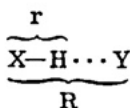
The intense, broad OH absorption observed in dialkylaminopropans and butylene glycol monomethyl ether is due to the formation of stable six- and seven-membered rings [166, 176]. The intensity decreases with decrease in ring size and there is little evidence of hydrogen bonding in ethylene glycol monomethyl ether and glycol monoformate [166, 176].

Internal hydrogen bonding is possible in ortho-substituted phenols containing an electronegative atom or group such as Cl, NO_2 , and CN [177, 178], resulting in cis and trans conformations, with the trans absorbing at a higher frequency. Two conformations are possible without hydrogen bonding if an alkyl is in the ortho position. Only one conformation is possible if both substituents are the same, as in diortho substituents either with hydrogen bonding (electronegative substituent) or without hydrogen bonding.

D. Solvent-Complexed

The OH stretching vibration of alcohols and phenols without internal bonding exists predominantly in the monomer form in dilute solution in carbon tetrachloride. Addition to such a solution of a basic, proton acceptor causes the free hydroxyl band near 3600 cm^{-1} to be replaced by a broader, more intense band at a lower frequency (Tables 27 and 28). For a given alcohol, the shift, increase in intensity, and increase in band half-width are measures of the basicity of the acceptor and the strength of the hydrogen bond formed [66, 159, 175]. For a series of alcohols the shifts observed with a reference acceptor are measures of the acidity of the OH group. The energy of the bonds can be determined by measuring the change in any of the altered parameters (frequency shift, band half-width, intensities) as a function of the reciprocal of the absolute temperature [160].

Either linear or smooth monotonic relations are observed among $\Delta\nu$, $\nu_{1/2}$, and B and among any of these parameters and the enthalpy, association constant, and other thermodynamic constants for the hydrogen-bonded complex. The observed shifts have also been correlated with the interatomic distances R and r:



The formation of a complex with pyridine is the basis of an analytical procedure for OH groups in steroids and other compounds [179].

TABLE 27
Frequencies and Intensities of Complexed Hydroxyl Stretching
Modes of Alcohols and Phenols^a

Alcohol	Base	$\Delta\nu$, cm^{-1}	$\nu_{1/2}$, cm^{-1}	$\frac{d(\Delta\nu)}{dT}$, $\text{cm}^{-1}/^\circ\text{C}$	B	$\frac{dB}{dT}$ $\times 10^{-2}$	$-\Delta H$, kcal/mole
Methanol	Acetone	112	132	0.50	1.73	1.84	2.52
	Benzophenone	88	100	0.40	1.06	1.84	2.16
	Ethyl acetate	84	100	0.24	1.22	1.66	2.52
	Dioxane	126	90	0.26	1.22	1.09	2.80
	Dimethylformamide	160	148	0.53	1.72	1.96	3.72
	Pyridine	286	180	0.56	2.46	2.54	3.98

Compound	Acceptor	Solvent	ν_{max} , cm^{-1}	$\nu_{1/2}$	ϵ_{max}	B
Phenol	$\text{C}_2\text{H}_2\text{Cl}_4$	CCl_4	3600	38	334	0.86
	Chlorobenzene	CCl_4	3583	40	358	0.97
	Acetonitrile	n-Heptane	3478	77	415	2.2
	Ethyl acetate	n-Heptane	3461	160	334	3.65
	Ethyl ether	n-Heptane	3362	115	444	3.5
	Hexamethylene tetramine	CCl_4	3070	280	281	5.4

^aRefs. [66, 175].

TABLE 28

Integrated Intensities and Frequency Shifts of OH Stretching Vibrations of Alcohols and Phenols in Basic Solvents^a

	ν_{CCl_4}	B	Ether		Triethylamine	
			$\Delta\nu$	B	$\Delta\nu$	B
tert-Butyl alcohol	3614	0.18	116	1.1	337	2.0
Isopropyl alcohol	3620	0.21	122	1.3	374	2.1
sec-Butyl alcohol	3623	0.25	123	1.4	375	2.3
Ethyl alcohol	3634	0.27	133	1.65	393	2.7
n-Butyl alcohol	3636	0.31	135	1.65	400	2.9
Methyl alcohol	3644	0.23	136	1.7	401	2.7
2-Ethoxyethanol	(3630)		143	1.5	424	3.1
2-Chloroethanol	(3630)		177	2.0	479	3.6
Phenol	3609	0.52	276	3.7		

^aRef. 168.

XI. INTENSITIES OF OTHER OH VIBRATIONS

The intensity of the first overtone of the free OH stretching vibration near 7600 cm^{-1} is about 0.015 unit and is particularly suitable for analytical purposes. The intensities of the OH bending mode near 1400 cm^{-1} and of CO bending modes near 1100 to 1200 cm^{-1} do not change much with hydrogen bonding, a fact cited in support of the charge transfer hypothesis in preference to the electrostatic hypothesis of hydrogen bonding [159]. The absence of overtones associated with hydrogen bonding has been considered prejudicial to the anharmonicity theory of the band broadening associated with H bonding.

XII. INTENSITIES OF NH STRETCHING VIBRATIONS

The question of the relationship of the integrated intensity of the NH stretching vibration to the polar properties of the bond has interested a number of investigators. By treating the NH vibration as a harmonic oscillator with fixed charges, Richards and Burton [180] were able to deduce a value of 0.8 D for the dipole moment of the linkage, assuming a bond length of 1.01 \AA . The electronegativity difference would suggest a bond moment of 0.9 D. No serious error was made by ignoring anharmonic effects because a calculation involving higher-order perturbations yielded values differing only 3% from the value for a harmonic oscillator.

Wulf and Liddell [181] measured the intensities of the first over-

tones of some amines, amides, and heterocyclics and found significant variations from one type to another, but the value for the NH group was roughly constant, suggesting that the NH overtone might be useful in analytical applications.

Russell and Thompson [182] determined extinction coefficients, band half-widths, and integrated intensities of aliphatic, aromatic, and heterocyclic amines and found a roughly inverse relation between integrated intensity and band half-width (except in the case of 2-nitrodiphenylamine, which appeared to undergo band broadening due to hydrogen bonding). The $\nu(\text{NH})$ intensities of aromatic amines were far higher than the values for aliphatic amines. The intensity ratios in the series aliphatic/alkylanilines/acetanilides/N-heterocyclics were roughly 0.5:20:30:60. The differences in intensities of the fundamentals and previously published data [181] for $\nu(\text{NH})$ overtones were interpreted as indicating a very significant difference in the nature of the NH bond in simple dialkylamines.

Comparison of the $\nu(\text{NH})$ and $2\nu(\text{NH})$ intensities of aliphatic and aromatic amines in a succeeding paper [183] revealed a marked variation in A_{01}/A_{02} [intensity ratio of $\nu(\text{NH})/2\nu(\text{NH})$] with a range 0.6 to 2 in aliphatic (secondary) amines to 60 in acetanilides and N-heterocyclic amines. The low ratio in aliphatic amines was explained as arising from the considerable electrical anharmonicity of the $\nu(\text{NH})$ vibration in alkylamines.

The effects of solvents and aromatic ring structure (ring substituents) on $\nu(\text{NH})$ intensities, frequencies, and band half-widths were systematically explored in papers by Krueger and Thompson [184] and Califano and Moccia [185] for substituted anilines. Their results were similar, showing that an inverse trend of the effect of p- and m-substituted ring substituents on $\nu(\text{NH})$ intensities and band half-widths of these compounds existed, with highest intensities and sharpest bands being observed with anilines containing substituents with high electron-attracting power (e.g., p-nitroaniline). These authors correlated the effect of the substituents on band frequencies, intensities, and band half-widths with the corresponding Hammett substituent factors.

The spread of intensities was greater for $\nu(\text{NH})$ symmetric and the corresponding bands were sharper than the values obtained for the higher-frequency antisymmetric band. The slope of the intensity vs. σ plot was also steeper for the symmetric mode in the m- and p-substituted compounds. Similar trends, complicated by steric and H-bonding effects, were observed in the o-substituted anilines.

Solvents had a marked effect on the intensities, with intensities increasing in the order $\text{CS}_2 < \text{CCl}_4 < \text{benzene} < \text{nitromethane} < \text{acetone}$, the range being roughly threefold for the increase.

Similar trends of the effects of substituents on intensity, frequency, and band half-widths were obtained with *N*-methylanilines, which show a single ν (NH) band near 3450 cm^{-1} in carbon tetrachloride, of intensity roughly equal to the intensity of the symmetric ν (NH) band of primary amines near 3400 cm^{-1} . In acetanilides the NH stretching vibration was found to be constant in intensity and not subject to a substituent effect [186].

The intensity of ν (NH) asymmetric of substituted anilines near 3500 cm^{-1} was found to be roughly the same as the intensity of the symmetric band within the range -0.2 to $+0.4\sigma$ for the substituent. For higher σ values the symmetric band was more intense, and for lower values the asymmetric band was more intense.

A linear correlation was obtained between ν asymmetric and ν symmetric of the NH stretching modes in substituted anilines containing *m* and *p* substituents [187]:

$$\nu^S = 1023 + 0.682\nu^A$$

A similar relation was reported earlier [187a]:

$$\nu^S = 345.5 + 0.876\nu^A$$

for several classes of compounds containing the NH_2 group.

Values for ortho-substituted compounds deviated from the correlation, possibly because of the effects of steric hindrance and hydrogen bonding on the frequencies.

Krueger and Thompson [187] suggested that a more satisfactory relationship for band intensity in substituted compounds could be obtained by the equation

$$\log_{10} A = C + \alpha\sigma_I + \beta\sigma_R$$

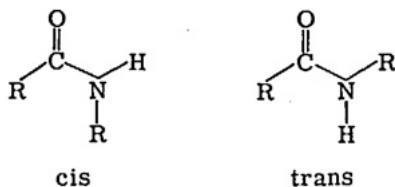
in which σ_I and σ_R are the inductive and resonance factors for each substituent and α and β are characteristic parameters for each functional group (their paper considered nitriles, anilines, phenols, and benzoates, encompassing CN, NH, OH, and C=O vibrations).

The ratio of α to β indicates the relative importance of each effect on the intensity.

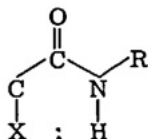
Brown [9] has explained the effects of electronegative substituents on the symmetric NH vibration intensity in aromatic amines as analogous to the results for phenols. The NH bond tends to become increasingly polar on stretching, the process being electron-releasing with respect to the aromatic ring. Electron-withdrawing meta and para groups favor the process by increasing the resonance stabilization of the charge-separated form.

Mason [188], Elliot and Mason [189], and others [190] have interpreted the effect of aromatic nuclei on the intensities of the NH stretching vibration in terms of the effect of the π electron system of the ring on the lone-pair electrons and electron density at the amino nitrogen atom. Delocalization tends to increase the s character of the overlapped $1s$ orbital of the hydrogen atom and the $2s-2p$ hybrid orbital of the nitrogen atom, thereby increasing the strength and polar character of the NH bond. These changes are reflected in the rise of both intensity and frequencies of the NH stretching vibrations in aromatic systems over the values in aliphatic amines.

Two possible configurations may occur for secondary amides in dilute solution:



According to Nyquist [190a] the predominant species is the trans form in the N-alkyl acetamides with a band near 3430 to 3480 cm^{-1} with an intensity of 0.15 to 0.2 unit due to the NH stretching vibration. The intensity is increased in α -substituted acetamides containing a halo or alkoxy substituent due to an intramolecular bonding effect,



with the trans form being the only observable species. The frequency is also lowered, consistent with an H-bonding effect.

Nyquist reported that the ν_{NH} frequency in para-substituted anilides decreased, whereas the intensity increased with increase in σ_p of the para substituent [150a]. These effects were reversed in the case of the $\nu_{\text{C=O}}$ vibration. The effect of α -halogen substitution was to increase the ν_{NH} intensity, caused by an intramolecular hydrogen bond, as in the α -substituted acetamides.

The integrated intensities and frequencies for the ν_{NH} selected from the literature are presented in Table 29 for dilute solutions in solvents. In concentrated solutions and in the solid state, hydrogen-bonding effects may alter the intensity and frequency. The spectra of amines are radically altered by conversion to the salt form, which

TABLE 29
 Integrated Intensities and Frequencies of NH Stretching
 Vibrations in Organic Compounds
 (Solvents: CCl_4 and CHCl_3)

Compound	Asymmetric		Symmetric		Ref.
	Band, cm^{-1}	B	Band, cm^{-1}	B	
Primary amines					
Aliphatics	3375	0.02	3310	0.01	188
Anilines	3450	0.1	3780	0.1	184
p-Nitroanilines	3510	0.2	3416	0.5	184
Polynuclearamines	3470	0.1	3390	0.1	189
N-Heterocyclics	3510	0.2-0.5	3410	0.2-0.4	188
Secondary amines, amides					
Aliphatic amines	3300	0.005-0.01			182
N-Alkylanilines	3440	0.1-0.2			184
Heterocyclic amines	3690	0.5			182
N-Alkyl acetamides	3450-3480	0.15-0.2			190a
N-Alkyl- α -halo- acetamides	3410-3450	0.3-0.5			190a
Acetanilides	3430-40	0.3			150a
α -Haloacetanilides	3400	0.4-0.5			150a
First overtone, $2\nu_{\text{NH}}$					
Aliphatic, secondary amines		0.01			183
Aromatic, secondary amines		0.005-0.01			183
Aromatic, primary amines		0.01-0.015			18

may be of value in diagnosis and in differentiation from the hydroxyl group.

XIII. INTENSITIES OF $-\text{NO}_2$ STRETCHING VIBRATIONS

The $-\text{NO}_2$ group is characterized by two strong bands near 1260 and 1640 cm^{-1} (alkyl nitrates) or 1350 and 1530 cm^{-1} (nitro), assigned to symmetric and antisymmetric stretching modes. The molar absorptivities of these two bands, and their ratios, have been determined in the alkyl nitrates [191]. The ratio is about 1.26, with the 1640- cm^{-1} band being somewhat more intense. The ratio of the integrated intensities of these two bands in nitro aromatics has been

found to be near unity, with a value of 0.65 unit per band [14]. The intensity of the symmetric mode was markedly increased in nitrobenzenes with an amino group in the para position.

XIV. INTENSITIES OF $-\text{SO}_2-$ STRETCHING VIBRATIONS

The SO_2 group displays two strong bands assigned to the symmetric (1100 to 1200 cm^{-1}) and antisymmetric (1300 to 1400 cm^{-1}) stretching vibrations. The frequencies of these vibrations are sensitive to inductive effects and their ratio has been shown to be nearly constant at a value of 1.6 [192]. The intensity of the $-\text{SO}_2-$ symmetric stretching vibration has been shown to increase with substitution of an electron-donating group (OH , NH_2 , $\text{O}-\text{CH}_3$) in the para position in phenyl methylsulfones [193]. The intensities of both vibrations appeared to decrease with increase in chain length in a homologous series of alkane sulfochlorides. A linear relation was observed between the integrated intensity and the logarithm of the hydrolysis rate constant [194]. A linear relationship was observed between the intensity and the corresponding Taft substituent constant. These constants varied linearly with the reciprocal of n , where n is the number of carbon atoms in the alkyl chain. The intensities of these vibrations in various types of compounds with the $-\text{SO}_2-$ group are presented in Table 30. The ratio of the symmetric to antisymmetric intensities are also included in this table. The log of this ratio has been shown to correlate with atomic localization energy and therefore with the electron density at the central atom in these and similar vibrations (nitro and amino groups) [195].

TABLE 30
Integrated Intensities of $-\text{SO}_2$ Stretching Modes
(Solvents: KBr (Ref. [14]); CS_2 (Ref. [194]))

	Symmetric		Antisymmetric		Ratio s/a	Ref.
	Band, cm^{-1}	B	Band, cm^{-1}	B		
Sulfonamides	1150	0.65	1310	0.65	1.0	14
Alkane sulfochlorides	1170	1.5-3	1380	4-5	0.5-0.7	194
Sulfones	1160	0.9	1325	0.9	1.0	14
Sulfonic acids ^a	1050	0.5	1200	2.4	0.2	14

^a These assignments are doubtful but are included for comparison.

XV. APPLICATIONS OF INTEGRATED INTENSITY DATA

In the course of a review of the literature, it appeared worthwhile to summarize some of the integrated intensity data associated with characteristic groups in the form of a frequency-intensity correlation chart in which both intensity and frequency are plotted. This chart (Fig. 5) is presented for the purpose of using intensity as an additional parameter to supplement frequency data in the characterization of chemical compounds by infrared spectroscopy. Two types of data are evident. Horizontal bars indicate a fairly good group intensity with a variable frequency range. Vertical bars indicate a good group frequency with intensity spread over a range, depending on substituents and electronic factors which effect intensity of a group vibration. Groups of the first type are especially amenable to functional analysis, whereas groups of the second type are of interest in chemical investigations in which the emphasis is on molecular structure and reactivity parameters.

Integrated intensities can be more closely related to chemical and molecular properties than molar absorptivities in certain cases, as in the determination of enthalpies of isomerization [196] or in correlation with resonance substituent constants σ_R^+ [197]. Thus a close correlation between the square root of the integrated intensity of the ν_{16} vibrations and the Hammett resonance parameter has been reported for monosubstituted benzenes. Such a relationship seems to have a theoretical basis in a molecular orbital model for infrared band intensities [198].

These relationships are especially interesting to the chemist because of the apparent parallel between electronic charge distribution in a vibrating group and the electronic distribution in the transition-state configuration. These correlations have apparently been successfully utilized in drawing inferences about electronic charge distribution in the substituted benzenes from infrared and reactivity data [199].

The assumptions implicit in Eq. (1) and in the correlations reported between integrated intensities and reactivity parameters indicate that integrated intensities of infrared vibrations are a probe of electronic structure and electronic shielding factors. A correlation between infrared intensities and NMR and PMR chemical shifts may be anticipated and such correlations have been reported [200]. The correlation of both infrared intensities [7, 8] and NMR chemical shifts with Hammett and Taft reactivity parameters [201] implies that both types of probes sense similar perturbations of electronic structure, although by completely different mechanisms (dipole-moment variations and changes in nuclear spin frequencies).

Recently it has been shown that the rotational motion of molecules

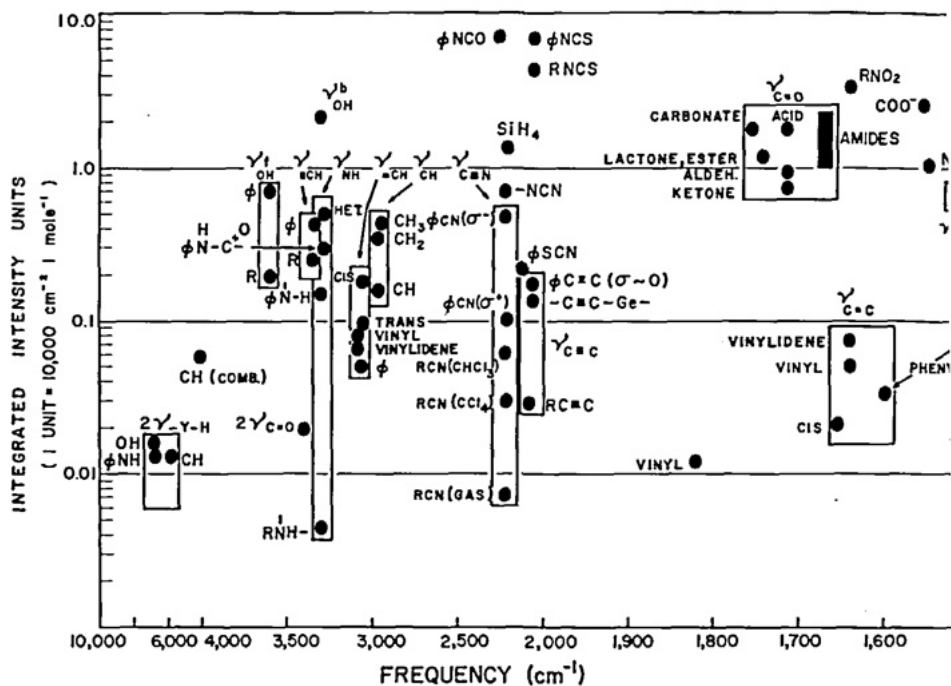
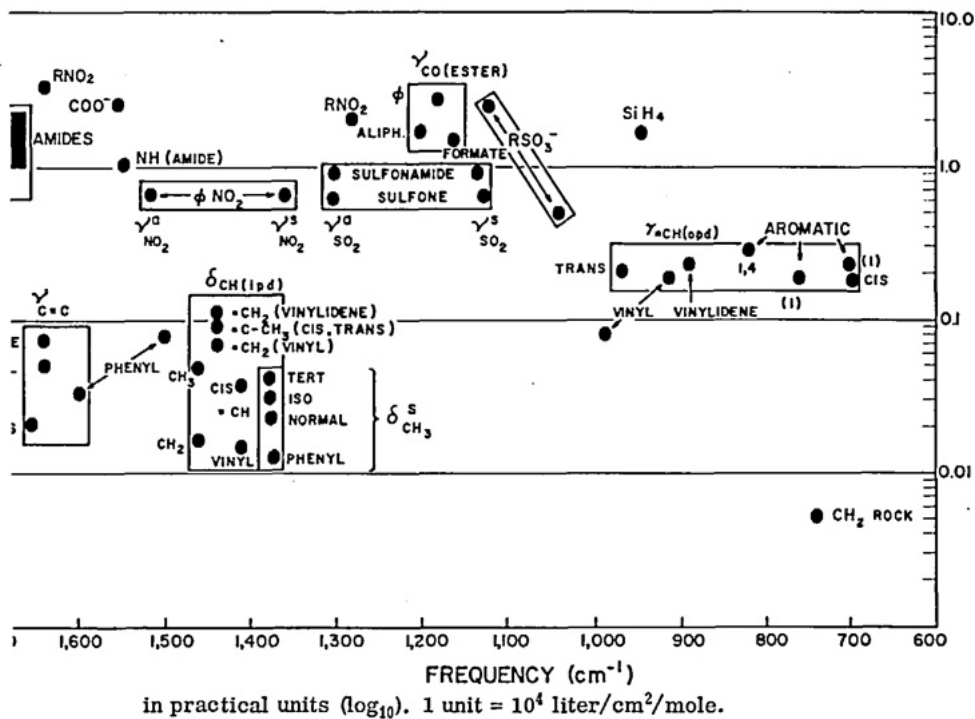


FIG. 5. Frequency-intensity infrared correlation chart. Intensity (RNO_2 refers to alkyl nitrates.)



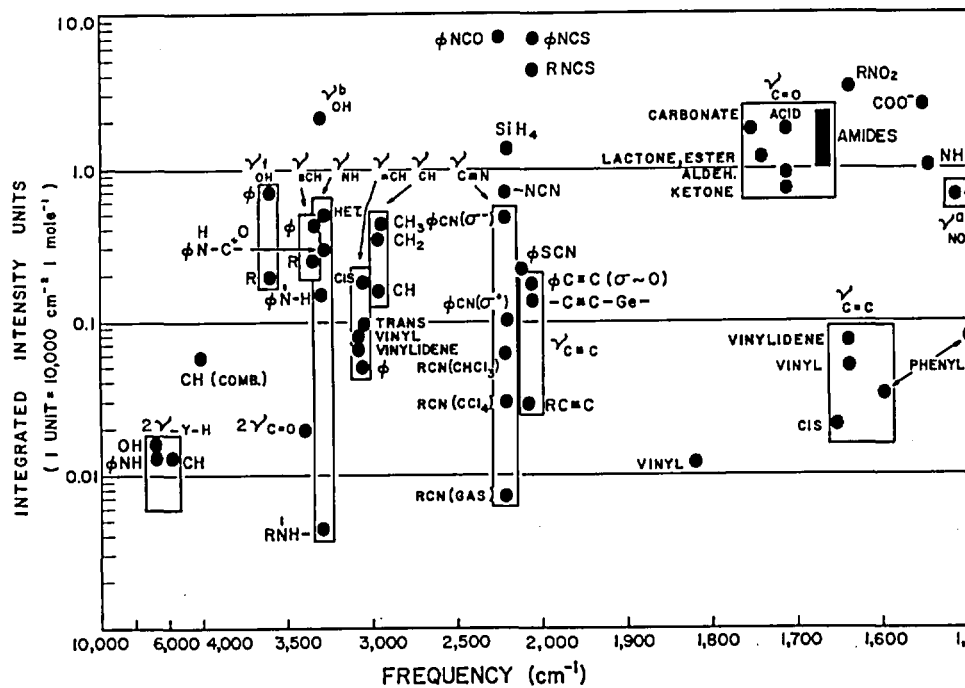
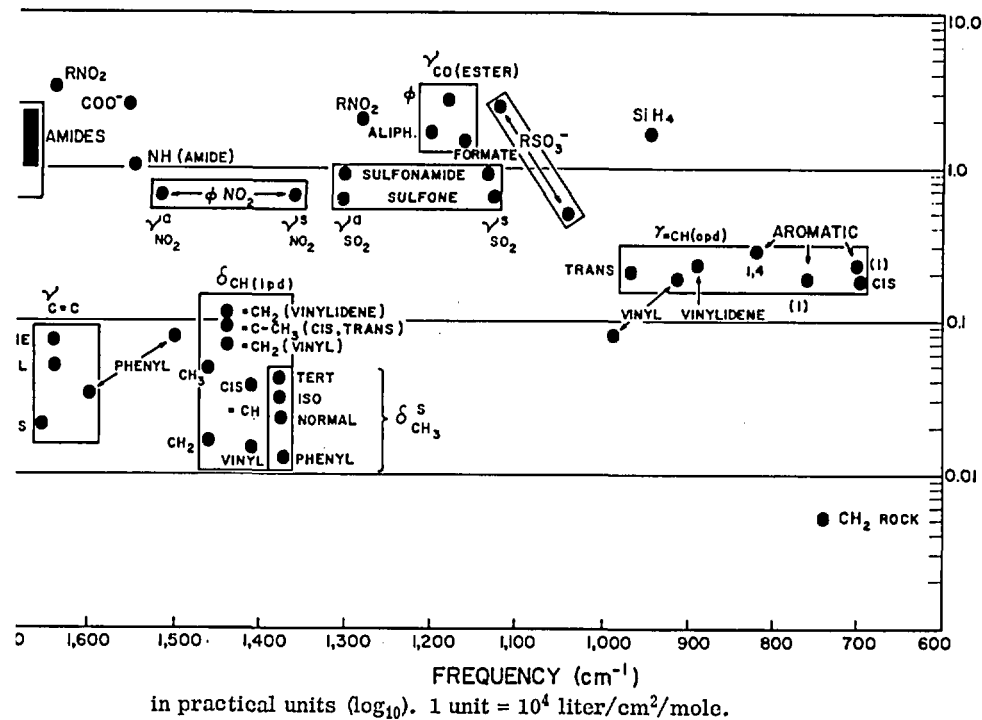


FIG. 5. Frequency-intensity infrared correlation chart. Intensity (RNO_2 refers to alkyl nitrates.)



in practical units (\log_{10}). 1 unit = 10^4 liter/cm²/mole.

can be described by correlation functions and correlation times relating randomizing processes such as Brownian motion to the orientation of a molecule over a period of time [202-205]. These processes affect band widths, intensities and moments of distribution, or spectral density. The representation of the spectral band shape in terms of the Fourier transform of the correlation functions apparently has theoretical significance in studies of molecular dynamics.

In addition to these examples, two other applications of integrated intensity data are evident which appeal to the specialist in one case and to the practitioner of general chemistry in the second case. The problem of accounting for properties of a molecule in terms of the observed infrared frequencies and intensities is a problem of general interest, appealing to the analytical, (in)organic, and physical chemist. This application ranges from such recondite problems as inferring molecular-moment distributions by means of Eq. (1) to the simple matter of determining the percentage of aromatics in crude naphtha fractions from an area measurement [206]. The converse problem is the accounting of the vibrational spectrum from a knowledge of molecular structure. Not until a successful analysis of the infrared spectrum has been made can the chemist be fully satisfied with a molecular formula, or for that matter with the question of identity of a compound or its purity. This analysis raises questions of conformational isomerism, associated species, and existence of states of a substance not readily detected by nonspectroscopic methods, which must be settled in accounting for the spectrum. Another problem is vibrational, such as that arising from coupling of different vibrational modes. Such information can be utilized to advantage in structure work, because coupling may be possible only in certain specific orientations, configurations, or positions within a molecule, or, more specifically, the degree and character of coupling may so vary.

ADDENDUM

The following material arrived too late to be included in the manuscript prior to copy reproduction. It is therefore attached as an addendum.

The polarity of the ring CH stretching vibration in benzene, pyridine, and their derivatives is predominantly $\overset{+}{C}-\overset{-}{H}$. The polarity may reverse in derivatives with strong electron-attracting substituents, judging from the observed correlation between integrated intensities and Taft substituent constants [207]. The integrated intensities of the ring CH stretching vibrations in monosubstituted benzenes and deu-

terobenzenes can be divided into contributions of CH or CD oscillators in ortho, meta, and para positions [208]. Correlations between intensities in para-substituted benzenes and the sum of the Hammett inductive parameters $\nu_1(x)$ and $\sigma_1(y)$ for substituents were observed, with inversion of polarity for sufficiently large values of the constants [209].

A functional relation which confirms the concept of a $\dot{C}-\bar{H}$ polarity for near-zero values of σ_1 was also observed between $\nu_{CH(ar)}$ intensities and substituent constants in the substituted pyridines [210]. The conclusions drawn from the experimental data are that (1) the $\nu_{CH(ar)}$ intensity is a function of σ_1 ; (2) the vibrations are well local localized in the CH bonds and the dipole-moment derivative $\partial\mu_j/\partial r_j$ is a function of the substituent inductive constants; (3) the $\nu_{CH(ar)}$ polarity for benzene and most of its derivatives is $\dot{C}-\bar{H}$; (4) σ_1 values greater than zero induce a $\dot{C}-\bar{H}$ polarity; and (5) in some para-disubstituted benzene derivatives, the dipole moments induced by substituents are so great as to lead to a $\bar{C}-\dot{H}$ polarity of the CH bond [207].

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