NEAR INFRARED SPECTRA OF ORGANIC COMPOUNDS

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I. INTRODUCTION

The part of the electromagnetic spectrum visible to the human eye extends to about 7500 A. (0.75 μ), while the infrared and microwave parts of the spectrum lie at successively higher wavelengths. The intermediate region between the visible and infrared is termed the near infrared; the far infrared is that part of the spectrum between the infrared and microwave regions. The infrared section of the spectrum is commonly taken as extending from about 2.0 μ to 25 μ (33, 41, 239), and the absorption maxima found in this region arise from the fundamental vibrations of covalent bonds in organic compounds. The near infrared region is below about 2.5 μ (268), and absorption bands correspond to the harmonics or overtones of the fundamental vibrations of the true infrared. The near infrared has also been termed the photographic infrared (33), since a photographic plate was formerly the only means of detecting this radiation. Recently the term "photoelectric infrared" has been used (151), since modern receivers are of this type, whereas thermal-sensitive devices are used in the true infrared. Earlier writers (186, 241) have used the term "near infrared" to denote the region to 23 μ and to distinguish it from the far infrared above this value. In this review the near infrared part of the spectrum will be taken to extend from 0.5 to 2.0 μ, since all the observable harmonics or overtones of simple vibrational groups occur in this region.

In chemistry data in the visible region of the spectrum are almost invariably expressed in wavelengths, using either Ångström units (A.) or millimicrons (mμ). Both wavelengths (in microns) and wave numbers (number of waves per centimeter, in cm.$^{-1}$) are used to express infrared data. In this review wavelengths only will be used, since the commercially available instruments are all calibrated directly in these units. Wavelengths (λ) and wave numbers (n) are related by $n = 1/\lambda$ (in centimeters), and 1 A. $= 10^{-4}\ \mu = 10^{-8}$ cm.

This review will not deal with general infrared spectra except in so far as the measurements assist in the interpretation of near infrared data. Excellent treatments of infrared spectra may be found in the books of Bellamy (41), Herzberg (156), and Randall, Fowler, Fuson, and Dangl (239), and the subject is periodically reviewed in *Analytical Chemistry* (144, 145; *cf.* 310). Measurements in the near infrared prior to 1929 have been reviewed by Ellis (94), and Kaye (173) has recently briefly discussed this topic.

II. HISTORICAL NOTE

As early as 1800, Herschel (155) observed that there existed, just beyond the visible spectrum, radiation which could blacken a photographic plate or increase the temperature of a thermometer. The first infrared spectrum of any organic compound was measured photographically from 0.7 to 1.2 μ by Abney and Festing in 1881 (1), who made the very astute observation that "the foundation of all absorption in these bodies is the hydrogen." After the development of the bolometer by Julius in 1892 (172) most absorption studies were restricted to the general infrared. However, much pioneer work in the near infrared was carried out by Coblentz (66, 67, 69), Donath (82), and Puccianti (236, 237, 238). Brackett, in 1928 (48), was the first to study large organic molecules under high resolution in the infrared, and he showed that primary, secondary, and tertiary hydrogen atoms attached to carbon give rise to bands at slightly different wavelengths near 1.2 μ.

III. THEORY

The absorption of light of a definite wavelength by a molecule results in an increase in the frequency of vibration of a bond between a pair of atoms. As a first approximation the vibration in the bond behaves as a simple harmonic motion. All energy changes within molecules are quantized, and there will be a definite frequency of vibration associated with the quantized change in vibrational energy. This definite change in energy will be produced by the absorption of light of a definite frequency, and this will result in an absorption band at a definite frequency or wavelength. In the case of a simple harmonic vibration the frequency of the absorbed light is equal to the frequency of vibration of the bond. However, the observed spectrum contains, apart from the strong absorption band, a number of other much weaker bands at nearly twice and three times the frequency (or one-half and one-third the wavelength) of the main band. These additional bands arise from the fact that vibrations in molecular bonds are not simple harmonic motions. From quantum-mechanical considerations (156) the frequencies (ν) of the various bands are given by

$$\nu = \{1 - (v + 1)x\}v \cdot \omega$$

where v is the vibrational quantum number, x is the anharmonicity constant to correct for anharmonic vibrations, and ω is the frequency of vibration of the bond. The vibrational quantum number, v, can have only the values of positive integers (1, 2, 3, etc.), and the corresponding vibrations (v_1, v_2, v_3, etc.) will be:

$$v_1 = (1 - 2x)\omega; \quad v_2 = (1 - 3x)2\omega; \quad v_3 = (1 - 4x)3\omega$$

The principal band (frequency ν_1) is termed the fundamental or first harmonic and the other much weaker bands (with frequency ν_2, etc.) are the first and second overtones, etc., or the second and third harmonics. To avoid confusion only the term "overtone" will be used in this review. The first, second, and third overtones then correspond to vibrational quantum numbers (v) of 2, 3, and 4. The value of the anharmonicity constant x is usually very small, so that the first and second overtones occur at nearly twice and three times the frequency (one-half and one-third the wavelength) of the fundamental band. Similar empirical equations have been used to relate the observed fundamental and overtone frequencies. Thus for chloroform (16) the equation

$$\nu_n = nv_0(1 - nx)$$

gives a good fit of the data, with $v_n = 3082$ cm.$^{-1}$ and $x = 0.0205$. For carbon–hydrogen vibrations x is generally between 0.01 and 0.05 (131, 132). A quadratic equation, such as

$$\nu = av - bv^2$$

where a and b are constants (and $a \gg b$) will often fit the data (156).

In polyatomic molecules the vibrations are not independent of each other and if changes in the vibrational energy levels of two or more bonds occur simultaneously, a new band, termed a combination band, will be observed. If terms for the anharmonicity of the vibrations and for interactions between vibrations are neglected, then the frequency of the combination bands is given by

$$\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3 + \cdots$$

where ν_1, ν_2, and ν_3 are the frequencies of the normal modes of vibration, and n_1, n_2, and n_3 are either small positive integers or zero. Simple combinations involving only two fundamental frequencies are more often observed, and these will correspond to $n_1 = 1$, $n_2 = 2$, and $n_3 = 0$ or $n_1 = 1$, $n_2 = 0$, and $n_3 = 2$, etc. (16).

Every vibrational energy change in a bond is accompanied by a number of changes in the smaller rotational energy about the bond, and these rotational energy changes give rise to absorption lines of lesser intensity on either side of the main vibrational absorption line. Under low dispersion the group of lines appears as a band or peak of absorption. These bands in the near infrared part of the spectrum, as in the case of ordinary infrared bands, can be resolved under high dispersion into a pattern of lines. The spacing of the rotational lines associated with one vibrational band can be used to determine interatomic distances (156), and measurements in the near infrared will supplement such information more easily obtained from ordinary infrared spectra. A complete quantitative interpretation of the spectra is possible only in the case of simple molecules, such as diatomic or symmetrical polyatomic molecules, and this subject is outside the scope of this review (see 156).

The frequency of vibration of the classical simple harmonic oscillator is given by

$$\nu = 1/2\pi/\sqrt{k/\mu}$$

where k is the force constant and is a measure of the "elasticity" of the bond and μ is the kinetic reduced mass of the pair of atoms forming the bond. In the case of two isotopes of an element the value of k, which depends on the charges on the atoms (or the atomic number) will be the same, while the value of μ, which depends on the atomic weights of the isotopes, will be different. The most pronounced "isotope effect" is shown by hydrogen and deuterium atoms, where the ratio of the atomic masses is 1 to 2. In the case of the hydroxyl (OH) and deuterohydroxyl (OD) groups the ratio of the reduced masses, $\mu_{\mathrm{OD}}/\mu_{\mathrm{OH}}$, is 1.89, and the ratio of their fundamental vibrational frequencies, $\nu_{\mathrm{OD}}/\nu_{\mathrm{OH}}$, is 0.728. Consequently the wavelength of absorption of a deuterated group is always considerably greater than that of the corresponding undeuterated group.

The vibrational frequencies most commonly observed are those of the bonds of hydrogen with carbon, oxygen, or nitrogen atoms. The reduced masses of these groups are, respectively, 0.85, 0.89, and 0.87; since these values are nearly equal, it would be expected that the absorption frequencies of these groups would be nearly indistinguishable (173). However, the force constant, k, varies considerably with the electronic nature of the bond and this largely controls the frequency of vibration (173). A change in motion within a molecule will be accompanied by absorption (or emission) of light only if the motion leads to a change in dipole moment. In the case of two unlike atoms the center of the electrical charge will not correspond to the center of gravity of the atomic masses and vibrations within the bond will result in a detectable infrared band. However, a pair of like atoms which are equally substituted will not give a detectable band, and atoms of only slightly different electrical charges will give bands of low intensity. Since the intensity of the overtones is considerably less than that of the fundamental band, only the overtones of polar groups which give strong fundamental bands will be easily detected. The intensity of a vibrational band also depends on the strength of the bond and is greater for those bonds which can be more easily caused to vibrate. A double bond accordingly has a much weaker absorption than a single bond, and a triple bond absorbs with very low intensity. The overtones of double bonds will be difficult to detect, and overtones of triple bonds will be extremely difficult to observe. Combination bands caused by the simultaneous vibration of more than two bonds will be of low probability, and only simple combination bands will be easily detected.

In a diatomic molecule there is only one possible mode of vibration: namely, a stretching vibration along the axis of the bond. However, in polyatomic molecules a second mode of vibration is possible, involving a bending or rocking of a bond between a pair of atoms about the axis joining them to a third atom. Stretching vibrations give rise to absorption between 2 and 10 μ (except for heavy halogen atoms) and bending vibrations between 10 and 25 μ. The overtones of the bending vibrations will occur as very weak bands in the 2–10 μ region and will generally be hidden by the much stronger vibrational stretching bands. However, most of the overtones of the fundamental stretching frequencies will occur below 2 μ, in a region which is otherwise free from absorption bands.

IV. INSTRUMENTATION

A. Optics

A spectrometer may use a prism, a grating, or a combination of both for the dispersion of radiation (201). The material for the prism in the near infrared presents no problem, since quartz, either natural or synthetic, can be used to about 3 μ (33, 151, 186, 201). Its maximum dispersion, moreover, is in this region at about 2.9 μ (186). Small absorption bands occur at 2.9–3 μ (173, 260), and quartz absorbs appreciably above about 3.0 μ. Flint glass absorbs above 1.5 μ (33, 151, 186) and has found only limited use in the near infrared. Certain salt crystals, such as lithium fluoride, sodium chloride, and fluorite (natural calcium fluoride), can also be used (33, 151, 201). Such crystals have potential use in instruments measuring from the far ultraviolet into the infrared, since their useful ranges are as follows: lithium fluoride, 120 mμ to 6.5 μ (201); sodium chloride, 200 mμ to 17.0 μ (151); calcium fluoride, 125 mμ to 9.0 μ (151).

Details of some of the prism spectrometers used in the earlier measurements have been given (81, 113, 126, 129, 189, 209, 213, 254). Grating spectrometers have been less frequently used, though the construction of a grating spectrometer using a photocell and galvanometer to record from 0.6 to 1.0 μ on a photographic plate (13) and of a recording echelette grating spectrometer (266) has been described. Vacuum spectrometers using a prism (70), a Littrow spectrograph with thermopile (184), and a grating (315) have also been used. The construction of a rapid scanning spectrometer with oscillographic presentation and covering the range 0.36–5 μ has been described (53). A simple quartz spectrometer has also been used to measure the absorption of water in polymers in the range 0.1–2.5 μ (170).

Commercial instruments are now available which measure to 2.8 or 3.30 μ (139). These are the Beckman D.K. 1 and 2 models, the Carey Model 14, and the Perkin-Elmer Spectracord Model 4000. Data on the performance and tests of the Beckman instruments have been published (54). The ordinary Beckman D.U. can be used effectively in the near infrared to 1.4 μ (149) and can be modified to read to 2.7 μ (175). Adaptations of the General Electric spectrophotometer for readings to 1.2 μ (271) and of the Perkin-Elmer Model 12 instrument to read to 2.0 μ (65, 161) have been described.

B. Sources of infrared radiation

Any heated body emits infrared radiation, and the maximum energy of emission of a Nernst filament is at about 1 μ (186). The most commonly used source is a heated filament, such as a tungsten element, protected by enclosure in a soft-glass envelope (207). Such a source gives a continuous spectrum up to 3 μ, but cannot be used above this because of the absorption by the glass. An ordinary incandescent lamp can be used up to 2 μ (201).

C. Receivers

The development of near infrared absorption studies was long delayed by the lack of a convenient and reliable type of receiver. In the older studies the absorption spectrum was recorded on photographic plates (1, 241) sensitized to infrared radiation with special photosensitizing dyes such as neocyanine (29). Commercial available plates could be further sensitized by washing with 3 per cent aqueous ammonia (171). The photographic method is tedious, since the plates must be developed and rapid determinations cannot be made because the exposure time is sometimes very long. The intensity of absorption can be obtained only by measuring the density of blackening of the plate with a photodensiometer (241), and reproducible readings of intensity will be obtained only by preparing and developing the plates under carefully standardized conditions. Certain special techniques have also been used, such as receiving the weak near infrared radiation on a phosphor, thus converting it to radiation of shorter wavelength which can be measured with a photomultiplier tube (80).

Although thermopiles have been used in the near infrared (170, 184), neither the thermopile nor the bolometer commonly employed in the infrared (268) can be used effectively at shorter wavelengths. Consequently some type of photoelectric cell must be utilized. The photoemissive type, in which the incident light causes the emission of electrons which produce an anode current in a radiotube circuit, is commonly used in the visible part of the spectrum. Such a cell with cesium on silver on a boron oxide support is sensitive to 0.75 μ, and one of cesium on cesium oxide on silver is sensitive to 1.2 μ (186). A selenium photovoltaic cell, in which light produces a voltage difference across a selenium film, can be used in the range 0.3–0.8 μ, although it is more sensitive from 0.5 to 0.6 μ (201). The only type of photocell which is operative throughout the near infrared region is the photoconductive type, in which the conduction of an inorganic salt changes with the intensity of the incident light, owing to the excitation of photoconductive electrons (151, 186, 207, 267, 268). Case, in 1917 (58), discovered that certain minerals such as galena (PbS), bismuthinite (Bi_2S_3), and stibnite (Sb_2S_3) were photoconducting (207). Selenium or "thalofide" (thallous oxysulfide) cells were first used; although they have maximum sensitivity at about 0.95 μ, they can be used effectively to 1.4 μ (151). The commercially available instruments all use near infrared detectors of synthetic lead sulfide which are sensitive to 3 μ (216, 257). Lead telluride cells can be used to 4.0 μ (208, 267); more recently lead selenide cells have been shown to be effective to 5.4 μ (43, 45, 134, 191, 262, 270, 275) or even to 7.0 μ (268). The range of these cells can be increased by cooling to a low temperature. At −183°C. lead sulfide, lead telluride, and lead selenide cells are useful to 4.3 μ (208), 5.8 μ (208, 233), and 7.2 μ (134, 245), respectively. A lead selenide cell is sensitive to 9 μ (233) at the temperature of liquid hydrogen. A recent publication (263a) describes the construction of an indium sulfide cell sensitive to 10 μ. The future should see the development of other such cells sensitive to still higher wavelengths.

The techniques of automatically recording the response of these cells have been discussed by Kaye (174).

D. Standards

The wavelength calibration of a spectrometer can be checked by comparing a measured emission or absorption spectrum with some accurately recorded data. Such data are available for the emission spectrum of a graphite arc from 0.25 to 1.8 μ (99) and for a mercury lamp from 0.5 to 2.5 μ (234). Accurate data for the gas-discharge spectra of neon (to 1.035 μ), argon (to 0.955 μ), krypton (0.46–1.34 μ), and xenon (0.65–1.405 μ) are also available (230). The refractivity of lithium fluoride from 0.4 to 5.9 μ has also been reported (282) for use in calibrating spectrometers. Absorption spectra are more easily determined with the commonly used instruments, and the absorption bands of water vapor at 1.1, 1.3–1.48, and 1.77–1.98 μ and of methane at 1.7 and 2.2 μ have been accurately measured (232). The maxima of ammonia at 1.98 μ and of carbon monoxide at 1.96 and 2.01 μ have also been recorded to ± 0.1 cm.$^{-1}$ (150). For routine checking the bands of atmospheric water vapor or carbon dioxide, of liquid films of methanol or 1,2,4-trichlorobenzene, or of a solid film of polystyrene would seem more convenient (234). The water vapor within the instrument can be used for calibration by operating it under single-beam conditions (173).

V. SOLVENTS

Although the absorption spectra of simple organic compounds can be studied in the vapor state (156), the vapor pressure of most organic compounds is too low at ordinary temperatures, and the spectra must be determined with the pure liquid or solid, or in solution.

No measurements have been made using liquid films. The only spectra of solids were determined with specimens of coal (56), using either thin sections mounted with "halothene" (halogenated polythene) or as evaporated films of pyridine extracts. Polytrichlorofluoroethylene has high transmission to about 0.7 μ (227) and can be used for mounting solids. Nujol mulls, which are commonly employed in the infrared, have not been used in the near infrared, although plates made by grinding the substance with potassium iodide have been used from 1 to 4 μ (102).

Many of the measurements in the near infrared have been carried out on solutions. A solvent must be chosen which either absorbs very weakly in this region or has groups which absorb at wavelengths different from those of the groups being studied in the solute. Carbon tetrachloride is the most useful solvent, since the fundamental stretching frequency of the carbon–chlorine bonds occurs at 12.55 μ (269), and it shows only very weak absorption in the near infrared at about 1.8 μ (301), a value which corresponds to the sixth overtone. Most substances are sufficiently soluble in this solvent to allow their spectra to be measured, and it has been used extensively in studies of the association of hydroxyl groups (7, 8, 142, 197, 209, 311). Carbon tetrachloride is hygroscopic (173) and is best stored over phosphorus pentoxide. Carbon disulfide, which has its fundamental at 6.62 μ (41), shows a small band at about 2.2 μ (128), which would be the second overtone. This solvent has found only limited use (7, 288) because of its low flash-point.

A number of organic liquids containing carbon–hydrogen bonds can be used as solvents if carbon–hydrogen overtones are not being studied. Thus, benzene and other aromatic hydrocarbons have been used to study the second overtone in methanol, and pseudocumene was used to study cyclohexanol at 135°C. (171). An alkoxide linkage with its fundamental frequency at 8.8–9.4 μ (33, 261) will absorb only very weakly below 2 μ, and ether and dioxane have been used to study the overtones of hydroxyl groups (125, 139). Chloroform has found some use (167), although the ethanol used as a preservative in the commercial material must first be removed.

Water-soluble organic compounds can be studied in aqueous solution (2, 72, 73, 88, 129), although hydroxyl groups cannot, of course, be studied. However, the oxygen–deuterium bands of heavy water occur at different wavelengths (91), and studies of the hydroxyl group could be made in this solvent (294).

The use of an alcohol as solvent will obscure both hydroxyl and carbon–hydrogen bands; hence ethanol (1, 88, 129) and methanol (44) have found very limited use.

VI. CHARACTERISTIC GROUPS

A. Predictions

As has been seen in Section III, those groups having strong fundamental bands in the region 3–5 μ will give easily detectable overtones in the near infrared. The most common are the carbon–hydrogen group, which has its fundamental stretching vibration at 3.3–3.5 μ (107, 108, 109), and the oxygen–hydrogen group with its fundamental at 2.7–2.9 μ (106, 110). Both these groups give relatively strong overtones below 2 μ (see table 1). A nitrogen–hydrogen group with its fundamental at 2.7–2.9 μ (69, 239) and a sulfur–hydrogen group with its fundamental at about 3.9 μ (41) will give weaker overtones, since the intensities of the fundamentals are less.

The single-bond carbon–carbon and the carbon–oxygen stretching vibrations give bands at 6.9–7.3 μ and 7.1–7.9 μ, respectively (41), and the band of the former is less intense. Thus only the third and higher overtones will occur below 2 μ and such overtones will be very difficult to detect. A carbon–carbon double

TABLE 1

Approximate theoretical wavelengths of overtones

Group	Overtone	λ	Intensity*	Group	Overtone	λ	Intensity*
		μ				μ	
C—H	1	1.7	s	C—C	3	1.75	vw
	2	1.1	m		4	1.4	n
	3	0.85	w	C—O	3	1.85	w
	4	0.7	vw		4	1.5	vw
O—H	1	1.4	s	C=C	3	1.5	vw
	2	0.95	m		4	1.2	n
	3	0.7	w	C=O	2	1.9	m
	4	0.55	vw		3	1.45	w
N—H	1	1.4	m		4	1.15	vw
	2	0.95	w	C≡C	2	1.6	m
	3	0.7	vw		3	1.15	vw
	4	0.55	n	C≡N	2	1.5	w
S—H	1	1.95	w		3	1.1	vw
	2	1.3	vw	C—F	4	1.6	vw
C—D	2	1.55	s	C—Cl	6	1.9	n
	3	1.15	m	Si—H	2	1.5	s
O—D	2	1.45	m		3	1.15	m
	3	1.1	w	P—H	2	1.4	w
N—H	2	1.35	w		3	1.05	vw
	3	1.0	vw				

* Relative intensities: s, strong; m, medium; w, weak; vw, very weak; n, not detectable or extremely difficult to detect.

bond absorbs at 5.95–6.15 μ (258, 259) with rather low intensity, so that its third overtone will occur as a very weak band below 2 μ. However, the carbon–oxygen double bond, with an intense fundamental at about 5.8 μ (33, 162), will have its second overtone just below 2 μ and should be more easily detectable. Triple bonds between carbon and carbon atoms, or between carbon and nitrogen atoms, absorb very weakly at about 4.5 μ (41), and although their second overtones will occur below 2 μ, they will not be easy to observe.

The fundamental stretching vibrations of carbon–fluorine and carbon–chlorine bonds give bands at 8.0 and 14.0 μ, respectively (41); although their absorption is very intense, only their fourth and sixth overtones, respectively, will occur in the near infrared region and they will be very difficult to detect. The bonds of carbon attached to bromine and iodine absorb at still higher wavelengths and will not give observable overtones below 2 μ. Silicon–hydrogen and phosphorus–hydrogen bonds have fundamentals at 4.35–4.75 and 4.1–4.25 μ, respectively (41), and their second overtones should be found below 2 μ.

The bonds of deuterium attached to heavier elements will give overtones at higher wavelengths than the corresponding bonds formed with hydrogen.

These predicted overtone wavelengths are summarized in table 1. The available experimental observations on these groups will be discussed in the following sections.

B. Carbon–hydrogen groups

The fundamental carbon–hydrogen stretching vibration gives rise to a band at about 3.3–3.5 μ (107, 108, 109), and the overtones of this vibration were early detected in the near infrared region. Thus Coblentz (63) and Puccianti (236) found bands at 1.7 μ in hydrocarbons which they attributed to an overtone of the carbon–hydrogen fundamental. In the early work the fundamental carbon–hydrogen stretching vibration was taken as occurring at 6.9 μ, and Ellis (90, 91) found bands in liquid hydrocarbons and simple derivatives at 2.3, 1.72, 1.38, 1.15, 0.99, 0.84, and 0.77 μ which he assigned to the second to eighth overtones of the 6.9 μ band and which should occur near 2.30, 1.73, 1.38, 1.15, 0.99, 0.86, and 0.77 μ, respectively. However, it is now known that the band at 6.9 μ is a carbon–hydrogen "bending" or deformation vibration (41) and that the true stretching vibration occurs near 3.5 μ. The true stretching overtones are then at 1.75, 1.15, 0.88, and 0.70 μ (first to fourth), and the other bands detected by Ellis and others (89) must be either overtones of the carbon–hydrogen bending vibration at 6.9 μ or combinations of this with stretching vibrational overtones.

In an early study of the near infrared spectra of organic vapors bands of relatively high intensity were detected at 1.7 and 2.3 μ and weaker bands at 1.15 and 1.4 μ (84). The first pair must be the first overtone of the fundamental carbon–hydrogen stretching vibration and the second overtone of the corresponding bending vibration, respectively, and the latter pair are probably the second overtones of the stretching vibration and the fourth overtone of the bending vibration. The third stretching overtone was early detected in hydrocarbons at 0.913 μ (57, 200).

The fundamental carbon–hydrogen stretching vibrations of methyl (CH_3), methylene (CH_2), and methine (CH) groups occur at slightly different wavelengths (107, 108, 109), the values increasing in the order given. Corresponding differences are found in the overtones of these groups (48). Thus the first overtone of the methyl and methylene groups appears as a doublet at 1.705 and 1.695 μ and at 1.765 and 1.725 μ, respectively (246). The first overtone of the nonaromatic methine group has not been observed in hydrocarbon spectra, since it will be submerged by the absorption of the larger number of methyl groups. The second overtone of the methyl group gives a band at 1.195 μ and that of a methylene group at 1.215 μ (100). With higher resolution (246) the band of the methyl groups appears as a doublet at 1.190 and 1.150 μ (the former is stronger), while the methylene group still gives only one band at 1.210 μ. The corresponding overtone of the methine group appears at 1.225 μ. Bands of methyl groups at 1.360 and 1.435 μ (this band is weaker), of methylene groups at 1.395 and 1.415 μ, and of methine groups at 1.440 μ must be combination bands. Another study (182) has shown that the methyl group gives rise to bands at 1.015, 0.90, and 0.7405 μ and the methylene group at 1.053, 0.9380, and 0.9185 μ (doublet) and at 0.7690 and 0.7520 μ (another doublet) (assigned to the third, fourth, and fifth overtones). The spectra of several normal hydrocarbons (31) also show doublets at 0.913 and 0.934 and at 0.746 and 0.762 μ. The latter pair will arise from methyl and methylene groups, respectively. The other pair must arise from combinations of other bands, although the bands at about 0.9 and 0.74 μ are near the values expected for the third and fourth stretching overtones. Similarly, *n*-octane has bands at 1.709 and 1.747 μ (218, 219), whereas the isomeric branched-chain hydrocarbons have bands at 1.697, 1.703, and 1.714 μ (219). Bands of the methyl group have also been reported at 0.75 and 0.915 μ and of the methylene group at 0.715, 0.76 and 0.875, 0.94 μ (18). The application of the differences between these groups to the identification and analysis of hydrocarbons is discussed in Section VIII.

The fundamental vibration of the bond of a hydrogen atom attached to a carbon atom of an aromatic ring [the aromatic methine group (CH)] gives a band at a lower wavelength (near 3.29 μ) than those of saturated bonds (105), and the same behavior is shown by the overtones. In benzene (30, 237, 238) itself, the first overtone occurs at 1.685 μ and the second at 1.143 μ, as well as combination bands at 1.417 and 1.446 μ (274). The third overtone is at 0.8741 μ in liquid benzene (27, 28) and at 0.88 μ in carbon tetrachloride solution (68, 177). A high-resolution study has shown (246) that the first overtone exists as three peaks at 1.695 μ, and the second overtone as peaks at 1.135–1.150 μ, with many weak combination bands from 1.350 to 1.565 μ.

Derivatives of hydrocarbons not containing strongly polar groups give wavelength values very similar to those of the hydrocarbons themselves. Thus in fatty acids and their derivatives the first overtones of methyl and methylene groups appear at 1.69 and 1.70 μ, respectively (164), and the third overtone of methylene groups in aliphatic alcohols is at 0.91 μ (177). It has been reported that bands at 1.75, 1.2, and 0.9 μ increase in intensity with each additional methyl group in branched-chain alcohols, whereas bands at 1.4 and 1.0 μ decrease in intensity (254). Clearly the former bands are due to methyl groups and the latter to methylene groupings. The band near 1 μ in alcohols has also been shown to be a doublet and to be displaced regularly to longer wavelength on ascending an homologous series (115). Small differences have been noted between the overtones of methylene groups in cyclohexyl and cyclopentyl rings (100). Thus the bands of cyclohexyl methylene groups are broader than normally and cyclopentyl methylene groups, while giving the usual band at 1.215 μ, also show a sharp peak at 1.195 μ. Similar differences have been noted in other overtones (62, 299) and in the fundamental vibration (228). Cyclopropane has its methylene band at 1.097 μ (263).

The wavelengths of carbon–hydrogen overtones do not vary with temperature over the range −70°C. to 120°C. (44) or from 20°C. to 250°C. (16). In the case of phenol only the oxygen–hydrogen overtones change in wavelength with temperature (16). The physical state of the compound can affect the wavelengths slightly. Thus in a series of isomeric octanes the bands are displaced very slightly to higher wavelength in the liquid state (219) as compared to the vapor (218). In many easily condensable gases, such as the alkyl halides, condensation generally raises the wavelength of carbon–hydrogen overtones (200) and in a series of overtones the reduction in relative frequency ($\Delta\nu/\nu$) is constant. These changes have been attributed to the presence of attractive forces in the liquid state. The wavelengths of the bands of liquid and vapor samples move together with increasing temperatures up to the critical point, above which they become constant (209). Measurements of the spectra of ethylene and acetylene near their melting points have shown that the spectra in the solid and liquid states contain a number of additional bands not shown by their vapors (244; *cf.* 202, 213).

The overtones of carbon–hydrogen fundamentals show only small differences between various solvents. The greatest changes are produced when hydrogen bonding occurs between the solute and solvent, as in the case of benzene in diethyl ether (267). The absorption of the terminal methylene group (CH_2=; see below) in ethyl acrylate at 1.62 μ has been studied in some seventeen solvents (132). The band remains unchanged in wavelength but solvents not containing oxygen, such as hydrocarbons, give high-intensity values (A_M = 0.314–0.327), whereas nonpolar oxygen-containing solvents, such as alcohols and ketones, give lower values (A_M = 0.279–0.289). Polar oxygen-containing solvents, such as ethers, give still lower values (0.250–0.265), and highly polar solvents such as dimethylformamide (A_M = 0.239) and dimethyl sulfoxide (A_M = 0.228) give the lowest values.

The presence of polar substituents can considerably change the wavelength and other absorption characteristics of a group. Thus, the first methyl group overtone is at 1.72 μ in methanol and at 1.73 μ in acetic acid (152) instead of at its normal value of 1.69 μ, and this same overtone occurs at 1.65 μ in methyl cyanide (272) and methyl isocyanide (309). The corresponding second overtone in methylamine and dimethylamine is at 1.18 μ (64) instead of being near 1.15 μ.

Highly polar substituents, such as the halogen atoms, give rise to large displacements from the normal wavelength values (13, 18, 283). The third and fourth overtones of the carbon–hydrogen vibrations are at 0.8836–0.8941 μ and at 0.7233–0.7297 μ, instead of the normal values near 0.9 and 0.75 μ, respectively. The corresponding overtones for bromo compounds appear as a doublet at 0.895 μ and at 0.730–0.753 μ (13). The effect of changing from chlorine to bromine to iodine in a normal halide is to increase the intensity and produce more fine structure (18). Thus ethyl bromide shows one maximum and an inflection, whereas ethyl iodide shows four maxima. Differences are also noted between methyl, methylene, and methine groups. The methyl group shows three bands, the two at shorter wavelength being more intense, while the methylene group appears at two bands (that at shorter wavelength is more intense) and the methine group gives one very sharp band. Similarly, band multiplicity has been noted in alkoxy organophosphorus compounds (191). Thus a methoxyl group shows two principal bands as well as several lesser ones, while an ethoxyl group has four bands, and *n*-propoxyl and isopropoxyl groups give three and four bands, respectively. Thiomethoxyl groups give stronger bands than methoxyl groups.

The second overtone of the carbon–hydrogen ring vibration in monoalkylated benzenes at 1.145 μ remains unchanged in wavelength and intensity with different alkyl substituents, but in the case of polysubstituted compounds the wavelength varies by about 0.015 μ (246). Similarly, for the third, fourth, and fifth overtones of benzene at 0.8736, 0.7137, and 0.6107 μ, alkyl groups produce only small displacements and the size of the group is unimportant (18); this is to be expected, since the inductive effects of various alkyls groups are only slightly different.

Polar substituents generally produce appreciable changes in the overtones of the aromatic methine group (49). Thus electronegative substituents, such as the halogens or a nitro group, shift the 1.0 μ band of benzene to shorter wavelength (126), since by attracting electronic charge they will increase the electron density and hence the force constant of the carbon–hydrogen bond, resulting in an increased frequency of vibration and a decreased wavelength. The effect of polar substituents on the third, fourth, and fifth overtones of benzene has been studied in detail (18). Electronegative groups, such as the halogens or cyano or nitro groups, invariably give displacements to lower wavelengths, whereas an electropositive group, such as an alkyl or an amino group, produces a displacement to longer wavelengths, as expected. Alkyl groups give shifts in the 0.87 μ band of 25–29 A. and shifts of 16–19 A. in the 0.71 μ peak. In benzyl chloride the opposing electronic effects of the chlorine atom and the methylene group result in smaller shifts of 16 A. in the 0.87 μ maximum, as compared with 26 A. for the methyl group in toluene. The direction of the displacement in disubstituted benzenes depends on the relative magnitudes of the inductive effects of the two groups. For groups having the same polar nature the shifts are greater for ortho and least for para substitution, and the displacement for the ortho compound is nearly double that in the monosubstituted compound. If the two substituents have opposite polarities, then the band of the ortho compound is simple, that of the meta compound is disymmetric, and that of the para compound appears as a doublet. The direction of the displacement of the ortho compound is determined by the more polar group, while the position of the bands in the para isomer is very near to the bands of the corresponding pair of monosubstituted compounds. Thus, *p*-chlorotoluene shows two bands at 0.8704 and 0.8747 μ (*cf.* chlorobenzene at 0.8711 μ and toluene at 0.8765 μ), and *p*-nitrotoluene has maxima at 0.8628 and 0.8763 μ (*cf.* nitrobenzene at 0.8626 μ). The displacements observed for trisubstituted benzenes are larger and are greatest for the symmetrically substituted isomer.

Heterocyclic aromatic rings have their carbon–hydrogen overtones at slightly different wavelengths from the normal aromatic values. Thus pyridine (149, 254) has the third and fourth overtones at 1.145 and 0.877 μ, respectively (254), and pyrrole (149, 185) has these overtones at 1.11 and 0.85 μ (149). Thiophene has the third overtone as a doublet at 1.11 and 1.12 μ (149) and the fourth overtone at 0.86 μ (3).

Some data have been published on the overtones of the bonds of hydrogen attached to carbon–carbon double bonds. Thus the overtone at 0.8780 μ shows three new bands on the shorter wavelength side in the spectra of 1-hexene and 1-dodecene (18) and these must be due to the H—C= grouping. A number of unsaturated fatty acids have additional bands at 1.60 and 1.80 μ, and the intensity of a maximum at 1.68 μ increases with increasing unsaturation (164). In a detailed study of unsaturated compounds (139) a band at 1.63 μ was assigned to the unsaturation. A trans double bond, however, has no unique band in the near infrared, whereas a cis double bond gives a relatively strong band at 2.14 μ. Terminal unsaturation is easier to detect, and the terminal methylene ($H_2C=$) group has a band at 1.62 μ. Propylene gas also shows a band at 1.629 μ

(187), attributed to the first overtone of the antisymmetrical methylene ($=CH_2$) stretching fundamental.

A band at 1.77 μ (64) is probably due to an overtone of the carbon–hydrogen stretching fundamental of an acetylene group ($H—C\equiv$). Allene ($H_2C=C=CH_2$) has the first carbon–hydrogen overtone at 1.629 μ and a combination band at 1.658 μ (186); its second and third overtones are at 1.16 and 0.85 μ (169).

The intensities of the various possible carbon–hydrogen overtones have been used in the identification and quantitative analysis of organic compounds. These applications are discussed in Section VIII.

C. Oxygen–hydrogen groups

The fundamental oxygen–hydrogen vibration of a nonbonded hydroxyl group occurs at 2.74–2.79 μ (106, 110). The first overtone, which should thus be observed near 1.4 μ, has been detected in saturated alcohols (44, 164) as a strong peak at 1.42 μ or near 1.55 μ (254). Carboxylic acids show only a very weak peak at these wavelengths (164, 254), since the fundamental of the hydroxyl group is also very weak (41). Under higher resolution the hydroxyl overtone of an alcohol is more complex (25) and many combination bands have been detected in the spectra of methanol (173).

The second overtone near 0.9 μ has been studied more. It occurs at 0.970 μ in simple alcohols (163, 166, 182, 213, 317) and at 0.9630 μ in liquid alcohols (115). It has also been reported at 0.95 μ in alcohols and at 0.98 μ in acids (209). Normal primary alcohols show this band at 0.9615 μ in carbon tetrachloride solution (182). Changes in the structure of the alcohol result in splitting of the band and systematic shifts in the range 0.9450–0.9850 μ (6); bicyclic triterpene alcohols have this hydroxyl overtone at 0.966 μ (290). A weak band at 0.975 μ in acetic acid has been assigned to the unassociated hydroxyl group (80), and a number of organic acids in the vapor phase have a band at 0.9700 μ (35).

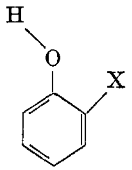
The third overtone, which should occur near 0.7 μ, has been detected at 0.7383 μ (13, 182, 209) in simple alcohols. However, methanol shows this band at 0.8230 μ (13) and formic acid has a band at 0.7525 μ (278). In a series of saturated aliphatic alcohols this overtone is displaced slightly to longer wavelength (from 0.7383 to 7439 μ) on ascending the homologous series (16, 209). This is in contrast to the behavior of the corresponding nitrogen–hydrogen overtone in homologous amines (*cf.* Section VI,E), which is displaced to shorter wavelength (16, 209). In passing from a primary to a secondary and a tertiary alcohol this overtone is also displaced to successively larger wavelengths (209).

The first overtone of the hydroxyl group of methanol has been studied in a number of solvents (171). In carbon tetrachloride the overtone appears at 0.9595 μ, as compared to 0.9491 μ in the vapor state. The shifts are greater in aromatic solvents, but this can be attributed to hydrogen bonding (see following section). In nonpolar solvents the shifts depend on the static dielectric constant (D) of the solvent and are proportional to $(D - 1)/(2D + 1)$ (171). Similar wavelength displacements of the 0.964 μ band in aliphatic alcohols in general have been observed (289). Changes of temperature can also result in displacements of wavelength; for simple alcohols the displacements of the 0.95 and 0.7 μ bands are proportional to the temperature (129). The second overtone has also been studied up to the critical temperature (209, 212). The wavelengths of the bands of the vapor and liquid move together up to the critical temperature, at which temperature the bands coincide. Above the critical point the wavelength does not vary with temperature. The changes in the structure of the bands of some alcohols (44) and of acetic acid (7) in solution are due to hydrogen bonding (see following section).

The presence of polar atoms near the alcohol grouping can displace the hydroxyl overtones. Thus 2,2,2-trichloro-1-propanol has a maximum at 1.49 μ, while 1-propanol absorbs at 1.46 μ (152). Similarly, $\beta,\beta,\beta,\beta',\beta',\beta'$-hexachloroisopropyl alcohol absorbs at 1.50 μ and β,β,β-trifluoroisopropyl alcohol at 1.47 μ, whereas isopropyl alcohol itself absorbs at 1.46 μ. The hydroperoxide group (—OOH) in methyl linoleate peroxide absorbs at 1.46 μ (164) and in peracetic acid at 1.930 μ (136).

Hydroxyl groups have been detected in polyvinyl alcohol polymers (138) and in cellulose and its derivatives (214) (*cf.* Section VIII).

The second overtone of the fundamental of phenol (11, 140, 287) occurs as a strong band at 1.00 μ and a second weaker band at 0.971 μ in carbon tetrachloride solution (311, 312). The third overtone appears as an intense band at 0.7466 μ, which is displaced by some 50 A. from the corresponding band of simple primary alcohols, and another weaker band at 0.7598 μ (16). *o*-Halogenophenols show a doubling of the hydroxyl overtones in dilute solution (314). Pauling (225; *cf.* 78, 321) suggested that the doublet arose from the existence of *s*-trans (I) and *s*-cis (II) forms of the phenol in equilibrium, the cis form (II) being stabilized by internal hydrogen bonding between the hydroxyl group and the halogen atom (311, 312). Monomeric phenol has a peak at 1.42 μ in carbon tetrachloride; *o*-chlorophenol has one peak at this wavelength and this must correspond to the trans form (I) (250). A second peak at 1.45 μ will correspond to the cis form (II), and this peak is about ten times as intense as the other. The ratio of the areas of the two peaks at different temperatures gives a value of the stabilizing energy of the cis form ($\Delta\Delta F$) of 1.4 kcal. mole^{-1}. The value for *o*-bromophenol in solution is 2.1 kcal. mole^{-1}; for *o*-iodophenol it is 1.4 kcal. mole^{-1} in solution and 2.8 kcal. mole^{-1} in the gas phase. The second and third overtones also appear as doublets, and the values for *o*-iodophenol are 1.009 μ (cis) and 0.9717 μ (trans) and 0.7820 μ (cis) and 0.7458 μ (trans), respectively. The fundamental hydroxyl stretching vibration of highly purified *o*-halogenophenols has been reëxamined



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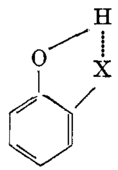


II

(10). A doublet is found in all these phenols except in the case of *o*-fluorophenol, where the trans peak is probably very weak and is submerged by the stronger cis band. The difference between the wavelengths of the trans and cis bands and the ratio of their intensities increases on passing from chloro through bromo to iodo. These observations demonstrate the increasing stability of the cis form in the order F $<$ Cl $<$ Br $<$ I.

The changes in the relative intensities of the doublet shown by phenol and substituted phenols in concentrated solution (16, 197, 255) are due to hydrogen bonding (see following section).

D. Hydrogen bonding

The formation of hydrogen bonds between hydroxyl groups results in a displacement of the fundamental stretching vibration from about 2.74–2.79 μ for a free hydroxyl group to 2.80–2.90 μ for a bonded group (106, 110). Corresponding shifts are observed in the case of the overtones (143, 162). Thus the associated dimer of acetic acid absorbs at 1.01 μ in carbon tetrachloride solution, whereas the unassociated hydroxyl group absorbs at 0.975 μ (8). The intensity of the former band increases at low temperatures because of increased association (7). The bands of methanol in carbon tetrachloride and of ethanol in carbon disulfide, at 0.9577 and 0.9658 μ, diminish in intensity with increased concentration (7); conversely, the intensity of the third overtone (near 0.75 μ) increases on dilution of chloroform or carbon tetrachloride solutions of these alcohols (16). Both these effects are due to increase in association of the hydroxyl group in more concentrated solution. The fundamental vibration of the bonded hydroxyl group of ethanol (143) in the vapor phase disappears at 70°C. (98), since hydrogen bonding is thermally unstable.

The degree of association (α) of a number of alcohols in various solvents has been studied (166) by measuring the change in intensity (ϵ) of the monomeric unbonded hydroxyl overtone at 0.970 μ at various concentrations (c). A graph of $1/\epsilon$ against c was extrapolated to zero concentration to obtain the intensity of absorption of the completely unassociated monomer (ϵ_∞).

If C_1 is the concentration of monomer at any other concentration and c is the concentration of the alcohol, then $\alpha = C_1/c = \epsilon/\epsilon_\infty$. A more detailed analysis has been carried out (97) to determine the association number (n) of several alcohols in carbon tetrachloride.

$$n\mathrm{ROH} \rightleftharpoons (\mathrm{ROH})_n$$

The concentration of the monomer is obtained as above and the concentration of the polymeric alcohol by the difference from the total concentration. The values of n for methanol, isobutyl alcohol, *tert*-amyl alcohol, and 2-octanol are between 3 and 4.

The third overtone of phenol is a doublet at 0.7466 and 0.7698 μ; on dilution the first band increases in intensity while the second decreases (16). The former band must correspond to the free hydroxyl group. The association of phenol in carbon tetrachloride solution has been studied by measuring the fraction of monomeric phenol from the intensity of the first and second hydroxyl overtones (197). Mean association energies were calculated from the change of intensity with temperature. The association of *o*-halogenophenols has also been studied recently (196) in the radiofrequency region.

The shifts in wavelength of methanol (171) in aromatic solvents are larger than those predicted by the dielectric constant relationship (see previous section). This has been attributed to hydrogen bonding between the hydroxyl group and the π electrons of the aromatic ring. Cyclohexanol shows a doublet in ψ-cumene which disappears at 135°C. Recently such hydrogen bonding has been observed within an aromatic alcohol (142). Thus, β-phenylethyl alcohol ($C_6H_5CH_2CH_2OH$) shows a doublet at 1.4084 and 1.4209 μ in carbon tetrachloride solution, whereas benzyl alcohol and 3-phenyl-1-propanol show only one band. The second weaker band of the doublet is assigned to internal hydrogen bonding between the hydroxyl group and the π electrons above the first ring carbon atom. 1,2-Diphenylethanol ($C_6H_5CH_2CHOHC_6H_5$) and 1-phenyl-2-propanol ($C_6H_5CH_2CHOHCH_3$) both show the same doublet, and *p*-methoxyphenylethanol gives a widely spaced doublet, although *p*-nitrophenylethanol shows only one peak. All compounds give a single maximum in benzene solution. The shifts of the doublets correspond to a bond energy of 0.88 and 0.98 kcal. mole^{-1} for β-phenylethanol and its *p*-methoxy derivative.

Steric effects within an alcohol can influence the extent of hydrogen bonding. In a series of tertiary cyclanols the spacial configuration can be obtained from the displacement of the hydroxyl overtone at 0.9363 μ, and the displacement is greatest when the hydroxyl group and the tertiary hydrogen atom are cis to each other (62). The effect of substitution on the hydrogen bonding of 3-pentanol has been studied in detail (265). The association hydroxyl band of this compound at 1.492 μ decreases in intensity with increasing branching. 3-Pentanol and its 3-methyl derivative have another band at 1.41 μ. This is at 1.40 μ in 2,2,4-trimethyl-3-pentanol, 2,2,4,4-tetramethyl-3-isopropyl-3-pentanol, and similar compounds. 2,2,3-Trimethyl-3-pentanol and 2,4-dimethyl-3-ethyl-3-pentanol show only a very weak band at 1.43 μ.

Hydrogen bonding between the hydroxyl group and nitrogen atom of salicylanil ($o\text{-}HOC_6H_4CH{=}NC_6H_5$) has been detected by the absorption at 1.4 μ (153) and this is not present in the hydroxyl-deuterated compound. Alterations in the absorption spectra of water and protein molecules, when water is bonded to gelatin, have also been noted (95, 96).

E. Nitrogen–hydrogen groups

The fundamental stretching vibration of the nitrogen–hydrogen bond in an amine group occurs at about 2.86 μ (67, 69). This is also the wavelength of absorption of the hydroxyl group fundamental, but the intensity of the maximum of the amine group is much less. Methylamine and dimethylamine gas show bands at 1.520 and 1.528 μ, respectively, and these have been assigned to the first overtone (185). Bands at 1.04–1.06 μ and at 1.03 μ in either compound must correspond to the second overtone (64). The band at 1.53 μ has been observed in long-chain aliphatic amines (164) and other aliphatic amines (168). In the case of aromatic amines, such as aniline or benzylamine, the band is at 1.50 μ (185). The amine band in propylamine at 1.55 μ remains unchanged in wavelength over the temperature range 70–120°C., in contrast to the band for the hydroxyl group, which varies considerably (44). However, this fact cannot be taken as evidence for the lack of hydrogen bonding in amines, since hydrogen bonding is known to produce only a very small shift (ca. 100 cm.$^{-1}$) in the fundamental band (127).

The presence of polar groups near the amine group can displace the overtones. Thus, the first nitrogen–hydrogen overtone of the amide (CONH) grouping in gelatin and silk fibroin is at 1.57 μ (34), and corresponding displacements occur in the fundamental (239, 269). An amine group attached to phosphorus shows its first overtone as a doublet at 1.481 μ and 1.488 μ (191) and the second amine overtone in pyrrole is at 0.99 μ (322), also slightly displaced from the normal aliphatic value.

Higher overtones of the nitrogen–hydrogen fundamental are difficult to detect because of their low intensity, and in a large molecule they will be hidden by much stronger carbon–hydrogen absorption. The third and fourth amine overtones of aniline vapor have been detected, at 0.79 and 0.648 μ, by using a long cell (92). These overtones have been studied for a series of amines and important generalizations were noted (122). The third overtone in primary amines occurs as a doublet at 0.806 μ and 0.779 μ. The latter band is more intense and its intensity increases with increasing chain length, whereas the intensity of the first decreases. The fourth overtone also appears as a doublet at 0.661 μ, although the second peak is very weak. Secondary amines, such as dimethylamine, diethylamine, di-*n*-propylamine, and di-*n*-butylamine, have their third and fourth overtones at 0.815 and 0.672 μ, respectively. Combination bands were also detected at 0.808 and 0.832 μ, except in the case of dibutylamine. Cyclic and aromatic amines also give doublets, and the band of a cyclic amine is displaced to higher wavelength by 0.025 and 0.021 μ for the third and fourth overtones, as compared with an acyclic amine. An aromatic amine has its overtones displaced to lower wavelength, and the values observed for aniline were 0.7915 and 0.6526 μ (122).

The effect of substituents on the near infrared absorption of aniline has recently been studied (304). Aniline, in carbon tetrachloride solution, shows a combination band at 1.97 μ and the first overtone as an asymmetric band at 1.45 μ and a symmetric band at 1.49 μ. The second overtone is at 1.02 μ. Substitution leads to values of the asymmetric first overtone of 1.432–1.460 μ and 1.472–1.513 μ for the symmetric band. The displacement of the combination band is only about one-half, within the range 1.959–1.9825 μ, while the second overtone has values of 1.003–1.035 μ. Para substitution results in the greatest displacements, while meta substituents produce only small shifts, and linear relationships exist between the frequency shifts and the substituent constants of Hammett (σ) and Brown (σ_p^*, σ^+). Hydrogen bonding, which occurs with some ortho substituents, leads to a splitting of the symmetric overtone to a doublet.

Hydrogen bonding has been observed between the NH bond of the amide group in gelatin and absorbed water (96). The intensity of the first amide (NH) overtone, near 1.5 μ, decreases in intensity with increased water content. The hydrogen bonding of the nitrogen–hydrogen bond of pyrrole has been studied in detail (318). Pure liquid pyrrole shows nitrogen–hydrogen overtones at 1.490 and 1.005 μ, whereas a solution in carbon tetrachloride has these bands at 1.460 and 0.995 μ, and this is attributed to hydrogen bonding within pure pyrrole itself. Pyrrole shows no hydrogen bonding to acetone, acetylacetone, or acetoacetic ester when dissolved in these substances. However, hydrogen bonding is observed with acetone and with pyridine in carbon tetrachloride solution. Pyrrole also bonds with pyridine when this is used as solvent, and this results in wavelength shifts of the first and second NH overtones. The decrease in intensity of these bands corresponds to about 7–8 per cent hydrogen bonding. In the presence of phenol the NH band remains unchanged, but the hydroxyl band of the phenol disappears, showing that this acts as the acceptor of bonding and pyrrole as the donor in this case.

The quantitative analysis of amine groups in organic compounds by their near infrared absorption is dealt with in Section VIII.

F. Carbonyl group

The only group which gives bands commonly encountered in the near infrared is the carbonyl group. This has a high-intensity fundamental stretching vibration at about 5.8 μ (33) and its overtones will be near 2.9, 1.95, 1.45, 1.16, and 0.97 μ (table 1). The first overtone will be very near the fundamental carbon–hydrogen stretching vibration, but it has been observed in cyclohexanone and acetophenone by using a lithium fluoride prism (204). The second to the fifth overtone has been observed in many aldehydes and ketones (52, 87, 93) at 1.96, 1.41–1.46, 1.24, and 0.96 μ, although the latter bands are very weak. Simple aldehydes, such as propionaldehyde, butyraldehyde, and valeraldehyde, show the third overtone very clearly (176). The position of the carbonyl stretching fundamental varies with the environment of the group (33, 41), and the second overtone occurs in acids at 1.90 μ (164) and at 1.90 and 1.95 μ in esters (93, 164). A double bond in conjugation with an ester group gives rise to splitting of the second overtone into multiple bands (164) and a similar behavior is found in the fundamental (41). The carbonyl overtone of acetone, at 1.97 μ, shows no change in wavelength over the temperature range -70°C. to 120°C., and there can be accordingly little association of this group. A band at 1.92 μ, attributable to the carbonyl group of the amide (CONH) grouping, has been observed in polypeptides (34, 86, 154) and in natural proteins (34, 86).

G. Miscellaneous groups

The overtones of stretching frequencies of bonds between hydrogen and another atom, other than those discussed above, should be detectable in the near infrared, but only a few data have been published. Ethyl mercaptan and 3-dimethylaminopropyl mercaptan show a small band at 1.740 μ (191), and this is probably the first overtone (301) of the fundamental sulfur–hydrogen stretching frequency, which occurs at 3.85–3.92 μ (41). The fundamental is weak and the overtone will be difficult to detect in other than simple compounds (301).

From a recent study of a number of organophosphorus compounds (191) it appears that the phosphorus–hydrogen bond gives rise to a band at 1.892 ± 0.001 μ, which is weak and diffuse. The fundamental, however, occurs at 4.10–4.25 μ (41). A hydroxyl group attached to phosphorus (P—OH) gives a band at 1.908 μ (191), which is considerably displaced with respect to the normal hydroxyl overtone. The fundamental band is also displaced (41) to 3.70–3.90 μ, and this has been attributed to the strong hydrogen bonding in phosphorus acids. The phosphorus–thiol group (P—SH) similarly shows a displacement of the normal thiol overtone to 1.970 and 1.999 μ. An amino group attached to phosphorus (P—NH) shows less displacement from the normal value, giving maxima at 1.481, 1.488, and 1.992 μ.

An overtone of the carbon–chlorine stretching frequency occurs at 1.86 μ (44) and this must be the sixth overtone, since the fundamental is at 13.3–14.3 μ (269). No other data have been published on overtones of heavier atoms (e.g., fluorine, silicon).

Since the stretching frequency of a bond depends on the mass of the vibrating atoms (Section III), the substitution of deuterium for hydrogen will result in a displacement of the frequency. Hexadeuterobenzene (C_6D_6) has bands at 1.01, 1.375, 1.56, and 1.90 μ, while the corresponding bands of benzene are at 0.84, 1.08, 1.25, and 1.65 μ (32). Monodeuteroacetylene ($HC\equiv CD$) has strong bands at 1.030 μ (50) and 0.5025 μ (192), and hexadeuteropropylene ($CD_3CD{=}CD_2$) has an overtone of the antisymmetric stretching frequency of the CD_2 group at

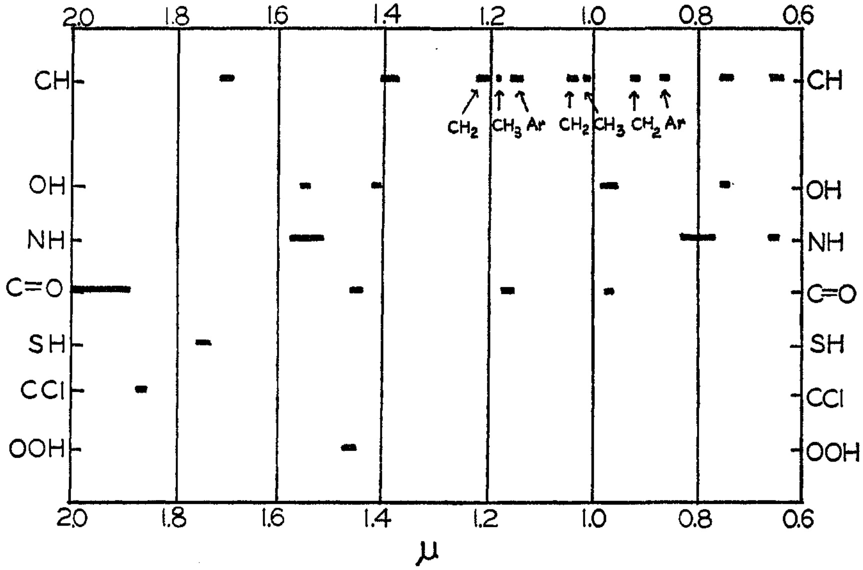


FIG. 1. Chart of characteristic wavelengths in microns

2.17 μ (187). Very few measurements have been made of the deuterated hydroxyl group (OD), although the hydrogen bonding present in salicylanil at 1.4 μ disappears on deuteration of the hydroxyl group (15). The replacement of hydrogen for deuterium in groups in which the hydrogen is easily exchanged (e.g., OH, NH, or SH) should be a useful method of identifying the bands associated with these groups, since only these bands would be displaced on substitution.

VII. GENERALIZATIONS

The experimental measurements discussed in the previous section can be used as a basis for deducing some generalizations concerning the wavelengths of commonly encountered overtones (figure 1). Lists of generalizations have been published (173, 203). In using these tables it should be remembered that interaction with a solvent or the presence of neighboring polar groups can result in shifts of the wavelengths from the generally observed values.

VIII. APPLICATIONS

Apart from the use of near infrared absorption in studying hydrogen bonding (Section VII,C), measurements in this region have found many analytical applications (*cf.* 273).

The absorption of colored organic compounds, such as dyes, in the region just beyond the red part of the visible spectrum has been much used for identifying them (76, 77, 103, 147, 235, 256, 271) and has also been used to analyze food dyes (135).

The generalizations (Section VII) as to the characteristic wavelengths of the overtones of various groups can be used to identify the groups present in compounds of unknown structure, and such an analysis could supplement similar information obtained from the normal infrared spectra. As has already been noted (Section VI,B), methyl and methylene groups absorb at slightly different wavelengths; accordingly there are small differences between the spectra of normal and isomeric hydrocarbons and these have been used to differentiate isomers and to identify hydrocarbons (119). In the case of pyridine methyl substitution produces displacements in the spectra, but these are not proportional to the number of methyl groups (in picoline, 2,6-lutidine, and 2,4,6-collidine). The differences between α- and β-picoline, however, are sufficient to differentiate them (224). Since the carbon–hydrogen overtones occur in well-defined and rather limited regions (near 1.2, 1.4, and 1.7 μ), impurities, containing other groups, can be detected at wavelengths between these values (139).

Near infrared measurements have been used to study natural polymers, such as wool (86, 105), silk (34, 86, 111), gelatin (34), and other peptides (154), as well as many synthetic polymers, such as polyglycine (86, 111), poly-L-alanine (86, 111), nylon (111, 137), polyvinyl alcohol (137, 138), polyvinyl chloride (137), polyvinylidene chloride (137), polystyrene (234), polyindene (269), and polythene (111, 137). The near infrared spectra of mixed organic oils (90), such as castor oil and essential oils (82), cottonseed oil (91), and various vegetable and animal oils (68, 269), have also been measured. The absorption between 1.0

and 2.2 μ of cellulose and its derivatives has been studied in relation to the hydroxyl groups present (214). An interesting application of near infrared absorption to the study of formyl (HCO•) and deuteroformyl (DCO•) free radicals has been recorded (159).

The intensity of the absorption bands can be used to determine quantitatively the number of groups in a molecule (187). The carbon–hydrogen overtones of the methyl (CH_3) group at 1.19 μ and of the methylene (CH_2) group at 1.21 μ have a nearly constant intensity per group, and by measuring the intensity of these peaks an estimate of the number of these groups per molecule can be made (48, 173, 184, 246, 291). Such an analysis has been carried out in detail for fifty-four hydrocarbons (247). For a normal hydrocarbon, if n_A and n_B are the number of methyl and methylene groups and α and β the molal absorption intensities per group, then the total absorption intensity K is given by

$$K = n_A\alpha + n_B\beta$$

Similarly for branched-chain and for cyclic and aromatic paraffins

$$K = n_A\alpha + n_B\beta + n_C\gamma + n_D\delta$$

where n_C and n_D are the number of aliphatic and aromatic methine (CH) groups and γ and δ are their respective molal absorption intensities per group. This method was employed to identify an "isononane" isolated from petroleum as 2,6-dimethylheptane. The ratio of the extinction coefficient of the aromatic CH band to the corresponding coefficient of the aliphatic CH band ("Varal" index) has been proposed (149) as a measure of the aromatic content of a hydrocarbon. The intensity of the carbon–hydrogen overtones in aliphatic alcohols is proportional to the number of carbon–hydrogen bonds present (319), and this could be used to determine the chain length.

The absorption intensity of the nitrogen–hydrogen overtone near 1.5 μ in a series of aliphatic and aromatic amines has also been studied in detail (185). Simple primary aromatic amines have a value of $\epsilon = 0.6$ per NH group. *N*-Methylation reduces the total absorption by two-thirds, but the value per NH group is increased (to 0.86), while *N*-ethylaniline and *N*-propylaniline have smaller values ($\epsilon =$ ca. 0.64). For normal aliphatic amines the values are less (0.4 per nitrogen–hydrogen bond), although the values are greater for secondary amines (0.60–0.64). It has been suggested that these differences could be used to analyze alkaloids (217).

A double bond with a pair of cis α,β-hydrogen atoms has characteristic bands at 1.18 and 1.68 μ, and these can be used to estimate the number of such groupings in a mixture (164). The band for the cis double bond, recorded at 1.62 μ (139), has ϵ values of 0.31–0.36 in most cases, and the intensity at this wavelength can be used to measure the content of the cis form of fatty acids or unsaturated hydrocarbons. 3-Chloro-3-chloromethylpropane can also be detected to a few hundred parts per million. The carbon–hydrogen overtone of a terminal epoxide group

TABLE 2

Near infrared spectra of organic compounds

Formula	Compound	References
CD_3Br	Deuteromethyl bromide	(305, 307)
$CHBr_3$	Bromoform	(13, 91, 173, 274)
$CHCl_3$	Chloroform	(13, 18, 27, 44, 83, 91, 133, 167, 173, 305, 307)
CHD_3	Trideuteromethane	(47, 306)
CHF_3	Fluoroform	(42, 243, 305, 307)
CH_2BrCl	Bromochloromethane	(229)
CH_2ClF	Chlorofluoromethane	(233)
CH_2Br_2	Dibromomethane	(13, 18, 91, 173, 229)
CH_2Cl_2	Dichloromethane	(91, 173, 229, 274)
CH_2I_2	Diiodomethane	(91, 229)
CH_2O_2	Formic acid	(35, 209, 278)
CH_3Br	Methyl bromide	(200, 206, 285)
CH_3Cl	Methyl chloride	(200, 206, 285)
CH_3D	Deuteromethane	(61)
CH_3I	Methyl iodide	(91, 160, 206, 274, 285, 305, 307)
CH_3NO_2	Nitromethane	(274)
CH_4	Methane	(60, 74, 205, 234, 240)
CH_4O	Methanol	(3, 6, 7, 13, 16, 44, 97, 129, 164, 171, 173, 182, 191, 197, 209, 213, 215, 234, 254, 299, 312, 317)
CH_5N	Methylamine	(63, 64, 122, 185, 277, 280)
C_2Cl_4	Tetrachloroethylene	(18)
C_2D_2	Dideuteroacetylene	(51, 231, 252)
C_2HCl_3	Trichloroethylene	(18)
C_2HCl_3O	Dichloroacetyl chloride	(13)
$C_2HCl_3O_2$	Trichloroacetic acid	(35)
C_2HCl_5	1,1,1,2,2-Pentachloroethane	(13, 18, 269, 274)
C_2HD	Deuteroacetylene	(50, 192)
C_2H_2	Acetylene	(51, 244, 276)
$C_2H_2Cl_2$	1,2-Dichloroethylene	(18, 264, 274)
$C_2H_2Cl_4$	*sym*-Tetrachloroethane	(11, 18, 264, 274)
$C_2H_2D_2$	Dideuteroethylene	(75)
$C_2H_3Cl_3$	1,1,1-Trichloroethane	(264, 293)
$C_2H_3Cl_3O$	2,2,2-Trichloroethanol	(152)
$C_2H_3F_3$	1,1,1-Trifluoroethane	(71, 157)
C_2H_3N	Methyl cyanide	(222, 274, 292)
	Methyl isocyanide	(309)
C_2H_4	Ethylene	(75, 226, 244)
C_2H_4BrCl	1-Bromo-2-chloroethane	(13)
$C_2H_4Br_2$	1,2-Dibromoethane	(13, 91)
$C_2H_4Cl_2$	1,2-Dichloroethane	(13, 91, 264, 269, 274)
$C_2H_4F_2O$	2,2-Difluoroethanol	(152)
C_2H_4O	Acetaldehyde	(87, 149)
	Ethylene oxide	(200)
$C_2H_4O_2$	Acetic acid	(7, 8, 35, 209, 256)
$C_2H_4O_3$	Peracetic acid	(136)
C_2H_4OS	Thioacetic acid	(199)
$C_2H_4S_2$	Dithioacetic acid	(199)
C_2H_5Br	Ethyl bromide	(13, 91, 129, 274)
C_2H_5Cl	Ethyl chloride	(91, 200)
C_2H_5ClO	Ethylene chlorohydrin	(44)
C_2H_5I	Ethyl iodide	(13, 91, 274)
$C_2H_5NO_2$	Nitroethane	(274)
$C_2H_5NO_3$	Ethyl nitrate	(274)
$C_2H_6N_2$	Ethylenediamine	(149)
C_2H_6O	Ethanol	(1, 3, 6, 7, 13, 16, 44, 88, 97, 129, 182, 191, 209, 215, 254, 256, 264, 299, 317)
$C_2H_6O_2$	Ethylene glycol	(6, 209, 317)
C_2H_6S	Ethyl mercaptan	(191)
C_2H_7N	Dimethylamine	(13, 17, 64, 122, 185)
	Ethylamine	(13, 116, 117, 122, 185)

TABLE 2—*Continued*

Formula	Compound	References
$C_2H_7O_4P$	Dimethyl phosphate	(191)
$C_2O_2Cl_2$	Oxalyl chloride	(320)
C_3D_6	Hexadeuteropropylene	(187)
C_3HD_3	Trideuteromethylacetylene	(158)
$C_3H_2Cl_6O$	1-Trichloromethyl-2,2,2-trichloro-1-propanol	(152)
C_3H_3N	Acrylonitrile	(139)
C_3H_4	Allene	(169, 186)
C_3H_4O	Acrolein	(139)
$C_3H_4O_2$	Acrylic acid	(139)
C_3H_5Cl	Allyl chloride	(200)
$C_3H_5F_3O$	3,3,3-Trifluoro-1-propanol	(152)
	3,3,3-Trifluoro-2-propanol	(152)
C_3H_5N	Ethyl cyanide	(274)
C_3H_6	Propylene	(187)
$C_3H_6Br_2$	1,2-Dibromopropane	(13)
$C_3H_6Cl_2$	1,2-Dichloropropane	(13)
	1,3-Dichloropropane	(13)
C_3H_6	Cyclopropane	(263)
C_3H_6O	Acetone	(44, 87, 91, 274)
	Allyl alcohol	(6, 16, 209)
	Propionaldehyde	(87, 176)
$C_3H_6O_2$	Methyl acetate	(87, 164, 254, 264)
	Propionic acid	(35, 84)
$C_3H_6O_3$	Dimethyl carbonate	(199)
	Trioxane	(149)
C_3H_7Br	*n*-Propyl bromide	(13, 274)
	Isopropyl bromide	(13, 91, 269, 274)
C_3H_7Cl	*n*-Propyl chloride	(274)
C_3H_7I	*n*-Propyl iodide	(13, 91, 274)
	Isopropyl iodide	(91, 274)
C_3H_7NO	*N*-Methylacetamide	(79)
C_3H_8O	1-Propanol	(6, 13, 16, 129, 152, 182, 209, 254, 317)
	2-Propanol	(6, 16, 97, 152, 199, 209, 254, 299, 317)
$C_3H_8O_2$	Dimethoxymethane	(274)
$C_3H_8O_3$	Glycerol	(3, 59, 209, 215, 317)
C_3H_9N	*n*-Propylamine	(13, 40, 44, 116, 117, 122, 254)
$C_3H_9O_4P$	Trimethyl phosphate	(191)
$C_4H_2D_3$	(Trideuteromethyl)allene	(169)
$C_4H_3F_7O$	2,2,3,3,4,4,4-Heptafluoro-1-butanol	(152)
C_4H_4S	Thiophene	(3, 18, 32, 149)
C_4H_5N	Pyrrole	(149, 185, 288, 317, 322)
$C_4H_5NO_2$	Succinimide	(198)
$C_4H_6Cl_2$	3-Chloro-2-chloromethyl-1-propene	(139)
C_4H_6DNS	*N*-Deuterothiobutyrolactam	(198)
C_4H_6O	Crotonaldehyde	(139)
	α-Methylacrolein	(139)
$C_4H_6O_2$	Vinyl acetate	(139)
	Crotonic acid	(164)
C_4H_7NS	Thiobutyrolactam	(198)
C_4H_8O	Butyraldehyde	(87, 176, 254)
	Ethyl methyl ketone	(254, 274)
$C_4H_8O_2$	Butyric acid	(254)
	Isobutyric acid	(209)
	p-Dioxane	(149, 193, 194, 200, 274)
	Ethyl acetate	(87, 254, 269)
C_4H_9Br	*n*-Butyl bromide	(13, 91, 269, 274)
	Isobutyl bromide	(91)
	tert-Butyl bromide	(13)
C_4H_9Cl	*n*-Butyl chloride	(13, 91, 274)
	Isobutyl chloride	(91)
	tert-Butyl chloride	(13)

TABLE 2—*Continued*

Formula	Compound	References
C_4H_9I	*n*-Butyl iodide	(13, 91, 274)
	Isobutyl iodide	(91)
C_4H_9NO	Morpholine	(149)
$C_4H_9NO_2$	*n*-Butyl nitrite	(91)
$C_4H_{10}O$	1-Butanol	(6, 13, 16, 44, 129, 182, 209, 254, 264, 317)
	sec-Butyl alcohol	(6, 13, 254)
	Isobutyl alcohol	(6, 13, 209, 254, 317)
	tert-Butyl alcohol	(6, 13, 16, 197, 254, 262, 299)
	Diethyl ether	(3, 87, 91, 149, 254, 264, 274)
	Methyl *n*-propyl ether	(264)
	Methyl isopropyl ether	(264)
$C_4H_{10}O_4S$	Diethyl sulfate	(87)
$C_4H_{11}N$	Diethylamine	(122, 185)
	n-Butylamine	(13, 40, 116, 117, 122, 185)
$C_4H_{11}O_3P$	Diethyl phosphonate	(199)
C_5H_5N	Pyridine	(149, 224, 249, 254)
C_5H_8	Cyclopentene	(139, 228, 300)
$C_5H_8O_2$	2-Pentenoic acid	(164)
	Allyl acetate	(139)
	Ethyl acrylate	(139)
	3-Methyl-2-butenoic acid	(164)
	Methyl methacrylate	(139)
C_5H_9N	*n*-Butyl cyanide	(274)
C_5H_{10}	Cyclopentane	(285, 300)
	2-Pentene	(139)
$C_5H_{10}O$	Cyclopentanol	(299)
	Diethyl ketone	(274)
	Methyl *n*-propyl ketone	(87)
	Valeraldehyde	(176)
	Isovaleraldehyde	(176)
$C_5H_{10}O_2$	Ethyl propionate	(264)
	n-Propyl acetate	(254, 264)
	Isovaleric acid	(164)
$C_5H_{10}O_3$	Diethyl carbonate	(191, 264)
	Ethyl lactate	(264)
$C_5H_{11}NO_2$	Isoamyl nitrite	(84)
C_5H_{12}	Pentane	(13, 29, 184, 236, 247, 274)
$C_5H_{12}O$	*n*-Amyl alcohol	(44, 182)
	Isoamyl alcohol	(74, 209, 254, 317)
	tert-Amyl alcohol	(16, 35, 97, 209, 264, 317)
	n-Butyl methyl ether	(264)
	sec-Butyl methyl ether	(264)
	Isobutyl methyl ether	(264)
	tert-Butyl methyl ether	(264)
	3-Pentanol	(260)
$C_5H_{13}N$	*n*-Amylamine	(13, 122)
	Isoamylamine	(40)
C_6D_6	Hexadeuterobenzene	(32)
C_6HCl_5O	Pentachlorophenol	(311, 312)
$C_6HF_{11}O_2$	Perfluorocaproic acid	(164)
$C_6H_3Br_3O$	2,4,6-Tribromophenol	(311, 316)
$C_6H_3Cl_3$	1,2,4-Trichlorobenzene	(234)
$C_6H_3Cl_3O$	2,4,6-Trichlorophenol	(311, 312)
$C_6H_3I_3O$	2,4,6-Triiodophenol	(311, 312)
$C_6H_4Cl_2$	*m*-Dichlorobenzene	(18, 274)
	o-Dichlorobenzene	(18, 274)
	p-Dichlorobenzene	(18)
$C_6H_4F_2$	*m*-Difluorobenzene	(18)
	o-Difluorobenzene	(18)
	p-Difluorobenzene	(18)
C_6H_5Br	Bromobenzene	(18, 274)
C_6H_5BrO	*o*-Bromophenol	(311, 312)
C_6H_5Cl	Chlorobenzene	(18, 177, 269, 274)

TABLE 2—*Continued*

Formula	Compound	References
C_6H_5ClO	*o*-Chlorophenol	(6, 16, 209, 311, 312)
	p-Chlorophenol	(16, 197, 209)
C_6H_5F	Fluorobenzene	(18)
C_6H_5I	Iodobenzene	(274)
C_6H_5IO	*o*-Iodophenol	(311, 312)
$C_6H_5NO_2$	Nitrobenzene	(18, 177, 274)
C_6H_6	Benzene	(3, 4, 14, 15, 18, 21, 27, 28, 30, 32, 44, 83, 84, 88, 91, 126, 129, 130, 132, 149, 173, 177, 184, 200 238, 247, 256, 274)
	Dimethyldiacetylene	(104)
C_6H_6O	Phenol	(6, 8, 18, 149, 182, 185, 190, 197, 209, 210, 211, 213, 286, 311, 312, 318)
$C_6H_6O_2$	Resorcinol	(209)
C_6H_7N	Aniline	(18, 44, 92, 122, 124, 149, 185, 178)
	α-Picoline, β-picoline	(224)
C_6H_{10}	Cyclohexene	(18, 149, 228, 300)
$C_6H_{10}O$	Cyclohexanone	(3, 254 300)
$C_6H_{10}O_2$	3-Hexenoic acid	(164)
$C_6H_{10}O_4$	Diethyl oxalate	(84, 191)
C_6H_{12}	Cyclohexane	(149, 164, 182, 184, 200, 247, 274, 300)
	Methylcyclopentane	(184, 247)
	1-Hexene	(18)
	cis-3-Hexene	(139)
	4-Methyl-2-pentene	(139)
$C_6H_{12}O$	*n*-Butyl vinyl ether	(139)
	Isobutyl vinyl ether	(139)
	Cyclohexanol	(3, 171, 200, 209, 299)
	3-Methyl-3-pentanol	(265)
$C_6H_{12}O_2$	*n*-Butyl acetate	(87, 254)
	Ethyl butyrate	(87, 254, 264)
	2-Ethylbutyric acid	(164)
	Hexanoic acid	(209)
	n-Pentyl formate	(264)
	n-Propyl propionate	(254)
	Paraldehyde	(84)
$C_6H_{13}N$	Cyclohexylamine	(122)
C_6H_{14}	2,3-Dimethylbutane	(184, 247)
	Hexane	(13, 44, 182, 200, 236, 247, 274)
	2-Methylpentane	(13, 184, 247)
	3-Methylpentane	(13, 184, 247)
$C_6H_{14}O$	1-Hexanol	(182, 317)
	Di-*n*-propyl ether	(87, 274)
	1-Ethylpropyl methyl ether	(264)
	Methyl *n*-pentyl ether	(264)
	Methyl isopentyl ether	(264)
	Methyl *tert*-pentyl ether	(264)
$C_6H_{14}O_4$	Triethylene glycol	(203)
$C_6H_{15}N$	Di-*n*-propylamine	(40, 122)
	Triethylamine	(274)
$C_6H_{15}O_3P$	Triethyl phosphite	(191)
$C_6H_{15}O_4P$	Triethyl phosphate	(191)
C_7F_{16}	Hexadecafluoroheptane	(220)
$C_7H_5Cl_3$	Benzotrichloride	(274)
C_7H_5N	Benzonitrile	(18, 274)
$C_7H_6Cl_2$	Benzal chloride	(274)
C_7H_6O	Benzaldehyde	(87, 149)
$C_7H_6O_2$	Benzoic acid	(209)
C_7H_7Br	*m*-Bromotoluene	(18)
	o-Bromotoluene	(18)
	p-Bromotoluene	(18)
C_7H_7BrO	*p*-Bromoanisole	(18)

TABLE 2—*Continued*

Formula	Compound	References
C_7H_7Cl	Benzyl chloride	(18, 84)
	m-Chlorotoluene	(18)
	o-Chlorotoluene	(18)
	p-Chlorotoluene	(18)
C_7H_7ClO	*p*-Chloroanisole	(18)
C_7H_7FO	*p*-Fluoroanisole	(18)
$C_7H_7NO_2$	*m*-Nitrotoluene	(18)
	o-Nitrotoluene	(18)
	p-Nitrotoluene	(18)
C_7H_8	Toluene	(3, 18, 27, 28, 30, 91, 149, 177, 184, 247, 274)
C_7H_8O	Benzyl alcohol	(18, 44, 142, 197, 209)
	o-Cresol	(197)
	p-Cresol	(197)
C_7H_9N	Benzylamine	(18, 122, 185)
	2,6-Lutidine	(224)
	N-Methylaniline	(18, 185)
	m-Toluidine	(173, 185)
	o-Toluidine	(185)
	p-Toluidine	(185)
C_7H_{12}	Cycloheptene	(139, 300)
$C_7H_{12}O_4$	Diethyl malonate	(87)
C_7H_{14}	Cycloheptane	(300)
	cis-1,2-Dimethylcyclopentane	(184, 247)
	trans-1,2-Dimethylcyclopentane	(247)
	Methylcyclohexane	(184, 247)
$C_7H_{14}O$	Methyl *n*-pentyl ketone	(87)
$C_7H_{14}O_2$	*n*-Amyl acetate	(264)
	Heptanoic acid	(209)
C_7H_{16}	2,2-Dimethylpentane	(184)
	2,3-Dimethylpentane	(184, 247)
	3,3-Dimethylpentane	(184, 247)
	2,4-Dimethylpentane	(184, 247)
	2,2,3-Trimethylbutane	(184, 247)
	3-Ethylpentane	(184, 247)
	Heptane	(13, 91, 139, 184, 247, 274)
	2-Methylhexane	(184, 247)
	3-Methylhexane	(184, 247)
	2,2,3-Trimethylbutane	(184, 247)
$C_7H_{16}O$	1-Heptanol	(44)
C_8H_7N	Phenylacetonitrile	(274)
	m-Tolunitrile	(18)
	o-Tolunitrile	(18)
	p-Tolunitrile	(18)
C_8H_8	Styrene	(138, 177, 269)
C_8H_8O	Acetophenone	(87)
	p-Tolualdehyde	(87)
$C_8H_8O_2$	Methyl benzoate	(84, 86, 264)
$C_8H_8O_3$	Methyl salicylate	(84, 264)
$C_8H_9NO_3$	β-(*p*-Nitrophenyl)ethanol	(142)
C_8H_{10}	Ethylbenzene	(18, 27, 28, 177, 184, 247, 269, 274)
	m-Xylene	(3, 18, 27, 28, 177, 184, 247, 274)
	o-Xylene	(3, 18, 27, 28, 177, 184, 247, 274)
	p-Xylene	(3, 18, 27, 28, 30, 91, 177, 184, 247, 274)
$C_8H_{10}O$	Benzyl methyl ether	(254)
	β-Phenylethanol	(142)
	1,3,2-Xylenol	(16)
	1,3,4-Xylenol	(16)
	1,3,5-Xylenol	(16)

TABLE 2—*Continued*

Formula	Compound	References
$C_8H_{11}N$	2,4,6-Collidine	(224)
	N,*N*-Dimethylaniline	(18)
	N-Ethylaniline	(185)
	N-Methyl-*p*-toluidine	(185)
	2-Phenylethylamine	(185)
	2,4-Xylidene	(185)
	2,5-Xylidene	(185)
	2,6-Xylidene	(185)
	3,5-Xylidene	(185)
$C_8H_{12}O$	1-Phenyl-2-propanol	(142)
	3-Phenyl-1-propanol	(142)
$C_8H_{12}O_2$	Ethyl sorbate	(164)
$C_8H_{13}NO_2$	Arecoline	(217)
$C_8H_{13}NO_2 \cdot HBr$	Arecoline hydrobromide	(217)
C_8H_{14}	Diethylbenzene	(27)
$C_8H_{15}NO$	Pelletierine	(217)
C_8H_{16}	Ethylcyclohexane	(246, 247)
	1-Octene	(139)
$C_8H_{15}O_2$	Caprylic acid	(164)
C_8H_{18}	2,2-Dimethylhexane	(218, 219)
	2,3-Dimethylhexane	(218, 219)
	2,4-Dimethylhexane	(218, 219)
	2,5-Dimethylhexane	(218, 219)
	3,3-Dimethylhexane	(218, 219)
	3,4-Dimethylhexane	(218, 219)
	3-Ethylhexane	(218, 219)
	3-Ethyl-2-methylpentane	(13, 218, 219)
	3-Ethyl-3-methylpentane	(218, 219)
	2-Methylheptane	(13, 218, 219)
	3-Methylheptane	(218, 219)
	4-Methylheptane	(13, 218, 219)
	n-Octane	(13, 91, 184, 219, 247)
	2,2,3,3-Tetramethylbutane	(218, 219)
	2,2,3-Trimethylpentane	(218, 219)
	2,2,4-Trimethylpentane	(13, 164, 178, 184, 219, 247)
	2,3,3-Trimethylpentane	(219)
	2,3,4-Trimethylpentane	(219)
$C_8H_{18}O$	Di-*n*-butyl ether	(87, 91)
	1-Octanol	(209)
	2-Octanol	(97, 209)
	2,2,4-Trimethyl-3-pentanol	(265)
$C_8H_{19}N$	Di-*n*-butylamine	(40, 122, 185)
	Diisobutylamine	(122)
$C_8H_{23}O_3P$	Di-*n*-butyl phosphonate	(191)
C_9H_8O	Cinnamaldehyde	(87, 254)
C_9H_{10}	α-Methylstyrene	(139)
$C_9H_{10}O$	Propiophenone	(87)
$C_9H_{10}O_2$	Ethyl benzoate	(87)
$C_9H_{10}O_3$	Ethyl salicylate	(264)
C_9H_{12}	Mesitylene	(27, 28, 30, 91, 149, 177, 184, 247)
	n-Propylbenzene	(18, 246, 247, 274)
	Isopropylbenzene	(246, 247)
	1,2,3-Trimethylbenzene	(184, 247)
	1,2,4-Trimethylbenzene	(184, 247)
$C_9H_{12}O_2$	β-(*p*-Methoxyphenyl)ethanol	(142)
$C_9H_{13}N$	*N*-Propylaniline	(185)
$C_9H_{15}N_3$	2,4,6-Triethyltriazine	(55)
C_9H_{20}	Nonane	(184, 247)
$C_9H_{20}O$	2,4-Dimethyl-3-ethyl-3-pentanol	(265)
$C_9H_{21}N$	Tri-*n*-propylamine	(40)
$C_9H_{21}O_6P$	Triisopropyl phosphite	(191)
$C_{10}H_8$	Naphthalene	(149)

TABLE 2—*Continued*

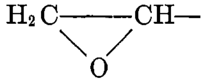
Formula	Compound	References
$C_{10}H_8N_2$	Dipyridyl	(217)
$C_{10}H_{12}$	Tetralin	(149)
$C_{10}H_{12}O$	Anethole	(84)
$C_{10}H_{14}$	Isobutylbenzene	(18)
	Diethylbenzene	(28)
$C_{10}H_{14}N_2$	Anabasine	(217)
	dl-Neonicotine	(217)
	Nicotine	(217)
$C_{10}H_{16}$	*d*-Pinene	(84)
	l-Pinene	(84)
	Limonene	(18)
$C_{10}H_{18}$	Decahydronaphthalene	(149)
$C_{10}H_{20}$	1-Decene	(18, 164)
$C_{10}H_{22}$	Decane	(13, 29, 184, 247)
	2-Methylnonane	(246, 247)
	3-Methylnonane	(246, 247)
	4-Methylnonane	(246, 247)
	5-Methylnonane	(246, 247)
	3,5,5-Trimethylheptane	(246, 247)
	3,4,5,5-Tetramethylhexane	(246, 247)
$C_{10}H_{22}O$	1-Decanol	(164)
	3-Ethyl-2,2,4-trimethyl-3-pentanol	(265)
$C_{10}H_{23}N$	Diisoamylamine	(40)
$C_{11}H_{10}O_2$	Methyl 2,8-decadiene-4,6-diynoate	(164)
$C_{11}H_{11}N$	*N*-Methyl-α-naphthylamine	(37)
$C_{11}H_{16}$	Isoamylbenzene	(18)
$C_{11}H_{16}N_2$	Methylanabasine	(217)
$C_{11}H_{16}N_2O_2$	Pilocarpine	(217)
$C_{11}H_{20}O_4$	Dimethyl azelate	(164)
$C_{11}H_{22}O_2$	Undecylanic acid	(164)
$C_{11}H_{24}$	Undecane	(184, 247)
$C_{11}H_{24}O$	3-Isopropyl-2,2,4-trimethyl-3-pentanol	(265)
$C_{12}H_{10}$	Biphenyl	(149)
$C_{12}H_{11}N$	Diphenylamine	(18, 185)
$C_{12}H_{13}N$	*N*-Ethyl-α-naphthylamine	(37)
$C_{12}H_{14}O_4$	Diethyl phthalate	(264)
$C_{12}H_{20}O$	α-Terpinyl vinyl ether	(139)
$C_{12}H_{24}$	1-Dodecene	(18)
$C_{12}H_{26}$	Dodecane	(13, 184, 247)
$C_{12}H_{26}O$	3-Propyl-2,2,4,4-tetramethyl-3-pentanol	(265)
	3-Isopropyl-2,2,4,4-tetramethyl-3-pentanol	(265)
$C_{12}H_{27}N$	Tri-*n*-butylamine	(40)
$C_{12}H_{27}O_3P$	Tri-*n*-butyl phosphite	(191)
$C_{12}H_{27}O_4P$	Tri-*n*-butyl phosphate	(191)
$C_{13}H_{10}O$	Benzophenone	(87)
$C_{13}H_{11}N$	Fluorylamine	(185)
$C_{13}H_{11}NO$	Salicylanil	(153)
$C_{13}H_{22}O_2$	Methyl 2,4-dodecadienoate	(164)
$C_{14}H_{10}$	Anthracene	(149)
	Phenanthrene	(149)
$C_{14}H_{12}$	Stilbene	(291)
$C_{14}H_{14}$	1,2-Diphenylethane	(291)
$C_{14}H_{14}O$	Dibenzyl ether	(254)
	1,2-Diphenylethanol	(142, 291)
$C_{14}H_{15}N$	Dibenzylamine	(39, 185)
$C_{14}H_{20}$	1-Cyclopentyl-3-phenylpropane	(100)
	1-Cyclohexyl-2-phenylethane	(100)
$C_{14}H_{24}$	Perhydroanthracene	(149)
	Perhydrophenanthrene	(149)
$C_{14}H_{28}$	1-Tetradecene	(18)
$C_{14}H_{28}O$	Myristaldehyde	(164)
$C_{14}H_{30}$	Tetradecane	(13)

TABLE 2—*Continued*

Formula	Compound	References
$C_{15}H_{26}N_2$	Sparteine	(217)
$C_{15}H_{26}N_2 \cdot H_2SO_4$	Sparteine sulfate	(217)
$C_{15}H_{33}N$	Triisoamylamine	(40)
$C_{16}H_{10}$	Pyrene	(149)
$C_{16}H_{16}$	1,2-Diphenyl-1-butene	(291)
$C_{16}H_{16}O$	1,4-Diphenyltetrahydrofuran	(291)
$C_{16}H_{18}$	1,2-Diphenylbutane	(291)
$C_{16}H_{18}O$	1,4-Diphenylbutanol	(291)
$C_{16}H_{18}O_2$	1,4-Diphenyl-1,2-butanediol	(291)
$C_{16}H_{24}$	Perhydropyrene	(149)
$C_{16}H_{32}$	1-Hexadecene	(164)
$C_{16}H_{32}O_2$	Palmitic acid	(164)
$C_{16}H_{34}$	Hexadecane	(164)
$C_{16}H_{34}O$	1-Hexadecanol	(164)
$C_{17}H_{18}$	1,2-Diphenyl-1-pentene	(291)
$C_{17}H_{20}$	1,2-Diphenylpentane	(291)
$C_{17}H_{34}O_2$	Methyl palmitate	(164)
$C_{17}H_{36}$	Heptadecane	(100)
$C_{18}H_{15}N$	Triphenylamine	(38, 185)
$C_{18}H_{20}O$	1,4-Dibenzyltetrahydrofuran	(291)
$C_{18}H_{22}O$	2,5-Diphenylhexanol	(291)
$C_{18}H_{22}O_2$	2,5-Diphenyl-2,5-hexanediol	(291)
$C_{18}H_{30}O_2$	Linolenic acid	(164)
$C_{18}H_{32}O_2$	Linoleic acid	(139, 164)
	Stearolic acid	(164)
$C_{18}H_{32}O_3$	12-Ketoelaidic acid	(164)
$C_{18}H_{32}O_4$	12-Keto-9,10-oxidostearic acid	(164)
$C_{18}H_{34}O_2$	Elaidic acid	(139, 164)
	Oleic acid	(139, 164)
$C_{18}H_{34}O_3$	9,10-Epoxystearic acid	(164)
$C_{18}H_{36}$	1-Octadecene	(139, 164)
$C_{18}H_{36}O_2$	Ethyl palmitate	(164)
	Stearic acid	(164)
$C_{18}H_{36}O_3$	Methyl 12-hydroxystearate	(164)
$C_{18}H_{38}$	Octadecane	(164)
$C_{18}H_{39}N$	*n*-Octadecylamine	(164)
$C_{19}H_{24}$	1,1-Diphenylheptane	(100)
$C_{19}H_{34}O_2$	Methyl linoleate	(139)
	Methyl *cis*-9-*trans*-11-linoleate	(100)
	Methyl *trans*-10-*trans*-12-linoleate	(164)
	Methyl linolelaidate	(164)
$C_{19}H_{34}O_4$	Methyl linoleate peroxide	(164)
$C_{19}H_{36}O_2$	Methyl elaidate	(164)
	Methyl oleate	(139)
$C_{20}H_{16}$	1,1,2-Triphenylethylene	(291)
$C_{20}H_{18}$	1,1,2-Triphenylethane	(291)
$C_{20}H_{18}O$	1,1,2-Triphenylethanol	(291)
$C_{20}H_{19}N$	2,2,2-Triphenylethylamine	(185)
$C_{20}H_{30}O$	Vitamin A	(164)
$C_{20}H_{32}O_2$	Arachidonic acid	(164)
$C_{20}H_{34}$	4,7-Diisobutyl-2,9-dimethyl-3,7-decadiene-5-yne	(291)
$C_{20}H_{36}$	4,7-Diisobutyl-2,9-dimethyl-3,5,7-decatriene	(291)
	5,8-Dibutyl-4,8-dodecadiene-6-yne	(291)
$C_{20}H_{36}O_2$	Ethyl *cis*-9-*trans*-12-linoleate	(164)
$C_{20}H_{40}$	5,8-Dibutyl-4,6,8-dodecatriene	(291)
$C_{20}H_{42}$	5,8-Dibutyl-5,7-dodecadiene	(291)
	4,7-Diisobutyl-2,9-dimethyl-5-decene	(291)
	5,8-Dibutyl-6-dodecene	(291)
$C_{20}H_{42}O$	11-Hydroxy-10-eicosanone	(164)

TABLE 2—*Concluded*

Formula	Compound	References
$C_{20}H_{44}$	4,7-Diisobutyl-2,9-dimethyldecane	(291)
	5,8-Dibutyldodecane	(291)
$C_{21}H_{21}N$	Tribenzylamine	(39)
	3,3,3-Triphenylpropylamine	(291)
$C_{22}H_{44}O_2$	Behenolic acid	(164)
$C_{24}H_{42}$	1-Phenyloctadecane	(246, 247)
$C_{24}H_{48}$	1-Cyclohexyloctadecane	(246, 247)
	1-Cyclopentyl-4-(3-cyclopentylpropyl)-dodecane	(100)
$C_{27}H_{46}O$	Cholesterol	(164)
$C_{28}H_{48}$	1-(7-Tetrahydronaphthyl)octadecane	(246, 247)
$C_{28}H_{66}$	5-Cyclohexyldocosane	(246, 247)
$C_{29}H_{50}O_2$	α-Tocopherol	(164)
$C_{29}H_{60}$	Nonacosane	(246, 247)
$C_{30}H_{46}$	1-(*p*-Diphenyl)octadecane	(246, 247)
$C_{32}H_{54}$	5-(7-Tetrahydronapththyl)-5-docosene	(246, 247)
$C_{32}H_{56}$	5-(7-Tetrahydronaphthyl)docosane	(246, 247)
$C_{32}H_{62}$	5-(2-Decahydronaphthyl)docosane	(246, 247)
$C_{34}H_{62}$	5-(*p*-Diphenylyl)-5-docosene	(246, 247)
$C_{35}H_{48}$	1-Cyclohexyl-3-(2-cyclohexylethyl)hendecane	(100)
$C_{35}H_{68}O_5$	Dipalmitin	(164)
$C_{35}H_{70}O$	Stearone	(164)
$C_{51}H_{98}O_6$	Tripalmitin	(164)
$C_{55}H_{72}MgN_4O_5$	Chlorophyll	(181)



at 1.650 ± 0.006 μ is of nearly constant intensity ($\epsilon = 0.2$) and can be used for analysis of mixtures, although the overtone of the aromatic CH group at 1.66 μ may interfere. Epichlorohydrin at 55 γ per milliliter of carbon tetrachloride can be easily detected (141). The application of near infrared spectra to the quantitative analysis of polymers and to end-group assay has been reviewed (203).

An interesting application of quantitative analysis to predict the spectra of organophosphorus compounds has been published (191). To predict the spectrum of diethyl methylphosphonate ($CH_3PO(OC_2H_5)_2$), for example, the band positions and intensities of one CH_3PO and two C_2H_5OP groups are summed. This type of summation can also be made instrumentally. Thus by placing cells containing equimolar quantities of $R'P(X)Y_2$, $R''P(X)Y_2$, and $R'''P(X)Y_2$ (where R', R'', and R''' are hydrogen-containing groups) in series, the spectrum of $R'R''R'''P(X)$ will be obtained. This type of analysis could be extended to other groups of similarly related compounds.

In the field of biochemistry near infrared measurements of hemoglobin derivatives have revealed (153) differences between the spectra of oxyhemoglobin and reduced hemoglobin and methemoglobin, metcyanohemoglobin, cyanohemoglobin, and carbonylhemoglobin. The changes in the latter are sufficient to analyze for carbon monoxide in the blood to < 1 per cent. The near infrared spectrum of zinc insulfate has also been recorded (164).

IX. TABLE OF COMPOUNDS

Table 2 lists a large number of organic compounds in the order of the number of carbon atoms present in the molecule, together with their names and the references to articles where data on their absorption spectra in the near infrared may be found.

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