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Spectroscopy of Organic Molecules in the Vacuum Ultraviolet

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INTRODUCTION

IN general, the longest wave-length electronic absorption bands of organic molecules are found farther and farther in the ultraviolet as we proceed from complex to simple molecular structures. Consequently, saturated compounds or compounds containing only isolated (unconjugated) double bonds are quite transparent throughout the region accessible to the quartz spectrograph, and their spectra must be studied in the vacuum ultraviolet with fluorite prism or concave grating spectrographs. These compounds are therefore distinguished from the more complex organic molecules by differences of spectroscopic technique and by a resultant paucity of well-established experimental data. Naturally, what data can be obtained on these simpler molecules are of more than average importance to the general theory of electronic spectra.

Experimental interest in spectra in the vacuum ultraviolet, however, will probably increase sharply in the next few years. Many compounds, such as the substituted ethylenes, of the greatest interest to industrial and biological spectroscopists have their characteristic electronic absorptions here, and it seems likely from recent studies that experimental technique can be simplified and put on a quantitative basis, and that the limitation to light, vaporizable compounds can be partially removed. For the benefit of prospective experimentalists, this paper will undertake to summarize the present state and some future possibilities of this field.

The discussion will be focused on organic absorption spectra obtained with vacuum spectrographs below 2000A. (Polyatomic emission spectra cannot be obtained because the molecules dissociate in a discharge.) Spectroscopists commonly recognize this limit as the point at which studies with vacuum apparatus begin to have appreciable advantages over studies with quartz or rock salt instruments in air. The latter techniques will not be discussed since they are already well known. Of course, no such separation by apparatus or wave-lengths is possible on the interpretative level, and these restrictions are somewhat relaxed in the tables and bibliography at the end.

I. EXPERIMENTAL TECHNIQUE

Special Problems

General spectrophotometric practice has been treated by Brode (141)* and vacuum ultraviolet problems have been exhaustively surveyed by Bomke (138) and Boyce (140). However, the study of organic vapors and solutions and their photometry in the vacuum region involves certain additional difficulties which are a cross-product of the need for excluding air (or, more specifically, oxygen), and the need for including the organic material in the optical path. Thus, while far ultraviolet technique requires a vacuum source, vacuum spectrograph, transparent windows with vacuum-tight seals, and ultraviolet sensitive photographic plates or photo-cells, organic studies need a continuous-spectrum light source, and, for solution work, transparent solvents. Also steps must be taken to prevent photochemical changes and contamination by vacuum waxes. Now that most of the survey work in this region has been done, more and more experimental arrangements will include in addition some provision for precise photometry, so that the groundwork can be laid for quantitative analysis.

How these various requirements are met will be sketched briefly, and then the main features

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* Numbers in ( ) refer to the bibliography at the end of this article.

of several different experimental set-ups will be examined.

As light sources, sparks in air between various metals were sometimes used by earlier workers, but it is better to employ continuous-spectrum sources, especially in vapor phase work, to make sure of detecting narrow bands. The hydrogen arc now in common use in the quartz region has a strong molecular continuum to 1650A and a many-line spectrum at shorter wave-lengths. It is stable enough for photometry in either the high-voltage or the low-voltage form. The Lyman spark discharge (142) through a quartz capillary produces a continuum overlaid by strong lines which extends to below 1000A, but the action of the disruptive spark on the capillary seems to be erratic and unsuited for precise photometry in its present form.

Spectrographs are either fluorite prism or concave grating instruments. Prism instruments are more compact and cheaper than the gratings but have smaller dispersions. This is not a serious disadvantage in studying polyatomic molecules because the narrowest absorption bands of vapors at low pressures are usually of the order of one angstrom wide, and the separation of such bands will not tax the dispersion of a prism spectrograph. In using gratings for work in the 1300A–2000A region, higher orders of shorter wave-lengths may be eliminated by a fluorite window.

It is possible to make absorption measurements to about 1850A in air at atmospheric pressure if advantage is taken of the transparent "windows" between the Schumann bands of oxygen below 2000A. (Some photodecomposition studies have also been made in air through the "window" at 1200A (124).) The absorption of compounds studied in this fashion is presumed to be continuous across the intervals between the "windows." A great deal of such work has been done with small quartz and rock salt prism spectrographs. To eliminate the Schumann bands and extend the range to shorter wave-lengths, it is necessary to remove the oxygen or to replace it by some transparent gas such as nitrogen. The oxygen partial pressure must be reduced to a few microns (an "oil pump vacuum") in order to make measurements through the most absorbing region at 1450A. This vacuum evidently must be maintained in the space between the source and the spectrograph as well as in the body of the spectrograph itself.

The prism and window materials which have been used in the far ultraviolet are quartz, rock salt, artificial sapphire,[1] fluorite, and synthetic lithium fluoride.[2] Small quartz or rock salt spectrographs can be used to about 1850A, and exceptional quartz crystals will transmit to 1600A in 2-mm thickness and to 1500A in 0.2-mm thickness. Duncan (22) used a fused quartz absorption cell to 1560A and thus completely avoided the difficulties other workers have had with waxed-on windows. Artificial sapphire (white sapphire, or corundum, Al_2O_3) is a uniaxial crystal which has been reported (143) as transparent to 1435A in $\frac{1}{16}''$ plates and which might be suitable for polarization work.

Fluorite (CaF_2) and lithium fluoride are the most transparent prism and window materials in this region. The former will transmit to 1350A in prism thicknesses ($\sim$1 cm), to 1250A in window thicknesses ($\sim$2 mm). The latter transmits about 100A farther, if it is quite free of impurities, but the present commercial variety cuts off at about 1400A in thicknesses of a few mm. Natural fluorite is not easy to obtain in this country in pieces suitable for prisms and windows.

On continued irradiation by ultraviolet light, both fluorite and lithium fluoride, especially the latter, become less transparent. Some of the transparency can be regained at first by cleaning with organic solvents and later by repolishing. Evidently windows should be protected from the source light as much as possible when exposures are not actually in progress. The repolishing is more troublesome for the lithium fluoride because of its greater softness and water solubility. The solubility of both substances is great enough to cause etching if they are used for cell windows in water solution studies. Both substances also have large thermal expansion coefficients, hence when wax is used to seal on

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[1] Manufactured by the Heller Hope Company, New York City.

[2] Manufactured by Harshaw Chemical Company, Cleveland, Ohio.

windows, heating must be done by careful irradiation rather than by an open flame.*

Photographic plates for the far ultraviolet include the sensitive but erratic Schumann plates, Ilford Q plates, and Eastman Ultraviolet Sensitized Type O plates. The sensitized plates have a fluorescent coating which is dissolved before development. They are apparently grainier and not quite as uniform as their unsensitized counterparts.

Plate calibration in vacuum offers its own peculiar problems. The inverse square method and the neutral wedge are obviously unsuitable. Step slits are hard to make in dimensions small enough for fluorite spectrographs and they cannot be used in grating spectrographs because of the astigmatism. The usual kind of sector disk is too bulky for use in a small vacuum system, although a compact variant has been devised for this purpose (147). Ladenburg and Van Voorhis (146) obtained an intensity calibration by placing symmetrical sector-shaped diaphragms over their condensing lenses in front of the spectrograph slit; this method assumes that the effective light intensity is properly distributed across the aperture. The use of calibrated wire screens in a similar way has been suggested (144), but does not seem to have been actually tried as yet in this region.

The commonest and simplest method of calibration in practice has been that of varying exposure times. This is subject to errors up to 30 percent in the value of the extinction coefficient unless correction is made for reciprocity failure in the kind of plates used. However, since Harrison and Leighton (144) have found that the characteristics of fluorescent plates are constant below the wave-length at which the fluorescence process begins to dominate the response, the reciprocity correction factor (Schwarzchild constant) can be determined conveniently in air at longer wave-lengths. The effects of pressure changes and desiccation in the vacuum system are assumed to be negligible. An even simpler method of calibration is suggested by the statement of Allen (137) that the intensity in the continuum from his hydrogen tube is proportional to the arc current.[3] If a linear law or some other law of change of intensity with current could be verified and found reproducible throughout the hydrogen molecular continuum for some particular arc design, calibration problems would disappear in the near as well as the far ultraviolet. The uncertainties which have been reported so far in determination of molar extinction coefficients by the photographic method are of the order of 20 percent, but there seems to be no reason why this cannot be decreased to below 5 percent by adherence to the best modern photographic spectrophotometric practice.

Some work has been done on extending photoelectric methods into the vacuum region. As early as 1901, Kreusler (145) used a hydrogen-filled platinum surface photo-tube to 1860A in studying the absorption of inorganic gases. He could not reach shorter wave-lengths because the fluorite double monochromator which he used could not be evacuated. Smakula and Wassermann (119) employed a double monochromator (in air) designed by Pohl (148) in which rock-salt prisms could be inserted to permit measurements to 1850A. The receiver was an evacuated potassium surface photo-tube, and the readings could be corrected for fluctuations in the source intensity by means of a second similar cell which received part of the unabsorbed light beam. The reported uncertainties in extinction values are as small as 2 to 3 percent. Powell (149) has constructed a vacuum grating spectrophotometer using an argon-filled platinum surface photo-tube with a waxed-on fluorite window and has employed it to measure the transmission of fluorite to 1250A.

The gas-filled photo-cells used by Kreusler and Powell have the disadvantage that their re-

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* *Note added in proof.* A new process of spraying fused quartz on a metal form may simplify the production of transparent windows and bulbs from that material. Some other possible window materials are Corning 791 ("Vycor") High Silica Glass, which is almost equal to fused quartz in transparency but is also almost equally hard to work and seal; and Corning 9741 glass, which cuts off at 1800A in 1-mm thicknesses, and which is more like ordinary glasses in its mechanical and thermal properties. The former does not lose its transparency ("solarize") under prolonged irradiation but the latter does.

A recently announced ultraviolet-transmitting glass made from aluminum metaphosphate [Chem. Eng. News, **23**, 288 (1945)], shows no promise of being transparent much below 2000A.

[3] Recently, however, Bosch and Anderson (139) have found deviations from linearity in their hydrogen arc at some wave-lengths.

sponse is non-linear, but they are simpler to make than vacuum photo-cells for this region. The latter require fused-on windows which must be in the form of thin in-blown bubbles if made of the relatively opaque fused quartz or the ultraviolet-transmitting glass mentioned below, or else must involve graded seals if artificial sapphire is used. Almost any metal can be employed for a photo-emissive cathode in this region, but platinum is preferred because of the high work function it has when carefully outgassed, which makes it insensitive to scattered radiation of wave-lengths longer than about 1960A. A platinum photo-cell is now advertised commercially.[4] It is reported as sensitive below 2100A to whatever limit is imposed by a window "a few microns thick" of a special ultraviolet-transmitting glass. ** The advent of this cell may make the general construction of vacuum spectrophotometers for this region more feasible.

Solvents in the ultraviolet are simply those compounds whose first absorption bands are at the shortest wave-lengths, that is, saturated compounds. Since they too are beginning to absorb, they must be used in thin cells. In 0.3-mm cells, methyl and ethyl alcohol transmit to 1900A, water to 1800A, iso-octane to 1780A, *n*-hexane and *n*-heptane to 1700A; cyclohexane has been used to 1850A and may be transparent below that. The need for purity in solvents is obvious as well as the need for keeping the solvents away from the waxes which hold on the cell windows.

Solution studies seem generally better suited for precise photometry than vapor studies, and consequently, attempts should be made to push the solution limit to shorter wave-lengths. This might be done by trying the lighter paraffins as solvents, say at low temperatures, or by squeezing the cell down to a film of only a few microns thickness as Ley and Arends (51) and Mohler (65) have done with quartz cells. In principle, with sufficiently thin cells spectra can be followed in solution as long as there remains a differential absorption between the solvent and the solute.

Photochemical changes in the substances being studied are minimized without too much difficulty in both liquids and vapors by a continuous flow technique. In vapor measurements, this procedure has led to some difficulty in controlling and measuring the vapor pressure, and as a result, absolute determinations of absorption coefficients for vapors have been less common than for solutions, even where the vapor spectra are favorable for such determinations.

A final peculiarity of the region is the matter of preventing interaction between the vapors or solutions being studied and the vacuum sealing compounds. How this problem has been met, or avoided, will be best seen by turning to some of the experimental arrangements.

Arrangement of Apparatus

Price and his co-workers (94–106), Duncan, and Noyes and their associates (19–23, 42, 47, 59, 88), Beynon and Evans (6, 7) and Rathenau (108) have used grating spectrographs with a Lyman source. As a result they have specialized in the precise determination of wave-lengths rather than intensities and have been able to measure spectra to below 1000A and to discover the short wave-length Rydberg series and ionization limits of many vapors. (Henning (30) used the helium continuum, 600A–900A, with a grating spectrograph to obtain spectra above the ionization limits.) In their arrangement usually no window covers the slit, and the source gas (H_2) diffuses through to mix with the vapor being studied in the body of the spectrograph. (Duncan has also used a quartz cell to hold the vapor, as mentioned earlier.) For plates, Price has employed an Ilford Q emulsion coated on special 0.2-mm thick microscope cover glass which can be bent to the focal curve of the grating spectrograph without breaking. Several sizes of spectrograph have been used from 40-cm radius, 30,000 lines/inch gratings at normal incidence (dispersion 10A/mm) to 2-meter, 30,000 lines/inch gratings at grazing incidence (dispersion about 2A/mm between 1000A and 2000A).

Carr, Stücklen, Pickett, and their collaborators

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[4] Westinghouse Electric Corporation, Bloomfield, New Jersey.

** *Note added in proof.* Dr. H. C. Rentschler of the Westinghouse Company informs us that this cell (WL 789) is made in a bulb of Corning 9741 glass. A photo-multiplier tube with the same kind of bulb is also reported to be in process of manufacture by another company.

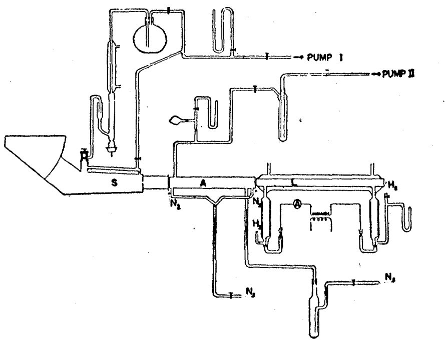

FIG. 1. Apparatus of Carr and Stücklen (11).

(9–16, 90, 91), Scheibe and his co-workers (37, 38, 112–116), Henrici and others (34–36), Hese, Rose, and zu Dohna (40), Leifson (48), and Woo, Badger, and Chu (5, 134, 135) have all used the hydrogen arc and fluorite spectrographs in the study of vapor spectra. Stark and his associates (125–128) used a fluorite spectrograph with spark source. The apparatus used by Carr and Stücklen (11) is shown in Fig. 1. *A* is the absorption cell between the light source, *L*, and the spectrograph *S*. The vapor to be studied is sent through the cell continuously. Streams of nitrogen fill the gaps at the ends of the cell, flow against the inside of the fluorite windows to protect the white shellac joints from the organic vapor, and flow into the spectrograph to drive out oxygen. The spectrograph used had a focal length of 25.4 cm and gave a dispersion of 2.5A/mm at 1400A and 27.8A/mm at 2200A. The plate holder took a Schumann plate (later Ilford Q) $6\frac{1}{2}'' \times 1\frac{1}{2}''$, on which ten exposures could be made without opening the instrument. Absolute intensity measurements with the apparatus at this laboratory have been reported only by Pickett (90), for the spectrum of furan, a substance which, it was found, could be left in the cell at constant pressure for long periods of time without photochemical or other reactions.

Scheibe, Povenz, and Linström (114) met the problem of window sealing by the method shown in Fig. 2. The source window was placed at the end of a long neck to reduce the sputtering of material on it from the nearest electrode. The ground joints were sealed with Picein wax on the side away from the vapors and the fluorite windows were put on with white shellac in the same way. In earlier studies with substituted alkyl compounds, Herzberg and Scheibe (37) also provided a gypsum buffer between the surface of the wax and the vapor. Absolute photometry was attempted with the apparatus of Fig. 2, but later, papers from the same laboratory have indicated intensity only by the "appearance pressures" of the absorption bands.

Organic solution spectra have been studied with fluorite spectrographs by Ley and Arends and others (51–56), by Mohler and Sorge and others (65–77), and by Platt, Rusoff, Klevens, and Burr (92, 110). These studies have been characterized by attempts at absolute intensity measurement and by emphasis on compounds which are not volatile enough to be studied in the vapor phase. For such compounds, information obtained from solution spectra may evidently be of considerable value in spite of the limited wave-length range available. In their early work, Ley and Arends employed for a source a silver-tungsten spark in air, the spark being placed 10 mm away from the quartz cell to reduce the air path as much as possible. In all the later work a hydrogen source has been used in an arrangement similar to that of Fig. 3, which was developed by Scheibe (150) for the study of ions in solution. The solution is held in a thin cell by surface tension. The cell is formed by the narrow gap between fluorite windows covering the source and the spectrograph, and it is accessible from the open air. One of the windows may be attached to its unit through a flexible metal bellows to simplify the alignment

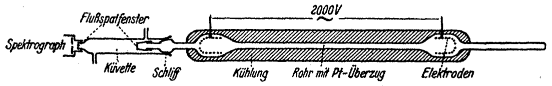

FIG. 2. Apparatus of Scheibe, Povenz and Linström (114).

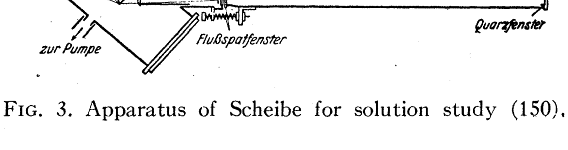

FIG. 3. Apparatus of Scheibe for solution study (150).

problem. Since an oil pump can evacuate the spectrograph sufficiently in two minutes, this arrangement of apparatus offers a simplicity and speed in operation comparable with that obtained in solution studies with quartz spectrographs in air.

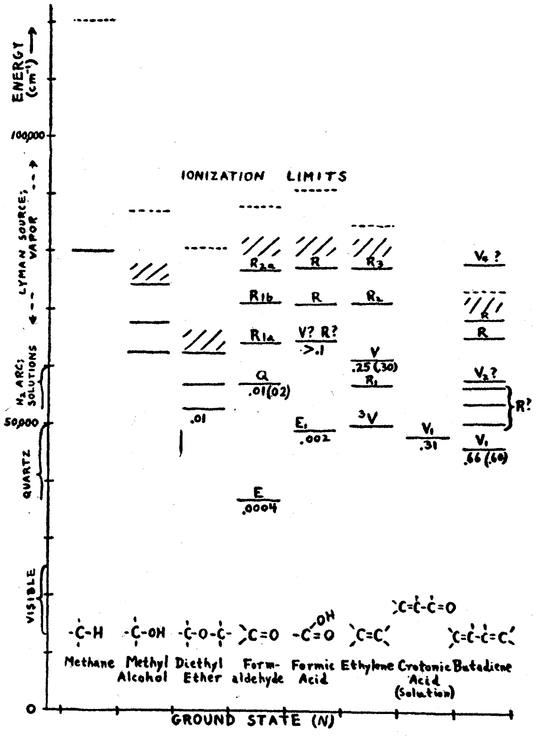

Fig. 4. Electronic energy states of vacuum ultraviolet chromophores. Slanted lines indicate close structure. Numbers are observed *f*-values (theoretical in brackets) for transitions from the ground state for the following molecules in heptane solution (92, 110, except as otherwise indicated): C—O—C, di-*n*-butyl ether; C=O, N→E, acetone (61), N→Q, methyl ethyl and diethyl ketone [theoretical, formaldehyde (61)]; COOH, caprylic and myristic acid; C=C, octene-3 [theoretical, ethylene (84)]; C=C—C=O, α-crotonic and α-heptadecenoic acid; C=C—C=C, 9,11-octadecadienoic acid [theoretical, 1,4-dimethyl-1,3-butadiene (84), using correction factor for chain dienes of 0.4].

II. REGULARITIES IN OBSERVED SPECTRA

Tables I to VI and the bibliography list the organic compounds whose spectra have been followed below 2000A. Sponer (123) and Sponer and Teller (124) have already given extremely complete tables of the electronic spectra of vapors, but it was felt that it would be of value for spectroscopists interested in studying compounds in the far ultraviolet to have the experimental references for this region, including solution studies, brought up to date and gathered together in one place. Some theoretical references which have a fairly direct bearing on the observed spectra have been included.

The organization and theoretical interpretation of the data in this field have already been dealt with in recent reviews by Mulliken (81, 82), Mulliken and Rieke (84), and by Sponer and Teller (124). The first two papers emphasize the discussion of intensities, and the last stresses the analysis of frequencies and vibrational structure. Other general discussions of the data in this field have been recently given by Stimson and Reuter (129) and by Anslow (3). We will mention here a few of the regularities which have been brought out by these reviews, after first recapitulating the more elementary laws which apply to all molecular spectra.

Rotation, Vibration, and Intensity Formulas

Absorption spectra in the visible and ultraviolet are all produced by electronic transitions, that is, transitions from the ground state rotational levels of the molecule (Fig. 4) (and possibly from such closely adjacent vibration-rotation states as may have an appreciable population at the operating temperature), to the vibration-rotation levels of some excited electronic state. The energy, E, absorbed in the transition is related to the absorbing wave-length, λ,

$$E = h\nu = hc/\lambda = hc\bar{\nu}$$

and may be expressed in the units of $\bar{\nu}$ (cm^{-1}). (The common usage will be followed here of omitting the bar and distinguishing $\bar{\nu}$ from ν by its units.) 2000A thus corresponds to 50,000 cm^{-1}, or 6.20 ev, since 1 ev is 8067 cm^{-1}.

The rotational structure is not resolved in polyatomic spectra in the vacuum region (except perhaps in the case of methyl iodide), because it involves the spacing constant

$$(h^2/8\pi^2)(1/I'' - 1/I'),$$

which is very small when the moments of inertia are large. ($''$ refers to ground state, $'$ to the excited states). In vapor spectra, a shading of the vibration bands to longer or shorter wave-lengths ("red" or "violet") may, however, be seen, according to whether I' is larger or smaller than I'', the first case being, of course, more common.

The vibrational structure in first approximation obeys the usual law,

$$\nu=\nu_{0,0}+\sum n_i'\nu_i'-\sum n_i''\nu_i'',$$

$$n_i'=1,\,2,\,3,\,\cdots,\quad n_i''=1,\,2,\,3\cdots,$$

In this region the structure would be complicated by the many possible vibrations of a polyatomic molecule, except that the excited vibrational levels of the ground state are thinly populated at room temperature, while a selection rule restricts strong transitions to just the totally symmetric vibrations of the upper state. Also progressions of the upper state vibrations often do not go to more than three terms (a striking exception being the C=C vibration in dienes), so that higher order terms are generally unnecessary in the formula above, and the bands cannot be followed to their convergence (dissociation) limits. By the Franck-Condon principle this shortness of the progressions means that the equilibrium dimensions of the molecule may not be greatly changed by the excitation of one electron. As in diatomic molecules, vibration frequencies are usually smaller in the upper electronic state because of the decreased force constants between the atoms when a bonding electron is excited.

The molar extinction, ϵ_ν, is the standard measure of the intensity of absorption in a transition. It is obtained from the Lambert-Beer law,

$$I/I_0=10^{-\epsilon_\nu ct},$$

where I and I_0 are the incident and transmitted light intensities, c is the concentration of the absorbing material (moles/liter), and t is the thickness (cm) of the absorbing layer. Since ϵ_ν varies over a range of 10^4, $\log_{10}\epsilon_\nu$ is commonly plotted instead of ϵ_ν in the presentation of results. If ϵ_ν is known throughout the region covered by an electronic band, it may be used to compute the oscillator strength of the transition,

$$f=10^3\log_{10}\epsilon\frac{mc^2}{\pi e^2N}\int\epsilon_\nu d\nu=4.32\times10^{-9}\int\epsilon_\nu d\nu,$$

and the dipole strength,

$$D=(3h/8\pi^2mc)f/\nu=3.98\times10^{-4}\int\epsilon_\nu(d\nu/\nu),$$

(where ν is in cm^{-1} and D is in A^2). The quantity f is the same as the oscillator strength which appears in the classical dispersion equation; this identity has been strikingly proved for O_2 by the vacuum absorption measurements of Ladenburg and Van Voorhis (146). The values of f and D may also be obtained theoretically from the relation

$$D=GQ^2\quad\text{where}\quad\mathbf{Q}=\int\psi'(\textstyle\sum_i\mathbf{r}_i)\psi''d\tau,$$

if suitable approximations for the wave functions of the electrons can be found.

The quantity f is measured most easily in solution spectra because the sharp bands, which in the vapor phase make the integration of ϵ_ν difficult, are broadened in solution by the perturbations of the surrounding solvent molecules. By classical theory, the influence of the dielectric solvent also should increase the observed f-value of an absorption band by a factor,

$$1/\gamma=(n_0^2+2)^2/9n_0$$

where n_0 is the index of refraction of the solvent (Chako (18)). This factor is about 1.3 for common solvents in this region. In the two valid tests of this prediction which have been made on these molecules (33, 91), the solution f-values were actually very close to the vapor f-values. Mulliken and Rieke (84), therefore, suggest that solution and vapor f-values be treated as equivalent until more data on this point are obtained.

Non-polar solvents, such as members of the paraffin series, produce smaller shifts of intensity and position and preserve the fine structure of bands better than the polar solvents, water and alcohol; the latter are therefore less desirable to use when data are to be compared with theoretical predictions.

Appearance of Spectra and Energy Levels

The first excited energy levels of organic molecules commonly involve an electron from some atom, or group of atoms, in the molecule which is less tightly bound than the electrons associated with the regular saturated hydrocarbon structure. Such a loosely binding atom or group is called a chromophore, and the characteristics of its electronic spectrum will be roughly duplicated in all the molecules in which it occurs even when other chromophores are present as long as the two groups are not so close together that they interact appreciably.

Since chromophore electrons are also responsible for the lowest ionization potential and for much of the chemical behavior of the molecule, the details of the electronic spectrum are perhaps more directly related to chemistry than is the case with infra-red and Raman spectra. Price and Tutte (104) have shown, for example, that shifts of the first long-wave absorption in alkylated ethylenes are nearly proportional to changes in their heats of hydrogenation; and Sklar (118) was actually able to predict the wave-length of the first band in several conjugated double-bond compounds from purely theoretical calculations in which the only parameter was determined by the heats of hydrogenation. In Fig. 4 it can be seen that the value of the ionization potential and the location of the first strong absorption band generally vary together. From this relation the ionization potential can be estimated when it cannot be determined more directly. Price (94) has also computed bond strengths from the position of predissociation bands (but Henkin and Burton (29) have questioned the validity of his procedure). Some other less striking correlations and minor parallels between spectra in this region and chemical behavior will be mentioned later.

The relations among the spectra will be better understood by reference to Figs. 4 and 5, showing respectively an energy level diagram (which since we are dealing with absorption spectra is equivalent to plotting the observed spectra vertically on a frequency scale) and the appearance of some actual spectra (ethylenes). Below 2500A, several kinds of bands may be distinguished by their position, intensity, and diffuseness.

1. Continua. These are observed in molecules with spherical symmetry such as CH_4, CCl_4, etc. They also characterize the C—C and C—H absorptions near 1300A. It is not certain whether any of these are true continua or whether they are only very complicated structures. The C—C and C—H bands increase with the number of such groups until in larger molecules they make the study of the sharp Rydberg series in the same region impossible, as may be seen in the last two spectra in Fig. 5.

2. Strong bands with very diffuse vibrational progressions. The strong $N \rightarrow V_1$, $N \rightarrow V_{2,3}$ and $N \rightarrow V_4$ transitions[5] in the conjugated dienes (Fig. 4) are of this character, with a series of maxima spaced about 1400 cm^{-1} apart (the C═C valence frequency). The analogous $N \rightarrow V$ transition in the ethylenes** (at 1600 to 1900A, depending on the particular molecule—Fig. 5) is thought to be of this type, but so complicated that it appears as a smooth continuum of type 1, several thousand cm^{-1} broad.

3. Very weak low frequency bands. A series of bands in ethylene just below 2000A ($N \rightarrow {}^3V$, not visible in the reproduction of Fig. 5) is of this type as are the aldehyde and ketone $N \rightarrow E$ bands, the acid $N \rightarrow Q$ band and the 2500A and 1900A benzene absorptions. These all seem to be forbidden transitions which borrow intensity from interactions with the first strong allowed transition at shorter wave-lengths.

4. Strong bands with sharp vibrational structure. The 1700A group in ethylene is of this character. It has been designated as the first member $N \rightarrow R_1$ of the Rydberg series which appears at higher frequencies, although, as would be expected even in atomic structure, it does not fit well into the series formula. With substitution, this band shifts regularly to lower frequencies, but becomes weaker and more diffuse, losing its Rydberg character, as Fig. 5 shows. (The spectra of heavier molecules generally become more diffuse as the symmetry decreases and the number of totally symmetric vibrations increases.) Carr, Pickett, and Stücklen (16) have shown that

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[5] Because of the small number of classified states involved in the discussion here, the simple Mulliken designations are used.

** The word "ethylenes" is generalized throughout this article to mean "compounds with one or more isolated double bonds" and includes mono-olefins, unconjugated polyenes, cycloenes, and compounds having an additional weaker chromophore such as the ethylenic acids because these molecules are all spectroscopically similar.

strong sharp bands of similar appearance occur in the dienes but disappear with end-substitution.

From type 4 bands, many vibrational frequencies are now known for the excited states of the molecules methyl iodide, ethyl iodide, formaldehyde, acetone, cyclopentadiene, and furan. The vibrational sequences are usually quite short, the $N \rightarrow R_1$ band of ethylene being an exception. The dominant frequency in these bands is expected to be that of the valence vibration of the chromophore bonds on which the excited electron is localized. This rule seems to be violated in the $N \rightarrow Q$ band of acetone according to Lawson and Duncan (47) who state that the strong 1200 cm^{-1} frequency is changed in deuteroacetone and, therefore, cannot be the $C{=}O$ vibration as was formerly thought but must be the CH_2 bending vibration. Discussion is continuing over the proper interpretation of the marked doublet structure (separation about 470 cm^{-1}) of the bands of type 4 in ethylene and cyclopentadiene. Mulliken (86) agrees with Price and Tutte (104) that in ethylene they may be due to the twisting frequency of CH_2, but this vibration is not totally symmetrical, and Sponer and Teller (124) say of the doubling, "No satisfactory explanation yet given." Pairs with separation 200–500 cm^{-1} and single lines which do not fit into series occur in many molecules.

5. Rydberg series; strong sharp lines. The definitely established series are mostly based on three to six band groups below 1400A whose 0,0 transitions fit into the usual Rydberg formula for atoms,

$$\nu = \nu_\infty - R/(n+a)^2,$$

where ν_∞ is the ionization limit, n takes a succession of integral values, and a is a constant less than unity. The convergence of several Rydberg groups toward the limit is easily seen in ethylene in Fig. 5. In the upper Rydberg states, the electron is traveling in essentially atomic orbitals which must be far larger than the chromophore section of the molecule. The terms are often multiple, but comparison with the spectra of deuterated compounds [Price and Wood (99) and Price and Tutte (104)] has shown that the multiplicity in several cases is electronic and not vibrational in origin. In many molecules Price and his co-workers have found two to four series with different Rydberg denominators, and in the alkyl halides Price (96) found convergence to two different ionization limits (ground states of the ion) which confirm the theoretical predictions of Mulliken as to the separation of these ionic states. The frequency ν_∞ expressed in volts is the ionization potential, V_i, a quantity which has also been determined for many of these same molecules by the method of electron impact. Such values are usually a few-tenths of a volt higher than the spectroscopic values, since the impact process produces "vertical" ionization (molecular dimensions unchanged) while the absorption process gives spectra converging to the "adiabatic" ionization limit, in which the molecule assumes its lowest energy configuration as the electron is removed.

In methyl iodide and some other molecules, a diffuseness due to predissociation can be observed in lines which apparently should be of types 4 or 5. The diffuseness sets in suddenly among these lines in going to higher frequencies and then diminishes until it is unobservable after a few thousand cm^{-1}. The broadening is explained by the usual pre-dissociation mechanism: when the energy of a state is just greater than that necessary for a dissociation of the molecule, so that a radiationless transition from the bound state to the dissociated state is fairly probable, then the mean lifetime, Δt, of the bound state is greatly decreased, and the uncertainty or width, ΔE, of its energy value is correspondingly increased according to the relation $\Delta t \Delta E \sim h/4\pi$. The point at which the diffuseness is first seen gives an upper limit for some dissociation energy. Information on the probable kind of dissociation process involved can be obtained from the symmetry properties shown in the spectra.

Red Shift with Alkylation

Some of the outstanding regularities in organic spectra in the far ultraviolet are the red shifts with alkyl substitution, the independent addition of isolated chromophores, and the phenomena resulting from the conjugation of double bonds.

Every successive alkyl substitution on the carbons in a chromophore bond produces a shift of all bands to lower frequencies. This is seen in Fig. 5 for the $N \rightarrow V$ bands in a series of ethylenes which have respectively 0, 1, 2, 3, and 4 alkyl groups attached to the two double bond carbons. Carr and Stücklen (11) have demonstrated the same effect in the $N \rightarrow R$ transition of ethylenes (Fig. 6), and analogous shifts are known for other chromophores in the quartz ultraviolet. As Figs. 5 and 6 show, it is the first methyl group substituted at a given position which produces the shift, and additional chain length adds very little to the effect. As the bands move to lower frequencies, the ionization limit decreases, and much of the change must therefore be due to the reduction of the binding energy, V_i, of the ground state with substitution. Price and his

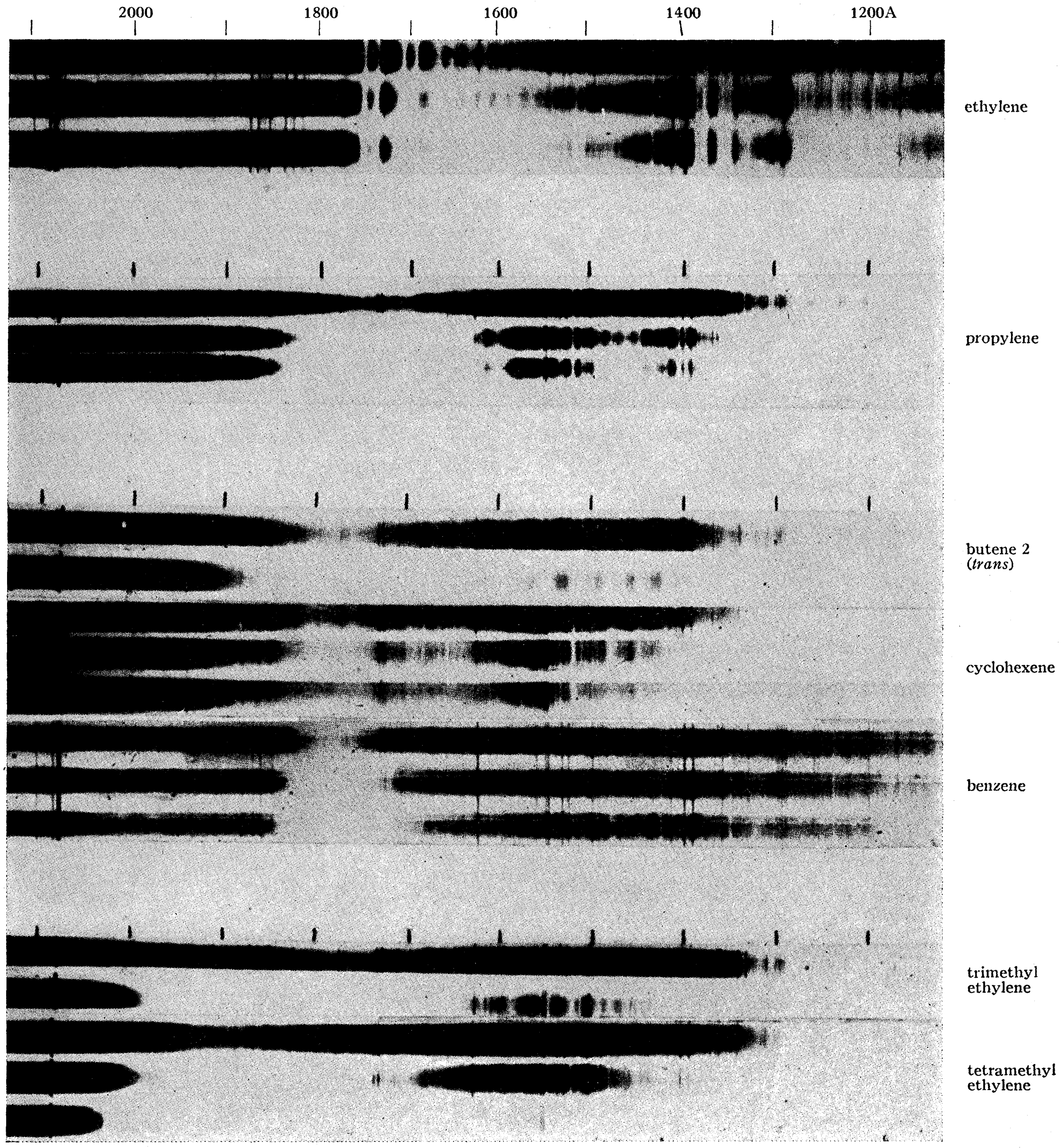


FIG. 5. Vapor spectra of ethylenes (104).

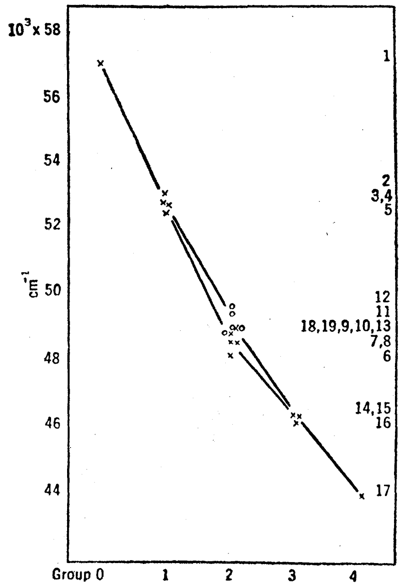


FIG. 6. Shift of first long-wave ($N \rightarrow R$) bands in ethylenes as function of number of alkyl substituents on the double bond carbons (11). 1, ethylene; 2, butene-1; 3, pentene-1; 4, heptene-1; 5, isopropylethylene; 6, *cis*-butene-2; 7, *trans*-butene-2; 8, pentene-2; 9, hexene-3; 10, heptene-3; 11, isobutene; 12, methyl-ethylethylene (unsym.); 13, diisobutylene I; 14, trimethylethylene; 15, diethyl methylethylene; 16, diisobutylene II; 17, tetramethyl-ethylene; 18, benzene; 19, diphenyl.

co-workers (104, 105) have attributed such a reduction largely to a purely inductive transfer of charge toward the bond caused by the presence of the substituent alkyl group which is less electropositive than the hydrogen atom it replaces.

Independence of Isolated Chromophores

The rule that isolated chromophores absorb independently is illustrated by Figs. 7–9. If two or more chromophores are present in a molecule, their effects are approximately additive on a molar basis providing at least two C—C single bonds separate or "insulate" them. Thus, propylene (Fig. 5) with a C=C double bond absorption modified by one alkyl substitution has its $N \rightarrow V$ and $N \rightarrow R$ peaks at the same position as the diallyl molecule (Fig. 7) which consists of two propylene groups, and the molar extinction of the diallyl is about twice as great.

The curves of Fig. 8 show that the combined absorption of an aliphatic acid and a dialkylated ethylene is equal within experimental error to the absorption of a long chain ethylenic acid.

Figure 9 demonstrates the same approximate addition of molar absorption and *f*-value in some unconjugated acids as the number of double bonds is increased, but changes in the curve shapes for the more unsaturated compounds indicate that two C—C single bonds between the chromophores do not quite insulate them completely, and some interaction is taking place.

Effects of Conjugation of Double Bonds

The changes of Fig. 9 are very small compared with the dramatic alteration of the spectrum (and of the chemical properties) when the C=C bonds are separated by just one C—C single bond, as in the 1,3-pentadiene of Fig. 7. This arrangement is called "conjugation" and its most obvious effect is to shift a major part of the $N \rightarrow V$ absorption several hundred angstroms toward the red for every additional —C=C— unit which is added to the chain. In long conjugated chains for which $N \rightarrow V_1$ has moved to the visible, this shift can be used to create sequences of dyes.

Theoretical treatment of this phenomenon has been very successful, especially in the computation of intensities. In the ethylenes with one double bond, the $N \rightarrow V$ transition is from a ground state N (or $^1A_{1g}$ for ethylene in the more usual notation) which has its two equivalent π electrons (unsaturation electrons of the double bond) both in bonding orbitals holding the molecule planar—to a state called ^1V or V (or

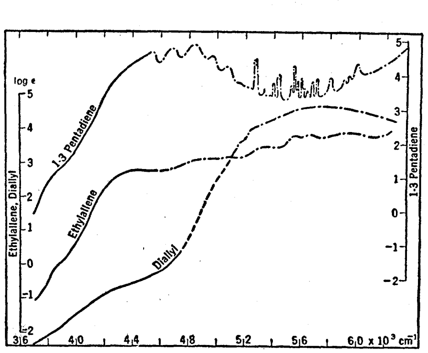


FIG. 7. Effect of separation of two double bonds (15). Diallyl, $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$, unconjugated; 1,3-pentadiene, $CH_2{=}CH{-}CH{=}CH{-}CH_3$, conjugated; ethylallene, $CH_2{=}C{=}CH{-}C_2H_5$, adjacent.

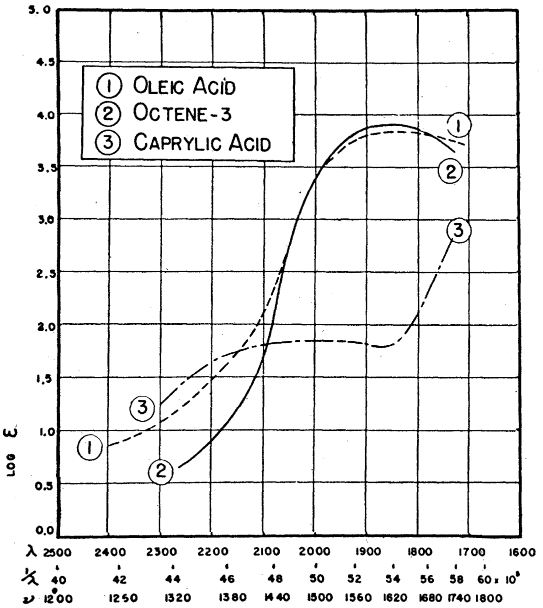
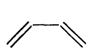
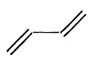


FIG 8. Addition of isolated chromophores (110). Oleic acid-9(*cis*), $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$; octene-3, $CH_3-(CH_2)-CH=CH-(CH_2)_3-CH_3$; caprylic acid, $CH_3-(CH_2)_6-COOH$. All in heptane solution.

$^1B_{1u}$) in which one of the π electrons is excited to an antibonding orbital. V is a "valence" or "ionic" state in which the excited electron remains localized much nearer the double bond than in the Rydberg states. The calculation of intensities has been carried out by Mulliken (81) using the common approximation that the orbital wave-function for each of the two unsaturation electrons around the double bond (the other electrons may be ignored in the computation) can be represented as a linear combination of atomic orbitals (in this case, the 2 p orbitals) around the two carbon atoms of the bond. The f-value computed by this method for ethylene is 0.30 (84) while that measured for octene-3 is 0.25 (from curve in (92)), an agreement well within the uncertainties both of the calculation and the measurement. The V state in these computations turns out to have a curious equilibrium configuration in which one of the CH_2 groups is turned 90° with respect to the other. This twist may account for the diffuseness and great width of the $N \rightarrow V$ band, and it has been suggested that it is a favorable situation for photochemical *cis-trans* conversion in the disubstituted ethylenes.

These ideas may be extended to dienes and polyenes. When two or more double bonds are conjugated, they interact across the intermediate single bond to establish a planar configuration for the whole molecule, and in fact, the orbitals of the excited electron may be thought of as extending the full length of the conjugated chain. But now the degeneracy which would be present if the double bonds were separated is removed by the strong interaction, and the V-level in dienes splits into four levels, V_1, V_2, V_3, V_4, with a total separation of the order of 50,000 cm^{-1}. In the planar molecule, two arrangements around the *single* bond are possible:


s-*cis*


s-*trans*

The selection rules for the $N \rightarrow V$ transitions are different for these two forms:

	$N \rightarrow V_1$	$\rightarrow V_2$	$\rightarrow V_3$	$\rightarrow V_4$
s-*cis*	weak	strong	strong	missing
s-*trans*	strong	missing	missing	weak.

Cyclic dienes are necessarily s-*cis*, and in their spectra the first absorption $N \rightarrow V_1$ is indeed comparatively weak. In straight chain dienes, both s-*cis* and s-*trans* can be present, probably in some equilibrium ratio at room temperature, but the strength of $N \rightarrow V_1$ and the weakness of $N \rightarrow V_2$ as actually observed indicates from these selection rules that s-*trans* is favored, particularly in the case of center substitution. Price and Walsh (89), however, have suggested that these selection rules may not be very binding because they found no s-*cis* ionization potential in straight chain dienes and they conclude that the $N \rightarrow V_{2,3}$ bands which are observed must come entirely from s-*trans* molecules.

The absolute values of the predicted intensities do not agree as well with experiment as in the case of the ethylenes, presumably because the approximations used in the computations are less accurate here. Nevertheless, relative predictions from one molecule to another are rather good, and if the theoretical values are multiplied by 0.4 for chain dienes and by 0.3 for cyclic dienes, the agreement of theory and experiment is similar to that shown in Fig. 4.

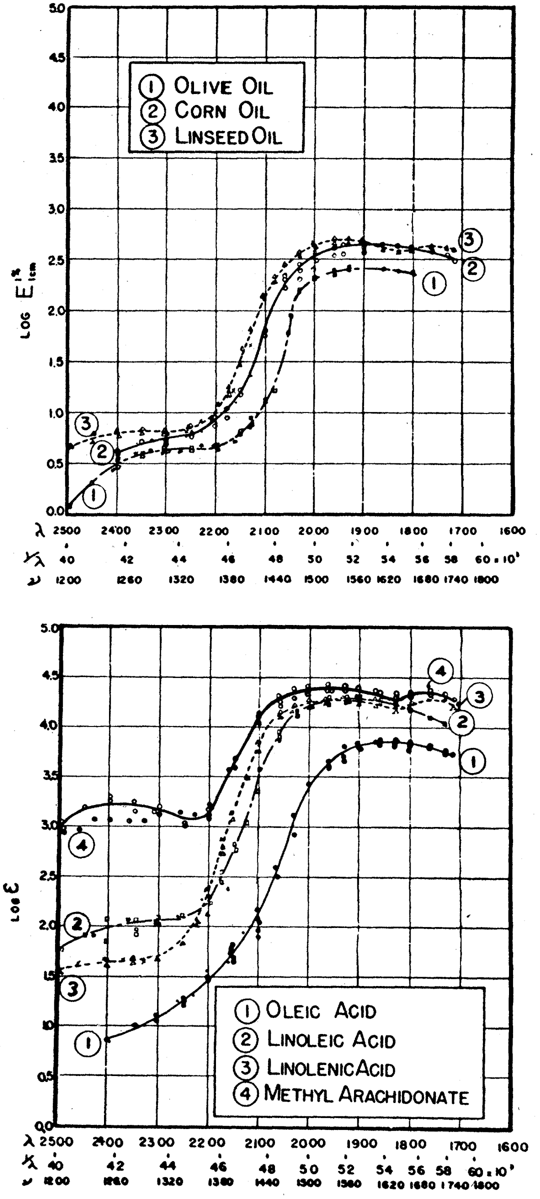


FIG. 9. Fatty acids and oils (110). Oleic acid-9(*cis*), $CH_3—(CH_2)_7—CH=CH—(CH_2)_7—COOH$; linoleic acid-9,12 (*cis, cis*), $CH_3—(CH_2)_3—(CH_2—CH=CH)_2—(CH_2)_7COOH$; linolenic acid-9,12,15, $CH_3—(CH_2—CH=CH)_3—(CH_2)_7—COOH$; methyl arachidonate-5,8,11,14, $CH_3—(CH_2)_3—(CH_2—CH=CH)_4—(CH_2)_3—COOCH_3$. All in heptane solution.

The red shifts of diene spectra with alkylation have been computed theoretically with fair success by Mulliken (86). He concludes that the theoretical procedure is generally correct "but . . . somewhat rough" since for example "it predicts larger shifts for the end-substituted dienes than for the central-substituted dienes, contrary to observation."

Because of the symmetry, the $N \rightarrow V$ transitions in benzene are simplified to a single band at 1800A like that of the ethylenes (Fig. 5). Its spectrum thus shows a striking loss of conjugated character compared to the straight-chain trienes, which have the strong $N \rightarrow V_1$ at 2700A followed by eight other $N \rightarrow V$ components. The benzene $N \rightarrow V$ intensity has been predicted theoretically (84) but it has not as yet been determined experimentally.

To explain such phenomena as the red shift of the cyclic dienes compared to the open chain dienes, Mulliken suggested that the CH_2 groups in the cyclics could act as a pseudo-double bond and enter into a kind of weak conjugation—"hyperconjugation"—with the true double bonds. Some such concept might account for the splitting, shown in Fig. 9, of the ethylene peak with increasing number of C=C groups, which may hyperconjugate with the CH_2 groups between them. For a time it was also thought possible to explain by hyperconjugation the shifts of $N \rightarrow V$ in the ethylenes with alkylation, but it now seems that it must play only a minor role in this phenomenon (86).

These theories about the $N \rightarrow V$ transition in double bonds and the changes with conjugation have been extended by McMurry and Mulliken (60–62, 80) to aldehydes, ketones, and acids, since the C=O and C=C double bonds are electronically similar. The weak (forbidden) long wave-length bands are different for the keto and carboxyl groups, but the $N \rightarrow V$ transition seems to be the same for all the C=O compounds. It is at shorter wave-lengths than $N \rightarrow V$ for C=C, corresponding to a higher ionization potential. Conjugated ketones, C=C—C=O, similarly have $N \rightarrow V_1$ at shorter wave-lengths than conjugated dienes C=C—C=C (61). The extension of conjugated electron orbitals for the full length of the chain, in this theory, throws light on the characteristic chemical behavior of the conjugated ketones such as the 1,4 addition reaction.

Intensity computations have also been carried out for some of the longer wave-length transitions in the acids, ketones, and aldehydes. These calculations have been used in deciding between alternative assignments for some of these bands.

The allenes (Fig. 7) have not yet been discussed theoretically, though Carr and Stücklen (15) have pointed out that the superposition in their spectra of the conjugated band at 46,000 cm^{-1} on the unconjugated band at 57,000 cm^{-1}, as shown in Fig. 7, is "parallel to the anomalous chemical reactivity of allene derivatives." Some other molecules which need further study are: cyclohexane, cyclohexadiene, cyclopentanone, cyclohexanone, conjugated acids, and amino acids; and the butadiene bands of type 4 need explanation, as well as the sharp doublets and doublet systems which occur in several molecules.

The experimental work of especial interest which needs to be done includes the determination of the *N*→*V* intensity in benzene, the study of photoisomerization of ethylenes in the *N*→*V* region, and a further check on the validity of the Lorentz-Lorenz correction by vapor and solution measurements on the same molecule. Also, more vapor spectra could profitably be analyzed along the lines followed by Price and Wood (99) on benzene and Lawson and Duncan (47) on acetone, that is, by comparing the fine structure of the spectra of the normal and deuterated compound as observed with a high dispersion spectrograph.

III. APPLICATIONS

As the preliminary mapping of organic spectra in the far ultraviolet nears completion, a number of possible applications appear, for the techniques of this region have their own role to play in the determination of chemical structure and in the analysis of mixtures.

For such purposes, the strength and the weakness of spectra in the vacuum ultraviolet just as in the quartz region is that they are very "unspecific" by comparison with infra-red and Raman data. The latter depend critically on vibrational and especially on rotational properties of molecules which are not of any direct chemical importance and which therefore may differ considerably even for related molecules. Consequently in these regions particular molecules may be uniquely earmarked. Ultraviolet spectra on the other hand tend to reveal to what

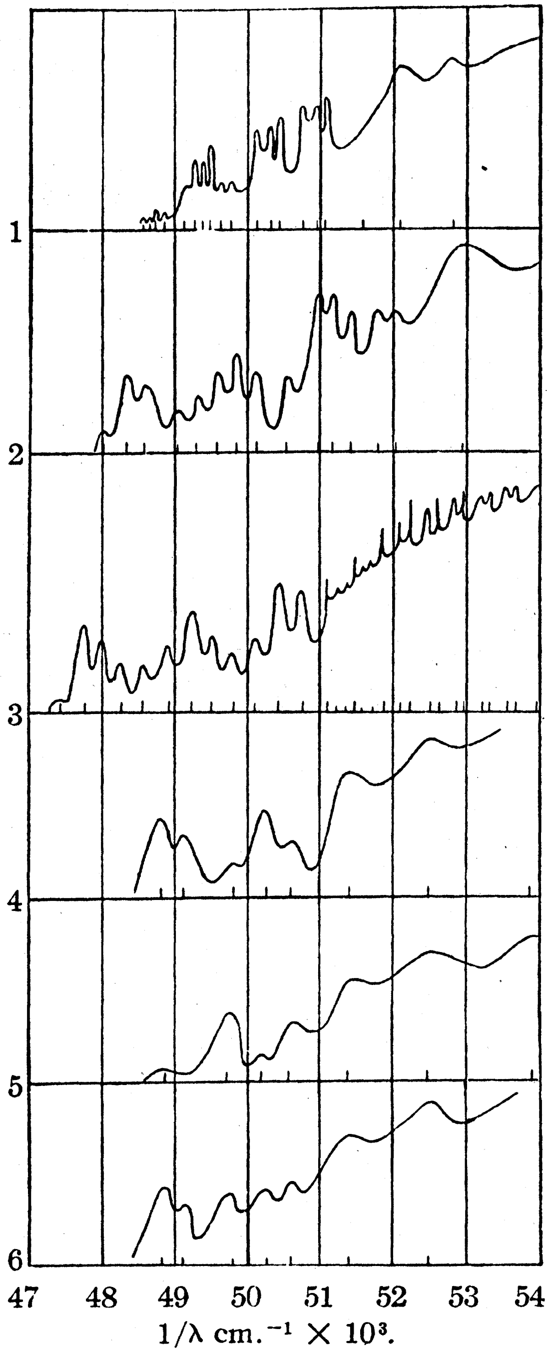


FIG. 10. *Cis-trans* isomerism (12). 1, low-boiling butene-2; 2, high-boiling butene-2; 3, cyclohexane; 4, high-boiling pentene-2; 5, low-boiling pentene-2; 6, pentene-2 from α-ethylcrotonic acid.

extent a given kind of linkage is present in a liquid or vapor without showing how it is distributed among the molecules or whether the non-absorbing parts of the molecules are long or short. In the vapor phase, this loss of specificity may be partly overcome by high resolving power instruments which can distinguish specific detail as in Lawson and Duncan's work on acetone (47); but no remedy is possible with solution spectra. Of course, for many purposes, the close correlation of ultraviolet spectra with chemical behavior will be more important than specificity.

To date, the actual applications in the vacuum region have not been very numerous. The possibility of mixture analysis is shown in Fig. 9 which illustrates how with somewhat improved photometry the composition of certain oils which are quite transparent in the near ultraviolet could be easily determined here. The experimental accuracy of the curves shown was not high enough to make an analysis worth while, but the increasing percentage of the more unsaturated fatty acids in going from olive oil to linseed oil is clearly seen, confirming the known composition of these oils.

Figure 10 gives a series of absorption curves by which Carr and Stücklen showed that the higher-boiling butene-2 and pentene-2 have spectra like cyclohexane in the first structure of their $N \rightarrow R$ bands, while the lower-boiling compounds are quite different; the former must therefore be *cis* as cyclohexene is, and the latter must be *trans*. This conclusion again confirms other chemical evidence. The last curve demonstrates how a mixture of the *cis*- and *trans*-pentenes could be analyzed by means of these spectral differences; the preparation shown appears to be 80–90 percent *cis*.

Scheibe and Pummerer (112) have also used spectra in this neighborhood to throw light on the arrangement of double bonds in the rubber molecule.

Further applications await only increased familiarity with and use of the vacuum spectrograph and improvements in photometry. Evidently, at present, the lighter hydrocarbons may be identified semi-quantitatively in vapor phase; while the ethylenes, the ethers, and possibly the alcohols, which cannot be analyzed in the quartz region, are accessible in solution in this region. A lowered solution limit might add the branched and heavier saturated hydrocarbons to this list.

IV. TABLES OF ORGANIC SPECTRA BELOW 2000A.

(Supplementary to tables in Sponer (123), and Sponer and Teller (124). The discussions of compounds from those tables are not repeated here.) B = bands, R = curve rising toward higher frequencies, V_i = first ionization potential (ev), ω = vibrational frequencies, C = continuum, P = peak, W = weak, D = diffuse, p = pressure, and L_a = limit of transparency.

TABLE I. Saturated compounds.
Theory: (80, 82, 123, 124).

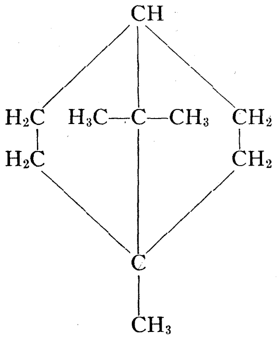
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
CH_4 methane					19, 40, 48, 111, 115, 123, 124
C_2H_6 ethane					94, 115, 123, 124
C_6H_{14} *n*-hexane					9, 92, 123, 125
C_7H_{16} *n*-heptane					9, 92, 123
$CH_3C(CH_3)_2CH_2CH(CH_3)_2$ *iso*-octane	56,000 58,000	1785 1725	R	L_a(liquid); $\log \epsilon \sim 1.0$ L_a(liquid); $\log \epsilon \sim 2.0$ Shift from *n*-heptane seems real.	92
$CH_2—CH_2—CH_2$ cyclopropane	52,600	1890	R(liq., vap.)	$\log \epsilon = \bar{1}.8$	4, 124
$CH_2—(CH_2)_4—CH_2$ cyclohexane	58,000	1725	P		115, 123, 125
 camphane	54,000	1850	WB	p = 1 mm; 20 cm cell	125
CH_3Cl methyl chloride					34, 37, 43, 96, 123, 124
C_2H_5Cl ethyl chloride					43, 100, 123, 124
C_3H_7Cl *n*-propyl chloride					43, 100, 114, 123, 124
$(CH_3)_2CHCl$ *iso*-propyl chloride					
C_4H_9Cl *n*-butyl chloride					
C_4H_9Cl *tert*-butyl chloride					
$C_5H_{11}Cl$ *n*-amyl chloride					
$C_5H_{11}Cl$ *iso*-amyl chloride					

TABLE I.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
CH_3Br methyl bromide					24, 34, 37, 43, 93, 96, 123, 124
C_2H_5Br ethyl bromide					43, 93, 100, 123, 124
C_3H_7Br *n*-propyl bromide					43, 123
C_3H_7Br *iso*-propyl bromide					
C_4H_9Br *n*-butyl bromide					43, 93, 100, 123, 124
C_4H_9Br *sec*-butyl bromide					43, 123
C_4H_9Br *tert*-butyl bromide					
C_4H_9Br *iso*-butyl bromide					
$C_5H_{11}Br$ *iso*-amyl bromide					
CH_3I methyl iodide					34, 35, 37, 39, 43, 96, 114, 116, 123, 124
C_2H_5I ethyl iodide					36, 43, 100, 114, 123, 124
C_3H_7I *n*-propyl iodide					43, 64, 123, 124
C_3H_7I *iso*-propyl iodide					
C_4H_9I *n*-butyl iodide					
C_4H_9I *sec*-butyl iodide					43, 64,114, 123
C_4H_9I *tert*-butyl iodide					
C_4H_9I *iso*-butyl iodide					
$C_5H_{11}I$ *iso*-amyl iodide					
CH_2Cl_2 methylene chloride					34, 43, 89, 123
CH_2Br_2 methylene bromide					
CH_2I_2 methylene iodide					34, 43, 89, 123, 124
$CHCl_3$ chloroform					
$CHBr_3$ bromoform					
CHI_3 iodoform					

TABLE I.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
CCl_4 carbon tetrachloride					34, 43, 48, 89, 123, 124
CBr_4 carbon tetrabromide					34, 89, 123, 124
CI_4 carbon tetraiodide					89
CH_3CHCl_2 1,1,-dichloroethane	45,900	2170		L_a, "max. vapor pressure"	43, 123
CH_2ClCH_2Cl 1,2-dichloroethane	44,700	2240			
CH_2BrCH_2Br 1,2-dibromoethane	37,000	2705			
CH_2ICH_2I 1,2-diiodoethane					
$CH_2ClCHCl_2$ 1,1,2-trichloroethane	45,900	2180			
$CHCl_2CHCl_2$ 1,1,2,2-tetrachloroethane	43,000	2330			
$CHBr_2CHBr_2$ 1,1,2,2-tetrabromoethane	40,700	2460			
CH_3OH methyl alcohol	52,900	1890	*R*	L_a(liquid); $\log \epsilon \sim .5$	7, 37, 43, 92, 98, 123, 124
C_2H_5OH ethyl alcohol	52,900 56,000	1890 1785	*R* *R*	L_a(liquid); $\log \epsilon \sim .6$ L_a(liquid); $\log \epsilon \sim 1.6$	6, 37, 43, 48, 92, 123, 124
C_3H_7OH *iso*-propyl alcohol					43
C_3H_7OH *n*-propyl alcohol				In heptane to 58,000. Samples not well purified. May be wide step-out near 54,000 in sec-alcohols, $\log \epsilon \sim 2.3, f \sim .01$	6, 43, 92, 124
C_4H_9OH *n*-butyl alcohol					
$CH_3CHOHC_2H_5$ *sec*-butyl alcohol					
$(CH_3)_3COH$ *tert*-butyl alcohol					
C_4H_9OH *iso*-butyl alcohol					
$C_5H_{11}OH$ *n*-amyl alcohol					
$(C_2H_5)_2CHOH$ diethyl carbinol					
$CH_3CHOHC_6H_{13}$ *sec*-octyl alcohol					
$C_5H_{11}OH$ *iso*-amyl alcohol	49,600	2020		L_a, "max. vapor pressure"	43, 123
$C_5H_{11}OH$ *sec*-amyl alcohol	47,000	2130			
$C_5H_{11}OH$ *tert*-amyl alcohol	49,700	2015			

TABLE I.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$C_6H_{13}OH$ *n*-hexyl alcohol	50,200	1995		L_a, "max. vapor pressure"	43, 123
$C_7H_{15}OH$ *n*-heptyl alcohol	50,400	1985			
$C_8H_{17}OH$ *n*-octyl alcohol	50,800	1970			
$C_{10}H_{21}OH$ *n*-decyl alcohol	52,800	1895			
$C_{12}H_{25}OH$ *n*-dodecyl alcohol	53,500	1870			
$(C_2H_5)_2C(OH)CH_3$ methyl diethyl carbinol					43, 124
$C_2H_4(OH)_2$ ethylene glycol					
$CH_2OHCH_2CH_2OH$ trimethylene glycol					
$C_3H_5(OH)_3$ glycerol					
CH_2ClCH_2OH ethylene chlorohydrin					
CH_2BrCH_2OH ethylene bromohydrin					
CH_2ICH_2OH ethylene iodohydrin					
$(CH_3)_2O$ dimethyl ether					115, 123, 124
$(C_2H_5)_2O$ diethyl ether	51,000	1960		L_a(liquid); log $\epsilon \sim .9$	92, 98, 115, 123, 124
$(C_4H_9)_2O$ di-*n*-butyl ether	55,000	1820		Step-out in heptane solution. log $\epsilon \sim 3.0$; $f \sim .01$. Sample not well purified.	92
$CH_3CH_2OCHClCH_3$ α-chloroethyl ethyl ether			*R*(Hex)	log $\epsilon = 2.2$ at 1800A	77
$CH_3CH_2OCH_2CH_2Cl$ β-chloroethyl ethyl ether			*R*(Hex)	log $\epsilon = 2.4$ at 2200A	
$CH_3CH_2OCHClCH_2Cl$ α,β-dichloroethyl ethyl ether	43,500	2300	*P*(Hex) *R*	log $\epsilon = 1.3$ log $\epsilon = 2.3$ at 1850A	
$CH_2ClCH_2OCH_2CH_2Cl$ β,β′-dichlorodiethyl ether			*R*(Hex)	log $\epsilon = 2.2$ at 1900A	
$CH_3CH_2OCHOHCH_3$ α-hydroxyethyl ethyl ether	45,400	2200	*P*(Hex) *R*	log $\epsilon = 1.6$ log $\epsilon = 2.0$ at 1950A	
$CH_2OHCH_2OCH_2CH_3$ β-hydroxyethyl ethyl ether			*R*(Hex)	log $\epsilon = 2.0$ at 1900A	
$(HOCH_2CH_2)_2O$ β,β′-dihydroxydiethyl ether			*R*(H_2O)	log $\epsilon = 2.0$ at 1900A	
$(CH_3CHO)_3$ paraldehyde	45,500	2200	*P*(H_2O)	Curve to 1950A	117

TABLE I.—*Continued.*

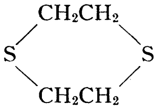
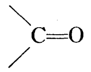
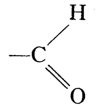
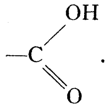
Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
CH_3SH methyl mercaptan					43, 124
C_2H_5SH ethyl mercaptan					43, 53, 98, 124
C_3H_7SH *n*-propyl mercaptan					43, 98, 123, 124
$(CH_3)_2CHSH$ *iso*-propyl mercaptan					
C_4H_9SH *n*-butyl mercaptan					
C_2H_5SNa sodium ethylmercaptide	$>45,500$	<2200	*R*(Alc)	log $\epsilon = 3.8$ at 1880A	53
$[S(C_2H_5)_3]Cl$ triethylsulfonium chloride	$>50,000$	<2000	*R*(Alc)	log $\epsilon = 3.9$ at 1850A	
$(C_2H_5)_2S$ diethyl sulfide	40,000 $>45,500$	2500 <2200	*P*(MeOH) *R*		53, 70, 77, 98, 124
$(C_3H_7)_2S$ di-*n*-propyl sulfide				Qualitative mention	98
$[(CH_3)_2CH]_2S$ di-*iso*-propyl sulfide					
$(C_4H_8)_2S$ di-*n*-butyl sulfide					
 diethylene disulfide	43,500 50,000	2300 2000	*P*(Hex) *P*	log $\epsilon = 2.5$ log $\epsilon = 3.9$	70, 77
$CH_3CH_2SCH_2CH_2Cl$ *β*-chloroethyl ethyl sulfide	43,500 48,800	2300 2050	*P*(Hex) *P*	log $\epsilon = 2.3$ log $\epsilon = 3.5$	77
$CH_2CHClSCHClCH_3$ *α*,*α*′-dichlorodiethyl sulfide	43,500 48,800	2300 2050	*P*(Hex) *P*	log $\epsilon = 2.8$ log $\epsilon = 3.3$	
$CH_2ClCH_2SCH_2CH_2Cl$ *β*,*β*′-dichlorodiethyl sulfide	49,500	2020	*P*(Hex)	log $\epsilon = 3.7$	66, 70, 75, 77
$CH_3CH_2SCH_2CH_2OH$ *β*-hydroxyethyl ethyl sulfide	50,000	2000	*P*(Hex)	log $\epsilon = 3.4$	77
$CH_2OHCH_2SCH_2CH_2OH$ *β*,*β*′-dihydroxydiethyl sulfide	52,700	1900	*P*(Hex)	log $\epsilon = 3.3$	70, 77
$(C_2H_5S)_2$ diethyl disulfide	40,000 $>50,000$	2500 <2000	*P*(Alc) *R*	log $\epsilon = 2.6$ log $\epsilon = 3.9$ at 1800A	53, 54, 77
$N(CH_2CH_2Cl)_3$ trichlorotriethyl amine	55,600	1800	*P*(Hex)	log $\epsilon = 3.5$	76
$[HN(CH_2CH_2Cl)_3]^+Cl^-$ trichlorotriethyl amine hydrochloride			*R*(Alc)	log $\epsilon = 3.2$ at 2000A	
$(C_2H_5)_2NH$ diethyl amine	$>42,000$	<2400	*R*(Hex)	log $\epsilon = 3.5$ at 1800A	54
$(C_2H_5)_2NH_2^+Cl^-$ diethylamine hydrochloride	$>50,000$	<2000	*R*(H_2O)	log $\epsilon = 3.8$ at 1840A	
$(CH_2)_5NH$ piperidine	$>45,000$	<2200	*R*(H_2O)	log $\epsilon = 3.4$ at 1840A	

Table I.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$(CH_2)_5NH_2^+Cl^-$ piperidine hydrochloride			$R(H_2O)$	log $\epsilon=3.7$ at 1850A	54
Cl_3CNO_2 chloropicrin	48,800	2050	P(Hex)	log $\epsilon=3.5$	73, 75
$Hg(CH_3)_2$ mercury dimethyl					123, 124, 130
CH_3HgI methyl mercury iodide					
$CH_3CH_2AsCl_2$ ethyl dichloroarsine	41,500	2410	P(Hex) R	log $\epsilon=3.3$ log $\epsilon=3.5$ at 2000A	75

Table II. Aldehydes, ketones, and acids

Theory: (60, 61, 62, 80).

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
H_2CO formaldehyde					38, 39, 95, 98, 123, 124
CH_3CHO acetaldehyde	50,800	1970	$P(H_2O)$	log $\epsilon=1.55$	58, 114, 117, 123
$(CH_3)_2CHCH_2CHO$ *iso*-valeraldehyde				Abs. curve in *n*-heptane to 54,000. Is shifted 2000 cm^{-1} higher than ketones	92
CH_3COCH_3 acetone CD_3COCD_3 deutero-acetone	50,000 to 56,000	2000 to 1785	B	$\omega'=1194$ $\omega'=1047$ $\omega'=714$ $\omega'=315$ $\omega'=269$ 0,0 band at 51,181 (multiple with many int. bands) Frequency 1194 not C=O as does not appear in deutero-acetone	20, 42, 47, 52, 55, 65, 74, 88, 92, 113, 114, 123
	53,500	1870	P(Hep)	log $\epsilon=2.9$; f∼.015. Second peak at 55,500?	
$CH_3COC_2H_5$ methyl ethyl ketone	53,800	1860	P(Hep)	log $\epsilon=2.9$; f=.016	21, 92, 124
$CH_3COC_3H_7$ methyl *n*-propyl ketone					22, 92, 124
$CH_3COCH(CH_3)_2$ methyl *iso*-propyl ketone					22, 124
$CH_3COC_5H_{11}$ methyl amyl ketone				Curve in heptane soln. to 54,000; abs. lower than any other ketones; sample not well purified.	92
$C_2H_5COC_2H_5$ diethyl ketone	53,000	1890	P(Hep)	log $\epsilon=2.6$; f=.008. Sample not well purified.	22, 92, 124

TABLE II.—*Continued.*

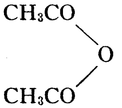
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$(CH_3)_3CCOC(CH_3)_3$ hexamethyl acetone					114, 123
$\underbrace{CH_2(CH_2)_3CO}$ cyclopentanone					69, 115, 123
$\underbrace{CH_2(CH_2)_4CO}$ cyclohexanone					69, 115, 123
$C_{10}H_{16}O$ thujone			R(Hex)	log $\epsilon=3.5$ at 1900A	69
$C_{10}H_{18}O$ *l*-menthone			R(Hex)	log $\epsilon=3.1$ at 1900A	
CH_3COCH_2Br bromoacetone	46,500	2150	P(Hex) R	log $\epsilon=2.6$ log $\epsilon=2.8$ at 1800A	74,75
$C_2H_5COCH_2Br$ bromomethyl ethyl ketone	47,000	2130	P(Hex) R	log $\epsilon=2.5$ log $\epsilon=2.8$ at 1800A	
HCOOH formic acid	48,500 52,000	2060 1925	$P(H_2O)$ R	log $\epsilon=1.8$	54, 101, 114, 123, 124
$HCOOCH_3$ methyl formate					114, 123
HCOONa sodium formate	49,000 52,000	2040 1920	R	Step-out in H_2O solution.	54
CH_3COOH acetic acid	49,000	2040	P(Hep) $P(H_2O)$	log $\epsilon=1.7$; lower than for heavier acids.	8, 51, 54, 92, 110, 114, 123
	$>60,000$	<1665	P(Hep)	log $\epsilon\sim2.0$, rising steeply; for next band, prob. $f>.1$	
CH_3COOCH_3 methyl acetate					114, 123
$CH_3COOC_2H_5$ ethyl acetate	47,500	2100	P(Alc)	log $\epsilon=1.8$	51, 54, 114, 123
CH_3COONa sodium acetate	$>52,000$	<1940	$R(H_4O)$	No true peak at 49,000. log $\epsilon=3.3$ at 1870A	51, 54
CH_3CONH_2 acetamide	$>54,000$	<1850	$R(H_2O)$	log $\epsilon=4.0$	54
CH_3COCl acetyl chloride	42,500 $>47,000$	2345 <2120	P(Hex) R	log $\epsilon=1.7$ log $\epsilon=2.4$ at 2000A	
CCl_3COCl trichloroacetyl chloride					107, 123
 acetic anhydride	46,000 $>52,000$	2170 <1930	P R	log $\epsilon=1.8$ log $\epsilon=2.4$ at 1840A	54, 114
C_4H_9COOH butyric acid	49,000 48,500 $>52,000$	2040 2060 <1930	P(Hep) $P(H_2O)$ R(Hep)	log $\epsilon=1.8$ log $\epsilon=2.5$ at 1840A	54, 92, 110
$C_7H_{15}COOH$ caprylic acid	49,000 $>60,000$	2040 <1665	P(Hep) P(Hep)	log $\epsilon\sim2.8$, rising steeply; prob. for next band $f>.1$. Ester shifted ~500 cm^{-1} to red. Alcohol solution shifted ~1000 cm^{-1} to red.	92, 110
$C_{13}H_{27}COOH$ myristic acid					
$C_{13}H_{27}COOCH_3$ methyl myristate					

TABLE II.—*Continued.*

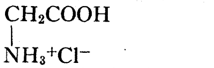
Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
$C_{15}H_{31}COOH$ palmitic acid	47,500	2100	$P(H_2O)$	log $\epsilon = 1.7$	54
HOOCCOOH (See Table IV) oxalic acid					
$HOOC(CH_2)_2COOH$ succinic acid	48,500 $>52,000$	2070 <1930	$P(H_2O)$ R	log $\epsilon = 2.0$ log $\epsilon = 2.4$ at 1840A	54
$NaOOC(CH_2)_2COONa$ disodium succinate	$>47,500$	<2100	$R(H_2O)$	log $\epsilon = 4.1$ at 1840A	
$(CH_3O)_2CO$ dimethyl carbonate	$>50,000$	<2000	$R(H_2O)$	log $\epsilon = 1.7$ at 1800A	
$(C_2H_5O)_2CO$ diethyl carbonate					114, 123
$NaHCO_3$ sodium bicarbonate	$>50,000$	<2000	$R(H_2O)$	log $\epsilon = 2.6$ at 1850A	54
$ClCOOCH_3$ methyl chloroformate				No selective absorption to 1850A	73, 75
$ClCOOCCl_3$ diphosgene					
NH_2CONH_2 urea	$>44,500$	<2250	$R(H_2O)$	log $\epsilon = 3.8$ at 1800A	54
$NH_2COOC_2H_5$ urethan (ethyl carbamate)	$>45,000$	<2200	$R(H_2O)$	log $\epsilon = 2.9$ at 1870A	
NH_2CH_2COOH glycine	$>43,500$	<2300	$R(H_2O)$	Step out about 2050. log $\epsilon \sim 3.8$ at 1850A	
$CH_3CH(NH_2)COOH$ alanine					
$C_4H_7N(OH)COOH$ hydroxyproline					
$(CH_2)_5NCH_2COOH$ piperidoacetic acid					
$(CH_3)_2CHCH(NH_2)COOH$ valine	$>43,000$	<2340	$R(H_2O)$	Abs. similar to that of amino acids above but displaced about 30A toward red.	
$(CH_3)_2CHCH_2CH(NH_2)COOH$ leucine					
$(C_4H_7NH)COOH$ proline	$>52,600$	<1900	$R(H_2O)$	log $\epsilon = 2.7$ at 1900A	
NH_2CH_2COONa sodium glycinate	$>54,000$	<1850	$R(H_2O)$	log $\epsilon = 3.8$ at 1850A	
$CH_3CH(NH_2)COONa$ sodium alaninate					
$(C_4H_7NOH)COONa$ sodium hydroxyprolinate	$>54,000$	<1850	$R(H_2O)$	log $\epsilon = 3.3$ at 1850 A	
$[SCH_2CH(NH_2)COONa]_2$ sodium cystinate	$>39,000$	<2560	$R(H_2O)$	Step-out at 2500A	
$(CH_2)_5NCH_2COONa$ sodium piperidoacetate			$R(H_2O)$	log $\epsilon = 3.7$ at 1840A	
 $\begin{array}{l}CH_2COOH\\ \vert\\ NH_3^+Cl^-\end{array}$ glycine hydrochloride			$R(H_2O)$	Step-out$\sim$2050A log $\epsilon = 3.8$ at 1850A	

TABLE II.—*Continued.*

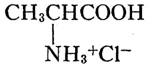
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
 $CH_3CH(NH_3^+Cl^-)COOH$ alanine hydrochloride			$R(H_2O)$	Step-out∼2100A log $\epsilon = 2.4$ at 1950A	54
$[SCH_2CH(NH_3^+Cl^-)COOH]_2$ cystine dihydrochloride			$R(H_2O)$	Step-out∼2400A log $\epsilon = 3.7$ at 1950A	

TABLE III. Compounds containing unconjugated double bonds

$\rangle C{=}C\langle$ $\rangle C{=}C{-}C{-}C{=}C\langle$ $\rangle C{=}C{-}C{-}C{=}O.$

Theory: (14, 15, 79, 80, 84, 86, 111).

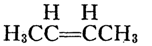
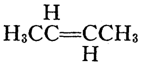
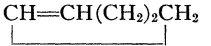
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$H_2C{=}CH_2$ ethylene $H_2C{=}CHD$ $D_2C{=}CD_2$ deuteroethylenes	57,000 to 62,500	1750 to 1600	Doublet series	$\omega' = 1370$ Sep. $= 470$ cm^{-1}. Price and Tutte (104) think 470 is CH_2 twist; Mulliken (86) agrees; Sponer and Teller (124) say "no satisfactory explanation."	41, 94, 104, 115, 122, 123, 124, 125, 128
$H_2C{=}CHCH_3$ propylene					4, 104, 124
$H_2C{=}CHC_2H_5$ butene-1					11, 123, 124
$H_2C{=}CHC_3H_8$ pentene-1					9, 11, 123, 124
$H_2C{=}CHC_5H_{11}$ heptene-1					9, 11, 123, 124
$H_2C{=}CHC_6H_{13}$ octene-1	>42,500	<2350	*C*	*P*∼3mm; 20 cm cell.	125
$H_2C{=}CHCH(CH_3)_2$ *iso*-propylethylene					11, 123, 124
 $H_3C\overset{H}{C}{=}\overset{H}{C}CH_3$ *cis*-butene-2					11, 12, 124
 $H_3C\overset{H}{C}{=}\underset{H}{C}CH_3$ *trans*-butene-2					11, 12, 104, 124
$H_3CCH{=}CHC_2H_5$ *cis*- *trans*-pentene-2					9, 11, 12, 123 124
$CH_3(CH_2)_2CH{=}CHCH_3$ hexene-2	>42,500	<2350	*R*	Sat. p. $= 105$ mm; 20 cm cell	125
$C_2H_5CH{=}CHC_2H_5$ hexene-3					11, 12, 124
$C_2H_5CH{=}CHC_3H_7$ heptene-3					10, 11, 12, 124
$C_2H_5CH{=}CHC_4H_9$ octene-3	54,300	1840	*P*(Hep)	log $\epsilon = 3.9$; f $= .25$	92
 $CH{=}CH(CH_2)_2CH_2$ cyclopentene					13, 124

TABLE III.—*Continued.*

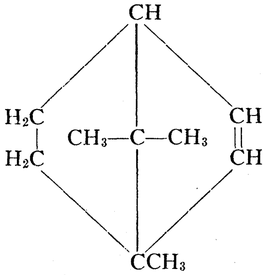
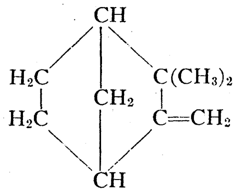
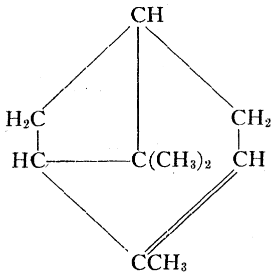
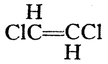
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$CH{=}CH(CH_2)_3CH_2$ cyclohexene					1, 13, 69, 104, 122, 124, 127
 bornylene	50,000 54,000	2000 1850	*P* *P*		125
$CH_2{=}C(CH_3)_2$ *iso*-butene					11, 124, 125, 128
$CH_2{=}C(CH_3)C_2H_5$ unsym. methyl ethyl ethylene $CH_2{=}C(CH_3)C_5H_{11}$ diisobutylene-I					11, 124
 camphene	50,000 54,000	2000 1850	*P* *P*		125
$CH_3CH{=}C(CH_3)_2$ trimethylethylene	$>47{,}500$ $>50{,}000$	<2100 <2000	*R*(Cyclohex) *R*(Hex)	log $\epsilon=3.7$ at 1900A log $\epsilon=4.0$ at 1923A	9, 11, 55, 57, 104, 109, 112, 122, 123, 124, 125
$CH_3CH{=}C(C_2H_5)_2$ diethyl methyl ethylene $C_4H_9CH{=}C(CH_3)_2$ diisobutylene-II					11, 124
 α-pinene	49,000 54,000	2040 1850	*P* *P*		125
$(CH_3)_2C{=}C(CH_3)_2$ tetramethylethylene					10, 11, 104, 124
 $\overset{H}{ClC}{=}\underset{H}{CCl}$ *trans*-dichloroethylene					43, 59, 123

TABLE III.—*Continued.*

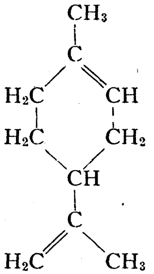
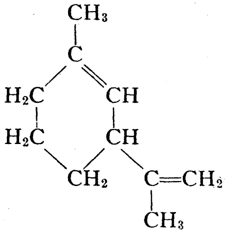
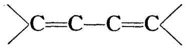
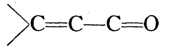
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$\underset{H}{ClC}=\underset{H}{CCl}$ *cis*-dichloroethylene					59, 123
$CHCl=CCl_2$ trichloroethylene					43, 123
$CCl_2=CCl_2$ tetrachloroethylene					43, 115, 123
$CHBr=CHBr$ α,β-dibromoethylene					43, 123
$CH_3CH=CHCl$ α-chloropropylene					
$CH_3CH=CHBr$ α-bromopropylene					
$CH_3CH=CHI$ α-iodopropylene					
$CH_2=CHCH_2Cl$ allyl chloride					100, 124
$CH_2=CHCH_2OH$ allyl alcohol	$>50,000$	<2000	*R*(Hex)	log $\epsilon=3.3$ at 1923A	7, 43, 57, 109, 124
$CH_2=CH(CH_2)_2HC=CH_2$ diallyl	56,500	1770	*P*	log $\epsilon=4.6$ f$\sim$1.0	15, 109, 112, 125
$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CH_2$ geraniolene	$>41,500$	<2410	*R*	Saturation $p=151$ mm; 20 cm cell	125
 *d*-limonene	$>54,000$	<1850	*B, C*		
 *d*-sylvestrene	$>54,000$	<1850	*B, C*		
$C_{10}H_{12}$ dicyclopentadiene (dimer of 1,3-cyclopentadiene)				Curve in hexane indicates loss of conjugation.	91
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ oleic acid-9 (*cis*)	54,500	1835	Broad *P*(Hep)	log $\epsilon=3.9$ f$=.24$	110
$CH_3(CH_2)_7CH=CH(CH_2)_7COOC_2H_5$ ethyl oleate-9 (*cis*)	54,500	1835	Broad *P*(Hep)	log $\epsilon=4.0$ f$=.27$	

TABLE III.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ elaidic acid-9 (*trans*)	53,200	1880	Broad P(Hep)	log $\epsilon = 3.9$ $f = .24$ Shifted about 1000 cm^{-1} to red of *cis*	110
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ linoleic acid-9,12 (*cis, cis*)	52,000	1920	P(Hep)	log $\epsilon = 4.25$ $f = .70$ Broader than oleic	
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOC_2H_5$ ethyl linoleate-9,12 (*cis, cis*)	53,000	1890	P(Hep)	log $\epsilon = 4.1$ $f = .60$ Broader than oleic; shifted about 400 cm^{-1} to red from acid.	
$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$ linolenic acid-9,12,15	51,000 57,500	1960 1735	P(Hep) P(Hep)	log $\epsilon = 4.3$ log $\epsilon = 4.25$ total $f \geq .76$	
$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOC_2H_5$ ethyl linolenate-9,12,15				Similar to linolenic acid	
$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOC_2H_5$ ethyl elaidolinolenate-9,12,15	50,000 56,500	2000 1770	P(Hep) P(Hep)	log $\epsilon = 4.1$ log $\epsilon = 4.1$ total $f = .65$ Shifted about 400 cm^{-1} to red from acid	
$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOCH_3$ methyl arachidonate-5,8,11,14	50,400 56,500	1980 1770	P(Hep) P(Hep)	log $\epsilon = 4.35$ log $\epsilon = 4.25$ total $f = .89$	
$(CH_3)_2C{=}NOH$ acetoxime	54,700	1830	P(Alc)	log $\epsilon = 3.7$	55
$CH_3CH{=}NOH$ acetaldoxime	55,500	1800	P(Alc)	log $\epsilon = 3.5$	
$C_{10}H_{18}$ 2,8-decadiene	53,200	1880	P(Hex)	log $\epsilon = 4.3$	68
$(CH_2{=}CH)_2S$ divinyl sulfide	40,800	2450	P(Hex) R	log $\epsilon = 3.8$ log $\epsilon = 3.6$ at 1950A	77
$ClCH{=}CHAsCl_2$ β-chlorovinyl dichloroarsine (Lewisite I)	46,800	2140	P(Hex)	log $\epsilon = 4.0$	73, 75
$(ClCH{=}CH)_2AsCl$ β,β′-dichlorodivinyl chloroarsine (Lewisite II)	47,800	2090	P(Hex)	log $\epsilon = 4.2$	
$(ClCH{=}CH)_3As$ β,β′,β″-trichlorotrivinyl arsine (Lewisite III)	48,300	2070	P(Hex)	log $\epsilon = 4.4$	
$C_{27}H_{45}OH$ cholesterol	53,200	1880	P(Hex)	log $\epsilon = 4.3$	68

TABLE IV. Compounds containing conjugated double bonds





$O{=}C{-}C{=}O$.

Theory: (46A, 49, 81, 86, 118).

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$CH_2{=}CHCH{=}CH_2$ butadiene-1,3	46,000	2170	P(Hex)	log $\epsilon = 4.3$	16, 105, 115, 120, 123, 124

TABLE IV.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$CH_2{=}CHCH{=}CHCH_3$ pentadiene-1,3	45,000 to 50,000	2200 to 2000	*DB*	$\omega' \sim 1400$ $N \rightarrow V_1$ Whole spectrum shifted ~ 1000 cm^{-1} to red of butadiene	15, 16
	52,000 to 58,000	1920 to 1725	Sharp bands		
$CH_3CH{=}CHCH{=}CHCH_3$ hexadiene-2,4	46,000 to 50,000	2170 to 2000	*DB*	$\omega' \sim 1400$ $N \rightarrow V_1$	16, 125, 128
	57,000	1750	*C*	$N \rightarrow V_{2,3}$(?) 1000 cm^{-1} to red of butadiene. End substitution eliminates 55,000 cm^{-1} sharp bands.	
$CH_2{=}C(CH_3)CH{=}CH_2$ isoprene	45,000	2200	*P*(Hex)	$\log \epsilon = 4.4$	16, 68, 105, 112, 120, 124, 125, 128
$CH_2{=}C(CH_3)(CH_3)C{=}CH_2$ 2,3-dimethyl butadiene-1,3	44,500	2250	*P*(Hex)	$\log \epsilon = 4.3$	16, 105, 120, 124, 125
$CH_2{=}C(CH_3)CH{=}CHCH_3$ 2-methyl pentadiene-1,3	45,000 to 48,000	2220 to 2080	*B*	$\omega' \sim 1300$ $N \rightarrow V_1$	16
	52,000 to 57,000	1920 to 1755	*WB*	$\omega' \sim 1600$	
$(CH_3)_2C{=}CHCH{=}CH_2$ 4-methyl pentadiene-1,3	38,000	2630	*C*	Saturation $p = 65$ mm; 20 cm cell	125
$(CH_3)_2C{=}CHCH{=}CHCH_3$ 2-methyl hexadiene-2,4	44,000 to 52,000	2270 to 1925	Progression	$\omega' \sim 1560$ $N \rightarrow V_1$ See note on hexadiene-2,4	16
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$ 2,5-dimethyl hexadiene-2,4	43,000 to 57,000	2320 to 1755	Progression	$\omega' \sim 1560$ Bands now fairly sharp.	
	44,000	2280	*B*	$N \rightarrow V_1$ Higher peaks here	
	57,000	1755	*B*	$N \rightarrow V_{2,3}$	
$CH{=}CHCH{=}CHCH_2$ cyclopentadiene	50,000 to 53,000	2000 to 1890	*B*	$\omega' \sim 1450$ $\omega' \sim 800$ $\omega' \sim 1070$ 0,0 at 50,380 cm^{-1} Pairs, sep. = 480 cm^{-1} Called CH_2 twisting vibration by Price and Walsh (106). Pickett *et al.* (91) list $\omega' \sim 930$ in addition.	13, 91, 106, 115, 123, 124
	60,140	1660	*B*	This band stronger than 45,000; agrees with Mulliken's (81) prediction. $\nu = 69{,}500 - R/(n+0.28)^2$	
	>60,000	<1665	*C*	$V_i = 8.58V$.	
$CH_2CH{=}CHCH{=}CHCH_2$ cyclohexadiene-1,3	>47,500	<2100	*R*(Cyclohex)	$\log \epsilon = 4.7$ at 1900A	1, 13, 33, 106, 124, 127

TABLE IV.—*Continued.*

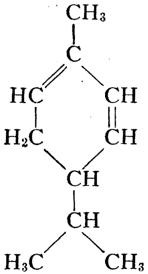
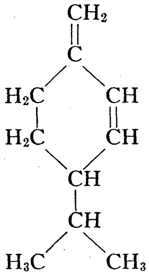
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
 α-phellandrene	38,800	2580	*P*		125
	47,600	2100	*P*		
 β-phellandrene	43,700	2290	*P*		
	50,600	1980	*P*		
$CH_2{=}CClCH{=}CH_2$ chloroprene					105, 124
$CH{=}CHCH{=}CHO$ furan	52,000 to 57,000	1925 to 1755	Sharp *B*	$\omega'=1410$ $\omega'=1068$ $\omega'=848$	77, 90, 106, 124
	60,000 to 71,000	1665 to 1400	*B*	$\nu=73{,}080-R/(n+0.90)^2$ $\nu=73{,}020-R/(n+0.50)^2$ $V_i=9.01$ V. V_{i2} est. 10.8 V.	
$CH{=}CHCH{=}CHS$ thiophene	41,000 to 48,000	2440 to 2080	*B*	$\omega'=1150$ (63) $\omega'=965$(106) $N\rightarrow V_1$ To short λ from cyclopentadiene.	63, 70, 77, 106
	53,000 to 63,000	1885 to 1590	*B*	$\omega'=1250$ $\omega''=675$? $N\rightarrow V_{2,3}$ Pairs; sep. = 540 cm^{-1}.	
	>67,000	<1490	*B*	$\nu=72{,}170-R/(n+0.90)^2$ $V_i=8.91$ V.	
$CH{=}CHCH{=}CHNH$ pyrrole	45,000 to 51,000	2220 to 1960	*B*	$\omega'\sim1400$?	106, 115, 123
	49,000	2040	*P* in *C*	Groups closer together than in thiophene.	
	54,500	1835			
	59,000	1695			
	57,000 to 59,000	1755 to 1695	*B*		

TABLE IV.—*Continued.*

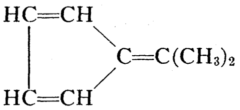
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
	$>66{,}000$	<1515	*B*	Rydberg structure like thiophene. V_i est. 8.9 V.	
 dimethyl fulvene	38,800 48,300	2580 2070	*P* *P*		125
$CH_2{=}CHCOOH$ acrylic acid	$>48{,}000$	<2080	*R*(Hex)	$\log \epsilon = 4.3$ at 2080 A	57
$CH_3CH{=}CHCOOH$ α-crotonic acid	48,000	2080	*P*(Hep)	$\log \epsilon = 4.1$ Curve (Alc) to 52,000 Curve (Hep) to 55,000	28, 55, 71, 110, 120
$CH_3(CH_2)_{13}CH{=}CHCOOH$ α-heptadecenoic acid	46,500	2150	*P*(Hep)	$\log \epsilon = 4.1$ Curve (Hep) to 59,000	110
$CH_3(CH{=}CH)_2CH_2CH_2COOH$ octadienoic-4,6 acid	44,000	2280	*P*(Hex)	$\log \epsilon = 4.3$	120
$CH_3(CH_2)_5(CH{=}CH)_2(CH_2)_7COOH$ octadecadienoic-9,11 acid	52,000 $>58{,}000$	1925 <1700	*WP*(Hep) *R*	$\log \epsilon = 3.3$	110
$CH_3(CH_2)_4(CH{=}CH)_2(CH_2)_8COOH$ octadecadienoic-10,12 acid	55,500	1800	*WP*(Hep)	$N \rightarrow V_2$?; $\log \epsilon \sim 3.4$ f∼.06?	
$CH_3(CH_2)_2(CH{=}CH)_3(CH_2)_8COOH$ pseudoeleostearic-10,12,14 acid	52,000	1920	*WB* in *C*	$\log \epsilon \sim 3.3$	
$CH_2{=}CHCH{=}CHCOOH$ vinyl acrylic acid	40,300	2480	*P*(Hex) *R*	$\log \epsilon = 4.3$ $\log \epsilon = 3.6$ at 1850A	120
$CH_3(CH{=}CH)_2COOH$ sorbic acid (hexadienoic-2,4 acid)	38,500	2600	*P*(Hex)	$\log \epsilon = 4.4$	28, 120
$CH_3CH{=}CHC(CH_3){=}CHCOOH$ β-methyl sorbic acid	38,000 50,000	2660 2000	*P*(Hex) *R*	$\log \epsilon = 4.3$ $\log \epsilon = 3.8$ at 1850A	120
$CH_3(CH{=}CH)_3COOH$ octatrienoic acid				Curve to 1800A	
$CH_3(CH{=}CH)_2C(CH_3){=}CHCOOH$ β-methyl octatrienoic acid	48,600	2100	*P*(Hex)	$\log \epsilon = 3.5$	
$CH_3CH_2(CH{=}CH)_3CH_2COOH$ decatrienoic acid			*R*(Hex)	$\log \epsilon = 4.0$ at 1850A	
$CH_3(CH{=}CH)_4COOH$ decatetrenoic acid				Curve to 1800A	28
HOOCCOOH oxalic acid NaOOCCOONa disodium oxalate	$>50{,}000$	<2000	*R*(H_2O)	Step out at ∼2500A $\log \epsilon = 3.6$ at 1840A	54
$H_3COOCCOOCH_3$ dimethyl oxalate	$>50{,}000$	<2000	*R*(MeOH)	Step out at ∼2400A $\log \epsilon = 3.0$ at 1980A	
$HOOCCH_2CH{=}CHCOOH$ glutaconic acid	49,000	2040	*P*(Alc)	$\log \epsilon = 4.1$	120
$HOOC(CH_2)_2CH{=}CHCOOH$ dihydromuconic acid	48,500	2050	*P*(Alc)	$\log \epsilon = 4.1$	
 $\begin{matrix} HOOC & COOH \\ \vert & \vert \\ HC & {=}CH \end{matrix}$ maleic acid (*cis*)			*R*(Alc)	$\log \epsilon = 3.9$ at 1940A	55, 132

TABLE IV.—*Continued.*

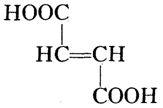
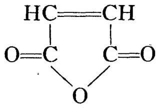
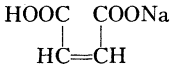
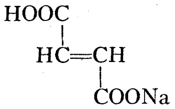
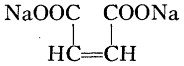
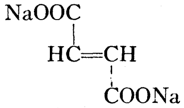
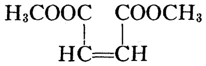
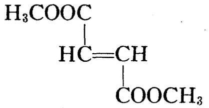
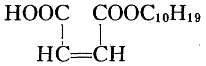
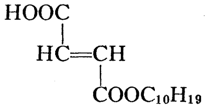
Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
 $\mathrm{HOOC{-}CH{=}CH{-}COOH}$ fumaric acid (*trans*)	48,300 47,500	2070 2100	P(Alc) P(Hex)	log $\epsilon=4.2$ log $\epsilon=4.1$	55, 120, 132
 $\mathrm{HC{=}CH{-}C({=}O){-}O{-}C({=}O)}$ maleic anhydride	49,000	2040	P(Alc)	log $\epsilon=4.0$	132
 $\mathrm{HOOC{-}CH{=}CH{-}COONa}$ mono-sodium maleate	47,700	2100	$P(H_2O)$	log $\epsilon=4.1$	
 $\mathrm{HOOC{-}CH{=}CH{-}COONa}$ mono-sodium fumarate	48,300	2070	$P(H_2O)$	log $\epsilon=4.2$	
 $\mathrm{NaOOC{-}CH{=}CH{-}COONa}$ disodium maleate	52,200	1920	$P(H_2O)$	log $\epsilon=3.9$	55, 132
 $\mathrm{NaOOC{-}CH{=}CH{-}COONa}$ disodium fumarate	49,000	2040	$P(H_2O)$	log $\epsilon=4.1$	
 $\mathrm{H_3COOC{-}CH{=}CH{-}COOCH_3}$ dimethyl maleate	51,500	1940	P(Hex)	log $\epsilon=3.8$	132
 $\mathrm{H_3COOC{-}CH{=}CH{-}COOCH_3}$ dimethyl fumarate	48,000	2080	P(Hex)	log $\epsilon=4.1$	
 $\mathrm{HOOC{-}CH{=}CH{-}COOC_{10}H_{19}}$ mono-*l*-menthyl maleate	51,000	1960	P(Alc)	Ester shift towards red 20A	132, 133
 $\mathrm{HOOC{-}CH{=}CH{-}COOC_{10}H_{19}}$ mono-*l*-menthyl fumarate	47,700	2100	P(Alc)		
di-*l*-menthyl and sodium *l*-menthyl fumarate di-*l*-menthyl and sodium *l*-menthyl maleate					132
$\mathrm{HOOCCH{=}CHCH{=}CHCOOH}$ muconic acid				Curve (Alc) to 1800A	28, 120
C_4H_3OCOOH α-furan formic acid (pyromucic acid)				Curve (Hex) to 1850A	28, 63, 120

TABLE IV.—*Continued.*

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
$C_4H_3OCH{=}CHCOOH$ α-furan acrylic acid				Curve (Hex) to 1850A	28, 120
$C_4H_3OCH_2CH{=}CHCH_2COOH$ α-furan pentenoic-3 acid	46,000	2180	*P*(Hex)	log $\epsilon=4.0$ Curve to 1850A	
$C_4H_3O(CH{=}CH)_2COOH$ α-furan pentadienoic acid				Curve to 1850A	
$C_4H_3OCH_2(CH{=}CH)_2CH_2COOH$ α-furan heptadienoic-3,5 acid	43,500	2300	*P*(Hex)	log $\epsilon=4.4$ Curve to 1850A	
$C_4H_3O(CH{=}CH)_3COOH$ α-furan heptatrienoic acid				Curve to 1850A	
$C_4H_2O(COOH)_2$ α,α′-furan dicarboxylic acid	52,500	1900	*P*(H_2O)	log $\epsilon=4.4$ Curve to 1850A	28
$CH_2{=}CHCHO$ acrolein	50,700	1975	*R*(Hex)	log $\epsilon=4.3$ at 2080A f = .69	32, 61
$CH_3CH{=}CHCHO$ crotonaldehyde	47,000	2110	*P*(Hex)	log $\epsilon=4.2$ Curve to 1850A f = .40	28, 61, 120
$CH_3CH{=}CHCH{=}CHC(CH_3)O$ crotylidene acetone	38,000	2640	*P*(Hex)	log $\epsilon=4.3$	120
$CH_3CH{=}CHC(CH_3)O$ ethylidene acetone	46,500	2150	*P*(Hex)	log $\epsilon=4.2$	
$CH_3(CH{=}CH)_2CHO$ sorbinaldehyde				Curve (Hex) to 1850A	28
$CH_3(CH{=}CH)_3CHO$ octatrienealdehyde					
$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}$ $CHCHO$ citral	43,000 >54,000	2330 <1850	*P*(Hex) *P*(Hex)	f = .28; log $\epsilon=4.0$ log $\epsilon=4.0$ at 1850A	61, 120
$CHOCHO$ glyoxal	>45,500	<2200	*R*(Hex)	Step out about 1950A at log $\epsilon=1.6$	57, 58
$O{=}C(CH_3)(CH_3)C{=}O$ diacetyl					23, 124
$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}$ $CHCH{=}CHCOCH_3$ pseudoionone	54,000	1850	*P*(Hex)	log $\epsilon=4.1$ at 1850A	120
$(CH_3)_2C{=}CHCOCH_3$ mesityl oxide	44,500	2250	*P*(Hex) *R*	log $\epsilon=4.0$ log $\epsilon=3.6$ at 1900A	55, 67
$CH_3C({=}NOH)CH{=}C(CH_3)_2$ β-mesityl oxide oxime	42,500	2350	*P*(H_2O) *R*	log $\epsilon=3.9$ log $\epsilon=3.8$ at 1850A	55
$C_6H_8O_6$ *l*-ascorbic acid	40,800	2450	*P*(Alc)	log $\epsilon=4.0$	71
$C_{10}H_{16}O$ *p*-menthenone (piperitone)	44,500	2250	*P*(Hex) *R*	log $\epsilon=3.8$ log $\epsilon=3.5$ at 1900A	69
$C_{27}H_{42}O$ ergosterol	51,200	1950	*P*(Hex)	log $\epsilon=4.2$	68
$C_{27}H_{44}O$ calciferol	45,500 52,500	2200 1900	*P*(Hex) *P*	log $\epsilon=4.2$ log $\epsilon=4.4$	

TABLE V. Aromatic compounds.

Theory: (25, 50, 124).

Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
C_6H_6 benzene C_6D_6 deuterobenzene					9, 11, 13, 17, 26, 31, 40, 63, 81, 87, 99, 104, 111, 118, 123, 124, 127, 128
$C_6H_5C_6H_5$ diphenyl					11, 124
$C_6H_5C_2H_5$ ethyl benzene	48,600	2060	*P*(Cyclohex)	$\log \epsilon = 4.5$	121
$C_6H_5CH{=}CH_2$ styrene	41,000 49,500	2450 2030	*P*(Hex) *P*(Hex)	$\log \epsilon = 4.2$ $\log \epsilon = 4.4$	120, 121
$C_6H_5CH{=}CHCH{=}CH_2$ phenyl butadiene	36,000 47,500 $>50{,}000$	2800 2100 <2000	*P*(Hex) *P*(Hex) *R*	$\log \epsilon = 4.3$ $\log \epsilon = 4.2$ $\log \epsilon = 4.2$ at 1850A	120
$C_6H_5NH_2$ aniline	50,500	1980	*P*(MeOH)	$\log \epsilon = 4.3$	56, 124
$C_6H_5N(CH_3)H$ monomethyl aniline	50,300	1990	*P*(MeOH)	$\log \epsilon = 4.2$	56
$C_6H_5N(CH_3)_2$ dimethyl aniline	50,000	2000	*P*(MeOH)	$\log \epsilon = 4.2$	
$C_6H_5CH_2COC_6H_5$ desoxybenzoin				Step out at 2050A $\log \epsilon = 4.4$ at 1950A	55
$(C_6H_5)_2CO$ benzophenone			*R*(Alc)	$\log \epsilon = 4.7$ at 1900A	
$C_6H_5COCH_2Cl$ α-chloroacetophenone	40,700 50,500	2460 1980	*P*(Hex) *P*	$\log \epsilon = 3.9$ $\log \epsilon = 4.2$	74, 75
$C_6H_5COCH_2Br$ α-bromoacetophenone	40,000 50,800	2500 1970	*P*(Hex) *P*	$\log \epsilon = 4.1$ $\log \epsilon = 4.5$	
$(C_6H_5CH_2)_2C{=}NOH$ dibenzyl ketoxime	52,500	1900	*P*(Alc)	$\log \epsilon = 5.0$	55
$C_6H_5CH_2OH$ benzyl alcohol					43, 124
$C_6H_5(CH_2)_2OH$ β-phenyl ethyl alcohol					
$C_6H_5(CH_2)_3OH$ γ-phenyl propyl alcohol					
$C_6H_4(C_3H_7)CH_2OH$ propyl benzyl alcohol					
$C_6H_5CH_2COCH_3$ phenyl acetone			*R*(Alc)	$\log \epsilon = 4.7$ at 1900A Step-out at 2100A	55
$(C_6H_5CH_2)_2CO$ dibenzyl ketone			*R*(Alc)	$\log \epsilon = 5.0$ at 1900A	
$C_6H_5CH_2Cl$ benzyl chloride					43, 124
$C_6H_5CH_2Br$ benzyl bromide					43, 74, 75, 124
$CH_3C_6H_4CH_2Br$ xylyl bromide	~47,200 50,200	~2330 1990	*P*(Hex) *P*	$\log \epsilon = 3.7$ $\log \epsilon = 4.4$	74, 75
$C_6H_5CHBrCN$ α-bromobenzyl cyanide	41,300	2420	*P*(Hex) *R*	$\log \epsilon = 3.7$ $\log \epsilon = 4.4$ at 1850A	

TABLE V.—*Continued.*

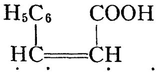
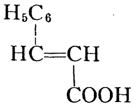
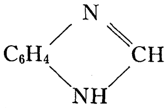
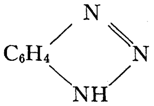
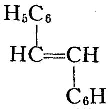
Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
$C_6H_5CH_2CN$ benzyl cyanide					43, 124
$C_6H_5C(CH_3)O$ acetophenone	41,800 to 43,650	2390 to 2290	*B*		45, 55
	50,150	1995	*B*		
	51,070	1960	*B*		
$C_6H_5COOCH_3$ methyl benzoate	43,650 to 46,050	2290 to 2170	*B*		45
	48,000	2080	*B*		
	48,850	2040	*B*		
C_6H_4OHCHO salicylic aldehyde					43, 124
 $\overset{H_5C_6}{HC}{=}\overset{COOH}{CH}$ *cis*-cinnamic acid				*Trans* compounds show two peaks at 2250A and 2000A *Cis* compounds show only step-outs in these regions.	119, 120
 $\overset{H_5C_6}{HC}{=}\underset{COOH}{CH}$ *trans*-cinnamic acid					
sodium *cis*-cinnamate					
sodium *trans*-cinnamate					
$C_6H_5(CH{=}CH)_2COOH$ phenyl pentadienoic acid	44,500	2250	*P*(Alc)	log $\epsilon=3.9$	120
	>46,500	<2150	*R*	log $\epsilon=4.0$ at 1950A	
$C_6H_5(CH{=}CH)_3COOH$ phenyl heptatrienoic acid	42,500	2350	*P*(Alc)	log $\epsilon=3.7$	
	>45,500	<2200	*R*	log $\epsilon=4.2$ at 1950A	
$C_6H_5CONH_2$ benzamide	44,500	2250	*P*(MeOH)	log $\epsilon=3.9$	56
	>48,000	<2080	*R*	log $\epsilon=4.6$ at 1900A	
$C_6H_5CON(CH_3)H$ methyl benzamide	44,500	2250	*P*(MeOH)	log $\epsilon=4.0$	
	>48,000	<2080	*R*	log $\epsilon=4.8$ at 1900A	
$C_6H_5CON(CH_3)_2$ dimethyl benzamide			*R*(MeOH)	log $\epsilon=4.3$ at 1900A Step-out $\sim$2200A	
$C_6H_5C(OC_2H_5){=}NH$ benziminoethyl ether	43,500	2300	*P*(MeOH)	log $\epsilon=4.0$	
	>47,000	<2120	*R*	log $\epsilon=4.6$ at 1900A	
 benzimidazol	50,000	2000	*P*(MeOH)	log $\epsilon=4.3$	
 benzotriazol	50,500	1980	*P*(MeOH)	log $\epsilon=4.4$	
 $\overset{H_5C_6}{HC}{=}\underset{C_6H_5}{CH}$ *trans*-stilbene	43,300	2260	*P*	*Trans* compounds show two peaks in these regions.	17, 119
	50,000	2000	*P*		

Table V.—*Continued.*

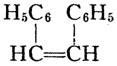
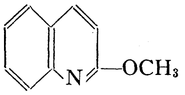
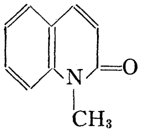
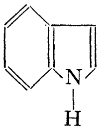
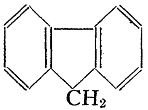
Molecule	Spectral region		Characteristics of transition	Remarks	Lit.
	cm^{-1}	A			
 $\underset{HC=CH}{\overset{H_5C_6\ \ C_6H_5}{|\ \ \ \ \ \ |}}$ *cis*-stilbene				*Cis* compounds show only step-outs.	17, 119
$C_6H_5(CH=CH)_2C_6H_5$ diphenyl butadiene				Curve to 1930A	17
$C_{18}H_{12}$ triphenylene	52,500	1900	*P*(Hex)	log $\epsilon=4.6$	72
$C_{21}H_{14}$ 1,2,3,4-dibenzofluorene	46,400	2150	*P*(Hex) *R*	log $\epsilon=4.3$ log $\epsilon=4.5$ at 1900A	
$C_{21}H_{16}$ cyclopentenotriphenylene	51,000	1960	*P*(Hex)	log $\epsilon=4.6$	
$C_{17}H_{12}$ cyclopentenophenanthrene-2,3	46,400	2150	*P*(Hex) *R*	log $\epsilon=4.4$ log $\epsilon=4.4$ at 1900A	
$C_6H_5CH_2CH=CHCH_2C_6H_5$ dibenzyl ethylene	>45,500	<2200	*R*(Hex)	log $\epsilon=4.5$ at 1950A	120
$C_6H_5CH_2(CH=CH)_2CH_2C_6H_5$ dibenzyl butadiene	42,500 >46,500	2350 <2150	*P*(Hex) *R*	log $\epsilon=4.4$ log $\epsilon=4.4$ at 1950A	
$C_6H_5CH_2(CH=CH)_3CH_2C_6H_5$ dibenzyl hexatriene	37,000 >42,500	2700 <2350	*P*(Hex) *R*	log $\epsilon=4.5$ log $\epsilon=4.2$ at 1950A	
$C_6H_5CH=CH[CH(OH)]_2CH=CHC_6H_5$ hydrocinnamoin	39,200 48,700	2560 2050	*P*(Alc) *P*	log $\epsilon=4.4$ log $\epsilon=4.5$	
$C_6H_5NHC(CH_3)=NC_6H_5$ diphenyl acetamidine	>43,500	<2300	*R*(MeOH)	log $\epsilon=4.7$ at 1900A	56
C_9H_7NO carbostyril	45,500	2200	*P*(MeOH)	log $\epsilon=4.6$	
 carbostyril-O-methyl ester	46,500	2150	*P*(MeOH)	log $\epsilon=4.4$	
 carbostyril-*N*-methyl ester	46,300	2160	*P*(MeOH)	log $\epsilon=4.6$	
 indole	46,600 >48,800	2150 <2050	*P*(Hex) *R*	log $\epsilon=4.4$ log $\epsilon=4.3$ at 1950A	63
 fluorene	48,800 >50,500	2050 <1980	*P*(Hex) *R*	log $\epsilon=4.6$ log $\epsilon=4.5$ at 1950A	63, 72
$C_{10}H_8$ naphthalene	47,900 46,700	2090 2140	*P* *P*		127
$(C_6H_5)_2AsCl$ diphenyl chloroarsine (Clark I)			*R*(Hex)	log $\epsilon=4.0$ at 2000A	73, 75

TABLE V.—*Continued.*

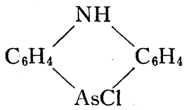
Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
$(C_6H_5)_2AsCN$ diphenyl cyanoarsine			*R*(Hex)	log $\epsilon = 5.2$ at 2000A	73, 75
 phenarsazinchloride (Adamsite)	45,500 50,500	2200 1980	*P*(Hex) *P*	log $\epsilon = 4.9$ log $\epsilon = 5.2$	

TABLE VI. Miscellaneous compounds.

Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
CO carbon monoxide					30, 123
CO_2 carbon dioxide					30, 48, 103, 108, 123, 124
COS carbonyl sulfide					103, 124
CS_2 carbon disulfide					27, 97, 102, 123, 124
$O=S(CH_2CH_2Cl)_2$ dichlorodiethyl sulfoxide	44,500 50,000	2250 2000	*P*(Alc) *P*	log $\epsilon = 3.1$ log $\epsilon = 3.5$	70
$O_2S(CH_2CH_2Cl)_2$ dichlorodiethyl sulfone			*R*(Alc)	log $\epsilon = 2.6$ at 1950A	
$CH_2{=}C{=}CHC_2H_5$ ethyl allene	40,000 to 62,000	2500 to 1610	*B*+*C*		15
$CH_3CH{=}C{=}CHCH_3$ dimethyl allene				No details, similar to ethyl allene.	16
$CH{\equiv}CH$ acetylene $CD{\equiv}CD$ deuteroacetylene					29, 38, 40, 46, 80, 94, 111, 123, 124, 126, 128
C_4H_2 diacetylene					123, 124, 135
$HC{\equiv}C(CH_2)_2C{\equiv}CH$ dipropargyl	41,000 49,800	2450 2010	*P* *P*		126, 128
HCN hydrogen cyanide					41, 95, 123
C_2N_2 cyanogen					78, 124, 134
KCN potassium cyanide	>46,000	<2175	*C*	KCN at 875°C.	131
CH_3CN methyl cyanide	55,600 to 64,500 60,700 67,000	1800 to 1550 1650 1500	*C* *P* *C*		37, 43

TABLE VI.—*Continued.*

Molecule	Spectral region cm^{-1}	A	Characteristics of transition	Remarks	Lit.
C_2H_5CN ethyl cyanide					43, 123
ICN iodocyanogen					5, 44, 78, 124
BrCN bromocyanogen					
ClCN chlorocyanogen					
$ClCH_2CN$ chloromethyl cyanide					43
CH_2CNCH_2OH ethylene cyanohydrin					43, 124

V. BIBLIOGRAPHY OF EXPERIMENTAL ORGANIC STUDIES BELOW 2000A.

V = vapor; S = solution; figures indicate lower wave-length limit of study in A; L = wave-length list; L_a = absorption limit only; R = reproduction of spectrum; C = absorption curve; N = no intensity estimate; E = visual estimate; P = order-of-magnitude photometry; A = absolute extinction values. Wave-length limit larger than 1840 indicates quartz spectrograph in air; lower than 1530 indicates vacuum grating spectrograph with Lyman source.

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S (cyclohexane) 1850 C L A, cyclohexene, 1,3-cyclohexadiene.

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S 1850 L N, phenylalanine, tyrosine, tryptophane, histidine.

3. G. A. Anslow, J. Appl. Phys. **16**, 41 (1945);
Review of organic spectra, especially proteins and vitamins in the near ultraviolet.

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V 1860 C, cyclopropane, propylene.

4A. R. K. Asundi, C. M. Bhaskar-Rao, and R. Samuel, Proc. Ind. Acad. Sci. **1A**, 54 (1935);
V 1500 C L, carbon monoxide, mercury dimethyl, mercury diethyl, phenyl mercury chloride, mercury diphenyl, ethyl mercury chloride.

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V 1900 L, iodocyanogen, bromocyanogen, chlorocyanogen.

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V 600 L, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol.

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V 600 L, methyl alcohol, allyl alcohol.

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S (alcohol, water) 1860 C A, acetic acid.

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V 1530 L N, *n*-hexane, *n*-heptane, 1-pentene, 2-pentene, 1-heptene, trimethylethylene, benzene.

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V 1600 C E, *n*-heptene-3, tetramethylethylene.

11. E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936)
V 1600 C L E, butene-1, *cis*-butene-2, *trans*-butene-2, *iso*-butene, pentene-1, pentene-2, *iso*-propyl ethylene, hexene-3, heptene-1, heptene-3, unsym. methyl ethyl ethylene, trimethylethylene, diethylmethylethylene, tetramethylethylene, di-*iso*-butylene-I, di-*iso*-butylene-II, benzene, diphenyl.

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V 1850 C E, *cis*-butene-2, *trans*-butene-2, *cis*-pentene-2, *trans*-pentene-2, *n*-hexene-3, *n*-heptene-3.

13. E. P. Carr and H. Stücklen, J. Chem. Phys. **6**, 55 (1938);
V 1650 C L R E, cyclopentene, cyclopentadiene, cyclohexene, 1,3-cyclohexadiene, benzene.

14. E. P. Carr and H. Stücklen, J. Chem. Phys. **7**, 631 L (1939).
Assignment of ethylene bands.

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1,3-pentadiene, ethyl allene, diallyl.

16. E. P. Carr, L. W. Pickett, and H. Stücklen, Rev. Mod. Phys. **14**, 260 (1942);
V 1700 C E, butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,4-hexadiene, 2-methyl-2,4-hexadiene, 2,5-dimethyl-2,4-hexadiene, dimethyl allene.

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S (hexane) 1930 C A, diphenyl ethylene, benzene, diphenyl butadiene.

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Classical theory of dielectric solvent effect on bands.

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V 1000 L N, methane.

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V 850 L E, acetone.

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V 800 L E, methyl ethyl ketone.

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V 800 L N, methyl *n*-propyl ketone, methyl *iso*-propyl ketone, diethyl ketone.

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V 1600 L E, diacetyl.

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V 1900 C A, methyl bromide.

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Computation of energies of first excited states of several aromatics.

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Calculation of position of first excited states in benzene.

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S (hexane, alcohol) 1850 C L A, crotonaldehyde, sorbinaldehyde, octatrienealdehyde, α-crotonic acid, sorbic acid, decatetrenoic acid, muconic acid, α-furan formic acid, α-furan acrylic acid, α-furan pentenoic-3-acid, α-furan heptatrienoic acid, α-furan heptadienoic-3,5-acid, α,α′furandicarboxylic acid.

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Bond strength and potential energy relationships in acetylene.

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V 600 (long limit 900) R L, carbon monoxide, carbon dioxide.

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S (pentane) 1940 C A, benzene.

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Compilation of organic solution data, principally in the quartz region.

33. V. Henri and L. W. Pickett, J. Chem. Phys. **7**, 439 (1939);
V S (hexane) 2200 C L A, 1,3-cyclohexadiene.

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V 1550 L N, methyl chloride, methyl bromide, methyl iodide, methylene chloride, methylene bromide, methylene iodide, chloroform, bromoform, iodoform, carbon tetrachloride, carbon tetrabromide.

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V 1960 L E, methyl iodide.

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V 1950 L P, ethyl iodide.

37. G. Herzberg and G. Scheibe, Trans. Faraday Soc. **25**, 716 (1929); Zeits. f. physik. Chemie **B7**, 390 (1930);
V 1550 L R C P, methyl alcohol, ethyl alcohol, methyl chloride, methyl bromide, methyl iodide, methyl cyanide.

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V 1600 L N, formaldehyde, acetylene.

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Theory of methyl iodide and formaldehyde; symmetry properties of polyatomic molecules.

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V 1300 L R N, methane, benzene, acetylene.

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V 1300 L, hydrogen cyanide, ethylene.

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Photodecomposition of acetone.

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V 1900 L R, acetophenone, methyl benzoate.

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V 1900 L, acetylene.

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Energy levels of conjugated double bond systems.

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V 1600 C L N, acetone, deuteroacetone.

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V 1200 R N, methane, ethyl alcohol, carbon tetrachloride, carbon dioxide.

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Theory and computations of bond energies and lengths in conjugated double bond systems.

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Theoretical computations of bond energies and lengths in aromatic molecules.

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S (water) 1850 C A, acetic acid, ethyl acetate, sodium acetate.

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S (hexane, water) 1800 C A, acetone.

53. H. Ley and B. Arends, Zeits. f. physik. Chemie **B15**, 311 (1931);
S (water, alcohol) 1850 C L A, ethyl mercaptan, sodium ethylmercaptide, diethyl sulfide, diethyl disulfide, triethylsulfonium chloride.

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S (water, alcohol, hexane) 1800 C L A, formic acid, sodium formate, acetic acid, ethyl acetate, sodium acetate, butyric acid, palmitic acid, dimethyl carbonate, sodium bicarbonate, oxalic acid, disodium oxalate, dimethyl oxalate, succinic acid, disodium succinate, acetyl chloride, acetic anhydride, diethyl disulfide, diethyl amine, diethyl amine hydrochloride, acetamide, urea, urethan, piperidine, piperidine hydrochloride, piperidoacetic acid, sodium piperidoacetate, glycine, sodium glycinate, glycine hydrochloride, alanine, sodium alaninate, alanine hydrochloride, valine, leucine, proline, hydroxyproline, sodium hydroxyprolinate, sodium cystinate, cystine hydrochloride.

55. H. Ley and H. Wingchen, Ber. d. D. Chem. Ges. **67**, 501 (1934);
S (alcohol, hexane, water) 1800 C L A, trimethylethylene, α-crotonic acid, maleic acid, fumaric acid, disodium maleate, disodium fumarate, acetone, phenyl acetone, dibenzyl ketone, acetophenone, desoxybenzoin, benzophenone, acetoxime, acetaldoxime, mesityl oxide, β-mesityl oxide oxime, dibenzyl ketoxime.

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S (methyl alcohol, methyl alcohol+sodium methoxide) 1930 C L A, aniline, monomethyl aniline, dimethyl aniline, benzamide, methyl benzamide, dimethyl benzamide, benziminoethyl ether, benzimidazol, benzotriazol, diphenyl acetamidine, carbostyril, carbostyril-N-methyl ester, carbostyril-O-methyl ester.

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S (alcohol, hexane) 1940 C A, trimethylethylene, glyoxal, allyl alcohol, acrylic acid.

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S (hexane) 1860 C A, glyoxal, acetaldehyde.

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Intensity computations for aldehydes and ketones.

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Intensity computations on acids, esters, and salts.

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S (hexane) 1850 C A, β,β′-dichlorodiethyl sulfide.

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S (hexane) 1850 C A, mesityl oxide.

68. H. Mohler, Helv. Chim. Acta **20**, 811 (1937);
S (hexane, alcohol) 1850 C A, decadiene-2,8, cholesterol, isoprene, ergosterol, calciferol.

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S (hexane) C L A, cyclopentanone, cyclohexanone, *l*-menthone, thujone, cyclohexene, *p*-menthenone (piperitone).

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S (alcohol, hexane) C A, diethyl sulfide, diethylene disulfide, β,β′-dichlorodiethyl sulfide, β,β′-dihydroxy diethyl sulfide, thiophene, dichlorodiethyl sulfoxide, dichlorodiethyl sulfone.

71. H. Mohler and H. Lohr, Helv. Chim. Acta **21**, 485 (1938);
S (water, alcohol) 1850 C L A, α-crotonic acid, *l*-ascorbic acid.

72. H. Mohler and J. Sorge, Helv. Chim. Acta **22**, 229 (1939);
S (hexane) 1850 C A, triphenylene, cyclopentenotriphenylene, 2,3-cyclopentenophenanthrene, fluorene, 1,2,3,4-dibenzofluorene, methyl benzopyrene, 7-methyl naphthafluorene, dihydrochrysene.

73. H. Mohler and J. Sorge, Helv. Chim. Acta **22**, 235 (1939);
S (hexane) 1850 C L A, methyl chloroformate, chloropicrin, diphosgene, β-chlorovinyl dichloroarsine (Lewisite I), β,β′-dichlorodivinyl chloroarsine (Lewisite II), β,β′,β″-trichlorotrivinyl arsine (Lewisite III), diphenyl chloroarsine (Clark I), diphenyl cyanoarsine (Clark II), phenarsazin chloride (Adamsite).

74. H. Mohler and J. Sorge, Helv. Chim. Acta **23**, 100 (1940);
S (hexane) C A, acetone, bromoacetone, bromomethyl ethyl ketone, α-chloroacetophenone, α-bromo-

acetophenone, benzyl bromide, xylyl bromide, α-bromobenzyl cyanide.

75. H. Mohler and J. Sorge, Helv. Chim. Acta **23**, 104 (1940);
S (hexane) 1850 C L A, bromoacetone, bromomethyl ethyl ketone, α-chloroacetophenone, α-bromoacetophenone, benzyl bromide, xylyl bromide, α-bromobenzyl cyanide, chloropicrin, diphosgene, ethyl dichloroarsine, β-chlorovinyl dichloroarsine, β,β′-dichlorodivinyl chloroarsine, β,β′,β″-trichlorotrivinyl arsine, phenarsazin chloride, diphenyl chloroarsine, diphenyl cyanoarsine, β,β′-dichlorodiethyl sulfide.

76. H. Mohler and W. Hämmerle, Helv. Chim. Acta **23**, 1211 (1940);
S (hexane, alcohol) 1850 C A, trichlorotriethylamine, trichlorotriethylamine hydrochloride.

77. H. Mohler and J. Sorge, Helv. Chim. Acta **23**, 1200 (1940);
S (hexane, water) 1850 C L A, diethylsulfide, diethyl disulfide, diethylene disulfide, β-hydroxyethyl ethyl sulfide, β-chloroethyl ethyl sulfide, α,α′-dichlorodiethyl sulfide, β,β′-dichlorodiethyl sulfide, β,β′-dihydroxydiethyl sulfide, α-chloroethyl ethyl ether, β-chloroethyl ethyl ether, α,β-dichloroethyl ethyl ether, β,β′-dichlorodiethyl ether, α-hydroxyethyl ethyl ether, β-hydroxyethyl ethyl ether, β,β′-dihydroxydiethyl ether, furan, thiophene, divinyl sulfide.

78. R. B. Mooney and H. G. Reid, Proc. Roy. Soc. (Edinburgh) **250**, 152 (1932); Nature **128**, 271 (1931);
V 1850 L E, cyanogen, bromocyanogen, chlorocyanogen, iodocyanogen.

79. R. S. Mulliken, Phys. Rev. **41**, 751 (1932); **43**, 279 (1933).
Quantum theory of ethylenes.

80. R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933), **3**, 375, 506, 514, 517, 564, 720 (1935).
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Theory of bond integrals.

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Theory, ethylenes, butadienes; red shifts.

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Interpretation of absorption systems of benzene vapor in far ultraviolet.

88. W. A. Noyes, Jr., A. B. F. Duncan, and W. M. Manning, J. Chem. Phys. **2**, 717 (1934);
V 1250 L R E, acetone.

98. Y. P. Parti and R. Samuel, Proc. Phys. Soc. (London) **49**, 568 (1937);
V 1950 C L, methylene iodide, methylene bromide, methylene chloride, iodoform, bromoform, chloroform, carbon tetraiodide, carbon tetrabromide, carbon tetrachloride.

90. L. W. Pickett, J. Chem. Phys. **8**, 293 (1940);
V 1600 C L A, furan.

91. L. W. Pickett, E. Paddock, and E. Sackter, J. Am. Chem. Soc. **63**, 1073 (1941);
V 1600 C L E, cyclopentadiene, dicyclopentadiene.

92. J. R. Platt, I. Rusoff, and H. B. Klevens, J. Chem. Phys. **11**, 535 (1943);
S (heptane) 1700 C A, acetic acid, butyric acid, caprylic acid, myristic acid, acetone, methyl ethyl ketone, diethyl ketone, methyl amyl ketone, methyl *n*-propyl ketone, *iso*-valeraldehyde, methyl alcohol, *n*-propyl alcohol, *n*-butyl alchol, *sec*-butyl alcohol, *tert*-butyl alcohol, *n*-amyl alcohol, diethyl carbinol, *sec*-octyl alcohol, di-*n*-butyl ether, octene-3. L_a, pure liquid: *n*-hexane, *n*-heptane, isooctane, methyl alcohol, ethyl alcohol, diethyl ether, acetone.

93. D. Porret and C. F. Goodeve, Proc. Roy. Soc. (London) **A165**, 31 (1938);
V 1900 C A, methyl bromide, ethyl bromide, butyl bromide.

94. W. C. Price, Phys. Rev. **45**, 843 L (1934); **47**, 444 (1935).
V 1050 R L E, ethane, ethylene, acetylene.

95. W. C. Price, Phys. Rev. **46**, 529 L (1934);
V 1150 N, formaldehyde, hydrogen cyanide.

96. W. C. Price, Phys. Rev. **47**, 510 L (1935), J. Chem. Phys. **4**, 539 (1936);
V 1000 L R N, methyl chloride, methyl bromide, methyl iodide.

97. W. C. Price, Phys. Rev. **47**, 788 A (1935);
V 1000, carbon disulfide.

98. W. C. Price, J. Chem. Phys. **3**, 256 (1935);
V 1000 R N, methyl alcohol, formaldehyde, diethyl ether, ethyl mercaptan, *n*-propyl mercaptan, *iso*-propyl mercaptan, *n*-butyl mercaptan, diethyl sulfide, di-*n*-propyl sulfide, di-*iso*-propyl sulfide, di-*n*-butyl sulfide.

99. W. C. Price and R. W. Wood, J. Chem. Phys. **3**, 439 (1935);
V 1000 R N, benzene, deuterobenzene.

100. W. C. Price, J. Chem. Phys. **3**, 365 L (1935), **4**, 547 (1936);
V 1100 L N, ethyl chloride, *n*-propyl chloride, *iso*-propyl chloride, *n*-buty chloride, *n*-amyl chloride, ethyl bromide, *n*-butyl bromide, ethyl iodide, allyl chloride.

101. W. C. Price and W. M. Evans, Proc. Roy. Soc. (London) **A162**, 110 (1937);
V 900 L R E, formic acid.

102. W. C. Price and D. M. Simpson, Proc. Roy. Soc. (London) **A165**, 272 (1938);
V 1000 R L N, carbon disulfide.

103. W. C. Price and D. M. Simpson, Proc. Roy. Soc. (London) **A169**, 501 (1938);
V 1000 R L N, carbon dioxide, carbonyl sulfide.

104. W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London) **A174**, 207 (1940);
V 1000 R N, ethylene, deuteroethylenes, propylene, *trans*-butene-2, trimethylethylene, tetramethylethylene, cyclohexene, benzene.

105. W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) **A174**, 220 (1940);
V 900 R N, butadiene, isoprene, 2,3-dimethyl butadiene, chloroprene.

106. W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) **A179**, 201 (1941);
V 900 R L E, cyclopentadiene, cyclohexadiene, pyrrole, thiophene, furan.

107. C. M. B. Rao and R. Samuel, Curr. Sci. **3**, 549 (1935);
trichloroacetyl chloride.

108. G. Rathenau, Zeits. f. Physik **87**, 32 (1934);
V 270 R L, carbon dioxide.

109. F. Riedel, Diss. Erlangen, 1928;
S 1850 P, trimethylethylene, allyl alcohol, diallyl.

110. I. Rusoff, J. R. Platt, H. B. Klevens, and G. O. Burr, J. Am. Chem. Soc. **67**, 673 (1945);
S (heptane) 1700 C A, acetic acid, butyric acid, caprylic acid, myristic acid, methyl myristate, oleic acid-9 (*cis*), ethyl oleate-9 (*cis*), elaidic acid-9 (*trans*), linoleic acid-9,12 (*cis, cis*), ethyl linoleate-9, 12 (*cis, cis*), linolenic acid-9,12,15, ethyl linolenate-9,12,15, ethyl elaidolinolenate-9,12,15, methyl arachidonate-5,8,11,14, α-crotonic acid, α-heptadecenoic acid, octadecadienoic acid-9,11, octadecadienoic acid-10,12, pseudoeleosteric acid-10, 12, 14.

111. J. Savard, J. de phys. et rad. **5**, 27 (1934).
Discussion of V_i for methane, ethylene, acetylene, benzene.

112. G. Scheibe and R. Pummerer, Ber. d. D. Chem. Ges. **60**, 2163 (1927);
S (hexahydrotoluol) 1850 C A L, isoprene, trimethyl ethylene, diallyl.

113. G. Scheibe and C. F. Linström, Zeits. f. physik. Chemie **B12**, 387 (1931);
V 1600 N, acetone.

114. G. Scheibe, F. Povenz, and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933);
V 1650 C L A, formic acid, methyl formate, acetic acid, methyl acetate, ethyl acetate, acetone, hexamethyl acetone, acetaldehyde, acetic anhydride, methyl iodide, ethyl iodide, *tert*-butyl iodide, *n*-butyl chloride, diethyl carbonate.

115. G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934);
V 1550 C P, methane, ethane, cyclohexane, dimethyl ether, diethyl ether, ethylene, butadiene, tetrachloroethylene, cyclopentadiene, cyclopentanone, cyclohexanone, pyrrole.

116. G. Scheibe, Zeits. f. physik. Chemie **B30**, 1 (1935);
V 1650 C P, methyl iodide.

117. S. A. Schou, Comptes rendus **184**, 1452 (1927);
S (water) 1950 C A, acetaldehyde, paraldehyde.

118. A. L. Sklar, J. Chem. Phys. **5**, 669 (1937).
Calculation of first excited states in benzene, cyclohexadiene and butadiene.

119. A. Smakula and A. Wassermann, Zeits. f. physik. Chemie **A155**, 353 (1931);
S (water, alcohol, hexane) 1850 C L A, *cis*-stilbene, *trans*-stilbene, *cis*-cinnamic acid, *trans*-cinnamic acid, sodium *cis*-cinnamate, sodium *trans*-cinnamate.

120. A. Smakula, Angew. Chem. **47**, 657 (1934);
S (alcohol, hexane) 1850 C A, butadiene, isoprene, 2,3-dimethyl butadiene, α-crotonic acid, sorbic acid, β-methyl sorbic acid, vinyl acrylic acid, octadienoic acid, octatrienoic acid, β-methyl octatrienoic acid, decatrienoic acid, muconic acid, fumaric acid, glutaconic acid, dihydromucunic acid, crotonaldehyde, citral, pseudoionone, ethylidene acetone, crotylidene acetone, pyromucic acid, α-furan acrylic acid, α-furan pentenoic-3 acid, α-furan pentadienoic acid, α-furan heptadienoic acid, α-furan heptatrienoic acid, cinnamic acid, phenyl pentadienoic acid, phenyl heptatrienoic acid, styrene, hydrocinnamoin, phenyl butadiene, dibenzyl ethylene, α,β,-dibenzyl butadiene, dibenzyl hexatriene.

121. A. Smakula, Angew. Chem. **47**, 777 (1934);
S (cyclohexane) 1850 C L A, ethyl benzene, styrene.

122. C. P. Snow and C. B. Allsopp, Trans. Faraday Soc. **30**, 93 (1934);
S (cyclohexane) 1850 C A; V 1850 C E, ethylene, trimethylethylene, cyclohexene.

123. H. Sponer, *Molekülspektren*, Vol. I (Tables), Vol. II (Text), (Julius Springer, Berlin, 1935, 1936).
Theory of molecular spectra, and bibliography and tables of spectra.

124. H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 75 (1941).
Theory of electronic spectra of polyatomic molecules, emphasizing methane derivatives and benzene derivatives; tables of compounds and bibliography.

125. J. Stark, W. Steubing, C. J. Enklaar, and P. Lipp, Jahr. Radioakt. Electronik **10**, 139 (1913);
V 1850 C P, *n*-hexane, cyclohexane, camphane, ethylene, octene-1, hexene-2, *iso*-butene, trimethylethylene, diallyl, isoprene, 1,1-dimethyl butadiene, 2,3-dimethyl butadiene, 2,4-hexadiene, camphene, bornylene, geraniolene, dimethyl fulvene, *d*-limonene, *d*-sylvestrene, α-pinene, α-phellandrene, β-phellandrene.

126. J. Stark and P. Lipp, Jahr. Radioakt. Elektronik **10**, 175 (1913);
V 1850 C P, acetylene, dipropargyl.

127. J. Stark and P. Levy, Jahr. Radioakt. Elektronik **10**, 179 (1913);
V 1850 C P, benzene, naphthalene, cyclohexene, cyclohexadiene.

128. J. Stark and P. Lipp, Zeits. f. physik. Chemie **86**, 36 (1913);
V 1850 C P, ethylene, *iso*-butene, isoprene, 2,4-hexadiene, acetylene, dipropargyl, benzene.

129. M. M. Stimson and M. A. Reuter, Inst. Divi Thomae **3**, 167 (1941).
Review of observed spectra, especially in the near ultraviolet.

130. A. Terenin and N. Prileshajewa, J. Chem. Phys. **2**, 441 L (1934) and Acta Physicochimica **1**, 759 (1935);
V 1850 R L (Photodissociation), mercury dimethyl, methyl mercury iodide.

131. D. S. Villars, J. Am. Chem. Soc. **53**, 405 (1931);
V 1950 P, potassium cyanide.

132. A. Wassermann and A. Smakula, Zeits. f. physik. Chemie **A155**, 366 (1931);
S (water, alcohol, hexane) 1850 C L A, maleic acid, maleic anhydride, mono-sodium maleate, di-sodium maleate, mono-*l*-menthyl maleate, di-*l*-menthyl maleate, sodium *l*-menthyl maleate, fumaric acid, mono-sodium fumarate, di-sodium fumarate, mono-*l*-menthyl fumarate, di-*l*-menthyl fumarate, sodium *l*-menthyl fumarate, dimethyl maleate, dimethyl fumarate.

133. A. Wassermann, Lieb. Ann. **488**, 211 (1931);
S (water, alcohol, hexane) 1850 C L A, mono-*l*-menthyl maleate, mono-*l*-menthyl fumarate.

134. S. C. Woo and R. M. Badger, Phys. Rev. **39**, 932 (1932);
V 1800 L R P, cyanogen.

135. S. C. Woo and T. C. Chu, Phys. Rev. **47**, 886 L (1935); J. Chem. Phys. **3**, 541 (1935);
V 1900 L E, diacetylene.

136. H. Zeise, Zeits. f. Elektrochemie **47**, 380, 595, 644 (1941); **48**, 425, 476 (1942).
Calculation of free energy, entropy, specific heat, and equilibrium, from spectroscopic data.

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140. J. C. Boyce, Rev. Mod. Phys. **13**, 1 (1941).
141. W. R. Brode, *Chemical Spectroscopy* (John Wiley and Sons, Inc., New York, 1944), 2nd Ed.
142. G. B. Collins and W. C. Price, Rev. Sci. Inst. **5**, 423 (1934).
143. S. Freed, H. L. McMurry and E. J. Rosenbaum, J. Chem. Phys. **7**, 853 L (1939).
144. G. R. Harrison and P. A. Leighton, J. Opt. Soc. Am. **20**, 313 (1930).
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146. R. Ladenburg and C. C. Van Voorhis, Phys. Rev. **43**, 315 (1933).
147. J. R. Platt, H. E. Clark, A. A. Cohen, and P. A. Caldwell, Rev. Sci. Inst. **14**, 85 (1943).
148. R. W. Pohl, Naturwiss. **15**, 433 (1927).
149. W. M. Powell, Jr., Phys. Rev. **45**, 154 (1934).
150. G. Scheibe, Zeits. f. physik Chemie **B5**, 355 (1929).

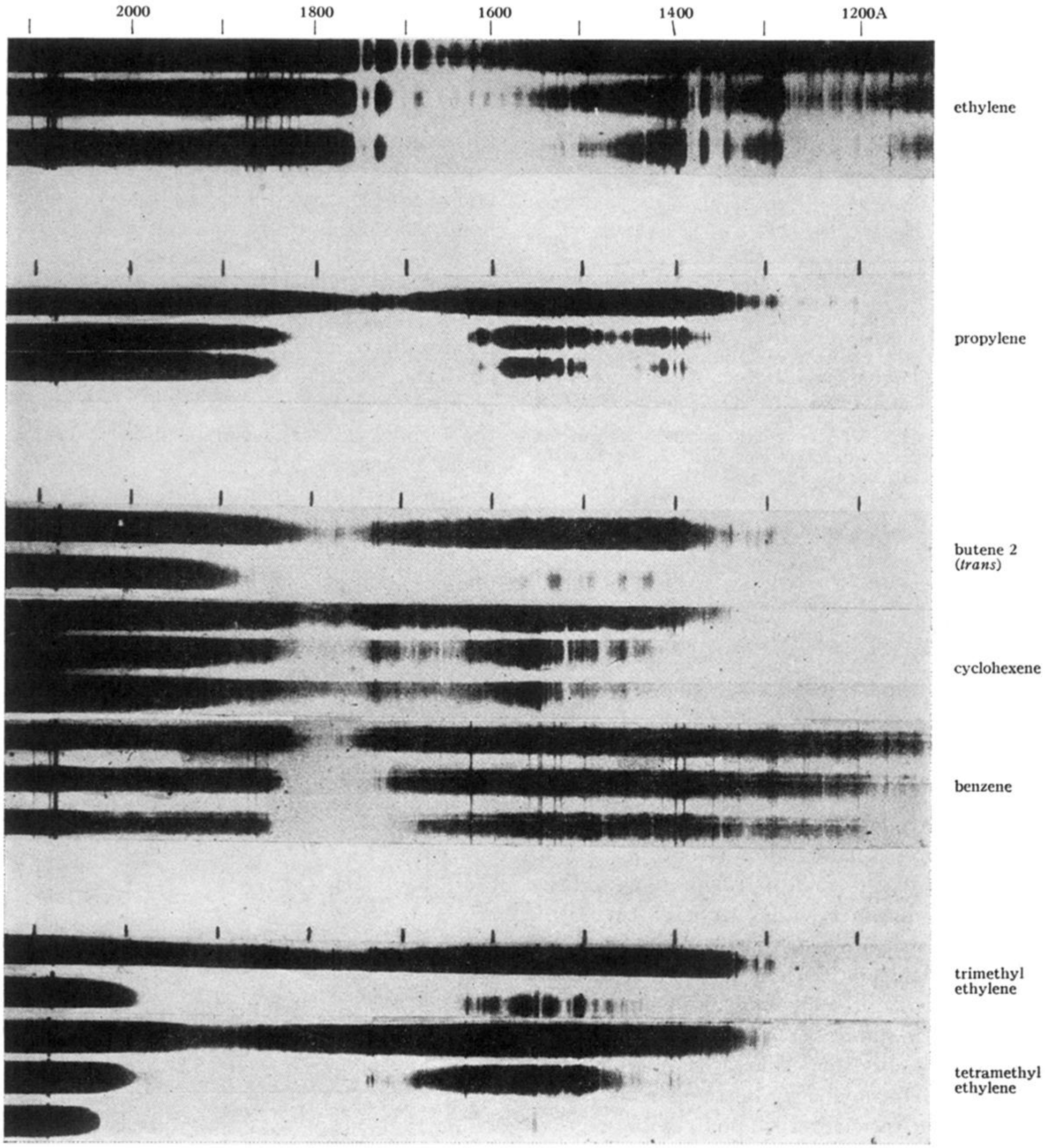

FIG. 5. Vapor spectra of ethylenes (104).