[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND CHEMISTRY OF OHIO STATE UNIVERSITY]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN

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RECEIVED MARCH 2, 1927 PUBLISHED MAY 10, 1927

Introduction

The recent developments in the theory of band spectra make it possible to understand the general mechanism of all absorption phenomena so that the study of the absorption spectrum of a vapor gives knowledge of the movements and structure of the molecules contained therein. In view of this fact, data on the absorption of light by vapors give valuable information concerning the properties and behavior of the molecules of the compound. Henri and his co-workers[2] have studied the absorption of light in the ultraviolet region of the spectrum in a number of organic vapors. They have been able to show that many of these absorption spectra consist of a certain number of groups, each group being made up of a series of bands and each band consisting of a certain number of fine and closely spaced lines. From these results conclusions can be drawn concerning the moment of inertia of the molecules and the effect of different substituents on the arrangement of the electrons, on the vibratory motion of the atoms or groups of atoms and on the rotation of the molecule about one or more of its axes.

In some cases it has been found possible to express the wave lengths of these band systems by means of equations formulated according to the modern theory of band spectra. In benzene four systems of such band spectra were located, each with a different origin. It is important to determine the groups of atoms from which these series of bands originate and the way in which they are influenced by changes in the constitution of the organic molecule.

Helen L. Wikoff[3] and Arthur J. Yaney,[4] working with dilute alcoholic solutions or thin films of the pure liquids, have shown that cyclohexene, ethyl ether and methyl-*n*-amyl ether give banded absorption patterns

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[2] (a) Henri, *J. phys. radium*, [6] 3, 181 (1922). (b) Henri and de Laszlo, *Proc. Roy. Soc.*, **105A**, 662 (1924). (c) de Laszlo, *Proc. Roy. Soc.*, **111A**, 355 (1926).

[3] Wikoff, Dissertation, Ohio State University, **1924**. Reported before the Organic Division, American Chemical Society, at Ithaca, September, 1924 [*Science*, **60**, 436 (1924)].

[4] Yaney, *Dissertation*, Ohio State University, **1925**. Reported before the Organic Division, American Chemical Society, at Baltimore, April, 1925 [*Science*, **61**, 496 (1925)].

in the ultraviolet region, similar to that of benzene. It seemed desirable, therefore, to photograph the ultraviolet absorption of these compounds through the vapors in order to determine what band systems are involved and whether they are identical with those characteristic of benzene. It should be pointed out that cyclohexene is closely related to benzene while ethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin differ widely from it in molecular structure.

Experimental Method

Source of Light.—An under-water spark between aluminum electrodes in distilled water was used as a source of continuous radiation. A condenser (Fig. 1) was charged by means of a 20-kv., 2.5-kw. Thordarson transformer and then discharged through an auxiliary spark gap and the under-water spark in series. To insure an abrupt discharge, compressed air was forced between the terminals of the auxiliary spark gap. The primary of the transformer was connected to the 60-cycle, 110-v. mains. The aluminum electrodes used in the under-water spark were cylindrical rods about 0.45 cm. in diameter, and the length of the under-water spark gap was 1 or 2 mm. The ends of the aluminum rods between which the sparks passed were wedge-shaped in order to localize the discharge so far as possible and to prevent it from shifting away from the axis of collimation. Suitable values of the capacity were chosen to give a discharge of high frequency and satisfactory intensity. The radiation from this source was continuous except for a few arc lines of aluminum which appeared as absorption lines in the under-water spark.

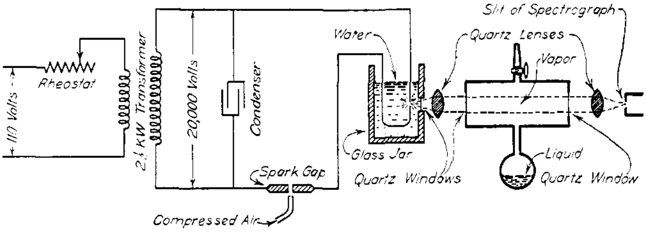

Fig. 1.

Spectrograph.—The radiation from the under-water spark passed directly through the quartz window in the side of the glass jar and then through two quartz lenses by means of which it was brought to a focus on the slit of a Hilger E_2 spectrograph with which the spectra were photographed. This instrument is provided with a quartz Cornu prism 41 mm. high, having a length of face of 65 mm. and with two lenses of focal length 61 cm. The length of the spectrum between 2700 and 2300 Å. is 52 mm.

Absorption Cells.—The vapors to be studied were introduced into the absorption cells (Fig. 1) which consisted essentially of cylindrical glass tubes 3.5 cm. in diameter, provided with quartz windows through which the radiation passed. The length of the cells was so chosen that the column of vapor would produce the proper amount of absorption to give a satisfactory definition of the absorption bands. In the course of the experiments cells with the following lengths were used: 2.5 cm., 10 cm., 30 cm. and 90 cm. A spherical bulb as indicated in Fig. 1 was sealed to the cylindrical cell. The liquid, the vapor of which was to be investigated, was introduced into this bulb. This saturated vapor filled the entire space above the liquid. The pressure of the vapor was controlled by regulating the temperature of the liquid in the bulb. The vapor pressures were so chosen that the column of vapor produced bands of suitable intensity and definition in the region of the spectrum being investigated.

Method of Observation.—After a suitable length of column of vapor and a suitable pressure of vapor in the tube had been found by experiment, a series of exposures was made through the column of vapor. The photograph in which the absorption bands were most sharply defined was chosen and the positions of the heads of the bands were measured on a comparator. The bands were shaded toward the red end of the spectrum. In measuring the positions of the bands, the cross wire of the micrometer microscope was set on the sharply defined head of the band which was always towards the violet end of the spectrum. A comparison spectrum from a copper arc was used to calibrate the wave-length scale and also to furnish the necessary reference lines for the measurement of the absorption bands. Except for a few bands which were too diffuse and indistinct for accurate measurement, the heads of the absorption bands could be measured with an accuracy of 0.1 Å.

In order to determine intensities of the different absorption bands, they were analyzed by means of a Moll microphotometer. This instrument gives a photographic record of the blackening of the photographic plate and hence, except for variation in the sensitivity of the plate, a direct measure of the intensities of the absorption bands.

Sources and Purities of Compounds

The compounds used in this investigation were carefully purified by fractional distillation. The original sources and physical characteristics of the final products are indicated below.

Benzene, C_6H_6.—(a) A sample of Baker's Analyzed C. P. benzene (thiophene free) gave a negative test with isatin. A 500cc. portion was treated with 100 cc. of concd. sulfuric acid and shaken in the cold for ten minutes. The resulting hydrocarbon layer was separated from the acid, washed first with sodium hydroxide solution, then with water, and dried over calcium chloride. The product was distilled twice, using a 48cm. column. That portion boiling at 79.7° (corr.) was saved.

(b) A sample of synthetic benzene was prepared from Powers, Weightman and Rosengarten benzoic acid and sodium hydroxide in the conventional way. The resulting product was shaken with a small quantity of concd. sulfuric acid and purified as described above. After the third fractionation, that portion boiling at 79.8° (corr.) was saved.

Cyclohexene, C_6H_{10}.—A sample of Eastman Kodak Company purified cyclohexene was redistilled thrice. That portion boiling at 82.7° was used.

Cyclohexane, C_6H_{12}.—Three hundred g. of crude cyclohexane was prepared by the catalytic hydrogenation of benzene, according to the method of Sabatier and Senderens.[5] In order to free the crude product from benzene it was shaken with small quantities of a mixture of sulfuric and nitric acids until the acid extract, upon dilution with water, showed no turbidity. It was washed with sodium hydroxide solution, then with water and dried over calcium chloride. After fractionating thrice, that portion boiling at 80.4° was saved.

Methyl-*n*-amyl Ether, $CH_3—O—(CH_2)_4CH_3$.—A 10g. sample of Eastman Kodak Company purified product was redistilled. That portion boiling at 100.6–101.6° (corr.) was used.

Ethylene Chlorohydrin, $Cl(CH_2)_2OH$.—The Eastman Kodak Company purified product was redistilled and that portion boiling at 127.1–128.1° (corr.) was saved.

Results

The photographs of the absorption spectra were taken under a great variety of conditions with respect to the time of exposure, the length of the column of vapor, and the pressure of the vapor in the absorption cell. The times of exposure ranged from 5 to 300 seconds and the pressures in the absorption cell corresponded to the vapor pressure of the liquid at a number of temperatures between 0 and 100°. In Fig. 2 are shown microphotographs obtained from the absorption band spectra in benzene, cyclohexene, ethylene chlorohydrin, ethyl ether and methyl-*n*-amyl ether. In the case of ethyl ether, methyl-*n*-amyl ether and cyclohexene, the length of the column of vapor was 90 cm. For ethylene chlorohydrin it was 10 cm. and for benzene it was 2.5 cm. The liquid in the bulb for the photographs from which these microphotographs were made was ordinarily kept at about room temperature (24–25°) and the density of the vapor in the absorbing column was that corresponding to the pressure of the saturated vapor at that temperature. The time of exposure was five or ten seconds.

From these microphotographs it is seen that the positions of the characteristic absorption bands are the same within the error of these observations and that the wave lengths of these systems of band spectra are not influenced by the structure of the molecules. The amount of absorption is quite different in the different vapors. No attempt has yet been made to study the way in which the intensity of the absorption changes from one substance to another or to find the relation between the amount of absorption for different bands. It is sufficient to point out here that

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[5] Sabatier and Senderens, *Compt. rend.*, **132**, 210 (1901).

whereas a column of benzene vapor 2.5 cm. long is sufficient to give a well defined absorption spectrum, it requires a column of vapor 90 cm. long at about the same vapor pressure to produce a much smaller amount of absorption in either of these ethers or in cyclohexene. Hence, the absorbing power of these vapors depends very largely on the nature and structure of the molecule. In fact, cyclohexane proved to be perfectly transparent in this region for all concentrations of vapor, up to the boiling point, in a 90cm. tube. Cyclohexadiene, on the other hand, proved so intensely absorptive that it was necessary to immerse the bulb in liquid air in order to secure a sufficiently attenuated vapor to permit photographing the same region through a 2.5cm. tube. Even so, the bands obtained were blurred and insufficiently resolved to permit any definite measurements to be made.

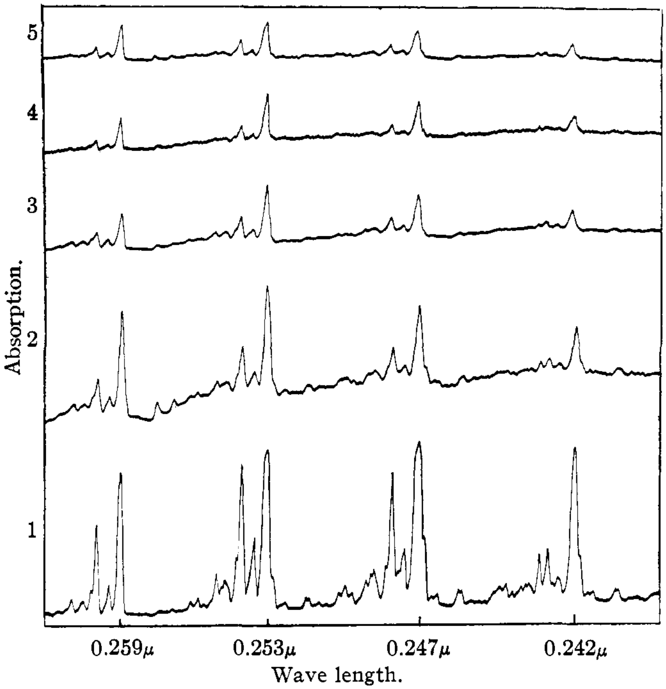

Fig. 2.—1, Benzene, 2.5cm. tube, t = 24°; 2, ethyl ether, 90cm. tube, t = 24°; 3, methyl-n-amyl ether, 90cm. tube, t = 25°; 4, ethylene chlorohydrin, 10cm. tube, t = 70°; 5, cyclohexene, 90cm. tube, t = 24°.

Table I gives in Ångström units the wave lengths of the heads of the absorption bands for ethyl ether, methyl-n-amyl ether, ethylene chlorohydrin and benzene. The values tabulated for benzene are those given by Henri. From a comparison of the wave lengths of the bands for

TABLE I

A COMPARISON OF THE MEASURED ULTRAVIOLET ABSORPTION BANDS OF THE ETHYL ETHER, METHYL-*n*-AMYL ETHER, ETHYLENE CHLOROHYDRIN AND CYCLOHEXENE WITH HENRI'S CALCULATED VALUES OF BENZENE

Series I $1/\lambda = 37{,}703 + 921.4\,n_1 - (159n_2 + 2n_2^2)$

n_1	n_2	Ethyl ether	Methyl-*n*-amyl ether	Ethylene chlorohydrin	Cyclohexene	Av.	Benzene
1	0	2589.3	2589.2	2588.9	2589.2	2589.1	2589.0
2	0	2528.5	2528.8	2528.5	2528.8	2528.7	2528.6
3	0	2471.0	2471.1	2470.9	2470.9	2471.0	2471.0
4	0	2415.8	2416.1	2415.9	2415.9	2415.9	2415.9
5	0	2363.4	....	....	....	2363.4	2363.6
1	1	2599.9	2600.0	2599.7	2599.9	2599.9	2599.9
2	1	2538.9	2538.9	2538.7	2538.9	2538.9	2539.0
3	1	2480.7	2480.9	2480.6	2480.6	2480.7	2480.8
4	1	2425.3	2425.8	2425.4	2425.4	2425.5	2425.3
1	2	2610.9	2611.1	2610.7	....	2610.8	2610.2
2	2	2549.4	2549.9	2549.6	....	2549.5	2549.6
3	2	2491.1	2491.2	2490.9	....	2491.1	2491.5
4	2	....	....	2435.3	....	2435.3	2435.4
1	3	....	....	2561.4	....	2561.4	2560.8
2	3	....	....	2502.4	....	2502.4	2502.5

Series II $1/\lambda = 37{,}613 + 921.4\,n_1 - (159n_2 + 2n_2^2)$

n_1	n_2	Ethyl ether	Methyl-*n*-amyl ether	Ethylene chlorohydrin	Cyclohexene	Av.	Benzene
1	0	2595.0	2594.9	2594.7	2595.1	2594.9	2595.2
2	0	2533.9	2534.4	2534.1	2534.6	2534.3	2534.6
3	0	2476.4	2476.6	....	2476.5	2476.5	2476.6
4	0	2421.5	2422.0	2421.7	2421.5	2421.7	2421.4
5	0	2368.6	....	....	....	2368.6	2368.7
1	1	2606.0	2606.2	2605.7	....	2606.0	2605.7
2	1	2544.5	2544.9	2544.9	....	2544.8	2544.9
3	1	2487.0	2486.9	2487.8	....	2487.2	2487.8

Series III $1/\lambda = 37{,}494 + 921.4\,n_1 - (159n_2 + 2n_2^2)$

n_1	n_2	Ethyl ether	Methyl-*n*-amyl ether	Ethylene chlorohydrin	Cyclohexene	Av.	Benzene
1	0	2603.3	....	2602.6	....	2603.0	2603.0
2	0	2541.7	....	2542.1	....	2541.9	2541.7
3	0	2483.8	....	....	....	2483.8	2483.7
4	0	2428.3	....	2428.3	....	2428.3	2428.5
5	0	2375.4	....	2375.1	....	2375.3	2375.2
1	1	....	....	2614.3	....	2614.3	2613.9
2	1	....	....	2552.7	....	2552.7	2552.5

benzene as recorded in the last column of this table with the mean values of the wave lengths of the corresponding bands for ethyl ether, methyl-*n*-amyl ether, ethylene chlorohydrin and cyclohexene as recorded in the last column but one, it is seen that except for a few cases when the bands were indistinct the wave lengths agree within 0.1 Å. From this agreement it seems necessary to conclude that the systems of bands are unchanged in these organic compounds and arise from electronic and vibrational conditions which are common to all compounds.

Henri found it possible to arrange the bands in the vapor of benzene in four series, each of which has a different origin. The intensities of the corresponding absorption bands decrease progressively as the origin of the band system is shifted toward the longer wave lengths. The intensities of the bands in the fourth series in which the origin lies farthest toward the red end of the spectrum are small, and no members of this series have been located with certainty in the vapors used in this investigation. The three remaining series differ only in the position of the origin. A large number of bands belonging to each of these series has been found in ethyl ether, methyl-*n*-amyl ether, ethylene chlorohydrin and cyclohexene. Since the observed wave lengths of the absorption bands of these vapors are the same as the corresponding wave lengths found by Henri in the absorption spectrum of benzene, it follows at once that these absorption bands can be expressed by the same formulas which were used for the band systems in benzene. In Table I the absorption bands have been arranged according to the three series used by Henri for benzene. A discussion of the development and meaning of these series is given later in this paper. Since no absorption bands belonging to the fourth series were located in these vapors, only three series are included in the table. If longer columns of the absorbing vapor were used, it would no doubt be possible also to find this fourth series of bands in these vapors.

Theory

According to the quantum theory of band spectra, each line of such a spectrum results from the simultaneous occurrence in a molecule of quantum jumps of three distinct types. Each of the three types of quantum numbers—electronic, molecular vibrational and molecular rotational—may have initially any one of a variety of values which may change either by a positive or by a negative integer. Consider the energy which is absorbed when a molecule passes from a less to a more excited state. Let E' denote the total energy of the molecule in its more excited state and E'' its total energy in the less excited state. Each of these energies, E' and E'', is a function of a set of electronic quantum numbers (e_1, e_2, $e_3 \ldots\ldots$), a quantum number n associated with the vibration of the nuclei and a quantum number m associated with the rotation of the nuclei about some axis in the molecule. Assume that the total energy can be divided into three parts which depend solely on m, n and the e's, respectively. Let E_e be the electronic energy depending only on the e's; E_n, the vibrational energy depending only on n; and E_m, the rotational energy depending only on m.

Then $E = f(e_1, e_2, e_3 \ldots\ldots n, m) = E_e + E_n + E_m,$

where $E_e = f(e_1, e_2, e_3 \ldots\ldots 0, 0),\ E_n = f(e_1, e_2, e_3 \ldots\ldots n, 0) - E_e,$

$E_m = f(e_1, e_2, e_3 \ldots\ldots n, m) - E_n.$ Since $h\nu = E' - E''$, the frequency of any line which is absorbed by the vapor is

$$\nu = \frac{E' - E''}{h} = \left(\frac{1}{h}\right)(E'_e + E'_n + E'_m) - \frac{1}{h}(E''_e + E''_n + E''_m) \quad \text{and}$$

$$\nu = \left(\frac{1}{h}\right)(\Delta E) = \left(\frac{1}{h}\right)(\Delta E_e + \Delta E_n + \Delta E_m). \text{ In general,}$$

$$\nu = \nu_e + \nu_n + \nu_m \tag{1}$$

$$\nu_e > \nu_n > \nu_m$$

The values of both ν_n and ν_m may be either positive or negative. In the near infra-red region of the spectrum, band spectra are characterized by the omission of the term ν_e. In the far infra-red, both the terms ν_e and ν_n are absent. In line spectra the term ν_e alone is present.

All of the lines on a band spectrum are collectively designated as a *band system.* Each individual band in a band system is determined by a pair of values (n_1, n_2). The structure of each band in a band system is determined by changes in m. The changes $m_1 \longrightarrow m_2$ are limited in accordance with the correspondence principle by the rules $(m_2 - m_1) = \pm 1$ or 0. Hence ν_m is usually relatively small. The origin of a band may be defined as frequency, $\nu = \nu_e + \nu_n$, corresponding to $\nu_m = 0$. Similarly, the origin of a band system may be defined as the frequency ν_e, corresponding to $\nu_n = 0$ and $\nu_m = 0$.

Making use of certain simplifying assumptions, Henri has undertaken to apply this kind of analysis to develop the equations which express the relation between the frequency numbers of the absorption lines observed in the vapor of benzene. Assume that by the absorption of the radiation, the molecule passes from the less excited state B to the more excited state A. In accordance with the Bohr theory of the atom, the electronic energy which depends on the e's may be assumed proportional to the Planck constant h. Hence, $E'_e = Ah;\ E''_e = Bh$, where A and B are constants, depending on the electronic configuration, and h is the universal Planck constant.

If linear harmonic vibrations with energy equal to an entire number of quanta are assumed, $E'_n = n_2\, a\, h;\ E''_n = n_1\, b\, h$, where n_1 and n_2 are integral numbers and a and b are constants.

The energy corresponding to the rotation of the molecule is $E'_m = \left(\frac{I}{2}\right)(2\pi\omega)^2 = \frac{1}{2}\, m_1 h\omega$, where I is the moment of inertia of the molecule; ω its frequency of rotation; m_1 an integral number and

$$\omega = \frac{m_1 h}{4\pi^2 I},\ E'_m = \frac{h^2 m_1^2}{8\pi^2 I},\ E''_m = \frac{h^2 m_2^2}{8\pi^2 I}.$$

Whence $$E'' = E''_e + E''_n + E''_m = Bh + n_2 bh + \frac{h^2 m_2^2}{8\pi^2 I}$$

$$E' = E'_e + E'_n + E'_m = Ah + n_1 ah + \frac{h^2 m_1^2}{8\pi^2 I}.$$

When the molecule passes from the less excited state B to the more excited state A the energy absorbed is

$$h\nu = E' - E'' = (A - B)\,h + (n_1a - n_2b)\,h + \frac{h^2}{8\pi^2 I}(m_1^2 - m_2^2)$$

$$\nu = (A - B) + (n_1a - n_2b) + \frac{h}{8\pi^2 I}(m_1^2 - m_2^2)$$

If the vibrations are not harmonic, $E''_n = n_2hb + n_2^2hb' + n_2^3hb'' +$, where b' and b'' are small in comparison with b, and $E'_n = n_1ha + n_1^2ha' + n_1^3ha''$, where a' and a'' are constants which can be neglected in comparison with a.

Using these expressions for energy instead of the corresponding ones when the vibrations of the oscillators are assumed harmonic, the frequency of the absorption line is given by the expression

$$1/\lambda = \nu = (A - B) + an_1 - (bn_2 + b'n_2^2) + \alpha(m_1^2 - m_2^2) \qquad (2)$$

where

$$\alpha = h/8\pi^2 I$$

In this expression a' and a'' are neglected in comparison with a. This approximation seems doubtful since there is little reason for assuming that the vibrations would depart less from harmonic conditions in State A than they do in State B. However, it may not be an unreasonable approximation.

Comparing Equation 1 with Equation 2, $\nu_e = A - B$; $\nu_n = a\,n_1 - (bn_2 + b'n_2^2)$; $\nu_m = h/8\pi^2 I\,(m_1^2 - m_2^2)$.

As already pointed out, Henri found four band systems in benzene vapor, each with a different value of $A - B = \nu_e$, the frequency number of the origin of the band system. Three of the band systems had the same values of a, b and b', which are related to the vibrational frequency number of the atoms through the equation $\nu_n = an_1 - (bn_2 + b'n_2^2)$.

In the fourth band system, b and b' had values slightly different from the corresponding values in the other three systems. It has been found in this investigation that the three prominent band systems which occur in benzene also occur unchanged in cyclohexene, ethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin. In terms of the preceding analysis it seems that this result should be interpreted as meaning that the electronic frequency number and the vibrational frequency number are not influenced by the composition and structure of these organic molecules. Hence, it becomes of importance to inquire concerning the atoms or groups of atoms from which these bands may arise and yet remain unchanged in these compounds. There are in the compounds under consideration only two common linkages, the carbon-hydrogen linkage and the carbon-carbon linkage. It seems probable that one or the other of these linkages gives rise to these systems of bands.

In a large number of organic liquids containing the carbon-hydrogen linkage, there are a number of absorption bands in the near infra-red region of the spectrum. These bands have been attributed by Ellis[6]

[6] Ellis, *Phys. Rev.*, [2] **27**, 298 (1926).

to the carbon-hydrogen linkage. If this assignment is correct and if the series band systems located in some of these same organic compounds in the ultraviolet also arise from the carbon-hydrogen linkages, it should be possible to calculate the positions of the bands in the near infra-red region from the equation

$$\nu_n = 921.4\, n_1 - (159\, n_2 + 2\, n_2^2)$$
$$\nu_n = 921.4\, n_1 - 159\, n_2, \text{ approximately} \qquad (3)$$

because when $\nu_e = 0$ and $\nu_m = 0$, ν_n of Equation 1 gives bands which lie in the near infra-red region of the spectrum.

In making such a calculation it must be remembered that most of the observations on the absorption band in the near infra-red have been made on liquids and that the position of the absorption band of the liquid is not necessarily identical with its position when the compound is in the vapor state. With this approximation in mind, a comparison of the observed and calculated wave lengths is shown in Table II. Col. 1 shows the observed values and Col. 3 those calculated by Equation 3. Henri has made similar calculations for some of these bands but the list has been extended to include the results of the recent work of Ellis. Ellis found that the positions of those absorption bands in the near infra-red can be expressed by the equation

$$\nu_n = 1579\, n - 26.1\, n^2 \qquad (4)$$

where n has the integral values 1, 2, 3, etc. In Col. 6 are recorded the wave lengths calculated by Equation 4. An examination of Table II

Table II

A Comparison of the Observed Infra-Red Absorption Bands with Those Calculated from Ultraviolet Absorption Bands as Measured in the Vapor Phase

Obs. values		Calcd. values				
		Henri's formula (3)			Ellis formula (4)	
λ in μ	ν	λ in μ	n_1	n_2	λ in μ	n
0.760	13,160	0.760	16	10	0.758	10
.835	11,980	.831	16	17	.827	9
.913	10,950	.910	14	12	.913	8
1.022	9785	1.022	12	8	1.023	7
1.172	8531	1.166	10	4	1.172	6
1.379	7252	1.370	10	12	1.375	5
1.695	5900	1.684	8	9	1.695	4
2.16	4630	2.19	6	6	2.22	3
2.49	4020	2.45	6	9	...	..
2.75	3640	2.74	5	6	...	..
3.25	3080	3.28	4	4	3.28	2
5.40	1850	5.53	3	6	...	..
6.7	1490	6.6	2	2	6.44	1
7.3	1370	7.3	2	3	...	..
8.7	1150	8.3	2	4	...	..
9.8	1020	9.6	2	5	...	..
11.8	848	11.4	2	6	...	..
13.0	769	13.1	1	1	...	..

shows that the formula proposed by Henri fits the facts over a larger range of wave lengths than the formula proposed by Ellis and that the difference between the observed and calculated values is of the same order of magnitude. The agreement between the observed values and those calculated by Henri's formula is sufficiently good, considering the approximations, to justify the conclusion that if these infra-red absorption bands are to be attributed to the carbon-hydrogen linkage, then the ultraviolet absorption band system found in benzene, cyclohexene, ethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin may also be attributed to this source.

Having thus disposed of the physical significance of the ultraviolet absorption of these compounds, let us consider briefly the chemical aspects of the foregoing facts. It would seem that the origin of light absorption by organic compounds is being slowly but surely traced back to the atoms which the compounds contain and to their linkages. It can be stated unequivocally that absorption by organic compounds does not owe its origin to any form of structural molecular vibration such as may occur in a molecular rearrangement. One may well ask, what then is the relation between absorption (color) and chemical constitution? The data available do not enable one to answer this question at the present time. A careful analysis of the facts, however, would seem to indicate the direction in which the answer is to be sought. First, the absorption bands tabulated in Table I represent the heads of bands which within themselves have a structure. Should it prove possible to resolve these bands, it is believed that this structure will involve the frequency factor ν_m and, therefore, the moment of inertia of the absorbing molecule. Second, the ultraviolet bands tabulated in Table I were measured by photographing through the vapors. When the absorption is photographed through thin layers of a solution or through films of the pure liquid, the oscillations are damped so that the bands become broadened to the point where they merge into finger-like bands, and if thicker layers are used these in turn merge into broad enveloping bands. It is usually these enveloping bands of which the organic chemist speaks when applying Witt's chromophoric theory or Nietzki's rule. As shown in Table I for ultraviolet absorption, $\nu = \nu_e + \nu_n$. In other words these frequencies originate in transitions of electrons from one energy level to another and the oscillations of the atomic nuclei. In so far as differences in the molecular structure change the energy levels which the electrons can occupy and in so far as they change the oscillations between the nuclei of constituent atoms, the absorption will depend upon the chemical constitution. Until these enveloping bands can be resolved into smaller bands and these smaller bands in turn resolved into lines, the final answer will not be known. We hope by work now in progress to shed additional light on this question.

Summary

1. Three series of band spectra which have previously been found in benzene have been found in cyclohexene, ethyl ether, methyl-*n*-amyl ether and ethylene chlorohydrin.

2. An analysis of these spectra on the basis of the quantum theory indicates that they can be attributed to the carbon-hydrogen linkage in the molecule.

3. The direction in which the experimental determination of the relation between absorption and chemical constitution lies, is pointed out.

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METHOXY-SUBSTITUTED TRIPHENYL CARBINOLS AND THEIR SALTS

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RECEIVED MARCH 7, 1927 PUBLISHED MAY 10, 1927

When to equimolecular quantities of carbinols dissolved in acetic acid containing some sulfuric acid, dil. alcohol is added until the color is discharged, the amount of dilution serves as the index of the relative ease with which the various carbinol salts are completely hydrolyzed. Although this procedure can give only approximately correct results—and this was recognized by Baeyer and Villiger[2]—nevertheless, it has frequently been used by later investigators, and mathematically formulated rules have been derived concerning the basic strength of these nitrogen-free bases. With Baeyer, it is assumed that the influence of the methoxy groups is as follows: triphenyl carbinol: mono-*p*-methoxy: di-*p*-: tri-*p*- = 1:6.3:34.0:286. The influence of each succeeding group is thus exponential. As regards orientation, it is assumed that the *para* is pre-eminently greater in its influence than the other positions: triphenyl carbinol: *m*, -*m*, -*m*-: *p*,-*o*,-*o*,: *p*,-*p*,-*p*,: 1:1.7: 7.6: 286.

The possible relation between increased basic strength of the carbinols on the one hand and their tendency to give rise to monomolecular triaryl methyls on the other, has been the subject of many investigations. In this Laboratory,[3] a number of mono- and dimethoxy triaryl methyls have been prepared in the solid state, and their molecular state determined. The results indicate that the methoxy groups, in addition to augmenting the basicity of the carbinols, exert an appreciable positive influence as

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[1] Denmark-America Society Fellow, 1923–1924; International Education Board (New York) Fellow, 1924–1925. The material here presented is from a dissertation submitted to the Faculty of the University of Copenhagen, Denmark, for the degree of Doctor of Philosophy, 1926.

[2] Baeyer and Villiger, *Ber.*, **35**, 1189 (1902).

[3] Gomberg and co-workers, THIS JOURNAL, **45**, 190, 207 (1923); **47**, 2392 (1925).