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Additional information on J. Chem. Phys.

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(Received June 9, 1934)

In this paper a first attempt is made to evaluate from published measurements the total strength and width of absorption bands of organic compounds, and to correlate that with the nature of the solvent and the constitution of the substance. It turns out that none of the quantities that one could consider from the theoretical standpoint remains constant.

INTRODUCTION

THE absorption spectrum has long been regarded as closely connected with the molecular structure of organic compounds. Many investigations have been made concerning the influence of substitution and (if, as is mostly the case, the compound is in solution) of the solvent on the wave-length of the absorption maximum, and it has been possible to formulate some general rules. But very little has been done concerning the two other quantities which are characteristic for a continuous absorption band, its width and its strength, and an attempt is made here to supply this deficiency.

THEORY

If a plane wave of frequency ν and wave-length λ in vacuum progresses through an absorbing medium, this can be characterized by a complex refractive index n'

$$n' = n(1 - ik), \tag{1}$$

so that the wave amplitude is given by

$$e^{2\pi i \nu(t - n' \, x/c)} = e^{-2\pi n k \, x/\lambda} e^{2\pi i(\nu t - n \, x/\lambda)}.$$

If we have μ mols per liter, the absorption of the light intensity (square of the amplitude) is given by $e^{-\epsilon \mu x}$, where

$$\epsilon = 4\pi n k/\lambda. \tag{2}$$

The theory of dispersion shows now that one has

$$n'^2 - 1 = n^2(1 - k^2) - 1 - 2n^2 ik$$
$$= \frac{e^2}{\pi m} N' \sum \frac{f_j}{\nu_j^2 - \nu^2 + i\gamma_j \nu}, \tag{3}$$

where the summation on the right is extended over all the absorption bands of frequency ν_j, γ_j is a quantity measuring the damping and responsible for the width of the band, f_j measures the strength. N' is the number of molecules per cc and will be written

$$N' = N\mu \tag{3'}$$

with $N = 6.06 \times 10^{20}$, finally it has been assumed that in the visible and ultraviolet one can put for e and m charge and mass of the electron. f_j, the strength of the band, would in classical theory be the number of electrons per molecule producing that band. In quantum theory, it measures the ratio of the probability of transition for the band to the probability of the standard classical band.[1] The sum of all the f_j is equal to the number of electrons.[2] It has turned out through recent investigations, that most of the characteristic absorption bands, e.g., the ones determining color, are weak bands, while the bands contributing the main part of the refractive index lie in the extreme ultraviolet.

If one considers the neighborhood of one weak absorption band removed from the others, one can write

$$2n^2 k = \frac{e^2}{\pi m} N' \frac{\bar{f}_j \gamma_j \nu}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2 \nu^2} \tag{4}$$

and if the band is weak enough, one can neglect the change in n which is contributed by this particular band and write for n the value due to all the other bands at ν.

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[1] R. Ladenburg, Zeits. f. Physik **4**, 451 (1921); R. Ladenburg and F. Reiche, Naturwiss. **11**, 584 (1923).

[2] F. Reiche and W. Thomas, Zeits. f. Physik **34**, 510 (1925); W. Kuhn, Zeits. f. Physik **33**, 408 (1925).

We find from (2) and (4)

$$\epsilon = \frac{2e^2}{cm}\frac{N}{n}\frac{\bar{f}_i\gamma_i\nu^2}{(\nu_i{}^2-\nu^2)^2+\gamma_i{}^2\nu^2}. \qquad (5)$$

If the band is sufficiently narrow, it follows

$$\int \epsilon d\nu = \frac{\pi e^2}{cm\nu_i{}^2}\frac{N}{n}\bar{f}_i \qquad (6)$$

independent of γ.

Similarly, Fuchtbauer[3] has shown that from the quantum standpoint one should get the integral on the left side of (6) to be proportional to the probability of transition, and for a gas $n=1$ one gets then

$$\int \epsilon d\nu = \frac{\pi e^2}{cm\nu_i{}^2}Nf_i. \qquad (6')$$

While this f cannot be interpreted as "electron number" for $n \neq 1$, it is also listed in the tables.

A closer inspection of his reasoning shows that this should be replaced for a broad band by

$$\int \epsilon\nu d\nu = (\pi e^2/cm\nu_i)Nf_i, \qquad (6'')$$

but numerically there is only a small difference between (6') and (6'') for the bands investigated here.

According to formula (5), one finds that the maximum adsorption, which occurs at $\nu=\nu_i$ is given by

$$\epsilon(\max) = \frac{2e^2N}{cm\nu}\frac{f_i}{\nu_i{}^2}\frac{1}{\gamma_i}$$

or

$$\gamma_i\epsilon(\max) = (2/\pi)\int \epsilon d\nu. \qquad (7)$$

Formula (5) has been used here to calculate $\bar{f}$ graphically from the published absorption curves. (7) is used to calculate γ.

If γ were independent of ν throughout the band (an assumption that can always be made for spectral lines), the half width of the band

[3] Chr. Fuchtbauer, Phys. Zeits. **21**, 322 (1920).

that is the distance between the places where $\epsilon=\epsilon(\max)/2$, would be given by

$$\Delta\nu = (c/\lambda)\Delta\lambda = 2\gamma. \qquad (8)$$

A comparison of γ calculated by (8) and (7) shows usually differences of not more than 10 percent.

In testing the influence of solvent and chemical substitutions on f, one has to consider that the classical theory predicts an influence of the neighboring molecules due to the Lorentz-Lorenz force, which is the force coming from the polarization of the surrounding molecules. Accordingly, the force acting on one molecule is

$$E+(4r/3)P = E+(4r/3)(n^2-1)E,$$

where P is the polarization per cc, E the field. This results in a replacement in (3) of n^2-1 by $3(n^2-1)/(n+2)$. Assuming a dilute solution, a solvent which has no absorption band at the place where the band of the dissolved compound which is studied is situated, calling furthermore n_0 the refractive index of the solvent at ν, one finds

$$\frac{n^2-1}{n^2+2} = 1 - \frac{3}{n^2+2}$$

$$= \frac{e^2}{3\pi m}N\left\{\mu_0\sum{}^0 + \mu\sum\frac{\bar{\bar{f}}_i}{(\nu_i{}^2-\nu^2)+i\gamma_i\nu}\right\}, \qquad (9)$$

where μ_0 is the number of mols of the solvent in 1 liter of the solution and the first sum extends over the absorption bands of the solvent.

If one puts $n=n_0+n'(1-ik)$ a short calculation leads to

$$\epsilon = \frac{e^2}{mc}N\frac{(n_0{}^2+2)^2}{18n_0}\frac{\bar{f}_i\gamma_i\nu^2}{(\nu_i{}^2-\nu^2)^2+\gamma_i{}^2\nu^2}, \qquad (10)$$

$$\int \epsilon d\nu = \frac{\pi e^2}{cm\nu_i{}^2}N\frac{(n_0{}^2+2)^2}{9n_0}\bar{\bar{f}}_i. \qquad (11)$$

$\bar{\bar{f}}_i$ is then the transition probability of the dissolved molecules if they were in the gaseous state. This is calculated from the measured value $\bar{f}_i$, the transition probability in solution

$$\bar{\bar{f}}_i = [9/(n_0{}^2+2)^2]\bar{f}_i \qquad (12)$$

under the assumption, that the Lorentz-Lorenz force is the only modifying influence. In quantum theory, the increase of f over $\bar{f}$ is due to an increased transition probability induced by the alternating fields of the neighboring polarized atoms.

To see whether, f, $\bar{f}$ or $\bar{\bar{f}}$ are better constants, both have been calculated for some substances measured in sufficiently different solvents (Tables I–XVII).

RESULTS

Tables I–XVII contain the results. The substances have been arranged according to their chemical constitution, λ is the (vacuum) wavelength of the maximum, $\bar{f}$ is calculated from (6), $\bar{\bar{f}}$ from (12), f from (7). The three f's are listed in the order of their size, namely, $\bar{f}, f, \bar{\bar{f}}$. They are given in 10^{-4} electron numbers, so that for example 3000 would correspond to 3/10th of an electron. The γ are in 10^{13} sec.$^{-1}$.

TABLE I. *Aliphatic compounds.*

Substance	Solvent	λ	f			γ
Iodoform[4]	hexane	3480	449	320	258	8.8
"	"	3052	412	290	234	11
"	ethyl alcohol	3385	445	320	259	9.6
"	" "	2480	423	302	243	12.6
"	chloroform	3479	468	320	242	8.8
"	"	3052	430	290	220	12.1
Ethyl iodide[4]	hexane	2590	13.	9	7.2	14.4
" "	chloroform	2560	19.5	13.1	10	16.5
" "	ethyl alcohol	2557	17.1	12.1	10.2	15
, " "	water	2510	6.55	4.92	4.10	17
Cyclohexene[4]	heptane	3455	5.85	4.11	3.27	16.2
Tetraethyl ammonium nitrate	chloroform	3125	2070	1410	1080	15
	water	3000	2100	1560	1300	14.2

TABLE II. *Acids.*[5]

Substance	Solvent	λ	f			γ
Formic	water	2065	28.8	21.6	18.3	26.1
Palmitic	ethyl alcohol	2105	29.5	20.5	16.1	27.2
Butyric	water	2060	31.5	23.7	20.0	27.2
Oxalic	water	2500	19.1	14.3	12.1	19
Succinic	water	2068	45.8	34.0	28.7	22

TABLE III. *Ketones.*

Substance	Solvent	λ	f			γ
Acetone[4]	hexane	2784	6.05	4.26	3.39	16.9
"	ethyl alcohol	2720	5.75	4.07	3.28	18.6
"	water	2645	6.1	4.6	3.82	18.8
"	water[6]	2648	6.69	4.97	4.19	18.4
"	10% CaCl$_2$ sol.	2609	6.14	4.48	3.68	17.4
Acetylacetone[6]	hexane	2688	4120	2900	2300	16
"	ethyl alcohol	2725	3050	2180	1750	13.6
"	water	2770	1580	1180	975	20.1
Methylacetylacetone[6]	ethyl alcohol or hexane	2864	834	590	474	16.2
"	water	2856	486	360	305	12.7
Menthon[7]	heptane	2893	5.88	4.11	3.25	18
"	methane	2894	6.96	5.17	4.32	14.6
"	ethyl alcohol	2953	7.15	5.11	4.10	14.7
Cyclopentanone[7]	heptane	2953	6.35	4.43	3.35	18.4
"	methanol	2897	6.33	4.68	3.90	18.4
"	"	2910	6.32	4.52	3.64	15.6

[4] G. Scheibe, Ber. d. chem. Ges. **58'**, 586 (1925).
[5] H. Ley and B. Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).
[6] P. Grossmann, Zeits. f. physik. Chemie **A109**, 305 (1924).

[7] H. L. Donle and G. Volkert, Zeits. f. physik. Chemie **B8**, 60 (1930).
[7a] J. Eisenbrand and H. v. Halban, Zeits. f. physik. Chemie **A146**, 234 (1930).

TABLE IV. *Unsaturated compounds and esters.*

Substance	Solvent	λ	f			γ
Acetylacetic ester[6]	hexane	2439	2520	1750	1370	15.6
" "	ethyl alcohol	2457	655	464	373	17
" "	water	2550	42.7	31.9	26.7	18.5
" "	ether	2439	4450	1170	147	15.6
Diethyl acetylacetic ester[6]	ethyl alcohol	2280	206	145	115	21.5
Crotonic ethyl ester[6]	hexane	2470	26.3	18.4	14.6	12.3
" "	"	1980	5850	3960	3010	15.2
β-ethoxycrotonic ethyl ester[6]	hexane	2289	6150	4260	3340	16
" " "	water	2393	6790	5100	4300	19.7
Acrylic acid[8]	hexane	2419	3160	2210	1750	12.7
Acrolein[8]	hexane	3350	5.04	3.6	2.89	20
"	ether	3350	5.76	4.2	3.46	18
"	ethyl alcohol	3278	5.15	3.7	3.0	21
"	water	3210	8.36	6.2	5.17	20
Crotonaldehyde[8]	hexane	3290	6.25	4.46	3.59	16.4
"	ethyl alcohol	3205	8.35	6.01	4.85	19
Mesetyloxide[4]	hexane	3267	13.4	9.6	7.7	17.2
"	"	2298	3620	2520	1970	13.6
"	methanol	3124	22	15	12.6	18.8
"	"	2380	3480	2520	2060	17
Phoron[4]	hexane	3764	25	18	14.5	15.3
"	"	2590	8430	5900	4670	17
"	ethyl alcohol	3547	40	29	23.7	17.6
"	" "	2635	8190	5800	4860	17
"	water	2727	8570	6350	5240	18.8
"	acetic acid	2666	7380	5500	4620	16.6
"	conc. sulfuric acid	3394	5740	3900	3000	11.5
"	" " "	2750	2300	1400	952	16.8

TABLE V. *Diazo compounds[9] in ethyl alcohol.*

Substance	λ	f			γ
Diazoacetone	3600	4.76	3.45	2.82	11.6
"	2750	1160	828	665	13.8
Diazoacetylacetone	3281	11.1	8	6.5	22
Diazoacetic-methyl ester	3640	5.25	3.8	3.12	
" "	2484	3040	2160	1750	13
Diazoacetic-n-butyl ester	3628	5.20	3.76	3.08	18.3
" "	2510	3760	2670	2140	9.7
Diazomalonic-diethyl ester	3450	7.51	5.43	4.45	13.5
" "	2542	2640	1910	1510	13
" "	3411	7.94	5.7	4.61	20.6
Diazoacetyl-acetic-methyl ester	3700	3.28	2.38	1.95	11.9
" "	2600	1620	1080	716	10
Diazoacetyl-acetic-ethyl ester	3625	6.76	4.9	4.06	13.2
" "	2585	4080	2890	2320	12.1
Diazosuccinic-diethyl ester	3970	4.60	3.4	2.79	13
" "	2530	2100	1490	1240	20.5

[8] A. Luthy, Zeits. f. physik. Chemie **A107**, 285 (1923).

[9] H. Lindermann, A. Walter and R. Gregor, Ber. d. chem. Ges. **63′**, 702 (1930).

TABLE VI. *Aromatic compounds—hydrocarbons.*

Substance	Solvent	λ	f			γ
Benzene	pentane[11]	2685	0.051	0.035	0.027	2.4
"	"	2606	0.68	0.46	0.35	1.7
"	"	2548	0.86	0.57	0.43	1.7
"	"	2486	0.78	0.52	0.40	2.2
"	"	2434	0.3	0.2	0.15	1.5
"	"	2338	0.20	0.13	0.10	2.4
"	"	2289	1.5	0.9	0.8	2.6
"	"	2067	440	278	196	3.4
"	"	2033	730	450	308	5.0
"	"	1878	1100	660	423	6.0
"	heptane[10]	2692	2.98	2.07	1.60	1.0
"	"	2600	4.43	3.06	2.37	1.1
"	"	2546	6.62	4.53	3.50	1.2
"	"	2490	4.72	3.23	2.50	1.2
"	"	2418	3.24	2.27	1.69	1.3
"	"	2384	2.65	1.80	1.39	1.7
"	methanol[10]	2594	3.25	2.37	1.95	1.2
"	"	2543	6.57	4.80	3.94	1.6
"	"	2479	4.42	3.23	2.65	1.2
"	"	2418	2.98	2.16	1.77	1.5
Hexamethylbenzene[12]	hexane	2680	47.9	33.7	26.8	10.5
Toluene[10]	heptane	2765	9.17	6.47	4.99	1.9
"	"	2693	14.8	10.2	7.9	2.3
"	"	2605	8.7	6.04	4.73	3.3
Trimethylbenzene[13]	10n. NaOH	2818	5120	3970	3120	10.5
Ortho-xylene[10]	heptane	2710	12.4	8.60	6.75	2.7
"	"	2640	43.8	30	23.2	7.7
Meta-xylene	"	2721	18.6	12.9	10.1	3.4
"	"	2678	37.4	25.9	20.4	6.2
Para-xylene	"	2750	24.9	17.2	13.5	2.6
"	"	2675	54.7	38	29.7	6.2

TABLE VII. *Chlorides.*[10]

Substance	Solvent	λ	f			γ
Monochlorbenzene	heptane	2720	10.5	7.3	5.7	2.1
"	"	2645	15.7	10.8	8.4	3.2
"	"	2580	21.4	14.7	11.4	5.2
"	methanol	2720	8.8	6.5	5.4	2.4
"	"	2640	14.1	10.3	8.4	3.5
"	"	2558	17.7	12.9	10.6	5.6
Toluolchloride ortho	in heptane	2740	15.5	10.8	8.5	2.5
" "	"	2665	26.6	18.5	14.5	3.7
" "	"	2580	23.0	17.2	13.4	5.3
" meta	"	2743	15.5	10.8	8.5	2.5
" "	"	2700	23.6	16.5	12.9	4.1
" "	"	2653	19.9	13.8	10.8	4.3
" para	"	2761	27.4	19.0	14.9	3.0
" "	"	2702	28.6	19.8	15.6	3.0
" "	"	2631	27.6	19.0	14.8	3.0
" "	"	2580	22.5	15.5	12.0	4.8
Dichlorbenzene ortho	"	2784	15.0	10.4	8.2	1.9
" "	"	2710	28.0	19.4	15.2	3.5
" "	"	2632	28.2	19.4	15.1	5.5
" meta	"	2784	14.8	10.3	8.0	1.5
" "	"	2710	28.0	19.4	15.2	3.5
" "	"	2632	25.0	17.2	13.4	4.7
" para	"	2825	18.6	12.9	10.1	2.0
" "	"	2740	34.2	23.4	18.6	3.3
" "	"	2650	43.8	30.2	23.4	7.2

[10] K. L. Wolf and W. Herold, Zeits. f. physik. Chemie B13, 201 (1931).
[11] V. Henri, J. de physique 3, 181 (1922).
[12] G. Scheibe, Ber. d. chem. Ges. 59[2], 2624 (1926).
[13] J. Eisenbrand and H. v. Halban, Zeits. f. physik. Chemie A146, 30, 101, 111 (1930).

TABLE VIII. *Nitrocompounds.*

Substance		Solvent	λ	f			γ
Nitrobenzene		hexane[12]	3388	26.6	19.0	15.3	10.2
"		"	2515	3480	2670	1930	19.1
"		heptane[10]	2500	4320	2960	2290	19.5
"		ether[12]	3360	37.0	27.0	22.2	11.7
"		"	2565	5250	2580	1260	20
"		methanol[12]	3409[9]	44.3	33.0	27.8	13.7
"		"	2600[12]	3800	2770	2280	21
"		"	2605[10]	3400	2490	2050	19
Chloronitrobenzene	ortho	heptane[10]	3365	344	242	193	12.1
"	"	"	2430	1780	1210	933	15.5
"	meta	"	2970	282	197	156	10.8
"	"	"	2500	2520	1730	1340	14.2
"	para	"	2660	4500	3100	2400	19
"	ortho	methanol[10]	2500	1290	940	775	14.6
"	meta	"	2565	3070	2240	1840	19
"	para	"	2700	4720	3450	2860	7

TABLE IX. *Phenols.*

Substance		Solvent	λ	f			γ
Phenol[10]		heptane	2744	147	102	79.7	2.9
"		"	2710	155	108	84.2	2.5
"			2650	155	108	84.2	4.0
"		methanol	2726	529	388	321	1.3
Kresol[10]	ortho	methanol	2786	116	86.3	72	2.7
"	"	"	2710	289	214	179	6.9
"	meta	"	2806	67.5	50.1	41.7	1.7
"	"	"	2720	225	164	135	5.6
"	para	"	2855	99	77.3	61.4	2.0
"	"	"	2793	92.2	68.3	57	2.3
"	"	"	2755	204	151	128	5.0
Chlorophenol[10]	ortho	heptane	2815	167	116	91	2.9
"	"	"	2740	199	138	109	3.4
"	"	"	2630	151	108.	84	4.3
"	para	"	2890	124	86	67.5	2.4
"	"	"	2825	137	95	74.6	2.5
"	"	"	2750	173	120	94.4	4.3

TABLE X.

Substance	Solvent	λ	f			γ
Benzonitril[12]	hexane	2769	37	26	20.7	2.1
"	"	2675	78.2	55	38.8	5.7
"	methanol	2770	52.1	38.6	32.2	3.4
"	"	2700	105.1	77.6	47.1	7.3

TABLE XI. *Ethers.*

Substance	Solvent	λ	f			γ
Anisol	hexane[12]	2780	92	64.7	51.5	2
"	"	2710	306	215	171	6.9
"	heptane[10]	2784	64.7	50.5	32.8	2.2
"	"	2722	141	97.8	75.7	2.3
"	"	2650	120	82.7	64	4.2
"	methanol[10]	2784	101	75	62.8	2.8
"	"	2722	148	97.8	78.4	3.0
"	"	2667	146	108	78.4	4.5
"	methanol[12]	2713	226	183	138	7.3
"	water[12]	2710	245	183	154	10
Phenetol[10]	heptane[10]	2784	101	70	54.8	1.9
"	"	2722	17.4	12	9.4	3
"	"	2675	155	108	84.5	4.6
"	methanol[10]	2775	87.5	64.7	54	2.2
"	"	2725	26.4	19.4	16	5.4

DISCUSSION OF METHODS

Three methods have been used to measure the absorption. A. Halban compares the intensity of the light passing through the pure solvent with that passing through the solution with the help of a photoelectric cell. This method can be used in the visible and ultraviolet, is very accurate and needs no assumptions. B and C are photographic methods in which the spectrum of the light passing through the pure solvent is compared with a series of spectra of the light passing through the solution. This series, printed on the same plate, is either made with different length of exposure t (method B, Henri) or with different openings t/t_0 of a rotating sector (method C, Scheibe). One determines the exposure time of the spectrum of the solution, that for a certain wave-length gives the same blackening of the plate as the same wave-length passing through the pure solvent, and calculates the absorption from

$$x = q \ln t/t_0,$$

where q is the Schwarzschild constant. This is determined by either printing marks with the source at several distances (method a) or by comparison with a photoelectric cell (method b).

In the following discussion, the numbers refer to the authors of the bibliography, the letters to the method:

4, 12) method C, q determined by b. Finds $q=1$, accuracy 1–2 percent.

5) method B, use same plates as (4) and assume $q=1$, without mentioning a separate determination.

6) method B, says nothing about q.

7) method C, follows exactly procedure in 10.

7a, 13) method A, accuracy $\frac{1}{2}$ percent.

8) method B, says that for his plates $q=0, 9$ (as for Henri, 11).

9) method C, do not say anything about q.

10) method C, do not say anything about q.

11) method B, determines $q=0, 9$ by method a.

14) method B, do not say anything about q, but same method as 5. $(q=1?)$.

15) method C, use $q=1$ without further justification.

16) method C; they use $q=1$; comparing their results for potassiumchromate in KOH with Halban (A) they find good agreement.

17) method C, uses $q=1$. Comparison of the result for pure azobenzene with Halban (A), shows good agreement.

18, 19) method C, q put equal 1. There is no difficulty as long as it is only a question of stating that the maximum absorption remains unchanged.

TABLE XII. *Ketones.*

Substance	Solvent	λ	f			γ
Benzophenone[12]	hexane[12]	3450	32.6	23.3	18.7	13
"	"	2484	6150	4300	3410	18.3
"	ethyl alcohol[12]	3270	51.6	37.2	30.5	8.2
"	"	2550	7350	5280	4240	17.8
"	propyl alcohol[10]	2547	6800	4680	3800	19.4
"	conc. sulfuric acid[12]	3430	45.6	31.0	23.9	11
"	" " "	2960	18800	12000	8550	8.2
Acetophenone[12]	hexane	3204	10.9	7.8	6.3	10.9
"	"	2761	186	131	104	11.2
"	"	2350	3740	2600	2040	14.8
"	ethyl alcohol	3220	9.8	7.04	5.7	8.4
"	"	2760	195	139	112	13.9
"	" "	2389	3690	2620	2010	14.3
"	water[12]	2770	316	236	195	13.5
"	"	2450	3860	2900	2440	16
"	conc. sulfuric acid[12]	2530	442	267	175	11

TABLE XIII. *Amines.*

Substance	Solvent	λ	f			γ
Aniline	hexane[12]	2660	422	299	210	10.6
"	heptane[10]	2864	423	296	234	11.0
"	ether[12]	2664	664	366	215	11
"	methanol[10]	2858[7]	378	280	232	13.2
"	"	2806[9]	375	276	231	10.2
"	water[12]	2643	324	240	200	11
Toluidine[10] ortho	in heptane	2850	435	302	237	9.6
" meta	"	2875	385	267	210	9.6
" para	"	2915	379	259	205	9.4
Chloraniline[10] ortho	in heptane	2538	570	416	342	10.6
" meta	"	2538	430	314	258	10.8
" para	"	2585	430	314	258	10.9
" "	"	2155	374	269	218	13.5

TABLE XIV. *Azoxy compounds in alcohol.*

Substance	λ	f			γ
Azoxybenzene[14]	2375	6100	4300	3420	20
Isazoxybenzene[14]	3400	2070	1490	1210	15.5
"	2488	4820	3390	2100	19.4
Azoxytoluene[14] *mm′*	3350	6130	4410	3560	21
Azoxytoluene[14] iso-*mm′*	3310	2300	1660	1340	19
"	2395	5050	3540	2830	22
Azoxytoluene[14] *p-p*	3350	8100	5830	4720	24.0
" iso *p-p′*	3350	3080	2200	1780	21.6
"	2476	7730	5480	4330	28
Azoxytoluene[15] *o-o*	3150	3820	2670	2120	23.5
" *o-o*-iso-	3220	1320	950	770	14.9
"	2430	4650	3280	2610	23
Dichloroazoxybenzene[15] *o-o′*-iso-	3120	3580	2500	1990	23
"	2400	4170	2930	2340	19.4
"	3140	1270	890	705	17
"	2390	7950	5600	4450	29.6
" *o-o′*	3150	4970	3470	2760	35
Azoxyanisol[14] *o-o′*-iso-	3356	2280	1640	1350	23.4
"	2410	6740	4740	3370	28.4
Bromazoxybenzene[17] *α*	3352	9040	6500	5260	23
" *β*	3329	10100	7300	5880	24.2
Nitrobromazoxybenzene[17] *α*	3389	11100	8000	6470	23
" *β*	3389	13300	9600	7750	28.9
Nitrobromazoxybenzene[17] *α*	3532	9920	7200	5900	21.6
" *α*	2613	9450	6700	5370	25.4
" *β*	3369	11500	8340	6700	23.8
Azoxybenzene[15]	2375	6100	4300	3420	20
Iso-azoxybenzene[15]	3400	2070	1490	1210	15.5
"	2488	4820	3390	2100	19.4
Azoxytoluene[15] *mm′*	3350	6130	4410	3560	21
Azoxytoluene[15] iso-*mm′*	3310	2300	1660	1340	19.2
"	2395	5050	3540	2830	22
Azoxytoluene[15] *p-p′*	3350	8100	5830	4720	24.1
" iso-*p-p′*	3350	3080	2200	1780	21.6
"	2476	7730	5440	4330	28
Azoxybenzene-methylether[17] *α*	3507	10500	7200	6220	21.3
" *α*	2490	6980	4950	3980	27.5
" *β*	3332	12800	9200	6460	28
Azoxybenzene-ethylether[17] *α*	3350	9920	7200	5900	20.8
" *α*	2520	4230	3000	2460	17.4
" *β*	3384	13600	9800	7930	28
Oxyazoxybenzene[17] *α*	3545	9520	6900	5650	21.5
" *β*	3332	11200	8060	6520	23
2-methyl-5-oxyazoxybenzene[17] *α*	3957	2880	2100	1730	13.8
" *α*	3260	4450	3200	2590	20.4
" *α*	2803	3500	2500	2020	19.5
" *β*	3229	9100	6550	5300	28

[14] H. Hunecke, Ber. d. chem. Ges. **60²**, 1451 (1927).
[15] E. Muller and E. Hory, Zeits. f. physik. Chemie **A162**, 281 (1932).

[16] S. Goldschmidt and F. Graef, Ber. d. chem. Ges. **61²**, 1858 (1928).
[17] L. Szego, Ber. d. chem. Ges. **61²**, 2087 (1928).

TABLE XV. *Quinones.*[16]

Substance	Solvent	λ		f		γ
Ortho quinone[16]	hexane	3630	955	882	545	16.1
" "	ether	5790	4.63	3.45	2.90	9.3
" "	"	3660	730	531	438	15.2
" "	chloroform	5730	4.95	3.45	2.78	7.8
" "	"	3750	629	430	332	17.0
Homo-ortho quinone[16]	hexane	3655	676	483	277	16.3
" "	ether	5750	4.96	3.70	3.10	11
" "	"	3760	593	430	355	15.3
" "	chloroform	5650	6.42	4.49	3.63	10.2
" "	"	3820	591	405	312	13.4
Paraquinone	hexane	4685	3.96	2.85	2.32	10.6
"	"	2840[12]	1030	730	580	16
"	"	2420[12]	6190	4300	3370	15.5
"	water	4200	6.70	4.85	3.98	14
"	"	2960[13]	993	733	614	15.9
"	"	2490[12]	516	389	327	13.8
β Naphthoquinone[16]	ether	5350	4.62	3.45	2.90	8
"	"	3985	500	367	302	11.2
"	"	3325	415	302	249	9.2
"	"	2495	10700	4400	1112	11.5
"	chloroform	5200	6.70	4.70	3.66	4.8
"	"	4050	550	381	295	11
"	"	3325	455	310	238	8.9
"	"	2300	5230	3450	2550	8.6
"	ethyl alcohol	4000	504	387	302	11.1
" "	" "	3370	420	302	244	9
"	" "	2505	6580	4660	3740	13

TABLE XVI. *Miscellaneous compounds.*

Substance	Solvent	λ		f		γ
Pyridin[13]	water	2531	720	540	457	11.4
Betain[13]	water	2631	172	128	108	9
Picolinic acid[13]	water	2617	1540	1150	965	14.2
Sodium picolinate[13]	water	2630	538	401	337	9.4
Nicolinic acid[13]	water	2596	850	834	531	11.6

TABLE XVII. *Pure ketones.*[18]

Substance	λ		f		γ
Acetone	2747	6.87	4.84	3.84	18
Methylethylketone	2770	8.06	5.6	4.37	20
Methylpropylketone*	2790	7.9	5.5	4.4	18.3
Methylisopropylketone	2820	8.8	6.2	4.92	19.5
Methylisobutylketone	2810	8.9	6.2	4.9	18.3
Pinacoline	2810	8.9	5.5	4.9	18.4
Diethylketone	2780	7.8	5.5	4.3	18.4
Ethylpropylketone	2800	8.3	5.6	4.3	18.5
Ethylisobutylketone	2820	9.24	6.2	4.7	19
Dipropylketone	2820	9.24	6.2	4.7	19
Hexamethylketone	2950	8.8	5.9	4.4	18.8

* Same values for methylbutylketone, methylhexylketone, methylnonylketone. $n = 3, 5, 8$.

[18] F. O. Rice, Proc. Roy. Soc. **A91**, 76 (1915).

The use of the photographic methods might introduce systematic errors which, however, probably are not large enough to obviate the general results.

DISCUSSION OF RESULTS

Most of the bands contained in the tables are weak bands, relatively few have f's larger than 0.1. Only benzophenone in concentrated sulphuric acid and some of the nitroazoxybenzene compounds have f's larger than 1. The large value of f for a band in the near ultraviolet (region of 3500A) in nitrobenzene and some of the azoxybenzenes of Table XV account for their high refractive index and dispersion.

In an attempt to find regularities the first impression is that no rules that are valid without exception can be deduced from the tables. Variation of the solvent shows that it is impossible to account for the influence of the solvent through the Lorentz-Lorenz force. The following is a compilation of the results.

For the solutions of iodoform (Table I), mesetyloxide (Table IV), benzene* (Table VI), acetophenone in hexane and alcohol (Table XII), the variations of the refractive index of the solvent are too small to permit a distinction between the equally good agreements of $\bar{\bar{f}}, f, \bar{f}$.

For ethyliodide (Table I), acetyl- and methylacetyl acetone (Table III), acetophenone in water and the esters (Table III), the ethers (Table XI), benzophenone (Table XII), the quinones (Table XVI), the variation in the three quantities $\bar{f}, f, \bar{\bar{f}}$, is about equally large.

For tetraethylammoniumnitrate in chloroform and water (Table I), aceton (Table III), ethoxycrotonic ethylester and phorone (Table IV), $\bar{f}, f$ are decidedly better constants than the value following from the Lorentz-Lorenz force, $\bar{\bar{f}}$. For nitrobenzene (Table VIII), f is best.

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* There is strong disagreement between benzene in pentane and heptane. These two solutions have been measured by different authors.

In the amines of (Table XIII) however $\bar{\bar{f}}$ is by far the most constant.

For crotonaldehydes (Table IV) and benzonitril (Table X) the values of f/γ which give the height of the maximum of the absorption curve, seem better constant than any one of the f's alone. This fact had already been remarked by F. O. Rice,[18, 19] who measured ketones in the pure form (Table XVI) and in solution, and found the height of the absorption curve the same.

In discussing the influence of substitutions it makes no difference which one of the f's we use because they differ by a factor referring to the solvent.

It is found in general that a substitution of Cl or CH_3 for H increases the f for the bands which have nearly the same wave-length in spite of the fact that for this reason these bands belong probably to a part of the molecule not directly affected by the substitution. Examples are found in the comparison of benzene and toluene (Table VI) of monochlorbenzene with toluene chloride and dichlorbenzene (Table VII). Very often we have for f

$$\text{meta} \leqq \text{ortho} < \text{para}.$$

This can be seen in xylol (Table VI), the chlorides (Table VII), the nitrocompounds (Table VIII) which have, however, meta > ortho.

In the phenols of (Table IX) however, we have

$$\text{ortho} > \text{para} > \text{meta}.$$

Here again f/γ (the maximum of absorption) seems better constant than anything else. We have also

$$\text{ortho} > \text{meta} = \text{para}$$

for toluidin and chloraniline (Table XIII).

In the fatty acids (Table II) f and γ are very accurately constant, while the values for oxalic and succinic acid are considerably different.

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[19] F. O. Rice, J. Am. Chem. Soc. **42**, 2665 (1920).