CXLIII.—*The Absorption Spectra of Aniline and its Homologues as Vapours, as Liquids, and in Solution.*

By JOHN EDWARD PURVIS.

THE aim of this communication is to give an account of a comparative study of the absorption spectra of aniline and its liquid homologues, in the state of vapours, liquids, and in solution, in order to ascertain, under these conditions, (1) the nature of the influence on the absorption of the radiant energy, and (2) how far the replacement of the hydrogen atoms by simple groups in the nucleus, or in the side-chain, affects the extent and type of the absorption bands.

The substances examined were aniline, mono- and di-methylaniline, mono- and di-ethylaniline, *o*- and *m*-toluidine, *o*-3-xylydine, *m*-2-xylydine, mesidine, and benzylamine. The substances were distilled several times before use.

EXPERIMENTAL.

Vapours.

The absorption spectrum of the vapour of aniline in a tube 1-dm. long, and at 35°, has been studied by Pauer (*Wied. Ann.*, 1897, **61**, 374), who measured the positions of sixteen absorption bands, employing the radiant energy of the Cd spark. More recently, Grebe (*Diss.*, Bonn, 1905; and *Zeitsch. wiss. Photochem.*, 1905, **3**, 363) studied the vapour of aniline at 25–30°, and used the continuous spectrum obtained when a powerful spark was passed between aluminium poles immersed in water. He noted the presence, and measured the positions of twenty-eight bands. Neither of these observers, however, investigated the effect of varying the temperature and pressure.

The author has already given an account of the absorption spectra of the vapours of pyridine and some of its derivatives (this

vol., pp. 692 and 1035), and the apparatus used in this investigation is described in the first cited paper. Each band was separately measured at the different temperatures and pressures, and on the more refrangible edge.

Aniline.

TABLE I.

The absorption bands in aniline vapour at various temperatures and pressures in a column 2-dcm. long. Barometric pressure=763 mm.

Abbreviations: w.=weak; mod. str.=moderately strong; str.=strong; v.w.=very weak; r.w.=rather wide; narr.=narrow; mod. w.=moderately weak; v. str.=very strong. The brackets of the wave-lengths represent the measurements of similar related bands; they are not measurements of the width of the bands.

14°. 763 mm.		30°. 807 mm.		45°. 833 mm.	
λ.		λ.		λ.	
2978 w.		2978 mod.w.		2981 w., narr.	
2977 w.		2977 w.		2978 mod.str., narr.	
2975·5 w.		2974·5 mod.str.		2977 w.	
2973 w.		2973 mod.w.		2975 str., narr.	
{ 2969·5 w.		{ 2970·5 mod.str.		2973 mod.str.	
{ 2966·5 mod.str.		{ 2967 "		2970·5 mod.str., wider	
2964 w.		2964 w., r.w.		than 2973	
2961·5 mod.str.		2962 mod.str.		2966·5 mod.str.	
2958 " "		2959 "		2963 "	
{ 2953·5 w.		{ 2954·5 w., r.w.		2962 "	
{ 2951 w.		{ 2951·5 w., r.w.		2958·5 " narr.	
{ 2949 w.		{ 2950·5 mod.str., narr.		{ 2954·5 w., wide	
{ 2945 mod.str.		{ 2946 "		{ 2951 "	
{ 2942·5 str.		{ 2943 v.str.		{ 2949 mod.str., narr.	
{ 2940 wider and		{ 2940 wider and		{ 2946 "	
stronger than 2942·5		stronger than 2943		{ 2942·5 str., wide "	
2935 mod.str.		2934 mod.str.		{ 2939 "	
{ 2931 v.w. } equally		{ 2930 w.		2934 str., narr.	
{ 2928 v.w. } strong		{ 2927·5 w.		{ 2931 w., wide	
{ 2923·5 v.w. }		{ 2924 w.		{ 2928·5 "	
2921·5 v.w.		2921·5 w., narr.		{ 2924·5 "	
{ 2919 mod.str.		{ 2918 str.		2921·5 w., narr.	
{ 2914 str.		{ 2913·5 wider and		{ 2918 str., wide	
2912·5 v.w.		stronger than 2918		{ 2913·5 " "	
2909 v.w.		2912·5 v.w.		2912 v.w.	
2907 v.w.		2910 w., wide		2909·5 w., narr.	
2901 mod.str.		2907 w., narrower		2906 w., wide	
2897·5 str.		than 2910		2900 "	
2894 v.w.		2900 mod.str., narr.		2897 v.w., wide	
2891·5 w.		2897 str.		2893 w.	
{ 2879 v.w.		2894 v.w.		2891 mod.str., wide	
{ 2877 v.w.		2891 mod.str., narr.		{ 2878·5 v.w.	
{ 2875 v.w.		{ 2878·5 w., narr.		{ 2877·5 v.w.	
{ 2874 v.w.		{ 2877·5 "		{ 2876 v.w.	
{ 2871 v.w.		{ 2876 "		{ 2875 v.w.	
{ 2870 v.w.		{ 2875 "		{ 2872 v.w.	
{ 2868 w., wide		{ 2872 "		{ 2871 v.w.	
{ 2866 w., wide		{ 2871 "		General absorption began	
{ 2864 w., narr.		{ 2868 w., wide		about λ 2850.	
{ 2862 w., narr.		{ 2866 "		36 bands.	

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14°. 763 mm.	30°. 807 mm.	60°. 863 mm.
λ.	λ.	λ.
2859·5 str., wide	{ 2864 w., narr.	3005 v.w., wide
2857 mod.str.	{ 2862 w., stronger	3000 " "
{ 2856 w., narr.	than 2864	2995 w., narr.
{ 2853·5 v.w.	2859·5 str., wide	2993 v.w., narr.
{ 2851·5 v.w., narr. } equal-	2857 mod.str.	2989 " "
{ 2848·5 " " } ly	{ 2856 w., narr.	2985 mod.str., wide
{ 2846 " " } strong	{ 2854·5 " "	2978 " "
{ 2844 " " }	{ 2851·5 v.w., narr.	2975 " "
{ 2841 " " }	{ 2849 " "	stronger than 2878
{ 2838 " " }	{ 2847 " "	2972 mod.str., wide
{ 2836 " " }	{ 2844·5 v.w., f.wide	2970 " "
{ 2834·5 w.	{ 2841·5 " "	2966 " "
{ 2832 w.	{ 2838 w., narr.	2962 " "
{ 2830 mod.w. } equally	{ 2836 " "	2958·5 " "
{ 2828 " " } strong	{ 2834·5 " "	
{ 2826·5 " " }	{ 2832·5 " "	
2821 head of wide	{ 2830·5 r.w.	General absorption began
band	{ 2828 " "	at about λ 2940; the Cd
{ 2814·5 v.w.	{ 2826·5 " "	line 2948 was just visible.
{ 2810·5 v.w.	2821 head of strong	13 bands.
{ 2807 v.w., stronger	wide band	
than other two	{ 2816 w., narr.	
2804·5 mod. str.	{ 2812 " "	
2798·5 w.	{ 2808·5 " "	
{ 2794·5 w.	2805 mod.str.	
{ 2791·5 w.	2799 w., r.w.	
2787 w., wide	{ 2795 " "	
2782 w., wide	{ 2791·5 " "	75°.
2781 v.w.	2787 " "	893 mm.
2779 v.w.	2783 " "	
{ 2770 v.w.	2781 v.w.	λ.
{ 2768·5 v.w.	2778 v.w., narr.	3005 w., wide
{ 2766 v.w.	{ 2770·5 w., narr.	3000 " "
{ 2764·5 v.w.	{ 2768·5 " "	2995 " "
2759 v.w.	{ 2766·5 " "	2993 " "
2757·5 v.w.	{ 2765·5 " "	2989 " "
2755 v.w.	2759·5 mod.str., wide	2985 " "
2739 v.w.	2757·5 w., narr.	
2737 v.w.	2754 mod.str., narr.	General absorption began
2729 w.	2744 v.w., narr.	at about λ 2980.
2730 mod.str.	2743 " "	
2726 v.w.	2740 w., wide	6 bands.
2725 v.w.	2737·5 " "	
2722 v.w.	2729 mod.str.	
2720·5 v.w., wide	2730 stronger than 2729	
2717·5 " "	2726·5 w., narr.	
	2725 " "	
	2723 " "	90°.
General absorption began	2720·5 w., wide	923 mm.
at about λ 2400; Cd lines	2717·5 " "	λ.
2321, 2313, 2288, 2265,		No bands and general
2194, 2144 were just vis-	General absorption began	absorption began at about
ible.	at about λ 2430.	λ 3070.

83 bands.

85 bands.

The absorption spectrum of aniline vapour was also observed at a constant temperature of 17·5° and at gradually diminished pressures. The number and position of the bands were the same

as those observed at 14° and 763 mm. pressure in the above table; but they became sharper and weaker as the pressure decreased, and the position of general absorption was shifted towards the more refrangible regions of the spectrum. For example, under 754 mm. pressure the general absorption began at about λ 2400, the Cd lines 2329, 2321, 2313, 2288, 2265, 2194, 2144 were very weak; under 474 mm. pressure the general absorption began at about λ 2390, and the Cd lines beyond were stronger; whilst under 24 mm. pressure the general absorption began at about λ 2370, and the Cd lines were very strong.

The bands are more of the nature of strong lines than of what is usually understood by a band; and the width of many of them is measurable to the same degree and in the same sense as the images of many of the bright lines in emission spectra. They are not nearly so wide as an Ångström unit, and the width of some of the narrow bands is not measurable at all. The constitution and appearance of the bands is completely different from those of the vapour of benzene as described by Hartley (*Phil. Trans.*, 1907, A, **208**, 475). Most of the latter appear to be wide bands, sharp and strong on the more refrangible edge.

The results prove that (1) an increase in the temperature and pressure produces a strengthening and widening of the bands, and the appearance of new bands on the less refrangible side; (2) a decrease in the pressure, the temperature remaining constant, produces a weakening and narrowing of the bands. At the same time, (3) an increase in the temperature and pressure produces a shift of the region of general absorption towards the red end; whilst (4) a decrease in the pressure, the temperature remaining constant, produces a shift in the opposite direction.

The bands observed in the vapour of aniline occur chiefly as a series of doublets and triplets; some of them are sharper on the more refrangible edge, whilst others have the edges equally sharp; some of the doublets appear to be equally strong, and some of them show the less refrangible of the two not quite so strong as the more refrangible one. Of the triplets, some have the three constituents equally strong, and of others the most refrangible constituent is the strongest. In addition to these general observations, an attempt has been made to arrange the bands in a definite and regular manner. The following table indicates fairly consistent differences in the wave-lengths of the majority of the bands, considered as a whole:

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Monomethylaniline.

t°	Pressure in mm.	
14°	755	The rays were transmitted to about λ 2500 and then absorbed; of the Cd lines, 2321, 2313, 2288, 2265, 2194, 2144 were just visible
30	799	The rays were transmitted to about λ 2750 and then absorbed; the Cd line 2573 was just visible.
45	825	The rays were transmitted to about λ 3050, and then all the rays beyond were absorbed.
60	855	The rays were transmitted to about λ 2990 and then absorbed.
75	885	The rays were absorbed from about λ 3130.
90	915	" " " λ 3150.
100	931	" " " λ 3165.

Dimethylaniline.

12·5	765	The rays were absorbed from about λ 2500, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about λ 2750, but the Cd line 2573 was visible.
45	835	The rays were absorbed from about λ 3020, although the Cd line 2981 was visible.
60	865	The rays were absorbed from about λ 3070.
75	895	" " " λ 3120.
90	925	" " " λ 3140.
100	941	" " " λ 3170.

Monoethylaniline.

13·5	765	The rays were absorbed from about λ 2470, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about λ 2540.
45	835	" " " λ 2700, but the Cd line 2573 was well marked.
60	865	The rays were absorbed from about λ 3050.
75	895	" " " λ 3080.
90	925	" " " λ 3120.
100	941	" " " λ 3150.

Diethylaniline.

12	766	The rays were transmitted to about λ 2450, and the Cd lines 2329 to 2144 were well marked.
100	942	The rays were absorbed from about λ 3150.

o-Toluidine.

13	760	The rays were transmitted to about λ 2470; the Cd lines from 2329 to 2144 were well marked.
30	804	The rays were transmitted to about λ 2540; the Cd lines 2321, 2313, 2288, 2265, 2194, 2144 were visible.
45	830	The rays were transmitted to about λ 2700; the Cd line 2573 was just visible.
60	860	The rays were transmitted to about λ 2980; the Cd line 2748 was just visible.
75	890	The rays were transmitted to about λ 3060.
90	920	" " " " λ 3100.
100	936	" " " " λ 3120.

m-Toluidine.

t°	Pressure in mm.	
13	759	The rays were transmitted to about λ 2480 ; the Cd lines 2329 to 2144 were well marked.
45	829	The rays were transmitted to about λ 2750, the Cd line 2748 ending sharply ; the Cd line 2573 was just visible.
75	889	The rays were transmitted to about λ 3050 ; the Cd line 2980 was just visible.
100	935	The rays were transmitted to about λ 3110.

o-3-Xylidine (b. p. 223°).

12	752	The rays were transmitted to about λ 2400 ; the Cd lines 2329 to 2144 were well marked.
30	796	The rays were transmitted to about λ 2450 ; the Cd lines 2329 to 2144 were visible.
60	852	The rays were transmitted to about λ 2600 ; the Cd line 2573 was well marked.

m-2-Xylidine (b. p. 215°).

12	752	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about λ 2380 ; the series of Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about λ 2470 ; the Cd lines from 2329 to 2144 were visible.

Mesidine (b. p. 233°).

13	759	The rays were transmitted to about λ 2350 ; the Cd lines 2321 to 2144 were strong.
45	829	The rays were transmitted to about λ 2420 ; the Cd lines 2321 to 2144 were well marked.
75	889	The rays were transmitted to about λ 2550 ; the Cd lines 2313 and 2268 were just visible.
100	935	The rays were transmitted to about λ 3000 ; the Cd lines 2880, 2837, and 2748 were visible.

Benzylamine.

12.5	752	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were visible.
45	822	The rays were transmitted to about λ 2420 ; the Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about λ 2500 ; the Cd lines from 2329 to 2144 were visible.
75	882	The rays were transmitted to about λ 2650 ; the Cd line 2573 was well marked.
90	910	The rays were transmitted to about λ 2900 ; the Cd lines 2880 2837, and 2748 were visible.

General Results of the Absorption Spectra of the Vapours.

The results of the preceding observations of the absorption spectra of the vapours of aniline and its homologues prove that (1) aniline vapour has a considerable number of absorption bands which show relationships amongst themselves both in structure and in differences of wave-lengths; (2) under the influences of increased temperature and pressure the aniline bands become wider; weak bands become stronger; new bands make their appearance; and the general absorption is shifted towards the less refrangible region; (3) with decreased pressure, the temperature remaining constant, the aniline bands become sharper and weaker, and the region of general absorption is shifted towards the more refrangible region of the spectrum; (4) the most remarkable fact is that none of the homologues of aniline show any of the bands characteristic of aniline; (5) under the influences of increased temperature and pressure, the general absorption of the vapours of the homologues of aniline is shifted towards the less refrangible region.

Solutions.

The experimental methods employed in the study of the absorption spectra of solutions have been described before.

Aniline, Monomethylaniline, and Dimethylaniline.—The ultra-violet absorption spectra of alcoholic solutions of aniline have been described by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 257), who observed two bands at λ 285— λ 274 and λ 240— λ 230. Baly and Collie (*Trans.*, 1905, **87**, 1342) state that they repeated the observations with identically the same results. They also plotted the absorption curves of the bands in alcoholic solutions of monomethylaniline and dimethylaniline, and they show that the difference in the persistence of the band in the three cases is very marked. The absorption curve of dimethylaniline showed also a second band on the more refrangible side. The author found similar results to those of Baly and Collie in $N/1000$ -solutions of these three substances, and the curves are therefore not reproduced.

Monoethylaniline and Diethylaniline.—The author has investigated the absorption spectra of the ultra-violet regions of $N/1000$ -alcoholic solutions of these substances. It will be noticed (Fig. 1) that diethylaniline shows a second band at about $1/\lambda$ 3850, which is absent in monoethylaniline. It is precisely similar to the phenomena observed by Baly and Collie in mono- and di-methylaniline. It is also noticeable that the characteristic band of these substances is not so persistent as the corresponding bands in aniline, mono- and di-methylaniline.

o-Toluidine.—Hartley (Trans., 1885, **47**, 685) described a large, persistent band, the head of which was about $1/\lambda$ 3040.

m-Toluidine.—Baly and Ewbank (Trans., 1905, **87**, 1358) described a large, persistent band, the head of which was about $1/\lambda$ 3045.

The author has repeated the observations with *N*/1000-solutions of *o*-toluidine and *m*-toluidine, and found similar results. The curves therefore are not reproduced.

o-3-Xylidine and *m*-2-Xylidine.—*N*/1000-alcoholic solutions of

FIG. 1.

Oscillation frequencies.

Continuous curve: *N*/100-alcoholic solution of benzylamine.
 Dot and dash curve: *N*/1000-alcoholic solution of monoethylaniline.
 Dash curve: *N*/1000-alcoholic solution of diethylaniline.

these substances were observed, and their absorption curves have been drawn (Fig. 2). The general form of the curves is not unlike that of the toluidines. The bands are strongly persistent, and their positions are more towards the red end than the corresponding bands of the toluidines.

Mesidine.—An *N*/1000-solution of this substance exhibits a band which is not very persistent (Fig. 2). It is of some interest to note

that the persistency of this band is not so marked as that of either the toluidines or the xylydines.

Benzylamine.—An $N/1000$ -solution transmitted the rays to about λ 2290 through a thickness of 30 mm., but an $N/100$ -solution showed a moderately strong band, the curve of which has been drawn (Fig. 1). The position of this band is more towards the regions

FIG. 2.
Oscillation frequencies.

of greater refrangibility than in any of the substances herein described. It is of some importance to notice that the band corresponds in position and general form with the band $1/\lambda$ 3850 of diethylaniline.

General Results of the Absorption Spectra of the Solutions.

The general results of the investigation of the absorption spectra of the solutions are that (1) in the replacement of the hydrogen

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of the amino-group of aniline by alkyl groups, the persistence of the curve is considerably reduced; (2) when the hydrogen of the nucleus is replaced by alkyl groups the band becomes large and persistent; (3) in mesidine the band is not very strong or persistent; and (4) in benzylamine the band is fairly strong.

Liquids.

Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 274) pointed out that it was only on dilution that the absorption bands of aromatic substances became visible. The thickness of the layer of liquid used by them was 0.75 inch.

In investigating the absorbent effect of liquids a special form of cell was used. It consisted of two quartz plates firmly cemented to a brass box or telescope. One of the quartz plates was attached to a movable micrometer screw, which could be moved by thousandths of a mm., whilst the other plate was rigidly attached to a brass stage. A drop of the liquid to be investigated was placed between the two quartz plates, and these were then screwed together to a distance of 0.05 mm. apart. The screw was turned so that the quartz plate attached to it was moved closer and closer to the rigidly placed plate until the distance between them was about 0.001 mm. The light of the Cd spark was passed through the film of liquid for five minutes during each observation. Even through the thinnest films of about 0.001 mm. no absorption bands were seen; and the following numbers state the regions where general absorption began under the above conditions, and through various thicknesses of the films.

<i>Aniline.</i>		<i>Methylaniline.</i>		<i>Dimethylaniline.</i>		<i>Ethylaniline.</i>	
Thickness of film, mm.	λ .	Thickness of film, mm.	λ .	Thickness of film, mm.	λ .	Thickness of film, mm.	λ .
0.050	3185	0.050	3305	0.050	3310	0.050	3260
0.030	3175	0.030	3295	0.030	3300	0.030	3250
0.010	3160	0.010	3270	0.010	3280	0.010	3220
0.004	3150	0.004	3260	0.004	3260	0.004	3210
0.001	3140	0.001	3250	0.001	3270	0.001	3200
<i>Diethylaniline.</i>		<i>o-Toluidine.</i>		<i>m-Toluidine.</i>		<i>o-3-Xylidine.</i>	
0.050	3325	0.050	3150	0.050	3180	0.050	3175
0.030	3310	0.030	3135	0.030	3170	0.030	3165
0.010	3285	0.010	3120	0.010	3140	0.010	3150
0.004	3275	0.004	3100	0.004	3130	0.004	3140
0.001	3265	0.001	3095	0.001	3125	0.001	3130

<i>m</i> -2- <i>Xylidine</i> .		<i>Mesidine</i> .		<i>Benzylamine</i> .	
Thickness of film, mm.	λ .	Thickness of film, mm.	λ .	Thickness of film, mm.	λ .
0.050	3200	0.050	3250	0.050	2745
0.030	3180	0.030	3210	0.030	2735
0.010	3160	0.010	3160	0.010	2730
0.004	3145	0.004	3140	0.004	2720
0.001	3140	0.001	3130	0.001	2710

General Results of the Absorption Spectra of the Liquids.

The more important points of interest in the above table are that (1) the constitution of the molecules of the various compounds influences the general absorption. For example, the positions of general absorption of the ortho-compounds are different from those of the isomeric meta-compounds; the differences in this respect are comparable with the differences observed in the absorption of their solutions; (2) isomeric substances like benzylamine, the toluidines, and methylaniline show differences in their positions of general absorption, which are also analogous to differences in the absorption of their solutions; (3) none of the substances when in the liquid condition exhibit absorption bands through the thinnest films of 0.001 mm. thick.

It is not possible to imply very much from these numbers, as it is conceivable that films thinner than 0.001 mm. are obtainable under greater pressure, which would allow more of the ultra-violet vibrations to pass through. On the other hand, such excessively thin films produced by pressure could no longer be considered as liquids. The physical condition of the molecules would then be more of the nature of a vapour under high pressure, and the results would hardly be comparable.

Discussion of Results.

In discussing the preceding observations we are confronted with the fact that the vapours of toluene, the xylenes, and mesitylene all exhibit absorption bands as described by Pauer, Grebe (*loc. cit.*), and by Hartley (*Phil. Trans.*, 1908, *A*, **208**, 475), and that the number of bands decreases as the number of methyl groups increases; but in the toluidines, not only do the bands of toluene vapour disappear, but also those characteristic of aniline vapour, and similar phenomena are observed in the xylidines and in mesidine. Further, the replacement of a hydrogen atom of the amino-group in aniline by an alkyl group produces a complete elimination of the bands characteristic of aniline vapour.

In the alcoholic solutions the type of absorption band is very similar in aniline and in the methyl- and ethyl-anilines, whereas

in the toluidines and the xylidines the bands are stronger, different in position, and much more persistent than in either toluene, the xylenes, or aniline. The position and intensity of the band in benzylamine is also quite different from that of either toluene or aniline, but it corresponds in form and position with the more refrangible band of diethylaniline.

In the liquids, the general absorption is so great that the ultra-violet light is absorbed over the regions covered by the bands found in the solutions even at thicknesses of the liquids represented by 0.001 mm.

The author has already discussed (*loc. cit.*) the absorption spectra of the vapours of pyridine and some of its derivatives from a consideration of the impacts of symmetrically and unsymmetrically oriented molecules. It seems to be possible to apply a similar explanation to the phenomena described in this communication. In the methyl- and ethyl-anilines the symmetrical orientation of the aniline molecule is distorted, and the vibrations of the more symmetrical aniline, which produce selective absorption, are destroyed. The vibrations producing the absorption bands in the vapours of toluene or the xylenes are wholly different from those producing the bands in aniline vapour; and in the vapours of the toluidines and the xylidines there is no trace of any of the series of bands. The symmetrical orientation of the atoms is absent in these compounds, and the vibrations no longer exercise a selective absorption of the radiant energy. The energy may be chiefly absorbed by the translatory energy of the molecules producing general absorption, which becomes more pronounced as the temperature and pressure are increased.

In the solutions, the solvent acts partly as a constraint on the vibrations of the molecules of the dissolved substance, partly as a barrier to the number of encounters, and partly as an absorbent of a portion of the radiant energy. The result of these influences is that the vibrations of the molecules are quite different from those of the vapours. The atoms of the molecules under these conditions vibrate or oscillate in a definite way characteristic of each substance; and molecules of the same type, for example, aniline and the methyl- and ethyl-anilines, exhibit bands having similar forms. They differ only in their relative positions and in their increased or decreased persistencies, which are regulated by the number, weight, and type of the substituted groups.

In the liquids, the molecules are more closely packed, and they exert a greater tensional effect on each other, so that the restraining influences on the vibrations are still more powerful. The radiant energy is absorbed by the molecules, for even when the film of

liquid was only 0.001 mm. thick, no bands of selective absorption were observed in any of the liquids. Nevertheless, the differences observed in the positions of general absorption of the ortho- and meta-compounds and in the isomeric substances, benzylamine, methylaniline, and the toluidines, indicate that, besides the weight of the molecule, the orientation is also a factor in determining the extent of the general absorption as distinct from selective absorption.

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