Near Ultraviolet Absorption Spectrum of Hydroquinone, Resorcinol, and Catechol

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(Received June 12, 1950)

The near ultraviolet absorption spectra of the three dihydroxybenzenes in the vapor state are measured. 0,0 values are chosen and compared with benzene. Frequency differences of the main bands are given and some vibrational assignments made.

I. INTRODUCTION

THE absorption spectrum of benzene and several singly and doubly substituted benzenes[1] in the near ultraviolet region of 2600A have been discussed during recent years. Phenol[2] with one OH substitution has also been investigated in this region and it was of interest to see the effect of the double substitution. This was done with the hope of finding the amount of pure electronic excitation, also vibrational frequencies in the ground and upper electronic states.

It can be shown from symmetry considerations that the electronic transition observed in this region is, for the three di-hydroxy-benzenes, thus described:

$C_6H_4(OH)_2(1,4)$ Hydroquinone

                    $(V_h$ symmetry), $A_{1g} \rightarrow B_{3u}$

$C_6H_4(OH)_2(1,3)$ Resorcinol

                    $(C_{2v}$ symmetry), $A_1 \rightarrow B_1$

$C_6H_4(OH)_2(1,2)$ Catechol $(C_{2v}$ symmetry), $A_1 \rightarrow A_1$.

From symmetry, these transitions are allowed. From the work of Klingstedt[3] on this u.v. absorption of these molecules in hexane solution, each of the three molecules show about ten times the total absorption strength of benzene. It is also to be expected, then, that these spectra in the vapor will show the features (Sponer-Teller[1]) of an allowed transition, namely, a strong 0,0 band and excitation of totally symmetrical vibrations, with non-totally symmetrical vibrations appearing as 0,0 1,1 $\cdots$ $v-v$ transitions, and more weakly as $\Delta v = 2, 4$, etc., and one would not expect the features of a forbidden transition to appear with any prominence. Unlike the case of substitution by a single atom, these three molecules do not strictly possess a V_h and probably not a C_{2v} type of symmetry, respectively. However, the change in electronic wave function should not be expected to be great.

Existing data comprise work[4] on the vapor spectrum
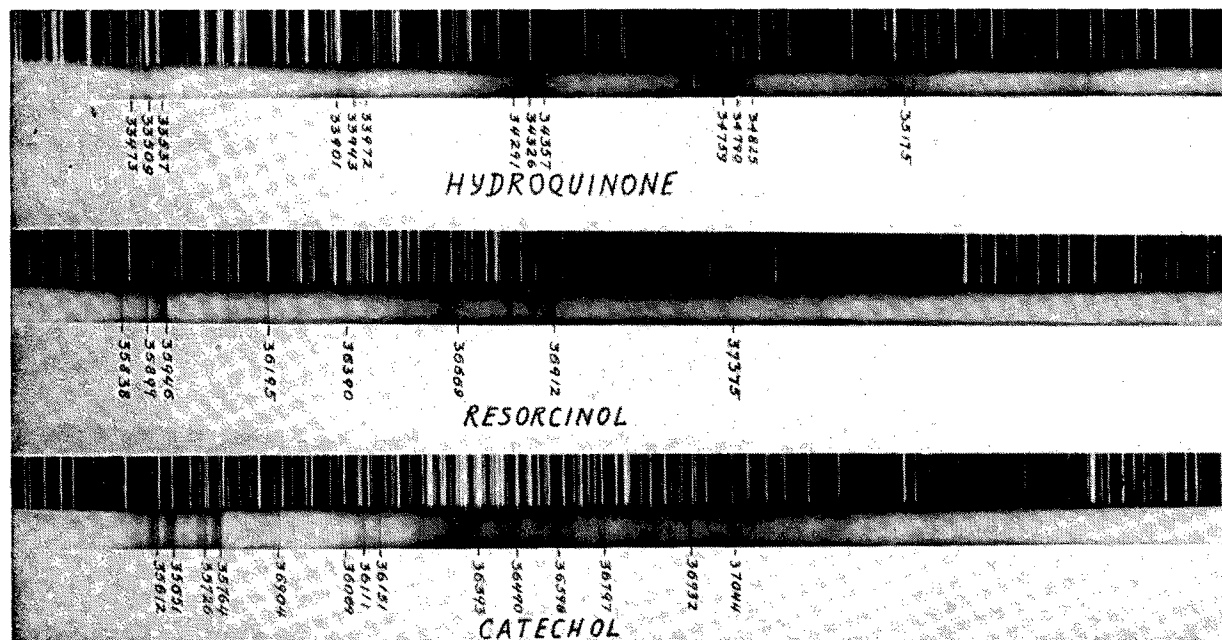
FIG. 1. Absorption spectra of hydroquinone, resorcinol, and catechol.

* This research was aided by the ONR Contract N6onr-255.

[1] H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 115 (1941); H. Sponer, Rev. Mod. Phys. **14**, 224 (1942).

[2] N. Ginsburg and F. A. Matsen, J. Chem. Phys. **13**, 167 (1945); M. B. Hall, Duke University, Ph.D. thesis, 1942.

[3] F. W. Klingstedt, Comptes Rendus **175**, 365 (1922).

[4] W. N. Hartley and A. G. G. Leonard, J. Chem. Soc. London **95**, 34 (1909), (Hydroq.); P. K. Seshan, Ind. Acad. Sci. **3**, 172 (1936), (Hydroq.); J. E. Purvis and N. R. McCleland, J. Chem. Soc. London **103**, 1088 (1913), (Catechol).

TABLE I. Hydroquinone.

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
33009	w	vBr	2	0−528
33017			2	
33029	w	Br	2	
33038	w		2	
33046	w		2	
33054	w	vBr	2	0−483
33075	w		2	0−462
33167	w		1	0−370
33177	w		2	
33197	w	vBr	1	
33230	w	vBr	2	
33251	w	Br	1	
33261	m		3	0−276
33277	w	vBr	1	
—				
33391	w	Br	1	0−146
33422	w	Br	3	
33432	w	Br	1	
33441	w	Br	4	0−96
33450	w		2	
33458	w	Br	2	
33473	m	Br	3	0−64
33502⎫	s		4	0−35
33509⎭	m		4	
33518	w	Br	1	
33527⎫	m	Br	2	
33537⎭	s		4	0−0
33553	w	Br	3	
33570	w	sh	2	
33589	w	sh	3	
33614	w	vBr	3	
33626	w	vBr	3	
33641	w	vBr	4	
33668	w	vBr	4	
33724	w	vBr	1	
—				
33757	w	Br	2	
—				
33791	w	vBr	2	
33812	w	Br	2	
33827	w		4	

TABLE I.—*Continued.*

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
33855	m	Br	5	
33868	w	Br	3	0+331
33878	m	Br	3	
33893	m	Br	4	
33908	s		4	0+435−64
33937⎫	s		4	
33943⎭	s		4	0+435−36 (?); 0+400
33953	w		1	
33959	w		3	
33968	w		1	
33972⎫	s		3	0+435
33986⎭	w	Br	1	
34262	w	Br	2	
34277	w	vBr	2	
34291	m		4	0+820−64
34314	w		2	
34326	m		2	0+820−36
34333	w	Br	1	
34346⎫	m		1	
34357⎭	s		3	0+820
34372	w		3	
34385	w		3	0+850
34578	w		2	
34727	w	vBr	4	0+820−64+435; 0−97+435+850
34759	m	Br	4	0+435−36+820; 0−64+435+850
34779	w	Br	4	
34790	s	vBr	4	0+435+820; 0−35+435+850
34826	m		4	0+435+850
35140	w		3	0+2×820−36
35167	m		4	
35175	m	Br	3	0+2×820
35195	w	Br	4	0+848+820
35213			4	
35224	m	Br	4	0+2×850
35259	w		2	
35558	m		4	
35608	m		4	0+435+2×820
35642	m		4	0+435+850+820
36011	w	Br	4	
36042	w	Br	4	
36074	w	Br	4	
36111	w	Br	2	

Note: Bands from 33473 up taken at about 115°C. Lower value bands taken progressively between 124°C and 138°C. Number of readings give some idea about difficulty of measurement because of diffuse and weak appearance.
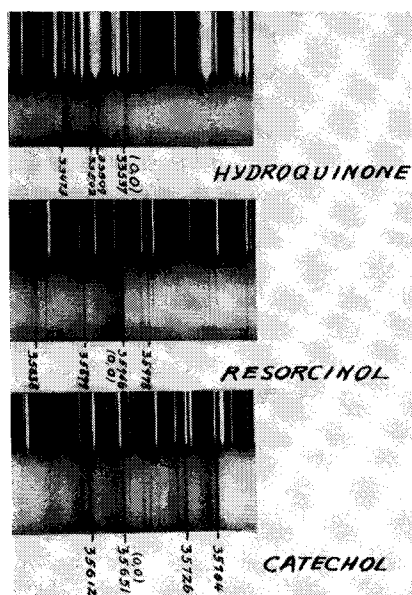

FIG. 2. Indicated 0,0 and surrounding region for hydroquinone, resorcinol, and catechol.

of hydroquinone and catechol and that of Klingstedt,[3] just mentioned, in solution. Some ground-state frequencies are known since Raman spectra[5] of the three molecules have been taken in the liquid state. No polarization data are given. however.

II. EXPERIMENTAL METHODS

A five-meter concave grating with a dispersion of 3.5A/mm, in the first order was used. The arrangement was the same as used in earlier work.[6] Bands were measured with a low power (9×) binocular microscope. The samples were of Eastman's highest grade. The bands were checked carefully for the presence of bands of phenol and the other two isomers in each case, and none were detected. A further check consisted in three

[5] K. W. F. Kohlrausch and A. Pongratz, Wien. Ber. **143**, 358 (1934); Mh. Chem. **65**, 6 (1935).
[6] W. F. Radle and C. A. Beck, J. Chem. Phys. **8**, 507 (1940).

TABLE II. Resorcinol.

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
35102	vw		2	
35108	vw		2	
35152	w		2	
35200	w		2	0−746
35398	w		2	0−548
35435	w		4	0−511
35448	w		2	0−498
35546	vw		1	
35564	s		4	0−382
35598	w		1	0−348
35675			1	
35687	w		1	
35730	m		4	
35735	w		4	0−211
35747	w		4	
35780	m		4	
35792	w		4	
35801	w		4	
35838	m		4	0−108
35851	m		4	
35899	m		4	0−47
35940 }	m		4	
35946 }	vs		4	0−0
35968	m		4	
35978	m		4	0−210+250 (?)
35986	w		4	
35999	w	Br	4	
36014	w	Br	4	
36045	w	Br	2	0−99
36051	w		4	
36059	w		4	0−210+333 (?)
36098	m		4	0+152
36147	w		4	0+250−47
36169		Br	4	
36188 }	w		2	
36195 }	m		4	0+250

TABLE II.—Continued.

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
36219	w	Br	4	
36226			4	0+332−47
36269	m		4	
36277	w		4	0+331
36312			1	
36344	w		1	
36354	w		1	
36390	w		4	0+444
36502	vw		2	
36518			2	
36532	vw		4	
36542	vw		4	0+703−108
36562	w		4	0+723−108
36576	vw	Br	1	
36589	vw		1	
36597	w		1	0+703−52
36623	w		4	0+723−47
36649	m		4	0+703
36669	m		4	0+723
36804	m	vvBr	4	0+966−108
36865	w		3	0+966−47
36906 }	w	Br	4	
36912 }	s		4	0+966
37108		Br	2	
37135	vw		1	
37156	m		3	0+1210
37178	w		3	0+1232 (?)
37245		Br	4	
37355		Br	1	0+2×703
37376	w		4	0+2×723 (?)
37486	w		2	
37613		vvBr	1	0+703+966
37638		Br	4	0+723+966
37867		Br	2	
37881	vw	Br	3	0+2×966

Note: Strongest bands of 0,0 and below measured at about 95°C. Bands lower than 0,0 measured progressively at temperatures between 95°C and 110°C.

times recrystallizing the benzene, after which the spectra appeared the same as before.

The whole cell with side arm was kept successively at the following temperatures and corresponding vapor pressures:

Hydroquinone   115   125   130   140°C
               at 0.02   0.6   1.0   2.0 mm Hg.

Resorcinol   70   80   90   100   110   135°C
    with pressures from roughly 0.1 to 5 mm.

Catechol   60   70   80   90°C
    with maximum pressure about 2 mm.

Values of precise vapor pressures at the required temperatures were not found in the literature, so those given were roughly estimated from data given by Stull.[7] Above these temperatures, it was not thought possible to bring out more bands to the red from 0,0 because of the increasing diffuseness of the spectrum.

Spectra at approximately liquid air temperature were taken with a special Dewar arrangement built by the Naval Research Laboratory, for taking absorption spectra at low temperatures. It was held immediately before the slit and consisted of two parts. Liquid air was

poured into one part, the copper end of which almost completely (i.e., except for the openings necessary for the light beam and insertion) surrounded the specimen, melted previously between two quartz plates. This part rested in a ground glass seal inside the other part containing quartz windows. The space between the two parts could then be evacuated.

III. RESULTS AND DISCUSSION

The general appearance of the spectra, seen in Fig. 1, shows that the bands become gradually more diffuse toward the high frequency side of the spectrum. This is much more pronounced than in benzene. Also, a continuous absorption seems to cover a large part of the spectrum, and this makes it more difficult to observe the bands. Surely for the bands of very diffuse appearance, and, also, for others, relatively sharper, frequency values are not easily measured with great accuracy. Overlapping of bands also is a source of some difficulty. The wave-number values of heads, given to the nearest unit, are accurate to about one wave number for the sharpest bands, but other bands may have an uncertainty of two or three or even more in some cases. The band edges become sharper in the contrast of prints, and

[7] D. R. Stull, Ind. Eng. Chem. 39, 517 (1947).

this seems to lead to a greater possibility of seeing rather broad bands. Very roughly estimated intensities are given in a column beside the wave numbers. Not much attempt to bracket close-lying bands, suggesting some closer relationship, as rotational branches, has been thought feasible. Due to the appearance of some bands, there is little doubt but that they, as in benzene, are composed of two or even in some cases three branches. Generally, the branch, lying to shorter wave-lengths which usually is the strongest has been taken in computing frequency differences. The bands for which this can be detected, degrade to the red in catechol and resorcinol, as in benzene, but to the violet in hydroquinone, so for the latter the setting is taken on the long wave-length edge for all bands. This unusual behavior in hydroquinone is discussed later.

Spectra of all three molecules were taken at the low temperature partly to aid in substantiating 0,0 values. The spectra are very broad but the whole pattern did indicate the same general trend as in the vapor, the whole spectrum simply being shifted to the red. These liquid air spectra are not reproduced, because they are of such a broad character with only a few main maxima showing.

A. Hydroquinone

About 85 band heads have been measured. The spectrum is shown in Fig. 1. The bands appear at about 100°C and there is complete take-out of the central region at about 130°C. The position of the whole band system is displaced to longer wave-lengths from that of benzene (Table IV, 0,0 transitions) and there is a considerable region of relative transparency between this system and a band system around 2000A. Many of the bands have a diffuse appearance although this does not seem to be as marked here as in catechol and resorcinol. This diffuseness in general increases with decreasing wave-length. For several reasons, including diffuseness, difficulty of locating the proper band head (double and triple branches), anharmonicity and overlapping, it is not always possible to give very accurate and unambiguous frequency assignments.
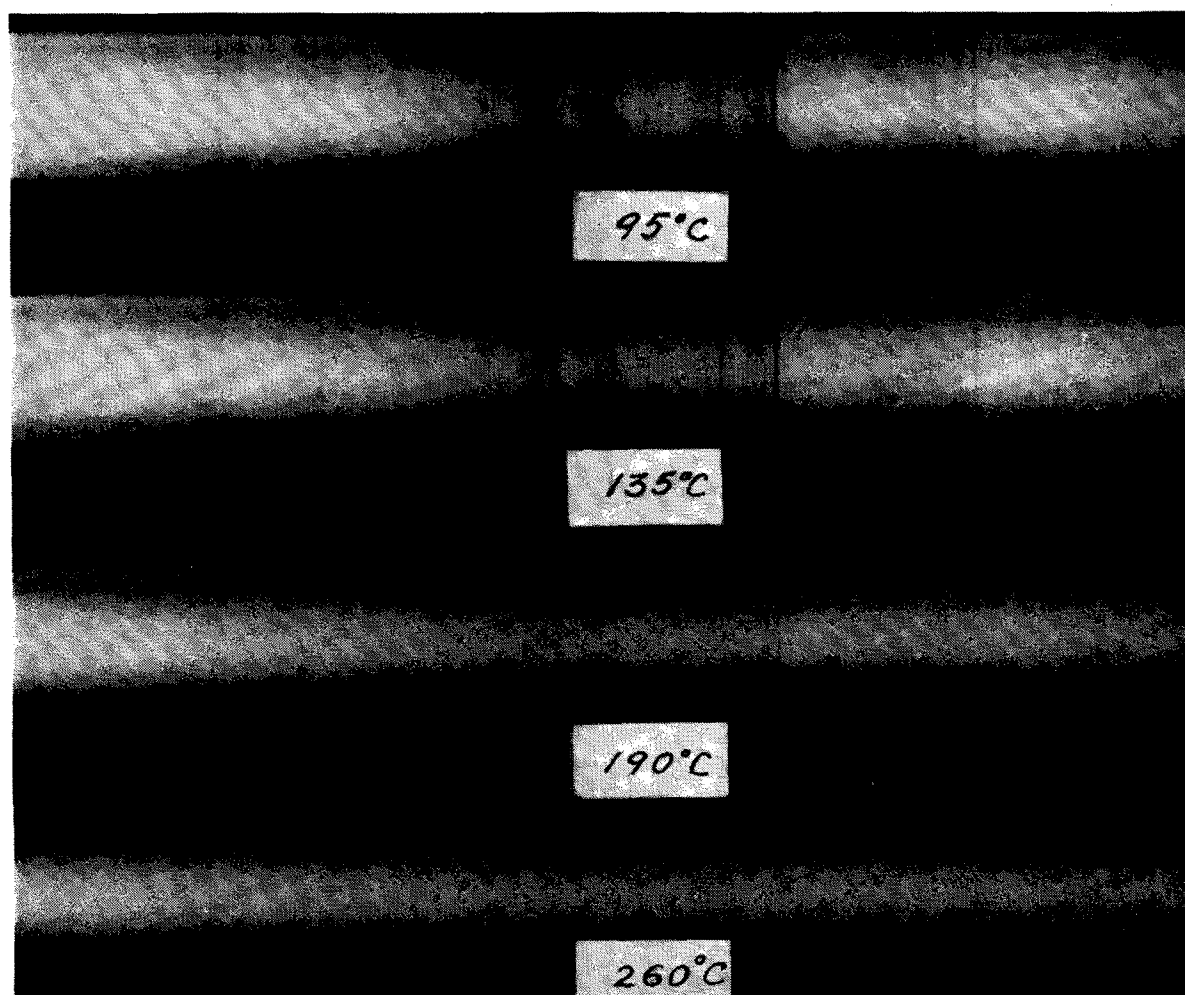

FIG. 3. Spectra of catechol with constant number of molecules at various temperatures.

TABLE III. Catechol.

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
34883	m	Br	2	0−768
34996	m		2	0−768+113
35050	w	Br	2	
35058	m	Br	2	
35079	m	Br	2	0−572
35144	m	Br		
35179	w	Br	2	0−572+100
35343	m		2	0−308
35383	m		4	0−268
35395	w	. Br	2	
35449	m		4	0−202
35459	m		2	0−308+116
35485	vw		2	
35528	m	Br	4	0−123
35569	m		4	0−82
35601	s		6	
35608	s		2	
35611	s		6	0−40
35630	m	vBr	2	
35643	m	Br	2	
35651	vs		6	0−0
35659	s		6	
35675	w		6	
35685	w		2	0+113−80
35692	w	Br	2	
35708	m		2	
35716	m		2	
35726	s		6	0+113−36
35756	m		6	
35764	vs		6	0+113
35771	m		4	
35843	m	Br	4	0+192
35861	vw	vvBr	2	
35869	vw	Br	2	
35877	m		4	0+227
35880			4	
35894	m		2	
35904	s		6	0+253
35917	w		2	
35948	vw	vBr	4	0+300
35991	w	vBr	2	
36018		vvBr	2	

TABLE III.—*Continued.*

Wave number (cm⁻¹)	Intensity		No. of readings	Assignment
36054	w	vBr	2	
36068	m	vvBr	4	0+500−83
36111	m	vvBr	4	0+500−41
36122	w	vBr	2	0+476
36136	w	vBr	2	
36151	m		4	0+500
36174			2	
36206			2	
36255	m	vBr	2	0+2×300 (?)
36294	m	vBr	4	
36333	m		2	
36352	m		4	
36375	m	Br	2	
36382	w		4	
36393	m		6	0+742
36453	w	vvBr	2	
36490	m		6	0+839
36557	m	vBr	2	
36596	m	vvBr	2	0+945 (2×476)?
36643	m	vBr	2	0+2×500
36675	m	vBr	2	
36703	w	vBr	2	
36759	m		2	
36797	m		6	0+1146
36859	m	vBr	2	
36897	w	vBr	4	
36932	m		6	0+1280
37035	w	Br	2	
37044	m		2	0+1280+113
37087	m	vBr	2	
37097	m	Br	2	
37135	m		2	0+2×742
37182	m		2	
37225	m	vBr	2	
37273	w		2	
37342	m		2	
37434	m	vBr	2	
37538	vw	Br	2	0+2×945
37573	vw	Br	2	
37767	w	vvBr	2	

Note. Strong bands from 35600 up measured at 60°C. Weaker bands measured at 70°C Bands below 35600 measured progressively at three temperatures ranging between 70°C and 90°C.

The gas spectrum contains four groups of bands. The high frequency bands in these four groups are located at 33537 cm⁻¹, 33972 (33537+435) cm⁻¹, 34357 (33537+820) cm⁻¹, 34790 (33537+435+820) cm⁻¹; the first two are much weaker than the last two. The 0,0 transition is taken to be 33537 cm⁻¹. If this interpretation is correct, the fact that the bands involving 0,820 and 0,435+820 transitions have higher intensity indicates a change in internuclear distance in the excited state. A very rough calculation leads to a change of the same order of magnitude as in benzene. In solution, the first strong peaks from the red lie at about 33000 cm⁻¹, with three or four following to shorter wave-length; the published data are not good enough to measure frequency differences, but do not contradict the estimate of about 400, 800, and 1200. As in the gas, the first two peaks are weaker than the next two.

The low temperature spectrum obtained was very broad and peaks were not clearly visible, so from this source the 0,0 is not established with certainty. The red end of the spectrum is shifted about 1100 cm⁻¹ toward the red from the assumed 0,0 transition in the gas.

The frequency assignments in Table I refer mainly to transitions from the vibrationless ground state. With the temperatures used, bands to about only 500 cm⁻¹ to the red from 0,0 were observed with sufficient intensity or clearness. For the purpose of correlation the papers of Sponer and Kirby-Smith[8] and the diagrams of Kohlrausch[9] were mainly used.

From the 0,0 group there is a group 435 cm⁻¹ to the violet, but it appears only once. We recall that there arise two components from the degenerate 606 vibration in benzene, one totally symmetrical and the other non-totally symmetrical. Kohlrausch[5,9] ascribes the 468 Raman line (value in liquid) to the symmetrical one. It is possible that the 435 frequency is of this type. We expect the other, non-totally symmetrical component to have a higher value. This is seen for example, in

[8] H. Sponer and Kirby-Smith, J. Chem. Phys. 9, 667 (1941).
[9] K. W F. Kohlrausch, Ramanspektren, Hand. und Jahrbuch der Chem. Phys. 9, 367 (1943)

TABLE IV. Frequency values of 0,0 transitions of hydroquinone, resorcinol catechol, and differences Δ from benzene.

	Vapor		Liquid		Solid	
Benzene	38089 (calc.)		37750		37828 (calc.)	
		Δ		Δ		Δ
Hydroquinone (p)	33537	4552	33000	4750	32500	5330
Resorcinol (m)	35946	2143	35800	1950	35900	1930
Catechol (o)	35764	2325	35200	2550	34000	3830

mono-deutero and para-deutero-benzene,[10] in mono-chloro[11] and the di-chloro-benzenes.[12] This other frequency may be the Raman 531; there is also a band, 33009, shifted to the red by about this amount.

The 406 in benzene splits in V_h symmetry into an A_{2u} and a B_{2u} but for neither are transitions $0-1$ or $1-0$ allowed.

In phenol the Raman frequency 810 is ascribed[13] to the totally symmetrical $C-OH$, the frequency 830 to some type of ring vibration.[14] One should expect that the corresponding frequencies in hydroquinone are not very different. 829 and 853 are found,[5] and it would seem right to ascribe the latter to the ring vibration (this agrees with a rough estimate from the square root ratio of the masses). In ortho- and meta-chlorofluoro benzenes also the ring vibration is chosen[15] as the higher of the two. It is now very curious that in our spectrum there are two bands at 820 and 850 cm⁻¹ to the violet of the 0,0 transition respectively. Both form progressions which, however, because of diffuseness cannot be followed much beyond the second members. 820 and 850 are practically identical with the above Raman frequencies, but refer to vibrations in the excited state. In no case up to now, for benzene or substituted benzenes, have the upper state frequencies been found to be so close to the ground state frequencies, but they were found to be 30 to 90, rarely more, wave numbers lower.

As is usual there is the recurring pattern of small frequency differences, probably n,n transitions. The difference 36 might be explained by the 370 vibration (33167) dropping in the upper state to 331 (band at 33868) or by 462 dropping to 435, although the latter difference being 9 cm⁻¹ off may not be plausible.

In benzene and in all the singly and doubly substituted benzenes which have come to our attention to date, the degradation of the bands is to the red. This means, of course, that at least one moment of inertia is higher in the excited state than in the ground state. Here, however, all those bands for which it is possible to observe a sharp edge (many bands are very diffuse)

behave oppositely. This is observed in an even more pronounced manner in para-chlorophenol, on which substance work by Y. C. Kao is in progress in this laboratory. This means that, for these substituted benzenes at one moment of inertia is lower in the excited state than in the ground state. The structural appearance of the bands is not uniform. For example, the 0,0 band has a different structure (2 branches only) than the band at $0,0-35$ (3 branches). The latter looks somewhat like a mirror image of the $A_0{}^0$ of benzene $(0,0+520)$.

B. Resorcinol

The vapor spectrum contains three outstanding groups of bands, the violet band of each is located at 35946, 36663, and 36912. The first one was chosen for the 0,0 transition (Table II).

In the low temperature spectrum, three peaks apparently corresponding to these three groups appear to be present. This substantiates the choice of the 0,0 position. All peaks were displaced by a rather constant small amount, roughly less than 400 cm⁻¹ to the red from the corresponding position in the gas.

In searching on the red side of the 0,0 for frequencies found in the Raman spectrum there is a band displaced by 748 cm, the value given by Kohlrausch, which is probably the totally symmetrical $C-OH$ vibration. In the upper state there are two bands at 36649 $(0+703)$ and 36669 $(0+723)$, both fairly strong. They probably correspond to the Raman 724 and the above 748.

The symmetrical ring vibration corresponds probably to the strong 1000 Raman frequency, which may drop in value to 966 in the upper electronic state. (Strong band at 36912.) Since bands to the red from the 0,0 of more than 850 cm⁻¹ were not in these spectra, the ground-state frequency was not observed.

A broad Raman line is reported at 531. There are bands to the red for 500, 513, and 550, and the Raman value may be an average of these. The relatively strong bands at 35735 $(0-211)$ and 35564 $(0-382)$ probably contain non-totally symmetrical vibrations and are considerably weaker than a mere Boltzmann decrease would predict.

On the violet side, other differences appear in prominent bands: 152, 250, 444, and others at 1210 and 1232 in bands not so strong. In the Raman spectra, there are in the region around 1000 several totally symmetrical vibrations which are rather independent of substituent, among which are 1000 and 1290. 1000 may drop in the higher state to 966 as stated above and 1290 to 1210.

Several small frequency shifts appear, e.g., 47 and 108, connected probably with 1,1 transitions. This could however be confirmed if bands belonging to $0-1$ and $1-0$ transitions with satisfactory frequency values were found. This is not the case, from which one may conclude that the vibrations involved are non-totally symmetrical.

[10] A. Langseth and R C. Lord, Det. Kgl. Danske Vidensk Selskab. 16, No. 6 (1943).
[11] H. Sponer and S. H. Wollman, J. Chem. Phys. 9, 816 (1941).
[12] H. Sponer, Rev. Mod. Phys. 14, 229 (1942).
[13] J. Lecomte, J. de phys. et rad. 8, 489 (1937).
[14] K. W. F. Kohlrausch, Physik. Zeits. 37, 68 (1936)
[15] A. M. Bass, Duke University, M.S. thesis, 1943

C. Catechol

Many bands towards shorter wave-lengths become extremely diffuse so that it becomes impossible to follow the progressions to higher frequencies. Many of the bands are diffuse on both sides, but the measurements were taken on the violet edge (Table III).

The spectrum contains two groups of bands; (Fig. 2) the group towards the red contains four bands, about 41 cm^{-1} distant from each other, the group of shorter wave-length surely two and perhaps also four bands, also 41 cm^{-1} apart. The wave number difference between the groups is 113 cm^{-1}. It was expected that one of these bands corresponded to the $0-0$ transition. To ascertain whether any ground-state vibration is involved, a series of exposures (Fig. 3) were taken, with a constant amount of the material (about one milligram) placed in the cell, and the temperature was raised from 60°C to 250°C. It was evident that at about 75°C all the material had evaporated. Above that temperature all the bands seemed to get weaker, but the edges seem fairly sharp even at elevated temperatures. At the same time a continuous background appears; its intensity increasing with temperature, so that at first glance the spectrum appears more diffuse. Since these results did not give decision on the 0,0 transition, spectra of a thin solid layer were taken next at liquid air temperature. While no separate bands are visible, there seem to be two broad maxima, about 100 cm^{-1} apart and of equal intensity (as are the two groups 113 cm^{-1} apart in the vapor state). There is no absorption further to the red, therefore it seems reasonable to identify these two peaks with the two groups of bands in the vapor state and conclude that they start from the vibrationless ground state. Accordingly it was concluded that the violet band of the band group located to larger wave-length, with a wave number of 35651, is the 0,0 band, while the other bands of this and the other band group, with wave-number differences of about 41, are probably n,n transitions (see the remarks at the end of the discussion on resorcinol). There are two possible explanations of the wave-number differences, 113 cm^{-1} between the two band groups: It may be a vibration frequency in the excited state, or an electronic doublet. A vibration frequency as low as 113 is not very probable.

From polarization data and the correlation diagram,[8] 202 seems to be non-totally symmetrical and weak as expected. If the 113 in the upper state represents this vibration, the difference gives 89 instead of 81 which is observed. This may be too far off to be plausible. The bands in general have more than one branch and an error of 20 cm^{-1} or even more could be made by a measurement to points which do not correspond to the same branch. Here, branches of corresponding, strong, intensity towards the violet side are taken.

The 308 does not seem to be a totally symmetrical vibration, and the band containing it is weak. The vibration 572 is probably a totally symmetrical one, and

appears with fairly good intensity. The Raman frequency 768 is probably the totally symmetric $C-OH$ valence vibration in the ground state. To it corresponds the band at 34883; considering the small Boltzmann factor involved, this band is fairly strong.

To the violet side of the 0,0 transition there lies another group of four bands (with differences of 41 cm^{-1} as described before). Its violet band lies at 36151, and is interpreted as $(0,0+500)$. There is another band at 35904 $(0,0+253)$. One might think that $500=2\times253$. However this band does not form part of a group of four; therefore it seems more probable that the two bands are of different origin. No interpretation for the two frequencies 253 and 500 is given.

The totally symmetric ring vibration is probably the Raman frequency 1036. There are two bands, 839 and 945 cm^{-1} respectively shifted to shorter wave-lengths from the 0,0 transition. Either 839 or 945 may be the totally symmetric ring vibration in the excited state. To decide between the two it would be useful to find the 1,1 transition, but this should be very weak because of the small Boltzmann factor.

Other bands to the violet, with frequency differences against 0,0 of 1146 and 1280 are observed. Because of the strength of these bands, the corresponding vibrations would seem to be totally symmetric. 1146 may be the excited state vibration corresponding to the Raman line 1263.

Band groups with small frequency differences of approximately 41 appear besides the three mentioned earlier. While it is probable that $n-n$ transitions are involved, it has not been possible definitely to assign them to any particular vibration. If the transitions belonged to the ground-state frequencies 202 or 306, there ought to be $0-1$ transitions at $35764+202-40 =35926$ or $35764+308-40=36032$. These bands are not visible on the plates. For the Raman frequency 454, the corresponding band would be at $35764+454-40 =36188$; this region is masked by several closely lying bands.

SUMMARY

In conclusion we wish to emphasize that the assignments here included, are not final in many cases because of the difficulties of setting up a complete unambiguous correlation table of vibration frequencies.

Table IV gives the comparison between assigned 0,0 transition values, measured in vapor, and very roughly estimated in solution[3] and solid, and the corresponding value in benzene. Here we notice a change from the usual order $p.m.o.$[16] This and also a general difficulty of interpretation may be related to a deviation from a true C_{2v} or V_h symmetry.

The various peaks in a given liquid appear to shift by approximately the same amount from their position

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[16] Miller and Thompson find in the substituted benzo-trifluorides the order of p and m to be reversed. C. H. Miller and H. W. Thompson, J. Chem Phys. 17, 845 (1949).

in the vapor. The same relation seems to hold also between solid and vapor.

Choice of 0,0's is greatly aided by low temperature spectra, and it is intended to include these spectra taken at lower temperatures in our future program.

The occurrence of degradation to the violet is of great interest, but the whole problem of the band shape is larger than could be contained in the scope of this paper.

The C—Br Bond Dissociation Energy in Benzyl Bromide and Allyl Bromide

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The pyrolysis of organic bromides in a stream of toluene is described as a method for the determination of the C—Br bond dissociation energies. The technique used makes it possible to discriminate between two mechanisms of decomposition:

$$R.Br \rightarrow R \cdot + Br \qquad (a)$$
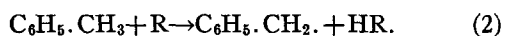$$R.Br \rightarrow olefin + HBr. \qquad (b)$$
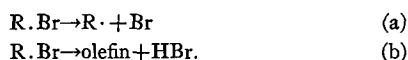
It was found that both benzyl and allyl bromide decomposed according to mechanism (a), the bromine atoms reacting readily with toluene to give hydrobromic acid. The rate of the primary dissociation process was measured by the rate of formation of HBr. It was proved that the thermal decompositions of benzyl and allyl bromide were homogeneous gas reactions obeying first order kinetics. The activation energies were calculated at 50.5 ± 2 kcal./mole and 47.5 ± 2 kcal./mole, and identified with $D(C_6H_5.CH_2-Br)$ and $D(CH_2:CH.CH_2-Br)$, respectively.

The fate of the allyl radical is discussed, and a rough estimate of the activation energy for the reaction

$$CH_2:CH.CH_2 \cdot + C_6H_5.CH_3 \rightarrow CH_2:CH.CH_3 + C_6H_5CH_2 \cdot$$
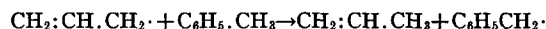
leads to a value of 14–17 kcal./mole.

The problem of ionic contribution in the C—Br bonds is discussed.

The estimation of the dissociation energies of the C—Br bonds of various organic bromides is of great interest since the values for these dissociation energies, combined with the heats of formation of the relevant bromides in the gaseous state, make it possible to determine the heats of formation of various organic radicals. Furthermore, the latter data in conjunction with the heats of formation of hydrocarbons enable us to calculate the various C—H and C—C bond dissociation energies and the resonance energies of the relevant radicals.

## THE METHOD OF DETERMINATION OF THE C—Br BOND DISSOCIATION ENERGY

IT was deduced by Baughan and Polanyi[1] that the C—Br bond dissociation energies are much lower than the respective dissociation energies of C—H or C—C bonds. In consequence one might expect that the thermal decomposition of an organic bromide RBr would result in rupturing the weakest C—Br bond with the formation of a radical R and a bromine atom, i.e.,

$$R.Br \rightarrow R + Br. \qquad (1)$$

The estimation of the rate of reaction (1) by a suitable experimental technique would lead to the determination of the C—Br bond dissociation energy. That has been achieved in our work by investigating the pyrolysis of organic bromides in a stream of toluene. As was shown in previous communications[2] toluene is very effective in removing various radicals which react with it according to Eq. (2)

$$C_6H_5.CH_3 + R \rightarrow C_6H_5.CH_2 + HR. \qquad (2)$$

The relatively stable benzyl radicals produced in this type of reaction dimerise to give dibenzyl which is one of the products of pyrolysis.

If the pyrolysis of RBr takes place according to the above scheme, then each decomposed molecule of RBr will give rise to one molecule of HBr, of RH, and of dibenzyl; and the rate of the primary dissociation process of the organic bromide could be measured by the rate of formation of HBr, RH, or dibenzyl. It is possible, however, that a molecule of an organic bromide could decompose into HBr and the corresponding olefin.[3] This case can be easily distinguished from the former, for although HBr would again be a product of pyrolysis, no dibenzyl would be produced. Hence, using toluene as a carrier gas one would be able to measure for an organic bromide both the rate of decomposition into radicals according to Eq. (1), and into HBr and olefin according to Eq. (3)

$$RBr \rightarrow HBr + olefin, \qquad (3)$$
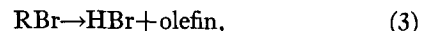
even if these reactions occurred simultaneously. The

[1] E. C. Baughan and M. Polanyi, Nature 146, 685 (1940).

[2a] M. Szwarc, J. Chem. Phys. 17, 432 (1949). [b] M. Szwarc, J. Chem. Phys. 17, 505 (1949) and Proc. Roy. Soc. A198, 267 and 285 (1949).

[3] E T. Lessig, J. Phys. Chem. 36, 2335 (1932). E. L. Vernon and F. Daniels, J. Am. Chem. Soc. 55, 922 (1933). P. Fugassi and F. Daniels, *ibid.* 60, 771 (1938) F. Daniels and P. L. Veltman, J. Chem. Phys. 7, 756 (1939).