SEPTEMBER 1, 1932 PHYSICAL REVIEW VOLUME 41

The Resonance Fluorescence of Benzene

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(Received July 18, 1932)

The fluorescence of benzene vapor has been studied at pressures varying from 25 to 0.01 mm mercury using, as a monochromatic excitation source, the 2536A mercury line. At the lowest investigated pressures the emission spectrum consists of several narrow line groups. Their spacing shows that emission occurs in transitions from a definite vibrational level of the excited state to various vibrational levels of the normal state. The following vibrational frequencies of the normal benzene molecule have been identified: 160, 793 (uncertain), 988, 1200, 1354, 1663 and 3139 cm^{-1}. The fine structure of the line groups has not been fully resolved. They appear to consist each of two strong lines with several weaker ones grouped around them. The ordinary, high pressure, fluorescence of benzene vapor is interpreted as being due to transitions from the lowest vibrational level of the excited state (or states). This level is reached by molecules as the result of inelastic collisions upon excitation. An apparently continuous emission present at the long wave-length end of the fluorescence spectrum at higher vapor pressures is attributed to two causes, decreased intensity of bands heads owing to an increased moment of inertia of the molecule in higher vibrational levels of the normal state, and a crowding of vibrational levels when the total vibrational energy is large. This conclusion is supported by observations of the fluorescence of toluene, which appears to be almost wholly continuous.

THE ultraviolet spectrum of benzene has attracted the attention of many investigators. Among the more recent studies should be mentioned those of Henri,[2] Pringsheim,[3] Shapiro, Gibbs and Johnson[4] on the absorption of the vapor, of Kronenberger[5] on the absorption and fluorescence of the solid at low temperatures, of Pringsheim and Reiman[6] on the fluorescence of the vapor and of McVicker, Marsh and Stewart[7] and of Austin and Black[8] on the high-frequency emission spectrum of benzene. Although notable success has been achieved by these workers in the interpretation of the ultraviolet bands of benzene, the analysis is still far from complete and certain.

The first absorption bands of the vapor set in at about 2742A and extend into the ultraviolet with increasing intensity. The beginning of the spectrum, at least, consists of clearly distinguishable band groups about 920 cm^{-1} apart. The closely spaced bands within each group are shaded to the red. The intensity within each group also falls off to the red. Below 2200A the bands become diffuse, predissociation setting in.[2]

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[1] M. Nelles, Charles A. Coffin Fellow.

[2] Henri, Structure des Molecules, Herman, Paris (1925).

[3] Pringsheim, Fluoreszenz und Phosphoreszenz, Springer, Berlin (1928).

[4] Shapiro, Gibbs, and Johnson, Phys. Rev. **38**, 1170 (1931).

[5] Kronenberger, Zeits. f. Physik **40**, 75 (1927); **63**, 494 (1930).

[6] Pringsheim and Reimann, Zeits. f. Physik **29**, 115 (1924); Ann. d. Physik **80**, 43 (1926).

[7] McVicker, Marsh and Stewart, J. Chem. Soc. **123**, 642 (1923).

[8] Austin and Black, Phys. Rev. **35**, 452 (1930).

It seems to be the consensus of opinion now that the major part of the spectrum can be represented by equations involving two upper electronic levels and several vibrational frequencies, of which one is about 920 cm^{-1}, and the other, 160 cm^{-1}. Although the equations proposed are essentially similar, they differ in many details. Shapiro and co-workers brought forward strong evidence that the 160 cm^{-1} frequency belongs to the normal state. This will probably necessitate some revision of earlier interpretations because Kronenberger finds a 160 cm^{-1} frequency to be present in absorption of the solid at 14°K. If his data can be applied to the vapor, it follows that both the normal and the excited electronic levels possess nearly the same vibrational frequency, a circumstance not considered in the above-mentioned eqations.

The fluorescence spectrum of benzene extends from about 2600A to the red. It is quite similar to the absorption spectrum, consisting also of band groups, but separated now by 980 cm^{-1}. Pringsheim and Reimann[6] describe the bands within each group by means of two progressions, each involving the 160 cm^{-1} frequency and being displaced one against the other by 83 cm^{-1}. Austin and Black[8] require six separate equations involving altogether five vibrational frequencies, a number so large as to be meaningless, to describe some hundred band heads found in emission in high-frequency discharge, a spectrum very similar to fluorescence.

Most of the work on the fluorescence of benzene has been done at relatively high pressures. Under these conditions the spectrum emitted is quite independent of the source of excitation. Pringsheim and Reimann[6] reported, however, that at 0.3 mm vapor pressure with illumination by the 2536A mercury line, a fluorescence spectrum is obtained which differs somewhat from that at higher pressures and polychromatic illumination. On the basis of this work, it seemed likely that, by using a monochromatic source of excitation and vapor pressures so low as to minimize the effect of inelastic collisions, one might obtain considerably simplified emission spectrum which would throw further light on the structure of benzene.

EXPERIMENTAL DETAILS

For these experiments a very intense source of monochromatic illumination was needed, the fluorescence of benzene being not strong even at high pressures. Use was made of the strong emission of the 2536A line by the low pressure mercury arcs. Fig. 1 shows the arrangement adopted, which is merely a suitable modification of variously described[9] controlled-vapor-pressure mercury arcs. The lower vertical part of the lamp is immersed in cold running water (15°C) and the arc is struck, by the application of a spark coil, between the mercury electrode *A* and a molybdenum electrode *B*. A metal disk *C* deflects mercury vapor to the cooled glass walls. The lamp is continuously evacuated by a fast diffusion pump. The current was usually kept at 25 amp., the potential drop being about 30 volts. The lamp ran very steadily on 110 volts d.c. Two quartz tubes, *D* and *E*, are mounted coaxically

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[9] Taylor and Bates, Proc. Nat. Acad. Sci. **12**, 692 (1926).

in the lamp. The De Khotinsky seals are indicated in Fig. 1 by the letter *K* while *P* is a somewhat flexible joint made of asbestos rope soaked in picein cement, the whole being covered by rubber. Benzene vapor flows very rapidly through the inner tube *E*. It is generated in a flask in which solid benzene is maintained at a constant temperature and is condensed, after passing *E*, in a liquid air trap followed by a pump. Through the annular space between the quartz tubings is passed either water or a 5 molal solution of acetic acid. The latter acts not only as a cooling agent but also as a light filter, the 2 mm layer of its absorbing all wave-lengths transmitted by quartz but shorter than 2400A. The 2536A line is absorbed by this solution only very slightly. Longer wave-lengths than this, besides being weak in a lamp of the present type are too feebly absorbed by dilute benzene vapor to contribute materially to excitation. Thus an almost monochromatic source of excitation is obtained, of intensity sufficient to produce a strong image of the fluorescence of benzene vapor at 25 mm pressure in one minute. With benzene at 0.01 mm pressure, exposures of ten hours' duration were required to obtain workable plates. A quartz Hilger E1 (Littrow) spectrograph was used throughout this work. The wave-length determinations were made in the usual way with an iron arc for the comparison spectrum.

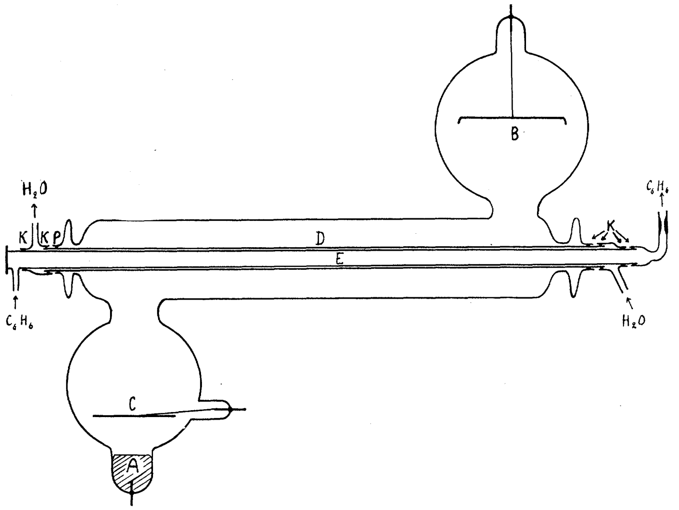

Fig. 1. The light source.

Some decomposition of benzene occurred on illumination, particularly when water and not acetic acid was used as the cooling agent. The decomposition products settled on the walls of tube *E* and made them opaque to mercury radiation. It was necessary, therefore, during protracted runs, to remove and clean this tube occasionally.

Results

Benzene fluorescence was studied at vapor pressures varying from 25 to 0.01 mm mercury. In this range no difference could be noticed between the photographs obtained with water as the cooling agent and those for which the acetic acid light filter was used. This shows that in a lamp of the described type only the 2536A line contributes materially to fluorescence. The spectrum emitted at pressures above about 1 mm is practically independent of pressure and, as our measurements indicate, is identical with that described by other workers. Fig. 2, curve 2, reproduces a microphotometer record of the short wave-length half of it. Two complete band groups and the beginning of a third can be seen on the figure. One progression in each group is marked by the figures 0, 1, 2 with subscripts. The entire spectrum on the plates obtained shows four such groups. They become weaker and less distinct towards the red.

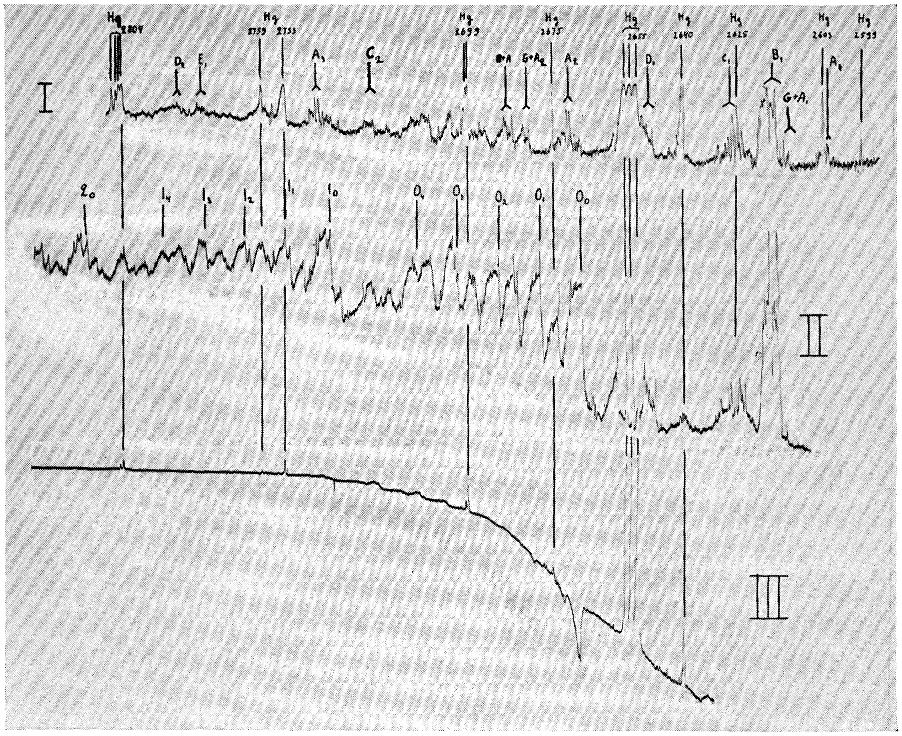

Fig. 2. Microphotometer records of fluorescence spectra. I. Benzene at low pressures. II. Benzene at high pressures. III. Toluene.

Below 1 mm pressure the appearance of the emission spectrum gradually changes. At about 0.1 mm the band heads nearly disappear and the spectrum consists of numerous unresolved line groups, of which more than two hundred have been measured between 38,400 and 34,500 cm^{-1}. As the following will show, this spectrum represents the transition to the real resonance fluorescence. It does not show obvious regularities except some which are similar to the high pressure fluorescence and the recording here of our measurements

TABLE I. *Emission lines in resonance fluorescence.*

λ (air)	cm^{-1}	*I*	λ (air)	cm^{-1}	*I*
2588.67	38618.4	1	2742.29	36455.1	5
2600.31	444.0	0d	43.26	442.2	5
01.56	427.0	1	44.04	431.8	1dd
01.96	421.1	1	44.77	422.2	2d
03.15	403.5	0	56.13	272.1	3
12.00	273.4	0	58.02	247.2	0d
12.98	258.5	1	58.73	237.9	0d
15.23	226.1	10	67.44	123.8	0d
16.01	214.7	3d	68.99	103.6	0
16.49	207.5	3d	72.92	052.4	0d
17.25	196.6	10	73.67	042.7	0d
18.54	177.8	3d	77.02	35999.8	0
18.96	172.7	2d	77.71	990.3	0
23.76	101.9	1d	78.46	980.5	0
24.48	091.4	0d	79.26	970.2	1
26.29	065.2	3	81.61	939.8	0
27.46	048.2	2d	83.33	917.5	0d
28.13	038.5	0d	84.78	898.9	0d
29.86	013.5	0	85.60	888.3	0d
30.18	008.9	0	2813.52	532.2	0d
47.55	37759.5	1	14.83	515.7	0
49.11	737.3	1d	15.65	505.3	0
67.17	481.8	0	16.21	498.3	0d
67.62	475.5	0d	16.91	489.5	0
68.09	468.6	0d	18.39	470.8	2
70.10	440.7	3	19.58	455.9	2
70.77	431.3	3	20.42	455.8	0
81.29	284.4	1	21.35	433.6	0d
82.96	261.2	1d	22.16	423.4	0d
86.13	217.2	2d	28.99	337.9	0
87.67	195.9	1d	29.84	327.3	0d
88.25	187.9	0d	31.58	305.6	0d
93.57	114.4	0dd	32.51	294.0	1
95.21	091.9	1d	35.35	258.6	1
96.50	074.1	1d	36.13	249.0	0d
97.33	062.8	0d	36.97	238.5	0
2703.28	36981.0	2	37.86	227.5	0d
03.77	974.4	1d	39.08	212.3	0dd
04.26	967.7	1d	40.63	193.1	0dd
06.68	934.1	0	44.31	147.6	0
09.66	894.1	1d	89.17	34601.9	0d
10.27	885.8	0d	90.17	589.9	0d
11.41	870.3	1d	91.31	576.3	0d
14.13	833.3	0dd	97.16	507.4	0d
14.82	824.0	0d	98.70	488.1	1
21.11	738.8	0d	2900.13	471.1	1
21.93	727.8	1	12.76	321.7	0d
23.62	705.0	1d	21.01	224.7	0d
24.32	695.5	0d	21.84	215.0	0d
25.96	673.5	0d	22.62	205.9	0d
26.98	659.8	0d	24.08	188.8	0
27.67	650.5	0d	25.69	170.0	0d
28.37	641.1	0d	3001.80	33303.7	0
36.18	536.5	1	04.75	271.0	0d
38.55	505.2	1	06.83	248.0	0dd
39.62	490.6	0	08.20	232.8	0d
40.88	473.8	2	09.47	218.8	0d

will be omitted since not much significance can be attached to them at the present time.

Still further pressure decrease produces a considerable simplification of the spectrum through a gradual disappearance of the majority of lines and the enhancement of the others. Table I gives the results of measurements on plates taken at 0.01 mm benzene vapor pressure. The accuracy of these wavelength determinations is rather low, an error of ± 1 cm^{-1} or even more being probable for most of the lines. This is due to the diffuseness of the lines and lack of contrast owing to a continuous background coming from the light source. Fig. 2, curve 1, gives the microphotometer record of the short wavelength part of this spectrum. It shows that the stronger emission lines form a system of doublets, several weaker lines being usually grouped around each of these. The whole resembles the well-known resonance fluorescence of iodine vapor discovered by Wood more than twenty years ago. Indeed, it can be interpreted on essentially the same basis, as representing transitions from a certain vibrational level attained on absorption of the 2536A line to different vibrational levels of the normal molecule. However, several modes of vibration being possible in benzene molecules, more than one progression of doublets is observed. As the following Table II shows, several vibrational frequencies can be identified with more or less certainty. This table presents in successive columns: (1) the assignment of the line group (2) the frequency separation of the center of the doublet from the exciting line (2536.6A) or, when the line group does not appear as a doublet the separation of its center of density; (3) the separation from the preceding line group of the same series; (4) the second frequency difference; (5) the doublet separation; (6) the intensity of the doublet lines. Table III compares the frequencies here obtained with some of those known from Raman spectra and from the infrared bands of benzene.[10] The correspondence is, on the whole, very good, since the 160 cm^{-1} frequency can be interpreted as the fundamental of the infrared band

TABLE II. *Vibrational frequencies in resonance fluorescence.*

Line group	Separation from the exciting line, cm^{-1}	$\Delta\nu$ cm^{-1}	$\Delta^2\nu$ cm^{-1}	Doublet separation cm^{-1}	Intensity
F_1	792.6	792.6			1
A_1	987.0	987.0		5.9	1
			+ 1.0		
A_2	1975.0	988.0		9.4	3
			− 0.6		
A_3	2962.4	987.4		12.9	5
			− 2.2		
A_4	3947.6	985.2		14.9	2
			− 1.4		
A_5	4931.4	983.8		17.0	1
B_1	1199.6	1199.6		29.5	10
C_1	1354.3	1354.3		17.0	3
			−14.0		
C_2	2694.6	1340.3		22.8	1
D_1	1662.6	1662.6		22.2	1
			−27.9		
D_2	3297.0	1634.7		20.2	0
E_1	3138.9	3138.9		?	3
			−92.3		
E_2 (?)	6185.2	3046.3		14.0	0
A^1+G	1145.0	158.0		14.9	2
A_2+G	2138.2	163.2		23.2	2

TABLE III. *Comparison of fluorescence, Raman and infrared frequencies.*

Fluorescence cm^{-1}	Raman lines cm^{-1}	Infrared bands cm^{-1}
160	—	—
—	—	310
—	—	442
—	—	515
—	605	—
793	—	—
—	849	—
988	991	—
1200	1178	1235
1354	—	1316
—	1583	—
1663	1605	—
—	2947	—
—	3047	3030
—	3060	—
3139	3164	—
—	3184	—

at 310 cm^{-1}, while the 791 cm^{-1} frequency is very doubtful anyway on account of the faintness of the single line observed there. It should be pointed out that in accordance with selection rules holding for electronic transitions, both Raman and infrared frequencies may appear in fluorescence. The numerical agreement of fluorescence data with the data from other sources is not as good as the probable errors of these measurements would seem to indicate. Part of this, at least, should be attributed to an error arising from the use here of the center of the doublets for the determination of the frequencies. Another reason why the data cannot be strictly compared is that liquid benzene is usually used for the infrared and Raman spectra, whereas the fluorescence was obtained with benzene vapor.

In addition to the line groups recorded in Table II, the plates show some diffuse groups which can be identified on the microphotometer record between the mercury lines 2753 and 2699A. Using some imagination one can assign these groups to additional frequencies of benzene or to combinations of those already described. This assignment is highly uncertain in view of the diffuse nature of the groups and it is omitted here. The possibility also exists that these groups are the last remnants of the high pressure fluorescence and will disappear on further lowering of benzene vapor pressure. Further work now being undertaken will probably settle this point.

The fine structure of the line groups observed in low pressure fluorescence can be, at least partially, understood from the point of view here developed. In the absence of any information to the contrary one might assume that the benzene molecule behaves as a symmetric top not only in the lower but also in the upper electronic levels. For this case it has been shown[11] that, if j is the quantum number of the total angular momentum, while k is that of the rotation around the axis of symmetry, the following rotational transitions

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[10] K. W. F. Kohlrausch, Der Smekal-Raman Effekt, Springer, Berlin (1931).

[11] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

take place depending on whether the bands are of the parallel or the perpendicular type:

parallel perpendicular

$$k \rightarrow k \begin{cases} j \rightarrow j + 1^* \\ j \rightarrow j \\ j \rightarrow j - 1^* \end{cases} \qquad k \rightarrow k + 1 \begin{cases} j \rightarrow j + 1^* \\ j \rightarrow j; \\ j \rightarrow j - 1 \end{cases} \qquad k \rightarrow k - 1 \begin{cases} j \rightarrow j + 1 \\ j \rightarrow j \\ j \rightarrow j - 1^* \end{cases}$$

For larger values of k the transitions marked by a star are the ones with the greatest *a priori* probability. Now, the 2536A mercury line happens to fall near the tail of a benzene band in the third band group of the absorption spectrum. This makes it probable that the molecules participating in the absorption process have a large value of k and therefore, irrespective of whether the bands are of the parallel or of the perpendicular type, one should expect in emission two strong and some weaker lines. The existence of the hyperfine structure in the 2536A line makes it probable that more than one rotational level of the upper electronic state is reached on absorption. This may account for the diffuseness of the emission lines. The feature which remain unexplained is the variation in the separation of the doublet components which is very regular in the long A progression of doublets and is quite beyond a possible experimental error. It increases with increasing vibrational quantum numbers, whereas it would be expected to decrease, if the explanation given above is right.

It throws considerable doubt on the correctness of the whole interpretation as given above. Professor G. H. Dieke pointed out to us in a personal discussion that the two components of each doublet may represent independent but degenerate vibrations and that the increase in the doublet separation is due to a gradual removal of the degeneracy in higher vibrational quantum levels.

The information presented on the preceding pages together with the earlier known facts allows some conclusions to be drawn concerning the high pressure fluorescence, or at least, that part of it which consists of the band groups 0, 1, 2, etc. Its independence of the exciting source suggests immediately that at higher pressures benzene molecules lose the vibrational part of their excitation energy in inelastic collisions prior to light emission. The transitions giving rise to fluorescence occur therefore from the lowest level of the electronic state or states. The latter is more probable because the 83 cm^{-1} separation, found in the high pressure band groups, does not appear in resonance fluorescence. It should therefore be attributed to the existence of two upper electronic levels, both of which are reached by molecules upon inelastic collisions. This interpretation of the ordinary fluorescence finds further support in the fact that the first absorption band group coincides with the first, "0," group of fluorescence. They differ only in that the intensity of the different bands within the group falls off more rapidly towards the red (that is, with increasing quantum number of the 160 cm^{-1} frequency) in absorption than in emission. This fact is readily understood if the 160 cm^{-1} frequency is attributed to the normal electronic state, as suggested by Shapiro. A point of difference between the resonance and the high pressure fluorescence is that in the short wave-length part of the latter only two frequencies, 920 and 160 cm^{-1} make their appearance. This might be attributed to particular transition probabilities characterizing the lowest level of the excited electronic states. An analogy to this is found in observations made with the absorption spectrum. Transitions from the nonvibrating level of the normal electronic state show also only one, the 920 cm^{-1}, frequency of the excited state. This holds, at any rate, for the longer wave-length part of the absorption spectrum, where the total vibrational energy of the molecule is small.

The structure of the fluorescence spectrum at vapor pressures in the neighborhood of 0.1 mm indicates that vibrational energy is much more readily exchanged on collisions than is rotational energy. Thus, here the bands, with their characteristic heads, are as yet undeveloped, but groups of lines are present throughout the spectral region in which these bands are located at higher pressures. The persistence of fluorescence even at atmospheric pressure or in the liquid state shows further that the benzene molecules are relatively stable against the loss of electronic energy on collisions. This is undoubtedly related to the exceptional sharpness of the absorption bands of benzene in the liquid state.[12]

Recently Almasy[13] in a short notice suggested that a predissociation occurs in the final state of the fluorescence transitions. He brings forward this suggestion to account for continuous emission, observed by him, which extends from 2670A to longer wave-lengths when benzene vapor is excited by the 2536A mercury line. The experiments here recorded lead us to disagree with Almasy both in matter of fact and in the conclusion. The emission at low pressures has been found to be wholly discontinuous. The plates, it is true, show a continuum extending from about 2650 to 3200A with a maximum at 3000A. However, several tests, made under conditions identical with the fluorescence experiments in every respect except that benzene vapor was absent from the inner quartz tube, showed conclusively that the entire continuum is due to scattered light from the light source. Only at high pressures of benzene vapor can the long wave-length end of the spectrum be described as continuous. The interpretation of Almasy, when applied to this continuum, meets, however, grave difficulties. The continuum starts at about 2800 and ends at 3200A. Thus, the energy left in the molecules after emission of radiation is less than one electron volt, even granting that the continuum is due to direct transitions from the excited level reached on absorption of the 2536A line. If, however, the molecules lose first some energy on collisions, as suggested on the preceding pages, the energy remaining upon emission of radiation is still less and does not exceed 0.5 electron volts. Predissociation has by now been definitely interpreted as due to radiationless transitions to continuous levels, that is, to a breaking up of the molecule. The well-known sta-

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[12] Arnold and Kistiakowsky, J. Am. Chem. Soc. **54**, 1713 (1932).

[13] Almasy, Naturwiss. **20**, 296 (1932).

bility of benzene, on the other hand, does not allow one to believe that a decomposition occurs with only some 15 cal. of vibrational or electronic energy in the molecule. The continuum may be interpreted without this difficulty, by considering that the absorption and emission bands are degraded to the red so that the moment of inertia of the excited molecule must be larger than that of the normal molecule. The moment of inertia in higher vibrational states has usually been found to be larger than that of the nonvibrating molecule. The result of this is that, as the transitions occur to higher and higher vibrational levels of the normal state of benzene, the moments of inertia of the initial and final states approach each other and the band heads become less prominent. The rotational structure of the bands being entirely unresolved, this will cause the appearance of an apparently continuous emission. Curve 2, Fig. 2, shows very clearly how the band heads gradually weaken towards the red.

Another cause may also contribute to the effect. As has been pointed out by Kassel,[14] the spacing of vibrational quantum states in polyatomic molecules decreases very rapidly with increasing total energy. If, in transitions to higher vibrational quantum levels, frequencies other than 980 and 160 cm^{-1} take part, this crowding of levels must contribute considerably to the continuous appearance of the long wave-length part of the fluorescence spectrum.

In extending the present investigation to molecules other than benzene, toluene has been already studied. The pressure range covered was 20 to 1 mm, the weakness of emission preventing further decrease of pressure. The fluorescence was found to be wholly continuous with the exception of some quite diffuse bands between 2750 and 2650A. Fig. 2, curve 3, shows a microphotometer record of a part of this spectrum. The continuum in the case of toluene is much more pronounced than with benzene. It would be necessary to assume that toluene becomes unstable even when possessing some 0.3 electron volts of energy in order to account for the continuum on the assumption of predissociation. The suggestion advanced here, on the other hand, readily accounts for these observations. The decreased symmetry and an increased number of atoms in toluene are favorable to a crowding of vibrational levels at lower total energies and thus agree with the appearance of the continuum at shorter wave-lengths.[15]

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[14] Kassel, J. Am. Chem. Soc. **53**, 2143 (1931).

[15] A note giving the above results and arguments was sent in June to Die Naturwissenschaften but was not accepted by the editor of that publication.

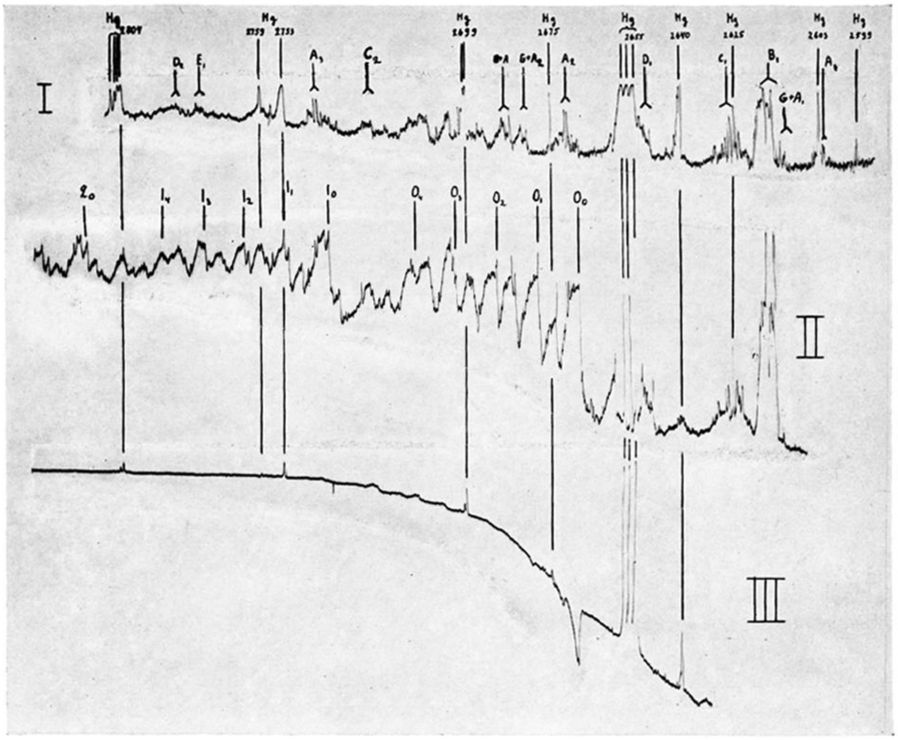

Fig. 2. Microphotometer records of fluorescence spectra. I. Benzene at low pressures. II. Benzene at high pressures. III. Toluene.