ON THE ABSORPTION SPECTRA OF SOME ORGANO-METALLIC COMPOUNDS.

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As a result of theoretical investigations regarding the term systems of polyatomic molecules, the absorption spectra of such molecules in the vapour state have received considerable attention during the past few years. For a summary of investigations done in this line we would refer to a paper by one of us.[1] In the present paper a report of experiments on the absorption spectra of some organo-metallic compounds is given. For the normal ultra-violet region the substances were introduced in a silicon absorption tube; the continuous hydrogen spectrum as the source of light and a Hilger E_3 quartz spectrograph as the resolving instrument were used. For the Schumann region a small fluorite vacuum spectrograph after Cario and Schmidt-Ott[2] was employed. In this case the vapours were introduced into a metal chamber permanently attached to the spectrograph and separated inside from it by a fluorite window and closed on the opposite side also by a fluorite window. The continuous hydrogen spectrum was produced in a discharge tube having a fluorite window. The tube was slightly pressed on to the outside window above referred to. In using such a disposition of the apparatus a thin layer of air of some tenths of a mm. cannot be avoided, but it does not prevent us from reaching down to wave-length of 1500 A.U. in favourable cases. As against the usual method where the source of light is also under vacuum, this procedure has the advantage that the source of light can be easily exchanged for a discharge tube showing the CO emission bands or the aluminium spark spectrum (in vacuum) which we used as standard wave-lengths.

Fig. 1 shows the CO emission bands, the continuous hydrogen spectrum through the vapour of mercury dimethyl and the continuous spectrum alone. The plates (Eastman Kodak type 3 U.V. sensitive for the Schumann region and anti-screen plates for the usual ultra-violet region) were then measured by the Zeiss recording microphotometer. Figs. 2 and 3 are reproductions of the microphotometer plates of $(CH_3)_2Hg$ and $(C_6H_5)HgCl$ respectively

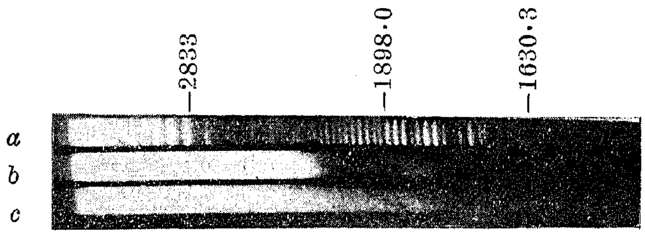

FIG. 1.
(*a*) CO Spectrum.
(*b*) Absorption through mercury dimethyl.
(*c*) Continuous Hydrogen Spectrum.

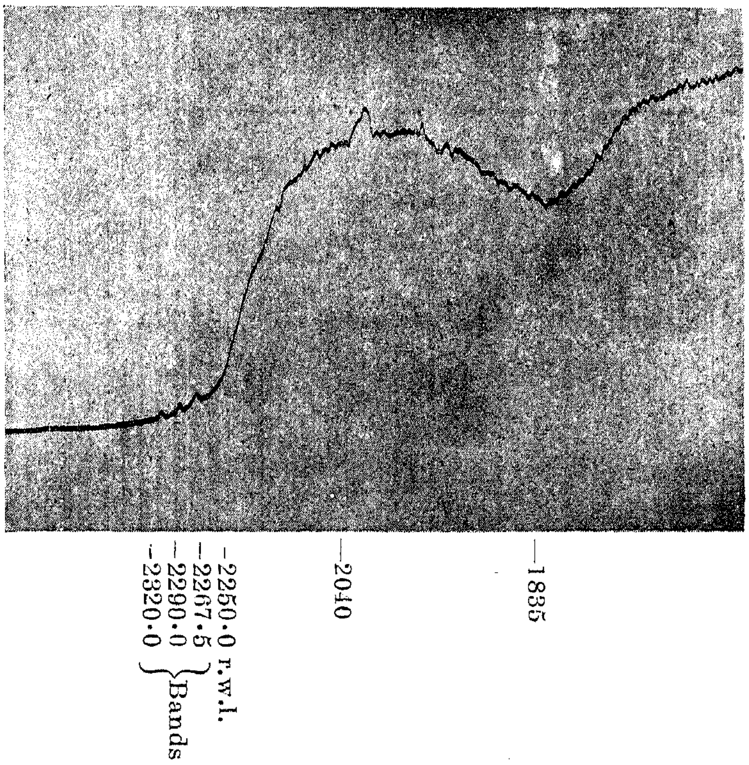

FIG. 2. $(CH_3)_2Hg$.

thus obtained. The grain of the U.V. sensitive plates is rather coarse and therefore it is difficult to distinguish weak absorption bands in a continuous background of kinks due to the grain. We have utilised only such bands as stand prominently above the general background and are always present on different microphotograms taken from the original plates, but it is quite likely that more genuine bands are present but difficult to distinguish,

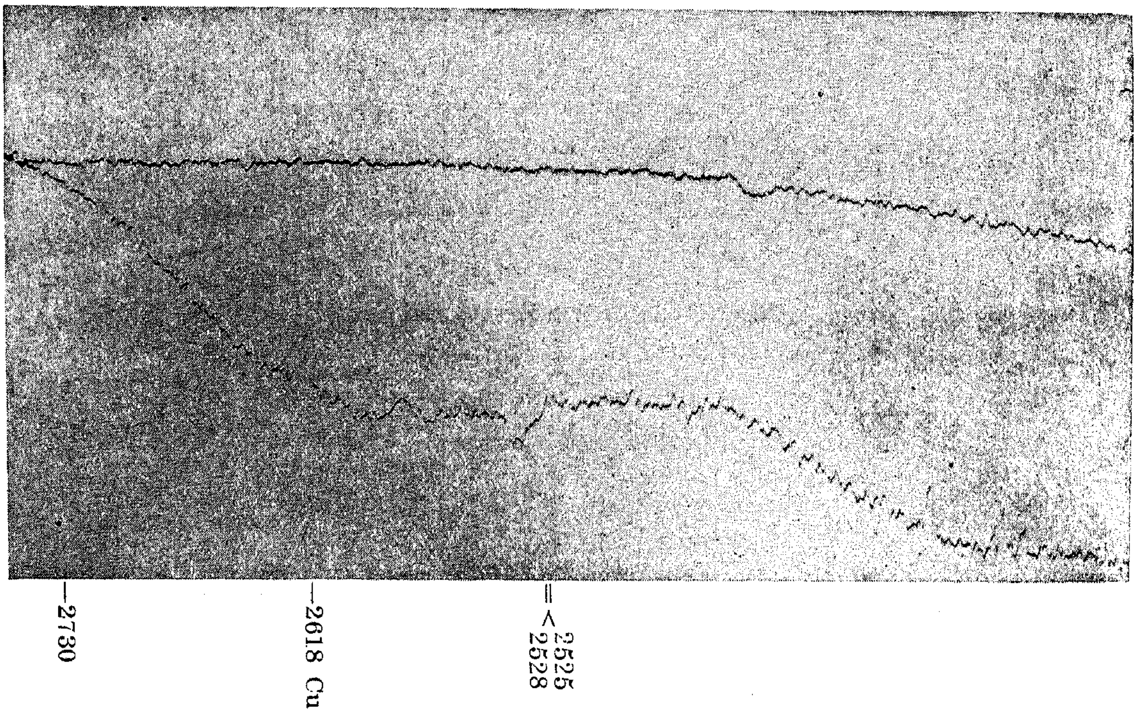

FIG. 3. $(C_6H_5)HgCl$.

Some of the substances used in this investigation were kindly put at our disposal by Dr. Lorenz of the Breslau University.

1. $(CH_3)_2Hg$.

Dimethyl mercury gives a continuous absorption spectrum which at 0·1 mm. pressure in the metal chamber 20 cm. long and at about 25°C. extends from 2250 A.U. onwards towards shorter wave-lengths. It shows two maxima at 2040 and 1660 A.U., the point of retransmission being at 1835 A.U. There are two sets of bands, one just on the long wave-length side before the absorption and the other in the neighbourhood of the first maximum and superimposed upon the absorption. The following table gives the data of these bands.

Band	λ (air)	ν (vac)	Band	λ (air)	ν (vac)
1	2320·0	43090	4	2062·0	48481
		564			522
2	2290·0	43654	5	2040·0	49003
		433			
3	2267·5	44087			

2. $(C_2H_5)_2Hg$.

At a pressure of 0·06 mm. in the metal chamber and at about 25°C., this shows a continuous absorption beginning at 2600 A.U. and extending towards the Schumann region till about 1650 A.U. It has two maxima at about 2250 and 1955 A.U. and the following bands at the neighbourhood of the point of retransmission.

Band	λ (air)	ν (vac)	
1	2065·0	48410	1078
2	2020·0	49488	247
3	2010·0	49735	

3. $(C_2H_5)HgCl$.

This is a solid and since the heating arrangement for the vacuum spectrograph is not yet complete we had to confine ourselves to the quartz region of the ultra-violet end for this and the rest of the substances. $(C_2H_5)HgCl$ shows a prominent continuous absorption beginning at about 3200 A.U. and a maximum at 2366 A.U. at 190°C. in a silicon tube 10 cms. long. No bands were found.

4. $(C_6H_5)_2Hg$.

The continuous spectrum starts at 2830 A.U. with a maximum at about 2600 A.U. Two very prominent bands were found in the neighbourhood of the maximum (temp. 205°C.; tube 10 cms.).

Band	λ (air)	ν (vac)	
1	2639·0	37896	852
2	2580·0	38748	

5. $(C_6H_5)HgCl$.

The red wave-length limit of the absorption spectrum lies at 2730 A.U. It shows two maxima of absorption at 2595 and 2378 A.U. and the following bands (temp. 260°C.; tube 10 cms.).

Band	λ (air)	ν (vac)		Band	λ (air)	ν (vac)	
1*a*	2567·1	38942	78	2*a*	2528·8	39532	60
1*b*	2562·3	39020		2*b*	2525·0	39592	

Band	λ (air)	ν (vac)	
3*a*	2505·5	39900	30
3*b*	2503·6	39930	

$2a-1a=590$ cm.$^{-1}$; $3a-2a=368$ cm.$^{-1}$.

6. $(C_6H_5)_4Pb$.

It shows a continuous absorption whose long wave-length limit lies at 2900 A.U. and whose maximum is at 2550 A.U. (temp. 225°C.; tube 10 cms.). No bands could be traced. This did not seem to agree with the strong bands recorded by Thompson[3] for tetra-ethyl-lead since one would expect to find rather a greater number of bands for $(C_6H_5)_4Pb$. We noted that the wave-lengths listed by Thompson agree very well with the main maxima of the complicated band system of benzene.[4] In order to satisfy ourselves about this point we took the absorption spectrum of benzene vapour in a silicon tube of 20 cms. length and at a pressure of about 0·05 mm. Hg with the result that the bands obtained with a Hilger medium quartz spectrograph agreed completely in wave-length and appearance with those recorded by Thompson. This evidently explains why Duncan and Murray[5] could not obtain these bands in their repetition of Thompson's experiments.*

Discussion.

The experimental results are summarised in Table I and Fig. 4. We shall first discuss the continuous absorption spectra. Evidently, we have to interpret them as transitions from the ground state to repulsive curves. The process of photo-dissociation obtained here is concerned with the C—Hg linkage since the C—H linkage itself has already a dissociation energy of about 100 K. Cal./mol. and a photo-dissociation involving two electronic levels will therefore give a higher value than what we obtain in these experiments. Indication of such a splitting of the C—H link is always

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* We have communicated our point of view to Dr. Thompson who agrees with us.

TABLE I.

No.	Substance	Red wave-length limit				1. Absorption Maximum				2. Absorption Maximum				Pressure	Temp.
		λ(air)A.U.	ν(vac)Cm.$^{-1}$	K. Cal/mol.	E. Volts	λ(air)A.U.	ν(vac)Cm.$^{-1}$	K. Cal./mol.	E. Volts	λ(air)A.U.	ν(vac)Cm.$^{-1}$	K. Cal/mol.	E. Volts		
1	$(CH_3)_2Hg$	2250	44430	126·27	5·47	2040	49003	139·26	6·04	1660	60240	171·20	7·42	0·1 mm..	25°C.
2	$(C_2H_5)_2Hg$	2600	38450	109·27	4·74	2250	44430	126·27	5·47	1955	51151	145·37	6·36	0·06 mm.	25°C.
3	$(C_2H_5)HgCl$	3200	31241	88·78	3·85	2366	42252	120·08	5·20	..	..	..	..	..	190°C.
4	$(C_6H_5)_2Hg$	2830	35325	100·39	4·35	2639	37896	107·70	4·67	2580	38748	110·12	4·77	..	205°C.
5	$(C_6H_5)HgCl$	2730	36619	104·07	4·51	2595	38524	109·48	4·74	2378	42952	119·51	5·18	..	260°C.
6	$(C_6H_5)_4Pb$	2900	34472	97·96	4·24	2550	39203	111·41	4·87	..	..	..	..	..	225°C.

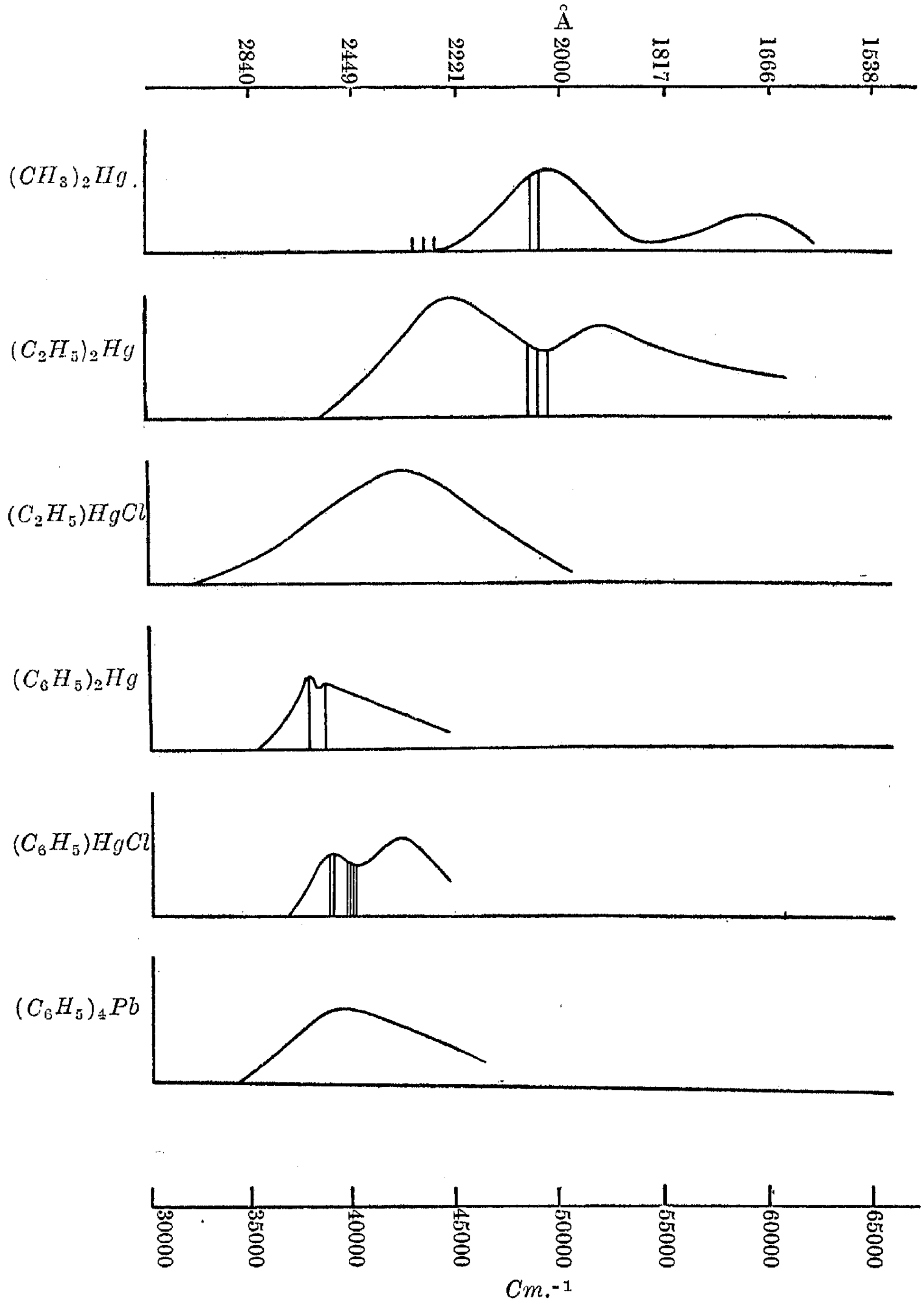

FIG. 4.

found in the Schumann region at much shorter wave-lengths only. We shall take for the red wave-length limit the value which we obtain as the *shortest* wave-length at which absorption starts. Moreover, it is quite possible to shift this limit towards higher wave-lengths with increase in temperature or pressure but this indicates only the presence of molecules in higher vibrational states, but does not give the real value of the photo-dissociation of the vibrationless molecule.† Since neither thermochemical data for the heat of dissociation of these molecules are known nor are the bands found numerous enough to extrapolate the heat of dissociation of the ground state, we have to consider all possibilities obtainable from Frank-Condon curves. The most probable of such curves are indicated in the three diagrams of Fig. 5.

If, however, we want to find out the *thermochemical* value of the energy of a C—Hg link and not the adiabatic dissociation of the ground level, we can confine ourselves only to diagrams *b* and *c*. Because for this purpose it is enough to know the difference between the ground state of the molecule and the level of the separated system R+HgR (unexcited). As in diagram *a*, if the energy curve for the ground state does not originate in this level of the separated systems but intersects the repulsive curve, the energy δ represents only an energy of activation which is unimportant for this purpose. In any case the red wave-length absorption value gives an upper limit to the thermochemical energy of dissociation. How much greater such a value is than the actual, depends firstly on the slope of the repulsive curves, as shown in the diagrams *b* and *c*. In order to decide if the lower of the two repulsive curves has to be correlated to the dissociation of the molecule into two unexcited radicals (R+HgR) or into two radicals one of which is excited, we take into account certain similarities between our measurements for diethyl mercury and those recorded by Scheibe and Grieneisen[6] for diethyl ether. From the diagrams in that paper, we evaluate for the energetic difference between the first two maxima of continuous absorption in diethyl ether 7200 cm.$^{-1}$; for diethyl mercury we get nearly the same figure, *i.e.*, 6600 cm.$^{-1}$; therefore it seems

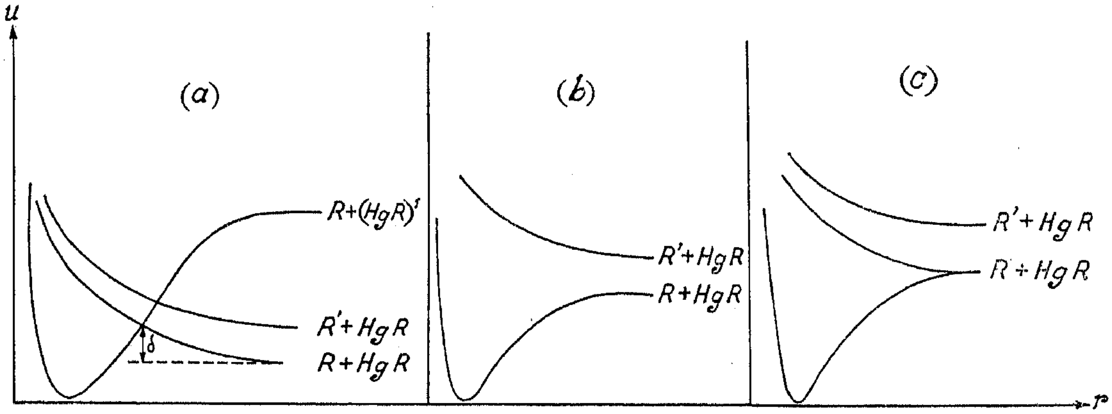

FIG. 5.

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† For detailed discussion of this point *vide* reference 1.

probable that this figure represents an energy of excitation of the radical C_2H_5. This radical is comparable in mass with the Cl atom but represents of course a different dynamical system. In such a system the effective nuclear field acting on the series electron will be considerably weaker than if it were moving in the field of a united atom which certainly the radical is not. The energy of excitation between the two spin components of the ground level will therefore be larger, as a matter of fact, in this case as large as in the iodine atom. If we assume therefore that in the absorption spectra of both of these substances, the upper repulsive curve is correlated to the same excited radical $(C_2H_5)^*$ the lower one will belong to two unexcited radicals $R+HgR$ and $R+OR$ respectively since an excitation of both the radicals in the upper curve is highly improbable. Therefore we rather favour diagram *c* which in this respect is identical with *a*.

In $(CH_3)_2Hg$ the corresponding radical CH_3 will have much smaller mass which is comparable with that of F but also the dynamical system is strengthened and is a better approximation to the united atom. As a result the energy difference will be considerably smaller and probably cannot be found in the absorption curves for the same reason that in NaCl the maxima due to the excitation of Cl cannot be found, whereas the corresponding maxima of I and Br have been found in many such alkali salts. So we assume that the second maximum in $(CH_3)_2Hg$ has a different origin.

In $(C_6H_5)HgCl$ the energetic difference between the two absorption maxima, *i.e.*, 3500 cm.$^{-1}$ probably represents the excitation energy of the C_6H_5 radical. The absorption curve of $(C_2H_5)HgCl$, however, is distinctly different from those of other mercury compounds since it extends considerably more to longer waves and does not show any bands. Probably in this case the Hg—Cl link is highly polarised and may be, it is this link which is affected first in this process by photo-dissociation.

To summarise, we assume that in substances 1, 2, 4 and 5, the red wave-length limits correspond to a photolytical splitting of the C—Hg link giving rise to unexcited radicals ; in cases 3 and 6, however, the splitting corresponds in the same way to the HgCl and C—Pb links respectively. The steepness of the repulsive curve can be judged from the breadth of the absorption region and also from the shift of the red wave-length limit of absorption by an increase of temperature or pressure.[7] This brings about molecules in higher states of vibration, and we thus obtain transitions from different parts of the Frank-Condon curve to the repulsive curve and this gives us a possibility of judging the steepness of the repulsive curve. In our case all continuous spectra are rather broad and we get a considerable shift in $(C_6H_5)_4Pb$ and $(C_6H_5)_2Hg$ but not in $(C_6H_5)HgCl$. The following table summarises these observations.

Substance	Temp.° C.	λ Red wave-limit
$(C_6H_5)HgCl$	210	~2730
	260	2730
	325	~2800
$(C_6H_5)_4Pb$	200	2900
	220	~3400
$(C_6H_5)_2Hg$	205	2830
	210	~2830
	250	~3300

This indicates that the repulsive curve is very steep at least for such compounds as do not contain an additional halogen atom. From the values given in Table I, we estimate about 60 K. Cal./mol.* as the heat of formation for the bond between Hg and an aliphatic carbon atom and probably slightly less between Hg and an aromatic carbon atom. Similarly, it is evident from Thompson's work[3] that the repulsive curve in the zinc dialkyls is also steep. In this case too we have to consider first the *highest* energy value for the red-wave limit as that of the *vibrationless* molecule and then correct this value for the steepness of the repulsive curve to arrive at the heat of formation. If we do this we obtain a value of about 50 K. Cal./mol. which represents the heat of formation of the Zn—C bond. Also the Raman frequencies for the zinc dialkyls are slightly less than those for the mercury dialkyls. Both these agree with the well-known fact that the ionisation potential of mercury is slightly higher than that of zinc on account of certain irregularities in the *d*-shell among the preceding atoms[8]; these react on the bond in the mercury derivatives.

Turning now to the bands observed, these give us some information regarding the excited molecules. In $(C_2H_5)_2Hg$ we observe bands due to an

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* This value agrees also with that estimated by Terenin, *J. Chem. Phys.*, 1934, **2**, 441.

upper electronic level which is binding and the energy of excitation of which is 48410 cm.$^{-1}$ The vibrational differences 1078 and 1325 may be taken as belonging to the C—H linkages, the deforming vibrations in the excited state of the molecule being known to be between 1250 and 1450; or it is quite possible that only the 1078 corresponds to such a deforming vibration of the C—H linkage and that superimposed upon it is a vibration of 247 due to the deforming vibration of the C—C link or of the two radicals against each other. In any case it appears that the vibration levels of these electronic states belong to the organic radicals corresponding to those which have been observed in the absorption spectra of methyl iodide, acetone, acetaldehyde, cyclo-pentane, cyclo-hexanone, etc.[6]

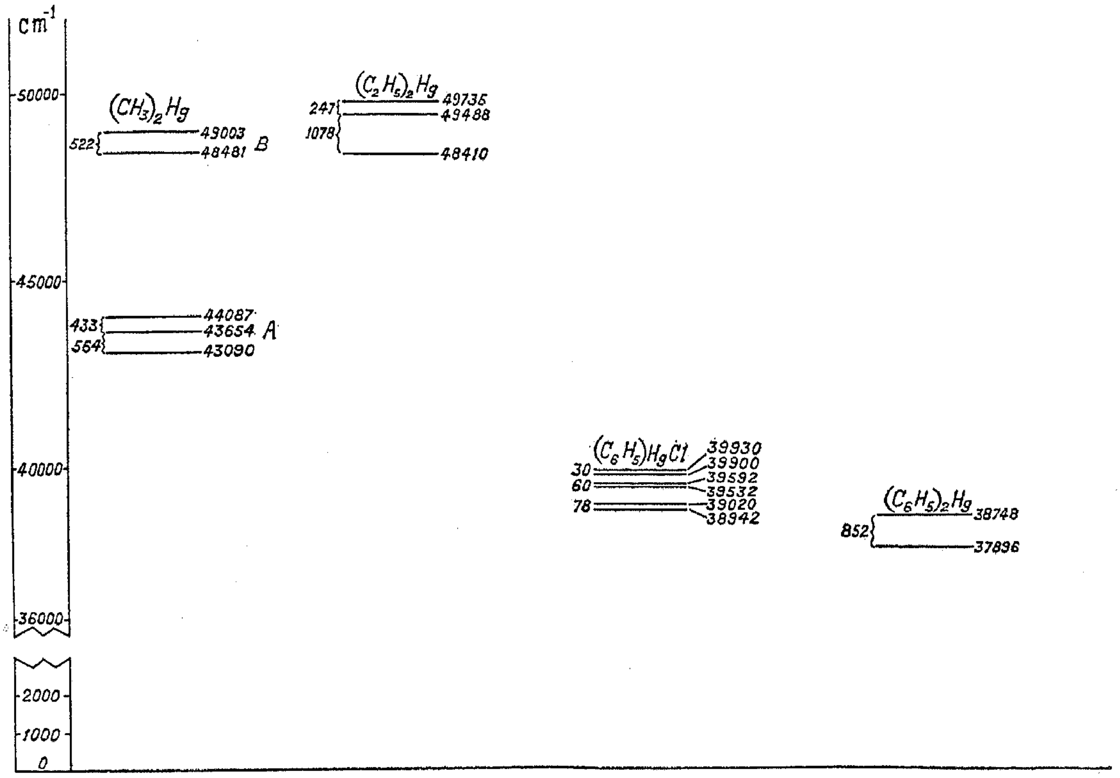

Fig. 6.

Fig. 6 gives a representation of the bands of the various molecules arranged according to the term scheme. We attribute the vibrations to the upper level since in absorption it is not likely that the ground level would show higher vibrational levels. The ground state is in all cases taken to be singlefold.

In mercury diphenyl we observe a vibration superimposed on the electronic level which is due to the phenyl radical. The value 852 and the marked intensity of these bands indicate that it is the total symmetric vibration of the benzene ring having a frequency of 991 in the Raman sprectrum which naturally is slightly diminished in the excited molecule.

In the two remaining molecules are observed bands which we attribute to the C—Hg bond. The Raman spectra of substances having such a bond are known only for mercury dimethyl and mercury diethyl.[*] The fundamental frequencies of mercury dimethyl are 515, 156 and 700 cm.$^{-1}$ and those of mercury diethyl 486, 140 and 633 cm.$^{-1}$ The order of magnitude of 564 for mercury dimethyl and 590 for phenyl mercury chloride from their respective band spectra agrees with that which is to be expected for the deforming vibration which is 700 in the unexcited mercury dimethyl. In $(CH_3)_2Hg$ it appears from the energetic difference and from the fact that one set of bands is before the absorption and the other set in the absorption region itself, that the two sets originate in two different excited electronic states. It looks as if the upper electronic state B corresponds to that found in $(C_2H_5)_2Hg$. The vibration frequency of 522 for the state B as compared to 564 of state A is of the right order of magnitude.[†] The unharmonicity factor for state A which can be calculated if we were allowed to treat the molecule as a diatomic one, will be 65·5, an unusually large value. In any case we think we can infer that the molecule in this state is rather unstable, that it is highly polarised and that it is non-linear. It is also possible to treat the difference of 433 cm.$^{-1}$, not as a second member of the same progression but as an independent superimposed vibration which would then be the valency vibration of C—Hg bond which is 515 cm.$^{-1}$ in the unexcited molecule. This interpretation, however, leads to the same conclusions as given above.

Similar frequencies of vibration are also found in $(C_6H_5)HgCl$. The frequency 590 agrees very well with 564 of state A for $(CH_3)_2Hg$. This coincidence incidentally indicates that these figures must be very near to the true vibration frequency of the excited levels and much importance need not be attached to the unusually big unharmonicity which, if real, could not, as is usually done, be neglected for the calculation of the real vibration frequency, and which is only derived from a pretended similarity of such a polyatomic molecule to a simple diatomic one. Another interesting feature of the bands observed in this molecule is the close doubling of the lines, the doublet separations being 78, 60, and 30 cm.$^{-1}$ This doubling has probably nothing to do with the multiplicity of the electronic level and the simplest

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[*] We are indebted to Prof. K. S. Krishnan for these data from a paper of Mr. N. Gopala Pai, *Proc. Roy. Soc.* (A), (in press) from his laboratory.

[†] It is not possible to say at present whether the state B is identical with that found by Terenin (*loc. cit.*) at low temperatures of −150°C., or not.

explanation seems to be that they are due to the presence of strong Q head in addition to the usual R or P heads. If this interpretation is true, taking the analogy of diatomic molecules we may say that since the ground state of such a saturated and diamagnetic molecule is certainly of the Σ type, the excited state must be of the Π type.

REFERENCES.

1. R. Samuel, Report on "Absorption Spectra and Chemical Linkage," Indian Acad. of Sciences, Bangalore, 1935.
2. G. Cario and H. D. Schmidt-Ott, *Zs. f. Phys.*, 1931, **69**, 719.
3. H. W. Thompson, *J.C.S.*, 1934, 790.
4. *Cf.* H. Ley, article on "Absorption Spectra" in *Handb. d. Phys.*, XXI.
5. A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.*, 1934, **2**, 636.
6. G. Scheibe and H. Grieneisen, *Zs. f. Phys. Chem.* (B), 1934, **25**, 52.
7. W. Finkelnburg, H. F. Schumacher and G. Stieger, *Zs. f. Phys. Chem.* (B), 1931, **15**, 127, *cf.* reference (1).
8. *Cf.* the discussion in R. Samuel and L. Lorenz, *Zs. f. Phys.*, 1929, **59**, 53.