170. *The Absorption Spectra of Some Polyatomic Molecules containing Methyl and Ethyl Radicals.*

By H. W. THOMPSON.

THE following is a preliminary account of some experiments which are in progress in which the spectra of the vapours of methyl and ethyl compounds of zinc, lead, mercury, phosphorus, nitrogen, oxygen, and sulphur are being examined. These measurements have a manifold purpose. First, they may give information to assist in the interpretation of the spectra of polyatomic molecules, in which direction little progress has so far been made. The presence of similar groups in the respective compounds of the series should provide standards of comparison and simplify the analysis. Secondly, the measurements should provide a knowledge of the structure and stability of the molecules in their normal and excited states. Thirdly, an insight should be gained into the mechanisms of the photochemical decomposition of the substances, which may then be compared with the corresponding thermal processes. It should be remembered that in inferring the mechanism of photochemical decomposition from the nature of an absorption spectrum, importance attaches not only to the occurrence of one type or another of diffuse region, but also to the discovery of the types and nature of vibrations which are induced in the excited states. The introduction of deformation vibrations rather than, or in addition to, purely valency vibrations, may be very important in a subsequent decomposition of the molecule. Finally, it is of interest to discover whether the different symmetry arrangements in molecule types such as diethylzinc, triethylphosphine, and tetraethyl-lead are reflected in the structure of their spectra.

The measurements now to be described relate to dimethyl- and diethyl-zinc and tetraethyl-lead. Since more detailed analysis will require a still higher dispersion and may not be completed for some time, several features already established are outlined.

Comparatively few measurements on the absorption spectra of polyatomic molecules are on record. Henri, Norrish, and others have studied aldehydes and ketones, the spectra of which in the quartz ultra-violet are connected with the properties of the chromophoric carbonyl group. Scheibe, Povenz, and Linström have extended these measurements to higher frequencies and the Schumann region, where the systems observed again probably involve a higher excitation of the carbonyl group. Herzberg and others have studied methylamine, where the spectrum observed can be attributed essentially to vibrations excited concurrently with an electronic excitation in the amino-group.

Investigations relevant to those described below, where the alkyl radicals are attached to a single atom in the molecule, are those on the methyl halides by Herzberg and Scheibe (*Z. physikal. Chem.*, 1930, *B*, **7**, 390), by Henrici (*Z. Physik*, 1932, **77**, 35), and by Scheibe, Povenz, and Linström (*Z. physikal. Chem.*, 1933, *B*, **20**, 283). Herzberg and Teller (*ibid.*, **21**, 410) have also discussed some of the results in connexion with theoretical considerations on the types of vibration induced by electronic excitation. With methyl iodide, bromide, and chloride, the spectrum consists of a region of continuous absorption on the longer-wave side of discrete band systems. With methyl iodide the maximum in the continuum lies at *ca.* 2590 Å., and the threshold at *ca.* 2950 Å. The first band occurs at 2063 Å. In passing from iodo- to chloro-compounds the whole spectrum is displaced towards higher frequencies. The threshold for the continuous absorption has been employed to determine the energy of the carbon–halogen link, which is supposed to break (cf. also Iredale and Mills, *Proc. Roy. Soc.*, 1931, **133**, *A*, 430; Iredale, *Z. physikal. Chem.*, 1932, *B*, **20**, 340). There is some doubt as to whether the discrete bands are connected with electronic excitation in the methyl group or in the carbon–halogen link. In view of all the facts, Herzberg and Teller favoured the former alternative but this has recently been questioned (Scheibe and Grieneisen, *Z. physikal. Chem.*, 1934, *B*, **25**, 52). The intervals between the stronger bands correspond to a deformation vibration frequency, 1090 cm.$^{-1}$, of the methyl group in the excited state. No intense bands appear which might be connected with excitation of carbon–halogen vibrations. The feebler bands are interpreted as being due to absorption from higher vibrational levels in the ground state, or to the excitation of $\perp$ vibrations. In general the types of vibration induced are those which would be expected from the theoretical considerations of Herzberg and Teller, the strongest involving totally symmetrical vibrations.

EXPERIMENTAL.

The dimethyl- and diethyl-zinc and tetraethyl-lead, supplied as pure by Messrs. Harrington Ltd. (Kahlbaum product), were repurified by vacuum distillation. The final products were colourless, had the correct vapour pressures, and were free from methyl and ethyl halides. The absorption vessels were cylindrical glass tubes 5—50 cm. long with polished quartz ends cemented on. Pressures were measured by a mercury manometer, and the apparatus evacuated by a Hyvac oil pump, suitable traps being introduced. The spectrograph was a Hilger instrument E 315 and the range studied 2100—7000 Å. The continuous source used was a hydrogen discharge tube consuming 3 kw.

Results.—Dimethylzinc. Pressures from 0·5 to 200 mm. of the vapour were used. Discrete absorption was never observed. With increasing pressures a continuous absorption starting at higher frequencies gradually extended towards longer wave-lengths. At the highest pressures used, the threshold for this continuum was at *ca.* 2600 Å. Fig. 1 shows photographs taken under the following conditions :

Column 16 cm. Exposure 5 mins. Temp. 18°.

No.	1	2	3	4	5	6	7	8	9	10
Press. of $ZnMe_2$, mm.	0	0·5	1·0	1·5	2·0	3·0	5·0	10·0	50	200

The absorption is quite marked at pressures less than 1 mm. The limit at 2600 Å. corresponds to 38460 cm.$^{-1}$, or absorption of *ca.* 108 kg.-cals. per g.-mol.

Diethylzinc. Pressures from 0 to 10 mm. were used. A region of continuous absorption similar to that found with dimethylzinc, but beginning at *ca.* 2800 Å. (102 kg.-cals. per g.-mol.), overlaps one of peculiarly spaced diffuse bands. Increase of pressure markedly favours the development of the continuous absorption. The striking feature of the band system is the occurrence of pairs of bands marked α, β, γ, δ in Fig. 2. These pairs are almost equidistantly spaced, are entirely diffuse, without a head, and have the general characteristics of predissociation bands. The four pairs here given occur at wave-lengths (centres of bands) *ca.* 2396·5, 2375·5; 2335·5, 2316; 2278, 2260; and 2224·5, 2216 Å. There may be other such pairs at higher frequencies, but it is difficult to develop them in the presence of the overlapping continuum. A much fainter and narrower band occurs at 2423 Å., and between each of the intense pairs is a group of three or four narrow bands and a single band. Measurement of the wave-lengths of these is difficult but will be more satisfactory with higher dispersion.

The photographs of Fig. 2 were taken under the following conditions : temperature 18°; exposure 5 mins.; column 16 cm. (Nos. 1—7), 5·5 cm. (Nos. 8—16). Table I gives the wave-lengths of the centres of the bands, and Fig. 3 shows the approximate spacings and interval relationships.

No.	1	2	3	4	5	6	7		
Press. of $ZnEt_2$, mm.	0·5	1·5	3·0	7·0	9·5	12·0	2·0		
No.	8	9	10	11	12	13	14	15	16
Press. of $ZnEt_2$, mm.	9·5	7	2·5	1·5	1·0	2	0·5	1·0	0

FIG. 3.

Diethylzinc.

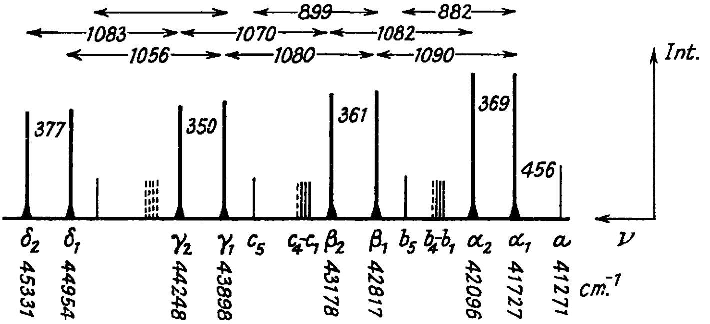


TABLE I.*

Diethylzinc.

Designation.	Wave-length, Å.	Remarks.	Designation.	Wave-length, Å.	Remarks.	Designation.	Wave-length, Å.	Remarks.
a	2423		b_5	2346·9		c_4	?	Doubtful
a_1	2396·5	Broad	β_1	2335·5	Broad	c_5	2287·5	
a_2	2375·5	,,	β_2	2316	,,	γ_1	2278	Broad
b_1	2363·1	Narrow	c_1	2303·5		γ_2	2260	,,
b_2	2360·6	,,	c_2	2300·7		δ_1	2224·4	,,
b_3	2357·8	,,	c_3	2297·6		δ_2	2206	,,
b_4	?	Doubtful						

* The wave-lengths given here may be amended slightly by subsequent work. Those of the prominent bands are given to the nearest 0·5 Å. The weaker bands are narrower and much closer; in these cases attempts are made to greater exactness, since the intervals are much smaller.

Tetraethyl-lead. Pressures of 0—5 mm. were used. The photographs of Fig. 4 were taken under the following conditions :

Column 20 cm. Exposure 10 mins. Temp. 18°.

No.	1	2	3	4	5
Press. of $PbEt_4$, mm.	1	2	2	4	0

Fig. 4*a* is an enlargement of some of the bands.

It is seen that a system of narrow, sharp bands occurs from *ca.* 2700 Å. towards shorter wave-lengths. Its structure is quite different from that given by diethylzinc, and there is no overlapping continuum, although a slight continuous absorption may begin below *ca.* 2200 Å. There are some six or seven prominent groups of bands, with sharp heads and degrading to the red. In each of these groups two intense bands stand out; the stronger has the higher frequency head and is more developed than that at lower frequency. Fine structure of the rotational levels cannot be detected in the bands, but in a heavy molecule of this type this is not surprising; and the occurrence of what appears to be a gap near the head of each of the bands, in addition to their sharp head, suggests that they are probably not diffuse. This gap may indicate that only *P* and *R* branches are involved, not *Q* branches.

Between the two prominent bands of each of the prominent groups occurs a fainter band. Between the prominent groups occur much fainter narrow bands which have almost the ap-

FIG. 1.

Dimethylzinc.

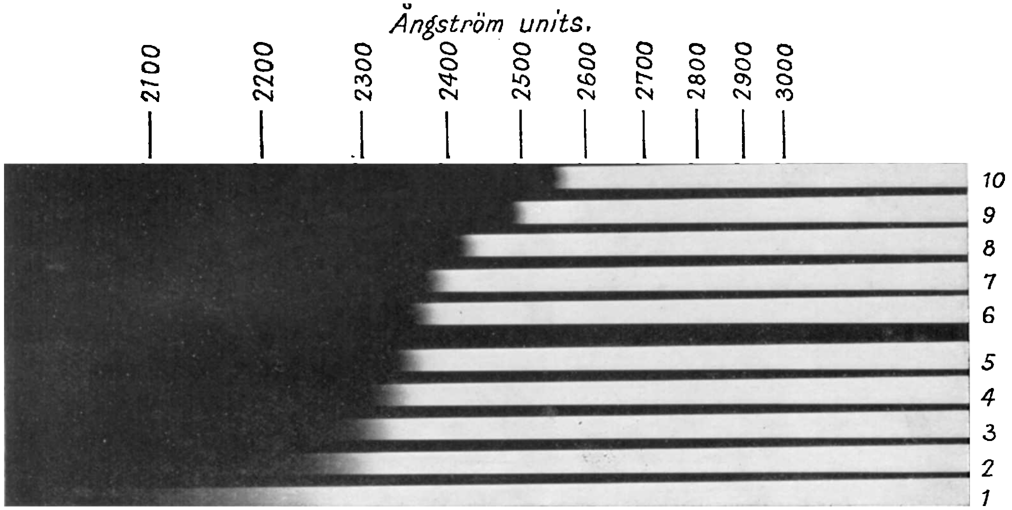


FIG. 2.

Diethylzinc.

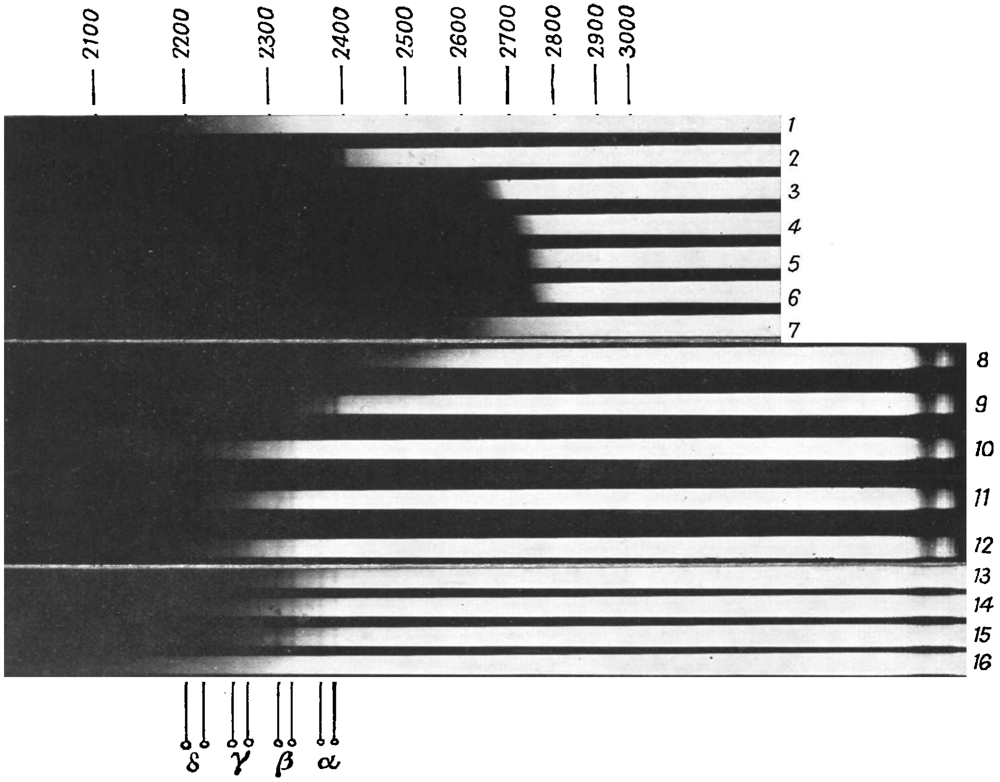


Fig. 4.

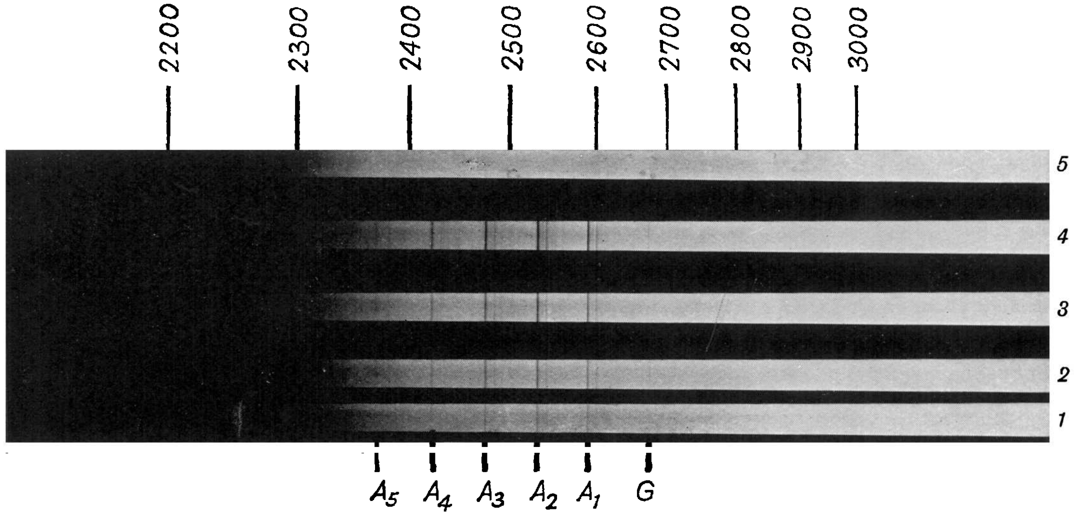
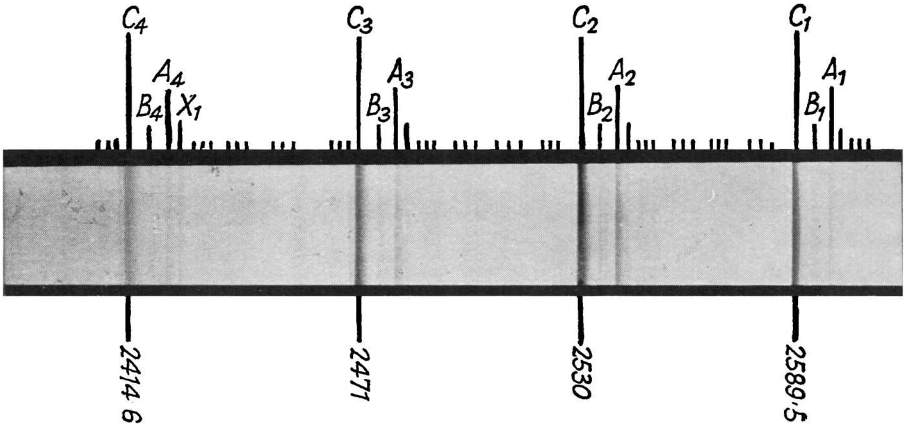

2200
2300
2400
2500
2600
2700
2800
2900
3000
5
4
3
2
1
A_5
A_4
A_3
A_2
A_1
G

Fig. 4a.


C_4
A_4
B_4
X_1
C_3
A_3
B_3
C_2
A_2
B_2
C_1
A_1
B_1
2414 6
2471
2530
2589,5

pearance of lines. These apparently occur in groups of three, the components of each triplet group not having equal intensity. There may be other lines not yet recorded. The intensity of the most prominent bands in the principal groups does not fall off uniformly on passing from longer to shorter wave-lengths; the second group band has the highest intensity. The spectrum and the approximate relative intensities are represented in Fig. 5. Table II gives the wave-lengths of band heads.

FIG. 5.

Tetraethyl-lead.

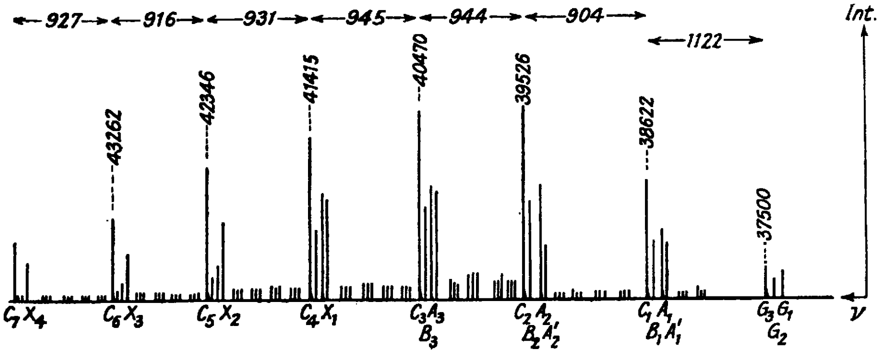


TABLE II.

Tetraethyl-lead.

Designation.	Wave-length, Å.	Designation.	Wave-length, Å.	Designation.	Wave-length, Å.	Designation.	Wave-length, Å.
G_1	2679·2	g_1	2562·5	j_2	2491·8	X_1	2427·7
G_2	2673	h_1	2559·5	k_2	2489·6	A_4	2425·2
G_3	2666·7	i_1	2556·4	l_2	2488·5	B_4	2420·2
g_0	— *†	j_1	2551	A_3	2481·3 ‖	C_4	2414·6
h_0	— *†	k_1	2549·8	B_3	2476	a_4	2413·5
i_0	2616	l_1	2547	C_3	2471	b_4	2411
j_0	2611	A_2	2540·7 §	a_3	2470	c_4	2409
k_0	2609	B_2	2535·7	b_3	2468·4	$d_4 \rightarrow l_4$	—
l_0	2606·5	C_2	2530	c_3	2465·2	X_2	2373·2
A_1	2600·3 ‡	a_2	2528·5	d_3	2457·2	A_5	2370·2
B_1	2595·7	b_2	2526·5	e_3	—	B_5	2366·6
C_1	2589·5	c_2	2523·6	f_3	—	C_5	2361·5
a_1	— †	d_2	2515·4	g_3	2446	X_3	2322·8
b_1	— †	e_2	2512	h_3	2442·6	C_6	2311·5
c_1	— †	f_2	2507·5	i_3	2440·5	X_4	2274·6
d_1	— *	g_2	2503	j_3	2435	C_7	2263
e_1	— *	h_2	2500	k_3	2433·2		
f_1	— *	i_2	2497·4	l_3	2431·4		

* Not measured. † Doubtful. ‡ Also at A_1' 2602(?). § Also at A_2' 2542(?).
‖ Also at A_3' 2483(?).

DISCUSSION.

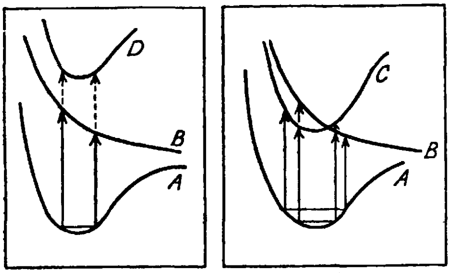
Continua.—The continuous absorption by dimethylzinc beginning at *ca.* 2600 Å. must be attributed to a dissociation process. The continuum differs from that observed with methyl iodide (Herzberg and Scheibe; Iredale, *locc. cit.*) in having no marked maximum, but rapidly becoming complete beyond the threshold. The continuous absorption is strongly affected by changes of pressure. The energy required to remove a hydrogen atom from the methyl group is probably at least 100 kg.-cals. If there were no excitation of the products of dissociation, the energy corresponding to the limit at 2600 Å. (108 kg.-cals.) might be just sufficient. A similar process might then be involved in the case of the ethyl iodide continuum, the small difference in the absorbed quantum (102 kg.-cals.) being reasonable. It is, however, certain that this process is not operative; if it were, tetraethyl-lead would probably give a similar continuous absorption, starting at approximately the same wave-length, but this does not occur. Herzberg and Scheibe, and also

Iredale, concluded that the methyl halide continua are not connected with the scission of a hydrogen atom, but with a breakage of the carbon–halogen link. Moreover, from the measurements on the alkyl compounds in general, it seems certain that the methyl radical does not absorb electronic energy at wave-lengths greater than 2000 Å. In addition, if the initial excitation occurred in the methyl group, followed by a subsequent transfer of energy to the zinc–carbon link, diffuse bands would probably be obtained.

It is therefore reasonable to attribute the continua in both dimethyl- and diethylzinc to the excitation and splitting of the zinc–carbon link. If it be legitimate to draw the potential-energy curves in their simple form, there will then be absorption from the stable ground state A (Fig. 6*a*) to an excited unstable state B, the primary act then being, *e.g.*, $ZnMe_2 + h\nu \longrightarrow ZnMe + Me$, one or both of the radicals probably being excited and carrying surplus kinetic energy. On this basis, the energy of the zinc–carbon link would be not greater than 100 kg.-cals. and probably appreciably less than this value, *i.e.*, by the amount of excitation energy of the products. Thermochemical data are not available for checking this, but it appears to be a reasonable value. It is impossible to make an estimate of the energy of excitation of the products here; in the case of methyl iodide it may be as much as 45 kg.-cals.

An alternative view of the mechanism of the dissociation, which might be suggested on the basis of photochemical work with other substances, is that a simultaneous fission of both alkyl groups occurs, *e.g.*, $ZnMe_2 + h\nu \longrightarrow Zn + 2Me$, the energy being absorbed by one zinc–carbon link and subsequently distributed between the two. Collisions might be expected to facilitate this partition, which would have to occur within the period required for some complete vibration. The development of the continuum towards longer wave-lengths is, indeed, markedly increased by increase of pressure. Again, the introduction of vibrations into one zinc–carbon link as a result of electronic excitation will almost certainly automatically induce vibrations in the other similar link. According to the structure and symmetry properties of the whole molecule, these induced vibrations will be of different types. The introduction of deformation vibrations into these links might well lead to a simultaneous scission of both alkyl groups.

FIG. 6.



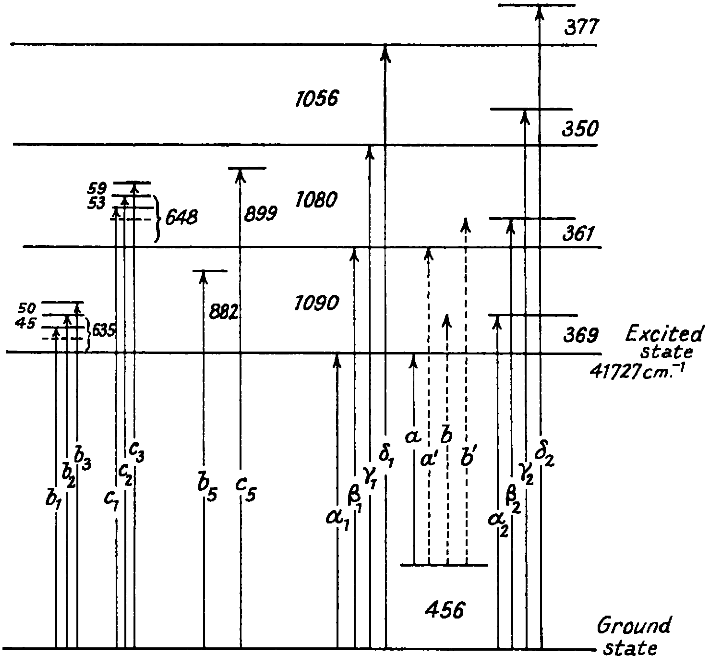
(*a*) (*b*)

Photochemical measurements and an analysis of the products of decomposition with compounds containing different alkyl groups, *e.g.*, ZnMeEt, are being carried out in order to decide which of the two mechanisms is operative.

Bands.—From the general character of the system and the relatively small intervals, it is supposed that all the bands observed with diethylzinc are connected with the same electronic transition. The existence of bands with this compound and their absence with the dimethyl compound might suggest that this excitation is in the ethyl radical, and indeed in the C–C link; but tetraethyl-lead does not give the same band system at all, and ethyl iodide (Scheibe, Povenz, and Linström, *loc. cit.*) gives no bands in the region concerned. It is very likely that with diethylzinc, two states of excitation of the zinc–carbon link exist, one unstable, like that of dimethylzinc (B), but the other stable with its potential-energy curve (C) intersecting that of the unstable state (Fig. 6*b*). This would explain the diffuse (predissociated) nature of the bands. A similar hypothesis was introduced by Herzberg and Scheibe for the methyl halides. It may be that, with dimethylzinc at much higher frequencies, discrete bands can be obtained corresponding to transitions from the state A to the state D (Fig. 6*a*). A similar displacement of the region of electronic absorption of the carbon–halogen link with the nature of the halogen has been found to occur.

The principal bands with diethylzinc can be interpreted by the energy-level scheme shown in Fig. 7. The more intense pairs of bands, α, β, γ, δ, are regarded as involving transitions from the ground state, and the feebler band designated *a* as a transition from the first vibration level (456 cm.$^{-1}$) of the ground state. That the intensity of the principal bands steadily decreases from the first onwards to higher frequencies, *i.e.*, does not first increase and then decrease, suggests in accordance with the Franck–Condon principle that there is little change in the binding on electronic excitation. At the temperatures employed, it is improbable that the molecule will possess more than one or two vibrational quanta of the magnitude involved here. The Boltzmann factor would suggest that the relative probability of the ground state and the 456 cm.$^{-1}$ level is about 1 : 10. This is the order of the relative intensities of bands a and α_1. The intervals between the two bands of each pair (369, 361, 350, 377) are interpreted as vibrations in the excited state corresponding to the 456 cm.$^{-1}$ vibration of the ground state. The other prominent interval is an excited state of frequency 1080—1090. Feebler bands suggest a vibration frequency in the excited state of *ca.* 890. Transitions from the first vibrational level of the ground state represented in Fig. 7 by b, a', may occur, but will be relatively feeble and lie so close to the α, β_1, . . . diffuse bands as to be undetected. The very weak bands marked b_1, b_2, b_3, c_1, c_2, c_3, have not yet been satisfactorily interpreted. It can be supposed that they arise from transitions from the ground state to a three- (or four-)fold level in the excited state, with frequencies grouped *ca.* 50 cm.$^{-1}$ about 635 cm.$^{-1}$. A consideration of the Raman frequencies (Venkateswaran, *Indian J. Physics*, 1930, **5**, 145) given for diethylzinc supports the above scheme. The three strongest frequencies are 474, 1174, and 2874. With dimethylzinc there are three corresponding frequencies 506, 1165, and 2883, so no marked alteration occurs with the change from methyl to ethyl groups. The value 2880 is prevalent in most alkyl compounds of very different types, and is generally regarded as a C–H valency vibration; 474 is almost certainly a valency vibration of the zinc–carbon link, and 1174 probably a deformation vibration. The normal valency vibration found for the ground state (456) agrees satisfactorily with the Raman value 474. This is presumably modified in the excited state to 369, etc. It is not yet clear whether the 1090 interval found is the 1174 Raman frequency modified in the excited state. Another possibility is that it represents a deformation frequency of the methyl radical which was found to be intense with methyl iodide and other alkyl compounds, and has exactly this value.

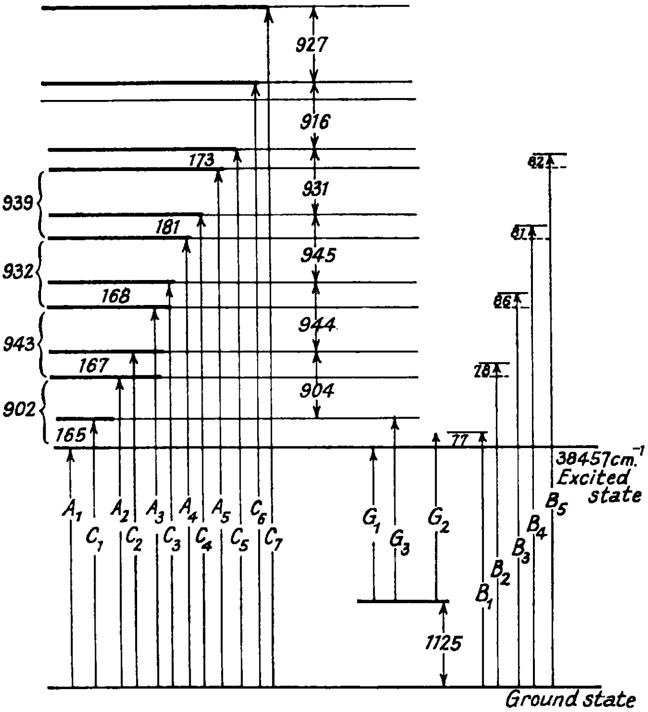
FIG. 7.



The frequency 890 and the split level about 640 are not at present explained. They may correspond to frequencies not detected in the Raman measurements; the infra-red spectrum has not been measured. Two feeble Raman frequencies, 933 and 987, are recorded, one of which may be amended here to 890. The splitting of the 640 group may be in accordance with the symmetry properties of the molecule (cf. Mecke, " Molekülstruktur," 1931, p. 51), and their low intensity may imply that they involve non-totally symmetrical vibrations.

The band system of tetraethyl-lead must arise from an electronic excitation in the lead–carbon link, and the intensity distribution of the strongest bands, which passes through a maximum, suggests that in the excitation the system behaves similarly to a diatomic molecule, *i.e.*, the alkyl groups are fairly rigid. The correlation into an energy-level scheme is more difficult than with diethylzinc owing to the peculiar intensity distribution of the weaker bands, and in addition, no data are available on either the Raman spectrum or the infra-red spectrum. According to Mecke (*op. cit.*), molecules with tetrahedral symmetry give two vibration levels which are each split three-fold—an antisymmetrical valency vibration and a symmetrical deformation. This suggests a possible interpretation of the observed weaker groups of three. With the stronger and more developed bands it is seen that the intervals G_1A_1, G_2B_1, G_3C_1, of 1132, 1114, and 1122, are markedly different from the spacing *ca.* 904—945 of the intense pairs of heads. Also G_1, G_2, G_3, are much weaker. This suggests that *ca.* 1125 is a vibration in the ground state. It may well be a deformation vibration similar to the 1174 of diethylzinc. The frequencies 904—945 may involve the same vibration modified in the excited state.

Fig. 8.



That the bands A_1, B_1 lie on the longer-wave side of the C_1 bands, and have a lower intensity, suggests that A_1, B_1 also represent absorption from higher vibration levels in the ground state; but in intensity $C_1 > A_1 > B_1$, and the G level is not single but gives a similar group of three. It must therefore be concluded that the A_1—C_1 intervals represent vibration levels in the excited state. This may also be true of the B_1—C_1 intervals, and the lower intensity of the B bands may be due to the type of symmetry change involved. A tentative scheme is given in Fig. 8. Explanation of the X_1 bands at higher frequencies, which become stronger than the A_1 bands, is postponed. They may be connected with those designated A_1', A_2', A_3'.

If the scheme given is correct, electronic excitation of the lead–carbon link is predominantly accompanied by an excitation of the valency vibration *ca.* 170 cm.$^{-1}$, and this type of vibration is induced to the exclusion of others more than was the case with diethylzinc.

Duncan and Murray (*J. Chem. Physics*, 1934, **2**, 146) have recently published work on the Raman spectrum of tetramethyl-lead. By analogy with dimethyl- and diethylzinc, the Raman frequencies of which are similar, as already stated, a close similarity might also be expected between tetramethyl- and tetraethyl-lead. With the former, the stronger frequencies found are 135, 458, 472, with somewhat weaker 2921, 3000, and 1155, and a few still feebler vibrations, *e.g.*, 930. It is noticeable that two strong pairs of frequencies occur, and that the 135 vibration is intense. The 170 vibration found in the ultra-violet absorption of tetraethyl-lead will then be related to a frequency corresponding to the 135 of tetramethyl-lead. The ultra-violet frequency 1125 may be connected with the Raman 1155, and the 940 may be the same frequency modified by the electronic excitation; but the very feeble frequency 930 found in the Raman spectrum may, by virtue of the type of vibration it involves, appear more strongly in the infra-red and ultra-violet absorption spectra, and it may be that this is the correct interpretation. It is, however, remarkable that the intense Raman frequencies 458 and 472 do not appear in the ultra-violet absorption. The 930 frequency might be a harmonic of one of these, but there seems to be no reason why such a harmonic should be particularly preferred to the fundamental vibration.

SUMMARY.

As the first part of a series in which the absorption spectra of certain polyatomic molecules containing methyl and ethyl radicals are being examined, the results with dimethyl- and diethyl-zinc and tetraethyl-lead are reported. The spectrum of the first is continuous, that of the second shows diffuse bands with an overlapping continuum, and that of the third gives a quite different, sharp, band system. Attempts are made to correlate the vibration levels induced by electronic excitation with types of vibration theoretically known to occur, and with the Raman frequencies.

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