ON THE CONTINUOUS EMISSION SPECTRA ASSOCIATED WITH ELECTRIC DISCHARGES THROUGH FLOWING VAPOURS OF SnCl₂, SnCl₄ AND SiCl₄

By R. K. Asundi, S. Mujtaba Karim and R. Samuel

(From the Department of Physics, Benares Hindu University, Benares)

During the course of an investigation on the emission bands of $SiCl_2$ and $SnCl_2$, a number of continuous emission bands have been recorded; the experimental procedure and conditions under which the spectra were obtained are described already in detail.[1] These are not repeated here but for ready reference the requisite data concerning the long-wave limits, maxima, etc., are reproduced in Tables I, II and III.

TABLE I. $SnCl_2$

(Vapour pressure less than 1 mm. of Hg.   Uncondensed discharge)

Long-wave-length limit			Maxima			Short-wave-length limit
A	Kcal./mol.	Electron-volts	A	Kcal./mol.	Electron-volts	A
5200	55·2	2·4	4500	62·5	2·7	4000
3400	82·8	3·6	3100	92·0	4·0	3000

TABLE II. $SnCl_4$

(Vapour pressure less than 1 mm. of Hg.   Uncondensed discharge)

Long-wave-length limit			Maxima			Short-wave-length limit
A	K. cal./mol.	Elctron-volts	A	K. cal./mol.	Electron-volts	A
5100	55·5	2·5	4525	62·5	2·7	3910
3470	82·0	3·5	3260	87·0	3·6	3210
2620	108·0	4·7	2580	110·0	4·8	2520
2520	112·5	4·9	2365?	120·0	5·1	2400

TABLE III. $SiCl_4$

(*Vapour pressure about 0·5 mm. of Hg. Uncondensed discharge*)

Long-wave-length limit			Maxima			Short-wave-length limit
A	K. cal./mol.	Electron-volts	A	K. cal./mol.	Electron-volts	A
6500	44·0	1·9	4022	70·5	3·0	3550
3550	80·0	3·5	3260	86·7	3·8	3160
2620	108·0	4·7	2570	110·5	4·8·	2535
2500	113·7	4·9	2450	116·0	5·0	2400

It is only recently that attention is being drawn to the continuous emission spectra observed in the discharge through gases and it appears that such spectra are generally due to electron radiation.[2] We cannot say whether the spectra observed by us are due to the same reason, but since the density of current and particularly the vapour pressure are much lower than in the above experiments, it is not unlikely that the continuous spectra observed by us are really emitted by the excited molecules of the vapour, *i.e.*, are due to some or other chloride of Si or Sn. This is even more probable, since the discrete bands observed,[1] as far as the experimental conditions are concerned, clearly appear to be connected with the continuous background in which they appear. We wish, therefore, to draw attention to a simple relation between the continuous spectra and the electron terms of the molecules in question, which possibly is the explanation of the existence of the continua.

At present, however, our knowledge of such spectra is very limited. In the case of continuous absorption spectrum we know at least that the initial state of the absorption process must be the ground level of the molecule, and thermochemical data are qualified to correlate the various regions of selective absorption with particular processes of photodissociation. In the case of a continuous emission spectrum we know nothing, *a priori*, but that the final level of the corresponding transitions must be a repulsive one and therefore cannot be the ground level of the molecule. Furthermore, the experimental determination of such spectra at present is even more difficult than that of absorption spectra and particularly the long-wave limit of such a spectrum cannot be ascertained with accuracy inside rather wide limits. For these reasons, it is obvious that we offer the following explanation only as a first and tentative discussion.

We consider at first, the spectrum (Sn + 4 Cl) since the heats of formation of $SnCl_4$ as well as of $SnCl_2$ are directly known. Parti and Samuel have recently investigated[3] the various processes of photodissociation of molecules of this type and have given a term scheme including stable as well as repulsive terms. The simplified Franck-Condon diagram of Fig. 1 is constructed according to the thermochemical figures calculated by them.
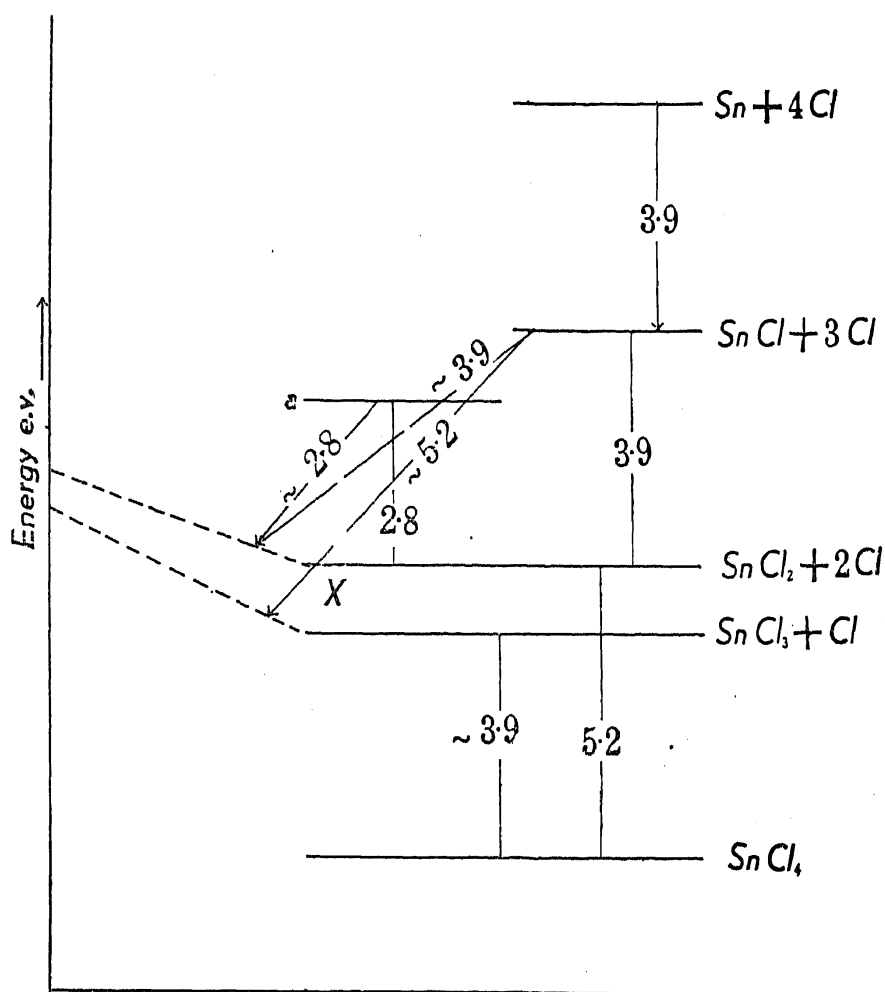

FIG. 1.

The combination of Sn and one Cl atom gives rise to the stable ground state of the molecule SnCl. The atomic heat of formation of $SnCl_2$ being D $(SnCl_2) = 180 \cdot 9$ K. cal./mol., this ground state lies $90 \cdot 5$ K. cal./mol. or about $3 \cdot 9$ e.v. below the level of dissociated atoms. The ground level of $SnCl_2$ obtains by the combination of the same SnCl molecule with a further Cl atom. That of $SnCl_4$, however, does not belong to this series but involves an excited $SnCl_2$ molecule (or an excited Sn atom) in which the repulsive s^2 group is already fissured. It lies lower than that of $SnCl_2$ by the difference D $(SnCl_4) - D(SnCl_2) = 300 \cdot 5 - 180 \cdot 9 = 119 \cdot 6$ K. cal./mol. $= 5 \cdot 2$ e.v. The ground level of $SnCl_3$ lies somewhere in between. Its exact position is not known for want of data on the ^5S term of Sn. According to the estimate[1]

of $2 \cdot 4$ e.v. for this term of Sn, the ground level of $SnCl_3$ is assumed to lie $3 \cdot 9$ e.v. above the ground level of $SnCl_4$.

From the absorption spectra of molecules of this type and their correlation to photodissociation process it is already known that these stable electronic levels are associated at the same time with repulsive potential curves. For instance, the approach of one or two Cl atoms towards the unexcited molecule $SnCl_2$ does not produce chemical combination (again on account of s^2 group) but an elastic collision only occurs. The corresponding potential curve has been found to be comparatively flat.[3] But also where chemical union becomes possible, e.g., at the approach of Cl towards SnCl or $SnCl_3$ it is highly probable for thermochemical reasons, that at least one repulsive curve is produced along with the attractive one. These repulsive curves are represented in the diagram by dotted lines. Finally, the excited term[1] of $SnCl_2$ at 22237 cm.$^{-1}$ or $2 \cdot 8$ e.v. is added.

The energy difference between the upper repulsive curve ($SnCl_2 + 2$ Cl) and the excited level of $SnCl_2$ is $2 \cdot 8$ e.v. at its lowest point and the difference of the same curve and the ground level of SnCl is roughly one e.v. larger, i.e., $3 \cdot 9$ e.v. The energy difference between the lower repulsive curve ($SnCl_3 +$ Cl) and the ground level of SnCl is about $5 \cdot 2$ e.v. As can be seen from Tables I and II, these are just the values needed for the interpretation of the continuous spectra. Not only do they agree quite well with the long-wave limits but what is more important, considering the unreliability of these determinations, these term differences are just slightly larger than the maxima of continuous emission, as should be expected for a transition to a repulsive potential curve (see inclined arrows in Fig. 1).

This suggested interpretation of these spectra, assuming they are due to the vapour molecules, appears plausible for the following reasons:

(1) It explains why the A bands[1] of $SnCl_2$ appear under the same experimental conditions as the continuous background, a($SnCl_2$) being the common initial level of both emissions.

(2) The extreme short wave maximum is double, viz., $4 \cdot 8$ and $5 \cdot 1$ e.v., with a separation of $0 \cdot 3$ e.v. between the two components. This is almost exactly the value of the electronic separation of the ground level of SnCl.

(3) This maximum is either absent or considerably weakened in the discharge through the vapour of $SnCl_2$, where the number of $SnCl_4$ molecules are naturally decreased.

A similar interpretation holds good for $SiCl_4$, but here the thermochemical data are not quite accurate. Utilizing the values already deduced,[1]

Fig. 2 is drawn in the same manner as Fig. 1, exactly similar remarks obtaining in this case also. The energy differences of 3·5, 3·7 and
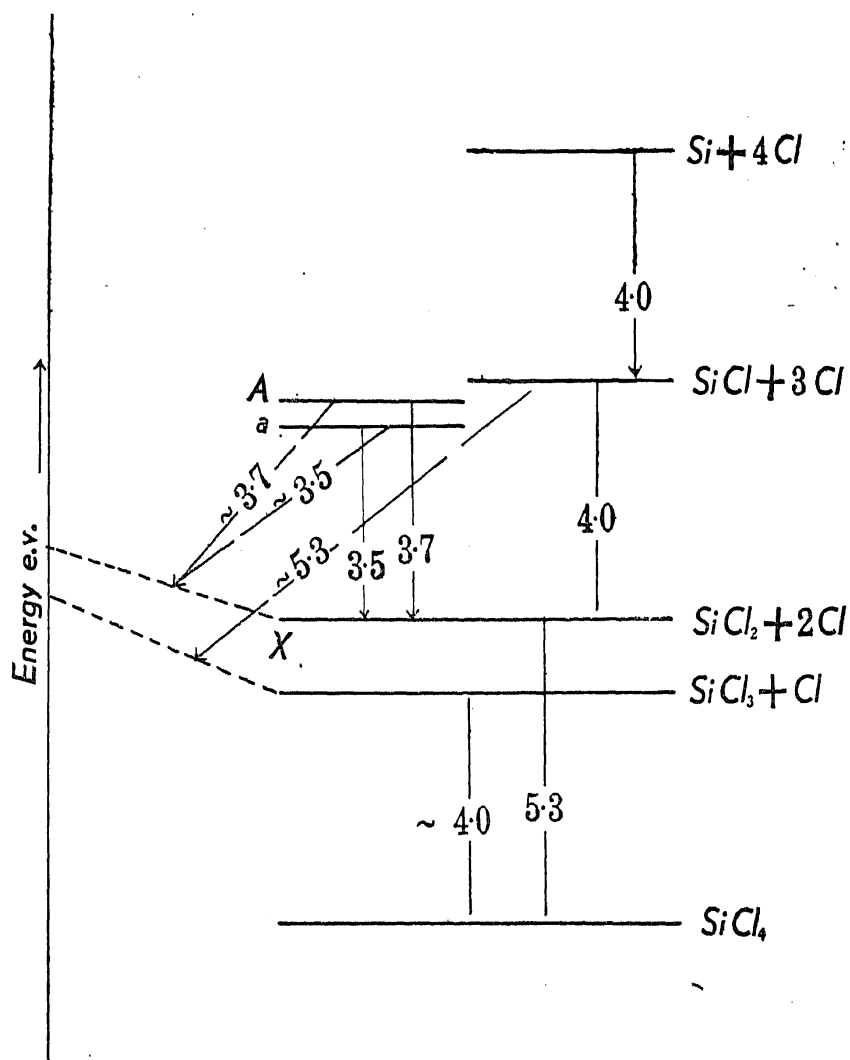

FIG. 2.

about 5·3 e.v., agree quite well with the values of the maxima recorded in Table III. The difference of 0·2 e.v., of the two last maxima is of course larger than the much smaller electronic separation of $^2\Pi$ (SiCl), but the same accuracy cannot be expected in such continuous spectra as in discrete band spectra. It is significant, however, that this value is smaller for $SiCl_4$ than for $SnCl_4$.

Summary

From the experimental conditions under which the spectra are obtained it is assumed that they are due to molecular radiation. Thermochemical and spectrascopic data enable one to illustrate the relation among the energy levels of the various systems in the formation of the multi-atomic molecules from their constituent atoms. Such simplified Franck-Condon diagrams are constructed for $SnCl_4$ (which includes $SnCl_2$) and $SiCl_4$. An interpretation,

R. K. Asundi and others

uniform in all cases, of the observed continuous bands in terms of the transitions among the energy levels, transitions, which of course involve a repulsive state for their final level, is suggested.

REFERENCES

1. R. K. Asundi, M. Karim   *Proc. Phys. Soc. Lond.*, 1938, **50**, 581–98.
   and R. Samuel

2. W. Finkelnburgh   .. *Zt. f. Phys.*, 1931, **70**, 375; 1934, **88**, 768.

3. Y. P. Parti and R. Samuel .. *Proc. Phys. Soc. Lond.*, 1937, **49**, 568.