

ON THE EMISSION SPECTRUM OF CCl_4 .*

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THE spectrum of the uncondensed discharge through flowing vapour of CCl_4 has been studied by Jevons.¹ In addition to the bands attributable to C_2 and CO , a prominent cluster of four bands was found in the ultra-violet. Continuous emission bands were observed but have not been recorded † We have photographed the spectrum of an uncondensed discharge from a 1.5 K.W. transformer delivering 50,000 volts through flowing CCl_4 vapour, pressure being maintained constant between 0.2 and 0.3 mm. of Hg. Medium Hilger quartz spectrograph has been used to photograph the spectrum in the ultra-violet region. The plates have been measured on the Abbe comparator using Cu arc lines as standards. The wave-lengths of the beginning, maximum and end of the continuous emission bands have been determined from microphotometer records, which were obtained on a Zeiss recording microphotometer. This shows continuous emission bands, the wave-lengths of whose maxima are approximately at $\lambda\lambda$ 4600, 3348, 3070, 2580, 2430, and (2345 ?). The full data on these continuous bands are given in Table I, and the accompanying microphotometer curve given in Fig. 1 shows the details. There was no trace of bands due to C_2 .

TABLE I.

Long wave-length limit A.U.	Maxima A.U.	Short wave-length limit A.U.
5850	4600	4000
4000	3348	3260
3260	3070	3000
2700	2580	2500
2500	2430	2380
2380	2300 ?	2250

* A preliminary note has been published in *Curr. Sci.*, 1937, 5, 474, which also contains a reproduction of the bands.

† Private communication from Dr. Jevons.

Among the CO bands the plate showed only a faint trace of the 0-0 band of the third positive carbon system. In addition to the continuous bands, the most characteristic feature of the spectrum was a prominent group of strong bands between $\lambda\lambda$ 2796 and 2777. Six heads could be distinguished of which four can be identified with bands observed by Jevons.¹ In addition to this group of bands the plate showed two more groups of weaker bands on either side of this region. All these bands are degraded towards shorter waves. The strong group of bands lies exactly in the region of the 0-1 bands of the 5B system of CO, but we have satisfied ourselves that it is different from 5B bands by obtaining direct spectrograms of CO. The differences in wave-lengths though slight, are outside the errors of observation and are confirmed by independent measurements of Jevons. Furthermore, the CCl_4 plates do not show any trace of the 0-0 band of 5B system which is about the same intensity as, if not slightly stronger than, the 0-1 band. Again the group of bands at λ 2846 which fortunately lies in the region free from CO bands definitely shows that the strong group also does not belong to CO. The accepted values of wave-lengths represent the mean of three measurements which agreed to within 0.2 A.U.

In Table II are listed the wave-lengths of the band heads observed here. Column 3 gives the wave-lengths as measured by Jevons.¹ The figures in brackets in each case represent visually estimated intensities. Column 4 contains the wave-lengths as recently measured on a heavily exposed plate by Dr. Jevons who has kindly communicated the results to one of us (R. K. A.).

In appearance these bands resemble very much the group of bands observed in the spectrum of the vapour of $SiCl_4$,² between $\lambda\lambda$ 2830 and 2770, and whose emitter is not yet definitely established. Some of the bands have a sharp line-like head as in these latter bands and show no indication of resolution. It is possible, however, to arrange them in the usual v' , v'' table (Table III). The band at λ 2724.3 coincides with a mercury line and was, therefore, omitted in the preliminary publication. In view of the fact, however, that the resonance line of Hg at λ 2536.7 is not present on the plates, this is regarded as a band belonging to the system described. The only band not shown in the analysis is that at λ 2786.5 which, however, will probably fit into the scheme as one of the (2-2) bands. It may be mentioned that the band at λ 2782.4 coincides with a chlorine line.

The analysis as displayed in Table III indicates that the bands are due to a diatomic molecule. Apparently the CCl molecule suggests itself as the emitter.

TABLE II.

Authors λ A.U.	Int.	Jevons	
		Earlier Measurements λ A.U.	New Measurements λ A.U.
2862.0	(0)
2857.0	(4)	..	2856.83
2849.4	(4)
2846.0	(4)	..	2845.84
2795.9	(6)
*2789.5	(8)	..	2789.85
*2788.3	(8)	2788.2 (4)	2788.32
2786.5	(5)	..	2786.68
*2782.4	(8)	2782.3 (2)	2782.27
*2778.9	(6)	2778.6 (1)	2778.71
*2777.7	(8)	2777.5 (4)	2777.59
*2724.3	(0)
2713.4	(0)

* Sharp line-like heads, or strong line superposed on head.

TABLE III.

v' \ v''	0			1		
	λ Air A.U.	ν Vac. cm. ⁻¹	$\Delta \nu$	λ Air A.U.	ν Vac. cm. ⁻¹	
0	2795.9 (6)	35756	826	2862.0 (0)	34930	
	2789.5 (8)	35838	846	2857.0 (4)	34992	
	2782.4 (8)	35930	845	2849.4 (4)	35085	135
	2778.9 (6)	35975	848	2846.0 (4)	35127	
$\Delta \nu$	858, 868			862, 863		
1		
	2724.3 (0)	36696	842	2788.3 (8)	35854	
		136
	2713.4 (0)	36843	853	2777.7 (8)	35990	

In Table IV are collected the data of the ground states of the known iso-electronic molecules formed by the atoms of the two short periods. It will

TABLE IV.

Molecule	No. of Electrons	Ground Term	$\Delta \nu_e$	ω_e''	$\omega_e'' x_e''$
CP	21	$^2\Sigma$..	1239.67	6.86
SiN	21	$^2\Sigma$..	1151.68	6.56
BeCl	21	$^2\Sigma ?$..	846.6	5.11
MgF	21	$^2\Sigma$..	690.75	3.95
CS	22	$^1\Sigma$..	1285.1	6.5
SiO	22	$^2\Sigma$..	1242.0	6.05
NS	23	$^2\Pi$	223	1220.0	7.75
PO	23	$^2\Pi$	224	1230.6	6.52

Data from Spomer's *Molekuel Spektren*, Berlin, 1936.

be seen that a close correspondence exists between the various constants in each pair of molecules. The data for BeCl are not definite to establish the term taken here as the ground state of the molecule. The discrepancy may be due to the possibility that this level may not really be the ground state of the BeCl molecule.

If the emitter of the bands is taken as CCl, we obtain the following correspondence (Table V) between the constants of this molecule and that of the

TABLE V.

Molecule	Ground State	$\Delta \nu_e$	$\omega_{\frac{1}{2}}$	$\omega_e'' x_e''$
CCl	${}^2\Pi$	136	843.6	?
SiF ⁴	${}^2\Pi$	161	844.7	4.7

iso-electronic molecule SiF. It may also be pointed out, as suggested by Dr. Jevons (private communication), that the constants here obtained fit very well as an extension to CCl, of the tables of constants given by Bashford, Briscoe and Jevons³ for the fluorides, chlorides and bromides of Si, Ge, Sn, and Pb.‡

If this is true, the bands are the analogues of the β -bands of the SiF system, which have been shown to be due the transition $B {}^2\Sigma \rightarrow X {}^2\Pi$. The excitation energy of the CCl band system is 4.4 e. volts and this also agrees with 4.29 e. volts, the excitation potential of the β -bands of SiF.⁴ The only constant which does not completely agree is the electronic doublet separation $\Delta \nu_e$ of the ground state which is 136 cm^{-1} for CCl and 161.1 cm^{-1} for SiF. The difference between the frequencies of vibrations in the initial and final states being small, the transitions in which Δv is large are not expected. The conditions are favourable for the development of long sequences which, however, are not observed. Evidently, it has not been possible to derive the vibrational functions. The electronic structure of the molecule in the two states is expected to be similar to that of SiF, but unless more data are made available, this statement cannot be put to test.

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‡ This is since shown in a paper by W. Jevons and L. A. Bashford, *Proc. Phys. Soc. Lond.*, 1937, **49**, 554.

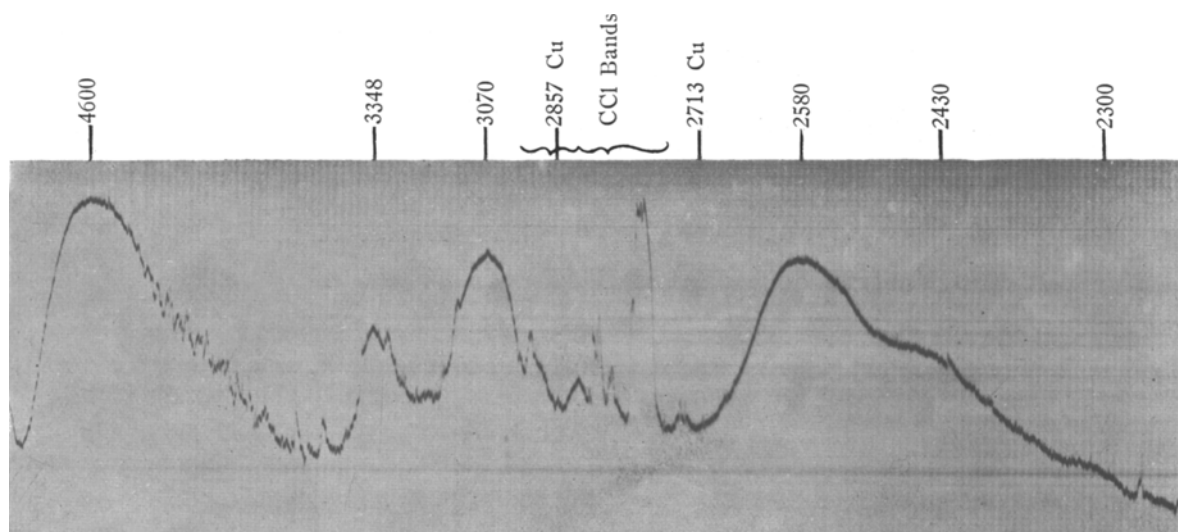


FIG. 1.