

on the different molecules. The average value $4.58_0 \pm 0.050$ is slightly lower than the earlier less accurate value.² Table V compares the nuclear coupling in HCN with that in the halogen cyanides. The higher value for HCN reveals a small but definite difference in the electronic structure of the CN bond. A slight difference

is also revealed by the shorter CN distance for HCN shown in Table V.

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On the Emission Bands of CCl

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Some new bands of CCl are recorded and these together with those reported by earlier workers are arranged in a vibrational scheme. The electronic transition is ${}^2\Sigma \rightarrow {}^2\Pi$, the doublet separation for the ${}^2\Pi$ state being 138 cm^{-1} . By way of comparison it is mentioned that the uncondensed transformer discharge gave CF_2 bands in the case of CF_4 , CCl, and Cl_2 bands in the case of CCl_4 and only Br_2 bands in CBr_4 . It is pointed out that the supposed CBr bands reported by Durie and Iredale are not due to CBr but due to Br_2 .

FLOWING vapor of carbon tetrachloride was excited by an uncondensed transformer discharge and the spectrum obtained was photographed on Medium Hilger quartz and E_1 -quartz (Littrow type) spectrographs. Besides the continuous bands of Cl_2 and the CCl bands reported by earlier workers,¹⁻³ some extra bands of CCl were recorded. The wave-lengths and the wave numbers together with the estimated intensities of the band heads, which are all degraded to shorter wave-lengths, are given in Table I. The intense bands were photographed in the second order of a 21-ft. Wadsworth mounting grating spectrograph, and the rotational structure of the bands could be seen, but the dispersion is not high enough to make any rotational analysis.

All the new bands, marked*, together with those reported by earlier workers can be arranged in the vibrational scheme shown in Table II, which represents an extension of the analysis of Asundi and Karim.¹ The electronic transition, as suggested by Asundi and Karim, appears to be ${}^2\Sigma \rightarrow {}^2\Pi$, ${}^2\Pi$ being the ground state. The doublet separation ${}^2\Pi_{3/2} - {}^2\Pi_{1/2}$ is 138 cm^{-1} . From the analysis the Q heads can be fairly well represented by the following formula.

$$\nu = \left. \begin{array}{l} 35834 \\ 35972 \end{array} \right\} + (866v' - 1.5v'^2) - (845v'' - 1.0v''^2).$$

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¹ R. K. Asundi and S. M. Karim, Proc. Ind. Acad. Sci. **6A**, 328 (1937).

² Asundi, Singh, and Mishra, Current Science **12**, 204 (1943).

³ Tadao Horie, Proc. Phys.-Math. Soc. Japan **21**, 143 (1939).

Horie³ gave a vibrational analysis of the CCl bands** which does not appear to be satisfactory for the following reasons: (1) Some of the extra bands obtained in the present experiments, namely 34098, 34169, and 36012 cm^{-1} do not fit in the scheme proposed by Horie. (2) The $\omega_e'x_e'$ value 18.8 cm^{-1} obtained by Horie's analysis appears to be too high and out of proportion with the value 3.5 cm^{-1} obtained by him for $\omega_e''x_e''$.

TABLE I.

Intensity	λ_{air}	ν_{vac}
1	2931.9	34098
1	2927.4	34150
?	2925.8	34169
1	2919.5	34242
1	2916.3	34280
3	2861.5	34936
5	2857.1	34990
4	2855.5	35010
4	2849.2	35087
5	2846.0	35127
?	2844.2	35149
4	2794.2	35778
6	2789.8	35834
10	2788.3	35854
5	2786.7	35874
8	2782.3	35931
7	2778.9	35975
10	2777.6	35992
?	2776.0	36012
1	2724.0	36700
2	2721.5	36734
?	2717.4	36789
2	2713.9	36836
1	2711.5	36869

** The isotope displacements due to CCl^{35} and CCl^{37} , reported by Horie for three of the bands are, however, not noticed in the present experiments.

TABLE II. Vibrational analysis.

v''	0	1	2	3
0	P 35778 842	34936 838	34098*	
	Q 35834 844	34990 840	34150	
	P 35931 844	35087 845	34242	
	Q 35975 848	35127 847	34280*	
	866,858,861	864,865	860	
1
	36700 846	35854 844	35010 841	34169*
	36789*	...	35149	
	36836 844	35992		
		864, 863		
2			...	
			35874	
			36012*	
			860,857	
3			...	
			36734	
			...	
			36869*	

(3) The O—C values for Horie's analysis can be seen to be in general high compared with the O—C values for the present analysis. (4) The transition responsible for the band system, as stated above appears to be ${}^2\Sigma \rightarrow {}^2\Pi$, with which Horie also agrees. ${}^2\Sigma \rightarrow {}^2\Pi$ transitions in the iso-electronic molecules SiF (β - and γ -systems),⁴ NS⁵ and Po⁶ (all of which have 23 electrons like CCl) clearly show P_1 , Q_1 , P_2 and Q_2 band heads. This is

⁴ R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. 3, 346 (1936).

⁵ A. Fowler and C. J. Bakker, Proc. Roy. Soc. London 136, 28 (1932).

⁶ P. N. Gosh and G. N. Ball, Zeits. f. Physik 71, 362 (1931).

true also for similar transitions in NO and SiCl.⁷ So it is quite natural to expect the P_1 , Q_1 , P_2 and Q_2 heads in the CCl band system. Indeed we see four band heads in the different groups of the present band system. Horie's analysis is based on the assumption that all the band heads are just either Q_1 or Q_2 heads and he does not take into consideration the possible existence of P_1 and P_2 heads at all. On the other hand, the present analysis (Table II) shows clearly the expected P_1 , Q_1 , P_2 and Q_2 heads.

It will be worth while, by way of comparison, to mention briefly some results obtained by the writer in other experiments using a similar uncondensed transformer discharge through CF₄ and CBr₄. In the case of CF₄, a new band system due to the CF₂ molecule is obtained. This will be dealt with in detail in a separate communication. But the excitation of CBr₄ gave only bands due to the bromine molecule and did not give any bands due to either CBr or CBr₂. It may be pointed out that Durie and Iredale⁸ reported some supposed CBr continuous bands^{**},⁹ obtained by high frequency discharge through CBr₄ vapor. We also got these bands by the transformer discharge through CBr₄ vapor, but the same bands were also obtained by exciting pure bromine vapor.¹⁰ Hence these bands must be due to the bromine molecule and not due to the CBr molecule.

The author wishes to express his thanks to Professor R. S. Mulliken for his kind interest in the work.

⁷ W. Jevons, Proc. Phys. Soc. 48, 563 (1936).

⁸ R. A. Durie and T. Iredale, Trans. Faraday Soc. XLIV, 806 (1948).

^{**} It may be mentioned that these continua agree well with those continuous emission bands obtained by Asundi and Karim (see reference 9) in the excitation of SiBr₄, which are also obviously due to Br₂.

⁹ See reference 1, p. 282.

¹⁰ P. Venkateswarlu, Proc. Ind. Acad. Sci. 25A, 138 (1947).