



which may therefore be assigned to ClO. The bands do not occur readily when chlorine is introduced into a carbon monoxide - oxygen flame, but have been observed, very weakly, in the outer cone of a methyl chloride - oxygen flame.

The bands, which are superposed on a fairly strong continuous background, are degraded to the red and appear to possess a fairly simple vibrational structure. Unfortunately, the heads are not well defined, and overlapping by strong bands of OH renders accurate measurement and reliable analysis difficult. Photographs have been taken with a medium quartz spectrograph (as in illustration), using plates of high contrast, and also with a large Littrow-type quartz spectrograph giving a dispersion of about 5 Å./mm. in the region of the bands. Under the large dispersion the rotational structure is seen to be complex; heads are difficult to locate, and the chlorine isotope effect could not be found owing to the complexity. With the smaller dispersion, the band heads listed in the accompanying table were measured; the measures

BAND HEADS OF ClO

λ	I	ν	ν'	ν''	λ	I	ν	ν'	ν''
4502	2	22206	4	10 + x	3991	8	25049	1	4 + x
4459	3	22420	3	9 + x	3957	7	25265	0	3 + x
4417	3	22833	2	8 + x	3874	10	25806	1	3 + x
4373	3	22861	1	7 + x	3841	10	26027	0	2 + x
4335	1	23062	3	8 + x	3761	9	26581	1	2 + x
4293	7	23341	2	7 + x	3729.5	7	26805	0	1 + x
4241	5	23573	1	6 + x	3652.5	6	27371	1	1 + x
4154	4	24066	2	6 + x	3625	3	27578	0	0 + x
4114	9	24300	1	5 + x	3587	2	27871	2	1 + x
4078	6	24515	0	4 + x					

are accurate to about 2 Å. in most cases, but in a few difficult cases there is a possibility of errors so large as 5 Å. The bands have been arranged into a provisional vibrational scheme using intervals of about 780 cm^{-1} , decreasing to less than 700 for ω'' and about 550 cm^{-1} for ω' . The bands fall on an open Franck-Condon parabola, and it is not possible to assign definite values for ν'' ; it would not be surprising if x in the table was about 3, making ω'' a little more than 800 cm^{-1} .

G. PANNETIER
A. G. GAYDON

Chemical Engineering Department,
Imperial College of Science and Technology,
London, S.W.7.

Oct. 22.

¹ Vaidya, W. M., *Proc. Indian Acad. Sci.*, 7 A, 321 (1938).

² Vaidya, W. M., *Proc. Indian Acad. Sci.*, 6 A, 122 (1937).

³ Coleman, E. H., and Gaydon, A. G., *Trans. Farad. Soc.*, in the press.

⁴ Urey, H. C., and Bates, J. R., *Phys. Rev.*, 34, 1541 (1929).

Interaction Terms in Molecular Vibrations

In a recent communication¹, Coulson, Duchesne and Manneback have pointed out that the positive sign of the cross-term constant, g_c , in the P.E. function of the water molecule

$$2V = f_1(\overline{\Delta r_1}^2 + \overline{\Delta r_2}^2) + 2f_{12} \cdot \Delta r_1 \cdot \Delta r_2 + r_1 r_2 f_{\theta} \cdot \overline{\Delta \theta}^2 + 2r_1 g_c (\Delta r_1 + \Delta r_2) \cdot \Delta \theta$$

can be accounted for by supposing that the hybridization of the oxygen bond-forming orbitals changes during a vibration. We had come to exactly the same conclusion, and our reasons for this are contained in a communication to the Faraday Society which is awaiting publication².

We were led to our conclusion more particularly by the sign of f_{12} , which is negative. This implies that, as one OH-bond contracts, the other tends to contract also. We had first supposed that the departure from the simple valency force-field might be due to repulsion between the hydrogen atoms. But, if this were so, movement of one hydrogen atom towards the oxygen atom would force the other away. We were therefore led to conclude that as one OH-bond contracts it assumes more s -character, which results in the other bond assuming more s -character and its equilibrium-length decreasing. This explanation was confirmed by the fact that it accounted for the positive sign of g_c also. So we concluded that the size of the HOH angle was due to the fact that the oxygen bond-forming orbitals in water had considerable s -character, rather than because of repulsion between the hydrogen atoms.

If the repulsion between the hydrogen atoms is given by

$$V = V_0 + A(\Delta R) + \frac{1}{2}B(\Delta R)^2$$

for small displacements, ΔR , from the HH distance in the equilibrium configuration, the contribution of A and B to the cross-terms f_{12} and g_c can be shown to be

$$\begin{aligned} 0.313 B - 0.124 A & \text{ to } f_{12} \\ 0.242 B + 0.160 A & \text{ to } g_c. \end{aligned}$$

The signs of the contributions to g_c and f_{12} will depend, therefore, on the signs and relative magnitudes of A and B . We cannot, therefore, agree with Coulson, Duchesne and Manneback that it is necessary "that the contributions to the interaction constants f_{12} and g_c that arise from the force between the two non-bonded atoms have the same sign". This will only be true when the first terms involving B , d^2V/dR^2 , outweigh the second terms involving A , dV/dR . However, in the present case, it does not seem that the force between the non-bonded atoms is an important factor. Urey and Bradley³ pointed out that this factor was important in accounting for the departures from the simple valency force-field in molecules such as carbon tetrachloride. We have developed their ideas somewhat further for the tetrahalides of some Group IV elements in two other papers that are awaiting publication⁴, and have shown that the repulsion that exists is of the magnitude that would be expected if it arises from Van der Waals' type interaction.

D. F. HEATH
J. W. LINNETT

Inorganic Chemistry Laboratory,
Oxford.
Dec. 8.

¹ Coulson, Duchesne and Manneback, *Nature*, 160, 794 (1947).

² Heath and Linnett, *Trans. Farad. Soc.*, in the press.

³ Urey and Bradley, *Phys. Rev.*, 38, 1969 (1931).

⁴ Heath and Linnett, *Trans. Farad. Soc.*, in the press.