The Force Fields of Cl_2O and Cl_2O_7

By B. BEAGLEY, A. H. CLARK, and D. W. J. CRUICKSHANK
(*Chemistry Department, University of Glasgow, Glasgow, W.2*)

THE results of normal-co-ordinate analyses by computer of the vibrational motions in Cl_2O and Cl_2O_7 show that certain aspects of earlier work reported in the literature require correction.

Rochkind and Pimentel[1] have derived the simple harmonic force field for Cl_2O by a comprehensive study of the infrared spectra of a number of isotopic species. Repetition of some of the calculations shows that in one aspect the reported force field is in error. The correct value of $f_{r\theta}$, the bond-stretching–angle-bending interaction force constant, is twice the published value. The revised field agrees well with that obtained by Herberich, Jackson, and Millen[2] from a microwave study. The situation is summarised in Table 1. As a further check on the force field, an electron-diffraction study of gaseous Cl_2O is being carried out to determine the root-mean-square amplitudes of vibration for Cl–O and Cl · · · Cl. These amplitudes have been calculated from the revised force field and are $u_{Cl-O} = 0{\cdot}051$ Å and $u_{Cl \ldots Cl} = 0{\cdot}067$ Å at 0°c.

For Cl_2O_7, a number of attempts[3–5] have been made to assign the observed vibrational frequencies to the appropriate modes of vibration. For the bridging part of the molecule, these assignments are listed in Table 2. Normal-co-ordinate calculations, making use of vibrational amplitudes

measured by electron diffraction,[6] show that none of the previous assignments is wholly correct.

Preliminary calculations were carried out treating Cl_2O_7 as a bent XOX system ($X \equiv ClO_3$) and assuming a completely diagonal (valence) force field. Thus the three fundamental frequencies ν_s, ν_b, ν_a, and two mean amplitudes u_{OX} and u_{XX} are dependent on the two parameters f_r and f_θ ($f_{rr} = f_{r\theta} = 0$). The bond-stretching force constant, f_r, was set equal to 2·75 md/Å, the value given in Table 1 for Cl–O in Cl_2O. This assumption is justified by the similarity in the experimental values for the lengths of the bridging bonds in Cl_2O and Cl_2O_7 (1·700 and 1·709 Å, respectively[2,6]). It follows at once that $\nu_a = 695$ cm.$^{-1}$ in agreement with two of the earlier assignments.[4,5] To find ν_s and ν_b, f_θ was steadily increased from zero until the calculated value of u_{XX} agreed with experiment[6] ($u_{Cl \ldots Cl} = 0{\cdot}055$ Å) within the limits of error of the approximations involved. Best agreement occurs when f_θ has the value $1{\cdot}45 \times 10^{-11}$ erg/rad.^{2}, which by calculation suggests the assignment $\nu_s = 595$ cm.$^{-1}$ and leads to $\nu_b = 195$ cm.$^{-1}$

The doubtfulness of the earlier assignments[2–5] can be further demonstrated by employing the full force-constant matrix in the XOX treatment and using a force-constant ellipse method. This method indicates all the possible harmonic force fields for a particular choice of ν_s, ν_b, ν_a. Each of the previously published assignments[2–5] was tested and could immediately be discarded because they lead to force fields with unreasonably large off-diagonal elements. The new assignment suggested by the simple diagonal-field approximation leads to a force field closely similar to that obtained for Cl_2O and to values of u_{OX} and u_{XX} which agree satisfactorily with experiment.[6]

A full normal-co-ordinate analysis of Cl_2O_7, now in progress, confirms the value of 595 cm.$^{-1}$ for ν_s. The band at 280 cm.$^{-1}$ which previous workers assign as ν_b or ν_s corresponds to a rocking mode of the ClO_3 groups.

The infrared spectrum[4] at present available for Cl_2O_7 has a lower limit of about 250 cm.$^{-1}$ Information about the far-infrared or Raman spectrum of Cl_2O_7 should confirm the presence of the angle-bending mode which is expected below 200 cm.$^{-1}$ There are also two torsional modes which should give bands near 100 cm.$^{-1}$

TABLE 1

Harmonic force field for Cl_2O

	Ref. 1	This work	Ref. 2
f_r (md/Å)	2·75	2·75	2·88
f_{rr} (md/Å)	0·40	0·40	0·31
$f_{r\theta} \times 10^3$ (dyne/rad)	0·13	0·26	0·28
$f_\theta \times 10^{11}$ (erg/rad^2)	1·32	1·32	1·22

TABLE 2

Frequency assignments for bridge in Cl_2O_7 (*cm.*$^{-1}$)

Mode	Ref. 3	Ref. 4	Ref. 5	This work
ν_a, Antisymmetric Cl–O(br) stretch	501 or 595	695	695	695
ν_b, Symmetric Cl–O(br)–Cl angle bend	—	280	<280	~195
ν_s, Symmetric Cl–O(br) stretch	—	495	280	595

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