Structure of $^2A_2$ Excited State of Chlorine Dioxide

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Summary The excited $^2A_2$ state of ClO_2 has the non-linear, symmetrical structure $r_e(ClO) = 1{\cdot}619$ Å, $\theta_e =$ 107° 0′, contrary to earlier suggestions that the ClO bond distances are unequal.

THE visible bands of ClO_2 have for many years been attributed to a $^2A_2 \leftarrow {}^2B_1$ transition, representing a π–π excitation in the m.o. description.[1,2] Although microwave work[3] has confirmed the orbital B_1 symmetry of the ground state, the excited state assignment depends upon a partial rotational analysis[1a] which indicates that the electronic bands have parallel polarization. The fact that two quantum changes in the ν_3 mode occur quite prominently in the vibrational structure of the electronic spectrum has prompted the very interesting suggestion[4] that the excited state structure may be unsymmetrical, with unequal bond distances; if so, its point symmetry is C_s but, because the potential barrier opposing interconversion of the conformers is easily overridden,[4] a classification in terms of a group isomorphous with C_{2v} is still admissable. A re-examination of the band structure was undertaken in order to settle some of these problems.

Since the bent states of ClO_2 are relatively asymmetric a full-matrix diagonalization procedure was employed to calculate the rotational term values. The ground state terms were computed from the microwave constants[3] and the excited state term values then fitted by a least-squares procedure using trial constants refined by iterations based on Taylor's theorem. It emerges that the bands are definitely type A, confirming the $^2A_2 \leftarrow {}^2B_1$ electronic assignment. Results for the $(v_1v_2v_3) = (100)$ level of the $^2A_2$ state are in the upper portion of the Table, the error estimates (in parentheses) being four times the statistical uncertainty; these constants reproduce the positions of about 750 lines with a weighted r.m.s. uncertainty of $< 0{\cdot}018$ cm.$^{-1}$. The earlier analysis[1a] gave $(B + C) =$ $0{\cdot}550$ cm.$^{-1}$, in agreement with present values.

Because rotational analysis cannot of itself show whether the two ClO bonds are equivalent, the relative intensities of vibronic bands were calculated on the assumption of a symmetrical C_{2v} structure. For this purpose the harmonic $(\omega_k, k = 1, 2, \text{ or } 3)$ and anharmonic $(x_{kk'})$ constants[5] were used together with a model potential function[6] to calculate the quadratic, cubic, and quartic constants of a vibrational potential function complete through quartic terms. From the cubic constants one may then by standard methods[7] determine the vibration–rotation interaction constants $\alpha_k^q (q = a, b, \text{ or } c)$ (central portion of Table), an hence the

Constants of the (100) *state of* $^2A_2$ $^{35}ClO_2$

A_{100}	1·05633(13) cm.$^{-1}$	ν_o	21722·087(20) cm.$^{-1}$	$10^3\tau_{aaaa}$	$-0·1529(1)$ cm.$^{-1}$ × 10^3
B_{100}	0·30950(6) cm.$^{-1}$	ϵ_{aa}	0·0762(48) cm.$^{-1}$	$10^3\tau_{bbbb}$	$-0·0077(3)$ cm.$^{-1}$ × 10^3
C_{100}	0·23815(6) cm.$^{-1}$	ϵ_{bb}	$-0·0184(56)$ cm.$^{-1}$	$10^3\tau_{aabb}$	0·0126(15) cm.$^{-1}$ × 10^3
Δ_{100}	0·3602(25)amu Å$_2$	ϵ_{cc}	$-0·0130(56)$ cm.$^{-1}$	$10^3\tau_{abab}$	$-0·0026(7)$ cm.$^{-1}$ × 10^3

Calculated vibration-rotation interaction constants (*cm.*$^{-1}$)

α_1^a	0·165	α_2^a	$-0·0035$	α_3^a	0·187
α_1^b	0·0014	α_2^b	$-0·0008$	α_3^b	0·0001
α_1^c	0·0018	α_2^c	0·0007	α_3^c	0·0018

Structure ($^2A_2$ *state*): r_e (ClO) = 1·619 Å, θ_e = 107° 0′

Intensities relative to 0–0 *band*

	Obs.	Calc.		Obs.	Calc.
$I(2\nu_1')$	21·5	21·9	$I(2\nu_1' + \nu_2')$	13·6	13·4
$I(2\nu_3')$	2·2	1·8	$I(\nu_1' + 2\nu_3')$	7·1	3·9
$I(\nu_2' + 2\nu_3')$	1·7	1·9	$I(\nu_1' + \nu_2' + 2\nu_3')$	5·9	8·4
$I(3\nu_1')$	38·4	41·6	$I(3\nu_1' + \nu_2')$	22·1	19·6

equilibrium constants A_e B_e, and C_e and the equilibrium geometry. This calculation was refined iteratively so that the potential constants were consistent with the final geometry. Finally, the *anharmonic* vibrational wavefunctions were used to compute the relative intensities of vibronic bands in the band system, the electronic transition moment being assumed constant. This calculation, summarized at the foot of the Table, satisfactorily reproduces the intensities of the $2\nu_3'$ group of transitions which, in effect, appear in consequence of intensity borrowed from the Franck-Condon favoured bands of the main $v_1\nu_1$ progression. Such borrowing is probably widespread in polyatomic spectra. The results emphasize the need for caution in drawing conclusions—here, of possible asymmetry in structure—from considerations based upon a purely harmonic model for vibrational motion.

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