

Evidence for a Double-Minimum Potential in an Excited State of ClO_2

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Evidence is presented which suggests the existence of a double-minimum potential in the anti-symmetrical vibrational co-ordinate of an excited electronic state of ClO_2 . A previously reported vibrational analysis of the 3600 Å absorption system of ClO_2 vapour proposes the excited state assignments $2\nu_3 = (1^+ - 0^+) = 1559 \text{ cm}^{-1}$ and $4\nu_3 - 2\nu_3 = (2^+ - 1^+) = 1640.5 \text{ cm}^{-1}$. In the present work, a two-parameter double-minimum potential function is adjusted to fit these levels of the Q_3' mode. The resulting function has a barrier of 2520 cm^{-1} , and at each potential minimum one bond is 0.065 Å shorter and one bond is 0.065 Å longer than the average bond of 1.620 Å . The isotope shift calculated for the interval $(1^+ - 0^+)$ agrees with the shift observed; however, the shift calculated for $(2^+ - 1^+)$ does not. A Franck-Condon calculation based on the vibrational wave functions of the double-minimum potential yields intensity ratios in approximate agreement with the experimental ratios. The isotope shifts and intensity ratios calculated assuming a harmonic potential in the Q_3' mode do not agree with experiment.

Recently¹ an intense progression of vibronic bands in the 3600 Å absorption system of ClO_2 has been given the assignment $(\nu_1', 0, 2) \leftarrow (0, 0, 0)$, and a less intense progression has been given the assignment $(\nu_1', 0, 4) \leftarrow (0, 0, 0)$. These progressions are labelled (c) and (d) respectively. The observed intensities of these progressions relative to the (a) progression $(\nu_1', 0, 0) \leftarrow (0, 0, 0)$ is much greater than is expected on the basis of a harmonic potential in the Q_3' co-ordinate, but a double-minimum potential explains the observed intensities qualitatively.¹ Furthermore, the isotope shift of $2\nu_3'$ as obtained from progressions (c) and (d) is about 25 % less than that expected for a harmonic potential. The purpose of this paper is to explain quantitatively the anomalous intensity and isotope shift in terms of a double-minimum potential function in the Q_3' co-ordinate.

Mulliken^{2a} and Walsh^{2b} have discussed the probability that not only ClO_2 but some excited states of SO_2 and NO_2 differ slightly from C_{2v} symmetry. Mulliken suggests that the $2b_1$ molecular orbital is responsible for these slightly unsymmetrical states.

1. THE POTENTIAL FUNCTION³

It is assumed that the potential function in the Q_3' co-ordinate has the form

$$V(Q) = \frac{\lambda}{2} Q^2 + A \exp(-a^2 Q^2) \quad (1.1)$$

where Q is a co-ordinate satisfying the condition $2T = \dot{Q}^2$. The minima of this three-parameter potential function are located at $\pm Q_m$ given by

$$Q_m^2 = \frac{1}{a^2} \ln \left(\frac{2a^2 A}{\lambda} \right). \quad (1.2)$$

A parameter ρ is introduced by writing

$$a^2 = \frac{\lambda}{2A} e^\rho. \quad (1.3)$$

A frequency ν_0 is defined by $\lambda = (2\pi c\nu_0)^2$, and a dimensionless parameter B is introduced such that the barrier height is $Bhcn\nu_0$. From eqn. (1.1), (1.2) and (1.3),

$$Bhcn\nu_0 = V(0) - V(Q_m) = A \frac{(e^\rho - \rho - 1)}{e^\rho}. \quad (1.4)$$

The barrier height in cm^{-1} is

$$b = B\nu_0, \quad (1.5)$$

and the minima are located at $\pm Q_m$ where

$$Q_m^2 = \frac{2\rho}{e^\rho - \rho - 1} \frac{h}{4\pi^2 c} \frac{B}{\nu_0}. \quad (1.6)$$

We may replace the parameters λ , A and a^2 by the parameters ν_0 , B and ρ . In the present application ρ is set equal to 1.5. For this value of ρ the minima are parabolic. The energy levels and wave functions of the potential function (1.1) have been determined³ for 60 different barrier heights ranging from $B = 0.0$ to $B = 6.0$ in intervals of 0.1. Machine calculations based on the secular equation of the linear variation method lead to wave functions of the form

$$\Psi(Q) = \sum_{k=0}^{23} a_k \phi_k(Q),$$

where the ϕ_k are harmonic oscillator wave functions corresponding to the frequency ν_0 . Numerical values of the dimensionless energy levels $G(0^+)/\nu_0$, $G(0^-)/\nu_0$, . . . , $G(4^+)/\nu_0$, $G(4^-)/\nu_0$ are given for each value of the dimensionless barrier height B . Here G is the energy above the potential minima in cm^{-1} . The coefficients a_k are tabulated against B for each of ten levels 0^+ , . . . , 4^- . This requires ten tables of coefficients. The energy level tables are available³ but the tables of a_k are too extensive to publish.

2. BARRIER HEIGHT AND BOND LENGTHS

The data used in this section are taken from Coon and Ortiz,¹

$$\begin{aligned} 2\nu'_3 &= G(1^+) - G(0^+) = 1559 \text{ cm}^{-1}, \\ 4\nu'_3 - 2\nu'_3 &= G(2^+) - G(1^+) = 1640.5 \text{ cm}^{-1}. \end{aligned} \quad (2.1)$$

Examination of the table giving the levels G/ν_0 for a barrier B described in § 1 reveals that only for $B = 2.050$ does the ratio

$$\frac{G(2^+)/\nu_0 - G(1^+)/\nu_0}{G(1^+)/\nu_0 - G(0^+)/\nu_0} \quad (2.2)$$

agree with the experimental value, 1640.5/1559. This establishes the value of B . The value of ν_0 is determined from the identity

$$\nu_0 = \frac{G(1^+) - G(0^+)}{G(1^+)/\nu_0 - G(0^+)/\nu_0} \text{ cm}^{-1}. \quad (2.3)$$

The result is $\nu_0 = 1229 \text{ cm}^{-1}$. Multiplication of tabulated values of G/ν_0 by this value of ν_0 yields the levels

$$\begin{aligned} G(0^+) &= 945 \text{ cm}^{-1}, & G(1^+) &= 2504 \text{ cm}^{-1}, & G(2^+) &= 4143 \text{ cm}^{-1}, \\ G(0^-) &= 1014 \text{ cm}^{-1}, & G(1^-) &= 3034 \text{ cm}^{-1}, & G(2^-) &= 5128 \text{ cm}^{-1}. \end{aligned} \quad (2.4)$$

Accordingly the $(0^+ - 0^-)$ separation is 69 cm^{-1} . It also follows that the barrier height is

$$b = B\nu_0 = 2520 \text{ cm}^{-1}. \quad (2.5)$$

In order to calculate the configuration of the molecule at the potential minima, consider fig. 1. Let r_0 be the bond length at the symmetrical configuration and let r be the change of bond length corresponding to an antisymmetrical displacement Q . For small displacements the kinetic energy T is given by $2T = \mu \dot{r}^2$, where

$$\mu = \frac{2mM}{2m \sin^2 \theta + M}. \quad (2.6)$$

For the excited state 2θ is $107^\circ 24'.$ Using $2T = \dot{Q}^2$ and setting $Q = Q_m$,

$$Q_m^2 = \mu r_m^2. \quad (2.7)$$

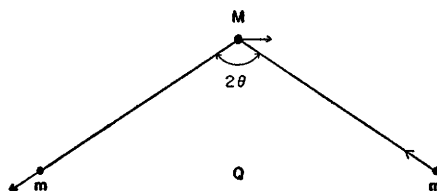


FIG. 1.

Since $\rho = 1.5$, eqn. (1.6) gives $Q_m^2 = 0.1414 \times 10^{-40} \text{ g cm}^2$. Consequently by eqn. (2.7), $r_m = 0.0651 \text{ \AA}$. Since the average bond length⁴ for the excited state is 1.620 \AA , the bond lengths at the potential minima are

$$\text{bond lengths} = 1.620 \text{ \AA} \pm 0.065 \text{ \AA}. \quad (2.8)$$

The displacement of the potential minima from the symmetrical configuration is considered to be within the range of small displacements.

3. THE ISOTOPE SHIFT

The values of B and v_0 determined in § 2 along with the assumed value of ρ are sufficient to determine a specific double-minimum potential function having the form of eqn. (1.1). The isotope shift calculated on the basis of this potential function and that calculated on the basis of a harmonic potential function may be compared with the isotope shift spectroscopically observed. Table 1 gives the isotope shift $\Delta\sigma = \sigma(\text{Cl}^{35}\text{O}_2) - \sigma(\text{Cl}^{37}\text{O}_2)$ observed for the three band progressions,

$$\begin{aligned} a(v) & (v'_1, 0, 0) \rightarrow (0, 0, 0), \\ c(v) & (v'_1, 0, 2) \rightarrow (0, 0, 0), \\ d(v) & (v'_1, 0, 4) \rightarrow (0, 0, 0). \end{aligned} \quad (3.1)$$

TABLE 1.—PEAK EXTINCTION COEFFICIENT ϵ IN (l./mole cm) AND THE ISOTOPE SHIFT $\Delta\sigma = \sigma(\text{Cl}^{35}\text{O}_2) - \sigma(\text{Cl}^{37}\text{O}_2)$ FOR THREE BAND PROGRESSIONS IN THE SPECTRUM OF CHLORINE DIOXIDE

v'_1	$\sigma^{(v)}_{\text{cm}^{-1}}$	$\Delta\sigma_{\text{cm}^{-1}}$	ϵ	$\sigma^{(v)}_{\text{cm}^{-1}}$	$\Delta\sigma_{\text{cm}^{-1}}$	ϵ	$\sigma^{(v)}_{\text{cm}^{-1}}$	$\Delta\sigma_{\text{cm}^{-1}}$	ϵ
2	22425.5		89	23960.6	20.9		25571.5	32.0	139
3	23119.2		233	24636.7	24.8	180	26232.2	35.9	168
4	23806.9		384	25307.6	31.6	295	26888.8	40.4	147
5	24488.2	24.1	491	25973.8	35.4	409	27540.7	44.9	106
6	25164.3	29.6	638	26635.5	41.2	495	28187.9	50.1	37
7	25835.7	34.5	900	27292.0	45.9	470			
8	26502.4	41.0	1076						
9	27164.1	44.9	1108						

These isotope shifts are obtained by averaging the shift measured by Urey and Johnston⁵ with that measured by Ku.⁶ For each progression $\Delta\sigma$ may be plotted against v'_i and a best straight line may be drawn through the points. The interval between the straight lines for progressions $a(v)$ and $c(v)$ gives an approximate value for the isotope shift of $2v'_3$,

$$(\text{experimental}) \Delta(2v'_3) = 11.6 \text{ cm}^{-1} \quad (3.2)$$

To calculate the isotope shift for a harmonic potential we may use

$$(2v'_3)^2/(2v'_3)_i^2 = \mu_i/\mu. \quad (3.3)$$

The subscript i refers to isotopic quantities. The reduced mass μ is given by eqn. (2.6) and μ_i contains the mass of Cl^{37} instead of Cl^{35} . Substituting $2v'_3 = 1559 \text{ cm}^{-1}$ into eqn. (3.3) leads to

$$(\text{harmonic}) \Delta(2v'_3) = 15.8 \text{ cm}^{-1}, \quad (3.4)$$

which deviates considerably from the observed value.

To calculate the isotope shift for the double-minimum potential it is noted that the barrier height Bv_0 and the position of the potential minima $\pm r_m$ do not change with isotopic substitution. Consequently eqn. (1.6) and (2.7) yield

$$(\mu_i/\mu)^{\frac{1}{2}} = v_0/v'_0 = B_i/B. \quad (3.5)$$

Using these relations the parameters B_i and v'_0 for the isotopic molecule may be determined and hence the energy levels may be obtained from the table of (G/v_0) . It follows that $[G(1^+) - G(0^+)]_i = 1547.6 \text{ cm}^{-1}$ which compared to 1559 cm^{-1} corresponds to

$$(\text{double min.}) \Delta(2v_3) = 11.4 \text{ cm}^{-1}, \quad (3.6)$$

in agreement with the observed isotope shift. However, the success of the double-minimum potential function in explaining the isotopic shift of the second observed interval is less marked:

$$\begin{aligned} (\text{expt.}) \Delta(4v'_3 - 2v'_3) &= 10.4 \text{ cm}^{-1}, \\ (\text{double min.}) \Delta[G(2^+) - G(1^+)] &= 26.0 \text{ cm}^{-1}. \end{aligned} \quad (3.7)$$

4. INTENSITY CALCULATION

Another method of checking the validity of the double-minimum potential function of §2 is to test the ability of the wave functions of this potential to produce observed intensity ratios. Let $\varepsilon/\sigma(1^+, 0)$ designate the peak extinction coefficient divided by the frequency for a band of the progression $c(v)$, and let $\varepsilon/\sigma(0^+, 0)$ designate the same for the corresponding band of progression $a(v)$. According to the Franck-Condon principle,

$$\frac{\varepsilon/\sigma(1^+, 0)}{\varepsilon/\sigma(0^+, 0)} = \left[\frac{R(1^+, 0)}{R(0^+, 0)} \right]^2, \quad (4.1)$$

where

$$R(v, 0) = \int \Psi'(v) \Psi''(0) dQ_3. \quad (4.2)$$

In this overlap integral, $Q'_3 = Q_3$.

The average value of the intensity ratio as determined from the data of table 1 is

$$\frac{\varepsilon/\sigma(1^+, 0)}{\varepsilon/\sigma(0^+, 0)} = 0.74. \quad (4.3)$$

The data for bands $\nu'_1 = 3, 4, 5$ and 6 are averaged. This experimental intensity ratio is to be compared with the value calculated from eqn. (4.1).

For the parameter $B = 2.050$ the tables described in § 1 give the coefficients a_k of the wave functions,

$$\begin{aligned}\Psi'(1^+) &= 0.706 \phi'_0 - 0.408 \phi'_2 - 0.570 \phi'_4 + \dots, \\ \Psi'(0^+) &= 0.623 \phi'_0 + 0.744 \phi'_2 + 0.241 \phi'_4 + \dots\end{aligned}\quad (4.4)$$

The ϕ'_k are harmonic oscillator wave functions corresponding to the frequency given by the double-minimum parameter $\nu_0 = 1229 \text{ cm}^{-1}$. The ground-state vibrational wave function is

$$\Psi''(0) = \phi''_0, \quad (4.5)$$

where ϕ''_0 is the harmonic oscillator wave function for $\nu'' = 0$ corresponding to the frequency $\nu''_3 = 1110.5 \text{ cm}^{-1}$. The ratio $R(1^+, 0)/R(0^+, 0)$ is easily evaluated by use of the formulae,

$$\begin{aligned}\frac{r(2, 0)}{r(0, 0)} &= \left(\frac{1}{2}\right)^{\frac{1}{2}} \left[\frac{\nu'_0 - \nu''}{\nu'_0 + \nu''} \right], & \frac{r(4, 0)}{r(0, 0)} &= \left(\frac{3}{8}\right)^{\frac{1}{2}} \left[\frac{\nu'_0 - \nu''}{\nu'_0 + \nu''} \right]^2, \\ \frac{r(6, 0)}{r(0, 0)} &= \left(\frac{5}{16}\right)^{\frac{1}{2}} \left[\frac{\nu'_0 - \nu''}{\nu'_0 + \nu''} \right]^3, & \frac{r(8, 0)}{r(0, 0)} &= \left(\frac{35}{128}\right)^{\frac{1}{2}} \left[\frac{\nu'_0 - \nu''}{\nu'_0 + \nu''} \right]^4,\end{aligned}\quad (4.6)$$

where

$$r(\nu, 0) = \int \phi'_\nu \phi''_0 dQ_3.$$

The result is

$$[R(1^+, 0)/R(0^+, 0)]^2 = 1.13, \quad (4.7)$$

which is in fair agreement with eqn. (4.3). A similar calculation yields

$$[R(2^+, 0)/R(0^+, 0)]^2 = 0.22, \quad (4.8)$$

which compares in order of magnitude to the intensity ratio of progression $d(\nu)$ to progression $a(\nu)$. These calculated intensities are a great improvement over those based on a harmonic potential in the Q'_3 mode. Using $\nu'_3 = 1559/2$ and $\nu''_3 = 1110.5 \text{ cm}^{-1}$ the harmonic potential leads to 0.015 and 0.00036 in the place of values given in eqn. (4.7) and (4.8) respectively.

DISCUSSION

The double-minimum potential function specified by ($\rho = 1.5$, $B = 2.050$, and $\nu_0 = 1229 \text{ cm}^{-1}$), having a barrier of 2520 cm^{-1} , explains the two observed vibrational intervals $1559 \text{ cm}^{-1} = 1^+ - 0^+$ and $1640.5 \text{ cm}^{-1} = 2^+ - 1^+$. However, this potential explains the small isotope shift of only the first interval. Calculations not reported above show that a potential function with a barrier of about 3500 cm^{-1} is able to explain the small isotope shift observed for both intervals. For such a high barrier the second vibrational interval is reduced to 75 % of the value observed. The fact that both of the intervals and the isotope shifts of both intervals can not be explained by a single double-minimum potential function constitutes a serious difficulty.

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