Theoretical elucidation of the infrared activity of "symmetry-forbidden" overtone bands of CO_2 induced by asymmetric isotopic substitution

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Abstract : Recently, the intensities of the $2v_3$ band in $^{12}C^{16}O^{17}O$ and $^{12}C^{16}O^{17}O$ isotopomers of CO_2 were measured by high resolution Fourier transform spectrometry [1,2]. One may recall that in a linear and symmetric triatomic molecule XYX, the states corresponding to the vibrations v_1, $2v_1$, $2v_3$ etc. are symmetry-forbidden for i.r. absorption and that their weak i.r. activity in the asymmetric isotopomer results from the mass disparity in the two isotopic atoms. The problem of quantifying the infrared activity of these forbidden bands is tractable under the Born-Oppenheimer approximation. In the present paper a theoretical framework for approaching the intensity problem is discussed in the context of the overtone band $2v_3$. This analysis is essentially a natural extension of our previous work [3] dealing with the mass asymmetry-induced infrared (Raman) activity of the fundamental v_1 (v_3). In particular, the present theory enables us to calculate, *ab initio*, the transition moment ratio $| \mu(2v_3, {}^{12}C^{16}O^{17}O)/\mu(2v_3, {}^{12}C^{16}O^{18}O) |$. The theoretical ratio compares well with the experimentally deduced value.

Keywords : Overtone bands of CO_2, infrared activity, transition dipole moments.

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Introduction

The present work has been motivated by the recent measurement [1,2] of the strength of the $2v_3$ band in the asymmetric isotopomers $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$ of the CO_2 molecule. One may recall that in a linear, symmetric triatomic molecule of the type X-Y-X, the stretching vibrations v_1, $2v_1$, $3v_1$ etc. and $2v_3$, $v_1 + 2v_3$ etc. carry the inversion symmetry label g, much like the ground state and therefore the corresponding states are inaccessible for electric dipole absorption. However, when one of the extreme atoms is replaced by its isotope, the forbidden bands become weakly allowed. It is intuitively clear that the electrical symmetry of the molecule is preserved despite isotopic substitution and that the small intensities that do arise for the forbidden bands like $2v_3$ must some how be related to the mass asymmetry in the X-Y-X' type of molecules. The present work is aimed at finding a rationale for understanding the

relative transition dipole moments for the $2v_3$ band observed in $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$, recently [1,2].

2. Theoretical details

2.1. Normal mode analysis of the stretching vibrations :

The first step in the theoretical approach to the intensity of the forbidden $2v_3$ band is the normal mode analysis of the stretching vibrations [4–6]. To this end let us consider the linear triatomic molecule X-Y-X'. Let us introduce the displacement coordinates $\zeta_1 = R_1 - R$ and $\zeta_2 = R_2 - R$ where R is the equilibrium bond distance.

1		2	1		2
●——————●——————●			●——————●——————————●		
X	Y	X'	X	Y	X'
|← R →|← R →|			|←—R_1—→|←—— R_2 ——→|		
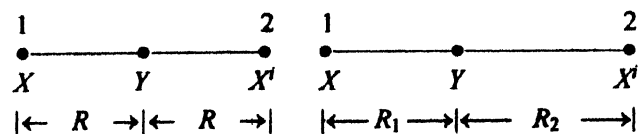
With the notation as in the figure above, the kinetic energy (K.E.) of the stretching motion is

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$$2 \times K.E. = \begin{pmatrix} \dot{\zeta}_1 & \dot{\zeta}_2 \end{pmatrix} \begin{pmatrix} M_{11} & M_{12} \\ M_{12} & M_{22} \end{pmatrix} \begin{pmatrix} \dot{\zeta}_1 \\ \dot{\zeta}_2 \end{pmatrix} \tag{1}$$

where $M_{11} = \dfrac{M_X(M_Y + M_{X'})}{M_X + M_Y + M_{X'}}$;

$$M_{12} = M_{21} = \dfrac{M_X M_{X'}}{M_X + M_Y + M_{X'}};$$

$$M_{22} = \dfrac{M_{X'}(M_Y + M_{X'})}{M_X + M_Y + M_{X'}} \tag{1a}$$

In the harmonic approximation, the potential energy $V(\zeta_1, \zeta_2)$ is given by

$$2 \times V(\zeta_1, \zeta_2) = \begin{pmatrix} \zeta_1 & \zeta_2 \end{pmatrix} \begin{pmatrix} k & k_{12} \\ k_{12} & k \end{pmatrix} \begin{pmatrix} \zeta_1 \\ \zeta_2 \end{pmatrix} \tag{2}$$

Here k and k_{12} are the force constants for the problem. Note that since the isotopic atoms X and X' are electrically equivalent, we require $V(\zeta_1, \zeta_2) = V(\zeta_2, \zeta_1)$ so that the diagonal term in eq. (2) becomes equal. Also, within the Born-Oppenheimer approximation, k and k_{12} can be treated as isotopic invariants. To make further progress we need values for k and k_{12} for which we make use of the known frequencies $\omega_{e1} = 1339.1$ cm^{-1}, $\omega_{e3} = 2374.1$ cm^{-1} of the v_1 and v_3 modes in the symmetric $^{16}O^{12}C^{16}O$ molecule. It can be shown that

$$2k = (2\pi c)^2 M_X \left(\dfrac{M_Y}{2M_X + M_Y} \omega_{e3}^2 + \omega_{e1}^2 \right)$$

$$2k_{12} = (2\pi c)^2 M_X \left(\dfrac{M_Y}{2M_X + M_Y} \omega_{e3}^2 - \omega_{e1}^2 \right)$$

Taking,

$M_X(^{16}O) = 15.994915$ amu; $M_Y(^{12}C) = 12.000000$ amu; 1 amu $= 1.6605402 \times 10^{-24}$ g

We finally obtain,

$k = 1.569430186 \times 10^6$ dynes/cm ;

$k_{12} = 0.1204600968 \times 10^6$ dynes/cm.

Using these force constants it is easy to derive the stretching eigenfrequencies of the isotopomers from the relation

$$\begin{vmatrix} k - \lambda M_{11} & k_{12} - \lambda M_{12} \\ k_{12} - \lambda M_{12} & k - \lambda M_{22} \end{vmatrix} = 0$$

[with $\lambda = (2\pi c \omega_e)^2$ and ω_e is in cm^{-1}] $\tag{3}$

Eq. (3) in combination with eq. (1a) yields

$\lambda_1 = 0.6172348388 \times 10^{29}$: $\omega_{e1} = 1318.9388$ cm^{-1} ;

$\lambda_3 = 1.983965611 \times 10^{29}$: $\omega_{e3} = 2364.648$ cm^{-1},

for $^{16}O^{12}C^{17}O$.

Similarly,

$\lambda_1 = 0.600037828 \times 10^{29}$: $\omega_{e1} = 1300.4353$ cm^{-1};

$\lambda_3 = 1.970275172 \times 10^{29}$: $\omega_{e3} = 2356.4752$ cm^{-1},

for $^{16}O^{12}C^{18}O$.

The next step is to make the normal coordinate transformation for which we use the relation

$$\begin{array}{cc} \lambda_1 & \lambda_2 \end{array}$$
$$\begin{pmatrix} \zeta_1 \\ \zeta_2 \end{pmatrix} = \begin{pmatrix} A_{11} & A_{13} \\ A_{21} & A_{23} \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_3 \end{pmatrix}$$

Here the normal coordinate Q_1, is associated with v_1 and with v_3. The column vectors in the A matrix are normalized to ensure that the following relations hold

$$\tilde{A}MA = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \tilde{A}KA = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_3 \end{pmatrix}$$

We find for

$^{16}O^{12}C^{17}O$, $A = \begin{pmatrix} A_{11} = 0.133269705 \times 10^{12} \\ A_{21} = 0.136986446 \times 10^{12} \end{pmatrix}$

$\begin{pmatrix} A_{13} = 0.26471064 \times 10^{12} \\ A_{23} = -0.258549043 \times 10^{12} \end{pmatrix}$

$^{16}O^{12}C^{18}O$, $A = \begin{pmatrix} A_{11} = 0.129759552 \times 10^{12} \\ A_{21} = 0.136650811 \times 10^{12} \end{pmatrix}$

$\begin{pmatrix} A_{13} = 0.266453075 \times 10^{12} \\ A_{23} = -0.254889962 \times 10^{12} \end{pmatrix}$

For the symmetric species like $^{16}O^{12}C^{16}O$, we would have had $A_{11} = A_{12}$ and $A_{13} = -A_{23}$. We shall presently see the small departure from the equality that holds for the symmetric species is what primarily causes the $2v_3$ band in the asymmetric species to pick up intensities. (Note that the numerical factors appearing in all the relations above, have been deliberately specified to more decimal places than warranted, so as to avoid rounding off errors).

2.2. *The electric dipole moment for stretching motion*

Since the intensities of the band are connected with the change of dipole moment of the molecule with vibration, we should now consider this aspect. The mere isotopic replacement of one of the atoms can not destroy the inherent charge symmetry of the molecule. Therefore, we expect the stretching dipole moment function $\mu(\zeta_1, \zeta_2)$ to display the following properties.

$$\mu(R_1, R_2) = \mu(\zeta_1, \zeta_2)$$

$$\mu(\zeta_2, \zeta_1) = -\mu(\zeta_1, \zeta_2)$$

The requirement in eq. (8) can be illustrated geometrically as follows
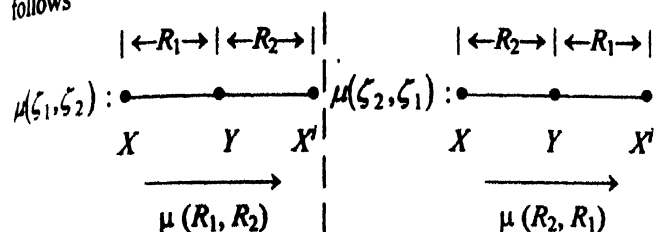
The Taylor series expansion of $\mu(\zeta_1,\zeta_2)$ in the displacement coordinates ζ_1,ζ_2 should be consistent with the eq. (8) above. Accordingly we have

$$\mu(\zeta_1,\zeta_2) = a_1(\zeta_1 - \zeta_2) + a_{20}(\zeta_1^2 - \zeta_2^2) + \qquad (9)$$

From eq. (4) we obtain

$$\zeta_1 = A_{11} Q_1 + A_{13} Q_3 \text{ and } \zeta_2 = A_{21} Q_1 + A_{23} Q_3.$$

Substitution of these values of ζ_1 and ζ_2 in eq. (9) gives

$$\mu(Q_1, Q_3) = a_1 [(A_{11} - A_{21}) Q_1 + (A_{13} - A_{23}) Q_3]$$
$$+ a_{20} \{(A_{11} + A_{21})(A_{11} - A_{21})Q_1^2$$
$$+ (A_{13} - A_{23})(A_{13} + A_{23})Q_1^2$$
$$+ Q_1Q_3 [(A_{11} + A_{21})(A_{13} - A_{23})$$
$$+ (A_{13} + A_{23})(A_{11} - A_{21})]\}. \qquad (10)$$

In this paper we are primarily concerned with the $2\nu_3$ band which derives intensity from the coefficient of Q_1^2 i.e. $a_{20}[(A_{13} - A_{23})(A_{13} + A_{23})]$. We realize that in the symmetric species $A_{13} = -A_{23}$ and therefore, this coefficient vanishes altogether and thus it is that the $2\nu_3$ band becomes forbidden. On the other hand, in the asymmetrically substituted isotopomer we can no longer require $A_{13} = -A_{23}$ [see eqns. (5) and (6)]. Therefore in the asymmetric isotopomer, the $2\nu_3$ band derives small intensities from the mass asymmetry.

3. Comparison of transition moment of the $2\nu_3$ band in $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$

We know that the intensity of a transition between the initial state $| i >$ and final state $| f >$ is proportional to $| <f| \mu | i > |^2$, where $<f| \mu | i >$ is the transition dipole moment. In eq. (10), we need the values of the coefficients a_{10}, a_{20}, etc. to be able to predict the absolute intensities of the vibrational transitions. In particular, to know the intensity $I(2\nu_3)$ we should have knowledge of the coefficient a_{20}. In the absence

of this we can only compare the ratios of the intensities of the $2\nu_3$ band in the two isotopomers $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$. Since this comparison eliminates a_{20} while the other coefficients A_{11}, A_{13} etc. are completely known through the dynamics of the problem we can make theoretical predictions of the intensity ratio or, equivalently, the ratio of the transition dipole moments (R_{vib}). A careful calculation leads to the following theoretical ratio

$$\frac{R_{vib}(2\nu_3; {}^{16}O^{12}C^{17}O)}{R_{vib}(2\nu_3; {}^{16}O^{12}C^{18}O)} =$$

$$\frac{[(A_{13} - A_{23})(A_{13} + A_{23})\omega_{e'}^{-1}]^{16}O^{12}C^{17}O}{[(A_{13} - A_{23})(A_{13} + A_{23})\omega_{e'}^{-1}]^{16}O^{12}C^{18}O} = 0.533$$

obtained after inserting the values of A_{13} and A_{23} from eqns. (5) and (6).

The experimental [1,2] value is 0.561

which is strikingly close to the theoretical ratio.

4. Conclusion

It is very gratifying that with only the observed frequencies of the ν_1, ν_3 modes in $^{12}C^{16}O_2$ and the isotopic masses we have been able to predict the ratio of the transition moment of the generically forbidden $2\nu_3$ band in the two asymmetrical species which agrees with the experimental ratio to within 6%. The small discrepancy may be ascribed to our restrictive treatment of the problem within the harmonic approximation. A more full blown methodology whereby other forbidden bands can be treated is under development.

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