

CHAPTER - 10VIBRATIONAL SPECTRA OF KHCO_3 AND ITS NORMAL COORDINATE ANALYSISABSTRACT

This chapter deals with the laser Raman Spectrum and infrared spectrum of potassium bicarbonate from 50 to 4000 cm^{-1} and 625 to 4000 cm^{-1} respectively. The spectrum has been analysed assuming C_{2v} symmetry. The fundamental frequencies of the bicarbonate ion are

$$\begin{aligned}\nu(A_1) &= 1019, 1400 \text{ and } 670 \text{ cm}^{-1} \\ \nu(B_1) &= 1603 \text{ and } 712 \text{ cm}^{-1} \\ \nu(B_2) &= 840 \text{ cm}^{-1}\end{aligned}$$

Further, the validity of the assignment has been confirmed through a normal coordinate analysis. Molecular constants such as force constants, compliance constants, mean amplitudes, Coriolis coupling constants and centrifugal distortion constants have been reported.

INTRODUCTION

Potassium bicarbonate has several industrial applications and hence the structural and spectroscopic data are of great value. Hence our attention has been turned to the vibrational frequencies and analysis of the spectrum of bicarbonate ion. In this chapter the laser Raman Spectrum and infrared spectrum of bicarbonate ion are reported. The vibrational frequencies of this molecule have been assigned on the basis of C_{2v} symmetry. The six fundamentals observed in the spectrum are assigned in the following manner; three belonging to A_1 species; two belonging to B_1 species and one belonging to B_2 species.

EXPERIMENTAL

The infrared spectrum of potassium bicarbonate has been recorded in Perkin Elmer IR 257 Double beam grating spectrophotometer in the region 625 to 4000 cm^{-1} . The laser Raman Spectrum has also been recorded on the Cary Model 82 Spectrophotometer equipped with Argon laser of power 4 Watts in the region 50-4000 cm^{-1} . The observed frequencies are listed in Table 10.1. The frequencies for all sharp bands are expected to be accurate to $\pm 1 \text{ cm}^{-1}$.

FREQUENCY ASSIGNMENT

Six fundamental absorption bands have been observed at 670, 712, 840, 1019, 1400 and 1603 cm^{-1} . The appearance of two high frequency infrared bands at 1400 and 1603 cm^{-1} suggest the C_{2v} symmetry for this molecule. These correspond to C-O symmetric and C-O asymmetric stretchings. This assignment is consistent with Bernitt (1). Also the assignments of high frequency fundamentals corresponding to the stretching modes is based on their relative intensities. The present assignment agrees quite well with HCO_3^- ion for all remaining bands.

THEORETICAL CONSIDERATIONS

The bicarbonate ion is of XYZ_2 planar type and belongs to C_{2v} point group. The nomenclature of the different parameters and the structure are given in Fig. 1. The normal vibrations of the XYZ_2 type molecules are represented in Fig. 2. These have six non-degenerate normal modes of vibrations which are classified as

$$\Gamma = 3A_1 + 2B_1 + B_2$$

The symmetry coordinates used are those used by Oka and Morino (2) and Ford and Orville - Thomas (3) are given below:

$$S_1 (A_1) = \Delta_D$$

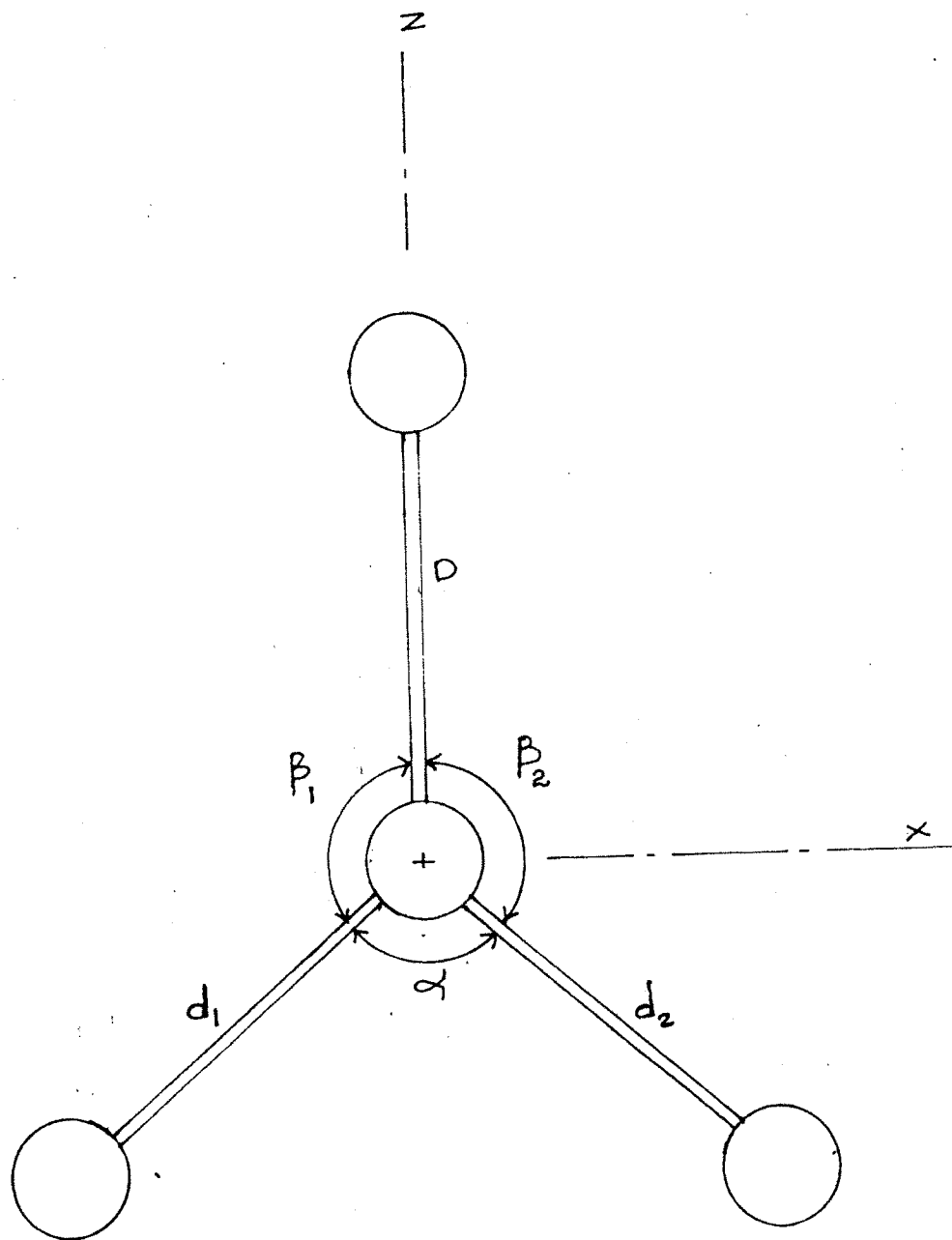


FIG 1 STRUCTURE AND NOMENCLATURE OF XYZ₂
 PLANAR TYPE BELONGING TO C_{2v} POINT GROUP

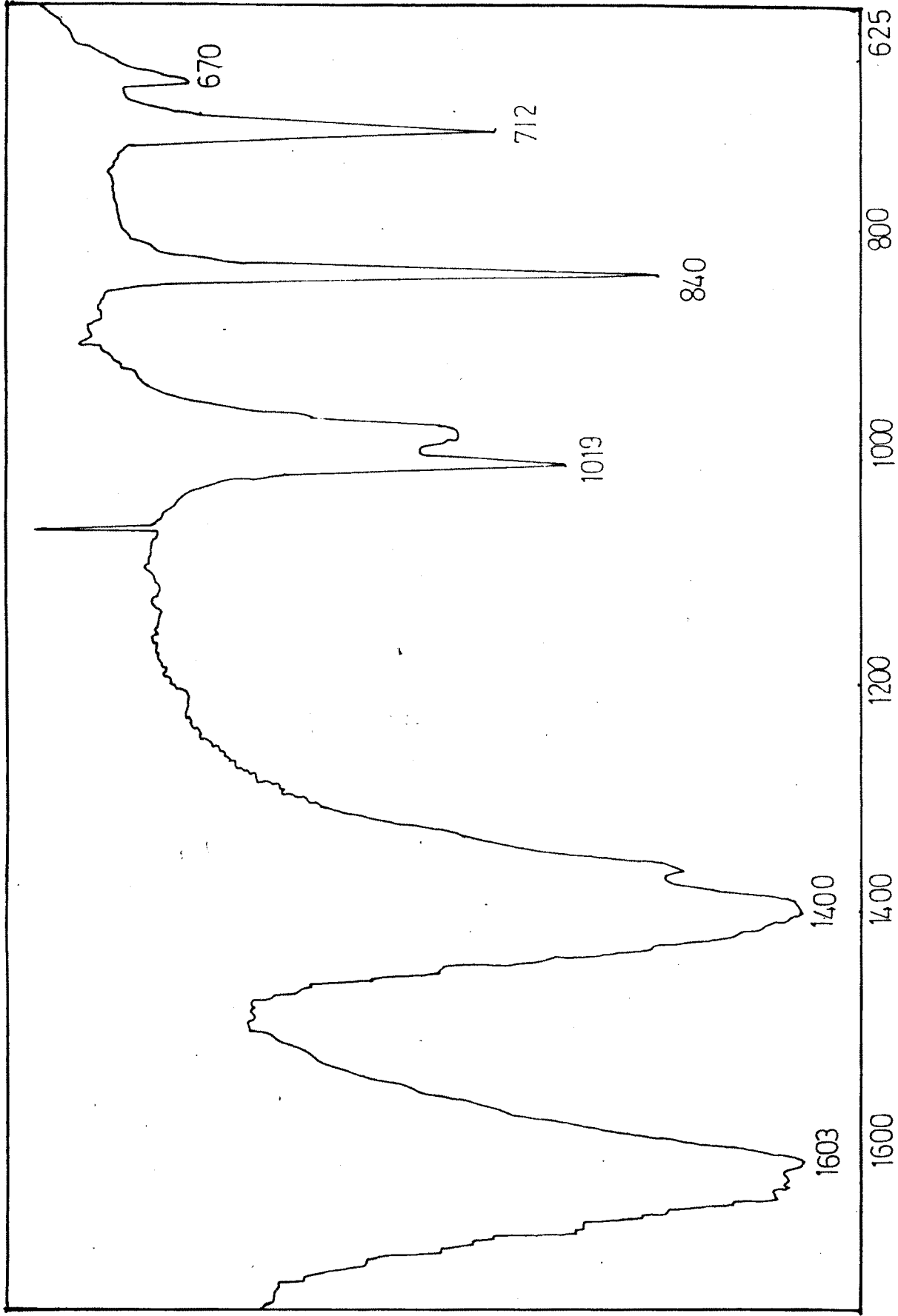


FIG 2 INFRARED SPECTRA OF POTASSIUM BICARBONATE.

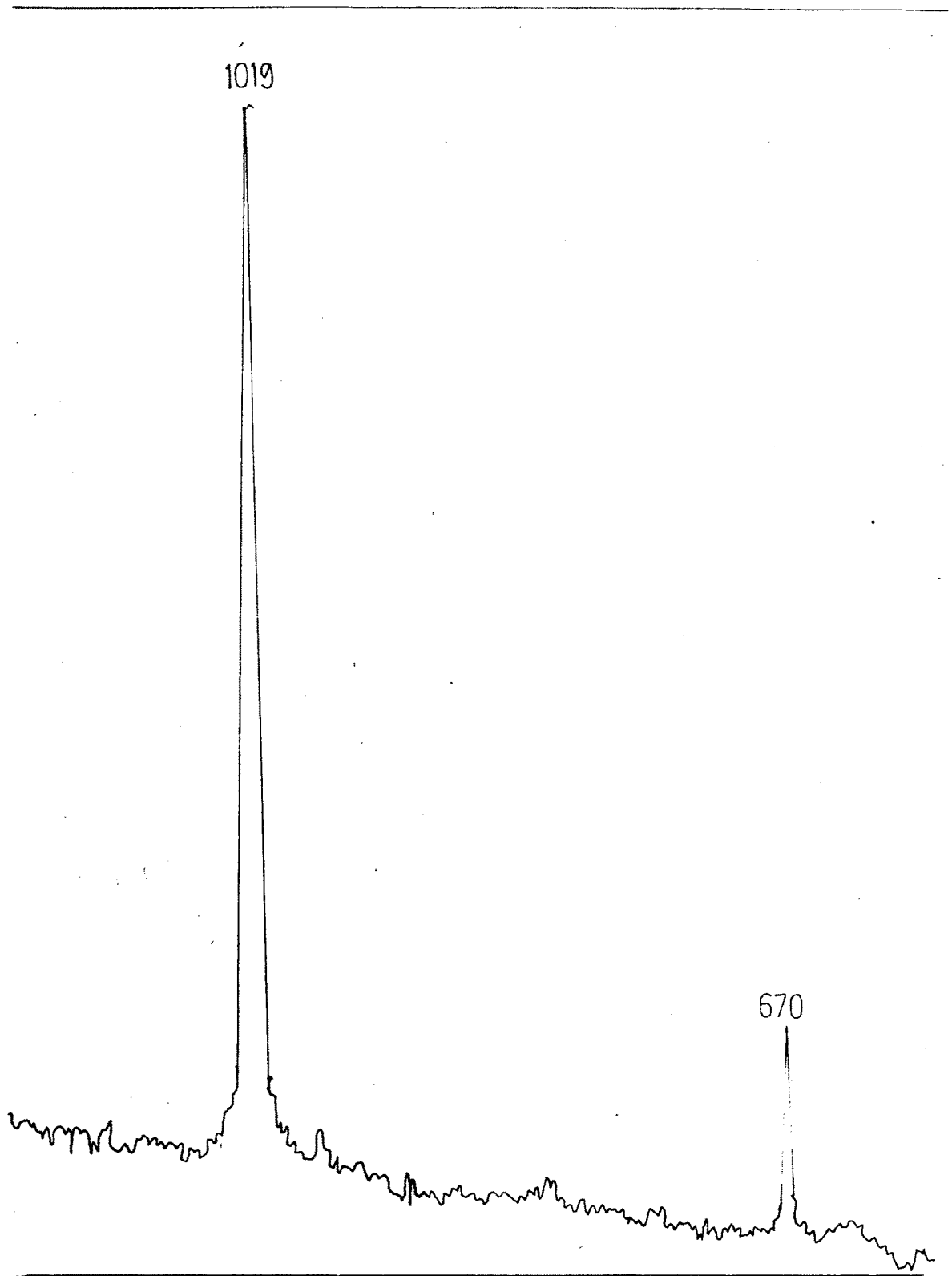


FIG 3 LASER RAMAN SPECTRA OF POTASSIUM BICARBONATE

$$\begin{aligned}
 S_2 (A_1) &= \frac{1}{\sqrt{2}} (\Delta d_1 + \Delta d_2) \\
 S_3 (A_1) &= \frac{1}{\sqrt{6}} d (2 \Delta \alpha - \Delta \beta_1 - \Delta \beta_2) \\
 S_r (A_1) &= \frac{1}{\sqrt{3}} d (\Delta \alpha + \Delta \beta_1 + \Delta \beta_2) \\
 S_4 (B_1) &= \frac{1}{\sqrt{2}} (\Delta d_1 - \Delta d_2) \\
 S_5 (B_1) &= \frac{1}{\sqrt{2}} d (\Delta \beta_1 - \Delta \beta_2) \\
 S_6 (B_2) &= d \Delta \delta
 \end{aligned}$$

The internal coordinates used in the symmetry coordinates are defined as follows

- ΔD is the change in X - Y bond distance
- $\Delta d'_1, \Delta d'_2$ are the changes in X - Z bond distance
- $\Delta \alpha$ is the change in $Z \hat{X} Z$ bond angle
- $\Delta \beta'_1, \Delta \beta'_2$ are the changes in $Y \hat{X} Z$ bond angle
- $\Delta \delta$ is the change in the angle relating to the out of plane bending mode.

The structure, bond distances and angles are schematically represented in Fig 10.1. The F matrix, G matrix, & K matrix are given below. (OH) is treated as point mass

POTENTIAL ENERGY EXPRESSIONS

F - Matrix

F matrix elements for different species have been evaluated using the expression

$$F = UfU'$$

Potential Energy Expression

The most general quadratic potential energy function in terms of the internal coordinates is given below:

$$\begin{aligned}
 2V = & f_D [(\Delta D)^2] \\
 & + f_d [(\Delta d_1)^2 + (\Delta d_2)^2] \\
 & + 2f_{Dd} [(\Delta D) (\Delta d_1 + \Delta d_2)] \\
 & + 2f_{dd} [(\Delta d_1) (\Delta d_2)] \\
 & + d^2 f_\alpha [(\Delta \alpha)^2] \\
 & + Ddf_\beta [(\Delta \beta_1)^2 + (\Delta \beta_2)^2] \\
 & + 2d(Dd)^{\frac{1}{2}} f_{\alpha\beta} [(\Delta \alpha)^2 (\Delta \beta_1 + \Delta \beta_2)] \\
 & + 2Ddf_{\beta\beta} [(\Delta \beta_1) (\Delta \beta_2)] \\
 & + 2(Dd)^{\frac{1}{2}} f_{D\beta} [(\Delta D + (\Delta \beta_1 + \Delta \beta_2))] \\
 & + 2f_\alpha [(\Delta d_1 + \Delta d_2) (\Delta \alpha)] \\
 & + 2(Dd)^{\frac{1}{2}} f_{d\beta} [(\Delta d_1) (\Delta \beta_1) + (\Delta d_2) (\Delta \beta_2)] \\
 & + 2(Dd)^{\frac{1}{2}} f_{d\beta} [(\Delta d_1) (\Delta \beta_1) + (\Delta d_2) (\Delta \beta_1)] \\
 & + Ddf_\delta [(\Delta \delta)^2]
 \end{aligned}$$

Notation of force and kinetic constants used.

Nature of the constant	Force Constant	Kinetic Constant
XY Stretching	f_D	k_D
XZ Stretching	f_d	k_d
XY/XZ interaction	f_{Dd}	k_{Dd}
XZ/XZ interaction	f_{dd}	k_{dd}
\wedge ZXZ bending	f_α	k_α
\wedge YXZ bending	f_β	k_β
\wedge XY/ZXZ interaction	$f_{D\alpha}$	$k_{D\alpha}$
\wedge XZ/ZXZ interaction	$f_{d\alpha}$	$k_{d\alpha}$
\wedge XZ ₁ /YXZ ₁ interaction	$f'_{d\beta}$	$k'_{d\beta}$
Out of plane bending	f_δ	k_δ

Following Ford and Orville - Thomas (3) the redundancy symmetry coordinates associated with A₁ species is utilised to reduce the general F matrix elements to the following simple form.

A₁ Species

$$F_{11} = f_d$$

$$F_{22} = f_d + f_{dd}$$

$$F_{33} = \frac{3}{r} (f_{\beta} + f_{\beta\beta})$$

$$F_{12} = \sqrt{2} f_{Dd}$$

$$F_{13} = \frac{3}{2} f_{D\alpha}$$

$$F_{23} = \frac{3}{r} (f'_{d\beta} + f''_{d\beta})$$

B₁ Species

$$F_{44} = f_d - f_{dd}$$

$$F_{55} = \frac{1}{r} (f_{\beta} - f_{\beta\beta})$$

$$F_{45} = \frac{1}{r} (f'_{d\beta} - f''_{d\beta})$$

B₂ Species

$$F_{66} = f_{\partial/}$$

$$\text{where } r = d/D$$

The redundancy constraints used to reduce the general F - matrix are given below :

$$\sqrt{r} f_D + 2 f_D = 0$$

$$\sqrt{r} f_d + f'_{d\beta} + f''_{d\beta} = 0$$

$$\sqrt{r} f_\alpha + 2f_{\alpha\beta} = 0$$

$$r f_\alpha - 2(f_\beta + f_{\beta\beta}) = 0$$

G Matrix

The G matrix elements obtained making use of Wilson's expression (4) are given below

A₁ Species

$$G_{11} = \mu_x + \mu_y$$

$$G_{22} = 2c^2 \mu_x + \mu_y$$

$$G_{33} = 3(2s^2 \mu_x + \mu_y)$$

$$G_{12} = \sqrt{2} c \mu_x$$

$$G_{13} = \sqrt{6} s \mu_x$$

$$G_{23} = \sqrt{12} cs \mu_x$$

B₁ Species

$$G_{44} = 2S^2 \mu_x + \mu_y$$

$$G_{55} = 2(r - c)^2 \mu_x + 2r^2 \mu_y + \mu_z$$

$$G_{45} = -2S(r - c) \mu_x$$

B_2 Species

$$G_{66} = (r - c^{-1})^2 \mu_x + r^2 \mu_y + (2c^2)^{-1} \mu_z$$

where $S = \sin \beta = \sin(\alpha/2)$

$C = \cos \beta = -\cos(\alpha/2)$

$r = d/D$

μ_x , μ_y and μ_z are the reciprocal masses of X, Y and Z atoms respectively.

Kinetic Constants

The elements of kinetic energy matrix have been used to arrive at kinetic constants. The K matrix elements are given below

A_1 Species

$$K_{11} = k_D$$

$$K_{22} = k_d + k_{dd}$$

$$K_{33} = \frac{3}{r} (k_\beta + k_{\beta\beta})$$

$$K_{12} = \sqrt{2} k_{Dd}$$

$$K_{13} = \left(\frac{3}{2}\right)^{\frac{1}{2}} k_{D\alpha}$$

$$K_{23} = \left(\frac{3}{r}\right)^{\frac{1}{2}} (k'_{d\beta} + k''_{d\beta})$$

B₁ Species

$$K_{44} = k_d - k_{dd}$$

$$K_{55} = \frac{1}{r} (k_{\beta} - k_{\beta\beta})$$

$$K_{45} = \frac{1}{r} (k'_{d\beta} - k'_{d\beta})$$

B₂ Species

$$K_{66} = \frac{1}{r} k_{\delta}$$

where $r = d/D$

METHOD OF KINETIC CONSTANTS

The method of kinetic constants for evaluating force constants have been applied successfully for different types of molecules (5-9).

The equations involving A₁ species and B₁ species of the type of ion are solved easily by using this method.

COMPLIANCE CONSTANTS

The Compliance Constants matrix N as introduced by Decius (10) is the inverse of force constant matrix. These compliance

constants are therefore obtained from the corresponding N ($N \equiv F^{-1}$) elements.

VIBRATIONAL MEAN AMPLITUDES

Utilising Cyvin's equation (11)

$$\Sigma = L \Delta L'$$

the symmetrised mean square amplitudes and hence the valence mean square amplitudes quantities for bonded and non bonded mean square amplitudes are given below:

Bonded:

$$\sigma_D = \Sigma_{11}$$

$$\sigma_d = \frac{1}{2} (\Sigma_{22} + \Sigma_{11})$$

$$\sigma_{dd} = \frac{1}{2} (\Sigma_{22} - \Sigma_{44})$$

$$\sigma_\beta = \frac{r}{6} (\Sigma_{33} + \Sigma_{55})$$

$$\sigma_{Dd} = \frac{1}{\sqrt{2}} \Sigma_{12}$$

$$\sigma_{D\alpha} = \frac{\sqrt{2}}{\sqrt{3}} \Sigma_{13}$$

$$\sigma_{d\beta} = \frac{V_r}{\sqrt{12}} (\Sigma_{23} + 3 \Sigma_{45})$$

$$\sigma_{d\beta} = -\frac{V_r}{\sqrt{12}} (\Sigma_{23} - 3 \Sigma_{45})$$

$$\sigma_{\beta\beta} = \frac{r}{6} (\Sigma_{33} - 6 \Sigma_{55})$$

$$\sigma_{\delta} = r \Sigma_{66}$$

The redundancy constraints used to simplify expressions are

$$\sigma_{D\alpha} + 2 \sqrt{r} \sigma_{D\beta} = 0$$

$$\sigma_{d\alpha} + \sqrt{r} (\sigma_{d\beta}' + \sigma_{d\beta}'') = 0$$

$$\sigma_{\alpha} + 2 \sqrt{r} \sigma_{\alpha\beta} = 0$$

$$\sigma_{\alpha} - 2r (\sigma_{\beta} + \sigma_{\beta\beta}) = 0$$

Non Bonded:

$$\sigma_p = p^{-2} [a^2 \sigma_D + b^2 \sigma_d + DdS^2 \sigma_{\beta} + 2ab \sigma_{Dd} - DS (a \sigma_{D\alpha} - 2b \sqrt{r} \sigma_{d\beta}')]$$

$$\sigma_q = 2S^2 (\sigma_d + \sigma_{dd}) + C^2 \sigma_{\alpha} - 4CS \sigma_{d\alpha}$$

Where p is the Y...Z distance

and q is the Z...Z distance

$$a = D-dC$$

$$b = d-DC$$

$$p = (D^2 + d^2 - 2 DdC)^{1/2}$$

$$C_{15} = \sqrt{2} [(r - c) \mu_x + r \mu_y]$$

$$C_{25} = 2C (r - c) \mu_x - \mu_z$$

$$C_{35} = \sqrt{12} S (r - c) \mu_x$$

$B_1 \times B_2$ Coupling

$$C_{46} = \frac{1}{\sqrt{2}} t [2(1 - rc) \mu_x + \mu_z]$$

$$C_{56} = \frac{1}{\sqrt{2}} [2(r - c)(r - c^{-1}) \mu_x + 2r^2 \mu_y + \mu_z]$$

Using these C_y elements and the inverse of normal coordinate transformation matrix L , the zeta matrix elements are evaluated from the relation

$$\zeta^\alpha = L^{-1} C^\alpha (L^{-1})'$$

CENTRIFUGAL DISTORTION CONSTANTS

Cyvin et al (14) have reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of the partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of Kivelson and Wilson (15,16). The quantities $t_{\alpha\beta\gamma\delta}$ have been obtained using Cyvin's relation and the non vanishing $T_{\alpha\beta,s}$ matrix elements evaluated in terms of the present symmetry coordinates are given below:

T matrix elements for the planar XYZ₂ molecular model is as follows:

T	XX	YY	ZZ	ZX
S ₁ (A ₁)	2D	2D	0	0
S ₂ (A ₁)	$\sqrt{8} dc^2$	$\sqrt{8} d$	$\sqrt{8} ds^2$	0
S ₃ (A ₁)	$\sqrt{24} dcs$	0	$-\sqrt{24} dcs$	0
S ₄ (B ₁)	0	0	0	$\sqrt{8} dcs$
S ₅ (B ₁)	0	0	0	$-\sqrt{8} ds^2$

The elements are evaluated from the relation

$$t_{\alpha\beta\gamma\delta} = -2 I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e \alpha\beta\gamma\delta$$

where expressions of moments of inertia are

$$I_{XX} = M^{-1} [D^2 m_Y (m_X + 2m_Z) + 2d^2 c^2 m_Z (m_X + m_Y) - 4 Ddc m_Y m_Z]$$

$$I_{ZZ} = 2 d^2 s^2 m_Z$$

here m_X , m_Y , m_Z and M stand for the masses of X, Y, Z atoms and the mass of the molecule respectively.

RESULTS AND DISCUSSIONS

A normal coordinate analysis of the bicarbonate ion has been carried out using Coriolis F-G matrix method on the basis of

C_{2v} point group using general quadratic potential function and molecular kinetic constants and a set of force constants have been reported.

The set of fundamental frequencies used and the other structural parameters are given in Table 10.1. The kinetic constants of the bicarbonate ion are given in Table 10.2. These constants can be grouped into three heads as

- a) those belonging to bond angle interaction
- b) those belonging to bending and angle-angle interactions
- c) those belonging to stretching and bond-bond interactions

The first set of complimentary kinetic constants namely bond angle interaction kinetic constants possess mutually complimentary roles and their algebraic sum vanishes. Again the sums of bending and the angle interaction kinetic constants i.e. the second set of kinetic constants are found to satisfy the following kinetic constants.

$$\left(\frac{d}{D}\right)^{\frac{1}{2}} K_{D\alpha} + 2 k_{dd} = 0$$

$$\left(\frac{d}{D}\right)^{\frac{1}{2}} k_{d\alpha} = k'_{d\beta} + k''_{d\beta} = 0$$

$$\left(\frac{d}{D}\right)^{\frac{1}{2}} k_{\alpha} + 2k_{\alpha\beta} = 0$$

$$\left(\frac{d}{D}\right)^{\frac{1}{2}} k_{\alpha} + 2 (k_{\beta} + k_{\beta\beta}) = 0$$

Hence only six kinetic constants namely k_D , k_d , k_{Dd} , k_{dd} , k_{α} and k_{β} are sufficient to indicate the nature of the molecular structure.

The other kinetic constants can be inferred from the six kinetic constants. It is seen from the table that bond angle interaction kinetic constant $K_{D\alpha}$ is negative as expected. The results are analogous to those obtained by Mohan et al (17).

The valence force constants of the bicarbonate ion are presented in table 10.3. It is seen from the table that the bond angle interaction force constant $f_{D\alpha}$ is negative. The high values of C-OH stretching force constant f_D and the C-O stretching force constant f_d and the bond-bond interaction constants f_{dd} and f_{Dd} indicates that there is heavy mixing of normal modes of vibration. Further the C-O stretching force constant f_d evaluated in the present investigation agrees quite well with C-O stretching values in COH_2 and COD_2 by Thirugnanasambandam et al (18).

The compliance constants calculated for this molecule by Decius method (10) are given in table 10.4. These show trends opposite to those of force constants.

Using the force constants in Cyvin secular equation (11) the symmetrised mean square amplitude elements and hence the vibrational mean amplitudes have been obtained. These values are reported in table 10.5. The values obtained are in the expected range. It is also seen that l_{0-0} is greater than l_{0-OH} .

This confirms the correctness of the assignments.

The coriolis coupling constants for A_1XB_2 , A_1XB_1 and B_1XB_2 couplings have been evaluated using the matrix relation

$$\gamma^\alpha = L^{-1} C^\alpha (L^{-1})^{-1}$$

The C^α ($\alpha = x, y, z$) matrix elements have been obtained by the vector method of Meal and Polo (13).

The Zeta values are listed in Table 10.6. The Coriolis coupling constants obey the following sum rules given by Oka et al (19) and Watson (20).

$$\zeta_{16}^z + \zeta_{26}^z + \zeta_{36}^z = 1$$

$$\zeta_{15}^z + \zeta_{25}^z + \zeta_{35}^z = 1$$

$$\zeta_{14}^z + \zeta_{24}^z + \zeta_{34}^z = 1$$

$$\zeta_{46}^z + \zeta_{56}^z = 1$$

The high values of ζ_{26}^z , ζ_{34}^z , ζ_{46}^x suggest that couplings concerned are stronger than others.

Knowledge of centrifugal distortion constants are necessary for the determination of exact vibrational energy levels of a

non rigid molecule. The centrifugal distortion constants of bicarbonate ion have been calculated by Cyvin's method(14) using the force constants obtained. They are reported in the table 10.7.

CONCLUSION

A complete vibrational analysis of bicarbonate ion using the observed vibrational frequencies obtained from Laser Raman and Infrared Spectrum on the basis of C_{2v} symmetry is available in the present study.

TABLE 10.1.α

INFRARED AND LASER RAMAN FREQUENCIES OF
BICARBONATE ION IN POTASSIUM BICARBONATE MOLECULE

I.R. Frequ- ency <small>cm⁻¹</small>	Inten- sity	Assignment	Laser Raman Frequency <small>cm⁻¹</small>	Inten- sity
670	W	ν_3 Symmetric bend	670	W
712	M	ν_5 Asymmetric bend		
840	M	ν_6 Out of plane		
1019	S	(C - OH) ν_1 Symmetric stretching	1019	S
1400	VS	(C - O) ν_2 Symmetric stretching		
1603	VS	(C - O) ν_4 Asymmetric stretching		

TABLE - 10.1.b

Structural parameters and fundamental frequencies of HCO_3 ion in potassium bicarbonate molecules.

Ion	D	ν_1 (A_1)	ν_4 (B_1)
	d	ν_2 (A_1)	ν_5 (B_1)
	\AA	ν_3 (A_1)	ν_6 (B_2)
		cm^{-1}	cm^{-1}
HCO_3	1.38	1019	1603
	1.28	1400	712
		670	840

TABLE - 10.2

Values of Kinetic Constants (10^{-26} kg) of HCO_3^- ion in potassium bicarbonate molecule.

k_D	2.0362
k_d	1.9586
k_{Dd}	0.3702
k_{dd}	0.3490
k_α	0.3580
k_β	0.3412
$k_{D\alpha}$	- 0.4275
$k_{d\alpha}$	0.2011
$k_{d\beta}$	0.4141
k_δ	0.1736

TABLE - 10.3

Values of potential constants (10^2 N/m) of HCO_3^- ion in potassium bicarbonate molecule.

f_D	6.6572
f_d	10.6319
f_{Dd}	1.2103
f_{dd}	1.2565
f_α	0.5703
f_β	0.6324
$f_{D\alpha}$	- 0.6808
$f_{d\alpha}$	0.3202
$f_{d\beta'}$	- 1.0185
f_δ	0.4342

TABLE - 10.4

Values of Compliance Constants (10^{-2} Nm^{-1}) of HCO_3^- ion in potassium bicarbonate molecule.

n_D	0.1850
n_d	0.1088
n_{Dd}	- 0.0256
n_{dd}	- 0.0150
n_α	0.9813
n_β	0.7390
$n_{D\alpha}$	0.1664
$n_{d\alpha}$	0.0555
$n_{d\beta}$	0.0930
n_δ	- 2.0139

TABLE - 10.5

Values of vibrational mean square amplitudes ($10^{-3} \overset{\circ}{\text{A}}^2$) - bonded and non bonded - and vibrational mean amplitudes ($10^{-2} \overset{\circ}{\text{A}}$) at 298.16 K for HCO_3^- ion in potassium bicarbonate molecule.

σ_D	2.0808
σ_d	1.6149
σ_{Dd}	- 0.4352
σ_{dd}	0.3447
σ_α	7.7648
σ_β	6.4404
$\sigma_{D\alpha}$	- 1.9819
$\sigma_{d\alpha}$	0.8219
$\sigma_{d\beta}$	1.5422
σ_θ	19.7261
σ_ρ	3.0162
σ_q	10.2058
l_D	4.5615
l_d	4.0186
l_q	10.1025
l_p	5.4919

TABLE - 10.6

Values of Coriolis Coupling Constants (ζ) of HCO_3^- ion in potassium bicarbonate molecule.

ζ_{16}^x	- 0.4036
ζ_{26}^x	0.8151
ζ_{36}^x	- 0.4157
ζ_{14}^y	- 0.3099
ζ_{24}^y	0.5953
ζ_{34}^y	- 0.7413
ζ_{15}^y	0.3006
ζ_{25}^y	0.6784
ζ_{35}^y	0.6704
ζ_{46}^z	- 0.9184
ζ_{56}^z	0.4050

TABLE - 10.7

Values of Centrifugal Distortion Constants (τ) in MHz of HCO_3^- ion in potassium bicarbonate molecule.

$$\tau_{xxxx} = -0.0040$$

$$\tau_{yyyy} = -0.0004$$

$$\tau_{zzzz} = -0.0052$$

$$\tau_{xxyy} = -0.0008$$

$$\tau_{xxzz} = 0.0008$$

$$\tau_{yyzz} = -0.0006$$

REFERENCES

1. D.L.Bernitt Spectrochim Acta., 23A, 223 (1967)
2. T.Oka and Y.Morino J.Molr. Spectrosc., 11, 349 (1963)
3. T.A.Ford and W.J.Oriville-Thomas Spectrochim Acta, 23A, 579 (1967)
4. E.B.Wilson (Jr.), J.C.Decius and P.C.Cross 'Molecular Vibrations', McGraw Hill, New York (1955)
5. S.Mohan Bull.Soc.Chim.Belges, 52A, 747 (1977)
6. S.Mohan Acta Phys. Pol. A57, 433 (1980)
7. S.Mohan, K.G.Ravikumar and S.Gunasekaran Actachim. Hungarica, 111, 59 (1982)
8. S.Mohan and K.G.Ravikumar Acta Phys. Pol. A63, 77, (1983)
9. S.Mohan and K.G.Ravikumar Indian J. Pure and Appl. Phys. 20, 417, (1982)
10. J.C.Decius J.Chem. Phys. 38, 241 (1963)
11. S.J.Cyvin 'Molecular Vibrations and mean square amplitudes', Elsevier, New York (1968)
12. H.A.Jahn Phys. Rev. 56, 680 (1939)
13. J.H.Meal and S.R.Polo J.Chem. Phys. 24, 1911, 1926 (1956)
14. S.J.Cyvin, B.N.Cyvin and G.Hogen Z.Naturforsch 23a, 1964 (1968)

Thus vibrational mean amplitudes for bicarbonate ion are evaluated from mean square amplitude quantities.

Coriolis Coupling Constants:

The non vanishing Coriolis Couplings arising from Jahn's rule (12) for planar XYZ_2 type molecules are given as $A_1 \times B_2$ along X axis, $A_1 \times B_1$ along the Y axis and $B_1 \times B_2$ along the Z axis. The C^α ($\alpha = x, y, z$) matrix elements have been evaluated by the vector method of Meal and Polo (13) are given below:

C_{ij}^α elements

$A_1 \times B_2$ Coupling

$$C_{16} = -[(r - c^{-1}) \mu_x + r \mu_y]$$

$$C_{26} = \frac{1}{\sqrt{2}} [2(1 - rc) \mu_x + \mu_z]$$

$$C_{36} = \frac{\sqrt{3}}{\sqrt{2}} t [2(1 - rc) \mu_x + \mu_z]$$

$A_1 \times B_1$ Coupling

$$C_{14} = -2S \mu_x$$

$$C_{24} = -2CS \mu_x$$

$$C_{34} = -3(2S^2 \mu_x + \mu_z)$$

15. D.Kivelson and E.B.Wilson (Jr) J.Chem Phys. 20, 1575 (1952)
16. D.Kivelson and E.B.Wilson (Jr.) J.Chem. Phys. 21, 1229, (1953)
17. S.Mohan and K.G.Ravikumar Acta Phys. Pol. A64, 671, (1983)
18. P.Thirugnanasambandam and N.Karunanidhi Indian J.Phys. 49, 658, (1975)
19. T.Oka and Y.Morino J.Molr. Spectrosc., 6, 472 (1961)
20. J.K.G. Watson J.Molr. Spectrosc. 39, 364 (1971)