

Vibrational spectra and normal coordinate analysis on an organic non-linear optical crystal-3-methoxy-4-hydroxy benzaldehyde

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The crystal 3-methoxy-4-hydroxy benzaldehyde (vanillin) is a potential non-linear organic crystal. The FTIR and laser Raman spectroscopy have been used to make a qualitative analysis and structural confirmation on vanillin. The molecular structure of vanillin belongs to C_s point group symmetry. A normal coordinate analysis of vanillin has been carried out following Wilson's F-G matrix method using the general quadratic valence force field. A set of orthonormalised symmetry coordinates satisfying the transformation properties is constructed. The validity of the vibrational assignments is supported evaluating the potential constants of the molecule of vanillin. Further, the potential energy distribution has also been evaluated to check, whether the chosen set of vibrational frequencies contribute to the maximum potential energy associated with the normal coordinate of the molecule.

Keywords: Normal coordinate analysis, FTIR, Laser Raman spectra, Non-linear optical, Vanillin, F-G matrix
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1 Introduction

Some organic crystalline solids that comprise highly polar molecules and form non-centro-symmetric crystal structures exhibit second order non-linear optical properties and laser damage thresholds that are potentially superior to those of currently available inorganic systems. The crystal 3-methoxy-4-hydroxy benzaldehyde (MHBA) also known as vanillin, exhibits good non-linear optical property. Several investigations^{1,2} have been carried out on MHBA to study the properties like optical transmission, refractive index, electro-optic effect, dielectric constant etc., MHBA is a trisubstituted benzene with $-CHO$, $-OCH_3$ and $-OH$ groups substituted at 1,3,4 positions of the ring. Its molecular formula is $C_6H_3(CH_3O)(OH)(CHO)$. MHBA crystals can be grown by Bridgman technique because its melting point is 82-83°C. It is also soluble in several common organic solvents and can be easily grown from solution by the temperature lowering method. MHBA crystallizes under the monoclinic non-centro symmetric class with space group P_{21} . The lattice parameters are: $a = 14.057 \text{ \AA}$, $b = 7.875 \text{ \AA}$, $c =$

15.037 \AA and $\beta = 115.45^\circ$ and the cell volume is $1503.30 (\text{ \AA})^3$. There are 8 molecules in the unit cell. The density of the crystal is 1.34 g/cm^3 . The inter molecular hydrogen bonds existing between the carbonyl and hydroxyl group play an important role in the stacking of molecules in the crystals. MHBA is a donor-acceptor substituted benzene derivative. There exists a charge transfer between the para donor hydroxyl ($-OH$) and carbonyl ($-CHO$) acceptor. The methoxy ($-OCH_3$) provides a minor contribution to the non-linearity, but plays an important role in promoting the formation of non-centro crystal structures.

The Mohs hardness of MHBA is 1.67 and the crystal is transparent over the region 375-1700 nm and hence the lower cut-off wavelength is 370 nm. The powder SHG efficiency of MHBA is 30 times higher than that of urea. The refractive indices of the MHBA along the three crystallographic axes are: $n_x = 1.703$, $n_y = 1.563$ and $n_z = 1.814$. The electro optic half wave voltage is 3.96 kV and the value of the electro optic coefficient is $r_{12} = 22.99 \text{ pm/V}$. MHBA is soluble in water and acetone + methanol is also a better solvent. It is also used in the preparation of perfumes, flavours, pharmaceuticals, some laboratory reagents etc. MHBA is extracted from the vanilla bean and lignin contained in sulphite waste pulp

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liquor. Hence, MHBA is a technologically an important organic system and in the present work, normal coordinate analysis on the molecular structure of MHBA has been carried out to elucidate the structural details of the molecule.

2 Experimental Details

Spectroscopically pure sample of MHBA has been procured from Sigma-Aldrich Company, USA and is used as such. The Fourier Transform Infrared spectrum has been recorded using BRUKER IFS 66V Spectrometer in the region $4000\text{--}400\text{ cm}^{-1}$ by KBr pellet method. The laser Raman spectrum of the sample has been recorded using DILOR Z 24 Raman Spectrometer equipped with 647 nm krypton ion laser instrument in the region $3500\text{--}50\text{ cm}^{-1}$. Both the spectra have been recorded at 303 K. The frequencies

of all the sharp bands are accurate to $\pm 1\text{ cm}^{-1}$. A spectral width of 4.29 cm^{-1} was used and spectra were measured with a scanning speed of 1.87 cm^{-1} per minute. All the spectra were recorded at Sophisticated Analytical Instrumentation Facility, Indian Institute of Technology, Chennai. The vibrational spectra of MHBA are presented in Fig. 1.

3 Normal Coordinate Analysis

The molecular structure of MHBA is presented in Fig. 2. The benzene ring, carbonyl group and the hydroxyl group of MHBA are arranged in a plane of the paper excepting the CH_3 group of $-\text{OCH}_3$. Hence, the molecular structure of MHBA belongs to C_s symmetry with 51 fundamental modes of vibration and is represented as $\Gamma_{\text{vib}} = 35 A' (\text{IR}, \text{R}) + 16 A'' (\text{IR}, \text{R})$ and both A' and A'' species are IR and Raman

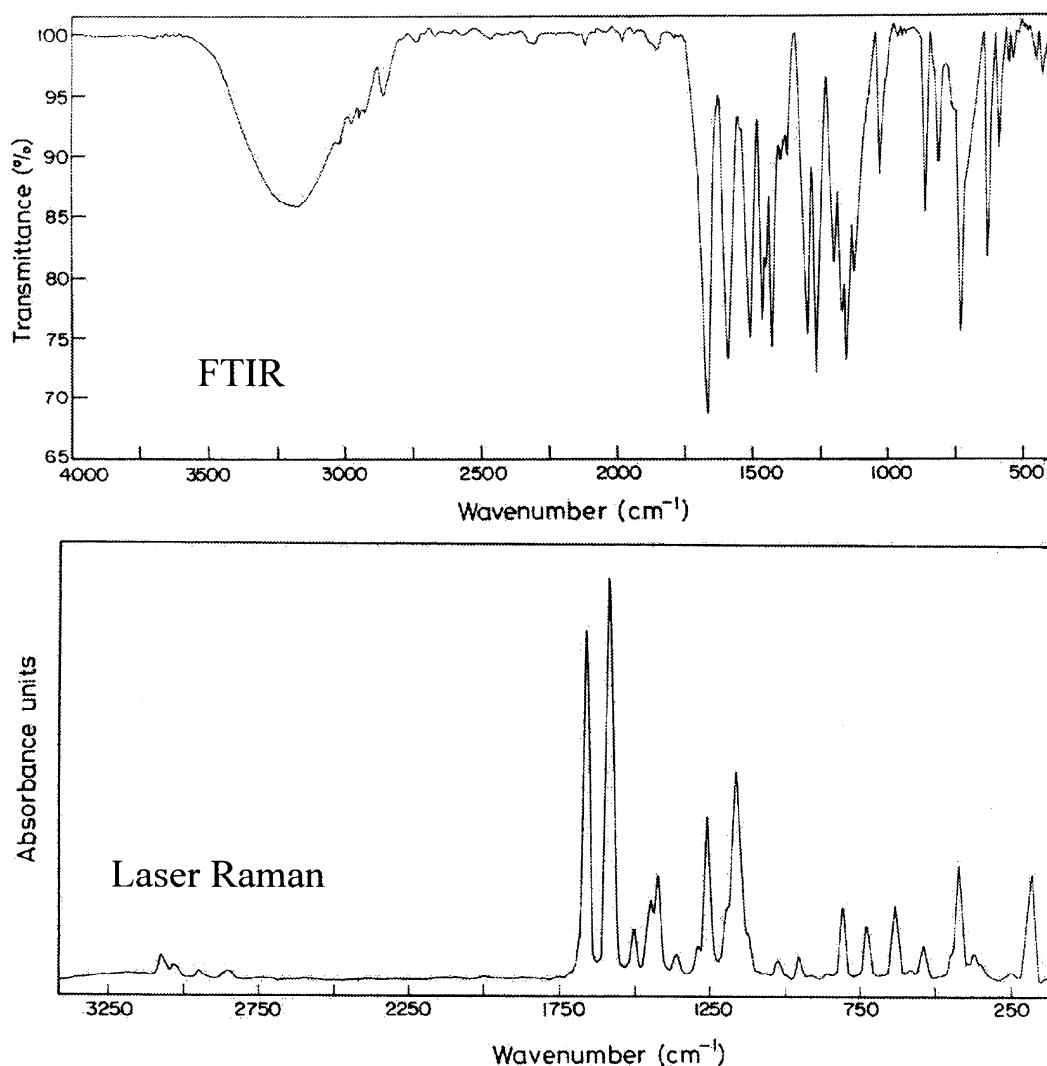


Fig.1—Vibrational spectra of MHBA

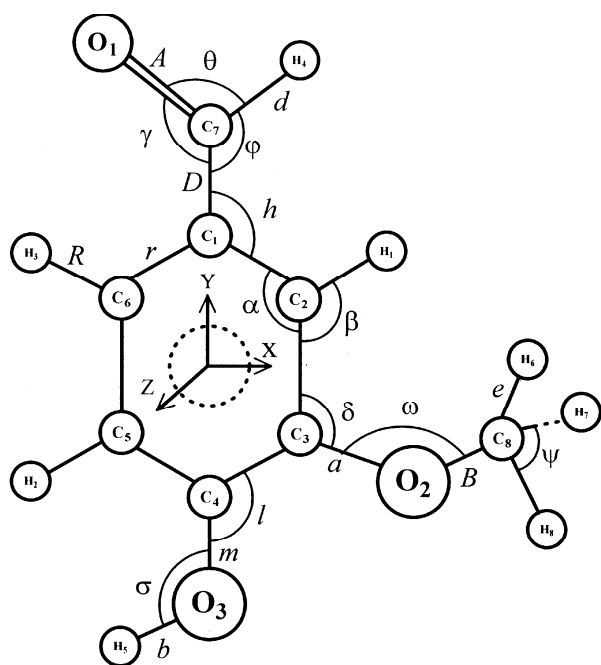


Fig. 2—Structure, nomenclature of the parameters and orientation of the principal axes of the molecule MHBA

active. In the present work, out of 51 fundamental modes, only 29 specific modes of vibrations are considered for the structural elucidation of the molecule. *Ortho* normal set of symmetry coordinates for some of the specific modes of vibration have been constructed from the sets of equivalent internal coordinates for the molecular structure of MHBA and they are as follows:

A' species:

- (1) $S_1 = (1/\sqrt{6}) [\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6]$
- (2) $S_2 = (1/\sqrt{3}) [\Delta R_1 + \Delta R_2 + \Delta R_3]$
- (3) $S_3 = \Delta D$
- (4) $S_4 = \Delta a$
- (5) $S_5 = \Delta m$
- (6) $S_6 = \Delta A$
- (7) $S_7 = \Delta d$
- (8) $S_8 = \Delta B$
- (9) $S_9 = \Delta b$
- (10) $S_{10} = (1/\sqrt{3}) [\Delta e_1 + \Delta e_2 + \Delta e_3]$
- (11) $S_{11} = (1/\sqrt{6}) [\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 + \Delta \beta_4 + \Delta \beta_5 + \Delta \beta_6]$
- (12) $S_{12} = (1/\sqrt{2}) [\Delta h_1 + \Delta h_2]$
- (13) $S_{13} = (1/\sqrt{6}) [\Delta l_1 + \Delta l_2]$
- (14) $S_{14} = \Delta \gamma$
- (15) $S_{15} = \Delta \phi$
- (16) $S_{16} = \Delta \theta$
- (17) $S_{17} = \Delta \omega$
- (18) $S_{18} = \Delta \sigma$
- (19) $S_{19} = (1/\sqrt{3}) [\Delta \psi_1 + \Delta \psi_2 + \Delta \psi_3]$

Table 1—Molecular parameters for MHBA

Nature of the bond length and bond angle	Description	Molecular parameter
CC ring	r	1.397 Å
CH ring	m	1.364 Å
C-OH	R	1.082 Å
C=O (aldehyde)	A	1.240 Å
C-CHO	D	1.480 Å
O-H	b	0.956 Å
C-H (aldehyde)	d	1.084 Å
C-OCH ₃	a	1.361 Å
O-CH ₃	B	1.423 Å
CH (methoxy)	e	1.110 Å
CCC-ring	α	120°
CCH-ring	β	120°
CC(OH)	l	120°
COH	σ	109°
CC(CHO)	h	120°
CCO (aldehyde)	γ	125°
CCH (aldehyde)	ϕ	115°
CC(OCH ₃)	δ	120°
OCH (aldehyde)	θ	109.47°
CO(CH ₃)	ω	120°
HCH (methyl)	ψ	109.47°

A'' species:

- (20) $S_{20} = (1/\sqrt{6}) [\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4 + \Delta r_5 - \Delta r_6]$
- (21) $S_{21} = (1/\sqrt{12}) [\Delta r_1 - 2\Delta r_2 + \Delta r_3 + \Delta r_4 - 2\Delta r_5 + \Delta r_6]$
- (22) $S_{22} = (1/\sqrt{6}) [2\Delta R_1 - \Delta R_2 - \Delta R_3]$
- (23) $S_{23} = (1/\sqrt{6}) [2\Delta e_1 - \Delta e_2 - \Delta e_3]$
- (24) $S_{24} = (1/\sqrt{6}) [\Delta \alpha_1 - \Delta \alpha_2 + \Delta \alpha_3 - \Delta \alpha_4 + \Delta \alpha_5 - \Delta \alpha_6]$
- (25) $S_{25} = (1/\sqrt{12}) [\Delta \alpha_1 - 2\Delta \alpha_2 + \Delta \alpha_3 + \Delta \alpha_4 - 2\Delta \alpha_5 + \Delta \alpha_6]$
- (26) $S_{26} = (1/\sqrt{6}) [\Delta \beta_1 - \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_4 + \Delta \beta_5 - \Delta \beta_6]$
- (27) $S_{27} = (1/\sqrt{2}) [\Delta h_1 - \Delta h_2]$
- (28) $S_{28} = (1/\sqrt{2}) [\Delta l_1 - \Delta l_2]$
- (29) $S_{29} = (1/\sqrt{6}) [2\Delta \psi_1 - \Delta \psi_2 - \Delta \psi_3]$

where Δ^s are the changes in the corresponding bonds and bond angles. The bond angles and bond lengths that are essential for calculations have been taken from literature² and are presented in Table 1.

A normal coordinate analysis on structure of MHBA has been carried out following Wilson's F-G Matrix method on the basis of C_s point group symmetry using a general quadratic valence force field. The method of kinetic constants for solving the secular equation has been found to give satisfactory results in different type of molecules. Evaluation of all the symmetry force constants in the case of a system of order $n_i > 1$ requires the incorporation of at least $n_i(n_i-1)/2$ additional data other than n_i

frequencies. According to the method of kinetic constants^{3,4}, the off diagonal and diagonal elements are related to the kinetic constants by the relation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$ ($i < j; j = 1, 2, 3 \dots n$).

The tedium of this methodology is that the possible number of combinations of diagonal F elements set to be tried is a very large number. By error and trial, it can be found whether a particular F matrix constitutes a valid solution and the F matrix for the given molecule which satisfies the secular equation is hence-forth arrived at the Potential Energy Distribution (PED) is evaluated by using the expression $F_{ij} L_{ij}^2 / \lambda_j$. PED is the contribution of the symmetric coordinate to the potential energy of vibration whose frequency is ν_j . F_{ij} is the force constant and L_{ij} is the L matrix element. In the present work, only the diagonal force constants were considered. The initial force constants for the diagonal elements of the present molecules were taken from benzene derivatives and phenol derivatives^{5,6}. The process of solving the secular equation and filtering of appropriate force constants were done using C++ program where the input to the computer includes the diagonal elements of G -matrix, initial set of force constants and the observed frequencies. The advantage of the program lies in the fact that the process allows the approximate set of force constants to adjust themselves to a proper fit for the present molecules.

4 Vibrational Band Assignments

Ring C—C vibrations

The ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm^{-1} . In general, the bands are of variable intensity and are observed at 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280 cm^{-1} form the frequency ranges given by Varsanyi⁵, for the five bands in this region. In the present work, the frequencies observed in the FTIR spectrum at 1590, 1539, 1511, 1465 and 1372 cm^{-1} have been assigned to CC stretching vibrations. The same vibrations appear in the laser Raman spectrum at 1593, 1512 and 1369 cm^{-1} . The in-plane deformation vibration is at higher frequencies than the out-of-plane vibrations. Shimanouchi *et al.*⁷ gave the frequency data for these vibrations for different benzene derivatives as a result of normal coordinate analysis. The weak bands observed at 763, 457 and 426 cm^{-1} are assigned to CCC deformations of phenyl ring.

Ring C-H vibrations

The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm^{-1} . A band up to five peaks may be observed in the region 3100-3010 cm^{-1} . The bands observed at 3011 cm^{-1} in the FTIR spectrum and 3030 and 3077 cm^{-1} in the laser spectrum are attributed to the C-H stretching vibrations. The in-plane aromatic C-H deformation vibrations occur in the region 1300-900 cm^{-1} . The bands are sharp but are weak to medium intensity. The medium and strong intensity bands at 1124 and 1300 cm^{-1} in the FTIR spectrum are due to in-plane CH deformations. The same vibration appears in the laser Raman spectrum at 1295 cm^{-1} with very weak intensity.

Vibrations of the aldehyde group

The CH stretching vibrations of the aldehyde group⁸ usually appear in the region 2806-2871 cm^{-1} . The weak band observed in the FTIR spectrum at 2859 cm^{-1} is due to CH stretching vibration of the aldehyde group. The in-plane CH deformation mode of aldehyde group is observed at 1397 cm^{-1} with weak intensity in the FTIR spectrum. The carbonyl (C=O) stretching vibrations in the substituted benzaldehydes is reported near 1700 cm^{-1} . The very strong band centered at 1666 cm^{-1} in both FTIR and laser Raman spectra are attributed to C=O stretching vibrations of the aldehyde group. Singh *et al.*⁹ have assigned the C=O in-plane bending vibrations for isomers of methoxy benzaldehydes in the region 585-620 cm^{-1} . Hence the weak band observed at 589 cm^{-1} could be assigned to C = O in-plane bending vibration. Hanken *et al.*¹⁰ have assigned the band at 173 cm^{-1} in the Raman spectrum of chlorobenzaldehyde as aldehyde out-of-plane wag. In MHBA, the weak band centered at 188 cm^{-1} in the Raman spectrum could be due to aldehyde out-of-plane wagging vibration. A weak to medium intensity band due to the aldehydic group CHO deformation vibration¹¹ is found in the region 975-780 cm^{-1} . In consonance with this, the weak intensity band at 813 cm^{-1} could be assigned to CHO out-of-plane deformation. The bands at 859 and 733 cm^{-1} are attributed to CC(CHO) out-of-plane vibrations.

Vibrations of the methoxy group

For the methoxy group compounds⁹, the asymmetric stretching mode appears in the range 2825-2870 cm^{-1} , lower in magnitude compared to its value in CH_3 compounds (2860-2935 cm^{-1}) whereas the asymmetric stretching modes for both the types of

compounds lie in the same region $2925\text{--}2985\text{ cm}^{-1}$. The weak bands observed at 2935 and 2978 cm^{-1} in the FTIR spectrum could be attributed to CH_3 asymmetric stretching vibration. The same vibration appears in the Raman spectrum at 2950 cm^{-1} with weak intensity. The weak band centered at 2850 cm^{-1} could be assigned to symmetric CH_3 stretching vibration. The asymmetric deformation of CH_3 is usually observed at around 1450 cm^{-1} for methyl substituted benzenes¹². As expected, medium and strong intensity bands are appeared at 1452 and 1430 cm^{-1} in the FTIR spectrum and this is due to CH_3 asymmetric deformation vibration. The corresponding vibration in the laser Raman spectrum appears at 1455 and 1430 cm^{-1} with weak intensity. The CH_3 symmetric deformation absorption occurs at 1369 cm^{-1} and this vibration overlaps with CC ring stretching vibrations. The medium intensity band

observed at 958 cm^{-1} in the FTIR spectrum could be assigned to C-OCH_3 stretching vibration. The CH_3 rocking vibration of anisoles appears at 1175 cm^{-1} . As expected, this vibration appears at 1172 cm^{-1} with strong intensity in FTIR spectrum and 1171 cm^{-1} with medium intensity in the laser Raman spectrum. For anisoles and substituted anisoles, O-CH_3 stretching vibration⁶ appears at 1035 cm^{-1} and the weak bands appeared in the spectra of MBHA at 1030 cm^{-1} could be attributed to O-CH_3 stretching vibration. The in-plane COC bending mode of MHBA is assigned at 551 cm^{-1} and the corresponding out-of-plane vibration appears at 254 cm^{-1} in the laser Raman spectrum.

Vibrations of the hydroxy group

In phenols⁶, the free O-H group absorbs at 3615 cm^{-1} while the associated group has a stretching frequency in the range $3200\text{--}3250\text{ cm}^{-1}$. This is due to

Table 2-Normal modes of vibration, potential constants and PED of MHBA

Fundamental Mode	Frequency (cm^{-1})		Assignment	Potential constant ($\times 10^2\text{ N/m}$)	PED(%)
	FTIR	Laser Raman			
$\nu_1 (A_1)$	1372 (w)	1369 (vw)	$\nu_s (\text{CC})$	6.5016	39
$\nu_2 (A_1)$	---	3030 (vw)	$\nu_s (\text{CH}) (\text{ring})$	5.0413	95
$\nu_3 (A_1)$	1266 (vs)	1267 (m)	$\nu (\text{C-CHO})$	5.3010	43
$\nu_4 (A_1)$	958 (m)	960 (vw)	$\nu (\text{C-OCH}_3)$	5.0111	66
$\nu_5 (A_1)$	1154 (vs)	---	$\nu (\text{C-OH})$	5.3324	48
$\nu_6 (A_1)$	1666 (vs)	1668 (vs)	$\nu (\text{C=O})$	10.1106	62
$\nu_7 (A_1)$	2859 (vw)	---	$\nu (\text{CH}) (\text{aldehyde})$	4.4138	98
$\nu_8 (A_1)$	1030 (s)	1295 (vw)	$\nu (\text{O-CH}_3)$	4.8843	40
$\nu_9 (A_1)$	3183 (m)	---	$\nu (\text{O-H})$	5.6100	99
$\nu_{10} (A_1)$	---	2850 (vw)	$\nu_s (\text{CH}) (\text{methyl})$	4.6382	98
$\nu_{11} (A_1)$	1124 (m)	---	$\delta_s (\text{CCH})$	0.4900	46
$\nu_{12} (A_1)$	733 (s)	736 (vw)	$\delta_s (\text{C-C-CHO})$	1.3378	60
$\nu_{13} (A_1)$	536 (vw)	543 (vw)	$\delta_s (\text{C-C-OH})$	1.0520	71
$\nu_{14} (A_1)$	589 (w)	585 (vw)	$\delta (\text{O-C=O})$	0.9989	65
$\nu_{15} (A_1)$	1397 (w)	---	$\delta (\text{C-C-H}) (\text{aldehyde})$	0.5136	90
$\nu_{16} (A_1)$	813 (w)	814 (vw)	$\delta (\text{O=C-H})$	0.9873	46
$\nu_{17} (A_1)$	551 (vw)	---	$\delta (\text{C-O-CH}_3)$	1.7121	39
$\nu_{18} (A_1)$	1200 (m)	1202 (vw)	$\delta (\text{C-O-H})$	0.7532	54
$\nu_{19} (A_1)$	1372 (w)	1369 (vw)	$\delta_s (\text{CH}_3)$	0.5130	42
$\nu_{20} (A_2)$	1511 (s)	1512 (vw)	$\nu_{as} (\text{CC})$	6.6121	68
$\nu_{21} (A_2)$	1590 (vs)	1593 (vs)	$\nu_{as} (\text{CC})$	6.6917	70
$\nu_{22} (A_2)$	---	3077 (vw)	$\nu_{as} (\text{CH}) (\text{ring})$	5.0622	95
$\nu_{23} (A_2)$	2978 (w)	---	$\nu_{as} (\text{CH}_3)$	4.6920	99
$\nu_{24} (A_2)$	426 (vw)	429 (vw)	$\delta_{as} (\text{CCC}) (\text{ring})$	0.8603	36
$\nu_{25} (A_2)$	763 (vw)	---	$\delta_{as} (\text{CCC}) (\text{ring})$	0.9500	40
$\nu_{26} (A_2)$	1300 (s)	1295 (w)	$\delta_{as} (\text{CCH}) (\text{ring})$	0.4965	51
$\nu_{27} (A_2)$	859 (m)	---	$\delta_{as} (\text{CC-CHO})$	1.3602	58
$\nu_{28} (A_2)$	632 (m)	636 (vw)	$\delta_{as} (\text{C-C-OH})$	1.0611	48
$\nu_{29} (A_2)$	1452 (m)	1455 (vw)	$\delta_{as} (\text{CH}_3)$	0.5211	84

vs-very strong, s-strong, m-medium, w-weak, vw-very weak

ν -stretching, ν_s -symmetric stretching, ν_{as} -asymmetric stretching, δ -bending, δ_s -symmetric bending, δ_{as} -asymmetric bending

the intermolecular hydrogen bonding. In the present work, the medium intensity broad band centered at 3183 cm^{-1} could be assigned to OH stretching vibration. The predominant contribution of in-plane bending vibration⁸ of OH is always centered at around 1220 cm^{-1} . The medium intensity band appeared in the FTIR spectrum at 1200 cm^{-1} is attributed to in-plane bending vibration of hydroxyl group. Since the energy range of C-H in-plane bending vibrations is very close to the energy range of C-O vibration, the absorption centered in this region may be attributed to C-O stretching vibrations¹³. The C-O stretching vibration appears at 1154 cm^{-1} with very strong intensity in the FTIR spectrum. The weak and medium intensity bands at 536 and 632 cm^{-1} in the FTIR spectrum could be attributed to CCO out-of-plane deformations. The same vibrations appear in the laser Raman spectrum at 543 and 636 cm^{-1} with weak intensities.

5 Results and Discussion

The normal modes of vibration, potential constants and PED for MHBA are given in Table 2. The calculated force constants were comparable with those of related molecules confirming the correctness of the present assignment. The potential energy distributions for all the vibrating modes were found to be satisfactory. From the Table 2, it is observed that the force constants involving ring CH vibrations is $5.0413 \times 10^2\text{ N/m}$ whereas that of methyl and aldehydic group are $4.6382 \times 10^2\text{ N/m}$ and $4.4138 \times 10^2\text{ N/m}$ respectively. The similar observations are reported in methoxy benzaldehydes. From the PED calculations, it is also observed that these vibrations have maximum contribution as these are not mixed with any other vibration of the molecule. Similarly, symmetric and asymmetric bending vibrations of the methyl group in the molecule also have the maximum contribution to the corresponding normal mode of vibration. Some other internal modes like $\nu(\text{C-CHO})$, $\nu(\text{C-OH})$ and $\delta(\text{C-O-CH}_3)$ have low PED values and this due to the mixed vibrations of the molecule with other modes.

6 Conclusion

A satisfactory vibrational band assignment has been made available for 3-methoxy-4-hydroxy benzaldehyde based on the measurements taken from the infrared and Raman spectra. A systematic set of potential constants has been computed using the method of kinetic constants on the basis of C_s symmetry. The potential constants evaluated have been compared with those of related molecules and are in good agreement with literature. To check whether the chosen set of symmetry coordinates contribute maximum to the potential energy associated with the normal coordinate of the molecule, the potential energy distribution has been evaluated which confirms the correctness of assignments based on C_s point group symmetry.

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