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Vibrational Spectra and Normal Coordinate Analysis of *p*-Anisaldehyde

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A normal coordinate analysis on *p*-anisaldehyde has been carried out with a systematic set of symmetry coordinates following Wilson's F-G matrix method. The potential constants evaluated for the molecule are found to be in good agreement with literature values thereby confirming the vibrational assignments. To check whether the chosen set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordinates of the molecule, the potential energy distribution has been evaluated.

Key Words: Normal coordinate analysis, FTIR and FT Raman spectra, *p*-Anisaldehyde.

INTRODUCTION

p-Anisaldehyde, an aromatic aldehyde with methoxy group, is a clear liquid having yellow colour on storage (limited shelf life 6 months) with molecular formula *p*-$CH_3OC_6H_4CHO$. It is chemically called as 4-methoxybenzaldehyde. It is soluble in alcohol and ether but insoluble in water. It is used in the synthesis of other organic compounds including pharmaceuticals (especially antihistamines), agrochemicals, dyes and plastic additives. It is an important intermediate for the processing of perfumes and flavouring compounds. Spectroscopic investigations on the title compound have been carried out by many researchers[1, 2]. However, the normal coordinate analysis and the potential energy distribution (PED) associated with each vibrational mode of *p*-anisaldehyde have not been carried out so far. Hence, in the present work, vibrational spectral analyses have been carried out on *p*-anisaldehyde using normal coordinate analysis. The characteristic vibrational frequencies of this compound have been identified and assigned on the basis of their relative intensity, characteristic positions and correlation of vibrational bands of related compounds. The present investigation has been undertaken to provide a satisfactory vibrational analysis of *p*-anisaldehyde through FTIR and FT Raman spectroscopy. To check whether the chosen

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set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordinates of the molecule, the potential energy distributions have been evaluated.

EXPERIMENTAL

High grade pure sample of *p*-anisaldehyde was procured from Sigma Chemical Company, USA and was used as such. The FTIR spectrum of the compound was recorded in the region 4000–400 cm^{-1} in evacuation mode using KBr pellet technique (solid phase) with 4.0 cm^{-1} resolution. The FT Raman spectrum was recorded in the region 4000–100 cm^{-1} in purge mode using YAG laser of 200 MW. Both the spectra were recorded using Bruker IFS 66V FTIR spectrophotometer at Sophisticated Instrumentation Analysis Facility, IIT, Chennai, India.

Normal Coordinate Analysis

The compound under consideration, *p*-anisaldehyde, belongs to C_s point group symmetry with the consideration of the methyl group as point mass. The number of normal modes of vibration are distributed as $\Gamma_{vib} = 26A' + 13\,A''$; all the fundamental modes of vibration are active both in Raman and Infrared spectra. Of the 26 modes of vibrations only 15 are considered in A′ species and out of the 13 fundamental modes in A″ species only six are considered in the present work. The structure, orientation of the principal axes and the nomenclature of the parameters of the *p*-anisaldehyde molecule are shown in Fig. 1. The molecular parameters are taken from Sutton table[3] and are given in Table-1.

The orthonormal set of symmetry co-ordinates for the molecule under study are constructed using the internal coordinates with the knowledge of the projection operator and with the help of the character table. The symmetry coordinates thus obtained are as follows:

A′ Species

$S_1 = 1/\sqrt{6}\,[\Delta p_1 + \Delta p_2 + \Delta p_3 + \Delta p_4 + \Delta p_5 + \Delta p_6]$

$S_2 = 1/2\,[\Delta q_1 + \Delta q_2 + \Delta q_3 + \Delta q_4]$

$S_3 = \Delta r$

$S_4 = \Delta d$

$S_5 = \Delta a$

$S_6 = \Delta f$

$S_7 = \Delta b$

$S_8 = 1/\sqrt{6}\,[\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6]$

$S_9 = 1/\sqrt{8}\,[\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6 + \Delta\beta_7 + \Delta\beta_8]$

$S_{10} = 1/\sqrt{2}\,[\Delta\Psi_1 + \Delta\Psi_2]$

$S_{11} = 1/\sqrt{2}\,[\Delta\tau_1 + \Delta\tau_2]$

$S_{12} = \Delta\phi$

$S_{13} = \Delta\theta$

$S_{14} = \Delta\nu$

$S_{15} = \Delta\delta$

A″ Species

$S_{16} = 1/\sqrt{12}\,[2\Delta p_1 - \Delta p_2 - \Delta p_3 + 2\Delta p_4 - \Delta p_5 - \Delta p_6]$

$S_{17} = 1/2\,[\Delta q_1 - \Delta q_2 - \Delta q_3 + \Delta q_4]$

$S_{18} = 1/\sqrt{12}\,[2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 + 2\Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6]$

$S_{19} = 1/\sqrt{8}\,[\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 - \Delta\beta_6 - \Delta\beta_7 + \Delta\beta_8]$

$S_{20} = 1/\sqrt{2}\,[\Delta\Psi_1 - \Delta\Psi_2]$

$S_{21} = 1/\sqrt{2}\,[\Delta\tau_1 - \Delta\tau_2]$

where Δ's represent the changes in corresponding bond distances and bond angles.

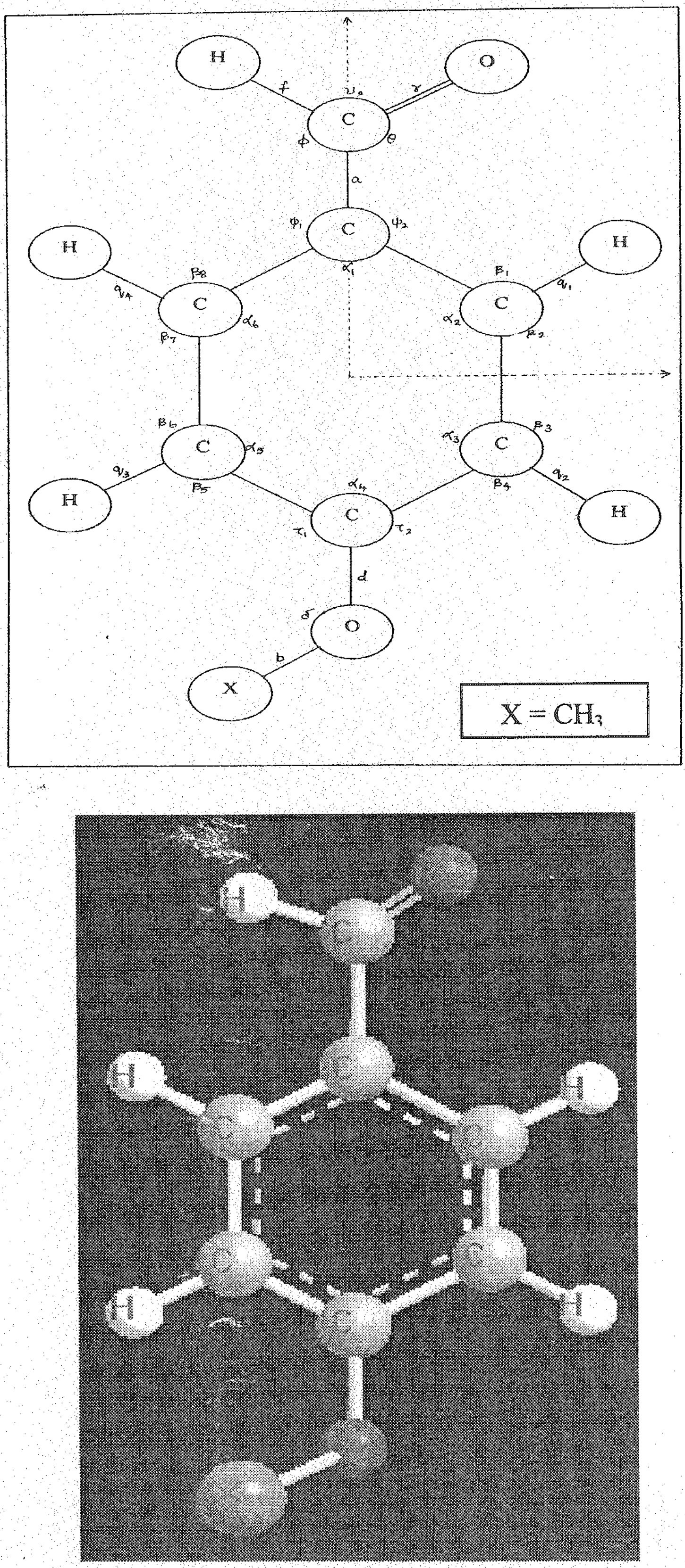

Fig. 1. Structure, nomenclature of parameters and orientation of the principal axes and 3D view of *p*-anisaldehyde

TABLE-1
MOLECULAR PARAMETERS OF p-ANISALDEHYDE

Nature of bond length / bond angle	Description	Molecular parameters of *p*-anisaldehyde	Nature of bond length / bond angle	Description	Molecular parameters of *p*-anisaldehyde
C_1-C_2	p_1	1.507 Å	C_2-C_3-H_{10}	β_3	119.8°
C_2-C_3	p_2	1.530Å	C_4-C_3-H_{10}	β_4	119.6°
C_3-H_{14}	q_1	1.100Å	C_3-C_4-C_5	α_4	120.0°
C_1-C_7	a	1.498Å	C_4-C_5-C_6	α_5	119.9°
C_3-C_4	p_3	1.519Å	C_4-C_5-H_{12}	β_5	120.0°
C_3-H_{10}	q_2	1.100Å	C_5-C_6-H_{12}	β_6	119.8°
C_4-C_5	p_4	1.420Å	C_5-C_6-C_1	α_6	120.0°
C_5-C_6	p_5	1.503Å	C_6-C_1-C_2	α_1	120.0°
C_5-H_{12}	q_3	1.100Å	C_5-C_6-H_{13}	β_7	119.9°
C_6-H_{13}	q_4	1.100Å	C_6-C_1-H_{13}	β_8	119.8°
C_7-H_{14}	f	1.113Å	C_1-C_2-C_7	ψ_1	119.9°
C_7-O_8	r	1.208Å	C_6-C_1-C_7	ψ_2	120.2°
C_4-O_{11}	d	1.355Å	C_1-C_7-O_8	θ	122.9°
O_{11}-X	b	1.613Å	C_7-C_1-H_{14}	ϕ	118.6°
			H_{14}-C_7-O_8	ν	119.9°
C_1-C_2-C_3	α_2	120.0°	C_5-C_4-O_{11}	τ_1	120.1°
C_2-C_1-H_9	β_1	119.8°	C_3-C_4-O_{11}	τ_2	119.7°
C_3-C_2-H_9	β_2	119.9°	C_4-O_{11}-X	δ	109.8°
C_4-C_2-C_3	α_3	120.1°			

Vibrational band assignment

IR and Raman spectra contain a number of bands at specific wavenumbers. The aim of the vibrational analysis is to decide which of the vibrational modes give rise to each of these observed bands. The assignments for the fundamental modes of vibrations have been made on the basis of band position shape and intensity. Vibrational frequencies of similar compounds like cresol, paracetamol have been taken into consideration for the assignment of fundamental vibrations of *p*-anisaldehyde[4, 5].

C—H Vibrations : The heteroaromatic structure shows the presence of C—H stretching vibrations[6, 7] in the region 3100–3000 cm^{-1} for asymmetric stretching and 2900–2810 cm^{-1} for symmetric stretching modes of vibration. Heterocyclic compound C—H vibration absorption bands are usually weak; in many cases it is too weak for detection. In the present work, the bands observed at 2841 and 3072 cm^{-1} in the FTIR spectrum and the bands at 2847 and 3078 cm^{-1} in FT Raman spectrum are assigned to C—H symmetric and C—H asymmetric stretching vibrations respectively.

C—C ring stretching : Benzene has two doubly degenerate modes and two non-degenerate modes of vibration due to stretching[8, 9] of C—C bonds. The ring C—C stretching vibrations occur in the region 1625–1430 cm^{-1}. In the present work the bands observed at 1427 and 1511 cm^{-1} in the FTIR spectrum and the bands at

1433 and 1516 cm^{-1} in FT Raman spectrum are assigned to ring C—C symmetric and asymmetric stretching vibrations respectively.

C=O stretching: The pyrimidines and purines have been extensively studied on account of their intrinsic interest as important biological compounds. Due to tautomerism, pyrimidines substituted with hydroxyl groups are generally in the keto form and, therefore, have a strong band due to carbonyl group. The carbonyl group exhibits a strong absorption band due to C=O stretching vibration and is observed in the region 1850–1550 cm^{-1}. Because of its high intensity[10–12] and the relatively interference-free region in which it occurs, this band is reasonably easy to recognize. In the present work, the band observed at 1685 cm^{-1} in the FTIR spectrum and the band at 1688 cm^{-1} in FT Raman spectrum are assigned to C=O stretching mode of vibration respectively.

C—O stretching: A great deal of structural information can be derived for the exact position of carbonyl stretching absorption peak. The interaction of carbonyl group with the other group present in the system does not produce such drastic and characteristic changes in the frequency of C—O stretch as it does by N—H stretch. Further if a compound contains carbonyl group the absorption caused by C—O stretching is generally strong among the strongest present[13, 14]. Consideration of these factors leads to assigning the strong band in the FTIR spectrum at 1217 cm^{-1} and the band at 1223 cm^{-1} in FT Raman spectrum is assigned to C—O stretching mode of vibration.

C—H bending: The C—H deformation frequencies in benzene and its derivatives are found to occur in the region 1200–1050 cm^{-1}.[15, 16] In the present work the bands observed at 1065 and 1161 cm^{-1} in the FTIR spectrum and the bands at 1072 and 1166 cm^{-1} in the FT Raman spectrum of *p*-anisaldehyde are assigned to C—H symmetric and asymmetric bending respectively.

C—C—C bending: The C—C—C bending bands always occur below 600 cm^{-1}. Isopropyl benzenes[17] have a medium intensity of band in the region 560–480 cm^{-1}. In the present work the band observed at 486 cm^{-1} and the band at 568 cm^{-1} are assigned to C—C— C symmetric and asymmetric bending modes of vibration respectively.

C—C—O bending: In saturated aliphatic ketones C—C—O deformation[13] is found to occur in the range 660–580 cm^{-1}. Based on the above, the band observed at 608 cm^{-1} in the FTIR spectrum and the band at 612 cm^{-1} in the FT Raman spectrum of *p*-anisaldehyde is assigned to C—C—O symmetric mode of deformation. Similarly the band observed at 658 cm^{-1} in the FTIR spectrum is assigned to C—C—O asymmetric mode of deformation respectively.

RESULTS AND DISCUSSION

A normal coordinate analysis for *p*-anisaldehyde has been carried out using the observed frequencies from the FTIR and FT Raman spectra. The evaluation of force constants has been made on the basis of general valence force field by applying Wilson's F-G matrix method[18]; the method of kinetic constants has been used to solve the secular equation. The correctness of the assignment has been verified by evaluating the potential energy distribution using the relation % PED = $F_{ij}L_{ij}^2/\lambda_j$. The observed frequencies along with the assignment, calculated force constants and potential energy distribution are presented in Table-2.

TABLE-2
VIBRATIONAL SPECTRAL ASSIGNMENTS, POTENTIAL CONSTANTS (10^2 N/m) AND PED VALUES OF *p*-ANISALDEHYDE

Symmetry coordinate	Frequency (cm^{-1})		Assignment	Force consnstant (10^2 N/m)	PED (%)
	FTIR	FT Raman			
A′ Species					
S_1	1427 s	1433 s	Ring C—C symmetric stretching	6.7966	92
S_2	2841 m	2847 m	C—H symmetric stretching	5.8913	95
S_3	1685 m	1688 s	C═O stretching	15.4596	89
S_4	1217 s	1223 m	C—O stretching	8.3497	86
S_5	1396 m	1400 w	C—C stretching	7.3490	91
S_6	2936 s	2942 s	C—H stretching	5.4926	95
S_7	1262 m	1266 s	O—X stretching	7.8745	97
S_8	486 s	480 w	C—C—C symmetric bending	0.8019	83
S_9	1065 s	1072 ms	C—H symmetric bending	0.6198	62
S_{10}	462 w	–	C—C═C bending	0.8102	93
S_{11}	608 m	612 m	C—C—O symmetric bending	0.6107	58
S_{12}	1025 s	–	C—C—H bending	0.6115	56
S_{13}	766 w	768 s	C—C═O bending	0.4154	49
S_{14}	540 m	–	H—C═O bending	0.5196	52
S_{15}	590 m	–	C—O—X bending	0.6117	41
A″ Species					
S_{16}	1511 s	1516 vs	Ring C—C asymmetric stretching	6.8401	89
S_{17}	3072 m	3078 m	C—H asymmetric stretching	5.9522	98
S_{18}	568 ms	–	C—C—C asymmetric bending	0.8196	62
S_{19}	1161 m	1166 w	C—C—H asymmetric bending	0.6197	51
S_{20}	519 s	512 w	C—C asymmetric bending	0.8154	43
S_{21}	658 m	–	C—C—O asymmetric bending	0.7148	59

The initial set of force constants for *p*-anisaldehyde were taken from the molecules of similar environment and they were subsequently refined using successive approximation technique. The force constants evaluated for this compound are compared with the previous works[15, 19]. The force constant of C—C stretching vibration of the compound is found to be around 6.79 × 10^2 N/m as expected and they contribute PED value of more than 92%. The symmetric and asymmetric C—H stretching vibrations of the molecule exhibit a force constant around 5.8 and 5.9 × 10^2 N/m respectively, contributing to the PED value of more than 95%. Similarly the force constant of C—O stretching vibration of the compound is found to be around 8.3 × 10^2 N/m and they contribute PED value of more than 86%. A PED value of around 89% is found to be calculated for

C═O stretching vibrations whose frequency is assigned around 1685 cm^{-1}. Apart from these major stretching vibrations, the compounds also have a number of bending vibrations. The force constants for these vibrations have been evaluated to be around 0.8–1.2 × 10^2 N/m as expected and contribute to the PED values of 40–60%. The potential energy distribution confirms the correctness of the frequency assignment done based on the C_s point group symmetry thus providing a strong support to the present work.

Conclusion

Thus a complete vibrational band assignment of *p*-anisaldehyde has been carried out using infrared and Raman spectra on the basis of C_s point group symmetry. A systematic set of symmetry coordinates has been constructed and the potential force constants have been calculated. The PED calculation regarding the normal modes of vibration provide a strong support for the frequency assignment on the highly complex molecule.

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