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Vibrational Spectra and Normal Coordinate Calculations of *para*-Methoxy Benzoic Acid

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The laser Raman, infrared and FTIR spectra of *p*-methoxy benzoic acid have been recorded in the regions 4000–30 cm^{-1}, 4000–600 cm^{-1} and 4000–200 cm^{-1} respectively in the solid phase. The observed frequencies of *p*-methoxy benzoic acid have been assigned to various modes of vibrations in terms of fundamentals, overtones and combinations assuming C_s point group symmetry. The normal coordinate analysis has been carried out to check the validity of the assignments. The potential energy distribution associated with normal modes was also reported here. The assignments of fundamental vibrations agree well with the calculated frequencies.

INTRODUCTION

A number of workers[1,2] have extensively studied the vibrational spectra of benzoic acid and substituted benzoic acids. Rastogi *et al.*[1] have reported about vibrational study of 3,5-dinitro benzoic acid. However, there is no report on the virational spectra of *p*-methoxy benzoic acid. It is a white coloured crystal soluble in alcohol and ether and used in medicine as an insect repellent and ovicide. Hence the aim of this investigation is to study the vibrational spectra of this compound by infrared FTIR and laser Raman studies and to assign the fundamental frequencies.

EXPERIMENTAL

Spectroscopically pure crystalline chemical, *p*-methoxy benzoic acid, was obtained from SISCO Chemical Industries, Bombay. The IR spectrum was recorded in the region 4000–600 cm^{-1} on Perkin-Elmer IR 983; the FTIR spectrum was recorded in the region 4000–200 cm^{-1} on Shimadzu FTIR 8101 spectrophotometer in KBr pellet method and the laser Raman spectrum was recorded in the region 4000–30 cm^{-1} on Carry Model 82 grating spectrophotometer using 488 nm radiation from an argon ion laser excitation operating at 4 W. The spectral width was 2 cm^{-1} and the scanning speed was 30 cm^{-1} min^{-1}. The frequencies for all sharp bands are accurate to $\pm$ 1 cm^{-1}.

Normal coordinate calculations: The major result of this work is the normal coordinate calculation which is very essential in providing a reliable and accurate

vibrational assignment of the normal modes of the molecule. Wilson's F.G. matrix method with the modified computer programme by Mink and Mink[3] was used for the normal coordinate analysis. The molecule under investigation belongs to C_s symmetry which leads to two types of vibrations distributed as

$$\Gamma_{CS} = 21a' \text{ (planar)} + 9a'' \text{ (non-planar)}$$

The 30 fundamental vibrations are active in both Raman and IR. Further a′ gives rise to polarized lines whereas a″ gives depolarized lines in the Raman spectrum. We have treated benzyl group as a local symmetry group in our assignment of the skeletal modes. Hence we assumed the degeneracy of some of the fundamentals as a result of this local symmetry. The structural parameters employed in the present work are assumed from benzene derivatives.

TABLE-1
INITIAL AND FINAL FORCE CONSTANTS OF *p*-METHOXY BENZOIC ACID

Types of constants	Parameters	Coordinates involved	Initial value	Final value
Diagonal constants				
Stretching	f_D	C=C	10.05	10.12
	f_d	C—C	5.13	5.42
	f_s	C—H	4.50	4.52
Bending	f_α	CCC	0.45	0.47
	f_β	CCC	0.55	0.51
	f_θ	CCC	0.50	0.58
	f_δ	CCH	0.31	0.39
Interaction constants				
Stretch-stretch	f_{Dd}	CC CC	0.06	0.12
	f_{Sd}	CH CC	0.19	0.34
	f_{SD}	CH CC	–0.19	0.09
Stretch-bend	$f_{d\alpha}$	CC CCC	0.30	0.18
	$f_{d\beta}$	CC CCC	0.12	0.21
	$f_{d\theta}$	CC CCC	0.18	0.28
	$f_{s\beta}$	CH CCC	0.30	0.41
	$f_{D\delta}$	CC CCH	0.34	0.44
	$f_{S\theta}$	CH CCC	0.20	0.18
Bend-bend	$f_{\beta\beta}$	CCC CCC	0.67	0.55
	$f_{\beta\delta}$	CCC CCH	0.08	0.10
	$f_{\alpha\theta}$	CCC CCC	0.71	0.78
	$f_{\alpha\delta}$	CCC CCH	0.07	0.18

The initial force constants were taken from similar benzene derivatives. This set of force constants was subsequently refined by keeping few interaction constants fixed throughout the refinement process, so that only 20 of the 30 force constants were refined. The final force constants obtained from the calculations,

which are the most important information regarding the dynamics of the molecules, are also given in Table-1. The potential energy distributions obtained using final set of force constants are given in Table-2 along with the observed and calculated frequencies, nature of absorption bands in terms of mixing vibrational assignments.

TABLE-2
OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR *p*-METHOXY BENZOIC ACID

Species	IR/ Intensity	FTIR/ Intensity	Laser Raman/ Intensity	Calculated frequency	Assignemnts/PED
	3975 w				3080 + 890
	3940 w				3200 + 732
	3833 w				2 × 1361 + 1100
	3800 w				2 × 1070 + 1670
	3602 w				2 × 1215 + 1158
	3275 m				O—H stretching*
a′	3200 m			3212	C—H stretching 94
a′	3155 m			3142	C—H stretching 92
a′	3080 m		3090 w	3070	C—H stretching 86
a′			3041 m	3053	C—H stretching 78
	2975 w				C—H stretching*
	2846 m				2 × 992 + 852
	2045 w	2030 w			2 × 506 + 1027
	1685 m	1690 m			C=O stretching*
a′	1670 m			1652	C=C stretching 72
			17634 vs	1630	C=C stretching 91
		1605m	1605 m	1614	C=C stretching 88
		1465 w	1479 vw		3090–1605
	1451 w	1450 w	1446 w		O—H in-plane bending*
a′	1361 m	1360 w		1349	C—C stretching 74
a′			1318 m	1310	C—OCH_3 stretching 65
		1300 m	1298 s		C—O stretching*
a′		1260 m		1250	C—C stretching 86
	1245 m		1235 w		C—O stretching*
a′	1215 m		1209 m	1216	C—C stretching 89
a′	1180 w		1182 w	1169	C—OCH_3 in-plane bending 61
a′	1158 s		1161 m	1142	C—COOH stretching 55
a′	1100 w	1108 w		1119	C—H in-plane bending 48
a′	1070 w			1061	C—H in-plane bending 67

Species	IR/ Intensity	FTIR/ Intensity	Laser Raman/ Intensity	Calculated frequency	Assignemnts/PED
a′	1029 w	1027 s	1038 s	1022	C—H in-plane bending 45
a′	1010 w			998	C—H in-plane bending 58
a″	992 m		980 vw	975	C—H out-of-plane bending 54
a″		925 s		912	C—H out-of-plane bending 61
a″	890 m		890 w	877	C—H out-of-plane bending 42
a″	852 m	845 s	853 s	842	C—H out-of-plane bending 59
	840 m	825 w			C—H out-of-plane bending*
	788 m	775 vs			O—C—O out-of-plane bending*
a′	732 m			723	C—C—C out-of-plane bending 61
	698 m	698 s	700 w		C=O out-of-plane bending*
a″	630 vs	632 s	643 w	629	C—C—C in-plane bending 68
	611 w	615 vs			C—C—O rocking*
a″		550 vs		534	C—OCH_3 out-of-plane bending 49
a′		506 s		515	C—C—C in-plane bending 59
a″		400 w		386	C—C—C out-of-plane bending 59
		378 w			C—OH in-plane bending*
a′		330 w	325 w	312	C—C—C in-plane bending 56
a′		328 w		310	C—COOH in-plane bending 47
a″		225 m		213	C—C—C out-of-plane bending 64
		214 m			C—OH out-of-plane bending*
		210 m		200	C—COOH out-of-plane bending 52
			111 s		Lattice vibration
			89 s		Lattice vibration

vs—Very strong; vw—Very week; s—Strong; ms—Medium strong; m—Medium; w—Week; *—Group vibrations.

RESULTS AND DISCUSSION

The observed frequencies along with their relative intensities of *p*-methoxy benzoic acid and probable assignments are presented in Table-2. The observed spectra are explained on the basis of C_s point group symmetry for the molecule under consideration by assuming carboxylic —COOH and the methoxy — OCH_3 moieties as point masses.

Phenyl ring vibrations

Carbon vibrations: Benzene has two doubly degenerate modes e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}) and two non-degenerate modes b_{2u} (1310 cm^{-1}) and a_{1g} (995 cm^{-1}) due to skeletal C—C stretching. The actual positions are determined not so much by the nature of substituents but by the form of substituents around the ring.[4] The doubly degenerate e_{2g} modes corresponding to

C—C stretching in benzene are assigned to the bands at 1670, 1634, 1605, 1361, 1260 and 1215 cm^{-1} in the *p*-methoxy benzoic acid. These assignments are in close agreement with literature.[5]

The in-plane carbon bending vibrations are obtained from the non-degenerate b_{1u} (1010 cm^{-1}) and degenerate e_{2g} (606 cm^{-1}) modes of benzene. The e_{2g} (606 cm^{-1}) degenerate mode splits into two totally symmetric vibrations under C_s symmetry and they are observed at 630 and 506 cm^{-1} in *p*-methoxy benzoic acid, which agree well with the work of Mukherjee *et al.*[6]

The carbon out-of-plane bending vibrations are generally assigned to the non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. The former is found to be constant in substituted benzenes and it is observed at 732 cm^{-1} in *p*-methoxy benzoic acid. The degenerate e_{2u} (404 cm^{-1}) vibration splits into two non-totally symmetric components and the bands are observed at 400 and 225 cm^{-1}. These assignments are in close agreement with the literature values[7].

C–H Vibrations: The substituted benzene gives rise to C—H stretching vibrations in the region 3100–3000 cm^{-1}, C—H in-plane bending in the region 1100–1000 cm^{-1} and C—H out-of-plane bending in the region 980–800 cm^{-1}. They are not affected by the nature of the substituents. In *p*-methoxy benzoic acid the frequencies 3200, 3115, 3080 and 3041 cm^{-1} are assigned to C—H stretching and these frequencies are in favourable agreement with Silver *et al.*[8] The frequencies 1100, 1070, 1029 and 1010 cm^{-1} are assigned to C—H in-plane bending and these assignments are in good agreement with the literature values.[9] The C—H out-of-plane bending assignments are made to the bands 992, 925, 890 and 845 cm^{-1} and these assignments are in good agreement with Varsanyi.[10]

C—OCH_3 vibrations: In *p*-methoxy benzoic acid, carbon methoxy stretching vibrations are assigned to the band at 1318 cm^{-1} while the band at 1180 cm^{-1} is assigned to C—OCH_3 in-plane bending vibration. The C—OCH_3 out-of-plane bending vibration is observed at 550 cm^{-1}. The above conclusions agree favourably well with the literature values.[11]

C—COOH Vibration: Usually the band around 1185 cm^{-1} is assigned to C—COOH stretching, 330 cm^{-1} is assigned to C—COOH in-plane bending and 209 cm^{-1} is assigned to C-COOH out-of-plane bending in *p*-methoxy benzoic acid the medium in laser Raman at 1161 cm^{-1} is assigned to C—COOH stretching; the band at 328 cm^{-1} to C—COOH in-plane and the band at 210 cm^{-1} to C—COOH out-of-plane bending.

Group vibrations: Group vibrations are determined in terms of the motions that the nuclei in a structural group in the molecule undergo during the vibration and they appear in fairly constant regions of the spectrum.

COOH group vibrations: The band observed at 3275 cm^{-1} has its origin in the O—H stretching vibration region. The C=O stretching is a characteristic frequency of carboxylic group. The dipole moment derivatives of the COO in-plane bending mode and C=O stretching mode are very large. Splitting with marked frequency differences may be expected for these modes. Further it is known that the out-of-plane C=O stretching mode should have a higher frequency than that of the in-plane mode[12]. The characteristic band appearing at

1685 cm^{-1} is assigned to C=O stretching vibration. OH in-plane bending and C—O stretching vibrations appear at 1451 cm^{-1} and 1298 cm^{-1} respectively. OH in-plane bending and C—O stretching vibrations are closely coupled. The OCO rocking vibrations appear at 775 cm^{-1} and 615 cm^{-1}. The OH out-of-plane bending vibrations and C=O out-of-plane bending vibrations give rise to bands at 840 cm^{-1} and 698 cm^{-1} respectively. C—OH in-plane bending vibrations and C—OH out-of-plane bending vibrations are assigned to frequencies 378 cm^{-1} and 222 cm^{-1}. These assignments well agree with Ahmad *et al.*[13]

O—CH_3 group vibraions: The band at 2975 cm^{-1} in *p*-methoxy benzoic acid is assigned to C—H stretching in methyl group. The C—O stretching vibration is assigned to the band at 1245 cm^{-1}. These assignments agree well with Prabhakaran *et al.*[14].

Potential energy distribution

To check whether a chosen set of assignments contributes maximum to the potential energy associated with normal coordinates of the molecules, the potential energy distribution (PED) has been calculated using the relation

$$PED = \frac{F_{ii}L_{ia}^2}{\lambda_a}$$

where F_{ii} are the force constants refined by the damped least square technique. The highest PED contributions corresponding to each of the observed frequencies alone are lined in the present work. The information supports and confirms the present assignments, particularly for the low frequency modes. The close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

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