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FT-IR and FT-Raman Spectra and Normal Coordinate Analysis of Poly methyl methacrylate

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ABSTRACT

Poly methyl methacrylate (PMMA) is a widely used polymer with various applications. Fourier transform infrared and Raman spectra of PMMA were recorded in range of 4000 – 400 cm⁻¹ and 4000 – 100 cm⁻¹, respectively. In the present investigation, detailed assignments of the observed fundamental bands of PMMA have been analyzed in terms of peak positions and relative intensities. With hope of providing more and effective information on the fundamental vibrations, a normal coordinate analysis has also been performed on PMMA by assuming C_s symmetry. The simple general valence force field (SGVFF) has been employed in normal coordinate analysis and the potential energy distribution (PED) has been calculated for each fundamental vibration. The PED contribution corresponding to each of the observed frequencies shows the reliability and accuracy of spectral analysis.

Keywords: Infrared, Raman, poly methyl methacrylate, potential energy distribution, vibrational spectroscopy.

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INTRODUCTION

Vibrational spectroscopy plays an important role in elucidation of molecular structure. A detailed analysis of its IR and Raman spectra provides an insight into intramolecular as well as intermolecular interactions. Poly methyl methacrylate (PMMA) is commercially the most important member of a range of acrylic polymers which may be considered structurally as a derivative of acrylic acid. Polymers made from PMMA are used primarily in plastic applications. PMMA is a high transparent common polymer, presenting excellent mechanical and chemical properties [1]. PMMA is put to a wide variety of uses, such as manufacture of dental [2] and medical applications [3]. As a useful biomaterial, PMMA is also used as bone cement and

cosmetic surgery with good safety records [4]. Being light, PMMA was recognized as an ideal glazing material for the aircraft industry and found it's first used in 1936 on the new British fighter planes [5]. Recently, PMMA was used as an extrinsic fibre optic displacement sensor for the measurement of amplitude and frequency of vibrations [6].

Polymethacrylates give a series of characteristic infrared bands at 7.8, 8.1, 8.55 and 8.7 μm and at 13.35 μm . The alcoholic constituents of these polymers may be differentiated by the characteristic bands [7-8]. Kaczmarczyk *et al.* [9] reported a high intensity C=O stretching vibration band of the carbonyl ester group at 1725 cm^{-1} in the IR region. Hummel *et al.* [10] reported that PMMA compounds can be easily distinguished by bands in-between $1260 - 1150\text{ cm}^{-1}$ involving C-O-C stretching mode. Partial vibrational analyses of PMMA were found in literature. The steric structure was determined by NMR spectroscopy of the methylene protons [11-12]. Stroupe and Hughes [13] proposed a (5/2)-helix model of isotactic PMMA whereas Spevacek and Schneider [14] discussed the possibility of the formation of a double helix. Takahashi *et al.* [15] reported the intermolecular interaction in mixed monolayers of isotactic and syndiotactic poly (methyl methacrylate) at the air-water interface. Furthermore, Liquori *et al.* [16] reported the formation of a crystalline complex between syndiotactic PMMA and isotactic PMMA in the molar ratio 2:1. In their paper, they noted that the Fourier Transform of a (5/2)-helix was inconsistent with the intensity distribution of the fiber X-ray diagram of isotactic PMMA. Spectroscopic properties of blends formed of PMMA doped with Europium (III) acetylacetonate have been studied recently by photoacoustic spectroscopy (PAS) and photoluminescent (PL) spectroscopy [17]. Further excitation spectra, excited state decay times, and quantum efficiency have also been evaluated by them. Direct insertion probe pyrolysis mass spectrometry (DIP-MS) analysis of PMMA was performed by Uyar *et al.* [18] to determine the thermal stability of the polymer. High-resolution ^1H NMR spectra of solutions of isotactic and syndiotactic conformations of PMMA in toluene- d_8 were measured by Spevacek and Schneider [19].

Although PMMA has been a widely used commercial polymer, there are no substantial vibrational assignments reported in the literature. Hence, the objectives of the present investigation are (i) to assign all observable vibrational frequencies of PMMA using FT-IR and FT-Raman spectra, (ii) to obtain the reasonable set of potential constants, (iii) to check the initial assignments through potential energy distribution, (iv) to estimate the amount of mixing skeletal modes of vibration, and (v) to discuss the nature of absorption bands.

RESULTS AND DISCUSSION

The FTIR and FT Raman spectra of PMMA are shown in Figure 2 and 3 respectively. The observed spectra of the compound are analyzed on the basis of C_s point group symmetry. The observed and calculated frequencies of PMMA in the infrared and Raman along with their relative intensities and proposed assignments are summarized in Table 1. Assignments have been made on the basis of relative intensities, magnitude of frequencies and mainly on the normal coordinate calculations as well as the literature data of polymers of similar structure. The purity of the normal modes is further confirmed by calculating the PED to each fundamental vibration.

Side Chain modes

The backbone consists of polyethylene chain with $\text{H}_3\text{C}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ and $\text{H}_3\text{C}-$ moieties attached to every second carbon atom. The asymmetric stretches and the symmetric

stretches of the methyl (CH₃) group in one structural repeat unit have been calculated at 3011 and 3002 cm⁻¹ and 2835 and 2732 cm⁻¹, respectively. The asymmetric stretches are assigned to Raman frequency at 3013 cm⁻¹ and IR frequency at 3000 cm⁻¹. The symmetric stretches are assigned to 2840 cm⁻¹ in both Raman and IR spectra and at 2732 cm⁻¹ in the Raman spectrum. The assigned values are in good agreement with that in the literature [26]. The observed values agree well with the calculated values and the PED shows that they are pure modes. The observed frequency at 1483, 1447, 1437, 1398 cm⁻¹ in IR and 1487 and 1446 cm⁻¹ in Raman has been assigned to the deformation modes of the CH₃ group which agrees with the calculated values 1480, 1446, 1430 and 1388 cm⁻¹. The rocking modes depend upon the environment of the CH₃ group. The frequencies calculated at 905 and 869 cm⁻¹ have major contributions from rocking modes. They are observed at 920 and 880 cm⁻¹ in the IR. They are in agreement with isotactic 1,4-trans poly (1, 3-pentadiene) (940 and 860 cm⁻¹) [27]. The bands at 1147 cm⁻¹ and 1050 cm⁻¹ in the infrared and at 1067 cm⁻¹ and 1046 cm⁻¹ in Raman are assigned to the CH₃ twisting and these values agree quite well with the calculated values 1138 cm⁻¹, 1064 cm⁻¹, and 1042 cm⁻¹. The wagging modes of the CH₃ group are observed at 1197 cm⁻¹ and 1187 cm⁻¹ in the IR and the Raman spectra respectively. Further, the bands at 1060 cm⁻¹ and 1127 cm⁻¹ in the Raman spectrum are assigned to the CH₃ wagging modes and they agree not only with the calculated values but also agree favorably with those of Samuel *et al* [28].

The C=O and the C-O bands often dominates the IR spectrum and the C-C modes dominates the Raman spectrum [29]. The C=O stretching usually lies in the region between 1500 to 2000 cm⁻¹. PMMA shows a band at 1724 cm⁻¹ assigned to C=O stretching. C-O stretching frequency is one of the intense bands that appear in the finger print region. This frequency is rather variable and usually appears within 1000 – 1400 cm⁻¹. Medium bands at 1267 cm⁻¹ and at 1239 cm⁻¹ are assigned to C-O stretching modes. The C=O in plane and out of plane bending is assigned to a very strong Raman band at 810 cm⁻¹ (calculated value 805 cm⁻¹) and a medium strong band in IR at 750 cm⁻¹ (calculated value 739 cm⁻¹) respectively. The C-O in plane and out of plane bending in one structural repeat unit has been calculated at 725 and 595 cm⁻¹ and 361 and 291 cm⁻¹, respectively. These bands are observed in the Raman spectrum at 733 and 600 cm⁻¹ and 367 and 300 cm⁻¹, respectively.

Backbone modes.

PMMA consists of three monomeric residue units in every structural repeat unit. The very strong IR band and strong Raman band at 2953 cm⁻¹ (calculated 2951 cm⁻¹) are assigned to methylene (CH₂) asymmetric stretching vibrations. The weak Raman band at 2760 cm⁻¹ is also assigned to CH₂ symmetric stretching. The deformation mode of CH₂ has been calculated at 1381 cm⁻¹ and observed at 1381 cm⁻¹. The above conclusion agrees well with those of Zwarich *et al.* [30] and Green and Harrison [31]. The CH₂ wagging and twisting are calculated at 1364 and 1320 cm⁻¹. The weak band appearing at 840 cm⁻¹ (calculated at 828 cm⁻¹) has been identified as CH₂ rocking vibration which in keeping with the assignment proposed by Srivastava *et al.* [32] and P.Nallasamy *et al.* [33].

Mixed Modes

These are generally dispersive nature. An interesting feature of the dispersive modes of PMMA is their tendency to bunch either towards the zone centre or at the zone boundary. The C-C in plane bending modes are assigned to 560, 513, and 487 cm⁻¹ and C-C out of plane bending modes are assigned to 267, 200 and 163 cm⁻¹ of the Raman spectra. The C-C torsion is assigned to 140 cm⁻¹ of Raman. PED is very useful to distinguish between pure and mixed modes.

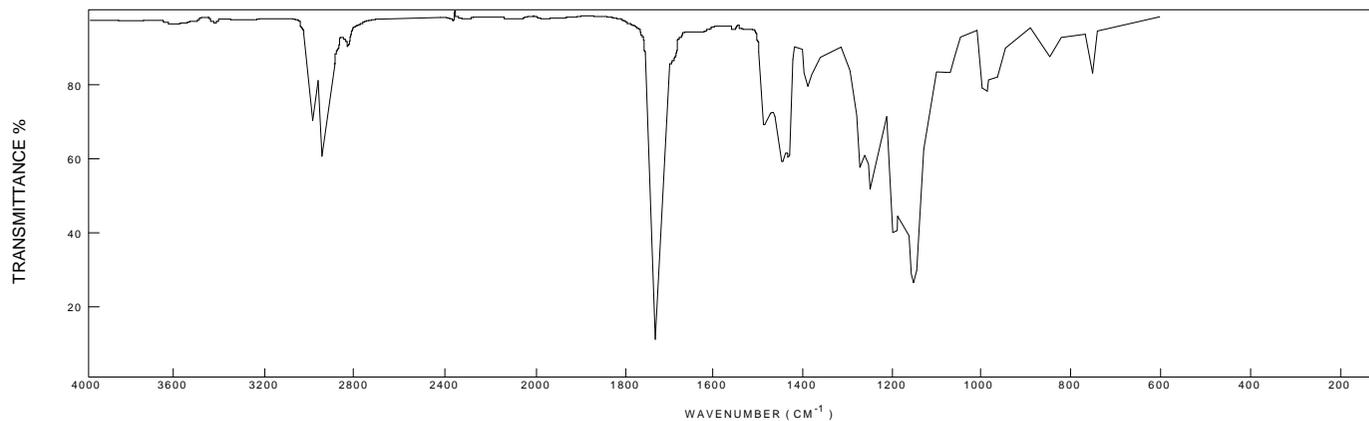


FIG 2 : FT - IR SPECTRUM OF OF POLY METHYL METHACRYLATE

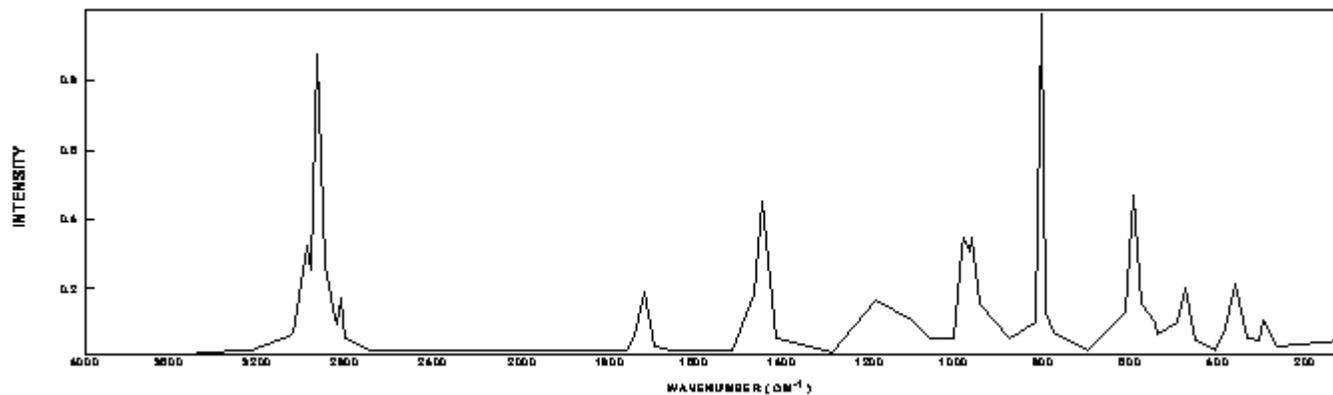


FIG 3 : FT - RAMAN SPECTRUM OF POLY METHYL METHACRYLATE

EXPERIMENTAL

Samples of PMMA were obtained from M/S Aldrich with high purity and used as such without any further purification. The laser power was fixed at 200 mW at the sample and the spectral resolution at 2 cm^{-1} . The FTIR spectrum of PMMA was recorded in solid phase on Bruker IFS 66V FTIR spectrometer in the region $4000 - 200\text{ cm}^{-1}$. The FT-Raman spectrum of the same compound is also recorded on the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at $1.06\mu\text{m}$ line with a scanning speed of $30\text{ cm}^{-1}\text{ min}^{-1}$ with a spectral width of 2.0 cm^{-1} .

Theoretical Consideration

Despite the extensive experimental work, it is impossible to obtain complete information on the polymer structure on the basis of these data only without spectroscopic analysis. The effective use of IR and Raman spectroscopy for polymer investigation is possible only with the sufficiently rigorous conclusions from the normal coordinate analysis. Thus the calculation methods are inevitable to obtain a complete assignment and determine the character of the bands in the vibrational spectra of polymers. The unit structure of PMMA is shown in Figure 1. The maximum number of potentially active observable fundamentals of a polymer in which the chemically repeating unit of a polymer chain contains N atoms equal to $3N-4$, ignoring three translation degrees of freedom and rotation of the polymer molecule about its own axis. The internal coordinates of PMMA are classified in accordance with IUPAC. The distribution of the normal modes among the irreducible representations under C_s point group symmetry is given by $\Gamma_{\text{vib}} = 26a' + 15a''$. Its forty one normal modes of vibration consists of 26 planar and 15 non-planar modes of species a' and a'' , respectively. All the vibrations are both infrared and Raman active. In the present work, both in-plane and out-of-plane vibrations are treated completely.

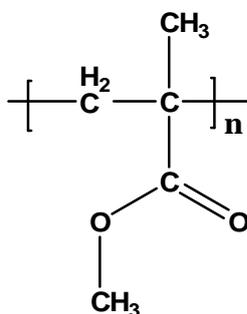


Figure 1 Structure of poly methyl methacrylate

Normal Coordinate Analysis

With the aim of gaining more complete knowledge on the vibrational spectra of PMMA a normal coordinate analysis calculation was carried out using Wilson's FG matrix method [20-22]. The simple valance force field is adopted to analyze both in-plane and out-of-plane vibrations. The computer program for normal coordinate calculations developed by Furher *et al.* [23] was suitably modified and used in the present work. The structural parameters employed in the present work are taken from Sutton table [24]. The initial sets of force constants are transferred from allied molecules. The force constants are refined by the least square method [25] to give the best agreement between the calculated and the observed wave numbers.

Potential Energy Distribution

To analyze the purity of the modes, the potential energy distribution (PED) associated with each normal modes are calculated using the relation

$$PED = \frac{F_{ii}L_{ik}^2}{\lambda_k}$$

Where F_{ii} are the force co. λ_k L_{ik} the normalised amplitude of the associated element (i, k) and λ_k , the eigen value for the corresponding vibrational frequency of the element k. The PED contribution corresponding to each of the observed frequencies over 10% are alone listed in the present work. The observed frequencies along with the assignments of various modes of vibration, calculated frequencies and PED are presented in Table 1.

Table 1 Observed and theoretical wavenumbers (cm⁻¹) and potential energy distribution (PED) for poly methyl methacrylate

Species	Observed frequency		Calculated wave number	Assignment	% PED
	FTIR	FTR			
a'		3013 m	3011	C-H asym stretching in CH ₃	88v _{asym} CH ₃
a'	3000 m		3002	C-H asym stretching in CH ₃	91v _{asym} CH ₃
a'	2953 vs	2953 ms	2951	C-H asym stretching in CH ₂	86v _{asym} CH ₂
a'	2840 w	2840 m	2835	C-H sym stretching in CH ₃	80v _{sym} CH ₃
a'		2760 w	2756	C-H asym stretching in CH ₂	82v _{sym} CH ₂
a'		2733 vw	2732	C-H sym stretching in CH ₃	89v _{sym} CH ₂
a'	1727 vs	1730 m	1724	C=O stretching	72v _{C=O} + 21v _{CC}
a'	1483 m	1487 m	1480	CH ₃ deformation	71δCH ₃ + 11δCH ₂
a'	1447 ms	1453 ms	1446	CH ₃ deformation	68δCH ₃ + 16δCH ₂
a'	1437 ms		1430	CH ₃ deformation	59δCH ₃ + 14δCH ₂
a'	1398 m		1388	CH ₃ deformation	74δCH ₃ + 16δCH ₂
a'		1387w	1381	CH ₂ deformation	61δCH ₂ + 10δCH ₃
a''	1367vw		1364	CH ₂ wagging	60ωCH ₂ + 20τCH ₂
a''		1327 w	1320	CH ₂ twisting	55τCH ₂ + 30ωCH ₂
a'	1267 w		1261	C-O stretching	74v _{C-O} + 11v _{C=O}
a'	1239 m	1240 w	1238	C-O stretching	82v _{C-O} + 12v _{CC}
a''	1197 m	1187 w	1190	CH ₃ wagging	49ωCH ₃ + 22τCH ₃
a''		1160 w	1155	CH ₃ wagging	56ωCH ₃ + 30τCH ₃
a''	1147 ms		1138	CH ₃ twisting	46τCH ₃ + 24ωCH ₃

a''		1127 w	1121	CH ₃ wagging	42 ω CH ₃ + 35 τ CH ₃
a''		1067 w	1064	CH ₃ twisting	51 τ CH ₃ + 31 ω CH ₃
a''	1050 w	1046 vw	1042	CH ₃ twisting	48 τ CH ₃ + 34 ω CH ₃
a'		1027vw	1022	C-C stretching	68 ν_{CC}
a'	990 m	990 m	981	C-C stretching	74 ν_{CC}
a'	967 w	970 m	968	C-C stretching	65 ν_{CC}
a'	913 vw	920 vw	905	CH ₃ rocking	71 ρ CH ₃ + 19 δ CH ₃
a'		880w	869	CH ₃ rocking	68 ρ CH ₃ + 21 δ CH ₃
a'	840 w	840 w	828	CH ₂ rocking	74 ρ CH ₂ + 20 δ CH ₂
a'	807 vw	810 vs	805	C=O in plane bending	66 $\beta_{C=O}$ + 30 β_{C-O}
a''	750 m		739	C=O out of plane bending	60 $\eta_{C=O}$ + 14 η_{C-O}
a'		733 w	725	C-O in plane bending	52 β_{C-O} + 16 $\rho_{C=O}$
a'		600 ms	595	C-O in plane bending	58 β_{C-O} + 28 $\rho_{C=O}$
a'		560 w	550	C-C in plane bending	62 β_{C-C} + 18 β_{C-CH_2}
a'		513 vw	502	C-C in plane bending	59 β_{CC} + 21 $\beta_{C=O}$
a'		487 m	478	C-C in plane bending	69 β_{CC} + 11 β_{C-CH_3}
a''		367 m	361	C-O out of plane bending	59 η_{C-O} + 12 $\eta_{C=O}$
a''		300 m	291	C-O out of plane bending	56 η_{C-O} + 10 $\eta_{C=O}$
a''		267 w	250	C-C out of plane bending	62 η_{C-C} + 16 η_{CH_2}
a''		200 w	192	C-C out of plane bending	59 η_{C-C} + 14 η_{CH_3}
a''		163 vw	169	C-C out of plane bending	51 η_{C-C} + 11 $\eta_{C=O}$
a''		140 vw	144	C-C torsion	42 τ_{CC} + 22 η_{C-C} + 10 η_{CH_3}

vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; v, stretching; δ , deformation; β , in-plane bending; η , out-of-plane bending; ρ , rocking; ω , wagging; τ , twisting.

CONCLUSION

A complete vibrational spectra and normal coordinate analysis is available in the present work for poly methyl methacrylate. The close agreement between the observed values and the calculated frequencies and the PED calculations confirms the validity of the present assignments.

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