

Normal Coordinate Analysis of Polyvinyl Acetate

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Fourier transform infrared (FT-IR) and FT-Raman spectra of polyvinyl acetate have been recorded in the range of 4000-400 and 4000-100 cm^{-1} , respectively. In the present investigation, a detailed assignment of the observed fundamental bands of polyvinyl acetate has been analyzed in terms of peak position and relative intensities. With the hope of providing more and effective information on the fundamental vibrations, a normal coordinate analysis has been performed on polyvinyl acetate by assuming C_s symmetry. The simple general valance force field (SGVFF) method has been employed in normal coordinate analysis. The potential energy distribution for each fundamental vibration has also been calculated. The potential energy distribution contribution corresponding to each of the observed frequencies shows the reliability and accuracy of spectral analysis.

Key Words: FTIR, FT-Raman, Polyvinyl acetate, Force field, Vibrational analysis.

INTRODUCTION

Polyvinyl acetate can be prepared by the free radical polymerization of vinyl acetate. Polymerization is carried out commercially by bulk, solution, suspension or emulsion polymerization techniques^{1,2}. The polyvinyl acetate is soluble in aromatic solvents, alcohol and ester and is used mainly in adhesives³, lacquers and gramophone records⁴. The dried polyvinyl acetate latex was found to have a wide application in the industries of synthetic fibers, adhesives, coatings and paints⁵. Currently, polyvinyl acetate is added to the vulcanizable rubber compositions to improve the processability of the compound which improves the tear strength and modulus of the rubber⁶. The polymer was found to reduce the number of mixing stages during compounding, resulting

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in lowering of the cost of operation and increasing plant productivity. Recently, flax fiber was modified using polyvinyl acetate and was found to improve interfacial behaviour of the fiber and matrix adhesion⁷. Structural study of polyvinyl acetate and its blends by fluorescence spectroscopy was carried out by Atvars *et al.*⁸. An integrated Thermogravimetry (TGA)-FTIR analysis on polyvinyl acetate was carried out by Compton *et al.*⁹. According to them a sharper peak at *ca.* 380 °C indicated weight loss due to water vapour and an organic material. Thermal degradation of polyvinyl acetate using TGA indicated the polymer degraded in two stages, around 360 and 440 °C, corresponding to deacetylation and disintegration of the polyolefinic backbone, respectively¹⁰⁻¹². The structural conformations of polyvinyl acetate repeating unit were studied by nuclear magnetic resonance spectroscopy^{13,14}. The polymer electrolytes composed of polyvinyl acetate with various stoichiometric ratios of lithium perchlorate and ammonium thiocyanate were studied by Selvasekarandian *et al.*^{15,16}. The FTIR and Laser Raman spectroscopy have been used to monitor polymer-salt complex formation, ion-ion and ion-polymer interactions as a function of salt concentration. An attempt has been made in the present work to analyze completely the vibrational spectra of polyvinyl acetate through FTIR and FTR as normal coordinate analysis.

EXPERIMENTAL

Spectroscopically pure chemicals were obtained from Aldrich Chemicals, USA and used as such for recording purposes. The FTIR spectrum of PVAC was recorded in solid phase on Bruker IFS 66V FTIR spectrometer in the region 4000-400 cm^{-1} . The FT-Raman spectrum of the same compound was also recorded in the region 4000-100 cm^{-1} on the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line with a scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 20 cm^{-1} . The frequencies for all sharp bands were accurate to $\pm 1 \text{ cm}^{-1}$.

Theoretical considerations: The structural unit of PVAC is shown in Fig. 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 is equal to (3N-4), ignoring three translational degrees of freedom and rotation of the polymer molecule about its own axis. With the aim to gain a complete knowledge of the vibrational spectra of polyvinyl acetate a normal coordinate calculation has also been carried out using Wilson's FG matrix method¹⁷⁻¹⁹. The computer program developed by Furher *et al.*²⁰, with suitable modification is used to calculate the vibrational frequencies and potential energy distribution (PED). The theoretical calculations on the vibrational modes are made by an appropriate model of the conformation of the polymer chain. In such an approach, it is imperative that

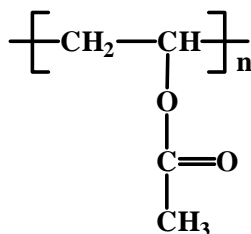


Fig. 1. Structure of polyvinyl acetate

a reliable force field be identified so that the molecular motions can be accurately described. Hence, a simple valance force field (SGVFF) show for both in plane and out of plane vibrations in normal coordinate calculation permits the transfer of valance force constants from allied molecules. The validity of the force constants helps to evaluate the calculated frequencies which can be compared with observed frequencies. The symmetry possessed by a molecule helps to determine and classify the actual number of fundamental vibrations of the system. The observed spectrum is explained on the basis of C_s point group symmetry. The 32 fundamental vibrations are distributed as $\Gamma_{\text{vib}} = 22a' + 10a''$. All vibrations are both infrared and Raman active. The observed frequencies have been assigned to various modes of vibration on the basis of intensity, frequency and from normal coordinate calculations.

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

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

where F_{ii} are the force constants, L_{ik}^2 the transformation matrix associated element (i, k) and λ_k the eigen value corresponding to the vibrational frequency of the element k. The observed frequencies along with the assignments of various modes of vibration, calculated frequencies and PED using final set of force constants are presented in Table-1.

RESULTS AND DISCUSSION

FTIR and FT Raman spectra of polyvinyl acetate are shown in Figs. 2 and 3, respectively. The observed spectra of the compound are analyzed on the basis of C_s point group symmetry. The purity of the normal modes is further confirmed by calculating the PED to each fundamental vibration.

TABLE-1
OBSERVED AND THEORETICAL WAVENUMBERS (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR POLYVINYL ACETATE

Species	Observed frequency		Calcd. Wave no.	Assignments	PED (%)
	FTIR	FTR			
a'	2973 m	2973 m	2970	C-H asym stretching in CH_3	$88\nu_{\text{asy}}\text{CH}$
a'	2933 ms	2940 vs	2933	C-H asym stretching in CH_2	$92\nu_{\text{asy}}\text{CH}$
a'	2853 w	2853 w	2856	C-H sym stretching in CH_3	$90\nu_{\text{sy}}\text{CH}$
a'	2733 vw		2728	C-H sym stretching in CH_2	$89\nu_{\text{sy}}\text{CH}$
a'	2546 vw		2537	C-H stretching	$95\nu\text{CH}$
a'	2466 vw		2458	C-H stretching	$96\nu\text{CH}$
a'	1740 vs	1733 m	1736	C=O stretching	$84\nu\text{C=O}$
a''		1493 w	1490	CH asym deformation in CH_3	$88\nu_{\text{asy}}\text{CH}$
a''	1433 ms	1443 ms	1442	CH_2 asym deformation	$79\delta_{\text{asy}}\text{CH}$
a''	1373 vs	1383 m	1381	CH_3 asym deformation	$69\delta_{\text{asy}}\text{CH} + 21\beta\text{CH}$
a'		1357 m	1250	CH_2 sym deformation	$74\delta_{\text{asy}}\text{CH} + 14\beta\text{CH}$
a'		1300 vw	1289	CH_3 sym deformation	$68\delta_{\text{sy}}\text{CH} + 28\beta\text{CH}$
a'	1240 vs		1233	C-H in plane bending	$71\beta_{\text{CH}} + 19\delta_{\text{CH}}$
a'	1127 s	1133 m	1129	C-O stretching	$79\nu_{\text{C-O}} + 11\nu_{\text{CH}_3}$
a'		1087 vw	1081	C-O stretching	$84\nu_{\text{C-O}} + 10\nu_{\text{CH}_3}$
a''	1040 s		1032	CH_2 wagging	$74\omega\text{CH}_2 + 19\tau\text{CH}_2$
a''	1027 vs	1023 m	1026	CH_2 twisting	$59\tau\text{CH}_2 + 28\omega\text{CH}_2$
a''	947 ms	947 vw	938	CH_3 wagging	$68\omega\text{CH}_3 + 30\tau\text{CH}_3$
a''		933 vw	926	CH_3 twisting	$60\tau\text{CH}_3 + 24\omega\text{CH}_3$
a'		900 vw	891	C-C stretching	$72\nu_{\text{CC}} + 28\nu_{\text{C-O}}$
a'		887 m	880	C-C stretching	$69\nu_{\text{CC}} + 14\nu_{\text{C-O}}$
a'		830 w	820	C-O-C in plane bending	$71\beta_{\text{COC}} + 19\rho\text{CH}_3$
a'	800 m	800 w	806	CH_3 rocking	$68\rho\text{CH}_3 + 22\beta_{\text{COC}}$
a'		740 vw	734	CH_2 rocking	$79\rho\text{CH}_2 + 11\beta_{\text{COC}}$
a'	660 w		656	C=O in plane bending	$88\beta\text{C=O} + 10\beta\text{C-CH}_2$
a''	633 m	633 ms	628	C=O out of plane bending	$69\eta\text{C=O} + 14\eta\text{C-CH}_2$
a'		577 w	568	C- CH_2 in plane bending	$74\beta\text{C-CH}_2 + 11\beta_{\text{CH}}$
a'		477 vw	475	C- CH_3 in plane bending	$80\beta\text{C-CH}_3 + 10\beta_{\text{CH}}$
a''		407 w	401	C-H out of plane bending	$66\eta\text{CH} + 19\eta\text{CO}$
a''		347 vw	333	C- CH_2 out of plane bending	$71\eta\text{C-CH}_2 + 24\eta\text{C=O}$
a''		313 vw	308	C- CH_3 out of plane bending	$68\eta\text{C-CH}_3 + 30\eta\text{C=O}$
a''		160 vw	168	C-C torsion	$51\eta\tau\text{CC} + 22\eta\text{C-O}$

ν = stretching; δ = deformation; β = in-plane bending; η = out-of-plane bending;
 ρ = rocking; ω = wagging; τ = twisting.

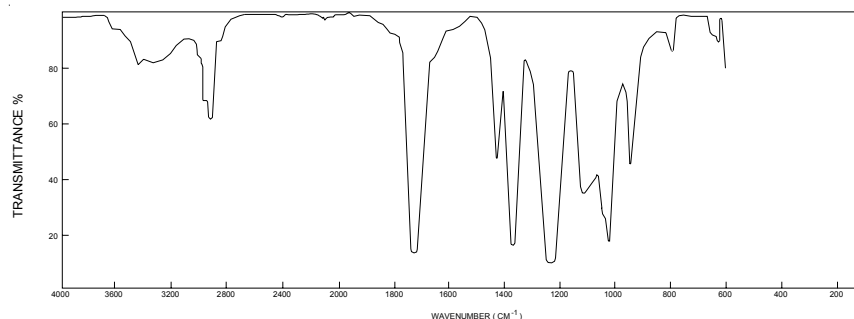


Fig. 2. FT-IR Spectrum of polyvinyl acetate

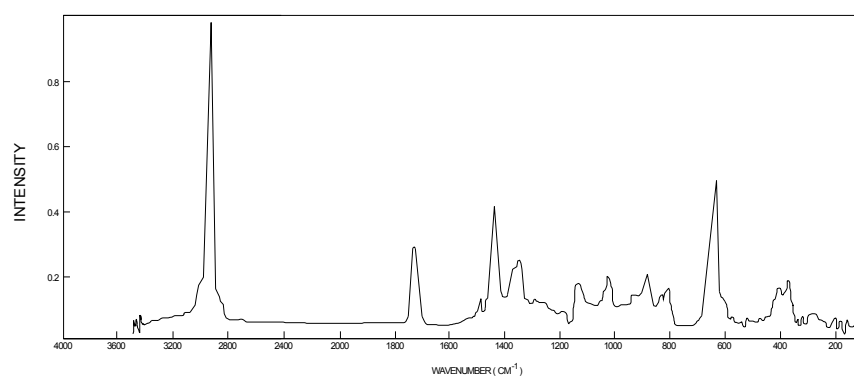


Fig. 3. FT-Raman spectrum of polyvinyl acetate

C-H Stretching: The C-H stretching of the methyl (CH_3) group is highly localized and is generally observed in the frequency range $3000\text{--}2800\text{ cm}^{-1}$ in all polymers²¹⁻²³. The asymmetric stretching mode of C-H in CH_3 is assigned to a medium band of 2973 cm^{-1} in both Raman and infrared spectra. The symmetric stretching mode of CH_3 is assigned to a weak band of 2853 cm^{-1} in both Raman and infrared spectra. The asymmetric stretching mode of methylene (CH_2) is assigned to a very strong band of 2933 cm^{-1} in Raman spectra and a medium strong band of 2940 cm^{-1} in infrared spectra. The symmetric stretching mode of CH_2 is assigned to a weak band of 2733 cm^{-1} . Very weak infrared bands at 2546 and 2466 cm^{-1} have been assigned to methine (C-H) stretching vibrations. The calculated values agree well with the observed values and the PED confirms these modes as pure modes.

C=O Stretching: The stretching vibration of carbonyl group ($\text{C}=\text{O}$) is normally found²¹ in the region $1800\text{--}1700\text{ cm}^{-1}$. A very strong infrared band at 1740 cm^{-1} and a medium Raman band at 1733 cm^{-1} have been assigned to $\text{C}=\text{O}$ stretching vibrations. The calculated wave number, 1736 cm^{-1} agrees well with the observed frequency as well as literature value²⁴. The PED

calculation for C=O stretching reveals that the stretching is pure mode with 84 % contribution.

C-O Stretching: The C-O stretching vibrations of ester are generally observed²⁵ in the region of 1300-1000 cm^{-1} . Two C-O stretching bands of PVAC are assigned as follows: First one is a very strong band of 1127 cm^{-1} at infrared spectra and 1133 cm^{-1} in Raman spectra. The second one is assigned to a very weak Raman band at 1087 cm^{-1} . The calculated wave numbers 1129 and 1081 cm^{-1} agree well with the observed frequencies. The PED reveals that both the stretching are mixed mode with 79 % C-O stretching and 11 % CH_3 stretching and 84 % C-O stretching and 10 % CH_3 stretching, respectively.

C-C Stretching: Symmetrical bands such as C=C and C-C manifest themselves by giving intense bands in the Raman spectra²⁶. The two C-C stretching vibrations of polyvinyl acetate have been assigned to medium Raman band at 887 cm^{-1} and weak Raman band at 900 cm^{-1} . They agree with the calculated frequencies 891 and 880 cm^{-1} , respectively. The PED for both the C-C stretching reveals a mixed mode with contributions from C-H stretching (28 %) and C-O stretching (14 %).

Methyl deformation: The observed frequency at 1493 cm^{-1} in Raman spectra, 1433 cm^{-1} in both Raman and infrared spectra, 1373 and 1383 cm^{-1} in infrared and Raman spectra respectively, have been assigned to the asymmetric degenerate deformation modes of the methyl groups which agree with the calculated values 1490, 1442 and 1381 cm^{-1} . The PED calculations for asymmetrical deformation shows all are pure modes except at 1350 cm^{-1} where there is 21 % contribution of C-H in plane bending. The calculated frequencies at 1350 and 1289 cm^{-1} have been matched with the weak Raman band at 1300 cm^{-1} and a very strong Infrared band at 1240 cm^{-1} . This observed mode is assigned as the symmetric deformation mode of the methyl group. The PED calculations for symmetrical deformation shows both the assignments are in mixed mode with 14 and 28 % contribution of C-H in plane bending respectively. The above assignment agrees well with the literature values²⁷.

In plane bending: At lower frequencies, the assignments become more complex since the bands no longer correspond to pure motions. They are complex mixtures of different internal coordinates or mixing of low lying deformations with lattice modes. In the case of vibrational analysis of a rather complex vibrating molecular system, the lower the symmetry the greater the attention it deserves. The Raman spectrum is particularly rich in the lower frequency range, where there is little absorbance in the infrared spectrum²⁸.

The C- CH_2 and C- CH_3 in plane bendings are assigned to weak Raman at 577 cm^{-1} and a very weak Raman at 475 cm^{-1} which agrees closely with

the calculated wave numbers 568 and 475 cm^{-1} , respectively. The PED calculations for C-CH₂ and C-CH₃ shows that the assignments are of mixed modes with 16 and 10 % contribution of C-H in plane bending, respectively. C=O in plane bending has been assigned to a weak infrared at 660 cm^{-1} which agrees quite well with the calculated value of 656 cm^{-1} . The frequencies calculated at 800 cm^{-1} (In both infrared and Raman) and 740 cm^{-1} have major contribution from rocking modes. The above mentioned conclusion agrees quite well with Nallasamy *et al.*²⁹. The PED data indicates a mixed mode assignment with contribution from C-O-C out of plane bending.

Out of plane bending: The C-H, C-CH₂ and C-CH₃ out of plane bending are assigned to weak Raman at 407 cm^{-1} , a very weak Raman at 347 cm^{-1} and a very weak Raman at 313 cm^{-1} which agrees with calculated wave numbers 401, 333 and 308 cm^{-1} , respectively. The PED calculation shows that all the assignments are of mixed modes. The C-H and C-CH₂ out of plane bending have 19 and 24 % contribution, respectively from the C-O out of plane bending. C-CH₃ has a contribution of 30 % of C=O out of plane bending. C=O out of plane bending is assigned to a medium infrared and a medium strong Raman at 633 cm^{-1} which agrees well with the calculated values at 628 cm^{-1} . The CH₃ wagging and twisting are assigned to 947 cm^{-1} (both in IR and Raman) and 933 cm^{-1} in Raman. The CH₂ wagging is assigned to 1040 cm^{-1} in IR and the wagging is assigned to 933 cm^{-1} .

Conclusion

A complete vibrational spectral analysis is available in the present work for polyvinyl acetate. The close agreement between the observed and calculated frequencies and potential energy distribution calculations confirm the validity of the present assignments.

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