Spectra and vibrational analysis of poly propanone

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Fourier transform infrared and Raman spectra of this polymer have been recorded in range of 4000 - 400 cm^{-1} and 4000 - 100 cm^{-1}, respectively. In this present investigation, detailed assignments of the observed fundamental bands of poly propanone 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 poly propanone by assuming C_s symmetry. The simple general valence force field (SGVFF) method 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.

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1. Introduction

Vibrational spectroscopy plays a vital role in the elucidation of molecular structure. The vibrational characteristics of any compound are determined by its conformational state and the nature of the force field. The present work focuses in the use of FTIR and Raman spectroscopy in vibrational studies. With the introduction of Fourier transform method, the IR spectroscopy has been used by many in the research field [1]. The IR spectrum characterises the vibrational modes of the molecule and its quantitative interpretation aided by computer data analysis allows researchers to explore polymer molecules and its tacticity and neighbouring group interactions [2] - [3]. Raman spectroscopy is a form of vibrational which arises from a change in the polarizibility and it given structural insights involving interplay between atomic positions, electron distribution and intermolecular forces [4]-[6]. To date, IR and Raman spectroscopic methods have contributed substantially to our understanding of the behaviour of polymers [7]-[10], its derivatives [11], elastomers [12-13], polymerised 1,3-dienes [14-15], polymer electrolytes[16-17] and polymer based composites [18-19]. The polymer under study is poly propanone which is polymerized from 2-propanone or methyl ketone. The monomer, 2-propanone is colourless, flammable liquid used extensively as a solvent, as in nail-varnish remover, and for making acrylic plastics. It boils at 56.5°C, mixes with water in all proportions, and has a characteristic odour.

Some spectroscopic work has been done on propanone derivatives. Yaylayan et al. [20] studied carbonyl-amine reaction and enolization of l-hydroxy-2-propanone by FTIR Spectroscopy. An NMR study on enolization of l-p-chlorophenyl-l-hydroxy-2-propanone was studied by Warren et al [21]. Phenyl-2-propanone was investigated by Allen et al. [22] by using capillary gas chromatography combined with vapor-phase FTIR**.**

In the present work, the FTIR and FT-Raman spectra of poly propanone were recorded and assignment of the observed frequencies were assigned to the fundamental vibrational modes of the molecule. A normal co-ordinate analysis was carried out for the proper assignment of the vibrational frequencies. This could not only help the proper assignment of the vibrational frequencies but also present a complete picture about the molecular dynamics of poly propanone.

2. Experimental

The poly propanone sample was obtained from Sigma with high purity and used as such without further purification to record the spectra. The FTIR spectrum of this compound has been recorded in the region 400-4000 cm^{-1} by a Brukker IFS 66V spectrometer with a scanning speed of 30cm^{-1} min^{-1} with a spectral width of 2.0cm^{-1}. The FT Raman spectrum of poly propanone was also recorded in the same instrument with a FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064μ line with 200 mW power in the wave number range 4000 - 100 cm^{-1}. The frequencies of all sharp bands were accurate to ± 1 cm^{-1}.

3. Normal coordinate analysis

The structure of poly propanone is show 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 more complete knowledge of the vibrational spectra of poly propanone, a normal co-ordinate analysis has been carried out in the present work.

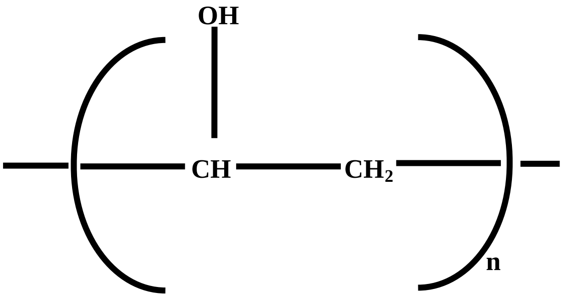

Fig. 1. Molecular Structure of Polypropanone.

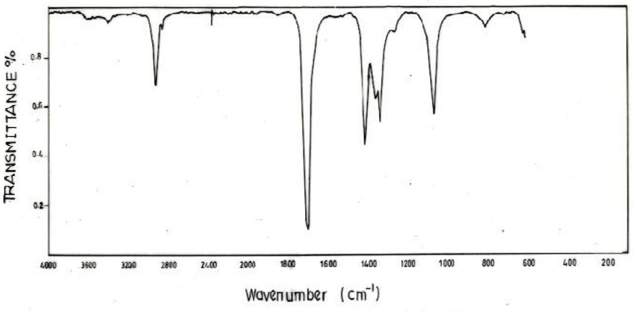

Fig. 2. FTIR spectrum of Polypropanone.

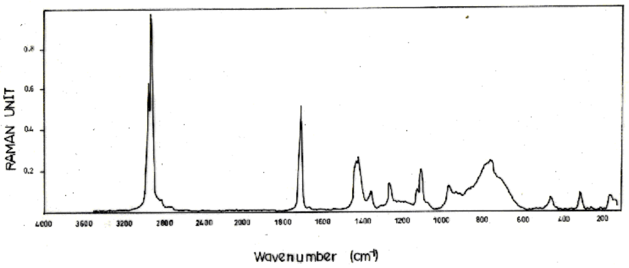

Fig. 3. FT Raman spectrum of polypropanone.

The computer program developed by Fuhrer et al [23] was used after a suitable modification to calculate vibrational frequencies and potential energy distributions (PED). This program follows the Wilson F-G matrix method [24]-[26] of vibrational analysis. The molecule under investigation, poly propanone, possesses a C_s symmetry. The structural parameters necessary for this compound is taken from the Sutton table [27]. Under C_s point group symmetry, the 20 fundamental vibrations are distributed as 13 in plane vibrations of a’ species and 7 out of plane vibrations of a" species. All the vibrations are both infrared and Raman active. A simple valance force field was adopted for both in plane and out of plane vibrations and the force constants were refined by the least square method [28]. The potential energy distributions (PED) calculated using final set of force constants are presented in the Table 1.

4. Results and discussions

The FTIR and FT-Raman spectra of PVA are shown in Figure 2 and 3. The observed spectra of the compound are analyzed on the basis of C_s point group symmetry. 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.

Stretching vibrations

C=O stretching

The stretching vibration of carbonyl group (C=O) is normally found in the region 1800 -1700 cm^{-1} [29]. A very strong infrared band at 1703 cm^{-1} and a medium strong Raman band at 1713 cm^{-1} have been assigned to C=O stretching vibrations. The calculated wave number, 1711 cm^{-1} agrees well with the observed frequency as well as literature value [30]. The PED calculation for C=O stretching reveals that the stretching is pure mode with 89% contribution.

C-C stretching

Symmetrical bands such as C-C and C=C manifest by giving intense band in the Raman spectra [31]. The two C-C stretching vibrations of poly propanone have been assigned to a medium strong Raman band at 1063 cm^{-1} and weak Raman band at 1120 cm^{-1}. They agree with the calculated frequencies 1056 and 1111 cm^{-1}, respectively. The above conclusions agree favorably with those of Zwarich et al. [32] and Green & Harrison [33].The PED for both the C-C stretching reveals a mixed mode with contributions from C-H stretching.

Methylene modes

The Raman bands and IR bands at 2947 and 2920 cm^{-1} are assigned to CH_2 asymmetric stretching vibrations. The IR band at 2853 and the Raman band at 2813cm^{-1} are assigned to CH_2 symmetric stretching vibrations. The methylene bending mode is commonly ascribed to a strong infrared band near 1475 cm^{-1} [34]. The medium strong IR band at 1407 cm^{-1} is assigned to CH_2 deformation. The weak Raman band at 1420 cm^{-1} is also assigned to CH_2 deformation mode. The weak bands at 747 and 727cm^{-1} in the Raman spectra were assigned to CH_2 rocking. This is in good agreement with Edwards and Farwell [35]. The twisting and wagging CH_2 normal modes occurs between 1151cm^{-1} and 1350 cm^{-1}. The CH_2 wagging modes are identified at a IR band at 1340 cm^{-1} and at a Raman band at 1353cm^{-1}. CH_2 twisting mode is assigned to 1260cm^{-1} in both the IR and the Raman spectra and 1173 cm^{-1} in the FI-IR spectra. The above mentioned conclusions agree quite well with those of Srivastava et al [36].

In- Plane and Out -of -Plane Bending

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 spectrum [9].C=O in plane bending has been assigned to a weak infrared at 807cm^{-1} which agrees quite well with the calculated value of 800 cm^{-1}. The above mentioned conclusion agrees quite well with Nallasamy et. al. [37]. The PED data indicates a mixed mode assignment with contribution from C-H in plane bending. In the present work, the band occurring at 460cm^{-1} in Raman is assigned to C-C-C in plane bending.

Out- of- Plane Bending

C=O out of plane bending is assigned to a weak Infrared at 680 cm^{-1} which agrees well with the calculated values at 671 cm^{-1}. The C-C-C out of plane bending is assigned to a Raman band at 310. This value agrees well with the calculated values. The C-C torsion is assigned to 168 cm^{-1} in Raman which agrees well with those of Samuel and Mohan [38] and the PED result reveals a mixed mode with a contribution from C=O out of plane bending.

The remaining observed frequencies are listed in Table 1. The frequencies obtained are accounted for the allowed combinations, overtones and fundamentals. These values give additional support for the allocations.

Potential energy distributions

The potential energy distribution is expressed in terms of the percentage contribution of each force constant or the displacement coordinate or symmetry coordinate to the potential energy of each normal mode. The potential energy distribution (PED) has been calculated using the relation

$$\mathbf{PED} = \frac{\mathbf{F_{ii}\,L^{2}_{ik}}}{\boldsymbol{\lambda_k}}$$

where F_{ii} are the force constant, 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 potential energy distribution calculated confirms the validity of the assignments. In the normal coordinate analysis potential energy distribution plays an important role for the characterization of the relative contributions from each internal coordinate to the potential energy associated with a particular normal coordinate of the molecule. The contribution to the potential energy from the individual diagonal elements gives rise to a conceptual link between the empirical analysis of the vibrational spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computational of the normal modes. The PED contributions corresponding to each of the observed frequencies are listed in Table 1.

5. Conclusion

A complete vibrational spectral analysis is available in the present work for poly propanone. The close agreement between the observed and calculated frequencies and PED calculations confirm the validity of the present assignments.

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Table 1. Observed and calculated frequencies and and potential energy distribution for poly propanone.

Species	**Observed Wave Number & Re. Intensity**		**Calculated wave Number cm^{-1}**	**Assignments**	**PED %**
	Infrared cm^{-1}	**Raman cm^{-1}**			
	3400 w			2947 + 460	
a'	2947 m	2947 s	2945	C-H asymmetric stretching in CH_2	$91\nu_{asy}CH$
a'	2920 s	2920 vs	2918	C-H asymmetric stretching in CH_2	$95\nu_{asy}CH$
a'	2853 w		2851	C-H symmetric stretching in CH_2	$89\nu_{sym}$ CH
a'		2813 w	2809	C-H symmetric stretching in CH_2	$92\nu_{sym}CH$
a'	1703 vs	1713 ms	1711	C=O stretching	89ν C=O

Species	Observed Wave Number & Re. Intensity		Calculated wave Number cm^{-1}	Assignments	PED %
	Infrared cm^{-1}	Raman cm^{-1}			
		1433 w		2920 - (2 x 747)	-
a'		1420 w	1415	CH_2 deformation	78δ CH_2 + 14ρ CH_2
a'	1407 ms		1405	deformation CH_2	70δ CH_2 +21ρ CH_2
	1367 w			2x680	
a''		1353 w	1351	CH_2 wagging	74ω CH_2+20τ CH_2
a''	1340 w		1330	CH_2 wagging	69ω CH_2+26τ CH_2
a''	1260w	1260 m	1248	CH_2 twisting	61τ CH_2 + 30ω CH_2
a''	1173 w		1166	CH_2 twisting	58τ CH_2 + 35ω CH_2
a'		1120 w	1111	C-C stretching	71ν C-C + 12ν CH
		1100 w		1260-160	78ν C-O+10ν CH_2
a'	1063 ms		1056	C-C stretching	84ν C-C + 14ν CH
		947		1260-(2x160)	-
a'	807 w		800	C=O in plane bending	82β C=O + 11β CH
a'		745 vw	733	CH_2 rocking	66β C-OH+12β CH_2
a'		727 vw	720	CH_2 rocking	60β C-OH + 28β CH_2
a''	680 vw		671	C=O out of plane bending	59η CO + 22 η CC
a'		460 w	451	C-C-C in plane bending	71β CCC+19β CH
a''		310w	302	C-C-C out of plane bending	66η CCC + 14η CH
a''		160 w	168	C-C torsion	49τ CC + 19 η CO

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

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