

Vibrational spectra and modified valence force field for N,N'-methylenebisacrylamide

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Raman and Fourier transform infrared (FTIR) spectra of N,N'-methylenebisacrylamide have been recorded. A 35-parameter modified valence force field has been evaluated using 38-in-plane vibrational frequencies of the molecule. Unambiguous vibrational assignments have been made using eigenvectors and potential energy distributions computed in the process.

Keywords: Vibrational spectra, Valence force field, FTIR, Raman spectra

1 Introduction

Spectroscopic investigations of amides¹⁻⁴ gained importance as their structure is related to molecules of biological importance such as polypeptides and proteins. The vibrational spectra and normal coordinate analysis of acrylamide have already been investigated by us^{5,6}. In the present paper, vibrational spectra and normal coordinate analysis of N,N'-methylenebisacrylamide (MBAC) has been studied as the later contains two monomers of acrylamide. Further, MBAC is known for its neurotoxic and stimulant properties and used as a cross-linking agent in the preparation of polyacrylamide gels by polymerization of acrylamide.

2 Experimental Details

The sample of MBAC was obtained from Sigma-Aldrich Chemical Co, USA. It was stated of purity as 98% and used without further purification. The infrared spectrum of MBAC was recorded in the range 4000-400 cm⁻¹ by employing KBr pellet technique using Perkin-Elmer Model-983 double beam spectrophotometer. The Fourier transform infrared (FTIR) spectrum of the same compound was measured in the spectral range 490-50 cm⁻¹ using Polytech FIR-3 Fourier transform far infrared spectrophotometer on polyethylene support. The laser Raman spectrum was recorded in the range 4000-30 cm⁻¹ using Dilor Z24 Raman spectrometer with spectral width 4.3 cm⁻¹. The exciting radiation at

488 nm was provided by an organ ion laser operating at 200 mW power. These spectra are shown in Figs 1-3.

3 Results and Discussion

In order to know the amount of mixing among the normal modes and to obtain a more accurate description of the fundamental vibrations of MBAC, a normal coordinate analysis was undertaken. Wilson's GF matrix method was used for the normal coordinate calculations⁷. The molecule was assumed to be planner with C_s point group symmetry as shown in Fig.4. In C_s structure, the 57 fundamentals of the molecule are distributed as 38 in-plane vibrations of a'-species and 19 out-of-plane vibrations of a''-species. All the vibrations are active in both infrared and Raman spectra. In the present paper, the results of a'-species are reported.

The structure parameters, internal coordinate system, method of dealing with redundancies, symmetry coordinates used and the method of computation in the present investigation are the same as those employed for N-methylacrylamide⁸. Thus, a 35-parameter modified valence force field was chosen for the normal coordinate analysis. The initial values of all the force constants were obtained from N-methylacrylamide⁸ except the bending force constant associated with NC'N', which was taken from dimethyl urea⁹. The interaction constants for which no values were available from related systems, were taken initially as zero. The initial set of force constants, thus, obtained was subsequently refined by

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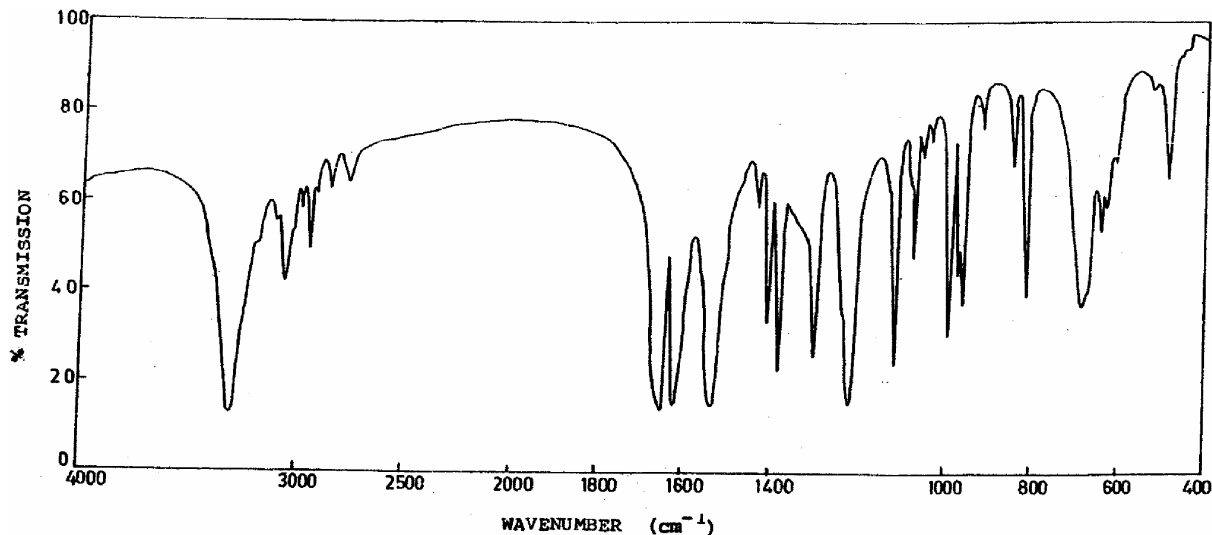


Fig. 1 — Infrared spectrum of N,N'-methylenebisacrylamide

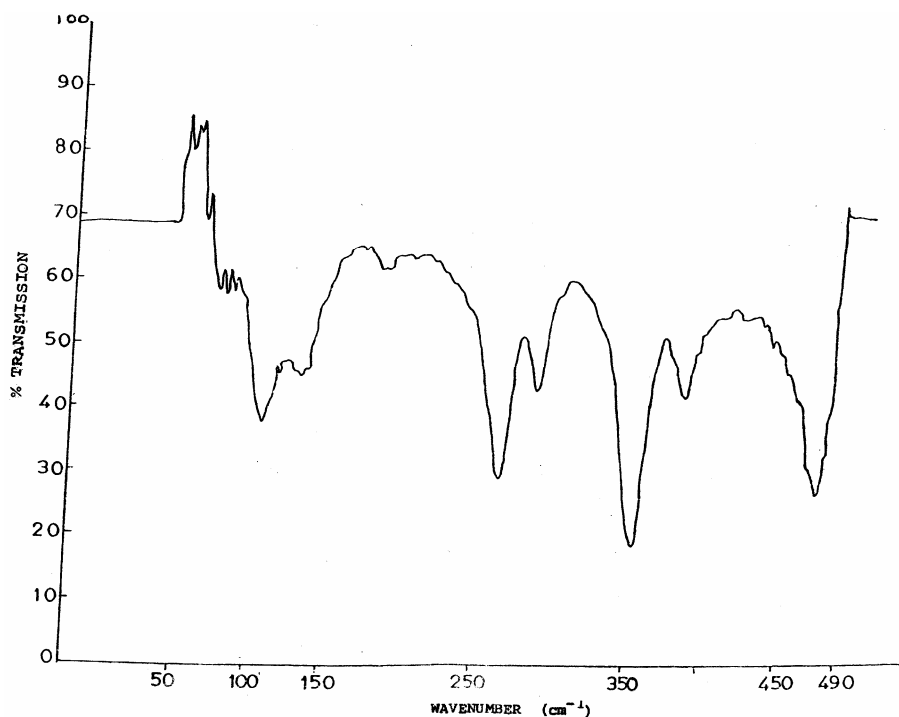


Fig. 2 — Fourier transform infrared (FTIR) spectrum of N,N'-methylenebisacrylamide

an overlay least-squares technique using Schachtschneider's program¹⁰ which was modified to suit the IBM computer with Pentium-IV processor.

The initial refinement of the force constants was carried through several cycles with a damping factor of 0.1 without fixing any of the force constants. In the final refinement, several of the interaction constants along with some diagonal constants were fixed, either because they were correlated, or could be determined inadequately with the available data. Then, damping

was reduced to zero. The refinement was continued until convergence was achieved with an average error of 9 cm^{-1} between the observed (infrared) and calculated frequencies.

The final force constants are presented in Table.1 together with the initial values and dispersions. A summary of vibrational assignments observed and calculated frequencies and potential energy distributions (PED) are presented in Table.2. PED contributions below 10% are not shown.

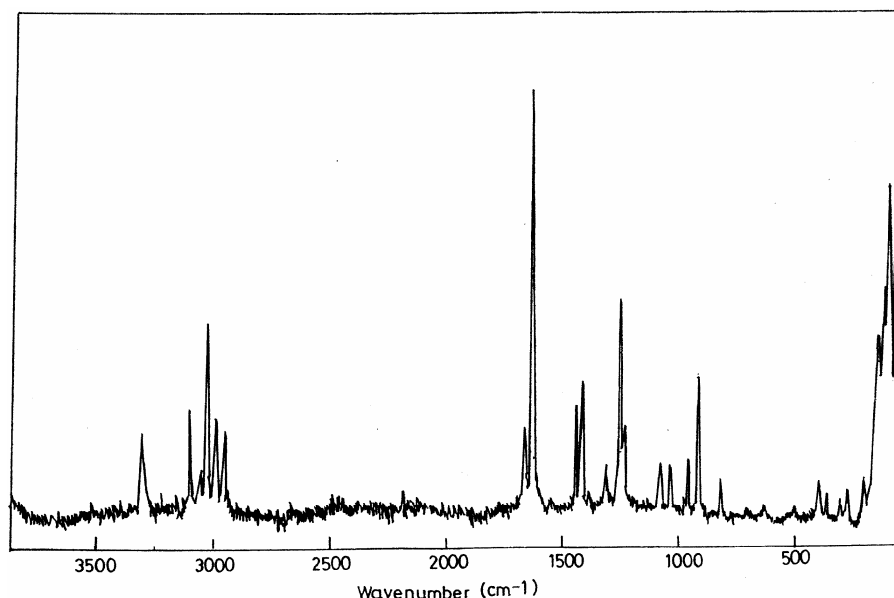


Fig. 3 — Laser Raman spectrum of N,N'-methylenebisacrylamide

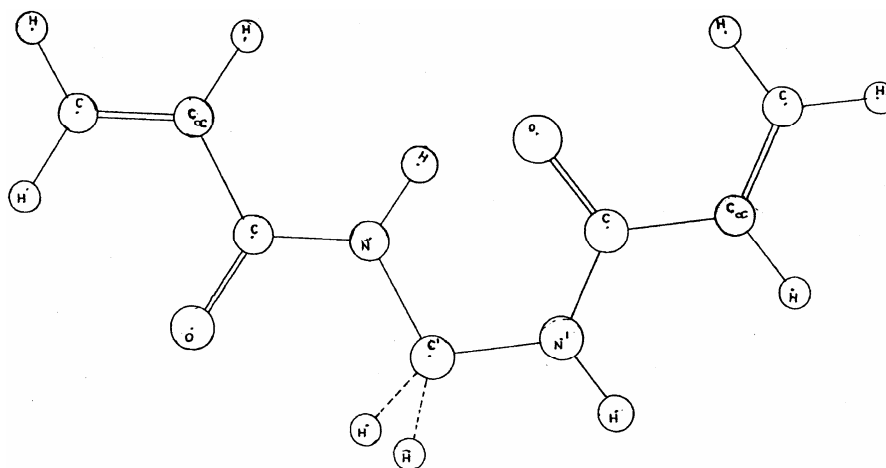


Fig. 4 — Structure of N,N'-methylenebisacrylamide

3.1 Final force field

The calculated and observed frequencies agree within reasonable limits of experimental error and anharmonicity corrections (Table 2), the final values of the force constants, especially, those of the diagonal ones, are close to their initial values. The dispersions of the force constants are small and the constants are comparable to those of related molecules. Hence, the final set of force constants satisfies the conditions of an acceptable force field and can be regarded as a reasonable set. Therefore, these can be used for the vibrational assignment of various fundamentals.

3.2 Vibrational assignments

The vibrational assignments of MBAC are guided by

- (i) Assignment of corresponding bands in the related systems;
- (ii) Infrared and Raman intensities (qualitative) and
- (iii) Potential Energy Distribution is given in Table 2.

The results presented in Table 2 are self-explanatory. However, the following elucidation may be in order in case of some of the important modes.

(a) Vibrations of the amide group

Table 1 — Force constants (in mdyne/Å, mdyne/rad) of in-plane vibrations of N,N' methylenebisacrylamide

Sr. No	Symbol	Coordinates involved	Common atoms	Initial value ^a	Final value	Dispersion ^b
<i>Diagonal force constants</i>						
<i>Stretch</i>						
1	K _d	N-H	-	5.929	6.019	0.0
2	K _f	C _α -H	-	4.225	4.370	0.0
3	K _h	C-H	-	5.066	5.166	0.0
4	K _a	C-N	-	6.697	6.994	0.0
5	K _b	C=O	-	8.373	8.403	0.216
6	K _c	C _α -C	-	6.314	6.513	0.324
7	K _g	C=C _α	-	7.625	7.526	0.0
8	K _e	N-C'	-	3.424	3.699	0.248
9	K _s	C'-H	-	4.715	4.783	0.0
<i>Bend</i>						
10	H _{de}	∠C'NH	-	0.633	0.793	0.361
11	H _{ae}	∠CNC'	-	0.479	0.210	0.271
12	H _{ab}	∠NC=O	-	1.102	1.159	0.0
13	H _{bc}	∠C _α C=O	-	1.018	0.635	0.321
14	H _{ac}	∠C _α CN	-	1.265	1.308	0.394
15	H _{cg}	∠CC _α =C	-	1.607	1.438	0.0
16	H _{cf}	∠CC _α H	-	0.550	0.480	0.316
17	H _{fg}	∠C=C _α H	-	0.233	0.232	0.322
18	H _θ	∠HCH	-	0.815	0.195	0.093
19	H _{gh}	∠C _α =CH	-	0.832	1.048	0.178
20	H _φ	∠HC'H	-	0.514	0.474	0.0
21	H _{es}	∠NC'H	-	0.801	0.715	0.0
22	H _{ad}	∠CNH	-	0.548	0.353	0.378
23	H _ω	∠NC'N'	-	1.154	0.027	0.0
<i>Interaction constants</i>						
<i>Stretch - Stretch</i>						
24	F _{a,c}	N-C, C-C _α	C	0.825	0.505	0.0
25	F _{a,b}	N-C, C=O	C	1.645	0.178	0.0
26	F _{b,c}	C=O, C-C _α	C	1.434	0.611	0.0
27	F _{c,g}	C-C _α , C _α =C	C	0.445	1.670	0.0
28	F _{a,e}	C-N, N-C'	N	0.0	1.451	0.0
29	F _{h,h}	C-H, C-H	C	0.087	1.011	0.0
30	F _{e,e}	N-C', N'-C'	C'	0.0	0.673	0.0
31	F _{s,s}	C'-H, C'-H	C'	0.064	0.271	0.0
<i>Stretch - Bend</i>						
32	F _{c,bc}	C-C _α , ∠C _α C=O	C-C _α	1.350	0.130	0.0
33	F _{f_c,ac}	C-C _α , ∠C _α CN	C-C _α	0.373	0.826	0.0
34	F _{e,es}	N-C', ∠NC'H	N-C'	0.315	0.564	0.0
<i>Bend - Bend</i>						
35	F _{es,es}	∠NC'H, ∠NC'H	N-C'	-0.050	0.060	0.0

^a Force constant at Sr. No 23 is taken from dimethyl urea⁹ and remaining constants are taken from N-methylacrylamide⁸

^b Force constants with zero dispersion are kept fixed after initial refinement

Table 2 — Observed and calculated frequencies (in cm^{-1}) and vibrational assignments of N,N'-methylenebisacrylamide

Sr. No	Mode	Obs freq.		Cal. freq	Vibrational assignment ^a
		IR	Raman		
<i>a' species</i>					
1	$\nu_s(\text{CH}_2)$	3060 s	3034 vs	3060	$97\nu_s(\text{CH}_2)$
2	$\nu_s(\text{CH}_2)$	3060 s	3034 vs	3060	$97\nu_s(\text{CH}_2)$
3	$\nu_{as}(\text{CH}_2)$	3105 w	3103 s	3105	$100\nu_{as}(\text{CH}_2)$
4	$\nu_{as}(\text{CH}_2)$	3105 w	3103 s	3105	$100\nu_{as}(\text{CH}_2)$
5	$\delta(\text{CH}_2)$	1428 ms	1441 s	1439	$37\delta(\text{CH}_2)+34\nu(\text{C-N})+27\nu(\text{C=C}_\alpha)$
6	$\delta(\text{CH}_2)$	1428 ms	1441 s	1438	$29\delta(\text{CH}_2)+36\nu(\text{C-N})+29\nu(\text{C=C}_\alpha)$
7	$\gamma(\text{CH}_2)$	987 vs	-	987	$45\gamma(\text{CH}_2)+28\nu(\text{N-C}')+14\delta(\text{CH}_2)$
8	$\gamma(\text{CH}_2)$	987 vs	-	972	$73\gamma(\text{CH}_2)+24\delta(\text{CH}_2)+11\delta(\text{C}_\alpha\text{-H})$
9	$\nu(\text{C=C}_\alpha)$	1620 vs	1635 vs	1620	$34\nu(\text{C=C}_\alpha)+22\nu(\text{C-N})+12\nu(\text{C=O})$
10	$\nu(\text{C=C}_\alpha)$	1620 vs	1635 vs	1601	$32\nu(\text{C-N})+20\delta(\text{N-H})+15\nu(\text{C=C}_\alpha)+12\nu(\text{C=O})$
11	$\nu(\text{C}_\alpha\text{-H})$	2845 ms	-	2844	$98\nu(\text{C}_\alpha\text{-H})$
12	$\nu(\text{C}_\alpha\text{-H})$	2845 ms	-	2845	$98\nu(\text{C}_\alpha\text{-H})$
13	$\delta(\text{C}_\alpha\text{-H})$	1070 s	1078 ms	1082	$46\gamma(\text{CH}_2)+32\delta(\text{C}_\alpha\text{-H})$
14	$\delta(\text{C}_\alpha\text{-H})$	1070 s	1078 ms	1088	$40\gamma(\text{CH}_2)+17\delta(\text{C}_\alpha\text{-H})+14\nu(\text{C-N})$
15	$\nu(\text{C-C}_\alpha)$	965 s	963 ms	957	$30\nu(\text{N-C}')+23\nu(\text{C-N})+20\nu(\text{C-C}_\alpha)+17\delta(\text{C}_\alpha\text{-H})$
16	$\nu(\text{C-C}_\alpha)$	965 s	963 ms	953	$56\delta(\text{C}_\alpha\text{-H})+18\gamma(\text{CH}_2)+14\nu(\text{C-C}_\alpha)$
17	$\delta(\text{C-C}_\alpha)$	293 s	310 w	305	$44\delta(\text{C-C}_\alpha)+27\delta(\text{C=C}_\alpha\text{-C})$
18	$\delta(\text{C-C}_\alpha)$	293 s	310 w	309	$33\delta(\text{C=C}_\alpha\text{-C})+31\delta(\text{C-C}_\alpha)$
19	$\delta(\text{C=C}_\alpha\text{-C})$	485 s	-	495	$40\delta(\text{O=C-N})+15\delta(\text{C=C}_\alpha\text{-C})$
20	$\delta(\text{C=C}_\alpha\text{-C})$	485 s	-	468	$42\delta(\text{O=C-N})+14\delta(\text{C=C}_\alpha\text{-C})$
21	$\nu(\text{C=O})$	1650 vs	1662 ms	1635	$27\nu(\text{C-C}_\alpha)+26\nu(\text{C=C}_\alpha)+15\nu(\text{C=O})+12\delta(\text{N-H})$
22	$\nu(\text{C=O})$	1650 vs	1662 ms	1631	$32\delta(\text{N}'\text{-H})+26\nu(\text{C=O})+14\nu(\text{C-C}_\alpha)$
23	$\nu(\text{C-N})$	1301 vs	1311 ms	1302	$28\nu(\text{C-C}_\alpha)+20\nu(\text{C-N})+16\delta(\text{N-H})$
24	$\nu(\text{C-N}')$	1301 vs	1311 ms	1298	$27\nu(\text{C-C}_\alpha)+25\nu(\text{C-N}')+18\delta(\text{N}'\text{-H})$
25	$\delta(\text{O=C-N})$	627 w	-	614	$27\delta(\text{C=C}_\alpha\text{-C})+26\delta(\text{O=C-N})$
26	$\delta(\text{O=C-N}')$	627 w	-	640	$28\delta(\text{O=C-N}')+27\delta(\text{C=C}_\alpha\text{-C})$
27	$\nu(\text{N-H})$	3305 vs	3308 s	3305	$99\nu(\text{N-H})$
28	$\nu(\text{N}'\text{-H})$	3305 vs	3308 s	3305	$99\nu(\text{N}'\text{-H})$
29	$\delta(\text{N-H})$	1535 vs	-	1546	$33\gamma(\text{CH}_2)+18\delta(\text{N-H})+12\nu(\text{C-C}_\alpha)$
30	$\delta(\text{N}'\text{-H})$	1535 vs	-	1550	$35\gamma(\text{CH}_2)+17\delta(\text{N}'\text{-H})+13\nu(\text{C=O})$
31	$\nu(\text{N-C}')$	955 vs	-	940	$30\nu(\text{N-C}')+25\gamma(\text{CH}_2)+15\nu(\text{C=O})$
32	$\nu(\text{N}'\text{-C}')$	955 vs	-	933	$64\nu(\text{N}'\text{-C}')$
33	$\delta(\text{C-N-C}')$	195 w	203 ms	180	$48\delta(\text{C-N-C}')+18\delta(\text{C-C}_\alpha)$
34	$\delta(\text{C}'\text{-N}'\text{-C})$	195 w	203 ms	176	$24\delta(\text{C}'\text{-N}'\text{-C})+22\delta(\text{NC}'\text{N})$
35	$\nu_s(\text{C}'\text{H}_2)$	2943 s	2957 ms	2943	$98\nu_s(\text{C}'\text{H}_2)$
36	$\delta(\text{C}'\text{H}_2)$	1405 s	1415 s	1405	$72\delta(\text{C}'\text{H}_2)+25\omega(\text{C}'\text{H}_2)$
37	$\omega(\text{C}'\text{H}_2)$	1380 vs	-	1379	$83\omega(\text{C}'\text{H}_2)$
38	$\delta(\text{NC}'\text{N}')$	70 s	67 vs	56	$55\delta(\text{C-N-C}')+20\delta(\text{NC}'\text{N}')$

^a The number before vibrational mode is %PED

- Not observed

There are two amide groups, each accounting for eight in-plane vibrations of MBAC. The strong infrared band near 3305 cm^{-1} with its strong Raman counterpart near 3308 cm^{-1} is assigned to N-H stretching vibration. This vibration is pure as it does not mix with any other vibration (Table.2). The strong IR band near 1650 cm^{-1}

which has a medium intense Raman counterpart near 1662 cm^{-1} is assigned to C=O stretching mode (the Amide I band). The strong IR band near 1535 cm^{-1} is assigned to deformation of (N-H) moiety (the Amide II band). The two $\delta(\text{N-H})$ vibrations mix with $\gamma(\text{CH}_2)$ vibration. C-N stretching vibration (the Amide III

band) is observed near 1301 cm^{-1} in IR with its Raman counterpart at 1311 cm^{-1} . Both the Amide I and Amide III bands mix with Amide II band. The strong absorption near 955 cm^{-1} in IR spectrum is assigned to N-C' stretching vibration. The stretching and bending vibrations of C-C $_{\alpha}$ bond are assigned to strong infrared bands near 965 and 293 cm^{-1} with their Raman counterparts near 963 and 310 cm^{-1} , respectively. The Amide IV band (i.e. in-plane deformation of O=C-N) is identified near 627 cm^{-1} .

(b) *Vibrations of the vinyl group*

There are two vinyl groups each accounting for 9 in-plane vibrations of MBAC. In this molecule, six distinct bands are expected in the range $2850\text{--}3100\text{ cm}^{-1}$ which can be assigned to two symmetric and two asymmetric vibrations of two CH $_2$ groups and two stretching vibrations of the two C $_{\alpha}$ -H moieties. The IR spectrum reveals three bands near 3105 , 3060 and 2845 cm^{-1} and the Raman spectrum shows only two bands around 3103 and 3034 cm^{-1} . According to normal coordinate calculations, the two asymmetric stretching modes of two CH $_2$ groups are calculated near 3105 and 3105 cm^{-1} and the two symmetric stretching vibrations at 3060 and 3060 cm^{-1} . Hence, the IR band near 3105 cm^{-1} with its Raman counterpart at 3103 cm^{-1} has been assigned to CH $_2$ asymmetric stretching mode. The strong IR band at 3060 cm^{-1} with intense Raman counterpart near 3034 cm^{-1} has been assigned to CH $_2$ symmetric stretching vibrations. The two C $_{\alpha}$ -H stretching vibrations are calculated near 2844 and 2845 cm^{-1} . Hence, a medium strong IR band at 2845 cm^{-1} is assigned to C $_{\alpha}$ -H stretching vibration. These vibrations are pure as these do not mix with any other vibrations. The strong IR band near 1620 cm^{-1} with its strong Raman counterpart at 1635 cm^{-1} is essentially due to C=C $_{\alpha}$ stretching mode, as these vibrations are calculated near 1620 and 1601 cm^{-1} . These two vibrations

mix with C-N stretching vibration (the Amide III band) which can be seen from Table 2. The medium intense IR band near 1428 cm^{-1} with its strong Raman counterpart at 1441 cm^{-1} and strong band near 987 cm^{-1} in IR are assigned to the $\delta(\text{CH}_2)$ and $\gamma(\text{CH}_2)$, respectively. The strong band near 1070 cm^{-1} in IR with its medium strong Raman counterpart at 1078 cm^{-1} is assigned to $\delta(\text{C}_{\alpha}\text{-H})$. The strong band near 485 cm^{-1} in IR spectrum is assigned to $\delta(\text{C}=\text{C}_{\alpha}\text{-C})$. Table 2 presents the entire deformation modes which exhibit mixed nature.

(c) *Vibrations of the methylene group (CH $_2$)*

The strong absorptions in IR near 2943 and 1405 cm^{-1} with their strong Raman counterparts near 2957 and 1415 cm^{-1} and strong IR band at 1380 cm^{-1} are assigned to $\nu_s(\text{C}'\text{H}_2)$, $\delta(\text{C}'\text{H}_2)$, and $\omega(\text{C}'\text{H}_2)$, respectively.

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