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### RESEARCH ARTICLE

#### RAMAN, FT RAMAN AND FTIR SPECTRA OF MOLLUSCAN SHELLS.

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#### Abstract

The present work reports the vibrational analyses of the FTIR and Raman spectra of few samples of molluscan shells procured locally for study. Raman spectra (including FT-Raman) show distinct band with highest intensity at  $1085\text{cm}^{-1}$  which is presumably due to symmetric mode of vibration of the  $(\text{CO}_3^{2-})$  group ( $\nu_1$ ),  $702\text{cm}^{-1}$  which is due to the in-plane bending mode and  $206\text{cm}^{-1}$  and  $274\text{cm}^{-1}$  which are characteristics of lattice vibrations of the crystal of calcium carbonate of aragonite type. The out of plane bending mode at  $860\text{cm}^{-1}$  and designated as  $\nu_3$  is completely absent in the Raman spectra, but this band appears with strong intensity in the infrared spectra.

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#### Introduction:-

We are concerned in the present work with the FTIR and Raman spectra of the Molluscan shells. Spectral investigations of carbonate minerals contained in biological systems are very useful in solving the sedimental petrology problems of  $\text{Mn}^{2+}$  concentration and its distribution non-equivalent positions within the corresponding mineral structure, as produced by mineral crystallization and evolution. Structural investigations of biominerals such as Molluscan shells were studied extensively by ESR and other techniques<sup>1,4</sup>. It is also well known that molluscan shells have a high environmental significance and provide information on physiological events (duration of spawning period, growth etc.); moreover, they are clearly related with taxonomy and phylogeny. In the first extensive study of Molluscan shell structures Boggild<sup>5</sup> described and classified the main categories from mineralogical, crystallographic and micro structural characters. The most widespread structure was the aragonite crossed lamellar layer. However, distinctive micro structural and mineralogical features were noticed in different families. In subsequent decades studies were mainly directed towards bivalve shells<sup>6,9</sup>. FTIR spectroscopy is relatively rapid, simple and accurate for detecting calcium carbonate because calcium carbonate shows strong absorption peaks in infrared spectrum at  $1430, 875$  and  $712\text{cm}^{-1}$ . These peaks are attributable to the vibration of carbon-oxygen double bond in the carbonate ion<sup>10</sup>. Especially the peak at  $875\text{cm}^{-1}$  is not overlapped with the peaks of other components, so it can be detected very easily and accurately in an unknown environment. However the main purpose of using FTIR will also be to identify the remaining organic components which are not easily found in Raman spectra. To analyse organic components in the samples of Molluscan shells which contain calcium carbonate as chief components (95 – 99.9%) and organic materials (5 – 0.1%)<sup>11,12</sup>, the extraction with organic solvents can be a solution. But it is not always adoptable, and the choice of the appropriate solvent is important. Nacre is an extraordinary example a hierarchical biological nanocomposite and is found in the interior of many Molluscan shells<sup>13,14</sup>. Though nacre is composed of exceedingly weak constituent materials, its unique and highly organized

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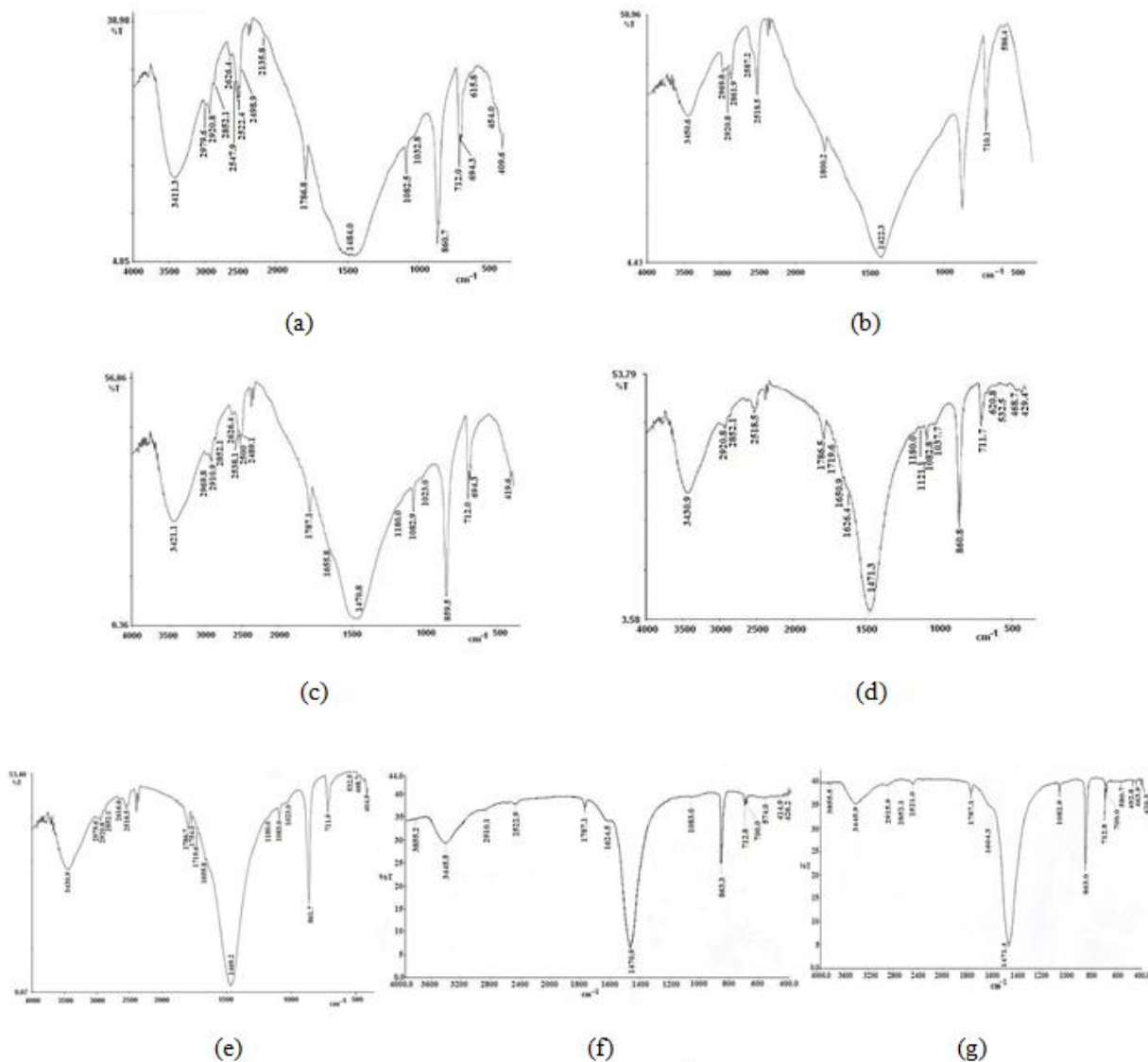
design at multiple length scales enables outstanding mechanical performance including an excellent combination of stiffness, strength, impact resistance and toughness<sup>13-18</sup>. The structure of nacre has been occasionally reviewed<sup>19,20</sup> and there is no doubt about its general structure. It is a composite material with a so called “brick-and-mortar” structure consisting of alternating layers of mineral tablets separated by thin layers of a biomacromolecular “glue”. Nacre is composed of ~ 95wt% pseudo-hexagonal, polygonal, or rounded aragonite tablets which have dimensions of ~5 – 20  $\mu\text{m}$  (plane with normal defined by the crystallographic c[100]-axis) and ~0.3 – 1.5  $\mu\text{m}$  in thickness (vertically parallel to the c[001]- axis)<sup>13,14</sup>. The organic matrix of the nacre has been studied in a number of reports<sup>21-34</sup>. The intertablet polymer layer has a thickness that varies between ~30-300 nm with pores for mineral bridges to pass through, and intercrystalline proteins are present within the tablets themselves. It has become increasingly evident that knowledge of the fine details of the nanoscales properties will be critical to the success of such theoretical approaches in their attempt to understand macroscopical mechanical function and performance. Research in this direction is just beginning and FTIR, Raman study of the organic matrices of Molluscan shells be great help in understanding the physics of shell formations. In a Raman spectrum usually two sharp bands due to the vibrations of the carbonate ions are observed at 1085  $\text{cm}^{-1}$  (symmetric stretching,  $\nu_1$ ) and 705  $\text{cm}^{-1}$  (in- plane bending,  $\nu_4$ ). The sharp bands at 207  $\text{cm}^{-1}$  and 154  $\text{cm}^{-1}$  are the characteristic of the aragonite structure<sup>35</sup>. Similarly the well known broadband on the FTIR spectrum is located at 3448  $\text{cm}^{-1}$  (OH and / or NH stretching modes of the organic matrix components). The 2800 – 3000  $\text{cm}^{-1}$  range is characteristic of the C-H stretching modes and exhibits a small band at 2846  $\text{cm}^{-1}$ . Protein complexes are demonstrated by the presence of intense bands at 1591  $\text{cm}^{-1}$  (carboxylate groups coordinated asymmetric stretching band) and 1409  $\text{cm}^{-1}$  (carboxylate symmetric stretching band). Smaller peaks detected at 1288, 1263, 921 and 850  $\text{cm}^{-1}$  are characteristic of sulfate group, while the 1000 – 1150  $\text{cm}^{-1}$  peaks correspond to the major polysaccharide absorption region. The presence of the bands at 1327 and 709  $\text{cm}^{-1}$  indicate amide group absorption (amide III C-N stretching vibration and amide V/ VII respectively).

Both FTIR and Raman spectroscopy are valuable tools for characterizing the microstructure of biogenic and synthetic carbonates. These methods can also detect organic materials such as carotenoid pigment that is closely associated with the mineral matrix of biogenic carbonate. Variations in the positions and half widths of the Raman-active modes provide evidence of the presence of rotational disordering of the carbonate ion in carbonate. This rotational disorder is evident in calcite, but not in aragonite, owing to the presence of solid solution between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and the greater concentration of trace impurities in calcite. Fourier transform infrared spectroscopy analyses of mineral and organic matrix from the shell of the Molluscan *Pinctada maxima* were made by Balmain et. Al<sup>36</sup> who showed that amide, amine, and carboxylic acid groups in the organic matrix of whole nacreous layer, with the  $\text{HCO}_3^-$  groups possibly present at the organic-mineral interface. Raman investigation of pigmentary molecules in the Molluscan biogenic matrix was recently made by Barnard and Coworker<sup>37</sup> using the 514.5 nm laser line of  $\text{Ar}^+$  laser. Shell species were chosen to obtain a variety of colour. The spectra obtained for the Molluscan pigments indicated that they are polyacetylenic in nature, and, from the spectral features it was deduced that the pigments were carotenoids with unmythylated polyacetylenic backbones of various conjugated lengths. Carotenoids are the dominant source of colour in nature and have been identified in many different body parts of marine invertebrates<sup>38-41</sup>. Molluscs are not able to synthesize carotenoids themselves, as these are synthesized afresh only in plant kingdom. The exact chemical nature of the marine carotenoids of Molluscan origin is not known, but they are believed to be carotenoid derivatives<sup>42,43</sup>. Raman spectral features have been used extensively for probing the structural nature of carotenoids<sup>44-46</sup> and of the carotenoids’ industrial counterparts, the polyacetylene derivatives<sup>47-52</sup>. Also the 514.5 nm laser wavelength falls within or close to the energy required for the electronic transition of most carotenoids or polyacetylene systems, resulting in the resonance Raman Effect that occurs for carotenoids. This feature makes Raman spectroscopy an ideal tool for in situ investigation of these pigments in the Molluscan matrix.

## Experimental Methods:-

### Fourier Transform Infrared Spectra:-

The samples of adult *Unio* were procured from the location – “Maguri Beel” of Dibru Saikhowa National Park, Tinsukia. The soft parts of the animal were removed and shells were rinsed with warm water, and then with cold water. The small pieces were ground into powder and the powdered samples were dried in an oven at 40<sup>0</sup>C for one night. All spectra were recorded in KBr by a sophisticated computer controlled Perkin Elmer 2000 Fourier transform spectrometer (FTIR) from 4000 to 450  $\text{cm}^{-1}$  with He-Ne laser as reference. The spectrometer was scanned at a resolution of 4  $\text{cm}^{-1}$  with steps of 1  $\text{cm}^{-1}$  and the results are shown in Fig. 1.1 (a, b, c, d, f, g, h). Table 1.1 shows the prominent peaks observed along with the assignments indicating the origin of the peaks.



**Fig 1.1:- (a, b, c, d, e, f, g)**  
FTIR Spectra of Molluscan Shells in powdered form (in KBR)

**Table 1.1:-** FTIR frequencies for Molluscan shells (cm<sup>-1</sup>) and their assignments

Sample	a	b	c	d	e	f	g	Assignment	
F R E Q U E N C I E S	3411(vs)	3451(vs)	3421(vs)	3431(vs)	3431(vs)	3445(s)	3446(s)	v (OH)	
	2979(ms)	2970(ms)	2970(s)					v (NH)	
	2921(s)	2921(ms)	2911(ms)	2921(ms)	2921(ms)	2910(vw)	2916(w)	v (C-H)	
	2852(w)	2862(ms)	2852(w)				2852(w)		
	2626(w)		2626(w)					(HCO <sub>2</sub> <sup>3-</sup> )	
	2548(w)		2538(ms)						
	2522(s)	2518(vs)	2518 (ms)	2518(w)	2518(w)	2523(w)			
	2499(ms)		2489(ms)						
	1787(s)	1800(s)	1787(s)	1786(ms)	1787(s)	1787(s)	1787(ms)	1787(s)	v (C=O)
			1655(w)			1656(w)			Amide-I
	1484(vs)	1422(vs)	1471(vs)	1471.3(vs)	1469(vs)	1471(s)	1471(s)	1471(vs)	v <sub>3</sub>
	1082(s)		1083(vs)	1083(s)	1083(ms)	1083(ms)	1083(ms)	1083(ms)	v <sub>1</sub>

	1033(w)			1037(w)	1023(w)			
	861(vs)	869(vs)	859(s)	861(vs)	862(vs)	863(vs)		$\nu_2$
	712(s)	710(vs)	712(vs)	712(s)	712(s)	713(s)	713(ms)	$\nu_4$
	616(ms)		694(s)			700(ms)	700(ms)	Amide V
				621(w)				
		586(w)						
	454(w)			468(w)			464(w)	
	410(ms)		419(w)	429(w)	405(w)			

The relative intensities are shown in the parentheses: s= strong, vs = very strong, ms= medium strong, w= weak

$\nu_1$  = symmetric stretching vibration of the carbonate ions

$\nu_2$  = out – of – plane bending

$\nu_3$  =  $\text{CO}_3^{2-}$  (asymmetric)

$\nu_4$  = in – plane – bending

From the data exhibited graphically in Fig 1.1, Table 1.1 has been prepared to exhibit the salient features in the FTIR spectra. There are few well known and prominent vibrational peaks which appear in the spectra and their interpretation are briefly described as follows. The strong and broad band located in the region  $3411$  to  $3451 \text{ cm}^{-1}$  is presumably due to the OH or NH stretching modes of the organic matrix components. The  $2800 - 3000 \text{ cm}^{-1}$  range is characteristic of the C-H stretching modes, and exhibits a group of frequencies. The group of frequencies in the range  $2500$  to  $2626 \text{ cm}^{-1}$  needs to be carefully interpreted as they do not appear under normal circumstances. It is reasonable to interpret them as originating from organic matrix (OH groups of carboxylic amino acids) and / or carbonate groups ( $\text{HCO}_2^{3-}$ ) present in the mineral component. The strong peak located at  $1787 \text{ cm}^{-1}$  is due to the C=O groups of the carbonate ions. In fact there is no ambiguity in this assignment. The weak bands at  $1655 \text{ cm}^{-1}$  and  $1656 \text{ cm}^{-1}$  are considered as amide-I bands. Similarly another reasonably strong band at about  $616 \text{ cm}^{-1}$  is identified as amide-V band. In addition to these bands we are left with the well known strong bands at  $1484 \text{ cm}^{-1}$ ,  $1471 \text{ cm}^{-1}$ ,  $1471.3 \text{ cm}^{-1}$ ,  $1469 \text{ cm}^{-1}$  and  $1422 \text{ cm}^{-1}$ . These bands are known as  $\nu_3$  band originating from asymmetric  $\text{CO}_3^{2-}$  stretching mode. It may be noted that this is the strongest band in the IR spectra with largest value of half width at half maxima (HWHM). The other bands at about  $1083$   $1422 \text{ cm}^{-1}$  are known as the  $\nu_1$  and  $\nu_3$  bands which originate from the symmetric and asymmetric stretching vibrations respectively of the carbonate ions. The band at  $861 \text{ cm}^{-1}$  is known as  $\nu_2$  band and is the characteristic band of out of plane bending vibration. The band at  $713 \text{ cm}^{-1}$  is also very strong and is due to in-plane-bending mode and is known as  $\nu_4$  band. The bands designated as  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  are well known absorption bands due to calcium carbonate. It is worthwhile to note that the relative intensities of these bands vary in different samples. The band at  $861 \text{ cm}^{-1}$  ( $\nu_2$ ) is reasonably strong in sample 1 while the band at  $1083 \text{ cm}^{-1}$  ( $\nu_1$ ) is completely absent in sample 2. As we have described so far calcium carbonate in the body of the shell can be detected very rapidly and easily by FTIR, paying attention to the absorption peaks at  $1484 \text{ cm}^{-1}$  ( $\nu_3$ ),  $1082 \text{ cm}^{-1}$  ( $\nu_1$ ),  $861 \text{ cm}^{-1}$  ( $\nu_2$ ) and  $712 \text{ cm}^{-1}$  ( $\nu_4$ ). These peaks are not overlapped with the peaks of other components, so they can be identified very accurately. However, our main purpose to use FTIR was to identify the remaining organic components in the samples. The organic components may be easily identified in the region of wave numbers of  $2000 - 4000 \text{ cm}^{-1}$ . However as shown in Fig 5.1 the absorption peak of calcium carbonate at  $1484 \text{ cm}^{-1}$  is sufficiently broad and this is possibly due to the overlapping of the absorption peaks of binding media.

#### Raman Spectra:-

The Raman spectra of the powdered samples of molluscan shells are recorded with the help of a Raman Spectrometer (Model Jobin Yvon 3000 V) with Triax monochromator. He-Cd laser line at  $442 \text{ nm}$  (cw) is used as the exciting radiation. The FT-Raman spectra of the powdered samples are recorded with a Bruker Spectrometer (model IFS 120 HR) equipped with an integrated FRA 106 Raman module. The  $1064 \text{ nm}$  radiation from Nd: YAG laser with an output of about  $150 \text{ mW}$  is used for excitation. The spectral range of interest is  $0 - 4000 \text{ cm}^{-1}$ . Fig 1.2(a,b,c) shows the FT-Raman spectra of three samples of molluscan shells and Fig 1.3(a,b,c,d,e) shows the Raman spectra of five samples excited by He – Cd laser line at  $442 \text{ nm}$  with maximum power of  $300 \text{ mW}$ . The spectral range considered in this case is  $0-200 \text{ cm}^{-1}$ .

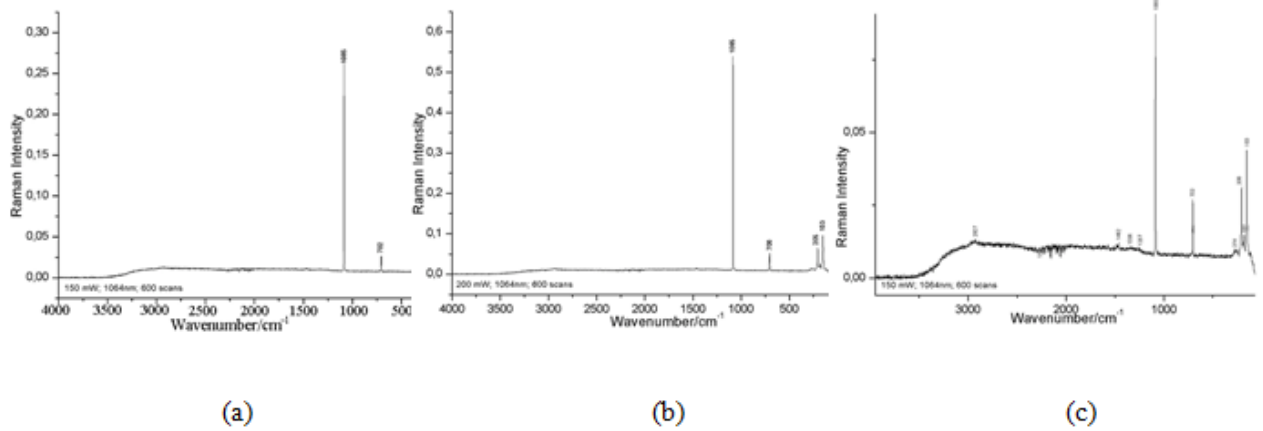


Fig 1.2:- (a, b, c) FT-Raman spectra Of molluscan shells.

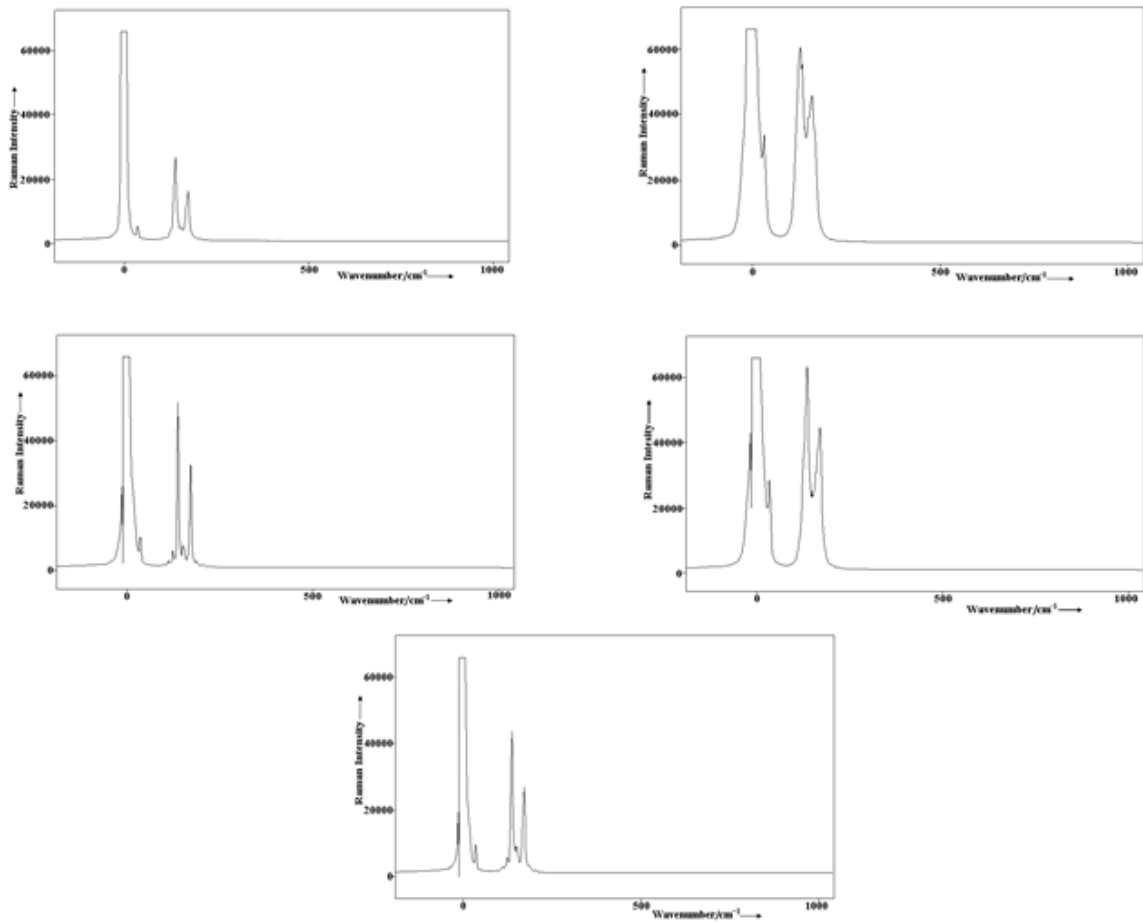


Fig 1.3:- (a, b, c, d, e), Raman spectra of five samples of molluscan shells in the range 0 – 200  $\text{cm}^{-1}$

**Table 1.2:-** FT-Raman frequencies of Molluscan Shells ( $\text{cm}^{-1}$ )

Sample a	Sample b	Sample c	Assignment
		2927 (w)	- CH Stretching
		1462 (w)	- $\text{CO}_3^{2-}$ ( $\nu_3$ )
		1336 (w)	-
		1257 (w)	-
1085 (vvs)	1085 (vvs)	1085 (vvs)	- $\text{CO}_3^{2-}$ ( $\nu_1$ )
702 (vs)	706 (vs)	702 (vs)	$\nu_4$
		274 (ms)	Lattice
206 (s)	205 (s)	206 (vs)	Lattice
		181 (ms)	Lattice
153 (s)	153 (s)	153 (vs)	Lattice

vvs = very very strong; vs = very strong; ms = medium strong; w = weak.

**Table 1.3:-** Raman frequencies in molluscan shells observed below  $200 \text{ cm}^{-1}$ .

Sample					Analysis
a	b	c	d	e	
37 (s)	40 (vs)	40 (s)	40 (ms)	40 (s)	Lattice
113 (w)					Lattice
			93 (w)		Lattice
			113 (w)		Lattice
126 (w)	127 (vs)		126 (ms)		Lattice
139 (vs)		133 (vs)	137 (vs)	139 (vs)	Lattice
145 (ms)	147 (w)		147 (ms)		Lattice
			149 (ms)		Lattice
165 (vs)	166 (s)	158 (s)	166 (s)	173 (s)	Lattice
184 (w)			186 (w)		Lattice
			203 (w)		Lattice

Intensities are given in the parenthesis

s = strong; w = weak; ms = medium strong; vs = very strong.

The FT-Raman spectra of the molluscan shells exhibit only three prominent bands. They are at  $1462 \text{ cm}^{-1}$  with extremely weak intensities which is due to antisymmetric stretching mode of  $\text{CO}_3^{2-}$  group ( $\nu_3$ ). This weak band is completely absent in the spectra of the remaining two samples. The band at  $1085 \text{ cm}^{-1}$  is due to the symmetric mode vibration of the  $\text{CO}_3^{2-}$  group ( $\nu_1$ ). Another strong band at  $702 \text{ cm}^{-1}$  ( $\nu_4$ ) is observed with very strong intensities in the Raman spectra. This band at  $702 \text{ cm}^{-1}$  is due to the in-plane-bending modes of carbonate ions. It may be noted here that the out of plane bending mode of vibration at  $860 \text{ cm}^{-1}$  and designated as  $\nu_2$  is completely absent in the Raman spectra whereas this band appears with strong intensity in the FTIR spectra. This is presumably due to the usual selection rule. The band due to  $\nu_2$  is not Raman active. The inorganic compound of molluscan shells primarily consists of  $\text{CaCO}_3$ .  $\text{CaCO}_3$  can exist as three polymorphs; calcite, aragonite and vaterite. It is possible to distinguish between the three phases by Raman spectroscopy, as each of them has unique, non-overlapping peaks. Vaterite has bands at  $738 \text{ cm}^{-1}$  and  $750 \text{ cm}^{-1}$ , aragonite a doublet at  $700 \text{ cm}^{-1}$  and  $705 \text{ cm}^{-1}$  and a calcite band at  $711 \text{ cm}^{-1}$ . From the consideration set forth here aragonite is the only form observed in the present case. The most intense band for all the three phases occurs at  $\sim 1086 \text{ cm}^{-1}$ , which is assigned to the symmetric  $\text{CO}_3^{2-}$  stretching mode. From this frequency it is not possible to distinguish between the three phases.

The medium intensity bands in the region of  $100 - 300 \text{ cm}^{-1}$  of the Raman spectra arise from the translational and rotational modes of lattice vibrations. Lattice vibrations of aragonite at  $206 \text{ cm}^{-1}$  and  $274 \text{ cm}^{-1}$  are clearly observed in the Raman spectra. The Raman bands observed below  $200 \text{ cm}^{-1}$ , as shown in Fig 1.3 and Table 1.3 indicate few features which have not been reported until now. Vibrational frequencies characteristics of the lattice modes are observed in large numbers. As for example ten frequencies are measured in sample d. In FT-Raman only three lattice vibrational modes have been identified. A proper identification of these low frequency modes will require a detailed investigation of the organic macromolecules in the growth of biogenic crystals, biogenic crystals differs in some aspects from its geological counterparts.

### Summary and Conclusion:-

The present work reports the vibrational analyses of the FTIR and Raman peaks observed in the samples of the molluscan shell. Raman spectra (including FT-Raman) show distinct peaks at  $1085\text{ cm}^{-1}$  which is due to symmetric mode of vibration of the  $\text{CO}_3^{2-}$  group ( $\nu_1$ ),  $702\text{ cm}^{-1}$  ( $\nu_4$ ) which is due to the in-plane-bending mode and  $206\text{ cm}^{-1}$  and  $274\text{ cm}^{-1}$  which are characteristic of lattice vibrations of the crystals of calcium carbonate of aragonite type. The out-of-plane bending mode at  $860\text{ cm}^{-1}$  and designated as  $\nu_2$  is completely absent in the Raman spectra, but this band appears with strong intensity in the infrared spectra.  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  bands are considered as fingerprint bands of calcium carbonate molecules. There are two common forms of calcium carbonate, aragonite and calcite. They differ in their crystal shape, yet their chemical formula is the same. Whether calcium carbonate becomes aragonite or calcite depends on the "seed crystals" growth pattern. The molluscan shells in the present work are composed of the aragonite form of calcium carbonate. Proteins and amino acids secreted by the polyp play role in the growth of the crystals of aragonite and probably determine whether aragonite or calcite forms. Raman and FTIR spectroscopy are valuable tools for characterizing the microstructure of biogenic and synthetic carbonates. This method can also detect organic materials that are closely associated with the mineral matrix of biogenic carbonate

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