Spectroscopic studies of molluscan shells

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The spectral characteristics of few naturally occurring molluscan shells have been investigated with the help of laser induced fluorescence, X-Rays, absorption and FTIR spectroscopic techniques. The laser induced fluorescence (LIF) or the stimulated laser induced fluorescence from molluscan shells exhibits diffuse bands in the region 5860-6350 Å and some discrete bands in the region 5000-5400 Å. The fluorescence spectra of different shells are found to be different. The FTIR spectra show predominantly the vibrational bands of CaCO₃. But there are additional bands, which are not characteristic of CaCO₃. The X-ray photograph and iridescence pattern of few shells are presented.

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1 Introduction

Sea shells and molluscan shells have attracted the attention of researchers for many physical phenomena exhibited by these objects. The study of shells is also important and fascinating subject because the shell is created by a living pulsating creature around itself as a cover for defense and it represents some sort of permanent phase which is irreversible. The materials of the molluscan shells present different appearances in different cases. It is hard, and white in shark, translucent in window-pane oyster, and iridescent in mother-of-pearl. It may be noted that the majority of the material of the shell is calcium carbonate. The carbonate is deposited as a secretion by the animal from the edges of its living substance and gradually builds up the substance of the shell. Little is known of the process of calcium carbonate formation and crystallization in the molluscan shell. Nature has plenty of examples that suggest that biological synthesis might be in many ways superior to conventional human synthesis of material. The shell of a molluscan built out of calcium carbonate has 3000 times higher fracture resistance than crystals of calcium carbonate. Shell growth involves increase in both area and thickness. Area increase is a function of increase of mantle area; increase in thickness relates to the deposition of calcium carbonate and organic matrix. The reference points for all analysis of bivalve shell grows are the umbones; the oldest part of the shell, situated more or less anteriorly above the hinge line. Many shells display concentric lines surrounding the umbones, these are growth lines. It may be noted that most shells are inequilateral, i.e. not symmetrical about a line drawn vertically downwards from the umbo. This reflects greater proportional growth posteriorly. As regards the shell pigmentation and ornamentation it may be noted that the lower bivalves commonly are pigmented with relatively simple acid soluble substance, usually pyrollic or indigold in structure. The majority of bivalves contain chromoproteins associated with the conchiolin of their shell valves and many of the melanoid pigments owe their origin to the biochemical activities associated with the quinone tanning of conchiolin. Several decades ago Raman and coworkers investigated experimentally various optical properties like iridescence structure and optical characters of shells. One may not know yet how the beautiful patterns on the shell surface originate. As in the case of Liesegang precipitation it appears that certain non-linearities called into play during the shell growth. Meinhart and Klingler have computer simulated many of the observed shell patterns using a suitable non-linear reaction diffusion model. Availability of laser as a strong source of...
Laser induced fluorescence of the specimen is observed when it is excited with the help of 500 mW Ar laser and is recorded photographically on a glass spectrograph and the intensity distribution of the fluorescence system is measured with the help of a densitometer. The finely powdered sample from the surface of the mother-of-pearl is kept between two firmly held glass plates. The optical path of the specimen thickness is 0.1 cm. Commercially available colour film is used to photograph the spectrum. We have also allowed the laser light to pass through the surface of the molluscan cell and observed its fluorescence. An exposure time of 5 min is adequate to photograph the fluorescence. Figs 1 and 2 show the nature of the fluorescence and its densitometer tracing.

X-rays — Fig. 3 shows few specimens of shells as observed in X-rays. The FTIR spectra of the powdered sample of a shell in KBR are recorded on a Perkin-Elmer infrared spectrometer type 2000 FTIR computer controlled within the range 400-4000 cm⁻¹. Figs 4 and 5 show the FTIR spectra of two powdered samples. Fig. 6 indicates the nature of the iridescence exhibited by four molluscan shells.
3 Results and Discussion

Laser induced fluorescence of the molluscan shell in the powdered form exhibits a well defined diffused system of the band in the yellow sector of the spectrum. The wavelength range is 5860 Å - 6350 Å. The wavelength range for the LIF belonging to another shell is slightly different. We have observed these distinguishing features for LIF for different molluscan shells, though the wavelength range lies in the red and yellow sector of the spectrum. The absorption spectrum as shown in Fig. 7 shows a discrete absorption at 6000 Å. Earlier researchers did not observe fluorescence from molluscan shells.14 This is to be understood because strong source of radiation or more precisely laser was not invented at that time. It is emphasized that we have allowed the laser radiation to be incident directly on the sample shell and the fluorescence is observed in the same direction. This procedure does not create any inconvenience because one can directly observe the fluorescence in the plate holder position of the spectrograph. In most of the experiments carried out in the laboratory, we have used this experimental set-up. This is similar to the experimental arrangement for observing stimulated Raman scattering (SRS). Thus, it is quite reasonable to term the present fluorescence as stimulated laser induced fluorescence (SLIF). Apart from the fluorescence or the diffuse band in the red yellow sector of the spectrum, there are some distinct bands or lines in the range 5000 Å - 5400 Å. They may also show characteristics of the material in the molluscan shell. These bands are not present in the SLIF of all the molluscan shells. The presence of these bands is interesting because their identification could not be made. They may be Raman bands or lines. As regards the origin of the diffuse fluorescence band in the region 5860 Å - 6350 Å, these presumably from organic material imbedded in the CaCO₃ matrix. It should be noted here that we have not been able to observe SLIF for pure CaCO₃. This strongly supports the view that CaCO₃ is not responsible for the SLIF recorded in the present experiment. Another conspicuous feature of the diffuse fluorescence band is that it is confined in a

Fig. 4 — FTIR spectrum of the powdered sample of molluscan shell and specimen No. 1

Fig. 5 — FTIR spectrum of molluscan shell. Specimen No. 2

Fig. 6 — Nature of iridescence exhibited by four molluscan shells
The spectrum. The Fig. 7 shows a strong source of not invented at researchers did not create any new because their shells — CaCO₃. Thus, there is indication here that, the molluscan shells are potential lasing material.

As may be inferred from Fig. 3, the X-ray photographs of six different shells show some interesting features. The ring structures usually observed in molluscan shells are strikingly demonstrated. As many as fifteen rings can be seen. There are some regions (rings) which are completely opaque for X-rays and there are some regions which are transparent or semi-transparent to X-rays. A proper analysis of the X-ray photograph of the type presented here has not been reported in any of the earlier works or literature. We believe that the rings will throw the much needed light on the evolution of molluscan shells and FTIR spectra show the prominent vibrational bands of CaCO₃ at 1471, 863, 713 cm⁻¹. There are however additional bands at 3446, 2916, 2521 and 1624 cm⁻¹ which are not of CaCO₃ origin. We conclude our discussion by indicating Fig. 6, which is about iridescence of some molluscan shells exhibiting beautiful iridescence patterns. Hundreds of molluscan shells have been studied but only 5% of these shells exhibit iridescence. Perhaps it is possible to further sub-classify the molluscan shells (unio) based on degree of iridescence.

4 Conclusion

In the present work we have reported for the first time the stimulated laser induced fluorescence of the molluscan (unio) shells. The laser induced fluorescence along with other spectroscopic and optical studies may be used to classify shells of natural origin. The materials of the shell may be regarded as promising candidate for laser materials.

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