RESONANCE RAMAN STUDIES ON SOME METALLOPORPHYRINS

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SYNOPSIS

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Porphyrins and their derivatives are of great biological importance and have received considerable attention during recent years.[1,2] They play a major role in the electron transfer reactions in many enzymes and form important chromophores in haeme proteins, chlorophylls, cytochrome oxidase etc. It is therefore important to study the physicochemical properties of metalloporphyrins and their aggregates in greater details which can provide useful insight into the mechanisms of their actions in various biological processes. Studies on these systems, however, do not stem exclusively because of their biological significance. This class of compounds offer ample opportunities to understand many fundamental problems of molecular physics, quite apart from their inherent interest in biology.

The advent of lasers and improved technical devices have stimulated considerable interest in the utility of resonance Raman (RR) spectroscopy as a probe to study the structure and dynamics of porphyrins and metalloporphyrins as well as their role in biological systems.[3-5] When the frequency of the exciting radiation is tuned through the electronic absorption region of the system, intensities of certain vibrational modes show preferential enhancement due to their coupling with either a single excited electronic state or through vibronic coupling between two nearby electronic states. The selectivity and sensitivity offered by the resonance Raman technique provides valuable informations about several molecular properties such as electronic and geometrical structure, intra and intermolecular forces, nature of the bond etc. and play a key role in understanding many fundamental problems of biology.

Resonance Raman studies of metalloporphyrins and haeme proteins are of great interest.[3-5] The early resonance Raman studies on porphyrins and metalloporphyrins were reported by Verma **et al.**[6-8] and it was shown that even peripheral and saturated substituents exert a profound influence on the vibrational pattern and depolarization ratios. Copper porphin was found to have D_{4h} symmetry[8] and vibrational modes of A_{2g} symmetry showed almost infinite depolarization ratio. During resonance Raman study of Manganese(III) aetioporphyrin-I, Asher and Sauer[9] could interprete the complicated electronic spectrum of the system by selective excitation of Raman spectra within charge transfer and $\pi \text{—} \pi^*$ transitions which showed dramatic changes in the resonance Raman spectra. Numerous resonance Raman studies have provided a great deal of knowledge about the metalloporphyrins as well as on haeme proteins and cytochromes.[3-5, 10]

However, in spite of several studies on porphyrins and metalloporphyrins, the role of haemoglobin in the control of oxygen binding is not fully understood. The specific role of vinyl groups in the cooperative binding of oxygen is also not clear. It has been proposed that the protein-haeme interactions occur via vinyl side chains and the role of such interactions in controlling O_2 binding is an area of growing research activity.[11-13] Therefore if the role of vinyl groups in the RR spectra of haeme proteins could be properly understood, it may be of great help in monitoring their role in important biochemical processes. However, there are several factors which add complexity to the RR spectra of haeme proteins. It is thus esential to understand the RR spectra of basic chromophore before attempting to investigate the effects of protein and other axial ligands on the vibrational modes of the chromophore in haeme proteins.

There has also been considerable interest in the study of Manganese(III) porphyrin complexes during recent years.[9,14-16] The absorption spectra of these complexes are strikingly different from the absorption spectra of normal metalloporphyrin complexes. This has been attributed to strong metal-porphyrin interactions, which modify the normal spectra and induce many new distinct features to appear in the absorption. However, unambigous assignment for these bands is still lacking and consequently a more detailed study is desirable.

Mn(III)-porphyrins have biological importance owing to their possible role in Manganese dependent green plant photosynthesis.[17] A thorough understanding of Manganese porphyrin complexes would also be valuable in sorting out the closely related and biologically important Iron systems, as well as for the understanding of metalloporphyrin structure and spectra, in general.

The axially bridged dimeric metalloporphyrin complexes have also drawn much attention to probe the energy transduction mechanisms in various biological systems. However, despite the utility of RR spectroscopy as a subtle and sensitive probe of environmental and structural factors, RR studies on these systems have not been carried out to a great extent.[18-21] Therefore, further systematic Raman investigations are necessary to achieve a proper understanding of these systems. In the present thesis we have attempted to resolve some of the outstanding problems on metalloporphyrins by combining resonance Raman, infrared (IR) and electronic absorption techniques.

The thesis is divided into seven chapters. Chapter I reviews the existing interpretations and their shortcomings as reported in literature on metalloporphyrins and related systems and introduces the problems under consideration.

Chapter II presents detailed theoretical background relevant to the present study. It discusses two well known techniques, viz., electronic absorption spectroscopy and resonance Raman spectroscopy and explains the types of informations which can be obtained by analyzing the resonance Raman data. Some pertinent aspects of IR technique are also given in this chapter.

Chapter III deals with the experimental techniques like sample preparation, instrumental set up which include various types of lasers, SPEX Raman spectrometer, photon counting arrangement etc. used in the present study.

Chapter IV describes the effect of vinyl groups on the RR spectra of protoporphyrin-IX. RR spectra of free base protoporphyrin-IX (PP), mesoporphyrin-IX (MP), and haematoporphyrin-IX (HP) having identical molecular symmetries, along with the copper and cobalt complexes of PP and MP have been compared to delineate the contributions of vinyl groups in the RR spectra of PP. The main conclusion of this work is that the vinyl groups in PP perturb the symmetry of the chromophore in the same way as the other substituents in the HP and MP, resulting in C_s symmetry for all the systems. This indicates either i) the conjugation of the vinyl groups with the porphyrin macrocycle in PP is decreased due to large steric interactions of the mesohydrogens with the vinyl group hydrogens in the coplanar configuration and/or ii) the vibrational modes of the vinyl groups are not effective in vibronic coupling of the excited electronic states of the macrocycle and therefore do not get enhanced in the RR spectra.[22]

Chapter V presents the resonance Raman studies of tetraphenylporphinato Manganese(III) chloride (Mn(III)TPPCl). Three aspects of these systems have been discussed in detail: the electronic structure, the state of conjugation of the phenyl rings with the macroring and the symmetry of the molecular system. It has been seen that due to strong metal porphyrin interactions, bands due to charge transfer transitions and singlet-triplet (π, π^*) transitions arise, which are not observed in the absorption spectra of normal metalloporphyrins. No direct evidence is found for the conjugation of phenyl rings with the macrocycle. The symmetry of the system is reduced from C_{4v}, probably because of the non-symmetric disposition of the phenyl rings.[23]

Chapter VI reports the resonance Raman spectra of oxygen-bridged Manganese(III) tetraphenylporphin dimer ($O-(MnTPPH_2O)_2$). The data obtained serves as a measure to probe the intradimer coupling, which is found to be non significant in this case. No direct contributions of the phenyl groups is found in the RR spectra of the dimer indicating thereby that the phenyl groups are not conjugated with the porphyrin macrocycle.[24]

Chapter VII gives the summary of the present work and important conclusions drawn from the study.

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