# DISTORTION INDUCED IR AND RAMAN ACTIVITY AND RELATED ASPECTS OF VIBRATIONAL DYNAMICS OF MOLECULAR UNITS IN CRYSTALS

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SYNOPSIS

# DISTORTION INDUCED IR AND RAMAN ACTIVITY AND RELATED ASPECTS OF VIBRATIONAL DYNAMICS OF MOLECULAR UNITS IN CRYSTALS

In the last few years, a significant number of papers (Luty and Rohleder 1972; Pimentel and McClellan 1952; Pimentel et. al. 1955; Suzuki et. al. 1968; Yamada and Person 1964) and reviews (Califano et. al. 1981; Person and Steele 1974) have appeared on the subject of Raman and infrared intensities of bands due to vibrational modes of molecular units in crystals. The main objective of all these reports has been to study : (i) the relative intensity of Davydov splitting (dichroic ratios), (ii) the change in intensity on condensation and (iii) the intensity of bands due to lattice modes. However, no attention seems to have been paid to formulate a quantitative theory of the phenomenon that activates the forbidden modes of a molecular unit which attains distorted structure and occupies a lattice site of symmetry lower than that of its free state. The phenomenon is associated qualitatively with the lowering of local symmetry of the unit and modified selection rules are derived using well known group theoretical techniques viz, the unit cell (Bhagavantam and Venkatarayudu 1939) and local symmetry approaches (Halford 1946; Hornig 1948; Winston and Halford 1949). Thus the main aim of this thesis is to give a

quantitative theory of the phenomenon, using group theory and perturbation methods. It has been revealed that these transitions become active due to structural distortion of the unit and they need to be ascribed as distortion induced transitions. Such transitions of different symmetry species are characterised by different order of distortion induced activity (DIA), i.e. DIA-I/DIA-II/..../DIA-h representing first/second/..../higher order effect of distortion. Normally, the transition occuring only as first order effect in the polar type of distortion are expected to gain observable intensity; others may result in perceptible intensity in exceptional situations. Therefore, for the better understanding of the observed IR and Raman spectra it is highly desirable to know the type and order of distortion induced activity (DIA) of the forbidden modes of a molecular unit. The usefulness of the theory in the study of the forbidden modes of molecular units in liquids and gases (under high pressure) has also been discussed. The intensity of such transitions has been quantitatively associated with the type and magnitude of distortion which is useful in understanding the microscopic mechanism of structural phase transition.

The thesis is divided into six chapters. Chapter I, presents various aspects of vibrations of molecules and crystals, IR and Raman spectroscopy, etc. relevant to the present investigation.

Chapter II, reviews the work pertaining to the vibrational selection rules for molecules in their gaseous as well as in crystalline states. It discusses at length the two well known techniques (alongwith their merits and demerits) i.e. the unit cell approach and the local symmetry approach applied to crystalline solids for determining IR and Raman active species. The application of these techniques has been illustrated by an example of our study and analysis of the IR and Raman spectra of Rochelle Salt ($NaKC_4H_4O_6.4H_2O$); this includes the details of experimental set up and techniques used for sample preparation and recording of the spectra.

Chapter III, describes the formulation of the theory of distortion induced activity (DIA) of forbidden modes of molecular units in crystals. The polar and non-polar site symmetry cases are discussed separately. The central idea of the work is that the crystal field which is non-uniform in strength serves as the source of perturbation and distorts the unit and hence modifies its dynamics and selection rules; the results have been analysed using group theory.

Chapter IV, presents the symmetry classification of forbidden modes of molecular units belonging to different point groups attaining first/second/..../higher order of DIA; in each case the results have been analysed for all possible site symmetries.

Chapter V, discusses the usefulness of the theory in the study of structural phase transition in crystals. The scope and the usefulness of the theory in determining the effective symmetry and the IR and Raman activity of molecular units in liquids and gases (under high pressure) has also been discussed.

Chapter VI, presents the summary of the work alongwith the important conclusions.

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