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PREVIEW

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**Raman and piezomodulated Raman spectroscopy of molecular  
crystals**

**White, Kenneth M., Ph.D.**

**The University of Nebraska - Lincoln, 1987**

PREVIEW

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Ann Arbor, MI 48106**

PREVIEW

RAMAN AND PIEZOMODULATED RAMAN SPECTROSCOPY  
OF MOLECULAR CRYSTALS

by

Kenneth M. White

A DISSERTATION

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The Graduate College in the University of Nebraska  
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RAMAN AND PIEZOMODULATED RAMAN SPECTROSCOPY

OF MOLECULAR CRYSTALS

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RAMAN AND PIEZOMODULATED RAMAN SPECTROSCOPY  
OF MOLECULAR CRYSTALS

Kenneth M. White, Ph.D.

University of Nebraska, 1987

Advisor: Dr. Craig J. Eckhardt

The intermolecular potential energy of the 1,2,4,5-tetrabromobenzene (TBB) molecular crystal has been studied using Raman and piezomodulated Raman spectroscopy and lattice dynamical calculations.

Polarized Raman spectra of single crystals of TBB were measured in the lattice mode energy region in both the beta phase at room temperature and the gamma phase at 330 K. Symmetry assignments for the modes in both phases have been determined from the experimental data. Assignments of the Raman active intramolecular modes in TBB as well as the lattice modes in 1,2,4,5-tetrachlorobenzene (TCB) were also obtained from polarized Raman spectra.

Piezomodulated Raman (PR) spectroscopy has been employed to determine the extent of anharmonicity in crystal vibrations in TBB. Strain-induced coupling constants have been derived from the relative intensities of the spectral bands observed for the various modes. Measurements at room temperature indicated that among all crystal vibrational modes the lattice modes exhibit the greatest amount of strain-induced coupling and the response is dependent on the direc-

tion of the applied stress. PR data for the molecular modes showed these vibrations to be less anharmonic, particularly for modes at high frequencies. PR spectra measured below the TBB phase transition at temperatures between 300 and 313 K have demonstrated that the most anharmonic mode in the crystal is also most affected by the phase transition. The strain produced in the crystal during the PR experiments is observed to drive the crystal toward the high temperature phase at temperatures just below the phase transition.

The PR spectra have been able to determine the molecular motions involved in the Raman active lattice modes in TBB. This is the first experimental technique known that directly probes lattice vibrations to obtain information about their eigenvectors.

Polarized Raman spectra of single crystals of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ<sup>o</sup>) have been measured to assign the lattice modes in this molecular crystal. Despite some coupling between internal and external modes, a frequency demarcation between them was observed.



To my mother and father

PREVIEW

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PREVIEW

## I. INTRODUCTION

A major goal in chemistry is to understand the forces that exist between atoms and molecules. It is generally held that the knowledge of covalent forces in molecules has advanced to the point where the synthetic chemist has at his disposal numerous methods for the creation of molecules that perform a particular function or possess an important property. On the other hand, progress in the investigation of interactions between molecules, which are characterized by dispersion forces and, to some extent, coulombic interactions, has come much more slowly. An understanding of intermolecular forces has a wide variety of applications: these forces control adsorption equilibria at surfaces, phase phenomena in liquid crystals, and even solvation processes in liquids, to name a few examples.

The study of intermolecular potentials is also vital to an understanding of molecular crystals. It is in these systems that intermolecular forces are most easily characterized. Furthermore, the benefits of such research in the crystalline state are manifold, since molecular interactions contribute to the mechanical, optical, electrical, and thermal properties of solids. Indeed, increased knowledge of the potential energy in molecular crystals could some day lead to the controlled use of intermolecular forces to regulate the packing of molecules in a crystal, thus ena-

bling solid state chemists to synthesize solids that would favor a specific reaction or optimize a particular solid state effect.

The determination of the potential energy of molecular crystals, by both theoretical and experimental means, has been an active area of research for many years. Perhaps the most effective approach for its calculation has involved the use of the parametrized Buckingham or Lennard-Jones potentials (Pertsin and Kitaigorodsky, 1987). These functions, which are employed to calculate interatomic interactions between molecules, are used widely and are appropriate to many different systems. The parameters, which are almost exclusively obtained from the consideration of the structure and energetics of organic molecular crystals, describe the relatively weak, short range forces that hold the molecular lattices together.

Experimental studies of the crystal potential energy often focus on the lattice dynamics that are governed by it. The lattice vibrational energies of a number of molecular crystals have been measured using Raman spectroscopy and in several cases, the symmetries of the modes have been assigned. A comparison of calculated and observed results shows that while the derived crystal potentials successfully predict frequencies and symmetries of lattice modes in some systems, they display significant inadequacies in others. Furthermore, in instances where the eigenvectors of the

modes have been calculated, only indirect tests of their validity by comparing observed and calculated Raman intensities have been possible.

The need to improve the functions and models used for the potential energies of molecular crystals is clearly evident. One important aspect to probe experimentally is the anharmonic contribution to the potential which is normally assumed to be insignificant when applying the harmonic approximation in studies of lattice dynamics (Born and Huang, 1954; Venkataraman et al., 1975). Anharmonicity is manifested by shifts of phonon frequencies from harmonic values and the finite lifetime of phonon states. It is also responsible for thermal expansion and stability of a crystal undergoing a phase transition and plays an important role in thermal and electrical conductivity (Bruesch, 1982). This coupling between vibrational modes in molecular crystals has been studied through various experimental methods, including measurements of Raman linewidths and frequency shifts as a function of temperature and pressure (Carlone et al., 1982; Anastassakis, 1980; Weinstein and Zallen, 1984). However, the anisotropy of the anharmonic crystal potential has not been investigated extensively.

The recent theoretical development of piezomodulated Raman spectroscopy (Luty and Eckhardt, 1985) has demonstrated that this experimental technique directly probes anharmonicity in vibrational modes in crystals by measuring

strain-induced coupling parameters for the modes. While the usefulness of such measurements in solids was alluded to by Cowley (1971), the coupling parameters are still largely unknown, particularly for molecular crystals. A significant advantage that piezomodulated Raman spectroscopy is expected to have over Raman measurements on strained molecular crystals already reported in the literature is that the experiment makes use of a small uniaxial stress, rather than a large hydrostatic one. This enables the elastic regime of the crystal to be probed and allows the extraction of directional information regarding the crystal potential energy. Furthermore, it provides a means whereby the motions of the molecules involved in the vibrational modes can be determined by observing how the frequencies of the vibrations change under stresses applied to the crystal in different directions.

Stress modulated transmission and reflectance spectroscopies are well known in the literature, but the majority of the work has been done on metals and semiconductors (Cardona, 1969). Its application to organic molecular crystals in more recent years has made use of both isotropic and uniaxial stresses in specular reflection experiments on aromatics (Merski and Eckhardt, 1981a,c; Anderson, 1985), charge transfer complexes (Merski and Eckhardt, 1981b), and dyes (Merski and Eckhardt, 1981d; Tristani-Kendra, 1984). The piezomodulated Raman experiment has been reported for a

polymer (Tzinis et al., 1978) and for the anthracene molecular crystal (White, Dye and Eckhardt, 1986); however, the former study lacked an underlying interpretation in terms of anharmonicity and data from the latter work did not display an unambiguous response as predicted by the theory due to the possible existence of an intergrowth phase.

The intent of this research has been to study strain-induced coupling in the lattice dynamics of 1,2,4,5-tetrabromobenzene (TBB) by means of piezomodulated Raman spectroscopy. By obtaining an unambiguous piezomodulated Raman response in a molecular crystal for the first time, an interpretation can be made based on the theory of Luty and Eckhardt (1985) that will quantify the anharmonic character of the various vibrational modes through the derivation of their respective coupling parameters. In so doing, the usefulness of the piezomodulated Raman experiment for the investigation of anharmonicity in the intermolecular potentials of molecular crystals will also be established.

TBB was chosen for this study for a number of reasons. Because of the distinct separation expected between its external and internal modes, it should be possible to determine the extent of strain-induced coupling exhibited by its lattice vibrations as compared to the intramolecular modes. This should provide a useful test of the theory that molecular vibrations, by being less coupled to the crystal lattice, are more harmonic than the lower frequency lattice