SPECTROSCOPIC TECHNIQUES and HINDERED

IOLECULAR

MOTION

Ferid Bashirov





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Preface

This monograph presents an advanced theoretical approach to the description of the spectroscopic study of the classical local thermal motion of small molecules and molecular fragments in crystals. The so-called extended angular jump model, which explores neither hydrodynamic theory nor dynamical methods, approximates the motion. This model of hindered molecular motion (HMM) is intermediate between the rotational diffusion model and the model of fixed angular jumps. Accounting for two point-symmetry groups of rotation-the symmetry group of molecular motion and that of its site, including distortion-enhances the power of the model. Symmetrized upon the irreducible representations of the crystallographic point symmetry group, the hindered states of the motion handle the transformation property of molecular quantities. Two phenomenological parameters of the model-the symmetrized correlation times and the dynamical weights of the motion-explore the fitted dynamic quantities of the theory. They allow us to obtain expanded knowledge of molecular dynamics as well as crystalline structure. We applied this innovative HMM theory to derive new analytical expressions describing quantitatively nuclear magnetic resonance relaxation rates and homogeneously broadened spectral lines offered by dielectric, infrared, Raman, Rayleigh, and incoherent neutron scattering spectroscopy techniques for both mono- and polycrystalline samples. The presented experimental spectroscopic investigations of HMM in molecular condensed substances make obvious the effectiveness of simulating HMM in the framework of the extended angular jump model. For example, we demonstrate that the experimental anisotropy of proton spin-lattice relaxation in ammonium chloride observed at low temperatures originates by structural distortion of the crystalline cubic unit cell. In addition, we establish theoretically that the nature of elastic and quasi-elastic incoherent neutron scattering is directly connected with the symmetry properties of HMM.

The treatment is classically phenomenological and should be useful primarily to experimentalists, and so we have included detailed derivations, tables of mathematical and numerical results, and comparisons of the theory with the experiments. Scientists, lecturers, and students of condensed matter physics can use the proposed monograph as a textbook as well as a manual in order to study microscopic peculiarities of the dynamics and the structure of molecular substances. Basic knowledge of the theory of stochastic processes, the theory of representations of the point symmetry groups, and some experimental practice in spectroscopy techniques would be beneficial in order to fruitfully exploit the contents of the book. I have not attempted to give a complete list of references, but I have occasionally inserted them when lack of space prevented me from making more than a mere allusion to the contents of the paper quoted.

Introductory comments added to some chapters will help graduate students readily assimilate the materials. I believe the book will stimulate new ideas and allow readers to better understand the structure and dynamics of condensed molecular media in the years to come. I would appreciate any comments as to possible errors or concerning corrections and improvements. At the same time, I expect that the statements presented here will find friendly acceptance and will be content if this book helps transfer some of the delight that I have experienced during my research in this fascinating field.

Acknowledgments

I would like to acknowledge the collaboration of my colleague Professor Nail Gaisin (Kazan Technological University). I take this opportunity to express my sincerest gratitude to Professor Albert Aganov (Kazan Federal University) for his generous and sympathetic help. Finally, I thank my wife, Khadycha, for her patience and encouragement; she made many efforts in order to give me the time I needed to write this book. This page intentionally left blank

Introduction

Determining the nature of intra- and intermolecular interactions as well as the character of molecular motion is one of the key problems of condensed state physics. Intermolecular interactions are feeble in gases and the motion of molecules is free during a mean time between two sequential collisions. The strong intermolecular interaction in a condensed substance converts a problem of statistical description of molecular motion into a many-body problem. Difficulties exhibited by dynamical and statistical theories of continuous medium have led to the involvement of alternative research techniques based on hypothetical models of the thermal molecular motion. At the same time, any model for approximating a physical phenomenon requires rigorous checking for its correspondence to actual events. Such checking is to be performed by experiments on real samples or, lacking those, by means of computer modeling.

Conformity of theoretical processing to experimental data and consistency of the results obtained by various experimental procedures are the major factors of quality in physical theory. Difficulties arising from the quantitative description of spectroscopic data that provide condensed molecular media give evidence to the fact that microscopic-level mysteries persist even today. Considering that the common physical properties of molecular solids and liquids are similar at temperatures close to fusion point, the solution of the thermal molecular motion problem in solids could accelerate elaboration of the general theory of condensed molecular media. This lack of a general theory impedes an understanding of the collected experimental data and the setup of new research.

The solution of the molecular motion problem in crystals has further value in the applied sense. A list that is by no means complete of those processes, phenomena, and understandings that would benefit from the study of molecular motion in crystals would include an understanding of the nature of structural phase transformation; the process of premelt crystallization; the phenomena of piezoelectricity, ferroelectricity, double refraction, and optical rotation; and the determination of the geometry of potential crystalline field, interatomic distances, the probabilities of elementary rotational displacements, and the energy barriers of molecular motion.

Liquid crystals present a classroom of substances for which studying orientational ordering shows a special significance. Organic compounds, polymers, pharmaceutical products, and biological systems consist of molecular fragments that possess rotational or conformational degrees of freedom, or there is an atomic exchange within. Determining laws of molecular motion allows one to obtain knowledge of that process and in what degree the interactions of various natures depend on each other. For example, magnetic and electrical interactions of nuclei and electrons depend on mechanical interactions and vice versa, as well as on external conditions: temperature, pressure, electrical and magnetic fields; composition and quantity of impurities; structural distortion, and so on. And knowledge of these laws stimulates growing new crystals and synthesizing new substances with the desired properties. It is clear that the noted examples do not exhaust all the various scientific and engineering problems for which experimental and theoretical study of the thermal molecular motion problem in condensed substances has paramount value.

The scope of this monograph is restricted to small molecules and molecular fragments such as N_2 , HC1, CO₂, CH₄, H₂O, NH₄, BeF₄, NH₃, CH₃, C₆H₆, SF₆, and other symmetrical atomic formations that exhibit local hindered motion in molecular condensed media: molecular and ionic crystals, molecular liquids, liquid crystals, polymeric solids, and biological objects. Chapter 1 presents the actual state of the theory of hindered molecular motion (HMM). Peculiarities of two well-known HMM models—the rotational diffusion model (RD model) and the model of fixed angular jumps (FAJ model)—are discussed. In Chapter 2, we describe the extended angular jump model (EAJ model) resulting from a selective choice of the priority ideas underlying two former models; then, by using the EAJ model, a rigorous solution of the HMM stochastic problem for molecular crystals is given.

The general and explicit forms of the angular autocorrelation functions of the unitary spherical tensor components adapted to the crystallographic point symmetry groups are derived for the EAJ model in Chapter 3.

The molecular spectroscopy applications of the HMM theory are given in Chapters 4–6. Frequency-dependent line shapes in dielectric, infrared absorption, and Rayleigh and Raman light scattering spectra show like peculiarities (Chapter 4). They consist of the sum of Lorentzians whose quantity is determined by the number of irreducible nonequivalent, nonidentical representations of a HMM symmetry group and do not exceed the number 3.

The application of the HMM theory to discussion of the exponential nuclear magnetic resonance relaxation is given in Chapter 5. We are concerned with the spin-lattice relaxation of the dipole and quadruple nuclei with respect to the laboratory and rotating reference frames in single- and polycrystalline samples. Explicit expressions are given for the relaxation rates in three- and four-spin systems. The experimental anisotropy of the proton relaxation rates in cubic ammonium chloride is explained by the tetragonal distortion of its cubic unit cell at low temperatures. A decrease of the proton relaxation rates in rotating three-spin systems with respect to predictions following the Bloembergen-Purcell-Pound (BPP) relaxation theory is interpreted in the framework of the EAJ model.

Incoherent neutron scattering application is discussed in Chapter 6. It is shown that HMM symmetrized solely in identical, irreducible representations of the point groups contributes to elastic incoherent neutron scattering; nonidentical representations originate quasi-elastic scattering. The interpretation of the experimental data on elastic incoherent neutron scattering in some polycrystalline samples is revised, and the realistic knowledge of the hindered motion of proton vectors and their site symmetry are obtained. This page intentionally left blank