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Structure and Dynamics of Non-Rigid Molecular Systems

Edited by
YVES G. SMEYERS
CSIC, Madrid, Spain

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FOREWORD

This volume contains a selection of scientific papers related to the structure and dynamics of non-rigid molecules. This frontline topic was born a few decades ago, when Longuet-Higgins proposed his famous theory of Molecular Symmetry Groups (*Mol. Phys.* **6**, (1962) 457).

Unfortunately, since this early paper, very few publications have been devoted to the study of non-rigid molecules. Let us mention some books which dedicate some chapters to them: *Induced Representations in Crystals and Molecules*, by S. L. Altmann, Academic Publishers, 1977; *Molecular Symmetry and Spectroscopy*, by P. R. Bunker, Academic Publishers, 1979; and finally *Large Amplitude Motion in Molecules*, Vols. I and II, by several authors, Springer Verlag, 1979.

More recently an International Symposium on Non-Rigid Molecules was held in Paris, France, from 1–7 July 1982, the proceedings of which were published in the volume entitled *Symmetries and Properties of Non-Rigid Molecules. A Comprehensive Survey*, edited by J. Maruani *et al.*, Elsevier, 1983.

Finally, we should mention the very specialized work *The Permutational Approach to Dynamic Stereochemistry*, by J. Brocas *et al.*, McGraw-Hill, 1983.

The purpose of this book is to fill in this information on the structure and dynamics of non-rigid systems. To this aim, we have gathered a collection of recent papers written by the most qualified specialists in the world, covering a large field from van der Waals molecules to inorganic complexes and organic polyrotor molecules, as well as considering statistical and dynamic aspects.

We wish to express here our thanks to all the authors of the different chapters of this book, and especially to Professor R. S. Berry of the University of Chicago for agreeing to write the preface.

Y.G. SMEYERS

PREFACE

R. STEPHEN BERRY
Department of Chemistry and The James Franck Institute,
The University of Chicago,
Chicago, IL 60637,
U.S.A.

The successes of the structural concept of molecules, firmly established by such achievements as the demonstration in the mid–1870s of the structure of benzene and the simultaneous clarification of the molecular basis of optical activity, made into dogma the idea that 'molecules have structures'. Modern molecular spectroscopy grew up on this dogma; atoms comprising a molecule have precise positions, relative to one another, around which the atoms undergo vibrations of very small amplitude, relative to the distances between atomic centres. Hence molecules are like near-rigid, quivering Tinkertoys or Meccano models, capable of rotating almost as if they were truly rigid structures. This picture allows us to describe the vibrational and rotational motions as almost independent, separable motions. Whatever deviations there may be from separability can be considered small perturbations, interpretable in the traditional context of centrifugal distortions and Coriolis interactions. With the advent of quantum mechanics, these ideas all found expression in the language of discrete states, still identifiable as states of small-amplitude oscillation, or of near-rigid rotation, or of a combination of both. The quantum equations were tractable enough that it was not even necessary to call upon the Correspondence Principle to find the wave functions and the energy eigenvalues for the states of molecular rotor-vibrators.

All this made the concept of a molecule very different from the concepts, more or less simultaneously developed, of the atom and of the nucleus. The concepts of their 'structures' quickly becoming models of free-flowing collections of component particles moving relatively independently. The most popular model of the nucleus for a long time was that of a liquid drop. The corresponding model of atoms was the quantum analogue of a solar system. The excitations of a nucleus became the excitation of collective modes of a fluid; those of an atom became the single-particle excitations of the individual electrons, notably from one shell to another.

The lore of almost-rigid molecules developed despite chemists' awareness of tautomerism, of the capacity of some special systems to rearrange. One of the most elegant and historically important was the cyclopentane molecule, a $(CH_2)_5$ ring, with four carbons in a common plane and the fifth, out of that plane. The special tautomerism of this system allows the out-of-plane carbon to return to the common plane and another carbon to move out of the plane; because of the identity of equivalent atoms, the isomer produced by this tautomerism looks like the initial species, just rotated, clockwise or counter-clockwise, by $2\pi/5$ or $4\pi/5$. In fact, the process involves both a permutation and a rotation, so is called a 'pseudo-rotation'. More elaborate motions are involved when species such as the trigonal bipyramids of PF_5 or $Fe(CO)_5$ pseudo-rotate to exchange axial and equatorial pairs of atoms. Still more complex systems are still being analysed, as illustrated by the chapter by Brocas in this book, on heptacoordinated systems.

By the 1960s, and even more still later, as it became possible to excite molecules to specific, high-energy vibrational states and to probe the internal dynamics of tautomerizing or rearranging molecules, the idea grew that molecules may be not so rigid, and that many of their kinetic properties are consequences of rearrangements. For example, the pseudo-rotation of 5-coordinate phosphorus compounds, originally introduced to interpret the equivalence of the NMR resonance frequencies of all five fluorines of PF_5, turned out to be the explanation also for the mechanism of very important biochemical process of phosphate ester hydrolysis.

As the subject grew, its fundamental mathematical and quantum-mechanical aspects challenged theorists. This aspect is reviewed and developed in the first chapter, by Boldyrev. Some of the traditional concepts, such as those associated with normal modes of vibration of a nearly rigid molecule, lose their meaning and must be replaced in some cases with new concepts that can be used outside the confines of validity of the older ideas; Natanson explores this topic, both how the traditional ideas break down and how we might be able to extend and replace them. Experimental approaches to probe non-rigid species, by fluorescence of jet-cooled species and by photodissociation, are the bases of the chapters by Laane and collaborators, and by Delgado-Barrio and Beswick, respectively. The fundamental physical generalities of non-rigid systems are the subjects of the chapters by Smeyers, on the symmetries and group theory of the problem, and by Weeks and Levine, on the nature of the coupling of the anharmonic modes, a subject closely related to that examined by Natanson, but from quite a different viewpoint. The underlying potential surfaces of non-rigid molecules is the subject of the chapter by Cárdenas-Jirón and her collaborators.

Together, these chapters provide a picture of much of what is going on at the frontiers of the very lively field of non-rigid molecules. For truly it has become a topic in itself, with tangent lines to chemical kinetics, phase transitions, theory of potential surfaces, chaotic and regular dynamics and the fields in which non-

rigid molecular processes play specific, crucial roles as in biochemistry. The book is probably immediately accessible to someone knowledgable in any of these subjects. It may require some background reading for others.

Only in relatively recent years have there been reviews of non-rigid molecular systems. Among them this writer and several others who have worked in the field have contributed. However, perhaps the most comprehensive, and one that would provide the most thorough background for this volume, is probably the 1986 monograph *Contemporary Theory of Chemical Isomerism* by Zdenek Slanina. That slim book reviews most of the concepts that Yves Smeyers and his co-authors have to assume, as they present the state of the art of non-rigid molecules.

R. STEPHEN BERRY
Spring 1994