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I. B. Bersuker V. Z. Polinger

Vibronic Interactions in Molecules and Crystals

With 86 Figures

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Professor Dr. Isaac B. Bersuker
Dr. Sci. Victor Z. Polinger
Department of Quantum Chemistry, Institute of Chemistry
Academy of Sciences, MoSSR, Grosul Street 3
SU-277028 Kishinev, USSR

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Preface

Vibronic interaction effects constitute a new field of investigation in the physics and chemistry of molecules and crystals that combines all the phenomena and laws originating from the mixing of different electronic states by nuclear displacements. This field is based on a new concept which goes beyond the separate descriptions of electronic and nuclear motions in the adiabatic approximation. Publications on this topic often appear under the title of the Jahn-Teller effect, although the area of application of the new approach is much wider: the term *vibronic interaction* seems to be more appropriate to the field as a whole.

The present understanding of the subject was reached only recently, during the last quarter of a century. As a result of intensive development of the theory and experiment, it was shown that the nonadiabatic mixing of close-in-energy electronic states under nuclear displacements and the back influence of the modified electronic structure on the nuclear dynamics result in a series of new effects in the properties of molecules and crystals. The applications of the theory of vibronic interactions cover the full range of spectroscopy [including visible, ultraviolet, infrared, Raman, EPR, NMR, nuclear quadrupole resonance (NQR), nuclear gamma resonance (NGR), photoelectron and x-ray spectroscopy], polarizability and magnetic susceptibility, scattering phenomena, ideal and impurity crystal physics and chemistry (including structural as well as ferroelectric phase transitions), stereochemistry and instability of molecular (including biological) systems, mechanisms of chemical reactions and catalysis.

The most interesting achievements of the theory of vibronic interactions are related to structural phase transitions in crystals (or, in a wider sense, to structural phase transformations in condensed media), the physics of impurity centers in crystals, and spectroscopy of polyatomic systems. In particular, structural aspects of the high-temperature superconductivity discovered recently have, beyond doubt, a vibronic nature.

This volume emerged from investigations on the theory of vibronic interactions carried out in collaboration with co-workers and colleagues at the Moldavian Academy of Sciences over a period of more than 25 years. It is the first book on this topic to be published for more than 15 years, during which time new ideas have been developed and some problems of primary importance have been solved. The authors hope that all main results on the theory of vibronic interactions in molecules and crystals obtained until now are well represented in this book, with the exception of some chemical and biological applications and some other special problems. Compared with the Russian book on which this edition is based, this

volume is more complete, in particular due to the addition of a survey of Green's function approaches, the solutions of multimode and multicenter problems, evaluations of additional interesting cases of optical and photoelectron spectra, polarizabilities and birefringence, Peierls transitions, and a general model for structural phase transitions in condensed media.

This book is mainly addressed to physicists – theoreticians and experimentalists (researchers, professors, graduate students, etc.) – specialists in the field of the structure and properties of molecules and crystals. However, this book may also be useful for specialists in related fields, in particular for chemists, biologists, and materials scientists; many new properties of materials have proved to be of vibronic origin.

I. B. Bersuker
V. Z. Polinger

Kishinev, January 1989

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