

49

Springer Series in Chemical Physics

Edited by Vitalii I. Goldanskii



# Springer Series in Chemical Physics

Editors: Vitalii I. Goldanskii Fritz P. Schäfer J. Peter Toennies

Managing Editor: H. K. V. Lotsch

- Volume 40 **High-Resolution Spectroscopy of Transient Molecules**  
By E. Hirota
- Volume 41 **High Resolution Spectral Atlas of Nitrogen Dioxide 559–597 nm**  
By K. Uehara and H. Sasada
- Volume 42 **Antennas and Reaction Centers of Photosynthetic Bacteria**  
Structure, Interactions, and Dynamics  
Editor: M. E. Michel-Beyerle
- Volume 43 **The Atom-Atom Potential Method.** Applications to Organic  
Molecular Solids  
By A. J. Pertsin and A. I. Kitaigorodsky
- Volume 44 **Secondary Ion Mass Spectrometry SIMS V**  
Editors: A. Benninghoven, R. J. Colton, D. S. Simons, and  
H. W. Werner
- Volume 45 **Thermotropic Liquid Crystals, Fundamentals**  
By G. Vertogen and W. H. de Jeu
- Volume 46 **Ultrafast Phenomena V**  
Editors: G. R. Fleming and A. E. Siegman
- Volume 47 **Complex Chemical Reaction Systems**  
Editors: J. Warnatz and W. Jäger
- Volume 48 **Ultrafast Phenomena VI**  
Editors: T. Yajima, K. Yoshihara, C. B. Harris, and S. Shionoya
- Volume 49 **Vibronic Interactions in Molecules and Crystals**  
By I. B. Bersuker and V. Z. Polinger
- Volume 50 **Molecular and Laser Spectroscopy**  
By Zu-Geng Wang and Hui-Rong Xia

Volumes 1–39 are listed on the back inside cover

---

I. B. Bersuker V. Z. Polinger

# Vibronic Interactions in Molecules and Crystals

With 86 Figures

Springer-Verlag Berlin Heidelberg New York  
London Paris Tokyo HongKong

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

*Series Editors*

Professor Vitalii I. Goldanskii

Institute of Chemical Physics  
Academy of Sciences, Kosygin Street 3  
Moscow V-334, USSR

Professor Dr. Fritz P. Schäfer

Max-Planck-Institut für  
Biophysikalische Chemie  
D-3400 Göttingen-Nikolausberg, FRG

Professor Dr. J. Peter Toennies

Max-Planck-Institut für Strömungsforschung  
Böttingerstrasse 6-8  
D-3400 Göttingen, FRG

*Managing Editor:* Dr. Helmut K. V. Lotsch

Springer-Verlag, Tiergartenstrasse 17  
D-6900 Heidelberg, Fed. Rep. of Germany

---

This edition is an updated version of the original Russian edition:

**Vibronnuie Vsaimodeistviya v Molekulakh i Kristallakh**

© Nauka, Moscow 1983

---

ISBN13:978-3-642-83481-3

e-ISBN-13:978-3-642-83479-0

DOI: 10.1007/978-3-642-83479-0

Library of Congress Cataloging-in-Publication Data. Bersuker, I. B. (Isaak Borisovich) [Vibronnye vzaimodeistviya v molekulakh i kristallakh. English] Vibronic interactions in molecules and crystals / I. B. Bersuker, V. Z. Polinger. p. cm.—(Springer series in chemical physics ; v. 49) Translation of: Vibronnye vzaimodeistviya v molekulakh i kristallakh. Bibliography: p. Includes index. ISBN 0-387-19259-X (U.S.) 1. Jahn-Teller effect. 2. Molecules. 3. Crystals. I. Polinger, V. Z. (Viktor Zigrifidovich) II. Title. III. Series. QD461.B46313 1989 539'.6—dc 19 88-16100

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its version of June 24, 1985, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1989

Softcover reprint of the hardcover 1st edition 1989

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: ASCO Trade Typesetting Ltd., Hong Kong  
2154/3150-543210 – Printed on acid-free paper

# 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.

Kishinev, January 1989

*I. B. Bersuker*  
*V. Z. Polinger*

## **Acknowledgements**

We are grateful to our co-workers and colleagues. Without our shared research and continuous personal contact the general presentation of the subject given in this book would not have been possible. With special pleasure we acknowledge fruitful discussions with B. G. Vekhter, M. D. Kaplan, I. Ya. Ogurtsov, Yu. E. Perlin, Yu. B. Rosenfeld, D. I. Khomskii and B. S. Tsukerblat.

We also acknowledge the discussions and cooperation with C. A. Bates, L. S. Cederbaum, R. Englman, F. S. Ham, V. V. Hizhnyakov, N. N. Kristoffel, K.-A. Müller, M. C. M. O'Brian, D. Reinen, H. Thomas and M. Wagner.

# Contents

<b>1. Introduction</b> .....	1
<b>2. Vibronic Interactions and the Jahn-Teller Theorem</b> .....	5
2.1 Adiabatic Approximation .....	5
2.1.1 Proper Adiabatic Approximation .....	5
2.1.2 Born-Oppenheimer Approximation .....	9
2.2 The Vibronic Hamiltonian .....	14
2.2.1 Reference Nuclear Configuration .....	14
2.2.2 Matrix Vibronic Hamiltonian .....	19
2.2.3 Primary Force Constants. Linear and Quadratic Vibronic Coupling .....	22
2.3 The Jahn-Teller Theorem .....	25
<b>3. Adiabatic Potentials</b> .....	31
3.1 The Orbital Doublet ( $E$ Term) .....	31
3.1.1 $E \otimes e$ Case: The Mexican Hat and the Tricorn .....	32
3.1.2 $E \otimes (b_1 + b_2)$ Case. The Method of Öpik and Pryce .....	40
3.2 Symmetry of Jahn-Teller Systems .....	45
3.2.1 Lee Symmetry of the Jahn-Teller Hamiltonian .....	45
3.2.2 Symmetry Properties of Adiabatic Potential Energy Surfaces	52
3.3 Triplet and Quadruplet Terms .....	55
3.3.1 $T \otimes d$ problem ( $d$ Mode Approximation) .....	55
3.3.2 $T \otimes (e + t_2)$ Problem .....	58
3.3.3 Cubic Quadruplet Terms: $T_8 \otimes (e + t_2)$ Problem .....	67
3.4 Pseudodegenerate Electronic Terms (Pseudo-Jahn-Teller Effect) ...	69
3.4.1 The Two-Level Case .....	69
3.4.2 Dipole Instability in Systems with an Inversion Center .....	75
3.4.3 Vibronic Origin of Molecular Dynamic Instability .....	79
3.5 Adiabatic Potentials for Multimode Systems .....	81
3.5.1 Ideal and Multimode Vibronic Systems .....	81
3.5.2 The Two-Mode $E \otimes (b_1 + b_1)$ Problem .....	82
3.5.3 General Case .....	85
3.6 The Jahn-Teller Effect in Polynuclear Clusters .....	90
3.6.1 Vibronic Interactions in a Bioctahedron .....	92
3.6.2 Electron Localization and Delocalization in Mixed-Valence Cluster Compounds .....	101



<b>4. Solution of Vibronic Equations. Tunneling Splitting</b> .....	107
4.1 Weak Vibronic Coupling. Perturbation Theory .....	107
4.1.1 Operator Version of Perturbation Theory .....	108
4.1.2 Weak Coupling Case in the $E \otimes e$ Problem .....	111
4.1.3 Perturbation Treatment of Other Jahn-Teller Problems ( $E \otimes b_1, E \otimes b_2, T \otimes e, T \otimes t_2, \Gamma_8 \otimes e, \Gamma_8 \otimes t_2$ ) .....	114
4.1.4 Weak Pseudo-Jahn-Teller Effect .....	117
4.2 Strong Vibronic Coupling. Free Rotation of Distortions .....	119
4.2.1 The Adiabatic Separation of Nuclear Motion. Elastically and Centrifugally Stabilized States .....	120
4.2.2 Quasi-Classical Approach to Jahn-Teller Problems .....	125
4.3 Hindered Rotations and Pulse Motions of Distortions. Tunneling Splitting .....	128
4.3.1 Warping Terms in the $E \otimes e$ Problem as Small Perturbations	129
4.3.2 Hindered Rotations of Jahn-Teller Distortions .....	130
4.3.3 Tunneling of Jahn-Teller Distortions Through Potential Bar- riers. Tunneling Splitting .....	134
4.3.4 Symmetry Properties and Group-Theoretical Classification of Tunneling States .....	142
4.4 Numerical Solutions of Vibronic Equations .....	145
4.5 Multiparticle Methods in the Theory of the Jahn-Teller Effect ...	158
4.5.1 General Relationships .....	159
4.5.2 The Case of Weak Coupling. Perturbation Theory in the Green's Function Method .....	163
4.5.3 The Method of Unitary Transformations .....	166
4.6 The Multimode Jahn-Teller Effect. Phonon Dispersion in Crystals	167
4.6.1 Qualitative Discussion .....	167
4.6.2 The Case of Weak Coupling. Perturbation Theory .....	170
4.6.3 Strong Coupling Case .....	174
4.6.4 Intermediate Coupling. Low-Energy Approximation .....	184
4.6.5 Other Models and Approximations .....	192
4.7 Factors of Vibronic Reduction .....	195
4.7.1 General Discussion .....	196
4.7.2 Concrete Analytical and Numerical Calculations of the Vibronic Reduction Factors .....	202
4.7.3 Vibronic Reduction in Second-Order Perturbation Theory ..	205
4.7.4 Vibronic Amplification of Nuclear Displacement Operators	207
<b>5. Spectroscopic Manifestations of Vibronic Effects</b> .....	209
5.1 The Shape of Optical Bands of Electron Transitions Between Degenerate Electronic Terms .....	209
5.1.1 General Theory of Multiplet-Multiplet Optical Transitions .	210
5.1.2 The Jahn-Teller Effect in the Excitation Spectrum of the $A \rightarrow E$ Transition .....	215

5.1.3	Manifestations of Vibronic Interactions in the Optical Spectra of the $A \rightarrow T$ Transition .....	223
5.1.4	Other Vibronic Effects in Electron Excitation Spectroscopy .....	226
5.1.5	The Jahn-Teller Effect in Radiative and Nonradiative Decay .....	229
5.1.6	Multimode Vibronic Effects in Electronic Spectra .....	231
5.1.7	The Method of Moments and Polarization Dichroism of Jahn-Teller Systems .....	235
5.2	Splitting of the Zero-Phonon Lines of the Optical Absorption and Luminescence .....	240
5.2.1	Vibronic Splitting and Broadening of the Zero-Phonon Line .....	242
5.2.2	Effect of External Field and Strain. Tunneling Splitting of the Zero-Phonon Line .....	247
5.3	Vibronic Effects in Infrared Absorption and Raman Spectra ....	251
5.3.1	Vibronic Effects in Vibrational Infrared Spectra .....	252
5.3.2	Rotational Vibronic Infrared Spectra of Free Oriented Molecules .....	260
5.3.3	Vibronic Nonresonant Raman Spectra .....	266
5.3.4	Vibronic Effects in Resonant Raman Scattering .....	273
5.3.5	Birefringence in Jahn-Teller Spherical Top Molecules .....	274
5.4	The Dynamic Jahn-Teller Effect in Magnetic Resonance Spectra ..	281
5.4.1	Effect of Vibronic Reduction of the Angular Momentum of Electrons in EPR Spectra. Two-State Model .....	282
5.4.2	Effect of Random Strain .....	285
5.4.3	Motional Narrowing of the EPR Broadened Band .....	290
5.5	Electron Paramagnetic Resonance. The Static Jahn-Teller Effect ..	296
5.5.1	Nature of the Isotropic EPR Spectrum of Cubic Paramagnetic Systems. Three-State Model .....	297
5.5.2	Effect of Random Strain. Angular Dependence of Spectra ..	302
5.5.3	Magnetic Resonance Spectra for Jahn-Teller Orbital Triplet Centers .....	312
<b>6.</b>	<b>Cooperative Phenomena. Structural Phase Transitions .....</b>	<b>317</b>
6.1	Ordering of Distortions in Crystals. Cooperative Jahn-Teller Effect ..	317
6.1.1	The Hamiltonian of the Jahn-Teller Crystal. Correlation of Local Distortions with Electronic States of Jahn-Teller Ions ..	319
6.1.2	Mean Field Approximation .....	322
6.1.3	A Simple Example: The $E \otimes b_1$ Jahn-Teller Crystal .....	324
6.1.4	Cooperative Jahn-Teller Effect in Cases of Weak, Strong and Intermediate Vibronic Coupling .....	328
6.1.5	Jahn-Teller Crystals with Insignificant Nonadiabaticity. Shift Transformation .....	334
6.1.6	Dynamics of Elementary Excitations .....	335
6.1.7	Interaction with the Macroscopic Deformations. Ferroelastic Phase Transitions .....	339

6.2 Pseudo-Jahn-Teller Mechanism of Spontaneous Polarization of Crystals. The Vibronic Theory of Ferroelectricity .....	344
6.2.1 The Simplest Case: Two-Band Model .....	345
6.2.2 Adiabatic Approach to Spontaneous Polarization .....	351
6.2.3 Perovskites .....	353
6.3 The Vibronic Theory of Structural Transformations in Condensed Media .....	359
6.3.1 Vibronic Origin of Instability of the High Symmetry Configuration of Dielectric Crystals .....	360
6.3.2 The Peierls-Fröhlich Theorem. The Band Jahn-Teller Effect .....	365
6.3.3 General Model of Structural Transformations in Condensed Matter .....	375
<b>Appendix A.</b> Expansion of the Full Vibrational Representation in Terms of Irreducible Ones .....	380
<b>Appendix B.</b> Expansion of the Symmetric and Antisymmetric Products of Degenerate Representations .....	389
<b>Appendix C.</b> Proof of the Jahn-Teller Theorem .....	391
<b>References</b> .....	397
<b>Subject Index</b> .....	419