**VIBRATIONAL-ROTATIONAL
EXCITATIONS IN
NONLINEAR MOLECULAR
SYSTEMS**

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Preface

"If there would be no God – then what a staff-captain am I?" – said one of the characters in a novel by Dostoevskii. In a similar way we can exclaim: "If there would be no nonlinearity – than what physics would that be?".

Really, the most interesting and exciting effects are described by nonlinear equations, and vanish in the linear approximation. For example, the general theory of relativity by A.Einstein comes to mind first — one of the most beautiful physical theories, which is in fact essentially nonlinear. Next, the phase transitions crystal – liquid and liquid – gas are due to the anharmonicity of inter-particle interactions, to dissociation and infinite motion. Similarly, transitions into the superconducting state or the superfluid would be impossible with purely harmonic interaction potentials. Another brilliant achievement in nonlinear physics was the construction of a laser and the subsequent development of nonlinear optics. The latter describes the interaction of the matter with light of super-high intensity, when multi-quanta intra-molecular transitions become essential. Last, we should note here the very beautiful mathematical theory – the theory of catastrophes. Its subject is the study of invariant general properties of multi-dimensional surfaces in the vicinity of bifurcation points with respect to continuous transformations. Assigning one or another physical meaning to multi-dimensional surfaces – for example, interpreting these either as potential surfaces of the interaction $U(R, r)$, or as a thermodynamic potential $\Phi(P, T, \eta)$, etc. – we can study the behavior of the systems in the vicinity of critical (bifurcation) points with the help of the theory of catastrophes.

Most monographs on intra - molecular vibrations and vibrational - rotational spectra of molecules are based on the theory of normal modes, while the nonlinearity is taken into account within perturbation theory. However, in high-intensity laser field the highly-excited intra-molecular vibrational-rotational modes are involved. The nonlinearity of motion plays then a decisive role and it should be taken into account properly in zero order approximation already. In the present book we will address the nonlinearity effects in polyatomic molecules exactly from that point of view. In the world of molecules we step away from the island of linearity into the intriguing ocean of nonlinearity. We hope, this journey will be interesting.

Recent progress in experimental laser technique provided extraordinary opportunities in the study of high vibrational / rotational overtones in the

spectra of polyatomic molecules. As it has been shown (A.A.Ovchinnikov, 1969), high excitations in nonlinear molecular systems give rise to local modes, which influence greatly the spectral properties and intramolecular kinetics. The theory of these effects is of great importance for the interpretation of experiments in IR spectroscopy, in the promising field of laser chemistry and molecular engineering (analysis, synthesis, and construction of complex organic molecules), in nonlinear optics, in the study of chemical transitions, etc. Besides, it forms an important inter-disciplinary part of fundamental theory at the border of chemical physics, physical chemistry, spectroscopy, quantum mechanics, and solid state physics.

This book is aimed at providing a comprehensive theoretical description of highly - excited long - living vibrational / rotational excitations in anharmonic molecules. It comprises the classical and quantum theory of local modes, their effect upon the infrared (IR) spectra of molecules and upon the kinetics of intramolecular relaxation, and presents a semi-empirical theory that relates the geometrical parameters of the molecule to the IR spectra. Besides, we added the material on breathers – local excitations of deformable lattices with inner vibrational structure, which attract much attention recently. At present the comprehensive analysis of the entire field is still lacking.

The following problems are considered in detail:

a) Classification of oscillation spectra of strongly excited molecules and molecular crystals. The principal idea is to explain the vibronic excitation formation, its long - living nature, and relaxation of vibration energy with the account of vibration nonlinearity for CH and OH bonds, with special emphasis on the nonperturbative nature of these effects;

b) Clusterization of vibrational and rotational energy levels;

c) Dynamical breakdown of symmetry of vibrational and rotational motion in polyatomic molecules;

d) Interpretation of IR spectra of organic molecules on the basis of local - mode theory;

e) Calculation of relaxation time for highly - excited vibrations in polyatomic molecules;

f) Existence of breathers, their stability and decay.

As to the form of the presentation of the material, our idea was to provide:

a) a systematic and comprehensive presentation (unified theoretical approach to the problems; inclusion of all the important topics in the field from the basics to up-to-date research);

b) a detailed form of presentation (only basic knowledge of quantum mechanics required as the background; all the important derivations performed in detail, without recourse to original literature);

c) suitability to a wide auditorium, ranging from graduate students, specializing in spectroscopy, molecular physics, optics, etc. up to academic

researchers.

The book is structured as follows: The Introduction provides the basics of the conventional normal - mode theory of vibrations and a brief survey of the principal ideas of the local - mode theory. In Chapter 2 and Chapter 3 the classical theory of localization of vibrational excitations is presented on the basis of the model of two coupled nonlinear oscillators and is generalized consequently to an arbitrary number of weakly interacting nonlinear oscillators. Criteria for local - mode formation and decay are formulated and studied. The theory of breathers and its relation to the theory of local modes is described in Chapter 4. The quantum theory of local modes and vibrational - rotational spectra of polyatomic molecules is considered in Chapters 5 and 6. On the basis of the model of two coupled Morse oscillators the conditions for the emergence of localized vibrational / rotational modes in polyatomic molecules are specified with the account of nonlinear interactions, both potential and kinematic ones. The effect of clusterization of stretching - vibrational levels in the spectrum is addressed. Construction of model Hamiltonians for the vibrational / rotational motion of molecules, along with the method of contact transformations is discussed. Clusterization of rotational levels in the spectrum within the semiclassical approach is studied in Chapter 7, with the account of the symmetry of the molecule and its rigidity. The account of interaction of vibrations and rotations, and its effect upon the spectrum and level clusterization is considered in Chapter 8. The influence of Fermi resonances upon the spectrum and the structure of phase space is discussed. Intramolecular relaxation of vibrational energy in the presence of local modes is studied in Chapter 9 and Chapter 10, both for isolated molecules and for molecular crystals. Correlation between the molecular structure and IR spectra of polyatomic molecules is investigated within a semi-empirical approach in Chapter 10 as well.

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Contents

1	Introduction	1
2	Classical theory of nonlinear vibrational systems; local modes	17
2.1	Survey of classical mechanics; introduction to local modes . .	17
2.2	Method of averaging	27
2.3	Two weakly coupled Morse oscillators: dynamics and local - mode formation	30
2.4	Analysis of phase trajectories with the help of Poincare sections, numerical results	46
3	Coupled nonlinear oscillators: formation and decay of local modes	55
3.1	Two weakly coupled nonlinear oscillators: decay of normal modes	56
3.2	Multi-oscillator systems: local modes' and normal modes' representations	60
3.3	Morse oscillators: calculation of resonance linewidths and criteria for the appearance of local modes	68
3.4	Coupled nonlinear oscillators: localized vibrational excitations and their asymptotic stability	77
3.5	Canonical transformation to local - mode representation . . .	89
4	Discrete breathers	97
4.1	Breathers in Hamiltonian lattices	97
4.2	Discrete breathers in one-dimensional chains	100
4.3	Arguments for the existence of discrete breathers: some mathematics	105
4.4	Discrete breathers: numerical experiments	107
4.5	Discrete breathers in lattices with a homogeneous potential .	112
4.6	An exactly solvable Hamiltonian lattice	115

5 Quantum theory of vibrational - rotational spectra in XY_2 - type molecules	119
5.1 Quantum theory of two Morse oscillators: stretching - vibration spectra in XY_2 molecules	121
5.2 Stretching - vibration spectra: nonresonant modes' effect upon clusterization of levels	130
5.3 Spectrum of stretching vibrations in XY_2 molecules: numerical studies	136
6 Quantum Hamiltonians of vibrational - rotational excitations in polyatomic molecules; method of contact transformations	143
6.1 Quantum Hamiltonian of polyatomic molecules	144
6.2 Molecular Hamiltonian in the inner basis representation 'coordinates - angles'	153
6.3 Contact transformation	160
6.4 Vibrational-rotational Hamiltonian for XY_2 molecule in the inner basis representation 'coordinates - angles'	168
7 Semiclassical rotational spectra of rigid and semi-rigid molecules; clusterization of levels and internal symmetry	177
7.1 Spectrum of polyatomic molecules: clusterization of rotational levels	178
7.2 Rotational spectrum of rigid and semi-rigid molecules: semiclassical approach	191
7.3 Symmetry - based analysis of rotational clusters	204
7.4 Tunnelling matrix	216
7.5 Violation of permutation symmetry and the super-hyperfine structure	229
8 Interaction of vibrations and rotations; polyads and their spectra	243
8.1 Interaction of local vibration modes and rotation in hydrides	244
8.2 Rotational - vibrational spectrum in the vicinity of bifurcation points	258
8.3 Spectral properties of systems with Fermi resonances	274
9 Intramolecular relaxation of vibrations in the presence of local modes	283
9.1 Localized long - living vibrational states in molecular crystals	286
9.2 Population inversion of localized long - living vibrational states in a cold lattice	294
9.3 Interaction of isolated levels with the continuous spectrum .	298

10 IR spectra and intramolecular relaxation	313
10.1 Redistribution of intramolecular energy: influence of multi-mode resonance	313
10.2 Relation between the absorption linewidths, intramolecular vibrations evolution, and unimolecular decay rates	324
10.3 Effect of anharmonicity on IR spectra of polyatomic molecules	330
10.4 Correlation between structure and IR spectra in polyatomic molecules	336
11 Conclusion	341
Bibliography	343
Index	353