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Manifestation of bifurcations and diabolic points in molecular energy spectra

D. A. Sadovskii

Institute of Spectroscopy, U.S.S.R. Academy of Sciences, Moscow Region, Troitzk, 142092, Union of Soviet Socialist Republics

B. I. Zhilinskii

Chemistry Department, Moscow State University, Moscow 119899, Union of Soviet Socialist Republics

J. P. Champion and G. Pierre

Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, Université de Bourgogne, 6 Bd Gabriel, 21100 Dijon, France

The general scheme of the qualitative analysis of finite-particle quantum problems is discussed. Theoretical methods for the qualitative analysis of energy spectra in quantum problems are applied to the study of the rovibrational energy levels of spherical top molecules. The existence of modifications in the rotational cluster structure and of redistributions of the energy levels between different branches under the rotational excitation is shown for the ν_2/ν_4 dyad of the $^{12}\text{CH}_4$ and $^{28}\text{SiH}_4$ molecules. An interpretation of the qualitative features of energy spectra in terms of bifurcations and formations of conical intersection points (diabolic points) on the energy surfaces of the corresponding classical problem is proposed.

I. INTRODUCTION

Rapid modernization of experimental spectroscopic methods produced a considerable increase of the accuracy and the number of known molecular energy levels. Alongside the study of the lowest levels, much more highly excited states become the object of attentive experimental and theoretical investigations. The main difficulty in the study of highly excited states of finite-particle system (molecules, atomic nuclei, and even quark systems) is the necessity of the description of a large number of admissible states, their classification, the extraction of some regular sequences of states and some exceptional states, and the study of their properties. In contrast to the lowest states which may be practically characterized individually, the excited states require an absolutely different approach. We have to try to characterize different groups or sequences of states rather than each state separately and to indicate some exceptional states if they exist. Such an analysis of quantum finite many-particle systems may be based on the same ideas as that used by Poincaré, Lyapunov, Hopf, and Andronov¹⁻⁵ for the qualitative study of classical mechanics problems. Their generalization to a much wider class of scientific problems is known now as the catastrophe theory and is applied to the study of qualitative changes of enormously different kinds of models.⁶⁻⁹

In past years a lot of papers were devoted to the study of transitions from regular to irregular spectra for some quantum finite particle systems, i.e., the following problem was studied: How to characterize in quantum problems the qualitative phenomena corresponding in classic mechanical systems to the well-known transition from quasiregular to chaotic motion.¹⁰⁻¹⁴ At the same time the much simpler question of the qualitative changes of regular spectra in quantum problems closely related to possible complications of the quasiregular motion in the corresponding classical systems (i.e., the bifurcation study) is rarely discussed in the

literature. Probably it is due to the fact that bifurcation analysis assumes the study of qualitative changes of the dynamic system under the variation of some parameters and therefore it is oriented to nonstationary problems where time, external fields, etc., are the natural parameters. Nevertheless, for conservative Hamiltonian systems, the analysis of the dynamics upon the variation of parameters become interesting and physically meaningful if the parameters themselves possess clear physical interpretation. For example, the parameters may play the role of integrals of motion (strict or approximate ones) such as the particle number, the energy, the angular momentum, etc.

Qualitative or topological analysis of classical dynamic systems includes, in the simplest case of conservative systems, the study of the topological properties of the set of classical trajectories. Similar analyses are suitable and useful for quantum systems as well. The topological properties of the trajectory sets for classical dynamic systems quickly become much more complicated under increase of the number of degrees of freedom (the phase space dimension). The most simple case corresponds to dynamic systems with one degree of freedom (two-dimensional phase space). The qualitative features of classical conservative dynamic problems with two-dimensional phase space is completely defined by a set of stationary points on the energy surface which specifies the topological structure of the set of classical trajectories.

A well-known molecular example of application of the qualitative methods to the rotational problem is the description of the rotational cluster structure. Although the qualitative description of the rotation of a rigid body in terms of stable and unstable rotation axes (i.e., in terms of stationary points of the rotational energy surfaces) has a long history (see, for example Landau and Lifshitz¹⁵) the application of the same qualitative ideas to explain the rotational energy level clustering in spherical top molecules was made only in 1972 by Dornay and Watson.¹⁶ The last ten years detailed

description of the rotational cluster structure was realized mainly by Harter, Patterson and their co-workers.¹⁷⁻²¹ A lot of different examples of energy level clusters were given. Graphical visualization of rotational surfaces enables one to see the semiclassical quantization for rovibrational problems and to understand better the relation between classical and quantum molecular rotation problems. The generalization of this approach to the two-dimensional vibrational problem was proposed as well.

In the present paper we limit ourselves to the discussion of qualitative changes which are typical for two-dimensional phase space. The example of such effects is the appearance or disappearance of new stationary points (bifurcation phenomena) or some other kinds of singular points on the energy surface under the variation of an integral of motion. The simplest typical effect is the qualitative change of the energy level system under the variation of the angular momentum value. The same effects are surely present for problems with larger numbers of degrees of freedom.

A classification of the qualitative changes may be done by taking into account the number of parameters and the constraints imposed by physical reasons (hermiticity, symmetry requirements etc.). For example, in the absence of symmetry and under the variation of one parameter, the only generic bifurcations (qualitative changes related to modifications of the system of stationary points) are those described by the fold catastrophe: two stationary points appear or disappear generically. Additional symmetry requirements result in new types of qualitative changes: the so-called equivariant bifurcations and catastrophes. The equivariant bifurcations received special attention in the last few years from both mathematicians and physicists.²²⁻²⁶ Finite groups are most frequently used for molecular problems. They are significantly simpler than continuous Lie groups appropriate for equivariant bifurcation theory in particle and nuclear physics, or in elasticity theory of continuum media.

It should be noted that the bifurcation analysis of quantum problems is not very popular now although the analogy between qualitative changes of quantum systems and phase transitions or critical phenomena in macroscopic systems was discussed several times by different authors either in the context of concrete physical problems^{27,28} or during the generalization of the catastrophe theory ideas to quantum problems.²⁹

In a series of works realized by Moscow physicists, a systematic study of qualitative effects in finite particle quantum systems under the variation of integrals of motion was performed.^{28,30-34} Qualitative features of energy spectra in quantum systems were mainly studied and some qualitative aspects of the eigenfunctions which influence the distribution of spectral line intensities were partially understood. The general theoretical analysis enables one to classify all possible critical phenomena appropriate for the rotational structure of isolated nondegenerate vibrational states under the variation of the rotational angular momentum.³⁰ All these critical phenomena are qualitative effects corresponding to the possible rearrangements of the cluster structure of rotational multiplets^{16,18,31,32} under the variation of the rota-

tion angular momentum. Some examples of these critical phenomena may be easily found, for example in Ref. 21, in figures showing the three-dimensional pictures of the rotational energy surfaces. Another type of qualitative effect was shown to exist^{31,33} for the rotational structure of quasi-degenerate vibrational states: the redistribution of the energy levels between different branches. This phenomenon is connected with the formation of conical intersection points (diaboloic points) on the energy surfaces. The existence of such conical intersection points of rotational energy surfaces was pointed out in Ref. 19. Excellent graphical visualizations of conical intersection points are given in Ref. 21. Such singularities are now under study in different areas of physics: particle and nuclear physics, superfluidity of ³He-A, stochasticity in classical mechanics.³⁵⁻³⁹ As an example of the problem specified by four or more phase variables the qualitative features of the vibrational polyads formed by degenerate or quasi-degenerate modes were analyzed from the same point of view.^{32,34} This problem is closely related to the investigations of the transition from normal to local modes^{40,41} and to the more general description of the formation of localized states.⁴²

It should be noted that until now model problems were studied only.^{30,33} It was shown that qualitative effects may exist but their experimental demonstration was not yet found in the existing molecular spectra and no new experiments were realized to verify or to reject the theoretical predictions. The aim of the present paper is to discuss shortly the main ideas of the theoretical approach to the study of qualitative effects and to demonstrate for the first time these effects using real systems of energy levels obtained from the fit of the most precise experimental data for spherical top molecules. In Sec. II we give a brief outline of the qualitative approach and in Sec. III we discuss the manifestation of bifurcations and the formation of diaboloic points on the basis of the analysis of experimental data in rovibrational spectra of spherical top molecules. We propose also a simple procedure for the visualization of the complicated effective Hamiltonians used for the analysis which seems to be useful for the interpretation of the intramolecular dynamics of molecular systems.

II. THEORETICAL BACKGROUND OF THE QUALITATIVE ANALYSIS

In the present paper, we limit ourselves to consideration of qualitative effects connected with the rearrangements of the rovibrational states in tetrahedral molecules. Spherical top molecules are especially suitable for this purpose due to the existence of easily seen rotational multiplets associated with one or several quasi-degenerate vibrational states and due to the formation of polyad structure of excited purely vibrational states caused by high degeneracy or quasidegeneracy of fundamental frequencies. Besides that, there exist many very accurate experimental data and corresponding phenomenological effective Hamiltonians for these molecules.

The subject of the theoretical analysis in the present paper is a family of effective operators depending on one parameter which has the physical meaning of an integral of motion. The purpose is to describe qualitative changes in the eigenvalue distribution under the parameter variation. That is we want to find and to describe typical modifications of the cluster structure under, for example, rotational excitations appropriate for real molecular systems. At the same time, we want to give a more general procedure, which may be applied to different physical problems rather than to particular molecular rotational problems. The general procedure of the theoretical analysis includes the following stages.

- (i) The construction of the effective Hamiltonian or its phenomenological expansion.
- (ii) Introduction of the classical limit manifold and determination on it of the symbol corresponding to quantum Hamiltonian.
- (iii) The determination of the action of the symmetry group on classical limit manifold and indication of all possible local symmetry groups, i.e., the stratification of the group action on the classical limit space.
- (iv) Analysis of the singularity points for different local symmetry groups for any isolated energy surface (degenerate stationary points or bifurcation points).
- (v) Analysis of the singularities appropriate for a system of energy surfaces (the degeneracy or diabolic points).

We present now the general scheme on different examples before treating the cases investigated experimentally.

A. Effective operators and classical limit manifolds

The simplest problem we shall consider is the description of the rotational structure of a nondegenerate vibrational state. Detailed analysis of the cluster structure in such a case was realized for some particular models about ten years ago,^{21,43} but here it is necessary to repeat Harter and Patterson arguments and to put them in slightly more general form appropriate for studying typical bifurcation phenomena for some wider classes of quantum molecular problems. A general effective rotational operator for an isolated vibrational state may be represented in a form of a power expansion in angular momentum operators.

$$\mathbf{H}_{\text{rot}} = \sum_{\alpha\beta\gamma} c_{\alpha\beta\gamma} (\mathbf{J}_x^\alpha \mathbf{J}_y^\beta \mathbf{J}_z^\gamma + \mathbf{J}_z^\gamma \mathbf{J}_y^\beta \mathbf{J}_x^\alpha). \quad (1)$$

The coefficients $c_{\alpha\beta\gamma}$ in Eq. (1) must satisfy requirements imposed by hermiticity, invariance with respect to time inversion and molecular symmetry group. The operator (1) may be written in several equivalent forms. It should be noted that the operator (1) may be studied independently for each value of the rotational quantum number J , i.e., for each eigenvalue of the operator \mathbf{J}^2 which is an integral of motion. If we consider J as a parameter the following question naturally arises: What are the qualitative changes in the distribution of the eigenvalues of Eq. (1) under J variation, i.e., under the rotational excitation.

The following important step is the introduction of the classical limit and in particular the definition of the one-parameter family of classical Hamiltonian functions corresponding to operator (1). The important notion for such a procedure is the classical problem. In the case of the rotational problem for nondegenerate vibrational states the classical limit manifold is a two-dimensional sphere S^2 , and the Hamiltonian (1) corresponds in a classical limit to a function defined on the sphere and depending on a parameter J being the integral of motion. We shall mainly consider the J dependence of the rotational Hamiltonian in this article with J playing the role of a parameter. The transformation to a classical limit may be performed by elementary formulas:

$$\mathbf{J}_x = j \sin \theta \cos \varphi, \quad \mathbf{J}_y = j \sin \theta \sin \varphi, \quad \mathbf{J}_z = j \cos \theta, \quad (2)$$

where \mathbf{J}_α are the projections of the classical angular momentum, j is the integral of motion, θ, φ take the role of the dynamic (phase) variables. The phase space of the rotation motion of the rigid body is formed by three Euler angles ϕ, ν, ψ and three conjugated momenta p_ϕ, p_ν, p_ψ . The absolute value of the angular momentum J and its projection $J_z = p_\phi$ on the z' axis of the laboratory fixed frame are the integrals of motion. It is suitable to perform the canonical transformation to new canonically conjugated variables J and q_J, J_z , and q_z, J_z and q_z . The phase space of the rotating body is really two-dimensional as q_J and q_z are cyclic variables. It can be mapped on the surface of the sphere of the radius J with the center at the origin of the body-fixed frame (the phase sphere, called also "Bloch sphere" in quantum optics). The point on the sphere specified by the coordinates θ, φ defines the orientation of the vector \mathbf{J} in the body fixed frame. The canonical transformation enables us to relate the conjugated variables J_z and q_z to the angles θ and φ . A more accurate treatment of the transition to classical limit must use the generalized coherent states.⁴⁴⁻⁴⁶ The representation of the coherent states enables one to generalize the construction of the classical limit from the purely rotational problem to much more complicated ones.⁴⁶

One evident generalization of the purely rotational problem for a nondegenerate vibrational state is the rotational problem for a group of degenerate or quasidegenerate states. An analysis of the rotational cluster structure for degenerate or quasidegenerate vibrational bands was made for some model problems by Harter *et al.*^{19,21} Different types of cluster structure were shown to exist and the application of cluster approach directly to the interpretation of the experimental data for heavy rotational tops was also proposed.^{19,47} Our purpose is to characterize (to classify and to describe) different typical qualitative effects which can take place for real molecular systems under rotational excitation for degenerate or quasidegenerate vibrational bands. The corresponding effective Hamiltonian may be represented in the form of a matrix operator

$$[\mathbf{H}] = [\mathbf{H}_{\alpha\beta} (\mathbf{J}_x, \mathbf{J}_y, \mathbf{J}_z)]. \quad (3)$$

The matrix elements $\mathbf{H}_{\alpha\beta}$ are some functions of the rotational angular momentum operators $\mathbf{J}_\alpha, \alpha = x, y, z$. Hermiticity and symmetry requirements put some restrictions on $\mathbf{H}_{\alpha\beta}$ which is similar to that for operator (1). The total an-

gular momentum \mathbf{J}^2 is the integral of motion for operator (3) and the classical limit manifold is a two-dimensional sphere. These facts are common for both operators (1) and (3). The symbol of Hamiltonian (3) in the classical limit is a matrix

$$[\mathbf{H}_{cl}] = [\mathbf{H}_{\alpha\beta}^J(\theta, \varphi)] \quad (4)$$

the elements of which are functions defined on S^2 and depending on one parameter J also.

The eigenvalues of the matrix (4) may be interpreted as rotational energy surfaces for different vibrational states.^{18,19,31} The qualitative analysis of the so obtained limiting classical problem must include both the qualitative study of each individual energy surface and the search for singularities caused by degeneracy points of different energy surfaces, i.e., the degeneracy of the eigenvalues of matrix (4).⁴⁸

The effective operators describing pure vibrational states (their relative positions within the polyads) formed by N degenerate or quasi-degenerate modes are another example. If we suppose the total number of quanta to be an integral of motion the effective operator may be written in terms of standard annihilation and creation vibrational operators a_k, a_k^+ as follows:

$$\mathbf{H} = \sum c_{n_1 \dots n_N m_1 \dots m_N} a_1^{n_1+} \dots a_N^{n_N+} a_1^{m_1} \dots a_N^{m_N}, \quad (5)$$

where n_i and m_i satisfy the following condition:

$$\sum_{i=1}^N n_i = \sum_{i=1}^N m_i \quad (6)$$

which means that operator (5) is a block-diagonal one with respect to the total number of vibrational quanta. For N vibrational degrees of freedom the introduction of the total number of quanta as an approximate integral of motion reduces the general problem to an effective Hamiltonian (5) possessing $(N-1)$ degrees of freedom and one integral of motion treated as parameter.

In the case of two-dimensional vibrational problem, operator (5) may be expressed in terms of pseudomoment operators by using the well-known Schwinger representation.⁴⁹ The similarity between the rotational problem and that of two-dimensional vibrational problem was used by Harter^{20,21} to study the cluster structure for the vibrational problem with two degrees of freedom.

More generally for K -dimensional vibrational problems operator (5) may be rewritten in terms of generators of the $SU(K)$ dynamic group.^{50,51} Vibrational states forming a given polyad belong to the degenerate irreducible representation of $SU(K)$ of the type $\square\square\square \dots \square\square$. To realize the transition to classical limit manifold in such a case one needs to use the generalized coherent states which are in one-to-one correspondence with the points of the complex projective space CP^{K-1} .⁴⁴⁻⁴⁶ It should be noted that the one-dimensional complex projective space CP^1 is the real two-dimensional sphere and this fact shows once more the equivalence of the purely rotational problem and the problem of the structure of vibrational polyads for two vibrational modes.²⁰ The analysis of vibrational polyads in the case of three-dimensional vibrational problems requires the qualitative study of Hamiltonian functions depending on four-phase variables and

one parameter—the total number of quanta. These problems are generally much more complicated due to possible transitions from quasi-regular to chaotic motion.^{5,10,13} Nevertheless, if we consider the qualitative changes of the quasi-regular motion we may separate the modifications associated with the changes of the stationary points on the energy surfaces.

Some other model situations may be proposed which result in effective Hamiltonians with the same formal structure as that mentioned above (from the point of view of the structure of the classical limit manifold and that of the symbol corresponding to the Hamiltonian of the quantum problem). The examples of such problems are: the rotational structure of vibrational polyads of several electronic states, the rotation structure of quasi-degenerate electronic states, the overlap between vibrational polyads for one electronic state, etc. We shall not consider them in detail and turn now to the discussion of the group action.

B. The group action

The next step in the qualitative analysis is the evaluation of the group action on the space of dynamic variables (phase space). The definition of the group action means that each point of the phase space is characterized by its orbit and its isotropy group (called also the local symmetry group). The orbit of a given point (x_0) includes all points which may be obtained by symmetry transformation of x_0 . The isotropy group of x_0 is a subgroup of the total symmetry group. It includes those elements which transform x_0 into itself. An equivalence relation in the orbit space may be introduced: Two orbits are equivalent if they possess conjugated isotropy groups. The set of equivalent orbits forms a stratum. It is the division of the phase space into strata that is the final purpose of the study of the group action. The importance of such a division of the phase space into strata is due to the fact that qualitative local behavior of a function invariant with respect to a given symmetry group in the neighborhood of the point x_0 is completely defined by the stratum which includes x_0 rather than by the position of x_0 within the stratum.

We shall name the process of the division of the phase space into strata with respect to a symmetry group action the stratification. There are two alternative ways for the study of the stratification under different group actions.

First, we may analyze all existing symmetry groups which may be considered as local symmetry groups of a point in a phase space. For problems with two-dimensional phase space the complete listing of such groups is well-known. It consists of two-dimensional point groups.⁵² Four-dimensional point groups are known as well but their enumeration is much more cumbersome.⁵³ The complete analysis of the groups admissible as local symmetry groups in a phase space of greater dimension is not of practical interest from the physical point of view.

An alternative approach to the study of different local symmetry groups is based on investigations of the stratification of the phase space for a given molecular symmetry group. For each molecular symmetry group this problem is only technical and it may be easily solved for not very com-

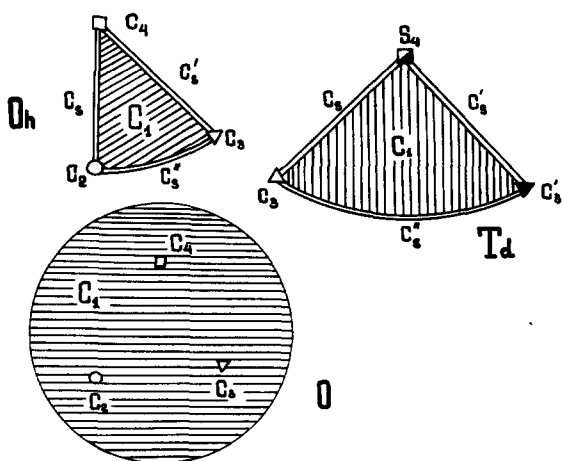


FIG. 1. Stratification of the two-dimensional sphere S^2 , under the action of the cubic symmetry point groups O , T_d , O_h .

plicated groups. As a simple example, Fig. 1 shows the stratification of the two-dimensional sphere S^2 under the action of the cubic symmetry point groups O , T_d , O_h . It should be noted that there are zero-, one-, and two-dimensional strata for the groups O_h and T_d whereas there are zero- and two-dimensional strata for the action of the group O on S^2 . Thus, the space of orbits (elementary cell) for the O_h and T_d groups is a part of a two-dimensional plane with the boundary being the one- and zero-dimensional strata. The space of orbits for the O group action is itself the two-dimensional sphere with three marked points—the zero-dimensional strata.

The stratification of the phase space may be realized also for much more complicated problems, for example in the case of classical limit manifold for vibrational polyads formed by triply degenerate vibrations. This manifold is the complex projective space CP^2 which is a four-dimensional real space.⁵⁴ It is important to remember also that the stratification of the phase space for different molecular symmetry groups and different types of vibrational operators may become identical because it depends on the group images in a given representation rather than on the initial symmetry group and the representation realized on the dynamic variables. The construction of the group images is widely used in the discussion of phase transitions.⁵⁵⁻⁵⁷ All group images for the irreducible representations of the crystallographic point groups are given in Refs. 56 and 58. The group images related to the polyad structure of two- and three-dimensional vibration problems are listed in Ref. 34.

As soon as the stratification of the phase space is given, one can study the local qualitative singularities for each local symmetry group in classical problems and study the corresponding effects in quantum problems.

C. Classical symbol singularities and quantum effects

The qualitative changes on the two-dimensional energy surfaces are connected with the variation and the stability of stationary points. All generic singularities of energy functions depending on only one parameter are discussed, for example, in Ref. 30. The singularities are classified accord-

ing to local symmetry groups. We limit ourselves here with the brief discussion of the critical phenomena appropriate for local symmetry groups C_{2v} , C_2 , C_s . All these local symmetry groups possess the same critical behavior.³⁰

The expansion of a function depending on one parameter J being the integral of motion and on two variables x, y in the neighborhood of a degenerate critical point $J \approx J_c$ in the case of the C_{2v} local symmetry group may be given in the form

$$E^J(x, y) = E_0 - \alpha(J - J_c)x^2 + a_{20}y^2 + a_{04}x^4, \quad (7)$$

where the coordinates x, y are chosen in such a way that $x = 0, y = 0, J = J_c$ correspond to a degenerate critical point. For the rotational problem considered below in Sec. III the x and y have clear physical meaning. They are the coordinates of the stereographic projections on the $z = J$ plane of the top of the vector \mathbf{J} defined in the body-fixed frame. x, y coordinates simply show the precession of the vector \mathbf{J} around the stationary rotation axis, possessing in this case the C_{2v} local symmetry. An analysis of the surface (7) close to a critical point shows that there are two types of critical phenomena depending on the relative signs of the coefficients a_{20} and a_{04} in the expansion (7). If a_{20} and a_{04} have opposite signs, the critical phenomenon corresponds to the formation of one stable point with C_{2v} local symmetry group and two equivalent nonstable stationary points with lower local symmetry (broken C_2 symmetry). The modification of the classical trajectory system for this critical phenomenon is shown in Fig. 2. It should be noted that the separatrix S remains the global curve and the critical phenomenon considered is nonlocal. At the same time new localized states are formed as a result of the critical phenomenon. These states are localized close to the stationary point with the C_{2v} local symmetry group.

The qualitative phenomenon mentioned above may be suitably represented by a bifurcation diagram showing in (E, J) coordinates the dependence of stationary energy points on the parameter J . We indicate in Fig. 3 the stable stationary points by a solid line and the unstable ones by a broken line. The bifurcation diagram for the considered non-

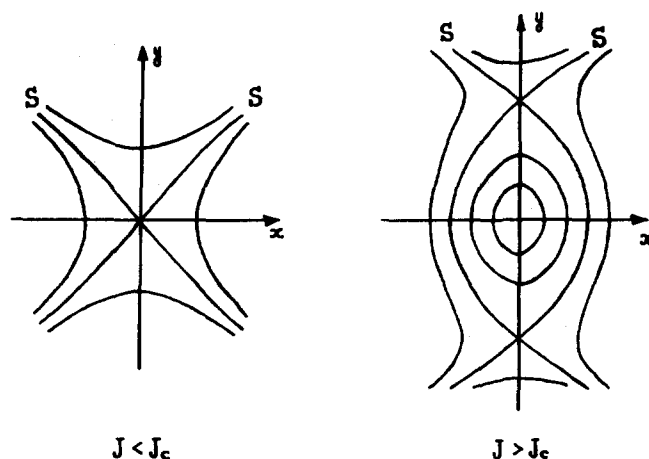


FIG. 2. The system of classical trajectories for nonlocal critical phenomena with C_{2v} local symmetry group.

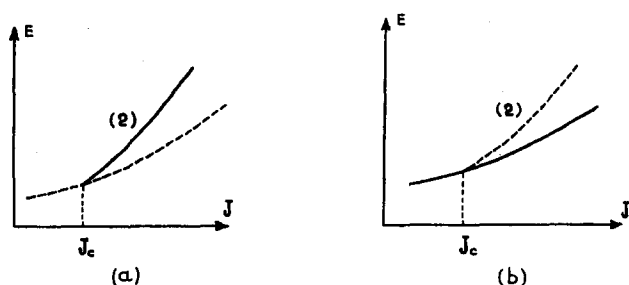


FIG. 3. Bifurcation diagrams for nonlocal (a) and local (b) critical phenomena with C_{2v} local symmetry group.

local critical phenomenon characterized by a broken C_2 local symmetry is shown in Fig. 3(a). The integers in parentheses over the lines indicate the number of equivalent stationary points existing for the problem considered. The number 1 is not shown for the sake of simplicity. If the classical model exhibits a critical behavior, the corresponding quantum problem is characterized by a redistribution of the energy levels. New regular sequence of states must appear (or disappear) under passing the parameter value over the critical one. The wave functions of these states should be localized close to the position of the new stable stationary point in the phase space.

If the coefficients a_{20} and a_{04} in (7) have the same sign the critical phenomenon is different. If, for example, α , a_{20} and a_{04} all are of the same sign, the stationary stable point of C_{2v} local symmetry goes over into unstable one and two new stable points equivalent with respect to C_2 operation and close to the C_{2v} symmetry point. The formation of two new points is associated with the broken C_2 symmetry. The typical change of the trajectory set for this type of critical phenomenon is shown in Fig. 4. The corresponding bifurcation diagram is shown in Fig. 3(b). This critical phenomenon in contrast to that mentioned above is a local one because the qualitative modification of the function takes place in a limited region of the phase space variables. This fact follows

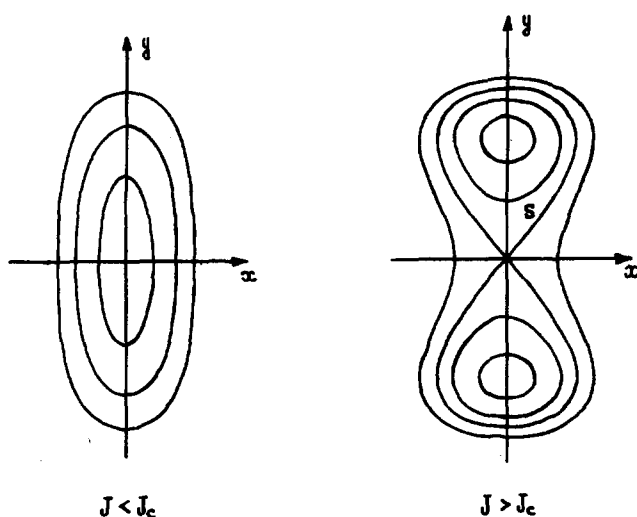


FIG. 4. The system of classical trajectories for local critical phenomena with C_{2v} local symmetry group.

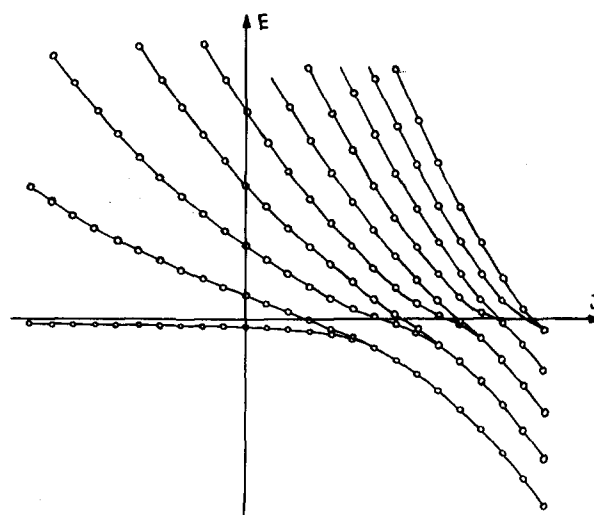


FIG. 5. Typical behavior of the energy level system of quantum problems under the variation of the integral of motion J in the neighborhood of a critical value for the local critical phenomenon with C_{2v} local symmetry group.

from the localization of the separatrix S at the critical value of parameter J_c .

The local character of the critical phenomenon enables one to describe it by an universal Hamiltonian which shows for the quantum problem the universal behavior of the energy levels for J values close to J_c .³⁰ The typical behavior of the energy levels at $J \approx J_c$ is shown in Fig. 5.

It consists in the formation of pairs of levels (or groups) from the regular sequence of states with appearance of a new regular sequence of states. A more detailed discussion and the general classification of the critical phenomena for the model problems with two-dimensional phase space and different symmetry groups may be found in Ref. 30. In the next section we discuss an example of molecular system which shows one of the types of critical behavior mentioned above under the increase of the rotational angular momentum.

Let us now consider the peculiarities of the energy level system for a quantum problem corresponding, in the classical limit, to matrix symbols. These problems along with qualitative features related to modifications of the set of stationary points for each energy surface possess singularities of a new type caused by the appearance of degeneracy points on the energy surfaces. In the general case the hermitian matrix depending on K parameters possesses a $(K - 3)$ dimensional subspace of degeneracy points.⁴⁸ Thus, the problem with two-dimensional phase space depending on one parameter generically have degeneracy points for isolated values of the parameter and for some discrete values of the phase variables. These degeneracy points are usually named conical intersection points (or diabolic points). The typical behavior of the two-dimensional energy surfaces near the degeneracy point is shown in Fig. 6. In problems with four-dimensional phase space and one parameter the degeneracy points form generically a two-dimensional surface in a five-dimensional space (four phase variables and one parameter). Thus two possibilities arise: (i) A two-dimensional surface of the

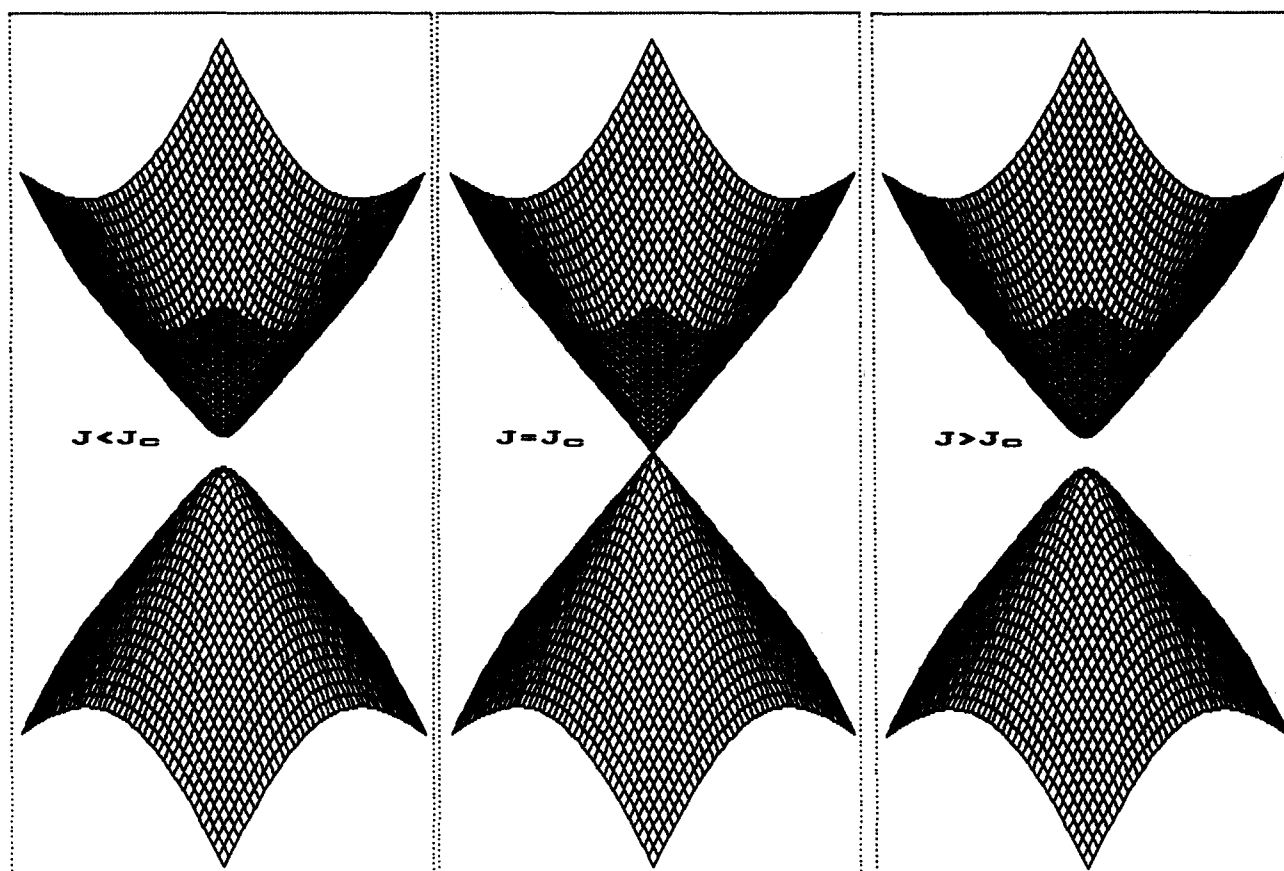


FIG. 6. Modification of the two energy surfaces showing the formation of a conical intersection (diabolic) point at $J = J_c$.

degeneracy points exists for a single value of the parameter; (ii) A one-dimensional line of the degeneracy points on the energy surfaces exists for a continuous region of the parameter variation. Symmetry requirements result in a much wider class of generic qualitative changes. For their classification the division of the phase space into strata should be done and each stratum should be considered separately.

III. THE MANIFESTATION OF BIFURCATIONS AND DIABOLIC POINTS IN THE EXPERIMENTAL DATA TREATMENT

A. Models for the experimental data treatment

In this section we consider the application of qualitative methods for the analysis of the energy level structure in concrete systems of rovibrational states found from experimental data. We restrict ourselves with the rovibrational levels of the ν_2/ν_4 dyad of tetrahedral molecules. There are a lot of very accurate experimental data for these molecules and the corresponding energy levels are known with high precision for a number of similar molecules such as CH_4 ,⁵⁹ CD_4 ,⁶⁰ SiH_4 ,⁶¹ GeH_4 ,⁶² and SnH_4 .⁶³ The comparative analysis of the ν_2/ν_4 dyads for various molecules is very useful from the point of view of the study of the generic origin of the qualitative effects mentioned above.

Experimental data treatments are usually based on effective phenomenological Hamiltonians which are suitably

represented for highly symmetrical molecules in terms of irreducible tensor operators⁵⁹⁻⁶⁶

$$\mathbf{H} = \sum_{ij} t_{ij} [\mathbf{v}_i^\Gamma \cdot \mathbf{R}_j^\Gamma]^{A_i}, \quad (8)$$

where \mathbf{V}^Γ are the vibrational operators having nonzero matrix elements only within the considered block of vibrational states. \mathbf{R}^Γ are the rotational operators, t_{ij} are the phenomenological coefficients which are the parameters fitted to experimental data. Different approaches make different choices of the basis of tensor operators, different notations of the phenomenological parameters and different schemes for the inclusion of the terms in the phenomenological expansion (8). This is mainly due to the fact that the general classification scheme which is based on the Born–Oppenheimer smallness parameter $\chi = (1/M)^{1/4}$ (where M is the average nuclei mass in the atomic units)⁶⁷ is rather crude and significant deviations from it may exist which are caused in particular, by various degree of quasi-degeneracy of the vibrational states. Moreover, it is well-known, that the general expansion (8) results in correlations between the parameters of the effective Hamiltonian. These correlations are due to ambiguities among effective operators caused by unitary transformations which do not change the form of the general expansion (8) and the general classification in small parameter but vary considerably the numerical values of the pa-

rameters within a given order of magnitude.^{66,68–70} Such ambiguities were analyzed in detail by Watson for the effective rotational Hamiltonians for the nondegenerate vibrational states,⁶⁸ and the general scheme for the construction of reduced Hamiltonians with unambiguous set of parameters was proposed. Last year a detailed study of the ambiguities of effective operators for spherical top molecules was performed.^{69–71} Effective Hamiltonians for degenerate and quasidegenerate vibrational states were analyzed. The explicit determination of correlations between effective parameters enables one to show the unitary equivalence between independent treatments of experimental data⁷⁰ and in some cases to simplify the mathematical optimization procedure of the parameter fitting which results in the possibility of including additional high-order parameters to improve the quality of fits.⁷¹

We use in our qualitative study the two most complete treatments of experimental data on the rotational structure of the ν_2/ν_4 dyads of $^{12}\text{CH}_4$ and $^{28}\text{SiH}_4$.^{72,73} The parameters of the phenomenological Hamiltonian (8) for methane and silane in the notation of Champion *et al.*^{65,70,74} are given in Tables I and II.

For $^{12}\text{CH}_4$ the data fitted are line positions of the ν_2/ν_4 dyad measured with precisions of 0.000 06 and 0.000 12 cm^{-1} using, respectively, 0.0055 and 0.011 cm^{-1} resolution spectra recorded with the Fourier Transform spectrometer at Kitt Peak (U.S.A.). Using a sixth-order reduced Hamiltonian, the ground state and the ν_2/ν_4 upper state parameters have been adjusted simultaneously. Standard deviations of $0.065 \times 10^{-3} \text{ cm}^{-1}$ involving data through $J = 23$ have been obtained. The majority of the predicted line positions have individual standard deviations of 10^{-4} cm^{-1} or better. Further details are reported in Ref. 72.

For $^{28}\text{SiH}_4$ infrared spectra of the ν_2/ν_4 dyad were recorded with the Fourier Transform Spectrometer at Paris by Valentin and Henry. The resolution of the spectrometer was adequate to observe lines within the Doppler–Fizeau width. A sixth-order reduced Hamiltonian, for the ground state and the (0100) and (0001) interacting states was used to fit simultaneously all the parameters. A standard deviation of 10^{-4} cm^{-1} involving data through $J = 25$ has been obtained. This work corresponds to an extension at the sixth order of the work reported in Ref. 73.

The presentation of the results of the data treatment in the form of a parameter table (such as Tables I and II) is not suitable for the purpose of the study of the intramolecular dynamics because it is practically impossible to make any even qualitative conclusions about the energy level system or about wave functions from the parameter values without numerical solution of the complete quantum problem. From another point of view the energy level system itself surely exhibits some clear qualitative features and regularities under J variation (see Figs. 7 and 8). The evidence for branches of rotational levels in the energy spectra and the redistribution of energy levels between different branches under the rotational excitation are crude examples of such qualitative features. The existence of rotational clusters and the modification of the cluster structure under J increase represent more sophisticated features.

Before going to the discussion of concrete molecular systems we formulate some possible advantages that the application of the qualitative methods may yield for molecular studies.

TABLE I. ν_2/ν_4 Hamiltonian parameters of $^{12}\text{CH}_4$.

| $\Omega(K\Gamma)$ | Γ_1 | Γ_2 | Values (standard deviation) |
|---------------------|---------------------|---------------------|----------------------------------|
| 0(0A ₁) | 0100 E | 0100 E | 1533.332 586(20) |
| 2(0A ₁) | 0100 E | 0100 E | 0.0 R ^a |
| 2(2E) | 0100 E | 0100 E | $-2.761\,672(53) \times 10^{-2}$ |
| 3(3A ₂) | 0100 E | 0100 E | $1.626\,21(37) \times 10^{-4}$ |
| 4(0A ₁) | 0100 E | 0100 E | $-4.0488(32) \times 10^{-6}$ |
| 4(2E) | 0100 E | 0100 E | $-8.02(12) \times 10^{-7}$ |
| 4(4A ₁) | 0100 E | 0100 E | 0.0 R |
| 4(4E) | 0100 E | 0100 E | 0.0 R |
| 5(3A ₂) | 0100 E | 0100 E | 0.0 R |
| 6(0A ₁) | 0100 E | 0100 E | $-1.568(48) \times 10^{-9}$ |
| 6(2E) | 0100 E | 0100 E | $-6.85(18) \times 10^{-10}$ |
| 6(4A ₁) | 0100 E | 0100 E | $-8.38(76) \times 10^{-11}$ |
| 6(4E) | 0100 E | 0100 E | $1.4(16) \times 10^{-11}$ |
| 6(6A ₁) | 0100 E | 0100 E | 0.0 R |
| 6(6E) | 0100 E | 0100 E | $5.95(15) \times 10^{-10}$ |
| 1(1F ₁) | 0100 E | 0001 F ₂ | $-9.312\,274(26)$ |
| 2(2F ₂) | 0100 E | 0001 F ₂ | $-7.591\,35(13) \times 10^{-2}$ |
| 3(1F ₁) | 0100 E | 0001 F ₂ | $-5.238\,53(75) \times 10^{-4}$ |
| 3(3F ₁) | 0100 E | 0001 F ₂ | $-2.0435(40) \times 10^{-4}$ |
| 3(3F ₂) | 0100 E | 0001 F ₂ | $-1.2907(77) \times 10^{-4}$ |
| 4(2F ₂) | 0100 E | 0001 F ₂ | $8.077(61) \times 10^{-7}$ |
| 4(4F ₁) | 0100 E | 0001 F ₂ | $-6.4(11) \times 10^{-7}$ |
| 4(4F ₂) | 0100 E | 0001 F ₂ | $-1.432(13) \times 10^{-6}$ |
| 5(1F ₁) | 0100 E | 0001 F ₂ | $-1.290(43) \times 10^{-8}$ |
| 5(3F ₁) | 0100 E | 0001 F ₂ | $1.67(11) \times 10^{-8}$ |
| 5(3F ₂) | 0100 E | 0001 F ₂ | $-3.11(16) \times 10^{-8}$ |
| 5(5F ₁) | 0100 E | 0001 F ₂ | $1.40(15) \times 10^{-8}$ |
| 5(5F ₂) | 0100 E | 0001 F ₂ | $-1.073(13) \times 10^{-8}$ |
| 5(5F ₃) | 0100 E | 0001 F ₂ | $-7.16(23) \times 10^{-8}$ |
| 6(2F ₂) | 0100 E | 0001 F ₂ | $1.230(58) \times 10^{-10}$ |
| 6(4F ₁) | 0100 E | 0001 F ₂ | $4.62(11) \times 10^{-10}$ |
| 6(4F ₂) | 0100 E | 0001 F ₂ | $1.13(12) \times 10^{-10}$ |
| 6(6F ₁) | 0100 E | 0001 F ₂ | $3.42(31) \times 10^{-10}$ |
| 6(6F ₂) | 0100 E | 0001 F ₂ | $2.27(15) \times 10^{-10}$ |
| 6(6F ₃) | 0100 E | 0001 F ₂ | $2.2(34) \times 10^{-12}$ |
| 0(0A ₁) | 0001 F ₂ | 0001 F ₂ | 1310.761 621 6(97) |
| 1(1F ₁) | 0001 F ₂ | 0001 F ₂ | 10.346 259 8(28) |
| 2(0A ₁) | 0001 F ₂ | 0001 F ₂ | $-5.610\,36(34) \times 10^{-3}$ |
| 2(2E) | 0001 F ₂ | 0001 F ₂ | $-2.957\,18(53) \times 10^{-3}$ |
| 2(2F ₂) | 0001 F ₂ | 0001 F ₂ | $-3.153\,379(42) \times 10^{-2}$ |
| 3(1F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 3(3F ₁) | 0001 F ₂ | 0001 F ₂ | $-2.6828(11) \times 10^{-4}$ |
| 4(0A ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 4(2E) | 0001 F ₂ | 0001 F ₂ | $-6.912(33) \times 10^{-7}$ |
| 4(2F ₂) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 4(4A ₁) | 0001 F ₂ | 0001 F ₂ | $-2.19(13) \times 10^{-7}$ |
| 4(4E) | 0001 F ₂ | 0001 F ₂ | $2.184(15) \times 10^{-6}$ |
| 4(4F ₂) | 0001 F ₂ | 0001 F ₂ | $2.3767(17) \times 10^{-6}$ |
| 5(1F ₁) | 0001 F ₂ | 0001 F ₂ | $5.13(12) \times 10^{-9}$ |
| 5(3F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 5(5F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 5(5F ₂) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(0A ₁) | 0001 F ₂ | 0001 F ₂ | $1.370(30) \times 10^{-9}$ |
| 6(2E) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(2F ₂) | 0001 F ₂ | 0001 F ₂ | $4.22(15) \times 10^{-10}$ |
| 6(4A ₁) | 0001 F ₂ | 0001 F ₂ | $1.351(75) \times 10^{-10}$ |
| 6(4E) | 0001 F ₂ | 0001 F ₂ | $-1.72(34) \times 10^{-10}$ |
| 6(4F ₂) | 0001 F ₂ | 0001 F ₂ | $-4.2(12) \times 10^{-11}$ |
| 6(6A ₁) | 0001 F ₂ | 0001 F ₂ | $3.14(10) \times 10^{-11}$ |
| 6(6E) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(6F ₂) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(6F ₃) | 0001 F ₂ | 0001 F ₂ | $5.10(26) \times 10^{-10}$ |

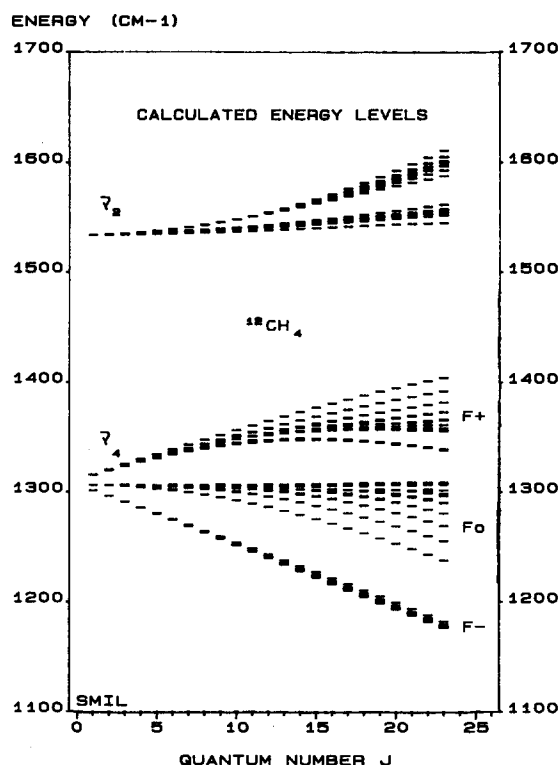
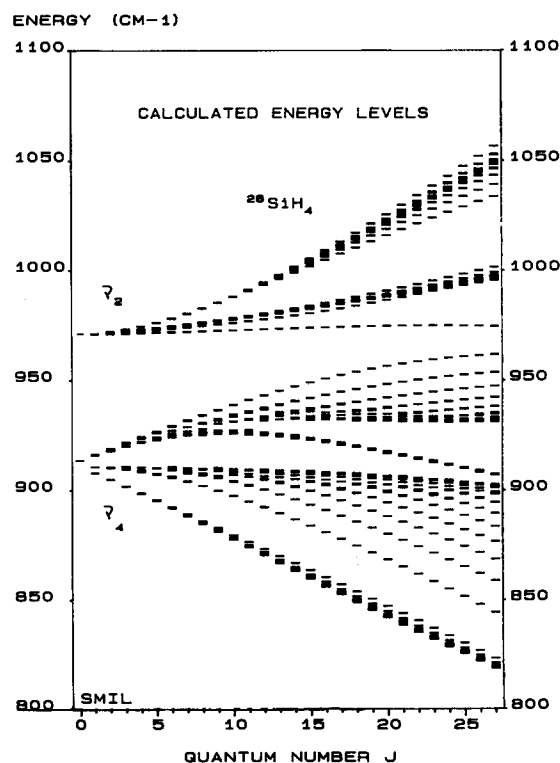
^a0.0 R means: fixed by reduction of the Hamiltonian. All values in cm^{-1} .

TABLE II. ν_2/ν_4 Hamiltonian parameters of $^{28}\text{SiH}_4$.

| $\Omega(K\Gamma)$ | Γ_1 | Γ_2 | Values (standard deviation) |
|---------------------|---------------------|---------------------|---------------------------------|
| 0(0A ₁) | 0100 E | 0100 E | 970.934 354(92) |
| 2(0A ₁) | 0100 E | 0100 E | 0.0 R ^a |
| 2(2E) | 0100 E | 0100 E | $-9.8160(19) \times 10^{-3}$ |
| 3(3A ₂) | 0100 E | 0100 E | $6.9983(69) \times 10^{-5}$ |
| 4(0A ₁) | 0100 E | 0100 E | $-1.076(11) \times 10^{-6}$ |
| 4(2E) | 0100 E | 0100 E | $-1.561(52) \times 10^{-7}$ |
| 4(4A ₁) | 0100 E | 0100 E | 0.0 R |
| 4(4E) | 0100 E | 0100 E | 0.0 R |
| 5(3A ₂) | 0100 E | 0100 E | 0.0 R |
| 6(0A ₁) | 0100 E | 0100 E | 0.0 R |
| 6(2E) | 0100 E | 0100 E | 0.0 R |
| 6(4A ₁) | 0100 E | 0100 E | $-2.46(40) \times 10^{-11}$ |
| 6(4E) | 0100 E | 0100 E | $-1.67(14) \times 10^{-10}$ |
| 6(6A ₁) | 0100 E | 0100 E | 0.0 R |
| 6(6E) | 0100 E | 0100 E | $1.29(11) \times 10^{-10}$ |
| 1(1F ₁) | 0100 E | 0001 F ₂ | $-5.069\,657(52)$ |
| 2(2F ₂) | 0100 E | 0001 F ₂ | $-2.407\,65(36) \times 10^{-2}$ |
| 3(1F ₁) | 0100 E | 0001 F ₂ | $-1.6251(12) \times 10^{-4}$ |
| 3(eF ₁) | 0100 E | 0001 F ₂ | $-3.9041(77) \times 10^{-5}$ |
| 3(3F ₂) | 0100 E | 0001 F ₂ | $-2.5010(70) \times 10^{-5}$ |
| 4(2F ₂) | 0100 E | 0001 F ₂ | $8.96(35) \times 10^{-8}$ |
| 4(4F ₁) | 0100 E | 0001 F ₂ | $1.41(10) \times 10^{-8}$ |
| 4(4F ₂) | 0100 E | 0001 F ₂ | $-6.22(61) \times 10^{-8}$ |
| 5(1F ₁) | 0100 E | 0001 F ₂ | $4.9(16) \times 10^{-10}$ |
| 5(3F ₁) | 0100 E | 0001 F ₂ | $1.35(20) \times 10^{-9}$ |
| 5(3F ₂) | 0100 E | 0001 F ₂ | $4.79(24) \times 10^{-9}$ |
| 5(5F ₁) | 0100 E | 0001 F ₂ | $-2.321(59) \times 10^{-9}$ |
| 5(5F ₁) | 0100 E | 0001 F ₂ | $-1.35(10) \times 10^{-9}$ |
| 5(5F ₂) | 0100 E | 0001 F ₂ | $-6.12(47) \times 10^{-9}$ |
| 6(2F ₂) | 0100 E | 0001 F ₂ | $-7.29(84) \times 10^{-11}$ |
| 6(4F ₁) | 0100 E | 0001 F ₂ | $1.12(87) \times 10^{-11}$ |
| 6(4F ₂) | 0100 E | 0001 F ₂ | $-9.81(90) \times 10^{-11}$ |
| 6(6F ₁) | 0100 E | 0001 F ₂ | $9.8(12) \times 10^{-11}$ |
| 6(6F ₂) | 0100 E | 0001 F ₂ | $-3.8(11) \times 10^{-11}$ |
| 6(6F ₂) | 0100 E | 0001 F ₂ | $1.8(61) \times 10^{-12}$ |
| 0(0A ₁) | 0001 F ₂ | 0001 F ₂ | 913.468 776(67) |
| 1(1F ₁) | 0001 F ₂ | 0001 F ₂ | 6.027 106(13) |
| 2(0A ₁) | 0001 F ₂ | 0001 F ₂ | $3.990(15) \times 10^{-4}$ |
| 2(2E) | 0001 F ₂ | 0001 F ₂ | $-3.0767(22) \times 10^{-3}$ |
| 2(2F ₂) | 0001 F ₂ | 0001 F ₂ | $-1.209\,79(19) \times 10^{-2}$ |
| 3(1F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 3(3F ₁) | 0001 F ₂ | 0001 F ₂ | $-1.160\,69(97) \times 10^{-4}$ |
| 4(0A ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 4(2E) | 0001 F ₂ | 0001 F ₂ | $-2.764(52) \times 10^{-7}$ |
| 4(2F ₂) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 4(4A ₁) | 0001 F ₂ | 0001 F ₂ | $-8.21(19) \times 10^{-8}$ |
| 4(4E) | 0001 F ₂ | 0001 F ₂ | $6.918(89) \times 10^{-7}$ |
| 4(4F ₂) | 0001 F ₂ | 0001 F ₂ | $7.367(72) \times 10^{-7}$ |
| 5(1F ₁) | 0001 F ₂ | 0001 F ₂ | $2.01(15) \times 10^{-9}$ |
| 5(3F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 5(5F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 5(5F ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(0A ₁) | 0001 F ₂ | 0001 F ₂ | $8.5(12) \times 10^{-11}$ |
| 6(2E) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(2F ₂) | 0001 F ₂ | 0001 F ₂ | $-1.556(96) \times 10^{-10}$ |
| 6(4A ₁) | 0001 F ₂ | 0001 F ₂ | $2.13(33) \times 10^{-11}$ |
| 6(4E) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(4F ₂) | 0001 F ₂ | 0001 F ₂ | $-1.87(14) \times 10^{-10}$ |
| 6(6A ₁) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(6E) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(6F ₂) | 0001 F ₂ | 0001 F ₂ | 0.0 R |
| 6(6F ₂) | 0001 F ₂ | 0001 F ₂ | $8.9(16) \times 10^{-11}$ |

^a0.0 R means: fixed by reduction of the Hamiltonian. All values in cm⁻¹.

The application of qualitative analyses enables us to represent the results of data treatments in a more compact and clear form by indicating bifurcation and diabolic points which are present in a given molecular system. New princi-

FIG. 7. Rovibrational energy levels for the dyad ν_2/ν_4 of $^{12}\text{CH}_4$. The parameters of the effective Hamiltonian are listed in Table I.FIG. 8. Rovibrational energy levels for the dyad ν_2/ν_4 of $^{28}\text{SiH}_4$. The parameters of the effective Hamiltonian are listed in Table II.

ples for the phenomenological Hamiltonian construction may be developed on the basis of the inclusion into the effective Hamiltonian of those terms which are of primary importance for the proper description of the possible qualitative changes. The location of the peculiarities in the energy spectra enables one to predict the preferable regions for the experimental spectroscopic study because the detailed investigation of a molecular system in a region close to singularity points gives in principle much more information about the intramolecular behavior than the wide study of the regular sequences of states. It is hoped that the knowledge of singularities may yield more reliable extrapolations to higher J values and to similar molecular systems.

B. Critical phenomena (bifurcations) in the rotational structure

The qualitative analysis of the effective rotational Hamiltonian (8) (Tables I and II) from the point of view of the appearance of degenerate critical points on the energy surfaces shows that for both $^{28}\text{SiH}_4$ and $^{12}\text{CH}_4$ the critical phenomenon associated with the C_2 local symmetry breaking under J variation is present. This critical phenomenon results in the appearance of a new stable C_2 rotation axis instead of an unstable one with the simultaneous appearance of a pair of unstable rotation axes close to each C_2 one. (See Figs. 2,3 and the corresponding discussion in Sec. III C). This critical phenomenon occurs in the lower of the two branches of the ν_2 (E) state. Figure 9 shows the fragment of the energy level system for the ν_2/ν_4 dyad of $^{28}\text{SiH}_4$ alongside with the energies of the stationary points on the rotational energy surfaces. To simplify the figure we show only the energies of the C_2 , C_3 , and C_4 axes. The stability of a stationary point on the energy surface is characterized by the Hessian value. As soon as the rotational energy surface $E^J(\theta, \varphi)$ depends on two phase variables (θ, φ) defined on the sphere S^2 (the classical limit manifold) the Hessian of the energy surface $E^J(\theta, \varphi)$ may be written in its standard form $[(\partial^2 E / \partial \theta^2) + (\partial^2 E / \partial \varphi^2) - (\partial^2 E / \partial \theta \partial \varphi)](1 / \sin^2 \theta)$. The Hessian is the determinant of the matrix of sec-

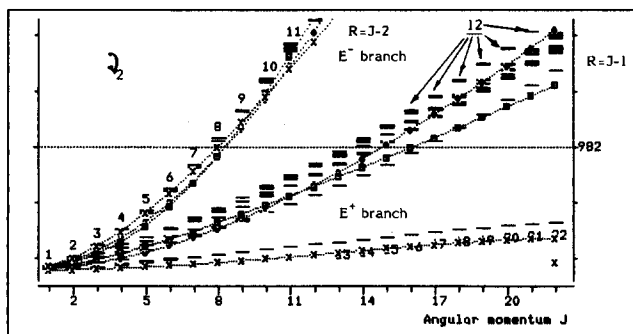


FIG. 9. Comparison between the energy level system and the classical energies of the C_2 , C_3 , C_4 stationary rotation axes in the neighborhood of the C_{2v} critical phenomenon for the ν_2 vibrational state of $^{28}\text{SiH}_4$. \times — C_4 axis energy, \square — C_3 axis energy, \circ — C_2 axis energy.

ond derivatives. So it is equal to the product of its eigenvalues, which for the stationary points completely characterize its stability. The Hessian is positive for maxima and minima and it is negative for saddle points. If the Hessian is equal to zero the stationary point is degenerate. Therefore, the Hessian passing through zero indicates the bifurcation. One must remember only that our rotational energy surface $E^J(\theta, \varphi)$ depends on the parameter J , the total angular momentum value and therefore the Hessian is J dependent. Figure 10 shows the Hessian value for the C_2 stationary axis for the lower branch of the E state. It is clear that the C_2 axis becomes a stable one at $J \approx 11$. Consequently, the formation of 12-fold rotational clusters is to occur for $J > 11$. From the qualitative point of view the wave functions corresponding to the energy levels forming 12-fold cluster differ significantly from some other functions due to their specific localization related to the localization of the corresponding classical precession motion of the angular momentum close to one of the equivalent C_2 axes.

The transitions to the levels incorporated into 12-fold clusters are present in the experimental data. Tables III and IV show 12-fold clusters existing in the energy level system of CH_4 and SiH_4 . An analysis of these transitions shows that the rotational levels of the ground vibrational state from which the transitions are observed to lie in the neighborhood of the separatrix for the energy surface of the ground vibrational state. The transitions of this type, although being not very intense, are nevertheless the most intense among other transitions because the wave functions of the ground state

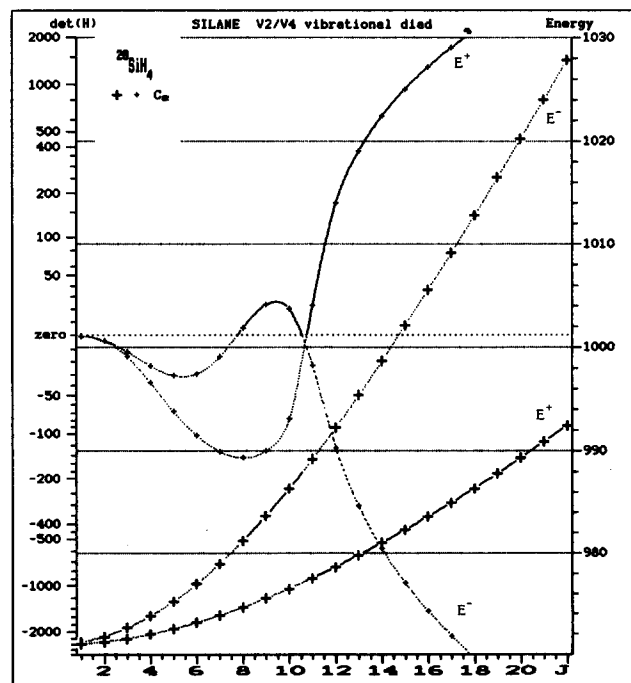


FIG. 10. Hessian values for the stationary C_2 rotation axis for the classical energy surface corresponding to the lower branch of the ν_2 state of $^{28}\text{SiH}_4$. $+$ is the energy of stationary points with C_2 local symmetry on the rotational energy surface. $+$ is the Hessian value for C_2 type stationary points.

TABLE III. 12-fold rotational clusters in the energy spectrum of $^{12}\text{CH}_4$.

| <i>J</i> symmetry type and energies of levels in the clusters (cm ⁻¹) | | | | Separation in energy from the closest | | |
|---|-----------------------|----|--------------|---------------------------------------|---------------------------------|---------------------------------|
| | | | | Cluster width (cm ⁻¹) | Upper level (cm ⁻¹) | Lower level (cm ⁻¹) |
| 12 | <i>F</i> ₁ | 13 | 2357.904 788 | 0.55 | 10.5 | 0.5 |
| 12 | <i>E</i> | 9 | 2357.860 680 | | | |
| 12 | <i>F</i> ₁ | 12 | 2357.740 393 | | | |
| 12 | <i>F</i> ₂ | 13 | 2357.630 423 | | | |
| 12 | <i>A</i> ₂ | 4 | 2357.355 851 | 0.33 | 12.1 | 1.0 |
| 13 | <i>F</i> ₂ | 14 | 2494.569 540 | | | |
| 13 | <i>E</i> | 9 | 2494.467 041 | | | |
| 13 | <i>F</i> ₁ | 14 | 2494.348 674 | | | |
| 13 | <i>A</i> ₁ | 5 | 2494.300 630 | 0.34 | 13.8 | 1.1 |
| 13 | <i>F</i> ₂ | 13 | 2494.237 198 | | | |
| 14 | <i>A</i> ₂ | 5 | 2641.567 524 | | | |
| 14 | <i>F</i> ₂ | 15 | 2641.484 712 | | | |
| 14 | <i>F</i> ₁ | 15 | 2641.417 247 | 0.30 | 15.3 | 1.5 |
| 14 | <i>E</i> | 10 | 2641.247 288 | | | |
| 14 | <i>F</i> ₁ | 14 | 2641.221 743 | | | |
| 15 | <i>F</i> ₂ | 16 | 2798.764 098 | | | |
| 15 | <i>A</i> ₁ | 5 | 2798.720 861 | 0.32 | 17.0 | 1.7 |
| 15 | <i>F</i> ₁ | 16 | 2798.684 588 | | | |
| 15 | <i>E</i> | 11 | 2798.621 582 | | | |
| 15 | <i>F</i> ₂ | 15 | 2798.458 606 | | | |
| 16 | <i>F</i> ₁ | 17 | 2966.264 290 | 0.23 | 18.0 | 1.9 |
| 16 | <i>E</i> | 11 | 2966.247 810 | | | |
| 16 | <i>F</i> ₁ | 16 | 2966.155 522 | | | |
| 16 | <i>F</i> ₂ | 17 | 2966.071 832 | | | |
| 16 | <i>A</i> ₂ | 6 | 2965.952 947 | 0.26 | 16.2 | 0.5 |
| 17 | <i>F</i> ₂ | 18 | 3144.000 141 | | | |
| 17 | <i>E</i> | 12 | 3143.911 174 | | | |
| 17 | <i>F</i> ₁ | 18 | 3143.863 189 | | | |
| 17 | <i>A</i> ₁ | 6 | 3143.841 769 | 0.22 | 17.9 | 0.7 |
| 17 | <i>F</i> ₂ | 17 | 3143.775 683 | | | |

TABLE IV. 12-fold rotational clusters in the energy spectrum of $^{28}\text{SiH}_4$.

| <i>J</i> symmetry type and energies of levels in the clusters (cm ⁻¹) | | | | Separation in energy from the closest | | |
|---|-----------------------|----|--------------|---------------------------------------|---------------------------------|---------------------------------|
| | | | | Cluster width (cm ⁻¹) | Upper level (cm ⁻¹) | Lower level (cm ⁻¹) |
| 14 | <i>A</i> ₂ | 5 | 1581.605 667 | 0.26 | 16.2 | 0.5 |
| 14 | <i>F</i> ₂ | 15 | 1581.539 325 | | | |
| 14 | <i>F</i> ₁ | 15 | 1581.479 692 | | | |
| 14 | <i>E</i> | 10 | 1581.387 901 | | | |
| 14 | <i>F</i> ₁ | 14 | 1581.342 038 | 0.22 | 17.9 | 0.7 |
| 15 | <i>F</i> ₂ | 16 | 1668.100 683 | | | |
| 15 | <i>E</i> | 11 | 1668.013 921 | | | |
| 15 | <i>F</i> ₁ | 16 | 1667.969 200 | | | |
| 15 | <i>A</i> ₁ | 5 | 1667.935 175 | 0.23 | 19.6 | 1.0 |
| 15 | <i>F</i> ₂ | 15 | 1667.885 390 | | | |
| 16 | <i>F</i> ₁ | 17 | 1760.262 672 | | | |
| 16 | <i>E</i> | 11 | 1760.256 652 | | | |
| 16 | <i>F</i> ₁ | 16 | 1760.180 643 | 0.16 | 21.0 | 1.0 |
| 16 | <i>F</i> ₂ | 17 | 1760.121 334 | | | |
| 16 | <i>A</i> ₂ | 6 | 1760.033 110 | | | |
| 17 | <i>F</i> ₂ | 18 | 1858.108 758 | | | |
| 17 | <i>A</i> ₁ | 6 | 1858.066 133 | 0.14 | 22.4 | 1.3 |
| 17 | <i>F</i> ₁ | 18 | 1858.055 310 | | | |
| 17 | <i>E</i> | 12 | 1858.027 375 | | | |
| 17 | <i>F</i> ₂ | 17 | 1857.947 292 | | | |
| 18 | <i>A</i> ₂ | 6 | 1961.605 533 | 0.11 | 23.8 | 1.3 |
| 18 | <i>F</i> ₂ | 19 | 1961.564 805 | | | |
| 18 | <i>F</i> ₁ | 19 | 1961.521 797 | | | |
| 18 | <i>E</i> | 13 | 1961.470 811 | | | |
| 18 | <i>F</i> ₁ | 18 | 1961.466 926 | 0.10 | 25.3 | 1.5 |
| 19 | <i>F</i> ₂ | 20 | 2070.662 857 | | | |
| 19 | <i>E</i> | 13 | 2070.611 973 | | | |
| 19 | <i>F</i> ₁ | 20 | 2070.602 380 | | | |
| 19 | <i>A</i> ₁ | 7 | 2070.596 850 | 0.10 | 25.3 | 1.5 |
| 19 | <i>F</i> ₂ | 19 | 2070.548 881 | | | |
| 20 | <i>F</i> ₁ | 21 | 2185.316 318 | | | |
| 20 | <i>E</i> | 14 | 2185.315 889 | | | |
| 20 | <i>F</i> ₁ | 20 | 2185.283 252 | 0.11 | 23.8 | 1.3 |
| 20 | <i>F</i> ₂ | 21 | 2185.249 474 | | | |
| 20 | <i>A</i> ₂ | 7 | 2185.211 596 | 0.10 | 25.3 | 1.5 |

must be sufficiently spread (delocalized) to overlap with the rotational wave functions of the upper vibrational state which are localized close to C_2 axes.

In order to show that 12-fold clusters may be easily separated from other levels we list in Tables III and IV the widths of the clusters and their separation in energy from the closest levels.

It should be noted that the appearance of 12-fold clusters was predicted by using the simple effective Hamiltonian for E state including only two tensor contributions³¹:

$$H = [(a_2^+ a_2)^E R^{2(2,E)}]^{A_1} + u[(a_2^+ a_2)^{A_2} R^{3(3,A_2)}]^{A_1}. \quad (9)$$

The classical problem for the Hamiltonian (9) can be solved exactly and yields the following dependence of the stationary points on the angular momentum quantum number J :

$$\begin{aligned} E(C_4) &= 4(2/3)^{1/2} J(J+1), \\ E(C_2) &= 2(2/3)^{1/2} J(J+1), \\ E(C_3) &= (2Z)^{1/2} J(J+1)/9, \\ E(C_s) &= 2J(J+1)[2[1 - (36/Z) + (432/Z^2)]/3]^{1/2}, \end{aligned} \quad (10)$$

where $Z = 32 uJ(J+1)$.

The positions of the stationary C_2 , C_3 , C_4 axes do not change under the variation of J . The stationary axes C_s exist only for $Z > 24$ and change their orientation with Z in accordance to the relations

$$\varphi = \pi/4, \quad \cos^2 \theta = 1 - 24/Z \quad (11)$$

which we give for one of the 24 equivalent C_s symmetry stationary points. The critical phenomenon for Hamiltonian (9) is identical to that discussed in Sec. II and demonstrated above for more complicated effective Hamiltonian for the CH_4 and SiH_4 molecules. It is interesting to note that using the very simple model Hamiltonian (9) with the numerical values of the parameters taken from the experimental treatment for the isolated E state model one gets the critical value of J close to the one actually observed. At the same time the transformation of the effective Hamiltonian for isolated E

state to the one for resonance model⁷⁴ shows that whereas the parameter $t_{2,2}^{(2,E)}$ changes slightly the variation of the $t_{2,2}^{(3,A_2)}$ parameter is very drastic. Therefore we may conclude that the qualitative phenomenon of the appearance of new stationary C_2 axes and the formation of 12-fold rotational clusters in the energy spectrum is mainly due to the interaction between the ν_2 and ν_4 vibration bands. This note may be useful for the study of microscopic theory of critical phenomena in spherical top molecules.

C. Energy level redistribution and diabolic points

The qualitative phenomena of the redistribution of rotational levels between branches in the rovibrational energy spectrum is clearly seen in Fig. 8 representing the energy levels for the ν_2/ν_4 dyad of SiH_4 . A similar situation takes place for CH_4 molecule (Fig. 7) but at much higher J values.

The redistribution of the levels between the $F+$ and $F0$ branches of the ν_4 vibrational state is particularly evident in Fig. 8. Under J increase the eight-fold cluster goes from the $F+$ to the $F0$ branch. It is seen also that the six-fold cluster begins to go from the lower branch of the ν_2 state to the $F+$ branch of ν_4 but this transition is less clear for the J values considered.

In Sec. II C we have shown using a simple model that the redistribution of energy levels may be interpreted by the formation of a diabolic point for two energy surfaces. Under such a supposal the redistribution of six- or eight-fold clusters is due to the formation of six- or eight-fold diabolic points equivalent by symmetry. This means that the redistribution of the sixfold (eightfold) clusters is associated with the formation of a diabolic point with C_4 (C_3) local symmetry group. It may be easily verified by the classical analysis of the corresponding quantum Hamiltonian. Figure 11 shows the energy levels of the ν_2/ν_4 dyad of SiH_4 along with the results of the classical analysis of all five energy surfaces. The energy of the C_2 , C_3 , C_4 stationary points for each energy surface is shown. It is clear from Fig. 11 that for the SiH_4 molecule the formation of diabolic points between $F+$ and $F0$ branches for the ν_4 state takes place at $J \approx 19$. The conical intersection point for the $F+$ branch and the lower E state branch is present at $J \approx 23$. Moreover, there is a tendency to form the diabolic point between the $F0$ and $F-$ branches of the ν_4 state at $J \approx 30$. The comparison of SiH_4 and CH_4 energy levels (Figs. 7 and 8) indicates that the same phenomena are appropriate for CH_4 but for higher J values. This is probably due to the larger difference between the vibrational frequencies for CH_4 with respect to SiH_4 . The closer resonance of the ν_2/ν_4 dyad in SiH_4 favors the redistribution of the energy levels at lower J values. The comparison of the CH_4 and CD_4 energy level systems verifies this conclusion.

Let us now give the qualitative explanation of the observed typical effect of redistribution of the energy levels for the ν_2/ν_4 dyad of tetrahedral molecules by using the simplest model. To do this we try to interpret this phenomenon in terms of recoupling of the vibrational and rotational angular momenta for the vibrational states considered. First of all we eliminate the tetrahedral structure which in some sense is

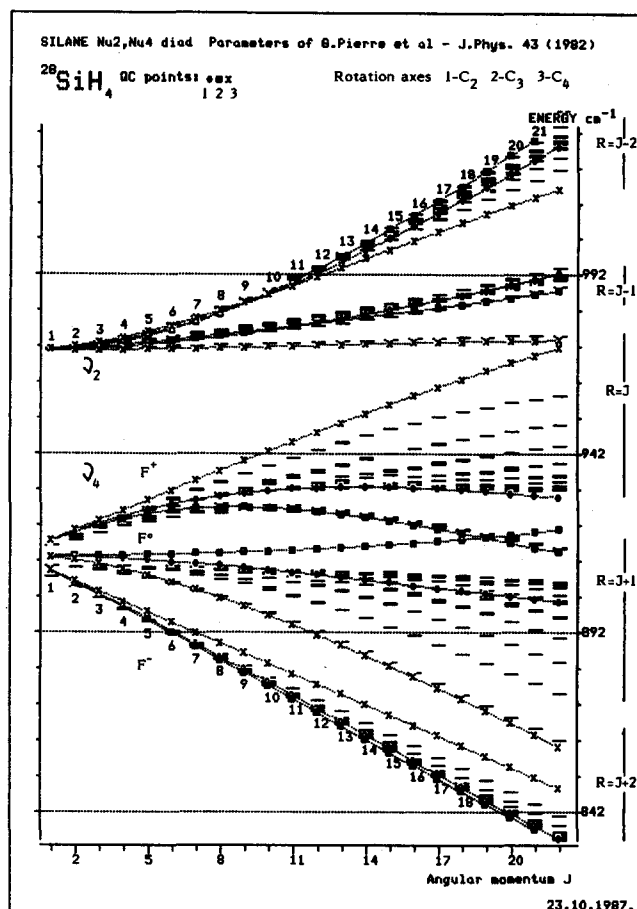


FIG. 11. The system of energy levels and the energy of the C_2 , C_3 , C_4 stationary points of the classical energy surfaces for the ν_2/ν_4 dyad of $^{28}\text{SiH}_4$. \times -energy of C_4 axis, \square -energy of C_3 axis, \circ -energy of C_2 axis.

a fine structure with respect to the distribution of branches we are discussing. We may do this by imposing the additional requirements for the rovibrational model Hamiltonian to be invariant with respect to the three-dimensional rotation group $\text{SO}(3)$. To do this we must indicate the irreducible representation of the $\text{SO}(3)$ group according which the vibrational operators are transformed. The simultaneous treatment of the ν_2/ν_4 dyad enables us to consider five vibrational annihilation (or creation) operators $a_1^E, a_2^E, a_x^{F_2}, a_y^{F_2}, a_z^{F_2}$ as transforming according to the irreducible representation of $\text{SO}(3)$ having the weight 2.⁷⁵ In such a case all rovibrational irreducible with respect to $\text{SO}(3)$ operators which may be included in the effective Hamiltonian may be written in the form

$$[(\mathbf{V} + {}^{(2)}\mathbf{V}^{(2)})^{(K)} \mathbf{R}^{\Omega(K)}]^{(0)}, \quad (12)$$

where the index K is the rank of the operators with respect to the $\text{SO}(3)$ group. We have generally five rovibrational operators for each value of $(\Omega - K) = 0, 2, 4, \dots$. The definition of the $\text{SO}(3)$ irreducible tensor operators may be naturally given in terms of the chain of groups $\text{SO}(3) \supset \text{O}^{76}$:

$$\begin{aligned}
 (\mathbf{V} + {}^{(2)}\mathbf{V}^{(2)})_p^{(K)} &= (-1)^K (2K+1)^{1/2} \\
 &\times \frac{1}{[\Gamma]^{1/2}} \sum K_{p_1 p_2 p}^{22K} (\mathbf{V}_{p_1} + {}^{(2)}\mathbf{V}_{p_2})^{(p)}, \\
 (p) &= (n, \Gamma),
 \end{aligned} \quad (13)$$

where $K_{p_1 p_2 p}^{22K}$ are the isoscalar factors for the chain of groups $\text{SO}(3) \supset \text{O}$.

All rovibrational states of the ν_2/ν_4 dyad under the additional supposal of $\text{SO}(3)$ symmetry are divided into five branches characterized by an auxiliary quantum number $R = J \pm 2, J \pm 1, J$. The so obtained classification is a natural generalization of the well-known classification of rovibrational states for a F_2 vibrational state split by Coriolis interaction. There are several schemes based on approximate $\text{SO}(3)$ symmetry for the construction of the effective Hamiltonian of tetrahedral molecules.⁷⁵ For our purposes it is important to take into account the lower in the rotational angular momentum terms [which are the most important ones from all terms of the form (12)] yielding the distribution of the energy branches in the energy spectra specified by the following sequence of R values: $J+2, J+1, J, J-1, J-2$. Each branch has $(2R+1)$ -fold degenerate levels. We do not take into account the $(2J+1)$ -fold degeneracy caused by different projections of the total angular momentum on the laboratory fixed frame.⁷⁷

The structure of branches which we obtain for the model mentioned above is similar to those taking place in tetrahedral molecules at the limit of sufficiently high J values. Indeed from Fig. 8 we see that after three consecutive redistributions of the energy levels between $F+$ and $F0$, lower E and $F+$, $F0$ and F -branches the resulting pattern is characterized by the following numbers of states in the branches: $2(J+2)+1$, $2(J+1)+1$, $2J+1$, $2(J-1)+1$, $2(J-2)+1$ with the energy increase. This effect has clear physical meaning. The Coriolis interaction (diagonal plus nondiagonal) is responsible for the formation of the branch structure in those regions of J values where the Coriolis splitting is larger than the $\nu_2 - \nu_4$ vibrational frequency difference.

Let us now take into account the most important terms leading to the breakdown of the $\text{SO}(3)$ invariance. The leading term is surely the splitting of purely vibrational states, i.e., $(\nu_2 - \nu_4)$ difference. Therefore we consider the model Hamiltonian including two operators only

$$\mathbf{H} = \Delta\nu(\mathbf{V}_{2,2} - \mathbf{V}_{4,4}) + t[(\mathbf{V} + {}^{(2)}\mathbf{V}^{(2)})^{(1)}\mathbf{R}^{(1)}]^{(0)}. \quad (14)$$

The first term is the detuning of the vibrational resonance. The second term is the Coriolis interaction between the ν_2 and ν_4 states under the supposal of $\text{SO}(3)$ invariance. The energy level system and the results of the classical analysis of the model Hamiltonian (14) is presented in Fig. 12. For low J values two groups of levels may be associated with the rotational structure of the ν_2 and ν_4 vibrational states because the $(\nu_2 - \nu_4)$ term is the leading one. The Coriolis interaction results in the splitting of triply degenerate F_2 state into three branches and to splitting of E state into two branches due to nondiagonal interactions. For higher J values the Coriolis interaction becomes the most important one

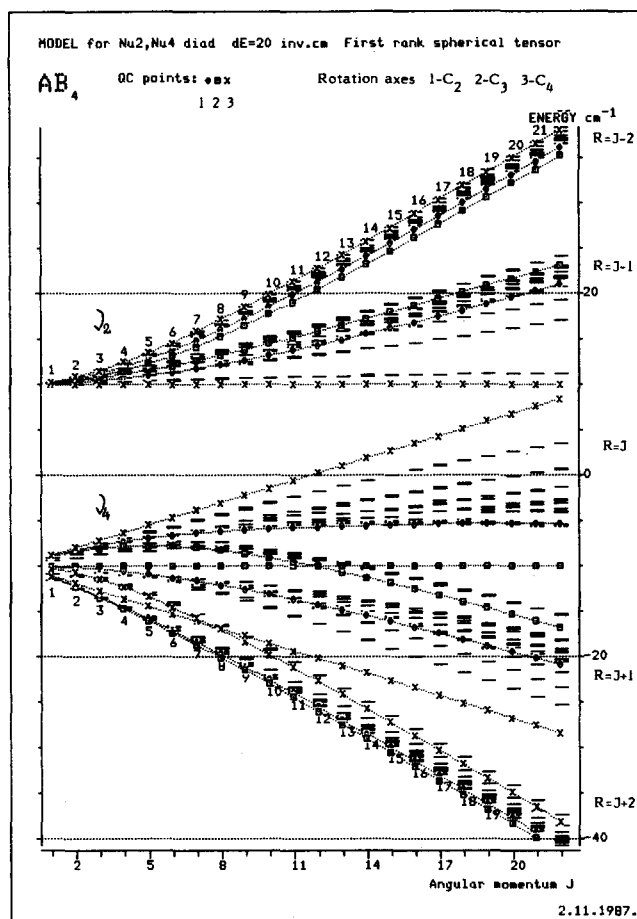


FIG. 12. Energy level system versus classical energies of the stationary C_2 , C_3 , C_4 axes for the model Hamiltonian (14). The notations are the same as in Fig. 11.

in Eq. (14). It leads to another distribution of the rotational branches whereas the tetrahedral splitting of each branch is exclusively due to the broken $\text{SO}(3)$ symmetry caused by the $(\nu_2 - \nu_4)$ term. The transition from one system of branches to another under J increase is connected to the formation of three conical intersection points. Therefore, from the qualitative point of view the redistribution of the energy levels between the branches for the model Hamiltonian (14) is in agreement with that observed for the SiH_4 and CH_4 molecules (Figs. 7, 8, and 11). To verify the application of the model Hamiltonian (14) to a qualitative description of rovibrational states of tetrahedral molecules we must demonstrate that we take into account all the most important terms in the classification scheme based on cubic molecular symmetry group rather than on approximate $\text{SO}(3)$ classification scheme. The difference between these two schemes lies in the number of independent operators of the first order (linear in the angular momentum operators). If we suppose the $\text{SO}(3)$ invariance of the rovibrational Hamiltonian there is only one operator linear in \mathbf{J}_α

$$[(\mathbf{V} + {}^{(2)}\mathbf{V}^{(2)})^{(1)}\mathbf{R}^{(1)}]^{(0)}. \quad (15)$$

The classification scheme based on cubic symmetry group gives two independent operators linear in \mathbf{J}_α

TABLE V. The Coriolis interaction parameters for tetrahedral molecules.

| Molecule | $^{12}\text{CH}_4$ | $^{12}\text{CD}_4$ | $^{28}\text{SiH}_4$ | $^{74}\text{GeH}_4$ | $^{120}\text{SnH}_4$ | ^a |
|---|--------------------|--------------------|---------------------|---------------------|----------------------|--------------|
| $\Delta\nu$ | 222.57 | 93.78 | 56.97 | 109.21 | 72.64 | 0 |
| $\frac{u_{2,4}^{1(1,F_1)}}{u_{4,4}^{1(1,F_1)}}$ | -0.9310 | -1.3794 | -0.9275 | -0.6894 | -0.6889 | $-\sqrt{2}$ |

^a The case of strict spherical symmetry.

$$\begin{aligned} & [(-)(\mathbf{V} + E\mathbf{V}F_2)F_1\mathbf{R}^{1(1,F_1)}]A_1, \\ & [(-)(\mathbf{V} + F_2\mathbf{V}F_2)F_1\mathbf{R}^{1(1,F_1)}]A_1, \end{aligned} \quad (16)$$

where $(-)\mathbf{A} = i(\mathbf{A} - \mathbf{A}^+)$.

The phenomenological Hamiltonian invariant with respect to the cubic symmetry group O up to terms linear in J_α must include the two operators (16) with independent coefficients. The scheme based on SO(3) supposed symmetry admits the only operator linear in J_α which is the linear combination of two operators (14) with fixed coefficients

$$\begin{aligned} & [(\mathbf{V} + {}^{(2)}\mathbf{V}F_2)(\mathbf{I})\mathbf{R}^{(1)}]^{(0)} \\ & = (5)^{-1/2}[(a + F_2aF_2)F_1\mathbf{R}^{1(1,F_1)}]A_1 \\ & - (2/5)^{1/2}[(-)(a + EaF_2)F_1\mathbf{R}^{1(1,F_1)}]A_1. \end{aligned} \quad (17)$$

Let us now consider whether the restriction imposed by fixed coefficients in (14) is a serious one for real molecular systems. The numerical comparison of the coefficients $t_{2,4}^{1(1,F_1)EF_2}$ and $t_{4,4}^{1(1,F_1)F_2F_2}$ of the nondiagonal and diagonal Coriolis terms shows that the ratio of these coefficients for the ν_2/ν_4 dyad of tetrahedral molecules is close to $(-\sqrt{2})$ [appropriate for the SO(3) invariant combination (17), see Table V]. Moreover, the parameter of the nondiagonal Coriolis term of the first order for the ν_2/ν_4 dyad may vary considerably due to the ambiguity of the effective Hamiltonian. Therefore, the effects caused by deviation of the linear combination of the Coriolis interaction operators from the SO(3) invariant operator (17) are of second order. The operator (14) is accurate up to the second-order terms and it properly describes the redistribution of the energy levels between different branches in the energy spectra. The redistribution phenomenon itself may be interpreted as the recoupling of the vibrational and rotational angular momenta under increase of the angular momentum quantum number.

IV. CONCLUSION

We have shown the rich possibilities which the method of the qualitative analysis yields for the investigations of complex molecular spectra. In conclusion we want to stress the following points.

(1) Qualitative methods enable one to clearly visualize the complicated effective Hamiltonian and to find their generic qualitative changes.

(2) The general phenomenological classification of the generic qualitative changes is based on the number of dynamic variables and on the molecular symmetry group.

(3) The proper knowledge of the singularities (bifurcation and diabolic points) is of primary importance for an adequate description of the dynamical systems. Accordingly, it is desirable to perform the experimental study of molecular systems close to the peculiarities of the energy spectra.

(4) The reasonable extrapolation of the experimental data for the same molecule or within some class of molecular systems might take advantage of a proper description of the qualitative changes, i.e., the singularity points.

(5) Along with the phenomenological Landau type theory of the qualitative changes discussed above the further next step is the formulation of the microscopic theory of qualitative changes.

(6) From the point of view of their possible applications to the study of qualitative features of excited states of quantum systems with small finite number of degrees of freedom, a more general comparative analysis of the qualitative methods of macroscopic physics is needed for further developments.

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