Chemical Physics 137 (1989) 1-13
North-Holland, Amsterdam

QUALITATIVE ANALYSIS OF VIBRATIONAL POLYADS: *N*-MODE CASE

B.I. ZHILINSKII
Chemistry Department, Moscow State University, 119899 Moscow, USSR

Received 2 February 1989

A general method for the qualitative analysis of vibrational polyads formed by *N* quasidegenerate modes is proposed. The construction of effective Hamiltonians for vibrational polyads and the general scheme of the qualitative analysis are outlined. The description of the limiting classic manifold is given and the analysis of the group action on it is performed. The three-mode problem is used as the simplest nontrivial example. The possible types of classical bifurcations and corresponding critical phenomena in the energy spectra of quantum systems appropriate for molecular problem with different symmetry groups are found. Brief discussion of different molecular problems tightly connected with the model considered is given along with some generalizations.

1. Introduction

Excited vibrational states of isolated molecules have been widely investigated the last years both by experimentators and theorticians (refs. [1-8] and references therein). In contrast to the lowest rovibrational states, the high density of excited vibrational states appropriate even for small polyatomics requires the development of a specific theoretical approach which should be adequate to correctly reproduce the general regularities in the energy level system and the corresponding wavefunctions, rather than the positions of the individual quantum levels.

One of the characteristic features of the system of excited vibrational states is the existence of vibrational polyads formed by several degenerate or quasidegenerate modes. The main question which we discuss in the present article is the description of the internal structure of vibrational polyads and its dependence on the energy (or quantum number) of the polyad. The internal structure of vibrational polyads depends on the number of vibrational degrees of freedom, their symmetry and intramolecular interactions. The simplest types of the energy level distribution within the polyad correspond to the so-called normal mode and local mode pictures. There exist many papers devoted to the study of these two possible limiting cases [3-15].

In a series of recent papers the method of the qualitative analysis of rotational and rovibrational problems [16-20] was developed and applied to the study of the qualitative features of the energy level distribution within the vibrational polyads [8,21-23]. Along with the general discussion of the construction of the effective Hamiltonians [8] one simple particular case of polyads formed by two (quasi)degenerate modes was investigated in detail [21-23]. Unfortunately, the theoretical analysis of the two-mode case [21-23] is based on the close equivalence between this particular vibrational problem and the purely rotational one and it cannot be generalized straightforwardly to more complicated vibrational problems.

This paper gives a general method for the qualitative analysis of vibrational polyads formed by *N* quasidegenerate modes. In section 2 the construction of effective Hamiltonians for vibrational polyads and a general scheme of the qualitative analysis are outlined. Sections 3 and 4 explain the construction of the limiting classic manifold and the analysis of the group action on it. We use the three-mode problem as the simplest nontrivial example. In section 5 we discuss the possible types of classical bifurcations and corresponding critical phenomena in the energy spectra of quantum systems appropriate for molecular problems with different symmetry groups. A brief discussion of different molecular problems tightly connected with the model considered is given in section 6 along with some generalizations.

2. Effective Hamiltonians for vibrational polyads and general scheme of the qualitative analysis

Effective operators for vibrational polyads may be easily written in terms of the vibrational creation and annihilation operators a_i^+, a_i satisfying the standard commutation relations

$$[a_i, a_j] = [a_i^+, a_j^+] = 0\,,$$
$$[a_i, a_j^+] = \delta_{ij}, \quad i, j = 1, ..., N\,. \qquad (1)$$

An effective Hamiltonian possesses the following power expansion in terms of a_i, a_j^+:

$$\mathscr{H} = \sum C_{n_1...n_N m_1...m_N} a_1^{+n_1} ... a_N^{+n_N} a_1^{m_1} ... a_N^{m_N}\,, \qquad (2)$$

with one additional condition to be imposed,

$$\sum n_i = \sum m_i\,. \qquad (3)$$

The condition (3) results in the block diagonal form of the Hamiltonian (2), i.e. the matrix elements of the operator (2) between wavefunctions corresponding to the states from different polyads are identically zero. In other words we suppose that the total number of vibrational quanta

$$K = \sum a_i^+ a_i \qquad (4)$$

is an integral of motion for the operator (2). Such a supposition is surely an approximation. It is not valid for a complete vibrational operator including all vibrational degrees of freedom. At the same time this approximation is physically reasonable in many interesting cases.

The limits of the applicability of the model considered can be described as follows. The vibrational level system of a real molecule must possess polyads well separated in energy formed by N quasidegenerate vibrations ν_1, ν_2, ..., ν_N. A crude estimate for the absence of the overlap of vibrational polyads is given by the inequality

$$(\nu_N - \nu_1)K < \nu_1\,, \qquad (5)$$

where K is the quantum number of a polyad (i.e. the total number of vibrational quanta) and $\nu_N - \nu_1$ shows the detuning of the vibrational resonances.

The second important condition of the applicability of the model considered is the absence of vibrational resonances with some other modes. Sometimes when such resonances (for example 1:2 Fermi resonance) systematically exist in the energy spectrum the model can be generalized to include the description of polyads taking into account some $n:m$ $(n \neq m)$ resonances.

Thus the initial point for the further qualitative analysis is the effective Hamiltonian (2) along with the additional requirement (3) showing the existence of the integral of motion (4). Accordingly, two slightly different problems may be formulated.

(A) The study of the qualitative structure of a single vibrational polyad characterized by a total number K of vibrational quanta.

(B) The study of the generic qualitative modifications in the internal structure of vibrational polyads under K variation.

The last problem is the question about generic changes in the one-parametric family of Hamiltonians with the integral of motion K playing the role of the parameter.

The general scheme of the qualitative analysis of the Hamiltonian (2) is similar to that developed earlier for the rotational problem [16–20]. So we just briefly summarize it and bring to attention some peculiarities of the vibration problem.

The general idea of the qualitative analysis is the transformation from the Hamiltonian to its classical analog and the application of the well-elaborated methods of bifurcation analysis to the study of classical problem. The first essential step is the construction of the classical limit manifold (i.e. the phase space) for the quantum problem considered and the determination of the symbol (classical Hamilton function) corresponding to the quantum Hamiltonian. The second step is the symmetry analysis of the group action on the classical limit manifold. The symmetry classification of the phase space points by their local symmetry group is the most important point for the study of possible types of bifurcations. It is just this step that we mainly study in the present paper.

3. Classical limit manifold

The general scheme of the construction of the classical limit manifold is based on the generalized coherent states method [24–30]. This procedure was discussed from a mathematical point of view in refs. [24–26]. Some physical application may be found in refs. [24,27–30]. We give here only a formal description of the correspondence between quantum and classical problems formulated especially for the case of effective vibrational Hamiltonians. We can take as dynamical variables for the quantum problem the vibrational creation and annihilation operators a_i^+, a_i supposing that they are introduced into the Hamiltonian only in the form of the product

$$a_1^{+n_1}...a_N^{+n_N}a_1^{n_1}...a_N^{m_N}\,, \tag{6}$$

satisfying the condition

$$n_1+...+n_N=m_1+...+m_N\,. \tag{7}$$

The action of any given operator (6) on any given wavefunction yields physically identical results if these wavefunction differ only by a common complex phase. This restrictions are to be taken into account under the transition to the classical limit.

To realize the transition to the classical limit one must introduce the complex variable z_i instead of a pair of operators a_i^+, a_i, to put the additional requirement $|z_1|^2+...+|z_N|^2=1$ and to equate the complex vectors which differ by a phase $(z_1, ..., z_N)$ and $(z_1e^{i\varphi}, ..., z_Ne^{i\varphi})$. From a mathematical point of view this procedure is the construction of the complex projective space CP^{N-1} which is locally a $(2N-2)$-dimensional real Euclidean space.

Below we limit ourselves to the example of the three-mode vibrational problem and investigate the two-dimensional complex projective space. To make further calculations we need the explicit form of the coordinate system on the complex projective space. We use the standard construction which is based on the introduction of several local maps.

Let (z_1, z_2, z_3) be the points of the three-dimensional complex Euclidean space C^3 which satisfy the requirement $|z_1|^2+|z_2|^2+|z_3|^2=1$. The projective images of all these points form the CP^2 space. We take as a first map in CP^2 that one which covers all the images of the points with $z_1\neq0$. The local coordinates of the images of (z_1, z_2, z_3), $z_1\neq0$ points in CP^2 in this map is given by $(1, w_2, w_3)$ where $w_2=z_2/z_1$, $w_3=z_3/z_1$. The second local map covers all points in CP^2 which are the images of (z_1, z_2, z_3) points with $z_2\neq0$. The local coordinates in this map are given by the relation

$$(z_1, z_2, z_3)\rightarrow(u_1, 1, u_3)\,;$$

$$u_1=z_1/z_2,\quad u_3=z_3/z_2\quad(z_2\neq0)\,.$$

At last the third map may be introduced which covers images of the points (z_1, z_2, z_3) with $z_3\neq0$,

$$(z_1, z_2, z_3)\rightarrow(v_1, v_2, 1)\,;$$

$$v_1=z_1/z_3,\quad v_2=z_2/z_3\quad(z_3\neq0)\,.$$

Three maps cover all points of the CP^2 space. The trivial generalization to the CP^k complex projective space shows that $k+1$ maps may be introduced in such a way that they cover the CP^k space. The maps introduced are overlapping. To reach the one-to-one correspondence between the points of the CP^2 space and the projective coordinates introduced above we can make the following choice, Let us fix three maps

$$\boldsymbol{M}^1=(1, w_2, w_3),\quad \boldsymbol{M}^2=(u_1, 1, u_3)\,,$$

$$\boldsymbol{M}^3=(v_1, v_2, 1)$$

and take all the points from the $\boldsymbol{M}^1$ map, the points with coordinates $(0, 1, u_3)$ from the $\boldsymbol{M}^2$ and the only $(0, 0, 1)$ from the $\boldsymbol{M}^3$ map. The unification of all these points gives the CP^2 space,

$$CP^2=(1, w_2, w_3)\oplus(0, 1, u_3)\oplus(0, 0, 1)\,. \tag{8}$$

The coordination introduced enables one to calculate the group action on the complex projective space which is induced by a symmetry properties of the initial quantum creation and annihilation operators.

4. Group action on the classical limit manifold

We have defined the classical limit manifold for the quantum Hamiltonian describing the vibrational polyads. It is the complex projective space CP^{N-1} (N is the number of vibrational modes forming the polyads). The next step is the definition of the group action on the classical phase space induced by the symmetry of the initial quantum problem. First of all it is necessary to find the group image for the problem considered starting from the molecular symmetry group and the symmetry types (the irreducible representations) of the dynamical variables. The important notion of "the group image" is widely used in solid state physics and especially in the theory of phase transitions [31,32]. The analysis of the group images for the effective Hamiltonians for vibrational polyads was given in the previous paper [8] where the complete list of the group images for the three-mode problems was given in particular. So we do not discuss this problem here and suppose that the group image is known for the molecular problem considered.

To specify the group action on the complex projective space it is necessary

(i) to define explicitly the action of all group elements on the points of the complex projective space (classical limit manifold),

(ii) to find the groups of isotropy for different points,

(iii) to give the decomposition of the carrier space into the sets of points with the same isotropy group (more strictly speaking the stratification of the orbit space must be given).

We start with the most trivial example. The three-dimensional vibrational space is characterized by two totally symmetric modes and one nonsymmetric mode. The group image is C_2 [8]. An example of such a situation is a three-atomic molecule AB_2 with a C_{2v} molecular symmetry group and a near degeneracy of all three modes. A more realistic example is the quasi-degeneracy of valence stretching modes ν_1, ν_3 and the overtone of the deformation mode $2\nu_2$. Under this supposition we can consider vibrational polyads of the form $(\nu_1, 2\nu_2, \nu_3)$, $\nu_1+\nu_2+\nu_3=\text{const.}$ but the symmetry of three modes remains the same, $2A+B$, with respect to C_2 group which is the group image for this special case considered.

We choose the vibrational annihilation and creation operators a_1, a_2, a_3, a_1^+, a_2^+, a_3^+ transforming according to irreducible representation of the C_2 group as

$$a_1 \sim B, \quad a_2, a_3 \sim A\,,$$
$$a_1^+ \sim B, \quad a_2^+, a_3^+ \sim A\,. \tag{9}$$

Thus the annihilation (creation) operators are transformed under the group action as

$$E(a_1, a_2, a_3) = (a_1, a_2, a_3)\,,$$
$$C_2(a_1, a_2, a_3) = (-a_1, a_2, a_3)\,. \tag{10}$$

We must now find the group action on the complex projective space CP^2 which is the classical limit manifold for the problem considered. It is a trivial task to define the group action on the space of classical complex variables z_i. It is necessary just to put

$$E(z_1, z_2, z_3) = (z_1, z_2, z_3)\,,$$
$$C_2(z_1, z_2, z_3) = (-z_1, z_2, z_3)\,. \tag{11}$$

Now we use the general procedure for the construction of the complex projective space and define the group action for different maps. The action of E is obvious in any map. To find the action of C_2 element in the map $\boldsymbol{M}^1$ we can use the explicit expression of the coordinates in terms of the variables z_i

$$C_2(1, w_2, w_3) = C_2(1, z_2/z_1, z_3/z_1)$$
$$= (1, -z_2/z_1, -z_3/z_1) = (1, -w_2, -w_3). \tag{12}$$

Similar we have for the CP^2 points from other maps $\boldsymbol{M}^2$ and $\boldsymbol{M}^3$

$$C_2(0, 1, u_3) = C_2(0, 1, z_3/z_2) = (0, 1, u_3)\,, \tag{13}$$

$$C_2(0, 0, 1) = (0, 0, 1)\,. \tag{14}$$

We can now easily find the set of points invariant with respect to the C_2 group, i.e. the set of points with C_2 local symmetry group. All such points are

$$(1, 0, 0) \oplus (0, 1, u_3) \oplus (0, 0, 1)\,. \tag{15}$$

It should be noted that $(0, 1, u_3) \oplus (0, 0, 1)$ is the CP^1 submanifold of CP^2 and the $(1, 0, 0)$ point is an isolated one.

A schematic visualization of the decomposition of the CP^2 space into subspace with different local symmetry groups is shown in fig. 1. It represents the S^2

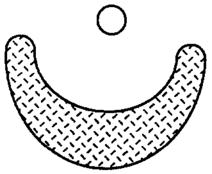

Fig. 1. C_2 group action on CP^2. Circle: isolated point with C_2 local symmetry, shaded area: S^2 surface with C_2 local symmetry.

surface and an isolated point in the CP^2 which is locally isomorphic to four-dimensional real Euclidean space.

Similar treatment may be realised for vibrational polyads with any symmetry properties and any number of vibrational degrees of freedom. We simply list here some results for three-mode cases with the most important for molecular symmetry properties.

In the case of three modes and the D_2 group image, the CP^2 phase space includes three S^2 surfaces with C_2 local symmetry group. Each two of these S^2 spheres has one common point with the D_2 local symmetry group. A schematic view of the D_2 group action on CP^2 space is shown in fig. 2. Table 1 gives the coordinates of different points along with their local symmetry groups. The same results are given in figs.3–5 and tables 2–4 for D_3, D_4 and O group actions on CP^2 space. The correspondence between molecular symmetry group and the irreducible representations of vibrational modes considered from one side and the image of group from the other is given in detail in ref. [8]. Here we list in table 5 examples of molecular symmetry groups which are reduced to group images C_2, D_2, D_3, D_4, O for three-mode problems.

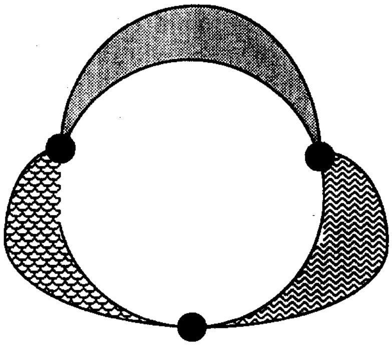

Fig. 2. D_2 group action on CP^2. (●) Isolated point with D_2 local symmetry.

Table 1
Stratification of CP^2 under the action of the D_2 group

Local symmetry group	Coordinates of points with given local symmetry group	Group operations from the local symmetry group
D_2	$(1, 0, 0)$ $(0, 1, 0)$ $(0, 0, 1)$	E, C_2^x, C_2^y, C_2^z
C_2	$(1, w_2, 0)$, $w_2 \neq 0, \infty$ $(1, 0, w_3)$, $w_3 \neq 0, \infty$ $(0, 1, u_3)$, $u_2 \neq 0, \infty$	E, C_2^x E, C_2^y E, C_2^z

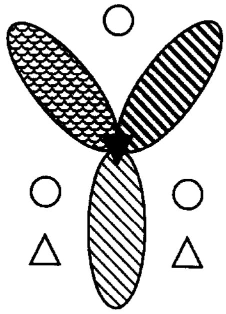

Fig. 3. D_3 group action on CP^2. (△, ▲) Isolated points with C_3 and D_3 local symmetry groups.

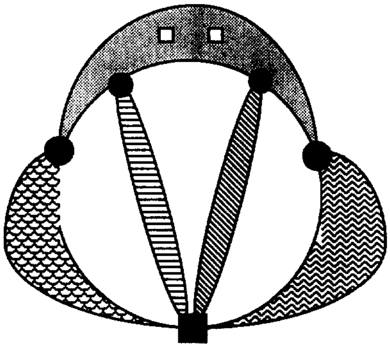

Fig. 4. D_4 group action on CP^2. (□, ■) Isolated points with C_4 and D_4 local symmetry groups.

5. Bifurcation analysis

We have given in section 4 the classification of the phase space points by their local symmetry. To reach the classification of the qualitative changes which can take place under the variation of one parameter it is necessary to find also the classification of the displacements from the point with given local symmetry group by the irreducible representations of the local symmetry group.

The types of bifurcations of the stationary points depend on the local symmetry group and on the cor-

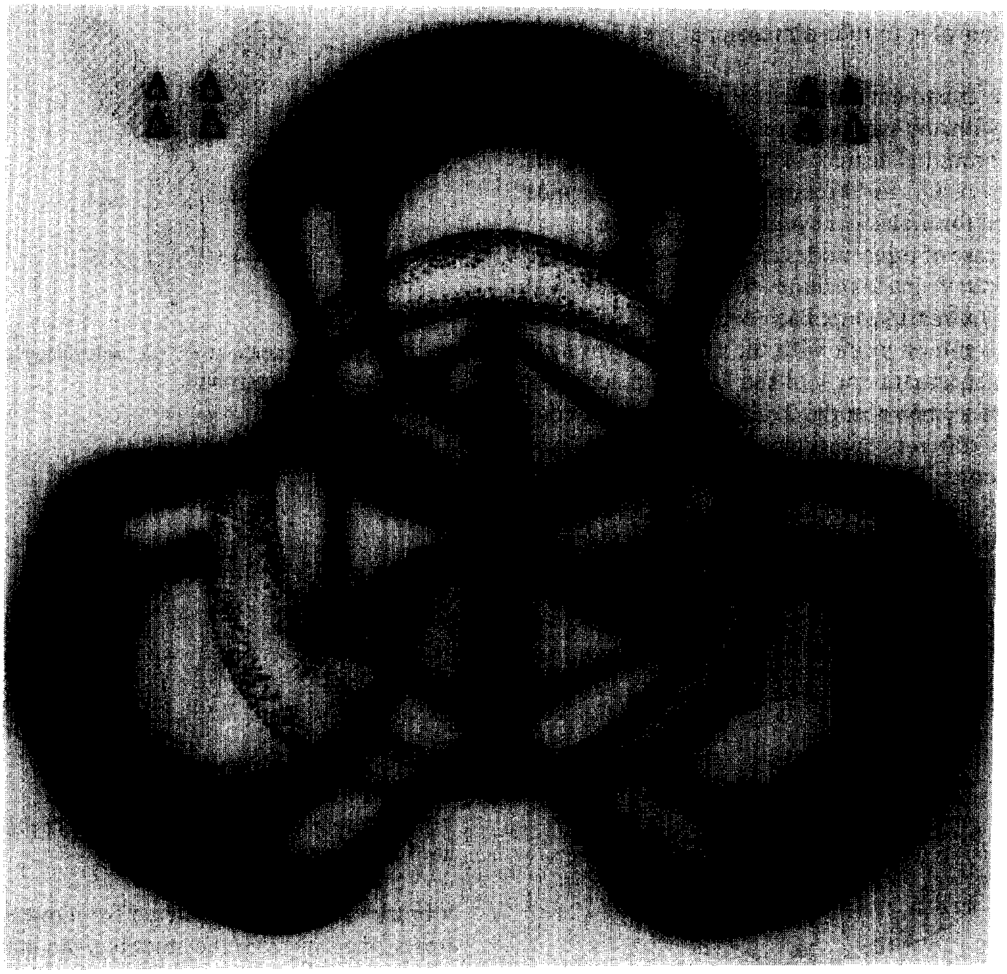

Fig. 5. O group action on CP^2.

responding symmetry types of small displacements rather than on the total symmetry groups and the symmetry classification of small displacements for the total symmetry groups.

As soon as under the variation of one parameter one irreducible representation may only be active, the types of the equivariant bifurcations appropriate for the problem considered are just the same as that studied earlier for purely rotational problems. Such a conclusion follows from the fact that only the molecular point groups are studied and the dependence on the only one parameter is considered. This conclusion shows in essence the absence of symmetry breaking phenomena for three-dimensional representation for the problem considered. It may be deduced also from the fact that the classical limit manifold (which has four real dimensions) admits the simplectic structure and therefore does not allow the three-dimensional representations for dynamic variables.

6. Molecular applications and generalization

The main physical supposition for the application of the model considered is the existence of isolated

Table 2
Stratification of CP^2 under the action of the D_3 group

Local symmetry group	Coordinates of points with given local symmetry group	Group operations from the local symmetry group
D_3	$(1, 1, 1)$	$E, C_3,$ $C_3^2,$ $C'_2,$ $C''_2,$ C'''_2
C_3	$(1, e^{2i\pi/3}, e^{4i\pi/3})$ $(1, e^{4i\pi/3}, e^{2i\pi/3})$	E, C_3, C_3^2
C_2	$(1, -1, 0)$ $(1, 1, w_3)\ w_3 \neq 1$	E, C'_2
	$(1, 0, -1)$ $(1, w_2, 1)\ w_2 \neq 1$	E, C''_2
	$(0, 1, -1)$ $(1, w, w)\ w \neq 1$	E, C'''_2

vibrational polyads. The most evident molecular problems verifying the abovementioned supposition are the stretching vibrations in AB_2, AB_3, AB_4, ... type molecules with heavy central atom A and light B atoms. The obvious obstacle is the existence of other vibrations possessing some kind of resonances with modes forming polyads. For example, the polyads formed by stretching vibrations of H_2O molecule are usually considered separately from the bending mode. At the same time such an approximation is rather crude because there is a near 2 : 1 resonance between bending and stretching modes. In such a case we can take into account bending and stretching modes simultaneously and consider larger polyads formed by three vibrational modes. The only modification is the consideration of two bending quanta as new ones. The notation of vibrational states in a polyad is $(\nu_1, 2\nu_2, \nu_3)$ or $(\nu_1, 2\nu_2+1, \nu_3)$ with $\nu_1+\nu_2+\nu_3=N$ being the effective total number of vibrational quanta. In such a case the polyads with odd and even bending vibrational quantum number should be considered separately. Another example is the C–H stretching vibrations in CHD_3 molecule [15]. This case corresponds to a near 2 : 1 Fermi resonance between doubly degenerate bending and single stretching modes. We again can consider separately the polyads formed by odd number bending quanta $(\nu_s, 2\nu_b)$ and by even number $(\nu_s, 2\nu_b)$.

Another kind of generalization is the description of the overlapping polyads. To describe the overlapping polyads one can introduce a more general effective operator for S polyads close to the Kth one. Such an effective Hamiltonian has the matrix form

$$H=(H_{ij}^K), \quad i,j=1, ..., S, \tag{16}$$

with each matrix element having the form

$$H_{ij}^K = \sum C_{n_1 \ldots n_N m_1 \ldots m_N} a_1^{+n_1} \ldots a_N^{+n_N} a_1^{m_1} \ldots a_N^{m_N}, \\ \sum n_\alpha = \sum m_\alpha . \tag{17}$$

The Hamiltonian (16) is represented in the clas-

Table 3
Stratification of CP^2 under the action of the D_4 group

Local symmetry group	Coordinates of points with given local symmetry group	Group operations from the local symmetry group
D_4	$(1, 0, 0)$	all group elements
C_4	$(0, 1, i), (0, 1, -i)$	$E, C_2^x, C_4^x, (C_4^x)^3$
D_2	$(0, 1, 0), (0, 0, 1)$	E, C_2^x, C_2^y, C_2^z
	$(0, 1, 1), (0, 1, -1)$	E, C_2^x, C'_2, C''_2
C_2	$(1, w_2, 0)\ w_2 \neq 0, \infty$	E, C_2^z
	$(1, 0, w_3)\ w_3 \neq 0, \infty$	E, C_2^y
	$(0, 1, u_3)\ u_3 \neq 0, \pm i, \pm 1, \infty$	E, C_2^x
	$(1, w, w)\ w \neq 0, \neq 1$	E, C'_2
	$(1, w, -w)\ w \neq 0, \neq 1$	E, C''_2

Table 4
Stratification of CP^2 under the action of the O group

Local symmetry group	Coordinates of points with given local symmetry group	Group operations from the local symmetry group
D_4	$(1, 0, 0)$	$E, C_2^x, C_2^y, C_2^z, C_4^x, (C_4^x)^3, C_2^{(5)}, C_2^{(6)}$
	$(0, 1, 0)$	$E, C_2^x, C_2^y, C_2^z, C_4^y, (C_4^y)^3, C_2^{(3)}, C_2^{(4)}$
	$(0, 0, 1)$	$E, C_2^x, C_2^y, C_2^z, C_4^z, (C_4^z)^3, C_2^{(1)}, C_2^{(2)}$
D_3	$(1, 1, 1)$	$E, C_2^{(1)}, C_2^{(3)}, C_2^{(5)}, C_3^c, (C_3^c)^2$
	$(1, -1, -1)$	$E, C_2^{(2)}, C_2^{(4)}, C_2^{(5)}, C_2^d, (C_3^d)^2$
	$(1, -1, 1)$	$E, C_2^{(2)}, C_2^{(3)}, C_2^{(6)}, C_3^b, (C_3^a)^2$
	$(1, 1, -1)$	$E, C_2^{(1)}, C_2^{(4)}, C_2^{(6)}, C_3^a, (C_3^a)^2$
C_4	$(1, i, 0), (1, -i, 0)$	$E, C_2^z, C_4^z, (C_4^z)^3$
	$(1, 0, i), (1, 0, -i)$	$E, C_2^y, C_4^y, (C_4^y)^3$
	$(0, 1, i), (0, 1, -i)$	$E, C_2^x, C_4^x, (C_4^x)^3$
C_3	$(1, e^{2i\pi/3}, e^{i\pi/3})$	$E, C_3^a, (C_3^a)^2$
	$(1, e^{5i\pi/3}, e^{4i\pi/3})$	
	$(1, e^{i\pi/3}, e^{2i\pi/3})$	$E, C_3^b, (C_3^b)^2$
	$(1, e^{4i\pi/3}, e^{5i\pi/3})$	
	$(1, e^{2i\pi/3}, e^{4i\pi/3})$	$E, C_3^c, (C_3^c)^2$
	$(1, e^{4i\pi/3}, e^{2i\pi/3})$	
	$(1, e^{i\pi/3}, e^{5i\pi/3})$	$E, C_3^d, (C_3^d)^2$
	$(1, e^{5i\pi/3}, e^{i\pi/3})$	
D_2	$(1, 1, 0), (1, -1, 0)$	$E, C_2^z, C_2^{(1)}, C_2^{(2)}$
	$(1, 0, 1), (1, 0, -1)$	$E, C_2^y, C_2^{(3)}, C_2^{(4)}$
	$(0, 1, 1), (0, 1, -1)$	$E, C_2^x, C_2^{(5)}, C_2^{(6)}$
C_2	$(1, w_2, 0)\ w_2 \neq 0, \pm i, \pm 1, \infty$	E, C_2^z
	$(1, 0, w_3)\ w_2 \neq 0, \pm i, \pm 1, \infty$	E, C_2^y
	$(0, 1, u_3)\ u_2 \neq 0, \pm i, \pm 1, \infty$	E, C_2^x
	$(1, w_2, -1)\ w_2 \neq 0, \pm 1, \infty$	$E, C_2^{(4)}$
	$(1, 1, w_3)\ w_3 \neq 0, \pm 1, \infty$	$E, C_2^{(1)}$
	$(1, -1, w_3)\ w_3 \neq 0, \pm 1, \infty$	$E, C_2^{(2)}$
	$(1, w, w)\ w \neq 0, \pm 1, \infty$	$E, C_2^{(5)}$
	$(1, w, -w)\ w \neq 0, \pm 1, \infty$	$E, C_2^{(6)}$
	$(1, w_2, 1)\ w_2 \neq 0, \pm 1, \infty$	$E, C_2^{(3)}$

sical limit by a matrix depending on the dynamic variables z_i and the parameter K showing the degree of vibrational excitation. For each K it gives S energy surfaces which are the eigenvalues of the classical matrix. The matrix symbol can show new types of qualitative peculiarities of the eigenvalues with respect to an isolated function. Along with bifurcations for every eigenvalue the degeneracy points of different energy surfaces can generally exist. The dimension of the set of degeneracy points depends on the number of parameters. We must treat as parameters the classical phase variables and the quantum number K which is supposed to be the integral of motion and is considered as parameter. The N-mode problem has $2N-2$ phase variables and one parameter K – the integral of motion. The abstract analysis of the matrix problems shows that the t-parameter-dependent family of Hermitian matrices possesses the $t-3$-dimensional set of doubly degenerate eigenvalues. This means that for the $N=2$ mode case $(t=3)$ the

Table 5
Three-dimensional vibrational problems which may be reduced to given group images

Abstract group isomorph to initial symmetry group	Symmetry of vibrations in G	Group image	Symmetry of bilinear combinations in the image	Local symmetry groups in the image
any	3Γ	C_1	9A	C_1
	Γ real			
any	$2\Gamma\oplus\Gamma'$ $(\Gamma\neq\Gamma')$	C_2	$5A\oplus 4B$	C_1, C_2
	Γ, Γ real			
any	$\Gamma\oplus\Gamma'\oplus\Gamma''$ $(\Gamma\neq\Gamma'\neq\Gamma''\neq\Gamma)$	D_2	$3A\oplus 2B_1\oplus 2B_2\oplus 2B_3$	C_1, C_2, D_2
	all real			
T	$A\oplus E$	C_3	$3\Gamma_0\oplus 3\Gamma_1\oplus 3\Gamma_1^*$	C_1, C_3
$T\times C_2$	$A_\alpha\oplus E_\alpha$ $(\alpha=g, u)$			
C_{3p}	$\Gamma_0\oplus\Gamma_p\oplus\Gamma_p^*$			
$C_{3p}\times C_2$	$\Gamma_{0\alpha}\oplus\Gamma_{p\alpha}\oplus\Gamma_{p\alpha}^*$ $(\alpha=g, u)$			
C_{6p}	$\Gamma_{3p}\oplus\Gamma_p\oplus\Gamma_p^*$			
$C_{6p}\times C_2$	$\Gamma_{3p\alpha}\oplus\Gamma_{p\alpha}\oplus\Gamma_{p\alpha}^*$ $(\alpha=g, u)$			
O	$A_i\oplus E$ $(i=1, 2)$	D_3	$2A_1\oplus A_2\oplus 3E$	C_1, C_2, C_3, D_3
$O\times C_2$	$A_{i\alpha}\oplus E_\alpha$ $(i=1, 2; \alpha=g, u)$			
D_{3p}	$A_i\oplus E_p$ $(i=1, 2)$			
$D_{3p}\times C_2$	$A_{i\alpha}\oplus E_{p\alpha}$ $(i=1, 2; \alpha=g, u)$			
D_{6p}	$B_i\oplus E_p$ $(i=1, 2)$			
$D_{6p}\times C_2$	$A_{i\alpha}\oplus E_\alpha$ $(i=1, 2; \alpha=g, u)$			
C_{4p}	$\Gamma_{i\alpha}\oplus\Gamma_p\oplus\Gamma_p^*$ $(i=0, 2p)$	C_4	$3\Gamma_0\oplus 2\Gamma_1^*\oplus 2\Gamma_1\oplus 2\Gamma_2$	C_1, C_2, C_4
$C_{4p}\times C_2$	$\Gamma_{i\alpha}\oplus\Gamma_{p\alpha}\oplus\Gamma_{p\alpha}^*$ $(i=0, 2p; \alpha=g, u)$			
D_{4p}	$\Gamma\oplus E_p$	D_4	$2A_1\oplus A_2\oplus B_1\oplus B_2\oplus 2E$	C_1, C_2, C_4, D_2, D_4
	$\Gamma=A_1, A_2, B_1, B_2$			
$D_{4p}\times C_2$	$\Gamma_\alpha\oplus E_{p\alpha}(\alpha=g, u)$			
	$\Gamma=A_1, A_2, B_1, B_2$			
T	F	T	$A\oplus E\oplus 2F$	C_1, C_2, C_3, D_2
$T\times C_2$	$F_\alpha(\alpha=g, u)$			
O	F_i $(i=1, 2)$	O	$A_1\oplus E\oplus F_1\oplus F_2$	C_1, C_2, C_3, C_4, D_2, D_3, D_4
O_h	$F_{i\alpha}$ $(i=1, 2; \alpha=g, u)$			

only possibility is the existence at some value of the parameter K of an isolated conical intersection point of two energy surfaces. For a general Hermitian matrix depending on t parameters the generic sets of degeneracy points are characterized in table 7 by the codimension which is the difference between the total number of parameters t and the dimension of the set of degeneracy points [33,34]. One can easily see that for the three-mode problem ($t=5$, four dynamic variables and one parameter) only the degeneracies of two energy surfaces are possible.

It was shown in ref. [19] that the appearance of isolated degeneracy points for the classical symbol corresponds in the case of two-phase variable problems to the regrouping of the energy levels between branches in the energy spectrum. The case of molecular model problems with a higher number of degrees of freedom is much more complicated due to the possibility of the formation of lines and surfaces of the degeneracy points in the phase space. This problem surely must be treated in detail separately.

Table 6
Examples of local symmetry groups occuring under the action of some symmetry groups on CP^2

Local symmetry group	Symmetry classification of small displacements	Group images possessing given local symmetry group
C_2	4B	C_2, D_3
	$2A \oplus 2B$	C_2, C_4, D_2, D_3, D_4, T, O
C_3	2E	C_3, D_3, T, O
C_4	$2\Gamma_2 \oplus E$	C_4, D_4, O
D_2	$2B_1 \oplus 2B_2$	D_2, D_4, T, O
D_3	2E	D_3, O
D_4	2E	D_4, O

Table 7
Codimensions of the generic sets of degeneracy points of the eigenvalues of parameter dependent Hermitian matrix

Type of degeneracy	Codimension
$E_i = E_j$	3
$E_i = E_j = E_k$	8
$E_{i1} = \ldots = E_{im}$	$m^2 - 1$
$E_i = E_j$; $E_k = E_l$	6

Appendix

The appendix is devoted to an intuitive explanation of some mathematical constructions which are either used in the main text or connected with the simplest applications of the results obtained for concrete molecular examples.

I shall discuss briefly the topological structure of the complex projective space which is the phase space for the problem considered. The relation between topological characteristics of the space and the system of stationary points of smooth functions on it will be formulated as well (the so-called Morse inequalities).

Some notions associated with the group action will be summarized and specified for the complex projective space. At last some simple conclusions about stationary points of functions defined on complex projective space and invariant with respect to a given symmetry group will be given.

One of the important characteristics of the global topological properties of the complex projective space, CP^n, are the Betti numbers. Betti number is an old mathematical terminology going back to the 19th century. Rang of the homology group is more appropriate in modern mathematical language.

Betti numbers may be found in some mathematical manuals on modern geometry. For CP^n space one has:

$$b_0 = b_2 = \ldots = b_{2n} = 1 \; ,$$

$$b_1 = b_3 = \ldots = b_{2n-1} = 0 \; . \qquad \text{(A.1)}$$

An intuitive interpretation of the Betti numbers may be given as follows.

Let us consider the connectivity of the space considered. If any two points of the space can be connected by a smooth curve it means that all the points are equivalent in some sense. This is the situation for the complex projective space. In such a case $b_0 = 1$. In contrast, the space of unimodular real matrices, for example, is characterized by $b_0 = 2$ because any matrix with determinant equal to $+1$ cannot be smoothly deformed into a matrix with determinant equal to -1.

Let us now consider different one-dimensional closed curves defined on CP^n. $b_1 = 0$ means that any closed one-dimensional curve may be smoothly deformed into a point. The same situation takes place for CP^1 space which is a bidimensional sphere S^2. It is evident that any closed curve on the bidimensional sphere may be deformed into a point. If one takes the bidimensional surface of the torus as an example, it is clear that there are some closed curves on it which may be deformed into a point but at the same time there are two nonequivalent types of closed curves which cannot be deformed into a point (two large circles on the torus). So for the bidimensional surface of the torus $b_1 = 2$ whereas for CP^1 (S^2) and more generally for CP^n $b_1 = 0$.

To explain the meaning of b_2 one must consider bidimensional closed surfaces and find all nonequivalent surfaces which cannot be reduced to an object of lower dimension. A further extrapolation is possible but it is sufficient to give here the relation between Betti numbers for CP^n:

$$b_k = b_{s-k} \; , \qquad \text{(A.2)}$$

where s is the real dimension of the manifold. (The real dimension of the complex projective space CP^n is equal to $2n$.)

The importance of Betti numbers is due to their relation to types and numbers of stationary points of Morse functions defined on the manifold considered. Some information concerning stationary points of Morse functions will be given below.

Let us consider a real smooth function f on the manifold M. The point $x_0 \in M$ is a stationary point of f if $\operatorname{grad} f(x_0) = 0$. The Hessian matrix

$$d^2 f = \frac{\partial^2 f}{\partial x_i \partial x_j} = (f_{x_i x_j}) \qquad (A.3)$$

is defined for a stationary point x_0. The stationary point x_0 is nondegenerate if the matrix $d^2 f$ is nondegenerate. All nondegenerate stationary points may be classified according to the number of positive and negative eigenvalues of the Hessian matrix.

The index of the stationary point x_0 is the number of negative eigenvalues of the Hessian matrix. For example, the function $f(x, y)$ depending on two variables possesses nondegenerate stationary points of the following types:

minima – stationary points of index 0,
saddle points – stationary points of index 1,
maxima – stationary points of index 2.

A function which possesses only nondegenerate stationary points is named a Morse function.

Let us now relate the number and types of stationary points of Morse functions defined on a given manifold with the Betti numbers of the manifold.

Let $c_k(f)$ be the number of stationary points of index k for the function f and $b_k(M)$ be the Betti numbers for a manifold M. The following set of relations holds:

$$b_0 - b_1 + b_2 - \ldots + (-1)^s b_s$$
$$= c_0(f) - c_1(f) + \ldots + (-1)^s c_s(f) \, , \qquad (A.4)$$

$$b_0(M) \leqslant c_0(f) \, ,$$
$$b_0(M) - b_1(M) \leqslant c_0(f) - c_1(f) \, ,$$
$$\ldots$$
$$b_0(M) - b_1(M) + \ldots + (-1)^k b_k(M)$$
$$\leqslant c_0(f) - c_1(f) + \ldots + (-1)^k c_k(f) \, ,$$
$$k < s \, . \qquad (A.5)$$

In particular, one has the simplified version of inequalities (A.5):

$$b_k(M) \leqslant c_k(f) \, . \qquad (A.6)$$

It follows immediately from (A.4) and (A.5) that one has the following set of inequalities for Morse functions defined on the bidimensional sphere S^2 ($b_0 = 1, b_1 = 0, b_2 = 1$).

$$c_0 - c_1 + c_2 = 2,$$
$$c_0 \geqslant 1, \quad c_2 \geqslant 1, \quad c_1 \geqslant c_0 - 1 \, .$$

The simplest solution $c_0 = 1, c_2 = 1, c_1 = 0$ shows that the simplest Morse function defined on the sphere S^2 possesses one minimum and one maximum and no saddle points.

For a function defined on CP^2 ($b_0 = b_2 = b_4 = 1$, $b_1 = b_3 = 0$) the equality takes the form

$$c_0 - c_1 + c_2 - c_3 + c_4 = 3 \, , \qquad (A.7)$$

and a set of inequalities may be represented in different forms, for example:

$$c_0 \geqslant 1, \quad c_2 \geqslant 1, \quad c_4 \geqslant 1 \, ,$$
$$c_1 \geqslant c_0 - 1, \quad c_3 \geqslant c_4 - 1 \, ,$$
$$c_0 - c_1 + c_2 \geqslant 2, \quad c_2 - c_3 + c_4 \geqslant 2 \, . \qquad (A.8)$$

It follows from (A.8) that the Morse function with the minimal number of stationary points possesses one point of index 0, one point of index 2, and one point of index 4 ($c_0 = c_2 = c_4 = 1, c_1 = c_3 = 0$).

To apply the Morse relations to functions which satisfy some symmetry requirements it is necessary to take into account the action of the symmetry group on the manifold because some stationary points may be due to a specific group action.

Let us consider the action of the group G on the manifold M. The action is given if the transformation of any point $x \in M$ under any element $R \in G$ is known. For each point $x_0 \in M$ one can define the local symmetry group H_{x_0} (an isotropy group) which includes all symmetry transformations leaving point x_0 invariant. An isotropy group H_{x_0} for any given point x_0 is a subgroup of the symmetry group G. The element $R \in G$, $R \notin H$ transforms x_0 into some other point. All such points form an orbit. The orbit of x_0 includes all the points that can be obtained from x_0 by the action of all the elements in the total symmetry group on it. It is possible to introduce the equivalence relation on the orbit space. The orbits are equivalent if they are characterized by the same isotropy group. The union of the orbits of the same type is called a stratum. The dimensions of the strata may generally vary from zero till the dimension of the manifold. The stratum of maximal possible dimension is called a generic one.

The function defined on the manifold necessarily possesses stationary points for all zero-dimensional strata. In some cases the simplest Morse function has stationary points only for zero-dimensional strata. In some other cases even the simplest Morse function possesses stationary points on one-, two-dimensional, or even generic strata. One may use Morse inequalities to answer the question: what kind of stationary points is appropriate and what strata are the stationary points placed on for the simplest Morse functions? Let us discuss some examples.

The action of the D_2 group on CP^2 (see fig. 2) leads to three points with D_2 local symmetry group. For these points the orbit consists of only one point because the isotropy group coincides with the total symmetry group. If the point x_0 has C_2 group as its isotropy group the corresponding orbit includes two points. There are three C_2 subgroups of the D_2 group (C_2^x, C_2^y, C_2^z) and the set of points possessing each C_2^i group as an isotropy group forms a two-dimensional sphere in CP^2 space. Therefore there are three two-dimensional spheres formed by points with C_2^i isotropy groups (two-dimensional strata).

All other points which do not belong to D_2 or C_2 isotropy groups (C_1 trivial isotropy group) form orbits including four points each. The space of these orbits is four-dimensional and it is a generic stratum.

The D_2 action on CP^2 results in zero-dimensional strata including three orbits (each includes one point) with D_2 isotropy group. Therefore the simplest Morse function invariant with respect to D_2 group possesses three stationary points which are placed on zero-dimensional strata. One stationary point has index 0, one has index 2, and one has index 4. The simplest D_2 invariant Morse function on CP^2 has the same system of stationary points as the generic nonsymmetrized Morse functions.

Let us consider the D_4 invariant Morse function defined on the CP^2 space. The analysis of the D_4 group action on CP^2 space (see table 3 and fig. 4) shows the existence of zero-, two-, and four-dimensional strata. Zero-dimensional strata include one stratum formed by one D_4 invariant orbit. This orbit includes one point because the isotropy group coincides with the total symmetry group. Another zero-dimensional stratum is formed by D_2 invariant orbits. Each orbit includes two equivalent points because D_2 is a subgroup of index 2 of the D_4 group. The C_4 invariant points form on orbit which forms itself a zero-dimensional stratum.

Let us now suppose that the simplest Morse function defined on CP^2 and invariant with respect to D_4 group possesses the stationary points on the zero-dimensional strata only. To verify such a conjecture it is necessary to show that all Morse relations can be satisfied. One may start with the equality (A.7) and take into account the supposition that the number of stationary points is equal to the number of points in orbits forming zero-dimensional strata

$$c_0+c_1+c_2+c_3+c_4=7\,. \tag{A.9}$$

From (A.7) and (A.9) it follows

$$c_1+c_3=2, \quad c_0+c_2+c_4=5. \tag{A.10}$$

From (A.10) and (A.8) it is easy to verify that the minimal number of stationary points (seven points which include three pairs of equivalent points) may be distributed between stationary points with different index in two ways

$$c_0=1, \quad c_1=0, \quad c_2=c_3=c_4=2\,;$$

$$c_0=c_1=c_2=2, \quad c_3=0, \quad c_4=1\,.$$

It is reasonable to suppose that the energy functions for the lowest polyads are the simplest Morse functions. The order of a polynomial required for a reasonable description of the lowest polyads is generally not too high to permit the formation of stationary points on the strata of high dimension and on the generic stratum in particular. Qualitative modifications of the energy surface or the energy level system for the corresponding quantum problem are associated with the formation of new stationary points under variation of the physical parameter. The appearance of new stationary points manifests itself by passing the determinant of the Hessian matrix through zero (i.e. by the formation of degenerate stationary points). All these critical phenomena depend only on the local isotropy group appropriate for an effective Hamiltonian for the three-dimensional vibrational problem.

References

[1] B.R. Henry, Accounts Chem. Res. 10 (1977) 204.
[2] M.L. Sage and J. Jortner, Advan. Chem. Phys. 47 (1981) 293.
[3] M.S. Child and L. Halonen, Advan. Chem. Phys. 57 (1984) 1.
[4] I. Mills and A.G. Robiette, Mol. Phys. 56 (1985) 743.
[5] C. Patterson, J. Chem. Phys. 83 (1985) 4618.
[6] M.E. Kellman, J. Chem. Phys. 83 (1985) 3843.
[7] F. Michelot and J. Moret-Bailly, J. Phys. (Paris) 48 (1987) 51.
[8] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Chem. Phys. 126 (1988) 243.
[9] C. Jaffe and P. Brumer, J. Chem. Phys. 73 (1980) 5646.
[10] K. Stefanski and E. Pollak, J. Chem. Phys. 87 (1987) 1079.
[11] R.H. Page, Y.R. Shen and Y.J. Lee, Phys. Rev. Letters 59 (1987) 1293.
[12] J. Makarewicz, J. Phys. B 21 (1988) 1803.
[13] L. Halonen and T. Carrington Jr., J. Chem. Phys. 88 (1988) 4171.
[14] W. Karrlein, J. Manz, V. Mohan, H.-J. Schreier and T. Spindler, Mol. Phys. 64 (1988) 563.
[15] M. Lewereng and M. Quack, J. Chem. Phys. 88 (1988) 5408.
[16] I.M. Pavlichenkov and B.I. Zhilinskii, Ann. Phys. 184 (1988) 1.
[17] D.A. Sadovskii and B.I. Zhilinskii, Mol. Phys. 65 (1988) 109.
[18] V.M. Krivtsun, D.A. Sadovskii and B.I. Zhilinskii, J. Mol. Spectry., in press.
[19] V.B. Pavlov-Verevkin, D.A. Sadovskii and B.I. Zhilinskii, Europhys. Letters 6 (1988) 573.
[20] D.A. Sadovskii, B.I. Zhilinskii, J.P. Campion and G. Pierre, submitted for publication.
[21] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Khim. Fiz. 6 (1987) 1459.
[22] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Opt. i Spektroskopya 64 (1988) 46.
[23] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Chem. Phys. 128 (1988) 429.
[24] R. Gilmore, Ann. Phys. 74 (1972) 391.
[25] B. Simon, Commun. Math. Phys. 71 (1980) 247.
[26] L.G. Yaffe, Rev. Mod. Phys. 54 (1982) 407.
[27] A.M. Perelomov, Generalized Coherent States and Their Applications (Springer, Berlin, 1986).
[28] D.H. Feng, R. Gilmore and S.R. Deans, Phys. Rev. C 23 (1981) 1254.
[29] W.M. Zhang, C.-L. Wu, D.H. Feng, J.N. Ginocchio and M.W. Guidry, Phys. Rev. C 38 (1988) 1475.
[30] R. Gilmore, Catastrophe Theory for Scientists and Engineers (Wiley, New York, 1981).
[31] L. Michel and J. Mozrzymas, Lecture Notes Phys. 79 (1977) 447.
[32] Yu.A. Izyumov and V.N. Syromyatnikov, Phase Transitions and Symmetry of Crystals (Nauka, Moscow, 1984).
[33] V.I. Arnol'd, Usp. Mat. Nauk 26 (1971) 101 [English transl. Russ. Math. Surv. 26 (1971) 29].
[34] J.E. Avron, A. Raveh and B. Zur, Rev. Mod. Phys. 60 (1988) 873.