Chemical Physics 128 (1988) 429–437
North-Holland, Amsterdam

REARRANGEMENTS OF THE VIBRATIONAL POLYADIC SPECTRA WITH EXCITATION: TWO-MODE CASE

V.B. PAVLOV-VEREVKIN and B.I. ZHILINSKII
Laboratory of Molecular Spectroscopy, Chemical Department, Moscow State University, Moscow 119899, USSR

Received 14 March 1988; in final form 5 July 1988

A simple approach permitting to explain the qualitative changes (rearrangements) of the vibrational polyads with excitation is developed and applied to the two-mode case. This approach is based on the analysis of the classical Hamilton function corresponding to the effective Hamiltonian for a vibrational polyad. The rearrangements of the vibrational polyads are related to certain bifurcations in the corresponding classical problem. A concept of localized vibrational states generalizing and unifying those of normal and local mode states is proposed. The influence of the symmetry properties of the problem on the rearrangements is studied. A complete group theoretical analysis is given and all the possible types of rearrangements in the two-mode case are listed.

1. Introduction

The experimental and theoretical studies of highly excited vibrational states of polyatomic molecules have given evidence to the existence of specific vibrational states – local modes (LMs). An extensive bibliography on this subject can be found in refs. [1–4]. From the classical viewpoint, LMs are vibrations with a highly asymmetrical distribution of the energy between different bond oscillators. LMs are very useful for describing the stretching spectra of molecules containing C–H bonds, such as H_2O, NH_3, CH_4, and many others. Each of these molecules possesses a group of (quasi)degenerate vibrations whose frequencies differ greatly from those of the other molecular vibrations. Such groups of (quasi)degenerate vibrations give rise to vibrational polyads (VPs) in the spectra of the corresponding molecules.

According to the usual normal mode (NM) model these VPs must consist of an equidistant sequence of energy levels. There are many examples where this is the case. But there are also many examples where the structure of the VPs deviates from the predicted one by the NM model and where it is better described by the LM.

A very interesting phenomenon occurs when the structure of the VPs changes qualitatively as the energy increases, e.g., passing from NM to LM type. Such rearrangements of the VPs indicate a drastic change in the intramolecular vibrational dynamics.

The existence of LMs raises many questions. We shall discuss some of them for a system of two coupled nonlinear (quasi)degenerate oscillators. The first question is whether it is possible to rationalize NMs and LMs in a unique fashion [5–10]. To answer this question we shall develop here a very simple approach based on the application of nonlinear mechanics and catastrophe theory analysis to the classical Hamilton function, H_{cl}, corresponding to the effective vibrational Hamiltonian, $H_{\mathrm{eff}}(N)$, which describes the structure of the Nth VP. We shall see that both, NMs and LMs, are characterized by the same kind of localization of the vibrations in the phase space: classical trajectories corresponding to both of them are localized in the vicinity of the isolated stable stationary points of H_{cl}.

This observation will permit us to combine the concepts of NMs and LMs in the frame of a more general concept of a localized vibrational state (LVS). From the classical viewpoint LVSs are vibrational states related to the trajectories localized in the vicinity of the isolated stable stationary points of the corresponding function H_{cl}.

In section 2 we shall give a brief outline of our for-

0301-0104/88/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

malism. In section 3 the physical model studied in this paper is presented. In section 4 an $H_{\mathrm{eff}}(N)$ is constructed for this model and in section 5 the qualitative theory of its spectrum is given. In section 6 this theory is applied to some simple examples. We shall see that besides the usual NMs and LMs, our formalism predicts other types of the LVSs.

The possibility of rearrangements of the VPs with excitation poses another interesting group of questions: how can we rationalize these rearrangements? What are the typical rearrangements for the system studied, and to what extent are they determined by the symmetry of the problem? We shall show that rearrangements of VPs are related to bifurcations in the corresponding classical problem. For the case of two vibrations the problem of classification of the possible VP rearrangements is mathematically equivalent to that for the purely rotational problem. So we shall apply in section 7 the known results about equivariant bifurcations in a rotational problem [11–13] to obtain a complete description of all possible VP rearrangements for any molecular symmetry. An important feature of our qualitative treatment is the study of general phenomena depending on the symmetry properties of the problem considered rather than on the concrete form of the $H_{\mathrm{eff}}(N)$.

2. Outline of the method [14,15]

In this paper we shall discuss the spectrum of two (quasi)degenerate vibrations in a polyatomic molecule under the following assumptions:

(i) The molecule possesses symmetry described by the point group G.

(ii) The vibrational operators a_1, a_2 corresponding to the two vibrations in question form the basis for some reducible or irreducible representation Γ of the group G.

(iii) The frequencies of the two vibrations differ significantly from the frequencies of the other molecular vibrations.

(iv) The interaction between states belonging to different VPs is small compared with the interaction between states within the same VP.

Due to assumptions (iii) and (iv), the spectrum of our two-mode system at low energies consists of weakly coupled VPs. The Nth VP is built from N levels $|n_1 n_2\rangle$ with the same total number of vibrational quanta: $n_1+n_2=N-1$. These assumptions permit us to study the structure of the VPs with the help of the effective Hamiltonians acting only within VPs. The assumption (iv) is crucial for the further analysis. Its exact mathematical formulation is not trivial at all. Here we shall note only that the assumption (iv) is much less restrictive than the assumption that the neighbour VPs do not overlap. For large enough energies assumption (iv) certainly fails.

The method of qualitative analysis of polyadic vibrational spectra implies three main steps. The first one is the construction of the effective Hamiltonian, $H_{\mathrm{eff}}(N)$, describing the structure of the Nth VP. This can be done in different ways. In section 3 we shall use one of them based on the contact transformation method which leads to $H_{\mathrm{eff}}(N)$ in the form of a power series in vibrational operators.

The next step is the transformation of $H_{\mathrm{eff}}(N)$ thus obtained to the form of the effective rotational Hamiltonian which is more suitable for the qualitative analysis. This transformation is easily performed by introducing the Schwinger pseudomomentum operators [16]. The main reason to do this is the existence of a well established qualitative theory of the effective rotational operators [11–13].

The last step consists in the construction of a classical Hamilton function, H_{cl}, corresponding to the H_{eff} obtained at the previous step, and in the analysis of the behaviour of the system of its stationary points with growth of the energy. As we shall demonstrate later, such analysis is a very useful and powerful tool to elucidate the main qualitative features of the VPs.

3. Model system

Our model system consists of two identical coupled oscillators described by a Hamiltonian of the form

$$\begin{aligned} H/\hbar\omega = {} & 0.5(P_1^2+Q_1^2+P_2^2+Q_2^2)+S(Q_1+Q_2) \\ & + AP_1P_2+BQ_1Q_2+C(Q_1^3+Q_2^3) \\ & + DQ_1Q_2(Q_1+Q_2)+E(Q_1^4+Q_2^4) \\ & + FQ_1Q_2(Q_1^2+Q_2^2)+UQ_1^2Q_2^2 \,. \end{aligned} \tag{1}$$

Here Q_k and P_k are dimensionless coordinates and momenta related to the ordinary ones, q_k and p_k, by

$$q_k=(\hbar/m\omega)^{1/2}Q_k\,,$$
$$p_k=(\hbar m\omega)^{1/2}P_k\,,\quad k=1,2\,, \tag{2}$$

where m and ω are the oscillator mass and fundamental frequency. The parameters A–F, S, U are also dimensionless with C–F, S, U being much less than 1 to satisfy assumptions (iii) and (iv).

Such a Hamiltonian can be obtained, e.g., from the usual LM Hamiltonian of Child and Lawton [3] by approximating the Morse potentials in the latter by their quartic expansions and by adding the anharmonic potential couplings. Truncation of the Morse potentials does not change the qualitative features of the problem at hand, whereas the inclusion of additional anharmonic potential couplings can lead to new phenomena not described by the standard LM Hamiltonian.

The Hamiltonian (1) can be viewed as an empirical one or it can be deduced in some way from the full vibrational Hamiltonian. The simplest possibility to accomplish this is to average the full vibrational Hamiltonian with respect to all unrelevant degrees of freedom. If necessary, it is possible in a standard fashion to improve the Hamiltonian thus obtained within perturbation theory or contact transformation approaches.

4. Effective Hamiltonian

A usual way to study VPs is to describe the structure of a given VP by its own effective Hamiltonian, $H_{\rm eff}(N)$. The recipe for obtaining such an $H_{\rm eff}(N)$ is well established. At first we shall rewrite the expression (1) with the help of the vibrational annihilation and creation operators defined by

$$Q_k=(a_k^+ + a_k)/\sqrt{2}\,,$$
$$P_k=\mathrm{i}(a_k^+ - a_k)/\sqrt{2}\,,\quad k=1,2\,. \tag{3}$$

$H_{\rm eff}$ for a VP must satisfy the so-called diagonal condition, that is, it must contain only those terms which prevent interaction between states belonging to different VPs. To transform the Hamiltonian (1) to such a diagonal form we shall use canonical transformation techniques, taking into account only the first nonzero contributions to $H_{\rm eff}$ from the different terms in (1). Thus only the first-order contributions from quartic and quadric terms and the second-order ones from linear and cubic terms shall be taken into account. This approximation is not crucial for the further discussion and is chosen to avoid the unnecessary technical complications.

Our next step is to transform $H_{\rm eff}$, thus obtained, to the form of the effective rotational operator using the Schwinger representation for the pseudomomentum operators

$$J_x=(a_1^+a_2+a_2^+a_1)/2\,,\quad J_y=(a_1^+a_2-a_2^+a_1)/2\mathrm{i}\,,$$
$$J_z=(a_1^+a_1-a_2^+a_2)/2\,,\quad J=(a_1^+a_1+a_2^+a_2)/2\,. \tag{4}$$

We can always do this because of the diagonality condition imposed on $H_{\rm eff}$. Note here that operator J is a constant within the VPs and is related to N by $2J+1=N$.

The above procedure gives us $H_{\rm eff}$ in the form of the effective rotational operator

$$H_{\rm eff}/\hbar\omega=H_0+sJ_x+tJ_x^2+uJ_z^2\,, \tag{5}$$

where

$$s=s_1+s_2(J+\tfrac{1}{2})\,,\quad s_1=A+B+4DS\,,$$
$$s_2=3F-\tfrac{10}{3}D^2-10CD\,,\quad t=U-4D^2+2CD\,,$$
$$u=(6E-U-15C^2-3D^2+14CD)/2\,, \tag{6}$$

and H_0 contains all irrelevant terms which are constant within VPs. A natural generalization of the Hamiltonian (5) in this two-mode case can be obtained by using a more general function of SU(2) group generators. It should be noted that similar algebraic approaches using generators of different continuous groups to construct $H_{\rm eff}$ for VPs became very popular last years [7–10,17–19].

The method described above permits the direct calculation of the parameters of the $H_{\rm eff}$ from the known molecular force field. Another possible way to use $H_{\rm eff}$ in the form (5) is to use it as a purely phenomenological effective Hamiltonian, and to obtain its parameters by fitting experimental data [7,8].

5. Qualitative description of the spectrum

To proceed further we shall build the classical Hamilton function, $H_{\rm cl}$, corresponding to the $H_{\rm eff}$. To do this it is sufficient to replace the quantum operators in (5) by their quasiclassical counterparts according to

$$J_x = L\cos\varphi\sin\theta\,,\quad J_z = L\cos\theta\,,$$
$$L = J + 1/2\,. \tag{7}$$

The length, L, of the classical pseudomomentum vector is related to N by $N=2L$.

We are interested in the isolated stationary points of the function $H_{\rm cl}$. This interest is motivated by the fact that in classical dynamics every stable stationary point (maximum or minimum) of the Hamilton function is surrounded by trajectories localized in the phase space in the vicinity of this stationary point. Under certain conditions, quantum states corresponding to such localized trajectories exist. Further, we shall refer to these quantum states as to localized vibrational states to emphasize their relation to the trajectories localized around the stationary stable points of $H_{\rm cl}$.

Omitting the insignificant term H_0, we can write the expression for $H_{\rm cl}$ in the form

$$H_{\rm cl} = (s_1 + s_2 L) L\cos\varphi\sin\theta$$
$$+\, tL^2\cos^2\varphi\sin^2\theta + uL^2\cos^2\theta\,. \tag{8}$$

In this paper, we shall study only the typical functions $H_{\rm cl}$. This means that no additional a priori restrictions are imposed on the parameters of $H_{\rm cl}$, besides those dictated by the symmetry of the problem. All stationary points and corresponding values of $H_{\rm cl}$ (8) are listed in table 1. We see that $H_{\rm cl}$ always has the nondegenerate stationary points (a) and (b) localized on the x-axis. The behaviour of the stationary points (c) and (d) with increase of L is more complicated. It is shown in table 2.

With increase of excitation (which corresponds to increase of L) the number and the nature of the stationary points of $H_{\rm cl}$ can change as L goes over some special values. This process, called bifurcation, leads to a qualitative change of the VPs structure and is further referred to as the rearrangement of the VPs. To illustrate this statement in section 6 we shall consider several simple examples.

6. Examples

(A) The simplest possible example is the system of two harmonic oscillators coupled by harmonic potential and kinetic terms. This system is equivalent to the system of two uncoupled harmonic oscillators with slightly different frequencies. The VPs contain the equidistant sequences of levels and their structure does not change with the growth of energy. In this case, the only nonzero parameter in (5) is s_1. This implies additional restrictions on the parameters of $H_{\rm eff}$; that is why this case is not directly covered by the analysis of section 5. The analysis along the lines of section 5 is trivial and leads to the conclusion that in this case $H_{\rm cl}$ has no other stationary points besides (a) and (b). These stationary points exist for all values of L, one of them being maximum and the other being minimum of $H_{\rm cl}$. It immediately follows that the bottom and the top of the VPs in this case are built from regular sequences of nondegenerate levels, and this structure does not change with increase of L, in accordance with the exact quantum results.

(B) Now, we shall generalize the previous case by

Table 1
Stationary points, P, and corresponding values of $H_{\rm cl}(\mathrm{P})$ (8). Here: $r_1 = (s_1 + s_2 L)/[2L(u-t)]$, $r_2 = -(s_1 + s_2 L)/2tL$

P	Coordinates of P		$H_{\rm cl}(\mathrm{P})$	Conditions of existence
	φ	θ		
(a)	0	$\pi/2$	$E_{\rm a} = s_1 L + (s_2 + t) L^2$	always
(b)	π	$\pi/2$	$E_{\rm b} = -s_1 L + (t - s_2) L^2$	always
($\mathrm{c}_{1,2}$)	$\pi[1 - \mathrm{sgn}(r_1)]/2$	$\pm\arcsin\lvert r_1\rvert$	$E_{\mathrm{c}_1} = E_{\mathrm{c}_2} = uL^2$ $+\ (s_1 + s_2 L)^2/4(u-t)$	$\lvert r_1\rvert \leqslant 1$
($\mathrm{d}_{1,2}$)	$\pm\arccos\lvert r_2\rvert$	$\pi/2$	$E_{\mathrm{d}_1} = E_{\mathrm{d}_2} = -(s_1 + s_2 L)^2/4t$	$\lvert r_2\rvert \leqslant 1$

Table 2
Domains of existence of the stationary points (c) and (d). Here: $L_1^{\pm}=|s_1/(2|u-t|\pm|s_2|)|$, $L_2^{\pm}=|s_1/(2|t|\pm|s_2|)|$

(c)			(d)		
sign of s_1s_2	sign of $\|s_2\|-2\|u-t\|$	domain	sign of s_1s_2	sign of $\|s_2\|-2\|t\|$	domain
+	+	absent	+	+	absent
+	–	$L \geqslant L_1^-$	+	–	$L \geqslant L_2^-$
–	+	$L_1^+ \leqslant L \leqslant L_1^-$	–	+	$L_2^+ \leqslant L \leqslant L_2^-$
–	–	$L \geqslant L_1^+$	–	–	$L \geqslant L_2^+$

taking into account the anharmonicity of the oscillators. It can be easily done by treating H_{eff} with nonzero parameters A, B, S, C, and E. This case is also degenerate due to the restrictions $s_2=t=0$. Analysis along the lines of section 5 shows that in such a system there always exists one bifurcation point at $L^*=|s_1/2u|$. Before this point, for $L<L^*$, there are two nondegenerate stable stationary points (a) and (b) and the structure of the VPs is the same as in the case (A): level spacings at the top and at the bottom of the VPs follow the NM model. At $L=L^*$ the bifurcation occurs: one of the stable stationary points (a) or (b) depending on the parameters of the problem, splits into two degenerate stable stationary points (c) of the same type as the parent stationary point, and one unstable stationary point. The appearance of two degenerate stable stationary points gives rise to the tendency of forming the regular sequence of quasidegenerate pairs of levels corresponding to the LVSs. The part of the VP formed from such pairs will be better described by the LM model, whereas level spacings at the other side of VP will follow the NM model.

What is the physical nature of the LVSs in this case? If the level spacings of the interacting oscillators decrease with the growth of energy (the usual situation), then the quasidegenerate pairs are formed at the bottom of the VP and are built from the zero-order vibrational states with a highly asymmetric distribution of the energy between the oscillators, that is to usual LMs. Thus, the formalism developed in the previous sections provides us with a very simple and clear classical picture of the formation of the LMs from the NMs with excitation. We see also that the formation of the LMs with excitation is a typical behaviour of the system in question.

In concrete molecules, too large or too small values of L^* can prevent the experimental observation of the rearrangements discussed above. In such cases, one will observe only one type of VPs: NM type if L^* is too large, and LM type if L^* is too small. In general, our analysis clearly shows that different parts of the same VP can be better described within different models.

(C) Now we are going to discuss the most general case when all parameters in (1) are nonzero. The inclusion of the quartic potential terms leads to two new effects: a new type of the LVSs corresponding to the stationary points (d) can arise in the system, and there may appear the LVSs with a finite domain of existence. For the moment it is not clear whether there is any fundamental difference between the LVSs corresponding to the stationary points (c) and (d) or not. The relation between LVSs of these two types and their relation with the ordinary LMs needs further study.

(D) Finally, we shall apply our analysis to model Hamiltonians describing two degenerate vibrations in several simple molecules using parameters given in [8]. Parameters ω, s_1, s_2, t, u of our model Hamiltonian (5) and those, ω_0, α_2, β, ϵ, δ', of the model Hamiltonian (2.37) from ref. [8] are related by

$$\omega=\omega_0\,,\quad s_1=\beta/\hbar\omega_0\,,\quad s_2=\epsilon/\hbar\omega_0\,,\quad t=4\delta'/\hbar\omega_0\,,$$

$$u=(\alpha_2+2\delta')/\hbar\omega_0\,. \tag{9}$$

The results of the model Hamiltonian analysis are listed in table 3.

While applying these results, it is necessary to take into account several points. First of all, one should be careful enough not to use the model H_{eff} beyond their domain of applicability. Secondly, when the bi-

Table 3
Bifurcation analysis of H_{eff} for some small molecules. Parameters for the model Hamiltonian (5) are taken from ref. [8]

Molecule	Domains of existence for the stationary points	
	(c)	(d)
H_2O	$L \geqslant 0.4$	$5.9 \leqslant L \leqslant 36.5$
SO_2	$L \geqslant 6.5$	$L \geqslant 13.7$
O_3	$L \geqslant 0.6$	$L \geqslant 10.8$
C_2H_2	$L \geqslant 0.4$	absent
C_2D_2	$L \geqslant 3.2$	$L \geqslant 22.8$

furcation value of L is large it is necessary to check whether the approximation of weakly interacting VPs is still valid. It should be mentioned also that the predictions of our approach are more accurate for large values of L. For small L our predictions have only qualitative character. Note in addition that for small L the rearrangements of VPs are very smooth functions of L. With this in mind we see that our approach locates the beginning of the VP rearrangements in good agreement with the results of the hindered rotator model [5,6].

From table 3 it follows that for real molecules the first bifurcation points often correspond to very small (H_2O and C_2H_2) or to very large (C_2D_2 and SO_2) values of L. In these cases, as already said, the structure of the VPs does not change with excitation in the experimentally studied domain of energies. More interesting are the cases when the bifurcation point lies within an experimentally studied domain of energies. In such cases it is possible to observe the transition from one type of the VPs to another. The spectrum of the stretching vibrations of the O_3 molecule may serve as one of such examples. In this case smooth formation of the LM polyads from the NM ones is clearly seen beginning from the second VP. The model spectrum of the C–D vibrations in C_2D_2 [8] is much more appropriate for demonstration of the VP rearrangements. In this case the bifurcation point lies high enough to ensure the existence of a large number of the typical NM VPs before bifurcation occurs and comparatively abrupt character of the transition to the LM VPs. Unfortunately, the bifurcation point in C_2D_2 lies in a domain not yet accessible to experiments.

We see that in all the molecules studied here, formation of the LMs is connected with the appearance of the stable stationary points (c). The stationary points (d) also exist for some molecules but they are too high in energy to have any physical significance.

7. Symmetry analysis

In the previous sections we have shown that when the vibrational energy exceeds some critical values the rearrangements of the VPs can occur. The method for locating such critical values of energy was developed and applied to some simple cases. In this section we shall treat the problem of the rearrangements from another point of view. Here we shall answer the two main questions. (i) What kind of rearrangements can occur in the two-mode vibrational problem? (ii) How does the symmetry of the problem manifest itself in these rearrangements?

According to our second assumption the vibrational operators, a_1 and a_2, used to construct H_{eff} have definite symmetry properties. If the two modes in question are NMs, then the vibrational operators will transform according to two one-dimensional or one two-dimensional irreducible representations of the molecular symmetry group G. If they are LMs the situation is a little bit different: a single LM does not possess the pure symmetry, but two of them always form a basis for some reducible or irreducible representation of the group G. This difference is not significant for further discussion. From the symmetry properties of the vibrational operators, it immediately follows that operators, J_α, also span some representation Γ' of the group G.

The essential notion for the further discussion is the notion of the symmetry group G* of the H_{eff}. The group G* depends not only on the molecular group G but also on the symmetry properties of the vibrational operators and is just the image of the group G in representation Γ' generated by the operators, J_α. For a more detailed discussion of the concept of the group image, see refs. [20–23].

We have determined and listed in table 4 all possible groups G* which can arise in the two mode vibrational problem. To do this, we have studied all different abstract groups to which the molecular point groups can be isomorphic. The isomorphism between abstract and point groups can be found, e.g., in

Table 4
Group images for the two-dimensional vibrational problem. Here: LCD is the largest common divisor; all the representations designated by Γ are one-dimensional; $q=\min(2m,\ n-2m)$; $k=\mathrm{LCD}(n, 2m)$; $j=\mathrm{LCD}(n, q)$; $\alpha=\mathrm{u}, \mathrm{g}$

Molecular group G	Symmetry of a_1, a_2 in G	Symmetry of J_α operators in G	Image G* as an abstract group
any finite	$\Gamma\oplus\Gamma$ Γ real	$3A_1$	C_1
any finite	$\Gamma\oplus\Gamma_1$ Γ, Γ_1 real $\Gamma\neq\Gamma_1$	$A_1\oplus 2\Gamma_2$ $\Gamma_2=\Gamma\otimes\Gamma_1$	C_2
C_n $n\geqslant 3$	$\Gamma_m\oplus\Gamma_m^*$ $1\leqslant m<n/2$	$\Gamma_0\oplus\Gamma_q\oplus\Gamma_q^*$	$C_{n/k}$
$C_n\otimes C_2$ $n=2p$, $p\geqslant 2$	$\Gamma_{m\alpha}\oplus\Gamma_{m\alpha}^*$ $1\leqslant m<n/2$	$\Gamma_{0g}\oplus\Gamma_{qg}\oplus\Gamma_{qg}^*$	$C_{n/k}$
D_n $n\geqslant 3$	E_m $m\neq n/4$	$A_2\oplus E_q$	$D_{n/j}$
$D_n\otimes C_2$ $n=2p$, $p\geqslant 2$	$E_{m\alpha}$ $m\neq n/4$	$A_{2g}\oplus E_{qg}$	$D_{n/j}$
D_{4p} $p\geqslant 1$	E_p	$A_2\oplus B_1\oplus B_2$	D_2
$D_{4p}\otimes C_2$ $p\geqslant 1$	$E_{p\alpha}$	$A_{2g}\oplus B_{1g}\oplus B_{2g}$	D_2
T	E	$A\oplus E$	C_3
$T\otimes C_2$	E_α	$A_g\oplus E_g$	C_3
O	E	$A_2\oplus E$	D_3
$O\otimes C_2$	E_α	$A_{2g}\oplus E_g$	D_3
D_∞	E_m	$A_2\oplus E_{2m}$	D_∞
$D_\infty\otimes C_2$	$E_{m\alpha}$	$A_{2g}\oplus E_{2mg}$	D_∞

ref. [24]. We see that in general the symmetry of H_{eff} does not coincide with G. Two vibrations in molecules with different symmetry may be described by H_{eff}'s having the same symmetry, and vice versa, the pairs of vibrations in the molecules with the same symmetry, or even different pairs of vibrations in the same molecule, may need for their description the effective Hamiltonians with different symmetry properties.

In the system described by the H_{eff} of a given symmetry G*, different types of bifurcations can take place. The type of bifurcation depends on the local symmetry group, G_L^*, of the point P in the phase space where this bifurcation occurs. G_L^* is defined as the group containing all elements of the group G* which do not move the point P.

In table 5 we have listed all possible local groups G_L^* which can arise in the two mode vibrational problem. Also, in the same table we have pointed out the numbers $K(G_L^*)$ which are equal to the numbers of points in the orbit of the point P in the group G*. They determine the number of different equivalent ways of localization of vibrations in the phase space and, hence, the (quasi)degeneracy of the vibrational levels in the quantum case. The infinite values of $K(G_L^*)$ in table 5 do not mean the infinite degeneracy of levels. They simply show that the corresponding stationary points are not isolated.

And at last in table 6 we have listed all different bifurcations possible in the two-mode vibrational problem.

To illustrate the use of this table, we shall discuss possible bifurcations for the local symmetry group C_2. In this case bifurcation occurs at the point P of the phase space located on the axis C_2. It leads to a change of the stability of this point which is followed by appearance or disappearance of two stationary points in general position (local group C_1). The stability of these stationary points given by the Hessian sign is opposite to that of the stationary point on the C_2 axis.

In this case there are two essentially different types of bifurcations. Bifurcations of the first type are local. For these bifurcations, the separatrix which divides the trajectories into localized and global ones, is itself localized in the neighbourhood of the stationary point in question. A separatrix for the bifurcations of the second type has a global character. The bifurcations of the second type occur in the full phase space and are called global. For a more detailed dis-

Table 5
Local groups, G_L^*, and corresponding (quasi)degeneracies, $K(G_L^*)$, for all group images G* possible in the two-mode vibrational problem

G*	G_L^*	$K(G_L^*)$	G*	G_L^*	$K(G_L^*)$
C_1	C_1	1	D_n	C_1	2n
C_2	C_1	2		C_2	n
	C_2	1		C_n	2
C_n	C_1	n	D_∞	C_1	∞
	C_n	1		C_2	∞
D_2	C_1	4		C_∞	2
	C_2	2			

Table 6
Possible bifurcations in the two-mode vibrational problem. Here: M – maximum, m – minimum, s – saddle point. In parentheses, the local group of the stationary point is given. All stationary points without parentheses have C_1 as the local group

G^*_L	Bifurcation
C_1	$M+s \Leftrightarrow 0$ $m+s \Leftrightarrow 0$
C_2	$M(C_2) \Leftrightarrow s(C_2)+2M$ $m(C_2) \Leftrightarrow s(C_2)+2m$ $s(C_2) \Leftrightarrow M(C_2)+2s$ $s(C_2) \Leftrightarrow m(C_2)+2s$
C_3	$m(C_3)+3s \Leftrightarrow M(C_3)+3s$
C_4	$m(C_4)+4s \Leftrightarrow M(C_4)+4s$ $M(C_4) \Leftrightarrow m(C_4)+4M+4s$ $m(C_4) \Leftrightarrow M(C_4)+4m+4s$
C_n $n \geqslant 5$	$M(C_n) \Leftrightarrow m(C_n)+nM+ns$ $m(C_n) \Leftrightarrow M(C_n)+nm+ns$
C_∞ [a)]	$M(C_\infty) \Leftrightarrow m(C_\infty)+\infty M+\infty s$ $m(C_\infty) \Leftrightarrow M(C_\infty)+\infty m+\infty s$

[a)] Index ∞ before the symbol of the SP signifies that this SP is not an isolated one.

cussion of this subject see refs. [11–13] where the complete analysis of the equivariant bifurcations for one-parameter family of the Hamiltonians in two-dimensional phase space is realized.

What kind of conclusions can we draw about the structure of the VPs using the formalism of this section? Suppose, e.g., that a local bifurcation

$$m(C_2) \Leftrightarrow s(C_2)+2m \qquad (10)$$

occurs in our system for $L=L^*$. In this case, for $L<L^*$, the VPs have a bounded from below regular sequence of levels with a $K(C_2)$-fold (quasi) degeneracy. For $L>L^*$ this sequence gradually disappears and, instead, there appears a new regular sequence of levels (also bounded from below) with $K(C_1)$-fold (quasi)degeneracy. From table 5 it follows that for all groups G^* $K(C_1)=2K(C_2)$. Thus, this bifurcation doubles the number of different equivalent ways of localization of the vibrations in the phase space.

8. Conclusions

We have studied here the structure and rearrangements with excitation of the two-mode vibrational polyads. A simple approach based on the construction and analysis of the classical Hamilton function corresponding to the effective Hamiltonian for VPs is proposed for this purpose. This approach permits the unified description of the usual NMs and LMs: both of them can be rationalized as examples of the localized vibrational states. From the classical viewpoint these localized vibrational states are related to the trajectories in the phase space which are localized near isolated stationary points of the corresponding Hamilton function. New types of localized vibrational states different from NMs and LMs are predicted in the two-dimensional vibrational problem.

Within our approach the rearrangements of the VPs with excitation are attributed to certain bifurcations in the corresponding classical problem. The possible types of rearrangements are determined by the symmetry properties of the problem in question, that is by the molecular symmetry group and by symmetry properties of the vibrational operators, rather than by the concrete form of the model Hamiltonian. The influence of the symmetry on the rearrangements of the VPs is studied and all different types of bifurcations possible in the two-mode vibrational problem are found.

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. Jaffe and P. Brumer, J. Chem. Phys. 73 (1980) 5646.
[6] E.L. Sibert III, W.P. Reinhardt and J.T. Hynes, J. Chem. Phys. 77 (1982) 3583;
E.L. Sibert III, J.T. Hines and W.P. Reinhardt, J. Chem. Phys. 77 (1982) 3595.
[7] M.E. Kellman, Chem. Phys. Letters 113 (1985) 489.
[8] M.E. Kellman, J. Chem. Phys. 83 (1985) 3843.
[9] R.D. Levine and J.L. Kinsey, J. Phys. Chem. 90 (1986) 3653.
[10] K. Stefanski and E. Pollak, J. Chem. Phys. 87 (1987) 1079.
[11] I.M. Pavlichenkov and B.I. Zhilinskii, Chem. Phys. 100 (1985) 339.
[12] B.I. Zhilinskii and I.M. Pavlichenkov, Zh. Eksp. Teor. Fiz. 92 (1987) 387.
[13] B.I. Zhilinskii and I.M. Pavlichenkov, Dokl. Akad. Nauk SSSR 288 (1986) 355.

[14] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Khim. Fiz. 6 (1987) 1459.

[15] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Opt. i Spektroskopiya 64 (1988) 46.

[16] J. Schwinger, in: Quantum theory of angular momentum, eds. L.C. Biedenharn and H. van Dam (Academic Press, New York, 1965).

[17] C. Patterson, J. Chem. Phys. 83 (1985) 4618.

[18] F. Michelot and J. Moret-Bailly, J. Phys. (Paris) 48 (1987) 51.

[19] M.E. Kellman and E.D. Lynch, J. Chem. Phys. 85 (1986) 7216.

[20] L. Michel, in: Regards sur la physique contemporaire. Actes du Colloque International en l'Honneur d'Antonie Visconti, 5-7 July 1979, Marseille (CNRS, Paris, 1980) p. 157.

[21] J.C. Toledano, L. Michel, P. Toledano and E. Brezin, Phys. Rev. B 31 (1985) 7171.

[22] L. Michel and J. Mozrymas, Lect. Notes Phys. 79 (1977) 447.

[23] M.V. Jaric, L. Michel and R.T. Sharp, J. Phys. (Paris) 45 (1984) 1.

[24] H.S.M. Coxeter and W.O.J. Moser, Generators and relations for discrete groups (Springer, Berlin, 1972).