

Bifurcation in rotational spectra of nonlinear AB₂ molecules

Igor N. Kozin and I. M. Pavlichenkov

Citation: *The Journal of Chemical Physics* **104**, 4105 (1996); doi: 10.1063/1.471223

View online: <http://dx.doi.org/10.1063/1.471223>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/104/11?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Ab initio potential energy surface, infrared spectra, and dynamics of the ion-molecule complexes between Br⁻ and H₂, D₂, and HD](#)

J. Chem. Phys. **125**, 114313 (2006); 10.1063/1.2355494

[Ab initio calculations of nonlinear optical rotation by several small chiral molecules and by uridine stereoisomers](#)

J. Chem. Phys. **124**, 184305 (2006); 10.1063/1.2196880

[Ab initio vibration-rotation-tunneling spectra and dynamics of H₂-F⁻ and its isotopomers](#)

J. Chem. Phys. **102**, 1295 (1995); 10.1063/1.468918

[SU\(2\) quantum group analysis of rotational spectra of diatomic molecules](#)

J. Chem. Phys. **96**, 5614 (1992); 10.1063/1.462709

[Rotational Structure in the Spectra of Diatomic Molecules.](#)

Phys. Today **25**, 54 (1972); 10.1063/1.3071095



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Bifurcation in rotational spectra of nonlinear AB₂ molecules

Igor N. Kozin^{a)}

Institute of Applied Physics, Uljanov Street 46, 603600 Nizhnii Novgorod, Russia

I. M. Pavlichenkov^{b)}

Russian National Center "Kurchatov Institute," 123182 Moscow, Russia

(Received 6 June 1995; accepted 7 December 1995)

A classical microscopic theory of rovibrational motion at high angular momenta in symmetrical nonlinear molecules AB₂ is derived within the framework of small oscillations near the stationary states of a rotating molecule. The full-dimensional analysis including stretching vibrations has confirmed the existence of the bifurcation predicted previously by means of the rigid-bender model [see B. I. Zhilinskii and I. M. Pavlichenkov, *Opt. Spectrosc. (USSR)* **64**, 413 (1988)]. The formation of fourfold energy clusters resulting from the bifurcation has been experimentally verified for H₂Se and it has been demonstrated in fully-dimensional quantum mechanical calculations carried out with the MORBID computer program. We show in the present work that apart from the level clustering, the bifurcation produces physically important effects including molecular symmetry-breaking and a transition from the normal mode to the local mode limit for the stretching vibrations due to the centrifugal forces. The application of the present theory with realistic molecular potentials to the H₂Te, H₂Se, and H₂S hydrides results in predictions of the bifurcation points very close to those calculated previously. However for the lighter H₂O molecule we find that the bifurcation occurs at higher values of the total angular momentum than obtained in previous estimations. The present work shows it to be very unlikely that the bifurcation in H₂O will lead to clustering of energy levels. This result is in agreement with recent variational calculations. © 1996 American Institute of Physics. [S0021-9606(96)04510-0]

I. INTRODUCTION

Energy level clustering in molecules is a very interesting phenomenon, which has been studied for about 20 years.¹⁻⁴ However the main interest was concentrated on highly symmetrical molecules like tetrahydrides. The possibility of fourfold cluster formation in the upper part of rotational multiplets of symmetrical nonlinear triatomic molecules has been predicted in the theoretical work by one of the authors and B. I. Zhilinskii.⁵ In that work the classical rovibrational dynamics of an asymmetric top molecule was investigated in the rigid-bender model.⁶ It has been shown that with the increasing of the angular momentum quantum number J the local precession around the axis with the smallest moment of inertia changes to delocalized precession around two equivalent axes at certain critical value J_c . This phenomenon can be referred to as a bifurcation. It manifests itself in the softening of the precessional mode, i.e., in the decreasing of the spacing between the upper levels of the rotational multiplets when J passes through the critical value J_c . The noticeable softening of the precessional modes in the ground and ν_2 vibrational states of H₂O and H₂S was interpreted as a possible bifurcation in these molecules.^{5,7} More precise numerical calculations based on the quantum Hamiltonian of the rigid-bender model were carried out soon after.^{8,9} They demonstrated the formation of fourfold energy clusters for J greater than J_c . The microscopic theory of bifurcations developed in Ref. 5 allowed the estimation of the critical an-

gular momentum J_c which determines the region of cluster formation. It was found in Refs. 7, 10 that J_c decreases with increasing mass of the central atom X in the H₂X molecule. This fact has been used in the experimental study of "level clustering" in the rotational spectrum of H₂Se.^{11,12} It was established that the energy levels in the vibrational ground state of H₂Se form groups of four quasi-degenerate levels at the top of the J -multiplets when the value of the total angular momentum J exceeds the critical value J_c . This phenomenon is very unusual for the rotational spectrum of a rigid asymmetric top.

Soon afterwards the MORBID program was successfully applied to the cluster analyses of the spectra of H₂Se,^{13,14} H₂S,¹⁵ and H₂Te.¹⁶ The MORBID program is a variational approach allowing the calculation of energy levels of the total rovibrational Hamiltonian of a molecule in an isolated electronic state.¹⁷ MORBID calculations based on fitted or *ab initio* molecular potentials showed good agreement with known experimental data and predicted the formation of fourfold clusters in highly excited rotational states of H₂Se, H₂S, and H₂Te. The MORBID calculations were also in good agreement with pure classical, semiclassical, and model quantum mechanical estimations of the critical angular momentum J_c for these three molecules. However preliminary calculations¹⁸ of the rotational levels up to $J=42$ in the ground vibrational state of the water molecule using the MORBID program with optimized potentials¹⁹ did not show evident fourfold clusters. Recently Polyansky *et al.* have reported a new optimized water potential.²⁰ Their calculations up to $J=35$ for the ground

^{a)}E-mail: nik@appl.sci-nnov.ru

^{b)}E-mail: pavi@kiae.su

vibrational state reproduce very well the available experimental energy levels but the authors concluded that the “rotational energy level structure in water is at least of a very different nature than the fourfold cluster structures observed for H₂Se and calculated for H₂S, H₂Se, and H₂Te.”²⁰ These two facts are in disaccord with all estimations of J_c for the water molecule; $J_c = 27$ – 28 in Ref. 5, $J_c = 26$ in Ref. 8 and with the calculations in Ref. 21, which predict quasidegeneracy of the levels $J_{J,0}$, $J_{J,1}$, $J_{J-1,1}$, and $J_{J-1,2}$ for $J > 32$.

These extensive calculations show that the role of stretching vibrations in the bifurcation phenomenon is not yet clear enough. The rigid-bender model used in the early microscopic theory⁵ assumes the bond lengths to be fixed at their equilibrium values. This theory cannot also answer the question if a bifurcation exists in the rotational bands of excited vibrational states. This deficiency is remedied in the present paper, which uses the fully-dimensional description of rovibrational motion in a triatomic molecule, the stretching vibrations being included. The analysis of the classical equations of motion is based on the study of small harmonic oscillations near stationary states of the system. Four-dimensional oscillations can be separated into *slow* precessional and *fast* vibrational motion. The approach of the present work differs from the standard adiabatic approximation by Born and Oppenheimer in that it considers the rovibrational motion to take place near the stationary states of a rapidly uniformly rotating molecule instead of having them take place near the equilibrium state of a nonrotating molecule. The difference has very important consequences because of the centrifugal distortion forces. First, the precessional motion of an AB₂ molecule around the axis with minimal moment of inertia becomes unstable at the bifurcation point J_c . For higher angular momenta, the fast uniform rotation of a molecule takes place around two axes situated in the molecular plane between the axes of maximal and intermediate moments of inertia. Owing to molecular symmetry, these two axes are equivalent. The delocalized precession around them may result in fourfold level clustering. This effect is the spectroscopic manifestation of the bifurcation. Another consequence is the asymmetrical deformation of the AB₂ molecule by centrifugal forces, whose anisotropic action on the B-atoms causes one A–B bond length to be longer than the other. This symmetry breaking of the molecular configuration in its turn changes the vibrational dynamics in such a way that the normal stretching modes ν_1 and ν_3 transform to the local vibrations of either of two A–B bonds. It is important to note that the transition from normal mode to local mode vibrations is caused in our case by rovibrational interaction and not by the anharmonicity of the vibrations as in customary local mode theory (see, for example, the review article, Ref. 22). The developed theory allows us to understand the relationship of local mode vibrations to a cluster formation in rotational spectra obtained by a model consideration in Ref. 23.

The classical method developed here has been applied to the hydrides H₂O, H₂S, H₂Se, and H₂Te to demonstrate that it produces consistency with purely quantum mechanical calculations for quantities like the critical angular momentum,

the bond length distortions, and the bending angle of the rotating molecule. The results obtained for the H₂Te, H₂Se, H₂S molecules are very close to those obtained previously, but for the lighter H₂O molecule the bifurcation is found to occur at J values significantly higher than those obtained in previous estimations. The most probable explanation of this is the neglect of the stretching vibrations in the earlier models. Furthermore, our analysis shows also that the stretching vibrations result in drastic reduction of the potential barrier, which separates the two regions of a delocalized precession. Thus it is very unlikely that the bifurcation in the vibrational ground state of H₂O can result in an observable fourfold cluster structure. The clustering of levels cannot therefore be the ultimate criteria of the bifurcation.

II. CLASSICAL EQUATIONS OF ROVIBRATIONAL MOTION FOR THE AB₂ MOLECULE

We begin with the classical rovibrational Hamiltonian which can be derived following the method of Wilson, Decius, and Cross.²⁴ Our treatment differs from theirs in that we do not use normal coordinates to have the possibility of considering the large displacements from the equilibrium configuration. With the standard choice of Euler angles²⁴ as rotational coordinates, the classical kinetic rovibrational energy in a rotating coordinate system with the origin in the center of mass of molecule has the form

$$T = \frac{1}{2} \sum_{ij} \omega_i I_{ij} \omega_j + \sum_i \omega_i g_i + \frac{1}{2} \sum_{\alpha i} m_{\alpha} v_{\alpha i}^2, \quad (1)$$

where the indices i and j run through the axes x , y , and z of this coordinate system, $\mathbf{r}_{\alpha}(x_{\alpha}, y_{\alpha}, z_{\alpha})$ is the position vector of nucleus α with mass m_{α} , \mathbf{v}_{α} is its velocity, and $\mathbf{g} = \sum_{\alpha} m_{\alpha} (\mathbf{r}_{\alpha} \times \mathbf{v}_{\alpha})$. I_{ij} is a matrix element of the inertia tensor, and ω_i are the projections of an angular velocity on the axes x , y , and z ,

$$\begin{aligned} \omega_x &= \dot{\theta} \sin \chi - \dot{\phi} \sin \theta \cos \chi, \\ \omega_y &= \dot{\theta} \cos \chi + \dot{\phi} \sin \theta \sin \chi, \\ \omega_z &= \dot{\phi} \cos \theta + \dot{\chi}. \end{aligned} \quad (2)$$

We consider a triatomic molecule B₁A₂B₃ with nuclear masses $m_1 = m_3 = m$ and $m_2 = M$. To define the rotating (molecule fixed) axis system we can use one of the methods suggested by Sutcliffe and Tennyson.²⁵ Let the molecule be placed in the (xz) plane, i.e., $y_i = 0$. Then we define the x -axis to be parallel to the bisector of the bond angle $\alpha = \angle B_1 A_2 B_3$. The axis directions are chosen so that z -axis points from B₃ to B₁, x -axis points from the center of mass to A₂ and the coordinate system is right-handed. It is natural to introduce three internal coordinates; the A₂–B₁ distance $r_1 \equiv q_1$, the angle $\alpha \equiv q_2$, and the A₂–B₃ distance $r_3 \equiv q_3$. These internal coordinates are connected with the Cartesian coordinates x_i and z_i as follows:

$$\begin{aligned}
x_1 &= \frac{mr_3 - (M+m)r_1}{M+2m} \cos \frac{\alpha}{2}, \\
x_2 &= \frac{m(r_1 + r_3)}{M+2m} \cos \frac{\alpha}{2}, \\
x_3 &= \frac{mr_1 - (M+m)r_3}{M+2m} \cos \frac{\alpha}{2}, \\
z_1 &= \frac{(M+m)r_1 + mr_3}{M+2m} \sin \frac{\alpha}{2}, \\
z_2 &= -\frac{m(r_1 - r_3)}{M+2m} \sin \frac{\alpha}{2}, \\
z_3 &= -\frac{mr_1 + (M+m)r_3}{M+2m} \sin \frac{\alpha}{2}.
\end{aligned} \tag{3}$$

With a molecule-fixed axis system defined in this way, the nonzero components of the inertia-tensor can be written as

$$\begin{aligned}
I_{xz} &= \frac{m(M+m)}{2(M+2m)} (r_1^2 - r_3^2) \sin \alpha, \\
I_{xx} &= \frac{m}{M+2m} [M(r_1^2 + r_3^2) + m(r_1 + r_3)^2] \sin^2 \frac{\alpha}{2}, \\
I_{zz} &= \frac{m}{M+2m} [M(r_1^2 + r_3^2) + m(r_1 - r_3)^2] \cos^2 \frac{\alpha}{2}, \\
I_{yy} &= \frac{m(M+m)}{M+2m} (r_1^2 + r_3^2) - \frac{2m^2}{M+2m} r_1 r_3 \cos \alpha,
\end{aligned} \tag{4}$$

and the components $g_i = \sum_\nu G_{i\nu} \dot{q}_\nu$, where due to a planar molecule only three $G_{y\nu}$ are nonzero,

$$\begin{aligned}
G_{y1} &= \frac{m^2}{2m+M} r_3 \sin \alpha, \\
G_{y2} &= \frac{m(m+M)}{2(2m+M)} (r_1^2 - r_3^2), \\
G_{y3} &= \frac{m^2}{2m+M} r_1 \sin \alpha.
\end{aligned} \tag{5}$$

With the introduced internal coordinates the kinetic energy (1) can be transformed to the form

$$T = \frac{1}{2} \sum_{ij} \omega_i I_{ij} \omega_j + \sum_{i\nu} \omega_i G_{i\nu} \dot{q}_\nu + \frac{1}{2} \sum_{\nu\nu'} \dot{q}_\nu a_{\nu\nu'} \dot{q}_{\nu'}, \tag{6}$$

where i and j again assume the values x, y, z , and ν and ν' run through 1, 2, 3, and the matrix elements $a_{\nu\nu'}$ depend on internal coordinates as follows:

$$\begin{aligned}
a_{11} &= a_{33} = \frac{m(M+m)}{M+2m}, \\
a_{22} &= \frac{m}{4(M+2m)} [(M+m)(r_1^2 + r_3^2) + 2mr_1 r_3 \cos \alpha],
\end{aligned}$$

$$a_{12} = a_{21} = \frac{m^2}{2(M+2m)} r_3 \sin \alpha, \tag{7}$$

$$a_{23} = a_{32} = \frac{m^2}{2(M+2m)} r_1 \sin \alpha,$$

$$a_{13} = a_{31} = -\frac{m^2}{M+2m} \cos \alpha.$$

It follows from Eq. (6) the impulse conjugated to q_ν is

$$p_\nu = \partial T / \partial \dot{q}_\nu = \sum_\nu a_{\nu\nu'} \dot{q}_{\nu'} + \omega_y G_{y\nu}. \tag{8}$$

Thus generally $p_\nu \neq 0$, when $\dot{q}_\nu = 0$, according to analogy between the Coriolis force [the middle term in Eq. (6)] and magnetic field. We introduce further the total angular momentum $\mathbf{J} = \sum_\alpha m_\alpha (\mathbf{r}_\alpha \times \dot{\mathbf{r}}_\alpha)$ with projections

$$\begin{aligned}
J_x &= p_\theta \sin \chi - p_\varphi \csc \theta \cos \chi + p_\chi \cot \theta \cos \chi, \\
J_y &= p_\theta \cos \chi + p_\varphi \csc \theta \sin \chi - p_\chi \cot \theta \sin \chi, \\
J_z &= p_\chi,
\end{aligned} \tag{9}$$

which are related to the angular velocity projections as follows:²⁴

$$J_i = \sum_j I_{ij} \omega_j + g_i. \tag{10}$$

The inversion of Eq. (10) leads to

$$\omega_j = \sum_i \tilde{\mu}_{ji} (J_i - g_i), \tag{11}$$

where $\{\tilde{\mu}_{ij}\}$ is the matrix inverse to $\{I_{ij}\}$ with the elements

$$\begin{aligned}
\tilde{\mu}_{xy} &= \tilde{\mu}_{yz} = 0, \\
\tilde{\mu}_{yy} &= 1/I_{yy}, \\
\tilde{\mu}_{xx} &= I_{zz} / (I_{zz} I_{xx} - I_{xz}^2), \\
\tilde{\mu}_{xz} &= I_{xz} / (I_{xz}^2 - I_{zz} I_{xx}), \\
\tilde{\mu}_{zz} &= I_{xx} / (I_{zz} I_{xx} - I_{xz}^2).
\end{aligned} \tag{12}$$

To obtain the Hamiltonian kinetic energy it is necessary to find from Eqs. (8) and (11) \dot{q}_ν as the function of p_ν and J_i and rewrite Eq. (6) in terms of J_i and p_ν . The result is

$$T = \frac{1}{2} \sum_{ij} J_i \mu_{ij} J_j - J_y \sum_\nu u_{y\nu} p_\nu + \frac{1}{2} \sum_{\nu\nu'} p_\nu b_{\nu\nu'} p_{\nu'}, \tag{13}$$

where $\{b_{\nu\nu'}\} = \{c_{\nu\nu'}\}^{-1}$ with $c_{\nu\nu'} = a_{\nu\nu'} - G_{y\nu} \tilde{\mu}_{yy} G_{y\nu'}$, assuming $\text{Det}\{c_{\nu\nu'}\} \neq 0$, $u_{y\nu} = \tilde{\mu}_{yy} \sum_{\nu'} G_{y\nu'} b_{\nu'\nu}$, and μ_{ij} is equal to $\tilde{\mu}_{ij}$ except $\mu_{yy} = \tilde{\mu}_{yy} (1 + \sum_\nu G_{y\nu} u_{y\nu})$. Thus μ_{ij} is the modified by the Coriolis force tensor, reciprocal to the instantaneous moment of inertia I_{ij} . The elements of $b_{\nu\nu'}$ matrix are identical to those given in Ref. 24,

$$\begin{aligned}
b_{11} &= b_{33} = \frac{1}{m} + \frac{1}{M}, \\
b_{22} &= \left(\frac{1}{m} + \frac{1}{M} \right) \left(\frac{1}{r_1^2} + \frac{1}{r_3^2} \right) - \frac{2 \cos \alpha}{M r_1 r_3}, \\
b_{12} &= b_{21} = -\frac{\sin \alpha}{M r_3}, \\
b_{23} &= b_{32} = -\frac{\sin \alpha}{M r_1}, \\
b_{13} &= b_{31} = \frac{\cos \alpha}{M}.
\end{aligned} \quad (14)$$

Finally the rovibrational Hamiltonian of the symmetrical AB₂ molecule is expressed by

$$\begin{aligned}
H &= \frac{1}{2} \sum_{ij} J_i \mu_{ij} J_j - J_y \sum_{\nu} u_{y\nu} p_{\nu} + \frac{1}{2} \sum_{\nu\nu'} p_{\nu} b_{\nu\nu'} p_{\nu'} \\
&+ V(r_1, \alpha, r_3),
\end{aligned} \quad (15)$$

where the second term is the Coriolis interaction and V is the nuclear potential, which is symmetrical with respect to permutations of identical nuclei. The obtained Hamiltonian allows to write Hamilton's equations of motion,

$$\dot{q}_{\nu} = \sum_{\nu'} b_{\nu\nu'} p_{\nu'} - J_y u_{y\nu}, \quad (16)$$

$$\begin{aligned}
\dot{p}_{\nu} &= -\frac{1}{2} \sum_{ij} J_i \frac{\partial \mu_{ij}}{\partial q_{\nu}} J_j + J_y \sum_{\nu'} \frac{\partial u_{y\nu'}}{\partial q_{\nu}} p_{\nu'} \\
&- \frac{1}{2} \sum_{\nu''} p_{\nu''} \frac{\partial b_{\nu\nu''}}{\partial q_{\nu}} p_{\nu''} - \frac{\partial V}{\partial q_{\nu}},
\end{aligned} \quad (17)$$

$$\dot{J}_i = \sum_{jkl} e_{ijk} J_j \mu_{kl} J_l + \sum_{kv} e_{iyk} u_{yv} J_k p_v. \quad (18)$$

Equation (18) is derived by using the Poisson bracket $\{J_i, J_j\} = e_{ijk} J_k$, where e is asymmetrical tensor. It is equivalent to the three equations,

$$\dot{J}_x = [\mu_{xz} J_x + (\mu_{zz} - \mu_{yy}) J_z] J_y + J_z \sum_{\nu} u_{y\nu} p_{\nu}, \quad (19)$$

$$\dot{J}_y = (\mu_{xx} - \mu_{zz}) J_x J_z + \mu_{xz} (J_z^2 - J_x^2), \quad (20)$$

$$\dot{J}_z = [-\mu_{xz} J_z + (\mu_{yy} - \mu_{xx}) J_x] J_y - J_x \sum_{\nu} u_{y\nu} p_{\nu}. \quad (21)$$

They are not independent since \mathbf{J}^2 is an integral of motion.

III. PRECESSIONAL AND VIBRATIONAL MOTIONS OF THE ROTATING AB₂ MOLECULE

Our analysis of the equations of motion is based on the study of rotation-vibrational motion near stationary states. In a stationary state, the time derivatives given in the left-hand sides of Eqs. (16)–(18) are equal to zero. Let us begin with Eqs. (19)–(21), which together with the conservation law for \mathbf{J}^2 define the axis of uniform rotation of the molecule, i.e.,

the total angular momentum vector \mathbf{J}_s in the molecular frame. Three projections of this vector are determined by four algebraic equations. Therefore, in a stationary state \mathbf{J}_s cannot have an arbitrary direction. There are two types of stationary states. In three *axial* stationary states $S_i: J_{si} = \pm J$, $i = x, y, z$, the molecule rotates uniformly around the i -axis. The molecular equilibrium configuration in the state S_i is defined by the three equations

$$\frac{1}{2} \frac{\partial \tilde{\mu}_{ii}}{\partial q_{\nu}} J^2 + \frac{\partial V}{\partial q_{\nu}} = 0 \quad (22)$$

with $\nu = 1, 2, 3$. The molecule has a symmetrical configuration with $r_{s1} = r_{s3} = r_s$ and α_s in an axial stationary state S_i . The energy of this state is

$$E_i = \frac{1}{2} \tilde{\mu}_{ii}(r_s, \alpha_s, r_s) J^2 + V(r_s, \alpha_s, r_s). \quad (23)$$

There is only one *plane* stationary state S_{xz} . In this state, the molecule rotates uniformly around one of two equivalent axes situated in the (xz) plane symmetrically relative to the x -axis. They form angles β_s and $(\pi - \beta_s)$ with the z -axis. The configuration of the molecule and the value of β_s are defined by the equations

$$\begin{aligned}
\frac{1}{2} \left(\frac{\partial \mu_{xx}}{\partial q_{\nu}} \sin^2 \beta_s + \frac{\partial \mu_{xz}}{\partial q_{\nu}} \sin 2\beta_s + \frac{\partial \mu_{zz}}{\partial q_{\nu}} \cos^2 \beta_s \right) J^2 + \frac{\partial V}{\partial q_{\nu}} \\
= 0, \quad \nu = 1, 2, 3,
\end{aligned} \quad (24)$$

$$\frac{1}{2} (\mu_{xx} - \mu_{zz}) \sin 2\beta_s + \mu_{xz} \cos 2\beta_s = 0. \quad (25)$$

It is interesting that in the state S_{xz} , the molecule has an asymmetric configuration with $r_{s1} \neq r_{s3}$. Of the two bond lengths, the one which initially forms the largest angle with the rotation axis will experience a larger elongation due to centrifugal distortion forces, and for increasing J this bond length will tend to become perpendicular to the rotation axis. The energy of the molecule in the S_{xz} state is equal to

$$\begin{aligned}
E_{xz} &= \frac{1}{2} J^2 (\mu_{xx} \sin^2 \beta_s + \mu_{xz} \sin 2\beta_s + \mu_{zz} \cos^2 \beta_s) \\
&+ V(r_{s1}, \alpha_s, r_{s3}).
\end{aligned} \quad (26)$$

Thus we see that the equilibrium configuration of a rotating molecule in a stationary state, i.e., the values of r_{s1} , α_s , and r_{s3} , is determined by the effective potential V_{eff} ,

$$V_{\text{eff}} = \frac{1}{2} \sum_{ij} J_i \tilde{\mu}_{ij} J_j + V, \quad (27)$$

as follows:

$$\frac{\partial V_{\text{eff}}}{\partial q_{\nu}} = 0, \quad \nu = 1, 2, 3. \quad (28)$$

The effective potential includes the centrifugal energy, which plays a central role in the dynamics of a rotating molecule. In particular, the configuration of a rotating molecule in a stationary state is different from that of nonrotating one. We will distinguish the corresponding values by indices s (for the stationary state) and e (for the nonrotating molecule in its equilibrium configuration), respectively. Although the func-

TABLE I. Action of $C_{2v}(M)$ group operators on the internal coordinates and the projections of the total angular momentum \mathbf{J} .

	E	$P(13)$	E^*	$P(13)E^*$
r_1	r_1	r_3	r_1	r_3
r_3	r_3	r_1	r_3	r_1
α	α	α	α	α
J_x	J_x	J_x	$-J_x$	$-J_x$
J_y	J_y	$-J_y$	J_y	$-J_y$
J_z	J_z	$-J_z$	$-J_z$	J_z

tion μ_{xz} is asymmetrical under the permutation of the coordinates r_1 and r_3 [see Eq. (4)], the effective potential [Eq. (27)], the total Hamiltonian [Eq. (15)], and the corresponding equations of motion are invariant under the operations of the $C_{2v}(M)$ permutation-inversion group of the AB₂ molecule²⁶ (see also Ref. 27). This group includes identity operator E , the $P(13)$ permutation operator of identical nuclei, the operator of inversion E^* and the product $P(13)E^*$ (see Table I). For example, when we have obtained one solution of Eqs. (24)–(25), the remaining three solutions can be easily obtained by using symmetry operations of the $C_{2v}(M)$ group. Because of a planar molecule the Coriolis force affects only the stationary state S_y resulting in the nonzero impulse

$$p_\nu = J \sum_{\nu'} c_{\nu\nu'} u_{\nu\nu'} . \quad (29)$$

The analysis of stationary states shows that an axial state has higher symmetry in the $C_{2v}(M)$ group than the plane state. This means that transitions from axial to plane state or vice versa are accompanied by a C_{2v} -type bifurcation.¹⁰ Such a bifurcation has been considered for the first time in rotational spectra of symmetrical triatomic molecules in Ref. 5. However, with the rigid-bender model with fixed bond lengths used in that work, it was not possible to show that the bifurcation results not only in the splitting of the stationary axis and consequently in level clustering but also in molecular symmetry-breaking. Due to this latter effect, the vibrational dynamics of the rotating molecule changes as we shall see below. Table II shows the centrifugal distortions $\Delta r_\nu = r_{s\nu} - r_e$ of the bond length from its equilibrium value r_e in the stationary state S_{xz} . The values were obtained numerically for the molecules H₂Se and H₂S by using the po-

TABLE II. Comparison of the molecular centrifugal distortions $\Delta r_\nu = r_{s\nu} - r_e$ for the stationary state S_{xz} at $J=20$ calculated in quantum and classical methods. The classical calculations correspond to molecular rotation around the stationary axis which is approximately perpendicular to the bond r_1 . Indexes s and e stand for the molecular equilibrium configurations of rotating and nonrotating molecule correspondingly.

Molecule	Quantum estimation		Classical estimation	
	$\Delta r_1/\text{\AA}$	$\Delta r_3/\text{\AA}$	$\Delta r_1/\text{\AA}$	$\Delta r_3/\text{\AA}$
H ₂ Se	0.023 ^a	0.004 ^a	0.025	0.002
H ₂ S	0.024 ^b	0.009 ^b	0.022	0.010

^aTaken from Ref. 14.

^bTaken from Ref. 15.

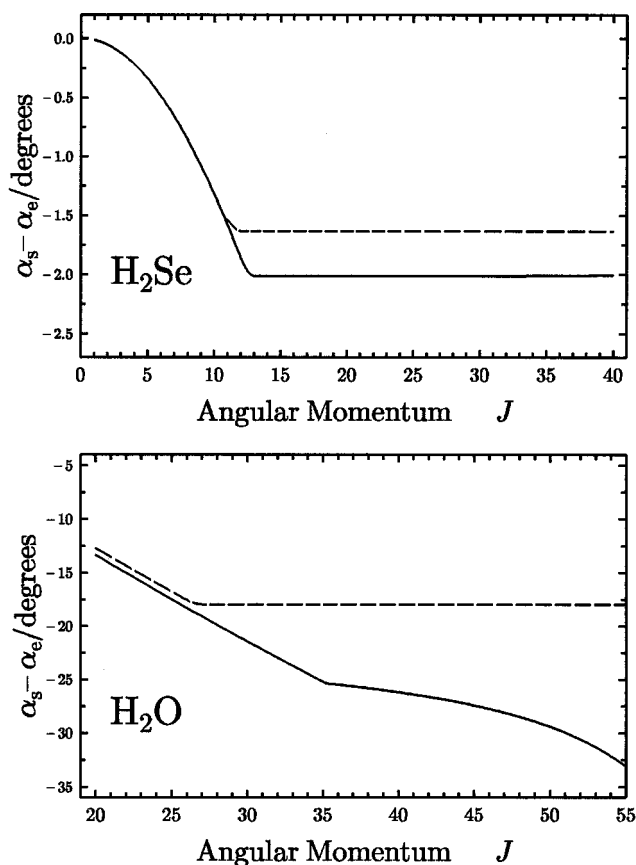


FIG. 1. J -dependence of the bending angle in the stationary states with maximal rotational energy (S_z if $J < J_c$ and S_{xz} if $J > J_c$) for the H₂Se and H₂O molecules. The angle is displayed relative to the equilibrium value α_e for the nonrotating molecule. The solid lines correspond to the stretching-bender model with the critical angular momentum $J_c = 12.5$ (H₂Se) and 35.2 (H₂O); the dashed lines represent the rigid-bender model ($J_c = 11.4$ for the H₂Se and 26.5 for the H₂O molecules).

tentials from Refs. 13 and 15, respectively. For comparison, the Δr_ν values obtained for the quantum cluster states in the upper part of the J -multiplets belonging to the ground vibrational state of these molecules are given in the same table. It is seen from Table II that classical and quantum estimates are in a good agreement.

Since the derivative $(\partial\mu_{zz}/\partial\alpha)$ is positive in the stationary state S_z , the bending angle α_s decreases with increasing J according to Eq. (22). After a bifurcation point, the angle α_s is stabilized at a constant value in the stationary state S_{xz} . In the rigid-bender model this angle is independent of J for $J > J_c$ (Refs. 5, 7) (see Fig. 1). For H₂Se, the rigid-bender and stretching-bender models give comparable results, but for H₂O the predictions of the stretching-bender model deviate significantly from those of the rigid-bender (Fig. 1). In the stretching-bender model, the bending angle value for H₂O continues to decrease significantly when J is above the critical value. Hence no stabilization at a constant value takes place. This effect can be explained as a competition between centrifugal force causing the hydrogen nuclei to bring together and their mutual repulsion.

In order to follow the change of molecular rotational

regimes as J increases, we must investigate the stability of the stationary states. To do this we consider the linearized set of Eqs. (16)–(18) for small displacements of the internal coordinates $Q_v = q_v - q_{sv}$ and the angular momentum projections $J'_i = J_i - J_{si}$ from their stationary values. Let us begin with the axial stationary state S_y . This is the only state where $p_{sv} \neq 0$. The linearized equations have the form

$$\begin{aligned} \ddot{Q}_v + J \sum_{v''} b_{vv''} \left[\frac{\partial(\tilde{\mu}_{yy} G_{yv''})}{\partial q_{v'}} - \frac{\partial(\tilde{\mu}_{yy} G_{yv'})}{\partial q_{v''}} \right] \dot{Q}_{v'} \\ + \sum_{v''} b_{vv''} \frac{\partial^2 V_{\text{eff}}}{\partial q_{v''} \partial q_{v'}} Q_{v'} = 0, \\ \ddot{J}_x + J^2 (\mu_{xx} - \tilde{\mu}_{yy})(\mu_{zz} - \tilde{\mu}_{yy}) J_x = 0. \end{aligned} \quad (30)$$

The coefficients of these equations are assumed to be taken in the stationary state, i.e., for $q_v = q_{sv}$ [see Eqs. (22)]. Note also that $J'_x = J_x$ because of $J_{sx} = 0$ in the considered stationary state. Equations (30) describe two independent harmonic motions, vibrational and precessional. The latter motion is characterized by the precession frequency

$$\Omega_y = J[(\mu_{xx} - \tilde{\mu}_{yy})(\mu_{zz} - \tilde{\mu}_{yy})]^{1/2}, \quad (31)$$

which has the same form as for a rigid top.²⁸ Obviously the precession is stable since μ_{zz} and μ_{xx} are greater than $\tilde{\mu}_{yy}$. The vibrational motion in the state S_y differs from that of the nonrotating molecule because the Coriolis force mixes together the asymmetric mode ν_3 with modes ν_1 and ν_2 . Besides the frequencies ω_1 , ω_2 , and ω_3 of the three new normal modes are determined by the effective potential and the equilibrium configuration of the rotating molecule. As a result they are shifted relative to those of the nonrotating molecule.

The linearized equations for the stationary state S_z ,

$$\begin{aligned} \ddot{Q}_v + \sum_{v'} \left[\sum_{v''} b_{vv''} \frac{\partial^2 V_{\text{eff}}}{\partial q_{v''} \partial q_{v'}} + J^2 u_{yv} \frac{\partial \mu_{xz}}{\partial q_{v'}} \right] Q_{v'} \\ + J \left[\sum_{v'} b_{vv'} \frac{\partial \mu_{xz}}{\partial q_{v'}} - u_{yv} (\mu_{zz} - \mu_{xx}) \right] J_x = 0, \\ \ddot{J}_x + J^2 \left[(\mu_{zz} - \mu_{yy})(\mu_{zz} - \mu_{xx}) + \sum_v u_{yv} \frac{\partial \mu_{xz}}{\partial q_v} \right] J_x \\ + J \sum_{vv'} \left[u_{yv'} \frac{\partial^2 V_{\text{eff}}}{\partial q_{v'} \partial q_v} - J^2 (\mu_{zz} - \mu_{yy}) \delta_{vv'} \frac{\partial \mu_{xz}}{\partial q_v} \right] Q_v = 0, \end{aligned} \quad (32)$$

describe coupled vibrational and precessional motions. It is not difficult to see that the coupling originates in the asymmetric variable $Q_a = (Q_1 - Q_3)/\sqrt{2}$. Thus Eqs. (32) split into two independent parts for the variables Q_a , J_x , and $Q_s = (Q_1 + Q_3)/\sqrt{2}$, Q_2 . The equations for Q_s and Q_2 are independent of the precessional motion and describe the ν_1 and ν_2 vibrational modes modified by the Coriolis and centrifugal forces. We can separate the precessional motion from the asymmetric vibration by using the inequality $\omega_3 \gg \Omega_z$ (adiabatic approximation), which is correct up to the critical point J_c (see below). In this approximation, the frequency of molecular precession around the z -axis is equal to

$$\Omega_z = J \left\{ (\mu_{zz} - \tilde{\mu}_{yy}) \left[\mu_{zz} - \mu_{xx} + J^2 \left(\frac{\partial \mu_{xz}}{\partial r_a} \right)^2 \right] / \frac{\partial^2 V_{\text{eff}}}{\partial r_a^2} \right\}^{1/2}, \quad (33)$$

where according to Eqs. (4) and (12),

$$\mu_{zz} - \mu_{xx} = \frac{2(M+m)}{mMr_s^2 \sin \alpha_s} \left(\frac{m}{M+m} - \cos \alpha_s \right). \quad (34)$$

For the hydrides considered, the equilibrium angle α_e is larger than 90° . So the precession frequency of Eq. (33) is real and the stationary state S_z is stable for small values of J . As we saw above, the stationary angle α_s decreases with increasing J due to a centrifugal distortion. So μ_{zz} approaches μ_{xx} and the precession frequency Ω_z vanishes when

$$\mu_{zz} - \mu_{xx} + J_c^2 \left(\frac{\partial \mu_{xz}}{\partial r_a} \right)^2 / \frac{\partial^2 V_{\text{eff}}}{\partial r_a^2} = 0. \quad (35)$$

Equations (35) and (22) (for $i = z$) define the critical angular momentum J_c . In the rigid-bender model, this point is determined by the bending angle,⁵

$$\alpha_c = \arccos \left(\frac{m}{M+m} \right), \quad (36)$$

for which $I_{xx} = I_{zz}$. The last nonadiabatic term in Eq. (35) takes into account the nonrigidity of the bond lengths r_1 and r_3 and becomes important when $\mu_{zz} - \mu_{xx}$ is close to zero. Since the correction term is positive, Eq. (35) gives higher values of J_c than the rigid-bender model. The term results from the centrifugal force only. Other nonadiabatic terms due to the Coriolis and centrifugal forces are contained in the expression $1 + a_1(\Omega_z/\omega_3)^2 + a_2(\Omega_z/\omega_3)^4 + \dots$, which appears as a multiplier in the right-hand side of Eq. (33). This multiplier does not change the value of J_c . Clearly, the more rigid the asymmetric stretching mode ν_3 , the closer is J_c to the value obtained in Ref. 7 in the rigid-bender approximation. Our numerical calculations of critical angular momentum for the set of the H₂X hydrides with the potentials from Refs. 13, 15, 16 give mainly slight corrections to the J_c values predicted previously. We obtained $J_c = 9.3$ for H₂Te, $J_c = 12.5$ for H₂Se, and $J_c = 18.9$ for H₂S compared to rigid-bender J_c values of 8.5, 11.4, and 16.9, respectively. It is seen that for lighter molecules, larger discrepancies are obtained. The water molecule shows the largest discrepancy of the J_c value. Using the potential from Ref. 19, $J_c = 26.5$ was obtained with the “frozen” bond lengths (which is close to all previous estimations) and $J_c = 35.2$ in the stretching-bender model.

For $J > J_c$, the stationary state S_z corresponds to an unstable saddle-type point. It is the top of a separation barrier between two symmetrical states S_{xz} which appears because of the bifurcation. The equations of a small amplitude motion near this state have the form

$$\ddot{Q}_v + \sum_{v'} \left[\sum_{v''} b_{vv''} \frac{\partial^2 V_{\text{eff}}}{\partial q_{v''} \partial q_{v'}} + J^2 u_{yv} B_{v'} \right] Q_{v'} + \frac{J}{\cos \beta_s} \left[\sum_{v'} b_{vv'} B_{v'} - \frac{u_{yv} (\mu_{zz} - \mu_{xx})}{\cos 2\beta_s} \right] J'_x = 0, \quad (37)$$

$$\begin{aligned} \ddot{J}'_x + J^2 \left[(\mu_{zz} - \mu_{yy} + \mu_{xz} \tan \beta_s) \frac{\mu_{zz} - \mu_{xx}}{\cos 2\beta_s} + \sum_v u_{yv} B_v \right] J'_x \\ - J \cos \beta_s \sum_v \left[J^2 B_v (\mu_{zz} - \mu_{yy} + \mu_{xz} \tan \beta_s) \right. \\ \left. - \sum_{v'} u_{yv'} \frac{\partial^2 V_{\text{eff}}}{\partial q_{v'} \partial q_v} \right] Q_v = 0, \end{aligned}$$

where the “coupling constant”

$$B_v = \frac{1}{2} \frac{\partial (\mu_{xx} - \mu_{zz})}{\partial q_v} \sin 2\beta_s + \frac{\partial \mu_{xz}}{\partial q_v} \cos 2\beta_s, \quad (38)$$

mixes all four motions; three vibrations and a precession. The last one can be decoupled from the vibrations in the adiabatic approximation for moderate values of J . In this approximation, the frequency of the precession around the S_{xz} state is

$$\Omega_{xz} = J \left\{ (\mu_{zz} - \tilde{\mu}_{yy} + \mu_{xz} \tan \beta_s) \left[\frac{\mu_{zz} - \mu_{xx}}{\cos 2\beta_s} + \frac{J^2}{\Delta} \sum_{v, v'} (-1)^{v-v'} \Delta_{vv'} B_v B_{v'} \right] \right\}^{1/2}, \quad (39)$$

where the determinant $\Delta = \text{Det}(\partial^2 V_{\text{eff}} / \partial q_v \partial q_{v'})$ and $\Delta_{vv'} = \Delta_{v'v}$ are the minors of this determinant. All the values in Eq. (39) are assumed to be taken in the stationary point determined by Eqs. (24) and (25). It is not difficult to show that the precession frequency Ω_{xz} vanishes in the critical point J_c . The higher nonadiabatic terms appear in Ω_{xz} in the same manner as in Ω_z [see the text following Eq. (33)].

The small amplitude motion near the state S_x is described by the equations which are very similar to Eqs. (32). As a result we get in the adiabatic approximation the following expression for the precession frequency around the x -axis:

$$\Omega_x = J \left\{ (\mu_{xx} - \tilde{\mu}_{yy}) \left[\mu_{xx} - \mu_{zz} + J^2 \left(\frac{\partial \mu_{xz}}{\partial r_a} \right)^2 \right] \frac{\partial^2 V_{\text{eff}}}{\partial r_a^2} \right\}^{1/2}, \quad (40)$$

where all the values are taken in the stationary state S_x . The last term in the braces is a small correction. Consequently, the stability of the S_x state is mainly defined by the value given in Eq. (34) which in turn depends on the angle α_s . Since this angle is larger than 90° for the molecules considered and increases with increasing J because the derivative $(\partial \mu_{xx} / \partial \alpha)$ is negative, the precession frequency Ω_x is

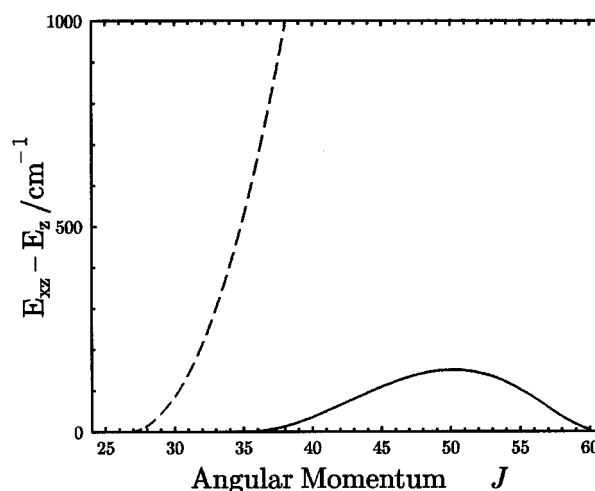


FIG. 2. Value of the barrier which separates two equivalent maxima of stationary state S_{xz} for water molecule calculated in the stretching-bender model (solid line) and the rigid-bender model (dashed line).

imaginary for reasonable values of J . Thus the state S_x corresponds to an unstable saddle-type point. The J -dependence of its energy is defined by Eq. (23).

Equations (23) and (26) (when the transition $S_z \rightarrow S_{xz}$ occurs) provide a good estimation of the maximal rotation energy in J -multiplet. The difference between our estimations and experimental data or variational calculations for H_2Te , H_2Se , H_2S , and H_2O molecules does not exceed 10%. This is also true for our estimations of the minimal rotational energy in the J -multiplet using Eq. (23) for the state S_y . The energy of the unstable stationary state S_x corresponds to the top of the barrier responsible for the K -doublets in the upper and lower parts of the J -multiplets.³ Another barrier appears because of the bifurcation for angular momentum at $J > J_c$. It separates two degenerate maxima of the stationary state S_{xz} . The barrier is responsible for the twofold clustering of the K -doublets. Its height is equal to the difference between the energies of the states S_z and S_{xz} . The higher the barrier is, the more apparent is the clustering. In the H_2Te , H_2Se , and H_2S molecules, the height of the barrier becomes significant as J increases. However, calculations carried for the H_2O molecule with potentials from Ref. 19 show that the height of the energy barrier increases very slowly with increasing J and its value is only 15 cm^{-1} at $J=40$ (see Fig. 2). This value is less than the precession frequency in the S_{xz} state so that such a barrier cannot result in fourfold clustering of levels. For higher J values the barrier increases further to its maximal value 150 cm^{-1} (which is about the precession frequency at this point) and then begins to decrease. In contrary, the barrier rapidly increases with increasing J for the rigid-bender model as it is seen from Fig. 2, where the dependence of the barrier height on angular momentum J is plotted. It is obvious that water represents a special case in the series of H_2X hydrides. Despite the bifurcation in the ground vibrational state of this molecule, no fourfold level clustering can be observed in the upper part of J -multiplets since the barrier is too small. This fact gives us a physical explanation to the

TABLE III. Normalized amplitudes of coordinate oscillations in the normal modes of precession-vibrational motion ($Q_4 = J_x/J$) around stationary state S_z for H₂Se molecule at $J = 10$.

Normal frequency/cm ⁻¹	Normalized amplitudes			
	Q_1/r_e	Q_2	Q_3/r_e	Q_4
$\omega_1 = 2426.4$	1 ^a	0.032	1	0
$\omega_2 = 1082.3$	-0.014	1 ^a	-0.014	0
$\omega_3 = 2437.5$	1 ^a	0	-1	-0.008
$\Omega_z = 15.7$	0.004	0	-0.004	1 ^a

^aSet to 1 due to normalization condition.

recent numerical calculations of water rotational spectrum with highly accurate optimized potentials,^{18,20} which failed to show any fourfold clusters.

The C_{2v} bifurcation has to exist also in rotational energy structure of excited vibrational states so far as the adiabatic approximation $\omega \gg \Omega$ is valid and allows to separate the precession from the vibrational motion. As to the energy clustering effect, we have seen above that this problem requires separate and more careful consideration. Preliminary analysis of experimental data showed the tendency of levels to cluster in ν_2 vibrational states of the H₂O and H₂S molecules.^{5,7} The cluster phenomenon has been found in variational quantum calculations for the excited vibrational states of H₂Se,^{13,14} H₂S,¹⁵ and H₂Te (Ref. 16) and very recently observed experimentally in the ν_1/ν_3 state of H₂Se.²⁹

Consider now in detail the molecular vibrational motion near the stationary states S_z for $J < J_c$ and S_{xz} for $J > J_c$. Four normal modes of precession-vibration motion are described by four coupled Eqs. (32) and (37) correspondingly. All these equations are not correct near the critical point J_c where the rovibrational motion is strongly nonlinear. It was shown above that the equations for the axial state S_z (and those for the state S_x) can be separated into two independent pairs when symmetrized stretching coordinates are introduced. When $J = 0$ the precessional motion is absent and the vibrational motion corresponds to the well-known picture of the normal vibrational modes ν_1 , ν_2 , and ν_3 .²⁴ This limit allows us to refer to the standard notations for a rotating molecule as well, i.e., the frequency ω_1 corresponds to the symmetrical stretching mode ν_1 , the frequency ω_2 corresponds to the bending mode ν_2 , and the frequency ω_3 corresponds to the asymmetric stretching mode ν_3 . The difference from a nonrotating molecule consists in the effective potential for vibrations and in the equilibrium configuration, which is symmetrical but differs from that of nonrotating molecule. This difference is a consequence of the centrifugal force only. Besides, the precessional mode with frequency Ω_z appears and the asymmetric stretching vibration mixes with the precessional motion because of the Coriolis and centrifugal interaction. However this mixing is very weak since the parameter $(\Omega_z/\omega_3)^2$ is small. This can be seen from Table III where the normalized amplitudes of four coordinates Q_1 , Q_2 , Q_3 , and $Q_4 = J_x/J$ involved in a normal mode oscillations are given for the H₂Se molecule at $J = 10$. It is seen from the table that the mixing of different types of motions is

TABLE IV. Normalized amplitudes of coordinate oscillations in the normal modes of precession-vibrational motion ($Q_4 = J'_x/J_{sz}$) near the equilibrium configuration of the H₂Se molecule uniformly rotating in stationary state S_{xz} at $J = 16$ around the axis which is approximately perpendicular to the r_1 bond ($\beta_s = 26.08^\circ$).

Normal frequency/cm ⁻¹	Normalized amplitudes			
	Q_1/r_e	Q_2	Q_3/r_e	Q_4
$\omega_1 = 2391.0$	1 ^a	0.018	0.097	-0.002
$\omega_2 = 1109.7$	-0.015	1 ^a	-0.013	0.024
$\omega_3 = 2436.1$	-0.097	0.012	1 ^a	0.003
$\Omega_{xz} = 39.5$	0.006	0.081	-0.008	1 ^a

^aSet to 1 due to normalization condition.

small and the character of the vibrations is close to the standard normal mode picture.²⁴

The character of the oscillations changes drastically after the critical point J_c . It is impossible to split the four equations (37) describing the small amplitude motion near the stationary state S_{xz} into two independent pairs because the molecular configuration is asymmetric and the uniform rotation of molecule around the axis in the (xz) plane mixes the symmetrical and asymmetric stretching vibrations. As a result, the standard picture of normal mode vibrations, which is correct for the S_z state, breaks down. This effect is illustrated in Table IV which shows normalized amplitudes of oscillations around the asymmetrical configuration of the state S_{xz} at $J = 16$ ($\beta_s = 26.08^\circ$). The precession of the angular momentum is described by dimensionless variable $Q_4 = (J_x - J_{sx})/J_{sz}$. Table IV shows also that the precessional motion is mixed mostly with the bending vibration. It is worth noting that the vibrations in the mode with the frequency ω_1 are localized predominantly on the bond r_1 and vibrations in the mode with the frequency ω_3 are localized on the bond r_3 . This feature is inherent in local mode vibrations.²² However usually the local mode motion appears due to the strong anharmonicity as the stretching vibrations are increasingly excited. In our case the normal to local mode transition is a result of the symmetry breaking, which leads to the different force constants for two bonds and favors the local mode picture in the competition between kinetic and potential coupling between the local bond oscillators. Accordingly the local character of the stretching motion

TABLE V. Normalized amplitudes of coordinate oscillations in the normal modes of precession-vibrational motion ($Q_4 = J'_x/J_{sz}$) near the equilibrium configuration of the H₂Se molecule uniformly rotating in stationary state S_{xz} at $J = 40$ around the axis which is approximately perpendicular to the r_1 bond ($\beta_s = 42.26^\circ$).

Normal frequency/cm ⁻¹	Normalized amplitudes			
	Q_1/r_e	Q_2	Q_3/r_e	Q_4
$\omega_1 = 2095.8$	1 ^a	0.030	0.015	-0.001
$\omega_2 = 1271.9$	-0.022	1 ^a	-0.009	0.130
$\omega_3 = 2438.0$	-0.015	0.003	1 ^a	0.004
$\Omega_{xz} = 211.7$	0.000	0.434	-0.009	1 ^a

^aSet to 1 due to normalization condition.

strengthens with increasing J . This follows from Table V which shows normalized amplitudes of oscillations around the state S_{xz} at $J=40$ ($\beta_s=42.26^\circ$) where Q_4 is defined as for Table IV.

The classical calculations of the present work have shown that in nonlinear AB₂ molecules, a normal to local mode transition can be brought about by rotational excitation. Similar results have been obtained in quantum numerical calculations with the MORBID program.¹⁴ The classical analysis of precession-vibrational motion of the present work gives a physical picture of the phenomenon. That is, the bifurcation in a ground vibrational state breaks the molecular symmetry and changes both rotational and vibrational motions of the nonlinear AB₂ molecule resulting in the fourfold clusters and in the normal to local mode transition. The physical reasons for these phenomena lie in the molecular symmetry and in the anisotropic centrifugal force. Therefore we should expect similar or even more interesting phenomena in the rapidly rotating molecules with higher symmetry.

ACKNOWLEDGMENTS

This work was supported by the Russian Fond for Fundamental Investigations (through Grant No. N 94-02-05424-a), International Science Foundation and Russian Government (through Grants Nos. MIW000, MIW300 and R8I000, R8I300). The authors are indebted to P. Jensen for critically reading the manuscript and suggesting improvements. I.N.K. is thankful to A. F. Krupnov for valuable comments on the manuscript. The authors would like also to thank the referee who pointed out on the existence of the Coriolis term in the Hamiltonian (15). The elimination of this defect allowed us to prove that all the effects considered above exist exclusively due to the centrifugal distortion force.

- ¹A. J. Dorney and J. K. G. Watson, *J. Mol. Spectrosc.* **42**, 135 (1972).
- ²W. G. Harter and C. W. Patterson, *J. Chem. Phys.* **80**, 4241 (1984), and references therein.
- ³W. G. Harter, *Comp. Phys. Rep.* **8**, 319 (1988).
- ⁴D. A. Sadovskii, B. I. Zhilinskii, J.-P. Champion, and G. Pierre, *J. Chem. Phys.* **92**, 1523 (1990).
- ⁵B. I. Zhilinskii and I. M. Pavlichenkov, *Opt. Spectrosc. (USSR)* **64**, 413 (1988).
- ⁶J. T. Hougen, P. R. Bunker, and J. W. C. Johns, *J. Mol. Spectrosc.* **34**, 136 (1970).
- ⁷I. M. Pavlichenkov, *Fizika atomnogo jadra, Materials of XXIVth winter school LIJaF*, 67, Leningrad 1989 (unpublished).
- ⁸J. Makarewicz and J. Pyka, *Mol. Phys.* **68**, 107 (1989); J. Makarewicz, *ibid.* **69**, 903 (1990).
- ⁹J. Pyka, *Mol. Phys.* **70**, 547 (1990).
- ¹⁰I. M. Pavlichenkov, *Phys. Rep.* **226**, 175 (1993).
- ¹¹I. N. Kozin, S. P. Belov, O. L. Polyansky, and M. Yu. Tretyakov, *J. Mol. Spectrosc.* **152**, 13 (1992).
- ¹²I. N. Kozin, S. Klee, P. Jensen, O. L. Polyansky, and I. M. Pavlichenkov, *J. Mol. Spectrosc.* **158**, 409 (1993).
- ¹³P. Jensen and I. N. Kozin, *J. Mol. Spectrosc.* **160**, 39 (1993).
- ¹⁴I. N. Kozin and P. Jensen, *J. Mol. Spectrosc.* **161**, 186 (1993).
- ¹⁵I. N. Kozin and P. Jensen, *J. Mol. Spectrosc.* **163**, 483 (1994).
- ¹⁶P. Jensen, Yan Li, G. Hirsch, R. J. Buenker, T. J. Lee, and I. N. Kozin, *Chem. Phys.* **190**, 179 (1995).
- ¹⁷P. Jensen, *J. Mol. Spectrosc.* **128**, 478 (1988); *J. Chem. Soc. Faraday Trans. 2* **84**, 1315 (1988).
- ¹⁸P. Jensen and I. N. Kozin (unpublished results).
- ¹⁹P. Jensen, *J. Mol. Spectrosc.* **133**, 438 (1989); P. Jensen, S. Tashkun, and V. G. Tyuterev, *ibid.* **168**, 271 (1994).
- ²⁰O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **101**, 7651 (1994).
- ²¹L. H. Coudert, *J. Mol. Spectrosc.* **154**, 427 (1992).
- ²²M. S. Child and L. Halonen, *Adv. Chem. Phys.* **57**, 1 (1984).
- ²³K. K. Lehmann, *J. Chem. Phys.* **95**, 2361 (1991).
- ²⁴E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- ²⁵B. T. Sutcliffe and J. Tennyson, *Mol. Phys.* **58**, 1053 (1986); *Int. J. of Quantum Chem.* **39**, 183 (1991).
- ²⁶P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, London, 1979).
- ²⁷P. Jensen and P. R. Bunker, *J. Mol. Spectrosc.* **164**, 315 (1994).
- ²⁸L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, Oxford, 1962).
- ²⁹J.-M. Flaud, C. Camy-Peyret, H. Bürger, P. Jensen, and I. N. Kozin, *J. Mol. Spectrosc.* **172**, 194 (1995).