EPJ manuscript No.
(will be inserted by the editor)

Qualitative analysis of molecular rotation starting from inter-nuclear potential

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Draft: Dunkerque, February 15, 1999; printed July 20, 1999

Abstract. We study how qualitative features of the molecular rotational dynamics can be derived directly from the internuclear (vibrational) potential. This approach is presented on the example of a tetrahedral molecule A_4 using several increasingly elaborated models of the potential.

PACS. 33.15.Mt Rotation, vibration, and vibration-rotation constants – 33.20.Vq Vibration-rotation analysis

1 Idea of the method

In this paper we combine two approaches to the description of molecular rotation, the effective or phenomenological approach and the theoretical or microscopic approach based on the adiabatic internuclear potential. We give both classical and quantum description in order to to show how qualitative features of molecular rotational dynamics can be analyzed directly on the basis of molecular parameters characterizing the equilibrium configuration [1] and inter-atomic potential (force field). The obvious advantage of such analysis is in the possibility to see the immediate effect of certain molecular parameters or their specific combinations on the qualitative structure of rotational levels such as clustering of rotational levels and its modifications. In particular, we can use simple parameter dependent models of inter-atomic forces and find those characteristics of the potential which are the most essential for qualitative changes in the rotational dynamics.

The main idea of the method can be explained on the well known example of rotational corrections to the vibrational potential of a diatomic molecule. This problem is described by the Hamiltonian

$$H_J(r,p_r) = \frac{p_r^2}{2\mu} + \frac{\mathbf{J}^2}{2\mu r^2} + V(r), \tag{1}$$

where the magnitude of the total angular momentum $\mathbf{J}^2 = J(J+1)$ is a strict integral of motion and can be considered as a *parameter*. For each *fixed* value of $|\mathbf{J}|$ (or the quantum number J), the two last terms of this Hamiltonian constitute an effective vibrational potential $V_J(r)$. We want to find the energy E_J of the ground vibrational state in this potential and to analyze its J-dependence. For example we want to know the value of J at which rotational dissociation begins. In the classical limit (that is, with the vibrational half quantum neglected and p_r set to 0) E_J is the minimum value of V_J at the internuclear distance $r_{\min}(J)$ and this minimum exists in most cases only for a limited range of J-values.

For a polyatomic molecule we should consider the classical rotational energy E_J for all possible axes of rotation. In other words, E_J is a function of axis position defined by spherical coordinates (θ,φ). This function is naturally defined on a 2-sphere and is often called rotational energy surface (RES) since the early works by Harter and coauthors [2,3]. As in the above example, we find E_J as a global minimum of the potential $V_J(\mathbf{q})$ which is a function of normal mode displacements $\mathbf{q} = q_1, q_2, \ldots,$ and parameter J. Two observations are crucial to the analysis: (i) in order to reconstruct qualitatively the whole of $E_J(\theta,\varphi)$ we can calculate this function only for a small set of *stationary axes* of rotation; (ii) the minimization is greatly simplified by using symmetry properties of stationary axes. By characterizing stationary axes of rotation, (energies of stationary points of RES, or relative equilibria) we obtain a qualitative description of the rotational dynamics as a whole and of the corresponding system of rotational energy levels.

2 Description of molecular rotation

Rotation of molecules [1,4] is traditionally described in terms of an effective rotational Hamiltonian which is constructed as a series in rotational operators J_x, J_y, and J_z, the components of the total angular momentum $\mathbf{J}$. In a suitably chosen molecule-fixed frame this Hamiltonian can be

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written in the form

$$H_{\text{eff}} = AJ_x^2 + BJ_y^2 + CJ_z^2 + \sum c_{\alpha\beta\gamma} J_x^\alpha J_y^\beta J_z^\gamma + \cdots, \quad (2)$$

where A, B, C, and $c_{\alpha\beta\gamma}$ are constants. The amplitude of the total angular momentum

$$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2 = \text{const} = J(J+1), \quad (3)$$

is an integral of motion and J is a dynamical parameter.

In classical mechanics, $\mathbf{J}^2$ and energy E are integrals of the Euler's equations of motion for dynamical variables J_x, J_y, and J_z. The phase space of the classical rotational problem with constant $|\mathbf{J}|$ is S_2, the two-sphere, with coordinates (θ, φ). The points on S_2 define the orientation of $\mathbf{J}$, i.e., the position of the axis and the direction of rotation. To interpret the quantum Hamiltonian we introduce the classical analogs of the operators J_x, J_y, and J_z,

$$\mathbf{J} \to \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} \sqrt{J(J+1)}\,, \quad (4)$$

and consider the rotational energy E as function of (θ, φ) and parameter J. Such classical interpretation has proven to be quite helpful in understanding the degeneracies of quantum rotational levels [5,2,3,6]. In fact, the analysis of the RES $E_J(\theta, \varphi)$ provides comprehensive information on the structure of quantum energy levels and localization of quantum wavefunctions. The main characteristics of RES are the location and type of its stationary points. In the simplest case [7,8] these characteristics are mere consequences of the S_2 topology of the phase space and the symmetry group of the problem (of the molecule). The qualitative study of molecular rotational dynamics is largely based on Morse theory of generic functions defined on S_2 in the presence of a certain *a priori* finite symmetry group. Furthermore, it is natural to consider the whole parametric family of RES's and to study qualitative changes or bifurcations [9,7,8] that occur in the system of stationary points of RES when the parameter J changes.

Parameters of effective Hamiltonians can be regarded as phenomenological constants that can be obtained from the analysis of experimental data. At the same time, these parameters can, in principle, be derived theoretically by reducing the initial "full" rotation-vibration Hamiltonian, known in molecular spectroscopy as Wilson-Howard Hamiltonian [4] simplified in the quantum case by Watson [10,11]. In fact, one of the goals of molecular spectroscopy is believed to be the inverse problem of recovery of molecular characteristics from phenomenological constants. Many theoretical formulae relating effective constants to the force field parameters, to the moment of inertia corrections, and to Coriolis constants can be found in the literature [12].

In our treatment, we eliminate the stage of effective Hamiltonian. In its most simple form presented in this paper, our method applies in the ground vibrational state of the molecule where vibrational kinetic energy is small and can be neglected and the difficulty of general reduction of the full vibration-rotation Hamiltonian can thus be bypassed by assuming "frozen" vibrations and considering the kinetic energy of rotation as a contribution in an effective potential V_J. Our problem turns into a static minimization of V_J on the space of vibrational coordinates q for a given axis of rotation defined by angles (θ, φ) and some value of J. The RES function $E_J(\theta, \varphi)$ is obtained as the result. Since this function is generally a formal power series in J with the known limited number of terms in each order, calculation of a small set of benchmark energies for stationary axes of rotation can be sufficient for reconstructing the whole of $E_J(\theta, \varphi)$ and the corresponding effective Hamiltonian to a certain order in J. The number, type, and orientation (θ, φ) of the stationary axes can often be determined entirely from symmetry arguments.

2.1 Symmetry analysis, relative equilibria

Symmetry plays an important role in our study. Symmetry of the molecular equilibrium configuration combines with the symmetry properties of the angular momentum vector $\mathbf{J}$ and results in the *a priori* symmetry $\mathfrak{G}$ of the rotational problem. The effective rotational Hamiltonian H_{eff} and the RES should be $\mathfrak{G}$-invariant. We assume that H_{eff} is a *generic* or Morse function $E_J(\theta, \varphi)$ on the sphere, and as such it should have at least a certain minimum set of stationary points [7,8]. The simplest system of stationary points is predicted entirely by arguments due to symmetry and topology, and we call the corresponding class of generic functions the class of simplest Morse functions on S_2 in the presence of $\mathfrak{G}$. The natural assumption is that at low rotational excitation (small values of J) the RES of the molecule is of this simplest kind.

Stationary points of the simplest Morse function exist regardless of how small the coefficients $c_{\alpha\beta\gamma}$ in eq. (2) may be, i.e., these points exist anywhere close to the limit of linearization (where H_{eff} is purely quadratic). Stationary points with such property are called *relative equilibria* [13]. Although their stability can be modified by bifurcations, relative equilibria exist in the whole range of values of the parameter J; we say that they can be *continued* for all J. In the rotational problem, relative equilibria correspond to stationary axes of rotation: when the molecule rotates around such an axis its angular momentum $\mathbf{J}$ is constantly aligned with the axis.

Relative equilibria of the reduced problem correspond to periodic orbits (PO's) of the initial problem, molecular rotation without reduction to constant J. A relative equilibrium considered for *all* values of J defines a family of PO's whose members exist at all J's and in particular, anywhere close to the linear limit of the rigid rotor. Such family of PO's is called *nonlinear normal mode* [14] or quasimode [15]. Existence and stability of nonlinear normal modes of the rotational problem have been recently analyzed by Montaldi and Roberts [16].

We explain our approach on the example of A_4, the simplest tetrahedral molecule whose three normal modes have different symmetry types. The symmetry group T_d of the equilibrium configuration of A_4 combines with the time reversal (or momentum reversal) symmetry $\mathcal{T}$ of the rotational Hamiltonian so that the total symmetry group of the rotational problem is $T_d \wedge \mathcal{T}$. This group is isomorphic to O_h and its action on the phase sphere S_2 (on the space spanned by three angular momenta where $\mathcal{T}$ is equivalent to momentum reversal, i.e. inversion C_i) is the same as the natural geometric action of O_h. Such high symmetry greatly restricts the number of possible nontrivial terms in the rotational Hamiltonian H_{eff} of A_4.

2.1.1 Effective rotational Hamiltonian

Due to its high symmetry the A_4 molecule is a spherical top [$A = B = C$ in eq. (2)] and its effective rotational Hamiltonian H_{eff} can be written as series in three basis polynomials [17] (with the appropriate symmetrization in the case of quantum operators) which can, for example, be chosen as

$$R_2 = J_x^2 + J_y^2 + J_z^2 = \mathbf{J}^2 = J^2, \tag{5a}$$

$$R_4 = J_x^4 + J_y^4 + J_z^4, \tag{5b}$$

$$R_6 = J_x^6 + J_y^6 + J_z^6, \tag{5c}$$

so that

$$H_{\text{eff}} = \sum h_{abc} R_2^a R_4^b R_6^c. \tag{6}$$

The spherically symmetric R_2 polynomial enters in the zero order rigid rotor term BJ^2, the powers of R_2 form scalar centrifugal corrections. Such corrections describe the increase of the size of the molecular frame (decrease of the moment of inertia) which is caused by rotational excitation (growing J) and which occurs without breaking the T_d symmetry of the equilibrium configuration. Polynomials R_4 and R_6 describe tensorial centrifugal distortions which break the T_d symmetry of the $\mathbf{J}$-dependent equilibrium configuration. Traditionally, such tensorial terms are classified using the $SO(3)$ group, i.e., using the group chain $SO(3) \supset O$ or $O(3) \supset O_h$. In the widely used spectroscopic notation originated by Watson [5,12], the corresponding tensors of ranks 4 and 6 are defined as

$$\Omega_4 = -\left[10R_4 - 6J^4 + 2J^2\right] \tag{7a}$$

$$\Omega_6 = \frac{77}{2}R_6 - \frac{35}{2}R_4(3J^2 - 7) + \frac{15}{2}J^4(2J^2 - 9) + 19J^2. \tag{7b}$$

In the slightly different notation by Moret-Bailly [?], the group chain approach is implemented more fully,

$$R^{N(0,A_{1g})} = \left(-\frac{4}{\sqrt{3}}R_2\right)^{N/2}, \quad N = 2, 4, 6, \ldots, \tag{8a}$$

$$R^{4(4,A_{1g})} = -\frac{4\sqrt{2}}{15}\Omega_4, \tag{8b}$$

$$R^{6(6,A_{1g})} = -\frac{64\sqrt{2}}{\sqrt{231}}\Omega_6. \tag{8c}$$

These latter definitions are used by the Dijon group in spectroscopic studies of spherical tops [18]. The spectroscopic effective rotational Hamiltonian of A_4 is quite simple.

Table 1. Principal stationary axes of tetrahedral molecules.

notation $\mathfrak{g} \subset O$	C_4	C_3	C_2
notation $\mathfrak{g} \subset O_h$	C_{4v}	C_{3v}	C_{2v}
notation $\mathfrak{g} \subset T_d$	S_4	C_{3v}	C_s
stabilizer of the axis	D_{2d}	C_{3v}	C_s
number of equivalent points (axes)	6(3)	8(4)	12(6)
example $[x, y, z]$	$[0,0,1]$	$\frac{1}{\sqrt{3}}[1,1,1]$	$\frac{1}{\sqrt{2}}[1,1,0]$

Up to order 6

$$\begin{aligned} H_{\text{eff}} &= BJ^2 - DJ^4 + D_t\Omega_4 + HJ^6 + H_{4t}J^2\Omega_4 + H_{6t}\Omega_6, \\ &= E_{\text{scalar}}(J) + D_t(J)\Omega_4 + H_t(J)\Omega_6. \end{aligned} \tag{9}$$

There is only one nontrivial term of degree 4, and one more is added at degree 6. It can be seen that to recover all coefficients in eq. (9) it is sufficient to compute the energy $E_J(\theta, \varphi)$ for the three non-equivalent by symmetry principal stationary axes (axes C_2, C_3, and C_4 in Table 1) up to order J^6 and solve a system of linear equations in each order.

2.1.2 Principal stationary axes of rotation

The action of the O_h group on the phase space S_2 of the rotational problem (with J = const) has three kinds of critical orbits (isolated fixed points on S_2) which are necessarily critical points of any generic O_h-symmetric Hamiltonian function on S_2 [7]. (Such points represent relative equilibria.) The local symmetry (stabilizer) $\mathfrak{g}$ and the number of points in the orbit for each kind are listed in Table 1. Below we tend to use the shorter O-group notation. Each stationary axis is represented by two diametrally opposite points on S_2 which correspond to two directions of rotation. Pairs of points with the same type of $\mathfrak{g}$ (pairs with conjugated stabilizers) represent *equivalent* stationary axes. The energy of rotation around equivalent axes is, of course, the same. Due to their high symmetry the C_3 and C_4 axes are stable, they correspond to maxima or minima of $E_J(\theta, \varphi)$. Axes C_2 can both be stable or unstable, in the latter case they correspond to saddle points of E_J.

Axes C_3, C_4, and C_2 are the only stationary axes in the case of the simplest Morse type rotational Hamiltonian of a spherical top molecule [7,8]. A combination of different terms where the R_4 term is dominant gives an example of such simplest Morse type Hamiltonian. In such case, axis C_2 is unstable and two possibilities exist (see fig. 1) : $E_J(C_3) > E_J(C_2) > E_J(C_4)$ when the coefficient before R_4 is negative or vice versa $E_J(C_4) > E_J(C_2) > E_J(C_3)$ when this coefficient is positive. In all other cases there are extra stationary axes (cf. fig. 1, center) which can appear, for example, in a pitchfork bifurcation of the C_2 axis when J becomes sufficiently large (see [9,7] for a complete classification of possible bifurcations).

Existence of equivalent stable stationary axes, i.e., of equivalent stable equilibria of H_{eff} has a well known quantum manifestation in the form of energy level *clusters* or

Fig. 1. Rotational energy surfaces for the A_4 molecule in the case of (left to right): the positive dominant contribution by R_4 ($D_t < 0$), the combination of R_4 and R_6 (such as $4J^2R_4 - 3R_6$ plotted), the negative dominant contribution by R_4 ($D_t > 0$).

quasi-degenerated groups of rotational levels [5,2,3]. The number of levels in a cluster depends on the symmetry type of the axis and equals the number of the corresponding equivalent equilibria. Thus in the simplest Morse case, the energy level spectrum consists of regular sequences of 6- and 8-fold clusters (corresponding to axes C_4 and C_3) separated by a transition region at energies near $E_J(C_2)$ which has no clusters.

2.2 Example of A_4

Our starting point is the vibration-rotation Hamiltonian which depends on the rotational dynamical variables J_x, J_y, J_z, as well as on the internal vibrational coordinates q, or the normal modes, and conjugated vibrational momenta p. The A_4 molecule has three normal modes which transform according to irreducible representations $\Gamma = A_1$, E and F_2 of the T_d group. Here is another advantage of our example: all normal modes have different symmetry and factorization of the principal (lowest order) terms in the Hamiltonian is straightforward.

The choice of the components of each normal mode is not unique. To avoid possible confusion, we give explicit representation of the six components of the normal modes $q_{\Gamma\sigma}$ in terms of the Cartesian displacements $\mathbf{r}_j = (r_{jx}, r_{jy}, r_{jz})$ of each atom $j = 1, \dots, 4$. The coordinate frame and the atom indices are set as shown in fig. 2. We represent $q_{\Gamma\sigma}$ as vectors $\mathbf{r}^k$ of dimension 12, with index $k = \Gamma\sigma = A_1$, E_a, F_{2x}, etc. These vectors transform according to the rows σ of the matrices of respective irreducible representations. Our matrices are defined by the polynomials $x^2 + y^2 + z^2$ (or simply a constant) for A_1, $[2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2)]$ for E, and $[x, y, z]$ for F_2. In general, for N atoms, vectors $\mathbf{r}^k$ form a $(3N-6) \times 3N$ block of the $3N \times 3N$ unitary matrix of correspondence between the $3N$ Cartesian displacements $\mathbf{r}_i$ of each atom on the one hand and the normal modes, three overall translations, and three overall (infinitesimal) rotations on the other.

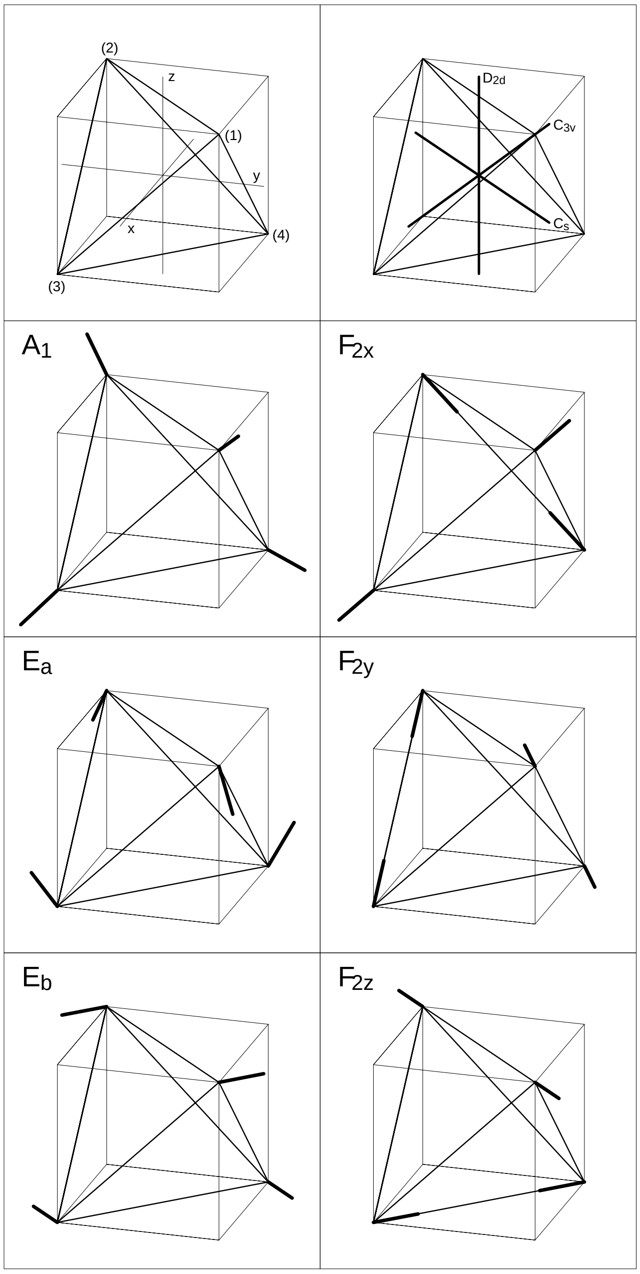

Fig. 2. Choice of coordinates, positions of atoms, axes of symmetry, and normal modes for the A_4 molecule.

3 Energy of rotation around stationary axes in the limit of frozen (absent) vibrations

The classical rotation-vibration Hamiltonian for a nonlinear N-atomic molecule with small amplitude vibrations about a well defined equilibrium configuration [1], the so-called Wilson-Howard Hamiltonian, is a function of the angular momentum $\mathbf{J}$, and of the $3N-6$ internal coordinates q_k and conjugated momenta p_k,

$$H_{\mathrm{rovib}} = (\mathbf{J} - \boldsymbol{\pi})^T \frac{\boldsymbol{\mu}(q)}{2} (\mathbf{J} - \boldsymbol{\pi}) + \sum_{k=1}^{3N-6} \frac{p_k^2}{2} + V(q), \quad (10)$$

where $\boldsymbol{\pi}$ is a vector bilinear in Cartesian coordinates and momenta which corresponds to the angular momentum induced by the vibrations, $\boldsymbol{\mu}$ is the inverse matrix of the modified inertia tensor, and V the inter-nuclear potential depending on internal coordinates $q = q_1, q_2, \dots, q_{3N-6}$.

Table 2. Normal modes of a T_d-symmetric molecule A_4 represented in terms of Cartesian displacements of the atoms; the 12-component vectors $\mathbf{r}^k$ are normalized to unity.

$\mathbf{r}_i^k$	A_1	E_a	E_b	F_{2x}	F_{2y}	F_{2z}
r_{1x}	1	1	-1	0	1	1
r_{1y}	1	1	1	1	0	1
r_{1z}	1	-2	0	1	1	0
r_{2x}	-1	-1	1	0	1	-1
r_{2y}	-1	-1	-1	1	0	-1
r_{2z}	1	-2	0	-1	-1	0
r_{3x}	1	1	-1	0	-1	-1
r_{3y}	-1	-1	-1	-1	0	1
r_{3z}	-1	2	0	-1	1	0
r_{4x}	-1	-1	1	0	-1	1
r_{4y}	1	1	1	-1	0	-1
r_{4z}	-1	2	0	1	-1	0
norm	$\sqrt{3}/6$	$\sqrt{6}/12$	$\sqrt{2}/4$	$\sqrt{2}/4$	$\sqrt{2}/4$	$\sqrt{2}/4$

Note that in our A_4 example (Sec. 2.2 and Table 2) index k takes the values A_1, E_a, E_b, F_{2x}, F_{2y}, and F_{2z}. We also remind that for the spherical top molecule of the type A_4, both the matrix of the inertia tensor and that of the quadratic part of the potential V can be diagonalized (see Sec. 2.2).

The main assumption of this work is that of *frozen* vibrations. In other words, we assume that all p_k and, consequently, the kinetic energy of vibrations [the second term in eq. (10)], the induced angular momentum $\boldsymbol{\pi}$, and the modifications of the inertia tensor incorporated into $\boldsymbol{\mu}$—all vanish. Furthermore, we will further simplify the problem by considering *only* the case of stationary axes of rotation where the Hamiltonian of the A_4 molecule in a suitably chosen reference frame becomes

$$H_{\text{static}} = V_J(q) = \frac{\mathbf{J}^2}{2I(q)} + V(q). \tag{11}$$

(Of course, this approximation is based on purely classical description of molecular rotation around a stationary axis. In quantum mechanics the angular momentum cannot have one fixed orientation, neither can vibrations be completely frozen.) The moment of inertia I in formula (11) can be calculated for any *stationary* axis of rotation as

$$I(q;\theta,\varphi) = \sum_{i=1}^{4} m \left[\left(\mathbf{R}_i + \sum_k q_k \mathbf{r}_i^k \right) \wedge \mathbf{n}(\theta,\varphi) \right]^2, \tag{12}$$

with the unit vector $\mathbf{n}$ defining the orientation of the axis, Cartesian displacement vectors $\mathbf{r}_i^k$ given in Table 2, and m the mass of each atom.

What happens to the molecule in the approximation of eq. (11)? Since vibrations are totally neglected we have a static problem with an effective potential H_{static} and one parameter $\mathbf{J}^2$ which, for the convenience of comparison to quantum mechanics, we will take as $J(J+1)$. In other words, depending on J the equilibrium configuration of the molecule gets distorted so that H_{static} in eq. (11) is at minimum at all J.

Table 3. Invariant distortions corresponding to each stationary axis of rotation of the A_4 molecule. Distortions are expressed in terms of normal modes as coefficients t_k^s and are normalized to unity. Different distortions invariant with respect to the same isotropy group (of the same axis) are labeled by an additional superscript (s).

k	$C_s^{(1)}$	$C_s^{(2)}$	$C_s^{(3)}$	$D_{2d}^{(1)}$	$D_{2d}^{(2)}$	$C_{3v}^{(1)}$	$C_{3v}^{(2)}$
A_1	1	0	0	1	0	1	0
E_a	0	1	0	0	1	0	0
E_b	0	0	0	0	0	0	0
F_{2x}	0	0	0	0	0	0	$3^{-1/2}$
F_{2y}	0	0	0	0	0	0	$3^{-1/2}$
F_{2z}	0	0	1	0	0	0	$3^{-1/2}$

When minimizing H_{static} we should take into account its isotropy symmetry group $\mathfrak{g}$ which is a common subgroup of the symmetry group of the potential, usually the symmetry group of the equilibrium configuration of the molecule G, and the axial symmetry of the kinetic part defined by $\mathbf{n}(\theta,\varphi)$ which includes all operations that preserve $\mathbf{n}$ or change its sign. If G contains some of these latter operations then $\mathfrak{g} \subset G$ is a nontrivial subgroup of G. For a generic axis $\mathbf{n}(\theta,\varphi)$ $\mathfrak{g} = C_1$ and we should minimize $H_{\text{static}}(q;J)$ using all $3N-6$ normal mode displacements q_k as independent parameters. At the same time, if the isotropy symmetry group $\mathfrak{g}$ (the stabilizer) of the axis is nontrivial we need a lesser number of free parameters. These latter correspond to such distortions δ_s of the initial equilibrium configuration of the molecule that are invariant with respect to $\mathfrak{g}$. In other words, out of all normal modes q_k we construct such combinations δ_s that are totally symmetric with regard to $\mathfrak{g}$, the subgroup of the symmetry group G. To find the number of free parameters δ_s we should consider the number of totally symmetric irreducible representations of $\mathfrak{g}$ in the decomposition of the representation of G spanned by normal modes q_k.

In our example of A_4, $G = T_d$ and normal modes span representation $\Gamma = A_1 \oplus E \oplus F_2$ of this group. The stationary axes C_2, C_3, and C_4 have stabilizers C_s, C_{3v}, and D_{2d}, so that the number of free parameters is 3, 2, and 2, respectively. The actual invariant distortions can be obtained by projecting the 6 components of Γ on the totally symmetric irreducible representations of the respective groups $\mathfrak{g}$. A multiplicity index $s(\mathfrak{g})$ will distinguish different such totally symmetric representations of each isotropy group $\mathfrak{g}$. For our A_4 example, we obtain invariant displacements for one representative of each class of equivalent axes, C_2, C_3, and C_4, exemplified in fig. 2 and Table 1. In Table 3 we list coefficients t_k^s with $k = A_1$, E_a, E_b, F_{2x}, F_{2y}, and F_{2z}, in the expression for resulting invariant displacements $\mathfrak{r}^{(s)}(\mathfrak{g})$ in terms of normal modes

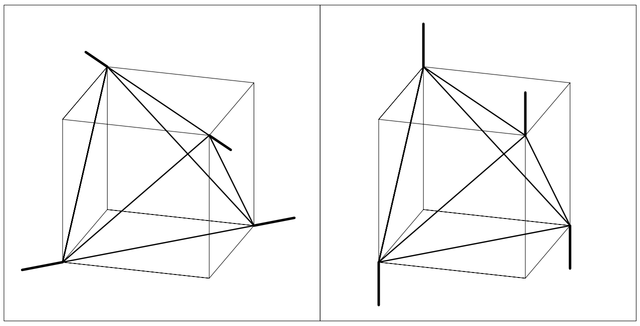

Fig. 3. Combinations of two invariant distortions for stationary axis C_4 with $\mathfrak{g} = D_{2d}$. See Table 3 and eq. (16).

$\mathbf{r}^k$,

$$\mathfrak{r}^{(s)}(\mathfrak{g}) = \sum_k t_k^s(\mathfrak{g})\ \mathbf{r}^k. \tag{13}$$

In general, coefficients $t_k^s(\mathfrak{g})$, with $k = 1, \dots, 3N-6$, form vectors $\mathbf{t}^s$. Like the normal modes $\mathbf{r}^k$ introduced in Sec. 2.2 in terms of Cartesian displacements (Table 2), vectors $\mathbf{t}^s$, $s = 1, \dots, K(\mathfrak{g})$ are orthonormal if they correspond to the same isotropy group $\mathfrak{g}$,

$$(\mathbf{t}^s(\mathfrak{g}), \mathbf{t}^{s'}(\mathfrak{g})) = \delta_{s,s'} \tag{14}$$

In other words, these vectors form a $K(\mathfrak{g}) \times (3N-6)$ block [with $K(C_s) = 3$, $K(C_{3v}) = 2$, and $K(D_{2d}) = 2$] of a unitary matrix of correspondence between the normal modes in some standard form and normal modes in a basis adapted to a particular subgroup $\mathfrak{g}$. Thus all twelve-component vectors $\mathfrak{r}^s(\mathfrak{g})$ in eq. (13) are orthonormal and form a $K(\mathfrak{g}) \times 12$ block of a unitary matrix :

$$(\mathfrak{r}^s, \mathfrak{r}^{s'}) = \sum_{k,l} t_k^s t_l^{s'} (\mathbf{r}^k, \mathbf{r}^l) = \sum_{k,l} t_k^s t_l^{s'} \delta_{k,l} = (\mathbf{t}^s, \mathbf{t}^{s'}). \tag{15}$$

To visualize the nature of these displacements it is sometimes helpful to decompose them into displacements (predominantly) parallel and orthogonal to the axis of rotation. For axes C_4 and C_3 this is most straightforward, resulting displacements for C_4,

$$\delta_{\|} = q_{A_1} - \sqrt{2}\, q_{E_a}, \quad \delta_{\perp} = \sqrt{2}\, q_{A_1} + q_{E_a}, \tag{16}$$

are shown in fig. 3. It can be seen that $\delta_{\|}$ does not change the moment of inertia with regard to axis C_4 (vertical axis in fig. 3), and is only needed to keep the center of mass in place. It follows that minimization in the case of C_3 and C_4 is one-dimensional with the only parameter of the type $\delta_{\perp}$.

We can now modify eq. (12) by using eq. (13) for particular axis (θ, φ) with stabilizer $\mathfrak{g}$,

$$I(\delta; \mathfrak{g}) = \sum_{i=1}^{4} m \left[\left(\mathbf{R}_i + \sum_s \delta_s \mathfrak{r}_i^s \right) \wedge \mathbf{n}(\mathfrak{g}) \right]^2, \tag{17}$$

where s is the multiplicity index. Similarly, we can express the potential term V in eq. (11) in terms of δ_s. If, like the moment of inertia, V is expressed in terms of N Cartesian displacement vectors $\mathbf{r}_i$, we replace these latter by

$$\mathbf{r}_i \to \sum_s \delta_s \mathfrak{r}^s. \tag{18a}$$

Otherwise, if V is expressed in terms of normal modes $\mathbf{q} = (q_1, q_2, \dots, q_{3N-6})$ we use $\mathbf{t}^s$ so that

$$q_k \to \sum_s \delta_s t_k^s. \tag{18b}$$

We then minimize with respect to all δ_s

$$\min_{\delta} \left[\frac{\mathbf{J}^2}{2I(\delta)} + V(\delta) \right], \tag{19}$$

i.e., solve a system of nonlinear equations of the type

$$\frac{\partial}{\partial \delta_s} \left[\frac{\mathbf{J}^2}{2I(\delta)} + V(\delta) \right] = 0. \tag{20}$$

In the simplest possible situation, δ_s can be regarded as very small and these equations can be linearized and solved straightforwardly. Corrections to $\{\delta_s\}_{\min}$ can be subsequently obtained by Newton's iteration.

4 Single parameter model of A_4

The most natural single parameter model of an A_4 molecule is the model with a pairwise interaction potential. Since in A_4 all four pairs of atoms (i, j) are equivalent, the harmonic approximation to a pairwise potential has only one harmonic force constant K characterizing the strength of the interatomic bond. In other words, we can represent V in eq. (11) as

$$V(r) = \frac{K}{2} \sum_{i}^{4} \sum_{j>i}^{4} \left[|\mathbf{R}_i + \mathbf{r}_i - \mathbf{R}_j - \mathbf{r}_i| - R \right]^2, \tag{21}$$

with $\mathbf{R}_i$ and $\mathbf{r}_i$ the equilibrium positions and Cartesian displacements of the four atoms, and

$$R = |\mathbf{R}_i - \mathbf{R}_j| \tag{22}$$

the equilibrium distance between the atoms.

In general, the A_4 molecule has three harmonic force constants, K_{A_1}, K_E and K_{F_2}, one for each normal mode. The model potential in eq. (21) imposes certain relations between them. To obtain these relations we use the definition of normal modes in Table 2 and represent $V(\mathbf{r})$ in eq. (21) in terms of normal modes q_k in eqs. (18a) and (18b). The Taylor expansion of $V(\mathbf{r})$ in q_k gives

$$\begin{aligned} V(q) = {} & \frac{K}{2} K_A q_{A_1}^2 + \frac{K}{2} K_E \left(q_{E_a}^2 + q_{E_b}^2 \right) \\ & + \frac{K}{2} K_F \left(q_{F_{2x}}^2 + q_{F_{2y}}^2 + q_{F_{2z}}^2 \right) \end{aligned} \tag{23}$$

with three dimensionless constants

$$K_A = 4, \quad K_E = 1, \quad K_F = 2\ . \tag{24}$$

To find the energy of rotation around a stationary axis with stabilizer $\mathfrak{g}$, we only allow for the $\mathfrak{g}$-invariant displacements. Thus, for axis C_2 with $\mathfrak{g} = C_s$ we use three displacements and express the energy in eq. (11) so that in the lowest order

$$\begin{aligned}\frac{E_{C_2}(\delta)}{B_0 J^2} = 1 &- \frac{2\sqrt{2}}{\sqrt{3}}\delta_1 + \frac{1}{\sqrt{3}}\delta_2 + \delta_3 + 2\left(1+\frac{1}{\tau}\right)\delta_1^2 \\ &- \frac{1}{2}\left(1-\frac{1}{\tau}\right)\delta_2^2 + \left(\frac{1}{2}+\frac{1}{\tau}\right)\delta_3^2 \\ &- \sqrt{2}\delta_1\delta_2 - \sqrt{6}\delta_1\delta_3 + \sqrt{3}\delta_2\delta_3,\end{aligned} \tag{25}$$

with B_0 the rotational constant of the equilibrium molecular configuration,

$$B_0 = \left(2mR^2\right)^{-1}, \tag{26}$$

δ_s dimensionless displacements chosen so that $R\delta_s$ give the change of atomic positions, and τ the dimensionless parameter,

$$\tau = J^2\epsilon > 0, \quad \epsilon = \frac{1}{2mKR^4} = \frac{B_0}{KR^2}. \tag{27}$$

We minimize the energy $E_{C_2}(\delta)$ by solving a system of three linear equations and find

$$\delta_1 = \frac{1}{\sqrt{6}}\tau - \frac{3\sqrt{3}}{4\sqrt{2}}\tau^2, \tag{28a}$$

$$\delta_2 = -\frac{1}{\sqrt{3}}\tau + \frac{\sqrt{3}}{2}\tau^2, \tag{28b}$$

$$\delta_3 = -\frac{1}{2}\tau + \frac{5}{4}\tau^2 \tag{28c}$$

Substitution of these solutions in the initial function $E_{C_2}(\delta)$ gives the energy of rotation around stationary axis C_2. The energy for axes C_3 and C_4 is obtained by the same procedure

$$E_{C_3} = B_0 J^2(1 - 2\tau/3), \tag{29a}$$

$$E_{C_2} = B_0 J^2(1 - 3\tau/4), \tag{29b}$$

$$E_{C_4} = B_0 J^2(1 - \tau). \tag{29c}$$

The three energies are such that $E_{C_3} > E_{C_2} > E_{C_4}$ (cf. fig. 1, right) and hence axes C_3 and C_4 are necessarily stable, while axis C_2 is unstable. Furthermore, relative splittings between these energies remain constant,

$$(E_{C_3} - E_{C_2})/(E_{C_2} - E_{C_4}) = 1/3, \tag{30}$$

and are equal to those produced by the Ω_4 term in eq. (7).

To reconstruct the parameters of the Hamiltonian in eq. (9) we consider its classical analog [cf. eqs. (4)] and calculate classical energies for axes C_3, C_4, and C_2 [for one axis (θ,φ) of each kind]. The latter should equal the energies in eqs. (29a) and this leads to equations for spectroscopic parameters B, D, etc, which are solved separately for each degree in J. As a result, spectroscopic parameters are expressed in terms of molecular parameters,

$$B = B_0\left(1+\frac{\epsilon}{10}\right), \quad D_t = B_0\frac{\epsilon}{20}, \quad D = B_0\frac{4\epsilon}{5}, \tag{31}$$

with ϵ defined in eq. (27). Here we draw attention to one simple consequence of the analysis made above. In the limit of small centrifugal distortions any A_4 molecule with pairwise potential has positive constant D_t. This means that in this case the sign of tetrahedral splitting of the rotational structure is unambiguous.

5 Full harmonic model of A_4

To account for all possible lowest order parameters of the molecular potential we consider the general form of the harmonic potential in eq. (23). Again, for each particular axis of rotation we allow only for a subset of distortions of the molecular equilibrium configurations δ which do not break the isotropy symmetry $\mathfrak{g}$ of the axis. We now use Table 3 and eq. (18b) to replace normal modes q in $V(q)$ by displacements δ, and use Tables 2 and 3 for the kinetic energy term. The subsequent minimization with regard to parameters δ yields the energies

$$E_J(C_i) = B_0 J^2\left(1 - \frac{4\tau}{3K_A} - E_i(K_E,K_F)\tau\right) \tag{32}$$

for the three axes C_i, $i = 2,3,4$, with

$$E_3 = \frac{2}{3K_F}, \quad E_2 = \frac{1}{2K_F} + \frac{1}{6K_E}, \quad E_4 = \frac{2}{3K_E}, \tag{33}$$

the first order splitting terms, and the same formal parameter τ as defined in eq. (27). As before, the values of the spectroscopic constants can be derived from the three rotation energies,

$$B = B_0\left[1 + \frac{\epsilon}{5}(K_E^{-1} - K_F^{-1})\right], \tag{34a}$$

$$D_t = B_0\frac{\epsilon}{10}(K_E^{-1} - K_F^{-1}), \tag{34b}$$

$$D = B_0\frac{2\epsilon}{15}\left(\frac{3}{K_F} + \frac{2}{K_E} + \frac{10}{K_A}\right). \tag{34c}$$

Since the totally symmetric vibration does not break the T_d symmetry of the equilibrium, the first order splitting terms E_3, E_2, and E_4, i.e., the tensorial part D_t of centrifugal distortion, do not depend on the constant K_A. Furthermore, these terms depend, essentially, on one parameter characterizing the ratio of K_E and K_F. We use the parameter α, such that

$$\tan\alpha = K_E/K_F, \quad 0 \le \alpha \le \pi/2, \tag{35}$$

and represent the splittings in the form

$$\frac{E_3}{S} = \sin\alpha, \quad \frac{E_2}{S} = \frac{3\sin\alpha - \cos\alpha}{4}, \quad \frac{E_4}{S} = \cos\alpha, \tag{36}$$

Table 4. Normal mode frequencies (cm^{-1}), masses (a.u.) and parameter α for tetrahedral molecules of the type A_4.

	ν_1	ν_2	ν_3	m	α/π	ref.
Bi_4	135	80	105	209	0.167	[19]
Sb_4	241	137	178	122	0.170	[19]
P_4	600	361	467	31	0.176	[20]
N_4	1672	887	1192	14	0.186	[21]
Ca_4	127	86	105	40	0.188	[22]
Be_4	663	469	571	9	0.191	[22]
Mg_4	192	147	171	24	0.203	[22]

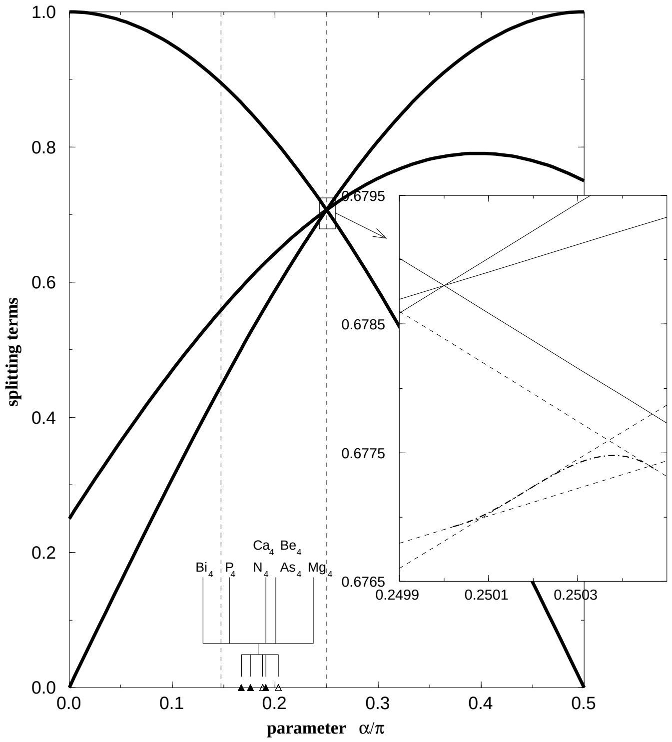

Fig. 4. First order splitting of the rotational energy E_J of the ground vibrational state of the A_4 molecule. Splitting terms for axes C_3, C_2, and C_4 defined in eq. (36) are shown as functions of $\alpha = \tan^{-1}(K_E/K_F)$. Molecular data from Table 4 are shown by triangle markers. Dashed vertical lines indicate crossover $K_F = K_E$ ($\alpha = \pi/4$) and the single parameter approximation $K_F = 2K_E$ [cf. eq. (24)]. Enhanced plot illustrates the distortion of the exact crossover due to higher order terms.

with common factor

$$S = \frac{2\sqrt{K_F^2 + K_E^2}}{3K_F K_E} = \frac{4}{3\sin 2\alpha}. \qquad (37)$$

As can be seen from eqs. (36) and fig. 4, two qualitatively different possibilities exist: $E_3 > E_2 > E_4$ when $\alpha > \pi/4$ and $E_4 > E_2 > E_3$ when $\alpha < \pi/4$. The point $\alpha = \pi/4$ ($K_E = K_F$) corresponds to the moment of *crossover*: if we (were able to) vary α smoothly and make it pass this point, the RES and the structure of the rotational multiplet gets inverted. In other words, in the first order approximation a molecule with $K_E = K_F$ behaves as a rigid spherical top. From the data in table 4 and fig. 4 we can see that real molecules correspond to an intermediate case between the crossover and the single parameter model of sec. 4.

Table 5. Approximation of the cubic force field of the A_4 molecule in the two-atom interaction model with Morse potential in eq. (44).

constant	model value	constant	model value
k_{AAA}	$-2\sqrt{6}\beta/3$	k_{EEE}	$\sqrt{3}(3+\beta)/6$
k_{AEE}	$\sqrt{3}(1-\beta)$	k_{EFF}	$(1+6\beta)/2$
k_{AFF}	$\sqrt{2}(1-3\beta)$	k_{FFF}	$-\sqrt{6}/2$

The RES $E_J(\theta,\varphi)$ in either of the above domains is of the simplest Morse type (fig. 1, left and right) with the minimal possible number of 26 stationary points. At $K_E = K_F$ maxima and minima of this RES are instantly switched. Such a transformation is not a generic one parameter phenomenon. It can be decomposed into a series of elementary bifurcations if we add higher order terms in eqs. (36). Then in the vicinity of the crossover point $K_E = K_F$ the RES will be of a more complicated Morse type with more stationary points than the minimum $\{C_3, C_4, C_2\}$ set of 26. Several sequences of bifurcations that modify the initial simplest Morse type RES and result in the crossover can be suggested [7,6,23,24]. In the most likely scenarios the crossover begins with the bifurcation at the C_2 point and the resulting 24 new unstable points (one pair per each C_2 point) depart on their roundabout along one of the C_s strata (in the symmetry planes). During the crossover (zoomed plot on fig. 4) the C_2 axis remains stable (fig. 1, center). To analyze qualitative features of the rotational energy surface in this region [25] we consider six order terms in eqs. (36) and the corresponding nonlinear terms of the vibrational potential in eqs. (23) and (21). These terms and their analysis are discussed in the next section.

6 Anharmonic model of A_4

The anharmonic potential of the A_4 molecule can be expressed as a series in normal coordinates q,

$$V(q) = V_0 + \frac{K}{R}\sum_{\Gamma\Gamma'} k_{\Gamma\Gamma'} V_{\Gamma\Gamma'} + \dots \, . \qquad (38a)$$

In this form it has six independent cubic terms (Table 5) and corresponding six constants k of the cubic force field. (Dimension of q^Γ equals that of R and factor K/R makes cubic constants dimensionless.) Explicit tensor product construction of these terms,

$$V_{\Gamma\Gamma'} = \left[\left(q^\Gamma \times q^\Gamma\right)^{\Gamma'} \times q^{\Gamma'}\right]^{A_1} = \sum_{\alpha\beta\gamma} \begin{pmatrix} \Gamma & \Gamma & \Gamma' \\ \alpha & \beta & \gamma \end{pmatrix} q^\Gamma_\alpha q^\Gamma_\beta q^{\Gamma'}_\gamma , \qquad (38b)$$

requires Wigner coefficients for the T_d group. We follow the convention of the Dijon group, see [18,26].

Rotational energy for the cubic potential in eq. (38a) can be found by the method already used in Sec. 5. For the three principal axes we obtain

$$E_J(C_i) = B_0 J^2 \left[1 \quad - \frac{4\tau}{3K_A} + \left(3 + \frac{\sqrt{6}k_{AAA}}{K_A}\right)\left(\frac{4\tau}{3K_A}\right)^2 - E_i\tau + E_i^{(2)}\tau^2 \right], \quad i = 2,3,4, \quad (39)$$

with the lowest order splitting terms as in eq. (36) and second order terms

$$E_3^{(2)} = \frac{4}{3K_F}\left(\frac{1}{K_F} + \frac{4}{K_A} + \frac{2\sqrt{2}}{3}\frac{k_{AFF}}{K_A K_F} + \frac{2\sqrt{6}}{9}\frac{k_{FFF}}{K_F^2}\right), \quad (40)$$

$$E_2^{(2)} = \left(\frac{4}{3K_A K_E} + \frac{4}{K_A K_F} + \frac{1}{K_E K_F} - \frac{1}{6K_E^2} + \frac{1}{2K_F^2} + \frac{2\sqrt{3}}{9}\frac{k_{AEE}}{K_A K_E^2} + \frac{2\sqrt{2}}{3}\frac{k_{AFF}}{K_A K_F^2} + \frac{\sqrt{3}}{18}\frac{k_{EEE}}{K_E^3} + \frac{1}{3}\frac{k_{EFF}}{K_E K_F^2}\right), \quad (41)$$

$$E_4^{(2)} = \frac{4}{3K_E}\left(\frac{1}{K_E} + \frac{4}{K_A} + \frac{2}{\sqrt{3}}\frac{k_{AEE}}{K_A K_E} - \frac{k_{EEE}}{\sqrt{3}K_E^2}\right). \quad (42)$$

Corresponding expressions for spectroscopic constants are too complicated to be reproduced here in full. We just remark that B and D receive corrections of order ϵ^2, D_t remains unchanged, and three constants of sixth degree terms with values of order ϵ^2 appear. In particular,

$$H_{6t} = B_0 \frac{4}{77}\left[3\left(\frac{1}{K_F} - \frac{1}{K_E}\right)^2 - \sqrt{3}\frac{k_{EEE}}{K_E^3} - 2\frac{k_{EFF}}{K_E K_F^2} - \frac{4\sqrt{2}}{\sqrt{3}}\frac{k_{FFF}}{K_F^3}\right]\epsilon^2. \quad (43)$$

We should further note that only parameters B, D, H, and H_{4t} which define scalar corrections depend on the harmonic constant K_A of the totally symmetric mode.

It is difficult to perform a study with so many free parameters. Furthermore, our purpose of the qualitative analysis of the influence of the nonlinear terms on the behavior of the RES near the crossover can be served by a simplier model which approximates the cubic force field by a Morse atom-atom potential

$$V(r) = E_{\rm diss} \sum_{i,j>i} \left\{ 1 - \exp\left[-\frac{\beta}{R}\Big(|\mathbf{R}_i + \mathbf{r}_i - \mathbf{R}_j - \mathbf{r}_j| - R \Big)\right]\right\}^2, \quad (44)$$

where the dissociation energy is related to the harmonic constant K (Sec. 4),

$$E_{\rm diss} = \frac{KR^2}{2\beta^2}. \quad (45)$$

Relations between the force constants implied by such an approximation are summarized in Table 5. It can be seen that, to analyze the system of stationary axes in the crossover region $K_E \approx K_F$ we will consider two extra parameters β and K_A at some fixed value of τ. To obtain an idea as to what changes are produced by the anharmonic corrections in eq. (40) we set $\beta = 0.35$ and $\tau = 0.01$, define the force constants so that

$$K = 1, \quad K_A = 4, \quad K_E^2 + K_F^2 = 9,$$

and correct the splittings E_i in eq. (36) using eqs. (39). The resulting splitting terms $(E_i - \tau E_i^{(2)})/S$ with $i = 2,3,4$ are shown in fig. 4.

To see the changes, the scale of this figure should be increased by a factor of 10^2. Then we can see well that to the second order in τ the energies of the rotation around the three axes do not cross at one point (dashed lines in the zoomed part of fig. 4 [25]) and that the crossover of the rotational multiplet happens in an interval of the values of parameter α. The RES on this interval is of a more complicated kind shown for one particular value of α in fig. (1), center. It possesses 24 additional unstable stationary points which are created in a "pitchfork" bifurcation of the C_2 axis. As the value of α increases, these points move quickly along the C_s stratum (the symmetry plane) participate in bifurcations at points C_3 and C_4, come back to C_2 and annihilate (see fig. 7.5 and 7.6 of [26], as well as [6,23,24]). Their energy is shown in the zoomed part of fig. 4. These points correspond to additional C_s symmetric relative equilibria which exist near the crossover point $K_E \approx K_F$ in a small interval of α. As we decrease rotational excitation, that is we decrease J, or more generally, as we decrease the value of the smallness parameter τ, the α interval becomes smaller, but, generically, it remains an interval anywhere close to the limit $J = \tau = 0$.

7 Discussion

This paper should be considered as complimentary to a number of previous studies [9,7,16,6,23,24,27,28]. On the one hand, our approach can be regarded as a simple way to obtain an approximate analog of the formulae which express spectroscopic constants, such as D, D_t, etc, in terms of molecular parameters, and which go back to the founding work by Watson [12]. Furthermore, we analyze our formulae to obtain the qualitative interpretation of the structure of the rotational multiplet in terms of stationary axes of rotation which also begins with Watson [5]. We discuss qualitative changes in the parametric family of the rotational multiplets and of the corresponding RES's which have been studied previously by Harter and Patterson [29,2,3] who considered the ratio D_t/H_{6t} as an external parameter, see also chap. 7 of [26]. Zhilinskií and Pavlichenkov suggested to treat the value of J as a dynamical parameter and considered the qualitative changes as classical bifurcations [9]. Later, the crossover of the rotational multiplet as a complex phenomenon corresponding to a sequence of classical bifurcations was studied in [6, 23,24]. Our approach gives a unifying description of the qualitative features of the rotational dynamics and the structure of the rotational multiplet with the advantage of tracing these features back to the parameters of the full molecular Hamiltonian. Another closely related paper is the recent work by Roberts and Kozin [30]. These authors use essentially the same idea and method to study a slightly different problem. They take a molecule with given concrete vibrational potential and consider how the equilibrium configuration of this molecule changes when the value of J increases.

Our method is presently restricted to the ground vibrational state where the kinetic energy of vibrations and Coriolis coupling can be neglected. It is natural, therefore, to ask whether this approach can be extended to excited vibrational states. We believe that an adiabatic generalization can be made possible by careful averaging over the vibrational degrees of freedom and we intend to consider such possibility in more detail in the future.

References

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