A CLASSICAL INSIGHT OF THE γ-CORIOLIS COUPLING IN ETHANE-LIKE MOLECULES*

C. DI LAURO, F. LATTANZI and R. AVELLINO

Dipartimento di Chimica Farmaceutica e Tossicologica, Università di Napoli
Via D. Montesano 49, I-80131 Napoli, Italy

The mechanisms of interaction between the deformations of the two moieties of ethane-like molecules in degenerate vibrational modes are investigated by simple methods of classical mechanics. Special attention is given to γ-Coriolis interaction in degenerate vibrational states, which generates first order vibration-torsion coupling.

It is shown that the level splitting due to tunneling through the torsional barrier in degenerate vibrational states is strongly affected by the value of the Coriolis ζ coefficient. Simple classical considerations can explain the recent experimental result that all degenerate normal modes of ethane form E_{1d}, E_{2d} paired representations of the $G_{36}(EM)$ molecular symmetry group.

Introduction

Ethane-like molecules consist of two identical coaxial rotors (top and frame or a and b) of threefold rotation symmetry, more or less coupled to each other.

The interaction between these two rotors basically manifests itself in two ways: i) the presence of a barrier hindering the internal rotation or torsion, and ii) the dependence of the vibrational deformations of a and b and their interactions on the internal rotation angle τ, or $\gamma = \tau/2$.

In the case of a low barrier the internal rotation is conveniently treated as an additional low frequency degree of freedom, and vibrational bands show both rotational and internal rotation structure. Moreover, degenerate vibrations can generate first order vibrational contributions to both angular momentum and internal rotation momentum. Therefore the spectra are very complex, and in fact the first rotational-torsional analysis of a high resolution band (CH_3-rocking system) of dimethylacetylene (with a barrier of 5.20 cm^{-1} in the ground vibrational state) only has been performed very recently [1].

In the case of a high or moderate barrier molecule, as ethane, the torsional motion behaves as a vibrational mode, which may have a large amplitude with the possibility of tunneling splitting. The infrared spectral features in general look much similar to those of rigid molecules, but if the tunneling splittings are resolved

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* Dedicated to Professor István Kovács on his eightieth birthday

the detailed analysis of the spectra requires the same basic theoretical methods of low-barrier molecules.

The theory of the mechanical behaviour of this class of molecules, mainly based on symmetry arguments, has been developed long before the first high resolution experimental studies. We mention here the leading papers of Hougen [2,3] and Bunker [4], mainly intended for dimethylacetylene, and the specific extension to ethane by Hougen [5].

The recent experimental high resolution results on dimethylacetylene [1] and ethane [6,7] have generated new interest in the theory, too, and especially in those aspects which depend on the peculiar mechanical properties of the specific molecules, beyond symmetry requirements [8,9]. Although all basic theoretical methods and their applications are based on symmetry and quantum mechanics, we believe that classical considerations can be helpful, too, and at least simplify the understanding of several fundamental physical concepts.

In this article we present a classical investigation of some fundamental aspects of the mechanics of ethane-like molecules and, in particular, of the so-called γ-Coriolis coupling of degenerate vibrational modes. We also discuss new results that will be treated by quantum mechanics in a forthcoming paper [9].

Three axis systems, all having a common z along the molecular skeleton rod, are defined as in previous works [8,10]. The a and b axis systems rotate about z with the molecular top and frame, respectively, and the x, y, z molecular axis system is defined in such a way that the planes zx and zy are bisectors of the dihedral angles zx_a, zx_b and zy_a, zy_b, respectively.

The z axis follows the molecule in its rotational tumbling. The molecular rotation is described with reference to x, y, z and a space-fixed axis system, as in rigid molecules. The torsional angle τ is described by the rotation about z of the a and b axis systems by γ and $-\gamma$, respectively, with $\gamma = \tau/2$. When we deal with vibrational and torsional effects in a non rotating molecule, the x, y, z axis system can be regarded as a space-fixed system.

z.-axis Coriolis coupling

The z-axis Coriolis coupling of two molecular vibrational modes consists of the energy transfer from one mode to the other by the effect of the rotation about z. Thus the two coupled modes cannot be excited independently of each other, in the presence of angular momentum about z.

Another way to look at the z-Coriolis coupling of two vibrational modes is to consider the ability of these modes, simultaneously excited, to generate angular momentum about z in the units a and b.

Here we only consider Coriolis interactions between components of degenerate vibrational modes, because these interactions can cause sensitive effects of vibration–torsion coupling which are peculiar of ethane-like molecules.

Typical cases are schematically illustrated in Fig. 1., where the displacements normal to z of corresponding atoms of top and frame in the x-oriented component

and the y-oriented component of two degenerate vibrational modes are represented by solid and dotted lines, and the arrows indicate the sense of their variation in time. If the displacements normal to z of corresponding atoms of top and frame are cis (Fig. 1a) or trans (Fig. 1b) in both the interacting vibrations, the two modes generate vibrational angular momentum about z (z-Coriolis interaction). This is most effective if the relative phases of these vibrational displacements of each atom are constant in time, that is the coupled modes have the same frequency. This is exactly the case of x-oriented and y-oriented components of the same double degenerate normal mode.
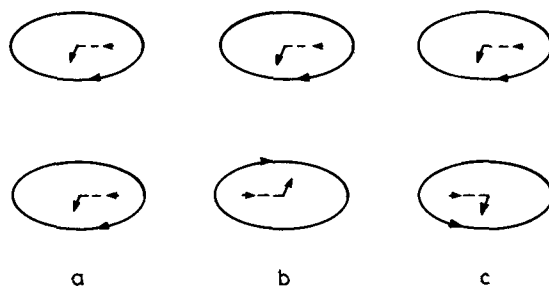

Fig. 1. Coupling of vibrational displacements in the molecular top and frame in degenerate modes. A vibrational angular momentum is generated in a) and b), whereas a vibrational internal rotation or torsional momentum is generated in c). See text

Figure 1c shows that if the displacements normal to z of corresponding atoms of top and frame are cis in one vibrational component and trans in the other one, then the vibrational angular momenta generated about z in the two molecular halves are opposite to each other, and this results in a vibrational contribution to the internal rotation or torsional momentum. This effect is called γ-Coriolis coupling [11] and implies an interaction between vibration and internal rotation. In the D_{3d} symmetry classification z-Coriolis coupling can occur between two E_u or two E_g modes, whereas γ-Coriolis coupling can occur between E_u and E_g vibrational modes.

In the case of free internal rotation one finds again that the γ-Coriolis coupling is most effective if the interacting vibrations have the same frequency. In the presence of a torsional barrier, the internal rotation generated by two vibrations of the same frequency, and then with constant dephasing, works as to wind up a spring whose torsional torque will hinder and eventually compensate for the effect of the Coriolis forces. If the interacting vibrations have not the same frequency, the vibrational torsional momentum changes periodically showing the presence of a periodic Coriolis torque. The γ-Coriolis interaction is most effective if the Coriolis and torsional torques are steadily tuned in phase.

Now the torsional torque has a frequency ν_τ and its phase changes sign with periodicity $\frac{T_\tau}{2} = \frac{1}{2\nu_\tau}$. The phase of the Coriolis torque resulting from the combination of two vibrational components is determined by their dephasing, $2\pi(\nu' - \nu'')t$,

and changes sign with periodicity Δt such that $2\pi(\nu' - \nu'')\Delta t = \pm\pi$. Therefore Coriolis and torsional torques are steadily tuned in phase if $\Delta t = \frac{T_\tau}{2}$, that is $\nu' - \nu'' = \pm\nu_\tau$.

Thus γ-Coriolis interaction is resonant if the frequencies of the coupled vibrational modes differ by ν_τ and their symmetries are E_u and E_g in D_{3d} or E' and E'' in D_{3h}. The state in which the vibration of lower frequency is excited must contain one more quantum of torsion with respect to the other one: in this way the interacting states have the same vibrational–torsional energy and symmetry.

The same results are obtained by combined symmetry and quantum mechanical considerations. Obviously the quantum mechanical treatment provides a powerful tool for quantitative evaluations, but the classical approach gives a vivid insight of the behaviour of the molecular dynamics.

Degenerate vibrations and internal rotation

In non degenerate vibrations the global displacements of groups of equivalent atoms are parallel to z in both top and frame, and do not change direction with the internal rotation. On the contrary, degenerate vibrations generate global displacements of groups of equivalent atoms with components normal to z in top and frame, whose relative orientations are affected by the internal rotation.

A consequence of this is that, contrary to non degenerate modes, the correlation of the symmetry species of the degenerate modes of ethane-like molecules from the staggered D_{3d} to the eclipsed D_{3h} conformation, through D_3, cannot be made univocally, but depends on how the relative orientation of displacements in top and frame changes with γ. This is determined by the peculiar properties of the molecule and of the specific vibration under consideration.

Degenerate deformations have a x_a-oriented component and a y_a-oriented component in the top, and similarly a x_b and a y_b component in the frame. When the two molecular moieties are fully uncoupled, so that the deformations of one molecular end are not affected by those of the other one, these components are all equivalent, and form a fourfold degenerate G_s mode of the extended molecular group $G_{36}(EM)$ [10].

The coupling of top and frame tends to generate two pairs of double degenerate modes from G_S, either E_{1d} and E_{2d} or E_{1s} and E_{2s} [5,8].

We consider first how the internal rotation can affect the relative orientation of the atomic displacements of top and frame in the case of full uncoupling of the two molecular moieties.

In each component of a degenerate mode the mass centers of all groups of equivalent atoms of a molecular moiety oscillate in a plane containing z, with given orientation in the x, y, z system at any instant. Such a plane will be called "plane of oscillation" for short. The planes of the two degenerate vibrational components in the same moiety are normal to each other, and we only need to consider one plane in each moiety in order to identify the relative orientation of the oscillation planes of top and frame.

It is in fact crucial to determine how the oscillation planes of top and frame rotate with respect to each other as a result of the internal rotation, as will be seen shortly in this article.

Uncoupled top and frame

In the case of no coupling between the two molecular halves, being the deformations of one end uncorrelated to those of the other one, the planes of oscillation of degenerate vibrations of top and frame can have any relative orientation, at any value of the torsional angle γ. However, their relative orientation can change continuously with the internal rotation.

One may think that, being top and frame independent, their oscillation planes should rotate about z with angular velocities $\dot{\gamma}$ and $-\dot{\gamma}$, just as top and frame do, and then their relative angular velocity should be $2\dot{\gamma}$. But this is not right, because we did not consider the inertial effects by which the oscillation planes should keep constant orientations in space, and then in the x, y, z system of a non-rotating molecule, just as in the pendulum. This can be explained by the effect of the Coriolis forces acting in the rotating systems of the a and b moieties [12].

However, molecular vibrations are quite different from the oscillations of a pendulum, in which the Coriolis force has full effect, because molecules can vibrate only in special modes described by their normal coordinates. The Coriolis forces are normal to the velocities of the atoms in a given vibrational mode (e.g. one component of a degenerate mode of top or frame), and only their components parallel to the displacements of the atoms in another mode (e.g. the other component of a degenerate mode of top or frame) are effective. Thus the effectiveness of the Coriolis forces is determined by the value of the Coriolis coefficient ζ [13,14].

Coriolis forces are fully effective if $\zeta = 1$, which implies perfect orthogonal atomic displacements in the two coupled vibrations. In this case the oscillation planes of top and frame do not rotate in space or in the x, y, z molecular system, and rotate with angular velocities $-\dot{\gamma}$ and $\dot{\gamma}$ in the respective a and b systems.

For $\zeta = 0$ the Coriolis forces are ineffective, and the planes of oscillation of a and b rotate with the two molecular halves (zero angular velocities in the respective top or frame axis systems, angular velocities $\dot{\gamma}$ and $-\dot{\gamma}$ in the molecular x, y, z system, relative angular velocity $2\dot{\gamma}$).

For a general value ζ of the Coriolis coefficient we find easily that the angular velocities about z of the planes of oscillations of a and b obey the following relations:

$$\omega_a^{(a)} = -\zeta\dot{\gamma} \qquad \text{in } x_a, y_a, z, \qquad (1)$$

$$\omega_b^{(b)} = \zeta\dot{\gamma} \qquad \text{in } x_b, y_b, z, \qquad (2)$$

$$\omega^{(a)} = (1-\zeta)\dot{\gamma} \qquad \text{in } x, y, z, \qquad (3)$$

$$\omega^{(b)} = -(1-\zeta)\dot{\gamma} \qquad \text{in } x, y, z, \qquad (4)$$

where the superscripts (a) and (b) denote angular velocities of the units a and b, and the subscripts a and b denote reference to the a and b axis systems.

The relative angular velocity of the oscillation planes of a and b, in any axis system, is

$$\omega^{(a)} - \omega^{(b)} = 2(1 - \zeta)\dot{\gamma}. \tag{5}$$

In fundamental vibrations ζ can assume values from -1 to 1. For negative values of ζ the planes of oscillation of top and frame rotate faster than the respective molecular moieties.

The orientations of the two components of a degenerate mode in the unit a or b are arbitrary, provided they are orthogonal to each other. A possible choice is to orient these components along x_a and y_a in the top and along x_b and y_b in the frame, with coordinates and fundamental vibrational wavefunctions $Q_{x_a}^{(a)}$, $Q_{y_a}^{(a)}$, $Q_{x_b}^{(b)}$, $Q_{y_b}^{(b)}$, and $\Psi_{x_a}^{(a)}$, $\Psi_{y_a}^{(a)}$, $\Psi_{x_b}^{(b)}$, $\Psi_{y_b}^{(b)}$. These vibrational coordinates and wavefunctions rotate with the molecular top and frame, with angular velocities $\dot{\gamma}$ and $-\dot{\gamma}$ in the x, y, z system. Henceforth they will be referred to as G_s vibrational coordinates and wavefunctions, being all partners of a fourfold degenerate representation of this symmetry in $G_{36}(EM)$.

We also can use components with different orientations, even depending on γ, by projecting the G_s-components belonging to a and b on other planes passing through z. If these planes rotate about z in the respective a or b axis systems, these projections will be γ-dependent.

The treatment of degenerate vibrational modes being easier with circular components, we define the circular G_s coordinates and wavefunctions

$$Q_{a\pm}^{(a)} = Q_{x_a}^{(a)} \pm iQ_{y_a}^{(a)},$$
$$Q_{b\pm}^{(b)} = Q_{x_b}^{(b)} \pm iQ_{y_b}^{(b)}, \tag{6}$$

$$\Psi_{a\pm}^{(a)} = \frac{1}{\sqrt{2}}(\Psi_{x_a}^{(a)} \pm i\Psi_{y_a}^{(a)}),$$
$$\Psi_{b\pm}^{(b)} = \frac{1}{\sqrt{2}}(\Psi_{x_b}^{(b)} \pm i\Psi_{y_b}^{(b)}). \tag{7}$$

Circular vibrational wavefunctions of a and b on planes that rotate with angular velocities $\omega^{(a)}$ and $\omega^{(b)}$ in the molecular x, y, z axis system are

$$\Psi_{\pm}^{(a,\omega^{(a)})} = e^{\pm i(\gamma-\omega^{(a)}t)}\Psi_{a\pm}^{(a)},$$
$$\Psi_{\pm}^{(b,\omega^{(b)})} = e^{\mp i(\gamma+\omega^{(b)}t)}\Psi_{b\pm}^{(b)}, \tag{8}$$

and similarly for vibrational coordinates.

Obviously, if $\omega_a^{(a)} = \dot{\gamma}$ and $\omega_b^{(b)} = -\dot{\gamma}$ the (8) give the G_s wavefunctions.

γ-Corio*less* planes and axes

We have shown in the previous Section that the components of degenerate vibrations actually can occur in planes of top and frame which rotate with angular velocities given in Eqs (1–5).

We are tempted to call these planes γ-Corio*less* planes. This may sound as a joke, but surely helps to remember that the Coriolis forces generated by the internal rotation have no effect on the components of degenerate vibrations oriented in these planes. Similarly, γ-Corio*less* axis systems are the axis systems of top and frame whose components normal to z are in the respective γ-Corio*less* planes.

The circular components of degenerate vibrational wavefunctions in these planes can be obtained from the Eqs (3–4) and (8):

$$\Psi_{\pm}^{(a)}(Cl) = e^{\pm i\zeta\gamma}\Psi_{a\pm}^{(a)},$$
$$\Psi_{\pm}^{(b)}(Cl) = e^{\mp i\zeta\gamma}\Psi_{b\pm}^{(b)}, \tag{9}$$

and similarly for vibrational coordinates.

For $\zeta = 0$ the axis systems of top and frame are γ-Corio*less* systems, as the planes of oscillations rotate with top and frame. For $\zeta = 1$ the γ-Corio*less* axis systems coincide with the molecular system x, y, z for both top and frame. This system does not rotate with γ, as can be seen in Eq. (3,4).

In overtones and combinations with the excitation of more than one quantum in the degenerate vibrations the value of ζ must be replaced by ζ_{eff}^i, whose absolute value also can be larger than 1: In this case, however, we must refer to the "planes of oscillation" of the wavefunctions, which are no longer the same as those of normal coordinates.

According to Eq. (5), in the case of uncoupled top and frame the value of ζ (or of ζ_{eff}^i) determines the relative angular velocity of the planes of oscillation of the two molecular moieties, but this does not require their dihedral angle to assume any particular value at any torsional conformation.

End-to-end coupling

When the end-to-end coupling is effective, the vibrational deformations of top and frame are no longer independent. Thus the degenerate vibrational coordinates or wavefunctions are conveniently expressed by linear combinations of the factors (9) of the two units, with γ-dependent coefficients:

$$\Psi_{E_1\pm} = \frac{1}{\sqrt{2}}(e^{\pm i\zeta\gamma}\Psi_{a\pm}^{(a)} + e^{\mp i\zeta\gamma}\Psi_{b\pm}^{(b)}),$$
$$\Psi_{E_2\pm} = \frac{1}{\sqrt{2}}(e^{\pm i\zeta\gamma}\Psi_{a\pm}^{(a)} - e^{\mp i\zeta\gamma}\Psi_{b\pm}^{(b)}), \tag{10}$$

and similarly for vibrational coordinates.

These are vibrational wavefunctions and coordinates of the whole molecule, contrary to G_s wavefunctions and coordinates whose components belong either to the top or to the frame. In particular, in the case of coupled top and frame degenerate vibrational coordinates and wavefunctions must span a degenerate symmetry of the point group D_{3h} (E′ or E″) and of D_{3d} (E_u or E_g) when the molecule assumes the eclipsed and staggered conformations.

Now the degenerate vibrational deformations of top and frame are "cis" in E_u and E′ and "trans" in E_g and E″, leading to four different possibilities. Coordinates which are E_{1d} in the molecular symmetry group $G_{36}(EM)$ correlate with E_u in D_{3d} and E′ in D_{3h}, and always have "cis" displacements in the two units, whereas E_{2d} coordinates correlate with E_g in D_{3d} and E″ in D_{3h}, always with "trans" displacements. Therefore, in these cases the planes of oscillation of top and frame have constant relative angular orientations, either 0 or π degrees, and correspond to the expressions (10) with $\zeta = 1$ (see also (5)). E_{1s} coordinates are "trans" (E_g) in D_{3d} and "cis" (E′) in D_{3h}, and E_{2s} coordinates behave just the opposite. In these cases the relative angular orientation of the planes of oscillation of top and frame changes by π when γ changes by $\pi/6$, at a rate $6\dot{\gamma}$ which corresponds to $\zeta = -2$ in (5) and (10).

Therefore the possible coupled wavefunctions (and coordinates), alternative to the fourfold G_s components, are:

$$\Psi_{E_{1d}\pm} = \frac{1}{\sqrt{2}}(e^{\pm i\gamma}\Psi_{a\pm}^{(a)} + e^{\mp i\gamma}\Psi_{b\pm}^{(b)}),$$

$$\Psi_{E_{2d}\pm} = \frac{1}{\sqrt{2}}(e^{\pm i\gamma}\Psi_{a\pm}^{(a)} - e^{\mp i\gamma}\Psi_{b\pm}^{(b)}), \tag{11}$$

$$\Psi_{E_{1s}\pm} = \frac{1}{\sqrt{2}}(e^{\mp i2\gamma}\Psi_{a\pm}^{(a)} + e^{\pm 2i\gamma}\Psi_{b\pm}^{(b)}),$$

$$\Psi_{E_{2s}\pm} = \frac{1}{\sqrt{2}}(e^{\mp i2\gamma}\Psi_{a\pm}^{(a)} - e^{\pm 2i\gamma}\Psi_{b\pm}^{(b)}), \tag{12}$$

and similar expressions for coordinates.

We recall that the value of ζ can range from -1 to 1 if only one quantum of the degenerate vibrational modes is excited. Values of ζ out of this range can occur with a multiple excitation of degenerate vibrational quanta. Vibrational normal coordinates and wavefunctions must have the same symmetry only in fundamentals. Pure E_d vibrational fundamental states, with $\zeta = 1$, generate overtones with $\zeta_{\text{eff}}^i = -2$, which are pure E_s vibrational states: However, both these fundamental and overtone states are based on E_d normal coordinates. Therefore, in general, it will be safer to talk of symmetry of degenerate vibrational functions, instead of normal coordinates, and of ζ_{eff}^i instead of ζ.

In degenerate vibrational states of ethane-like molecules the problem exists whether a G_s, or E_{1d}, E_{2d}, or E_{1s}, E_{2s} set provides the best approach to the vibrational mechanics. This problem has a clear cut solution only in relation to

"unpaired" degenerate vibrational modes, such as the C-Me-C skeletal bending of H_3C-Me-CH_3 molecules, with Me=Zn, Cd, Hg, whose wavefunctions are conveniently written in terms of E_{1d} normal coordinates.

In the other cases knowledge of the form and magnitudes of the end-to-end coupling energy terms is required, but also the value of ζ (or ζ^i_{eff}) has an important effect, which often is determinant.

Low-barrier molecules

In low-barrier molecules the internal rotation is almost free, and its kinetic energy tends to uncouple top and frame through the γ-Coriolis interaction of E_1 and E_2 vibrational states. Since a low-barrier also implies a weak potential coupling of the deformations of top and frame, the two molecular halves are easily uncoupled, leading to G_s vibrational states. The only exception occurs when the deformations of top and frame in a given vibrational coordinate have at the least one common atom, as in the skeletal bending of dimethylacetylene. In this case the a and b components of the vibrational mode are strongly coupled by kinetic energy terms, leading to E_{1d}, E_{2d} normal coordinates and vibrational wavefunctions consistent with them [8]. In fact all the fundamental vibrational systems of dimethylacetylene are G_s, except the skeletal bending system which is E_{1d}, E_{2d}.

In H_3C-Me-CH_3 compounds we can predict that the CH_3 rocking, being the Me atom common to the rocking coordinates of both units, forms a E_{1d}, E_{2d} system. All other degenerate fundamentals are expected to be G_s, with the exception of the "unpaired" C-Me-C bending, which is E_{1d}.

Moderate barrier: ethane

We define "moderate" a barrier hindering the internal rotation to the extent that the torsion behaves as a vibrational mode, but not so high to prevent "barrier tunneling", with the related torsional level splitting. This is the case of ethane.

With a moderate barrier the molecule is trapped in a torsional potential well, and if it can get over the barrier, it it trapped again in another well. In this situation top and frame cannot be effectively uncoupled by the kinetic energy of the torsional motion, and coupled double degenerate E-normal modes must occur. Whether they will give E_d or E_s vibrational states depends on the values of the different end-to-end coupling terms and on the value of ζ^i_{eff}. A value of ζ^i_{eff} close to 1 favours E_{1d}, E_{2d} states while a value close to -2 favours E_{1s}, E_{2s} states. In fundamental states, or in general in states where only one quantum is excited in the degenerate vibrational modes, $|\zeta|$ cannot exceed 1. Thus E_d or E_s modes are favoured, depending on whether ζ is larger or smaller than -0.5.

E_d and E_s vibrational states simply differ by the inversion of the order of the tunneling split vibro-torsional components [5], the order in $E_{2s}(E_{1s})$ vibrational levels being just the inverse of that in $E_{1d}(E_{2d})$ vibrational levels, when the torsional

potential energy is a minimum at the staggered conformations. Therefore, as an E_{1d}, E_{2d} system transforms towards an E_{2s}, E_{1s} system the splitting typical of the E_d system must decrease and pass through zero, before inverting to that which is appropriate for an E_s system. Thus, for given values of the end-to-end coupling terms, the torsional splitting is like to achieve the maximum values in pure E_d or E_s vibrational states, whereas the smallest value is like to occur in between, that is near $\zeta_{eff}^i = -0.5$.

In the CH_3 rocking system of ethane the estimated values of ζ in the two E-components are 0.26 and 0.41 [15], which favours E_{1d}, E_{2d} vibrational states. Moreover, the CH_3 rocking of top and frame in common both carbon atoms, which generates a strong kinetic energy coupling term which favours again E_{1d}, E_{2d} vibrational states [8].

In the CH_3 stretching system the estimated values of ζ are 0.02 and 0.20 [15], which again is in favour of an E_{1d}, E_{2d} vibrational system.

The values of ζ in the CH_3 deformation bands are estimated by Duncan et al, -0.30 and -0.34 [15], still larger than -0.5, but a tiny amount. The harmonized vibrational frequencies of the two E-components differ by a few wavenumbers [15], showing that the end-to-end coupling terms are presumably very small [8]. Therefore it is unlike that the end-to-end coupling contains any large term, and in particular a large term that would favour E_{1s}, E_{2s} vibrational fundamentals, and we conclude that also this system has to be E_{1d}, E_{2d}.

Thus the simple theory presented in this article, based on classical considerations, allows one to conclude that all the degenerate vibrational fundamentals of ethane, and then the related normal coordinates, form E_{1d}, E_{2d} systems. This is consistent with the experimental results of [7], obtained by the detailed analysis of the tunneling splitting in the rotational structure of numerous degenerate vibrational bands.

We recall here that Susskind [16] remarked that the observed tunneling splitting in the $\nu_4 + \nu_{11}$ combination of ethane (a combination with one quantum of a CH_3 deformation and one quantum of torsion) was smaller than that in the $\nu_4 + \nu_{12}$ combination (one quantum of torsion plus one quantum of a CH_3 rocking). He assumed that this required the torsional barrier to be larger in a state with one quantum of ν_{11} excited than in a state with one quantum of ν_{12} excited, which was in disagreement with the theoretical predictions of Kirtman et al [17]. This is not necessarily true, because the relatively small torsional splitting in $\nu_4 + \nu_{11}$ does not necessarily imply an increase of the barrier height when ν_{11} is excited. Rather, it can be very well explained by the fact that the value of ζ_{11} is not far from -0.5, the value where the torsional splitting is like to approach zero before inverting its sign to that appropriate to an E_{2s}, E_{1s} system.

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