Perturbation Treatment of Doublet Splittings in Rotational Spectra of Molecules with Two Equivalent Conformations Separated by Nonequivalent Energy Barriers

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A method is described for analyzing doublet splittings in rotational spectra caused by tunneling between two equivalent conformations, under the restriction that the tunneling motion be effectively aperiodic. The splittings can mainly be fitted with three parameters: the purely torsional doublet splitting ΔE and two Euler angles β and γ, which characterize the transformation between the principal-axis system and the Eckart-axis system. The method is numerically very fast when the splittings are small enough to allow the use of perturbation theory. Examples are given to show that a simple correlation between β and γ with the path of the tunneling process is possible.

INTRODUCTION

Molecules with internal rotations around single bonds frequently have several equivalent minima in the potential energy. This may result in observable line splittings in the rotational spectrum; a well-known example is the occurrence of $A-E$ doublet splittings caused by the internal rotation of a methyl group, where three equivalent potential energy minima exist. In this paper we shall consider a somewhat less well known case, where the internal rotor has two equivalent minima in the potential energy, separated by nonequivalent barriers.

Figure 1 shows our definition of the dihedral angle ϕ, chosen so that $\phi = 0°$ corresponds to a maximum in the potential energy. The simplest example is a molecule with a C_s rotor attached to a C_s frame with two equivalent *gauche* conformations at $\phi_e \approx 60°$. Often there is another, nonequivalent, potential energy minimum at $\phi = 180°$, but in other cases this might be a maximum or the nature of the potential energy in that region might be unknown.

As shown in Fig. 1, the energy levels which correspond to the *gauche* conformations are split into doublets with energy separation $h\Delta E$, corresponding to torsional wavefunctions which are symmetric (T^+) and antisymmetric (T^-) in ϕ. Hirota (*1*) has pointed out that for the case cited above two electric dipole moment components are even functions of ϕ, so that the allowed transitions are $T^+ \leftrightarrow T^+$ and $T^- \leftrightarrow T^-$. In the rotational spectrum the transitions whose intensity depends on these two dipole moment components will exhibit only a small doublet splitting. On the other hand, the third dipole moment is an odd function of ϕ, so only $T^+ \leftrightarrow T^-$ transitions will be allowed and the splittings in the corresponding rotational transitions will be approximately $2\Delta E$.
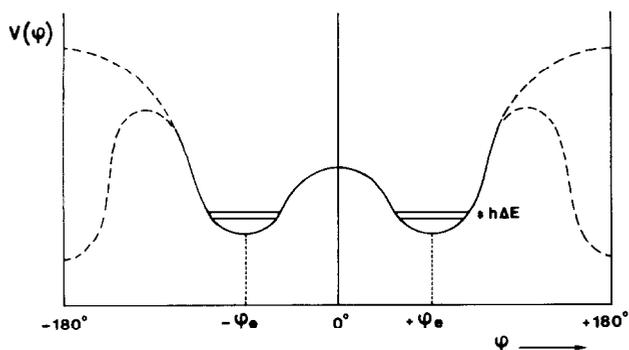
FIG. 1. Potential energy $V(\phi)$ as function of the dihedral angle ϕ, showing doublet splitting $h\Delta E$ and equilibrium angles $\pm\phi_e$. Two possibilities for $V(\phi = \pm 180°)$ are given.

A recent monograph (2) surveys the molecules that have been found to exhibit this behavior. For OH– and SH– tops (3–11) the spectra are relatively well explained by the simple theory described above, the splittings in the "non-inverting" transitions being only a few percent of the splittings in the "inverting" transitions. When the top is heavier than just one hydrogen atom (1, 12–18) the splittings are considerably smaller, and they can often only be observed in excited torsional states. Moreover, the doublet splittings of the "noninverting" transitions are no longer negligible with respect to ΔE. We have recently investigated two molecules (difluoroacetic acid and cis-2-pentene), where the splittings in the two types of transitions are of comparable magnitudes, and it was this observation that prompted the work reported in this paper.

The general theory to account for the splittings has been given by Quade and Lin (19), who specified it for threefold barriers as encountered in molecules with a partly deuterated methyl group. Meakin et al. (13) extended the theory to the more general case where each Fourier term of the potential energy function $V(\phi)$ may contribute. The effective Hamiltonian matrix for the rotational levels belonging to the T^+ and T^- doublet states has nonzero elements $\langle TJKM|H|T'JK'M\rangle$; it can be divided into four subblocks:

$$\begin{pmatrix} \langle JKM|H^{++}|JK'M\rangle & \langle JKM|H^{+-}|JK'M\rangle \\ \langle JKM|H^{-+}|JK'M\rangle & \langle JKM|H^{--}|JK'M\rangle \end{pmatrix}. \tag{1}$$

The effective operators appearing here can be expressed in ΔE and the components of the angular momentum operator in the molecule-fixed axis system, P_g ($g = x, y, z$):

$$H^{\pm\pm} = h\{\sum_g R^{\pm}_{gg}P^2_g + R^{\pm}_{xy}(P_xP_y + P_yP_x) \mp (1/2)\Delta E\}, \tag{2}$$

$$H^{+-} = h\{R_{yz}(P_yP_z + P_zP_y) + R_{xz}(P_xP_z + P_zP_x) + iG_xP_x + iG_yP_y\}, \tag{3}$$

when z is chosen to be the unique axis. In Refs. (13) and (19) the orientation of

the axis system is fixed to a fragment of the molecule, so that large torsion–rotation interactions exist even in the limit where the barrier is so high that the splittings vanish. It is preferable to use an instantaneous principal-axis system, so that the terms in $R_{gg'}$ are minimized for $g \neq g'$ (6, 10).

Both methods have been used successfully to interpret many of the spectra cited above, but a few drawbacks remain:

(i) The calculations tend to become lengthy for high values of J, as large matrices have to be diagonalized.

(ii) It is not an easy matter to relate the parameters in Eqs. (2) and (3) to a model that describes the mechanics of the tunneling process. The parameters will depend strongly on the barrier height; one consequence is that they may change dramatically upon isotopic substitution or change of torsional state.

In this paper an approach will be described which, at a slight loss of generality, largely eliminates these drawbacks.

HAMILTONIAN

Our Hamiltonian is based on the treatment by Pickett (20), who showed that for one aperiodic coordinate (in our case the torsional angle ϕ) it is possible to eliminate the interaction terms in the Hamiltonian between this coordinate and the overall rotation of the molecule. In practice this means that we must use the Eckart system for the torsion. Dreizler and co-workers (21, 22) have used the same approach for other vibrations of large amplitude.

This shows at once the limitation of our treatment: ϕ should be effectively aperiodic, and therefore the tunneling through $\phi = 180°$ should be negligible with respect to the tunneling through $\phi = 0°$. (Or vice versa, in which case the origin can be shifted by 180°.) The problem is then to a large extent mathematically comparable to the more familiar case of inversion or ring puckering. For levels which are well below the barrier at $\phi = 0°$ this limitation does not seem to be severe, since doublet splittings decrease very quickly with increasing barrier height and it is improbable that two nonequivalent barriers should produce splittings of comparable magnitudes. However, molecules with too much symmetry (e.g., phenol) or with more than one internal motion of large amplitude are excluded.

The coordinate system (x,y,z) is defined primarily at $\phi = 0°$, where it is equivalent to the principal-axis system (a,b,c) with the understanding that z is the unique axis. (Usually z will be perpendicular to a plane of symmetry, but in exceptional cases z might coincide with a twofold axis.) Upon internal rotation the axis system (x,y,z) does not remain a principal-axis system, but it is defined by the Eckart requirements,

$$\sum_i m_i \mathbf{r}_i = 0, \tag{4}$$

$$\sum_i m_i \mathbf{r}_i \times \frac{\partial \mathbf{r}_i}{\partial \phi} = 0, \tag{5}$$

where the summations are over all the atoms in the molecule.

In this system the parameters $R_{gg'}^{\pm}$ of Eq. (2) can be directly related to the inverse of the instantaneous inertial moment tensor I,

$$R_{gg'}^{\pm} = \frac{h}{8\pi^2}\langle T^{\pm}|I_{gg'}^{-1}|T^{\pm}\rangle \qquad (gg' = xx, yy, zz, xy), \tag{6}$$

whereas in Eq. (3) $G_x = 0$, $G_y = 0$, and

$$R_{gg'} = \frac{h}{8\pi^2}\langle T^{+}|I_{gg'}^{-1}|T^{-}\rangle \qquad (gg' = xz, yz). \tag{7}$$

Without loss of generality the wavefunctions $|T^{+}\rangle$ and $|T^{-}\rangle$ can be taken to be real.

To gain more insight in the physical meaning of $R_{gg'}^{\pm}$ and $R_{gg'}$, we start by defining the localized function

$$|L\rangle = \frac{1}{2^{1/2}}|T^{+}\rangle + \frac{1}{2^{1/2}}|T^{-}\rangle, \tag{8}$$

which is only significantly different from zero near one of the two equivalent potential energy minima of Fig. 1. The matrix elements of Eqs. (6) and (7) can now be redefined as

$$R_{gg'}^{\pm} = R_{gg'} \pm (1/2)\Delta R_{gg'} \qquad (gg' = xx, yy, zz, xy), \tag{9}$$

$$R_{gg'} = \frac{h}{8\pi^2}\langle L|I_{gg'}^{-1}|L\rangle \qquad \text{(every } gg'\text{)}, \tag{10}$$

with

$$\Delta R_{gg'} = \frac{h}{8\pi^2}\{\langle T^{+}|I_{gg'}^{-1}|T^{+}\rangle - \langle T^{-}|I_{gg'}^{-1}|T^{-}\rangle\}. \tag{11}$$

It should be noted that $R_{gg'}$ is just the expectation value of the corresponding quantity in a localized, noninverting, *gauche* molecule. For the levels that we are interested in, $\Delta R_{gg'}$ should be some orders of magnitude smaller than $R_{gg'}$.

From the properties of the matrix elements $\langle JKM|P_g P_{g'}|JK'M\rangle$ it follows that the nonzero matrix elements $\langle TJKM|H|T'JK'M\rangle$ must satisfy $K' - K = 0$, ± 2 for $T = T'$ [Eq. (6)], or $K' - K = \pm 1$ for $T \neq T'$ [Eq. (7)]. Therefore the Hamiltonian is blockdiagonal in the following two subblocks:

$$\begin{array}{llll} \text{I:} & K^{\text{even}}, T^{+} & \text{and} & K^{\text{odd}}, T^{-}, \\ \text{II:} & K^{\text{even}}, T^{-} & \text{and} & K^{\text{odd}}, T^{+}. \end{array}$$

This factorization is not lost in cases where the linear terms in $G_x P_x$ and $G_y P_y$ should be retained, as can be verified by inspection of the symmetry properties of the corresponding matrix elements or from group theoretical considerations (23).

Combining Eqs. (1)–(3) with (9) and (10) it is found that the Hamiltonians for the two subblocks can be written as

$$H_{\text{I}} = H^{(0)} + H^{(1)},$$
$$H_{\text{II}} = H^{(0)} - H^{(1)}, \tag{12}$$

where

$$\langle JKM|H^{(0)}|JK'M\rangle = h \sum_g \sum_{g'} R_{gg'}\langle JKM|P_g P_{g'}|JK'M\rangle \qquad (13)$$

and

$$\langle JKM|H^{(1)}|JK'M\rangle$$

$$= (1/2)h(-1)^K\{-\Delta E\delta_{KK'} + {\sum_g}' {\sum_{g'}}' \Delta R_{gg'}\langle JKM|P_g P_{g'}|JK'M\rangle\}. \qquad (14)$$

The $\sum'$ in Eq. (14) means that the summation is only over $gg' = xx, yy, zz, xy, yx$. It should be noted that for an infinitely high barrier $\Delta E = 0$ and $\Delta R_{gg'} = 0$; the Hamiltonian is then reduced to Eq. (13), which is the same as for a molecule which is permanently in one semirigid *gauche* conformation.

SELECTION RULES AND DOUBLET SPLITTINGS

The selection rules are easily derived by combining the torsional and the rotational selection rules:

Dipole moment component	Allowed transitions
μ_x, μ_y	$K^{\text{even}} \leftrightarrow K^{\text{odd}}$
μ_z	$K^{\text{even}} \leftrightarrow K^{\text{even}}$, $\qquad K^{\text{odd}} \leftrightarrow K^{\text{odd}}$
$\mu_g(\phi)$ odd	$T^+ \leftrightarrow T^-$
$\mu_g(\phi)$ even	$T^+ \leftrightarrow T^+$, $\qquad T^- \leftrightarrow T^-$

We can consider two possibilities:

Case A: The molecule has a plane of symmetry at $\phi = 0°$, so that μ_z is odd, μ_x and μ_y are even. Only transitions from block I to block II and vice versa are allowed.

Case B: The molecule has a twofold axis at $\phi = 0°$, so that μ_z is even, μ_x and μ_y are odd. Only transitions within each subblock are allowed.

Case A is the one which is commonly encountered; the two *gauche* conformations are mirror images of each other. Case B, where the two conformations are identical, is very rare but has been recently encountered in ethylene diamine (*24*).

As suggested by the form of Eq. (12), the doublet splittings are best calculated by perturbation theory. To the first order the unperturbed levels are found from the observed average doublet frequencies, which can be processed to obtain rotational constants and wavefunctions in the principal-axis system (a,b,c) with the usual methods for a semirigid rotor with centrifugal distortion. On the other hand, Eq. (13) shows that the rotational constants should also be obtained by diagonalizing the matrix R as defined in Eq. (10),

$$RU = UD, \qquad (15)$$

where the diagonal matrix D contains the rotational constants, and U is the matrix which transforms the three components of a vector from the (a,b,c)

system to the (x,y,z) system. Note that $R = D$ only at $\phi = 0°$ and not at $\phi = 180°$ or multiples thereof.

The rotational wavefunctions $|J\tau M\rangle$ can be expanded in symmetric rotor functions $|JKM\rangle$; the expansion coefficients are denoted by $p_{\tau K}^{(J)}$ and $q_{\tau K}^{(J)}$ in the (x,y,z) and (a,b,c) systems, respectively. The transformation between the two sets of coefficients is given by the formula (25)

$$p_{\tau K}^{(J)} = e^{iK\alpha} \sum_{K'} q_{\tau K'}^{(J)} d_{KK'}^{(J)}(\beta) e^{iK'\gamma}, \tag{16}$$

where α, β, and γ are Euler angles related to the matrix U; $d_{KK'}^{(J)}$ can be calculated with aid of formulas given in Ref. (25). Some care has to be taken in the definition of the Euler angles, as the angular momentum matrix elements are chosen by various authors in different ways. We have adhered to the conventions commonly used in microwave spectroscopy (26), and have found that Eq. (16) is then applicable when the Euler angles are defined by

$$\cos \beta = U_{z3},$$

$$\sin \alpha = U_{x3}/\sin \beta, \qquad \cos \alpha = -U_{y3}/\sin \beta,$$

$$\sin \gamma = U_{z1}/\sin \beta, \qquad \cos \gamma = U_{z2}/\sin \beta, \tag{17}$$

where $(1,2,3)$ are to be identified with (a,b,c) in such a way that $(1,2,3)$ $= (x,y,z)$ for $\phi = 0°$.

On the basis of the rotational wavefunctions $|J\tau M\rangle$ the matrix $H^{(0)}$ is diagonal; the matrix elements of the perturbation term $H^{(1)}$ are given by

$$\langle J\tau M|H^{(1)}|J\tau'M\rangle = \sum_{K} \sum_{K'} p_{\tau K}^{(J)*} p_{\tau'K'}^{(J)} \langle JKM|H^{(1)}|JK'M\rangle \tag{18}$$

and the first-order shift $h\Delta\nu_\tau$ in the energy level τ is just the diagonal element. The doublet splitting is $2\Delta\nu_\tau$, as seen from Eq. (12).

It may happen that the shift $h\Delta\nu_\tau$ is not small with respect to the energy difference between level τ and one or more other levels τ'. In this case it is necessary to use second-order perturbation theory or, in extreme cases such as K degeneracy, direct diagonalization of the τ, τ' block. Now the shifts in the two subblocks I and II will no longer be equal in absolute magnitude, and a correction must be applied to the mean frequency that was used in the determination of the rotation constants and wavefunctions. For large second-order effects this requires an iterative treatment of the data, and it may then be preferable to fit all parameters simultaneously by direct diagonalization of the Hamiltonian.

From Eqs. (18), (16), and (14) it is seen that the doublet splittings depend on α, β, γ, ΔE, and four $\Delta R_{gg'}$ constants. However, these parameters are not independent: if we had initially rotated the (x,y,z) system at $\phi = 0°$ through a certain angle about the z axis Eqs. (13) and (14) would remain valid. Such a rotation corresponds to a change in α, ΔR_{xx}, ΔR_{yy}, and ΔR_{xy}. Therefore only seven parameters can be determined, of which β, γ, and ΔE are the most important: α may be chosen at will and the four $\Delta R_{gg'}$ contribute relatively little to the doublet splittings.

It can be verified from the symmetry properties of the matrix elements $U_{gg'}$ or $d_{Kk'}^{(J)}(\beta)$ that the results of the calculation are invariant with respect to the operations

$$\beta \rightarrow -\beta,$$

$$\beta \rightarrow 180° - \beta, \qquad \gamma \rightarrow -\gamma,$$

$$\gamma \rightarrow 180° + \gamma,$$

$$\gamma \rightarrow -\gamma, \qquad \alpha \rightarrow -\alpha, \qquad R_{xy} \rightarrow -R_{xy},$$

$$\alpha \rightarrow 180° + \alpha. \tag{19}$$

Therefore the quadrants of β and γ cannot be determined, and we might arbitrarily require these angles to be between 0 and 90°.

MODEL CALCULATIONS

The values of β and γ as determined from the spectrum can be compared with results from a model calculation. A unit vector $\boldsymbol{\lambda}$, passing through a point with coordinates $\mathbf{r}_0$, represents the axis of internal rotation, and a set of vectors $\mathbf{p}_i$ is defined as

$$\mathbf{p}_i = 0 \qquad \text{(frame atoms)},$$

$$\mathbf{p}_i = \boldsymbol{\lambda} \times (\mathbf{r}_i - \mathbf{r}_0) \qquad \text{(top atoms)}. \tag{20}$$

The displacement of an atom i is now found from

$$\Delta \mathbf{r}_i = \left\{ \mathbf{p}_i - \frac{1}{M} \sum_j m_j \mathbf{p}_j - [\mathbf{s} \times \mathbf{r}_i] \right\} \Delta \phi, \tag{21}$$

where

$$s_g = \sum_{g'} I_{gg'}^{-1} \sum_j m_j [\mathbf{r}_j \times \mathbf{p}_j]_{g'} \tag{22}$$

thus ensuring that the Eckart conditions (4) and (5) are satisfied. After the atoms are shifted by the infinitesimal amount $\Delta \mathbf{r}_i$ the calculations have to be repeated, since all quantities in Eqs. (20)–(22) have changed. A numerical treatment with $\Delta \phi = 1°$ was found to be satisfactory, provided that care is taken not to deform the molecule by the successive operations (21) which are only equivalent to a true internal rotation in the limit $\Delta \phi = 0°$.

When the calculation is started at $\phi = 0°$ the matrices I and U, and hence the Euler angles α, β, and γ, are easily found as functions of ϕ. Apart from the ambiguities introduced by Eq. (19), a comparison with the observed β and γ should be possible at $\phi = \phi_e$, although some discrepancies are to be expected. One reason is that the expectation value of $I_{gg'}^{-1}$ [Eq. (10)] should have been taken instead of just the value at $\phi = \phi_e$, another that we have implicitly made the assumption that ϕ is the only molecular parameter which changes upon internal rotation. Still, it should be possible to determine, for instance, whether the tunneling occurs through the *trans* or the *cis* barrier.

In contrast to β and γ, a knowledge of the potential energy $V(\phi)$ is necessary to calculate the parameters ΔE and $\Delta R_{gg'}$. Since the torsional energy levels

are independent of the overall rotation of the molecule there is no need to calculate them in the aperiodic Eckart-like axis system used so far, and we can find ΔE by subtracting the appropriate eigenvalues of the usual torsional Hamiltonian

$$H_T = -h \, \frac{\partial}{\partial\phi} \, F(\phi) \, \frac{\partial}{\partial\phi} \, + \, V(\phi) \, + \, V'(\phi), \tag{23}$$

where $V'(\phi)$ is the pseudopotential defined in Ref. (20), and where

$$F(\phi) = \frac{h}{8\pi^2} \left\{ \sum_i m_i \left(\frac{\partial \mathbf{r}_i}{\partial\phi} \right)^2 \right\}^{-1}, \tag{24}$$

which may be found from Eq. (21) since it is independent of the axis system (20). The eigenvectors of Eq. (23) can be used to calculate the four $\Delta R_{gg'}$ parameters according to Eq. (11). This equation shows that it is the *change* in $I_{gg'}^{-1}$ with ϕ that determines the value of $\Delta R_{gg'}$, so there is no reason to neglect ΔR_{xy} with respect to the other three parameters as one might intuitively be inclined to do. It should be noted that $I_{gg'}^{-1}$ is not a periodic function of ϕ, and therefore only the interval between $\phi = -180°$ and $\phi = +180°$ must be used; besides, the wavefunctions should be essentially zero at $\phi = \pm 180°$. This is, of course, equivalent to the condition that the only significant tunneling occurs at $\phi = 0°$.

When the results for two torsional states are compared, β and γ should remain essentially the same whereas ΔE and $\Delta R_{gg'}$ are to be multiplied by a considerable factor. Some experience suggests that this factor is approximately the same for each of these five parameters.

APPLICATIONS

The theory discussed above has been implemented in three ALGOL-60 programs. The first performs the geometrical model calculations, which yield $F(\phi)$, $I_{gg'}^{-1}(\phi)$, and $U(\phi)$. The second program uses experimental values of rotational constants and centrifugal distortion constants to calculate the coefficients $q_{\tau K}^{(J)}$, which are then stored in the background memory of the computer. Finally, the main program performs the calculations indicated in Eqs. (16) and (18), and adjusts the seven parameters β, γ, ΔE, and $\Delta R_{gg'}$ to the observed doublet splittings by the least-squares method.

The Euler angle α is treated as a fixed-input parameter. When it is desired to compare the four values of $\Delta R_{gg'}$ with results from a model calculation it is convenient to set α equal to the value found from the model, although from a computational view the simple choice $\alpha = 0°$ would be preferable. It should perhaps be repeated here that the choice of α does not affect β, γ, and ΔE. Another point of interest is that γ is difficult to determine when β is small, as can be seen from the properties of the Euler angles.

Examples from the literature and from our own laboratory are given in Table I. As stated above, it was found that β, γ, and ΔE are sufficient to explain the main features of the spectra; only when a large variety of transitions is measured can the four $\Delta R_{gg'}$ parameters be determined with significant reliability. In the literature quite a few unsplit lines are reported; the calcula-

TABLE I

Fitting of the Parameters to Observed Spectra with Doublet Splittings and Comparison with Model Calculations

Substance	1-butene	allyl amine	3-fluoropropene	ethylene diamine	propanal	difluoroacetic acid	cis-2-pentene
Formula	$CH_2=CHC_2H_5$	$CH_2=CHCH_2NH_2$	$CH_2=CHCH_2F$	$NH_2CH_2CH_2NH_2$	CH_3CH_2CHO	CHF_2COOH	$CH_3CH=CHC_2H_5$
Remarks		Conf. NGLT		Conf. I.			
Reference	12	15	1, 13	24	14	27	28
Unique axis	c	c	c	b	c	c	c
Case	A	A	A	B	A	A	A
T	2	3	2	0	0	2	2
ϕ_e	60.1 ± 0.3°	60°	53 ± 3°	63 ± 2°	55°	62 ± 2°	61.5 ± 3°
N	23	16	13	26	10	33	41
J_{max}	15	16	9	58	5	33	28
ΔR_{gg}, fitted	no	no	no	yes	no	yes	yes
β	20.0 ± 0.3°	22.7 ± 0.2°	7.3 ± 0.2°	2.5 ± 1.5°	8.0 ± 0.8°	48.4 ± 0.1°	24.9 ± 0.1°
γ	-	-	-	-	-	3.7 ± 0.1°	3.5 ± 0.1°
ΔE (MHz)	5.35 ± 0.03	36.0 ± 0.1	185.7 ± 0.2	86.4 ± 0.1	472 ± 5	27.7 ± 0.4	28.6 ± 0.1
s (MHz)	0.12	0.35	0.70	0.30	1.05	0.33	0.06
β (model)	8.9°	7.9°	2.5°	-	9.2°	48.2°	22.0°
γ (model)	3.3°	3.7°	6.5°	-	2.8°	2.3°	3.6°
ϕ_e' (model)	64°	65°	65°	-	54°		

T: torsional quantum number

N: number of transitions used

J_{max}: highest value of J used

s: root mean square deviation of the fit

tions either confirmed this or indicated the occurrence of large second-order splittings with one component almost at the same frequency as the reported unsplit line.

The first three molecules in Table I have the chemical formula $CH_2{=}CH{-}CH_2X$, with $X = CH_3$, NH_2, F. In all cases the data were insufficient to determine γ, which oscillated within a few degrees near $\gamma = 0°$. The values of β found were higher than those predicted by model calculations, but the latter are very sensitive to small changes in ϕ. To illustrate this the values of ϕ which reproduce the observed β are given in row ϕ'_e.

Ethylene diamine is a very interesting molecule as the selection rules follow Case B. Marstokk and Møllendal (24) have already stated that the NCCN framework of the molecule is fixed during the tunneling process, which is confirmed by these selection rules. As inversion as well as rotation of the NH_2 groups around the C–N bonds may be involved, no model calculations were made.

Propanal shows very little inversion splitting, as only a-type transitions are observed. However, Pickett and Scroggin (14) discovered an accidental degeneracy from which they were able to determine $\Delta E = 471.80 \pm 0.07$ MHz and a parameter F, which we can translate into $\beta = 7.945 \pm 0.005°$, $\gamma = 0°$. Our program gave the same results, but not to the same accuracy, and we conclude that for this case an alternative treatment is preferable.

Difluoroacetic acid and cis-2-pentene are two examples where the doublet splittings are very irregular. Details will be published together with other results for these molecules; in both cases double resonance measurements have allowed us to verify the selection rules given in a preceding section.

One other case was studied: divinylether (17). Here no satisfactory reproduction of the published frequencies could be obtained. This is not surprising as the tunneling process has two degrees of freedom, and the theory is obviously not designed for this case. The same could have been said for ethylene diamine, but from the observation that the splittings could be reproduced by the theory one might conclude that here the internal motion is in effect one dimensional.

DISCUSSION

In the Introduction the idealized Case A was discussed where the doublet splittings are zero for x- and y-type transitions and $2\Delta E$ for z-type transitions.

Neglecting the relatively small effects of $\Delta R_{gg'}$, we can deduce from Eqs. (16) and (18) that this will occur when no degenerate levels are involved in the transition and when $\beta \approx 0°$. This means that the movement of the (a,b,c) axes with respect to the (x,y,z) axes should be negligible, which can happen for light tops as –OH or –SH, where only a hydrogen atom moves. For heavier internal rotors, and especially when two principal inertial moments are close to each other for any value of ϕ between $0°$ and the equilibrium value ϕ_e, β may be large and the idealized splittings will not even be found as a first approximation.

A comparison of the method described here with Eqs. (1)–(3) is in order. The latter are, of course, more general and can also be applied for energy levels close to or above the barrier to internal rotation at $\phi = 0°$. But in many cases only the lower levels are observed, and our method then has the following advantages:

(i) The transition to the infinitely high barrier case is immediately obvious.

(ii) The parameters β and γ can be much more easily correlated to the path of the tunneling process than the parameters G_x and G_y. Moreover, the former are expected to be nearly invariant for isotopic substitution or change of torsional state.

(iii) The method described here uses little computer time as long as perturbation theory can be applied, so it is especially suitable for analyzing doublet splittings which are small with respect to the average spacings between rotational energy levels.

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