

transitions by the Stark effect is difficult, the estimated b component of about 0.7 D seems reasonable. The line intensities for the tunneling-rotation transitions are by about one order of magnitude weaker than those of the pure rotational transitions, consistent with the calculated dipole moment ratio (μ_b/μ_a) of about 0.22.

C. Dynamics of proton tunneling

We consider the tunneling-rotation motion of tropolone using a one-dimensional model. The main aim of this discussion is to clarify what the spectroscopic constants obtained in the present study mean as well as to confirm that the tunneling-rotation interaction constant F is within an acceptable range of magnitude. For this purpose, use of a multidimensional model would only lead to unnecessary complication, although such models have frequently been employed for interpreting the vibrational dependence of the tunneling splitting.^{13–15} The present treatment partially parallels the one-dimensional analysis of proton tunneling dynamics in malonaldehyde by Baughcum *et al.*²⁵

The one-dimensional model is characterized by giving the coordinates $[a_i(x), b_i(x), c_i(x)]$ of each atom referred to the molecule-fixed Cartesian axes as functions of the tunneling coordinate x , which describes the degree of the molecular deformation during the tunneling motion. We assume that the potential function $U(x)$ has two equivalent minima at $x = \pm x_{\min}$, and $x=0$ corresponds to the top of the barrier. As usual, the origin of the axis system is chosen at the center of mass of the molecule. The c axis is perpendicular to the molecular plane, and $c_i(x)=0$ for all atoms. The orientation of the a and b axes can be chosen so that the angular momentum caused by the tunneling motion vanishes when viewed from the molecule-fixed axis system, i.e.,

$$\sum_i m_i [a_i (db_i/dx) - b_i (da_i/dx)] = 0. \quad (8)$$

Note that the a and b axes do not coincide with the instantaneous principal axes.

The classical kinetic energy for the tunneling-rotation motion is then written as

$$T = (1/2)I_{aa}(x)\omega_a^2 + (1/2)I_{bb}(x)\omega_b^2 + (1/2)I_{cc}(x)\omega_c^2 + I_{ab}(x)\omega_a\omega_b + (1/2)G(x)(dx/dt)^2, \quad (9)$$

where $I_{\alpha\beta}(x)$ is an element of the inertial tensor, ω_α an angular velocity component, and $G(x)$ is the reduced mass defined by

$$G(x) = \sum_i m_i [(da/dx)^2 + (db/dx)^2]. \quad (10)$$

The reduced mass, in general, depends on the tunneling coordinate x . However, an appropriate definition of x reduces $G(x)$ to a constant G_0 . Then the quantum mechanical Hamiltonian is derived by a standard method as

$$H = A(x)J_a^2 + B(x)J_b^2 + C(x)J_c^2 + F(x)(J_a J_b + J_b J_a) - Kd^2/dx^2 + U(x), \quad (11)$$

where K is a constant inversely proportional to the reduced mass G_0 . The coefficients $A(x)$, $B(x)$, $C(x)$, and $F(x)$ are the rotational constants and the tunneling-rotation interaction constant in frequency units as functions of the tunneling coordinate x ,

$$A(x) = (h/8\pi^2)I_{bb}(x)/[I_{aa}(x)I_{bb}(x) - I_{ab}(x)^2], \quad (12a)$$

$$B(x) = (h/8\pi^2)I_{aa}(x)/[I_{aa}(x)I_{bb}(x) - I_{ab}(x)^2], \quad (12b)$$

$$C(x) = (h/8\pi^2)[1/I_{cc}(x)], \quad (12c)$$

$$F(x) = -(h/8\pi^2)I_{ab}(x)/[I_{aa}(x)I_{bb}(x) - I_{ab}(x)^2]. \quad (12d)$$

When the Schrödinger equation for the tunneling motion,

$$[-Kd^2/dx^2 + U(x)]|n\rangle = \epsilon_n|n\rangle, \quad (13)$$

is solved, the first and second lowest eigenstates correspond to the 0^+ and 0^- components, respectively, of the tunneling doublet. The rotational constants observed for the 0^+ and 0^- states correspond to the averages of $A(x)$, etc., over the respective eigenfunctions,

$$A_\pm = \langle 0^\pm | A(x) | 0^\pm \rangle \text{ etc.}, \quad (14)$$

whereas the tunneling-rotation interaction constant is given by

$$F = \langle 0^+ | F(x) | 0^- \rangle. \quad (15)$$

Note that $A(x)$, etc., are even functions of x but $F(x)$ is an odd function, and that the eigenfunctions $|0^+\rangle$ and $|0^-\rangle$ are even and odd with respect to x . If the double minimum potential has a high barrier as in the present case, the eigenfunctions $|0^\pm\rangle$ have their amplitudes concentrated in the vicinity of the potential minima. Therefore, A_\pm , etc., would be close to $A(x_{\min})$, the value at the potential minimum, and F to $F(x_{\min})$.

Now we present the results of some sample calculations with assumption of a simple linear trajectory model, in which each atom traverses a straight path,

$$a_i(x) = (1/2)[a_i^R + a_i^L] + (1/2)[a_i^R - a_i^L](x/x_{\min}), \quad (16a)$$

$$b_i(x) = (1/2)[b_i^R + b_i^L] + (1/2)[b_i^R - b_i^L](x/x_{\min}), \quad (16b)$$

connecting (a_i^R, b_i^R) and (a_i^L, b_i^L) , which denote the positions of the atom corresponding to the two potential minima. The molecule takes the right-hand side (R) conformation when $x = x_{\min}$, and the left-hand side (L) one when $x = -x_{\min}$. With an assumption of the molecular shape at a minimum, these coordinates are uniquely determined in accordance with the condition of vanishing angular momentum [Eq. (8).]

If the ab initio optimized structure by Takada and Nakamura¹⁴ [Table IX (A)] is arbitrarily assumed as the equilibrium conformation, we obtain $F(x_{\min}) = -6.0$ MHz. This conformation corresponds to $A(x_{\min}) = 2751.4$, $B(x_{\min}) = 1652.2$, and $C(x_{\min}) = 1032.3$ MHz, in good agreement with the experimentally obtained rotational constants. However, another calculation done on the equilibrium conformation only slightly distorted from the above structure gave $F(x_{\min}) = 22.8$ MHz. These two structures differ by less than 0.01 Å and 0.8° in bond lengths and angles, respectively. It is