

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 ( $\mu_b/\mu_a$ ) 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.<sup>13–15</sup> The present treatment partially parallels the one-dimensional analysis of proton tunneling dynamics in malonaldehyde by Baughcum *et al.*<sup>25</sup>

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,  $\omega_\alpha$  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

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

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 Nakamura<sup>14</sup> [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