The interaction of rotation and local mode tunneling in the overtone spectra of symmetric hydrides. II. The spatial properties of the XH₄ eigenstates

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The matrix elements of the XH₄ rotation-tunneling Hamiltonian are given for basis states with all of the vibrational excitation in a single bond. A basis set of symmetrized rovibrational wave functions is given that are eigenfunctions in the limit in which the local mode tunneling rate is much smaller than the rotational precession rate. Using this basis, it is demonstrated that, in this limit, vibrational tunneling occurs with a simultaneous reorientation of the molecule, such that the spatial properties of the excited bond are the same as if tunneling did not take place at all. A resonant two-photon dissociation experiment is proposed that could observe this effect. It is found that as one moves away from this limit, the polarization properties of the F₂ symmetry vibrational state retain much of the symmetric top structure.

I. INTRODUCTION

The study of highly excited vibrational states provides a rich diversity of physical phenomena. Among the most studied and best characterized is the phenomenon of local modes. In a molecule with n equivalent hydrogen atoms, the normal mode XH stretching motions are delocalized over the n atoms. Classically, anharmonicity leads to a localization of the vibrational action on a single bond, if that bond starts with sufficient action. Quantum mechanically, the nondegenerate eigenstates must have equal excitation on each bond, but when the classical motion is localized, the quantum states with m quanta of excitation form a cluster of n states whose energy splitting reflects tunneling through a dynamical barrier. This splitting decreases exponentially with increasing vibrational action. Our understanding of this type of dynamics in well developed. The review by Child and Halonen provides an excellent summary of the modern work in this field.

Less well understood is how rotation interacts with this local mode tunneling. The first systematic study of this topic was the work of Halonen and Robiette. In an earlier paper (referred to as I), I extended their work by freeing it of several extreme approximations and showed how the effects they predicted followed naturally from an inversion of the normal time scales for vibrational and rotational motion. When the local mode tunneling rate is much slower than the rotational precession rate, then the rotational motion should reflect the dynamically reduced symmetry of the local mode state, where the excited bond is dynamically inequivalent to the others. This results in each local mode state having its own inertial principal axis system. Local mode tunneling is then between equivalent rovibrational states, and the eigenstates can be approximated by symmetrized linear combinations of rovibrational states. In general, one finds that local mode tunneling rates of these rovibrational states are reduced from the pure vibrational rates by rotational overlap integrals. This reduction was interpreted in I as arising from the fact that, in addition to transferring the vibrational action in the rotating molecule, one must also reorient the angular momenta in the body-fixed frame to obtain an equivalent state. This rotational effect on the tunneling rate was not noticed in previous theoretical work, which only considered the case where the rate was zero, but is observed in the first overtone spectrum of SnH₄.

In contrast, when the local mode tunneling rate is much faster than the rotational precession rate, then the rotational motion should reflect the full symmetry of the molecule and, thus, each vibrational state has the same principal axis system, aligned with the symmetry axes of the molecule. In this case, the eigenstates can be approximated by rotational wave function multiplied by symmetrized combinations of vibrational wave functions. In the intermediate case, where the tunneling rate and precession rate are comparable, the wave functions are strongly mixed in either the symmetrized vibrational or rovibrational basis.

By reference to expected orders of magnitude of different terms in I, phenomenological effective rotation-tunneling Hamiltonians were written down for the molecules XH₄ in the n pure local mode states with m quanta of excitation in a single bond. These effective Hamiltonians were transformed to a symmetrized vibrational basis which diagonalized the vibrational tunneling, but resulted in Jₔ Jₔ off-diagonal coupling between the symmetrized vibrational states. Explicit calculations were done in this vibrationally symmetrized basis, and the resulting energy level pattern was interpreted successfully in terms of the physical model described above.

This paper examines the spatial characteristics of the eigenstates of the effective rotation-tunneling Hamiltonian for the XH₄ molecule. Such spatial properties can be explored via polarization experiments and provide a view of the molecular dynamics that is different from the energy level structure. In addition, the spatial properties of the eigenstates are important if one wants to understand possible inelastic scattering or chemical reactions following overtone excitation. I find that these spatial properties can also be interpreted successfully in terms of the above physical mod-
and $J,K,$ and $M$ are the quantum numbers of a symmetric top function which has the symmetry axis defined along the nth XH bond (i.e., $e_4$). In this basis, the diagonal terms are the symmetric top energies $G_0 + BJ(J + 1) + (A - B)K^2$. Quartic and higher-order centrifugal distortion constants can easily be included; they will be identical in form to an $A_1$ level of a symmetric top. The only vibrationally off-diagonal terms ($n' \neq n$) come from the tunneling term and are given by

$$\langle n',J',K',M' | H_{\text{eff}} | n,J,K,M \rangle = \lambda D^J_{K,K'}(\alpha, \beta, \gamma) \delta_{J,J'} \delta_{M,M'},$$

where $D^J_{K,K'}$ are the Wigner $D$ matrix elements and $\alpha$, $\beta$, and $\gamma$ are the Euler angles needed to convert the principal axis system aligned along bond $n$ to that aligned along bond $n'$. It is seen that the Hamiltonian is block diagonal in $J$ and $M$ (which will, for now, be dropped explicitly from the wave function labels). Thus, we need to diagonalize a $(2J + 1)$ block of basis functions. In order to define the problem, we must give the principal axis system for each local mode vibrational state. While the choice of the $z$ axis is unique, one is free to choose any orientation for the $x,y$ axis. The Hamiltonian can be set up with any choice, but experience has demonstrated that the block symmetrization of the Hamiltonian is more convenient with some relative orientations. The coordinate systems used in this paper place bonds 1 and 2 in the $x,z$ plane when either bond 1 or 2 is excited, and bonds 3 and 4 in the $x,z$ plane when either bond 3 or 4 is excited. Table 1 gives the transformation Euler angles between these coordinate systems.

The matrix elements of Wigner $D$ matrix are given by

$$D^J_{K,K'}(\alpha, \beta, \gamma) = e^{-ik\alpha}a_k D^J_{K,K'}(\beta)e^{iK\gamma}$$

and it proves convenient to use the relationship

$$D^J_{K,K'}(\alpha, -\beta, \gamma) = (-1)^K D^J_{K',K}(\alpha, \beta, \gamma)$$

II. THE HAMILTONIAN IN A BASIS OF SYMMETRIZED ROVIBRATIONAL BASIS FUNCTIONS

In I, it was shown that the effective rotation-tunneling Hamiltonian for the local mode states of XH molecules can be written as

$$H = \sum_{J=1}^{4} \left[ (\epsilon_4 + B J^2 + (A - B)(\epsilon_4 J^2)) | k \rangle \langle k | 
+ \lambda \sum_{k=1}^{4} |k \rangle \langle l | \right]$$

where $G_0$ is the vibrational energy, $A$ and $B$ are the rotational constants for the local mode state which has the dynamical symmetry of a symmetric top with the excited bond defining the symmetry axis $e_4$, and $\lambda$ is the local mode tunneling integral that determines the frequency at which the vibrational excitation jumps from one bond to another. Child and Zhu showed that the same Hamiltonian can be obtained starting with the Hamiltonian of Halonen and Robiette. A natural basis for this representation of the Hamiltonian is the product functions $| n,J,K,M \rangle$, where $n$ denotes a vibrational function with $m$ quanta of vibrational excitation in bond $n$,

| TABLE I. Euler angles to transform principal axis systems $K(\alpha, \beta, \gamma)$. |
|-----------------|-------|-------|-------|
| $\alpha$ | $\beta$ | $\gamma$ |
| $2 \rightarrow 1$ | $\pi$ | $-\theta_1$ | 0 |
| $1 \rightarrow 2$ | 0 | $\theta_1$ | $\pi$ |
| $3 \rightarrow 1$ | $\pi$ | $-\theta_1$ | $2\pi$ |
| $1 \rightarrow 3$ | $-\pi/3$ | $\theta_1$ | $\pi/3$ |
| $4 \rightarrow 1$ | $-\theta_1$ | 0 | $-2\pi$ |
| $1 \rightarrow 4$ | $2\pi$ | $\theta_1$ | $\pi/3$ |
| $2 \rightarrow 3$ | $-\pi/3$ | $0$ | $-2\pi$ |
| $4 \rightarrow 2$ | $2\pi$ | $-\theta_1$ | $3\pi$ |
| $2 \rightarrow 4$ | $2\pi$ | $0$ | $\pi/3$ |
| $4 \rightarrow 3$ | $0$ | $-\theta_1$ | $\pi$ |
| $3 \rightarrow 4$ | $\pi$ | $\theta_1$ | 0 |
to express all matrix elements in terms of $d_{K,K}^\ell(\theta_i)$, where $\theta_i$ is the tetrahedral angle defined by $\cos(\theta_i) = -1/3$. It is seen that the matrix elements are, in general, complex. If one defines $\epsilon = e^{\imath \phi}$, then a $K' = K + \Delta K,K'$ block of the tunneling Hamiltonian can be written as

$$H_{K+\Delta K,K} = \lambda d_{K+\Delta K,K}^\ell(\theta_i)(-1)^K \begin{pmatrix} 0 & 1 & e^{2\Delta K} & e^{-2\Delta K} \\ 1 & 0 & e^{-2\Delta K} & e^{2\Delta K} \\ e^{-2\Delta K} & e^{2\Delta K} & 0 & 1 \\ e^{2\Delta K} & e^{-2\Delta K} & 1 & 0 \end{pmatrix}.$$ 

The rows and columns label the value of $n$ in the basis functions. In order to block diagonalize the Hamiltonian, we define the following simplified basis functions:

$$|a,K\rangle = \frac{1}{\sqrt{2}}(|1,K\rangle + |2,K\rangle + |3,K\rangle + |4,K\rangle),$$

$$|F_+,K\rangle = \frac{1}{\sqrt{2}}(|1,K\rangle - |2,K\rangle + |3,K\rangle - |4,K\rangle),$$

$$|F_-,K\rangle = i|e^{\imath \phi/K}|(|1,K\rangle - |2,K\rangle + |3,K\rangle - |4,K\rangle).$$

Because these are linear combinations of states that are degenerate in the rotational Hamiltonian, the vibrationally diagonal elements of that operator are not changed. In terms of these functions, the only nonzero terms in the tunneling Hamiltonian are

$$\langle a,K + 3N | H_I | a,K \rangle = 3(-1)^K \lambda d_{K+3N,K}^\ell(\theta_i),$$

$$\langle F_+,K + \Delta K | H_I | F_+,K \rangle = \langle F_+,K + \Delta K | H_I | F_-,K \rangle$$

$$= \langle F_+,K + \Delta K | H_I | F_+,K \rangle$$

$$= (-1)^K \lambda d_{K+\Delta K,K}^\ell(\theta_i) \times [1 - \cos(2\Delta K\pi/3)],$$

where $N$ is an integer. Notice that $[1 - 2 \times \cos(2\Delta K\pi/3)] = -1$ for $\Delta K = 3N$ and $2$ for $\Delta K = 3N \pm 1$. I have checked that the eigenvalues obtained by diagonalizing the above Hamiltonian agree with those calculated using the program written earlier in a symmetrized vibrational basis. We can further reduce the Hamiltonian by introducing Wang functions that are symmetric and antisymmetric combinations of functions $+ K$ and $- K$ projections. For $K > 0$,

$$|\Gamma,K \rangle \pm = \frac{1}{\sqrt{2}} (|\Gamma,K \rangle \pm |\Gamma,-K \rangle),$$

while for $K = 0$,

$$|\Gamma,0 \rangle = |\Gamma,0\rangle,$$

where $\Gamma = a, F_+, F_-, or F_-$. This provides states with different inversion symmetries. Using the fact that $d_{K,K}^\ell(\theta) = (-1)^K d_{-K,-K}^\ell(\theta)$, it can be shown that the states $|\Gamma,K \rangle$ are coupled to $|\Gamma,K \rangle \pm (2N + 1) \rangle$ and $|\Gamma,K \rangle \pm 2N \rangle$. Notice that the $|a,K\rangle$ basis functions only have nonzero matrix elements for $K$ differing by $3N$. Thus, for $K = 3N \pm 1$, the Wang combinations are degenerate and span an $E$ representation of $T_d$. The Wang combinations of the $a, K = \pm 3N$ basis functions produce an $A_1, A_2$ pair of levels with the $+ Wang$ function being $A_1$ for $(-1)^{J+K} = +1$ and $A_2$ for $(-1)^{J+K} = -1$. Likewise, the $F_+, K \pm$ states produce an $F_1, F_2$ pair of triply degenerate basis functions with the $+ Wang$ function being $F_1$ for $(-1)^{J+K} = +1$ and $F_2$ for $(-1)^{J+K} = -1$.

We define the symmetric top limit as $(A - B) \gg |\lambda_i|$, because in that limit, the above basis functions will be the eigenfunctions of the Hamiltonian and the energy level pattern will be given by

$$\langle a,K \pm | H_I | a,K \rangle = (-1)^K 3(\lambda_1 \pm \lambda_2),$$

for $K = 3N,$

$$\langle a,K \pm | H_I | a,K \rangle = (-1)^K 3\lambda_1,$$

for $K = 3N \pm 1,$

$$\langle F_\pm,K \pm | H_I | F_\pm,K \rangle = (-1)^K (\lambda_1 \pm 2\lambda_2).$$

for $K = 3N \pm 1,$

where $\lambda_1 = \lambda a_{K,K}^o(\theta_i)$ and $\lambda_2 = \lambda a_{-K,K}^o(\theta_i).$ This result was first derived by Child and Zhu.9

Because of reduced symmetry, the local mode basis functions should have a diagonal, vibrationally induced, dipole moment $\mu$ directed along the excited bond. Application of an external field will result in an off-diagonal matrix element between a $J,K$ pair of Wang basis functions equal to $\mu E K M / J(J+1)$. Because of the exact degeneracy of the two Wang states making up the $E$ representation, these states will show a true symmetric top, first-order Stark effect even for infinitesimal fields (but Stark energies still bigger than the spin–rotation interactions). For the $(A_1, A_2)$ and $(F_1, F_2)$ pairs, the Stark matrix element connects states that are split by a fraction of the tunneling splitting and thus will not have a first-order Stark effect until the Stark energy overwhels the rovibrational tunneling rate. It is well known, based on group theory, that $E$ rovibrational levels of $T_d$ are the only ones that can have true first-order Stark effects. In the present model, this appears quite clearly. As discussed in I, for high $J,K$ levels, $\lambda_1$ and $\lambda_2$0 exponentially and, thus, effective symmetric top linear Stark effects will be easily reached for all the symmetry species. While the Stark effect of fundamentals of a spherical top has been considered before, in those cases, the first-order Coriolis interaction was assumed to dominate over the tensor splitting which, in the present case, reflects the off-diagonal $(A - B)$ terms, but as discussed in I and previously, the effective Coriolis interaction decreases exponentially as the vibrational quantum number increases and, thus, the approximations used in the fundamentals will not be applicable for the local mode states.

For a quantitative treatment of a real spectrum, the Coriolis interaction, though small, will likely need to be included. For this reason, the matrix elements of this operator will be derived in our symmetrized local mode basis.

Coriolis coupling between states with excitation in bonds $k$ and $l$ will be induced by rotation in the direction of $\varepsilon_k \times \varepsilon_l$. Using the coordinate systems we considered above, we find
\[ H_c = -2B_c^2 \mathbf{J} \cdot \pi = \sqrt{2} B_c^2 \mathbf{J} \cdot \pi \left[ |2\rangle \langle 1|_{J,p_1} + |4\rangle \langle 1| \left( -\frac{1}{2} J_{p_1} - \frac{\sqrt{3}}{2} J_{x_1} \right) + |3\rangle \langle 1| \left( -\frac{1}{2} J_{p_2} + \frac{\sqrt{3}}{2} J_{x_2} \right) \right. \\
\left. + |1\rangle \langle 2|_{J,p_2} + |3\rangle \langle 2| \left( -\frac{1}{2} J_{p_2} - \frac{\sqrt{3}}{2} J_{x_2} \right) + |4\rangle \langle 1| \left( -\frac{1}{2} J_{p_2} + \frac{\sqrt{3}}{2} J_{x_2} \right) \right. \\
\left. + |3\rangle \langle 4|_{J,p_3} + |1\rangle \langle 4| \left( -\frac{1}{2} J_{p_3} - \frac{\sqrt{3}}{2} J_{x_3} \right) + |2\rangle \langle 4| \left( -\frac{1}{2} J_{p_4} + \frac{\sqrt{3}}{2} J_{x_4} \right) \right], \]

where \( \pi \) is the vibrational angular momentum operator, \( J_{\alpha} \) denotes the \( \alpha \) component angular momentum in the coordinate system of local mode vibrational state \( n \), and \( B_c^2 \) is an effective Coriolis interaction constant. In terms of the symmetrized basis functions we introduced above, we find that the only nonzero matrix elements of \( H_c \) are

\[ \langle a,K \mid H_c \mid a,K \rangle = \langle - \rangle \frac{3}{\sqrt{2}} \frac{B_c^2}{2} \left[ d_{K-3N,K-1}^{J+1} (\theta_1) f_{-} (J,K) - d_{K+3N,K+1}^{J-1} (\theta_1) f_{+} (J,K) \right] \]

\[ \langle F,K \mid H_c \mid F,K \rangle = \langle - \rangle \frac{3}{\sqrt{2}} \frac{B_c^2}{2} \left[ 1 - 2 \cos \frac{2(K'-K)\pi}{3} \right] \left[ d_{K'-K-1}^{J} (\theta_1) f_{-} (J,K) - d_{K'-K+1}^{J} (\theta_1) f_{+} (J,K) \right], \]

where \( f_{\pm} (J,K) = \sqrt{J(J+1) - K(K \pm 1)} \) and other symbols are as before. I have established, with these expressions for the Coriolis matrix elements, that the energy levels calculated for \( (A-R) \ll |B_c^2| \ll |\lambda| \) agree with the standard expressions for the first-order Coriolis splittings of a spherical top.12

III. SPATIAL PROPERTIES OF EIGENSTATES

Now consider the spatial properties of the excited bond. The rotational wave function for a state \( |n',J,K,M\rangle \) is given by the symmetric top function \((-1)^M \rho - \frac{1}{8} \rho^2 \delta_{M-M',K}(\phi,\theta,\chi)\), where \( \phi, \theta \), and \( \chi \) are the Euler angles needed to transform the molecular axis system for the vibrational state with bond \( n \) excited to the laboratory frame.13 Since the excited bond is, by definition, along the molecular z axis regardless of which bond is excited, the probability that the excited bond makes an angle \( \theta_1 \) with the laboratory Z axis is given by the diagonal matrix elements of \( \delta(\theta - \theta_1) \), where \( \theta \) is the Euler angle in the rotational wave function.14 As long as we neglect terms proportional to the overlap of the local mode vibrational functions (i.e., that \( \langle n'|n\rangle = \delta_{n',n} \)), we find that

\[ \langle n',J,K',M'| \delta(\theta - \theta_1) \mid n,J,K,M \rangle = \delta_{n',n} \delta_{K',K} \delta_{M',M} \left( \frac{2J+1}{8\pi^2} \right) \rho_{MK} (\theta_1)^2 \sin \theta_1. \]

The \( \delta \)'s in \( n, K, \) and \( M \) arise out of integration over the vibrational coordinates \( \chi \) and \( \phi \), respectively. Thus, this operator is diagonal in the local mode basis set and is diagonal in our symmetrized rovibrational basis functions as well since the symmetry equivalent states have the same diagonal matrix elements. The neglected overlap of local mode vibrational functions is on the order of \( |\lambda|/\rho_0 \) which is very small (\( < 10^{-3} \) or less) in the local mode limit.

The key point is that the above matrix elements are exactly the same as for the direction of the XH bond in \( XY_3 \) (i.e., our symmetrized \( |\Gamma,J,K,M\rangle \) basis states have the same spatial properties as a \( |J,K,M\rangle \) state of a symmetric top). In the symmetric top limit, however, the \( XH_4 \) eigenstates will be symmetric, and antisymmetric combinations of the \( |\Gamma,J,K,M\rangle \) states. For \( \Gamma = A \) or \( F \), these combinations will be split in energy by terms proportional to the effective local mode tunneling rate. This implies that the eigenstates will have the same static alignment as a single \( J,K,M \) symmetric top eigenstate, but that if we create an orientation, this will time average to zero because of the local mode tunneling. For the \( \Gamma = E \) states, the symmetric and antisymmetric combinations are degenerate and thus the orientation will be maintained. This leads to the first-order Stark effect for the \( E \) states, but not for the \( A \) or \( F \) rovibrational states. In the presence of a small static electric field, orientation can be maintained in all the states.

Let us consider the two-step photodissociation process discussed earlier for a symmetric top molecule \( XY_3 \). If we prepared the molecule in a single \( J,K,M \) state of the excited vibrational level, we would find that the absorption cross section for the second laser will be proportional to

\[ \left[ 1 - P_{JKM} (\chi) \right], \] where \( \chi \) is the angle that the dissociation laser polarization makes with respect to the laboratory Z axis. If the transition moment for the dissociation excitation is along the molecular symmetry axis, then straightforward angular momenta algebra shows that

\[ P_{JKM} = 2 \left[ 3M^2 - J(J+1) \right] \left[ 3K^2 - J(J+1) \right] \frac{J(J+1)(2J+3)(2J-1)}{J(J+1)(2J+3)(2J-1)}. \]

If we do not excite a single \( M \) level, but in fact we create an alignment with the overtone pump polarization (which defines the Z axis), we find, after \( M \) averaging, the same functional dependence for the photodissociation vs laser polarization, but with
\[
\beta_Q = \frac{2}{5} \frac{[3K^2 - J(J + 1)]}{J(J + 1)}, \\
\beta_R = -\frac{1}{10} \frac{[3K^2 - J(J + 1)]}{J(J + 1)}
\]

depending on whether we excite the \(J, K\) level on an \(R\) branch or \(Q\) branch transition. In all cases, we get anisotropy \((\beta)\) that is proportional to \(\beta_K = \frac{[3K^2 - J(J + 1)]}{2J(J + 1)}\). \(\beta_K\) is just \((P_2(\cos \theta))\), where \(\theta\) is the angle between the symmetry axis and the direction of \(J\) (i.e., it is the anisotropy in the molecular frame).

We now consider what happens when we excite the \(XH_4\) molecule to a local mode state with a polarized laser. In the symmetric top limit, where only one \([\Gamma, K, M, \pm]\) makes a significant contribution to each eigenstate, the polarization anisotropy will be exactly the same as for a symmetric top, since the angular distribution of the wave functions are identical. Further, since there are no off-diagonal terms in the distribution function, as we move away from the symmetric top limit, we will get the same functional form, but with \(K^2\) replaced by \(\langle K^2 \rangle\), where the average is over the eigenstate. Notice that if we have an even distribution over all \(K\) values, then \(\langle K^2 \rangle = \frac{3}{2}J(J + 1)\), and we will get zero anisotropy. Therefore, we expect that the anisotropy will decrease as we move away from the symmetric top limit. The eigenstates of the effective rotation-tunneling Hamiltonian depend only on the dimensionless ratio of \(\lambda\) to \((A - B)\). It is useful to examine the distribution over \(K\) for the individual eigenstates of the effective Hamiltonian in order to assess how quickly the symmetric top anisotropy is decreased as the tunneling rate increases. Increasing \(\lambda\) will increase our mixing of different \(K\) states and will, when \(|\lambda| \gg (A - B)\), lead to having traditional tetrahedral rotational manifolds in two well-separated vibrational states.

Figure 1 represents a correlation diagram for \(J = 6\) computed as a function of \(|\lambda|/(A - B)\). It is seen that, as we move away from the symmetric top limit, the different rotational levels (with the same \(J\)) of the \(A\) symmetry vibrational state collapse. When \(|\lambda| \gg (A - B)\), the splittings within a \(J\) manifold can be neglected, compared to the \(A - F\) vibrational energy separation. In this limit, straightforward manipulation of the rotation-tunneling Hamiltonian in symmetrized vibrational functions [Eq. (13) of I] shows that the interaction of the \(A\) and \(F\) vibrational states can be replaced (via second-order perturbation theory) by the rotational operators

\[
\pm \frac{(A - B)^2}{36\lambda} \left[ (J_x^2 + J_y^2 + \frac{1}{2}J_z^2) - \hbar^2 J^2 \right],
\]

which can be incorporated in other terms in the effective rotational Hamiltonian.

As shown above, the spatial properties of any eigenstate are determined by the distribution of symmetric top wave functions that make it up. Figures 2 and 3 show these distributions for the lowest and the highest eigenstates, with \(J = 10\) for several values of \(|\lambda|/(A - B)\). The wave function for the lowest state is essentially unchanged as \(\lambda\) is made larger than \(30(A - B)\) or less than \(-100(A - B)\). The highest eigenstate is unchanged for \(\lambda < -100\) and slowly approaches an asymptotic distribution as \(\lambda\) increase beyond \(100(A - B)\). The behavior near zero is as expected; only a single \(K\) value makes significant contribution to each eigenfunction, with the lowest being entirely \(K = 0\) and the highest \(K = J\). For \(\lambda \gg (A - B)J^2\), the lowest eigenstate is part of the \(F_1\) symmetry vibrational state, while the highest is part of the \(A_1\) vibrational state. For \(\lambda \ll (A - B)J^2\), the opposite occurs. It is seen that in both limits, the rotational function of the \(A\) vibrational state is made up of the full range
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Looking at the full range of eigenstates, we find that when $|\lambda| > (A - B)J^2$, the $J = 10$ rotational levels of the $A$ vibrational state have an energy spread of only $300 \times (A - B)^2 \times |\lambda|^{-1}$ compared with a spread of $100 \times (A - B)$ when $\lambda = 0$. If we look at the anisotropy $\beta_K$, we find values from $- (3 - 10) \times (A - B) \times \lambda^{-1}$. Thus, the levels approach the pattern expected for a spherical top.

If we look at the rotational levels corresponding to the $F_2$ vibrational state, we find that for $|\lambda| \gg (A - B)J^2$, they span an energy range of $79 \times (A - B)$ and a range of $\beta = -0.47$ to 0.60. For a symmetric top, $\beta_K = -0.5 (K = 0)$ to 0.86 ($K = J = 10$). We thus see that the rotational levels of the $F_2$ symmetry vibrational state retain much of the character of the symmetric top limit, even when

FIG. 2. The population (sum of the squares of the coefficients) of the lowest $J = 10$ eigenvalue as a function of $K$ for different values of the ratio $\lambda/(A - B)$. (a) 30; (b) 0.1; (c) -10; (d) -30; (e) -100.
the $A$-$F$ vibrational states are well separated and interact only weakly. The reason is that, even in this limit, there exists a rotational coupling among the three degenerate vibrational functions that make up the $F_2$ state. This result would not appear to depend on being in the local mode limit at all. However, it must be recalled that we have neglected the Coriolis coupling between the degenerate components of the $F$ state. For fundamental transitions, we expect the Coriolis interaction to dominate over the tensor splittings induced by $(A - B)$. 

In order to characterize how Coriolis coupling will change this pattern, consider the case $\lambda = 10^4 \times (A - B)$ and $B_\xi = 10^2 \times (A - B)$ which are reasonable parameters for a fundamental vibration. The $F_2$ vibrational state splits into three well-separated components $F^+, F_0$, and $F^-$ with energy shifts $+ 2B_\xi J$, $- 2B_\xi$, and $- 2B_\xi (J + 1)$, respectively. For $J = 10$, the tensor components of the $F^+$ states have a spread in energy of $0.23 \times (A - B) \times J^2$ and a range of $\beta_K$ of $-0.30 - 0.0$. For $F^0$, the energy spread and range of $\beta_K$ are $0.33 \times (A - B) \times J^2$ and $+0.15$ to $+0.60$, respec-
tively, while for $F^-$, they are $0.11 \times (A - B) \times J^2$ and $-0.30 - 0.15$. We conclude that the anisotropy is still quite strong, even when the Coriolis interaction is present.

IV. CONCLUSIONS

This paper has provided two principal results. First, the matrix elements for the effective local mode rotation-tunneling Hamiltonian are derived and given in terms of symmetrized rovibrational basis functions that lead to a factorization of $H_{eff}$ by symmetry. Second, it is demonstrated that in the symmetric top limit where $|\lambda| \ll (A - B)$, the spatial properties of the excited bond in an individual eigenstate are identical to those of a symmetric top molecule in a Wang function. Physically, this demonstrates that the molecule reorients itself in the laboratory frame when the vibrational energy quanta tunnels from one bond to another, such that the excited bond continues to point in the same direction in space as before. It is proposed that this can be detected via the polarization dependence of a two-step photodissociation experiment. It is found that, as one moves away from the symmetric top limit to the limit of a pair of well-separated $A_1$ and $F_2$ vibrational bands, the rotational functions of the $A_1$ vibrational state have an anisotropy that rapidly approaches zero, but that the rotational functions of the $F_2$ state retain most of the anisotropy of the symmetric top despite the vibrational tunneling frequency being much higher than the rotational precession rate.

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