Vibration–rotational spectroscopy of XH₂ and XH₃ type molecules near the local mode limit

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Present work studies the effective rotational Hamiltonians and their vibration–rotational parameters for XH₂ and XH₃ type molecules near the local mode limit by including the diagonal matrix elements of coordinate operators when the bond anharmonicity is significant. An improved ‘‘α relation’’ is given for the local mode limit by taking the anharmonic bond oscillator wave function as the basis function. Then the rotational tunneling approach is extended to model the effect of nonzero interbond coupling for XH₂ and XH₃ type molecules, which provides a dynamical view of the rovibrational structure of the local mode states. © 1996 American Institute of Physics. [S0021-9606(96)00141-9]

I. INTRODUCTION

Recently there has been much effort to study the vibration–rotational energy level structure of local mode vibrational states both theoretically1–7 and experimentally.5–13 The most striking feature of the XH₂ type molecules near the local mode limit is that the overtone spectra of XH₂ type molecules look like parallel bands of symmetric top, which has been observed in GeH₄,8 SiH₄,9 and SnH₄.10 In the case of XH₃ type molecules, the rotational energy level structure of the highly excited stretching states of SbH₃ (Ref. 11) and AsH₃ (Ref. 12) (particularly the ν=3 and 4 stretching state) has been found to qualitatively resemble that of an asymmetric rotor. In the case of XH₄ type molecules, the C₄ symmetry asymmetric top rotational structure has recently been observed by us in the ν=6 stretching states of H₂Se while the ν=2 and 3 stretching states exhibit this tendency but still retain the C₂ᵥ symmetry.13 In the normal mode representation that the overtone spectra are fitted using a Hamiltonian of close coupling of symmetric and antisymmetric stretching fundamentals, all the above features can be well established by assuming certain simplifications among the effective spectroscopic parameters resulting from the fitting, i.e., the degeneracy of the two bands,14 the quenching of the Coriolis interaction5,15,16 and particularly the so-called ‘‘α relation’’1,3,6 between the parameters of the H₂2 term whose two subscripts denote the total power in the vibrational operator and angular momentum operator, respectively. Specifically for the XH₃ type molecules to be discussed in this paper, the α relation for the effective parameters is6,6

\[ \alpha_A^B = \alpha_E^B, \quad \alpha_A^C = \alpha_E^C, \quad -2q_{\text{eff}} = \sqrt{2}\alpha_{\text{eff}}^{BB}, \]

\[ 4\sqrt{2}r_{\text{eff}} = \alpha_{\text{eff}}^{BC}. \]  (1)

When denoted the coefficients of Hamiltonian terms, the parameters in the above expression are conventionally written as: \( \alpha_1^B \), \( \alpha_1^C \), \( \alpha_2^B \), \( q_3 \), \( r_3 \), and \( \alpha_1^{13} \) with the first four parameters describing the vibrational dependence of rotational constants, \( q_3 \) and \( r_3 \) being the coefficients of \( l \) and \( r \) resonance within the antisymmetrical stretching fundamental \( \nu_3 \), respectively, and \( \alpha_{13}^{13} \) and \( \alpha_{13}^{13} \) being the coefficients of \( \alpha \) resonance between the symmetrical stretching fundamental \( \nu_1 \) and \( \nu_3 \).

In Ref. 6, Lehmann has obtained Eq. (1) by starting from a local mode Hamiltonian and transformed it into the normal mode representation. Furthermore in Lehmann’s second paper,7 the matrix elements of the interbond coupling term in this local mode Hamiltonian under the rovibrational basis of symmetric top are explicitly given. This rotational tunneling approach, equivalent to the conventional approach of close coupling of two normal mode states, provides a dynamical view of the rovibrational structure.

Lukka and Halonen have also obtained Eq. (1) using a different approach. Under the local mode limit condition that bending modes and the interbond coupling are negligible, the vibrational wave function is simply the symmetrized local mode wave function. Then by averaging the vibrational operators by this symmetrized local mode wave function, they were able to obtain Eq. (1). However in their derivation, the local mode wave function is harmonic. In addition, by defining a hypothetical rovibrational local mode limit that rovibrational cross terms do not introduce any rotational coupling between different local mode states they found that the \( H^{11} \) coefficients obey the same relationship (1) as their corresponding effective parameters.

Another approach to studying the rotational energy level structure is to obtain the effective rotational Hamiltonian by averaging the vibration–rotational Hamiltonian using the unsymmetrized local mode wave function. Using this approach, Child and Zhu have derived the effective vibration–rotational Hamiltonian of XH₄ (Ref. 4) and \( \nu_n \) (\( n=2, 3 \), and 4) type molecules5 at the local mode limit. However their derivation is based on an approximation \( \langle n|q|n \rangle = 0 \), which is reasonable in some cases since \( \langle n|q|n \rangle = o(k^{-1}) \),14 where \( k = \omega/\omega_x \) is usually a large number. But when the anharmonicity is significant, for example for XH type Morse oscillators typically \( k = 50 \), the \( \langle n|q|n \rangle \) is comparable to \( \langle n+1|q|n \rangle \) and should not be omitted.

The following part of this paper is organized as follows:
In Sec. II we will give the improved \( \alpha \) relation by taking the anharmonic bond oscillator wave function as the basis function and derive the effective rotational Hamiltonian by including the nonzero \( \langle n|q|n \rangle \) elements. In Secs. III and IV, we will extend the rotational tunneling approach proposed by Lehmann\(^6,7\) to \( \text{XH}_3 \) and \( \text{XH}_2 \) type molecules to explicitly give the matrix elements of interbond coupling term and Coriolis operator under the unsymmetrized local mode basis.

II. THE EFFECTIVE VIBRATION–ROTATIONAL PARAMETERS FOR \( \text{XH}_3 \) AND \( \text{XH}_2 \) TYPE MOLECULES AT THE LOCAL MODE LIMIT

The coordinate system for \( \text{XH}_3 \) type oblate symmetric top molecules with \( C_{3v} \) symmetry is defined by assigning the \( z \) axis as the \( \text{C}3 \) axis and setting one \( \text{XH} \) bond in the \( xz \) plane along the positive \( x \) axis. Then assuming the stretching vibrations are separable from bending vibrations, the stretching vibration–rotational Hamiltonian can be written by using dimensionless normal coordinates as\(^1,5\)

\[
H = (B_e - q_i^2 \alpha_1^1 - q_j^2 \alpha_1^1)(J_x - J^2) + (C_e - q_i^2 \alpha_1^1 - q_j^2 \alpha_1^1)J_z
- \frac{1}{2}q_i^2(q_i^2 - q_j^2)(J_x - J^2) + 2q_i^3q_j(J_x - J^2) \nonumber \\
+ 2r_3(q_i^2 - q_j^2)(J_x - J^2) - 2q_i^3q_j(J_x - J^2) \nonumber \\
+ \alpha_1^5q_i^3(J_x - J^2) - q_i^3q_j(J_x - J^2) \nonumber \\
+ \alpha_1^5q_i^3q_j(J_x - J^2).
\]

(2)

where \( q^2 = \frac{1}{2}(q^2 + p^2) \), \( q_i, q_j = q_i q_j + p_i p_j \), etc. and \( \{J, J\} = J_x J_y + J_y J_x \), etc. The dimensionless mode coordinates and the dimensionless bond displacement coordinates have the following relationship:

\[
q_1 = \frac{1}{\sqrt{3}} (\beta_1/\beta_m)^{1/2} (q_a + q_b + q_c),
\]

\[
p_1 = \frac{1}{\sqrt{3}} (\beta_1/\beta_m)^{-1/2} (p_a + p_b + p_c),
\]

\[
q_{3x} = \frac{1}{\sqrt{6}} (\beta_3/\beta_m)^{1/2} (2q_a - q_b - q_c),
\]

\[
p_{3x} = \frac{1}{\sqrt{6}} (\beta_3/\beta_m)^{-1/2} (2p_a - p_b - p_c),
\]

\[
q_{3y} = \frac{1}{\sqrt{2}} (\beta_3/\beta_m)^{1/2} (q_b - q_c),
\]

\[
p_{3y} = \frac{1}{\sqrt{2}} (\beta_3/\beta_m)^{-1/2} (p_b - p_c),
\]

and

\[
\beta_m = \left( \frac{2 \pi \hbar \omega_m}{\hbar g_{rr}} \right)^{1/2},
\]

with \( \omega_m \) being the Morse bond oscillator frequency. Here and throughout the paper, the bond oscillator is modelled by a Morse oscillator. With the approximation \( \beta_1 = \beta_3 = \beta_m \) applied, Eq. (3) is simplified as

\[
q_1 = \frac{1}{\sqrt{3}} (q_a + q_b + q_c), \quad p_1 = \frac{1}{\sqrt{3}} (p_a + p_b + p_c),
\]

\[
q_{3x} = \frac{1}{\sqrt{6}} (2q_a - q_b - q_c), \quad p_{3x} = \frac{1}{\sqrt{6}} (2p_a - p_b - p_c),
\]

\[
q_{3y} = \frac{1}{\sqrt{2}} (q_b - q_c), \quad p_{3y} = \frac{1}{\sqrt{2}} (p_b - p_c).
\]

Since at the local mode limit, the wave function of a local mode state is simply the product of three bond-oscillator wave functions, i.e., \( \langle n|q|n \rangle = \langle n|0 \rangle \langle 0|q|0 \rangle \), we can replace the dimensionless normal coordinates in Eq. (2) by the dimensionless bond displacement coordinates using Eq. (4), then use the local mode state wave function \( \langle n|0 \rangle \) to average this Hamiltonian over all vibrational coordinates. Including the nonzero matrix elements \( \langle n|q|n \rangle \) in the calculation, we find that the effective rotational Hamiltonian of an \( \text{XH}_3 \) type molecule at the local mode limit can also be transformed into that of an asymmetric top with the following three different effective rotational constants\(^5\):

\[
A = \frac{1}{2}[(B_e + C_e + E) + [(B_e - C_e + E)^2 + 4G^2]^{1/2}],
\]

\[
C = \frac{1}{2}[(B_e + C_e + E) - [(B_e - C_e + E)^2 + 4G^2]^{1/2}],
\]

\[
B = B_e - E,
\]

where

\[
E = \frac{1}{3}N(-q_3 + \sqrt{2}a_{13}^B + \frac{1}{3} \Delta (q_3 + \frac{\sqrt{2}}{2} a_{13}^B)),
\]

\[
G = \frac{4}{3}N \left( r_3 + \frac{\sqrt{2}}{4} a_{13}^C \right) + \frac{1}{3} \Delta \left( -r_3 + \frac{\sqrt{2}}{8} a_{13}^C \right),
\]

\[
B_e = B_0 - \frac{1}{2}N(a_1^B + 2a_3^B) - \frac{1}{2} \Delta (a_1^B - a_3^B),
\]

\[
C_e = C_0 - \frac{1}{2}N(a_1^C + 2a_3^C) - \frac{1}{2} \Delta (a_1^C - a_3^C),
\]

and \( N \) and \( \Delta \) are defined as

\[
N = \langle n|q^2|n \rangle - \langle 0|q^2|0 \rangle,
\]

\[
\Delta = \langle n|q|n \rangle \langle 0|q|0 \rangle - \langle 0|q|0 \rangle^2,
\]

where \( \langle n|q^2|n \rangle = \langle n|q^2|n \rangle + \langle n|p^2|n \rangle /2 \). In the case of \( \Delta = 0 \), they are the same as the previous results of Eq. (13) of Ref. 5.

However, since the vibration–rotational Hamiltonian in terms of normal coordinates has been commonly used and spectroscopists often derive the effective parameters from experimental data by treating the overtone spectra as if they are close coupled stretching fundamental pairs, it is conve-
nient to derive the expressions for these effective parameters at the local mode limit and find their relations with the parameters \( E \) and \( G \). For XH\(_4\) type molecules, the four effective vibrationally off-diagonal parameters of the \( H_{22} \) term are\(^1\)

\[
q_{\text{eff}} = (-2) \left( \phi_{n_00E} \right) \left( -\frac{1}{2} \phi_{q_3q_3} \right) + \frac{1}{2} \phi_{q_3q_3} \left( \phi_{q_3q_3} \right),
\]

\[
\alpha_{BB}^{\text{eff}} = (2 \sqrt{2}) \left( \phi_{n_00A_1} \right) \left( -\frac{1}{2} \phi_{q_3q_3} \right) + \frac{1}{2} \phi_{q_3q_3} \left( \phi_{q_3q_3} \right),
\]

\[
\alpha_{BC}^{\text{eff}} = (2 \sqrt{2}) \left( \phi_{n_00A_1} \right) \left( -\frac{1}{2} \phi_{q_3q_3} \right) + \frac{1}{2} \phi_{q_3q_3} \left( \phi_{q_3q_3} \right),
\]

where \( \phi_{n_00A_1} \) and \( \phi_{n_00E^+/-E^-} \) are the wave functions of the stretching states in question with symmetries \( A_1 \) and \( E \), which can be simply expressed as the symmetrized local mode state wave function \( |n_00A_1\rangle \) and \( |n_00E^\pm\rangle \) at the local mode limit. Then again replacing the normal coordinates \( q_1 \) and \( q_3 \pm \) in Eq. (9) by the bond displacement coordinates and incorporating the relations of Eq. (6), one obtains

\[
-2q_{\text{eff}} = 2E - \frac{8}{3} \left( q_3 + \frac{\sqrt{2}}{2} \phi_{BB}^{\text{eff}} \right) \left( |n\rangle \langle q|0\rangle \right)^2,
\]

\[
\sqrt{2} \alpha_{BB}^{\text{eff}} = 2E + \frac{4}{3} \left( q_3 + \frac{\sqrt{2}}{2} \phi_{BB}^{\text{eff}} \right) \left( |n\rangle \langle q|0\rangle \right)^2,
\]

\[
4\sqrt{2} r_{\text{eff}} = \sqrt{2} G - \frac{16\sqrt{2}}{3} \left( -r_3 + \frac{\sqrt{2}}{8} \phi_{BC}^{\text{eff}} \right) \left( |n\rangle \langle q|0\rangle \right)^2,
\]

\[
\alpha_{BC}^{\text{eff}} = \sqrt{2} G + \frac{8\sqrt{2}}{3} \left( -r_3 + \frac{\sqrt{2}}{8} \phi_{BC}^{\text{eff}} \right) \left( |n\rangle \langle q|0\rangle \right)^2,
\]

where \( \left( |n\rangle \langle q|0\rangle \right)^2 = (|n\rangle \langle q|0\rangle)^2 + \langle |n\rangle \langle n|0\rangle \rangle^2) / 2 \). Similarly the effective vibrationally diagonal parameters of the \( H_{22} \) term can also be obtained as

\[
\alpha_{A}^{\text{eff}} = \frac{1}{2} N \left( \alpha_{B}^{\text{eff}} + 2 \alpha_{C}^{\text{eff}} \right) + \frac{1}{2} \Delta \left( \alpha_{A}^{\text{eff}} - \alpha_{A}^{\text{eff}} \right),
\]

\[
\alpha_{C}^{\text{eff}} = \frac{1}{2} N \left( \alpha_{B}^{\text{eff}} + 2 \alpha_{C}^{\text{eff}} \right) + \frac{1}{2} \Delta \left( \alpha_{A}^{\text{eff}} - \alpha_{A}^{\text{eff}} \right),
\]

\[
(\sigma = B, C),
\]

which are improved \( \alpha \) relation. It is interesting to note that Eq. (13) of the vibrationally diagonal \( H_{22} \)-type parameters is the same as Eq. (7) obtained with the effective rotational Hamiltonian approach.

The effective parameters in Eq. (9) can also be evaluated by using the vibrational wave function obtained from the normal mode model with Darling–Dennison resonances included (NMDD model)\(^9,20\) and the results agree surprisingly well with the experimental values.\(^11,12\) This method also works for the \( \text{XH}_4 \) \text{ type molecules.}\(^3\) This NMDD model is equivalent to the harmonically coupled anharmonic oscillator model (HCAO model)\(^14,21\) when the basis bond function is the harmonic oscillator function instead of a more accurate anharmonic oscillator such as Morse oscillator. Under this harmonic bond oscillator approximation, \( |(n\rangle \langle q|0\rangle) |^2 \) and \( \Delta \) are zero and \( N = n \) since vibrational quantum number \( n \) for the overtones. Applying them to Eqs. (6), (10) and (7), (11) leads to the following relations, respectively:

\[
-2q_{\text{eff}} = \sqrt{2} \alpha_{BB}^{\text{eff}} = \frac{2}{n} (q_3 + \sqrt{2} \alpha_{BB}^{\text{eff}}),
\]

\[
4\sqrt{2} r_{\text{eff}} = \alpha_{BC}^{\text{eff}} = \frac{4\sqrt{2}}{3} \left( r_3 + \frac{\sqrt{2}}{4} \alpha_{BC}^{\text{eff}} \right),
\]

\[
\alpha_{A}^{\text{eff}} = \frac{1}{n} (\alpha_{C}^{\text{eff}} + 2 \alpha_{A}^{\text{eff}}),
\]

which show that under the harmonic bond oscillator approximation, the relationships between the parameters remain unchanged but their values change considerably.

For practical calculations of the effective vibration–rotational parameters, one can use the more accurate coordinate relationship (3) and the vibrational wave function such as \( \phi_{n_00A_1} \) and \( \phi_{n_00E^+/-E^-} \) which can be obtained variationally from the coupled Morse oscillators model.\(^22\) An example of such calculation is given in Ref. 9. It is found that use of Eq. (3) does not produce significantly different results for molecules near local mode limit, thus confirming the use of simplified Eq. (4) in the above discussion.

The vibration–rotational Hamiltonian of an \( \text{XH}_4 \) type molecule can be treated in the same way. Its coordinate system is defined by assigning \((x, y, z)\) axes as the \((b, c, a)\) principal axes. Then the stretching vibration–rotational Hamiltonian can be written as\(^1,5\)

\[
H = (B_x - q_1^2 \alpha_{1A} - q_2^2 \alpha_{1C}) J_x^2 + (C_x - q_3^2 \alpha_{1C} - q_3^2 \alpha_{1A}) J_y^2 + (A_x - q_1^2 \alpha_{1A} - q_3^2 \alpha_{1C}) J_z^2 + d_{13} q_1 q_3 J_x J_z,
\]

Again at the local mode limit, replacing the normal coordinates by the bond displacement coordinates and averaging the vibration–rotational Hamiltonian using the local mode state wave function \( |n\rangle = |n\rangle |0\rangle \), it was found that the effective rotational Hamiltonian of an \( \text{XH}_4 \) type molecule can be transformed again into that of a \( C_s \) symmetry asymmetric top with three different effective rotational constants\(^5\)
Similarly the effective vibrationally diagonal parameters of the $H_{22}$ term can be written

$$B = \frac{1}{2}(B_v + A_v) - \frac{1}{2}[ (B_v - A_v)^2 + (Nd_{13})^2 ]^{1/2},$$

$$A = \frac{1}{2}(B_v + A_v) + \frac{1}{2}[ (B_v - A_v)^2 + (Nd_{13})^2 ]^{1/2},$$

$$C = C_v,$$

where

$$A_v = A_0 - \frac{1}{2}N(a_A^4 + a_A^3) - \frac{1}{2}\Delta(a_A^4 - a_A^3),$$

$$B_v = B_0 - \frac{1}{2}N(a_B^4 + a_B^3) - \frac{1}{2}\Delta(a_B^4 - a_B^3),$$

$$C_v = C_0 - \frac{1}{2}N(a_C^4 + a_C^3) - \frac{1}{2}\Delta(a_C^4 - a_C^3).$$

On the other hand, in terms of dimensionless normal coordinates the effective vibrationally off-diagonal parameters of the $H_{22}$ term can be expressed as

$$d_{13,21} = 2d_{13}(\langle \varphi_{n0,A} | \tilde{q}_1 \tilde{q}_3 | \varphi_{n0,B} \rangle).$$

At the local mode limit substitution of the symmetrized local mode state wave function $|n0: A_1/B_2 \rangle$ into Eq. (19) gives

$$d_{13,21} = Nd_{13}.\tag{20}$$

Similarly the effective vibrationally diagonal parameters of the $H_{22}$ term can also be evaluated as

$$\alpha_{a_1}^{\sigma} = \frac{1}{2}N(a_A^\sigma + a_A^{\sigma'}) + \frac{1}{2} \Delta(\sigma - \sigma'),$$

$$\alpha_{a_2}^{\sigma} = \frac{1}{2}N(a_A^\sigma + a_A^{\sigma'}) + \frac{1}{2} \Delta(\sigma - \sigma') \quad (\sigma = A, B, C).\tag{21}$$

If $|\langle n | \tilde{q} | 0 \rangle|^2$ is omitted, we have

$$\alpha_{a_1}^{\sigma} = \frac{1}{2}N(a_A^\sigma + a_A^{\sigma'}) + \frac{1}{2} \Delta(\sigma - \sigma'),$$

$$\alpha_{a_2}^{\sigma} = \frac{1}{2}N(a_A^\sigma + a_A^{\sigma'}) + \frac{1}{2} \Delta(\sigma - \sigma') \quad (\sigma = A, B, C).\tag{22}$$

Applying the bond oscillator approximation to Eqs. (18) and (19), we obtain the following relations, respectively:

$$d_{13,21} = nd_{13},$$

$$\alpha_{a_1}^{\sigma} = \alpha_{a_2}^{\sigma} = \frac{1}{2}n(a_A^\sigma + a_A^{\sigma'}) \quad (\sigma = A, B, C).\tag{23}$$

III. THE EFFECT OF INTERBOND COUPLING FOR $XH_3$ TYPE MOLECULES

Now the problem confronting us is how to formulate the vibration–rotational spectroscopy in the unsymmetrized local mode basis when interbond coupling is nonzero? An approach to studying the vibration–rotational energy level structure of $XH_3$ type molecules with nonzero interbond coupling was proposed by Lehmann. The following discussion is the extension of his work on XH$_4$ type molecules.

When interbond coupling is nonzero, i.e., $\lambda \neq 0$, the rotational Hamiltonian of $XH_3$ type molecule can be written as

$$H = H_0 + H' = \sum_{k=1}^{3} [ G_0 + A J_k^2 + C J_k^2 + B J_k^2 ] |n_k\rangle \langle n_k| + \lambda \sum_{k \neq l} |n_k\rangle \langle n_l|,\tag{24}$$

where $|n_k\rangle$ stands for the local mode state with vibrational quanta $n$ on the $k$th bond. There are three such local mode states which are degenerated when $\lambda = 0$. For the vibration–rotational basis, we use the product function $|n_k; J \rangle = |n_k\rangle J \rangle$, where $|J \rangle$ is the eigenfunction of the total angular momentum $J$ and its component along $z$ axis. The three asymmetric top principal axes for local mode state $|n_k\rangle$ are as follows: $b$ axis is perpendicular to the plane defined by the excited bond $k$ and the ground state $C_3$ axis; $a$ and $c$ axis have been rotated by a $\theta$ angle from their equilibrium positions in the above mentioned plane toward the excited bond $k$.

When $\lambda \neq 0$, the vibrational tunneling term $H'$ in Eq. (24) will lift the degeneracy of $H_0$. The interacting matrix elements are

$$\langle n', J' K' | H' | n; J \rangle = \lambda D_{J' K' K}^J(\alpha, \beta, \gamma) \delta_{n',n} \delta_{J',J}.\tag{25}$$

Although the space-fixed and molecule-fixed $D_{J' K' K}^J$ lead to the same results when dealing with the Hamiltonian terms involving $J^2$-type operators, we found that the space-fixed $D_{J' K' K}^J$ definitions will cause irreconcilable errors when dealing with the Coriolis interaction terms involving $J$-type operators.

The $(x, y, z)$ coordinate system for the rotational Hamiltonian of Eq. (24) is chosen to coincide with the $(a, c, b)$ principal axes since this coordinate system provides the simplest, if not unique, way to determine the Euler angles needed to convert the principal axes system from one local mode state $|n\rangle$ to another $|n'\rangle$. It is worth noting that the definition of $D_{J' K' K}^J(\alpha, \beta, \gamma) = e^{-i(\alpha K' + \gamma K)\Delta_{J' K' K}^J(\beta)}$ and the formulas for $d_{J' K' K}$ in Ref. 23 refer to the space-fixed angular momenta. When referred to the molecule-fixed angular momenta, owing to the anomalous commutation relations of the molecule-fixed angular momenta, the definition of $D_{J' K' K}^J$ should be

$$D_{J' K' K}^J(\alpha, \beta, \gamma) = e^{i(\alpha K' + \gamma K)\Delta_{J' K' K}^J(\beta)}.\tag{26}$$

The $(x, y, z)$ coordinate system for the rotational Hamiltonian of Eq. (24) is chosen to coincide with the $(a, c, b)$ principal axes since this coordinate system provides the simplest, if not unique, way to determine the Euler angles needed to convert the principal axes system from one local mode state to another. This choice of coordinate system differs from Ref. 6. The orientation of the coordinates of the three local mode states with respect to the $C_3$ symmetry coordinate system are written out in Table I. The three locally vibrational bonds are numbered clockwise with respect to the $C_3$ axis. Then the Euler angles are given by

$$\begin{align*}
(\theta, 2\pi/3, -\theta) & \text{ for bond } n \text{ to bond } n', \\
(\theta, -2\pi/3, \theta) & \text{ for bond } n' \text{ to bond } n,
\end{align*}$$

where $n, n' = 1, 2, 3$ are the labels of three $XH$ bonds which carries local mode vibration. They take the value of (1,2), (2,3), or (3,1). Substituting Eq. (26) in Eq. (25) and using the properties of function $d_{J' K' K}^J(\beta)$, we obtain the following Hamiltonian matrix elements between $|n'; J' K' \rangle$ and $|n; J \rangle$ states (the quantum number $J$ is omitted here for the sake of brevity):
TABLE I. The coordinate axes direction of the three local mode states \(|n_k\rangle\) for XH\(_3\) type molecules with respect to the \(C_{3v}\) symmetry coordinate system defined in Sec. II.

<table>
<thead>
<tr>
<th>Bond 1</th>
<th>Bond 2</th>
<th>Bond 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_k)</td>
<td>((\cos \theta, 0, -\sin \theta))</td>
<td>(-\frac{1}{2} \cos \theta, \frac{\sqrt{3}}{2} \cos \theta, -\sin \theta)</td>
</tr>
<tr>
<td>(y_k)</td>
<td>((\sin \theta, 0, \cos \theta))</td>
<td>(\frac{1}{2} \sin \theta, \frac{\sqrt{3}}{2} \sin \theta, \cos \theta)</td>
</tr>
<tr>
<td>(z_k)</td>
<td>((0, -1, 0))</td>
<td>(\sqrt{3} \frac{1}{2} \cdot \frac{1}{2} \cdot 0)</td>
</tr>
</tbody>
</table>

\[H'_{K'} = \chi e^{i\theta(K' - K)} d_{K', K}^J(2 \pi/3)\]

\[\langle 1; K' | \langle 2; K' | \langle 3; K' |\]

\[\times \begin{bmatrix}
0 & 1 & (1 - K' - K) \\
(1 - K' - K) & 0 & 1 \\
1 & (1 - K' - K) & 0
\end{bmatrix} \begin{bmatrix}
1; K \\
2; K \\
3; K
\end{bmatrix} \]

(27)

Using the following vibrationally symmetrized basis functions:

\[|A; K\rangle = \frac{1}{\sqrt{3}} \left( |1; K\rangle + |2; K\rangle + |3; K\rangle \right),\]

\[|E^+; K\rangle = \sqrt{3} \left( |1; K\rangle + e^{2i\pi/3}|2; K\rangle + e^{i2\pi/3}|3; K\rangle \right),\]

\[|E^-; K\rangle = \sqrt{3} \left( |1; K\rangle + e^{-2i\pi/3}|2; K\rangle + e^{-i2\pi/3}|3; K\rangle \right),\]

with \(e = e^{i\pi/3},\)

the Hamiltonian matrix is divided into three blocks which have the matrix elements

\[\langle A; K' | H' | A; K\rangle = \chi e^{i\theta(K' - K)} [(-1)^{K' - K} + 1] \times d_{K', K}^J(2 \pi/3),\]

\[\langle E^+; K' | H' | E^+; K\rangle = \chi e^{i\theta(K' - K)} [e^{-i\pi/3}(-1)^{K' - K} + e] \times d_{K', K}^J(2 \pi/3),\]

(29)

\[\langle E^-; K' | H' | E^-; K\rangle = \chi e^{i\theta(K' - K)} [e^{-i\pi/3}(-1)^{K' - K} + e^*] \times d_{K', K}^J(2 \pi/3).\]

While the matrix elements of \(H_0\) remain unchanged, the \(E^+\) and \(E^-\) block eventually produce the \((2J + 1)\) same eigenvalues corresponding to doubly degenerated \(E\) symmetry rovibrational levels in the normal mode approach of close coupling of \(A\) and \(E\) vibrational states. Note also that the matrix elements of Eq. (29) are complex. They will become real after introducing the following Wang function:

\[|\Gamma; +\rangle = \frac{1}{\sqrt{2}} (|\Gamma; K\rangle + |\Gamma; - K\rangle),\]

(30a)

\[|\Gamma; -\rangle = \frac{i}{\sqrt{2}} (|\Gamma; K\rangle - |\Gamma; - K\rangle),\]

for \(K > 0\), and

\[|\Gamma; 0+\rangle = |\Gamma; 0\rangle\]

(30b)

for \(K = 0\) with \(\Gamma = A\), \(E^+\), or \(E^-\). An extra phase factor \(i\) has been added to function \(|\Gamma; - K\rangle\). Then the \(H'\) matrix elements become

\[\langle A; K' \pm | H' | A; K\pm\rangle = 2\chi \left[ \cos(K' - K) \theta d_{K', K}^J \left( \frac{2\pi}{3} \right) \mp \cos(K' + K) \theta d_{K', -K}^J \left( \frac{2\pi}{3} \right) \right] \text{ for } K' - K = 2n;\]

\[\langle A; K' + | H' | A; K-\rangle = -2\chi \left[ \sin(K' - K) \theta d_{K', K}^J \left( \frac{2\pi}{3} \right) - \sin(K' + K) \theta d_{K', -K}^J \left( \frac{2\pi}{3} \right) \right] \text{ for } K' - K = 2n;\]

(31)

\[\langle E^+; K' \pm | H' | E^+; K\pm\rangle = -\chi \left[ \cos(K' - K) \theta d_{K', K}^J \left( \frac{2\pi}{3} \right) \pm \cos(K' + K) \theta d_{K', -K}^J \left( \frac{2\pi}{3} \right) \right] \text{ for } K' - K = 2n;\]

\[= -\sqrt{3} \chi \left[ \sin(K' - K) \theta d_{K', K}^J \left( \frac{2\pi}{3} \right) \pm \sin(K' + K) \theta d_{K', -K}^J \left( \frac{2\pi}{3} \right) \right] \text{ for } K' - K = 2n + 1;\]
\begin{align*}
\langle E^+; K' + | H^+ | E^+; K' - \rangle &= \lambda \left[ \sin(K' - K) \theta d_{K'K} \left( \frac{2\pi}{3} \right) - \sin(K' + K) \theta d_{K',-K} \left( \frac{2\pi}{3} \right) \right] \quad \text{for } K' - K = 2n; \\
&= -\sqrt{3} \lambda \left[ \cos(K' - K) \theta d_{K'K} \left( \frac{2\pi}{3} \right) - \cos(K' + K) \theta d_{K',-K} \left( \frac{2\pi}{3} \right) \right] \quad \text{for } K' - K = 2n + 1.
\end{align*}

For $|\Gamma; 0+\rangle$, the coefficient of the above expression should be modified.

Another advantage of using Wang function is that the asymmetric top Hamiltonian $H_0$ is usually manipulated in the same way giving four subblocks $e^\pm$ and $o^\pm$, so that we can conveniently find how the threefold degeneracy is lifted due to the interbond coupling. Specifically, for the $A$ symmetry block, the matrix elements of the interbond coupling are nonzero only when the difference between quantum number $K$ is an even number [see Eq. (31)]. Therefore, the $A$ symmetry block is further divided into $K$ even and $K$ odd blocks. In other words, $e^+$ and $e^-$ symmetry asymmetric top energy levels are coupled together due to the interbond coupling. So are the $o^+$ and $o^-$ symmetry levels. A close examination of the symmetry properties shows that $K$ even and $K$ odd blocks correspond to the rovibrational $A_1$ and $A_2$ levels, while for the $E$ symmetry block all the four asymmetric top blocks are coupled together to give the $E$ levels in the approach of close coupling of $A_1$/$E$ vibrational states.

It is known that both $z$-type and $xy$-type Coriolis interactions are quenched at the local mode limit.\textsuperscript{2,15,16} But for a real case where the interbond coupling is nonzero, it is necessary to formulate the Coriolis interactions in the present approach. Starting from the usual $z$-type and $xy$-type Coriolis operators expressions expressed using the vibrational state projection operators, we can write

\begin{align*}
H^z_- &= -2C \xi_1^2 (|E^+\rangle \langle E^+| - |E^-\rangle \langle E^-|) J_z, \\
H^z_+ &= \sqrt{2} B \Omega_{13} \xi_1^2 [(|A_1\rangle \langle E^+| - |A_1\rangle \langle E^-|) J_+ \\
&+ (|E^+\rangle \langle A_1| - |A_1\rangle \langle E^-|) J_-],
\end{align*}

and replacing the normal mode vibrational basis by the local mode basis, and then further replacing the angular momenta operators in terms of $C_3$, symmetry coordinates by those in terms of the coordinates for the three local mode states using the relations in Table I, we found the Coriolis operators

\begin{align*}
H^z_+ &= \frac{2}{\sqrt{3}} C \xi_1^2 \sum_{n\bar{k},l} \left[ |k\rangle \langle l| ( - \sin \theta J_{x_l} + \cos \theta J_{y_l} ) \\
&- |l\rangle \langle k| (- \sin \theta J_{x_k} + \cos \theta J_{y_k} ) \right] \\
H^z_- &= -i \sqrt{2} B \Omega_{13} \xi_1^2 \sum_{n\bar{k},l} \left[ |k\rangle \langle l| ( \cos \theta J_{x_l} + \sin \theta J_{y_l} ) \\
&+ \sqrt{3} J_z ) - |l\rangle \langle k| ( \cos \theta J_{x_k} + \sin \theta J_{y_k} - \sqrt{3} J_z ) \right],
\end{align*}

where the summation index $(k, l)$ takes the value of (1,2), (2,3), and (3,1). These two Coriolis operators have the following nonzero matrix elements in the symmetrized basis of Eq. (28):

\begin{align*}
\langle A; K' \pm | H^z_+ | A; K \pm \rangle &= - \frac{2}{\sqrt{3}} C \xi_1^2 [ \cos(K' - K) \theta z_{K'K} \pm \cos(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n; \\
\langle A; K' + | H^z_+ | A; K' - \rangle &= \frac{2}{\sqrt{3}} C \xi_1^2 [ \sin(K' - K) \theta z_{K'K} - \sin(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n; \\
\langle E^+; K' \pm | H^z_+ | E^+; K \pm \rangle &= \frac{1}{\sqrt{3}} C \xi_1^2 [ \cos(K' - K) \theta z_{K'K} \pm \cos(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n; \\
&= C \xi_1^2 [ \sin(K' - K) \theta z_{K'K} \pm \sin(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n + 1, \\
\langle E^+; K' + | H^z_- | E^+; K' - \rangle &= - \frac{1}{\sqrt{3}} C \xi_1^2 [ \sin(K' - K) \theta z_{K'K} - \sin(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n; \\
&= C \xi_1^2 [ \cos(K' - K) \theta z_{K'K} - \cos(K' + K) \theta z_{K',-K} ] \\
&\quad \text{for } K' - K = 2n + 1.
\end{align*}
with
\[ c_{K',K} = f_+(J,K)d_{K',K+1}(\frac{3}{2}\pi) - f_-(J,K)d_{K',K-1}(\frac{3}{2}\pi), \]  
(34)
and
\[ \langle A;K'\pm|H'|A;K\pm \rangle = 2\sqrt{2}B\Omega_{13}\xi_{13}[\sin(K'-K)\theta_y J_{K',K},\pm\sin(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n; \)
\[ \langle A;K'\pm|H'|A;K\pm \rangle = 2\sqrt{2}B\Omega_{13}\xi_{13}[\cos(K'-K)\theta_y J_{K',K},\pm\cos(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n; \)
\[ \langle E^+;K'\pm|H^+;K\pm \rangle = -\sqrt{2}B\Omega_{13}\xi_{13}[\sin(K'-K)\theta_y J_{K',K},\pm\sin(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n; \)
\[ = \sqrt{2}B\Omega_{13}\xi_{13}[\cos(K'-K)\theta_y J_{K',K},\pm\cos(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n+1; \)
\[ \langle E^+;K'\pm|H^+;K\pm \rangle = -\sqrt{2}B\Omega_{13}\xi_{13}[\cos(K'-K)\theta_y J_{K',K},-\cos(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n; \)
\[ = -\sqrt{2}B\Omega_{13}\xi_{13}[\sin(K'-K)\theta_y J_{K',K},-\sin(K'+K)\theta_y J_{K',K},-K] \]  
for \( K'-K = 2n+1, \)
with
\[ J_{K',K} = \frac{1}{2}f_+(J,K)d_{K',K+1}(\frac{3}{2}\pi) + \frac{1}{2}f_-(J,K)d_{K',K-1}(\frac{3}{2}\pi) + \sqrt{3}Kd_{K',K}(\frac{3}{2}\pi), \quad f_\pm(J,K) = [J(J+1) - K(K\pm1)]^{1/2}. \]  
(35)

We have found that the eigenvalues calculated by using the matrix elements above agree with those calculated by the approach of close coupling of \( A_1|E \) vibrational states.

**IV. THE EFFECT OF INTERBOND COUPLING FOR XH\(_2\) TYPE MOLECULES**

The rotational Hamiltonian of XH\(_2\) type molecule, possessing \( C_\sigma \) symmetry is written as
\[ H = H_0 + H' = \sum_{k=1}^{2} [G_0 + B J_{k,k}^2 + C J_{k,k}^2 + A J_{k,k}^2] |n_k\rangle\langle n_k| \]
\[ + \lambda(|n_1\rangle\langle n_2| + |n_2\rangle\langle n_1|). \]  
(36)

This \( C_\sigma \) symmetry Hamiltonian arises out of the \( C_{2\pi} \) symmetry Hamiltonian by a \( \theta \) angle rotation of the \( a \) and \( b \) principle axes on the X–H–X plane. The rotational energy levels of \( H_0 \) in Eq. (36) are doubly degenerated. The introduction of interbond coupling term \( H' \) will destroy this degeneracy so as to give rise to the rovibrational levels of \( C_{2\pi} \) asymmetric top closely coupled \( A_1|B_2 \) vibrational states. The matrix elements of \( H' \) which couple the rotational levels of two local mode states \( |n_1\rangle \) and \( |n_2\rangle \) are
\[ \langle n_2;J_2K_2|H'|n_1;J_1K_1\rangle = \lambda D^{j_1j_2}_{K_2K_1}(\alpha,\beta,\gamma) \delta_{n_2n_1} \delta_{j_2j_1}. \]  
(37)

Unlike XH\(_3\) type molecules, all the labeling schemes for the \((x,y,z)\) coordinate system are applicable here, in Eq. (36) we have chosen the \((x,y,z)\) coordinate system to coincide with the \((b,c,a)\) principal axes. Then the Euler angles can be uniquely determined as \((0,\pi+2\theta,\pi)\) for converting local mode state \( |n_1\rangle \) to \( |n_2\rangle \) and \((-\pi,\pi-2\theta,0)\) vice versa. Substituting these values of Euler angles in Eq. (37) yields the following matrix elements of the interbond coupling term
\[ \langle n_2;J_2K_2|H'|n_1;J_1K_1\rangle = \lambda \delta_{n_2n_1} \delta_{j_2j_1}. \]  
(38)

Using the vibrationally symmetrized basis functions
\[ |A;K\rangle = \frac{1}{\sqrt{2}} (|1;K| + |2;K|), \]  
(39)
\[ |B;K\rangle = \frac{1}{\sqrt{2}} (|1;K| - |2;K|), \]  
we obtain
\[ \langle A;K'|H'|A;K\rangle = -\lambda(1)^{j_1j_2}d_{K_2,K_1}(2\theta). \]  
(40)

There are no nonzero coupling matrix elements between \( A \) and \( B \) states. Therefore the \( A \) and \( B \) states without the interbond coupling Eq. (40) are two degenerate symmetric top states since \( A \) and \( B \) states are linear combinations of the states that are degenerate in \( H_0 \) [see Eq. (39)], and the \( A \) and \( B \) states are isolated as the interbond coupling term has effect only inside the \( A \) and \( B \) states, respectively. Using the Wang functions for the \( A \) and \( B \) states:
\[ |\Gamma;K\rangle = \frac{1}{\sqrt{2}} (|\Gamma;K\rangle + |\Gamma;K\rangle), \quad \Gamma = A \text{ or } B, \]  
(41)
the matrix elements of the interbond coupling are...
\[ \langle A; K' | -H' | A; K \rangle = - \langle B; K' | -H' | B; K \rangle \]
\[ = \lambda (-1)^i [d_{K', K} (2\theta) \pm d_{K', K} (2\theta)] \quad \text{for} \ K' - K = 2n; \]
\[ \langle A; K' + | H' | A; K \rangle = - \langle B; K' + | H' | B; K \rangle \]
\[ = \lambda (-1)^i [d_{K', K} (2\theta) \pm d_{K', K} (2\theta)] \quad \text{for} \ K' - K = 2n + 1 \]

which show that the \( e^+ \) and \( o^- \), also \( e^- \) and \( e^- \) symmetry blocks are coupled together to give rise to four blocks: \((A; e^+ / o^-), (A; e^- / e^-), (B; e^+ / o^-), \) and \((B; e^- / e^-). \) They are found to correspond to the \((A_1; e^+ / B_2; o^-), (A_1; e^- / B_2; e^-), (B_2; e^+ / A_1; o^-), \) and \((B_2; e^- / A_1; e^-) \) symmetry blocks in the approach of close coupling of \( A_1 / B_2 \) vibrational states.

In the approach of close coupling of \( A_1 / B_2 \) vibrational states, the Coriolis operator in the coordinate system defined in Sec. II can be expressed using the vibrational state projection operators as:

\[ H^0 = 2C_{12} | \langle A_1 | B_2 | B_1 \rangle - | B_2 | A_1 \rangle | J_y. \]

Through a transformation of vibrational basis and angular momentum operators, the expression of the Coriolis operator in the present approach is obtained as:

\[ H^0 = 2C_{12} | \langle n_1 | n_2 | J_y \rangle + | n_2 | n_1 \rangle | J_y \rangle. \]

Using the symmetrized basis (41), the matrix elements of the Coriolis operators can be written as:

\[ \langle A; K' \pm | H^0 | A; K \rangle = - \langle B; K' \pm | H^0 | B; K \rangle \]
\[ = (-1)^i [d_{K; K} (2\theta) \pm d_{K; K} (2\theta)] \quad \text{for} \ K' - K = 2n; \]
\[ \langle A; K' + | H^0 | A; K \rangle = - \langle B; K' + | H^0 | B; K \rangle \]
\[ = (-1)^i [d_{K; K} (2\theta) \pm d_{K; K} (2\theta)] \quad \text{for} \ K' - K = 2n + 1 \]

with:

\[ \begin{align*}
    u_{K'K}^+ &= -f_+(J,K) d_{K',K} (2\theta) \\
    &+ f_-(J,K) d_{K',K} (2\theta).
\end{align*} \]

If the coordinates are chosen in a different way, the Euler angles and the subsequent expressions will be different, but the final results should be the same. For example, another good choice could be to coincide the \((x,y,z)\) coordinate axes with the \((a,b,c)\) principal axes. Then the Euler angles for converting local mode state \((n_1)\) to \((n_2)\) are \((0, -2\theta)\). The subsequent manipulations are very similar to that we have discussed. One can also choose the \((x,y,z)\) coordinate axes as the \((a,b,c)\) principal axes as used in Ref. 6. In this case, the Euler angles have infinite possible choices given by \([\alpha, \pi, -2\theta \pm \alpha]\) where \(\alpha\) has an arbitrary value. However, the resulting coupling matrix elements will be complex number involving a factor of \(e^{\pm 2\theta i}\). Introducing a pure imaginary number \(i\) in one of the Wang function will make the matrix elements real again.

We also found that the eigenvalues calculated by using the matrix elements presented here agree with those calculated by the approach of close coupling of \( A_1 / B_2 \) vibrational states.

V. DISCUSSION

It is interesting to find that the rotational tunneling approach with nonzero interbond coupling \( \lambda \neq 0 \) gives the same \( \alpha \) relation as that obtained by the traditional effective rotational Hamiltonian approach at the local mode limit. This is because the present rotational tunneling approach does not include the vibration–rotational interactions which will affect all the \( \alpha \) parameters. In fact, the interbond coupling term \( H^0 \) also mixes the vibrational wave functions, and, in turn, has effect on the rotational constants and other vibration–rotational parameters which could be thought as the second order effect of the interbond coupling. Further work is in progress to improve the rotational tunneling approach by including such high-order effect.

It is also very interesting to note that the highly excited rotational energy levels of some spherical top molecules become clustered and result in the symmetric top pattern.\(^{24,25}\)

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References
