The torsional and asymmetry splittings in HSOH

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\textbf{A B S T R A C T}

We refine the analytic treatment developed by Yamada et al. [K.M.T. Yamada, G. Winnewisser, P. Jensen, J. Mol. Struct. 695–696 (2004) 323] to explain the torsional splittings observed for HSOH. Here we find that in addition to the cis- and trans-tunnelling matrix elements, \( W_c \) and \( W_t \), the parameter originating from the torsion-rotation cross-term, \( \langle \vec{J}_c \vec{J}_b \rangle \), is also important. The torsional splittings of HSOH have a peculiar nature in that their magnitudes change cyclically with K with a period of approximately three. The previous treatment reproduced one cycle of this variation. Adjusting the three parameters of the current version to experimental data, which now extend to \( K = 5 \), the calculated splittings reproduce the experimental results quite well. The cyclic pattern is now calculated to extend over at least three cycles.

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\textbf{1. Introduction}

In recent years we have been interested in the torsional tunneling splittings observed in HSOH. HSOH and similar 4-atom skew-chain molecules present the simplest examples of internal rotation with asymmetric moieties. Yamada, Winnewisser, and Jensen [1] (hereinafter denoted YWJ) presented analytical expressions for the torsional splittings using the high-barrier matrix formalism proposed by Hougen [2,3]. The most important prediction presented by YWJ is that the magnitude of the torsional splitting should change cyclically with \( K \), with a period of about three. The number three derives from the approximately 1:2 ratio of the moments of inertia of the two internal rotor moieties: OH and SH.

The torsional quantum tunnelling splittings in HSOH and related skew-chain molecules exhibit unusual mass and \( K \)-dependence. In work performed by various combinations of the present authors, along with others, these unusual splittings have been the subject of a multi-level “attack”. The approaches include: a consideration of the limiting cases of hindered and free internal rotation which gives a clear qualitative explanation of these dependencies [4]; the use of the empirical algebraic model of YWJ which has a small number of fittable empirical parameters (whose improvement is the subject of the present work); the least-squares fitting of a reduced-dimension model, the Generalized Semi Rigid Bender (GSRB) [5]; and, finally, a full dimensional ab initio based TROVE calculation [6]. Each of these complementary approaches has added to our understanding of the physical origin of the splittings, and our ability to calculate and understand the quantum energy levels of such molecules.

Since YWJ, Baum et al. have made great progress in the observation of high \( K \) transitions and in their analysis using an effective Hamiltonian [7]. In the present study we have reanalyzed the torsional splitting at the \( J \rightarrow 0 \) limit using the YWJ method. The present analysis is different from the previous YWJ paper in that:

1. We can now include the recently reported transition frequencies of the \( 'Q_3 \) and \( 'R_4 \) branches of Baum et al. [7]. With this new data, the period of three predicted by the YWJ theory is clearly evident.
2. The new data shows that the magnitude of the torsional splittings for high \( K \) is almost independent of \( J \). Because the \( B_{ab} \) term in YWJ leads to a strong \( J \) dependence for all \( K \)'s we must therefore set it to zero. The strong \( J \) dependence of the torsional splitting observed in the low \( K \)'s \( 'Q_3 \) and \( 'Q_4 \) transitions is, in fact, mainly due to the inertial asymmetry.
3. Instead of incorporating the \( B_{ab} \) term we find that including a new term, neglected in YWJ, is important.
Since YWJ is a very bulky piece of work, we repeat the necessary equations here.

2. High-barrier matrix method

Following YWJ we consider various sets of \( K \) values in turn.

2.1. Splitting in the \( K = 3n \) states

The torsional–rotational energies of HSOH for \( K = 3n \) \((n \neq 0)\) states can be readily given by the diagonal elements of the \( 4 \times 4 \) Hamiltonian matrix in the basis set given in Eq. (93) of YWJ. The four basis functions are

\[
\begin{align*}
\psi_1^+ & : [J, K, m, 0] |A_1 \rangle, \\
\psi_2^+ & : [J, K, m, 1] |A_2 \rangle, \\
\psi_2^- & : [J, K, m, 0] |A_2 \rangle, \\
\psi_1^- & : [J, K, m, 1] |A_1 \rangle,
\end{align*}
\]

where the superscript on the \( \psi \) indicates the overall parity. The Wang linear combination of rotational wavefunctions is denoted rotational parity:

\[
\Delta \text{rot} = W_\text{c} + W_t.
\]

By assuming that the rotational part of the Hamiltonian is diagonal in the Wang basis, and by neglecting the cross-term neglected in YWJ, Section 5.2.1 of YWJ determined the energies to be

\[
\begin{align*}
\epsilon_1^+ & = E_{\text{rot}}^{(0)} + Q + W_\text{c} + W_t, \\
\epsilon_2^+ & = E_{\text{rot}}^{(1)} + Q - W_\text{c} - W_t, \\
\epsilon_2^- & = E_{\text{rot}}^{(0)} + Q - W_\text{c} - W_t, \\
\epsilon_1^- & = E_{\text{rot}}^{(1)} + Q + W_\text{c} + W_t,
\end{align*}
\]

Here \( E_{\text{rot}}^{(0)} \) and \( E_{\text{rot}}^{(1)} \) are the rotational energy of the Wang basis states \([J, K, m, 0]\) and \([J, K, m, 1]\), respectively. \( Q \) is the diagonal contribution from the torsional part of the Hamiltonian, \( W_\text{c} \) is the off-diagonal matrix element between the levels neighbouring through the cis-barrier, and \( W_t \) is that through the trans-barrier (see Eq. (52) of YWJ).

In the present study we account for the off-diagonal contribution of the cross-term neglected in YWJ, \( J_\text{c} J_\text{t} \), by using second order perturbation theory. This leads to

\[
\begin{align*}
\epsilon_1^+ & = E_{\text{rot}}^{(0)} + Q + W_\text{c} + W_t - \frac{(D_{\text{c}2})^2 K^2}{2(W_\text{c} + W_t)}, \\
\epsilon_2^+ & = E_{\text{rot}}^{(1)} + Q - W_\text{c} - W_t + \frac{(D_{\text{c}2})^2 K^2}{2(W_\text{c} + W_t)}, \\
\epsilon_2^- & = E_{\text{rot}}^{(0)} + Q - W_\text{c} - W_t + \frac{(D_{\text{c}2})^2 K^2}{2(W_\text{c} + W_t)}, \\
\epsilon_1^- & = E_{\text{rot}}^{(1)} + Q + W_\text{c} + W_t - \frac{(D_{\text{c}2})^2 K^2}{2(W_\text{c} + W_t)},
\end{align*}
\]

where, for the evaluation of the denominator of the second order perturbation term, we use the symmetric top approximation. That is, we assume \( E_{\text{rot}}^{(0)} \approx E_{\text{rot}}^{(1)} \), which is valid for \( K = 1 \) in a Wang basis and is therefore valid for the case of \( K = 3, 6, \ldots \) treated here.

The new parameter \( D_{\text{c}2} \) is defined by

\[
D_{\text{c}2} = \zeta \langle A_2 | J_\text{c} | A_1 \rangle = -\zeta \langle A_1 | J_\text{c} | A_2 \rangle.
\]

The energy order of the four components given by Eq. (3) depends on the values of the matrix elements, \( W_\text{c}, W_t, \) and \( D_{\text{c}2} \). We introduce an empirical index \( t = 1, 2, 3, \) and 4 for these components, indicating their energy order; i.e. \( E_1 \leq E_2 \leq E_3 \leq E_4 \). The \( t \) indices used here are not otherwise related to the nature of the wavefunction.

2.1.1. The \( K = 0 \) state

\( K = 0 \) is a special case, where only two components exist, \( \psi_1^+ \) and \( \psi_2^- \), the rotational parts of which are, as usual for \( K = 0 \), pure symmetric rotor functions. Thus

\[
\begin{align*}
\psi_1^+ & : [J, 0, m] |A_1 \rangle, \\
\psi_2^- & : [J, 0, m] |A_2 \rangle.
\end{align*}
\]

The corresponding energy eigenvalues \( \epsilon_1^+ \) and \( \epsilon_2^- \) are given in Eq. (2), which is equivalent to Eq. (3) when \( K = 0 \). With only two components for \( K = 0 \) we choose the index \( t \) as 3 for the lower energy one and 4 for the higher energy one. From Eq. (2) the torsional splitting between these levels is

\[
\Delta_3 = E_4 - E_3 = 2|W_\text{c} + W_t|,
\]

as given by Eq. (96) of YWJ. The energy splitting for even-\( J \) levels with \( K = 0 \) in the ground vibrational state is illustrated schematically in Fig. 1.

2.1.2. The \( K = 3n \) \((n \geq 1)\) states

For \( K = 3, 6, \ldots \), the symmetric top approximation can again be safely applied. Thus \( E_{\text{rot}}^{(0)} \approx E_{\text{rot}}^{(1)} \) so that \( E_1 \approx E_2 \) and \( E_3 \approx E_4 \). Then Eq. (3) shows that the torsional splittings, which are the energy differences between these pair of levels, are

\[
\Delta_4 = 2|W_\text{c} + W_t - K^2 D_{\text{c}2}/2(W_\text{c} + W_t)|.
\]

Note that Eq. (7) includes Eq. (6) as a special case.

The energy splitting of even-\( J \) levels with \( K = 3 \) in the ground vibrational state is illustrated schematically in Fig. 2, which is equivalent to Fig. 7 of YWJ, with the addition of the newly defined index \( t \).

2.2. Splitting in the \( K = 3n \pm 1 \) states

For \( K = 3n \pm 1 \) states the basis set of Eq. (97) of YWJ is used, where the index \( P \) represents the overall parity. We obtain the tor-

\[
K = 0, J \text{ even}
\]

\[
\begin{align*}
E_1 & \quad \Gamma^\text{\text{tor}} = +, \\
E_2 & \quad \Gamma^\text{\text{tor}} = +,
\end{align*}
\]

\[
\begin{align*}
J_{0, J} & \quad \Gamma^\text{\text{rot}} = +, \\
\delta_\text{\text{tor}} & \quad \Gamma^\text{\text{tor}} = -.
\end{align*}
\]

Fig. 1. The torsional splitting is shown schematically for a \( K = 0 \) even-\( J \) level in the ground vibrational state. The symmetry of the rotational part of the wavefunction for the \( E^* \) operation, i.e. parity, \( \Gamma^\text{\text{rot}} \), and that of the torsional part of the wavefunction, \( \Gamma^\text{\text{tor}} \), are indicated. The split components are labeled by \( E_t \) where the energy order index \( t \) is defined in the text. The overall parity of each level is given on the right. For odd-\( J \) the diagram is the same but with rotational and overall \( z \) parities reversed.
$K = 3$, $J$ even

2.2.1. The $K = 1$ state

Eq. (11) can be rewritten for $K = 1$, to give a good approximation for the asymmetry doubling in terms of the rotational constants $B$ and $C$.

\[
A_{\text{rot}}^{K=1} |_{K=1} = \frac{1}{2} (B - C) J (J + 1).
\]

(14)

Remembering that $q = -1$ for $K = 1$, Eq. (12) can be rewritten, as

\[
W_{jk}^{(P)} |_{K=1} = 2 B_{ab} [J (J + 1)] - D_{ab} - (-1)^{J + P} C_{ab} J (J + 1).
\]

(15)

Substituting Eqs. (14) and (15) into Eq. (10), the square of the splitting of the $K = 1, P = 0$ (positive overall parity) level is

\[
|H_{ab}^{(2)} |_{K=1} = \left\{ \left[ (B - C) / 2 - (-1)^{J} C_{ab} J (J + 1) + W_{c} - W_{l} / 2 \right]^2 + 2 B_{ab} [J (J + 1)] - D_{ab} \right\}^2 + 3 W_{l}^2 / 4.
\]

(16)

Since, as mentioned above, the experimentally derived torsional splittings do not exhibit a $J$-dependence for high $K$ states, $B_{ab}$ should be very small. We therefore neglect $B_{ab}$ and Eq. (16) becomes

\[
|H_{ab}^{(2)} |_{K=1} \approx \left\{ \left[ (B - C) / 2 - (-1)^{J} C_{ab} J (J + 1) + W_{c} - W_{l} / 2 - D_{ab} \right]^2 + 3 W_{l}^2 / 4.
\]

(17)

Similarly, for $P = 1$ (negative overall parity), we find

\[
|H_{ab}^{(1)} |_{K=1} \approx \left\{ - \left[ (B - C) / 2 - (-1)^{J} C_{ab} J (J + 1) + W_{c} - W_{l} / 2 - D_{ab} \right]^2 + 3 W_{l}^2 / 4.
\]

(18)

In the case of HSOH the $K = 1$ asymmetry splitting is very much larger than the torsional splitting, therefore

\[
|(B - C) / 2 - (-1)^{J} C_{ab} J (J + 1)
\]

is the dominant factor in Eqs. (17) and (18), and the resulting energy level pattern is shown in Fig. 3. (In the ground state of HSOH this relative dominance is true even for $J = 1$.)

The “larger” splittings, $\delta_{\text{asym}} = |E_{t} - E_{a}| / 2 - |E_{1} - E_{2}| / 2$, are mainly due to the inertial asymmetry ($K$-type doubling), expressed by Eq. (14). The “smaller” splittings, $\delta_{\text{tor}} = E_{4} - E_{2} \approx E_{2} - E_{1}$, represent the torsional splitting. This can be calculated for $K = 1$ from Eq. (119) of YWJ.

$K = 1$, $J$ even

\[
J_{1, J-1}
\]

$K = 3$, $J$ even

We now inspect the value $|H_{ab}^{(q)}|$ for the three special cases: $K = 1$, $K = 2$, and in the symmetric-top limit. To do this we need to find $A_{\text{rot}}^{K=1}$ and $W_{jk}^{(P)}$ for $K = 3n \pm 1$.
by using a first order expansion in terms of the quantity of Eq. (19) (which is large) to obtain the square roots of Eqs. (17) and (18). Using these in Eq. (20) then gives the torsional splitting at the asymmetric top limit as

\[ \Delta_1 \approx 2|W_c + W_r/2 - D_{ab}|. \]  

(21)

In order to validate the asymmetric top approximation of Eq. (21), we have calculated the splitting given by Eq. (20), using Eqs. (17) and (18), with observed \( B \) and \( C \), and assuming \( C_{ab} = 0 \) and \( D_{ab} = 0. \) \( \Delta_1 \) is then calculated to be 32.9 MHz for \( J = 1 \) and reaches the asymmetric top limit value \( \Delta_1 = 33.0 \) MHz at \( J = 9. \) Therefore the \( J \)-independent torsional splitting expression of Eq. (21) is a valid approximation.

2.2.2. The \( K = 2 \) state

In the YWJ treatment it is assumed that the rotational part of the full Hamiltonian of Eq. (8) is diagonal in the Wang basis. Neglect of the off-diagonal elements is valid as a first order approximation. In the rigid rotor approximation \( \Delta_{ab}^R = 0 \) for \( K = 2 \) states if only diagonal contributions to \( \Delta_{tot}^R \) for \( K = 2 \):

\[ \Delta_{tot}^R|_{K=2} = 2d[J(J+1)|J(J+1) - 2|. \]  

(22)

From Eq. (12) we obtain for \( K = 2 

\[ W_{k0}^R|_{K=2} = 2B_{ab}[J(J+1) - 4] + 2D_{ab}. \]  

(23)

Recalling Eq. (12) this corresponds to Eq. (15) for \( K = 1 \), noting that \( q = +1 \) and \( \delta_{1K} = 0 \) for \( K = 2 \). Substituting Eqs. (22) and (23) into Eq. (10), the off diagonal elements \( |H_{ab}^R|_{K=2} \) can be evaluated for even \( J \) as described for \( K = 1 \) in Section 2.2.1. Since the value of \( \Delta_{tot}^R \) in Eq. (22) is small for low \( J \), the torsional splitting for very low \( J \) levels can be evaluated by the symmetric top approximation as described in the next section.

For \( K = 2 \) of HSOH in the ground vibrational state one can roughly estimate that the asymmetric top limit is reached at about \( J = 20 \). It should be noted that the “smaller” splitting, \( E_1 - E_2 \approx E_2 - E_1 \), corresponds to asymmetry doubling at low \( J \) and to torsional doubling at high \( J \). Fig. 4 shows an example of the intermediate case. When the torsional doubling is larger than illustrated there, the rotational components of the \( t = 2 \) and \( t = 3 \) levels may switch after the level crossing.

2.2.3. High \( K \) states, symmetric top approximation

For high \( K \) states, say \( K \geq 4 \), the unperturbed \( K \)-type doubling \( (\text{Eq. (11)}) \) is vanishingly small, i.e.

\[ \Delta_{ab}^{K} \approx 0. \]  

(24)

The energy level pattern in this case is illustrated in Fig. 5 which is essentially the same as Fig. 9 of YWJ. The \( t = 1 \) and \( 2 \) levels are almost degenerate as are \( t = 3 \) and \( 4 \). In this case the torsional splitting, which is represented by the splitting \( E_4 - E_2 \) or \( E_3 - E_1 \), is derived from Eq. (9) as

\[ \Delta_{k} = 2|H_{ab}^{(0)}| - 2|H_{ab}^{(1)}|. \]  

(25)

Substituting Eq. (24) into the expression for \( H_{ab}^{(0)} \) (Eq. (10)), we obtain

\[ \Delta_{k} = 2\sqrt{(W_c - W_r/2 + D_{ab}qK)^2 + 3W_r^2/4} \]  

(26)

(Eq. (123) of YWJ), where \( q = -1 \) for \( K = 4, 7, 10, \ldots \) and \( q = +1 \) for \( K = 5, 8, 11, \ldots \).
Since the approximations used for using the more accurate energy-splitting expression (Eq. (10)) for $K = 1$ and 2, respectively. The fitting might be further improved by taking those splittings were weighted less by a factor of 100 and 4, respectively. The torsional splittings of HSOH in the ground state for each $K$-state strongly supports the adequacy of the present method for this type of problem.

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**References**


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Table 1

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<th>$K$</th>
<th>$\Delta_{nu}$</th>
<th>Observed$^a$/MHz</th>
<th>Calculated$^b$/MHz (present work)</th>
<th>Calculated$^c$/MHz (Ref. [6])</th>
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<tr>
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<td>W_c + W_t</td>
<td>$</td>
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</tr>
<tr>
<td>1</td>
<td>$2</td>
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<td>37.8</td>
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<td>20.0</td>
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</table>

$^a$ Reference [7].

$^b$ Calculated with the fitted values $W_c = -3.89(3)$ MHz, $W_t = -28.1(2)$ MHz, and $D_{12} = D_{ab} = -1.26(2)$ MHz.

$^c$ Calculated for $J = 1$ and 2. The disagree-
ments for $K = 1$ and 2 indicate that the torsi-
onal splittings are strongly $J$-dependent for these low $K$-states. It should be noted here that the present results are for the limit of $J = K$ while the TROVE results are for $J = 10$.

We believe that the present results provide a qualitative explana-
tion of the torsional splitting observed in HSOH, viz. that the torsion-
al splitting varies cyclically with $K$ with a period of approximately three. The good agreement with the TROVE results for high $K$-states strongly supports the adequacy of the present method for this type of problem.