Reduced dimension rovibrational variational calculations of the S1 state of C2H2. II. The S1 rovibrational manifold and the effects of isomerization

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Reduced dimension variational calculations have been performed for the rovibrational level structure of the S\textsubscript{1} state of acetylene. The state exhibits an unusually complicated level structure, for various reasons. First, the potential energy surface has two accessible conformers, trans and cis. The cis conformer lies about 2700 cm\textsuperscript{-1} above the trans, and the barrier to cis-trans isomerization lies about 5000 cm\textsuperscript{-1} above the trans minimum. The trans vibrations \nu\textsubscript{4} (torsion) and \nu\textsubscript{6} (asym. bend) interact very strongly by Darling-Dennison and Coriolis resonances, such that their combination levels and overtones form polyads with unexpected structures. Both conformers exhibit very large \chi\textsubscript{36} cross-anharmonicity since the pathway to isomerization is a combination of \nu\textsubscript{3} and \nu\textsubscript{5} (sym. bend). Near the isomerization barrier, the vibrational levels show an even-odd \(K\)-staggering of their rotational levels as a result of quantum mechanical tunneling through the barrier. The present calculations address all of these complications, and reproduce the observed \(K\)-structures of the bending and C–C stretching levels with good qualitative accuracy. It is expected that they will assist with the assignment of the irregular patterns near the isomerization barrier. © 2014 AIP Publishing LLC.

I. INTRODUCTION

Few excited electronic states of polyatomic molecules have been as extensively studied as the S\textsubscript{1} \((A^1A_u)\) state of acetylene, C\textsubscript{2}H\textsubscript{2}. Several decades of spectroscopy performed by many workers,\textsuperscript{1–14} as well as numerous theoretical studies,\textsuperscript{15–34} have shown that the molecule is trans-bent, and have given a complete vibrational assignment up to 4500 cm\textsuperscript{-1} of vibrational energy. A second conformer, where the molecule is cis-bent, was discovered recently.\textsuperscript{13} It lies 2670 ± 10 cm\textsuperscript{-1} above the trans conformer,\textsuperscript{34} and the barrier to isomerization is estimated to lie 4979 cm\textsuperscript{-1} (plus or minus a few hundred cm\textsuperscript{-1}) above the trans minimum.\textsuperscript{33} Since the S\textsubscript{1}-cis state transforms as \(a_2\) in the C\textsubscript{2v} point group, transitions to it from the \(\Sigma^+_g\) electronic ground state are dipole-forbidden.

The primary complication of the trans manifold’s rovibrational structure is the interaction between the nearly degenerate modes \nu\textsubscript{4} (torsion) and \nu\textsubscript{6} (asym. bend). These modes interact via Darling-Dennison resonance\textsuperscript{11,35} and both \(a\)- and \(b\)-axis Coriolis coupling.\textsuperscript{7} The result of these interactions is that the group of states with quantum numbers \(\nu\textsubscript{4} + \nu\textsubscript{6} = n\) forms a bending polyad, abbreviated \(B^n\). The bending polyads in trans C\textsubscript{2}H\textsubscript{2} have been quite successfully modeled by effective Hamiltonian treatments,\textsuperscript{11,12,14} in which the interaction parameters from high energy polyads scale in simple ways with those of low energy polyads, enabling a bootstrapped procedure of predicting high energy polyad structures from empirical fits of simpler low energy polyads. As nearly every vibrational level in the trans manifold belongs to a polyad, the robustness of the polyad patterns has been essential to successfully assigning the spectra of the S\textsubscript{1} state.

It is now known, however, that the addition of quanta of \nu\textsubscript{3} (sym. bend) to trans bending polyads progressively breaks apart and eventually destroys the polyad structure because of the large \(x_{36}\) cross anharmonicity associated with the approach to the half-linear isomerization transition state.\textsuperscript{12,14,34} The existence of a saddle point in the potential energy surface tests the limits of effective Hamiltonian treatments rooted in the assumption that the potential energy surface supports just one minimum and can be accurately represented as a relatively low-order power series expansion in the coordinates. Such difficulties have been noted before, for example, in Jacobsen and Child’s semiempirical, semiclassical inversion model of large amplitude motion in HCP,\textsuperscript{36} and in Barnes and Kellman’s approach to the isomerization in HO\textsubscript{2}.\textsuperscript{37,38} Though new empirical methods\textsuperscript{39} have been proposed to model the multi-mode vibrational level structure resulting from the existence of a saddle point, an \textit{ab initio} calculation that predicts the global rovibrational energy level structure and the associated wavefunctions is particularly useful for understanding both the physical nature and spectroscopic details of the emergent patterns caused by the isomerization.
A further consequence of isomerization in the $S_1$ state is that cis vibrational levels appear weakly in the $\tilde{A} - \tilde{X}$ spectra via tunneling into the trans well. The identification and assignment of these states\textsuperscript{13,14} has required parallel ab initio efforts.\textsuperscript{33,34} Continuing to push the assignment threshold to higher energies, up to and beyond the barrier to isomerization, is an additional motivation for the calculations presented in this paper.

The most recent ab initio study of $S_1$ acetylene prior to these calculations is the second-order vibrational perturbation theory (VPT2) treatment performed by some of the authors of the present work.\textsuperscript{34} Those calculations are realistically targeted to levels with two or fewer quanta of excitation. They achieved excellent agreement with experimental values, especially for stretching modes, but they performed much more poorly for the low energy bending modes. As Section IV of that reference shows in detail, the difficulty can be traced to the implicit use of rectilinear coordinates. In contrast, the use of curvilinear coordinates in a variational calculation provides for a much more accurate treatment of such motions.

Finally, it has been recently observed that barrier-proximal states, which can tunnel through the barrier to isomerization, exhibit a tunneling splitting in the form of $K$-staggering within their rotational manifolds.\textsuperscript{13,14} Though group theory allows for the possibility of these staggerings,\textsuperscript{40} their sign and magnitude cannot be easily predicted a priori. Understanding these staggerings and gaining a foothold on quantitative estimates of them is essential for continued progress in the study of $S_1$ C$_2$H$_2$.

This paper is the second of two parts. Paper I (Ref. 41) contains details of the methodology and implementation, and the reader is directed there for full documentation of the computational methods. Paper II presents our variational results. In Sec. II, we examine the predicted fundamental frequencies as a means of evaluating the quality of the calculations. In Sec. III, the structure of the trans bending polyads is explored, as well as the effects of isomerization on their structure. Section IV contains predictions regarding the cis vibrational manifold. Finally, in Sec. V, we discuss $K$-staggering and its effects on the $S_1$ rovibrational level structure.

II. FUNDAMENTAL FREQUENCIES

For the reader who has not read Paper I, the following information is necessary for interpreting the results:

- A reduced dimension approximation is made by freezing two CH bond lengths ($r_1$ and $r_2$), while leaving free the CC bond length ($r_3$), the two CCH bending angles ($\beta_1$, $\beta_2$) and the torsional angle ($\alpha$); these degrees of freedom span, to a good approximation, modes $\nu_2$, $\nu_3$, $\nu_4$, and $\nu_6$ of both trans and cis acetylene.
- Total molecular rotation is explicitly included, permitting the calculation of different $J$ and $K$ states.
- A multivalued internal coordinate system is employed, requiring the use of the $C_2^{\infty_v}$ extended complete nuclear permutation inversion (CNPI) symmetry group.\textsuperscript{40}
- A constrained, analytic reduced dimension rovibrational kinetic energy operator (KEO) is used, which properly accounts for the frozen CH bond lengths.
- Using a basis contraction scheme, a (3+3)D bending-torsion-rotation calculation (3 vibrational and 3 rotational degrees of freedom) is performed first; the eigenfunctions from this calculation are used to form a direct product basis with CC stretch basis functions to perform a (4+3)D calculation.

The sizes of the basis sets of each symmetry-$J$ block of the rovibrational Hamiltonian were given in Table III of Paper I. The absolute convergence error of the lowest eigenvalues of these basis sets is $<0.1$ cm$^{-1}$. Relative energies are converged to perhaps another order of magnitude. For the highest states of interest, lying around 5000 cm$^{-1}$ above the trans zero-point energy, the absolute convergence errors are of the order of 1 cm$^{-1}$.

As a means of evaluating the quality of our potential surface and the accuracy of our methods, we compare the observed and calculated fundamental frequencies for the trans and cis conformers in Table I. Only the modes approximately spanned in our reduced dimension internal coordinate space ($\nu_2$, $\nu_3$, $\nu_4$, and $\nu_6$ of each conformer) are included. Rough values are available for all of the cis frequencies, except $\nu_2$. For it we list the vibrational fundamental as given by VPT2 anharmonic force field calculations.\textsuperscript{34}

Examining modes of the trans conformer, for which all fundamentals are experimentally measured, it is clear that the 3D bending-torsion-rotation calculation is sufficient to describe the low frequency bends ($\nu_4$ and $\nu_6$), but fails to accurately reproduce the symmetric bending mode, $\nu_3$. The residual for this mode is significantly reduced by the addition of the $r_3$ stretch in the 4D calculation, which is consistent with

<table>
<thead>
<tr>
<th>Mode</th>
<th>Obs.</th>
<th>3D w/ unconstrained KEO</th>
<th>4D w/ unconstrained KEO</th>
<th>4D w/ constrained KEO</th>
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</thead>
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<tr>
<td>trans</td>
<td>$\nu_2$ ($\nu_{CC}$ stretch)</td>
<td>1387\textsuperscript{a}</td>
<td>...</td>
<td>1443</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$ (sym. bend)</td>
<td>1048\textsuperscript{a}</td>
<td>1109</td>
<td>1074</td>
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<tr>
<td></td>
<td>$\nu_4$ (torsion)</td>
<td>765\textsuperscript{b}</td>
<td>764</td>
<td>762\textsuperscript{c}</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$ (asym. bend)</td>
<td>768\textsuperscript{b}</td>
<td>770</td>
<td>769\textsuperscript{c}</td>
</tr>
<tr>
<td>cis</td>
<td>$\nu_2$ ($\nu_{CC}$ stretch)</td>
<td>(1503\textsuperscript{d})</td>
<td>...</td>
<td>1595</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$ (sym. bend)</td>
<td>740 $\pm$ 10\textsuperscript{e}</td>
<td>783</td>
<td>776</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$ (torsion)</td>
<td>865 $\pm$ 10\textsuperscript{e}</td>
<td>865</td>
<td>861\textsuperscript{f}</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$ (asym. bend)</td>
<td>622\textsuperscript{f,i}</td>
<td>618</td>
<td>615\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 3.
\textsuperscript{b}Reference 7.
\textsuperscript{c}These "4D" values for $\nu_4$ and $\nu_6$ were calculated on a 3D grid adiabatized along the $r_3$ coordinate.
\textsuperscript{d}This fundamental has not been observed. We instead quote recent VPT2 calculations (Ref. 34) for comparison.
\textsuperscript{e}Reference 13.
\textsuperscript{i}Estimated from the 2$\nu_4$ frequency divided by 2.
normal mode analyses that demonstrate a non-negligible contribution of \( r_3 \) displacement to \( \nu_5 \). The \( \nu_4 \) and \( \nu_6 \) predictions indicate that our calculated potential energy surface is of sufficiently high quality to generate spectroscopic accuracy (a few cm\(^{-1}\)) even for an excited electronic state. The fact that these predictions worsen in the 4D calculation is possibly a result of the coarser grid point sampling of the 4D potential surface (as detailed in Paper I), but we cannot entirely rule out that it is an artifact of the constrained KEO.

The CC stretching mode \( \nu_3 \) treated with an unconstrained KEO shows a considerably large residual. This may be at first unexpected as \( \nu_3 \) is spanned almost exclusively by \( r_3 \) and therefore the current dimension reduction should treat this mode adequately. The source of the discrepancy, however, can be traced to the use of an unconstrained, full dimensional KEO. As is often done when using a full dimensional KEO in a reduced dimension calculation, the only change made to the KEO is to ignore terms with derivatives with respect to frozen coordinates (in this case the two \( r_{CH} \) bond lengths). We expect the kinetic energy of the \( r_3 \) stretch to be determined largely by the KEO term containing its second derivative, which, in the unconstrained KEO, is

\[
\frac{-h^2}{2 \mu_{CC}} \frac{1}{\mu_{CC}} \frac{\partial^2}{\partial r_3^2}. \tag{1}
\]

This expression indicates that the effective reduced mass of the \( r_3 \) stretch is equal to \( \mu_{CC} \), i.e., the unconstrained KEO treats the \( r_3 \) stretch as that between two carbon atom masses, as opposed to two CH fragments, which is intuitively what one would expect. In fact, replacing the C-C reduced mass, \( \mu_{CC} = m_C/2 \), with a CH dimer reduced mass, \( \mu_{CH,CH} = (m_C + m_H)/2 \approx (13/12)\mu_{CC} \), should lower the stretch frequency by \( \sqrt{12/13} \). Scaling the calculated unconstrained KEO frequency of 1443 cm\(^{-1}\) by this ratio yields 1386 cm\(^{-1}\), almost exactly the observed \( \nu_3 \) frequency. This suggests that, indeed, the unconstrained KEO incorrectly treats reduced masses (among other details) when naïvely applied to reduced dimension systems. The corresponding second derivative term in the constrained KEO (see the Appendix of Paper I) equals

\[
\frac{-h^2}{2 \mu_{CC}} \left[ \frac{1}{\mu_{CC}} - \frac{\mu_{CH}}{m_C} (\cos^2 \beta_1 + \cos^2 \beta_2) \right] \frac{\partial^2}{\partial r_3^2}. \tag{2}
\]

The effective \( r_3 \) stretching mass is geometry-dependent according to the middle factor of the above expression. At linear geometries (\( \beta_1 = \beta_2 = 0 \)), the mass factor is exactly the inverse CH dimer reduced mass, as expected. When \( \beta_1 = \beta_2 = 90^\circ \), both cosine terms are zero and the effective mass is that of two carbon atoms. At other geometries, the effective mass equals some intermediate value.

The calculated \( \text{trans} \) fundamental frequencies using the constrained KEO are shown in the right-most column of Table I. The \( \nu_3 \) frequency clearly improves, matching the observed value to less than 1 cm\(^{-1}\), demonstrating the necessity of a properly constrained reduced dimension KEO, as discussed in Paper I. The low frequency bends, \( \nu_4 \) and \( \nu_6 \), actually worsen. As mentioned above, this is likely due to the more sparsely sampled 4D PES grid. It will be seen, however, that these small errors in the fundamental frequencies have relatively little effect on the calculated local polyad structures of high lying overtones and combination bands of \( \nu_4 \) and \( \nu_6 \).

The \( \text{cis} \) fundamental frequency predictions behave in a similar way to those of the \( \text{trans} \) conformer. \( \nu_4 \) and \( \nu_6 \) are expected to be the most accurate of the 3D calculation. In fact, \( \nu_4 \) is in perfect agreement with the experimentally observed value, and the \( \nu_6 \) frequency is reproduced quite well, within 1% error. For the same reason as above, the \( \text{cis} \) \( \nu_5 \) fundamental frequency in the 3D calculation is overestimated. The 4D calculation shows a similar degradation of the \( \nu_4 \) and \( \nu_6 \) frequencies. The \( \nu_5 \) frequency improves with the inclusion of \( r_3 \) displacement, while the \( \nu_3 \) frequency with the constrained KEO is in relatively good agreement with the VPT2 prediction.\(^{34} \) At least some of the current \( \text{cis} \) predictions’ discrepancies can be attributed to the fact that the PES was calculated with CH bond lengths constrained to their \( \text{trans} \) equilibrium values, \( r_{CH} = 1.0963 \) Å, which is about 0.2% smaller than the \( \text{cis} \) equilibrium value, \( r_{CH} = 1.0983 \) Å.\(^{33} \)

### III. BENDING POLYADS AND THE ONSET OF ISOMERIZATION

A complete \( J = K = 0 \) level list of predicted vibrational states with assignments from the \( \text{trans} \) origin to 5000 cm\(^{-1}\) of internal energy is included in the Appendix. It would be both tedious and mostly uninformative to compare the calculated structure to the observed levels state-by-state; instead, we examine specific representative cases.

An overview diagram of the observed and calculated \( \text{trans} \) and \( \text{cis} J = 0 \) level structure is shown in Figure 1.

Apart from the slight overestimation of the \( \nu_3 \) frequency, the overtones and combination bands involving \( \nu_3 \) and \( \nu_4 \) are reproduced quite well (left side of Figure 1). These levels display very little interesting structure and conform to simple anharmonic oscillator energy level patterns.

The first challenge for \( \text{ab initio} \) calculations involves the overtones of modes \( \nu_4 \) and \( \nu_6 \). Errors in the calculated bending fundamental frequencies, as discussed above, lead to some clearly-seen systematic offsets of the higher lying bending polyads. However, the \( \text{internal} \) structure of each polyad is reproduced with impressive accuracy. Figure 2 shows the observed and calculated (4D) \( J = K = 0 \) level structure of \( B^4 \), the polyad containing the zero-order \{4\,\,4, 4\,\,6\,\,1, 4\,\,6\,\,2, 4\,\,6\,\,3, 6\,\,1\} vibrational states. Overall, the complicated course of the perturbed asymmetric top levels is well reproduced, despite the small discrepancies in the \( \nu_4 \) and \( \nu_6 \) fundamental frequencies. After correcting for the net offset of the calculated polyad, the intrapolyad structure has a rms residual of only 4.9 cm\(^{-1}\). Other calculated polyads throughout the \( \text{trans} \) manifold have similar intrapolyad structure rms residuals. These residuals are about the same as those of effective Hamiltonian models that use interaction parameters from lower energy polyads to predict the structure of higher lying levels.

Variational eigenfunctions provide important insight into the physical nature of rovibrational dynamics. One notable result of polyad effective Hamiltonians in \( \text{trans} \) acetylene is that the polyad members possess approximate vibrational angular momentum.\(^{11} \) Inspection of the variational wavefunctions for the \( B^4 \) polyad elaborated upon in the preceding paragraph
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FIG. 1. Observed and calculated $S_1$ vibrational levels (energies in cm$^{-1}$). $J = 0$ vibrational energies are shown for almost all vibrational levels under 5000 cm$^{-1}$ of internal energy. Assigned observed levels are shown in blue (left side of each stack). Calculated levels are in red (right side of each stack). All levels are trans except for the rightmost column labeled “cis.” An offset of 240 cm$^{-1}$ was subtracted from the calculated cis levels such that the calculated and empirically estimated value of the cis $v = 0$ origin (2670 ± 10 cm$^{-1}$, Ref. 34) coincide. The cis origin is indicated with a dashed line, as it remains unobserved.

FIG. 2. Observed (blue, left) and calculated (red, right) $J = K = 0$–2 levels of the $B^4$ polyad, which contains five vibrational members. Only eight of the 15 expected $K$-stacks with $K = 0$–2 have been assigned. For unassigned states, calculated values based on parameters from lower bending polyads are given (Ref. 11). Bold lines indicate $J = K = 0$ levels, which are the same as those shown for this polyad in Figure 1. The “center of gravity” of the polyad has been subtracted to compare only the intrapolyad structure, ignoring systematic offsets. The bending polyads deviate significantly from the normal $E\times K^2$ prolate top rotational energy level pattern. Despite the fact that the $J = K = 0$–2 levels span 400 cm$^{-1}$, the 4D calculated structure has an rms residual of only 4.9 cm$^{-1}$.

FIG. 3. Variational wavefunctions of the $B^4$ polyad ($|\Psi|^2$ is plotted). The coupling between modes $v_4$ and $v_6$ is manifest. The angular nodal patterns (shown with solid lines) are consistent with the expected vibrational angular momentum quantum number $\ell \sim 0$, 2, 4. Member states of $B^4$ are labeled in absolute energy order by Roman numerals.

FIG. 4. As discussed above, effective Hamiltonian models begin to break down for $3^m6^n$ combination levels because of the large $x_{36}$ cross anharmonicity associated with the approach to the barrier to isomerization. Prior reduced dimension discrete variable representation (DVR) vibrational calculations of the $S_1$ state have shown that such levels are increasingly delocalized across the cis-trans isomerization barrier. This work, by including the torsional degree of freedom, extends this result by enabling an examination of the wavefunctions for all states of $3^m6^n$ polyads, among which isomerizing states are especially interesting. Figure 4 compares the $\{\beta_1, \beta_2, \alpha\}$ projections of the wavefunctions of $B^4$, $3^1B^4$, and $3^2B^4$ polyads as given by the 4D calculation. As a reminder, $\beta_1$ and $\beta_2$ are CCH bending angles and $\alpha$ is the torsional out-of-plane angle (see Paper I). For the pure bending polyad, $B^4$, the coupled vibrational angular momentum structure is the same as that seen in Figure 3. The addition of one or two quanta of $v_3$ begins to alter the polyad coupling patterns. The lowest member is decoupled from the remainder of the polyad. This selective and incremental decoupling can be seen in the loss of vibrational angular momentum structure in the wavefunction and the onset of delocalization into the cis well, especially for $3^26^4$ in the lower left plot of the figure. This decoupling is associated with the large cross-anharmonicity of $v_3$ and $v_6$. The predicted magnitude of the (negative) cross-anharmonicity in this calculation is smaller than experimentally observed (for example, we predict $3^16^1$ to lie, erroneously, above $3^14^1$); however, the general pattern of $3^m6^n$ combination bands is still well reproduced.
FIG. 4. Decoupling of the $3^1B^4$ polyads. The bending-torsion projections of 4D, $J = 0$ wavefunctions for the $B^4$, $3^1B^4$, and $3^2B^4$ polyads are shown in the first, second, and third rows, respectively. Isosurfaces of the squared amplitude ($|\Psi|^2$) are plotted. The lowest energy polyad member is on the far left of each row. As $v_3$ increases, the lowest member of the polyad becomes decoupled from the rest of the polyad, restoring its nominal $3^6$ character. $3^26^4$ (lowest left-most wavefunction) exhibits cis-trans delocalization and tunneling through the isomerization barrier.

broken apart by the effects of isomerization are difficult to predict with effective Hamiltonian models. Variational treatments generate the complete rovibrational manifold in a single calculation and thus allow us to understand—both globally and in detail—the patterns of the rovibrational structure of isomerizing systems.

IV. cis VIBRATIONAL MANIFOLD

The vibrational assignments of the experimentally observed cis states$^{13,14}$ have been guided to some extent by ab initio calculations$^{33,34}$ of cis vibrational frequencies. Completing the identification and assignment of the remaining cis vibrational levels below and near the barrier to isomerization will undoubtedly benefit from continued theoretical studies. We summarize in Table II the observed and calculated positions of the low energy cis vibrational manifold. Despite residuals of tens of cm$^{-1}$ in the variational results, the level structure is sufficiently sparse to confirm the vibrational assignments with confidence. It should be noted that the variational PES was optimized for trans geometries (i.e., trans $r_{C1}$ bond lengths), which results in systematically larger residuals for the cis predictions than for the trans. As mentioned above, the residuals in the variational predictions for the cis frequencies are expected to improve if a finer PES grid spacing is used around the equilibrium configuration, as well as allowing for relaxation of the CH distances.

V. K-STAGGERING AND TUNNELING INTERACTIONS

For any molecule with low barriers between local equilibrium geometries, barrier crossings and tunneling interactions will have an important qualitative impact on barrier-proximal states and their level structure. $S_1 C_2 H_2$ is an especially interesting case in that there are both several non-equivalent wells

<table>
<thead>
<tr>
<th>cis state</th>
<th>Obs.</th>
<th>Calc. (VPT2)</th>
<th>Calc. (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v = 0$</td>
<td>0$^a$</td>
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<td>$6^1$</td>
<td>...</td>
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<tr>
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<td>...</td>
<td>...</td>
<td>1815</td>
</tr>
</tbody>
</table>

$^a$The cis zero point has not been observed. Its value is derived to be 44 870 ± 10 cm$^{-1}$ based on the observation of cis $3^1$ and $3^2$ and the VPT2 calculation of cis $x_3$.

$^b$These VPT2 values include an empirical correction of the $v_4$ and $v_5$ frequencies (see Ref. 34 for details).
(cis and trans conformers) and two conceivable isomerization pathways between these wells (i.e., in-plane bending involving a mixture of symmetric and asymmetric bending modes and out-of-plane torsion). Though such properties make cis-trans isomerization in acetylene a complicated problem, they create patterns that encode details about cis-trans interactions and the associated isomerization dynamics.

It is convenient to divide the energy region where cis-trans tunneling is important into two parts. The lower energy part includes states where the tunneling interaction energies are much smaller than the spacing between localized cis and trans vibrational levels. The upper energy part includes states near the top of the isomerization barrier where tunneling effects are no longer perturbative, and interactions between wells dominate the level structure. In reality, of course, there is a continuous distribution between these regimes, but this distinction will help frame the discussion of tunneling patterns.

The simplest tunneling case is an interaction between degenerate localized states in identical potential wells. Figure 5(a) shows a 2D contour plot of the $S_1$ PES for planar geometries ($\alpha = 0$). The axes correspond to the two CCH bond angles $\beta_{1,2}$. The upper right and lower left quadrants contain two equivalent cis wells, while the upper left and lower right are trans. We consider localized wavefunctions in the two cis wells, which interact to form symmeterized tunneling components: a symmetric and antisymmetric linear combination. In Figure 5(b), we show transformations that may be applied to such wavefunctions. For the symmetric tunneling component, moving from configuration (1) to (3) via in-plane bending (2) leaves the value of the wavefunction unchanged (with no sign change), while the wavefunction of the antisymmetric component acquires a negative sign. A $180^\circ$ rotation about the body-fixed $z$-axis returns the molecule to the same space-fixed coordinates as (1), and therefore the total wavefunction must return to its original value. This implies that the rotational factor of the total wavefunction must undergo no sign change for symmetric tunneling components, but must acquire a negative sign for antisymmetric components. The phase change of such a rotation about the $z$-axis is $\exp(-i\pi K) = (-1)^K$. Thus symmetric tunneling components can only have rotational factors with even $K$ and antisymmetric tunneling components can only have rotational factors with odd $K$. Tunneling splittings in acetylene will therefore appear as a staggering between the even and odd $K$ levels of a vibrational state. This is distinct from how tunneling splittings appear in ammonia or methyl rotors.

The relevant extended CNPI group theory for treating isomerization in $S_1$ acetylene using the $G_4$ symmetry group is fully treated by Hougen and Merer in Ref. 40. It can be shown that nearest-neighbor tunneling interactions should lead to an even/odd $K$-staggering for in-plane isomerization. If torsional isomerization is feasible, then an additional staggering between $K = 4n$ and $K = 4n + 2$ states should occur.

A summary of observed and calculated staggerings is given in Table III. Because of the small number of observed cis levels and their respective $K$ rotational manifolds, few $K$-staggering measurements have been reported for this conformer. It is difficult to determine $K$-staggerings in trans polyads because the strong $a$-axis Coriolis coupling distorts the structure. Some $K$- levels that are not parts of polyads, like high overtones of $\nu_3$, are unaffected by such perturbations and have readily identifiable staggerings. For the two experimental cis data points available, the predictions agree in the direction and approximate magnitude of the $K$-staggering. The $K$-staggering for the cis origin level is predicted to be quite small and we anticipate that it will not be distinguishable from other factors affecting the rotational structure. Only one bending quantum higher than the levels where staggerings have been observed, the staggerings are predicted to be an order of magnitude larger (e.g., cis $K=6^2$ and $6^3$). There are two related contributions to this trend. First, the simple tunneling interactions between degenerate vibrational states belonging to identical wells (i.e., cis-cis or trans-trans tunneling) become larger as the barrier is approached. Second, resonant interactions between nearby cis and trans states are introduced. Because the CNPI symmetries of the rotational levels depend on $K$, the possible cis-trans interactions are

![FIG. 5. Tunneling in cis vibrational states. (a) 2D in-plane bending potential with two equivalent cis and trans wells. Degenerate localized wavefunctions in each equivalent well form symmetric and antisymmetric tunneling linear combinations. (b) A molecule in the lower left cis well (1) can isomerize via in-plane bending (2) to an equivalent cis well (3), which can be transformed back to the original orientation via a $180^\circ$ rotation about the CC-axis (4). The requirement of a single-valued wavefunction entails that symmetric tunneling components have only even $K$ states and antisymmetric tunneling components have only odd $K$ states.]
different for even or odd $K$. This gives a further contribution to the $K$-staggering.

The patterns associated with this latter type of cis-trans staggering are expected to be less consistent, as the level shifts depend sensitively on the relative positions of near-resonant cis and trans states. Even within this calculation, the sign of the shift can change, as it does, for example, with the 3D $\nu_4$ and 4D $K$-staggering prediction for trans $3^2\delta^2$, although the magnitude remains approximately the same. From a perturbation theory perspective, small cis-cis and trans-trans tunneling interactions between identical wells are a first-order effect, while K-dependent cis-trans interactions are a second-order effect.

It may be impossible to distinguish empirically between these two types of interactions in the observed spectra. However, in the variational wavefunctions, K-dependent cis-trans interactions are readily identified. As one example, the $\alpha = 0$ cross-section of the trans $3^2\delta^2$ wavefunction, for which the magnitude of the $K$-staggering could be as large as 60 cm$^{-1}$, is shown in Figure 6. The figure shows the calculated vibrational wavefunctions for both the $K = 0$ and 1 rotational components. Both rotational components show extensive cis-trans delocalization. However, the $K = 0$ component interacts with cis $3^2\delta^2$, and the $K = 1$ with cis $3^2\delta^2$, leading to a large predicted staggering between even and odd $K$ states. These asymmetric cis-trans interactions are especially sensitive to local resonances between the two wells, making it difficult for ab initio calculations to predict the detailed interactions between the uncorrelated zero-order structures of the cis and trans manifolds. However, these calculations provide qualitative patterns that are valuable when attempting to analyze spectra of the near-barrier region.

VI. CONCLUSIONS

In this paper, we have presented the highest dimension rovibrational variational calculations of $S_1$ acetylene to date. We have reproduced some of the most complicated aspects of this electronic state’s rovibrational structure, which include the $\nu_4/\nu_6$ bending polyads, the effects of cis-trans isomerization on the level structure of $3^2\delta^2$ combination bands, and the presence of $K$-staggering in levels that tunnel through barriers to isomerization. One strength of this variational treatment is that the entire global structure is generated with a single calculation, which allows patterns to be examined over large ranges of internal energy.

Though our calculations have contributed significantly to our understanding of cis-trans tunneling interactions, improving the quantitative accuracy of $K$-staggering predictions should be a primary goal of future theoretical studies of $S_1$ C$_2$H$_2$. The issue of sensitivity to local cis-trans level patterns may perhaps be overcome with a low dimension empirically fit effective potential, such as a 2D CCH bending model. However, it could very well be that a full dimensional treatment is required to obtain spectroscopically accurate predictions of $K$-staggerings.

In the Introduction, we alluded to an extended effective Hamiltonian approach to the isomerization of HO$_2$. However, we are less hopeful that such a model could be developed for cis-trans isomerization in $S_1$ C$_2$H$_2$ due to a number of significant complications: (i) acetylene exhibits an essentially complete mixing of normal modes along the isomerization path, whereas HO$_2$, though requiring both stretch and bend excitation to isomerize, dominantly proceeds along the bending coordinate; (ii) acetylene contains other resonances, such as the coupling between trans $\nu_4$ and $\nu_6$, which are not directly involved with the isomerization but would need to be accounted for in an effective Hamiltonian, complicating any conceivable model; and (iii) perhaps most importantly, the asymmetric double minimum potential of $S_1$ acetylene is a qualitatively distinct and more difficult system than that of a symmetric double well potential.

Exclusive attention has been devoted in this paper to the calculated rovibrational structure below and up to the barrier to isomerization. These calculations, of course, give predictions for the structure above the barrier as well. This predicted structure, however, has yet to be analyzed. Qualitatively new level patterns will emerge resulting from unhindered large amplitude internal motions. Among these is the development of approximate vibrational angular momentum about the out-of-plane (c) axis. Ab initio calculations conducted in parallel with the analysis of high energy spectra will certainly prove necessary in order to understand the undoubtedly complicated level structure of such energy regions.

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APPENDIX: J = K = 0 LEVEL LIST

See Table IV.
TABLE IV. Calculated 4D $J = K = 0$ level list. Assignments for all vibrational states up to 5000 cm$^{-1}$ above the zero point are included. States are organized by their $G^a_{2h}$ symmetry (with correlations to $C_{3h}$ and $C_{2v}$ labels provided). Local interactions which mix zero-order states of the same symmetry are indicated by superscript letters prefixed explicitly by "cis." States are prefixed explicitly by "cis."