

Extended permutation-inversion groups for simultaneous treatment of the rovibronic states of trans-acetylene, cis-acetylene, and vinylidene

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ABSTRACT

The electronic ground state potential surface of acetylene ($H-C\equiv C-H$) has a minimum at the linear conformation, but the excited electronic states may have potential minima at a variety of nonlinear equilibrium shapes. This work is concerned with the group theoretical ideas necessary to treat simultaneously the symmetry properties of rovibronic states associated with three different planar acetylene equilibrium configurations, namely trans bent acetylene, cis bent acetylene, and vinylidene ($H_2C=C$). We make use of three different kinds of groups: (i) point groups, (ii) permutation–inversion (PI) groups, and (iii) extended PI groups. The PI group is G_4 or G_8 , depending on whether C–H bond breaking is impossible (no bent acetylene \leftrightarrow vinylidene interconversion) or possible. The extended PI groups are $G_4^{(2)}$ and $G_8^{(2)}$, respectively, when the only large amplitude motions are the CCH bends at each end of the molecule, and $G_4^{(8)}$ and $G_8^{(8)}$, respectively, when internal rotation is added as a third large amplitude motion. Applied to acetylene, the results indicate that there will be no splittings of the rovibronic levels unless CH bond breaking occurs. Even without bond breaking, however, states of the cis and trans isomers just below their interconversion barrier will show “staggerings” in their K -structures, i.e., a given vibrational level will have three tunneling components at slightly different energies: one component will have levels with $K = 4n$ only (where n is an integer), a second component will have levels with $K = 4n + 2$ only, and the third will have only odd- K levels. New experimental results for the S_1 -cis electronic state of acetylene [21] are reviewed, and are found to be consistent with the group theory in so far as comparison is possible.

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1. Introduction

Acetylene ($H-C\equiv C-H$) is linear in its ground electronic state, but its excited electronic states exhibit a variety of equilibrium shapes. This paper is concerned with the group theoretical ideas necessary to treat simultaneously the symmetry properties of the rovibronic states of three different planar acetylene structures, namely trans bent acetylene, cis bent acetylene, and vinylidene ($H_2C=C$), although the formalism below has been carried further for situations where the vinylidene structure is excluded, i.e., for situations where no chemical bonds are broken. We make use of three different kinds of groups: (i) point groups [1,2], (ii) permutation–inversion (PI) groups [3,4], and (iii) extended PI groups [5], starting with the more familiar point-group ideas and gradually working up to the less familiar extended-PI group ideas. To make the paper more readable, we review a number of concepts already described in the literature.

In this paper we restrict consideration to electronic potential surfaces for C_2H_2 which have a very high barrier to linearity, so that

we can avoid all the complications that arise when the A rotational constant approaches infinity [6], and the a -axis rotational degree of freedom becomes a component of a degenerate bending vibrational degree of freedom.

Motions of the $N = 4$ atoms in acetylene give rise to $3N = 12$ degrees of freedom. For spectroscopic applications, we immediately remove the three translations from consideration. When considering only non-linear acetylenic structures (i.e., trans bent, and cis bent $H_1-C_a\equiv C_b-H_2$), it is logical to group the three bond stretches (H_1-C_a , $C_a\equiv C_b$, and C_b-H_2) together as small-amplitude vibrations (SAVs). This leaves us with the six degrees of freedom of interest for this paper, which are traditionally divided into three rotational angles χ , θ , ϕ describing the orientation of the non-linear equilibrium configuration in the laboratory, two C–C–H non-degenerate bends (i.e., $H_1-C_a\equiv C_b$ and $C_a\equiv C_b-H_2$) and one H–C–C–H torsion. If trans–cis interconversion is to be considered, the two bends and the torsion must be treated as large-amplitude motions (LAMs) in the spectroscopic formalism.

Because group theoretical symmetry operations must ultimately be applied to the variables in the molecular wavefunctions, and because some confusion arises as a result of the different coordinate systems used to describe wavefunctions for the different

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C_2H_2 equilibrium structures, we make extensive use of an equation relating laboratory-fixed Cartesian coordinates to the rovibrational coordinates used to describe the rovibronic wavefunctions of interest. This equation has the general form

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\text{LAMs}) + \mathbf{d}_i], \quad (1)$$

where \mathbf{R}_i represents the Cartesian coordinates of atom i in a laboratory-fixed axis system, \mathbf{R} represents the center of mass of the molecule in this same laboratory-fixed coordinate system, $S^{-1}(\chi, \theta, \phi)$ represents a direction cosine matrix relating the laboratory-fixed X, Y, Z axes to some molecule-fixed x, y, z axes, $\mathbf{a}_i(\text{LAMs})$ represents the position of atom i in the molecule-fixed axis system as a function of the large-amplitude-motion coordinates, and \mathbf{d}_i represents the small-amplitude vibrational displacement of atom i . (The use of the 12 components of the \mathbf{d}_i vectors to represent the less than 12 SAV degrees of freedom in our spectroscopic formalism will ultimately require suitable constraints on the \mathbf{d}_i .) The direction cosine matrix $S^{-1}(\chi, \theta, \phi)$ is taken from [7] and has the form

$$S^{-1}(\chi, \theta, \phi) = \begin{bmatrix} c\chi c\theta c\phi - s\chi s\phi & -s\chi c\theta c\phi - c\chi s\phi & s\theta c\phi \\ c\chi c\theta s\phi + s\chi c\phi & -s\chi c\theta s\phi + c\chi c\phi & s\theta s\phi \\ -c\chi s\theta & +s\chi s\theta & c\theta \end{bmatrix}, \quad (2)$$

where $c\chi s\theta = \cos\chi \sin\theta$, etc. A pedagogical discussion of the physical reasoning, algebraic manipulations, etc. associated with group-theoretical treatments based on Eqs. (1) and (2) can be found in Ref. [8]. Some familiarity with that material will greatly facilitate the reading of the rest of this paper.

2. Point group treatments

Fig. 1a–d shows schematic structures, atom labeling, and molecule-fixed Cartesian axis systems for trans and cis acetylene and for vinylidene. As is well known [1,2], these three equilibrium structures are traditionally treated using the point groups C_{2h} and C_{2v} (which are in fact both isomorphic to the abstract mathematical four-group). Table 1 gives character tables for these two point groups, using the structures and x, y, z axis labels in Fig. 1a–d. These axis labels do not necessarily follow the Mulliken convention [9], because the z axis in Fig. 1 is always chosen to lie along, or approximately along, the C–C bond. This is convenient

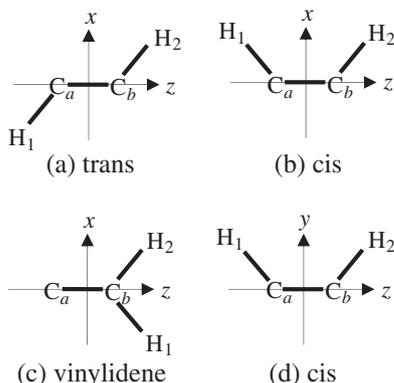


Fig. 1. Schematic structures for trans-bent and cis-bent acetylene and for vinylidene, together with atom labels and molecule-fixed x, y, z axis systems. The y axis is not shown in (a–c), but points up from the plane of the molecule (up from the page). The x axis is not shown in (d), but points down from the page. For conceptual simplicity, the z axis in these schematic structures always lies along the C_a – C_b bond. Appropriate translations and rotations of the axis systems shown will thus be required to obtain the principal inertial axes.

when rotational energy levels must be considered, since the z axis defined in this way is always nearly coincident with the principal inertial a axis of the molecule. For the structures in Fig. 1a–c, the y axis has been chosen to be perpendicular to the molecular plane, which causes it to lie always along the principal inertial c axis. For the structures in Fig. 1a and d the y axis is always the C_2 symmetry axis. These two structures will prove useful in the discussion of internal rotation in Section 7. We include the nuclear spin statistical weights for the rovibronic states of trans and cis acetylene and vinylidene in Table 2.

The point group operations of Table 1 can be converted to PI operations [3,4] by defining for each of them a transformation [10] of the coordinates $\mathbf{R}, \chi, \theta, \phi$, and the \mathbf{d}_i in Eq. (1). If we make the assumption that no LAMs exist, as is appropriate when point groups are used, then the quantities $\mathbf{a}_i(\text{LAMs})$ in Eq. (1) are replaced by equilibrium positions \mathbf{a}_i^0 , which are constants unaffected by the symmetry operations. We then obtain a simplified version of Eq. (1),

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i^0 + \mathbf{d}_i]. \quad (3)$$

It should be noted that Eq. (3) represents three very different equations for trans acetylene, cis acetylene and vinylidene because the equilibrium position vectors \mathbf{a}_i^0 are not the same for these isomers. As a result, the symbols χ, θ, ϕ and \mathbf{d}_i represent different mathematical variables in the wavefunctions for the three structures [11], hinting at the difficulties that will arise if point groups are used to classify their wavefunctions.

Table 3 lists the transformation properties of the rotation-vibration coordinates in Eq. (3) under the various point group operations in Table 1. The column labeled \mathbf{R} gives transformations for the center of mass. It is actually of little interest here. The column labeled χ, θ, ϕ gives transformations for the rotational angles [10]. These transformations determine the symmetry species of the rotational basis functions, and are often named by their “equivalent rotations” [4], as indicated in the next column to the right. The last two columns give the transformations of the small amplitude vibrational displacement vectors, \mathbf{d}_i , which are needed because linear combinations of them form the basis for the symmetry coordinates and the normal coordinates for the small-amplitude vibrations [7]. Column 8 identifies the atom j whose equilibrium position is reached when a given point-group operation acts on the equilibrium or reference position of atom i . The point group operation of column 2 is then applied to the displacement vector \mathbf{d}_j , and the result is the transformed vibrational displacement vector \mathbf{d}_i of atom i [5,7,10]. When these transformed quantities are substituted on the right of Eq. (3), with choices for the constant equilibrium positions \mathbf{a}_i^0 that are appropriate for the equilibrium geometry under consideration, the transformed values for the coordinates \mathbf{R}_i on the left-hand side of Eq. (3) are related to the original values by the PI operations indicated in Table 1. (The transformation of infinitesimal vibrational displacement vectors under point group operations is discussed more fully in Chapter 5 of Ref. [7], and is shown pictorially for a plane of reflection in Fig. 5–8 there.)

Table 3 can be used in two ways. First, it can be used to determine the point-group symmetry species for the vibrational and rotational wavefunctions of trans acetylene, cis acetylene and vinylidene when these three “molecules” possess only small amplitude vibrations and are not capable of interconversion. Second, it illustrates the difficulties of using only point groups when these three entities are considered as interconverting isomers of the same molecule, since some operations from the full permutation-inversion group (see Section 3) occur twice, with different vibrational and rotational transformation properties, e.g., $(ab)(12)$, and some do not occur at all, e.g., (ab) .

Table 1
Character tables (a)–(d) for the point groups of the C₂H₂ structures in Fig. 1a–d.

(a) G ₄ = C _{2h} for trans bent acetylene					(b) G ₄ = C _{2v} for cis bent acetylene				
PG ^a	E	C ₂ (y)	<i>i</i>	σ(xz)	PG ^a	E	C ₂ (x)	σ(xy)	σ(xz)
PI ^b	E	(ab)(12)	(ab)(12)*	E*	PI ^b	E	(ab)(12)	(ab)(12)*	E*
A _g	1	1	1	1	A ₁	1	1	1	1
A _u	1	1	–1	–1	A ₂	1	1	–1	–1
B _g	1	–1	1	–1	B ₁	1	–1	1	–1
B _u	1	–1	–1	1	B ₂	1	–1	–1	1
(c) G ₄ = C _{2v} for vinylidene					(d) G ₄ = C _{2v} for cis bent acetylene				
PG ^a	E	C ₂ (z)	σ(yz)	σ(xz)	PG ^a	E	C ₂ (y)	σ(xy)	σ(yz)
PI ^b	E	(12)	(12)*	E*	PI ^b	E	(ab)(12)	(ab)(12)*	E*
A ₁	1	1	1	1	A ₁	1	1	1	1
A ₂	1	1	–1	–1	A ₂	1	1	–1	–1
B ₁	1	–1	1	–1	B ₁	1	–1	1	–1
B ₂	1	–1	–1	1	B ₂	1	–1	–1	1

^a Point group operations for C_{2h} (a) and C_{2v} (b–d) for the C₂H₂ structures and x, y, z axis systems shown in Fig. 1a–d, respectively.

^b Permutation-inversion operations to which these point group operations correspond for the structures in Fig. 1a–d, respectively, when using the relation between laboratory-fixed and molecule-fixed coordinates given in Eq. (3) and the variable transformations given in Table 3.

Table 2
Statistical weights for rovibronic states of the C₂H₂ isotopomers with no bond breaking.

	¹² C ₂ H ₂	¹³ C ₂ H ₂	¹² C ₂ D ₂	¹³ C ₂ D ₂
<i>Trans or cis acetylene</i> ^a				
^{evr} A _g , A _u , A ₁ , A ₂	1	10	6	15
^{evr} B _g , B _u , B ₁ , B ₂	3	6	3	21
<i>Vinylidene</i> ^b				
^{evr} A ₁ , A ₂	1	4	6	24
^{evr} B ₁ , B ₂	3	12	3	12

^a Rovibronic symmetry species for the PI group G₄ given in Table 1a,b,d.

^b Rovibronic symmetry species for the PI group G₄ given in Table 1c.

3. Permutation-inversion group treatments

It is well known that when large amplitude motions are possible, point group treatments must usually be abandoned in favor of PI group treatments, so in this section we reconsider the three acetylene structures of interest from this point of view. The full (i.e. maximum possible) PI group for C₂H₂ is very simple, since it

is generated from the three operations (ab), (12), and E*. This full PI group has order 2³ = 8, and is known as G₈; it happens to be isomorphic to D_{2h}. The character table is shown in Table 4. This PI group is appropriate for a simultaneous treatment of rovibronic symmetry species for all three frameworks in Fig. 1a–c, i.e., trans and cis acetylene and vinylidene, and such a treatment has been carried out in the literature [12]. As we will see below, extended versions of the PI groups are needed when: (i) symmetry species must be assigned to individual factors of the total rovibronic wavefunction (electronic, small-amplitude-vibrational, large-amplitude-vibrational, and rotational), or (ii) the various possible tunneling splittings and staggerings are to be considered.

When the breaking of C–H bonds is treated as not feasible, such as when only cis and trans acetylene are considered, the appropriate PI group is G₄. It contains the four PI operations E, (ab)(12), (ab)(12)*, and E*.

Some conceptual problems remain even when PI group ideas are used. For example, in a G₈ treatment of C₂H₂, the PI operation (12) involves no breaking of C–H bonds when rovibronic functions associated with vinylidene are considered, whereas (12) involves breaking both C–H bonds when functions associated with

Table 3
Transformation properties of the coordinates **R**, χ , θ , ϕ , and the **d_i** on the right of Eq. (3) under the point group operations in Table 1a–d.

PI ^a	PG ^b	Molecule ^c	R ^d	χ , θ , ϕ ^e	Equiv. Rot. ^f	d_i ^g	<i>j</i> (<i>i</i>) ^h
E	E	a, b, c, d	R	χ , θ , ϕ	E	E d_i	<i>j</i> = <i>i</i>
(ab)(12)	C ₂ (y)	a, d	R	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	C ₂ (y)	C₂(y) d_i	a_j⁰ = C₂(y) a_i⁰
(ab)(12)*	<i>i</i>	a	– R	χ , θ , ϕ	E	i d_i	a_j⁰ = i a_i⁰
E*	σ(xz)	a, b, c	– R	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	C ₂ (y)	σ(xz) d_i	a_j⁰ = σ(xz) a_i⁰
(ab)(12)	C ₂ (x)	b	R	$-\chi$, $\pi - \theta$, $\pi + \phi$	C ₂ (x)	C₂(x) d_i	a_j⁰ = C₂(x) a_i⁰
(ab)(12)*	σ(xy)	b, d	– R	$\pi + \chi$, θ , ϕ	C ₂ (z)	σ(xy) d_i	a_j⁰ = σ(xy) a_i⁰
(12)	C ₂ (z)	c	R	$\pi + \chi$, θ , ϕ	C ₂ (z)	C₂(z) d_i	a_j⁰ = C₂(z) a_i⁰
(12)*	σ(yz)	c	– R	$-\chi$, $\pi - \theta$, $\pi + \phi$	C ₂ (x)	σ(yz) d_i	a_j⁰ = σ(yz) a_i⁰
E*	σ(yz)	d	– R	$-\chi$, $\pi - \theta$, $\pi + \phi$	C ₂ (x)	σ(yz) d_i	a_j⁰ = σ(yz) a_i⁰

^a Permutation-inversion operations from Table 1.

^b Point group operations from Table 1.

^c The letters a,b,c,d refer to the trans bent acetylene, cis bent acetylene, and vinylidene structures in Fig. 1a–d, respectively, and indicate the molecules to which each symmetry operation applies.

^d Laboratory-fixed center-of-mass vector.

^e Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^f As defined in Bunker and Jensen [4].

^g Small-amplitude molecule-fixed vibrational displacement vectors.

^h The subscript *j* as a function of *i* is defined by evaluating the right side of the equations in this column and then looking for the **a_j⁰** which is equal to this right side. See Fig. 1 for the *i* = a, b, 1, 2 atom labels. Note that this prescription will give no result for *j* for all operations in the second column that do not actually correspond to point-group operations for the trans-bent, cis-bent, or vinylidene shape under consideration.

Table 4Character table^{a,b} for the full PI group G_8 for C_2H_2 with bond breaking, and with atom labels as in Fig. 1.

E	(ab)	(12)	$(ab)(12)$	E^*	$(ab)^*$	$(12)^*$	$(ab)(12)^*$	Statistical weights			
								$^{12}C_2H_2$	$^{13}C_2H_2$	$^{12}C_2D_2$	$^{13}C_2D_2$
A_1^+	1	1	1	1	1	1	1	1	1	6	6
A_2^+	1	1	–1	–1	1	1	–1	–1	3	3	3
B_1^+	1	–1	1	–1	1	–1	–1	–1	0	3	18
B_2^+	1	–1	–1	1	1	–1	1	1	0	9	9
A_1^-	1	1	1	1	–1	–1	–1	–1	1	1	6
A_2^-	1	1	–1	–1	–1	–1	1	1	3	3	3
B_1^-	1	–1	1	–1	–1	1	–1	–1	0	3	18
B_2^-	1	–1	–1	1	–1	1	1	1	0	9	9

^a Since this group is isomorphic to D_{2h} (the abelian group G_8 containing only elements of order two), the sequence of the symmetry operations at the top of the table is somewhat arbitrary. We have chosen to put the pure permutations first, and the permutation-inversions second, in such a way that: (i) A and B species are symmetric and antisymmetric with respect to (ab) = exchange of the two C atoms; (ii) subscript 1 and 2 species are symmetric and antisymmetric with respect to (12) = exchange of the two H atoms; and (iii) superscript + and – species are of positive and negative parity. The PI operation $(ab)(12)$ corresponds to the C_2 point group operation for trans or cis bent acetylene; (12) corresponds to the C_2 point group operation for vinylidene; E^* corresponds to a point group reflection in the plane of the molecule. All eight PI operations in this table would correspond to the point-group operations of an actual C_2H_2 molecule if the two C's were symmetrically located on the positive and negative z axis and the two H's were symmetrically located on the positive and negative x axis. (Note that the G_8 symmetry species labels here differ from the G_8 labels used in Refs. [7,9,12,16].)

^b Statistical weights for rovibronic states of the C_2H_2 isotopomers when bond breaking is feasible are given in the last four columns.

acetylene are considered. Similarly, in a G_4 treatment of C_2H_2 , it can be shown from Tables 1 and 3 that the PI operation $(ab)(12)$ corresponds to a C_2 rotation about the b inertial axis of cis acetylene (in-plane), while also having to correspond to a C_2 rotation around the c inertial axis of trans acetylene (out-of-plane). Clearly some care will be required to get consistent definitions of the effects of these PI operations, given the contradictory requirements above.

Problems such as those just described can be solved using extended PI groups. These may seem like an unnecessary extra mathematical complexity, but we shall see in the next section that extended PI groups follow naturally from a spectroscopically reasonable choice for the three large-amplitude coordinates that allow interconversion among trans acetylene, cis acetylene, and vinylidene. The determination of the appropriate extended PI groups and their application to the LAM energy levels of C_2H_2 is the main goal of this paper.

4. Large-amplitude coordinates for acetylene

Two large amplitude coordinates appropriate for the trans \leftrightarrow cis problem in acetylene are the $H_1C_aC_b$ and $C_aC_bH_2$ bending angles β_1 and β_2 (which can be thought of as local bending modes at each end of the molecule). Bending through the linear configuration at one end of the molecule can clearly be used to pass from the trans to the cis configuration. This appears to be what actually happens in the trans–cis isomerization of the S_1 state of acetylene, where *ab initio* calculations [13,14] indicate that the transition state has a half-linear structure in which one of the CCH angles is roughly 120° , while the other end of the molecule is nearly linear. Positive and negative values for these two angles are schematically illustrated in Fig. 2. Another large amplitude coordinate relevant to the trans \leftrightarrow cis problem is the internal rotation angle α about the C_a – C_b bond, since changes in this angle can also be used to pass from the trans to the cis configuration.

Assume the molecule is initially in configuration (a) of Fig. 2, and then take it to configuration (b) by changing β_1 and β_2 to $-\beta_1$ and $-\beta_2$. Next rotate the whole configuration (b) about the z axis, by letting the rotational angle $\chi \rightarrow \chi + \pi$. This brings the numbered atoms of the molecule back into perfect coincidence with the configuration in (a), so that the transformation $(\beta_1, \beta_2, \chi) \rightarrow (-\beta_1, -\beta_2, \chi + \pi)$ corresponds to the identity operation E in the PI group. We call such an operation a “limited identity” because it does not function as a true identity only when limited to the PI group; it does not function as an identity when it appears in the extended

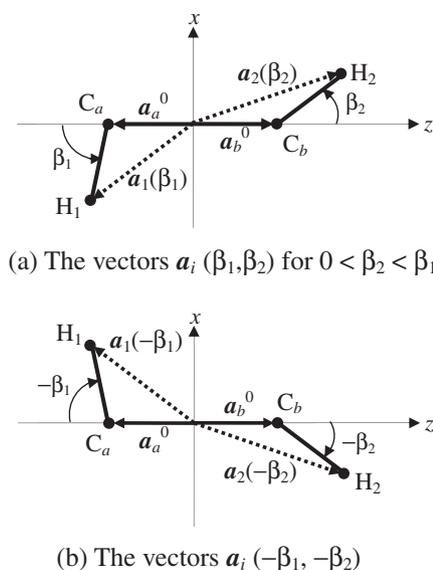


Fig. 2. Illustration of the vectors $a_i(\beta_1, \beta_2)$ in Eq. (5) for $i = a, b$ (shown as solid arrows) and $i = 1, 2$ (shown as dashed arrows). The small contribution of the center-of-mass position $A(\beta_1, \beta_2)$ has been neglected to simplify the drawing of the diagram. (a) A distorted conformation $a_i(\beta_1, \beta_2)$ of trans acetylene with $\pi/2 > \beta_1 > \beta_2 > 0$. (b) The conformation $a_i(-\beta_1, -\beta_2)$ obtained by reversing the signs of β_1 and β_2 , as specified for two of the symmetry operations in Table 5. Note that this change in sign of the LAM vibrational variables β_1 and β_2 leads to a structure in (b) which can be brought back into exact coincidence with that in (a) by using the rotational-variable transformation $\chi \rightarrow \chi + \pi$ to perform a $C_2(z)$ operation on the structure in (b). This combined LAM-rotation operation is the limited identity E_b occurring in Table 5.

PI group, where multiple-valued coordinates are used to express the molecular wavefunction. We will label this limited identity E_b in Section 6 and elsewhere to indicate that it is associated with the local mode bending vibrations. Similarly, another limited identity is given by the transformation $(\alpha, \chi) \rightarrow (\alpha + \pi, \chi + \pi)$, since an internal rotation of each C–H group by π followed by a z -axis overall rotation through π also brings configuration (a) of Fig. 2 back into perfect coincidence with itself. This limited identity is called E_t in Section 7 and elsewhere to indicate that it is associated with the torsional motion. Finally, the product of these two limited identities $(\beta_1, \beta_2, \alpha) \rightarrow (-\beta_1, -\beta_2, \alpha + \pi)$, is also a limited identity. It is called $E_b E_t = E_t E_b$ in Section 8 and elsewhere. These limited identities only arise when the coordinate system used for the molecular

wavefunctions is multiple-valued, i.e., when there is more than one set of coordinates that describes an identical arrangement of atoms in the laboratory (in other words an identical set of \mathbf{R}_i on the left of Eq. (1)). When there are n different coordinate transformations that correspond to the PI identity operation (no exchange of atoms, no laboratory-fixed inversion), we call the resulting group an n -fold extended PI group.

If we generalize the large-amplitude local bending angles β_1 and β_2 to describe motion on an appropriate ellipse with one C atom located at each focus, then changes in these angles can also be used to treat the trans \leftrightarrow cis \leftrightarrow vinylidene problem. The change from hydrogen motion on circles centered at each carbon atom to motion on an ellipse enclosing both carbons is illustrated in Fig. 3. This change in coordinates leads to no additional limited identities.

5. Extended PI group treatment for linear acetylene

We digress briefly to point out that an extended PI group is routinely (although mostly unknowingly) used by all high-resolution spectroscopists to treat linear acetylene. The PI group appropriate

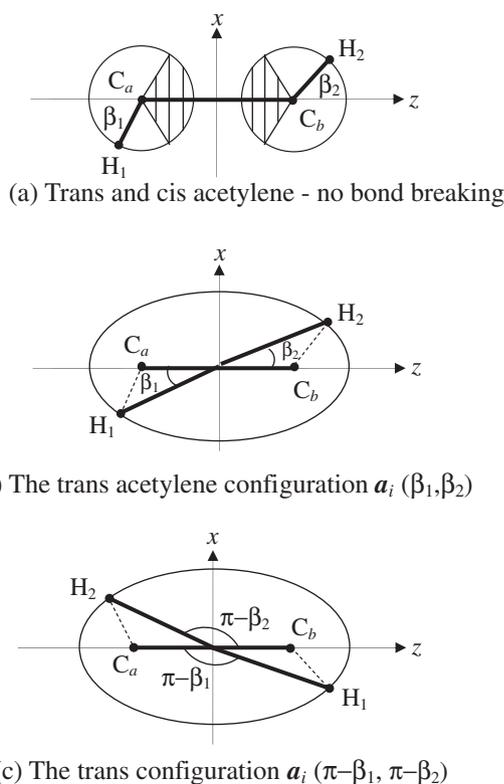


Fig. 3. Illustration of the range of motion of the two hydrogen atoms in C_2H_2 for the planar trans/cis acetylene problem and for the planar trans/cis acetylene problem with vinylidene. (a) Motion of the hydrogens on circles centered on each carbon atom. The requirement $-2\pi/3 < \beta_1, \beta_2 < +2\pi/3$ following Eq. (5) prevents the hydrogens from bending into the area containing the vertical shading, i.e., prevents the hydrogens from bending back into the $\text{C}_a\text{--C}_b$ bond. (b) Motion of the two hydrogen atoms on an (approximate) ellipse enclosing both carbon atoms, as appropriate for treating the trans and cis acetylene and vinylidene problem. This diagram is drawn for the same configuration as in (a), but values of β_1 and β_2 now describe angles of lines from the center of mass to the hydrogen atoms, rather than angles from the carbon atoms to the hydrogen atoms as in (a). The requirement $\beta_1 < \beta_2 + \pi < \beta_1 + 2\pi$ following Eq. (21) prevents either one of the hydrogens from overtaking the other on the elliptical path shown. (c) Example of a motion of the two hydrogens on the ellipse which involves breaking and reforming the two C–H bonds. The transformations of β_1 and β_2 depicted in this panel occur in two symmetry operations of the double group $G_4^{(2)}$ shown in Table 11, namely $C_2(x)$ and $\sigma(xy)$, which correspond to the PI operations (ab) and $(ab)^*$, respectively. (As might be intuitively expected, PI operations involving (12) in that table, require some interchange of the β_1 and β_2 angles.)

for linear acetylene is again G_4 , containing the four PI operations E , $(ab)(12)$, E^* , and $(ab)(12)^*$. This group has no degenerate symmetry species (see Table 1), but it is well known that linear acetylene has two doubly degenerate bending vibrations, belonging, respectively, to the π_g and π_u symmetry species of the point group $D_{\infty h}$. $D_{\infty h}$ is not isomorphic to G_4 , but is actually an infinite-fold extended group of G_4 [15], where each of the infinite number of arbitrary rotations C_α about the linear axis is a limited identity, since each such rotation causes the electronic and vibrational cylindrical coordinate angle variables to increase by α , but leads to no exchange of identical particles and to no inversion E^* .

A discussion of correlations between the rovibronic levels of linear acetylene and the rovibronic levels of both trans and cis bent acetylene, making use of the double group $G_4^{(2)}$, has been presented [16], but the results are not of direct interest here, since linear acetylene is excluded from consideration.

6. Trans and cis acetylene with only two local CCH in-plane bending LAMs

We begin our extended PI group treatments with this problem, because all configurations generated by the large amplitude motions are planar, which greatly simplifies the geometrical aspects of the problem. For this case, the expression $\mathbf{a}_i(\text{LAMs})$ in Eq. (1) must be replaced by $\mathbf{a}_i(\beta_1, \beta_2)$, where β_1 and β_2 are the $\text{H}_1\text{--C}_a\text{--C}_b$ and $\text{C}_a\text{--C}_b\text{--H}_2$ bending angles, respectively:

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\beta_1, \beta_2) + \mathbf{d}_i]. \quad (4)$$

The functions $\mathbf{a}_i(\beta_1, \beta_2)$, shown schematically in Fig. 2, can be defined algebraically in terms of appropriate constant vector positions \mathbf{a}_i^0 for the atoms. Even though this is a bending problem, it will be convenient to take the \mathbf{a}_i^0 vectors to correspond to the linear configuration, with all atoms on the z axis and the origin at the center of mass. This leads to

$$\begin{aligned} \mathbf{a}_i(\beta_1, \beta_2) &= \mathbf{a}_i^0 - \mathbf{A}(\beta_1, \beta_2) \quad \text{for } i = a, b \text{ (carbon atoms)} \\ \mathbf{a}_1(\beta_1, \beta_2) &= S^{-1}(0\beta_1 0)(\mathbf{a}_1^0 - \mathbf{a}_a^0) + \mathbf{a}_a^0 - \mathbf{A}(\beta_1, \beta_2) \\ \mathbf{a}_2(\beta_1, \beta_2) &= S^{-1}(0\beta_2 0)(\mathbf{a}_2^0 - \mathbf{a}_b^0) + \mathbf{a}_b^0 - \mathbf{A}(\beta_1, \beta_2), \end{aligned} \quad (5)$$

where $\mathbf{A}(\beta_1, \beta_2)$ is defined so that the center of mass of the arbitrarily bent structure $\mathbf{a}_i(\beta_1, \beta_2)$ is always at the origin. To constrain the LAM β_1, β_2 motions to something resembling a “normal bend,” i.e., to prevent the H atoms from passing through the $\text{C}\equiv\text{C}$ bond, we require $-2\pi/3 < \beta_1, \beta_2 < +2\pi/3$, as suggested by the top panel of Fig. 3.

It can be seen from Eq. (5) that if the small contributions from the center-of-mass position $\mathbf{A}(\beta_1, \beta_2)$ are ignored, then $\mathbf{a}_a(\beta_1, \beta_2)$ and $\mathbf{a}_b(\beta_1, \beta_2)$ are independent of β_1 and β_2 , while $\mathbf{a}_1(\beta_1, \beta_2)$ depends only on β_1 and $\mathbf{a}_2(\beta_1, \beta_2)$ depends only on β_2 . (The bending motions β_1 and β_2 are called “in-plane” in the heading of this section to emphasize the fact that each bend is associated with only one degree of freedom, unlike the bends in linear acetylene, which are doubly degenerate and are therefore each associated with two degrees of freedom.)

Table 5 gives a set of eight symmetry operations, which when applied to the right side of Eq. (4), produce on the left side of Eq. (4) transformed coordinates corresponding to the PI operations shown in Table 5. It is important to note that the four feasible PI operations for C_2H_2 with no C–H bond breaking each occur twice in Table 5, which means that we are dealing with a double group $G_4^{(2)}$ of the PI group G_4 containing the limited identity E_b . As explained in Section 4, the double-valued coordinate system in Eqs. (4) and (5) arises because we can achieve an apparent $C_2(z)$ rotation of a bent acetylene structure either (i) by carrying out an actual overall C_2 rotation of the molecule about the z axis via the

Table 5

Transformation properties of the coordinates \mathbf{R} , χ , θ , ϕ , β_1 , β_2 , and the \mathbf{d}_i on the right of Eq. (4) under symmetry operations of the double group $G_4^{(2)}$ of G_4 (see Table 1) appropriate for simultaneously treating trans bent and cis bent acetylene with only in-plane local mode C—C—H bending motions at each end as the two LAMs.

PI ^a	PG ^b	\mathbf{R}^c	χ, θ, ϕ^d	Equiv. Rot. ^e	β_1, β_2^f	\mathbf{d}_i^g	$j(i)^h$
E	E	\mathbf{R}	χ, θ, ϕ	E	β_1, β_2	$E \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_j^0$
(<i>ab</i>)(12)	$C_2(y)$	\mathbf{R}	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	β_2, β_1	$C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_j^0$
(<i>ab</i>)(12) [*]	<i>i</i>	$-\mathbf{R}$	χ, θ, ϕ	E	β_2, β_1	$i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_j^0$
E [*]	$\sigma(xz)$	$-\mathbf{R}$	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	β_1, β_2	$\sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_j^0$
E	E_b	\mathbf{R}	$\pi + \chi, \theta, \phi$	$C_2(z)$	$-\beta_1, -\beta_2$	$C_2(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_j^0$
(<i>ab</i>)(12)	$C_2(y)E_b$	\mathbf{R}	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$-\beta_2, -\beta_1$	$C_2(x) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_j^0$
(<i>ab</i>)(12) [*]	<i>i</i> E_b	$-\mathbf{R}$	$\pi + \chi, \theta, \phi$	$C_2(z)$	$-\beta_2, -\beta_1$	$\sigma(xy) \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_j^0$
E [*]	$\sigma(xz)E_b$	$-\mathbf{R}$	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$-\beta_1, -\beta_2$	$\sigma(yz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_j^0$

^a The PI operations in this column are obtained when the variable transformations in the columns to the right are substituted in Eq. (5). Note that every PI operation occurs twice, since this is a double group of the feasible PI group.

^b Operations of the extended PI group. E, $C_2(y)$, *i*, and $\sigma(xz)$ are very similar to the C_{2h} point group operations in Table 1a and Table 3, so the C_{2h} names have been retained in this double group of C_{2h} . E_b is the limited identity in this local-mode LAM bending problem.

^c Laboratory-fixed center of mass vector.

^d Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^e Equivalent rotation, as defined in Bunker and Jensen [4].

^f The two LAM local-mode H—C—C and C—C—H bending angles.

^g Small-amplitude molecule-fixed vibrational displacement vectors, which are needed to describe the three SAV bond stretches and the (SAV by hypothesis) torsion.

^h The subscript *j* as a function of *i* is defined by evaluating the right side of the equations in this column and then looking for the \mathbf{a}_j^0 which is equal to this right side. Note that $j = i$ for the first, fourth, fifth, and eighth rows.

rotational angle transformation $\chi \rightarrow \chi + \pi$, or (ii) by carrying out large-amplitude bending motions through the linear configuration at each end of the molecule via the bending angle transformation $(\beta_1, \beta_2) \rightarrow (-\beta_1, -\beta_2)$ (see Fig. 2).

This double-valued coordinate system could be avoided if the molecule fixed *x*, *y*, *z* axes were locked in the H—C—C group at one end of the molecule and the bending angle at that end were restricted to only positive values, but such a coordinate system treats the two symmetrically equivalent halves of acetylene in an unsymmetrical manner, so that group theoretical coordinate transformations cannot easily take all aspects of the molecular symmetry into account.

The symmetry species and characters for the double group $G_4^{(2)}$ containing the operations in Table 5 are given in Table 6. The SAV row in the heading, which has no analog in the character Table 1a–d, indicates which four of the eight symmetry operations can be

kept when trans acetylene (C_{2h}) or cis acetylene (C_{2v}) are considered to have only small-amplitude vibrations (SAV). This selection of symmetry operations can be understood with the help of Fig. 4, which gives a schematic representation of the *ab initio* potential surface [14] for the S_1 state of planar acetylene. Fig. 4 indicates that the two trans minima are located at $\beta_1 = \beta_2 = \pm\beta_{trans}$, where $\beta_{trans} \approx +60^\circ$, and that the two cis minima are located at $\beta_1 = -\beta_2 = \pm\beta_{cis}$, where $\beta_{cis} \approx +60^\circ$ (as shown also schematically in Fig. 2). Harmonic-oscillator-like SAV wavefunctions localized in each of these four wells can be represented schematically as

$$\begin{aligned} \psi_{UL} &= N_{trans} \exp[-k_{trans}(\beta_1 - \beta_{trans})^2] \exp[-k_{trans}(\beta_2 - \beta_{trans})^2] \\ \psi_{LR} &= N_{trans} \exp[-k_{trans}(\beta_1 + \beta_{trans})^2] \exp[-k_{trans}(\beta_2 + \beta_{trans})^2] \\ \psi_{UR} &= N_{cis} \exp[-k_{cis}(\beta_1 - \beta_{cis})^2] \exp[-k_{cis}(\beta_2 + \beta_{cis})^2] \\ \psi_{LL} &= N_{cis} \exp[-k_{cis}(\beta_1 + \beta_{cis})^2] \exp[-k_{cis}(\beta_2 - \beta_{cis})^2], \end{aligned} \quad (6)$$

Table 6

Character table^a for the double group $G_4^{(2)} = C_{2h}^{(2)} = G_8$ containing the symmetry operations in Table 5.

PI ^b	E	(<i>ab</i>)(12)	(<i>ab</i>)(12) [*]	E [*]	E	(<i>ab</i>)(12)	(<i>ab</i>)(12) [*]	E [*]			
$C_{2h}^{(2)c}$	E	$C_2(y)$	<i>i</i>	$\sigma(xz)$	E_b	$C_2(y)E_b$	<i>i</i> E_b	$\sigma(xz)E_b$			
SAV ^d	Both	C_{2h}	C_{2h}	Both		C_{2v}	C_{2v}		C_{2h}^e	C_{2v}^e	$(\mathbf{J}, \boldsymbol{\mu})^f$
A_{gs}^b	1	1	1	1	1	1	1	1	A_g	A_1	J_x, J_y, J_z
A_{us}^b	1	1	-1	-1	1	1	-1	-1	A_u	A_2	μ_x, μ_y, μ_z
B_{gs}^b	1	-1	1	-1	1	-1	1	-1	B_g	B_1	J_z
B_{us}^b	1	-1	-1	1	1	-1	-1	1	B_u	B_2	μ_z
A_{gd}^b	1	1	1	1	-1	-1	-1	-1	A_g	B_2	J_y
A_{ud}^b	1	1	-1	-1	-1	-1	1	1	A_u	B_1	μ_y
B_{gd}^b	1	-1	1	-1	-1	1	-1	1	B_g	A_2	J_x
B_{ud}^b	1	-1	-1	1	-1	1	1	-1	B_u	A_1	μ_x

^a This group is appropriate for a simultaneous treatment of trans bent and cis bent acetylene when the only LAMs are a local-mode in-plane C—C—H bending vibration at each end of the molecule. Symmetry species names follow their C_{2h} counterparts, except that the subscript *s* or *d* indicates single-valued and double-valued representations of C_{2h} (see footnotes b and c), and the superscript *b* indicates applicability to C_2H_2 with local bending LAMs.

^b PI operations of acetylene to which transformations in the next row correspond, when they are substituted into Eq. (4). Representations of $G_4^{(2)}$ that are also representations of the PI group G_4 must have the same character χ in any pair of columns headed by the same PI operation, i.e., $\chi[E] = \chi[E_b]$, $\chi[C_2(y)] = \chi[C_2(y)E_b]$, etc. These “single-valued” representations occur in the first four rows of this table.

^c Symmetry operations from Table 5. The first four operations have the same names as their C_{2h} counterparts in Table 1. The last four are the first four multiplied by the limited identity E_b (see Section 4).

^d Point-group operations that are retained for trans (C_{2h}) acetylene or cis (C_{2v}) acetylene when no LAMs are present (see Section 6).

^e Correlations of the $C_{2h}^{(2)}$ species with the species for trans (C_{2h}) acetylene or cis (C_{2v}) acetylene in Table 1a and b.

^f Symmetry species of the laboratory-fixed (*X, Y, Z*) and molecule-fixed (*x, y, z*) components of the total angular momentum \mathbf{J} (excluding nuclear spin) and the electric dipole moment $\boldsymbol{\mu}$.

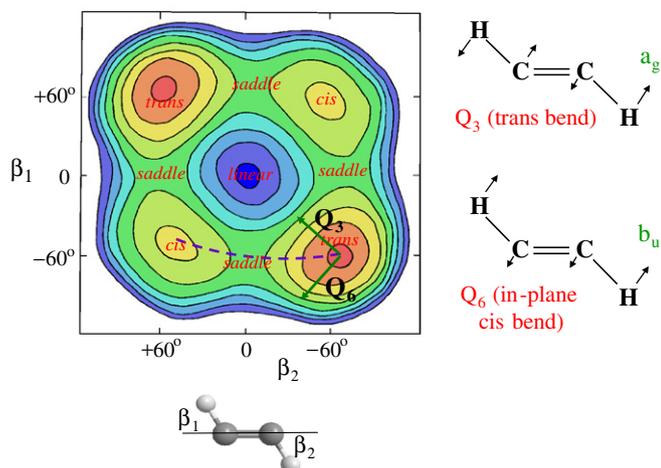


Fig. 4. Left side: Schematic representation of the S_1 potential surface $V(\beta_1, \beta_2)$ for planar acetylene, together with the trans–cis isomerization path (after Ref. [14]). (Regions of lowest potential energy are colored red in the web version, and those of highest potential energy blue; in between the colors follow the spectral sequence.) Two equivalent trans acetylene minima can be seen near $\beta_1 = \beta_2 = +60^\circ$ and $\beta_1 = \beta_2 = -60^\circ$. Similarly, two equivalent cis acetylene minima can be seen near $\beta_1 = -\beta_2 = +60^\circ$ and $\beta_1 = -\beta_2 = -60^\circ$. In the high-barrier case, tunneling between equivalent minima is expected to lead to “sum and difference” wavefunctions with slightly different energies. Note the very high barrier to linearity in this potential surface, which essentially prevents tunneling paths from passing through the linear configuration. Right side: Definition of the vibrational normal coordinates Q_3 and Q_6 , which when combined correspond closely to the isomerization coordinate.

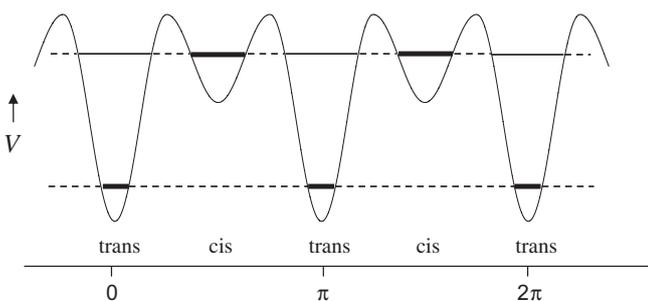


Fig. 5. The potential curve obtained by taking a “cut” along an approximately circular path in Fig. 4 that connects the four wells, i.e., trans \rightarrow cis \rightarrow trans \rightarrow cis \rightarrow repeat. The thick lines at $\gamma = 0, \pi$, and 2π , corresponding to points on the circle, represent the lowest vibrational level in the trans wells. The dashed line at the same energy represents the trans \leftrightarrow trans tunneling path through the classically forbidden region. The thick lines at $\gamma = \pi/2$ and $3\pi/2$ represent the lowest vibrational level in the cis wells. The dashed lines at the same energy represent the parts of the cis \leftrightarrow cis tunneling path that pass through a classically forbidden region. The thin solid lines represent the parts of the cis \leftrightarrow cis tunneling path that pass through classically allowed regions (above the trans minima). In these classically allowed regions the cis wavefunction will be small in amplitude, but will exhibit oscillatory behavior rather than exponential decay.

where the subscripts UL, LR indicate the upper left, lower right trans wells and UR, LL indicate the upper right, lower left cis wells in Fig. 4, and where N_{trans}, k_{trans} , etc. are suitable normalization and scaling factors. Under the assumption of only SAV motions, we must reject any symmetry operations in Table 5 that would change a wavefunction localized in one well into a wavefunction localized in one of the other wells. The vibrational coordinates that need to be constrained are β_1 and β_2 . It can easily be seen that the transformations $(\beta_1, \beta_2) \rightarrow (\beta_1, \beta_2)$ and $(\beta_1, \beta_2) \rightarrow (\beta_2, \beta_1)$ in Table 5 leave both sets of trans vibrational wavefunctions in their original wells, while $(\beta_1, \beta_2) \rightarrow (\beta_1, \beta_2)$ and $(\beta_1, \beta_2) \rightarrow (-\beta_2, -\beta_1)$ leave both sets of cis

vibrational wavefunctions in their original wells. These two criteria lead to the entries C_{2h}, C_{2v} , and “both” under selected PI operations in the SAV row of Table 6. As expected, the set of four operations kept for C_{2h} and the set of four kept for C_{2v} each contain the four PI elements of G_4 once and only once. Comparison with the PI-group characters in Table 1a and b then allows us to derive the symmetry species correlations given on the right-hand side of Table 6.

We now apply the group theory of this section to the vibrational, rotational, and vibration-rotation wavefunctions appropriate for the potential energy surface in Fig. 4. (A newer *ab initio* version of this surface has recently been used for accurate calculations of the energy levels using a Discrete Variable Representation [17].)

We consider the trans conformation first, assuming initially that the cis minima can be ignored. Simple tunneling considerations lead one to expect eigenfunctions given by the sum and difference of the localized basis functions

$$\begin{aligned}\psi_{trans,sum} &= 2^{-1/2}(\psi_{UL} + \psi_{LR}) \\ \psi_{trans,diff} &= 2^{-1/2}(\psi_{UL} - \psi_{LR}),\end{aligned}\quad (7)$$

where the lowest-energy state with a sum wavefunction (which is nodeless) is expected to lie below the lowest-energy state with a difference wavefunction. Application of the symmetry operations in Table 5, and comparison of the resultant characters with Table 6, indicates that $\psi_{trans,sum}$ and $\psi_{trans,diff}$ have vibrational species ${}^v\Gamma = A_{gs}^b$ and A_{gd}^b , respectively, in $G_4^{(2)}$. Similarly, applying the equivalent rotations in Table 5 to the asymmetric rotor functions J_{KaKc} (recalling that $z = a$ and $y = c$, and that $C_2(x) = C_2(y)C_2(z)$), we find from Table 6 that J_{ee}, J_{eo}, J_{oe} , and J_{oo} have rotational symmetry species ${}^r\Gamma = A_{gs}^b, B_{gs}^b, A_{gd}^b$ and B_{gd}^b in $G_4^{(2)}$. The four vibration-rotation species associated with either $\psi_{trans,sum}$ or $\psi_{trans,diff}$ in Eq. (7) are then ${}^{vr}\Gamma = {}^v\Gamma \otimes {}^r\Gamma = A_{gs}^b, B_{gs}^b, A_{gd}^b$ and B_{gd}^b .

It turns out that we have now stumbled upon one of the traditional quandaries in the treatment of certain bending vibrational problems using tunneling ideas. If we consider a single set of asymmetric-rotor quantum numbers J, K_a and K_c , the treatment above appears to predict two rotational energy levels, one associated with the lower tunneling component and one with the upper. But there is really only one possible trans acetylene equilibrium structure for an atom-labeled acetylene molecule $H_1-C_a \equiv C_b-H_2$ when breaking of the C–H bonds is not permitted, since all other trans equilibrium structures that can be drawn can be brought into exact coincidence (including atom labels) with the first structure by simple rotation and translation. Thus, only one vibration-rotation level J_{KaKc} is possible.

This dilemma can be overcome as follows. The PI group for this problem is G_4 , as given in Table 1a. Any complete wavefunction for the system can in principle be expressed in terms of the laboratory-fixed Cartesian coordinates \mathbf{R}_i occurring on the left of Eq. (4). Therefore, any complete wavefunction for the system must transform as some species (irreducible representation) of the PI group G_4 . (This requirement does not apply when the individual vibrational, torsional and rotational factors in the total wavefunction are considered separately, since these individual factors cannot be converted to functions of the \mathbf{R}_i without knowledge of the values of the coordinates in the other factors.) If a function is to transform as a species of G_4 , it must belong to a single-valued representation of $G_4^{(2)}$, since the single-valued representations are defined as those where all operations corresponding to a given PI operation have the same character.

Revisiting the conclusions following Eq. (7) above with these considerations in mind, we see that $\psi_{trans,sum}$ vibrational basis functions can only be combined with $K_a = \text{even}$ asymmetric-rotor functions, and that $\psi_{trans,diff}$ vibrational functions can only be combined with $K_a = \text{odd}$ rotational functions. This requirement

$$\mathbf{H} = \begin{bmatrix}
 E_0 & 2H_{12} & H_{13} & H_{13} & 0 & 0 & H_{13} & H_{13} \\
 2H_{12} & E_0 & H_{13} & H_{13} & 0 & 0 & H_{13} & H_{13} \\
 H_{13} & H_{13} & E_0 & 2H_{12} & H_{13} & H_{13} & 0 & 0 \\
 H_{13} & H_{13} & 2H_{12} & E_0 & H_{13} & H_{13} & 0 & 0 \\
 0 & 0 & H_{13} & H_{13} & E_0 & 2H_{12} & H_{13} & H_{13} \\
 0 & 0 & H_{13} & H_{13} & 2H_{12} & E_0 & H_{13} & H_{13} \\
 H_{13} & H_{13} & 0 & 0 & H_{13} & H_{13} & E_0 & 2H_{12} \\
 H_{13} & H_{13} & 0 & 0 & H_{13} & H_{13} & 2H_{12} & E_0
 \end{bmatrix}$$

A_{1g}^+

B_{1g}^+

E_g

E_g

E_1

E_1

E^+

E^+

Fig. 6. The 8×8 tunneling Hamiltonian matrix and its (unnormalized) eigenvectors. This matrix is appropriate for a tunneling problem with one vibrational ground state wavefunction localized in each of the eight trans minima in Eq. (15) or in each of the eight cis minima in Eq. (16), and rows and columns are labeled by these eight minima. The matrix element for the $1 \rightarrow 2$ nearest-neighbor tunneling path in the bending coordinates β_1 and β_2 (and all group-theoretically equivalent paths) is indicated by $2H_{12}$, where the factor of 2 arises because there are two equivalent paths from minimum 1 to minimum 2 in Fig. 4 (one clockwise, one counterclockwise). The matrix element for the $1 \rightarrow 3$ nearest-neighbor tunneling path in the torsional coordinate α (and all group-theoretically equivalent paths) is indicated by H_{13} . Eigenvectors are shown below the Hamiltonian matrix. Symmetry species labels below these eigenvectors are correct for the trans minima. For the cis minima, E_g must be replaced by E_u .

removes exactly half of the vibration-rotation wavefunctions generated in $G_4^{(2)}$, and thus resolves the number-of-states dilemma. It also leads to the conclusion that a staggering in energy of even- K_a and odd- K_a levels will be observed, with the magnitude of the energy staggering equal to the magnitude of the $\psi_{trans,sum}$ versus $\psi_{trans,diff}$ tunneling splitting. (As it happens, such K -level energy staggers occur frequently in molecules where extended-group symmetry analyses are appropriate [5].) As a final point we note that the vibration-rotation wavefunctions allowed by the above procedure, which transform as A_{gs}^b and B_{gs}^b in $G_4^{(2)}$, correlate with A_g and B_g in the group C_{2h} in Table 1, i.e., with the ground state rovibrational species expected in a single-well C_{2h} point-group treatment of trans acetylene.

All of these ideas can be repeated for a treatment of cis-well tunneling. We now expect

$$\begin{aligned}
 \psi_{cis,sum} &= 2^{-1/2}(\psi_{UR} + \psi_{LL}) \\
 \psi_{cis,diff} &= 2^{-1/2}(\psi_{UR} - \psi_{LL}),
 \end{aligned} \quad (8)$$

where the energy of $\psi_{cis,sum}$ is again below that of $\psi_{cis,diff}$ and where the $\psi_{cis,sum}$ and $\psi_{cis,diff}$ vibrational species are A_{gs}^b and B_{ud}^b , respectively, in $G_4^{(2)}$. Application of the equivalent rotations in Table 5 to the asymmetric rotor functions is unchanged from the trans case (because $z = a$ and $y = c$ is still valid), so J_{ee}, J_{eo}, J_{oe} , and J_{oo} again have the rotational symmetry species $A_{gs}^b, B_{gs}^b, A_{gd}^b$ and B_{gd}^b in $G_4^{(2)}$. Keeping only single-valued representations for the vibration-rotation wavefunctions, we find that $\psi_{cis,sum}$ has only $K_a = \text{even}$ levels, with vibration-rotation species A_{gs}^b and B_{gs}^b , while $\psi_{cis,diff}$ has only $K_a = \text{odd}$ levels, with vibration-rotation species A_{us}^b and B_{us}^b , and that

there is again an even- K_a vs odd- K_a energy staggering equal in magnitude to the $\psi_{cis,sum}$ versus $\psi_{cis,diff}$ tunneling splitting. For the cis tunneling case, the $G_4^{(2)}$ vibration-rotation species A_{gs}^b and B_{gs}^b for $K_a = \text{even}$ correlate in Table 6 with A_1 and B_1 in the group C_{2v} , while ${}^u\Gamma = A_{us}^b$ and B_{us}^b for $K_a = \text{odd}$ correlate with A_2 and B_2 , i.e., with the species expected for a single-well C_{2v} point-group treatment of cis acetylene.

7. Trans and cis acetylene with only an internal rotation LAM

This is essentially the H_2O_2 situation, which has been discussed in the literature [18], so we summarize here only the main points. The expression \mathbf{a}_i (LAMs) in Eq. (1) must be replaced by $\mathbf{a}_i(\alpha)$, where α is the internal rotation angle, to give

$$\mathbf{R}_i = \mathbf{R} + S_i^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\alpha) + \mathbf{d}_i]. \quad (9)$$

The functions $\mathbf{a}_i(\alpha)$ can again be defined in terms of appropriate constant vector positions for the atoms, \mathbf{a}_i^0 , taken for convenience to correspond to the trans bent conformation in Fig. 1a, with the C_a and C_b atoms at $-z_C$ and $+z_C$ on the z axis. This leads to

$$\mathbf{a}_i(\alpha) = S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}(\alpha), \quad (10)$$

where the internal-rotation matrices are

$$\begin{aligned}
 S_i^{-1}(\alpha, 0, 0) &= S^{-1}(0, 0, 0) \quad \text{for } i = a, b, \\
 S_i^{-1}(\alpha, 0, 0) &= S^{-1}[(-1)^i \alpha, 0, 0] \quad \text{for } i = 1, 2,
 \end{aligned} \quad (11)$$

and the constant vectors of atomic positions are

$$\begin{aligned}
 \mathbf{a}_a^0 &= -Z_C \mathbf{k} \\
 \mathbf{a}_b^0 &= +Z_C \mathbf{k} \\
 \mathbf{a}_1^0 &= -X_H \mathbf{i} - Z_H \mathbf{k} \\
 \mathbf{a}_2^0 &= +X_H \mathbf{i} + Z_H \mathbf{k},
 \end{aligned} \tag{12}$$

where Z_C , X_H , and Z_H are all positive. $\mathbf{A}(\alpha)$ is the center of mass of the structure $S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0$. In the structures $S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0$ obtained from Eq. (11) the C atom positions do not change with α , but the H atoms are rotated in equal amount and opposite sense about the C–C bond, so that the trans configuration occurs for $\alpha = n\pi$ and the cis configuration for $\alpha = (n + 1/2)\pi$, where n is an integer. Note that this way of carrying out the internal rotation maintains the y axis as the C_2 symmetry axis, so we can still use Table 1a for the trans configurations, but must use Table 1d for the cis. Furthermore, while the z axis remains nearly coincident with the principal a axis during the internal rotation motion, the y axis lies along the inertial c axis for trans conformations, but along the inertial b axis for cis conformations.

The last six columns of Table 7 give a set of eight symmetry operations which, when applied to the right side of Eq. (9), yield the same result as applying the PI operations shown in the first column of the table to the left side of Eq. (9). Just as in Table 5, the four feasible PI operations for C_2H_2 with no C–H bond breaking each occur twice in Table 7. The associated double-valued coordinate system, which gives rise to the limited identity E_t , could be avoided by locking the molecule fixed x , y , z axes in one of the two H–C–C groups, though again, as in Section 6, at the expense of hiding some of the full symmetry of the system.

Table 8 gives the character table of the group G_8 containing all the operations in Table 7. These are labeled in PI notation in the first row of the heading and in $C_{2h}^{(2)}$ notation in the second. The third row (SAV) gives the operations that can be retained when the molecule remains localized in one of the minima. As mentioned above, the two trans minima occur at $\alpha = 0$ and $\alpha = \pi$, so that symmetry operations involving $\alpha \rightarrow \alpha$ and $\alpha \rightarrow -\alpha$ in Table 7 do not move localized torsional wavefunctions (with approximate form $\exp[-k_{trans}(\alpha - 0)^2]$ and $\exp[-k_{trans}(\alpha - \pi)^2]$) out of either of these trans minima. The cis minima occur at $\alpha = +\pi/2$ and $\alpha = +3\pi/2$, so that symmetry operations involving $\alpha \rightarrow \alpha$ and $\alpha \rightarrow \pi - \alpha$ in Table 7 do not move localized torsional wavefunctions (with approximate

form $\exp[-k_{cis}(\alpha - \pi/2)^2]$ and $\exp[-k_{cis}(\alpha - 3\pi/2)^2]$) out of either of these cis minima. Again, the sets of elements retained for trans (C_{2h}) and cis (C_{2v}) acetylene each contain the four elements of the G_4 PI group once and only once, so that it is easy to derive the species correlations given in the second and third last columns by comparing characters with those in Table 1a and d.

We do not discuss the $C_{2h}^{(2)}$ group for the LAM torsional situation further, since by itself it is not likely to be useful for acetylene. Furthermore, its application to the torsion-rotation problem in H_2O_2 has been extensively described in the literature [16,18,19]. We note finally that: (i) the bodies of Tables 6 and 8 are the same, but some of the column headings are different, and (ii) the correlation to C_{2v} species is different for the double-valued representations in Tables 6 and 8.

8. Trans and cis acetylene with two C–C–H bends and internal rotation, giving three LAMs

Here we combine the treatments of Sections 6 and 7 to develop a formalism for treating the S_1 state of C_2H_2 near the isomerization barrier, where states with excitation of the torsional mode and the cis and trans bending modes occur (see Section 12). The expression \mathbf{a}_i (LAMs) in Eq. (1) must be replaced by $\mathbf{a}_i(\alpha, \beta_1, \beta_2)$, where α is the internal rotation angle and β_1 and β_2 are the $H_1-C_a-C_b$ and $C_a-C_b-H_2$ bending angles, to give

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\alpha, \beta_1, \beta_2) + \mathbf{d}_i]. \tag{13}$$

The functions $\mathbf{a}_i(\alpha, \beta_1, \beta_2)$ can be defined in terms of constant vector positions for the atoms, \mathbf{a}_i^0 , where, as in Section 6, these positions are chosen to correspond to the linear configuration, with all atoms on the z axis. This leads to

$$\begin{aligned}
 \mathbf{a}_i(\alpha, \beta_1, \beta_2) &= \mathbf{a}_i^0 - \mathbf{A}(\alpha, \beta_1, \beta_2) \quad \text{for } i = a, b \\
 \mathbf{a}_1(\alpha, \beta_1, \beta_2) &= S^{-1}(-\alpha, 0, 0) S^{-1}(0, \beta_1, 0)(\mathbf{a}_1^0 - \mathbf{a}_a^0) + \mathbf{a}_a^0 - \mathbf{A}(\alpha, \beta_1, \beta_2) \\
 &= S^{-1}(0, \beta_1, -\alpha)(\mathbf{a}_1^0 - \mathbf{a}_a^0) + \mathbf{a}_a^0 - \mathbf{A}(\alpha, \beta_1, \beta_2) \\
 \mathbf{a}_2(\alpha, \beta_1, \beta_2) &= S^{-1}(+\alpha, 0, 0) S^{-1}(0, \beta_2, 0)(\mathbf{a}_2^0 - \mathbf{a}_b^0) + \mathbf{a}_b^0 - \mathbf{A}(\alpha, \beta_1, \beta_2) \\
 &= S^{-1}(0, \beta_2, +\alpha)(\mathbf{a}_2^0 - \mathbf{a}_b^0) + \mathbf{a}_b^0 - \mathbf{A}(\alpha, \beta_1, \beta_2),
 \end{aligned} \tag{14}$$

Table 7
Transformation properties of the coordinates \mathbf{R} , χ , θ , ϕ , α , and the \mathbf{d}_i on the right of Eq. (9) under symmetry operations of the double group $G_4^{(2)}$ (see Table 8) of G_4 (see Table 1) appropriate for simultaneously treating trans bent and cis bent acetylene with internal rotation as the only LAM.

PI ^a	PG ^b	\mathbf{R}^c	χ, θ, ϕ^d	Equiv. Rot. ^e	α^f	\mathbf{d}_i^g	$j(i)^h$
E	E	\mathbf{R}	χ, θ, ϕ	E	α	E \mathbf{d}_j	$\mathbf{a}_j^0 = E\mathbf{a}_i^0$
(<i>ab</i>)(12)	$C_2(y)$	\mathbf{R}	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	α	$C_2(y)$ \mathbf{d}_j	$\mathbf{a}_j^0 = C_2(y)\mathbf{a}_i^0$
(<i>ab</i>)(12)*	<i>i</i>	$-\mathbf{R}$	χ, θ, ϕ	E	$-\alpha$	<i>i</i> \mathbf{d}_j	$\mathbf{a}_j^0 = i\mathbf{a}_i^0$
E*	$\sigma(xz)$	$-\mathbf{R}$	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	$-\alpha$	$\sigma(xz)$ \mathbf{d}_j	$\mathbf{a}_j^0 = \sigma(xz)\mathbf{a}_i^0$
E	E_t	\mathbf{R}	$\pi + \chi, \theta, \phi$	$C_2(z)$	$\pi + \alpha$	$C_2(z)$ \mathbf{d}_j	$\mathbf{a}_j^0 = E\mathbf{a}_i^0$
(<i>ab</i>)(12)	$C_2(y)E_t$	\mathbf{R}	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$\pi + \alpha$	$C_2(x)$ \mathbf{d}_j	$\mathbf{a}_j^0 = C_2(y)\mathbf{a}_i^0$
(<i>ab</i>)(12)*	<i>i</i> E_t	$-\mathbf{R}$	$\pi + \chi, \theta, \phi$	$C_2(z)$	$\pi - \alpha$	$\sigma(xy)$ \mathbf{d}_j	$\mathbf{a}_j^0 = i\mathbf{a}_i^0$
E*	$\sigma(xz)E_t$	$-\mathbf{R}$	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$\pi - \alpha$	$\sigma(yz)$ \mathbf{d}_j	$\mathbf{a}_j^0 = \sigma(xz)\mathbf{a}_i^0$

^a The PI operations in this column are obtained when the variable transformations in the columns to the right are substituted in Eq. (9). Note that every PI operation occurs twice, since this is a double group of the feasible PI group.

^b Operations of the extended PI group. E, $C_2(y)$, *i*, and $\sigma(xz)$ are very similar to the C_{2h} point group operations in Table 1a and Table 3, so the C_{2h} names have been retained in this double group of C_{2h} . E_t is the limited identity in this LAM torsional problem.

^c Laboratory-fixed center of mass vector.

^d Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^e As defined in Bunker and Jensen [4].

^f The LAM internal rotation angle.

^g Small-amplitude molecule-fixed vibrational displacement vectors, which are needed to express the three SAV bond stretches and the two SAV (by hypothesis) C–C–H angle bends.

^h The subscript j as a function of i is defined by evaluating the right side of the equations in this column and then looking for the \mathbf{a}_j^0 which is equal to this right side. Note that $j = i$ for the first, fourth, fifth, and eighth rows.

Table 8Character table^a for the double group $G_4^{(2)} = C_{2h}^{(2)} = G_8$ containing the symmetry operations in Table 7.

PI ^b	E	(ab)(12)	(ab)(12)*	E*	E	(ab)(12)	(ab)(12)*	E*			
$C_{2h}^{(2)c}$	E	$C_2(y)$	i	$\sigma(xz)$	E_t	$C_2(y)E_t$	iE_t	$\sigma(xz)E_t$			
SAV ^d	Both	Both	C_{2h}	C_{2h}			C_{2v}	C_{2v}	C_{2h}^e	C_{2v}^e	(J, μ) ^f
A_{gs}^t	1	1	1	1	1	1	1	1	A_g	A_1	J_x, J_y, J_z
A_{us}^t	1	1	-1	-1	1	1	-1	-1	A_u	A_2	μ_x, μ_y, μ_z
B_{gs}^t	1	-1	1	-1	1	-1	1	-1	B_g	B_1	J_z
B_{us}^t	1	-1	-1	1	1	-1	-1	1	B_u	B_2	μ_z
A_{gd}^t	1	1	1	1	-1	-1	-1	-1	A_g	A_2	J_y
A_{ud}^t	1	1	-1	-1	-1	-1	1	1	A_u	A_1	μ_y
B_{gd}^t	1	-1	1	-1	-1	1	-1	1	B_g	B_2	J_x
B_{ud}^t	1	-1	-1	1	-1	1	1	-1	B_u	B_1	μ_x

^a This group is appropriate for a simultaneous treatment of trans bent and cis bent acetylene when the only LAM is internal rotation. Symmetry species names follow their C_{2h} counterparts, except that the subscript *s* or *d* indicates single-valued and double-valued representations of C_{2h} (see footnotes b and c of Table 6), and the superscript *t* indicates applicability to C_2H_2 with only a torsional LAM.

^b PI operations of acetylene to which transformations in the next row correspond, when they are substituted into Eq. (9). Representations of $G_4^{(2)}$ that correspond to single-valued representations of the PI group G_4 must have the same character in each pair of columns headed by the same PI operation.

^c Symmetry operations from Table 7. The first four operations have the same names as their C_{2h} counterparts in Table 1. The last four are these operators multiplied by the limited identity E_t (see Section 4).

^d Point-group operations that are retained for trans (C_{2h}) or cis (C_{2v}) acetylene, i.e., retained when no LAMs are present (see Section 7).

^e Correlations of these $C_{2h}^{(2)}$ species with the species for trans (C_{2h}) and cis (C_{2v}) acetylene in Table 1a and d.

^f Symmetry species of the laboratory-fixed (X, Y, Z) and molecule-fixed (x, y, z) components of the total angular momentum J (excluding nuclear spin) and the electric dipole moment μ .

where $A(\alpha, \beta_1, \beta_2)$ is defined so that the center of mass of the $\mathbf{a}_i(\alpha, \beta_1, \beta_2)$ structure is always at the origin, and where we again require $-2\pi/3 < \beta_1, \beta_2 < +2\pi/3$.

It turns out that we can find eight trans minima in this coordinate system, lying at

$$\alpha = 0, \quad \beta_1 = +\beta_2 = \pm\beta_{trans} \approx \pm 2\pi/6 \quad (15a)$$

$$\alpha = \pi/2, \quad \beta_1 = -\beta_2 = \pm\beta_{trans} \approx \pm 2\pi/6 \quad (15b)$$

$$\alpha = \pi, \quad \beta_1 = +\beta_2 = \pm\beta_{trans} \approx \pm 2\pi/6 \quad (15c)$$

$$\alpha = 3\pi/2, \quad \beta_1 = -\beta_2 = \pm\beta_{trans} \approx \pm 2\pi/6, \quad (15d)$$

and eight cis minima, lying at

$$\alpha = 0, \quad \beta_1 = -\beta_2 = \pm\beta_{cis} \approx \pm 2\pi/6 \quad (16a)$$

$$\alpha = \pi/2, \quad \beta_1 = +\beta_2 = \pm\beta_{cis} \approx \pm 2\pi/6 \quad (16b)$$

$$\alpha = \pi, \quad \beta_1 = -\beta_2 = \pm\beta_{cis} \approx \pm 2\pi/6 \quad (16c)$$

$$\alpha = 3\pi/2, \quad \beta_1 = +\beta_2 = \pm\beta_{cis} \approx \pm 2\pi/6. \quad (16d)$$

Fig. 4 can be taken as an illustration of the $\alpha = 0$ minima in Eqs. (15) and (16), where the potential surface is now not imagined to be plotted in the vertical direction, but merely to be indicated by contour lines in the plane of the figure. For visualization purposes, we can imagine stacking three more versions of Fig. 4 above the original Fig. 4 to represent the $\alpha = \pi/2$, $\alpha = \pi$, and $\alpha = 3\pi/2$ cuts through $V(\alpha, \beta_1, \beta_2)$, but with the additional adjustment that each of the upper three figures be rotated about the vertical axis by its α value, so that the β_1 and β_2 axes used for the $\alpha = 0$ layer will apply to the other three layers as well.

The presence of eight trans minima in this $(\alpha, \beta_1, \beta_2)$ coordinate system indicates that we will be dealing with an eightfold extended group $G_4^{(8)} = G_{32}$ of the original PI group G_4 . Table 9 gives a set of 32 symmetry operations, which when applied to the right side of Eq. (13), give the same result as applying the PI operations shown in the first column of the table to the left side of Eq. (13). As expected, the four feasible PI operations for C_2H_2 with no C–H bond breaking each occur eight times in Table 9, with one true identity and seven limited identities. The seven limited identities transform a vibrational wavefunction localized in the first trans well of Eq. (15), represented schematically by $\exp[-k_{trans}^2(\alpha - 0)^2] \exp[-k_{trans}^2(\beta_1 - \beta_{trans})^2] \exp[-k_{trans}^2(\beta_2 - \beta_{trans})^2]$, into a wavefunction localized in one of the other trans wells in Eq. (15). They

also transform a vibrational wavefunction in the first cis well of Eq. (16) into a wavefunction in one of the seven other cis wells in Eq. (16).

Trial and error shows that all of the variable transformations in Table 9 can be expressed in terms of only four generating operations, i.e., in terms of only four of the operations occurring in Table 9. There is some flexibility in choosing the four generators. To achieve maximum compatibility with Ref. [20], we take

$$\begin{aligned} a &= iE_c \\ b &= C_2(y)E_b \\ c &= \sigma(xz)E_t \\ d &= E_t, \end{aligned} \quad (17)$$

which can be shown (by considering their effects on $\mathbf{R}, \chi, \theta, \phi, \alpha, \beta_1, \beta_2$, and the \mathbf{d}_i) to obey the ten relations

$$a^4 = b^2 = c^2 = d^2 = e \quad (18a)$$

$$ba = a^3b \quad (18b)$$

$$ca = acd \quad (18c)$$

$$da = ad, \quad cb = bc, \quad db = bd, \quad dc = cd, \quad (18d)$$

where e is the identity. Eq. (18a) gives the order of each of the generators. Eq. (18d) indicates that d commutes with the other three generators, and that b and c commute with each other. A general element of the group $G_4^{(8)}$ can now be written in the form

$$a^p b^q c^r d^s, \quad (19)$$

where (from Eq. (18a)) p takes the integer values 0, 1, 2, 3 and q, r, s take the values 0, 1.

It turns out that the relations given in Eq. (18), which are appropriate for acetylene when the two local bends and the internal rotation are treated as feasible LAMs, are formally identical to the relations that would be obtained for the operators a, b, c , and d defined in Table 2 of Merer and Watson [20], which are appropriate for ethylene when internal rotation is considered feasible. Because the relations are identical, the group G_{32} here is isomorphic to the group G_{32} there (and therefore also has the same symmetry species and character table). The character table for G_{32} given in [20] is reproduced here in Table 10. The choice of generators for use in Eq. (17) makes the transformations of the rotational

Table 9
Transformation properties of the coordinates R , χ , θ , ϕ , α , β_1 , β_2 , and the \mathbf{d}_i on the right of Eq. (13) under the symmetry operations of the eightfold extended group $G_4^{(8)}$ (see Table 10) of G_4 (see Tables 1 and 3) appropriate for simultaneously treating trans bent and cis bent acetylene with internal rotation and with local mode C—C—H bending motions at each end as the three LAMs.

PI ^a	Gen ^b	PG ^c	R ^d	χ , θ , ϕ ^e	Equiv. Rot. ^f	α , β_1 , β_2 ^g	\mathbf{d}_i ^h	$j(i)$ ⁱ
E	e	E	R	χ , θ , ϕ	E	α , β_1 , β_2	$E \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	a^2b	$C_2(y)$	R	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)$	α , β_2 , β_1	$C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	a^2bcd	i	$-R$	χ , θ , ϕ	E	$-\alpha$, β_2 , β_1	$i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	cd	$\sigma(xz)$	$-R$	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)$	$-\alpha$, β_1 , β_2	$\sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	a^2	E_b	R	$\pi + \chi$, θ , ϕ	$C_2(z)$	α , $-\beta_1$, $-\beta_2$	$C_2(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	b	$C_2(y)E_b$	R	$-\chi$, $\pi - \theta$, $\pi + \phi$	$C_2(x)$	α , $-\beta_2$, $-\beta_1$	$C_2(x) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	bcd	$i E_b$	$-R$	$\pi + \chi$, θ , ϕ	$C_2(z)$	$-\alpha$, $-\beta_2$, $-\beta_1$	$\sigma(xy) \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	a^2cd	$\sigma(xz)E_b$	$-R$	$-\chi$, $\pi - \theta$, $\pi + \phi$	$C_2(x)$	$-\alpha$, $-\beta_1$, $-\beta_2$	$\sigma(yz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	d	E_t	R	$\pi + \chi$, θ , ϕ	$C_2(z)$	$\pi + \alpha$, β_1 , β_2	$C_2(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	a^2bd	$C_2(y)E_t$	R	$-\chi$, $\pi - \theta$, $\pi + \phi$	$C_2(x)$	$\pi + \alpha$, β_2 , β_1	$C_2(x) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	a^2bc	$i E_t$	$-R$	$\pi + \chi$, θ , ϕ	$C_2(z)$	$\pi - \alpha$, β_2 , β_1	$\sigma(xy) \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	c	$\sigma(xz)E_t$	$-R$	$-\chi$, $\pi - \theta$, $\pi + \phi$	$C_2(x)$	$\pi - \alpha$, β_1 , β_2	$\sigma(yz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	a^2d	E_bE_t	R	χ , θ , ϕ	E	$\pi + \alpha$, $-\beta_1$, $-\beta_2$	$E \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	bd	$C_2(y)E_bE_t$	R	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)$	$\pi + \alpha$, $-\beta_2$, $-\beta_1$	$C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	bc	$i E_bE_t$	$-R$	χ , θ , ϕ	E	$\pi - \alpha$, $-\beta_2$, $-\beta_1$	$i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	a^2c	$\sigma(xz)E_bE_t$	$-R$	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)$	$\pi - \alpha$, $-\beta_1$, $-\beta_2$	$\sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	abc	E_c	R	$\pi/2 + \chi$, θ , ϕ	$C_4(z)$	$\pi/2 + \alpha$, β_1 , $-\beta_2$	$C_4^{-1}(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	ac	$C_2(y)E_c$	R	$3\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4(z)$	$\pi/2 + \alpha$, β_2 , $-\beta_1$	$C_4^{-1}(z)C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	a	$i E_c$	$-R$	$\pi/2 + \chi$, θ , ϕ	$C_4(z)$	$\pi/2 - \alpha$, β_2 , $-\beta_1$	$C_4^{-1}(z) i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	ab	$\sigma(xz)E_c$	$-R$	$3\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4(z)$	$\pi/2 - \alpha$, β_1 , $-\beta_2$	$C_4^{-1}(z) \sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	a^3bc	E_bE_c	R	$-\pi/2 + \chi$, θ , ϕ	$C_4^{-1}(z)$	$\pi/2 + \alpha$, $-\beta_1$, β_2	$C_4(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	a^3c	$C_2(y)E_bE_c$	R	$\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4^{-1}(z)$	$\pi/2 + \alpha$, $-\beta_2$, β_1	$C_4(z)C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	a^3	$i E_bE_c$	$-R$	$-\pi/2 + \chi$, θ , ϕ	$C_4^{-1}(z)$	$\pi/2 - \alpha$, $-\beta_2$, β_1	$C_4(z) i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	a^3b	$\sigma(xz)E_bE_c$	$-R$	$\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4^{-1}(z)$	$\pi/2 - \alpha$, $-\beta_1$, β_2	$C_4(z) \sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	$abcd$	E_tE_c	R	$-\pi/2 + \chi$, θ , ϕ	$C_4^{-1}(z)$	$-\pi/2 + \alpha$, β_1 , $-\beta_2$	$C_4(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	acd	$C_2(y)E_tE_c$	R	$\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4^{-1}(z)$	$-\pi/2 + \alpha$, β_2 , $-\beta_1$	$C_4(z)C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	ad	$i E_tE_c$	$-R$	$-\pi/2 + \chi$, θ , ϕ	$C_4^{-1}(z)$	$-\pi/2 - \alpha$, β_2 , $-\beta_1$	$C_4(z) i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	abd	$\sigma(xz)E_tE_c$	$-R$	$\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4^{-1}(z)$	$-\pi/2 - \alpha$, β_1 , $-\beta_2$	$C_4(z) \sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$
E	a^3bcd	$E_bE_tE_c$	R	$\pi/2 + \chi$, θ , ϕ	$C_4(z)$	$-\pi/2 + \alpha$, $-\beta_1$, β_2	$C_4^{-1}(z) \mathbf{d}_j$	$\mathbf{a}_j^0 = E \mathbf{a}_i^0$
(ab)(12)	a^3cd	$C_2(y)E_bE_tE_c$	R	$3\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4(z)$	$-\pi/2 + \alpha$, $-\beta_2$, β_1	$C_4^{-1}(z)C_2(y) \mathbf{d}_j$	$\mathbf{a}_j^0 = C_2(y) \mathbf{a}_i^0$
(ab)(12)*	a^3d	$i E_bE_tE_c$	$-R$	$\pi/2 + \chi$, θ , ϕ	$C_4(z)$	$-\pi/2 - \alpha$, $-\beta_2$, β_1	$C_4^{-1}(z) i \mathbf{d}_j$	$\mathbf{a}_j^0 = i \mathbf{a}_i^0$
E*	a^3bd	$\sigma(xz)E_bE_tE_c$	$-R$	$3\pi/2 - \chi$, $\pi - \theta$, $\pi + \phi$	$C_2(y)C_4(z)$	$-\pi/2 - \alpha$, $-\beta_1$, β_2	$C_4^{-1}(z) \sigma(xz) \mathbf{d}_j$	$\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$

^a The PI operations in this column are obtained when the variable transformations in the columns to the right are substituted in Eq. (13). Note that every PI operation occurs eight times.

^b Notation of Eq. (17).

^c The operations E, $C_2(y)$, $\sigma(xz)$, and i are very similar to the C_{2h} point group operations, so the C_{2h} names have been retained in this octuple group $G_4^{(8)}$ of the feasible PI group G_4 . E_b and E_t are the limited identities for the local-mode H—C—C and C—C—H bending problem and for the torsional problem, respectively, as found in Tables 5 and 7. E_c is a limited identity for the combined bending and torsional problem. Four other limited identities are obtained by taking binary and tertiary products of these three.

^d Laboratory-fixed center of mass vector.

^e Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^f The equivalent rotations $[4] C_4^{-1}(z)$ are of order four, but $C_2(y)C_4^{-1}(z) = C_2(y = \pm X)$ are of order two.

^g The LAM internal rotation angle and the two LAM local-mode H—C—C and C—C—H bending angles.

^h Small-amplitude molecule-fixed vibrational displacement vectors; linear combinations of these are used to express normal (or symmetry) coordinates for the three small-amplitude bond stretches.

ⁱ The subscript j as a function of i is defined by evaluating the right side of the equations in this column and then looking for the \mathbf{a}_j^0 which is equal to this right side. Note that $j = i$ whenever the equation has the form $\mathbf{a}_j^0 = E \mathbf{a}_i^0$, which occurs for all the limited identities, or the form $\mathbf{a}_j^0 = \sigma(xz) \mathbf{a}_i^0$, which occurs in eight other rows.

angles χ , θ , ϕ and the torsional angle α in Table 9 agree with the analogous transformations in Table 2 of Ref. [20], so that the species for rotational and torsional functions here are the same as those in Table 4 of Ref. [20]. The physical conclusions drawn from these two isomorphic groups will sometimes be different, however, because G_{32} here represents an eightfold extended group of the PI group G_4 for acetylene, i.e., $G_{32} = G_4^{(8)}$, whereas G_{32} there represents a twofold extended group of the PI group G_{16} for ethylene, i.e., $G_{32} = G_{16}^{(2)}$. One example of how analogies between the G_{32} group theory for acetylene and ethylene should not be pushed too far is the fact that single-valued representations of the acetylene PI group G_4 correspond to the four species A_{1g}^+ , A_{2g}^- , B_{2u}^+ , and B_{1u}^- in Table 10, whereas single-valued representations of the eth-

ylene PI group G_{16} correspond to the four A, four B, and E^+ and E^- species in Ref. [20].

It may at first seem surprising that the extended PI group for LAM bending and torsion in acetylene is isomorphic with that for the LAM torsion problem in ethylene. This fact can be made to seem intuitively reasonable by noting that the LAM acetylene bends give rise to an average planar structure of $(0.5H)_2-CC(0.5H)_2$, which is essentially the structure of ethylene. The degenerate representations in Table 10 arise because this hypothetical structure can pass through the D_{2d} point group when internal rotation is considered [20]. A second surprising group theoretical result, at least to the authors, is that three of the seven limited identities (a^2, d, a^2d) are each in a class by themselves,

Table 10
Character table^a for the group $G_4^{(8)}$, which is identical to that for $G_{16}^{(2)}$ [20]^b

Species ^c	<i>e</i>	<i>d</i>	<i>a</i> ²	<i>a</i> ² <i>d</i>	<i>c</i>	<i>a</i> ² <i>c</i>	<i>b</i>	<i>bd</i>	<i>bc</i>	<i>a</i> ² <i>bc</i>	<i>a</i>	<i>ac</i>	<i>ab</i>	<i>abc</i>	C_{2h} ^d	C_{2v} ^d	$(J, \mu)^e$
											<i>a</i> ³	<i>a</i> ³ <i>c</i>	<i>a</i> ³ <i>b</i>	<i>a</i> ³ <i>bc</i>			
A_{1g}^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	A_g	A_1	J_x, J_y, J_z
A_{2u}^+	1	1	1	1	1	1	−1	−1	−1	−1	1	1	−1	−1	B_u	B_2	
A_{1u}^-	1	1	1	1	−1	−1	1	1	−1	−1	1	−1	1	−1	A_u	A_2	
A_{2g}^-	1	1	1	1	−1	−1	−1	−1	1	1	1	−1	−1	1	B_g	B_1	J_z
B_{1g}^+	1	1	1	1	1	1	1	1	1	1	−1	−1	−1	−1	A_g	A_1	
B_{2u}^+	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	B_u	B_2	μ_z
B_{1u}^-	1	1	1	1	−1	−1	1	1	−1	−1	−1	1	−1	1	A_u	A_2	μ_x, μ_y, μ_z
B_{2g}^-	1	1	1	1	−1	−1	−1	−1	1	1	−1	1	−1	−1	B_g	B_1	
E^+	2	2	−2	−2	2	−2	0	0	0	0	0	0	0	0	$A_g \oplus B_u$	$A_1 \oplus B_2$	
E^-	2	2	−2	−2	−2	2	0	0	0	0	0	0	0	0	$A_u \oplus B_g$	$A_2 \oplus B_1$	
E_1	2	−2	2	−2	0	0	2	−2	0	0	0	0	0	0	$A_g \oplus A_u$	$A_1 \oplus A_2$	
E_2	2	−2	2	−2	0	0	−2	2	0	0	0	0	0	0	$B_g \oplus B_u$	$B_1 \oplus B_2$	
E_g	2	−2	−2	2	0	0	0	0	2	−2	0	0	0	0	$A_g \oplus B_g$	$A_2 \oplus B_2$	$\{J_x, J_y\}$
E_u	2	−2	−2	2	0	0	0	0	−2	2	0	0	0	0	$A_u \oplus B_u$	$A_1 \oplus B_1$	$\{\mu_x, \mu_y\}$

^a This group is appropriate for a simultaneous treatment of trans bent and cis bent acetylene when the three LAMs are internal rotation and a local-mode in-plane C–C–H bending vibration at each end of the molecule. Symmetry operations have been named to emphasize the isomorphism of the group of 32 elements used here for acetylene to the group of 32 elements used in Ref. [20] for ethylene. The effect on the variables on the right of Eq. (13) of the four operations *a*, *b*, *c*, and *d* used to generate all 32 elements of this group is given by the transformations in Table 9. Multiplication properties of these four operations are given in Eq. (18).

^b Elements in the last four classes in this character table are of order 4, 4, 2, and 4, respectively, e.g., $a^4 = (ac)^4 = (ab)^2 = (abc)^4 = e$.

^c Symmetry species and characters in this table have been taken without change from Ref. [20]. Representations of $G_4^{(8)}$ that correspond to single-valued representations of the PI group G_4 must have the same character in all columns corresponding to a given PI operation. In particular, they must have a character of +1 for all limited identities (see Table 9). The single-valued representations here thus consist only of the four representations with character +1 for *d*, *a*², *a*²*d* and the class containing *abc*, namely A_{1g}^+ , A_{2g}^- , B_{2u}^+ and B_{1u}^- .

^d Correlation of these $G_4^{(8)}$ species to the species of C_{2h} trans acetylene and of C_{2v} cis acetylene.

^e Symmetry species of the laboratory-fixed (*X, Y, Z*) and molecule-fixed (*x, y, z*) components of the total angular momentum *J* (excluding nuclear spin) and the electric dipole moment μ .

while the other four limited identities (*abc*, *a*³*bc*, *abcd*, *a*³*bcd*) are in the same class.

9. Trans and cis acetylene and vinylidene with only two delocalized H “in-plane bending” vibrations

For this problem, breaking the C–H bonds is considered to be a feasible operation. Fig. 3 illustrates an ellipse-like path along which the H atoms can travel as they move from one carbon atom to the other. (Note that moving the H atoms along this ellipse, in other words choosing the angles β_1 and β_2 appropriately in Fig. 3, allows the C_2H_2 molecule to assume trans bent, cis bent, and vinylidene-like structures.) From the point of view of mathematical expressions, the treatment in this section will be quite similar to that in Section 6.

The \mathbf{a}_i (LAMs) can again be represented as $\mathbf{a}_i(\beta_1, \beta_2)$, but it is now convenient to define β_1 and β_2 as angles giving the positions of the hydrogen atoms relative to the center of the C_b – C_a bond. Chemically this seems reasonable, since H_1 , for example, is no longer exclusively associated with C_a . The basic equation is thus formally identical to Eq. (4),

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi) [\mathbf{a}_i(\beta_1, \beta_2) + \mathbf{d}_i]. \quad (20)$$

The functions $\mathbf{a}_i(\beta_1, \beta_2)$ could again be defined (as in Eq. (5)) by applying rotations about the out-of-plane *y* axis through angles of 0, β_1 , or β_2 to a set of four constant vectors \mathbf{a}_i^0 ($i = a, b, 1, 2$) chosen to correspond to a linear $D_{\infty h}$ reference configuration lying along the *z* axis. This leads to

$$\begin{aligned} \mathbf{a}_i(\beta_1, \beta_2) &= \mathbf{a}_i^0 - \mathbf{A}(\beta_1, \beta_2) & \text{for } i = a, b \\ \mathbf{a}_1(\beta_1, \beta_2) &= S^{-1}(0, \beta_1, 0) \mathbf{a}_1^0 - \mathbf{A}(\beta_1, \beta_2) \\ \mathbf{a}_2(\beta_1, \beta_2) &= S^{-1}(0, \beta_2, 0) \mathbf{a}_2^0 - \mathbf{A}(\beta_1, \beta_2), \end{aligned} \quad (21)$$

where $\mathbf{A}(\beta_1, \beta_2)$ keeps the center of mass of $\mathbf{a}_i(\beta_1, \beta_2)$ at the origin, and where the values of the angles β_1 and β_2 are now (in contrast

to Section 6) unconstrained, except for $\beta_1 > \beta_2 - \pi > \beta_1 - 2\pi$, which prevents H_1 from overtaking H_2 and H_2 from overtaking H_1 . But Eq. (21) forces the hydrogens to follow a circular path centered at the origin, which seems less chemically reasonable than the elliptical path shown in Fig. 3. We therefore replace Eq. (21) by

$$\begin{aligned} \mathbf{a}_i(\beta_1, \beta_2) &= \mathbf{a}_i^0 - \mathbf{A}(\beta_1, \beta_2) & \text{for } i = a, b \\ \mathbf{a}_1(\beta_1, \beta_2) &= \mathbf{a}_1^0(\beta_1) - \mathbf{A}(\beta_1, \beta_2) \\ \mathbf{a}_2(\beta_1, \beta_2) &= \mathbf{a}_2^0(\beta_2) - \mathbf{A}(\beta_1, \beta_2), \end{aligned} \quad (22)$$

where the functions $\mathbf{a}_i^0(\beta)$ and $\mathbf{a}_2^0(\beta)$ are defined only implicitly, but with the requirements that:

$$\mathbf{j} \cdot \mathbf{a}_i^0(\beta) = 0 \quad \text{for } i = 1, 2 \quad (23a)$$

$$\mathbf{a}_i^0(\pi + \beta) = C_2(y) \mathbf{a}_i^0(\beta) \quad \text{for } i = 1, 2 \quad (23b)$$

$$\mathbf{a}_i^0(-\beta) = C_2(z) \mathbf{a}_i^0(\beta) \quad \text{for } i = 1, 2 \quad (23c)$$

$$\mathbf{a}_1^0(\beta) = C_2(y) \mathbf{a}_2^0(\beta). \quad (23d)$$

In Eq. (23a) \mathbf{j} is the unit vector along the *y* axis, so that the hydrogens are restricted to motion in the *xz* plane. Eqs. (23b) and (23c) require that the “tracks” for the LAM hydrogen bending motions each have D_{2h} symmetry. Eq. (23d) forces the LAM bending tracks to be the same for both H atoms.

The PI group for this problem is G_8 , with the character table shown in Table 6. Table 11 gives a set of 16 symmetry operations, which when applied to the right side of Eq. (20), give the same results as when the PI operations shown in Table 11 are applied to the left side of Eq. (20). The eight feasible PI operations for C_2H_2 (including those for C–H bond breaking) each occur twice in Table 11, so we are dealing with a double group $G_8^{(2)}$ of the PI group G_8 . The limited identity associated with this double group is again labeled E_b , and has essentially the same properties as the limited identity in Table 5. Note that no new limited identities are introduced when we extend the PI group of the planar bending problem of Section 6 to include CH-bond-breaking operations. The character

Table 11
Transformation properties of the coordinates R , χ , θ , ϕ , β_1 , β_2 , and the d_i on the right of Eq. (20) under symmetry operations of the double group $G_8^{(2)}$ appropriate for simultaneously treating trans bent and cis bent acetylene and vinylidene, with only in-plane H atom bending motions as the two LAMs (see Fig. 3).

PI ^a	PG ^b	R ^c	χ, θ, ϕ^d	Equiv. Rot. ^e	β_1, β_2^f	d_i^g	$j(i)^h$
E	E	R	χ, θ, ϕ	E	β_1, β_2	E d_j	a, b, 1, 2
(ab)(12)	C ₂ (y)	R	$\pi - \chi, \pi - \theta, \pi + \phi$	C ₂ (y)	β_2, β_1	C ₂ (y) d_j	b, a, 2, 1
(ab)(12)*	i	-R	χ, θ, ϕ	E	β_2, β_1	i d_j	b, a, 2, 1
E*	$\sigma(xz)$	-R	$\pi - \chi, \pi - \theta, \pi + \phi$	C ₂ (y)	β_1, β_2	$\sigma(xz) d_j$	a, b, 1, 2
(12)	C ₂ (z)	R	$\pi + \chi, \theta, \phi$	C ₂ (z)	$\pi - \beta_2, \pi - \beta_1$	C ₂ (z) d_j	a, b, 2, 1
(ab)	C ₂ (x)	R	$-\chi, \pi - \theta, \pi + \phi$	C ₂ (x)	$\pi - \beta_1, \pi - \beta_2$	C ₂ (x) d_j	b, a, 1, 2
(ab)*	$\sigma(xy)$	-R	$\pi + \chi, \theta, \phi$	C ₂ (z)	$\pi - \beta_1, \pi - \beta_2$	$\sigma(xy) d_j$	b, a, 1, 2
(12)*	$\sigma(yz)$	-R	$-\chi, \pi - \theta, \pi + \phi$	C ₂ (x)	$\pi - \beta_2, \pi - \beta_1$	$\sigma(yz) d_j$	a, b, 2, 1
E	E _b	R	$\pi + \chi, \theta, \phi$	C ₂ (z)	$-\beta_1, -\beta_2$	C ₂ (z) d_j	a, b, 1, 2
(ab)(12)	C ₂ (y)E _b	R	$-\chi, \pi - \theta, \pi + \phi$	C ₂ (x)	$-\beta_2, -\beta_1$	C ₂ (x) d_j	b, a, 2, 1
(ab)(12)*	i E _b	-R	$\pi + \chi, \theta, \phi$	C ₂ (z)	$-\beta_2, -\beta_1$	$\sigma(xy) d_j$	b, a, 2, 1
E*	$\sigma(xz)E_b$	-R	$-\chi, \pi - \theta, \pi + \phi$	C ₂ (x)	$-\beta_1, -\beta_2$	$\sigma(yz) d_j$	a, b, 1, 2
(12)	C ₂ (z)E _b	R	χ, θ, ϕ	E	$\pi + \beta_2, \pi + \beta_1$	E d_j	a, b, 2, 1
(ab)	C ₂ (x)E _b	R	$\pi - \chi, \pi - \theta, \pi + \phi$	C ₂ (y)	$\pi + \beta_1, \pi + \beta_2$	C ₂ (y) d_j	b, a, 1, 2
(ab)*	$\sigma(xy)E_b$	-R	χ, θ, ϕ	E	$\pi + \beta_1, \pi + \beta_2$	i d_j	b, a, 1, 2
(12)*	$\sigma(yz)E_b$	-R	$\pi - \chi, \pi - \theta, \pi + \phi$	C ₂ (y)	$\pi + \beta_2, \pi + \beta_1$	$\sigma(xz) d_j$	a, b, 2, 1

^a The PI operations in this column are obtained when the variable transformations in the columns to the right are substituted in Eqs. (20) and (22). Note that every PI operation occurs twice, since this is a double group of the feasible PI group G_8 (see Table 4).

^b The operations E, C₂(y), i, and $\sigma(xz)$ are very similar to the C_{2h} point group operations for trans bent acetylene in Fig. 1, so the C_{2h} names have been retained in this double group of G_8 ; C₂(z) and $\sigma(yz)$ are very similar to the C_{2v} operations for vinylidene in Fig. 1, so these C_{2v} names have also been retained. The first eight point group operations in this column would be appropriate for a D_{2h} acetylene molecule with the C's on the z axis and the H's on the x axis. E_b is the limited identity in this delocalized planar H-bending problem.

^c Laboratory-fixed center of mass vector.

^d Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^e As defined in Bunker and Jensen [4].

^f The two LAM local-mode H—C—C and C—C—H bending angles.

^g Small-amplitude molecule-fixed vibrational displacement vectors.

^h The four atom labels in each row of this column give values of the function $j(i)$ for $i = a, b, 1, 2$, respectively, for the symmetry operation at the left of the row.

Table 12

Character table^a for the double group $G_8^{(2)}$ appropriate for C₂H₂ when two LAM planar bending angles are considered which permit simultaneous description of trans acetylene, cis acetylene, and vinylidene.

	E	(ab)	(12)	(ab)(12)	E*	(ab)*	(12)*	(ab)(12)*	E	(ab)	(12)	(ab)(12)	E*	(ab)*	(12)*	(ab)(12)*	(J, μ) ^b
	E	C ₂ (x)	C ₂ (z)	C ₂ (y)	$\sigma(xz)$	$\sigma(xy)$	$\sigma(yz)$	i	E _b	C ₂ (x)E _b	C ₂ (z)E _b	C ₂ (y)E _b	$\sigma(xz)E_b$	$\sigma(xy)E_b$	$\sigma(yz)E_b$	iE _b	
A _{1s} ⁺	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	J _x , J _y , J _z
A _{2s} ⁺	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	
B _{1s} ⁺	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	μ_z
B _{2s} ⁺	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	
A _{1s} ⁻	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	μ_x, μ_y, μ_z
A _{2s} ⁻	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1	
B _{1s} ⁻	1	-1	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	J _z
B _{2s} ⁻	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1	
A _{1d} ⁺	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	
A _{2d} ⁺	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	μ_x
B _{1d} ⁺	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	
B _{2d} ⁺	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	J _y
A _{1d} ⁻	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	
A _{2d} ⁻	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1	J _x
B _{1d} ⁻	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1	
B _{2d} ⁻	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1	μ_y

^a The symmetry operations are defined in Table 11. The symmetry species of $G_8^{(2)}$ are divided into single-valued (subscript s) and double-valued (subscript d) representations of G_8 . This direct product character table contains four copies of Table 4, three multiplied by +1 and one (lower right) multiplied by -1.

^b Symmetry species of the laboratory-fixed (X, Y, Z) and molecule-fixed (x, y, z) components of the total angular momentum J (excluding nuclear spin) and the electric dipole moment μ .

table for $G_8^{(2)}$ is shown in Table 12, which has the simple form of a direct product group of G_8 with {E, E_b}.

10. Trans and cis acetylene and vinylidene with two delocalized H bending (migration) vibrations as well as internal rotation about the C—C bond

The last set of LAMs that we consider for the acetylene problem corresponds to the case of two delocalized H bending motions, which allow for C—H bond breaking, and an internal rotation about

the C—C bond. The treatment in this section is thus related to that in Section 8 much as the treatment in Section 9 was related to that in Section 6. In particular, no new limited identities arise (i.e., we have the same seven limited identities as in Section 8) and our final group G_{64} will be an octuple group $G_8^{(8)}$ of the PI group G_8 in Table 4.

There are many subtle conceptual problems associated with considering simultaneously vibrations and rotations for the three different molecular geometries in this section. We do not discuss any of these in detail, nor do we attempt spectroscopic applications

of the group theory. Instead we merely set up a coordinate system that allows passage among the three geometries, and then derive the group theoretical transformations associated with this coordinate system.

Eq. (1), relating the laboratory-fixed Cartesian coordinates and the molecule-fixed coordinates, becomes

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\alpha, \beta_1, \beta_2) + \mathbf{d}_i], \quad (24)$$

with reference positions defined by

$$\begin{aligned} \mathbf{a}_i(\alpha, \beta_1, \beta_2) &= \mathbf{a}_i^0 - \mathbf{A}(\alpha, \beta_1, \beta_2) & \text{for } i = a, b \\ \mathbf{a}_1(\alpha, \beta_1, \beta_2) &= S^{-1}(-\alpha, 0, 0)\mathbf{a}_1^0(\beta_1) - \mathbf{A}(\alpha, \beta_1, \beta_2) \\ \mathbf{a}_2(\alpha, \beta_1, \beta_2) &= S^{-1}(+\alpha, 0, 0)\mathbf{a}_2^0(\beta_2) - \mathbf{A}(\alpha, \beta_1, \beta_2). \end{aligned} \quad (25)$$

The functions $\mathbf{a}_i^0(\beta)$ and $\mathbf{a}_2^0(\beta)$, which essentially define the “tracks” on which the hydrogen bending vibrations take place, are again defined only implicitly, and are again required to satisfy Eq. (23).

One of the questions that we do not discuss in this paper is the problem of what happens to the torsion of trans and cis bent acetylene when the molecule takes a vinylidene shape. A vinylidene minimum occurs in Eq. (25) when $\alpha = 0$, $\beta_1 = \beta_{\text{vinyl}} = \text{constant}$ (with $0 < \beta_{\text{vinyl}} < \pi/2$), and $\beta_2 = \pi - \beta_{\text{vinyl}}$ (see Fig. 3). For this configuration, small displacements from zero of the coordinate α give rise to the out-of-plane umbrella vibration of vinylidene. It thus seems probable that the group theoretical treatment devised here will preserve the three stretches (one C–C and two C–H) and the two C–C–H local bends in all three molecular geometries, but that the torsion in trans and cis acetylene will “turn into” the umbrella motion in vinylidene. A further complication is the fact that the torsion of cis bent acetylene has a C_{2v} species of A_2 , while the umbrella mode of vinylidene has a C_{2v} species of B_1 .

Since Eqs. (24) and (25) are formally very similar to Eqs. (13) and (14), Table 9 and Eqs. (17)–(19) can be used to define symmetry transformations for Eq. (24) that do not involve breaking either C–H bond. It is then sufficient to add to the four generators in Section 8 one more generator g , which does break the C–H bonds. In PI notation there are four operators to choose from: (12), (ab) , $(12)^*$, and $(ab)^*$. It turns out that the direct-product structure of the resulting group G_{64} is most clearly seen if g is chosen to be one of the four $(ab)^*$ operations that is in a class by itself. (The reason why the eight $(ab)^*$ operations are distributed into four classes of order one and one class of order four is not intuitively obvious, but presumably derives from our unsymmetrical treatment of the carbon and hydrogen motions in the multi-valued coordinate system of Eq. (24).) The analog of Eq. (19) for a general element of G_{64} then becomes

$$a^p b^q c^r d^s g^t, \quad (26)$$

where p takes the integer values 0, 1, 2, 3, and q, r, s , and t take the values 0, 1, leading to a group of order 64. (To avoid confusion, the generating operations are not labeled by the letter e , which conventionally denotes the identity, or f , which conventionally denotes a function.) We take the precise transformation of molecular variables caused by the new generator g to be

$$gf(\mathbf{R}, \chi, \theta, \phi, \alpha, \beta_1, \beta_2, \mathbf{d}_i) = f(-\mathbf{R}, \chi, \theta, \phi, \alpha, \pi + \beta_1, \pi + \beta_2, \mathbf{id}_i), \quad (27)$$

where $j(i) = i$ for $i = 1$ or 2 , but $j(a) = b$ and $j(b) = a$. The generator g defined in Eq. (27) can be shown to lead to the PI operation $(ab)^*$ when its transformations are substituted in Eqs. (24) and (25). The 32 new transformations obtained by multiplying the 32 transformations in Table 9 by g are shown in Table 13.

It can also be shown that the definition for g in Eq. (27) leads to the following additions to the relations in Eq. (18)

$$g^2 = e \quad (28a)$$

$$ga = ag, \quad gb = bg, \quad gc = cg, \quad gd = dg. \quad (28b)$$

Since g commutes with all elements of $G_4^{(8)}$ in Table 10, G_{64} is a direct product of $G_4^{(8)}$ with the group $\{e, g\}$. G_{64} thus has 28 classes. The first 14 classes, containing only elements with $t = 0$ in Eq. (26), turn out to be identical to those at the top of Table 10. The second 14 classes, containing all the elements with $t = 1$ in Eq. (26), are these same classes, but with every element multiplied by g . They are used to label the columns in the G_{64} character table. Since G_{64} has exactly the same seven limited identities as $G_4^{(8)}$, we refer to G_{64} as $G_8^{(8)}$ from this point on. The character table for $G_8^{(8)}$ is given as Table 14. Its symmetry species are named according to the left side of Table 10, with the addition of s and a subscripts, which indicate species that are symmetric and antisymmetric with respect to g .

11. Application of the present formalism to trans and cis acetylene with high tunneling barriers and no bond breaking

We now apply the results of Section 8 to the 46000 cm^{-1} region of the S_1 – S_0 transition of acetylene [21]. States of trans and cis acetylene are both present, but transitions or interactions involving states of vinylidene are absent. This region lies just below the cis–trans interconversion barrier, so that the various LAM motions taking place will lead to “tunneling-sized” displacements, rather than gross rearrangement of the rovibronic energy levels.

The permutation operations for vinylidene given in Table 1c include (12), which is a bond-breaking operation for trans and cis bent acetylene. In this section we show that, when vinylidene is excluded from consideration, i.e. when bond-breaking operations are not feasible, there will be no splittings of the asymmetric rotor energy levels of the trans or cis bent isomers as a result of tunneling effects, though some of the levels will be systematically shifted, leading to K -staggerings instead of splittings.

11.1. Inter-conformational perturbations

The first question that arises is which cis acetylene levels can perturb which trans acetylene levels. The importance of this question lies in determining how intensity is transferred from S_1 -trans levels (to which absorption from the ground state is allowed) to S_1 -cis levels at nearly the same energy (to which absorption from the ground state is forbidden). In the high-barrier tunneling case, this question can be answered from a consideration of only point groups and permutation-inversion groups. No extended group considerations are needed. In fact, this question has already been answered by Lundberg [12], making use of the full permutation-inversion group G_8 for C_2H_2 . Since Lundberg used a group containing bond-breaking operations, the application of his results to the no-bond-breaking case can lead to some confusion. We therefore reproduce his results using arguments based only on the permutation-inversion group G_4 .

The high-barrier tunneling approximation allows us to begin by considering the energy levels of trans and cis acetylene using small-amplitude vibrations and point-group operations, i.e., we can work out the positions of, and classify the electronic, vibrational, and rotational states as is conventionally done using the C_{2h} point group for trans and the C_{2v} point group for cis acetylene. We then introduce the appropriate permutation-inversion group, containing whatever feasible tunneling operations are to be considered, and use Watson’s “reverse correlation method” [22] to determine the number and symmetry species (but not the relative or absolute positions) of the components into which each point-group rovibronic level splits.

The present situation is unusual, because the point groups for trans and cis acetylene contain the same number of operations as

Table 13

Transformation properties of the coordinates \mathbf{R} , χ , θ , ϕ , α , β_1 , β_2 , and the \mathbf{d}_i on the right of Eq. (24) under half (see Table 9 for the other half) of the symmetry operations of the eightfold extended group $G_8^{(8)}$ of G_8 (see Table 4) appropriate for simultaneously treating trans bent and cis bent acetylene and vinylidene with internal rotation and local mode C–H bending motions at each end as the three LAMs.

PI ^a	Gen ^b	PG ^c	\mathbf{R}^d	χ, θ, ϕ^e	Equiv. Rot. ^f	$\alpha, \beta_1, \beta_2^g$	\mathbf{d}_i^h	$j(i)^i$
(ab)*	g	$\sigma(xy)E_b$	–R	χ, θ, ϕ	E	$\alpha, \pi + \beta_1, \pi + \beta_2$	$i \mathbf{d}_j$	b, a, 1, 2
(12)*	a^2bg	$\sigma(yz)E_b$	–R	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	$\alpha, \pi + \beta_2, \pi + \beta_1$	$\sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	a^2bcdg	$C_2(z)E_b$	R	χ, θ, ϕ	E	$-\alpha, \pi + \beta_2, \pi + \beta_1$	$E \mathbf{d}_j$	a, b, 2, 1
(ab)	cdg	$C_2(x)E_b$	R	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	$-\alpha, \pi + \beta_1, \pi + \beta_2$	$C_2(y) \mathbf{d}_j$	b, a, 1, 2
(ab)*	a^2g	$\sigma(xy)$	–R	$\pi + \chi, \theta, \phi$	$C_2(z)$	$\alpha, \pi - \beta_1, \pi - \beta_2$	$\sigma(xy) \mathbf{d}_j$	a, b, 1, 2
(12)*	bg	$\sigma(yz)$	–R	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$\alpha, \pi - \beta_2, \pi - \beta_1$	$\sigma(yz) \mathbf{d}_j$	a, b, 2, 1
(12)	bcdg	$C_2(z)$	R	$\pi + \chi, \theta, \phi$	$C_2(z)$	$-\alpha, \pi - \beta_2, \pi - \beta_1$	$C_2(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	a^2cdg	$C_2(x)$	R	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$-\alpha, \pi - \beta_1, \pi - \beta_2$	$C_2(x) \mathbf{d}_j$	b, a, 1, 2
(ab)*	dg	$\sigma(xy)E_bE_t$	–R	$\pi + \chi, \theta, \phi$	$C_2(z)$	$\pi + \alpha, \pi + \beta_1, \pi + \beta_2$	$\sigma(xy) \mathbf{d}_j$	b, a, 1, 2
(12)*	a^2bdg	$\sigma(yz)E_bE_t$	–R	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$\pi + \alpha, \pi + \beta_2, \pi + \beta_1$	$\sigma(yz) \mathbf{d}_j$	a, b, 2, 1
(12)	a^2bcg	$C_2(z)E_bE_t$	R	$\pi + \chi, \theta, \phi$	$C_2(z)$	$\pi - \alpha, \pi + \beta_2, \pi + \beta_1$	$C_2(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	cg	$C_2(x)E_bE_t$	R	$-\chi, \pi - \theta, \pi + \phi$	$C_2(x)$	$\pi - \alpha, \pi + \beta_1, \pi + \beta_2$	$C_2(x) \mathbf{d}_j$	b, a, 1, 2
(ab)*	a^2dg	$\sigma(xy)E_t$	–R	χ, θ, ϕ	E	$\pi + \alpha, \pi - \beta_1, \pi - \beta_2$	$i \mathbf{d}_j$	b, a, 1, 2
(12)*	bdg	$\sigma(yz)E_t$	–R	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	$\pi + \alpha, \pi - \beta_2, \pi - \beta_1$	$\sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	bcdg	$C_2(z)E_t$	R	χ, θ, ϕ	E	$\pi - \alpha, \pi - \beta_2, \pi - \beta_1$	$E \mathbf{d}_j$	a, b, 2, 1
(ab)	a^2cg	$C_2(x)E_t$	R	$\pi - \chi, \pi - \theta, \pi + \phi$	$C_2(y)$	$\pi - \alpha, \pi - \beta_1, \pi - \beta_2$	$C_2(y) \mathbf{d}_j$	b, a, 1, 2
(ab)*	abcg	$\sigma(xy)E_bE_c$	–R	$\pi/2 + \chi, \theta, \phi$	$C_4(z)$	$\pi/2 + \alpha, \pi + \beta_1, \pi - \beta_2$	$C_4^{-1}(z) i \mathbf{d}_j$	b, a, 1, 2
(12)*	acg	$\sigma(yz)E_bE_c$	–R	$3\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4(z)$	$\pi/2 + \alpha, \pi + \beta_2, \pi - \beta_1$	$C_4^{-1}(z) \sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	ag	$C_2(z)E_bE_c$	R	$\pi/2 + \chi, \theta, \phi$	$C_4(z)$	$\pi/2 - \alpha, \pi + \beta_2, \pi - \beta_1$	$C_4^{-1}(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	abg	$C_2(x)E_bE_c$	R	$3\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4(z)$	$\pi/2 - \alpha, \pi + \beta_1, \pi - \beta_2$	$C_4^{-1}(z) C_2(y) \mathbf{d}_j$	b, a, 1, 2
(ab)*	a^3bcg	$\sigma(xy)E_c$	–R	$-\pi/2 + \chi, \theta, \phi$	$C_4^{-1}(z)$	$\pi/2 + \alpha, \pi - \beta_1, \pi + \beta_2$	$C_4(z) i \mathbf{d}_j$	b, a, 1, 2
(12)*	a^3cg	$\sigma(yz)E_c$	–R	$\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4^{-1}(z)$	$\pi/2 + \alpha, \pi - \beta_2, \pi + \beta_1$	$C_4(z) \sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	a^3g	$C_2(z)E_c$	R	$-\pi/2 + \chi, \theta, \phi$	$C_4^{-1}(z)$	$\pi/2 - \alpha, \pi - \beta_2, \pi + \beta_1$	$C_4(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	a^3bg	$C_2(x)E_c$	R	$\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4^{-1}(z)$	$\pi/2 - \alpha, \pi - \beta_1, \pi + \beta_2$	$C_4(z) C_2(y) \mathbf{d}_j$	b, a, 1, 2
(ab)*	abcdg	$\sigma(xy)E_bE_tE_c$	–R	$-\pi/2 + \chi, \theta, \phi$	$C_4^{-1}(z)$	$-\pi/2 + \alpha, \pi + \beta_1, \pi - \beta_2$	$C_4(z) i \mathbf{d}_j$	b, a, 1, 2
(12)*	acdg	$\sigma(yz)E_bE_tE_c$	–R	$\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4^{-1}(z)$	$-\pi/2 + \alpha, \pi + \beta_2, \pi - \beta_1$	$C_4(z) \sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	adg	$C_2(z)E_bE_tE_c$	R	$-\pi/2 + \chi, \theta, \phi$	$C_4^{-1}(z)$	$-\pi/2 - \alpha, \pi + \beta_2, \pi - \beta_1$	$C_4(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	abdg	$C_2(x)E_bE_tE_c$	R	$\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4^{-1}(z)$	$-\pi/2 - \alpha, \pi + \beta_1, \pi - \beta_2$	$C_4(z) C_2(y) \mathbf{d}_j$	b, a, 1, 2
(ab)*	a^3bcdg	$\sigma(xy)E_tE_c$	–R	$\pi/2 + \chi, \theta, \phi$	$C_4(z)$	$-\pi/2 + \alpha, \pi - \beta_1, \pi + \beta_2$	$C_4^{-1}(z) i \mathbf{d}_j$	b, a, 1, 2
(12)*	a^3cdg	$\sigma(yz)E_tE_c$	–R	$3\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4(z)$	$-\pi/2 + \alpha, \pi - \beta_2, \pi + \beta_1$	$C_4^{-1}(z) \sigma(xz) \mathbf{d}_j$	a, b, 2, 1
(12)	a^3dg	$C_2(z)E_tE_c$	R	$\pi/2 + \chi, \theta, \phi$	$C_4(z)$	$-\pi/2 - \alpha, \pi - \beta_2, \pi + \beta_1$	$C_4^{-1}(z) \mathbf{d}_j$	a, b, 2, 1
(ab)	a^3bdg	$C_2(x)E_tE_c$	R	$3\pi/2 - \chi, \pi - \theta, \pi + \phi$	$C_2(y)C_4(z)$	$-\pi/2 - \alpha, \pi - \beta_1, \pi + \beta_2$	$C_4^{-1}(z) C_2(y) \mathbf{d}_j$	b, a, 1, 2

^a The PI operations in this column are obtained when the variable transformations in the columns to the right are substituted in Eq. (24). Every PI operation occurs eight times.

^b Notation of Eqs. (19) and (26).

^c The operations $C_2(x)$, $C_2(y)$, $C_2(z)$, $\sigma(xy)$, $\sigma(yz)$, $\sigma(xz)$, and i are very similar to the D_{2h} point group operations, so the D_{2h} names have been retained in this octuple group $G_8^{(8)}$ of the feasible PI group G_8 . (See Table 9 for the other 32 elements of $G_8^{(8)}$.) E_b and E_t are the limited identities for the local-mode H–C–C and C–C–H bending problem and for the torsional problem, respectively, as found in Tables 5 and 7. E_c is a limited identity for the combined bending and torsional problem, as found in Table 9.

^d Laboratory-fixed center of mass vector.

^e Rotational variables = Eulerian angles in the direction cosine matrix of Eq. (2) [7].

^f As defined in Bunker and Jensen [4].

^g The LAM internal rotation angle and the two LAM local-mode H–C–C and C–C–H bending angles.

^h Small-amplitude molecule-fixed vibrational displacement vectors; linear combinations of these are used to express normal (or symmetry) coordinates for the three small-amplitude bond stretches.

ⁱ The four atom labels in each row of this column give values of the function $j(i)$ for $i = a, b, 1, 2$, respectively, for the symmetry operation at the left of the row. Note that $j = i$ does not occur for the 32 bond-breaking elements of $G_8^{(8)}$ given in this table.

the PI group needed when C–H bond breaking is not feasible. This leads group-theoretically to the conclusion that no splittings of rovibronic energy levels will be observed as long as bond-breaking does not occur. The same conclusion could be reached by noting that both trans and cis acetylene have only one framework when C–H bond breaking is forbidden, i.e., it is impossible to draw two non-superimposable trans acetylene equilibrium structures using the labeled atoms C_a , C_b , H_1 and H_2 , when H_1 must (by hypothesis) be attached to C_a .

Furthermore, the PI group G_4 for trans and cis acetylene without C–H bond breaking is isomorphic to both C_{2h} for trans acetylene and C_{2v} for cis acetylene. Thus, from the PI group point of view, the C_{2h} and C_{2v} symmetry labels are just two different sets of labels for the same PI group symmetry species, i.e., the point-group labels are rigorously identical in pairs, with: $A_g(C_{2h}) = A_1(C_{2v})$, $A_u(C_{2h}) = A_2(C_{2v})$, $B_g(C_{2h}) = B_1(C_{2v})$, and $B_u(C_{2h}) = B_2(C_{2v})$. This pairing also indicates which C_{2h} rovibronic states can perturb which C_{2v} rovibronic states, e.g., $^{evr}A_g(C_{2h})$ can perturb $^{evr}A_1(C_{2v})$, etc.

(Note that we are following Mulliken's recommendation [9] that the B species of C_{2v} be labeled such that in-plane vibrations are of species B_2 rather than B_1 .) The most important consequence [12,21] of these rovibronic selection rules is that a given trans vibronic state and a given cis vibronic state cannot perturb each other for both even and odd K values.

These rovibronic selection rules remain valid when perturbations driven by electron spin are considered. Spin splittings in C_2H_2 are expected to be small compared to rotational spacings, so that Hund's case (b) applies. The laboratory-fixed electron spin functions used in case (b) do not involve the nuclear coordinates, so they are unchanged by any nuclear permutation. Since the spin is an angular momentum, spin functions are invariant under the laboratory-fixed inversion operation E^* . Case (b) electron spin functions thus belong to the totally symmetric species in any PI group, so that the electron-spin-rovibronic species, $^{evrs} \Gamma$, of any case (b) spin component of a rovibronic state is always the same as that of the rovibronic state, $^{evr} \Gamma$. Electron spin driven

Table 14
Character table^{a,b} for the group $G_8^{(8)}$.

Species	<i>e</i>	<i>d</i>	<i>a</i> ²	<i>a</i> ² <i>d</i>	<i>c</i>	<i>a</i> ² <i>c</i>	<i>b</i>	<i>bd</i>	<i>bc</i>	<i>a</i> ² <i>bc</i>	<i>a</i>	<i>ac</i>	<i>ab</i>	<i>abc</i>	<i>g</i>	<i>dg</i>	<i>a</i> ² <i>g</i>	<i>a</i> ² <i>dg</i>	<i>cg</i>	<i>a</i> ² <i>cg</i>	<i>bg</i>	<i>bdg</i>	<i>bcg</i>	<i>a</i> ² <i>bcg</i>	<i>ag</i>	<i>acg</i>	<i>abg</i>	<i>abcg</i>	
					<i>cd</i>	<i>a</i> ² <i>cd</i>	<i>a</i> ² <i>b</i>	<i>a</i> ² <i>bd</i>	<i>a</i> ² <i>bcd</i>	<i>bcd</i>	<i>a</i> ³	<i>a</i> ³ <i>c</i>	<i>a</i> ³ <i>b</i>	<i>a</i> ³ <i>bc</i>					<i>cdg</i>	<i>a</i> ² <i>cdg</i>	<i>a</i> ² <i>bg</i>	<i>a</i> ² <i>bdg</i>	<i>a</i> ² <i>bcdg</i>	<i>a</i> ³ <i>dg</i>	<i>a</i> ³ <i>cg</i>	<i>a</i> ³ <i>bg</i>	<i>a</i> ³ <i>bcg</i>		
A _{1gs} ⁺	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A _{2us} ⁺	1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1	-1
A _{1us} ⁻	1	1	1	1	-1	-1	1	1	-1	-1	1	-1	1	-1	1	1	1	1	-1	-1	1	1	-1	-1	1	-1	1	-1	-1
A _{2gs} ⁻	1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1	-1	1	1
B _{1gs} ⁺	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1
B _{2us} ⁺	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1
B _{1us} ⁻	1	1	1	1	-1	-1	1	1	-1	-1	-1	1	-1	1	1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	1	-1	1
B _{2gs} ⁻	1	1	1	1	-1	-1	-1	-1	1	1	-1	1	1	-1	1	1	1	1	-1	-1	-1	-1	1	1	-1	1	1	-1	-1
E _s ⁺	2	2	-2	-2	2	-2	0	0	0	0	0	0	0	0	2	2	-2	-2	2	-2	0	0	0	0	0	0	0	0	0
E _s ⁻	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0	0
E _{1s}	2	-2	2	-2	0	0	2	-2	0	0	0	0	0	0	2	-2	2	-2	0	0	2	-2	0	0	0	0	0	0	0
E _{2s}	2	-2	2	-2	0	0	-2	2	0	0	0	0	0	0	2	-2	2	-2	0	0	-2	2	0	0	0	0	0	0	0
E _{gs}	2	-2	-2	2	0	0	0	0	2	-2	0	0	0	0	2	-2	-2	2	0	0	0	0	2	-2	0	0	0	0	0
E _{us}	2	-2	-2	2	0	0	0	0	-2	2	0	0	0	0	2	-2	-2	2	0	0	0	0	-2	2	0	0	0	0	0
A _{1ga} ⁺	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
A _{2ua} ⁺	1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	1	1
A _{1ua} ⁻	1	1	1	1	-1	-1	1	1	-1	-1	1	-1	1	-1	-1	-1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	-1	1
A _{2ga} ⁻	1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	1	1	-1	-1
B _{1ga} ⁺	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
B _{2ua} ⁺	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	-1	-1
B _{1ua} ⁻	1	1	1	1	-1	-1	1	1	-1	-1	-1	1	-1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	-1	1	-1	1	-1
B _{2ga} ⁻	1	1	1	1	-1	-1	-1	-1	1	1	-1	1	1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1	1	-1	-1	1	1
E _a ⁺	2	2	-2	-2	2	-2	0	0	0	0	0	0	0	0	-2	-2	2	2	-2	2	0	0	0	0	0	0	0	0	0
E _a ⁻	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0	-2	-2	2	2	2	-2	0	0	0	0	0	0	0	0	0
E _{1a}	2	-2	2	-2	0	0	2	-2	0	0	0	0	0	0	-2	2	-2	2	0	0	-2	2	0	0	0	0	0	0	0
E _{2a}	2	-2	2	-2	0	0	-2	2	0	0	0	0	0	0	-2	2	-2	2	0	0	2	-2	0	0	0	0	0	0	0
E _{ga}	2	-2	-2	2	0	0	0	0	2	-2	0	0	0	0	-2	2	2	-2	0	0	0	0	-2	2	0	0	0	0	0
E _{ua}	2	-2	-2	2	0	0	0	0	-2	2	0	0	0	0	-2	2	2	-2	0	0	0	0	2	-2	0	0	0	0	0

^a This group is appropriate for a simultaneous treatment of trans bent and cis bent acetylene and vinylidene when the three LAMs are internal rotation and a local-mode in-plane C–C–H bending vibration at each end of the molecule.

^b Symmetry species of various operators are: $\Gamma(\mu_x) = \Gamma(\mu_y) = \Gamma(\mu_z) = B_{1ua}^-; \Gamma(J_x) = \Gamma(J_y) = \Gamma(J_z) = A_{1gs}^+; \Gamma\{\mu_x, \mu_y\} = E_{ua}; \Gamma(\mu_z) = B_{2ua}^+; \Gamma\{J_x, J_y\} = E_{gs};$ and $\Gamma(J_z) = A_{2gs}^-.$

perturbations in C₂H₂ (e.g., singlet-triplet perturbations) thus cannot violate the rovibronic selection rules of the previous paragraph.

The rovibronic selection rules above do not remain valid when nuclear spin driven perturbations are considered, but observation of such perturbations is likely to be rare in the electronic spectrum of acetylene. Furthermore, a discussion of the changes in rovibronic selection rules is lengthy, involves consideration of the operator $\mathbf{F} = \mathbf{J} + \mathbf{I}$, and is different for different isotopic species, so we present only the final conclusion here: In acetylene with no bond breaking, perturbations between a given pair of cis and trans vibronic levels are rovibronically allowed for one (even or odd) set of K values and rovibronically forbidden for the other, but they are nuclear spin allowed (between levels of the same F value) for both even and odd K .

11.2. Tunneling splittings in the multivalued coordinate system of Section 8

It turns out that cis and trans acetylene do not exhibit doublings of their rovibronic energy levels when bond breaking motion is not feasible, though tunneling splittings of the LAM bending-torsional levels are expected when the use of a multiple valued coordinate system (designed to take maximum advantage of the vibrational symmetry) leads to the “creation” of a number of different frameworks. In this section we consider the energy level patterns of these vibrational tunneling splittings. In Section 11.3 we show how these splittings manifest themselves as staggerings of the K -structure when rotation is taken into account. Such staggerings often arise in quantum mechanical tunneling situations; the use of multiple valued coordinates greatly simplifies their qualitative understanding.

It is useful to recall some (pictorial) concepts associated with multidimensional, multi-minimum high-barrier tunneling problems, such as that suggested by the potential surface shown in Fig. 4. Fig. 5 shows a cut of this surface obtained by traveling around the circumference of a circle with its center at the linear configuration and its radius chosen to reach from the center to one of the trans minima. Such a cut passes in turn through a trans minimum, a cis minimum, a trans minimum, and a cis minimum, before returning again to the trans minimum starting point, and the energy along the cut can be displayed as a periodic function of an angular coordinate γ , given by $\tan^{-1}(\beta_2/\beta_1) - \pi/4$. In Fig. 5 we have taken the trans wells to be significantly deeper than the cis wells, as in the S_1 state of acetylene near 46000 cm⁻¹ [17,21].

Consider first a tunneling motion that starts from the lowest energy level in the trans well and moves along the angular coordinate γ around the circle. This trajectory passes “under” both cis wells, and thus corresponds to a traditional “ammonia-like” tunneling motion, in the sense that the entire region between the two identical trans wells is classically forbidden. The only difference from ammonia lies in the fact that the top of the potential barrier “mountain” is missing, because of the presence of the cis well “crater.” However, the tunneling splitting associated with this trans \rightarrow trans tunneling trajectory is characterized in the quantum mechanical high-barrier tunneling treatment by only a single parameter, namely the tunneling splitting frequency. The detailed shape of the top of the potential barrier, which is in any case almost “invisible” to the low-amplitude portion of the wavefunction passing under it, has little influence on the tunneling frequency, which is essentially determined by an integral along the path s under the barrier of the form $\int_{s_1}^{s_2} \{(2m/\hbar^2)[V(s) - E]\}^{1/2} ds$, i.e., by the usual function [23] of the tunneling mass (m), barrier height ($V - E$), and path length ($s_2 - s_1$) that arises in discussions of transmission coefficients for quantum mechanical wave propagation through a barrier.

Now consider a tunneling motion that starts from the lowest energy level in the cis well. This trajectory passes through the barrier separating the cis from the trans well, but passes above the minimum of the trans well, so there is a tendency to think of this as a tunneling from cis to trans acetylene. As is well known [23], however, the amplitude of the wavefunction will be extremely low in its oscillatory region above the trans minimum, and will only regain its original large magnitude when the tunneling trajectory reaches the other cis well. Thus, while this trajectory technically has a cis \rightarrow trans tunneling aspect to it, it is more reasonable to think of it as a cis \rightarrow cis tunneling, where the very-low-amplitude “tunneling” part of the wavefunction has an oscillatory (rather than an exponentially decaying) segment at its center. The quantum mechanical “purpose” of this oscillatory segment is to maintain a correct node-count, i.e., the lowest level in the cis well must have an eigenfunction with a node count one greater than the trans-well eigenfunction immediately below it in energy. Reasoning intuitively leads to the following suppositions, which we adopt here. (i) The tunneling splitting will still be characterized by a single parameter, which is determined by path integrals of the form $\int_{s_1}^{s_2} \{(2m/\hbar^2)[V(s) - E]\}^{1/2} ds$ along the two segments of the path under the barrier on either side of the trans-well oscillatory region. (ii) The very low amplitude oscillatory part of the wavefunction passing over the classically allowed trans minimum part of the path will correspond to a transmission coefficient of unity, and will give a negligible contribution to the cis \rightarrow cis tunneling frequency. (iii) The high-amplitude parts of the tunneling wavefunction will still occur only in the two cis wells.

We now turn to a more careful treatment of the eight-well tunneling problem associated with the multivalued coordinate system of Section 8. Following the discussion above, we will consider tunneling splittings caused by trans \rightarrow trans tunneling among a given set of eight isoenergetic localized trans minimum states entirely separately from splittings caused by cis \rightarrow cis tunneling among eight different localized cis minimum states.

Symmetry species for linear combinations of bending-torsional (bt) vibrational wavefunctions localized in the eight trans minima of Eq. (15) of Section 8 can be determined much as they were for the two-well problem of Section 6. The $\nu = 0$ harmonic-oscillator (Gaussian) bending-torsional basis functions localized in the eight trans wells span the representation

$${}^{bt}\Gamma_{trans} = A_{1g}^+ \oplus B_{1g}^+ \oplus E^+ \oplus E_1 \oplus E_g \quad (29)$$

of $G_4^{(8)}$. A similar set of Gaussian harmonic-oscillator basis functions localized in the eight cis wells span the $G_4^{(8)}$ representation

$${}^{bt}\Gamma_{cis} = A_{1g}^+ \oplus B_{1g}^+ \oplus E^+ \oplus E_1 \oplus E_u. \quad (30)$$

It is relatively simple to estimate the splittings of the levels in Eqs. (29) and (30) by carrying out a pure bending-torsion tunneling treatment. A complete treatment of the tunneling problem must obviously also include rotational effects, but such a treatment [24,25] is beyond the scope of this work, so we content ourselves here with deriving only the (presumably dominant) $J = 0$ splitting patterns.

We can understand the tunneling paths between the eight trans equilibrium configurations given by the various sets of α , β_1 , β_2 values in Eq. (15) pictorially, by imagining four copies of Fig. 4 (which are energy displays above the β_1 , β_2 plane), stacked on top of each other, in such a way that the vertical spacing between each copy is the same, but with the second copy rotated by 90° with respect to the first, the third copy rotated by 180°, and the fourth copy by 270°, corresponding to the four α values in Eqs. (15a)–(15d). We can then number the trans minima from $n = 1$ to 8, and use harmonic oscillator $\nu = 0$ vibrational functions in each of these minima (as in Sections 6 and 7) as a basis set to set up an 8×8 tunneling

matrix. To define the numbering of the minima in a group theoretically unique way, we act with powers of a^3cd in Table 9 on a bending-torsional function localized in trans minimum $n = 1$, occurring at $\alpha = 0$, $\beta_1 = \beta_2 = +\beta_{trans} \approx +2\pi/6$ in Eq. (15a), to generate bending-torsional functions localized in minima $n = 3, 5$, and 7 , i.e., $(a^3cd)^p|n = 1\rangle = |n = 1 + 2p\rangle$ for $0 \leq p \leq 3$, or act in a similar way on a bending-torsional function in trans minimum 2 , occurring at $\alpha = 0$, $\beta_1 = \beta_2 = -\beta_{trans} \approx -2\pi/6$ in Eq. (15a), to generate bending-torsional functions in minima $4, 6$, and 8 . In addition, $|n=2\rangle \equiv a^2|n=1\rangle$. This numbering scheme puts minima 1 and 2 from Eq. (15a) in the first layer, minima 3 and 4 from Eq. (15b) in the second, etc.

The “nearest-neighbor” in-plane bending tunneling motions take place within each layer, and can be represented as $1 \leftrightarrow 2$, $3 \leftrightarrow 4$, $5 \leftrightarrow 6$, and $7 \leftrightarrow 8$. These motions give rise to the tunneling matrix elements $2H_{12} = 2H_{21} = 2H_{34} = 2H_{43} = 2H_{56} = 2H_{65} = 2H_{78} = 2H_{87}$ in the 8×8 Hamiltonian matrix shown in Fig. 6. It can be shown by group theoretical arguments [24–26] that these tunneling elements all have the same magnitude and sign. (The factor of 2 is added to allow for the fact that there are two equivalent tunneling paths in Fig. 4, one going clockwise through one cis minimum, the other going counterclockwise through the other cis minimum.)

There are four equivalent internal-rotation tunnelings from minima 1 and 2 in the first layer to minima 3 and 4 in the second layer, i.e., $1 \leftrightarrow 3$, $1 \leftrightarrow 4$, $2 \leftrightarrow 3$, and $2 \leftrightarrow 4$. Counting all four layers, there are 32 equal (again by group theoretical arguments) matrix elements H_{13} at appropriate positions in the Hamiltonian of Fig. 6. Diagonalization of this matrix yields the eigenvectors shown at the bottom of Fig. 6, and the energy levels

$$\begin{aligned} E\left({}^{bt}A_{1g}^+\right) &= E_0 + 2H_{12} + 4H_{13} \\ E\left({}^{bt}B_{1g}^+\right) &= E_0 + 2H_{12} - 4H_{13} \\ E\left({}^{bt}E_g\right) &= E_0 - 2H_{12} \\ E\left({}^{bt}E_1\right) &= E_0 + 2H_{12} \\ E\left({}^{bt}E^+\right) &= E_0 - 2H_{12}, \end{aligned} \quad (31)$$

for the $G_4^{(8)}$ symmetry species levels in Eq. (29). We expect both H_{12} and H_{13} to be negative in the ground vibrational state [26], so that the eigenfunction for the lowest energy state has no nodes. The tunneling Hamiltonian matrix in Fig. 6 thus gives rise to five energy levels, whose relative energies are functions of two tunneling parameters: H_{12} , which is associated with tunneling involving the LAM local mode C–C–H bends at each end of the molecule, and H_{13} , which is associated with internal rotation tunneling of the two C–H groups about the C–C bond.

A similar treatment for the cis–cis tunneling problem yields energy levels

$$\begin{aligned} E\left({}^{bt}A_{1g}^+\right) &= E_0 + 2H_{12} + 4H_{13} \\ E\left({}^{bt}B_{1g}^+\right) &= E_0 + 2H_{12} - 4H_{13} \\ E\left({}^{bt}E_u\right) &= E_0 - 2H_{12} \\ E\left({}^{bt}E_1\right) &= E_0 + 2H_{12} \\ E\left({}^{bt}E^+\right) &= E_0 - 2H_{12}, \end{aligned} \quad (32)$$

for the symmetry species in Eq. (30).

11.3. Tunneling splittings become tunneling staggerings upon returning from $G_4^{(8)}$ to the PI group G_4

The derivation of tunneling staggering effects has two parts. First, we set up and diagonalize an LAM tunneling matrix in a multivalued coordinate system, which is needed if we are to define the LAM coordinates and their domain as symmetrically as possible for the two equivalent halves of the molecule. All group-theoretical

considerations at this stage are performed using the extended PI group $G_4^{(8)}$, as in Section 11.2.

Next we multiply the LAM tunneling wavefunctions by five other factors, namely the three small amplitude vibrational (SAV) wavefunctions, the electronic wavefunction, and the J_{KaKc} asymmetric-rotor wavefunction. Following this we discard any total rovibronic product functions having $G_4^{(8)}$ symmetry species that do not transform according to single-valued representations of the G_4 PI group. It is this group-theoretical discarding process (the subject of this section), that leads to the staggering. (To simplify the logic in this section, we assume that the SAV and electronic wavefunctions are all totally symmetric, so that they can be ignored. The full complexity of the symmetry of the total wavefunction will be dealt with in Sections 11.4 and 11.5.)

It is important to note that we are not discarding wavefunctions because of the requirements of Bose–Einstein or Fermi–Dirac statistics (which can also lead to energy level staggering, as, for example, in the Λ -doubling components of ${}^1\Pi$ states of O_2). That discarding is based on fundamental quantum mechanical assumptions concerning transformation properties of wavefunctions under exchange of identical bosons or fermions. It is a separate process that takes place after the discarding process of this section, which is necessary only because of our choice of a multiple-valued coordinate system and does not reflect any fundamental physics.

The symmetry species ${}^r\Gamma$ in $G_4^{(8)}$ of the asymmetric rotor functions J_{KaKc} are (from Ref. [20] or Tables 9 and 10)

$$\begin{aligned} {}^r\Gamma(J_{4n,e}) &= A_{1g}^+ \\ {}^r\Gamma(J_{4n,o}) &= A_{2g}^- \\ {}^r\Gamma(J_{4n+2,e}) &= B_{1g}^+ \\ {}^r\Gamma(J_{4n+2,o}) &= B_{2g}^- \\ {}^r\Gamma(J_{0e}, J_{0o}) &= E_g, \end{aligned} \quad (33)$$

where we have converted from Wang function notation [20] to J_{KaKc} notation by noting that $C_2(c)|J, K, M\rangle = C_2(y)|J, K, M\rangle = (-1)^{J-K}|J, -K, M\rangle$, so that $C_2(c)|J, K^\pm\rangle = \pm(-1)^{J-K}|J, K^\pm\rangle$; K_c thus has the same parity as $\pm(-1)^J$ when K is even. These rotational species are the same in the wells with $\alpha = 0$ and π as in the wells with $\alpha = \pi/2$ and $3\pi/2$, even though the b and c principal axes interchange when α increases by $\pi/2$.

The product wavefunctions formed by multiplying the bending-torsion wave functions by the rotational wavefunctions will have a variety of $G_4^{(8)}$ symmetry species, but we can only keep vibration-rotation (total) wavefunctions that belong to single-valued representations of G_4 , because: (i) any complete molecular wavefunction can always be expressed in terms of the laboratory-fixed Cartesian coordinates of the atoms in the molecule; (ii) laboratory-fixed Cartesian coordinates are a single-valued coordinate system, and (iii) the Longuet-Higgins PI group is the correct group for wavefunctions in such a coordinate system. (Note that any bending, torsional, or rotational factor by itself does not contain enough information to locate the atoms in the laboratory, and we are therefore not restricted to using the Longuet-Higgins PI group when studying such “partial” wavefunctions.)

The multiplication table for $G_4^{(8)}$ and the requirement that the tunneling-rotational product function must belong to a single-valued representation of G_4 then lead, for trans acetylene in its ground vibrational state, to the conclusions that: (i) $K_a = 4n$ rotational functions, with ${}^r\Gamma = A_{1g}^+$ or A_{2g}^- , can only be associated with the tunneling energy $E\left({}^{bt}A_{1g}^+\right) = E_0 + 2H_{12} + 4H_{13}$; (ii) $K_a = 4n + 2$ rotational functions, with ${}^r\Gamma = B_{1g}^+$ or B_{2g}^- , can only be associated with the tunneling energy $E\left({}^{bt}B_{1g}^+\right) = E_0 + 2H_{12} - 4H_{13}$; and (iii) $K_a = \text{odd}$ rotational functions, with ${}^r\Gamma = E_g$, can only be associated with the

tunneling energy $E(^bE_g) = E_0 - 2H_{12}$. This has the effect of discarding 7/8 of the vibration-rotation wavefunctions from the $G_4^{(8)}$ treatment, which brings us back to a one-framework count of quantum states. It has the further effect of introducing a staggering of the K_a stacks of energy levels in trans acetylene, that divides them into three categories according to the above rules. Two important points should be mentioned, however. First, group theory alone will not tell us the relative magnitudes of $|H_{12}|$ and $|H_{13}|$, i.e., cannot tell us whether the local-bend tunneling splittings are greater or less than the internal rotation tunneling splittings. Thus, without further modeling or some spectral fitting, we cannot predict whether $K_a = \text{odd}$ levels will be “staggered above” or “staggered below” the $K_a = 4n + 2$ levels. All we can say is that in the ground vibrational state the $K_a = 4n$ levels should be “staggered below” the other two sets (in keeping with our assumption that the lowest-energy wavefunction will be nodeless). Second, the $K_a K_c = oe$ and oo asymmetric rotor functions belong to the doubly degenerate representation rE_g of $G_4^{(8)}$. These rE_g functions must be combined with the bE_g tunneling component to form allowed tunneling-rotational functions of species ${}^{btr}A_{1g}^+$ and ${}^{btr}A_{2g}^-$. It is almost certain that cases will arise where the “group-theoretical splitting” associated with this ${}^{btr}E_g \times {}^rE_g = {}^{btr}A_{1g}^+ \oplus {}^{btr}A_{2g}^- \oplus {}^{btr}B_{1g}^+ \oplus {}^{btr}B_{2g}^-$ product will be large enough to influence in some way the apparent “asymmetry doubling” of a given pair of $K_a = \text{odd}$ levels (e.g., the $K_a = 1$ levels). Thus, while the present extended group model clearly predicts a staggering of K_a levels into three groups, working out the finer details of this staggering will require a proper tunneling-Hamiltonian treatment of levels with $J > 0$ [24–26].

The combination of bending-torsional and rotational functions for cis acetylene is basically the same, except that rE_g rotational functions will combine with ${}^{btr}E_u$ bending-torsional functions to give allowed ${}^{btr}B_{2u}^+$ and ${}^{btr}B_{1u}^-$ rovibronic functions. Keeping only single-valued representations of G_4 introduces a very similar staggering in the K_a stacks of the cis molecule.

11.4. Symmetry species in $G_4^{(8)}$ of the S_1 electronic state of acetylene

The S_1 electronic state of acetylene is known to have the electron configuration $\pi_g^2\pi_u$ and to transform as ${}^1\Sigma_u^-$, 1A_u or 1A_2 when the appropriate point group symmetry is $D_{\infty h}$, C_{2h} or C_{2v} , respectively. The correlations at the right of Table 10 show that these C_{2h} and C_{2v} orbital species are consistent with four possible $G_4^{(8)}$ symmetry species: A_{1u}^- , B_{1u}^- , E^- , and E_1 . Since the S_1 state is nondegenerate even in the linear configuration, the existence of a partner state seems unlikely, so we discard the two E possibilities. We now show that it is possible to construct two types of electronic states with the point-group correlation properties above, one of which is A_{1u}^- in $G_4^{(8)}$, the other B_{1u}^- .

At this point it is necessary to define the “molecule-fixed” electronic coordinates. It seems reasonable to require that all electrons be treated in the same way, since antisymmetrization requirements will eventually require exchanging electron coordinates. The most obvious way to do that within the spirit of the present treatment is to use the following equation

$${}^e\mathbf{R}_s = \mathbf{R} + S^{-1}(\chi, \theta, \phi){}^e\mathbf{r}_s, \quad (34)$$

where ${}^e\mathbf{R}_s$ and ${}^e\mathbf{r}_s$ represent, respectively, the laboratory-fixed and molecule-fixed Cartesian coordinates of electron s , and \mathbf{R} and $S^{-1}(\chi, \theta, \phi)$ are defined as in Eq. (13), which deals with the LAM part of the trans and cis acetylene problem when two local bends and internal rotation are considered as LAMs. It turns out that this definition for the molecule-fixed electron coordinates causes each set of coordinates $\{{}^eX_s, {}^eY_s, {}^eZ_s\}$ to transform exactly like the molecule-fixed components of the dipole moment operator $\{\mu_x, \mu_y, \mu_z\}$ in Table 10.

For symmetry purposes, we approximate the molecular orbitals by linear combinations of atomic orbitals (LCAOs), where the atomic orbitals are expressed as atomic wavefunctions in spherical coordinates with Condon and Shortley phase factors, i.e., in the form $R_{nl}(r)Y_{lm}(\theta, \phi)$ [27,28]. An additional complication arises however, because we want the arguments in the atomic wavefunctions to represent the polar coordinates of a vector from a given atom to the electron, rather than from the origin to the electron. This can be accomplished by defining the vector \mathbf{r}_{si} from atom $i = a, b, 1, 2$ to electron s as

$$\mathbf{r}_{si} = S^{+1}(\chi, \theta, \phi)[{}^e\mathbf{R}_s - \mathbf{R}_i] = {}^e\mathbf{r}_s - [\mathbf{a}_i(\alpha, \beta_1, \beta_2) + \mathbf{d}_i]. \quad (35)$$

It turns out that this definition for the \mathbf{r}_{si} causes them to transform exactly like the \mathbf{d}_i in Table 9, including the replacement of i by $j(i)$. It is the polar coordinates $\{r_{si}, \theta_{si}, \phi_{si}\}$ associated with the vectors $\mathbf{r}_{si} = (r_{si}\sin\theta_{si}\cos\phi_{si})\mathbf{i} + (r_{si}\sin\theta_{si}\sin\phi_{si})\mathbf{j} + (r_{si}\cos\theta_{si})\mathbf{k}$ that will be used as arguments in the atomic wavefunctions.

If the (unnormalized) π_g and π_u molecular orbitals for electron 1 are constructed only from $2p$ atomic orbitals on the carbon atoms a and b , we can write (in $R_{nl}(r)Y_{lm}(\theta, \phi)$ notation)

$$\begin{aligned} \pi_{g\pm}(1) &= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi_{1a}) - R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi_{1b}) \\ \pi_{u\pm}(1) &= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi_{1a}) + R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi_{1b}). \end{aligned} \quad (36)$$

These functions can be shown (after some algebra) to have the following transformation properties under the generators of the group $G_4^{(8)}$ in Eq. (17).

$$\begin{aligned} a\pi_{g\pm}(1) &= (\mp i)\pi_{g\pm}(1) \\ b\pi_{g\pm}(1) &= +\pi_{g\mp}(1) \\ c\pi_{g\pm}(1) &= +\pi_{g\mp}(1) \\ d\pi_{g\pm}(1) &= -\pi_{g\pm}(1) \\ a\pi_{u\pm}(1) &= (\pm i)\pi_{u\pm}(1) \\ b\pi_{u\pm}(1) &= -\pi_{u\mp}(1) \\ c\pi_{u\pm}(1) &= +\pi_{u\mp}(1) \\ d\pi_{u\pm}(1) &= -\pi_{u\pm}(1). \end{aligned} \quad (37)$$

We are now in a position to define the first of two possible electronic states correlating with 1A_u and 1A_2 in trans and cis bent acetylene. For simplicity, we consider the two-electron configuration $\pi_g\pi_u$, which is known [29] to give rise to the same final states as the four electron configuration $\pi_g^2\pi_u$, and construct an (unnormalized) two-electron wavefunction of the form

$$\begin{aligned} \{[\pi_{g+}(1)\pi_{u-}(2) - \pi_{g-}(1)\pi_{u+}(2)] + [\pi_{g+}(2)\pi_{u-}(1) \\ - \pi_{g-}(2)\pi_{u+}(1)]\}(\alpha_1\beta_2 - \alpha_2\beta_1). \end{aligned} \quad (38)$$

This function is a singlet, since the two-electron spin function $(\alpha_1\beta_2 - \alpha_2\beta_1)$ is a singlet. It is also antisymmetric with respect to exchange of electrons 1 and 2, and transforms as B_{1u}^- in Table 10 under the symmetry operations of $G_4^{(8)}$ in Table 9.

Now consider the second possible wavefunction. In Eq. (36) the ϕ_{1a} and ϕ_{1b} angles, describing rotation of electron 1 about the C_a-C_b bond are measured from the same zero. This corresponds, for example, to keeping the $2p_x$ orbitals on the two carbon atoms always “lined up” together. Instead we can require the $2p_x$ orbital on C_a to be aligned with the $H_1-C_a-C_b$ plane, and the $2p_x$ orbital on C_b to be aligned with the $C_a-C_b-H_2$ plane. It then makes sense to measure the ϕ angles from these planes, rather than from a common origin. These two planes rotate in opposite direction as the internal rotation angle α changes, and given the sense of rotation defined in Eq. (14), it (again intuitively) makes sense to replace ϕ_{1a} by $\phi'_{1a} \equiv \phi_{1a} + \alpha$ and ϕ_{1b} by $\phi'_{1b} \equiv \phi_{1b} - \alpha$. Consider thus a set of alternative π orbitals (with ' superscripts) defined by

$$\begin{aligned}
\pi'_{g\pm}(1) &= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi'_{1a}) - R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi'_{1b}) \\
&= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi'_{1a})e^{\pm iz} - R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi'_{1b})e^{\mp iz} \\
\pi'_{u\pm}(1) &= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi'_{1a}) + R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi'_{1b}) \\
&= R_{2,1}(r_{1a})Y_{1,m=\pm 1}(\theta_{1a}, \phi'_{1a})e^{\pm iz} + R_{2,1}(r_{1b})Y_{1,m=\pm 1}(\theta_{1b}, \phi'_{1b})e^{\mp iz}.
\end{aligned} \tag{39}$$

These π' orbitals give rise to an (unnormalized) two-electron wavefunction of the form

$$\begin{aligned}
&\left\{ \left[\pi'_{g+}(1)\pi'_{u-}(2) - \pi'_{g-}(1)\pi'_{u+}(2) \right] \right. \\
&\quad \left. + \left[\pi'_{g+}(2)\pi'_{u-}(1) - \pi'_{g-}(2)\pi'_{u+}(1) \right] \right\} (\alpha_1\beta_2 - \alpha_2\beta_1).
\end{aligned} \tag{40}$$

This function is again a singlet and is again antisymmetric with respect to exchange of electrons 1 and 2, but transforms as $A_{1u}^{(8)}$ under the symmetry operations of Table 9.

An unambiguous way to determine whether Eq. (38) or Eq. (40) better describes the S_1 electronic state of acetylene would be to follow carefully how the phases of various coefficients in the LCAO-type molecular orbitals change during an *ab initio* calculation “going around the circle” of Fig. 5. In the rest of this paper, we simply assume that the $2p$ orbitals on the carbon atoms maintain their alignment with respect to each other during internal rotation, rather than with respect to the CCH planes. This is equivalent to assuming that the S_1 electronic state has $B_{1u}^{(8)}$ symmetry in $G_4^{(8)}$.

11.5. Normal mode vibrational coordinates and harmonic oscillator functions localized in each of the eight minima of cis acetylene

Since the vibrational states considered in Section 12 both belong to cis acetylene, we consider the vibrational problem in detail for the eight cis minima. (A treatment for the trans minima would follow the same procedure with very slight modifications.) The goal of this section is to obtain symmetrized coordinates approximating the normal modes for the vibrations in cis bent acetylene, and then to construct harmonic-oscillator-like wavefunctions localized in each cis minimum, which can be excited with a given number of quanta, and which are suitable for use in a high-barrier tunneling basis set.

Consider first (unnormalized) infinitesimal coordinates δ for the three small-amplitude (by hypothesis) stretching vibrations, defined (for the purpose of symmetry considerations) by

$$\begin{aligned}
\delta_{CC} &= |\mathbf{R}_a - \mathbf{R}_b| - R_{CC}^0 \\
\delta_{ss} &= |\mathbf{R}_1 - \mathbf{R}_a| - R_{CH}^0 + |\mathbf{R}_2 - \mathbf{R}_b| - R_{CH}^0 \\
\delta_{as} &= |\mathbf{R}_1 - \mathbf{R}_a| - |\mathbf{R}_2 - \mathbf{R}_b|,
\end{aligned} \tag{41}$$

where the \mathbf{R}_i with $i = a, b, 1, 2$ are laboratory-fixed Cartesian coordinates for the atoms, $|\mathbf{R}_a - \mathbf{R}_b|$ is the length of the vector $\mathbf{R}_a - \mathbf{R}_b$, the R^0 quantities are equilibrium bond lengths, and the subscripts *ss* and *as* refer to the symmetric and asymmetric CH stretch, respectively. It can easily be seen that δ_{CC} and δ_{ss} are of species A_{1g}^+ , and δ_{as} is of species B_{2u}^+ in $G_4^{(8)}$. If we represent harmonic oscillator wavefunctions of the stretching variables δ with vibrational quantum number ν by $h_{\nu}(\delta)$, then all such functions are of symmetry A_{1g}^+ except for $h_{\nu as}(\delta_{as})$, which are of symmetry B_{2u}^+ when ν_{as} is odd.

Consider next the two LAM in-plane bending angles β_1 and β_2 , with equilibrium values of $\pm\beta_{cis}$ in the various cis minima of Eq. (16). Even though these two variables are angles, they are not permitted to take values outside the range $-2\pi/3 \leq \beta \leq +2\pi/3$, so the question of 2π periodicity does not arise. The species of $\{\beta_1, \beta_2\}$ is E^+ in $G_4^{(8)}$, which correlates with $A_1 \oplus B_2$ in cis acetylene, but this correlation is rather subtle, since $\beta_1 + \beta_2$ and $\beta_1 - \beta_2$ are of species B_2 and A_1 , respectively, in the C_{2v} point group containing the operations *e*, *b*, *bcd*, *cd*, as appropriate for the cis minima in Eqs. (16a) and (16c), but they are of species A_1 and B_2 , respectively, in the

C_{2v} point group containing *e*, a^2b , a^2bc and *c*, as appropriate for the cis minima in Eqs. (16b) and (16d). To help separate the different types of vibrational functions, we use the symbol $g_{\nu}(x)$ for harmonic oscillator wavefunctions of linear combinations of the β variables. To maintain group-theoretically determined phase factors, we define the harmonic oscillator functions for the symmetric bend (*sb*) and asymmetric bend (*ab*) only for framework 1 (as defined in connection with Fig. 4) and generate the rest using operations from $G_4^{(8)}$, as indicated below.

$$\begin{aligned}
|1_b\rangle &= g_{vsb}(+\beta_1 - \beta_2 - 2\beta_{cis})g_{vab}(+\beta_1 + \beta_2) \\
|2_b\rangle &= a^2|1_b\rangle = g_{vsb}(-\beta_1 + \beta_2 - 2\beta_{cis})g_{vab}(-\beta_1 - \beta_2) \\
|3_b\rangle &= a^3cd|1_b\rangle = g_{vsb}(-\beta_2 - \beta_1 - 2\beta_{cis})g_{vab}(-\beta_2 + \beta_1) \\
|4_b\rangle &= a^3cd|2_b\rangle = g_{vsb}(+\beta_2 + \beta_1 - 2\beta_{cis})g_{vab}(+\beta_2 - \beta_1) \\
|5_b\rangle &= (a^3cd)^2|1_b\rangle = a^2d|1_b\rangle = g_{vsb}(-\beta_1 + \beta_2 - 2\beta_{cis})g_{vab}(-\beta_1 - \beta_2) \\
|6_b\rangle &= (a^3cd)^2|2_b\rangle = a^2d|2_b\rangle = g_{vsb}(+\beta_1 - \beta_2 - 2\beta_{cis})g_{vab}(+\beta_1 + \beta_2) \\
|7_b\rangle &= (a^3cd)^3|1_b\rangle = ac|1_b\rangle = g_{vsb}(+\beta_2 + \beta_1 - 2\beta_{cis})g_{vab}(+\beta_2 - \beta_1) \\
|8_b\rangle &= (a^3cd)^3|2_b\rangle = ac|2_b\rangle = g_{vsb}(-\beta_2 - \beta_1 - 2\beta_{cis})g_{vab}(-\beta_2 + \beta_1),
\end{aligned} \tag{42}$$

where the subscript *b* is meant to imply that only bending coordinates are present in these localized harmonic oscillator basis functions. (The point of localization can be obtained by setting the argument in $g_{vsb} = 0$. For example, $|6_b\rangle$ is centered at $+\beta_1 - \beta_2 - 2\beta_{cis} = 0$, i.e., at $\beta_1 = +\beta_{cis}$ and $\beta_2 = -\beta_{cis}$.)

By applying the operations used in Eq. (42) to the matrix element $\langle 1_b|H|1_b\rangle$, i.e., by considering $a^2\langle 1_b|H|1_b\rangle = \langle 2_b|H|2_b\rangle$, etc., it is possible to show that all eight diagonal elements are equal for any pair of bending quantum numbers ν_{sb} and ν_{ab} . Similarly, it is possible to show by considering $a^3cd\langle 1_b|H|2_b\rangle = \langle 3_b|H|4_b\rangle$, etc., that the eight nearest neighbor bending tunneling matrix elements are all equal. By applying the symmetry operations occurring in Eq. (42) to the torsional tunneling matrix element $\langle 1_b|H|3_b\rangle$, we can generate a set of eight equal matrix elements. By noting that the nondegenerate harmonic oscillator wave function $|1_b\rangle$ can be taken to be real, which makes all of the $|n_b\rangle$ real, we can take Hermitian conjugates of the first eight equal matrix elements to obtain a total of 16 equal matrix elements. We then note that

$$\begin{aligned}
a^2b|1_b\rangle &= g_{vsb}(+\beta_2 - \beta_1 - 2\beta_{cis})g_{vab}(+\beta_2 + \beta_1) = (-1)^{\nu_{ab}}|2_b\rangle \\
a^2b|3_b\rangle &= g_{vsb}(-\beta_1 - \beta_2 - 2\beta_{cis})g_{vab}(-\beta_1 + \beta_2) = (-1)^{\nu_{ab}}|3_b\rangle,
\end{aligned} \tag{43}$$

where we have used the property of harmonic oscillator functions that $g_{\nu}(-x) = (-1)^{\nu}g_{\nu}(x)$. Eq. (43) can be used to show that $a^2b\langle 1_b|H|3_b\rangle = \langle 2_b|H|3_b\rangle$, from which, applying the earlier procedures, a total of 32 torsional tunneling matrix elements equal to $\langle 1_b|H|3_b\rangle$ are obtained, for any set of ν_{sb} and ν_{ab} .

Consider finally the internal rotation angle α , which has 2π periodicity. We use the notation $f_{\nu t}(\alpha)$ to represent a harmonic-oscillator-like wavefunction centered at $\alpha = 0$, except that this function, as defined in the interval $-\pi \leq \alpha \leq +\pi$, must actually be expressed as a Fourier series in $\cos n\alpha$ with integer n for even ν_t , and as a Fourier series in $\sin n\alpha$ with integer n for odd ν_t , to insure that it has 2π periodicity. The procedure illustrated in Eq. (42) yields

$$\begin{aligned}
|1_t\rangle &= |2_t\rangle = f_{\nu t}(\alpha) \\
|3_t\rangle &= |4_t\rangle = f_{\nu t}(\alpha - \pi/2) \\
|5_t\rangle &= |6_t\rangle = f_{\nu t}(\alpha - \pi) \\
|7_t\rangle &= |8_t\rangle = f_{\nu t}(\alpha - 3\pi/2).
\end{aligned} \tag{44}$$

Applying the operations in Eq. (42) to the matrix elements $\langle 1_t|H|1_t\rangle$, $\langle 1_t|H|2_t\rangle$, and $\langle 1_t|H|3_t\rangle$ we again generate three sets of eight elements equal to the original. Choosing $|1_t\rangle$ to be real leads to

$\langle 1_t | H | 3_t \rangle = \langle 3_t | H | 1_t \rangle^* = \langle 3_t | H | 1_t \rangle$. The definitions in Eq. (44) indicate that $\langle 1_t | H | 3_t \rangle = \langle 2_t | H | 3_t \rangle$. So we again obtain 32 matrix elements equal to $\langle 1_t | H | 3_t \rangle$.

As a consequence of the equalities obtained above, the Hamiltonian matrix set up in the basis set $|n\rangle = |n_b\rangle|n_t\rangle$, for $n = 1-8$, has the form given in Fig. 6 for any set of values of the bending and torsional harmonic oscillator quantum numbers. The numerical entries in the eigenvectors in Fig. 6 and their associated energy level expressions in Eq. (32) also remain unchanged. What does change with vibrational excitation, however, is the symmetry species Γ of these various eigenfunctions. Their species can be obtained by acting with one element from each class of $C_4^{(8)}$ on the eigenfunctions, as illustrated by the following example for the operation ab :

$$(ab)[c_1|1\rangle + c_2|2\rangle + c_3|3\rangle + c_4|4\rangle + c_5|5\rangle + c_6|6\rangle + c_7|7\rangle + c_8|8\rangle] \\ = (-1)^{v_{ab}+v_t}[c_1|4\rangle + c_2|3\rangle + c_3|2\rangle + c_4|1\rangle + c_5|8\rangle + c_6|7\rangle \\ + c_7|6\rangle + c_8|5\rangle], \quad (45)$$

where the eight coefficients c_i represent the numerical entries in one of the eigenvectors of Fig. 6, and where the $(-1)^{v_{ab}+v_t}$ factor arises, as in Eq. (43), because of sign changes in the harmonic oscillator functions that occur when a transformed function is brought back into one of the standard forms given in Eqs. (42) and (44). It turns out there are four sets of bending torsional symmetry species ${}^{bt}\Gamma$, depending on the (e)ven or (o)dd character of v_{ab} and v_t .

$${}^{bt}\Gamma(v_{ab}v_t = ee) = A_{1g}^+ \oplus B_{1g}^+ \oplus E_u \oplus E_1 \oplus E^+ \quad (46a)$$

$${}^{bt}\Gamma(v_{ab}v_t = eo) = B_{1u}^- \oplus A_{1u}^- \oplus E_g \oplus E_1 \oplus E^- \quad (46b)$$

$${}^{bt}\Gamma(v_{ab}v_t = oe) = A_{2u}^+ \oplus B_{2u}^+ \oplus E_g \oplus E_2 \oplus E^+ \quad (46c)$$

$${}^{bt}\Gamma(v_{ab}v_t = oo) = B_{2g}^- \oplus A_{2g}^- \oplus E_u \oplus E_2 \oplus E^-, \quad (46d)$$

where the symmetry species are given in the same order as the eigenvectors in Fig. 6, and where Eq. (46a) corresponds to the previously derived Eq. (30).

A corresponding set of equations for trans bent acetylene takes the form

$${}^{bt}\Gamma(v_{ab}v_t = ee) = A_{1g}^+ \oplus B_{1g}^+ \oplus E_g \oplus E_1 \oplus E^+ \quad (47a)$$

$${}^{bt}\Gamma(v_{ab}v_t = eo) = B_{1u}^- \oplus A_{1u}^- \oplus E_u \oplus E_1 \oplus E^- \quad (47b)$$

$${}^{bt}\Gamma(v_{ab}v_t = oe) = A_{2u}^+ \oplus B_{2u}^+ \oplus E_u \oplus E_2 \oplus E^+ \quad (47c)$$

$${}^{bt}\Gamma(v_{ab}v_t = oo) = B_{2g}^- \oplus A_{2g}^- \oplus E_g \oplus E_2 \oplus E^-, \quad (47d)$$

where v_{ab} and v_t again represent the number of quanta in the anti-symmetric bend and in the torsion, respectively.

12. Application to specific vibrational states of S₁-cis acetylene

12.1. The 3¹6¹ state of cis acetylene near 46 200 cm⁻¹

The 3¹6¹ vibrational state of cis bent acetylene, near 46 200 cm⁻¹, has one quantum of excitation in $v_3 = v_{sb}$ and one in $v_6 = v_{ab}$. We thus take the tunneling splittings from Eq. (32) and the bending-torsional symmetry species from Eq. (46c). We take the electronic symmetry species to be B_{1u}^- from Section 11.3, so that the vibronic species ${}^{ebt}\Gamma$ become

$${}^{ebt}\Gamma(v_{ab}v_t = oe) = B_{2g}^- \oplus A_{2g}^- \oplus E_u \oplus E_2 \oplus E^-. \quad (48)$$

Following the procedure in Section 11.3, we find that: (i) $K_a = 4n$ rotational wavefunctions are associated with ${}^{ebt}\Gamma(v_{ab}v_t = oe) = {}^{ebt}A_{2g}^-$; (ii) $K_a = 4n + 2$ rotational functions are associated with ${}^{ebt}B_{2g}^-$; (iii) $K_a = \text{odd}$ rotational functions are associated with ${}^{ebt}E_u$, and (iv) no rotational functions are associated with ${}^{ebt}E_2$ and ${}^{ebt}E^-$, so these two tunneling components “do not exist.”

The observed spectrum [21] gives the separations between the $K_a = 0, 1$ and 2 subbands, which can be expressed from the present formalism (ignoring asymmetric rotor and centrifugal distortion effects) as

$$E(J = 2, K_a = 2) - E(J = 2, K_a = 0) = 4[A - (B + C)/2] + 8H_{13} \quad (49a)$$

$$E(J = 2, K_a = 1) - E(J = 2, K_a = 0) = [A - (B + C)/2] + 4H_{13} - 4H_{12}. \quad (49b)$$

For low-lying levels in trans acetylene, we could now have invoked the rule that both H_{12} and H_{13} must be negative, to insure that the lowest-energy wavefunction has no nodes, but these signs cannot be deduced so simply for low-lying levels in cis acetylene. Fig. 5 indicates that the lowest (zero-point) level in cis bent acetylene passes through a region that lies above the bottom of the trans well, where the wavefunction oscillates and picks up some unknown number of additional nodes. Since the tunneling components lie at slightly different energies, and since the wavefunction carries out many oscillations high above the bottom of the trans potential well, it is conceivable that different tunneling components could pick up different numbers of nodes. Arguments based on node counts thus appear dangerous (at least in the absence of further study), so the authors prefer to use the signs of the cis tunneling parameters as adjustable parameters.

As it happens [21], the experimentally observed value of $E(K = 2) - E(K = 0)$ is almost the same as the *ab initio* value of $4[A - (B + C)/2]$, suggesting that $H_{13} \approx 0$, which is equivalent to saying that the effects of internal rotation tunneling are too small to be observed in the 3¹6¹ state. Setting $H_{13} = 0$ in Eqs. (49a) and (49b) then leads to the conclusion that the band origin difference $E(K = 1) - E(K = 0)$ should be $[A - (B + C)/2] - 4H_{12}$. The experimental observations [21] give $4H_{12} = -3.9 \text{ cm}^{-1}$. The fact that the $K = 1$ level is seriously displaced from its expected position can thus be understood in terms of the present theory, which then further predicts (on the basis of the H_{12} and H_{13} values just determined) that the $K = \text{even}$ levels of the cis 3¹6¹ state should behave normally, but that all $K = \text{odd}$ levels should be displaced upward by about 3.9 cm^{-1} from their expected position. Unfortunately, the experiments of Ref. [21] do not allow these higher K levels to be observed, so that this theoretical prediction cannot be tested.

The negative sign for H_{12} determined above happens to agree with the sign that would be predicted if the energy differences in Eq. (49) were for the ground vibrational state, and if the nodes above the trans well could be ignored. Since the state in question is not the ground vibrational state, a calculation similar to that presented in Eq. (7) of Ref. [30] must be carried out to determine how the sign of H_{12} should change when one quantum is excited in each of the two bends. Even this information would not be immediately useful, however, since we cannot predict the sign of H_{12} in the vibrational ground state of cis acetylene because of the node problem above the trans well.

12.2. The 4¹ state of cis acetylene near 45 700 cm⁻¹

The cis 4¹ vibrational state of acetylene, near 45 700 cm⁻¹, has only one quantum of vibrational excitation in $v_4 = v_t$, so the bending-torsional symmetry species should be taken from Eq. (46b). This leads to vibronic species of

$${}^{ebt}\Gamma(v_{ab}v_t = eo) = A_{1g}^+ \oplus B_{1g}^+ \oplus E_u \oplus E_1 \oplus E^+, \quad (50)$$

with $K_a = 4n$ levels associated with ${}^{ebt}A_{1g}^+$, $K_a = 4n + 2$ levels associated with ${}^{ebt}B_{1g}^+$, and $K_a = \text{odd}$ levels associated with ${}^{ebt}E_u$. The intervals for $K_a = 0, 1$, and 2 states then become

$$E(J = 2, K_a = 2) - E(J = 2, K_a = 0) = 4[A - (B + C)/2] - 8H_{13} \quad (51a)$$

$$E(J = 2, K_a = 1) - E(J = 2, K_a = 0) = [A - (B + C)/2] - 4H_{13} - 4H_{12}. \quad (51b)$$

Unfortunately only $K_a = 0$ and 2 levels have so far been observed for the cis 4^1 state.

It might be expected that internal rotation tunneling effects, represented by the parameter H_{13} , would become large enough to see when one quantum of torsion is excited, but experimentally, the $E(K=2)-E(K=0)$ splitting is only about 4 cm^{-1} larger than the *ab initio* value of $4[A - (B + C)/2]$, so it is difficult to decide whether tunneling effects or other small effects (e.g., centrifugal distortion) are the cause. If torsional tunneling effects are just barely observable in 4^1 , they should be clearly observable in 4^2 , but this state has not yet been identified.

13. Conclusions

This paper deals with the extended permutation-inversion groups that are needed to classify the rovibronic states of electronically-excited acetylene when large amplitude vibrational motions allow the interconversion of three non-linear isomers, cis, trans and vinylidene. It is assumed that there is always a large potential maximum at the linear configuration, so that the complications that arise when the a -axis rotation of a bent conformer becomes a component of a degenerate vibration of the linear molecule are not considered.

Specifically, we first consider the group theory for the interconversion of cis and trans isomers when the large amplitude vibrations allowing the interconversion are assumed to be (i) local CCH bends at the two ends of the molecule, (ii) internal rotation or (iii) a combination of local CCH bends and internal rotation. The PI group for these cases is always G_4 , but the extended PI groups are $G_4^{(2)}$, $G_4^{(2)}$, and $G_4^{(8)}$, respectively. After that we consider the interconversion of cis and trans acetylene to vinylidene, where the large amplitude vibrations are taken to be hydrogen migrations, (iv) without or (v) with internal rotation. The PI group for these cases is always G_8 , but the extended PI groups are $G_8^{(2)}$ and $G_8^{(8)}$, respectively. The group theoretical results indicate that there will be no splittings of the rovibronic levels unless CH bond breaking occurs. Even with no bond breaking, however, states of the cis and trans isomers just below their interconversion barrier will show “staggerings” in their K -structures. A given vibrational level will have three tunneling components, at different energies: one component will have levels with $K = 4n$ only (where n is an integer), a second component will have levels with $K = 4n + 2$ only, and the third will have only odd- K levels.

The group theory mentioned above consists mainly of: (i) a choice of large amplitude coordinates that capture the essence of the feasible motions and their symmetries, (ii) explicitly defined coordinate transformations for all elements of the molecular symmetry group, and (iii) character tables, which for the twofold and

eightfold extended PI groups contain one or seven limited identities, respectively.

The new experimental results for the S_1 -cis electronic state of acetylene [21] are reviewed in the light of the group theory results, and are found to be consistent with them in so far as comparisons are possible.

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