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

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The electronic ground state potential surface of acetylene (H-C≡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. The first part of 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 ($H_2C=C$). The second part of the work is concerned with the high-barrier tunneling ideas necessary to determine energy level splittings and staggerings. The third part involves (a still rather limited) comparison of the theoretical results with high-resolution experimental data available for states in the trans-bent and cis-bent minima of the S_1 state of C_2H_2.

We make use of three different kinds of groups: (i) point groups, (ii) permutation-inversion (PI) groups, and (iii) extended PI groups. As is well known, the PI group for C_2H_2 is G_4 or G_8, depending on whether C-H bond breaking is impossible (no bent acetylene ↔ vinylidene interconversion) or possible. If we number the atoms H_1-C_a-C_b-H_2, then G_4 contains E, $(ab)(12)$, $(ab)(12)^*$, and E*, while G_8 contains the preceding four elements plus (12), (12)*, (ab), and $(ab)^*$.

In order to apply group theory to the quantum mechanical Hamiltonian and its eigenfunctions, it is necessary to determine which coordinate transformation corresponds to each group operation. This is straightforward when the Hamiltonian and its eigenfunctions are written in terms of laboratory-fixed Cartesian coordinates, since then the atom-exchange operations of the PI group simply involve exchanging atom labels on the coordinates, e.g.
$(12)\ \Psi(X_1,Y_1,Z_1;\ X_2,Y_2,Z_2;\ X_a,Y_a,Z_a;\ X_b,Y_b,Z_b) = \Psi(X_2,Y_2,Z_2;\ X_1,Y_1,Z_1;\ X_a,Y_a,Z_a;\ X_b,Y_b,Z_b)$.

Significant problems usually arise, however, when one tries to apply the group operations separately to the electronic, vibrational, and rotational variables that are used both to write the individual factors in the molecular basis functions, and also to write the separated-variable Hamiltonians used to define these basis functions. In the present work, we focus on molecule-fixed coordinates for the C_2H_2 problem with no CH bond breaking, i.e., we focus on considering simultaneously only trans-bent and cis-bent acetylene, without vinylidene. We can then define the following molecule-fixed coordinates. Molecular orbitals for the electronic wavefunction are written as linear combinations of atomic orbitals (LCAOs), with each atomic orbital localized on a given atom. Vibrational coordinates are divided into a set of three small-amplitude vibrations (SAVs), which include the H_1-C_a, C_a-C_b, and C_b-H_2 stretches, and a set of three large-amplitude vibrations (LAMs), which include the H_1-C_a-C_b and C_a-C_b-H_2 local-mode bends (β_1 and β_2) at each end of the molecule and the H_1-C_a-C_b-H_2 torsion (α). Rotational coordinates are the usual three Eulerian angles (χ, θ, ϕ) describing the orientation of an *xyz* axis system fixed somehow in the molecule. To avoid the many complications associated with quasi-linear molecules, it is necessary to assume that the

C_2H_2 configuration never becomes linear. This assumption is valid for the first excited singlet state S_1 considered here, because *ab initio* calculations predict a very high energy barrier at the linear configuration.

The coordinate system described above turns out to be multiple-valued, since the bending-angle transformation $(\beta_1, \beta_2) \rightarrow (-\beta_1, -\beta_2)$ can be shown to be equivalent both to the torsional transformation $(\alpha) \rightarrow (\alpha+\pi)$ and also to the overall rotational transformation $(\chi) \rightarrow (\chi+\pi)$. When group theory is applied to this multiple-valued coordinate system, an eight-fold extended group $G_4^{(8)}$ of the original PI group G_4 is generated. This eight-fold extended PI group contains one true identity, and seven "limited identities," which are identities in the PI group G_4, but not in the extended group $G_4^{(8)}$. The main group theoretical conclusions of the present work are that a group of 32 elements is appropriate for simultaneously treating cis-bent and trans-bent acetylene, while 64 elements are required when vinylidene is included.

The multiple-valued coordinate system also leads to the existence of eight equivalent minima in the $G_4^{(8)}$ LAM bending-torsion problem of C_2H_2 with no CH bond breaking. A relatively simple high-barrier tunneling Hamiltonian can be written down for the rotationless problem, leading to a splitting of the $J = 0$ state into five components. Two of the five are non-degenerate, the other three are doubly degenerate. As is well known, we must return from $G_4^{(8)}$ to the original PI group G_4 in order to describe the complete rovibronic wavefunction. This causes the $G_4^{(8)}$ tunneling "splittings" to change into G_4 tunneling "staggerings," because: (i) rotational levels with $K_a = 4n$ can only be associated with one of the two non-degenerate $G_4^{(8)}$ tunneling components, (ii) levels with $K_a = 4n + 2$ can only be associated with the other non-degenerate $G_4^{(8)}$ tunneling component, and levels with $K_a =$ odd can only be associated with one of the three $G_4^{(8)}$ doubly degenerate tunneling components.

The $3^1 6^1$ vibrational state of cis bent acetylene, near 46 200 cm^{-1}, has one quantum of excitation in ν_3 (the antisymmetric bend) and one in ν_6 (the symmetric bend). The procedures described above give separations between the $K_a = 0$, 1 and 2 subbands (ignoring asymmetric rotor and centrifugal distortion effects) of

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

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

where H_{12} and H_{13} represent the bending and torsional tunneling frequencies, respectively.

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 $3^1 6^1$ state. Setting $H_{13} = 0$ then leads to the conclusion that that the subband origin difference $E(K=1) - E(K=0)$ should be $[A - (B+C)/2] - 4H_{12}$. The experimental observations give $4H_{12} = -3.9$ 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 $K_a =$ even levels of the cis $3^1 6^1$ state should behave normally, but that all $K_a =$ odd levels should be displaced upward by about 3.9 cm^{-1} from their expected position. Unfortunately, the molecular beam experiments do not allow higher K levels to be observed, so that this theoretical prediction cannot be tested at present.