Symmetry analysis of internal rotation

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Additional information on J. Chem. Phys.

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Research papers and textbooks addressing the problem of internal rotation in a molecule explain symmetry properties of the torsional potential by local geometrical symmetries of the molecule. It is shown here that symmetry properties of a torsional potential derive from permutation inversion symmetry and a peculiar nature of torsional dynamics but have no relation to actual geometrical symmetries. To confirm the validity of our symmetry analysis a minimum energy torsional potential curve has been determined *ab initio* for acetaldehyde, resulting in exact $2\pi/3$ periodicity that no previous *ab initio* calculations achieved. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1506156]

I. INTRODUCTION

During internal rotation a group of atoms, called the top, rotates with respect to another group, called the frame, within a molecule. Internal rotation, one of the most fascinating of internal motions in molecules, has been the focus of experimental and theoretical studies since 1930.[1,2] Yet, our knowledge about internal rotation potential curves still contains discrepancies. Consider, for example, torsion of the methyl group in the acetaldehyde molecule. The corresponding experimental spectra are described by a torsional potential of $2\pi/3$ periodicity.[3,4] Up to now, however, no first principles calculation has given a torsional potential of minimum energy and $2\pi/3$ periodicity for acetaldehyde. Despite the fact that analyses of experimental data[5,6] and *ab initio* electronic structure calculations[7] agree that the methyl group in acetaldehyde does not have C_3 symmetry axis, standard arguments[8–10] used to justify $2\pi/3$ periodicity assume C_3 geometric symmetry for the methyl group, and even theoretical investigations employing the molecular symmetry (MS) group[11,12] assume a reference configuration with a methyl group of C_3 symmetry. This paper explains the origin of and a solution to these discrepancies.

II. DEFINITION OF THE TORSIONAL COORDINATE

To describe the torsional motion in acetaldehyde most researchers would choose one of the three independent dihedral angles, ρ_1, ρ_2, and ρ_3 defined in Fig. 1. Nevertheless, there is no compelling reason to single out one of the dihedral angles as the most suitable. Therefore, let us define new coordinates, τ_1, τ_2, and τ_3, through invertible linear combinations of the dihedral angles:

$$\tau_1 = \tfrac{1}{3}(\rho_1 + \rho_2 + \rho_3 - 2\pi), \tag{1}$$

$$\tau_2 = \tfrac{1}{2}(\rho_1 - \rho_2), \tag{2}$$

$$\tau_3 = -\tfrac{1}{4}\rho_1 - \tfrac{1}{4}\rho_2 + \tfrac{1}{2}\rho_3. \tag{3}$$

When a rigid top rotates with respect to a rigid frame, i.e., when there is no geometry relaxation, and by assuming a methyl group of C_{3v} symmetry,

$$\rho_1 = \rho, \quad \rho_2 = \rho + \frac{2\pi}{3}, \quad \rho_3 = \rho + \frac{4\pi}{3}$$

and

$$\tau_1 = \rho, \quad \tau_2 = -\frac{\pi}{3}, \quad \tau_3 = \frac{\pi}{2},$$

with ρ denoting the angle of rigid internal rotation. Of the new coordinates τ_1 is clearly the only reasonable choice for describing the torsional motion since the other two coordinates cannot be used to describe even the rotation of a rigid top around a rigid frame. We shall use Eq. (1) as the defining equation of the torsional coordinate. τ_2 and τ_3 will be chosen to be two of the 14 additional internal coordinates, which will be denoted collectively by s, of acetaldehyde.
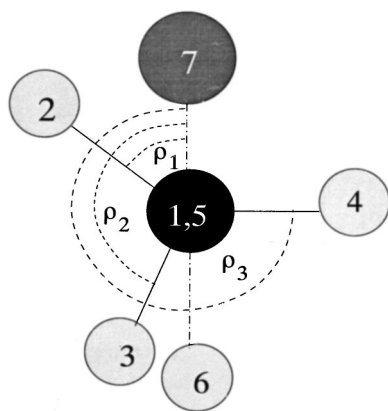
III. SYMMETRY ANALYSIS OF THE TORSIONAL MOTION

The MS group[13,14] of acetaldehyde is $C_{3v}(M)$. The potential energy surface (PES), $V(\tau_1, s)$, is invariant under the permutation and permutation-inversion of identical nuclei, and thus under the operations of the MS group. Therefore, with symmetry operators $\hat{g}$, $\hat{g} \in C_{3v}(M)$,

$$V(\tau_1, s) = \hat{g}V(\tau_1, s) = V(\hat{g}^{-1}\tau_1, \hat{g}^{-1}s), \tag{4}$$

must hold. An effective torsional potential, $V(\tau_1)$, is obtained by averaging the global PES over an eigenfunction,

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FIG. 1. The definition of the dihedral angles ρ_1, ρ_2, and ρ_3.

TABLE I. Transformation properties of the dihedral angles ρ_1, ρ_2, and ρ_3 given in Fig. 1 and the coordinate τ_1 defined by Eq. (1) under the elements of the $C_{3v}(M)$ molecular symmetry group.

	E	243	234	$(23)^*$	$(24)^*$	$(34)^*$
ρ_1	ρ_1	ρ_2	ρ_3	$-\rho_2$	$-\rho_3$	$-\rho_1$
ρ_2	ρ_2	ρ_3	$2\pi+\rho_1$	$-\rho_1$	$-\rho_2$	$2\pi-\rho_3$
ρ_3	ρ_3	$2\pi+\rho_1$	$2\pi+\rho_2$	$2\pi-\rho_3$	$-\rho_1$	$2\pi-\rho_2$
τ_1	τ_1	$\tau_1+2\pi/3$	$\tau_1+4\pi/3$	$-\tau_1-2\pi/3$	$-\tau_1-4\pi/3$	$-\tau_1$

$$V(\tau_1) = V\left(\tau_1 + \frac{2\pi}{3}\right) = V\left(\tau_1 + \frac{4\pi}{3}\right) = V\left(-\tau_1 - \frac{2\pi}{3}\right)$$

$$= V\left(-\tau_1 - \frac{4\pi}{3}\right) = V(-\tau_1), \tag{10}$$

follows. Therefore, the torsional potential energy curve is a periodic, with period length $2\pi/3$, and even function of the torsional coordinate τ_1. This conclusion remains valid regardless of the actual geometrical symmetry of the methyl top and aldehyde frame, since our derivation made no assumptions about geometrical symmetry. This explains why analyses of experimental spectra based on the assumption of $2\pi/3$ periodic torsional potentials were successful.

To our best knowledge all *ab initio* electronic structure calculations on the internal rotation of acetaldehyde employed a single dihedral angle as the torsional coordinate. With the help of Table I and an equation similar to Eq. (10), one can find that, when employing a dihedral angle, say ρ_1, as the torsional coordinate, $2\pi/3$ periodicity of the potential curve can occur only in the very special case when $\rho_2 = \rho_1 + 2\pi/3$ and $\rho_3 = \rho_1 + 4\pi/3$. As observed in *ab initio* studies[7,18] and spectroscopic experiments[5,6] this requirement is not satisfied even in the lowest-energy conformation of the acetaldehyde molecule. Therefore, when using a dihedral angle as the torsional coordinate, one cannot obtain a torsional potential that is along a minimum energy path and of $2\pi/3$ periodicity at the same time. This explains the failure of previous *ab initio* calculations[7,19] in determining torsional potentials of minimum energy and $2\pi/3$ periodicity. If one is to derive the torsional potential of minimum energy and $2\pi/3$ periodicity of acetaldehyde the torsional coordinate defined in Eq. (1) must be employed.

$\Psi(s)$, of an appropriate vibrational Hamiltonian. By using the invariance property of the PES under operations of the molecular symmetry group and the notation $s' = \hat{g}^{-1}s$, one can find that

$$V(\tau_1) = \int ds\, \Psi^*(s) V(\tau_1, s) \Psi(s)$$

$$= \int ds\, \Psi^*(s) V(\hat{g}^{-1}\tau_1, \hat{g}^{-1}s) \Psi(s)$$

$$= \int ds'\, \Psi^*(s') V(\hat{g}^{-1}\tau_1, s') \Psi(s')$$

$$= V(\hat{g}^{-1}\tau_1), \tag{5}$$

with appropriate limits of integration. Therefore, the symmetry properties, including periodicity, of the torsional potential $V(\tau_1)$ may be obtained by finding the transformation properties of the torsional coordinate. To establish the transformation properties of the torsional coordinate τ_1 we use its defining equation Eq. (1) along with the transformation properties of the dihedral angles.

It is important to notice that the dihedral angles are not completely independent coordinates. The PES has barriers of infinite (or at least very large) height at $\hat{g}\rho_i = \hat{g}\rho_j$, $i \neq j$, i, $j = 1, 2, 3$, and at $\hat{g}\rho_1 = \hat{g}\rho_2 = \hat{g}\rho_3$, which limit the available configuration space of the dihedral angles to

$$0 \leq \hat{g}\rho_1 < \hat{g}\rho_2 < \hat{g}\rho_3, \tag{6}$$

$$0 < \hat{g}\rho_2 - \hat{g}\rho_1 < 2\pi, \tag{7}$$

$$0 < \hat{g}\rho_3 - \hat{g}\rho_1 < 2\pi, \tag{8}$$

$$0 < \hat{g}\rho_3 - \hat{g}\rho_2 < 2\pi, \tag{9}$$

for all $\hat{g} \in C_{3v}(M)$. That is, the hydrogens of the methyl group cannot ''overtake'' each other (similarly to the hydrogens of a model devised to describe tunneling in the vinyl cation[15]). The transformation properties of the dihedral angles and of τ_1 must be determined by taking into account this correlation, but no other geometrical constraints are imposed. The transformation properties so derived are summarized in Table I.

From Eq. (5) and the results given in Table I,

IV. THE TORSIONAL POTENTIAL OF ACETALDEHYDE

We have used the ACES II electronic structure package[16] to minimize the total molecular energy (the sum of nuclear–nuclear repulsion and electronic energy) and to optimize the molecular geometry of acetaldehyde while keeping the torsional coordinate τ_1 fixed at values 0, 15, 30, ..., 180 deg, respectively. We have done similar calculations using the dihedral angle ρ_1 as the torsional coordinate. Since our goal has been merely to demonstrate the validity of our symmetry analysis, we have used the 6-31G** basis, a simple but reasonably good basis for the problem considered.
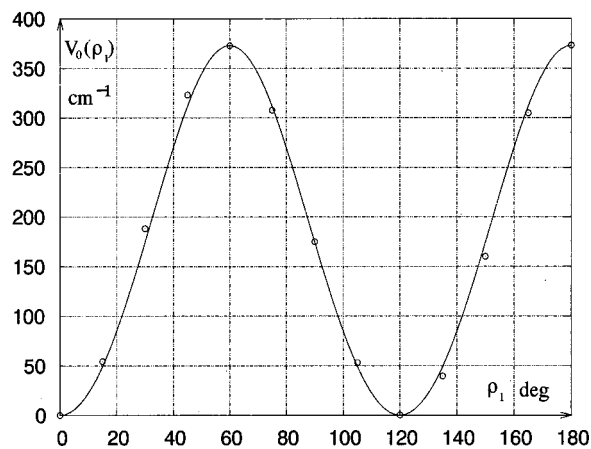
The total molecular energies calculated at various fixed values of the torsional coordinate are samples along the minimum energy torsional path, $V_0(\tau)$ with $\tau = \tau_1$ and $\tau = \rho_1$, when all (but the torsion) internal motions are frozen.

TABLE II. Torsional potentials of acetaldehyde. The total energies given are referenced to $E(\tau_1 = \rho_1 = 0) = -152.922\,587\,15$ hartrees.

τ_1/ρ_1 (deg)	$V_0(\tau_1)$ (cm^{-1})	$V_0(\rho_1)$ (cm^{-1})	ZPVE(τ_1) (cm^{-1})	$V_0(\tau_1)+$ZPVE(τ_1) (cm^{-1})
0.00	0.00	0.00	0.00	0.00
15.00	49.63	54.29	1.66	51.29
30.00	176.42	188.18	7.11	183.53
45.00	313.41	323.16	14.85	328.26
60.00	373.19	372.79	18.81	392.00
75.00	313.41	307.56	14.85	328.26
90.00	176.42	174.88	7.11	183.53
105.00	49.63	53.12	1.65	51.28
120.00	0.00	0.32	0.00	0.00
135.00	49.63	39.63	1.66	51.29
150.00	176.43	159.99	7.11	183.54
165.00	313.41	304.82	14.85	328.26
180.00	373.19	373.19	18.81	392.00

FIG. 3. The minimum energy torsional path along ρ_1.

The values obtained are given in Table II. The numbers show that the potential curve of minimum energy is $2\pi/3$ periodic when employing τ_1 as the torsional coordinate whereas it lacks this periodicity when ρ_1 is used. The same can immediately be seen from Figs. 2 and 3, where the total molecular energy values are plotted as points along the curves obtained by fitting the function $V(\tau) = 1/2[V_3(1-\cos 3\tau) + V_6(1 -\cos 6\tau) + V_9(1-\cos 9\tau)]$ to the total energies. The points almost perfectly match the fitted curve when employing τ_1. When employing ρ_1, however, there is clear deviation from $2\pi/3$ periodicity.

Points corresponding to configurations related by symmetry operations must lie on horizontal lines. While this is exactly what can be observed in Fig. 2, Fig. 3 shows the loss of symmetry. To correct for the loss of periodicity, according to a standard treatment,[7,19] one would carry out a least-squares fit of the total energies by using the function $V(\tau = (\rho_1 + \rho_2 + \rho_3 - 2\pi)/3)$ instead of the function $V(\tau = \rho_1)$. This amounts to assuming that the minimum energy path along a dihedral angle is related to the minimum energy path along τ_1 by simple coordinate transformation. Save special points, the stationary points on the torsional–vibrational PES, this assumption, however, is not correct, since the requirements of being on the minimum energy path along a dihedral angle, e.g., ρ_1, do not imply the satisfaction of the
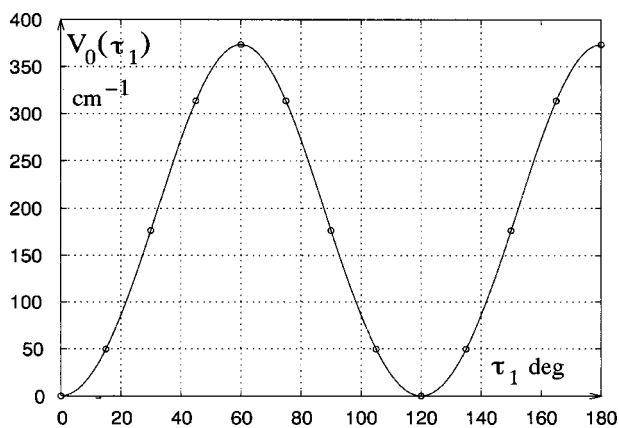
FIG. 2. The minimum energy torsional path along τ_1.

equations required on the minimum energy path along τ_1. Therefore, this method does not restore but (mistakenly) assumes periodicity. Several other methods have been proposed for recovering $2\pi/3$ periodicity,[20–22] but they can be questioned either on theoretical or practical grounds. $2\pi/3$ periodicity of the torsional potential of methyl-type internal rotors is a fundamental property that derives from dynamical symmetry. A theoretically sound *a priori* approach to calculating such a potential should obviate the need of any *a posteriori* symmetry restoration.

As our symmetry analysis has shown, the effective torsional potential of acetaldehyde must be a $2\pi/3$ periodic function of the torsional coordinate τ_1. The effective torsional potential of acetaldehyde that is the simplest next to $V_0(\tau_1)$ incorporates zero-point vibrational energy (ZPVE) contributions from the remaining 14 vibrational modes. Assuming that these vibrations are harmonic, the zero-point energy contribution is just the half of the sum of the 14 harmonic frequencies. The harmonic frequencies depend on the torsional coordinate. We have determined the harmonic frequencies and the ZPVE at fixed values of τ_1 with the following method. The Cartesian force constant matrix is calculated by the GAUSSIAN 98 program[17] at each of the optimized geometries obtained when sampling the potential $V_0(\tau_1)$. Then at each fixed value of τ_1 a projected force constant matrix is calculated with a projector matrix corresponding to the Eckart–Sayvetz conditions.[23,24] Diagonalization of a projected force constant matrix gives seven zero eigenvalues corresponding to three translational, three rotational, and the torsional mode, as well as 14 nonzero eigenvalues. The latter are equal to the square of the harmonic frequencies at the value of τ_1 considered. The numerical results summarized in Table II show that the effective torsional potential is indeed a $2\pi/3$ periodic function. A least-squares fit of the functional form $V(\tau_1)$ to the ZPVE corrected total energies (see Table II) gave the values $V_3 = 391.85$ cm^{-1}, $V_6 = -12.46$ cm^{-1}, and $V_9 = 0.16$ cm^{-1}, which compare favorably with the experimental values $V_3 = 407.95$ cm^{-1}, $V_6 = -12.92$ cm^{-1},[3] or $V_3 = 407.72$ cm^{-1}, $V_6 = -12.07$ cm^{-1}, and $V_9 = -0.19$ cm^{-1}.[4]

In passing it is worth noting that according to our calculations the geometry parameters of acetaldehyde not involv-

ing the methyl hydrogens are $2\pi/3$ periodic, whereas parameters involving methyl hydrogens are not $2\pi/3$ periodic functions of τ_1. All of the elements of the four dimensional generalized tensor of inertia[24] are, however, $2\pi/3$ periodic functions of τ_1.

V. SUMMARY

Barriers of infinite (or very large) height prevent certain rearrangements of the atoms in a molecule from occurring and therefore the complete nuclear permutation inversion (CNPI) group of the molecule can be reduced.[13,14] We pointed out, in the example of the acetaldehyde molecule, that some barriers of infinite height, in addition to reducing the CNPI group, constrain torsional dynamics explicitly and influence how the torsional coordinate transforms under the MS group. Then, having shown that there is a coordinate most reasonable for describing torsional motion, we have proved that the symmetry properties of the torsional potential do not depend on the geometrical symmetry of either the top or the frame.

Up to now research papers[7,25,26] and textbooks[9,10] kept relying on assumptions about the geometrical symmetry of the top and the frame when explaining the symmetry properties of torsional potentials, and dynamical models of internal rotation were being constructed by assuming reference configurations with methyl tops of threefold symmetry.[27,28] There were well known but unresolved discrepancies.[7,20–22] Our analysis explained the origin and resolved these discrepancies. The results of our symmetry analysis have been confirmed in all respects by numerical, first principles calculations of the torsional potential curve of acetaldehyde.

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