Ab initio torsional potential and transition frequencies of acetaldehyde

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High-level *ab initio* electronic structure calculations, including extrapolations to the complete basis set limit as well as relativistic and diagonal Born–Oppenheimer corrections, resulted in a torsional potential of acetaldehyde in its electronic ground state. This benchmark-quality potential fully reflects the symmetry and internal rotation dynamics of this molecule [J. Chem. Phys. **117**, 6489 (2002)] in the energy range probed by spectroscopic experiments in the infrared and microwave regions. The torsional transition frequencies calculated from this potential and the *ab initio* torsional inverse effective mass function are within $2\,\mathrm{cm}^{-1}$ of the available experimental values. Furthermore, the computed contortional parameter ρ of the rho-axis system Hamiltonian is also in excellent agreement with that obtained from spectral analyses of acetaldehyde. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1633260]

I. INTRODUCTION

Everyone learning chemistry at higher levels is familiar with the so-called ethane torsional potential, having three energy wells (minima) during a complete rotation through $2\pi(360°)$, thus having a periodicity of $2\pi/3$. One can ask three simple and fundamental questions concerning this curve presented or described in many textbooks (e.g., Ref. 1): (1) Are such high-periodicity curves characteristic only for the internal rotation of ethane-type highly symmetric or of a larger class of molecules? (2) What is the origin of the periodicity? (3) What is the exact shape and what forces are responsible for the shape of this periodic curve?

The answer to the first question is that all molecules having a methyl group must exhibit a methyl internal rotation curve of $2\pi/3$ periodicity, independently of the actual geometry of the molecule.[2] The related answer to the second question is that permutation-inversion symmetry of the like nuclei (in this case the three H atoms) and a peculiar property of torsional dynamics[2] are responsible for the periodicity. The interesting answer to the latter part of question 3 is that hyperconjugation rather than steric repulsion is responsible for the exact shape of the periodic potential required by symmetry.[3,4]

In this article we extend our previous theoretical study[2] on the methyl internal rotation of acetaldehyde, CH_3CHO, in its electronic ground state and present the shape of the torsional potential at the current technical limit.

Acetaldehyde has long been considered a prototypical molecule for studying the internal rotation of the methyl group. Consequently, numerous experimental[5,6] and quantum chemical[2,7–12] studies have been published which aimed at determining the torsional barrier and the shape of the torsional potential in acetaldehyde.

The best test of the quality of a first-principles torsional potential is through the calculation of the corresponding tor-sional energy levels and transition frequencies and their comparison with the available experimental data. Apart from the most recent attempt[2] all previous *ab initio* calculations of the torsional potential of acetaldehyde failed to provide a strictly $2\pi/3$ periodic potential and omitted the zero-point vibrational energy (ZPVE) correction arising from the nontorsional modes. Furthermore, due to the use of lower levels of electronic structure theory for the computation of the potential, the torsional transition frequencies calculated using these potentials agreed only semiquantitatively with experimental data. Our previous study[2] was also executed at a low level [6-31G** RHF (restricted Hartree–Fock)] of electronic structure theory. A principal aim of this study was to obtain a benchmark-quality *ab initio* torsional potential and subsequent transition frequencies for the methyl internal rotation of acetaldehyde. Consequently, the article is organized as follows. Details of the *ab initio* calculations and derivation of the torsional potential are described in Sec. II. In Sec. III the *ab initio* torsional potential and molecular geometries are used to calculate torsional energy levels and transition frequencies, and the contortional parameter ρ,[1] which are then compared to experimental data and the results of other *ab initio* calculations. Section IV summarizes the results.

II. THE *AB INITIO* TORSIONAL POTENTIAL

Recent developments in electronic structure theory, in particular our improved understanding of electronic structure effects beyond the usual nonrelativistic Born–Oppenheimer treatment, as well as advances in computer technology have facilitated the computations necessary for the theoretical determination of high-accuracy potential energy hypersurfaces (see, e.g., Ref. 13). Theory is now capable, over a rather large range of geometries, of obtaining potential energy values which lead to predictions of near spectroscopic accuracy, defined as $1\,\mathrm{cm}^{-1}$, for the rovibrational energy levels of small many-electron molecular systems.

TABLE I. Valence focal-point analysis of the rotational barrier of acetaldehyde.[a]

Basis set	RHF	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]
cc-pVDZ(62)	498.3	−8.7	−24.9	−1.3	−1.6
aug-cc-pVDZ(105)	470.8	−52.0	−12.7	−8.2	−1.9
aug-cc-pCVDZ(117)	468.8	−51.1	−12.1	−8.5	
cc-pVTZ(146)	446.8	−24.5	−12.8	−6.3	−1.0
aug-cc-pVTZ(230)	442.8	−29.6	−7.4	−7.2	
aug-cc-pCVTZ(269)	443.8	−28.1	−7.4	−7.1	
cc-pVQZ(285)	445.0	−31.2	−7.9	−7.4	
aug-cc-pVQZ(424)	444.5	−39.2	−4.9	−8.0	
aug-cc-pCVQZ(511)	443.3	−36.4	−5.3	−7.7	
cc-pV5Z(493)	443.9	−37.4	−5.0	−7.9	
aug-cc-pV5Z(701)	443.7	−36.7			
cc-pV6Z(784)	443.7	−37.1			
aug-cc-pV6Z(1075)	443.7				
Extrapolated(CBS)	443.7	−36.9	[−5.0]	[−7.9]	[−1.0]

[a]The energy values are given in units of wave numbers. The number of contracted Gaussian functions is given in parentheses after each basis set. The underlying reference structures have been optimized at the cc-pCVTZ CCSD(T) level. The CBS RHF barrier has been obtained from aug-cc-pV[Q,5,6] RHF results, the correlation contribution to the CBS MP2 barrier has been obtained from cc-pV[5,6]Z MP2 results (see text). No extrapolation was attempted beyond δ[MP2].

The largest computational error in today's approximate, wave function based solutions to the time-independent non-relativistic electronic Schrödinger equation results from the truncation of the n-electron basis of all Slater determinants that constitute the full configuration interaction (FCI) wave functions. Nevertheless, highly efficient techniques have been devised to get accurate approximate wave functions. The coupled-cluster approach,[14] employed extensively in this study, is the most advantageous one for the present problem. Determination of molecular quantities at the complete one-electron basis set limit has also received considerable attention. These studies show that Hartree–Fock (HF) energies converge almost exponentially toward the complete basis set (CBS) limit,[15,16] while correlation energies seem to follow an X^{-3} dependence,[15,17,18] where X is the cardinal number of the correlation-consistent (cc) Gaussian basis sets[19,20] well suited for such extrapolations. Once the CBS FCI asymptote is approached and relativistic effects[21] as well as diagonal corrections to the Born–Oppenheimer approximation[22] are included in the *ab initio* treatment, the electronic structure results are of quality approaching the desired spectroscopic accuracy.

During the present study we have used a local version of the ACESII electronic structure package[23,24] to optimize the molecular geometry of acetaldehyde while keeping the torsional coordinate τ, defined as $\tau = 1/3(\rho_1 + \rho_2 + \rho_3 - 2\pi)$,[2] where ρ_i are the dihedral angles H_iCCO, fixed at values very near to 0°, 15°, 30°, 45°, and 60°. The $2\pi/3$ torsional potential of acetaldehyde is an even function and thus the region 0° (minimum) to 60° (maximum) completely determines the shape of the potential. The constrained optimizations have been performed at the all-electron cc-pCVTZ CCSD(T) level.[25]

Valence-only MP2, CCSD, CCSD(T), and CCSDT correlation energies, keeping the 1s orbitals of C and O frozen during the calculations, have been computed with the (aug-)cc-pVXZ, $X=2$(D), 3(T), 4(Q), 5, and 6 basis sets. These calculations allow efficient extrapolations to the valence-only CBS limits. The CBS Hartree–Fock (HF) limiting values were obtained with the three-parameter formula $E^X = E_{CBS} + a\exp(-bX)$ using the best three HF values computed, while the computed correlation energies were extrapolated to their CBS limit employing the two-parameter formula $E^X = E_{CBS} + cX^{-3}$.

The core correlation energy contributions at each geometrical reference point were estimated at the aug-cc-pCVTZ CCSD(T) level by taking the difference in total energies obtained from all-electron and frozen-core computations.

To account for further small electronic structure effects the one-electron mass-velocity and Darwin (MVD1) relativistic energy correction[21,26] was obtained at the same five reference points, again employing the ACESII package[23,24] and cc-pCVTZ CCSD(T) wave functions.

Computation of the diagonal Born–Oppenheimer corrections (DBOC)[22,27] was performed at the Hartree–Fock level within the formalism of Handy, Yamaguchi, and Schaefer[22] using the BORN program operating within the PSI package.[28] A TZ2P basis set has been employed for these calculations.

Zero-point vibrational energy (ZPVE) corrections arising from the nontorsional modes were taken from Ref. 2 and were computed at the 6-31G** RHF level. Since harmonic frequencies are usually systematically overestimated at this level of theory, the ZPVE corrections have been scaled, at all computed points, by a single scale factor of 0.91.

Based on the above computations, a valence focal-point analysis[15] of the torsional barrier of acetaldehyde is presented in Table I. The largest aug-cc-pV6Z RHF computations employed 1075 contracted Gaussian functions (CGF), while the largest CCSD(T) computations, employing the aug-cc-pCVQZ basis set, used 511 CGFs. The valence focal-point-type analysis displays facile convergence toward the one- and n-particle limits. The cc-pVDZ RHF barrier is more than 50 cm^{-1} (or 10%) too high, as inferred from the Hartree–Fock limit of 443.7 cm^{-1}. The unreliability[29] of energies based on the subcompact cc-pVDZ set is clear from

TABLE II. Anatomy of the *ab initio* torsional potential of acetaldehyde.[a]

τ	CCSDT	+CC	+Rel	+DBOC	+ZPVE	Experiment	
0	0.00	0.00	0.00	0.00	0.00		
15	51.46	51.68	51.71	51.78	53.29		
30	183.51	184.28	184.41	184.66	191.13		
45	328.58	329.99	330.25	330.71	344.22		
60	392.94	394.73	395.06	395.60	412.72		
						b	c
V_3	392.43	394.16	394.49	395.04	412.08	407.95	407.72
V_6	-12.95	-13.10	-13.12	-13.13	-15.23	-12.92	-12.07
V_9	0.52	0.57	0.57	0.57	0.64	$\cdots$	-0.19

[a]The energy values are given in units of wavenumbers at different values of the torsional coordinate τ (see text). τ is given in units of degrees. The energy values were fitted to the functional form $V(\tau) = \frac{1}{2}[V_3(1-\cos(3\tau)) + V_6(1-\cos(6\tau)) + V_9(1-\cos(9\tau))]$. CCSDT = RHF + valence-only scaled (see text) complete basis set (CBS) CCSD(T) and CCSDT energy corrections; +CC = CCSDT + core correlation correction (see text); +Rel = CCSDT + CC + relativistic energy correction obtained at the MVD1 level (see text); +DBOC = CCSDT + CC + Rel + diagonal Born–Oppenheimer correction obtained at the TZ2P RHF level (see text); +ZPVE = CCSDT + CC + Rel + DBOC + zero-point vibrational energy correction arising from the non-torsional modes, computed at the 6-31G** RHF level.
[b]Reference 5.
[c]Reference 6.

the associated aug-cc-pVDZ and aug-cc-pCVDZ values. Nevertheless, all basis sets past cc-pVTZ give RHF results within 5 cm^{-1} of the HF limit. Variation of the second-order (MP2) correlation increment is considerably greater than that of the HF values, approaching an apparent limit of -37 cm^{-1} relatively slowly and somewhat erratically. In contrast, the δ[CCSD] values of about -5 cm^{-1} are remarkably stable, consistent with focal-point trends observed elsewhere.[15] The δ[CCSD(T)] correction is also small, only about -8 cm^{-1}, becoming slightly more negative with larger basis sets. The higher-order δ[CCSDT] term is only -1 cm^{-1}, or probably even less. It is safe to assume that the missing post-CCSDT correction is less than 1 cm^{-1} at the CBS limit.

Since rehybridization of valence electron pairs does not accompany torsional motion in acetaldehyde, both the relativistic ($+0.3$ cm^{-1}) and core correlation ($+1.8$ cm^{-1}) corrections to the barrier are minuscule (cf. Table II). In addition, the DBOC effect ($+0.5$ cm^{-1}) is also almost negligible. Applying all these corrections to the CBS CCSDT value, obtained as 392.9 cm^{-1}, yields the final net (electronic) barrier of $392.9 + 1.8 + 0.3 + 0.5 = 395.5$ cm^{-1}. Given the nearly ideal focal-point convergence and the diminutive nature of the small electronic structure corrections we are confident that this value is within ± 5 cm^{-1} of the true net barrier of acetaldehyde.

The penultimate total energies at each reference point along the methyl internal rotation curve included the valence-only CBS CCSD(T) energies, computed from aug-cc-pV[D,T,Q] CCSD(T) wave function results extrapolated to the RHF and correlation energy limits separately, corrected for core correlation and relativistic effects, and the DBOC term. Since a somewhat lower level of electronic structure theory has been used for calculation of the valence-only CCSDT part of the torsional potential than that used for the net barrier, the resulting slight change in the barrier has been incorporated into the final potential via the functional form

$$\Delta V^{\mathrm{corr}}(\tau) = \frac{\Delta V^{\mathrm{barr}}}{2}[1-\cos(3\tau)], \qquad (1)$$

with $\Delta V^{\mathrm{barr}} = +1.9$ cm^{-1}.

As it is clear from Table II, summarizing the anatomy of the net and effective torsional potential curves, computation of the effective torsional potential curve is somewhat troublesome due to the fact that the effect of the zero-point vibrations of the nontorsional modes is significant, adding $+17.1$ cm^{-1} to the net barrier height. Therefore, it is clear that the largest remaining computational error is due to the treatment of the vibrations. Further progress in the first-principles computation of the effective torsional potential of acetaldehyde will require a more sophisticated treatment of the vibrational motions of this polyatomic molecule.

The convergence behavior of the computed V_3 values has been discussed before. The CBS CCSD(T) value differs from the final net value by only -2.6 cm^{-1}. The V_6 and V_9 values also show extremely small variations; the change from the CBS RHF to the final net values are $+0.05$ and -0.59 cm^{-1}, respectively. Again, the zero-point corrections are much more substantial, being $[+7.04, -2.10, +0.07]$ cm^{-1} for $[V_3, V_6, V_9]$. While further studies are needed to establish the correct V_6 value, it seems that the experimental V_9 value of -0.19 cm^{-1} should be revised. Overall, this study provides further evidence to our previous observation[15,30,31] that *ab initio* computation of potential energy curves describing internal motion of the methyl group is less demanding than that of most other large-amplitude motions (see, e.g., Ref. 32).

III. CALCULATION OF THE TORSIONAL FREQUENCIES AND THE SPECTROSCOPIC PARAMETER ρ

This section discusses the calculation of the torsional (transition) frequencies and the spectroscopic contortional parameter ρ of the rho-axis-system Hamiltonian[1,33] from the molecular geometries and the torsional potential derived first principles in Sec. II.

TABLE III. Torsional transition frequencies and the ρ value of acetaldehyde.

	This work		HF/6-31G(d,p)[a]		MP2/6-31G(d,p)[a]		Experiment[b]	
	A	E	A	E	A	E	A	E
Zero point	75.78	75.86	77.08	77.18	75.87	75.97		
$0 \rightarrow 1$	145.25	143.30	144.64	141.83	142.04	139.18	143.74	141.92
$1 \rightarrow 2$	112.84	129.22	100.54	121.65	97.62	118.80	111.78	127.45
$2 \rightarrow 3$	157.14	81.70	160.03	71.95	157.60	70.07		
	This work				Xu et al.[c]		Experiment[d]	
ρ	0.3277				0.3384		0.3316	0.3291

[a]Reference 7.
[b]Reference 37.
[c]Reference 11.
[d]Reference 6.

The calculation of the inverse torsional effective mass function, $g(\tau)$, which is needed to calculate torsional energy levels, and the calculation of the spectroscopic parameter ρ require the determination of the four-dimensional generalized tensor of inertia[34] defined by the equation

$$\mathcal{I} = \begin{pmatrix} \mathbf{I}_R & \mathbf{I}_{R\tau} \\ (\mathbf{I}_{R\tau})^T & I_{\tau\tau} \end{pmatrix}, \qquad (2)$$

where superscript T denotes transposition, $\mathbf{I}_R$ is the rotational tensor of inertia, and the column vector $\mathbf{I}_{R\tau}$ and the scalar $I_{\tau\tau}$ are given by

$$\mathbf{I}_{R\tau} = \sum_{i=1}^{N} m_i \mathbf{a}_i \times \frac{d\mathbf{a}_i}{d\tau} \qquad (3)$$

and

$$I_{\tau\tau} = \sum_{i=1}^{N} m_i \frac{d\mathbf{a}_i}{d\tau} \cdot \frac{d\mathbf{a}_i}{d\tau}, \qquad (4)$$

respectively, where $\mathbf{a}_i$ is the column vector of the coordinates of the ith atom taken in a molecule fixed system of axes whose origin is at the center of mass, and N is the number of atoms in the molecule. Naturally, the atomic coordinates are functions of the torsional coordinate τ.

Calculation of the rotational tensor of inertia is straightforward. To obtain $\mathbf{I}_{R\tau}$ and $I_{\tau\tau}$ one must calculate the derivatives of the atomic coordinates with respect to the torsional coordinate. At any fixed value of τ one can accurately approximate these derivatives and thus avoid fitting the atomic coordinate functions to account for geometry relaxation. This is described as follows.

Assume a rigid internal rotation model. In this simple model the atomic coordinates and their derivatives can be expressed analytically in terms of the torsional and the other internal coordinates. To account for geometry relaxation, for any fixed value of the torsional coordinate we employ the internal coordinate values appropriate to the fully relaxed geometry at the particular torsional angle considered.

The inverse torsional effective mass function is related to the elements of the four dimensional generalized tensor of inertia by the expression[34]

$$g(\tau) = [I_{\tau\tau} - (\mathbf{I}_{R\tau})^T (\mathbf{I}_R)^{-1} \mathbf{I}_{R\tau}]^{-1}. \qquad (5)$$

Employing Eq. (5) and the *ab initio* reference geometries (see Sec. II) $g(\tau)$ can be calculated pointwise. The values obtained were fitted by an even, $2\pi/3$ periodic function resulting in

$$g(\tau) = 7.702\,84 + 0.052\,129\,7 \cos(3\tau)$$
$$+ 0.000\,748\,301 \cos(6\tau) - 0.000\,054\,74 \cos(9\tau), \qquad (6)$$

where the coefficients are given in units of wave numbers.

This corresponds to the following torsional Hamiltonian for acetaldehyde:

$$\hat{H} = -\frac{d}{d\tau}[7.702\,84 + 0.052\,129\,7 \cos(3\tau)$$
$$+ 0.000\,748\,301 \cos(6\tau) - 0.000\,054\,74 \cos(9\tau)]$$
$$\times \frac{d}{d\tau} + \frac{1}{2}[412.08(1 - \cos(3\tau))$$
$$- 15.23(1 - \cos(6\tau)) + 0.64(1 - \cos(9\tau))], \qquad (7)$$

where the coefficients are given in units of wave numbers.

The time-independent Schrödinger equation involving $\hat{H}$ was solved by a DVR-like method developed by Meyer[35] and the transition frequencies were computed. The results obtained are given in Table III.

The facile convergence of all-electron calculations to the one- and n-particle limits makes previous, lower-level computations rather accurate, especially for the $0 \rightarrow 1$ transition, as can be seen by the computed torsional transitions reported in Table III. Nevertheless, for the higher $1 \rightarrow 2$ transitions the differences between the old and new theoretical transition frequencies is a substantial 10 (or more) cm^{-1}, our values being in almost perfect agreement with the experimental values, with deviations hardly exceeding 1 cm^{-1}. We expect a similar precision for the $2 \rightarrow 3$ transitions.

The parameter ρ describes the strength of the coupling between the torsional momentum and the z component of the total angular momentum, as calculated in the so-called rho-axis system, and by assuming that all vibrational displacements except those due to the torsion are equal to zero. The rho-axis system is defined by the requirement of vanishing the x and y components of the angular velocitylike vector

$$\boldsymbol{\omega} = (\mathbf{I}_R)^{-1} \mathbf{I}_{R\tau}. \qquad (8)$$

Since ρ is free of vibrational contributions and depends only on the molecular geometry and on the variation of the molecular geometry with respect to the torsional coordinate, its experimentally determined value can be used to check the
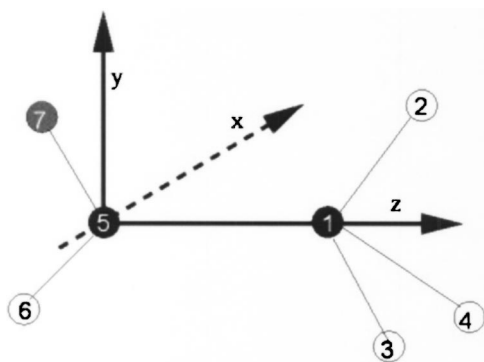
FIG. 1. The initial molecule fixed system of axes: The z axis coincides with the CC bond. The hydrogen atom of number 2 is in the yz plane when the dihedral angle $\angle 7512 = 0$.

quality of *ab initio* molecular geometries and the correctness of our definition of the torsional coordinate.

We have shown in Ref. 33 that the parameter ρ is identical to the positive central eigenvalue of a Floquet matrix that is constructed by employing the angular velocitylike vector $\boldsymbol{\omega}$. A least-squares fit to the *ab initio* determined $\boldsymbol{\omega}$ values (i.e., to the values of $\boldsymbol{\omega}$ at fixed torsional angles) gave

$$\omega_x = -0.000\,800\,442\sin 3\tau_1 + 0.000\,012\,0637\sin 6\tau_1$$
$$-1.3521\times10^{-7}\sin 9\tau_1,$$
$$\omega_y = -0.104\,641 - 0.001\,310\,54\cos 3\tau_1, \qquad (9)$$
$$\omega_z = 0.310\,517 + 0.005\,113\,23\cos 3\tau_1,$$

where the subscripts x, y, and z refer to coordinates in the Cartesian system of axes whose origin is at the center of mass while its axes are parallel to the axes of the initial Cartesian coordinate system depicted in Fig. 1.

Following the prescriptions in Refs. 33 and 36 we calculated ρ. The result, agreeing nicely with those derived experimentally,[6] is given in Table III.

IV. CONCLUDING REMARKS

The torsional potential, the torsional transition frequencies, and the contortional parameter have been obtained for acetaldehyde by high-level *ab initio* calculations. The theoretically derived contortional parameter and transition frequencies are in excellent agreement with the corresponding experimental values. In fact, no previous theoretical calculation led to such a good agreement. At the same time, somewhat unexpectedly, the theoretical values for V_6 and V_9 of the torsional potential deviate substantially from those obtained by the analysis of experimental spectra (see Table II).

ACKNOWLEDGMENTS

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