

# Methyl Torsion in Propene Initiates Ethylenic Hydrogen Wagging and Twisting<sup>†</sup>

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**Abstract:** We have examined the methyl torsional barrier, potential function, and frequencies in propene by pure ab initio methods using various flexing models, extended basis sets, and systematically increased correlation levels. The principal conclusions are the following: (1) a physically reasonable internal rotation potential function can be obtained only when out-of-plane ethylenic skeletal hydrogen flexing motions which include ethylenic twisting are part of the torsional motion; (2) the internal rotation barrier is calculated using MP4(SDTQ)/6-311G(3df,2p) ab initio theory at 689 cm<sup>-1</sup>, only 5 cm<sup>-1</sup> below the experimental barrier obtained from microwave and far infrared measurements; (3) correlation and basis set effects beyond MP2 and 6-311G(d,p) levels are very important for accurate ab initio calculation of the propene methyl torsional barrier, the correlation effect alone exceeding 85 cm<sup>-1</sup>; (4) both the fundamental and first overtone frequencies are calculated at the MP4(SDTQ)/6-311G(3df,2p) level within 1 cm<sup>-1</sup> of experimental values using a purely theoretical kinetic energy constant ( $F = 7.1731$  cm<sup>-1</sup>) calculated from MP2/6-311G(3df,2p) fully optimized conformer geometries.

## 1. Introduction

The minirevolution in infrared (IR) spectroscopy resulting from development of the Fourier transform infrared (FTIR) spectrometer has had no greater impact than on determination of methyl torsional fundamental frequencies. Because these large amplitude vibrational modes have very low frequencies, secure values for the fundamentals (and frequently overtones) had remained in limbo, 10–15-cm<sup>-1</sup> uncertainties not being uncommon. The precise frequency measurements (usually within 0.1 cm<sup>-1</sup>) made possible by FTIR spectroscopy provided a challenge for theoretical models for methyl torsions.

The failure of the rigid frame model (i.e., no alteration of the molecular frame or of methyl group hydrogen atom orientations during the methyl rotation) initially applied to predict torsional frequencies in such basic methyl group molecules as acetaldehyde, dimethyl ether, and acetone proved that internal rotation involves a more complex physical phenomenon than pure torsion.<sup>1</sup> The next step involved prediction of the torsional fundamental frequencies by relaxed model ab initio calculations.<sup>1–4</sup> In this model the methyl internal rotation is coupled to skeletal motions by allowing internal degrees of freedom to adjust during internal rotation. Thus both skeletal flexing and hydrogen folding motions result from methyl group rotation. These considerations were carried out at Hartree–Fock (HF) and electron correlated levels with basis sets up to 6-31G(d,p), the correlation corrections at Møller–Plesset second-order perturbation theory<sup>5</sup> (MP2). Very recently, the methyl torsion problem in acetaldehyde was reconsidered rigorously at the 6-311G(3df,2p) level, with MP4-(SDTQ) and coupled cluster theory correlation corrections.<sup>6</sup> The effects of the extensive polarization functions and correlation on

the acetaldehyde torsional barrier are very large, leading to up to 100-cm<sup>-1</sup> corrections.

The striking feature of these calculations is that even at the relatively modest HF/6-31G(d,p) level of calculation, theoretical simulations of experimental fundamental torsional frequencies are within 1–3 cm<sup>-1</sup> for one series of molecules (acetone, dimethyl ether, and acetaldehyde<sup>2–4</sup>), while for a second group consisting of the ethylenic molecules, propene, and isobutene, the disparity between experiment and theory exceeds 10 cm<sup>-1</sup>.<sup>1</sup> In particular, the propene fundamental is predicted by this approach at 203 cm<sup>-1</sup>, contrasted to the 188-cm<sup>-1</sup>. FTIR experimental frequency (compare to <1-cm<sup>-1</sup> disparity for the corresponding acetaldehyde fundamental). Inasmuch as the gas-phase far IR spectrum of propene has been determined at resolution levels which reveal detailed rotational structure with <0.1-cm<sup>-1</sup> uncertainty,<sup>7,8</sup> this discrepancy is meaningful.

The principal difference between the two types of molecules seems to lie in the ethylenic group. The close proximity of methyl rotor and ethylenic parts in propene suggests that the physics of interaction of the methyl group with the molecular skeleton is more complex for ethylenic molecules than for carbonyls. However, in light of the rigorous acetaldehyde calculations,<sup>6</sup> the effect of the limited 6-31G(d,p) basis set cannot be ignored.

The goal of the present paper is to determine what skeletal motions accompany internal rotation in propene. We address this problem by studying the methyl torsional potential for propene in detail using rigorous ab initio theory. Propene was chosen as the simplest model system for ethylenic molecules containing methyl groups. Advantage can be taken of propene's small size, allowing detailed study of basis set, electron correlation, and skeletal flexing effects on the predicted frequencies up to the MP4(SDTQ)/6-311G(3df,2p) level. This extended size basis set corrected by high-order electron correlation corrections allows the internal rotation barrier in acetaldehyde to be accurately predicted.<sup>6</sup>

## 2. Calculations

The standard theoretical approach predicting methyl internal rotation in a molecule where there is an appreciable hindering barrier to the rotation

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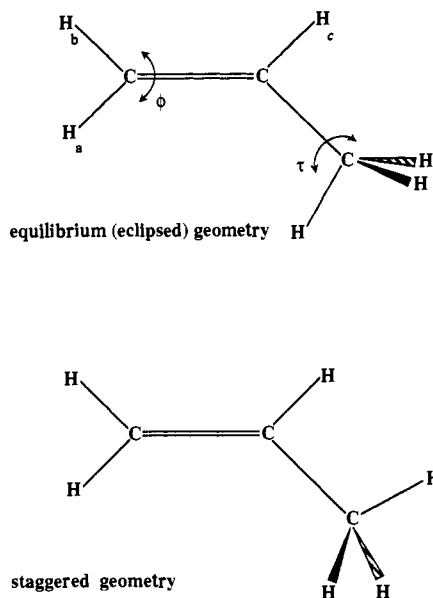
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**Figure 1.** Most stable (eclipsed,  $\tau = 0^\circ$ ) and least stable (staggered,  $\tau = 60^\circ$ ) methyl conformers of propene, showing hydrogen numbering designation. The ethylenic twist angle is represented by  $\phi$ .

is to assume a pure torsional Hamiltonian.<sup>9</sup> This Hamiltonian neglects interaction of the torsional motion with overall molecular rotation and allows expansion of the internal rotation potential function:  $V(\tau)$  in a Fourier series in the torsional angle  $\tau$ . Only cosine terms arise if the torsional axis lies in the molecular symmetry plane:

$$V(\tau) = \frac{1}{2} \sum V_n (1 - \cos n\tau) \quad (1)$$

Of these, only  $V_3, V_6, V_9, \dots$  are nonzero for  $C_{3v}$  methyl top symmetry, i.e.,

$$V(\tau) = \frac{1}{2} V_3 (1 - \cos 3\tau) + \frac{1}{2} V_6 (1 - \cos 6\tau) + \frac{1}{2} V_9 (1 - \cos 9\tau) + \dots \quad (2)$$

Even though the methyl group in propene does not have a  $C_3$  axis of symmetry, the  $120^\circ$  conformer differs from the  $\tau = 0$  conformer only in the labeling of the H atoms. For this reason, the three-term potential, eq 2, is used to ensure that a  $120^\circ$  rotated methyl group has the same energy as  $\tau = 0$  (see Appendix 1). The torsional energy levels are then determined by a Schrödinger equation constructed from the internal rotation Hamiltonian:

$$H = Fp^2 + V(\tau) \quad (3)$$

The kinetic energy coefficient  $F$  is determined by the moments of inertia. In principle,  $F$  depends on the torsional state; in practice, a single average  $F$  is usually assumed. There are many discussions of the internal rotation problem in the microwave spectroscopy literature, because the various terms in the Hamiltonian,  $F$  and  $V_n$ , directly relate to microwave spectral measurement.<sup>10</sup> In diagonalizing the Hamiltonian matrix associated with the Schrödinger equation constructed from (3), we use a 21-term free rotor basis set for propene, since this truncation only incurs  $<0.01\text{-cm}^{-1}$  error for the first few torsional levels.<sup>11</sup> Because the fundamental and first overtone energy levels are well below the top of the barrier, the neglected interactions described above are not expected to significantly affect these torsional energies.

The torsional potential function for the propene ground state was determined by calculating the total molecular energies for between 10 and 13 methyl rotational conformers obtained by rotating the methyl group successively every  $15^\circ$  up to  $180^\circ$ , as we have previously discussed for acetaldehyde.<sup>4</sup> The equilibrium geometry is the eclipsed conformation shown in Figure 1. This geometry defines  $\tau = 0$ . The top of the barrier corresponds to the staggered conformation,  $\tau = 60^\circ$ .

(9) E.g.: Livingston, R. C.; Grant, D. M.; Strong, K. A.; Brugger, R. M. *J. Chem. Phys.* **1973**, *58*, 1438.

(10) E.g.: Belov, S. P.; Tretyakov, M. Y.; Kleiner, I.; Hougen, J. T. *J. Mol. Spectrosc.* **1993**, *160*, 61.

(11) There is a misprint in eq 5A of ref 4. It should read  $\langle m|H|m \rangle = 9Fv^2$ , where  $v$  is the vibrational quantum number.

To determine what skeletal motions are important determinants of the methyl internal rotation potential in propene, we compare ab initio potentials calculated using five models incorporating progressively increasing restrictions for flexing motion during the methyl rotation.

**Model I.** Fully relaxed model involving complete geometry optimization, including independent optimization of all skeletal hydrogen ( $H_a, H_b, H_c$ ) out-of-plane wagging angles. This model has no constraints.

**Model II.** The optimization in I has been restricted by clamping the  $\text{CH}_2$  hydrogen (i.e.,  $H_a$  and  $H_b$  in Figure 1) out-of-plane motions. All  $H_c$  internal degrees of freedom are allowed to adjust.

**Model III.** The optimization in I has been restricted by clamping the skeletal hydrogen ( $H_c$ ) adjacent to the methyl group out-of-plane motion. All  $H_a$  and  $H_b$  degrees of freedom are allowed to adjust.

**Model IV.** The optimization in I has been restricted by clamping all skeletal hydrogen atom ( $H_a, H_b, H_c$ ) out-of-plane motions.<sup>1</sup>

**Model V.** Primitive rigid frame model (no flexing). The skeleton and skeletal hydrogens are fixed at the geometry of the eclipsed conformer. The methyl group is regarded as a rigid  $C_{3v}$  symmetry top with identical in-plane and out-of-plane C–H distances taken as the average methyl group C–H length computed in model I.

In each of the models, the potential can be expressed as a threefold symmetric potential function with energy levels corresponding to  $A$  and  $E$  high barrier limit rotor states.<sup>9</sup> The imposition of equal methyl C–H bond lengths in model V means that this model does not use the equilibrium (optimized) structure of propene as a starting point ( $\tau = 0$ ) description. Its usefulness, despite this flaw, is that it reveals the effect of skeletal relaxation on the potential function during methyl rotation, playing a parallel role to a valence bond structure in discussing energy effects. A related model, which avoids this fault, optimizes (only) the methyl group hydrogen atom orientations. Since this torsional potential does not have  $120^\circ$  periodicity (i.e., the energy will differ only through labeling of the H atoms) and thus becomes unphysical, we do not pursue it further. Models II–V all assume a  $0^\circ$  methyl tilt angle.

To understand the physics of the torsional process, we use MP2/6-311G(3df,2p) level calculations performed for each of the five flexing models to show that in the case of propene, only model I leads to a reasonable torsional potential function. Since the outcome of these calculations reveals that this basis set has the proper physical behavior, we use it to compare single-point correlation corrections at MP2, MP3, up to MP4(SDTQ) levels using the appropriate MP2 reference geometries. Additionally, three sets of calculations with progressively increasing basis sets, 6-31G(d,p), 6-311G(d,p), and 6-311G(3df,2p), were performed using model I to delineate basis set effects. Full geometry optimization of each rotamer was carried out at MP2 levels for each of these basis sets.

Calculations were carried out on a Cray C-90 processor using Gaussian 92 software. Default geometry optimization thresholds were as previously described.<sup>4</sup> The energy surface around the staggered conformation was interrogated to ensure that the staggered conformer is not a saddle point. The effect of methyl group  $C_3$  symmetry deviations was assessed by generating more than the required number of conformer energies to fit the three-term potential function (2). Since this potential function satisfies our criterion that all 10 conformer energies fall within  $\sim 1\text{ cm}^{-1}$  of the potential curve described by eq 2 (Appendix 1), we conclude that the  $C_3$  deviations do not lead to serious error. We avoided introducing angular dependence of  $F$  in the torsional Hamiltonian by employing the average calculated value of  $F$  for the nine conformers given in Appendix 2.

One further point needs to be mentioned. For the rigid frame model calculation (model V), the internal rotation angle is fully defined. This is not the case for any of the relaxed model calculations. In calculations using these models, the internal rotation angle  $\tau$  is defined as the average of the three hydrogen atom rotations from the equilibrium ( $\tau = 0$ ) conformer. (See Appendix 1 and our discussion of the internal rotation angle problem in acetaldehyde.<sup>4</sup>)

### 3. Results

MP2/6-311G(3df,2p) and MP2/6-31G(d,p) calculations on the eclipsed and staggered conformers with full geometry optimization are compared in Table I. The largest bond length difference is  $0.003\text{ \AA}$  in the C=C bond; the largest bond angle difference is only  $0.2^\circ$ . The HF geometries will not be discussed in light of the well-known improvement obtained at the MP2 level. The large basis set calculations confirm the conclusion obtained from smaller basis sets that the molecular frame is planar in both the equilibrium  $\tau = 0^\circ$  and in the staggered  $\tau = 60^\circ$

**Table I.** Propene Experimental and ab Initio Optimized Conformer Geometries<sup>a</sup>

	exptl ( $r_s$ ) <sup>b</sup>	MP2/6-311G(3df,2p)		MP2/6-31G(d,p)	
		eclipsed	staggered	eclipsed	staggered
Bond Lengths (Å)					
C=C	1.336	1.3323	1.3326	1.3357	1.3360
C-H <sub>a</sub>	1.091	1.0827	1.0832	1.0811	1.0816
C-H <sub>b</sub>	1.081	1.0808	1.0806	1.0794	1.0792
C-H <sub>c</sub>	1.090	1.0855	1.0844	1.0841	1.0833
C-C	1.501	1.4952	1.5049	1.4960	1.5047
C-H <sub>ip</sub>	1.085	1.0887	1.0873	1.0878	1.0865
C-H <sub>op1</sub>	1.098	1.0907	1.0896	1.0897	1.0889
C-H <sub>op2</sub>	1.098	1.0907	1.0896	1.0897	1.0889
Bond Angles (deg)					
C=C-C	124.3	124.5	124.1	124.5	124.2
H <sub>a</sub> -C=C	120.5	121.1	121.4	121.3	121.5
H <sub>b</sub> -C=C	121.5	121.5	121.4	121.6	121.5
H <sub>c</sub> -C=C	119.0	118.8	118.4	118.9	118.6
C-C-H <sub>ip</sub>	111.2	111.1	111.6	111.0	111.4
C-C-H <sub>op1</sub>	110.7	111.0	111.1	111.1	111.2
C-C-H <sub>op2</sub>	110.7	111.0	111.1	111.1	111.2
H <sub>ip</sub> -C-H <sub>op1</sub>	109.0	108.3	107.7	108.2	107.7
H <sub>ip</sub> -C-H <sub>op2</sub>	109.0	108.3	107.7	108.2	107.7
H <sub>op1</sub> -C-H <sub>op2</sub>	106.1	106.9	107.5	107.1	107.5

<sup>a</sup> Hydrogen atom designations are shown in Figure 1. <sup>b</sup> Experimental ( $r_s$ ) geometry is from D. R. Lide and D. Christensen: Lide, D. R.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374.

conformers. We note that models I-IV yield identical  $C_3$  symmetry geometries for both eclipsed and staggered conformers. However, this is not so for the model V rigid frame calculation because of the artificial  $C_3$  methyl group symmetry constraint. For the case of the polar molecule, acetaldehyde, inclusion of an extensive set of polarization functions in the basis set significantly affects bond length and angle differences between eclipsed and staggered conformers. The geometry differences for the two conformers in propene are only slightly changed (i.e., by  $\leq 0.001$  Å and  $\leq 0.2^\circ$ ) on going from the modest 6-31G(d,p) basis to the best used one, 6-311G(3df,2p). It appears unlikely that further significant changes will be incurred at still larger basis sets.

Propene barrier heights calculated using the basis sets and correlation corrections discussed in section 2 are compared to those obtained from lower level studies in Tables II. Comparison of internal rotation potential constants calculated at the MP2/6-311G(3df,2p) level for the five flexing models is given in Table III. Correlation effects calculated at this basis set using the fully relaxed model I are shown in Table IV. Fundamental and first overtone frequencies are given in Table V. Table VI contains predicted torsional energy levels for both propene- $h_6$  and propene deuterium isotopomers calculated using MP4/6-311G(3df,2p) fully relaxed model potential constants.

#### 4. Internal Rotation Potential Function

(a) **Barrier.** Durig, Guirgis, and Bell, as part of their thorough study of the propene gas-phase FTIR and Raman spectra,<sup>8</sup> review the microwave and infrared work leading to the torsional potential barrier. The quest of many experimental studies for the barrier, starting with Lide and Mann's 1957 microwave  $692 \pm 6$ -cm<sup>-1</sup> estimate,<sup>12</sup> has been quite extensive, and all studies, microwave and IR, conclude that the torsional potential barrier is near 700 cm<sup>-1</sup> (Table II). The best estimate, obtained from combined microwave and IR information, seems to be 694 cm<sup>-1</sup>.<sup>8</sup>

We first discuss the basis set dependence of the ab initio calculated potential barrier, given in Table II. Theoretically, the barrier height can be calculated as an energy difference between the eclipsed and staggered conformers. Small basis set HF predictions up to the double- $\zeta$  level at 635 cm<sup>-1</sup> are much too low. Hartree-Fock predictions made using larger basis sets, starting with 6-31G(d) up to 6-311G(3df,2p), are too high. It is clear

**Table II.** Ab Initio Calculated Barriers and Experimentally Determined Potential Energy Constants (cm<sup>-1</sup>) for Internal Rotation in Propene

Ab Initio			
method	ref	$V_{\text{eff}}$	
HF/STO-3G	<i>e</i>	539.9	
HF/3-21G	<i>e</i>	621.1	
HF/4-21G	<i>f</i>	632.1	
HF/DZ	<i>b</i>	635.4	
HF/6-31G(d)	<i>e</i>	724.3	
HF/6-31G(d,p)	this work	724.1	
HF/6-311G(d,p)	this work	737.0	
HF/6-311G(3df,2p)	this work	774.4	
CISD/6-311G(3df,2p) <sup>a</sup>	this work	727.3	
MP2/6-31G(d)	<i>e</i>	684.8	
MP2/6-31G(d,p)	this work	693.0	
MP2/6-311G(d,p)	this work	686.6	
MP2/6-311G(3d,2p)	this work	706.2	
MP2/6-311G(3df,2p) <sup>a</sup>	this work	718.5	
MP3/6-31G(d)	<i>e</i>	660.6	
MP3/6-311G(3df,2p) <sup>a</sup>	this work	695.5	
MP4(SDTQ)/6-31G(d,p)	this work	660.4	
MP4(DQ)/6-311G(3df,2p) <sup>a</sup>	this work	689.1	
MP4(SDQ)/6-311G(3df,2p) <sup>a</sup>	this work	692.0	
MP4(SDTQ)/6-311G(3df,2p) <sup>a</sup>	this work	689.3	
Experimental			
ref	$V_3$	$V_6$	$V_{\text{eff}}$
<i>b</i>	693.7	-14.0	693.7
<i>c</i>	692.4 ± 6		692.4 ± 6
<i>d</i>	698.4 ± 0.5	-13 ± 2	698.4 ± 0.5
<i>g</i>	682.9		682.9

<sup>a</sup> Calculated at MP2/6-311G(3df,2p) optimized geometries. All other calculations are at geometries optimized at the calculation level. <sup>b</sup> Durig, J. R.; Guirgis, G. A.; Bell, S. *J. Phys. Chem.* **1989**, *93*, 3487. <sup>c</sup> Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868. <sup>d</sup> Hirota, E. *J. Chem. Phys.* **1966**, *45*, 1984. <sup>e</sup> Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035. <sup>f</sup> Bowers, P.; Schäfer, L. *J. Mol. Struct.* **1980**, *69*, 233. <sup>g</sup> Souter, C. E.; Wood, J. L. *J. Chem. Phys.* **1970**, *52*, 674.

**Table III.** Flexing Model Dependence of MP2/6-311G(3df,2p) ab Initio Calculated Potential Constants (cm<sup>-1</sup>) for Internal Rotation in Propene

method	$V_3$	$V_6$	$V_9$
experiment <sup>a</sup>	693.7	-14.0	
model I <sup>b</sup>	718.4	-15.0	0.2
model II <sup>c</sup>	718.6	8.1	-0.1
model III <sup>d</sup>	719.3	-2.8	-0.8
model IV <sup>e</sup>	718.1	12.0	0.4
model V <sup>f</sup>	733.1	-0.6	0.0

<sup>a</sup> Reference *b* of Table II. <sup>b</sup> All skeletal and methyl group hydrogen optimizations independently included. <sup>c</sup> Optimizations in model I calculation restricted by clamping H<sub>a</sub> and H<sub>b</sub> (i.e., CH<sub>2</sub> hydrogens) out-of-plane motions. H<sub>c</sub> out-of-plane motion remains free. <sup>d</sup> Optimizations in model I calculation restricted by clamping H<sub>c</sub> (hydrogen adjacent to methyl group) out-of-plane motion. H<sub>a</sub> and H<sub>b</sub> out-of-plane motions remain free. <sup>e</sup> All skeletal hydrogen out-of-plane motions clamped. <sup>f</sup> Rigid frame calculation with a  $C_3$  symmetry methyl group having identical C-H lengths and HCH angles.

from the calculated barriers in Table II that convergence has not been reached at the HF level.

It is also clear from Table II that inclusion of the correlation correction is very important. In a number of cases it exceeds 50 cm<sup>-1</sup>. This conclusion is parallel to the results of our extensive correlation calculations for the acetaldehyde torsional potential barrier,<sup>6</sup> where the correlation correction to the much lower barrier in this molecule also exceeds 50 cm<sup>-1</sup>. The higher level correlation calculations demonstrate that the apparent reasonable agreement of the MP2/6-31G(d,p) barrier (693 cm<sup>-1</sup>) with experiment is fortuitous and that it is necessary to go to a more accurate reference geometry in conjunction with a higher order electron correlation correction. In fact, an MP4(SDTQ)/6-31G(d,p) calculation at MP2/6-31G(d,p) geometry predicts a much smaller barrier, 660

**Table IV.** Electron Correlation Dependence of 6-311G(3df,2p) Completely Relaxed ab Initio Calculated Propene Internal Rotation Potential Constants (cm<sup>-1</sup>)<sup>a</sup>

method	$V_3$	$V_6$	$V_9$
experiment <sup>b</sup>	693.7	-14.0	
HF <sup>c</sup>	774.5	-14.3	0.0
MP2	718.4	-15.0	0.2
MP3	695.4	-13.0	0.1
MP4(DQ)	689.1	-12.9	0.0
MP4(SDQ)	692.3	-12.9	-0.2
MP4(SDTQ)	689.1	-13.5	0.2

<sup>a</sup> All potential constants are calculated using the fully relaxed model I. <sup>b</sup> Reference b of Table II. <sup>c</sup> Calculated using HF optimized geometries. All correlated level calculations are at the MP2/6-311G(3df,2p) optimized geometries.

**Table V.** Electron Correlation Dependence of 6-311G(3df,2p) Completely Relaxed ab Initio Calculated Propene Fundamental and First Overtone Frequencies (cm<sup>-1</sup>)<sup>a</sup>

method	fundamental <sup>b</sup>		first overtone <sup>c</sup>	
	$A$	$E$	$A$	$E$
experiment <sup>d</sup>	188.1		357.7	359.3
HF	201.1	201.0	383.9	385.3
MP2	192.5	192.4	366.4	368.4
MP3	189.7	189.5	360.0	362.3
MP4(DQ)	188.7	188.6	358.0	360.4
MP4(SDQ)	189.1	189.0	359.0	361.3
MP4(SDTQ)	188.5	188.4	357.8	360.2

<sup>a</sup> Calculated using fully relaxed model I potential constants of Table IV. All calculations utilize the fully relaxed ab initio MP2/6-311G(3df,2p)  $F$  constant = 7.1731. See footnote c to Table IV. <sup>b</sup>  $1(A) \leftarrow 0(A)$  and  $1(E) \leftarrow 0(E)$  transitions. <sup>c</sup>  $2(A) \leftarrow 0(A)$  and  $2(E) \leftarrow 0(E)$  transitions. <sup>d</sup> Reference b of Table II.

cm<sup>-1</sup>. We note that models I–IV yield essentially the same barrier since they yield identical  $C_2$  symmetry geometries for both eclipsed and staggered conformers.

**(b) Potential Constants.** All of the experimentally derived potential constants for internal rotation in propene, whether originating from microwave, infrared, or Raman data, lead to a substantial negative  $V_6$  term (Table II). The generally accepted value is -14.0 cm<sup>-1</sup>,<sup>8,13</sup> although there is a not well-resolved Raman spectra study, suggesting that  $V_6$  has a larger negative value.<sup>14</sup>

We now compare potential constants calculated with the various models using the MP2/6-311G(3df,2p) basis set (Table III). All models give essentially the same value for the  $V_3$  term (the rigid frame model V excepted). As we have discussed earlier, the barrier height determining  $V_3$  term depends only on combined basis set correlation effects. The magnitude of  $V_9$  is calculated to be small, <1 cm<sup>-1</sup> in all cases. However, the  $V_6$  term, which is of monumental importance to the potential function shape, strongly depends on the choice of flexing model.

The model IV calculations represent the same physical model which proved to be successful for prediction of the methyl torsional fundamental frequencies for non-ethylenic molecules.<sup>2-4</sup> It flexes the methyl ethylene skeleton but imposes the condition that the skeleton including the skeletal hydrogen atoms remain planar during the methyl torsional rotation. The outcome is that  $V_6 > 0$ . This conclusion regarding the sign of  $V_6$  holds at all levels of HF and electron-correlated calculations.

The next step (in model II) introduces, in addition to the in-plane coordinate optimization, out-of-plane motion of the skeletal hydrogen atom adjacent to the methyl group, H<sub>c</sub>. Although the magnitude of  $V_6$  is somewhat reduced from that in model IV,  $V_6$  is still >0.

Model III represents another step in removing the classical assumption that the CH<sub>2</sub>=C< group remains planar and that the hydrogens in the ethylenic group are stationary during internal

**Table VI.** Propene Torsional Energy Levels Calculated from MP4/6-311G(3df,2p) Potential Constants (cm<sup>-1</sup>)<sup>a</sup>

energy level	$A$	$E$
Propene- $h_6$ ( $F = 7.17312$ )		
zero-point	98.05	98.05
1	188.55	188.40
2	357.74	360.10
3	518.63	499.28
4	592.68	640.78
5	846.83	735.95
Propene- $d_3$ ( $F = 4.42753$ )		
zero-point	77.63	77.63
1	150.78	150.77
2	291.62	291.74
3	421.45	419.87
4	525.35	535.79
5	656.57	612.24
6	677.43	740.41
Propene- $d_2$ ( $F = 6.83418$ )		
zero-point	95.79	95.79
1	184.41	184.30
2	350.89	352.72
3	507.61	491.79
4	585.84	628.68
5	822.76	718.85
Propene- $d_1$ ( $F = 6.80272$ )		
zero-point	95.57	95.57
1	184.02	183.91
2	350.24	352.03
3	506.58	491.07
4	585.20	627.56
5	820.53	717.28
Propene- $d_6$ ( $F = 3.85271$ )		
zero-point	72.55	72.55
1	141.25	141.24
2	274.06	274.10
3	397.20	396.57
4	502.70	507.89
5	615.93	589.18
6	648.67	694.81
7	848.18	766.55

<sup>a</sup> Potential constants  $V_3 = 689.12$ ;  $V_6 = -13.53$ ;  $V_9 = 0.24$  cm<sup>-1</sup>. Average  $F$  constants are calculated from MP2/6-311G(3df,2p) conformer geometries (see Appendix 2).

rotation. It introduces, in addition to the in-plane optimizations of model IV, out-of-plane motions of the CH<sub>2</sub> hydrogens. The outcome is different from that from models II and IV. The sign of  $V_6$  is reversed from that in model IV, but the magnitude of  $V_6$  is too small.

The final stage of our study of flexing motions in propene takes into account (in model I) independent wagging distortions of all three skeletal hydrogens. The result is dramatic. The magnitude of  $V_6$  is large, 15.0 cm<sup>-1</sup>, and its sign is negative.

To investigate the effect of electron correlation, we retain the 6-311G(3df,2p) basis set but vary the correlation correction from none to MP4(SDTQ) (Table IV). The outcome is that all levels of calculation lead to reasonable agreement with the -14.0-cm<sup>-1</sup> experimental  $V_6$  value. At the MP4(SDTQ) level,  $V_6$  is calculated as -13.5 cm<sup>-1</sup>.

## 5. Internal Rotation Frequencies

To predict torsional frequencies,  $F$  is required. We take the tack of employing a pure ab initio calculation of an average  $F = 7.1731$  from nine MP2/6-311G(3df,2p) fully optimized conformer geometries (see Appendix 2).

We start with the fully relaxed model I prediction of the propene fundamental frequency (Table V) using the MP4(SDTQ)/6-311G(3df,2p) potential function (Table IV). The complete set of torsional energy levels for propene and several deuterium isotopomers calculated from this potential function and the ab initio predicted average  $F$  constants is given in Table VI.

(13) Hirota, E. *J. Chem. Phys.* 1966, 45, 1984.

(14) Engeln, R.; Reuss, J. *J. Chem. Phys.* 1991, 156, 215.

Comparison to the Durig, Guirgis, and Bell 188.05-cm<sup>-1</sup> FTIR gas-phase frequency<sup>8</sup> (Table V) shows impressive agreement, i.e., to within 1 cm<sup>-1</sup>! Table V also shows that there is slightly poorer agreement with the experimental fundamental for lower MP4 correlation levels, with more severe degradation at MP2 and HF levels of calculation. *Removal of the various hydrogen out-of-plane flexings carried out individually or in concert, but with retention of the MP4(SDTQ) correlated level 6-311G(3df,2p) basis set, causes large disparity.* The litmus test for the importance of skeletal hydrogen out-of-plane displacements to the frequency predictions is that their removal (model IV) generates nearly 15-cm<sup>-1</sup> disparity at the MP2 level, actually slightly worse than that found with the medium-size basis set MP2/6-31G(d,p) prediction and much worse than that for any of the non-ethylenic molecules that we have studied.

Durig, Guirgis, and Bell<sup>8</sup> also observed the first overtone transition in the Raman spectrum of gaseous propene at 358 cm<sup>-1</sup>. The overtone frequency is again impressively predicted at 357.8 cm<sup>-1</sup> (!) by the *fully relaxed* MP4(SDTQ)/6-311G(3df,2p) potential function. Large disparities between the Raman overtone frequency and model IV flexing predictions at all basis sets and correlation levels are found. These disparities are larger than those for the fundamental, i.e., the model IV calculated overtone frequencies are 15-20 cm<sup>-1</sup> too high, a deficiency much worse than for the non-ethylenic molecules. As with the fundamental, introduction of either ethylenic CH<sub>2</sub> or H<sub>c</sub> wagging motion *alone* produces only minor improvements.

## 6. Discussion

An important conceptual conclusion can be drawn from the flexing calculations. The large negative  $V_6$  term in the internal rotation potential function can be understood only by requiring degrees of freedom that allow independent out-of-plane wagging motion of the skeletal hydrogen atoms. Examination of the CH<sub>2</sub> hydrogen atom out-of-plane displacements ( $z_a$  and  $z_b$ ) as the methyl group rotates shows that the two CH<sub>2</sub> hydrogens move in concert (but not equivalently) in opposite directions. Projection of the calculated  $z_a$  and  $z_b$  displacements onto primitive ethylenic twisting and CH<sub>2</sub> wagging coordinates,  $S_\phi = (z_a - z_b)/\sqrt{2}$  and  $S_\omega = (z_a + z_b)/\sqrt{2}$ , is useful to obtain understanding. The outcome is that the coefficient of  $S_\phi$ ,  $\alpha_\phi$ , is much greater than the coefficient of  $S_\omega$ ,  $\alpha_\omega$ , for any angle,  $\tau > 0$ .<sup>15</sup> *Thus the CH<sub>2</sub> out-of-plane displacements are dominantly twisting of the ethylenic CH<sub>2</sub> group.* The hydrogen atom adjacent to the methyl group out-of-plane displacement, H<sub>c</sub>, somewhat exceeds the CH<sub>2</sub> twisting displacement, as shown in Figure 2.<sup>16</sup> The maximum ethylenic twisting angle is  $\sim 3^\circ$  and the maximum H<sub>c</sub> wagging angle is  $\sim 4^\circ$ , both occurring when  $\tau$  is near  $30^\circ$ .

We conclude that *internal rotation in propene initiates both ethylenic twisting and out-of-plane wagging of H<sub>c</sub>*. These simultaneous motions are important determinants for the internal rotation potential shape; without these motions, neither the fundamental nor the overtone torsional frequencies can be reasonably understood.

No opportunity for these motions exists in the double methyl compounds acetone and dimethyl ether. We discuss the hydrogen wagging motion in acetaldehyde in another publication.<sup>17</sup>

One additional point follows from the projection calculation by regarding the torsion as coupled to normal modes involving CH<sub>2</sub> twist [990 cm<sup>-1</sup> (*A'*) and 1188 cm<sup>-1</sup> (*E*)], CH<sub>2</sub> wag [912 cm<sup>-1</sup>], and H<sub>c</sub> wag [575 cm<sup>-1</sup>].<sup>18</sup> The approximate equivalence of the CH<sub>2</sub> wag and CH<sub>2</sub> twist frequencies—far above the 188-

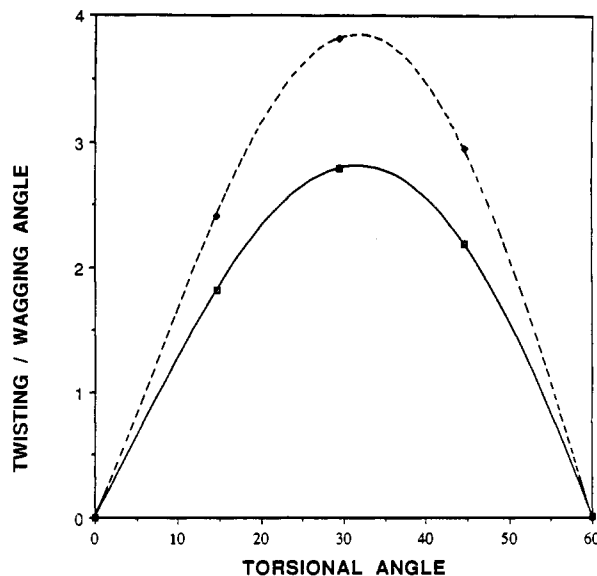


Figure 2. Dependence of ethylenic hydrogen twisting angle,  $\phi$  (solid line), and ethylenic H<sub>c</sub> wagging angle (dashed line) on the methyl rotation angle  $\tau$ . Angles are in degrees. The twist angle  $\phi$  is calculated from the average of the fully relaxed model MP2/6-311G(3df,2p) calculated H<sub>a</sub> and H<sub>b</sub> displacements (see text).

cm<sup>-1</sup> methyl torsion frequency—taken together with the projection calculation result,  $\alpha_\phi \gg \alpha_\omega$ , implies that for the coupling matrix element between torsion and twist,  $H(Q_\tau, Q_\phi) \gg H(Q_\tau, Q_{CH_2\omega})$  (the latter involving CH<sub>2</sub> wag). A similar line of reasoning implies that  $H(Q_\tau, Q_\phi) > H(Q_\tau, Q_{H_c\omega})$  and also that  $H(Q_\tau, Q_\phi, Q_{H_c\omega})$  is substantial. Spectroscopic exemplifications of the strong coupling envisioned between torsion and skeletal hydrogen out-of-plane normal modes will be isotopic frequency, IR intensity, microwave fine structure, and intramolecular vibrational relaxation effects.

## 7. Summary and Conclusions

The principal conclusions from this study of flexing attendant to internal rotation in propene are first that the large amplitude motion inherent in methyl torsional rotation initiates ethylenic skeletal hydrogen out-of-plane motions. The dominant induced motions are ethylenic twist and wagging of the hydrogen atom adjacent to the methyl carbon. The torsional fundamental and first overtone frequencies in propene cannot be understood without appreciation of this highly impure torsional motion. Thus methyl torsion in propene is more complex than that in small methyl carbonyl molecules. Triggering of ethylenic twisting motion by methyl torsional rotation strongly suggests important intramolecular vibrational relaxation effects in the electronic spectra of propene.

The second conclusion is that electron correlation and polarization function effects on the torsional barrier are large and must be considered in any attempt to understand and accurately predict, by an initio calculation, propene internal rotation potential functions and frequencies. Our calculations show a 50-cm<sup>-1</sup> increase in the barrier on going from a 6-31G(d,p) basis set to 6-311G(3df,2p) at the HF level. At the latter level, the predicted barrier is more than 80 cm<sup>-1</sup> too high. The importance of the correlation effect is seen from nearly 90-cm<sup>-1</sup> flattening of the potential barrier by an MP4(SDTQ) correlation correction using the 6-311G(3df,2p) basis. Even a modest MP2 correlation correction decreases the barrier by nearly 60 cm<sup>-1</sup>.

When extensive polarization functions and high-order correlation corrections are included, i.e., at the MP4(SDTQ)/6-311G(3df,2p) level, the barrier is calculated at 689 cm<sup>-1</sup>, only 5 cm<sup>-1</sup> below the experimentally established barrier.

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(15) E.g., at  $\tau = 30^\circ$ ,  $\alpha_\phi/\alpha_\omega > 3$ .

(16) Since  $\alpha_\phi \gg \alpha_\omega$ , we neglect  $\alpha_\omega$  and determine  $\phi$  from the average of the H<sub>a</sub> and H<sub>b</sub> displacements.

(17) Goodman, L.; Leszczynski, J.; Kundu, T. *J. Chem. Phys.* **1994**, *100*, Jan 15.

(18) Silvi, B.; Labarbe, P.; Perchard, J. P. *Spectrochim. Acta* **1973**, *29A*, 263.

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#### Appendix 1. Remarks on the Torsional Angle $\tau$ .

Table VII shows differences between the MP2/6-311G(3df,2p) computed C=C—C—H<sub>methyl</sub> dihedral angles and the "reference" hydrogen rotation angle,  $\tau_{H_1}$ . The differences among the three hydrogen rotation angles are, in general, 1–2°. To get around this ambiguity in the torsional angle, we define the internal rotation angle,  $\tau$ , as the average of the three hydrogen atom rotations from the equilibrium (eclipsed) geometry. These values are designated as  $\tau_{av}$  in Table VII. This is the methyl rotation angle utilized in the potential function fits. As can be seen from Table VII, all of the 10 conformer MP4(SDTQ)/6-311G(3df,2p) energies fall within 1.1 cm<sup>-1</sup> of the potential curve.

#### Appendix 2. The Kinetic Energy Coefficient $F$ .

The kinetic energy coefficient is conventionally expressed by  $F = h^2/8\pi^2 r I$ , in terms of the methyl top moment of inertia about its symmetry axis,  $I_\tau$ , and the quantity  $r = 1 - (\lambda_a^2 I_\tau / I_a) - (\lambda_b^2 I_\tau / I_b)$ . The direction cosines,  $\lambda_a$  and  $\lambda_b$ , between the (in-molecular-plane) methyl rotor axis and the molecular principal axes,  $a$  and  $b$ , respectively, define moments of inertia  $I_a$  and  $I_b$ .

The  $F$  values calculated for propene from the nine methyl conformer MP2/6-311G(3df,2p) optimized geometries are given in Table VIII. The torsional angle ( $\tau_{av}$ ) dependence of  $F$  causes <5% change between the eclipsed and staggered conformers. Because of this insensitivity, we calculate the average  $F$  value for the nine conformers and then employ this value in the torsional Hamiltonian without explicitly introducing angular dependence. In effect, we are neglecting kinetic energy coupling. A calculation of the sensitivity of the predicted frequencies to  $F$  {MP4(SDTQ)/6-311G(3df,2p) potential constants} shows that the fundamental varies by 1 cm<sup>-1</sup> and the overtone by 2 cm<sup>-1</sup> for a 0.1-cm<sup>-1</sup>  $F$  variation. The turning points for the fundamental and first

**Table VII.** Propene Methyl Torsional MP4(SDTQ)/6-311G(3df,2p) Potential Fits (cm<sup>-1</sup>)

$\tau_{H_1}$	$\tau_{H_2}$	$\tau_{H_3}$	$\tau_{av}$	energy	fitted energy <sup>a</sup>	difference
0.00	0.60	-0.60	0.00	0.00 <sup>b</sup>	0.00	0.00
15.00	15.03	13.92	14.65	89.81	90.18	-0.37
30.00	29.57	28.79	29.45	322.36	321.25	1.11
45.00	44.59	44.22	44.60	575.75	576.03	-0.28
60.00	59.83	60.35	60.06	689.30	689.36	-0.06
75.00	75.67	76.42	75.70	571.67	571.88	-0.21
90.00	90.50	91.55	90.68	318.33	318.92	-0.59
105.00	104.77	105.72	105.17	92.16	92.32	-0.16
120.00	118.84	119.45	119.43	-0.20	0.14	-0.34
180.00	180.20	179.80	180.00	689.66	689.36	0.30

<sup>a</sup> Fitted to eq 2 with potential constants  $V_3 = 689.12$ ;  $V_6 = -13.53$ ;  $V_9 = 0.24$  cm<sup>-1</sup>. <sup>b</sup> Conformer energies relative to eclipsed conformer energy,  $E = -117.672$  5428 hartrees.

**Table VIII.** Propene Kinetic Energy Coefficients  $F$ , Calculated from MP2/6-311G(3df,2p) ab Initio Optimized Methyl Conformer Geometries (cm<sup>-1</sup>)

$\tau_{av}$ <sup>a</sup>	$F$	$\tau_{av}$ <sup>a</sup>	$F$
0.00	7.195 59	75.70	7.132 67
14.65	7.196 35	90.68	7.132 13
29.45	7.194 54	105.17	7.161 79
44.6	7.188 82	119.43	7.193 71
60.06	7.162 42	average	7.173 12

<sup>a</sup>  $\tau_{av}$  values are from Table VII.

overtone torsional vibrations are computed from eq 2 at 28° and 38°, respectively. Thus, the <0.01-cm<sup>-1</sup> variation in  $F$  over  $\tau = 0$ –38° leads to ~0.2-cm<sup>-1</sup> error in the fundamental and 0.3-cm<sup>-1</sup> error in the first overtone frequencies calculated with a single averaged kinetic energy coefficient. The MP2/6-311G(3df,2p) ab initio averaged  $F$  constant (7.1713 cm<sup>-1</sup>) is only in fair agreement with Hirota's value of  $F = 7.1007$  cm<sup>-1</sup> obtained from microwave data, but in general lower values of  $F$  have been obtained from microwave splittings than those calculated from a structure.