



# An ab initio calculation of the rotation and internal-rotation energy levels of the ethyl radical

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## Abstract

By ab initio calculation at ten values of the internal-rotation angle we have determined the minimum energy path for internal-rotation in the ethyl radical  $C_2H_5$ . Bond-length and bond-angle relaxation are allowed via full optimization, using unrestricted second-order Møller–Plesset perturbation theory, for each choice of torsional dihedral angle. We find that the only significant relaxation is a wagging (or inversion) of the  $CH_2$  group through  $\pm 9^\circ$  about a planar  $C-CH_2$  geometry as the internal-rotation proceeds. The torsional potential can be accurately fitted to a  $V_6$  function and the barrier to internal-rotation is calculated to be  $26\text{ cm}^{-1}$ . Using our general rotation–contortion Hamiltonian and computer program we have calculated the rotation–torsion energy levels of the molecule using this minimum-energy path. Brief comparison is made to recent experimental measurements of the rotational fine structure of the  $\nu_9 = 1$  fundamental. © 1998 Elsevier Science B.V.

## 1. Introduction

In connection with our work on the  $CH_5^+$  molecular ion [1] we have developed a general rotation–contortion Hamiltonian and computer program that can be used to calculate the rotation–contortion energy levels of any molecule that has one large amplitude (contortional) degree of freedom [2]. The most significant aspect of this Hamiltonian is its ability to incorporate a parametrized geometrical path of any desired flexibility, hence avoiding any approximations or perturbation treatment for the large amplitude mode. In the present paper we use the program to calculate the rotation and internal-rotation energy levels of the ethyl radical  $C_2H_5$ . We use ab initio calculations to determine the optimized structure of the molecule, and the potential energy, along the minimum energy path for internal-rotation.

Our work has been inspired by the observation and analysis of a high resolution spectrum of a fundamental band of the ethyl radical in the gas phase by Sears et al. [3], having a band origin at  $528.1\text{ cm}^{-1}$ . This fundamental ( $\nu_9$ ) corresponds to the out-of-plane or umbrella inversion motion at the  $CH_2$  radical center (the  $CH_2$  wagging motion [4,5]). In this spectrum there is clear evidence for almost free internal-rotation, and from the analysis a torsional barrier height of about  $20\text{ cm}^{-1}$  was determined in Ref. [3]. The approximate model Hamiltonian used in Ref. [3] was unable to precisely fit the data, and we hope that our calculations will lead to a precise simulation of this spectrum.

Previous ab initio calculations at correlated levels of theory [6,7] have been concerned with determining the equilibrium structure, harmonic frequencies, and internal-rotation barrier height for use in the

study of hyperfine structure [6] and rate constants for the  $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$  reaction [7]. There has been no previous calculation of the rotation and internal-rotation energy levels of the ethyl radical based on an ab initio potential surface.

## 2. The internal-rotation minimum energy path

Our ab initio calculations were performed at the unrestricted second-order Møller–Plesset (UMP2) level of theory [8] with the cc-pVTZ basis set [9], using the GAUSSIAN94 program package [10]. Initially, geometry optimizations and harmonic frequencies were determined for the internal-rotation minimum and maximum conformations (see Fig. 1). The minimum energy conformation is traditionally called “staggered” (see Pacansky and Dupuis [11]) but has unfortunately been called “eclipsed” by some authors [3,6]; at this conformation the bisector of the  $\text{CH}_2$  group is in the same plane as one of the CH bonds of the  $\text{CH}_3$  group and it is tilted towards this CH bond out of collinearity with the CC bond by  $9.2^\circ$  (the out-of-plane wag angle). The saddle point between the successive internal-rotation minima has the plane of the  $\text{CH}_2$  group in the same plane as one

of the CH bonds in the  $\text{CH}_3$  group, and the bisector of the  $\text{CH}_2$  group is tilted away from that CH bond out of collinearity with the CC bond by  $0.5^\circ$  (the in-plane rock angle); we call this conformation the “eclipsed” conformation.

In 1991, Suter and Ha [6] published UMP2 eclipsed and staggered structures and harmonic frequencies of  $\text{C}_2\text{H}_5$  obtained with the smaller 6-31G(d, p) basis set. Our new results are but little different. The cc-pVTZ bond lengths are 0.1% smaller, and all of the harmonic frequencies are 1–2% smaller except for the umbrella mode, which matches the 6-31G(d, p) result ( $470 \text{ cm}^{-1}$ ) at the minimum conformation, and is  $50 \text{ cm}^{-1}$  higher than the 6-31G(d, p) result ( $390 \text{ cm}^{-1}$ ) at the maximum conformation. This is of some relevance to the separability of the internal-rotation mode from the umbrella mode, as the difference in harmonic umbrella frequency between eclipsed and staggered conformations is now only  $29 \text{ cm}^{-1}$  ( $470 \text{ cm}^{-1}$  at the minimum and  $441 \text{ cm}^{-1}$  at the internal-rotation maximum), reflecting a smaller amount of coupling than would previously have been thought.

Hase and coworkers [7] have more recently determined geometries and harmonic frequencies for the minimum at six different levels of ab initio theory. Again their results are similar to ours; the only significant improvement is a reduction of the out-of-plane wag angle by  $1.0^\circ$  at equilibrium with improved (post-MP2) correlation.

For the determination of the minimum energy path (MEP) for internal rotation, we performed full geometry optimizations at the UMP2/cc-pVTZ level of theory at eight more values of the dihedral angle  $\text{H}_7\text{C}_2\text{C}_1\text{H}_3$  (denoted  $\tau_{73}$ , measured in a right-handed sense about  $\text{C}_2 \rightarrow \text{C}_1$ ; see Fig. 1). The torsional angle  $\tau$  is defined as the average of all six dihedral angles between the CH bonds of the  $\text{CH}_3$  and  $\text{CH}_2$  rotors. At each calculated point the values of the dihedral angle  $\tau_{73}$ , of the angle  $\tau$ , and of the resulting potential energy  $V$ , are given in Table 1. We can fit this potential using a simple  $V_6$  function of  $\tau$ , and the values of this fitted function are also given in Table 1. This fitted function has an internal-rotation barrier height of  $36 \text{ cm}^{-1}$ , which we can correct with the zero-point vibrational energies (ZPVE) of the other  $3N - 7 = 14$  vibrational modes (taken as half the sum of the UMP2/cc-pVTZ harmonic frequen-

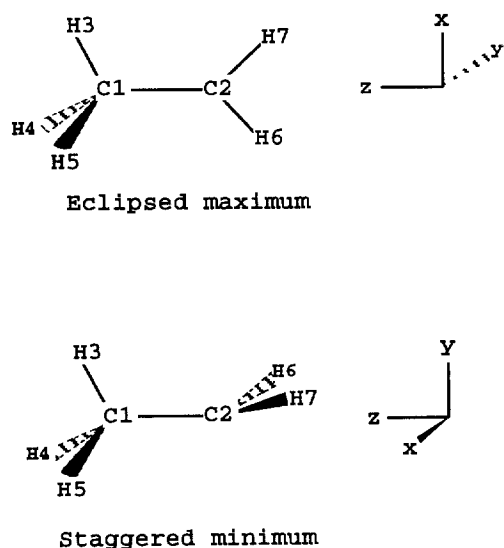


Fig. 1. The structure of the ethyl radical at equilibrium, and at the saddle point for the internal-rotation, including the molecule fixed ( $xyz$ ) axis system.

Table 1

Calculated values of the  $\text{H}_7\text{C}_2\text{C}_1\text{H}_3$  dihedral angle  $\tau_{73}$ , internal-rotation parameter  $\tau$  and the electronic energy  $V_{\text{elec}}$  at the ten optimized points, and the fitted value of  $V_{\text{elec}}$  obtained using a  $V_6$  cosine potential<sup>a</sup>

$\tau_{73}$	$\tau$	$V_{\text{elec}}$	$V_{\text{elec}}^{\text{fitted}}$
0.00	0.00 <sup>c</sup>	36.4	36.5
5.00 <sup>b</sup>	4.16	34.7	34.8
10.00 <sup>b</sup>	8.31	30.1	30.0
15.00 <sup>b</sup>	12.52	23.0	23.0
20.00 <sup>b</sup>	16.77	15.1	14.9
25.00 <sup>b</sup>	21.11	7.5	7.4
30.00 <sup>b</sup>	25.57	2.0	1.9
34.86	30.00 <sup>c</sup>	0.0	0.0
35.00 <sup>b</sup>	30.25	0.0	0.0
40.00 <sup>b</sup>	34.97	2.6	2.4

<sup>a</sup> Angles in degrees, energies in  $\text{cm}^{-1}$ .

<sup>b</sup> This value frozen during geometry optimization.

<sup>c</sup> This value determined by symmetry.

cies), obtaining an effective barrier height of  $26 \text{ cm}^{-1}$ . This matches exactly the previous results of Suter and Ha with the smaller basis set [6], although their electronic barrier height and ZPVE correction were almost double ours in size.

The  $\tau$ -dependent values of the various other internal coordinates were accurately fitted by the following analytical functions (where bond lengths are in Å and bond angles are in degrees):

$$r_{\text{C}_1\text{C}_2} = 1.4864 + 0.0001 \cos 6\tau, \quad (1)$$

$$r_{\text{C}_1\text{H}_7} = 1.0768 + 0.0006 \cos 3\tau - 0.0002 \cos 6\tau, \quad (2)$$

$$r_{\text{C}_1\text{H}_3} = 1.0906 - 0.0041 \cos 2\tau + 0.0003 \cos 4\tau, \quad (3)$$

$$\alpha_{\text{C}_1\text{C}_2\text{H}_7} = 120.89 + 0.58 \cos 3\tau + 0.14 \cos 6\tau, \quad (4)$$

$$\alpha_{\text{C}_2\text{C}_1\text{H}_3} = 111.63 + 0.03 \cos 2\tau + 0.06 \cos 4\tau, \quad (5)$$

and

$$\tau_{73} = \tau - 0.72 \sin 2\tau + 5.45 \sin 3\tau. \quad (6)$$

Other internal coordinates are obtained by symmetry, eg.  $r_{\text{C}_1\text{H}_4}(\tau) = r_{\text{C}_1\text{H}_3}(\tau + 2\pi/3)$ . These equations define the minimum energy path we use in the next section. The  $\tau$ -dependence of the bond lengths is almost negligible. The most significant relaxation effect is the  $\text{CH}_2$  wag ( $5.45 \sin 3\tau$  in  $\tau_{73}$ ), with

minor effects being methyl torsional defects ( $-0.72 \sin 2\tau$  in  $\tau_{73}$ ) and  $\text{CH}_2$  rocking ( $0.58 \cos 3\tau$  in  $\alpha_{\text{C}_1\text{C}_2\text{H}_7}$ ). This accords with the theoretical discussion of the problem given by Sørensen [12]. The structure relaxation can be rationalized in terms of the need to minimize non-bonded H–H interactions. There is practically no methyl tilting ( $0.03 \cos 2\tau$  in  $\alpha_{\text{C}_2\text{C}_1\text{H}_3}$ ), in accord with the results of the fitting to the data [3].

### 3. The rotation internal-rotation energy levels

The internal-coordinate functions of Eqs. (1)–(6) were first transformed analytically to Cartesian coordinate functions, employing molecule-fixed  $xyz$ -axes. These axes were chosen such that the origin was at the centre of mass, the  $z$ -axis parallel to the C–C bond axis, and the  $xz$ -plane parallel to a line passing through  $\text{H}_6$  and  $\text{H}_7$  (see Fig. 1). From the Cartesian coordinate functions we can determine the elements of the  $4 \times 4$  extended moment of inertia matrix at any given value of the torsional coordinate  $\tau$  (see Ref. [2]). Inverting this  $\tau$ -dependent matrix gives the  $\tau$ -dependent  $\mu$  matrix elements that we need for the kinetic energy part of the exact rotation–contortion Hamiltonian:

$$\hat{H} = \hat{H}^{\text{rot}} + \hat{H}^{\text{rot},\tau} + \hat{H}^{\tau}, \quad (7)$$

where

$$\hat{H}^{\text{rot}} = (1/2) \sum_{\alpha} \sum_{\beta}^{\text{xyz}} \mu_{\alpha\beta} \hat{J}_{\alpha} \hat{J}_{\beta} \quad (8)$$

$$\begin{aligned} \hat{H}^{\text{rot},\tau} = (1/2) \sum_{\alpha}^{\text{xyz}} [\hat{J}_{\tau}, \mu_{\alpha\tau}] \hat{J}_{\alpha} \\ + (1/2) \sum_{\alpha}^{\text{xyz}} \mu_{\alpha\tau} (\hat{J}_{\alpha} \hat{J}_{\tau} + \hat{J}_{\tau} \hat{J}_{\alpha}), \end{aligned} \quad (9)$$

and

$$\begin{aligned} \hat{H}^{\tau} = (1/2) \mu_{\tau\tau} \hat{J}_{\tau}^2 + (1/2) [\hat{J}_{\tau}, \mu_{\tau\tau}] \hat{J}_{\tau} \\ + (1/2) |\mu|^{1/4} [\hat{J}_{\tau}, \mu_{\tau\tau} |\mu|^{-1/2} [\hat{J}_{\tau}, |\mu|^{1/4}]] \\ + V(\tau). \end{aligned} \quad (10)$$

In Eqs. (8) to (10)  $\hat{J}_x$ ,  $\hat{J}_y$  and  $\hat{J}_z$  are the components of the total angular momentum operator along molecule-fixed axes,  $\hat{J}_\tau$  is the torsional momentum

Table 2

The rotation–torsion energy levels (in  $\text{cm}^{-1}$ ) and zero-point energy (ZPVE) obtained for  $J = 0, 1$ , and 2

$J$	$K$	$K_i$	Symmetry	Energy
2	2	3	$A_1''$	282.892
			$A_2''$	57.894
			$A_2''$	282.892
			$A_1''$	57.894
			$A_1''$	282.892
		2	$E'$	173.470
			$E'$	22.776
			$E''$	91.293
				16.645
			0	$A_1''$
	$A_2''$	39.522		
	3	$A_1'$		200.549
		$A_2'$		87.508
		$A_2'$		200.568
	1	2	$A_1'$	87.490
			$E''$	108.168
			$E''$	33.813
			$E'$	46.365
			$E'$	8.998
		0	$A_2''$	13.268
$A_1''$			13.102	
3			$A_1''$	141.732
			$A_2''$	128.749
			$E'$	62.372
2	0	$E''$	18.910	
		$A_2''$	4.404	
		3	$A_2'$	197.618
			$A_1'$	84.566
			$A_1'$	197.625
	2	$A_2'$	84.560	
		$E''$	105.232	
		$E''$	30.877	
		$E'$	43.428	
		$E'$	6.061	
1	0	$A_1''$	10.277	
		$A_2''$	10.221	
		3	$A_1''$	138.796
			$A_2''$	125.812
			$E'$	59.435
	2	$E''$	15.972	
		$E''$	1.468	
		$A_2''$	137.328	
		$A_1''$	124.344	
		$E'$	57.967	
0	0	$E''$	14.504	
		$E''$	0.000	
		$A_1'$	0.000	
		ZPVE	12.973	

Table 3

The wavenumbers (in  $\text{cm}^{-1}$ ) for selected  $\nu_9 = 1$  transitions in  $\text{C}_2\text{H}_5$

$J$	$K_i$	$K_{\text{upper}}$	$K_{\text{lower}}$	$\gamma^a$	Observed <sup>b</sup>	Calculated
1	0	1	0	0	536.829	536.853
2	0	1	0	0	536.783	536.798
3	0	1	0	0	536.702	536.716
4	0	1	0	0	536.593	536.607
5	0	1	0	0	536.460	536.473
2	1	2	1		535.350	535.747
3	1	2	1		535.354	535.740
4	1	2	1		535.333	535.722
5	1	2	1		535.309	535.687
4	-2	-3	-2		534.005	534.610
5	-2	-3	-2		533.993	534.596
4	3	4	3	0	532.819	533.487
4	3	4	3	1	532.819	533.487
5	3	4	3	0	532.808	533.481
5	3	4	3	1	532.808	533.481

<sup>a</sup> This quantum number is for transitions involving  $K_i = 0, 3, 6, 9$ , etc.

<sup>b</sup> Ref. [3].

operator, and  $|\mu|$  is the determinant of the  $\mu$  matrix. For the potential function we take

$$V(\tau) = (V_6/2)(1 + \cos 6\tau);$$

$$V_6 = 26 \text{ cm}^{-1}. \quad (11)$$

This Hamiltonian is solved by a combination of numerical integration and matrix diagonalization as described in Ref. [2]. In making this calculation of the rotation and internal-rotation energies we found that satisfactory convergence in the matrix diagonalization stage could be achieved with a basis set that included internal-rotation functions up to those having  $K_i = 12$ , where  $K_i$  is the internal rotation quantum number. The energies, and symmetries in the  $G_{12}$  molecular symmetry group, are given in Table 2.

We also converted our Table 2 results to  $\nu_9 = 1$  rovibrational transition wavenumbers by calculating the appropriate  $\Delta K = 1$  differences and adding the experimental band origin value of  $528.1 \text{ cm}^{-1}$ , and in Table 3 compare some of these results to those assigned by Sears et al. [3].

#### 4. Discussion

It is clear that the internal-rotation motion in the ethyl radical is almost free with a barrier of about  $25 \text{ cm}^{-1}$ , and that a rigid coaxial  $C_{3v}-C_{2v}$  internal-rotation model neglects primarily only the out-of-plane  $\text{CH}_2$  wagging relaxation. We do not achieve a close fitting of the data with this purely ab initio calculation. The next stage is to attempt a least squares fitting of the data, in which we adjust the minimum energy path and internal-rotation potential parameters, both in the ground state and in the wagging fundamental. Centrifugal distortion will almost certainly also have to be included. Work along these lines will be initiated, in collaboration with the authors of Ref. [3], in the hope of precisely understanding their spectrum and what is required to reproduce it.

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