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Inversion-torsional motion in the ethyl radical

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ABSTRACT

The two dimensional potential energy surface for inversion of the methylene group and torsion of the methyl group in the ethyl radical has been calculated using B3LYP method and the aug-cc-pVQZ basis set. The potential was corrected for harmonic zero-point vibrational energies of remaining 13 motions and fitted to the mixed Fourier expansion. The rotation-inversion-torsion energies were calculated using a semi rigid model allowing relaxation of the molecular structure. The ab initio PES was modified to reproduce spectroscopic data. The effective barrier to internal rotation is as low as 2.2 cm^{-1} comparing to the ab initio value of 18.9 cm^{-1}.

1. Introduction

Alkyl radicals have long been of great interest from both experimental and theoretical point of view since they play crucial roles in diverse chemical processes, as well as in atmospheric and interstellar chemistry. The ethyl radical, C_2H_5, as other open-shell highly reactive hydrocarbons, is particularly important due to its kinetic properties in fossil fuel combustion [1]. Moreover, it is considered a prototype for larger alkyl radicals. In ethyl radical a hyperconjugative effect occurs and it is believed that in higher radicals this effect becomes even more significant. All this makes ethyl radical an interesting object for detailed spectroscopic study of hyperconjugation and internal rotation motions in open shell systems.

Extensive spectroscopic research has been carried out to determine structural properties of ethyl radical. For the first time, Pacansky and Dupuis [2] obtained a qualitative description of the structure of the ethyl radical from its infrared spectrum, claiming that the radical has a staggered configuration with a distorted methyl group and a methylene group slightly off axis which results in a single tunneling path for torsional motion. This pathway goes along the torsional angle involving only slight changes in the inversion angle. Several other ab initio calculations [3–5] of the ethyl radical confirmed the displacement of the equilibrium geometry of the methylene group only by a few degrees from planarity.

Simultaneously with theoretical considerations, ethyl radical received also a great experimental interest. The first detection of the high resolution gas spectrum of C_2H_5 was performed by Sears et al. [6]. Many of the stronger subband structures were assigned, structural parameters were determined, and an experimental estimate of the height of the torsional barrier was obtained. The band origin of the CH_2 wagging fundamental, ν_9, was found to be at 528.1 cm^{-1}. Since an approximate model of rigid-top-rigid-frame torsional Hamiltonian was applied, it was not possible to fit the spectral observations to the level of the experimental accuracy. It has been concluded that there is almost free internal rotation in C_2H_5. In the one-dimensional analysis the torsional barrier was estimated to be about 20 cm^{-1}. This letter inspired East and Bunker [3] to carry out a precise simulation of the spectrum. Ab initio calculation of the purely electronic barrier to internal-rotation resulted in a value of 36 and 26 cm^{-1} when zero-point vibrational corrections were added. A new set of measurements of the ethyl radical $-CH_2$ wagging vibrational fundamental was reported by infrared diode laser transient absorption spectroscopy [7]. The analysis of this spectrum indicated the band origin at approximately 530 cm^{-1} and the height of the torsional barrier at 17 cm^{-1} in the zero-point level, which in the excited vibrational level decreased to 10 cm^{-1}. Although the quality of the fit was better than in previous work [6], it was still one order of magnitude higher than the measurement accuracy. Another work by Johnson and Sears considered interaction between the internal rotation and the vibrationally wagging excited fundamental, ν_9, of the ethyl radical and its influence on the magnitude of the barrier [4]. Ab initio calculations have been carried out using B3LYP and MP2 methods, and the torsional barriers in the ground state and in the first excited wagging state stayed very close to the experimental values from the previous work [7]. The best calculated value for the wagging frequency was about 30 cm^{-1} lower than the experimental one. In all referenced Letters, it was assumed that the methyl top rotates almost unhampered and thus, only one-dimensional calculations could be performed. However, one can anticipate that despite almost free movement of the methyl top, coupling between the inversion of the CH_2 and torsion of the CH_3 group should be taken into account. Such a suggestion was presented by Bhatta et al.

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[8]. It seems obvious that the zero-point correction for the wagging motion includes a significant part of the effective torsional barrier height and the torsion and inversion motions should not be treated separately. In Ref. [9] it has been emphasized that the combination of the two large amplitude motions (inversion of CH_2 and torsion of CH_3) plays a dominant role in the internal structure of two rovibrational progressions corresponding to the symmetric and antisymmetric stretches of the CH_2 group, which have been obtained from the first jet-cooled high resolution spectra of C_2H_5 in the CH stretch region. The progressions were assigned and analyzed with a near prolate top Hamiltonian and the band origins were found in agreement with the ab initio predictions and rotational constants were achieved for the ground and the two vibrational excited CH_2 stretch states. Later, high-resolution rovibrational spectra of the ethyl radical have been obtained for all three CH-stretch fundamentals of the methyl group [10]. Among ethyl radical studies and calculations, it is also worth mentioning a detection of the pure rotational spectrum of the ethyl radical with Fourier transform millimeter-wave spectrometer by Kim and Yamamoto [11] where about 20 lines of fine and hyperfine structure in the 1_{01}–0_{00} transition were assigned. In the recent Letter by Ratson et al. [12] the ethyl radical has been detected and spectroscopically studied in He nanodroplets, and all five fundamental CH stretch bands were observed, shifted by less 2 cm^{-1} from those reported from a gas phase [9].

The results of all these Letters showed that the one-dimensional model can explain well the rovibrational structure of the ethyl radical. However, our previous experience shows that the separation of vibrational motions leads to good understanding of the molecular dynamics when large amplitude vibrations are separated from small amplitude vibrations. In case of ethyl radical the separation goes between two large amplitude motions – the torsional and wagging motions. Thus, the question arises, how much this approach influences the estimation of the potential barrier for internal rotation, how effective is this barrier. The answer requires a rigorous application of the 2-dimensional model where both large amplitude motions are treated explicitly at the same level of approximation. In such a model only small amplitude vibrations give effective contributions to calculated parameters of the 2-dimensional potential surface.

The main goal of this work is to calculate the ab initio 2-dimensional potential function of the ethyl radical and then to solve a rovibrational Schrödinger equation, where internal rotation around the C—C bond and inversion (wagging) of the methylene group are treated explicitly. This potential has been corrected by comparison with experimental data. Besides, we were intrigued by the conclusion in Letter [4] where the DFT was considered superior over the MP2 method on the ground of the following argument: since the experimental value for the CH_2 wagging frequency is 528 cm^{-1} [6] and the theoretical harmonic frequencies obtained by Johnson and Sears with the 6–31++G(d,p) basis set are 491 and 463 cm^{-1} for DFT and MP2 methods, respectively, the DFT results being closer to the experimental one should be considered as superior with respect to the MP2 method. The question arises, whether the harmonic model can justify the choice of a method when the problem is highly anharmonic.

The Letter is divided into the following parts: (2) description of the coordinate-system used in the two-dimensional model, (3) a form of the inversion-torsion-rotation Hamiltonian and the solution of the respective Schrödinger equation, (4) building of the 2-dimensional potential surface, (5) ab initio calculation of the potential surface, (6) solution of the inversion-torsion-rotation problem and fitting to experimental data, (7) conclusions.

2. The mass-center Cartesian coordinates in the ethyl radical

The relaxation model of the ethyl radical is presented in Figure 1, where the inversion coordinate ρ is defined as an angle between the bisector of the HCH angle of the methylene group and the C—C bond, and the torsional coordinate τ is an angle between one of the CCH planes of the methyl group and the bisector plane perpendicular to the HCH plane of the methylene group. The ε angle is an angle between the z molecular axis and the C—C bond.

The Cartesian coordinates in a molecular system with the origin at the center of mass are given below:

$$a_{1x} = a_{2x} = -r_1 \cos\gamma \sin(\rho - \varepsilon) + a_{3x} \tag{1a}$$

$$a_{1y} = -a_{2y} = r_1 \sin\gamma \tag{1b}$$

$$a_{1z} = a_{2z} = r_1 \cos\gamma \cos(\rho - \varepsilon) + a_{3z} \tag{1c}$$

$$\begin{aligned} a_{3x} = \frac{1}{m}\{&-2m_1 r_1 \cos\gamma \sin(\rho - \varepsilon) + (m_4 + 3m_5) r_3 \sin\varepsilon \\ &- m_5(r_5 + r_6 + r_7)\cos\beta \sin(\varepsilon)\} \end{aligned} \tag{1d}$$

$$a_{3y} = 0 \tag{1e}$$

$$\begin{aligned} a_{3z} = \frac{1}{m}\{&-2m_1 r_1 \cos\gamma \cos(\rho - \varepsilon) + (m_4 + 3m_5) r_3 \cos\varepsilon \\ &- m_5(r_5 + r_6 + r_7)\cos\beta \cos(\varepsilon)\} \end{aligned} \tag{1f}$$

$$a_{4x} = -r_3 \sin\varepsilon + a_{3x} \tag{1g}$$

$$a_{4y} = 0 \tag{1h}$$

$$a_{4z} = -r_3 \cos\varepsilon + a_{3z} \tag{1i}$$

$$\begin{aligned} a_{5+j,x} = {}& r_{5+j} \sin\beta \cos\left(\tau + j\frac{2\pi}{3}\right)\cos(\varepsilon) - r_3 \sin\varepsilon \\ &+ r_{5+j}\cos\beta \sin(\varepsilon) + a_{3x} \end{aligned} \tag{1j}$$

$$a_{5+j,y} = r_{5+j} \sin\beta \sin\left(\tau + j\frac{2\pi}{3}\right) \qquad j = 0, 1, 2 \tag{1k}$$

$$\begin{aligned} a_{5+j,z} = {}& r_{5+j} \sin\beta \cos\left(\tau + j\frac{2\pi}{3}\right)\sin(\varepsilon) - r_3 \cos\varepsilon \\ &+ r_{5+j}\cos\beta \cos(\varepsilon) + a_{3z} \end{aligned} \tag{1l}$$

$$\gamma = \frac{1}{2}\alpha_{12} \tag{1m}$$

$$\beta = \alpha_{35} \tag{1n}$$

where r_1 and r_2 are the lengths of the CH bonds of the methylene group, r_3 that of the CC bond, and r_5, r_6 and r_7 those of the CH bonds of the methyl group.

In the semi-rigid model the bond lengths and angles are the functions of large amplitude coordinates ρ and τ. In the expressions below only the most important terms are included. Without any loss for the final conclusions other terms in the semi-rigid model can be neglected.

$$r_i = r_{i0} + r_{i1}\cos(\rho) \qquad i = 1, 2, 3 \tag{2a}$$

$$\gamma = \gamma_0 + \gamma_1 \cos(\rho) + \gamma_2 \cos(2\rho) \tag{2b}$$

$$r_k = [r_{k0} + r_{k1}\cos(\rho)]\left[1 + c_r \cos\left(\tau + (k-5)\frac{2\pi}{3}\right)\right] \quad k = 5, 6, 7 \tag{2c}$$