Ab initio determination of the far infrared spectra of some isotopic varieties of ethanol

M. L. Senent, Y. G. Smeyers, R. Domínguez-Gómez, and M. Villa

Citation: *J. Chem. Phys.* **112**, 5809 (2000); doi: 10.1063/1.481155

View online: <http://dx.doi.org/10.1063/1.481155>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v112/i13>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast
www.goodfellowusa.com

Ab initio determination of the far infrared spectra of some isotopic varieties of ethanol

M. L. Senent^{a)} and Y. G. Smeyers

Departamento de Química y Física Teóricas, Instituto de Estructura de la Materia, C.S.I.C., Serrano 113 bis, Madrid, E-28006, Spain

R. Domínguez-Gómez

Departamento de Ingeniería Civil, Cátedra de Química, E.U.I.T. Obras Públicas, Universidad Politécnica de Madrid, c/Alfonso XIII, 3-5, 28014 Madrid, Spain

M. Villa

Departamento de Química, UAM-I Purísima y Michoacan, s/n, CP 09340, Mexico, D.F., México

(Received 12 November 1999; accepted 11 January 2000)

The far infrared (FIR) spectra of various isotopic species of ethanol ($-h_6$, $-d_1$, and $-d_3$) are analyzed from MP4((SDQT) *ab initio* calculations using models in one and two dimensions. From the calculated frequencies and intensities, previous assignments of ethanol- h_6 and $-d_1$ bands are reviewed. The position of several combination bands are predicted. Ethanol shows two conformers, *trans* and *gauche*, and two interacting torsional modes. The torsional barriers have been calculated to be $V_3^{(\text{trans})} = 1226.7 \text{ cm}^{-1}$, $V_3^{(\text{gauche})} = 1296.3 \text{ cm}^{-1}$, $V_{\text{OH}}(\alpha = 62^\circ) = 404.1 \text{ cm}^{-1}$, and $V_{\text{OH}}(\alpha = 180^\circ) = 423.3 \text{ cm}^{-1}$. The flexible models in one and two dimensions yields the same OH torsional frequencies, whereas they differ in the methyl group state calculations. The fundamental bands of the ethanol- h_6 have been evaluated at 205.5 cm^{-1} (OH torsion) and 257.0 cm^{-1} (CH_3 torsion) and their corresponding intensities to be 18.650×10^{-4} and 0.662×10^{-4} . © 2000 American Institute of Physics. [S0021-9606(00)51613-4]

I. INTRODUCTION

Ethanol is a well known molecule of chemical and astrophysical interest. Relatively large proportions of the isolated molecule have been detected in the interstellar clouds. The vibrational and rotational spectra have been recorded in gas phase, in nitrogen and argon matrices, and in condensed phases.^{1–24}

Several effects that display special concern make it difficult for the far infrared (FIR) spectra interpretation. Two interacting torsional modes lay below 300 cm^{-1} and confer nonrigidity to the molecule. At relatively high pressures, ethanol has the tendency of forming dimers and polymers with additional bands arising from the hydrogen bonds, which can be detected in an argon matrix.^{4,16,19} They lay below 200 cm^{-1} close to the torsions making the assignments arduous. Their rigorous analysis is of interest for knowledge of the properties of the condensed phases of ethanol,¹⁷ because large isotopic effects for the excess contributions to the specific heat of the disordered phases have clear correlates in the low-frequencies spectra. The crystal packing shows hydrogen bonding where the molecules are linked forming infinite chains.¹⁷

At the electronic ground state, ethanol shows two stable conformers, *trans* and *cis-gauche* that are almost isoenergetic and interconvert by the torsion of the hydroxyl group.^{25–27} The three OH minima and the three equivalent ones of the methyl internal rotation design “an egg box”

potential energy surface with nine minima that are almost equivalent and separated by relatively low barriers. As a result, each vibrational level splits onto nine subcomponents. Both torsional motions are perpendicular vibrations and provide type-c IR bands with prominent *Q*-branches.

Recently, Durig and Larssen¹¹ have analyzed the torsional spectra using two different one-dimensional models for each torsional mode. They have considered the two torsions as independent. From the experimental fundamental frequencies and overtones, they calculated the torsional barriers to be 402.8 cm^{-1} (*trans-gauche*), 364.3 cm^{-1} (*gauche-trans*), 399.1 cm^{-1} (*gauche-gauche*), 1185 cm^{-1} (methyl group barrier at the *trans*-conformer), and 1251 cm^{-1} (methyl group barrier at the *gauche*-conformer). The energy difference between the two conformers has been determined to be 45 cm^{-1} from the infrared data¹¹ which is in a good agreement with the value of 39.2 cm^{-1} obtained from the millimeter wave-spectrum.¹³ All the potential parameters in Ref. 11 are calculated assuming that both vibrational modes were independent.

However, recently, we have performed a harmonic analysis of the monomers and dimers of ethanol where the two internal coordinates seem to interact strongly.²⁴ The numerical results for both torsional modes are not acceptable for a proper spectra assignments, nevertheless it is evident that the coupling between them is stronger than found in similar molecules. Two normal vibrations appear at 305.5 cm^{-1} and 250.4 cm^{-1} and represent a mixture of the two torsional internal coordinates. The weight of each coordinate in the normal mode fluctuates between 40% and 60%. The

^{a)}Author to whom correspondence should be addressed. Electronic mail: imtl2c@pinar2.csic.es

contribution of the methyl to the mode at 250.4 cm^{-1} is slightly larger than that of the OH torsion, whereas it is smaller for the mode at 305.5 cm^{-1} . This study has been done with a model for semirigid molecules which represents a more suitable first approximation for the methyl torsion than for the OH one taking into account the barriers heights. In order to clarify how strong these dependencies are a rigorous study is necessary in a two-dimensional model for nonrigid molecules to be able to describe the interactions between torsional coordinates and torsional motions hindered by low barriers.^{28,29}

In this paper, we analyze the FIR spectrum of several isotopic species of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol- h_6), $\text{CH}_3\text{CH}_2\text{OD}$ (ethanol- d_1), and $\text{CD}_3\text{CH}_2\text{OH}$ (ethanol- d_3), using *ab initio* calculations with full optimization of the geometry. As they contribute to the analysis, the levels of $\text{CD}_3\text{CD}_2\text{OD}$ (ethanol- d_6) and $\text{CH}_3\text{CD}_2\text{OH}$ (ethanol- d_2) are also evaluated. The torsional levels are determined variationally with one-dimensional and two-dimensional models results of which are compared. From the dipole moment variation, the absolute intensities of the bands are determined. We discuss previous assignments from the determination of the intensities of the bands.

II. THEORY

In this paper, the two torsional modes of ethanol are considered independently from the remaining coordinates. The roto-vibrational Hamiltonian, which is written as the sum of three terms,²⁹

$$H = H_V + H_{\text{rot}} + H_{VR} \quad (1)$$

is specified in terms of internal coordinates. H_V , H_{rot} , and H_{VR} are the vibrational (torsional) Hamiltonian, the pure rotational Hamiltonian and the roto-torsional operators. The two variables θ and α are defined as functions of the two dihedral angles HOC_2C_1 and $\text{HC}_1\text{C}_2\text{O}$ ($\theta = 180^\circ$, $<\text{HC}_1\text{C}_2\text{O}$ and $\alpha = 180^\circ$, HOC_2C_1). For $J=0$, the roto-vibrational operator coincides to H_V that can be written as

$$\begin{aligned} \hat{H}_{\text{vib}} = & -\left(\frac{\partial}{\partial\theta}\right)B_{11}\left(\frac{\partial}{\partial\theta}\right) - \left(\frac{\partial}{\partial\theta}\right)B_{12}\left(\frac{\partial}{\partial\alpha}\right) \\ & - \left(\frac{\partial}{\partial\alpha}\right)B_{12}\left(\frac{\partial}{\partial\theta}\right) - \left(\frac{\partial}{\partial\alpha}\right)B_{22}\left(\frac{\partial}{\partial\alpha}\right) \\ & + V'(\theta, \alpha) + V(\theta, \alpha), \end{aligned} \quad (2)$$

where V represents the potential energy surface and V' is the pseudopotential given by

$$\begin{aligned} V' = & \frac{1}{4} \sum_{k=1}^2 \sum_{l=1}^2 \left[\left(\frac{\partial}{\partial q_k} \right) B_{kl} \left(\frac{\partial \ln g}{\partial q_l} \right) - \left(\frac{\partial \ln g}{\partial q_k} \right) \right. \\ & \times B_{kl} \left(\frac{\partial}{\partial q_l} \right) \left. \right] + \frac{1}{16} \sum_{k=1}^2 \sum_{l=1}^2 \left(\frac{\partial \ln g}{\partial q_k} \right) \\ & \times B_{kl} \left(\frac{\partial \ln g}{\partial q_l} \right) \quad (q_1 = \theta, \quad q_2 = \alpha). \end{aligned} \quad (3)$$

In these equations, g is the determinant of the $\mathbf{G}^{-1}$ matrix.²⁹ B_{11} , B_{22} , and B_{12} are the methyl torsion, hydroxyl

torsion, and torsion–torsion interactions kinetic energy parameters. In cm^{-1} , they coincide to the torsional elements g_{44} and g_{55} and g_{45} of the $\mathbf{G}$ matrix [$B_{11} = (\hbar^2/2)g_{44}$, $B_{22} = (\hbar^2/2)g_{55}$, and $B_{12} = (\hbar^2/2)g_{45}$] (1 = methyl torsion, 2 = hydroxyl torsion). The definitions are specified in Ref. 29.

As a flexible model is employed, the $3N-8$ remaining coordinates are allowed to be relaxed during the variation of θ and α . They can be expressed as functions of the independent coordinates,

$$q_j = f(q_1, \dots, q_n) \quad j = n+1, n+2, \dots, 3N-6. \quad (4)$$

The trial function employed for the variational calculations of the torsional levels, are solutions of the free rotor (for the one-dimensional calculations) or solutions of the double free rotor (for the two-dimensional calculation).

The intensities of the transition between the i and j states are determined with the equation,³⁰

$$I = \frac{q}{3R^2 e^2 B} \omega (P_j - P_i) \langle \Psi_i | \mu_\gamma | \Psi_j \rangle^2 \quad \gamma = x, y, z, \quad (5)$$

where i and j represent two connected states. R is the radius of the rotor, $B = (B_{11} \times B_{22})^{1/2}$, μ_γ are the dipole moment components, and P_K represents the Boltzmann population. ω is the frequency and q is the nuclear statistical weight.

III. SYMMETRY

The most stable structure of ethanol may be classified according to the C_s symmetry point group and the G_6 full-non-rigid group which is identical to the restricted-non-rigid-group. The character table is shown in Appendix A. The group is defined by the semidirect product,^{31,32}

$$G_6 = C_3^I \wedge V^I, \quad (6)$$

The two subgroups C and V^I contain the operations,

$$C_3^I = E + C_3 + C_3^2, \quad V^I = E + V^I, \quad (7)$$

where E and C_3 are the identity and the threefold rotation. V is the double switch operator,

$$Vf(\theta, \alpha) = f(-\theta, -\alpha). \quad (8)$$

The Hamiltonian has to be totally symmetric, therefore the analytic form for the potential and the pseudopotential may be the symmetry adapted Fourier series,

$$\begin{aligned} V(\theta, \alpha) = & \sum_{N=0} \sum_{L=0} (A_{NL}^{cc} \cos 3N\theta \cos L\alpha \\ & + A_{NL}^{ss} \sin 3N\theta \sin L\alpha) \end{aligned} \quad (9)$$

formally identical equations may be employed for B_{11} , B_{22} , B_{12} , V' , and g_{ij} ($ij = 11, 22, 33, 12, 14, 15, 24$, and 25). For g_{ij} ($ij = 13, 23, 16$, and 26) the analytic form can be

$$\begin{aligned} g_{ij}(\theta, \alpha) = & \sum_{N=0} \sum_{L=0} (A_{NL}^{cs} \cos 3N\theta \sin L\alpha \\ & + A_{NL}^{sc} \sin 3N\theta \cos L\alpha). \end{aligned} \quad (10)$$

Appendix B shows the symmetry eigenvectors which can be obtained by applying the projection operator on the trial function to be employed in the variational calculations.

FIG. 1. The two-conformers of ethanol, *trans*, and *gauche*.

In the case of ethanol, the statistical weights are 2:1 for the *A* and *E* representations for the species ethanol and ethanol-*d*₁, and it is 11:8 for *A* and *E* for ethanol-*d*₃.³³ For the nondegenerate representations of the three isotopic varieties, *q* is taken equal to 1, 1, and 0.815. For the *E* the

TABLE I. Structural parameters of the two ethanol conformers.^a

	<i>trans</i> -ethanol	<i>gauche</i> -ethanol
C1C2	1.504094	1.509682
O3C2	1.418899	1.417911
H4C1	1.085082	1.085973
H5C1	1.084138	1.086756
H6C1	1.084138	1.084207
H7C2	1.089328	1.089538
H8C2	1.089328	1.083750
H9O3	0.958892	0.959632
O3C2C1	107.352	112.438
H4C1C2	110.613	110.837
H5C1C2	110.079	110.662
H6C1C2	110.079	110.169
H7C2C1	109.911	110.238
H8C2C1	109.911	110.186
H9O ₃ C ₂	107.953	107.318
H4C1C2O3	180.000	177.050
H5C1C2H4	120.023	119.672
H6C1C2H4	-120.023	-120.524
H7C2C1O3	120.694	124.352
H8C2C1O3	-120.694	-117.188

^aDistances are in Å, and angles are in deg.TABLE II. Kinetic and potential parameters of the two ethanol conformers.^a

	<i>trans</i> -ethanol	<i>gauche</i> -ethanol
α	0.000	120.159
<i>A</i>	1.181 084 22	1.183 049 81
<i>B</i>	0.318 538 34	0.303 866 95
<i>C</i>	0.276 577 76	0.270 082 29
κ	-0.911 332 2	-0.928 630 4
<i>B</i> ₁₁	6.584 595 78	6.666 125 08
<i>B</i> ₂₂	22.190 549 74	21.967 410 39
<i>B</i> ₁₂	0.292 296 22	-0.152 857 81
<i>V'</i>	0.145 033 84	-0.108 383 44
<i>V</i> ₃ ^(trans)	1226.7	<i>V</i> ₃ ^(gauche) 1296.3
<i>V</i> _{OH} ($\alpha = 62^\circ$)	404.1	ΔH 18.8
<i>V</i> _{OH} ($\alpha = 180^\circ$)	423.3	

^aRotational constants, *A*, *B*, and *C*, torsional kinetic parameters *B*_{*ij*}, the barriers, and the pseudopotential *V'* are in cm⁻¹.

weights are multiplied by two and *q* is taken equal to 1, 1, and 1.186.

IV. COMPUTATIONAL DETAILS

The potential energy surface and the kinetic parameters of the Hamiltonian have been determined from *ab initio* calculations performed with the GAUSSIAN 94 program.³⁴ The calculations have been achieved with the Dunning correlation consistent triple zeta basis set³⁵ and the Möller-Plesset

TABLE III. Relative energies^a (in cm⁻¹) of the selected conformations corresponding to θ (methyl torsion) and α (OH torsion).

θ	α	<i>E</i>	θ	α	<i>E</i>
<i>E</i> (θ, α)					
0	0	0.000 ^b	0	180	442.075
90	0	617.246	90	180	1138.094
180	0	1226.712	180	180	1896.186
0	30	193.160	0	150	225.183
90	30	890.343	90	150	985.274
180	30	1438.210	180	150	1632.483
-90	30	752.662	-90	150	841.340
0	60	412.744	0	120	25.619
90	60	1154.039	90	120	803.580
180	60	1669.368	180	120	1328.506
-90	60	939.656	-90	120	556.223
0	90	230.609			
90	90	989.155			
180	90	1478.1155			
-90	90	726.749			
<i>E</i> (θ)					
<i>trans</i> -ethanol			<i>gauche</i> -ethanol		
0	0.0	0.000 ^b	0	120.6	25.553
90	-4.7	610.708	90	119.4	803.810
180	0.0	1226.712	180	115.2	1321.821
-90	4.7	610.708	-90	116.5	552.663
<i>E</i> (α)					
0.0	0	0.000 ^b	2.9	120	18.789
2.5	30	188.535	1.3	150	224.362
3.5	60	403.557	0.0	180	442.075
3.8	90	219.306			

^aCalculated with MP4 (SDQT)/cc-pVTZ.^b*E* = -154.843 465 a.u.

FIG. 2. The one-dimensional potential energy surface of ethanol as a function of the methyl torsional coordinate.

perturbation theory up to the four order (MP4). All the electrons have been correlated incorporating double, triples and quartic substitutions (MP4(SDQT, full)). The geometry has been fully optimized at the MP2(full)/cc-pVTZ level. The convergence criteria of the gradient has been taken equal to 10^{-6} . A basis set containing diffuse functions has been employed for the computations of the electric properties.

The kinetic parameters have been computed from the optimized geometries with the KNP.F program.³⁶ The band positions and the intensities have been calculated with the programs UNADIM.f and BIDIM.f that incorporate symmetry conditions.

V. RESULTS AND DISCUSSION

In the electronic ground state, ethanol exhibits one conformer *trans* at $\alpha=0^\circ$ and a double minimum *cis-gauche* at 120.159° and -120.159° (see Fig. 1). They may be classified in the C_s , C_1 , and C_1 point groups. Table I shows the MP2(full)/cc-pVTZ structural parameters. In accordance

FIG. 3. The one-dimensional potential energy surface of ethanol as a function of the hydroxyl torsional coordinate.

FIG. 4. The two-dimensional potential energy surface of ethanol.

with the microwave measurements,⁵ the bending angle O3C2C1 is the internal coordinate that displays the major OH internal rotation dependence. It shifted approximately 5° during the torsion (from 107.352° in the *trans* conformer to 112.438° in the *gauche* geometries). With the OH internal rotation, the methyl group loses the C_{3v} symmetry and the central bond C1C2 increases from $1.504\,094\text{ \AA}$ (*trans*) up to $1.509\,682\text{ \AA}$ (*gauche*) for minimizing the steric interactions.

Table II shows the vibrational kinetic parameters, the internal rotational barriers and potential parameters, and the rotational constants at the minima. The energy difference between the conformers (ΔH) has been calculated to be 18.8 cm^{-1} , which is of an order of magnitude of the experimental data reported (41.2 cm^{-1} in Ref. 8; 39.2 cm^{-1} in Ref. 13, and 45 cm^{-1} in Ref. 11). As follows from experiments, the *trans*-conformer calculated with cc-pVTZ appears as the most stable geometry. The *trans*-conformer is prolate ($\kappa = -0.928\,630\,4$). The MP2(full)/cc-pVTZ rotational constants for the *trans*-conformation are $1.181\,084\,22$, $0.318\,538\,834$, and $0.276\,577\,77\text{ cm}^{-1}$ and those of the *gauche*-conformations are $1.183\,049\,81$, $0.303\,866\,95$, and $0.270\,082\,29\text{ cm}^{-1}$. All these structural data can be compared with the previous results performed with a shorter basis set.²⁴

Calculations achieved with a modest basis set invert the relative order of stabilities of the minima.²⁵ The current work was started using smaller basis set as cc-pVDZ and Aug-cc-pVDZ. Although, it is unnecessary to detail the initial results, it may be remarked that the shortest basis set cc-pVDZ gives erroneously the *gauche*-conformer as the most stable geometry. It is well known that the cc-pVDZ basis set contains a large intramolecular superposition error.³⁷

The methyl torsion barrier V_3^{trans} and V_3^{gauche} have been evaluated to be 1226.7 cm^{-1} and 1296.3 cm^{-1} with MP4(SDQT, full)/cc-pVTZ/MP2(full)/cc-pVTZ, whereas the experimental values obtained in one dimension¹¹ are 1185 ± 16 and $1251 \pm 2\text{ cm}^{-1}$. The calculated hydroxyl torsion *trans-gauche* and *gauche-gauche* barriers are placed at $\alpha = 62^\circ$ and $\alpha = 180^\circ$, and their heights are 404.1 cm^{-1} and 423.3 cm^{-1} , respectively. The FIR experimental measures carry the effect of the isotopic substitution, that is ignored on the *ab initio* calculations. They yield values of 402.8 ± 0.1 for the *trans-gauche*, 364.3 ± 0.1 for the *gauche-trans* and $399.1 \pm 0.2\text{ cm}^{-1}$ for the *gauche-gauche* barriers for ethanol-

TABLE IV. Comparison between the nondegenerate energy levels of ethanol- h_6 , calculated in one and two dimensions.

v	v'	Symmetry	1D		2D		Expt. (Ref. 11)
			OH	CH ₃	Fac1		
0	0	A ₁	0.0	0.0	0.0	51.2	0.0
0	0 ⁺	A ₁	25.5	18.8	25.5	42.3	
0	0 ⁻	A ₂	28.5	18.8	28.5	42.1	
0	1	A ₂	205.8		205.5	32.2	202.6
0	1 ⁺	A ₁	232.9		233.0	26.1	
0	1 ⁻	A ₂	279.2		278.3	34.4	
0	2	A ₁	351.4		352.8	21.8	
0	2 ⁻	A ₂	469.2		470.2	19.9	
0	2 ⁺	A ₁	470.0		473.2	24.9	
1	0	A ₂		252.4	257.0	69.1	244.4
1	0 ⁻	A ₂		283.6	294.4	59.5	
1	0 ⁺	A ₁		283.6	294.6	66.8	
2	0	A ₁		484.6	499.2	73.9	475.6
2	0 ⁺	A ₁		529.0	532.1	67.4	
2	0 ⁻	A ₂		529.0	541.8	75.6	
1	1	A ₁			456.5	54.8	
1	1 ⁻	A ₂			497.4	49.3	
1	1 ⁺	A ₁			550.7	56.9	

h_6 .¹¹ It has to be remarked that the calculated and experimental *trans-gauche* barrier are in a very good agreement. The calculated $V_3^{(trans)}$ and $V_3^{(gauche)}$ are overestimated.

As we wanted to evaluate the importance of the vibrational interactions between the two torsion modes, results obtained in one (1D) and two dimensions (2D), are compared. The 1D and 2D potential energy surfaces have been evaluated by fitting the energies of Table III. $E(\theta, \alpha)$ are the two-dimensional energies. They have been calculated by freezing two coordinates during the optimization of the geometry whereas the one-dimensional energies, $E(\theta)$ and $E(\alpha)$, have been evaluated by freezing only one variable. For this reason, the 1D and 2D selected conformations are not equivalent.

Our experience shows that the third and four order of the

Möller–Plesset calculations do not significantly improve the MP2 geometries, and the energies have been determined at the MP4(SDQT,full) level, whereas the geometries were optimized with MP2(full)/cc-pVTZ. The two-dimensional potential energy surface, $V(\theta, \alpha)$, was obtained with a least square fitting to Eq. (9) with the $E(\theta, \alpha)$ energies of 26 nuclear conformations selected using symmetry criteria. As is well known, the methyl group loses its “static C_{3v} symmetry” at the nonplanar conformations during the relaxation process, although the “dynamical symmetry” is preserved. In order to elude the static-dynamic symmetry dilemma the calculations have been performed for $\theta=0^\circ, 90^\circ, 180^\circ$ and -90° .³⁸ The hydroxyl torsion coordinate has been taken to be equal to $\alpha=0^\circ, 30^\circ, 60^\circ, 90^\circ, 120^\circ, 150^\circ$, and 180° . The reference structure $(\theta, \alpha)=(0^\circ, 0^\circ)$ is the *trans*-ethanol with the methyl group antieclipsed.

Three different one-dimensional surfaces may be determined. $V^{trans}(\theta)$ and $V^{gauche}(\theta)$ restrict the motion of the methyl group while the OH remains at the *trans* or *gauche* positions (see Fig. 2). $V(\alpha)$ hinders the hydroxyl group motion. In this case, the methyl group remains at the energy minimum (see Fig. 3). The three functions obtained with a least square fitting of the one-dimensional energies of Table III, are

$$V(\alpha) = 212.598 - 19.894 \cos(\alpha) - 0.996 \cos(2\alpha) - 201.935 \cos(3\alpha) + 7.574 \cos(4\alpha) + 0.791 \cos(5\alpha) + 1.863 \cos(6\alpha), \quad (11)$$

$$V^{(trans)}(\theta) = 612.032 - 613.356 \cos(3\theta) + 1.324 \cos(6\theta), \quad (12)$$

$$V^{(gauche)}(\theta) = 675.962 - 648.134 \cos(3\theta) - 125.573 \sin(3\theta) - 2.275 \cos(6\theta). \quad (13)$$

The two-dimensional potential energy surface is given in Fig. 4 and the corresponding function is

$$V(\theta, \alpha) = 867.114 - 649.982 \cos(3\theta) + 0.917 \cos(6\theta) - 58.396 \cos(\alpha) + 12.296 \cos(2\alpha) - 211.549 \cos(3\alpha) + 3.180 \cos(4\alpha) + 0.769 \cos(5\alpha) + 1.841 \cos(6\alpha) + 46.224 \cos(3\theta) \cos(\alpha) - 23.221 \cos(3\theta) \cos(2\alpha) + 11.239 \cos(3\theta) \cos(3\alpha) + 3.002 \cos(3\theta) \cos(4\alpha) - 0.613 \cos(3\theta) \cos(5\alpha) - 0.005 \cos(3\theta) \cos(6\alpha) - 133.849 \sin(3\theta) \sin(\alpha) + 5.662 \sin(3\theta) \sin(2\alpha) - 3.201 \sin(3\theta) \sin(3\alpha) - 3.857 \sin(3\theta) \sin(4\alpha) - 0.556 \sin(3\theta) \sin(5\alpha) - 6.244 \cos(6\theta) \cos(\alpha) + 4.380 \cos(6\theta) \cos(2\alpha) - 2.425 \cos(6\theta) \cos(3\alpha) + 1.566 \cos(6\theta) \cos(4\alpha). \quad (14)$$

The least square fit of the *ab initio* energies (Table III) produces a surface containing 23 terms. The description of the CH₃ and the OH torsion requires two and five independent terms at least. The $\sin \chi \sin$ products arise from the energy differences between pairs of nonplanar conformations

where the torsional groups are rotated in the same and in different senses. We usually call “gearing” to this effect.²⁸ The $\cos \chi \cos$ terms appear from the variation of the methyl barriers with the hydroxyl torsion.

The kinetic parameters of the roto-vibrational Hamil-

tonian have been determined with the KNP.F program.³⁵ For this purpose, the internal coordinates have been fitted to an adapted symmetry Fourier series to obtain the relations between the dependent and independent coordinates [Eq. (4)].

Table II shows the vibrational parameters B_{11} , B_{22} , B_{12} , and V' of the two conformers. The values for each conformation have been fitted to a completely symmetric periodic function. For ethanol- h_6 the resulting surfaces are [Eq. (15)]

$$\begin{aligned}
 B_1(\theta, \alpha) = & 6.5482 - 0.0845 \cos(3\theta) + 0.2147 \cos(6\theta) - 0.0999 \cos(\alpha) + 0.0307 \cos(2\alpha) + 0.0061 \cos(3\alpha) \\
 & - 0.0190 \cos(4\alpha) + 0.0151 \cos(5\alpha) - 0.0092 \cos(6\alpha) + 0.0250 \cos(3\theta)\cos(\alpha) - 0.0723 \cos(3\theta)\cos(2\alpha) \\
 & + 0.0134 \cos(3\theta)\cos(3\alpha) + 0.0104 \cos(3\theta)\cos(4\alpha) - 0.0103 \cos(3\theta)\cos(5\alpha) + 0.0068 \cos(3\theta)\cos(6\alpha) \\
 & - 0.0019 \sin(3\theta)\sin(\alpha) + 0.0264 \sin(3\theta)\sin(2\alpha) + 0.0001 \sin(3\theta)\sin(3\alpha) - 0.0055 \sin(3\theta)\sin(4\alpha) \\
 & + 0.0070 \sin(3\theta)\sin(5\alpha) - 0.0087 \cos(6\theta)\cos(\alpha) + 0.0688 \cos(6\theta)\cos(2\alpha) + 0.0083 \cos(6\theta)\cos(3\alpha) \\
 & + 0.0153 \cos(6\theta)\cos(4\alpha), \\
 B_2(\theta, \alpha) = & 22.7540 - 0.0545 \cos(3\theta) - 0.0128 \cos(6\theta) - 1.0846 \cos(\alpha) + 0.3763 \cos(2\alpha) - 0.1528 \cos(3\alpha) \\
 & + 0.1375 \cos(4\alpha) + 0.1222 \cos(5\alpha) - 0.0577 \cos(6\alpha) + 0.0535 \cos(3\theta)\cos(\alpha) + 0.0577 \cos(3\theta)\cos(2\alpha) \\
 & - 0.0605 \cos(3\theta)\cos(3\alpha) + 0.0188 \cos(3\theta)\cos(4\alpha) - 0.0514 \cos(3\theta)\cos(5\alpha) + 0.0022 \cos(3\theta)\cos(6\alpha) \\
 & - 0.0138 \sin(3\theta)\sin(\alpha) - 0.0671 \sin(3\theta)\sin(2\alpha) + 0.0858 \sin(3\theta)\sin(3\alpha) + 0.0166 \sin(3\theta)\sin(4\alpha) \\
 & + 0.0867 \sin(3\theta)\sin(5\alpha) - 0.0319 \cos(6\theta)\cos(\alpha) + 0.0471 \cos(6\theta)\cos(2\alpha) + 0.0126 \cos(6\theta)\cos(3\alpha) \\
 & + 0.0038 \cos(6\theta)\cos(4\alpha), \\
 B_{12}(\theta, \alpha) = & -0.8842 - 0.0665 \cos(3\theta) - 0.0158 \cos(6\theta) + 1.2769 \cos(\alpha) - 0.1462 \cos(2\alpha) + 0.0306 \cos(3\alpha) \\
 & + 0.0432 \cos(4\alpha) - 0.0315 \cos(5\alpha) + 0.0180 \cos(6\alpha) + 0.0101 \cos(3\theta)\cos(\alpha) + 0.0640 \cos(3\theta)\cos(2\alpha) \\
 & - 0.0256 \cos(3\theta)\cos(3\alpha) - 0.0281 \cos(3\theta)\cos(4\alpha) + 0.0026 \cos(3\theta)\cos(5\alpha) - 0.0104 \cos(3\theta)\cos(6\alpha) \\
 & + 0.1253 \sin(3\theta)\sin(\alpha) - 0.1104 \sin(3\theta)\sin(2\alpha) - 0.0616 \sin(3\theta)\sin(3\alpha) + 0.0280 \sin(3\theta)\sin(4\alpha) \\
 & - 0.0081 \sin(3\theta)\sin(5\alpha) + 0.0148 \cos(6\theta)\cos(\alpha) + 0.1129 \cos(6\theta)\cos(2\alpha) - 0.0096 \cos(6\theta)\cos(3\alpha) \\
 & - 0.0017 \cos(6\theta)\cos(4\alpha).
 \end{aligned} \tag{15}$$

We omitted the inclusion of the pseudopotential function $V'(\theta, \alpha)$, the order of magnitude of which is 1 cm^{-1} , and will produce a very small improvement on the torsional levels. The relations [Eq. (4)] between dependent and independent coordinates and the equations which defined the Cartesian coordinates as functions of the internal coordinates, are also omitted.

VI. ASSIGNMENTS

Table IV shows the nondegenerate energy levels A_i of ethanol- h_6 calculated variationally in one 1D and two dimensions (2D). They are labeled using the vibrational quanta numbers (v and v') and the irreducible representations of the nonrigid group of ethanol. The 2D levels have been determined solving the Hamiltonian of Eq. (2). The 1D Hamiltonian operators are defined in Ref. 29. As a consequence of the double minima, each *gauche* level splits in two subcomponents labeled as v'^{+} and v'^{-} , v' represents a *trans*-level. The methyl barrier produces the splitting of each subcomponent in three microstates, one nondegenerate A_i and two de-

generate E_i which energy difference is inappreciable. As result, nine microstates corresponding to the nine potential energy wells appear on the surface.

The torsional energies of the isotopic species $\text{CH}_3\text{CH}_2\text{OD}$ (ethanol- d_1), $\text{CD}_3\text{CH}_2\text{OH}$ (ethanol- d_3), $\text{CD}_3\text{CD}_2\text{OD}$ (ethanol- d_6), and $\text{CH}_3\text{CD}_2\text{OH}$ (ethanol- d_2) have been also calculated (Table V), although, only infrared experimental data are available for ethanol- d_1 . The evaluation of the levels of the remaining species, especially ethanol- d_3 , may help the assignments.

The two modes interact strongly making difficult the classification of the energy levels determined variationally. For this reason, two properties have been calculated for labeling the torsional states; the expectation values of the one-dimensional Hamiltonian operators on the two-dimensional torsional functions and the probability integrals in the potential energy wells.

The expectation values permit the assignment of the energies to each torsional mode. They are calculated with the equations,

TABLE V. Calculated energy levels of isotopic species of ethanol (in cm^{-1}).

v	v'	Symmetry	$\text{CH}_3\text{CH}_2\text{OD}$	$\text{CD}_3\text{CH}_2\text{OH}$	$\text{CD}_3\text{CD}_2\text{OD}$	$\text{CH}_3\text{CD}_2\text{OH}$
0	0	A_1	0.0	0.0	0.0	0.0
0	0^+	A_1	25.0	24.4	23.1	25.1
0	0^-	A_2	25.4	27.4	23.5	28.0
0	1	A_2	171.4	214.4	168.7	205.4
0	1^+	A_1	200.6	224.5	194.5	232.8
0	1^-	A_2	209.2	279.2	201.5	277.0
0	2	A_1	297.9	349.8	294.7	351.6
0	2^-	A_2	352.0	468.8	345.5	467.4
0	2^+	A_1	349.0	468.2	342.1	469.6
1	0	A_2	255.7	189.4	193.5	253.1
1	0^-	A_2	290.4	230.1	226.4	289.1
1	0^+	A_1	290.4	240.4	225.7	290.1
2	0	A_1	492.7	375.8	379.4	491.6
2	0^+	A_1	537.4	426.7	421.0	527.0
2	0^-	A_2	537.1	420.0	418.3	533.3
1	1	A_1	427.0	413.1	358.4	453.0
1	1^-	A_2	466.8	442.6	389.0	493.2
1	1^+	A_1	471.3	485.0	395.1	541.8

$$\langle H_i \rangle = \langle \phi_n | H_i | \phi_n \rangle \quad i=1,2, \quad (16)$$

$$H_i = -B_{ii}^0 + V(i,0) + V'(i,0),$$

where B_i represents the parameters B_{11} or B_{22} . ϕ_i are the 2D torsional functions. The factor,

$$\text{fac1} = \frac{100\langle H_1 \rangle}{\langle H_1 \rangle + \langle H_2 \rangle} \quad (17)$$

is a measure (%) of the methyl torsion (mode number 1) in each of the two-dimensional calculations. If $\text{Fac1} > 60$ and $\text{Fac1} < 40$, the levels are assigned to the methyl and hydroxyl torsion, respectively. Levels with $\text{Fac1} \approx 50\%$ are considered combination states.

The levels are classified as *trans* or *gauche* states by solving the probability integrals around the potential energy surface wells,

$$\int_{\gamma-\Delta\gamma}^{\gamma+\Delta\gamma} \Phi_i^* \Phi_i d\gamma \quad \gamma = \theta, \alpha. \quad (18)$$

In ethanol- h_6 , the 2D zero vibrational (253.8 cm^{-1}) splits into three subcomponents at 0.0, 25.5, and 28.5 cm^{-1} . The energy difference between *gauche* components, $(vv') = (00^+)$ and $(vv') = (00^-)$, has been calculated to be 3.012 cm^{-1} with the one-dimensional model and to be 3.008 cm^{-1} in two dimensions (Table IV). For ethanol- d_1 and ethanol- d_3 , it was found to be 0.476 cm^{-1} and 2.96 cm^{-1} , respectively. Experimentally, the values are 3.227 cm^{-1} (hydrogenated) and 0.570 cm^{-1} (deuterated).¹¹ As V_3 is three times higher than the hydroxyl barriers, the splitting arising from the methyl torsion is very small. In the ethanol- h_6 vibrational ground state, the energy differences among methyl torsional components are of an order of magnitude of 10^{-3} cm^{-1} . When $(vv') = (2,0)$, they increase up to 10^{-2} cm^{-1} . As was expected, the size of the splittings is lower in the deuterated species.

It has to be remarked that the hydroxyl torsion behaves as an independent coordinate, whereas the methyl torsion is affected by the interactions. For example, the OH torsional

levels (00), (01), and (02) have been calculated to be 0.0, 205.5, and 352.8 cm^{-1} in two dimensions, and to be 0.0, 205.8, and 351.4 cm^{-1} in one dimension. The values for the CH_3 torsion are not so accurate. An inconsistency appears from the flexible models employed in which the neglected vibrations are partially considered; the OH torsion seems to be independent on the CH_3 one, whereas the methyl torsion seems to be dependent on the OH one. To understand this, the two modes have to be considered as interacting. In the 1D calculations the second torsional mode is not absolutely neglected. Flexible models are more or less accurate depending on the interactions strength they have with the other amplitude modes. In ethanol, they appear to be optimal for the OH torsion because the differences between calculated and experimental values are small for the hydroxyl group, whereas the deformation coordinates of the methyl group appear to be poorly described.

The comparison of isotopic species levels clarifies the

FIG. 5. The variation of the dipole moment and the atomic charges with the hydroxyl torsional coordinate.

assignments (Table V). The deuteration of the $-\text{CH}_2-$ group imparts the largest effects on the CH_3 levels, which shows the dependencies of the methyl group torsion on other vibrations (Table V). The two fundamentals displace to 168.7 and 193.5 cm^{-1} when the molecule is fully deuterated. They are found at 205.4 and 253.1 cm^{-1} for ethanol- d_2 . The corresponding values for ethanol- h_6 are 205.4 cm^{-1} (OH torsion) and 257.0 cm^{-1} (methyl torsion).

The prominent Q branches observed in the experimental

spectra¹¹ correspond to type-c bands. Their intensities depend on the variation of the out-of-plane dipole moment component. For this reason, the dipole moments along the C principal axis of each selected conformation, have been fitted to symmetry adapted periodic series. The “in-plane” μ_a , and μ_b components transform as the totally symmetric representation A_1 and the “out-of-plane” μ_c transforms as the antisymmetric nondegenerate A_2 . The analytic form of $\mu_c(\theta, \alpha)$ is,

$$\begin{aligned} \mu_c(\theta, \alpha) = & -0.012\,742 \sin(3\theta) + 1.480\,681 \sin(\alpha) + 0.064\,699 \sin(2\alpha) - 0.039\,283 \sin(3\alpha) - 0.002\,75 \sin(4\alpha) \\ & + 0.003\,285 \sin(5\alpha) - 0.002\,412 \cos(3\theta) \sin(\alpha) - 0.001\,357 \cos(3\theta) \sin(2\alpha) - 0.001\,350 \cos(3\theta) \sin(3\alpha) \\ & + 0.009\,192 \sin(3\theta) \cos(2\alpha) + 0.008\,333 \sin(3\theta) \cos(3\alpha) + 0.007\,992 \sin(3\theta) \cos(4\alpha) \\ & + 0.008\,352 \sin(3\theta) \cos(5\alpha) + 0.004\,108 \sin(3\theta) \cos(6\alpha). \end{aligned} \quad (19)$$

As is evident, the c -component of the dipole moment depends strongly on the hydroxyl torsion and slightly on the methyl torsional coordinate. It may be expected that the OH internal rotation transitions yield the largest intensities. Figure 5 shows the dipole moment and the absolute atomic charges variations with respect to α .

Intensities are determined with the oscillator strength equation [Eq. (5)]. Tables VI, VII, and VIII show the frequencies and intensities of the most prominent methyl torsional bands, hydroxyl torsional bands, and combination bands. Bold characters are employed for the most significant transitions. The largest intensities correspond to the levels with low Fac1 factors [Eq. (17)]. The experimental values shown on the tables are from Ref. 11. The parentheses correspond to assignments suggested in the present paper for the

first time. The calculations allow us to predict approximate band locations where the background of the experimental spectra shows protuberances.

Finally, we study independently the spectra of ethanol- h_6 , ethanol- d_1 , and ethanol- d_3 . It has to be pondered that the accuracy of the potential energy surface is not uniform. The credibility of the calculations is optimally close to the *trans* well and decreases in the *gauche* one. In addition, the calculated OH torsional levels are more accurate than the methyl torsion energies because the methyl rotation barriers are overestimated.

A. Ethanol- h_6

On the basis of previous measurements,^{4,6,7} Durig and Larssen¹¹ have assigned the Q branches observed at 202.6,

TABLE VI. Methyl torsional frequencies (in cm^{-1}) and absolute intensities of the ethanol isotopes.

$\nu\nu\rightarrow\nu'\nu'$	Sym.	$\text{CH}_3\text{CH}_2\text{OH}$			$\text{CH}_3\text{CH}_2\text{OD}$			$\text{CH}_3\text{CH}_2\text{OH}$	
		Freq.	Int(10^{-4})	Obs.	Freq.	Int(10^{-4})	Obs.	Freq.	Int(10^{-4})
<i>trans</i> $\rightarrow$ <i>trans</i>									
00 $\rightarrow$ 10	$A_1\rightarrow A_2$	257.0	0.662	244.4	255.7	0.246	244.3	189.4	5.117
	$E\rightarrow E$	257.0	0.662		255.7	0.246		189.4	7.441
10 $\rightarrow$ 20	$A_2\rightarrow A_1$	242.2	0.954	231.1	236.9	0.203	231.0	186.4	0.340
	$E\rightarrow E$	242.2	0.954		236.9	0.203		186.4	0.494
<i>gauche</i> $\rightarrow$ <i>gauche</i>									
00 $^+\rightarrow$ 10 $^-$	$A_1\rightarrow A_2$	268.9	1.342		265.5	0.159		205.6	0.033
	$E\rightarrow E$	268.9	1.342		265.5	0.159		205.6	0.047
00 $^-\rightarrow$ 10 $^+$	$A_2\rightarrow A_1$	266.1	0.182		265.5	0.061		213.1	0.384
	$E\rightarrow E$	266.1	0.182		265.5	0.061		213.1	0.567
10 $^-\rightarrow$ 20 $^+$	$A_2\rightarrow A_1$	237.7	0.235		246.7	0.098		196.6	0.006
	$E\rightarrow E$	237.7	0.235		246.7	0.098		196.6	0.008
10 $^+\rightarrow$ 20 $^-$	$A_1\rightarrow A_2$	247.3	0.126		246.9	0.067		179.6	0.314
	$E\rightarrow E$	247.6	0.126		246.9	0.067		179.6	0.456
<i>trans</i> $\rightarrow$ <i>gauche</i>									
10 $\rightarrow$ 20 $^+$	$A_2\rightarrow A_1$	275.1	0.437		281.7	0.001		237.2	1.011
10 $^{-1}\rightarrow$ 20	$A_2\rightarrow A_1$	204.9	0.124		202.2	0.004		145.7	0.006
00 $\rightarrow$ 10 $^-$	$A_1\rightarrow A_2$	294.4	0.334		290.4	0.002		230.1	1.960
00 $^+\rightarrow$ 10	$A_1\rightarrow A_2$	231.5	0.334		230.8	0.003		165.0	0.003

TABLE VII. Hydroxyl torsional frequencies (in cm^{-1}) and absolute intensities of the ethanol isotopes.

$\nu\nu\rightarrow\nu'\nu'$	Sym.	CH ₃ CH ₂ OH			CH ₃ CH ₂ OD			CD ₃ CH ₂ OH	
		Freq.	Int(10 ⁻⁴)	Obs.	Freq.	Int(10 ⁻⁴)	Obs.	Freq.	Int(10 ⁻⁴)
<i>trans</i> → <i>trans</i>									
00→01	$A_1\rightarrow A_2$	205.5	18.650	202.6	171.4	12.873	169.3	214.5	11.509
	$E\rightarrow E$	205.5	18.650		171.4	12.873		214.5	16.733
10→02	$A_2\rightarrow A_1$	147.3	7.692	(152)	126.4	5.796	(125)	135.3	3.205
	$E\rightarrow E$	147.3	7.692		126.4	5.796		135.3	4.660
<i>gauche</i> → <i>gauche</i>									
00 ⁺ →01 ⁻	$A_1\rightarrow A_2$	252.8	4.321	243.1	184.2	3.764	175.1	254.8	5.505
	$E\rightarrow E$	252.8	4.321		184.2	3.764		254.8	8.004
00 ⁻ →01 ⁺	$A_2\rightarrow A_1$	204.5	7.929	195.8	175.1	4.278	162.6	197.8	3.622
	$E\rightarrow E$	204.5	7.929		175.1	4.278		197.8	5.266
01 ⁻ →02 ⁺	$A_2\rightarrow A_1$	194.9	6.410	(192)	139.8	4.059	(125)	189.0	7.580
	$E\rightarrow E$	194.9	6.410		139.8	4.059		189.0	11.021
01 ⁺ →02 ⁻	A_1+A_2	237.2	0.705		151.5	0.859		244.2	0.139
	$E\rightarrow E$	237.2	0.705		151.5	0.859		244.2	0.203
<i>trans</i> → <i>gauche</i>									
00→01 ⁺	$A_2\rightarrow A_1$	278.3	3.362		209.2	0.305		279.3	2.681
01→02 ⁺	$A_2\rightarrow A_1$	267.7	0.747		177.5	1.460		253.7	0.308

243.1, and 195.8 cm^{-1} to the OH torsional mode, and the branches at 244.4 cm^{-1} and 231.6 cm^{-1} to the methyl torsion. The band at 243.6 cm^{-1} is supposed to be a hot band.¹¹

As expected, the transitions with the largest calculated intensities are related to the OH torsional bands where the dipole moment variation is significant. The most probable transitions are the *trans*-fundamental calculated to be at 205.5 cm^{-1} ($I_A=18.650\times 10^{-4}$) and the first sequence determined to the 147.3 cm^{-1} ($I_A=7.692\times 10^{-4}$). As is evident, the band observed at 202.6 cm^{-1} is the *trans*-fundamental in agreement with Ref. 11 results. It can be suggested that the (00→01) frequency can be observed at 150 cm^{-1} .

The *gauche* fundamentals (00⁺→01⁻) and (00⁻→01⁺) calculated to be at 252.8 cm^{-1} ($I_A=4.321\times 10^{-4}$) and 204 cm^{-1} ($I_A=7.929\times 10^{-4}$) correspond to the observed frequencies of 243.1 and 195.8 cm^{-1} , a difference of 10 cm^{-1} between experimental and computed frequencies around the *gauche* minima is evident. It may be inferred that the first sequence determined at 194.9 cm^{-1} ($I_A=6.410\times 10^{-4}$) is that observed experimentally at 192 cm^{-1} . The remaining OH torsion transitions show low intensities.

The ratio between OH torsional intensities and CH₃ torsional intensities is 1:15. The calculated positions of the methyl fundamental and the first sequence are 257 cm^{-1} and 242.2 cm^{-1} and the intensities $I_A=0.662\times 10^{-4}$ and 0.954

TABLE VIII. Frequencies (in cm^{-1}) and absolute intensities of the combination bands.

		CH ₃ CH ₂ OH			CH ₃ CH ₂ OD			CD ₃ CH ₂ OH	
$\nu\nu\rightarrow\nu'\nu'$	Sym.	Freq.	Int(10 ⁻⁴)	Obs.	Freq.	Int(10 ⁻⁴)	Obs.	Freq.	Int(10 ⁻⁴)
<i>trans</i> → <i>trans</i>									
10→11	A ₂ →A ₁	251.0	0.268		171.3	3.305	(169)	223.7	2.145
	E→E	251.0	0.268		171.3	3.305		223.7	3.119
01→11	A ₂ →A ₁	199.5	4.172	(201)	255.6	0.007		198.7	1.510
	E→E	199.5	4.172		255.6	0.007		198.7	2.195
<i>gauche</i> → <i>gauche</i>									
10 ⁺ →11 ⁻	A ₂ →A ₁	202.8	1.713	(201)	176.4	0.630		202.3	0.679
	E→E	202.8	1.713		176.4	0.630		202.3	0.987
10 ⁻ →11 ⁺	A ₂ →A ₁	256.3	0.734	(190)	180.9	0.864		254.8	2.321
	E→E	256.3	0.734		180.9	0.864		254.8	3.375
01 ⁺ →11 ⁻	A ₁ →A ₂				266.2	0.192		218.1	1.081
	E→E				266.2	0.192		218.1	1.571
01 ⁻ →11 ⁺	A ₂ →A ₁	272.4	0.469		262.2	0.002		205.7	0.024
	E→E	272.4	0.469		262.2	0.002		205.7	0.036
<i>trans</i> → <i>gauche</i>									
10 ⁻ →11	A ₂ →A ₁	162.1	0.114		136.6	0.003		183.0	0.003
01 ⁻ →11	A ₂ →A ₁	178.2	0.229		217.8	0.009		133.9	0.003
10→11 ⁺	A ₂ →A ₁				215.6	0.041		295.5	0.337
01→11 ⁺	A ₂ →A ₁	293.8	0.331		299.9	0.006		270.4	0.160

FIG. 6. The calculated and observed far-infrared spectra of ethanol- h_6 . The observed spectrum is from Ref. 11.

$\times 10^{-4}$. As the barrier is overestimated, they may be correlated with the bands at 244.4 cm^{-1} and 231.6 cm^{-1} assigned by Durig and Larssen,¹¹ although the Q branches look quite intense. From the differences between experimental and calculated results, we inferred that the calculated band at 268.9 cm^{-1} would be observed at 255 cm^{-1} .

Some combination bands (Table VII) show important intensities. The intensities of $(01 \rightarrow 11)$ and $(10^+ \rightarrow 11^-)$ calculated at 199.5 cm^{-1} and 202.8 cm^{-1} are $I_A = 4.172 \times 10^{-4}$ and 1.713×10^{-4} . They have to be searched around 200 cm^{-1} . However, the Q branch¹¹ observed at 243.6 cm^{-1} is not a combination of the two torsional modes. It corresponds to a transitions connecting exciting levels of one of the $3N-8$ neglected modes.

Finally, the calculated spectra show mixed bands ($\text{trans} \leftrightarrow \text{gauche}$) around 270 cm^{-1} . They show relatively large probability because the OH barriers are very low. The transition $(10 \rightarrow 20^+)$, that appears at 275.1 cm^{-1} has $I_A = 0.437 \times 10^{-4}$. The frequency of $(00 \rightarrow 01^+)$ is 278.3 cm^{-1} and the intensity is $I_A = 3.362 \times 10^{-4}$ (see Fig. 6).

B. Ethanol- d_1

The most intense bands of ethanol- d_1 coincide with those of ethanol- h_6 . The prominent $(00 \rightarrow 01)$ transition calculated at 171.4 cm^{-1} ($I_A = 12.873 \times 10^{-4}$) is the OH fundamental one observed at 169.3 cm^{-1} . As in the ethanol- h_6 the first sequence calculated at 126.4 cm^{-1} has not been assigned before and it could be placed around 125 cm^{-1} . The *gauche*

FIG. 7. The calculated and observed far-infrared spectra of ethanol- d_1 . The observed spectrum is from Ref. 11.

transitions $(00^+ \rightarrow 01^-)$ and $(00^- \rightarrow 01^+)$ laying at 184.2 cm^{-1} ($I_A = 3.764 \times 10^{-4}$) and 175.1 cm^{-1} ($I_A = 4.278 \times 10^{-4}$) have been observed at 243.1 and 195.8 cm^{-1} . It could be predicted that $(01^- \rightarrow 02^+)$ lies around 125 cm^{-1} .

For the methyl torsion (Table VI), the frequencies calculated to be 255.7 cm^{-1} and 236.9 cm^{-1} are the *trans*-fundamental and the first sequence observed at 244.3 cm^{-1} and 231.0 cm^{-1} . The remaining transitions show low intensities. At 171.3 cm^{-1} , a combination band $(10 \rightarrow 11)$ has been found laying close to the OH fundamental torsion (see Fig. 7).

C. Ethanol- d_3

To our knowledge, there is not experimental information available concerning ethanol- d_3 . However, we believe that the current predicted intensities and frequencies may help future interpretations on the basis of the isotopic substitution effects.

The differences in the intensities of the transitions connecting nondegenerate levels are lower than those of the E_i levels arising from the statistical spin weights. The methyl torsion fundamental appears as a very intense band in comparison with ethanol- h_6 and $-d_1$. The frequency is 189.4 cm^{-1} and the intensities are $I_A = 5.117 \times 10^{-4}$ and $I_E = 7.441 \times 10^{-4}$. The torsional functions of the low energy levels assigned to the methyl mode show a relatively low *Fac1* factor. The OH torsion contribution on this levels is

very large [the factor Fac1 of the level $(\nu\nu')=(10)$ of ethanol- h_6 , ethanol- d_1 , and ethanol- d_3 are 69.1, 79.1, and 57.6].

Tables VI, VII, and VII show the predicted spectrum.

VII. CONCLUSIONS

The two torsional modes of ethanol interact strongly, although the 1D flexible model appears to be powerful enough for the determination of the OH frequencies. The MP4(SDQT) calculations are accurate enough for describing the OH torsion around the *trans*-well. The *gauche* levels and the methyl torsional levels show errors of an order of magnitude of 10 cm^{-1} .

We confirm previous assignment of Ref. 11 for ethanol- h_6 and ethanol- d_1 . In addition, the intensities allow us to suggest the assignments of several transitions which positions have been calculated at $152\text{ cm}^{-1}(10\rightarrow 02)$ and $192\text{ cm}^{-1}(01^-\rightarrow 02^+)$ for ethanol- h_6 , and $125\text{ cm}^{-1}(10\rightarrow 02)$ and $125\text{ cm}^{-1}(01^-\rightarrow 02^+)$ for ethanol- d_1 . Some combination bands are calculated around 175 cm^{-1} .

ACKNOWLEDGMENTS

This work has been supported by the "Comision Interministerial de Ciencias y Tecnologia" of Spain through Grant No. PB 96-0882.

APPENDIX A

Character table of the G_6 nonrigid group.

G_6	E	C_3^{-1} C_3	VC_3, VC_3^{-1} V	Dipole moment
A_1	1	1	1	μ_a, μ_b
A_2	1	1	-1	μ_c
E_1	2	-1	0	

APPENDIX B

Torsional symmetry eigenvectors

1-Symmetry A_1 $\cos 3K\theta \cos L\alpha$; $\sin 3K\theta \sin L\alpha$	2-Symmetry A_2 $\cos 3K\theta \sin L\alpha$; $\sin 3K\theta \cos L\alpha$
3-Symmetry E_{1x} $\cos(3K\pm 1)\theta \cos L\alpha$; $\sin(3K\pm 1)\sin L\alpha$;	4-Symmetry E_{1y} $\cos(3K\pm 1)\theta \sin L\alpha$; $\sin(3K\pm 1)\cos L\alpha$

¹J. P. Perchard and M. L. Josien, J. Chim. Phys. **65**, 1834 (1968).

²J. P. Perchard and M. L. Josien, J. Chim. Phys. **65**, 1856 (1968).

³M. Takano, Y. Sasada, and T. Satoh, J. Mol. Spectrosc. **26**, 157 (1968).

⁴A. J. Barnes and H. E. Hallam, Trans. Faraday Soc. **66**, 1932 (1970).

⁵Y. Sasada, M. Takano, and T. Satoh, J. Mol. Spectrosc. **38**, 33 (1971).

⁶J. R. Durig and C. W. Hawley, J. Phys. Chem. **75**, 3993 (1971).

⁷J. R. Durig, W. E. Bucy, C. J. Wurrey, and L. A. Carreira, J. Phys. Chem. **79**, 988 (1975).

⁸R. K. Kakar and C. R. Quade, J. Chem. Phys. **72**, 4300 (1980).

⁹F. J. Lovas, J. Phys. Chem. Ref. Data **11**, 251 (1982).

¹⁰B. J. Van der Veken and P. Coppens, J. Mol. Struct. **142**, 359 (1986).

¹¹J. R. Durig and R. A. Larssen, J. Mol. Struct. **238**, 195 (1989).

¹²J. C. Pearson, K. V. L. N. Sastry, M. Winniewisser, E. Herbst, and F. C. de Lucia, J. Phys. Chem. Ref. Data **24**, 1 (1995).

¹³J. C. Pearson, K. V. L. N. Sastry, E. Herbst, and F. C. de Lucia, J. Mol. Spectrosc. **175**, 246 (1996).

¹⁴Chun Fu Su and C. R. Quade, J. Mol. Spectrosc. **175**, 390 (1996).

¹⁵A. Anderson and W. Smith, Chem. Phys. Lett. **257**, 143 (1996).

¹⁶M. Ehbrecht and F. Huiskens, J. Phys. Chem. A **101**, 7768 (1997).

¹⁷C. Talón, M. A. Ramos, S. Viera, G. J. Cuello, F. J. Bermejo, A. Criado, M. L. Senent, S. M. Benington, H. E. Fischer, and H. Schober, Phys. Rev. B **58**, 745 (1998).

¹⁸Chun Fu Su and C. R. Quade, J. Mol. Spectrosc. **188**, 1 (1998).

¹⁹S. Coussan, Y. Bouteiller, J. P. Perchard, and W. Q. Zheng, J. Phys. Chem. **102**, 5789 (1998).

²⁰R. D. Suernram, F. J. Lovas, C. R. Quade, and Chun Fu Su, J. Mol. Spectrosc. **188**, 9 (1998).

²¹I. Mukhopadhyay, Spectrochim. Acta A **54**, 1471 (1998).

²²M. A. Natal-Santiago and J. A. Dumesic, J. Catal. **175**, 252 (1998).

²³W. O. George, T. Has, M. F. Hossain, B. F. Jones, and R. Lewis, J. Chem. Soc., Faraday Trans. **94**, 2701 (1998).

²⁴M. L. Senent, R. Domínguez-Gómez, and Y. G. Smeyers, Prog. Theor. Chem. (submitted).

²⁵C. H. Görbitz, J. Mol. Struct.: THEOCHEM **262**, 209 (1992).

²⁶R. Ludwog, F. Weinhold, and T. C. Farrar, Mol. Phys. **97**, 465 (1999).

²⁷R. Ludwog, F. Weinhold, and T. C. Farrar, Mol. Phys. **97**, 479 (1999).

²⁸Y. G. Smeyers, F. J. Melendez, and M. L. Senent, J. Chem. Phys. **106**, 1709 (1997); A. Vivier-Bunge, V. H. Uc, and Y. G. Smeyers, *ibid.* **109**, 2279 (1998).

²⁹M. L. Senent, J. Mol. Spectrosc. **191**, 265 (1998).

³⁰Y. G. Smeyers, A. Hernández-Laguna, and P. Galera-Gómez, Anal. Quim. (Madrid) **76**, 67 (1980).

³¹Y. G. Smeyers, "Introduction to Group Theory for Nonrigid Molecules," in *Advances in Quantum Chemistry*, edited by P. O. Lowden (Academic, New York, 1992), Vol. 24, pp. 1-77.

³²Y. G. Smeyers, "Group Theory for Three-Dimensional Nonrigid Molecular Problems: Application to the Double Equivalent C_{3v} Rotation Plus Bending, Wagging or Torsion Mode," in *Structure and Dynamics of Nonrigid Molecular Systems*, edited by Y. G. Smeyers (Kluwer Academic, New York, 1994).

³³E. Bright Wilson Jr., J. Chem. Phys. **3**, 276 (1935).

³⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN 94, Revision E.2, Gaussian, Inc., Pittsburgh, PA, 1995.

³⁵D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. **98**, 1358 (1993); R. A. Kendal, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); T. H. Dunning, Jr., *ibid.* **90**, 1007 (1989).

³⁶M. L. Senent, Chem. Phys. Lett. **296**, 299 (1990).

³⁷M. L. Senent and S. Wilson (in preparation).

³⁸Y. G. Smeyers and M. Villa, Chem. Phys. Lett. **235**, 587 (1995); M. Villa, Q. G. Herrera-Perez, and Y. G. Smeyers, *ibid.* **306**, 78 (1999).