2080 *J. Phys. Chem. A* **2004,** *108,* 2080−2086

Dimers of Ethanol

Volker Dyczmons[†]

Institut für Physikalische Chemie, Universität Göttingen, Tammannstr.6, D-37077 Göttingen, Germany

Received: July 30, 2003; In Final Form: November 21, 2003

The energy difference between the gauche and trans structures of ethanol is determined at the CCSD(T)/aug-cc-pVTZ level. Five classes of dimer structures exist due to the two monomer conformations. In a systematic way 600 structures were generated as initial structures for the dimer geometry optimization. On the MP2/6-311++(3df,2p) level the following minima on the potential energy surface were found: 10 conformations with oxygen as the proton donor and 14 conformations with only carbon as the proton donor. Saddle points and barrier heights of five rearrangement reactions were calculated on the MP2/6-31++G-(2d,p) level. The consequences of these rearangement reactions are: only six conformations of the ethanol dimers exist with oxygen as the proton donor and at low temperatures some conformations with only carbon atoms as the proton donor may be stable. A qualitative agreement exists between the experimental OH stretching spectrum and the corresponding calculated spectrum by use of the double harmonic approximation.

1. Introduction

Hydrogen-bonded clusters[1] play an important role in many fields of chemistry and biochemistry. They have received much attention in recent literature. Small and medium-sized clusters are recognized as ideal model systems for the study of solvation phenomena. Especially alcohol represents an important role in solvent−solvent interaction.

In contrast to methanol clusters up to now only a few theoretical investigations have been performed for ethanol complexes.[1−3] Ehbrecht and Huisken[2] calculated three dimer (D_{tt}, D_{tg}, and D_{gg}) and three trimer conformations derived from the experimental monomer geometries of Alagona and Tani[5] and of the intermolecular pair potential of Jorgensen.[6] Here the subscript t means the trans monomer and the subscript g means the gauche monomer. The gauche structure is favored by a statistical factor of 2. Gonzáles et al.[2] determined on the B3LYP/6-311+G(3df,2p) level four dimer structures (D_{tt}, D_{tg}, D_{gt}, and D_{gg}). Here D_{tg} means that the donor is a trans and the acceptor a gauche conformation, and for D_{gt} it is vice versa. However, it is argued that up to nine enantiomeric pairs of stable ethanol dimer conformations may exist.[7] Häber et al.[8] and Provencal et al.[4] have measured the OH stretching vibrations of jet-cooled ethanol. By means of MP2/6-311+G(d,p) calculations for four dimer conformations a first attempt for the interpretation of the spectrum was performed by Provencal et al.[4]

It is our intention to obtain all most stable ethanol dimers because reliable information about the properties of $(CH_3CH_2OH)_2$ can be achieved only in this way. So a systematic search is necessary. Further important rearrangement reactions must be investigated for finding the stable conformations of the ethanol dimers and for the interpretation of the spectrum.

2. Computational Details

Geometry optimization of all intermolecular and intramolecular parameters was performed for all analyzed conformations of the ethanol dimer at the MP2/6-31G, MP2/6-31++G(2d,p), and MP2/6-311++(3df,2p) levels, whereby sets of five d-type and seven f-type polarization functios were used. The trans and gauche monomer structures were optimized also with the CCSD(T)/aug-cc-pVTZ method; here aug-cc-pVTZ is the augmented correlation consistent polarized valence triple basis set of Dunning.[9,10] All MP2[11] calculations were carried out with the GAUSSIAN 98 program,[12] and the CCSD(T) calculations[13−15] were performed with the MOLPRO suite of programms[16] on workstations of the Abteilung für Theoretische Chemie at Göttingen.

3. The Ethanol Monomer

Three minima exist on the potential energy surface (PES) for the ethanol monomer: one trans structure M_t and two equivalent gauche monomers M_g due to the two possible orientations of the hydroxyl group. These two enantiomer gauche structures are in the following denoted as M_{g1} and M_{g2}. Up to now no reliable values exist for the energy difference between M_t and M_g and the barrier heights between M_t and M_g and between the two gauche structures M_{g1} and M_{g2}. The calculated values with and without zero point correction (ZPC) are listed in Table 1. The most reliable results are for the gauche−trans barrier, 3.9 kJ mol^{-1}, and for the cis barrier (barrier between M_{g1} and M_{g2}), 4.6 kJ mol^{-1}, both on the CCSD(T)/avtz//MP2/avtz level. Due to the low barrier height and the low mass of the hydrogen atom, tunneling takes place between all three monomers. For the relevant small energy difference between the trans and gauche structures, ΔE_{gt}, different results from the MP2 and the CCSD(T) calculations are obtained. With the CCSD(T)/aug-cc-pVTZ method we get $\Delta E_{gt} = 0.522$ kJ mol^{-1}; this is up to now the most accurate theoretical value. With the inclusion of the zero point correction (ZPC) calculated on the MP2/6-311++(3df,2p) level, ΔE_{gt} reduces to 0.514 kJ mol^{-1}. This is in an excellent agreement with the experimental value of 0.493 ± 0.06 kJ mol^{-1} of Kakar and Quade.[17]

4. Binding Energies and Geometries of the Dimers

According to the three monomer structures, M_t, M_{g1}, and M_{g2}, five different classes exist for the dimers of ethanol: (1) The

---

[†] E-mail address: vdyczmo@gwdg.de. Fax number: +49-551-393144.

10.1021/jp030930f CCC: $27.50

TABLE 1: Rotation Barriers (kJ mol^{-1}) of Ethanol

method	gauche−trans		cis barrier		$E_{gauche} - E_{trans}$	
		with ZPC		with ZPC		with ZPC
MP2/6-31++(2d,p)	4.093	2.591	5.501	4.154	1.189	1.189
MP2/6-311++(3df,2p)	3.613	2.158	4.852	3.568	1.178	1.045
MP2/avtz)	3.882		4.552	3.294	0.902	0.894
CCSD(T)/avtz//MP2/avtz	3.929		4.550		0.517	0.511[b]
CCSD(T)/avtz					0.522	0.514[b]
exp[c]						0.493

[a] avtz means the aug-cc-pVTZ basis of Dunning.[9,10] [b] The ZPC was taken over from the MP2/avtz calculation. [c] Kakar and Quade.[17]

combination of two trans monomers is denoted with D_{tt} according to Gonzáles et al.[3] Because we only consider dimer structures in this work, we use the abbreviation tt. (2) and (3) the combination of one trans and one gauche structure, tg or gt. Here the first symbol corresponds to the donor molecule. (4) and (5) two different combinations of the gauche structures M_{g1} and M_{g2}. We denote gg for the combination of the monomers M_g with M_g or M_{g2} with M_{g2} (homochiral) and gga for the combinations M_{g1} with M_{g2} or M_{g2} with M_{g1} (heterochiral). For each conformation an enantiomer structure also exists.

To get all relevant dimer structures, the following strategy was used for each of the four classes tt, tg (gt is here included), gg and gga: We fix one of the monomers in the origin of a coordinate system. The other monomer is placed on the positive and negative coordinate axes. For the distance between the gravity centers of the two monomers 5.25 Å was chosen. For the three Eulerian angles the values 0°, 90°, 180°, and 270° were taken. Altogether one obtains 576 initial structures. In a first step geometry optimization at the MP2/6-31G level ended in 71 “stable” conformations. In a second step we obtained 43 converged conformations at the MP2/6-31++G(2d,p) level. A harmonic frequency check reduced the number of “conformations” to 26. This shows drastically the risk to search minima of the PES for floppy systems with small basis sets and without a control of imaginary frequencies. From these 26 conformations 12 have oxygen as proton donor and for 15 conformations carbon is the proton donor. In a last step, optimization on the MP2/6-311++(3df,2p) level reduced the number of minima on the PES to 24.

The optimized structures on the MP2/6-311++(3df,2p) level are shown in Figures 1 and 2, and the binding energies with respect to their appertaining monomers are shown in Tables 2 and 3. At first we discuss those conformations with an O atom as the proton donor listed in Table 2. All of them have C_1 symmetry. The listed binding energy $E_{be}(j)$ ($j = 1-10$) of the dimer D_j is the difference between the energy of the conformation $E(D_j)$ and its appertaining monomers M_1 and M_2:

$$E_{be} = E(D_j) - E(M_1) - E(M_2) \qquad j = 1-10 \qquad (1)$$

The energy gaps are relatively small, with maximum 3 kJ mol^{-1}. The energetic sequence of the six most stable conformations is the same for the MP2/6-31++G(2d,p) and the MP2/6-311++G(3df,2p) method. Conformation gg2 is a minimum of the PES only on the MP2/6-31++G(2d,p) level. The conformation gg1 has the largest binding energy. Conformation gg1 is the global minimum in contrast to previous calculations.[2−4] According to (1) the absolute energy of a dimer D_j is given by

$$E(D_j) = E_{be}(j) + E(M_1) + E(M_2) = E_{be} + 2E(M_g) + i\cdot(E(M_t) - E(M_g)) \qquad i = 0, 1, 2$$

Here $i = 2$ corresponds to the tt conformers, $i = 1$ to the tg and gt conformers, and $i = 0$ to the gg and gga conformers. The relative energies with respect to the global minimum gg1 are then

$$\Delta E = E(\mathrm{gg1}) - E(Dj) = E_{be}(\mathrm{gg1}) - E_{be}(j) + i\,(E(M_t) - E(M_g)) \qquad i = 0, 1, 2$$

For getting more reliable results we take for the E_{be} values the MP2/6-311++G(3df,2p) results but for the energy difference between gauche and trans ΔE_{gt} we make use of the zero point corrected CCSD(T)/avtz value of Table 1.

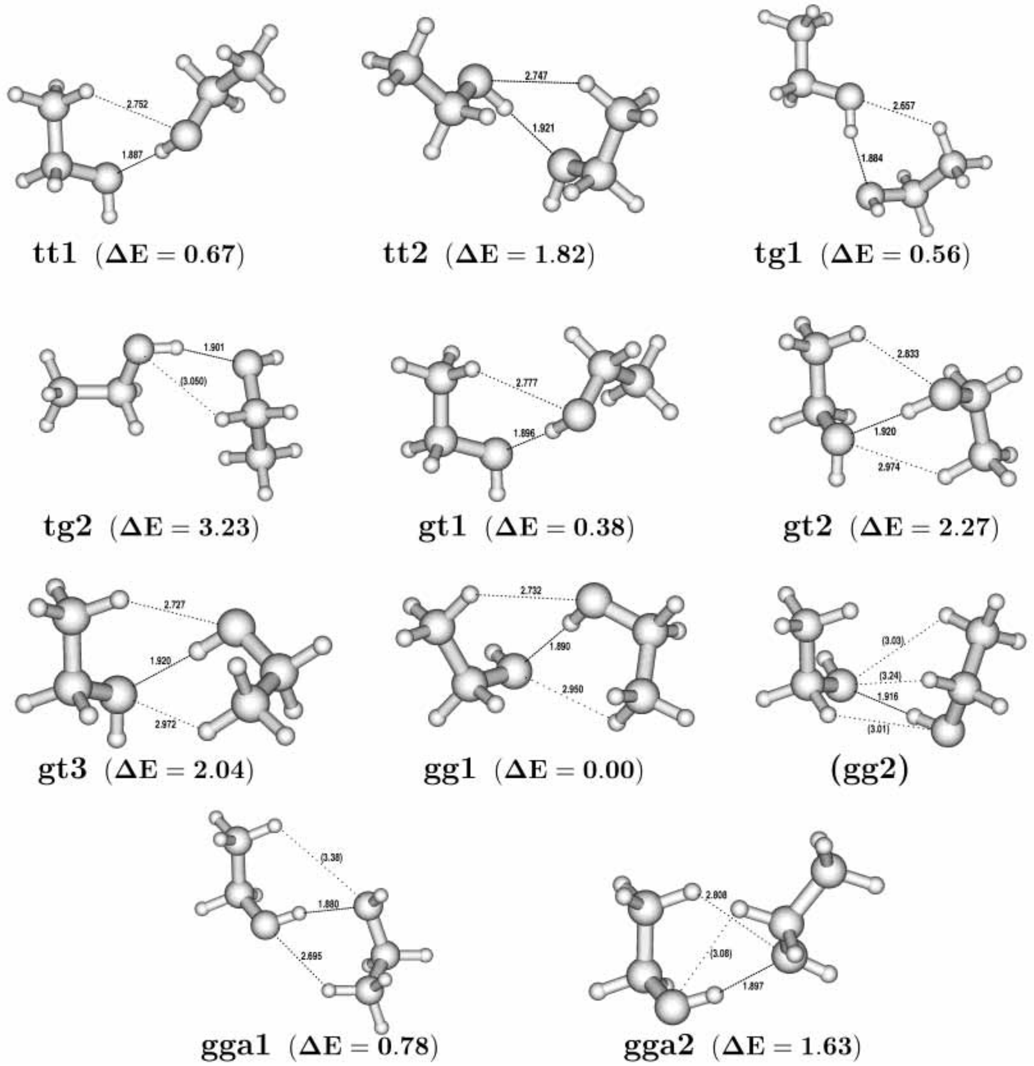
The length of the hydrogen bonds, where oxygen is the proton donor, is qualitatively a good measurement for the magnitude of the binding energy. One remarkable result is the following: All conformations in Figure 1 have one relativly strong hydrogen bridge (HB) with an O atom as proton donor (HB(O)). These strong HB(O) determine mainly the distance of the monomers and the OH···H angle. Additionally, one or two weak HB exist with C atoms as the proton donor (HB(C)). This can be seen from the large average length of 2.87 Å for the strongest HB(C) bonds. The average bond length of those conformations that have only HB(C) bonds (see Figure 2) is only 2.53 Å. These weak HB(C) determine only the angle of rotation about the corresponding OH···H hydrogen bonds. So one expects small rotation barriers for the rotation about the HB(O) bonds.

Dimers of ethanol that have only HB(C) bonds are investigated for the first time. In the first optimization procedure on the MP2/6-31G level about 30% of the obtained stable structures were of this type. Altogether, 14 minima on the PES were found. The HB(C) binding energies are surprisingly large. Cooperative effects are mainly responsible for this. The binding energies on the MP2/6-311++G(3df,2p) level lie between 7.1 and 12.6 kJ mol^{-1}. Also with the inclusion of the zero point energy 6 conformations have binding energies larger than 6 kJ mol^{-1}. So for very low temperatures some of them may exist. The conformations with C_2 and C_i symmetry are the most stable confomers. For the most weakly bonded conformations it holds that only one oxygen atom is incorporated into the HB(C)’s.

5. Some Rearrangement Reactions

To investigate the stability of the ethanol dimers, both tunneling processes and rearrangement reactions must be analyzed.

A necessary condition for successful tunneling is that the quantum levels are close together in the reactant well and in the product well, because otherwise the intensity of thermal fluctuations is too low to be effective. The monomers of ethanol have low tunneling barriers (see Table 1) and, of course, the wells are the same or similar for educt and product. Tunneling therefore takes place. The same is true for those conformations possessing an O atom that is not involved in hydrogen bonds. This is true only for the weakly bonded conformations of Table 3.



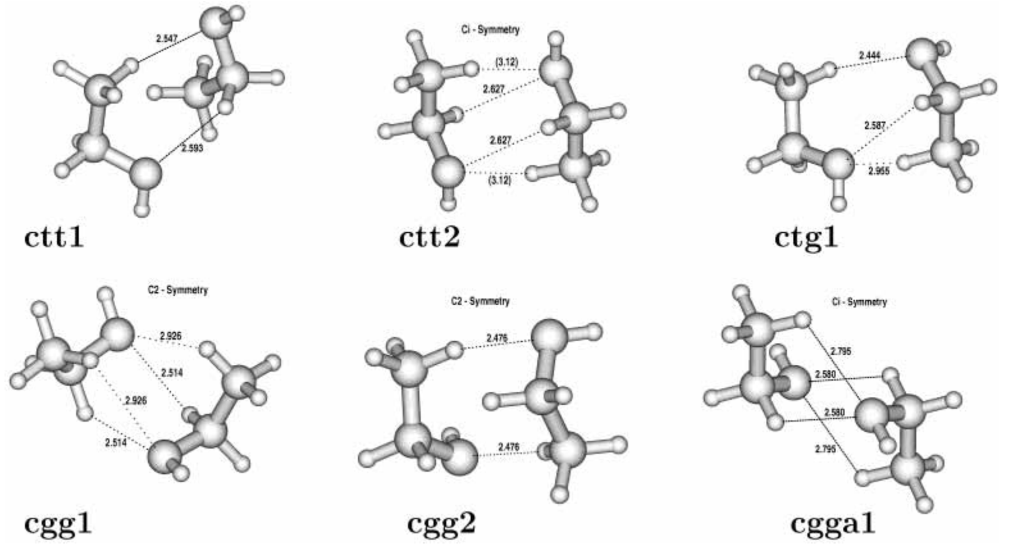
tt1 ($\Delta E = 0.67$) **tt2** ($\Delta E = 1.82$) **tg1** ($\Delta E = 0.56$)

tg2 ($\Delta E = 3.23$) **gt1** ($\Delta E = 0.38$) **gt2** ($\Delta E = 2.27$)

gt3 ($\Delta E = 2.04$) **gg1** ($\Delta E = 0.00$) **(gg2)**

gga1 ($\Delta E = 0.78$) **gga2** ($\Delta E = 1.63$)

Figure 1. : Dimer structures with oxygen as proton donor calculated at the MP2/6-311++G(3df,2p) level. Binding energies with respect to the appertaining monomers in kJ mol^{-1} and distances in Å.



ctt1 **ctt2** **ctg1**

cgg1 **cgg2** **cgga1**

Figure 2. Six most stable dimer structures with carbon as proton donor calculated at the MP2/6-311++G(3df,2p) level. Binding energies with respect to the appertaining monomers listed in Table 3; distances in Å.

For all other dimer structures tunneling of a OH group breaks at least one hydrogen bond. This increases the barrier to rotation. If the product well has a higher energy than the zero point level in the reactant, then tunneling is impossible. This means: starting from a stable conformation, the new structure generated by a tunneling process must be "close" to the geometry of a more stable conformation. This is not the case for all investigated conformations.

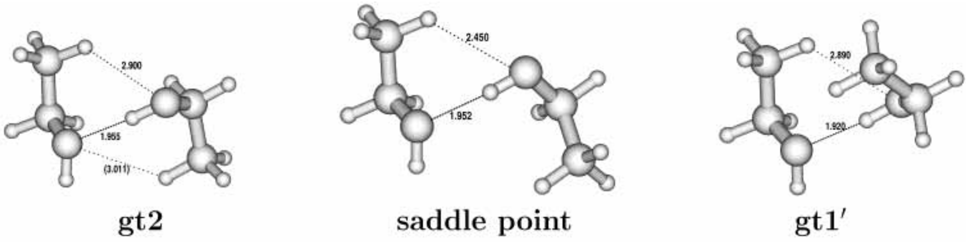


Figure 3. Rearrangement reaction **gt2** → **gt1′**. Here **gt1′** is the enantiomer of **gt1**. The barrier height at the MP2/6-31++G(2d,p) level with the inclusion of the CPC and ZPC is −0.21 kJ mol^{-1}.

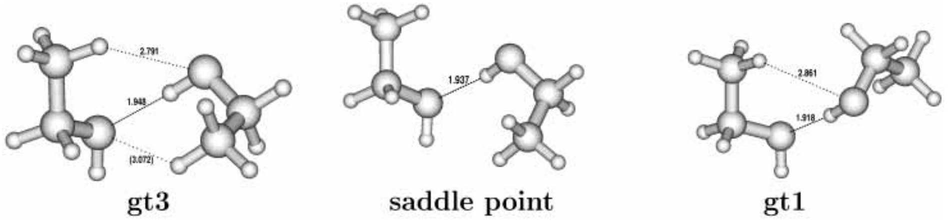


Figure 4. Rearrangement reaction **gt3** → **gt1**. The barrier height at the MP2/6-31++G(2d,p) level with the inclusion of the CPC and ZPC is −0.19 kJ mol^{-1}.

TABLE 2: Conformations with an O Atom as Proton Donor [Binding Energies with Respect to the Corresponding Monomers with and without Zero Point Correction and Deformation Energies (E_d, kJ mol^{-1})]

	MP2/6-31++G(2d,p)		MP2/6-311++G(3df,2p)				
conf		with CPC[a]		with CPC[a]	with ZPC[b]	E_d	ΔE[c]
tt1	−28.2	−22.5	−28.6	−24.1	−19.0	0.26	0.67
tt2	−26.3	−20.5	−27.4	−22.6	−17.8	0.68	1.82
tg1	−28.8	−23.1	−29.0	−24.8	−19.7	0.62	0.56
tg2	−26.5	−21.6	−26.6	−22.4	−17.0	0.61	3.23
gt1	−29.2	−23.3	−29.7	−25.1	−19.8	0.57	0.38
gt2	−27.0	−20.6	−27.9	−23.0	−17.9	0.64	2.27
gt3	−26.9	−21.0	−27.6	−22.9	−18.2	0.61	2.04
gg1	−30.2	−24.4	−30.7	−26.2	−20.8	0.59	0.00
(gg2)	−27.4	−22.3					
GGA1	=29.5	−23.9	−29.6	−25.2	−20.0	0.61	0.78
gga2	−28.09	−22.6	−28.3	−24.1	−19.1	0.60	1.63

[a] Including counterpoise correction. [b] The zero point correction is calculated at the MP2/6-31++(2d,p) level by use of harmonic frequencies. [c] Relative energies with respect to the global minimum **gg1**; here the energy difference between the trans and the gauche conformations calculated at the CCSD(T)/avtz level is included.

TABLE 3: Conformations with Only C Atoms as Proton Donors [Binding Energies with and without Zero Point Correction and Deformation Energies (E_d, kJ mol^{-1})]

		MP2/6-31++G(2d,p)		MP2/6-311++G(3df,2p)			
conf	sym		with CPC[a]		with CPC[a]	with ΔE_{ZPE}[b]	E_d
ctt1	C_1	−12.2	−7.9	−12.7	−9.6	−7.2	0.19
ctt2	C_i	−12.4	−8.0	−13.4	−9.5	−7.1	0.12
CTT3	C_1	−9.2	−5.8	−9.5	−7.1	−5.5	0.16
CTG1	C_1	−11.9	−8.2	−12.9	−9.8	−7.8	0.28
ctg2	C_1	−10.0	−6.5	−10.2	−7.8	−6.0	0.17
ctg3	C_1	−9.9	−6.2	−10.3	−7.6	−5.7	0.09
ctg4	C_1	−9.5	−6.2	−9.3	−7.3	−5.3	0.15
cgg1	C_2	−15.04	−10.6	−15.6	−12.2	−9.9	0.37
cgg2	C_2	−11.9	−8.2	−13.2	−9.9	−7.7	0.21
cgg3	C_1	−10.2	−6.6	−10.4	−7.9	−6.3	0.17
cgg4	C_1	−10.1	−6.6	−10.4	−7.9	−6.2	0.13
cgga1	C_i	−15.8	−11.0	−16.1	−12.6	−10.1	0.42
cgga2	C_1	−10.8	−7.0	−11.2	−8.5	−6.6	0.12
cgga3	C_1	−9.8	−6.4	−10.0	−7.5	−5.9	0.17

[a] Including counterpoise correction. [b] The zero point correction is calculated at the MP2/6-31++(2d,p) level by use of harmonic frequencies.

Due to the floppy nature of the dimers of ethanol the calculation of the minima of the PES is not sufficient for the search of stable conformations. Important rearrangement reactions must also be analyzed. In the following we use for all reactions the MP2/6-31++G(2d,p) method together with the inclusion of the CPC[18] and the ZPC.

At first we will examine those rearrangement reactions between "conformations" of Figure 1 where a rotation about the OH···H HB takes place. We investigate the following rearrangement reactions: gt2 → gt1 and gt3 → gt1. They are presented in Figures 3 and 4. Here only weak HB(C) are broken. Please notice that in Figure 3 the product gt1′ of the reaction gt2 → gt1 is the enantiomer structure of gt1. The barrier heights are 0.52 and 0.05 kJ mol^{-1}, with the CPC 0.34 and 0.01 kJ mol^{-1}, respectively. Adding up the zero point correction (ZPC) one obtains −0.21 and −0.19 kJ mol^{-1}. Thus the "conformations" gt2 and gt3 are not stable. It is plausible that analogously the "conformations" tt2 and tg2 are also not stable.

Next we consider the rearrangement reaction gga2 → gga1 presented in Figure 5. Here the situation is more complex. The reaction path does not correspond to a simple rotation about the OH···H HB. Additionally, one has to move from one lone pair of the acceptor O atom to the other one. So a larger barrier height is expected. With the same procedure we obtain 3.14 kJ mol^{-1} for the barrier height; with the CPC 2.35 kJ mol^{-1} and with inclusion of the ZPC one obtains 1.26 kJ mol^{-1}. So it is suggested that conformation gga is stable for low temperatures.

Of interest is also the rearrangement reaction between different classes. As an example we take the reaction tt1 → gt1 (see Figure 6). We get for the barrier height 3.80 kJ mol^{-1} and with adding up the ZPE one gets 3.37 kJ mol^{-1}. For the reaction gt1 → tt1 the barrier height with the inclusion of CPC and ZPC is 2.89 kJ mol^{-1}. The difference of 1.2 and 0.73 kJ mol^{-1}, respectively, from the gauche−trans barrier (see Table 1) demonstrates the weakness of the HB(C) bonds of the conformations tt1 and gt1. It is concluded that the most stable conformations of each class are stable at low temperatures.

In a last step we have to analyze whether some of those conformations that have only HB(C) are stable. Here we have analyzed the rearrangement reaction ctt2 → tt1 (see Figure 7). This complex reaction is composed of two steps: first, a shifting of the right monomer downward and forward, and then a turning about the OH···H HB. The barrier height is 1.46 kJ mol^{-1} and reduces with the inclusion of the CPC and ZPC to 1.01 and 0.39 kJ mol^{-1}, respectively. From this we assume that for low

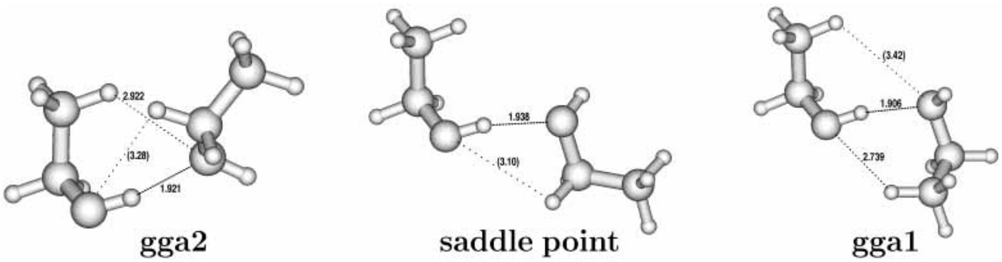


Figure 5. Rearrangement reaction **gga2** → **gga1**. The barrier height at the MP2/6-31++G(2d,p) level with the inclusion of the CPC and ZPC is 1.25 kJ mol^{-1}.

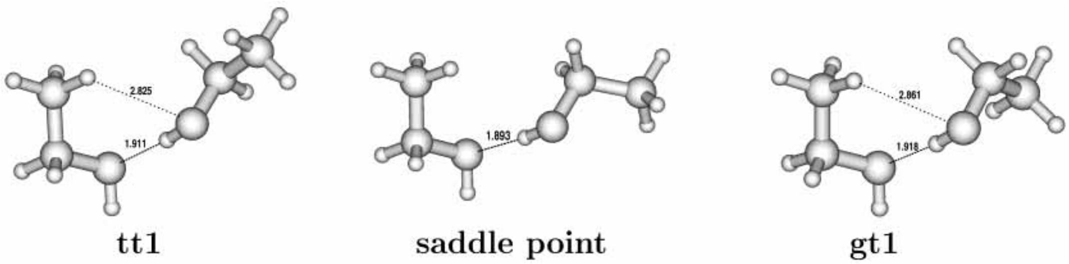


Figure 6. Rearrangement reaction **tt1** → **gt1** calculated with the MP2/6-31++G(2d,p) method. The barrier height with the inclusion of CPC and ZPC is 3.37 kJ mol^{-1} and for the reverse reaction 2.89 kJ mol^{-1}.

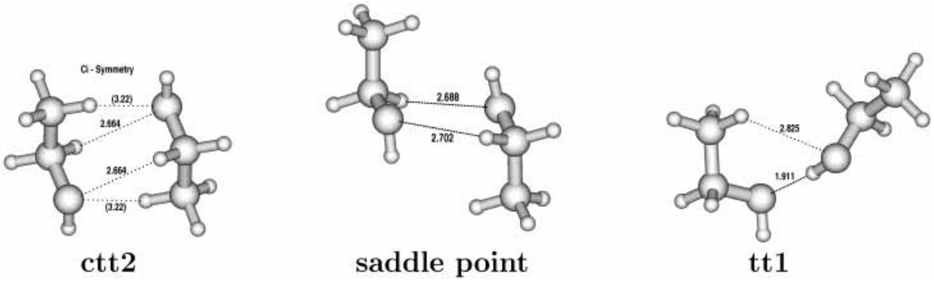


Figure 7. Rearrangement reaction **ctt2** → **tt1**. The barrier height at the MP2/6-31++G(2d,p) level with the inclusion of the CPC and ZPC is 0.39 kJ mol^{-1}.

temperatures some conformations, especially cgga1 and cgg1, may be stable.

6. Spectrum of the Red-Shifted O−H Stretching Modes

Infrared cavity ringdown laser absorption spectroscopy was performed by Provencial et al.[4] for the study of jet-cooled ethanol. Strong bands were measured at $\upsilon_1 = 3531.2$, $\upsilon_2 = 3539.5$, and $\upsilon_3 = 3547.5$ cm^{-1} for the red-shifted donor stretches of the dimers. The detection of these three bands suggests that at least three dimers were present in the molecular beam.

For comparison with experiment harmonic frequencies of the OH stretching modes were calculated. We obtain 10.92 cm^{-1} and 9.96 cm^{-1}, respectively, for the differences between the harmonic OH stretching frequencies of the monomers M_t and M_g at the MP2/6-31++G(2d,p) and MP2/aug-cc-pVTZ levels. The corresponding experimental harmonic and anharmonic values of Fang and Swofford[19] are 14 and 16 cm^{-1}. The appropriate differences of the stable conformations tt1 and tg1 on the one side and gt1, gg1, and gga1 on the other side are much smaller (see Table 4).

Due to the floppy nature of the dimers of ethanol, care must be exercised to compare theoretical and experimental values. One reason for this floppiness is the absence of saddle points between tt1 and tt2, tg1, and tg2 and between gt1, gt2, and gt3. One has to take new conformations $\overline{\text{tt1}}$, $\overline{\text{tg1}}$, and $\overline{\text{gt1}}$ between them but near to the conformations tt1, tg1, and gt1. The structures tt2, tg2, and gt3 have significantly smaller shift values (see Table 4) than the corresponding stable conformations tt1, tg1, and gt1. This holds also for the appropriate saddle points of Figures 3 and 4. Therefore it is expected that also these new conformations $\overline{\text{tt1}}$, $\overline{\text{tg1}}$, and $\overline{\text{gt1}}$ have slightly smaller shift values. As a rough estimate we take as first fit parameter a reduction of 3 cm^{-1} for the shift values of these conformations.

TABLE 4: Frequency Shifts (cm^{-1}) of the OH Stretching Vibrations of the Ethanol Dimer Due to the OH Stretching Frequency of the Trans Monomer Calculated with the MP2/6-31++G(2d,p) Method [IR Intensities (km mol^{-1}) in Parentheses]

conform	type	red shifts	type	blue shifts
tt1	t	−169.0 (494.8)	t	14.3 (47.9)
tt2	t	−145.7 (390.4)	t	10.9 (46.7)
tg1	t	−170..9 (487.2)	g	22.6 (37.1)
tg2	t	−165.0 (566.6)	g	24.5 (39.4)
gt1	g	−169.8 (418.9)	t	15.3 (47.9)
gt2	g	−153.0 (333.1)	t	12.8 (43.9)
gt3	g	−160.7 (375.5)	t	12.6 (41.8)
gg1	g	−173.3 (403.8)	g	24.2 (37.6)
gga1	g	−178.8 (432.7)	g	24.0 (37.4)
gga2	g	−159.3 (444.0)	g	22.4 (39.6)

To get a theoretically predicted spectrum, a scaling parameter was chosen in such a way that the calculated line of conformation gg1 has the frequency $\upsilon_2 = 3539.5$ cm^{-1}. Additionally, one needs the abundances of the six stable conformations in the molecular beam. The experimental values depend in an essential way on the carrier gas used. For He as carrier gas one obtains for the three strong lines nearly the same values (see Häber et al.[8] and Provencal et al.[4]). Yet with an Ar admixture (see Suhm et al.[20]) the low-frequency peak ($=\upsilon_1$) dominates

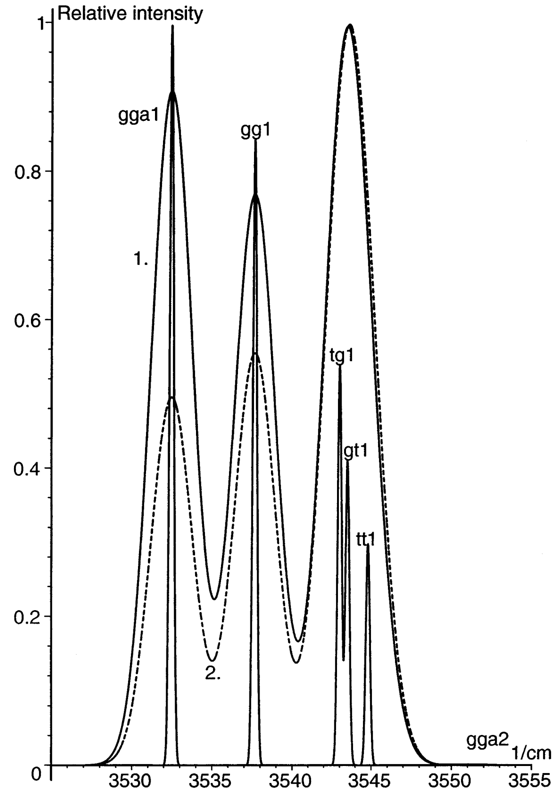


Figure 8. Calculated spectra for the red shifted OH stretching vibrations of the dimers of ethanol, whereby the half-width values of 3.0 and 0.3 cm^{-1} were taken. Curve 1 represents the rapid cooling case with a frozen in temperature of 200 K, and curve 2 (broken line) the limiting case of a Boltzmann distribution at 150 K.

under more efficient collision conditions. So the situation is complex. We propose two different limiting mechanisms:

(1) The abundances of our dimers are mainly determined by the abundances of the monomers at their formation temperature T_1. For the ratio of the abundances of M_g to M_t $a = 2 \cdot \exp[-0.514/0.008314T_1]$ is taken (see Tabel 1). No Boltzmann distribution is taken into account for the six stable conformations. This is plausible for a rapid cooling in the nozzle because the barriers of the corresponding rearrangement reaction are high and because one needs often two rearrangement reactions to come from one conformation to the other (gg ↔ tt) and (gt ↔ tg). Yet due to the lower barrier height of the rearrangement reaction gga2 → gga1 a Boltzmann distribution between these two conformations is expected for all temperatures above 30 K. So we obtain for the individual relative abundances: $1c_1$ for tt, ac_2 for tg1, ac_3 for gt1, a^2c_4 for gg, a^2c_5 for gga1, and a^2c_6 for gga2. The constants c_i are determined by the individual cross sections. For simplicity we assume that all individual cross sections c_i ($i = 1-6$) are approximately given by the Boltzmann distribution at temperature $T_1 = 200$ K.

(2) The formation temperature is higher and a slow drop of temperature in the nozzle takes place: here as limiting case a Boltzmann distribution is taken into account for the most stable conformations. We make use of a procedure that was successful for the interpretation of the spectrum of the trimers of hydrazine[21]: The Boltzmann distribution is frozen in for a certain temperature T_2 during the decrease of temperature. We take just as in case (1) for the rearrangement reaction gga2 → gga1 a Boltzmann distribution with a frozen-in temperature of 30 K.

By using the ΔE from Table 2 we consider at first case 1 (curve 1 in Figure 8): Here one gets a good qualitative accordance with the measured spectrum of Häber et al.[8] and Provencal et al.[4]: (1) The three calculated maxima are close together. (2) The intensities of these maxima are roughly the same. (3) The blue-shifted line (gga2) has a negligible intensity. At a first glance the accordance between the experimental and the calculated OH stretching spectrum is excellent, yet the caculated lines are closer together (roughly by a factor of 2/3). This rapid cooling process (case 1) is shown in Figure 8; hereby the half-width value of 3.0 cm^{-1} was taken.

For the other limiting case 2 (full Boltzmann distribution for $T_2 = 150$ K) the accordance with experiment is poor (see Figure 8 broken line). So a rapid cooling process seems to be more plausible.

For an Ar admixture up to now no agreement with experiment (Emmeluth and Suhm[20]) could be gained. So further investigations are desirable.

7. Conclusions

For the first time a systematic search for all minima on the PES of the dimers of ethanol were performed with the MP2/6-31G, MP2/6-31++G(2d,p), and MP2/6-311++G(3df,2p) methods. The number of the minima depends stronly on the used basis set. In this case also the MP2/6−61++G(2d,p) method is not suitable for getting stable structures. Calculation of the barrier heights of five rearrangement reactions shows that of the 24 minima on the PES probably only 6 structures are stable at low temperatures. The global minimum is a conformation of the gg type, in contrast to the results of earlier publications. This is caused by the fact that the energy difference between the monomer gauche and trans structures was calculated in this work more precisely (CCSD(T)/avtz method). The calculated harmonic frequencies of the red-shifted OH stretching mode are in a qualitative agreement with those measurements using He as carrier gas: (1) It was possible to assign the three measured lines to the calculated six stable conformers. (2) The calculated intensities correspond qualitatively with the experimental one's. Yet the calculated lines are by a factor of two-thirds closer together than the measured bands.

For the measurement with Ar admixture up to now no explanation for the domination of the low-frequency peak was found.

Acknowledgment. I thank Prof. M. A. Suhm for helpful discussions and Dr. R. Oswald for his help with computer hardware and software. Financial support by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 357 is gratefully acknowledged. Thanks are due to the Gesellschaft für wissenschaftliche Datenverarbeitung Göttingen for providing computer time.

References and Notes

(1) Hadzi, D., Ed. *Theoretical Treatments of Hydrogen Bonding;* John Wiley & Sons: Chichester, U.K., 1997.

(2) Ehbrecht, M.; Huisken, F. *J. Phys. Chem. A* **1997**, *101*, 7768.

(3) Gonzáles, L.; Mó, O.; Yáñez, M. *J. Chem. Phys.* **1999**, *111*, 3855.

(4) Provencal, R. A.; Casaes, R. N.; Roth, K.; Paul, J. B.; Chapo, C. N.; Saykally, R. J.; Tschumper, G. S.; Schaefer, H. F., III. *J. Phys. Chem. A* **2000**, *104*, 1423.

(5) Alagona, G.; Tani, A. *J. Chem. Phys.* **1981**, *74*, 3980.

(6) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.

(7) Schaal, H.; Häber, T.; Suhm, M. A. J. *Phys. Chem. A* **2000**, *104*, 265.

(8) Häber, T.; Schmitt, U.; Suhm, M. A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5573.

(9) Dunning, T. H. J. *Chem. Phys.* **1989**, *90*, 1007.

(10) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(11) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, C.; Cammi, R.; Menucci, B.; Pomelli, C.; Adamo, C.; Cliffort, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Ciu, Q.; Morokuma, K.; Malik, D. K.; Rabuck, A. D.; Raghavachari, K.; Forseman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Hampel, C.; Peterson K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(14) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(15) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(16) MOLPRO2000 is a package of ab initio programs written by H.-J. Werner, and P. J. Knowles, Eds., with contributions from R. D. Amos, A. Bernhardson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schiitz, H. Stoll, A. J. Stone, R. Tarroni, and R. Thorsteinsson.

(17) Kakar, R. K.; Quade, R. *J. Chem. Phys.* **1980**, *72*, 4300.

(18) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(19) Fang, L.; Swofford, R. L. *Chem. Phys. Lett.* **1984**, *105*, 5.

(20) Emmeluth, C.; Suhm, M. A. Unpublished results.

(21) Dyczmons, V. *J. Phys. Chem. A* **2002**, *106*, 5031.