

# Proton transfer dynamics in the propionic acid dimer from path integral molecular dynamics calculations

Piotr Durlak · Zdzisław Latajka

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**Abstract** The double proton transfer process in the cyclic dimer of propionic acid in the gas phase was studied using a path integral molecular dynamics method. Structures, energies and proton trajectories were determined. Very large amplitude motions of the skeleton of a propionic acid molecule were observed during the simulations, and almost free rotation of the  $C_2H_5$  group around the  $C_\alpha$ -C bond. A double-well symmetric potential with a very small energy barrier was determined from the free energy profile for the proton motions. Infrared spectra for different isotopomers were calculated, and comparative vibrational analysis was performed. The vibrational results from CPMD appear to be in qualitative agreement with the experimental ones.

**Keywords** Hydrogen bond · Propionic acid dimer (PAD) · Path integral molecular dynamics (PIMD) · Double proton transfer (DPT) · Quantum effects · IR spectra

## Abbreviations

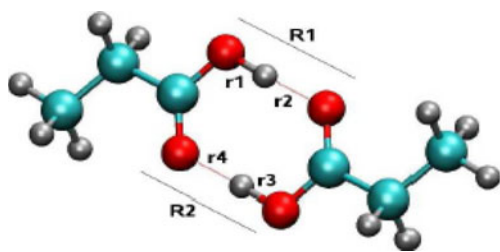
CPMD	Car–Parrinello molecular dynamics
DFT	Density functional theory
DPT	Double proton transfer
IR	Infrared spectrum
ISR	Isotopic ratio
MP2	Second-order Møller–Plesset perturbation method
UV	Ultraviolet spectroscopy
PBE	Perdew–Burke–Ernzerhof generalized gradient functional

PIMD	Path integral molecular dynamics
PI8	Eight polymer-bead model
PI16	Sixteen polymer-bead model
SPT	Single proton transfer

## Introduction

The most recent research into the double proton transfer (DPT) mechanism in biological systems is the study presented by Pérez and coworkers [1]. Those authors performed an ab initio path integral molecular dynamics study of double proton transfer in realistic models of Watson–Crick base pairs. Moreover, the hydrogen bond in monocarboxylic acids has been the subject of a vast body of experimental and theoretical studies for many years, because it can also be considered a very simple model of proton transfer in biological systems. Formic and acetic acid dimers have been the subject of many studies (see for example [2–14]). An interesting property of these dimers is the double proton transfer (DPT) process. The complete mechanism of DPT under classical conditions was first described by Ushiyama and Takatsuka [6]; in this mechanism, the protons being transferred are required to hop, but not tunnel, through any existing reaction barrier. From the viewpoint of classical molecular dynamics, the DPT is asynchronous, meaning that the two protons do not pass through the midpoints of their respective hydrogen bonds at the same time. On the other hand, the proton is a light particle, so it could be expected to quantum tunnel through a barrier. The mechanism that allows for quantum tunneling was first proposed by Miura and coworkers [4], who

P. Durlak (✉) · Z. Latajka  
Faculty of Chemistry, University of Wrocław,  
F. Joliot-Curie 14,  
50-383 Wrocław, Poland  
e-mail: piotr@elrond.chem.uni.wroc.pl  
URL: <http://kwanty.wchuwr.pl>



**Fig. 1** Structure and bond labels for the propionic acid dimer

suggested a much more dynamic mechanism without clear-cut classical mechanism steps.

Despite the very large number of papers devoted to formic and acetic acid dimers, there has been very limited experimental work on hydrogen bonds in propionic acid (propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ ) dimer. Sander and Gantenber studied the aggregation mechanism of propionic acid in low-temperature argon matrices using a pulse deposition technique [15]. The vibrational spectrum and vacuo UV spectroscopy of neutral and ionic monomers and clusters of propionic acid have been studied by Hu et al. [16]. Using IR-pump IR-probe spectroscopy, Koller and coworkers demonstrated strong coupling of the OH stretch vibration to CO stretching and OH/CH bending modes [17].

The main goal of this paper was to perform theoretical studies of the hydrogen bond dynamics in propionic acid dimers in vacuo. It is worth mentioning that propionic acid is the first in the series of monocarboxylic acids to form crystals consisting of isolated dimer pairs of molecules linked by a double hydrogen bonds [18], whereas formic and acetic acids form infinite chains of hydrogen-bonded molecules. Therefore, our study, which focuses on the gas phase, also represents a good model for a system in the crystal phase.

In our previous papers, we showed that quantum effects are important for describing proton transfer in hydrogen-bonded systems [19–24]. Therefore, in this study of double proton transfer in a propionic acid dimer, we have mainly used path integral molecular dynamics (PIMD) [25–27], which allows us to explore the quantum behavior of nuclear motion. In other words, it maps the problem of a quantum particle onto one of a classical ring polymer model with  $N$  beads that interact through temperature- and mass-dependent spring forces. In practice, the representation of each atom in the system as a group of  $N$  beads requires  $N$  electronic structure calculations, and is therefore much more computationally expensive than Car–Parrinello molecular dynamics (CPMD). It should also be mentioned that “real” properties of the quantum system are obtained only when there are an infinite number of beads.

### Computational details

A series of geometry optimizations together with vibrational harmonic and anharmonic frequency calculations were undertaken to localize the key stationary points on the potential energy surface (PES) of the propionic acid dimer. Calculations were performed using the Gaussian 03 package [28], utilizing the DFT method with the PBE1PBE functional [29]. Calculations were carried out with the aug-cc-pVTZ [30–33] and 6-311++G(2d,2p) [34, 35] basis sets. We also carried out calculations utilizing the Møller–Plesset [36] method truncated at the second-order (i.e., MP2) coupled with the aug-cc-pVDZ [30–33] basis set. The anharmonic vibrational spectra for the propionic acid dimer system were calculated using a second-order perturbative vibrational

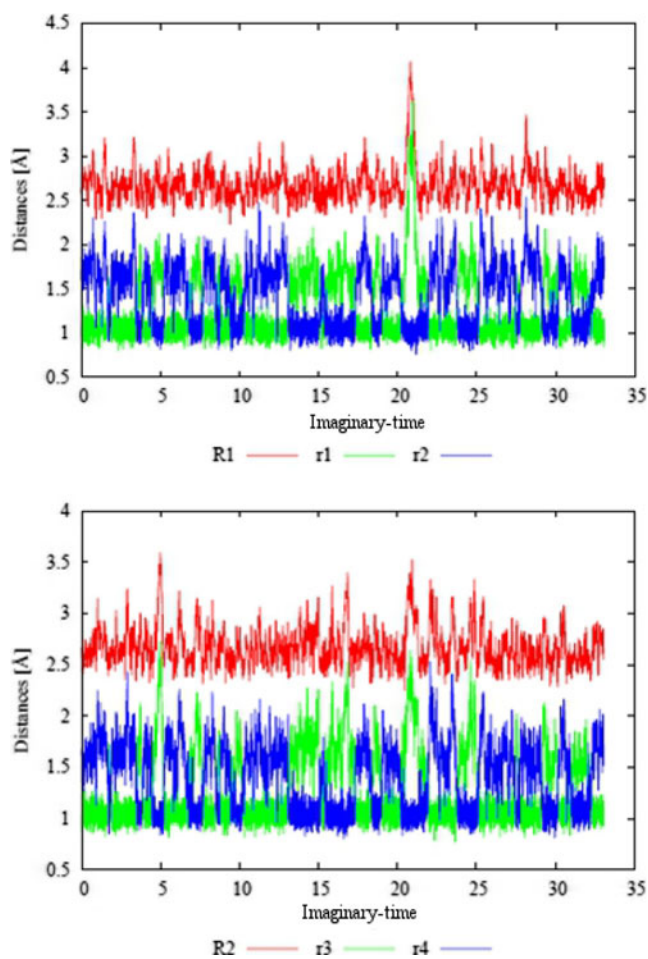
**Table 1** Calculated selected geometrical parameters after optimization compared with the existing experimental data for the propionic acid dimer system (bond lengths are in Å, angles are in degrees)

Parameter	PBE1PBE		PCG/PBE	MP2	Experimental <sup>a</sup>
	6-311++G(2d,2p)	aug-cc-pVTZ	80 Ry	aug-cc-pVTZ	
R1	2.658	2.598	2.611	2.626	2.711
R2	2.658	2.598	2.611	2.626	2.711
r1	1.001	1.001	1.031	0.998	1.030
r3	1.001	1.001	1.031	0.998	1.030
r2	1.658	1.590	1.581	1.628	-
r4	1.658	1.590	1.581	1.628	-
C–O	1.320	1.306	1.326	1.315	1.329
C=O	1.226	1.225	1.241	1.226	1.232
∠ R1	179.1	178.5	177.4	177.9	
∠ R2	179.1	178.5	177.4	177.9	

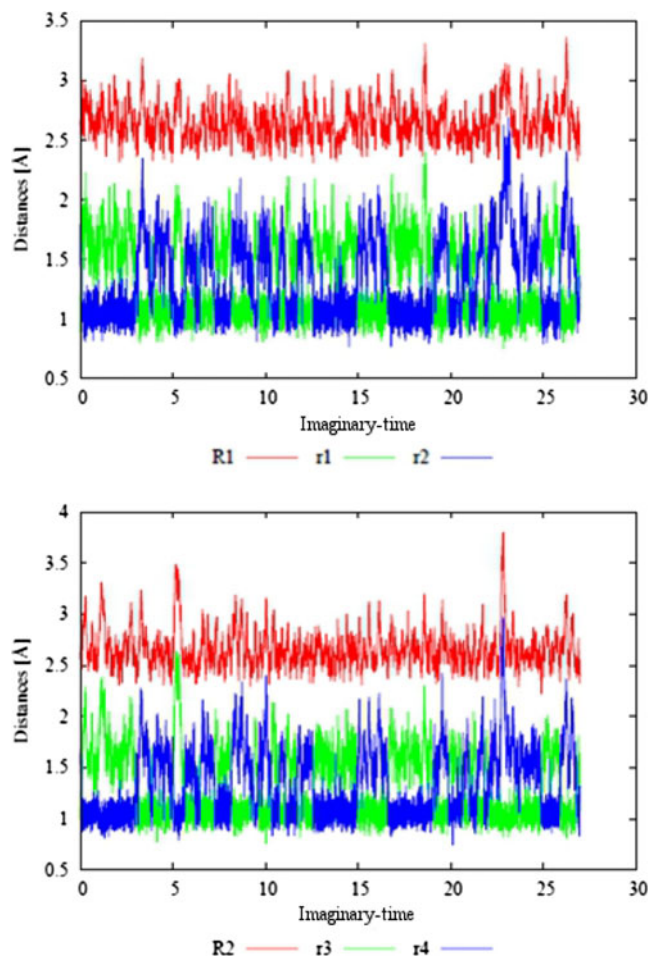
<sup>a</sup> Gas phase electron diffraction at 328 K, from [49]

treatment based on quadratic cubic and semidiagonal quartic force constants as implemented by Barone [37, 38] only at the DFT method level.

Molecular dynamics calculations have been carried out using the CPMD software, version 3.13.1 [39], with the initial molecular configuration for the propionic acid dimer optimized by the preconditioned conjugate gradient (PCG) method. The dimer was located in a simple cubic box of size 15.0 Å. Molecular dynamics and path integral simulations (NVT ensemble) were carried out at 450 K with a time step of 3.0 a.u. (0.072566 fs), coupled to a Nosé–Hoover chain thermostat [40] at a frequency of 3200 cm<sup>-1</sup>. An electronic mass parameter of 400 a.u. was employed. Electronic exchange and correlation were modeled using the gradient-corrected functional of Perdew, Burke and Ernzerhof (PBE) [41]. Core electrons were treated using the norm-conserving atomic pseudopotentials (PP) of Troullier and Martins [42], while valence



**Fig. 2** The evolutions of the bonds involved in the hydrogen bonding at 450 K, obtained using PIMD PI8 calculations (based on the positions of the bead centroids)



**Fig. 3** The evolutions of the bonds involved in the hydrogen bonding at 450 K, obtained using PIMD PI16 calculations (based on the positions of the bead centroids)

electrons were represented in a plane-wave basis set truncated at an extended energy cutoff of 80 Ry. Following the initial equilibration period, data were accrued for a further 34 and 27 ps (imaginary time) for the path integral dynamics simulation for 8 (PI8) and 16 (PI16) polymer beads (Trotter replicas), respectively, using the normal mode variable transformation. The data were visualized using the VMD software [43], with the path integral data first processed with a script by Kohlmeyer to calculate the centroid position of each set of polymer beads [44]. The proton distribution function and the free energy profile for proton motion of the PIMD simulations were calculated from the bead distribution.

The vibrational spectra were generated using the program by Forbert and Kohlmeyer [45] that calculates the spectrum using the inverse fast Fourier transform of the classical autocorrelation function of the total dipole moment (obtained from dipole trajectories generated by

the CPMD with a classical “one bead” simulation of nuclei), including all contributions (nuclear and electronic). To simulate the IR spectra, a massive Nosé–Hoover chain thermostat was used with the following options: massive Nose ions, 450 K,  $3200\text{ cm}^{-1}$ , with default parameter values for thermostat control.

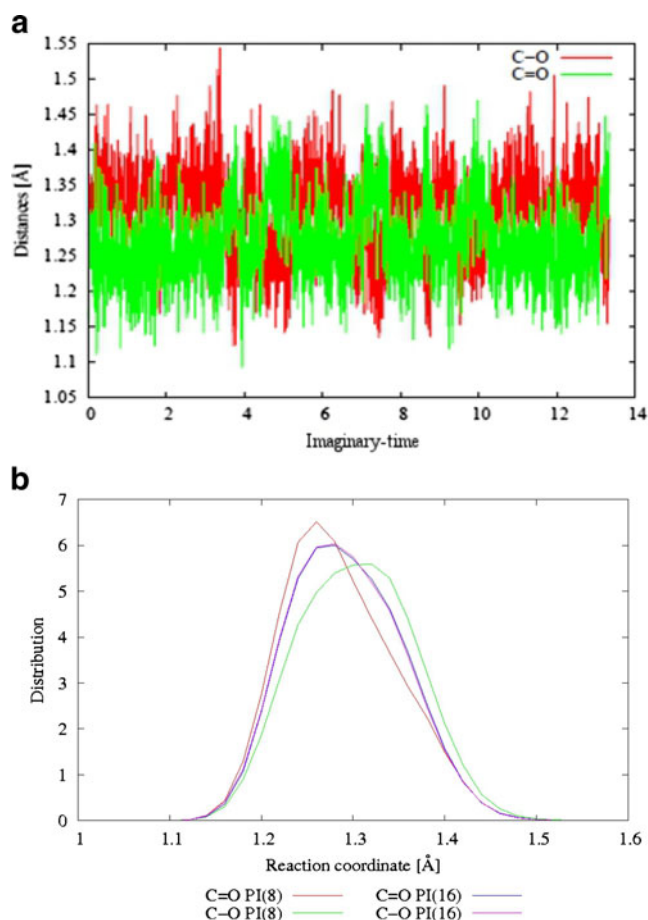
According to studies by Zhao and Truhlar [46], the density functionals (PBE and PBE1PBE) used in this work give good performance for hydrogen-bonded systems.

## Results and discussion

For the first part of the computational studies, MP2 (aug-cc-pVTZ) and DFT calculations with the PBE1PBE density functional and two basis sets—6-311++G(2d,2p) and aug-cc-pVTZ—were applied to investigate the molecular structure of the propionic acid dimer in vacuum. The structure of the studied dimer is presented in Fig. 1, whereas selected calculated geometrical parameters are listed in Table 1. The geometrical parameters that are most sensitive to the choice of basis set are the O...O bond distances, which are a little short when compared with the gas electron diffraction experimental results [47]. The remaining geometrical parameters are in reasonable agreement with the experimental data. It is worth noting that the O–H...O bond deviates only slightly from linearity (ca.  $179^\circ$ ).

The standard “static” ab initio calculations are useful for obtaining information on the localization of critical points (minima) on the PES. Because hydrogen-bonded systems are not static but fluctuate on an ultrashort time scale, we decided to use a molecular dynamics approach in the PIMD formalisms. Table 1 gives selected geometric parameters from the optimized athermal geometry of CPMD calculations.

Figures 2, 3, 4a and 5a are presented to indicate the nature and courses of the simulations, but they not provide any physical information for the structural analysis. The evolution of the bonds directly involved in both O–H...O hydrogen bridges at 450 K—calculated on the basis of the centroid positions of the beads—are presented in Fig. 2 (PI8) and Fig. 3 (PI16). The protons are very mobile in both hydrogen bonds, and double proton transfer (DPT) is observed. Detailed analysis shows that there are two distinct behaviors of the system: the so-called rest period, where each proton remains closely associated with one oxygen atom and exhibits normal O–H vibrational behavior, and an active period, where both protons quickly transfer to the other well on the potential energy surface. Moreover, an analysis of the trajectories of the atoms during the PIMD simulation clearly shows that a

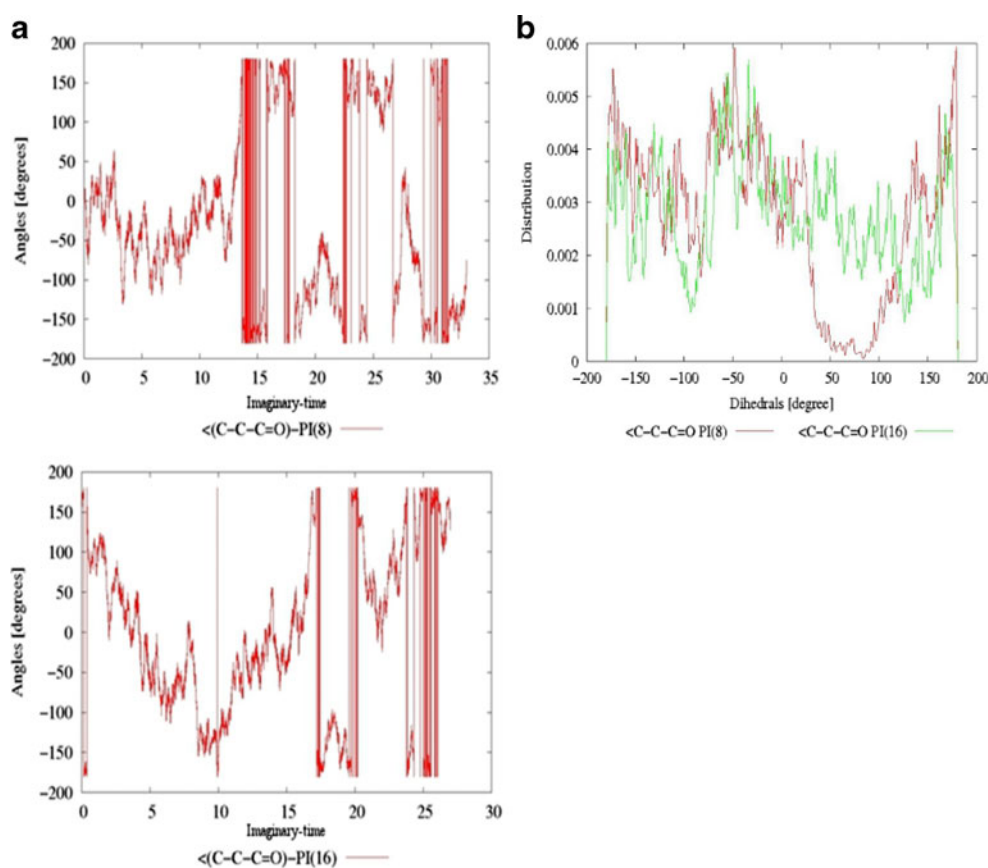


**Fig. 4** **a** C–O and C=O bond distances, obtained using path integral dynamics simulations (based on the positions of the bead centroids); **b** distribution functions for the lengths of the C–O and C=O bonds at 450 K, obtained from PIMD simulations (of 8 and 10 beads) of the propionic acid dimer in the gas phase

proton transfer event will occur for a contraction in the O...O distance to below  $2.5\text{ \AA}$ . The decrease in the hydrogen bond distance results in a drop in barrier height on the potential energy surface and an increase in the tunneling probability. In addition to observing the active DPT periods, which occur very frequently, there are also a small number of transient single proton transfer (SPT) events, where a proton transfers from one oxygen to the other and almost immediately moves back. The picture of DPT under PIMD conditions observed in this work is similar to that previously observed for the chloroacetic acid dimer [18] and the formic acid dimer in vacuo [4]. We also note that the motions of the two protons are synchronized, which agrees with previously reported PIMD studies on related systems.

During the DPT process, very large atomic motions of the skeletons of propionic acid monomers are observed during the PIMD simulations. The dynamics

**Fig. 5** **a** The evolution of the C–C–C=O dihedral angles (based on the positions of the bead centroids); **b** distribution functions for the dihedral angles C–C–C=O at 450 K from PIMD (8 and 16 beads) simulations of the propionic acid dimer in the gas phase

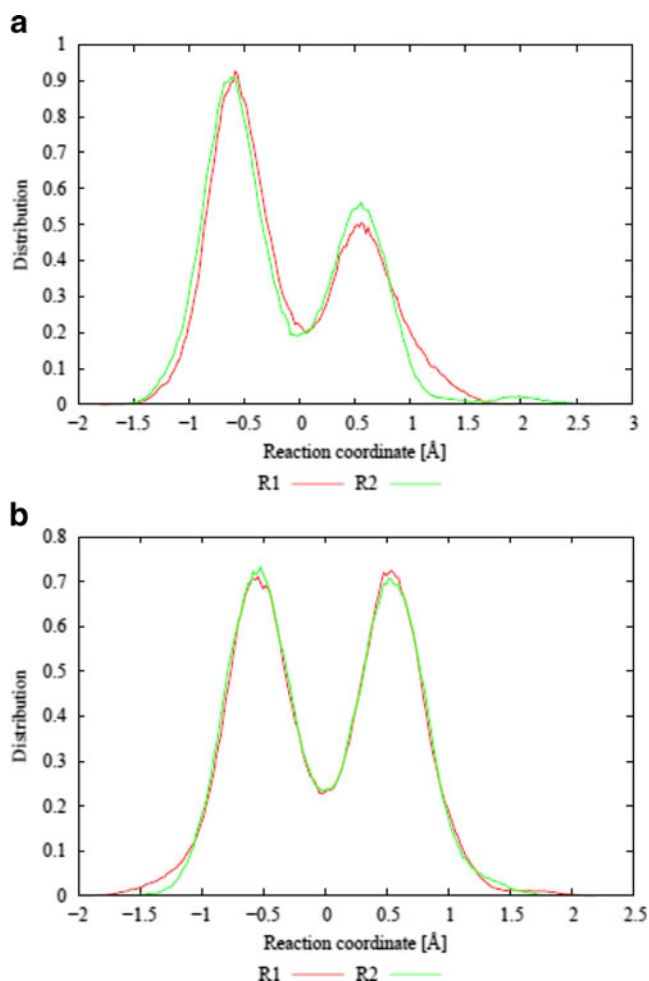


of proton transfer are also characterized by the evolution of the C–O/C=O bond lengths, as presented in Fig. 4a, and the bond distribution, as presented in Fig. 4b. Due to the proton transfer, the single carbon–oxygen bond becomes a double bond, and vice versa. The O=C–O angle has an average value of  $124^\circ$  but rotates with an amplitude of  $\pm 11^\circ$ , whereas the O–H...O angle varies by  $\pm 30^\circ$  (PI8 simulations).

Ab initio calculations carried out by Maçõas and coworkers predicted four stable conformers for the isolated propionic acid molecule [48]. These structures, denoted  $T_t$ ,  $T_g^\pm$ ,  $C_t$  and  $C_g^\pm$ , differ in terms of the arrangement around the C–O and  $C_\alpha$ –C bonds. The most stable is the  $T_t$  conformer, presented in Fig. 1, and this form is only present at 8 K after the deposition of an argon matrix containing propionic acid [49]. As presented by Maçõas et al., the MP2/6-311++G(2d,2p) calculations indicate that the second most stable conformer is the degenerate gauche configuration  $T_g^\pm$ , with a C–C–C=O dihedral angle of approximately  $\pm 75^\circ$ , and is higher in energy than the *trans* forms by ca.  $0.97 \text{ kcal mol}^{-1}$ . The estimated barrier to internal rotation around the  $C_\alpha$ –C bond was found to be approximately  $1.14 \text{ kcal mol}^{-1}$ . The results of the ab initio calculations are supported by experimental studies. The

electron diffraction studies of Derissen [47] suggest that, in addition to the  $T_t$  conformer, structures bearing a nonplanar C–C–C=O skeleton also contribute to the gas phase equilibrium conformation distribution, with an estimated population of ca. 40% at  $T=488 \text{ K}$ . Because our PIMD calculations are performed at a similarly high temperature (450 K), it can be expected that the C–C–C=O dihedral angle will change greatly during the simulations. In Fig. 5a, b, we present the evolution and the distribution of this angle. During the simulations we observed very large changes in the C–C–C=O dihedral angle, clearly indicating the rotation of  $C_2H_5$  group around the  $C_\alpha$ –C bond. Careful analysis of the trajectories does not indicate coupling between this motion and double proton transfer events.

Significant delocalization of the bridging protons in the O–H...O hydrogen bonds is even more visible in Fig. 6, where the proton distributions in both hydrogen bonds are presented versus the reaction coordinate. The midpoint position of the proton in the O–H...O bridge corresponds to a reaction coordinate ( $\delta=r_{O-H}-r_{H...O}$ ) of zero. Figure 6 presents the distributions of the protons from the PIMD simulations. At the PI8 level, an asymmetric proton distribution is seen in both hydrogen bonds. This may



**Fig. 6** Distribution functions for the protons from the PIMD simulation: *upper* PI8, *lower* PI16

suggest that the PI8 model is not sufficient to fully capture the quantum nature of this system, so the (artificial) asymmetric distribution arises from the statistical error. Increasing the number of polymer beads to 16 leads to a better description of quantum effects, and gives a symmetric proton distribution at both minima on the potential energy surface. A relatively wide proton distribution is observed in both simulations in the region of the energy barrier for the proton transfer, which is classically forbidden.

Figure 7 shows the free energy profiles for proton motion obtained from PIMD results. Free energy profiles were calculated from the equation

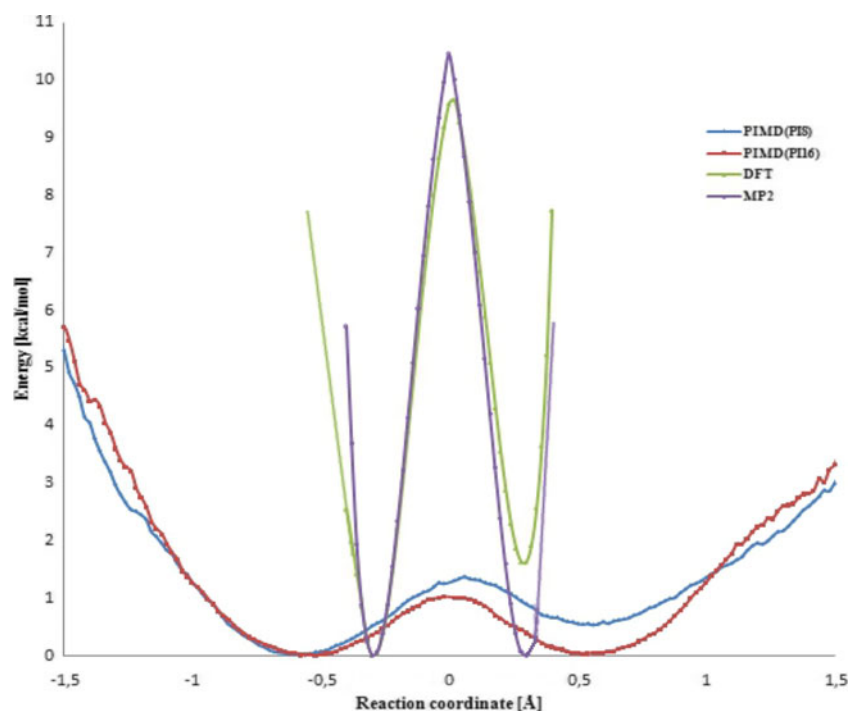
$$\Delta F = -kT \ln[P(\delta)], \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the simulation temperature, and  $P(\delta)$  is the proton distribution as a

function of  $\delta$  (the reaction coordinate). As expected, a double well potential successfully describes the proton motion. However, this motion is slightly asymmetric in the PI8 simulations, whereas symmetric motion is observed for the PI16 calculations. Including quantum effects reduces the effective barrier height to a value of ca.  $1.3 \text{ kcal mol}^{-1}$  for the 8-polymer-bead simulations and ca.  $1.0 \text{ kcal mol}^{-1}$  for the 16-polymer-bead calculations. The small asymmetry in the free energy profile for PI8 calculations explains the observed shape of the proton distribution in the O–H...O hydrogen bond. On the other hand, the energy barriers from the static calculations performed at the DFT and MP2 method levels indicate central barrier heights of around  $9.58 \text{ kcal mol}^{-1}$  and  $10.44 \text{ kcal mol}^{-1}$ , respectively. The PIMD calculations show that the hydrogen bridges are not rigid, with the distances  $R1$  and  $R2$  being described by large-amplitude motions. It is also important to note that the standard ab initio calculations only give us the value of the barrier height along the proton reaction path; this cannot be considered the absolute criterion for the possibility of proton motion.

The band shape of the OH stretching mode in carboxylic acid dimers is very complex. Instead of a single band, a very broad, structured absorption pattern is found in the gas phase [2, 9, 13, 49]. Different mechanisms such as Fermi resonance, Davydov splitting, and the Franck–Condon principle in combination with hydrogen bond modes have been used in models that attempt to reproduce the experimental band shape. The vibrational spectra for  $(\text{C}_2\text{H}_5\text{COOH})_2$ ,  $(\text{C}_2\text{H}_5\text{COOD})_2$  and  $(\text{C}_2\text{D}_5\text{COOD})_2$  have been calculated using Fourier transformation of the dipole autocorrelation function obtained for dipole trajectories generated by CPMD simulation. This approach includes all of the vibrational modes and anharmonic effects. Selected characteristic vibrational frequencies, together with harmonic and anharmonic PBE1PBE [6-311++G (2d,2p) and aug-cc-pVTZ basis sets] frequencies and available experimental data, are presented in Table 2. The IR spectra calculated by the CPMD method for three isotopomers are presented in Fig. 8. Calculated spectra, especially those at the anharmonic level, show good agreement with experimental results. For example, the OH stretching mode calculated by CPMD simulation arises at about  $2990 \text{ cm}^{-1}$ , while it is observed experimentally at  $3130 \text{ cm}^{-1}$  [48]. Moreover, the complicated and broad band shape of the OH stretching mode is also qualitatively replicated by the CPMD calculations. The main reason for this is that, during CPMD simulations, all possible mode couplings due to the oscillations of the atoms in molecules are taken into account. Moreover, when this approach is used, there is no limitation on mode couplings, in contrast

**Fig. 7** Quantum P18 (*blue*) and quantum P16 (*red*) free-energy profiles compared with the static energy barrier from DFT (*green*) and MP2 (*violet*) calculations for double proton transfer in the propionic acid dimer



to theoretical models that usually take into account only a few mode couplings.

In this work, vibrational stretching O–H...O modes for the hydrogen bridge in the dimer were investigated. CPMD places this mode at  $160\text{ cm}^{-1}$ , which is slightly higher than

the value obtained from anharmonic BPE1PBE calculations (ca.  $118\text{ cm}^{-1}$ ).

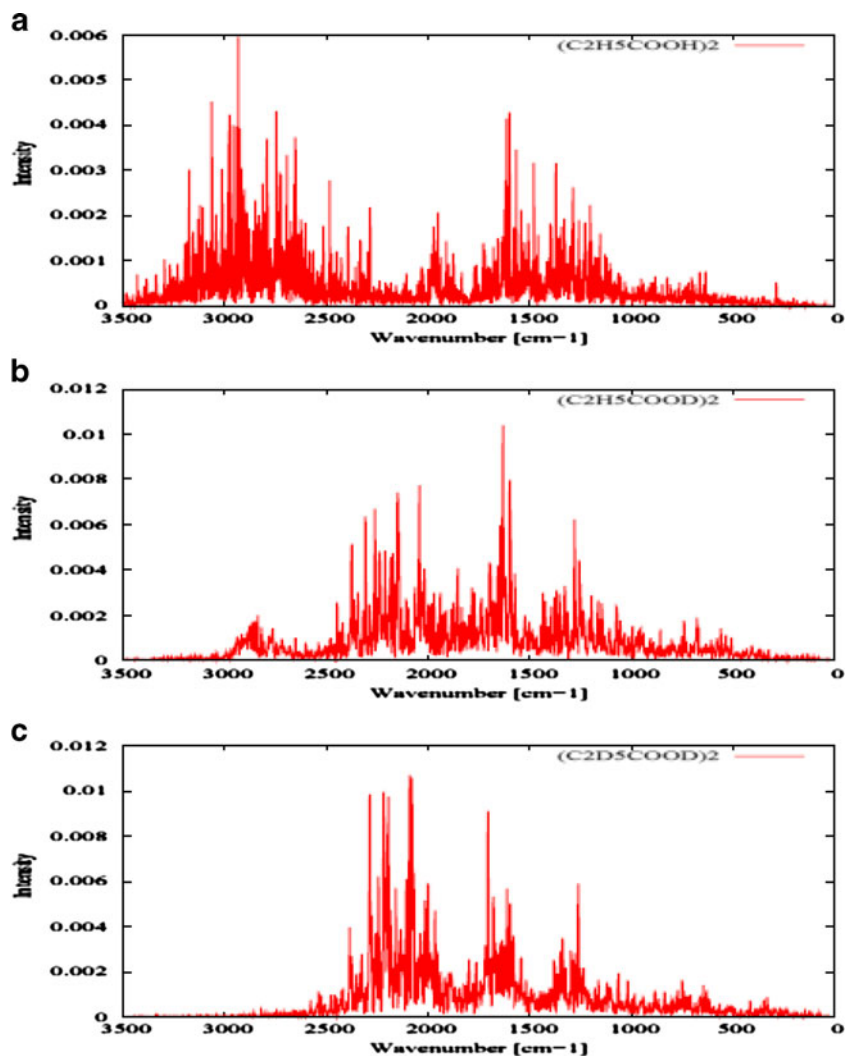
One of the most important parameters related to the IR properties of the hydrogen bond is the isotopic effect, as defined by the isotopic ratio (ISR):  $\nu(\text{OH})/\nu(\text{OD})$ . In

**Table 2** Selected calculated and experimental vibrational frequencies (in  $\text{cm}^{-1}$ ) for the propionic acid dimer and its deuterated analog

Frequency	PBE1PBE/6-311++G(2d,2p)		PBE1PBE/aug-cc-pVTZ		CPMD/PBE/80Ry	Experimental <sup>a</sup>
	Harmonic	Anharmonic	Harmonic ( $\text{C}_2\text{H}_5\text{COOH}$ ) <sub>2</sub>	Anharmonic		
$\nu\text{O-H}$	2945.5	2837.5	3049.8	2891.5	2990	3130
$\delta\text{O-H}$	1492.4	1453.3	1495.8	1448.5	1420	1419
$\nu\text{C=O}$	1712.6	1630.8	1775.3	1755.8	1720	1735
$\nu\text{C-O}$	1372.5	1332.1	1381.8	1337.1	1350	-
$\nu\text{O-H...O}$	134.5	119.6	134.4	118.2	160	-
			$(\text{C}_2\text{H}_5\text{COOD})_2$			
$\nu\text{O-D}$	2239.2	2186.7	2215.8	2158.9	2300	
$\delta\text{O-D}$	1125.8	1120.8	1120.1	1098.7	1380	1380
$\nu\text{C=O}$	1735.1	1698.8	1665.4	1642.5	1680	1725
$\nu\text{C-O}$	1379.7	1362.3	1346.5	1287.4	1280	-
$\nu\text{O-D...O}$	160.9	146.1	133.0	123.7	155	-
			$(\text{C}_2\text{D}_5\text{COOD})_2$			
$\nu\text{O-D}$	2239.1	2178.4	2225.4	2095.7	2300	
$\delta\text{O-D}$	1121.1	1197.0	1110.9	1054.6	1370	-
$\nu\text{C=O}$	1731.7	1698.2	1662.7	1654.7	1680	-
$\nu\text{C-O}$	1369.3	1340.6	1321.3	1275.6	1270	-
$\nu\text{O-D...O}$	156.9	140.7	126.4	120.1	140	-

<sup>a</sup> Gas-phase IR spectrum from [50]

**Fig. 8a–c** Simulated IR spectra at 450 K for the propionic acid dimer and its selectively deuterated isotopomers, obtained from CP molecular dynamics simulation: **a**  $(\text{C}_2\text{H}_5\text{COOH})_2$ , **b**  $(\text{C}_2\text{H}_5\text{COOD})_2$ , **c**  $(\text{C}_2\text{D}_5\text{COOD})_2$



normal hydrogen-bonded systems, the IRS value is less than  $\sqrt{2}$ . The calculated ISR from the CPMD simulations is equal to 1.3, very close to the CPMD [51] and experimental [49] ISR values for the acetic acid dimer in the gas phase. Similar IRS values were obtained from DFT calculations.

## Conclusions

This paper presents the results of a study of the double proton transfer dynamics of the propionic acid dimer in the gas phase at 450 K using PIMD simulations. Both protons are very mobile in the hydrogen bridges, and the DPT is synchronized under the control of quantum effects. Simulations at the PI16 level clearly show a symmetrical distribution of protons in the O–H...O bridge. Moreover, a relatively high probability of finding protons is also observed in the region of the energy barrier. The effective

barrier to proton motion, determined on the basis of the free energy profile, is relatively low ( $\sim 1$  kcal mol $^{-1}$ ). On the other hand, the energy barriers from static calculations performed at the DFT and MP2 method levels have central heights of around 9.58 kcal mol $^{-1}$  and 10.44 kcal mol $^{-1}$ , respectively. It is also important to note that standard ab initio calculations only gives the value of the barrier height along the proton's reaction path; it cannot be considered the absolute criterion for the possibility of proton motion.

During the simulations, very high deformation of the propionic acid skeleton was observed. Moreover, almost free rotation of the  $\text{CH}_3\text{CH}_2$  group was seen.

CPMD IR spectra reproduce the broad band shape of the OH stretching mode. Good agreement with experimental spectra from the gas phase was found for the calculated vibrational frequencies. The calculated isotopic ratio,  $\text{ISR} = \nu(\text{HO})/\nu(\text{OD}) = 1.3$ , is very close to the experimental value obtained for the acetic acid dimer in the gas phase.



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