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**Title:** Ab initio molecular dynamics study of overtone excitations in formic acid and its water complex

**Year:** 2018

**Version:** Accepted version (Final draft)

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**Please cite the original version:**

Järvinen, T., Lundell, J., & Dopieralski, P. (2018). Ab initio molecular dynamics study of overtone excitations in formic acid and its water complex. *Theoretical Chemistry Accounts*, 137(7), Article 100. <https://doi.org/10.1007/s00214-018-2280-6>

# Ab Initio Molecular Dynamics Study of Overtone Excitations in Formic acid and its Water Complex

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Received: date / Accepted: date

**Abstract** In this article we present results from ab initio molecular dynamics simulation of overtone excitation in formic acid monomer and its water complex in the gas phase. For the monomer a conformation change is observed employing both OH and CH vibrational excitation, which supports experimental findings. In the water conformed a conformer interconversion also takes place but it proceeds via hydrogen exchange together with the water molecule. Simulations raise a questions on effect of quantum and matrix effects to the results. Also a small testing of different computation methods was done on the system.

**Keywords** formic acid · overtone · proton exchange · vibration induced chemistry

## 1 Introduction

The high overtone induced processes are initiated by promoting a molecule or a complex to chemically relevant energies in high vibrational excited states through the thermal excitation or direct absorption of visible or near-infrared radiation. Unlike the thermally induced processes, the reactions initiated by vibrational overtone-pumping of ground electronic state molecule through direct absorption of photon can be treated without the need to consider collisional activation processes. In general, it is required that the energy is deposited into

the initially excited vibrational state and subsequently transferred by intramolecular vibrational redistribution to other modes of the molecule including the reaction coordinate. For example, it has been demonstrated that high overtone excitation of OH groups in carboxylic acids isolated in low temperature matrices leads to two different unimolecular processes: isomerization and/or decomposition of the molecules [1, 2, 3, 4]. Moreover, overtone pumping was used, for example, in the case of formic acid dimers to produce high-energy conformers within the hydrogen-bonded complexes [5, 6, 7].

In case of formic acid it has been shown to change conformation from trans to cis [1], see figure 1, and that formed cis conformer reorganises back to trans form via a tunneling mechanism [8]. But in formic acid water complex this conversion back from trans to cis does not happen [9].

The aim of this study was to try to simulate using ab-initio molecular dynamics these conformation changes that have been observed in experiments. In particular the aim was to try to see if 532 nm excitation energy could produce these results, as this has been the laser wavelength used to produce high-overtone interconversions, for example, for formic, oxalic and glyoxylic acids [2, 10].

## 2 Method

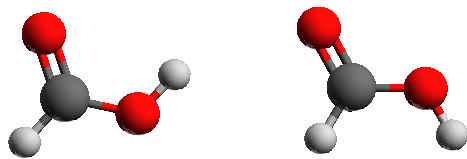
Ab-initio molecular dynamics simulations were done with Car-Parrinello method [11, 12], using CPMD v. 4.1 [13]. Calculations were done using BLYP functional with D2 dispersion correction, using Troullier-Martins pseudo potentials [14] with 90 ry cutoff, 3 au time step and 400 au fictitious electronic mass. Simulation box was cubic 10 Å for monomer and 14 Å for water com-

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**Fig. 1** Trans (left) and cis (right) conformers of formic acid.

plex. Periodic images were decoupled using Martyna-Tuckerman Poisson solver [15]. Simulation box sizes were verified by increasing box sizes and doing geometry optimization, which had no difference in energy or geometry. The plane wave cutoff was chosen because it has been used on a similar system [16].

To generate trajectories system was first propagated using velocity rescaling thermostat for  $\sim 1$  ps, in NVT conditions, followed by  $\sim 5$  ps using Nose-Hoover chain thermostat [12,17], in global mode. After which a total of 100 snapshots were saved in every  $\sim 1$  ps, while continuing with Nose-Hoover chain thermostat.

To simulate vibration excitations velocities in these snapshots were modified, so that kinetic energy is increased by a desired amount. According to hypothesis energy is added to OH stretching vibration. Also for formic acid monomer CH stretching excitations were done. Velocities were changed so that center of mass velocity does not change and that O and H atoms move away from each other. Due to mass difference this means that hydrogen will take most of the added kinetic energy in relation to mass difference. It also should be noted that because only O and H atoms, which form OH bond, have their velocities changed, there is also a little bit of energy added to COH bending and OCOH torsion motions. After adding velocities each snapshot was propagated forward in NVE conditions, thus creating a total of 100 trajectories.

For formic acid monomer the trajectories were propagated for about 1 ps. For water complex the trajectories had to be cut to about 200 fs, because complex dissociates due to added energy and fragments fly out of the simulation box. Also water complex is not stable in 300 K, and thus only 15 K and 200 K trajectories were generated, while for monomer 15 K, 100 K, 200 K and 300 K trajectories were generated. These temperatures are arbitrary chosen, to see how temperature affects the system and such they have no specific meaning. Also when temperature is addressed later in this

article, it always refers to these values before excitation was applied.

In these trajectories we are interested in question is there is a conformation change. This means that results from these trajectories are in form of probabilities to find something, which can be considered to behave like a binomial-distribution. To assess these probabilities and errors Bayesian-statistics [18] was used. In Bayesian-statistics binomial-distribution has a Bayesian-interface via beta-distribution, from which a probability to find a desired result can be taken as mean and error from associated cumulative distribution function. Even likelihood,  $\beta(1,1)$ -distribution, was used as a prior. In presented results errors (dotted lines) represent 95% confidence interval.

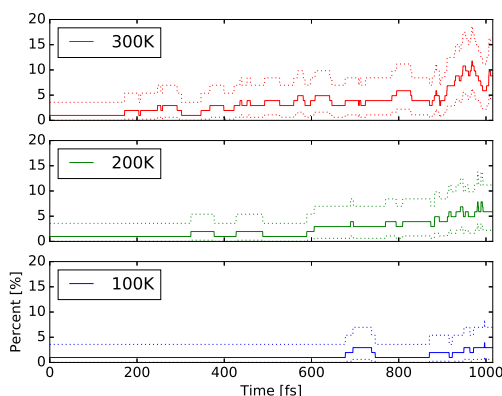
### 3 Results

#### 3.1 Monomer

Results from trajectories excited by 532 nm excitations to OH vibration are shown in figure 2. The most prominent feature is that conformation change is more probable in higher temperatures and it was not observed at all in 15 K. In case of CH excitation, figure 3, the conformation change is much more probable and temperature has only a minor effect. Conformation change was observed when excitation energy 1200 nm ( $8300\text{ cm}^{-1}$ ) or more, when CH bond was excited. We didn't find any conformation changes with 1700 nm ( $6000\text{ cm}^{-1}$ ) excitation energy. However due to statistical nature of results, we can only say this in about 95 % certainty. With OH excitation conformation change was observed when energy was 700 nm ( $14000\text{ cm}^{-1}$ ) or more and was not observed when energy was 800 nm ( $12500\text{ cm}^{-1}$ ).

To see how energy is transferred in molecule movement of certain parameters describing molecule was visualized see figures 4 and 5. Kinetic energy is related to square of change, so parameters chosen are square of change in distance and square of change in angle, although it should be noted that for e.g. bending motion kinetic energy depend on angular velocity and bond lengths, so care must be kept in mind when interpreting these figures.

From OH excited case, figure 4, gradual decrease of motion in OH bond and gradual increase of motion in other modes. COH bending motion seem to be excited earlier than OCOH torsional motion. Which could suggest that energy energy transfers from OH stretching to COH bending and then to OCOH torsion. To test this hypothesis a new set of trajectories was generated with an added constraint on COH bending, which fixed COH angle to its initial value. In these trajectories no



**Fig. 2** Probability to find cis conformer after OH excitation (532 nm) in different initial temperatures.

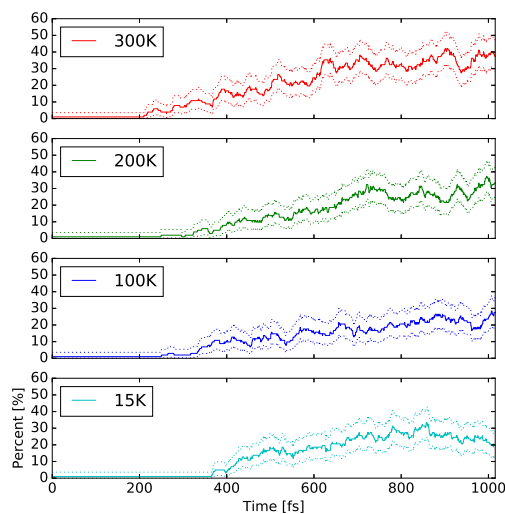
conformation changes were observed, which supports our hypothesis.

CH excitation data, figure 5, differs from OH excitation that OCH bending gains initially some energy and then starts to decrease. This points on possibility of this mode being part of energy channel and to test this a set of trajectories was made with a constraint on OCH motion. This lowered conformation change probability by ten fold of its initial value. From the figure can also be seen that COH bending motion is excited before OCOH torsion, so we could expect it to be part of energy channel, as it is in OH excitation. To test this a set of trajectories was again generated with a constraint on COH angle. This lowered conformation change probability to one third of its initial value. This suggest that there are two channels for energy transfer a one from CH stretch  $\rightarrow$  OCH bending  $\rightarrow$  OCOH torsion and an other from CH stretch  $\rightarrow$  COH bending  $\rightarrow$  OCOH torsion. However these two depend on each other, as the OCH constraint decreases movement in COH bending considerably. Which suggest that a third channel exists where energy transfers along path CH stretch  $\rightarrow$  OCH bending  $\rightarrow$  COH bending  $\rightarrow$  OCOH torsion.

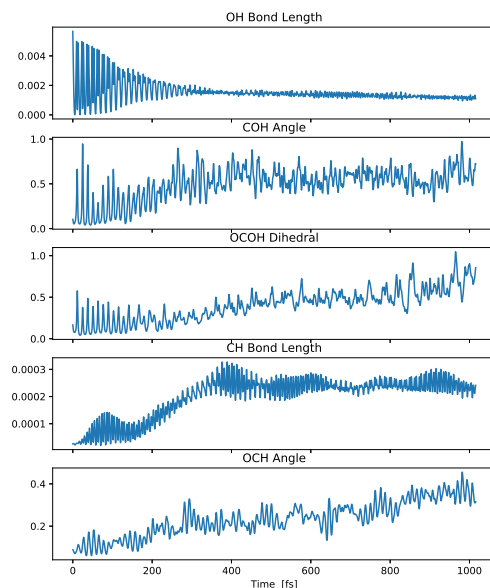
Also worth of mentioning is that energy added to COH bending and OCOH torsion motions due to our method of exciting molecule is small, as can be seen from the figures at time zero, and thus is not expected to affect results.

### 3.2 Water Complex

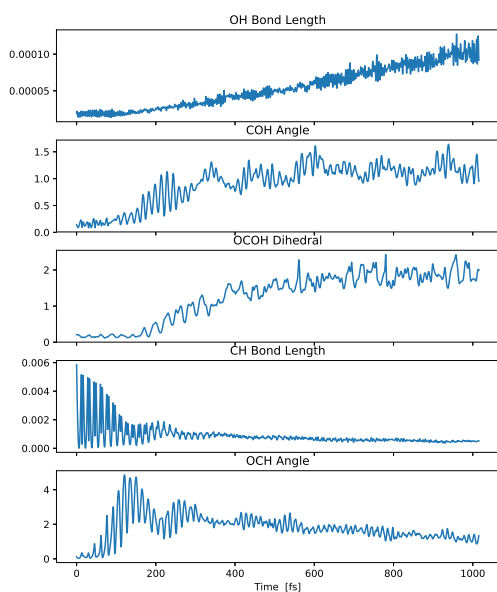
The most prominent feature of trajectories is hydrogen exchange with water molecule (see figure 6). This happens in all trajectories sampled from 15 K temperature (figure 7), while at 200 K the exchange probability diminishes due to increased rotation of the water



**Fig. 3** Probability to find cis conformer after CH excitation (532 nm) in different initial temperatures.



**Fig. 4** Square of change in some parameters describing molecule after exciting OH bond. This data is taken from trajectories sampled at 200 K and excited with 532 nm excitation. Note that y-axis is arbitrary and can be used only to make relative estimates of change.



**Fig. 5** Square of change in some parameters describing molecule after exciting CH bond. This data is taken from trajectories sampled at 200 K and excited with 532 nm excitation. Note that y-axis is arbitrary and can be used only to make relative estimates of change.

molecule. The exchange could be found in trajectories (200 K) when excitation energy used was 1200 nm ( $8300\text{ cm}^{-1}$ ) or more.

First step of the reaction is formation of  $\text{H}_3\text{O}^+$  and formate ions, figure 8, and after that one of the hydrogens from the  $\text{H}_3\text{O}^+$  is given back to the formate ion. This hydrogen can then bounce back to the water molecule to form an  $\text{H}_3\text{O}^+$  ion again, which can be seen in figure 8 as a second peak. While hydrogen exchange maximum, figure 6, is between these two peaks. Again the  $\text{H}_3\text{O}^+$  ion gives up one of its hydrogens to form formic acid and water. This can be repeated for a third time, see small peak appearing at ca. 60-70 fs in figure 8. Ultimately water and formic acid dissociate.

In some rare events formic acid first exchanges hydrogen with water and then changes conformation. This happens in 3 out of 100 trajectories both at 15 K and 200 K, but only at near end of the trajectories close to 200 fs, which compares well with the monomer results, figure 2, with the exception that now it happens in 15 K as well.

Transition state for hydrogen exchange reaction is a little bit of complicated. When transition state is calculated with traditional quantum chemistry methods, by searching a saddle point (done with ORCA v. 3.0.3 [19]), results in geometry represented in figure 9. While

in trajectories transition state is usually like a geometry in second from right in figure 6 and in a few cases close to what is represented in figure 9. This would suggest that there are two different reaction paths and associating transition states. This however is not the case.

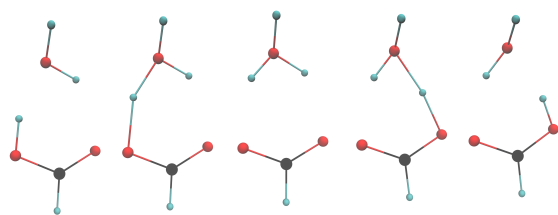
By inspecting trajectories more reveals that the rarer case is never present in first wave of exchanges, which can be seen in figure 7 as the first peak in around 25 fs. Also in the transition state the distance between water and formic acid is about  $0.5\text{ \AA}$  shorter than what it's in minimum energy geometry of the complex. So to get to the "true" transition state, water and formic acid would have to move closer. Here comes the fact that we have a lot of energy and that hydrogens move a lot of faster than oxygen. So when hydrogen is transferred to the water, the oxygen does not have enough time to move closer and instead one of the hydrogens will just fly away from the the  $\text{H}_3\text{O}^+$  ion. In an analogy this could be thought of like playing billiard, when one ball hits hard a group of balls next to each other, or like Newton's cradle.

Energies calculated with different methods and basis for the transition state, figure 9, are listed in tables 1 and 2. These values differ a lot from method to method, which is inspected more later. This calculated energy represent the minimum energy path. But the true energy depends on how long the distance is between the two molecules, which can be explained by a potential energy between two ions increasing with distance. When the distance is around the minimum energy geometry of the complex transition state energy is a little bit over  $12000\text{ cm}^{-1}$ , which can be estimated by a simple calculation with constraining the distance or by potential energy along a trajectory (see figure 10). It should be noted too that  $\text{H}_3\text{O}^+$  and formate ions is not a local minimum energy configuration, when their distance is around the minimum energy distance of the complex. Only when the distance would be more than  $0.5\text{ \AA}$  longer would it be a local minimum.

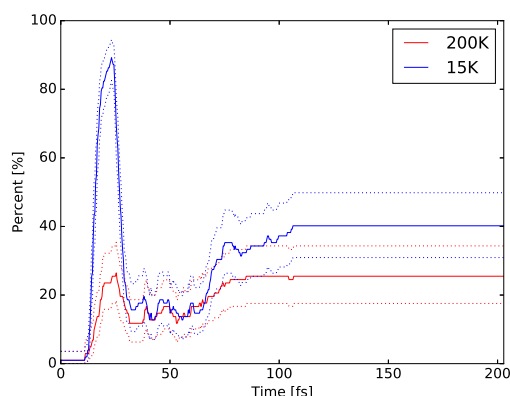
All this sums up that depending of reaction path the exchange reaction can have over  $7000\text{ cm}^{-1}$  difference in potential energy barrier.

#### 4 Comparing different calculation methods

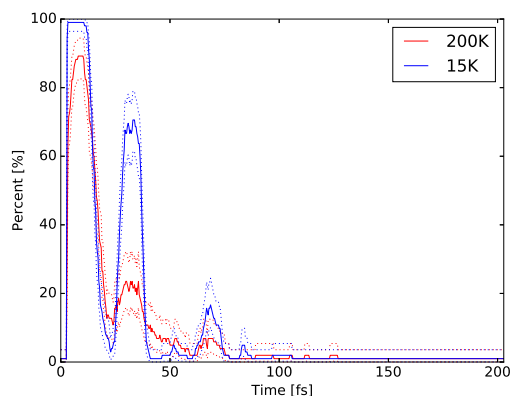
The large spread of transition state energies between different methods, table 1, in raised a question on accuracy of different methods in general are describing geometries present in trajectories. To get more information in this matter a few trajectories where picked and potential energy was calculated with different methods among them. Some high lights of these calculations are depicted in figures 10, 11 and 12. Basis sets used in these



**Fig. 6** Hydrogen exchange reaction from left to right after exciting formic acid OH bond.



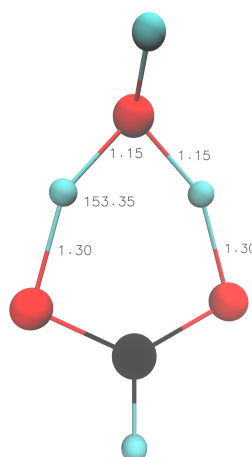
**Fig. 7** Hydrogen exchange probability after exciting (532 nm) formic acid OH bond in water complex.



**Fig. 8** Chance to find  $\text{H}_3\text{O}^+$  ion after exciting (532 nm) formic acid OH bond in water complex.

calculations are ma-def2-TZVPP with DFT and aug-cc-pVTZ with MP and DLPNO-CCSD(T). The program used in calculations was ORCA v. 4.0.0.2.

The most important information from these calculations is that ions are problematic. When ever formic acid water complex is in ionic form there is a large spread in potential energy among different methods. While all methods give in practice same results when



**Fig. 9** Transition state geometry for the hydrogen exchange reaction, DLPNO-CCSD(T)/aug-cc-pVTZ. Note that there is a symmetry plane in the middle.

**Table 1** Transition state energy comparison for different methods. Dispersion correction (D3BJ) was used with DFT methods.

Method	Transition energy / $\text{cm}^{-1}$
B2PLYP <sup>1</sup>	4952
B3LYP <sup>1</sup>	4811
BLYP <sup>1</sup>	4084
PBE <sup>1</sup>	3102
TPSS <sup>1</sup>	3680
TPSSH <sup>1</sup>	4083
DLPNO-CCSD(T) <sup>2</sup>	5485
MP2 <sup>2</sup>	4688

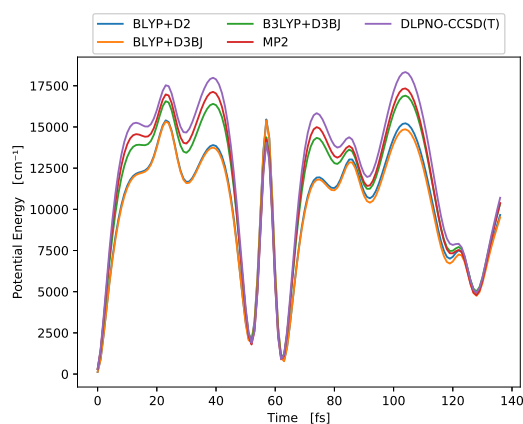
1. ma-def2-TZVPP
2. aug-cc-pVTZ

**Table 2** Transition state energy comparison for different basis with BLYP+D3BJ.

Basis	Transition energy / $\text{cm}^{-1}$
def2-SVP	3020
def2-TZVP	3820
def2-TZVPP	4006
ma-def2-SVP	3649
ma-def2-TZVPP	4084
ma-def2-QZVPP	4166

system is in form of formic acid and water molecules. The energy difference can be as high as  $5000 \text{ cm}^{-1}$ .

If we make a assumption that DLPNO-CCSD(T) would give the best results, we can then rank the other methods against it. This would mean that BLYP is the worst method clearly. It does not give the correct potential energy curve shape and it gives energies that can be thousands of wave numbers off of values given by DLPNO-CCSD(T). B3LYP is a large improvement over



**Fig. 10** Potential energy calculated along a trajectory with different methods in formic acid water complex hydrogen exchange reaction. Initial point of this trajectory is sampled from 15 K simulation and it is the point when energy has been added to the system. So this trajectory represents what is visualized in figure 6, as a back and forth reaction. So formic acid and water exist at 0 fs, 45-65 fs and around 130 fs. While the structure is ionic in between.

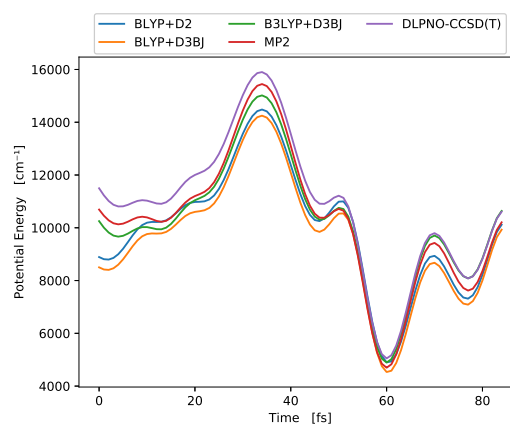
BLYP, but it too fails when system is ionic in form. It does however give the correct shape of potential energy curve. MP2 is within a few exception better option than B3LYP. A special note also to fact that D2 performs better than D3BJ.

For formic acid monomer trajectories, figure 12, the difference between different methods is a lot smaller. Only BLYP gives considerably different values from the other methods. In practice this means that when OH or CH bond is long enough BLYP fails. B3LYP gives very good values for OH bond, but it too will fail a bit on CH bond. But the magnitude of difference to DLPNO-CCSD(T) is of order for few hundred of wave numbers, while for BLYP it can be thousands. But these differences are present only when energy is over 15000  $\text{cm}^{-1}$ . MP2 and DLPNO-CCSD(T) on the other hand give in practice same values.

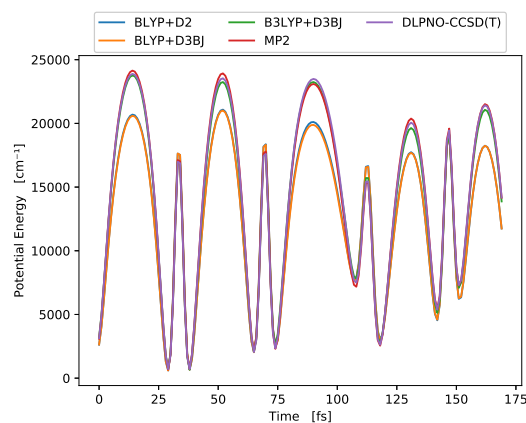
## 5 Discussion

### 5.1 Monomer

Simulations show conformation change as is observed in experiments when the OH bond is excited, but not at the temperatures used in experiments. This raises a question on role of quantum effects in the process. We already know that transition back from cis to trans happens with tunneling [8] and the whole process is about movement of hydrogen. So we can expect quantum effects, like tunneling and zero-point motion, to be important in trans to cis interconversion too. The



**Fig. 11** Potential energy calculated along a trajectory with different methods in formic acid water complex hydrogen exchange reaction. In this trajectory snapshot initial point is near minimum energy transition state and then moves somewhat around it to form formic acid and water around 60 fs, which then goes back to formate and oxonium ions again.



**Fig. 12** Potential energy calculated along a trajectory with different methods in formic acid monomer excitation case. Trajectory start from the point when energy is added. Its initial point is sampled from 300 K simulation. So initial potential energy represents thermal excitation at the beginning. Excitation in this trajectory is 532 nm on OH.

fact that we can not see any trans to cis change in simulation when nucleons are treated classically, can be considered as an evidence that not only are quantum effects important, but they are actually crucial for the hole process.

Our simulations showed that increasing temperature increases the probability of the conformational interconversion. This was expected, as formic acid in it's minimum energy configuration is a planar and for symmetry reasons the OH stretch, that is plane symmetric, can not excite torsion, which is not plane symmetric. In quantum nucleons case zero-point motion (and uncertainty principle) distorts molecule a little bit from

plane. Which is somewhat similar to effect of increased temperature.

In the case of CH excitation the importance of zero-point motion is not that clear, as in the simulations the temperature, where initial points of trajectories were generated, had only a minor effect to the final outcome of the simulations. The same symmetry reasoning applies also for the CH stretching mode. This implicates that the CH stretching motion is more strongly coupled to the torsional motion, than the OH stretching mode. Which is also evident based on the finding that the conformational interconversion is much more probable, when excitation is applied to the CH stretching than to the OH.

Because our simulation used classical nuclei, we didn't have tunneling in our simulations. Thus it's expected to need more energy to achieve the conformational interconversion. In our simulation we needed  $14000\text{ cm}^{-1}$  with excitation on the OH bond, which is about two and a half times more than what is observed experimentally. This difference does sound to be too large effect to be caused by miss of tunneling. As a comparison, in a recent study by Tew and Mizukami [20]. They calculated formic acid vibration overtones and showed that 6th and 7th excited states in torsion-mode tunnel trough barrier to cis conformer. Which in practice meant that barrier of about  $4500\text{ cm}^{-1}$  height is effectively only about  $3700\text{ cm}^{-1}$ . So we could expect tunneling to lower barrier by about  $1000\text{ cm}^{-1}$ .

This could mean that our simulations are too short and running a longer time would show the conformational interconversion happening with less energy. This brings us to the question of role of matrix, which absorbs all the thermal energy [1]. But in what time scale? However dynamics studies of matrix and steric effects of the systems studied here are outside the scope of the current paper.

Third possibility is that we have a wrong excitation. It is assumed that the excitation happens on the OH vibration and that when it happens with  $532\text{ nm}$  it excites 6th vibrational state of the OH stretching, based on experimental parameters [21]. But we do not know for sure. Thus it would be good to develop a better method to apply an excitation than a simple velocity rescaling.

In addition to repeating simulations with matrix atoms, it might be a good idea to do path integral simulations, to see how much quantum effects matter. These methods have some problems themselves, but could still be good to see how they differ from purely classical nuclei.

For formic acid monomer the poor performance of BLYP is probably not an issue. Because we did get same results when excitation energy was smaller than

the area where BLYP miss performs. But there could be some effect on probability and to how long it takes for conformational interconversion to happen.

## 5.2 Water complex.

Hydrogen exchange is well along with chemical intuition and it's already studied in many cases [22]. The novelty here is that it can be induced with vibrational excitations and that it can be an intermediate step in a total reaction. But because formic acid is symmetric it cannot be proven experimentally without isotope substitution.

While this study can not provide reason to why in formic acid water complex cis conformer does not tunnel back to trans form. It does imply that mechanism for conformational interconversion very likely includes hydrogen exchange and that this may also be a part of the reason why cis is stable, as was observed by Marushkevich et.al. [9].

A big question for the water complex calculations come from accuracy of the used method BLYP+D2. Normally it would be good idea to do the calculations with a better method. But to do B3LYP calculations with CPMD would need appropriate pseudopotentials, which we do not have. But in the future B3LYP or MP2 calculation should be minimum for the water complex calculations.

Then is the question of, how does the poorly performing method affect results from these simulations. If we look at the figure 10. We see that in that trajectory BLYP does get the shape right, it's only lower. Thus we could expect to get same kind of trajectory, if we just use more energy. So the hydrogen exchange reaction does most likely happen with other methods too. It's only about how much energy it needs and how probable it is. And in any case, this analysis of performance of different methods will prove to be useful in future works regarding the water complex.

## 6 Summary

The simulation results show that conformational interconversion takes place when OH and CH stretching vibrations are excited, which are in agreement with previous experimental observations. But the simulations also raise questions regarding a role of quantum and matrix effects. For excitations upon the OH vibrational mode, conformational interconversion does not happen at matrix isolation temperatures according to the simulations presented here. This points to the role of zero-point motion. Tunneling is also most likely important, because



in simulations much more energy was needed than what has been shown to work in experiments.

Water complex simulation could not explain explicitly the observed stability of the cis-HCOOH water complex. To address this issue, most likely a simulation with added matrix atoms is needed to mimic the experimental conditions better. In water complex simulations hydrogen exchange reaction was found and it's expected that trans to cis transformation happens via it. Testing accuracy of used method BLYP+D2 raised issues when calculating system when it's in ionic form, which will most likely affect the magnitude of excitation energy needed and reaction probability.

**Acknowledgements** The CSC - Center for Scientific Computing (Espoo, Finland) is thanked for the computational time allocated to this research. This research was supported by the Academy of Finland research project "Vibrational excitation induced chemistry" (Proj. No 286844) and we (P.D.) gratefully acknowledge financial support from the National Science Center Poland (2016/23/B/ST4/01099).

## References

1. M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *Journal of the American Chemical Society* **119**(48), 11715 (1997). DOI 10.1021/ja972362l. URL <http://dx.doi.org/10.1021/ja972362l>
2. A. Olbert-Majkut, J. Ahokas, M. Pettersson, J. Lundell, *The Journal of Physical Chemistry A* **117**(7), 1492 (2013). DOI 10.1021/jp311749z. URL <http://dx.doi.org/10.1021/jp311749z>. PMID: 23324029
3. A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *Phys. Chem. Chem. Phys.* **12**, 7138 (2010). DOI 10.1039/B926658E. URL <http://dx.doi.org/10.1039/B926658E>
4. A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *Journal of Raman Spectroscopy* **42**(8), 1670 (2011). DOI 10.1002/jrs.2909. URL <http://dx.doi.org/10.1002/jrs.2909>
5. K. Marushkevich, L. Khriachtchev, M. Räsänen, M. Melavuori, J. Lundell, *The Journal of Physical Chemistry A* **116**(9), 2101 (2012). DOI 10.1021/jp209714e. URL <http://dx.doi.org/10.1021/jp209714e>. PMID: 22280475
6. K. Marushkevich, L. Khriachtchev, J. Lundell, A. Domanskaya, M. Räsänen, *The Journal of Physical Chemistry A* **114**(10), 3495 (2010). DOI 10.1021/jp911515f. URL <http://dx.doi.org/10.1021/jp911515f>. PMID: 20166691
7. K. Marushkevich, L. Khriachtchev, J. Lundell, M. Räsänen, *Journal of the American Chemical Society* **128**(37), 12060 (2006). DOI 10.1021/ja064154b. URL <http://dx.doi.org/10.1021/ja064154b>. PMID: 16967943
8. M. Pettersson, E.M.S. Maçõas, L. Khriachtchev, J. Lundell, R. Fausto, M. Räsänen, *The Journal of Chemical Physics* **117**(20), 9095 (2002). DOI 10.1063/1.1521429. URL <http://dx.doi.org/10.1063/1.1521429>
9. K. Marushkevich, L. Khriachtchev, M. Räsänen, *The Journal of Physical Chemistry A* **111**(11), 2040 (2007). DOI 10.1021/jp070363m. URL <http://dx.doi.org/10.1021/jp070363m>. PMID: 17388271
10. A. Olbert-Majkut, J. Lundell, M. Wierzejewska, *The Journal of Physical Chemistry A* **118**(2), 350 (2014). DOI 10.1021/jp409982f. URL <http://dx.doi.org/10.1021/jp409982f>. PMID: 24354336
11. R. Car, M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985). DOI 10.1103/PhysRevLett.55.2471. URL <http://link.aps.org/doi/10.1103/PhysRevLett.55.2471>
12. D. Marx, J. Hutter, *Ab Initio Molecular Dynamics* (Cambridge, 2009)
13. URL <http://www.cpmc.org/>. CPMD, Copyright IBM Corp 1990-2015
14. N. Troullier, J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991). DOI 10.1103/PhysRevB.43.1993. URL <https://link.aps.org/doi/10.1103/PhysRevB.43.1993>
15. G.J. Martyna, M.E. Tuckerman, *The Journal of Chemical Physics* **110**(6), 2810 (1999). DOI 10.1063/1.477923. URL <http://dx.doi.org/10.1063/1.477923>
16. S.D. Ivanov, I.M. Grant, D. Marx, *The Journal of Chemical Physics* **143**(12), 124304 (2015). DOI 10.1063/1.4931052. URL <https://doi.org/10.1063/1.4931052>
17. M.E. Tuckerman, M. Parrinello, *The Journal of Chemical Physics* **101**(2), 1302 (1994). DOI 10.1063/1.467823. URL <http://dx.doi.org/10.1063/1.467823>
18. P.M. Lee, *Bayesian Statistics An Introduction*, 4th edn. (Wiley, 2012)
19. F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2**(1), 73 (2012). DOI 10.1002/wcms.81. URL <http://dx.doi.org/10.1002/wcms.81>
20. D.P. Tew, W. Mizukami, *The Journal of Physical Chemistry A* **120**(49), 9815 (2016). DOI 10.1021/acs.jpca.6b09952. URL <http://dx.doi.org/10.1021/acs.jpca.6b09952>. PMID: 27973803
21. E.M. Maçõas, J. Lundell, M. Pettersson, L. Khriachtchev, R. Fausto, M. Räsänen, *Journal of Molecular Spectroscopy* **219**(1), 70 (2003). DOI [https://doi.org/10.1016/S0022-2852\(03\)00018-3](https://doi.org/10.1016/S0022-2852(03)00018-3). URL <http://www.sciencedirect.com/science/article/pii/S0022285203000183>
22. S. Alavi, M. Taghikhani, *Chemical Physics* **402**, 105 (2012). DOI <http://dx.doi.org/10.1016/j.chemphys.2012.05.004>. URL <http://www.sciencedirect.com/science/article/pii/S030101041200208X>