Computational Approach Towards Vibrational Spectroscopic Detection of Molecular Species Relevant to Atmospheric Chemistry and Climate Science: The Formic Acid Rotamers

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Abstract—**A rigorous but still feasible computational approach is implemented that aims to provide a fundamental theoretical basis for an in-depth understanding of vibrational spectroscopic properties of molecular systems relevant to atmospheric chemistry and climate science. The mentioned properties are, on the other hand, crucial in the context of experimental detection of the title molecular species and their noncovalently bonded clusters. Rotamers of formic acid are treated as particular example. Potential energy surface of free formic acid was thoroughly explored at Möller-Plesset perturbation theory level, including corrections up to the second order with a rather flexible basis set for orbital expansion (MP2/6-311++G(3df,3pd)), as well as employing density functional tight binding approach (DFTB). Anharmonic O-H(D) stretching vibrational frequencies were calculated using several algorithms. It was found that MP2 level of theory leads to excellent agreement between theory and experiment without using any arbitrary scaling factor when the difference between O-H(D) stretching frequencies in the case of both rotamers is in question. DFTB performs significantly inferior to MP2 with this respect, while reproducing the absolute frequencies of individual rotamers rather well. Fully relaxed HCOH torsional potential was calculated as well and the frequencies of HCOH torsion in the cis- and trans- well were calculated either by solving the torsional Schrödinger equation variationally or by second-order perturbation theory. The agreement between theory and experiment is again excellent in cases when experimental data are available.**

Keywords—formic acid; atmospheric chemistry; chemistry-climate; O-H stretching; computational chemistry; intramolecular torsion

I. INTRODUCTION

Any serious attempt to understand the fundamental physical basis of processes responsible for climate changes must rely on an in-depth understanding of the physics and chemistry of molecular species which constitute Earth's atmosphere. It is therefore self-understood that new milestones in climate science should aim at the molecular-level understanding of the aforementioned phenomena. In other words, climate science has to undergo a substantial paradigmatic shift, from mesoscale-level models to molecular models. In this context, the establishment of chemistry-climate models should be emphasized, aiming to address at a fundamental molecular level the essential issues such as long-term ozone trends as well as methane lifetime etc.

In relation to these issues, organic acids have been thoroughly investigated as possible candidates for precursors in the process of formation of aerosols, which play one of the crucial roles in atmospheric, as well as health sciences [1,2].

Among the organic acids, formic acid – the simplest representative of this class of compounds, is at the same time the most abundant, and also ubiquitous organic acid in the atmosphere [3-8]. The reported concentrations of this molecule are of the order of 10 parts per billion, with slightly higher values in urban areas. Besides in aerosols and in gas phase, formic acid has also been identified in atmospheric precipitates (acid rain). Both anthropogenic and biogenic emissions have been pointed out as main sources of this compound in the atmosphere. In a much wider context, formic acid is also important in the human metabolitic processes. Also, notable interest for this simple molecular system has been shown in relation to its astrophysical relevance [1]. Formic acid is the simplest organic acid that has been first identified in the interstellar medium [9]. The chemistry and physics of its formation in interstellar and cometary ices has been addressed as well [9].

Aside from all arguments that have previously been outlined, one should bear in mind that the simplest molecule belonging to the class of organic acids is at the same time a prototypical model system for the whole class of compounds. A number of phenomena related to the physics and chemistry of organic acids may therefore be modeled and understood in a much easier way taking the simplest member as a representative example. Formic acid is also a sort of prototype for systems exhibiting intramolecular rotational (*i.e.* conformational) isomerism, as it can exist in two planar geometries that are mutually interconnected by rotation of the OH group (*i.e.* variation of the HCOH torsional angle – Fig. 1). The two conformations are known as *cis-* and *trans-*isomers, or by the systematic nomenclature, *Z* and *E* forms (Fig. 1).
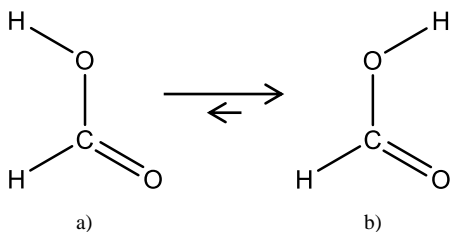
Fig. 1. Schematic presentation of the geometry of cis- (*i.e. E*) (a) and trans- (*i.e. Z*) (b) formic acid conformers.

Though being small, the formic acid molecule is thus relevant to very fundamental issues related to molecular structure and dynamics.

Due to all of the previously outlined reasons, formic acid has been studied a lot, both experimentally and theoretically, within a wide variety of contexts [1-8 and references therein]. In the current study, we focus on certain issues which are relevant to both climate science and atmospheric chemistry on one hand, and to the fundamental molecular chemical physics as well. As vibrational spectroscopic techniques have been proven to be rather powerful to study the structure, dynamics and certain properties of both individual molecules as well as of noncovalently bonded molecular clusters that they build up [10], we hereby focus on modeling of basic spectroscopic features of the two conformers of the title molecular system. Especially in the context of noncovalent intermolecular interactions, the O-H stretching vibrational modes are crucial for detection of formic acid under realistic conditions, as well as for detection of its noncovalently bonded species with various atmospherically relevant molecules and for structural elucidations thereof. Instead of relying on the rather crude harmonic approximation that is usually assumed in the course of these studies (even sometimes in a pretty much implicit way), we hereby consider exact anharmonic O-H stretching vibrational potential in the case of both conformers and we aim to understand the main features thereof. We also aim to establish a feasible computational method that could allow for accurate computation of absolute frequency values as well as of frequency shifts between the conformers. This is a first step towards establishing a more general computational approach that could be helpful in structural elucidations of various noncovalently bonded molecular species relevant to atmospheric chemistry and climate science.

II. COMPUTATIONAL DETAILS

A. General Theoretical Methodology

Geometries of the two conformers of free formic acid molecule (*cis-* and *trans*-isomers) were fully optimized using Schlegel's gradient optimization algorithm [11], at two levels of theory: i) Möller-Plesset perturbation theory including corrections up to the second order (*i.e.* truncating the Möller-Plesset expansion at second-order corrections - MP2 [12]); ii) Density functional tight binding semi-empirical approach (DFTB [13,14]). The rather large Pople-type 6-311++G(3*df*,3*pd*) basis set was used for orbital expansion in solving the HF equations and subsequent computations of Möller-Plesset correlation energy corrections. The DFTB approach, was, on the other hand, implemented in the DFTB-A variant [14], *i.e.* using the analytic expressions for the matrix elements instead of the tabulated ones. Subsequently to locating the minima on the explored molecular potential energy surfaces (PESs), their character was investigated by

computation of the corresponding second-derivative (Hessian) matrix. The absence of negative eigenvalues of the Hessian matrices (*i.e.* absence of imaginary vibrational frequencies) was used as a test whether the particular stationary point corresponds to a real minimum or to a saddle point on the PES. At the same time, by diagonalization of the mass-weighted second-derivative matrices, harmonic vibrational frequencies of the studied molecular systems were computed. All calculations in the present study were carried out by Gaussian09 series of programs [15].

B. Calculation of Anharmonic O-H Stretching Vibrational Frequencies

As implied before in the paper, intramolecular motions involving hydrogen atoms are particularly anharmonic. If one wants to, therefore, rely on theoretical computations in the course of interpretation of experimental vibrational spectroscopic data, it is crucial to go beyond the harmonic approximation. For the purpose of the present study, we have computed the anharmonic O-H stretching vibrational frequencies of the two rotamers of formic acid molecule implementing a localized mode approach, in the following manner [16 and references therein]. Starting from the equilibrium geometries (corresponding to the minima on the considered PESs), a series of configurations were generated by moving simultaneously the oxygen and hydrogen atoms in a manner that resembles the realistic motion taking place during the excitation of the O-H stretching vibration, varying the O-H distance from 0.85 to 1.55 Å. To generate these configurations, we have used our in-house developed FORTRAN code. A series of 15 pointwise energy calculations were further carried out for the series of geometries generated this way to compute the vibrational potentials $V(r_{OH})$. Subsequently, the $V = f(r_{OH})$ dependencies were fitted to a fifth-order polynomial in Δr ($\Delta r = \Delta r_{OH} = r_{OH} - r_{OH,e}$, $r_{OH,e}$ denoting the equilibrium value of r_{OH}):

$$V(\Delta r) = V_0 + k_2\Delta r^2 + k_3\Delta r^3 + k_4\Delta r^4 + k_5\Delta r^5 \qquad (1)$$

The polynomials of the form (1) were further truncated after the fourth order term and transformed into the Simons-Parr-Finlan (SPF) type coordinates of the form [16]:

$$\rho = (r_{OH} - r_{OH,e}) / r_{OH} \qquad (2)$$

To obtain the spectrum of the vibrational Hamiltonian, the 1D vibrational Schrödinger equation was subsequently solved with the variational method, using harmonic oscillator eigenfunctions as a basis set. 15 basis functions were sufficient to obtain convergent results. Frequencies of the fundamental $|0\rangle \rightarrow |1\rangle$ vibrational transitions were calculated from the energies of the ground ($|0\rangle$) and first excited ($|1\rangle$) vibrational energy levels. The SPF type coordinates have been shown to be rather superior over the ordinary bond stretch ones when one needs to solve the vibrational Schrödinger equation, as they allow for an extended region of convergence as well as a much faster convergence of the Hamiltonian eigenvalues with the number of basis functions used [16].

In parallel, anharmonic vibrational frequencies of the considered molecular systems were also computed with the second-order perturbative approach developed by Barone [17].

C. Calculation of Anharmonic HCOH Torsional Potentials and Diagonalization of the Torsional Hamiltonian

Assuming separability of the HCOH intramolecular torsional motion from all other motions, the torsional Hamiltonian acquires the form [18]:

$$\hat{H}_{torsion} = -\frac{\hbar^2}{2I_\varphi}\frac{\partial^2}{\partial\varphi^2} + V(\varphi) \qquad (3)$$

To solve the torsional Schrödinger equation, we have computed the fully relaxed torsional potential $V(\varphi)$, where φ actually denotes the HCOH dihedral angle. This was done by fixing the torsional angle at a series of values (sequentially increasing by 10 °), ranging from 0 to 180 °, and subsequently performing partial geometry optimization with respect to all other intramolecular parameters. The obtained potential was fitted to a truncated cosine Fourier series of the form:

$$V(\varphi) = \frac{1}{2}a_0 + \sum_k a_k\cos(k\varphi) \qquad (4)$$

The resulting Hamiltonian eigenvalue problem was solved with the variational method, using free rotor basis functions of the form:

$$\psi_{ml}(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im_l\varphi) \qquad (5)$$

where $m_l = 0, \pm1, \pm2, \ldots$ For the purpose of present study, we have used a flexible basis set with m_l raging up to ±100 (*i.e.* using 201 basis functions).

III. RESULTS AND DISCUSSION

Geometries of the two conformers of free formic acid corresponding to the minima on MP2/6-311++G(3*df*,3*pd*) potential energy surface (PES) are shown in Fig. 2.
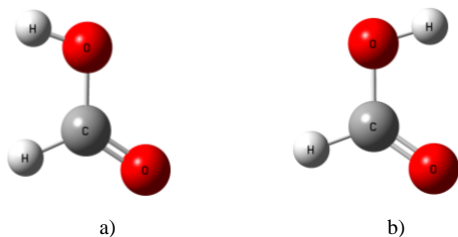

Fig. 2. Optimized geometries of cis- (a) and trans- (b) formic acid at MP2/6-311++G(3*df*,3*pd*) level of theory.

The corresponding computed structural parameters at both DFTB-A and MP2/6-311++G(3*df*,3*pd*) levels of theory are compared to the available experimental data in Tables I and II. Table III, on the other hand, contains the theoretical and experimental values of the changes in structural parameters of this molecular system upon trans → cis interconversion.

A. Structure

As can be seen from Tables I and II, concerning structural parameters of cis- and trans-formic acid, Möller-Plesset perturbation theory that includes corrections up to the second order agrees remarkably well with the available experimental data [1-8]. DFTB level of theory, on the other hand, performed somewhat poorer. Perhaps more important finding, that can be deduced from Table III, is that MP2 level predicts remarkably well the *changes* in intramolecular structural parameters of formic acid upon trans → cis interconversion. This is

especially important finding when one aims to establish a method for computation of the changes of O-H stretching vibrational frequencies upon the mentioned interconversion process (caused by intramolecular hindered rotation).

TABLE I. STRUCTURAL PARAMETERS OF TRANS-FORMIC ACID CONFORMER COMPUTED AT THE EMPLOYED THEORETICAL LEVELS TOGETHER WITH THE EXPERIMENTAL DATA

Parameter	Exp.	MP2	DFTB
R_{C-H} / Å	1.097	1.093	1.135
R_{C-O} / Å	1.342	1.343	1.377
R_{O-H} / Å	0.972	0.968	0.982
$R_{C=O}$ / Å	1.203	1.202	1.211
$\theta_{HCO(-H)}$ / °	112.0	109.7	112.6
θ_{COH} / °	106.3	106.5	107.9
θ_{HCO} / °	123.2	125.2	125.8
θ_{OCO} / °	124.8	125.1	121.6

TABLE II. STRUCTURAL PARAMETERS OF CIS-FORMIC ACID CONFORMER COMPUTED AT THE EMPLOYED THEORETICAL LEVELS TOGETHER WITH THE EXPERIMENTAL DATA

Parameter	Exp.	MP2	DFTB
R_{C-H} / Å	1.105	1.099	1.153
R_{C-O} / Å	1.352	1.350	1.379
R_{O-H} / Å	0.956	0.963	0.978
$R_{C=O}$ / Å	1.195	1.195	1.202
$\theta_{HCO(-H)}$ / °	114.6	113.5	112.9
θ_{COH} / °	109.7	108.9	110.4
θ_{HCO} / °	123.2	124.1	124.6
θ_{OCO} / °	122.1	122.4	122.5

TABLE III. CHANGES OF STRUCTURAL PARAMETERS UPON TRANS-CIS INTERCONVERSION OF FORMIC ACID COMPUTED AT THE EMPLOYED THEORETICAL LEVELS TOGETHER WITH THE EXPERIMENTAL DATA

Parameter	Exp.	MP2	DFTB
ΔR_{C-H} / Å	0.008	0.006	0.018
ΔR_{C-O} / Å	0.010	0.007	0.002
ΔR_{O-H} / Å	-0.016	-0.005	-0.004
$\Delta R_{C=O}$ / Å	-0.008	-0.007	-0.009
$\Delta\theta_{HCO(-H)}$ / °	2.6	3.8	0.3
$\Delta\theta_{COH}$ / °	3.4	2.4	2.5
$\Delta\theta_{HCO}$ / °	0.0	-1.1	-1.2
$\Delta\theta_{OCO}$ / °	-2.7	-2.7	0.9

B. O-H Stretching Vibrational Frequencies

The structural changes induced upon intramolecular torsional motion reflect correspondingly in the values of vibrational frequencies of intramolecular modes. In the context of the present study, we have focused on the values of O-H stretching vibrational frequencies, as this mode is of crucial importance for detection of formic acid, its rotamers, as well as its noncovalently bonded complexes under atmospheric (and even astrochemical) conditions [1-8]. The O-H stretching mode, in this context, can be treated as a sort of "vibrational chromophore", sensitive to both intra- and intermolecular environment. This chromophore can therefore be applied as a probe to sense both the different intra- and intermolecular environments. For these purposes, establishing a computational methodology for accurate computation of vibrational frequency of this particular vibrational mode seem crucial if one wants to gain deeper insights into the experimental spectroscopic data employing computational chemical physics as a support.

Tables IV-VII contain both experimental and theoretical values of the O-H stretching frequencies in the case of both conformers of the free (gas-phase) formic acid monomer. Anharmonic and harmonic frequency values have been computed either by variational solution of the vibrational Schrödinger equation on the basis of 1D stretching potentials computed by MP2 or DFTB methods, or by a second-order perturbation theory approach, as explained in methodological section. The computed O-H stretching potentials of the cis- and trans- rotamers at MP2/6-311++G($3df$,$3pd$) level of theory are shown in Fig. 3.
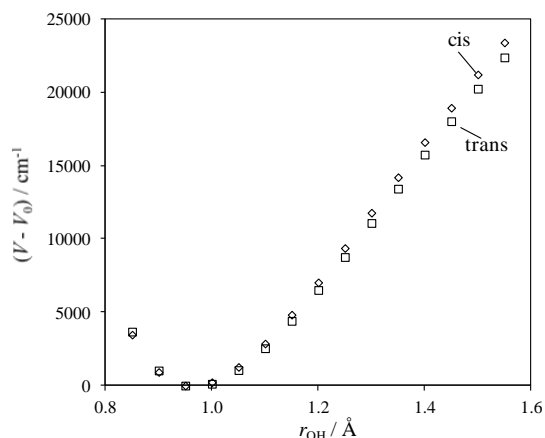

Fig. 3. The O-H stretching potentials of the cis- and trans- rotamers of formic acid computed at MP2/6-311++G($3df$,$3pd$) level of theory.

TABLE IV. EXPERIMENTALLY MEASURED O-H AND O-D STRETCHING FREQUENCIES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL ANHARMONIC VALUES COMPUTED ON THE BASIS OF 1D ANHARMONIC VIBRATIONAL POTENTIALS (SEE TEXT FOR DETAILS)

Parameter	Exp.	MP2	DFTB
cis			
v_{O-H} / cm^{-1}	- (3618.0)^{ftn}	3712.6	3568.0
v_{O-D} / cm^{-1}	2685.0	2906.4	2794.7
trans			
v_{O-H} / cm^{-1}	3568.0 (3570, 3570.5, 3569.0) (3550.5)^{ftn}	3642.8	3524.4
v_{O-D} / cm^{-1}	2632.0 (2631.0)	2852.6	2761.1
Δv_{O-H} / cm^{-1}	67.5	69.8	43.6
Δv_{O-D} / cm^{-1}	53.0	53.7	33.6

It is important to discuss to some extent the nature of experimental data that are available in relation to the O-H stretching vibration of formic acid rotamers [1-8]. Due to the larger stability of trans-formic acid, this form is the dominant one under usual spectroscopic conditions. For example, in gas phase at 298 K, the ratio of populations of cis- and trans-rotamers has been estimated to be of the order of 10^{-3}, so that the cis- isomer is far less abundant than the trans- one. As a consequence of this, it seems that the formic acid cis- rotamer has escaped non-elusive identification in gas phase with IR (and other vibrational spectroscopic techniques). However, it is possible to capture the less stable conformer in low-

temperature cryogenic matrices, in which it persists for a sufficiently long period that enables the detection of these molecular species by IR spectroscopy [1-8].

TABLE V. EXPERIMENTALLY MEASURED O-H AND O-D STRETCHING FREQUENCIES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL HARMONIC VALUES COMPUTED ON THE BASIS OF 1D ANHARMONIC VIBRATIONAL POTENTIALS (SEE TEXT FOR DETAILS)

Parameter	Exp.	MP2	DFTB
cis			
v_{O-H} / cm^{-1}	- (3618.0)^{ftn}	3866.6	3724.5
trans			
v_{O-H} / cm^{-1}	3568.0 (3570, 3570.5, 3569.0) (3550.5)^{ftn}	3798.6	3682.0
Δv_{O-H} / cm^{-1}	67.5	68.0	42.5

TABLE VI. EXPERIMENTALLY MEASURED O-H AND O-D STRETCHING FREQUENCIES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL ANHARMONIC VALUES COMPUTED WITH THE SECOND-ORDER PERTURBATION THEORETICAL APPROACH (SEE TEXT FOR DETAILS)

Parameter	Exp.	MP2	DFTB
cis			
v_{O-H} / cm^{-1}	- (3618.0)^{ftn}	3665.0	3506.6
v_{O-D} / cm^{-1}	2685.0	2706.9	2587.7
trans			
v_{O-H} / cm^{-1}	3568.0 (3570, 3570.5, 3569.0) (3550.5)^{ftn}	3589.9	3464.9
v_{O-D} / cm^{-1}	2632.0 (2631.0)	2646.3	2549.5
Δv_{O-H} / cm^{-1}	67.5	75.1	41.7
Δv_{O-D} / cm^{-1}	53.0	60.6	38.2

TABLE VII. EXPERIMENTALLY MEASURED O-H AND O-D STRETCHING FREQUENCIES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL HARMONIC VALUES COMPUTED WITH THE SECOND-ORDER PERTURBATION THEORETICAL APPROACH (SEE TEXT FOR DETAILS)

Parameter	Exp.	MP2	DFTB
cis			
v_{O-H} / cm^{-1}	- (3618.0)^{ftn}	3856.5	3667.0
v_{O-D} / cm^{-1}	2685.0	2807.7	2672.6
trans			
v_{O-H} / cm^{-1}	3568.0 (3570, 3570.5, 3569.0) (3550.5)^{ftn}	3785.5	3615.9
v_{O-D} / cm^{-1}	2632.0 (2631.0)	2752.6	2632.6
Δv_{O-H} / cm^{-1}	67.5	71.0	51.1
Δv_{O-D} / cm^{-1}	53.0	55.1	40.0

The experimental O-H stretching frequency shifts upon trans → cis interconversion, shown in Tables IV-VII, have therefore been calculated from the matrix isolation studied at cryogenic conditions. Assuming essentially equivalent influence of the cryogenic matrix on both O-H stretching modes (in the case of cis- ad trans- rotamers), which seems rather reasonable, the experimentally measured frequency

shifts in cryogenic matrices may be considered as being rather close to the gas-phase shifts.

In relation to our computational results, as can be seen from Tables IV-VII, the agreement between theory and experiment is excellent in essentially all aspects when the MP2 theoretical level is implemented to compute equilibrium geometries and 1D vibrational stretching potentials of the O-H vibrational chromophore. Of course, it is of essential importance to be able to predict the frequency changes upon rotamer interconversion (or, in a broader sense, upon noncovalent intermolecular interaction), instead of predicting the absolute frequencies themselves. With respect to this, MP2 level of theory significantly outperforms the DFTB approach, and it can be said that the agreement between theory and experiment is quantitative for any practical purpose. However, considering the absolute O-H stretching frequency values, reflecting energy differences between the ground and first excited vibrational levels, the performance of DFTB is rather good.

C. Torsional Barrier and Intrawell Torsional Transitions

The torsional dynamics of formic acid has been addressed from numerous aspects. Again, as this compound is a prototype system representing the whole class of compounds – organic acids, insights gained into the possibilities to control the torsional dynamics in molecular systems by studying this particular molecule can have enormous impact in the field of development of highly controllable organic synthetic methods, involving even the possibility of conformationally-controlled (*i.e.* conformation-specific) reactivity [1-8].

The computed fully relaxed HCOH torsional potential of formic acid at MP2/6-311++G(3*df*,3*pd*) level of theory is shown in Fig. 4. It can be seen that the trans- rotamer is the lower-energy conformer. The cis-rotamer is higher in energy by 1482 cm^{-1} at MP2/6-311++G(3*df*,3*pd*) level of theory, which is in very good agreement with the experimental estimation of 1364 cm^{-1}. The corresponding DFTB value is 1323 cm^{-1}, which is in excellent agreement with the experiment [1-8].
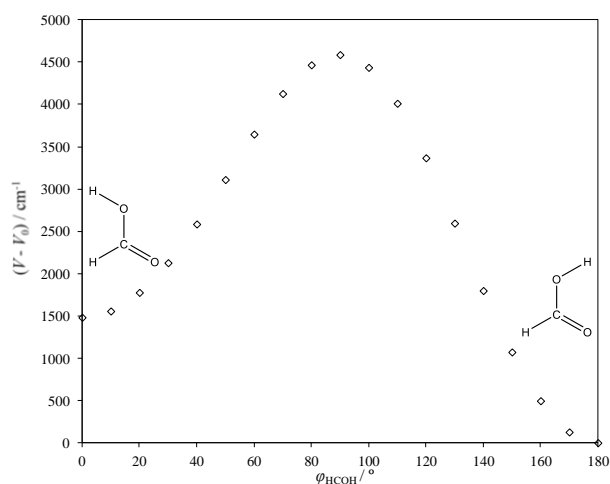

Fig. 4. The fully relaxed HCOH torsional potential of formic acid computed at MP2/6-311++G(3*df*,3*pd*) level of theory (the cis- rotamer corresponds to φ = 0 ° and the trans- rotamer corresponds to φ = 180 °).

TABLE VIII. EXPERIMENTALLY MEASURED FREQUENCIES OF THE O-H TORSIONAL MODES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL ANHARMONIC VALUES COMPUTED WITH THE SECOND-ORDER PERTURBATION THEORETICAL APPROACH (SEE TEXT FOR DETAILS)

Parameter	Exp.	MP2	DFTB
cis			
$\tau_{O\text{-}H}$ / cm^{-1}	503.0	503.7	405.9
trans			
$\tau_{O\text{-}H}$ / cm^{-1}	642.0	649.6	546.4
$\Delta\tau_{O\text{-}H}$ / cm^{-1}	-139.0	-145.9	-140.5

TABLE IX. EXPERIMENTALLY MEASURED FREQUENCIES OF THE O-H TORSIONAL MODES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL HARMONIC VALUES (SEE TEXT FOR DETAILS)

Parameter	Exp.[a]	MP2	DFTB
cis			
$\tau_{O\text{-}H}$ / cm^{-1}	503.0	533.4	436.0
trans			
$\tau_{O\text{-}H}$ / cm^{-1}	642.0	681.4	584.5
$\Delta\tau_{O\text{-}H}$ / cm^{-1}	-139.0	-148.0	-148.5

TABLE X. EXPERIMENTALLY MEASURED FREQUENCIES OF THE O-H TORSIONAL MODES IN TRANS- AND CIS-FORMIC ACID AND THEIR CHANGES UPON TRANS-CIS INTERCONVERSION TOGETHER WITH THE THEORETICAL ANHARMONIC VALUES COMPUTED FROM THE VARIATIONAL SOLUTION OF THE TORSIONAL SCHRÖDINGER EQUATION (SEE TEXT FOR DETAILS)

Parameter	Exp.[a]	MP2	DFTB
cis			
$\tau_{O\text{-}H}$ / cm^{-1}	503.0	435.5	365.9
trans			
$\tau_{O\text{-}H}$ / cm^{-1}	642.0	566.0	484.1
$\Delta\tau_{O\text{-}H}$ / cm^{-1}	-139.0	-130.5	-118.2

The computed barrier to cis → trans interconversion is 3031 cm^{-1} while the corresponding value for the reverse trans → cis interconversion is 4588 cm^{-1}. The later value is in excellent agreement with the corresponding experimental estimation of 4842 cm^{-1}. The corresponding values computed at DFTB level are 2069 cm^{-1} and 3447 cm^{-1} respectively.

The frequencies of the HCOH torisonal modes computed at the employed MP2 and DFTB theoretical levels with the algorithms described in the methodology section are presented in Tables VIII-X, together with the available experimental data. As can be seen, the anharmonic MP2 values are in excellent agreement with the experiment, in the case of both absolute frequency values as well as when frequency shifts induced by the trans → cis interconversion are in question. The overall performance of MP2 methodology is again superior to DFTB, though the overall performance of the later method with this respect may be considered as rather satisfactory, considering its cost-effectiveness.

IV. CONCLUSIONS

In the present study, we have implemented several theoretical methodologies to compute the vibrational frequencies of intramolecular modes of formic acid which are relevant to its spectroscopic detection in the context of atmospheric chemistry and climate science. The main focus

was put on the O-H stretching mode in the case of both cis- and trans- rotamers of the title molecule. We have demonstrated that the local mode approach based on computation of the 1D O-H stretching vibrational potential at MP2/6-311++G($3df,3pd$) level of theory followed by solution of the vibrational Schrödinger equation leads to excellent agreement with the experimental data for the frequency shifts of this mode upon trans → cis interconversion. The same level of theory was also applied to compute the fully relaxed HCOH torsional potential. Subsequent solution of the torsional Schrödinger equation leads to HCOH torsional frequencies and frequency shifts which are in excellent agreement with the experimental data. Our further efforts will be directed towards extension of the currently implemented approaches to compute the parameters related to cis → trans tunneling dynamics, which are relevant to certain aspects of photochemical behavior of the title system.

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