

## COMPUTATIONAL STUDY OF INTRAMOLECULAR O-H STRETCHING VIBRATIONS IN THE TWO ROTAMERS OF FREE FORMIC ACID

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*Abstract.* O-H stretching vibrations of the two formic acid rotamers were studied using a static approach, based on calculation of the corresponding 1D vibrational potential and subsequent solution of the vibrational Schrödinger equation, and with a dynamic approach, based on Born-Oppenheimer molecular dynamics simulations, followed by computation of partial autocorrelation functions and their subsequent Fourier transformation. All calculations were performed at second-order Møller-Plesset perturbation theory level, using the 6-311++G(3df,3pd) basis set for orbital expansion. Emphasis has been put on the usage of these results in the course of spectroscopic detection of this compound, with unique atmospheric chemistry significance, under realistic conditions.

*Key words:* formic acid, O-H stretching vibrations, rotamers, vibrational Schrödinger equation, BOMD, first-principles MD, partial autocorrelation functions.

### 1. INTRODUCTION

Recent advances in climate science have been undoubtedly related to the adoption of molecular-level approach towards an in-depth understanding of processes relevant in this context. On the basis of molecular modeling approaches, one can build up much more reliable mesoscale models, which can be further used for certain predictions (related, *e.g.* to long-term ozone trends, lifetime of methane etc.). Organic acids have been seen as perhaps most serious possible candidates for precursors to formation of aerosols. Aerosols, on the other hand, seem to play substantially important roles both in atmospheric chemistry and in health sciences [1, 2]. The simplest, and at the same time the seemingly most abundant organic acid in the Earth's atmosphere is formic acid. This simple prototypical organic compound has been identified as a constituent of atmospheric precipitates (*e.g.* acid

rain), aside from its presence in free form and in aerosols. Concerning the origin of atmospheric formic acid, it has been related to both biogenic and anthropogenic emissions [3–8]. Aside from being relevant to the Earth's atmospheric chemistry, formic acid has been identified in the interstellar medium as well. Its relevance in the context of physics governing the phenomena occurring within interstellar and cometary ices has been pointed out as well [9].

Other simple organic acids are also relevant in the previously mentioned molecular-level climate science context [3–8]. However, as the formic acid is the simplest, yet prototypical model of this class of compounds, in-depth understanding of its physics and chemistry is of certain both fundamental and applicative significance. Formic acid exists in two conformers (rotamers): cis- and trans- (shown in Fig. 1 a) and b) respectively).

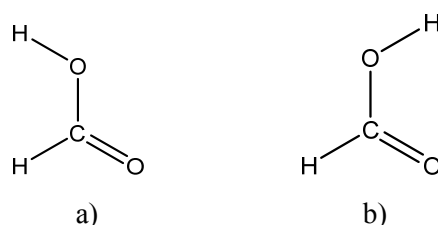


Fig. 1 – Molecular structure of the cis- (a) and trans- (b) conformers of formic acid.

Perhaps the most relevant vibrational spectroscopic characteristic of this simple molecular system, especially in the context of its identification as well as identification of its complexes with various molecular species under realistic atmospheric conditions is the O-H stretching vibration (and O-D as well, upon isotopic substitution of the parent compound). This normal mode, which is quite localized within the O-H moiety, *i.e.* practically decoupled from other intramolecular modes, is most easily detectable with vibrational spectroscopic techniques. At the same time, it is most sensitive to external perturbations, such as, *e.g.* involvement into noncovalent intermolecular interactions of various types, incorporation into condensed phases, nanodroplets etc. [10]. Therefore, understanding of this particular normal vibration is of high relevance if one wants to understand the processes and phenomena in which this molecule is involved, both in the context of climate science and atmospheric chemistry, as well as in a wide variety of biomedical contexts. At the same time, it is of essential importance to be able to describe this vibration in an exact quantum mechanical manner, and to predict accurately its vibrational frequency, in the case of both free molecular species, as well as in various noncovalently bonded clusters. In the present study,

we implement two exact methodologies to compute the anharmonic vibrational frequency of this mode in the case of both cis- and trans- conformers of formic acid. The first approach is in a sense a “static” one, based on calculation of anharmonic vibrational potential of the O-H stretching mode. The second one, which is inherently dynamical, relies on sequential Born-Oppenheimer molecular dynamics simulation (BOMD) [11, 12], followed by construction and further analysis/transformation of the relevant partial autocorrelation functions.

## 2. COMPUTATIONAL DETAILS

As outlined in the introductory section, we hereby apply two computational approaches to calculate in an exact manner the O-H stretching frequency of the cis- and trans- conformers of formic acid molecule. All computations were carried out at the second-order Møller-Plesset perturbation theoretic level (MP2), using the rather large and flexible 6-311++G(3*df*,3*pd*) basis set for orbital expansion, augmented with both diffuse and polarization functions on both hydrogen and non-hydrogen atoms. Thorough explorations of the MP2/6-311++G(3*df*,3*pd*) potential energy hypersurface (PES) of free (gas-phase) formic acid molecule, in particular in the vicinity of the cis- and trans- conformers, were carried out with Schlegel’s gradient optimization algorithm [13]. The located stationary points on the mentioned PES were subjected to harmonic vibrational analysis, which was carried out by diagonalization of the computed mass-weighted second derivative matrices (Hessians). The absence of negative eigenvalues of the mass-weighted Hessians indicated that a true minimum on the PES has been located. The located stationary points on the PES have subsequently been analyzed by the static and dynamic approaches described below. All quantum mechanical calculations for many-electron systems in the present study have been carried out using the Gaussian 09 series of codes [14]. All other computations described in the paper have been carried out with our locally developed codes.

### 2.1. “STATIC” COMPUTATION OF THE O-H STRETCHING FREQUENCIES

For the located minima on the MP2/6-311++G(3*df*,3*pd*) PES of free formic acid, corresponding to the cis- and trans- conformers, series of pointwise energy calculations were carried out, by stretching the O-H bonds, in a manner such that the center-of-mass of the O-H bond is kept constants, while the two atoms involved

in the vibration move in opposite directions. In this way, a pretty realistic description of the atomic movements is achieved in the course of excitation of the normal mode in question [15 and references therein]. The resulting potential energy function  $V(\Delta r)$  was subsequently fitted to a fifth-order polynomial in  $\Delta r$ :

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

where  $\Delta r = \Delta r_{\text{OH}} = r_{\text{OH}} - r_{\text{OH,e}}$ ,  $r_{\text{OH,e}}$  denoting the equilibrium value of  $r_{\text{OH}}$ . Subsequently, this polynomial was truncated after the fourth-order term, and transformed into the Simons-Parr-Finlan (SPF) type coordinates of the form [15]:

$$\rho = (r_{\text{OH}} - r_{\text{OH,e}}) / r_{\text{OH}}. \quad (2)$$

The 1D vibrational Schrödinger equation was solved variationally in the SPF coordinates, using 15 harmonic oscillator basis functions for expansion. Actually, the SPF-type coordinates have been shown to enable much wider region of convergence and sufficient convergence even with a modest number of basis functions [15 and references therein]. Finally, anharmonic vibrational frequencies of the fundamental  $|0\rangle \rightarrow |1\rangle$  vibrational transitions (*i.e.* actually the anharmonic vibrational wavenumbers, which are directly comparable to the experimental spectroscopic data) were calculated from the energies of the ground ( $|0\rangle$ ) and first excited ( $|1\rangle$ ) vibrational energy levels. Of course, the implemented 1D treatment of the O-H stretching vibrational motion within the static approach actually neglects the coupling of this mode with the other intramolecular vibrations (and neglect of any “accidental degeneracies” between intramolecular vibrational states). On the basis of our previous experience with the title system, including second-order perturbational treatment of its intramolecular motions, we have concluded that this assumption is justifiable in the present case.

## 2.2. “DYNAMIC” COMPUTATION OF THE O-H STRETCHING FREQUENCIES

Within the dynamic approach, Born-Oppenheimer molecular dynamics (BOMD) simulations of both *cis*- and *trans*- conformers of formic acid have been performed in gas phase, at temperature of 10 K at MP2/6-311++G(3*df*,3*pd*) level of theory. Dynamical simulations were started from the minima located at MP2/6-311++G(3*df*,3*pd*) PES. BOMD is actually a classical simulation of the nuclear dynamics (*i.e.* classical trajectory calculation), with forces computed from the implemented *ab initio* methodology in an “on the fly” manner. The total BOMD simulation was run for 1.44 ps in the case of both conformers. A total number of 1000 BOMD steps were computed by numerical integration of the Newton’s equations of motions.

Subsequently to the BOMD simulations, the contribution of the O-H stretching local mode to the overall IR spectrum of each of the formic acid conformers was computed, utilizing the method of partial autocorrelation functions (pACF) [16–18 and references therein]. In particular, we have used the following definition of the pACF:

$$C_{\zeta}(t) = \langle \dot{\zeta}(0) \dot{\zeta}(t) \rangle. \quad (3)$$

Then, the contribution to the overall IR intensity spectrum of this particular pACF is given by a Fourier transformation:

$$I_{\zeta}(\omega) = \int_0^{\infty} \exp(-i\omega t) C_{\zeta}(t) dt \quad (4)$$

or, finally:

$$I_{\zeta}(\omega) = \int_0^{\infty} \exp(-i\omega t) \langle \dot{\zeta}(0) \dot{\zeta}(t) \rangle dt. \quad (5)$$

In our particular case,  $\zeta$  is defined as the O-H distance of the vibrating hydroxyl group. Thus, the time series  $\zeta(t)$  is extracted from the BOMD trajectory, subsequently numerical first-order time derivatives were computed and the correlation function  $\langle \dot{\zeta}(0) \dot{\zeta}(t) \rangle$  was calculated. By a subsequent Fourier transformation, the contribution (5) has been obtained. Actually, (5) gives the contribution of this particular local mode to the overall vibrational density of states (VDOS), *i.e.* it represents the corresponding partial vibrational density of states (pVDOS) corresponding to the O-H stretching vibration.

### 3. RESULTS AND DISCUSSION

It should be mentioned at the very beginning of this chapter, that a non-elusive assignment and interpretation of experimental spectroscopic data in the case of molecular species with certain intramolecular torsional flexibility is not always possible. Thus, in the case of our studied title system, on the basis of thermodynamical and energetic data for the intramolecular *cis* → *trans* conversion process, it has been estimated [1–8] that the ratio of populations of the *cis*- to *trans*-conformers at 298 K should be close to  $10^{-3}$ . Therefore, the *cis*-rotamer is much less abundant and it is quite far from a trivial task to unequivocally detect it in a realistic gas-phase sample, on the basis of vibrational spectroscopy data. In the course of this task, computational methods can be especially useful. In the present

study, we rely on the experimental data obtained for formic acid rotamers captured in cryogenic matrices, where it is possible to detect the vibrational transitions of the cis- conformer relevant to the present study [1–8].

### 3.1. RESULTS FROM THE “STATIC” APPROACH

The structures corresponding to the minima on the MP2/6-311++G(3df,3pd) PES of the cis- and trans- rotamers of the free (gas-phase) formic acid are shown in Fig. 2.

In this context, we pay attention only to the agreement of our theoretical prediction with the experimental data for the structural parameter that is most relevant to the present study – the O-H distance within the carboxylic hydroxyl group. For example, the experimental O-H distance in the trans- conformer is 0.972 Å, while our theoretically predicted value is 0.968 Å. The corresponding experimental and theoretical values for the cis- conformer are 0.956 and 0.963 Å respectively [1–8]. The agreement between theory and experiment is thus excellent, the relative error of prediction being 0.4 % in the case of trans- and 0.7 % in the case of cis- conformers.

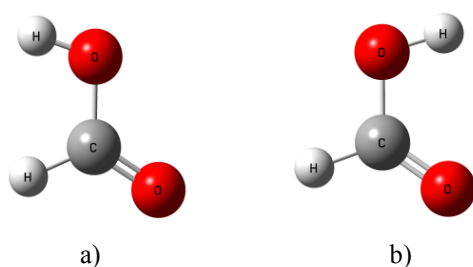


Fig. 2 – The geometries corresponding to the minima located on the MP2/6-311++G(3df,3pd) PES of the cis- (a) and trans- (b) conformers of formic acid.

Table 1 summarizes the theoretical results from the current study (obtained from the “static” approach), expressed through the anharmonic wavenumbers of the O-H stretching frequencies in the case of the cis- and trans-formic acid conformers. The agreement between theory and experiment is again excellent, especially when one compares the most relevant parameter for gas-phase detection of the two considered formic acid rotamers – the difference in the anharmonic vibrational wavenumbers of the O-H stretching mode. The computed O-H stretching vibrational potentials, on the basis of which the values presented in Table 1 have been computed, are shown in Fig. 3.

Table 1

The theoretically computed values of the O-H stretching frequencies in the case of cis- and trans-conformers of free (gas-phase) formic acid by the “static” approach, together with the corresponding experimental data

	Exp.	MP2
cis		
$\nu(\text{O-H}) / \text{cm}^{-1}$	3618.0	3712.6
trans		
$\nu(\text{O-H}) / \text{cm}^{-1}$	3550.5	3642.8
$\Delta\nu(\text{O-H})_{\text{cis-trans}} / \text{cm}^{-1}$	67.5	69.8

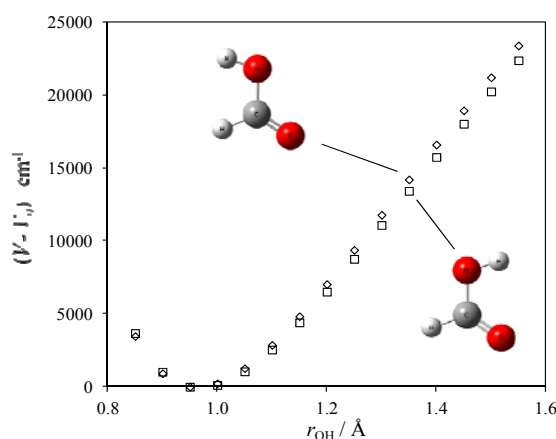


Fig. 3 – The O-H stretching vibrational potentials computed at MP2/6-311++G(3df,3pd) level of theory for cis- and trans- conformers of formic acid (for the geometries corresponding to the minima on the same PES).

### 3.2. RESULTS FROM THE “DYNAMIC” APPROACH

The calculated pACFs corresponding to the O-H stretching vibrational coordinates (the “local modes”) from the computed BOMD trajectories of the cis- and trans- rotamers of the free (gas-phase) formic acid are shown in Fig. 4a and Fig. 5a. In Fig. 4b and 5b, on the other hand, the corresponding Fourier transforms of these correlation functions are shown (*i.e.* the real parts thereof), which actually correspond to the contributions of the O-H stretching local modes to the overall IR spectra in the case of each of the formic acid conformers. As discussed before, Fig. 4b and 5b actually show the computed pVDOS corresponding to the O-H stretching modes of the cis- and trans-conformers.

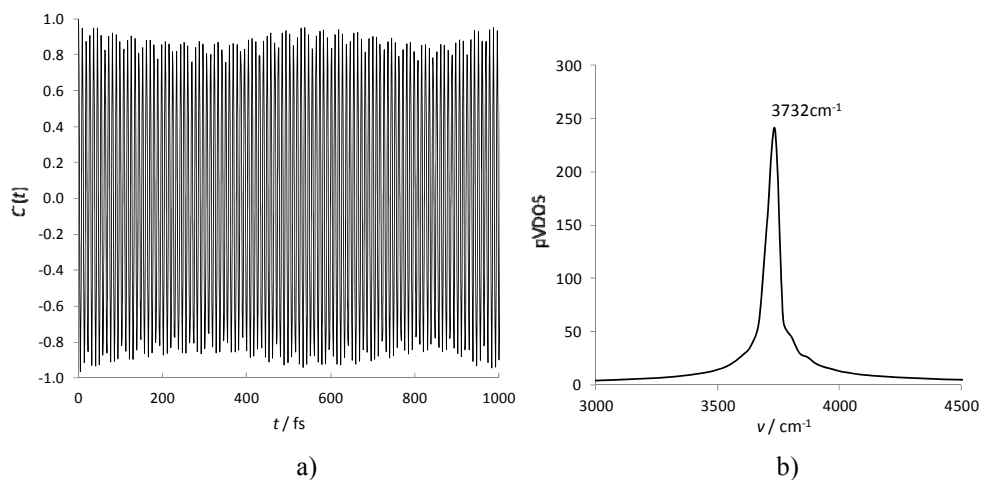


Fig. 4 – a) The pACF for the O-H stretching coordinate time derivative computed from BOMD/MP2/6-311++G(3df,3pd) trajectory for cis- conformer of formic acid and b) the corresponding pVDOS computed by sequential Fourier transformation of  $C(t)$ .

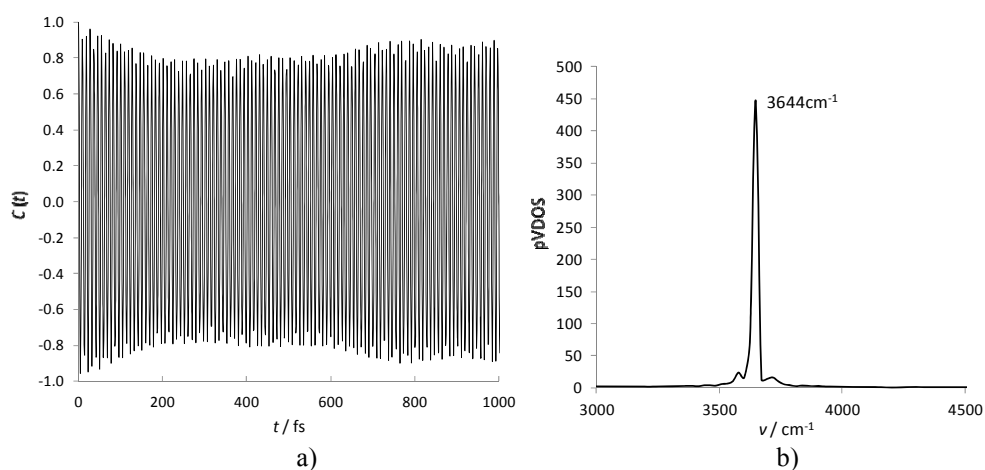


Fig. 5 – a) The pACF for the O-H stretching coordinate time derivative computed from BOMD/MP2/6-311++G(3df,3pd) trajectory for trans- conformer of formic acid and b) the corresponding pVDOS computed by sequential Fourier transformation of  $C(t)$ .

As can be seen, the band maxima in the pVDOS are positioned at  $3732$  and  $3644 \text{ cm}^{-1}$  in the case of cis- and trans- rotamers respectively. Having in mind that the corresponding experimental O-H stretching frequencies are  $3618$  and  $3550 \text{ cm}^{-1}$ , it may be concluded again that the agreement between theoretical predictions and the experimental data is rather good, having in mind the relative error, and the fact



that no scaling factors have been used. The same conclusion is valid for the vibrational frequency shifts corresponding to the cis  $\rightarrow$  trans interconversion (88 vs. 67.5  $\text{cm}^{-1}$ , theory vs. experiment respectively). Table 2 summarizes these data. Better agreement between theory and experiment in the case of anharmonic frequency shifts computed by the “static” approach may be attributed to a better sampling of the anharmonic part of the vibrational potential in the former case.

Table 2

The theoretically computed values of the O-H stretching frequencies in the case of cis- and trans-conformers of free (gas-phase) formic acid by the “dynamic” approach, together with the corresponding experimental data

	Exp.	BOMD-MP2
cis		
$\nu(\text{O-H}) / \text{cm}^{-1}$	3618.0	3732
trans		
$\nu(\text{O-H}) / \text{cm}^{-1}$	3550.5	3644
$\Delta\nu(\text{O-H})_{\text{cis-trans}} / \text{cm}^{-1}$	67.5	88

The rather good agreement between theoretical results obtained with the “static” and “dynamic” approach actually indicate that sufficient part of the “anharmonic” region of the O-H stretching motions has been sampled in the course of *ab initio* BOMD simulations. In theory, the pVDOS computed by Fourier transformation of the pACF should indeed give the anharmonic frequency. However, if the “anharmonic” region of the corresponding vibrational motion is not adequately sampled, one may finally arrive at the harmonic spectrum. The fact that, on the other hand, both the “static” and “dynamic” approach lead to O-H stretching frequency values which are still somewhat higher than the experimental ones in the case of both conformers (Tables 1 and 2), indicates that further methodological improvements are required to achieve an even better agreement between theory and experiment. Such improvements could be directed towards a better description of dynamical electron correlation effects, *e.g.* implementation of a multireference method, usage of an even larger and more flexible basis set for orbital expansion etc.

#### 4. CONCLUSIONS

In summary, in the present study we have calculated the O-H stretching vibrational frequencies of the two formic acid conformers in gas phase. The

calculations were carried out by two approaches: static and dynamic ones. The static approach is based on computation of anharmonic vibrational potentials and subsequent variational solution of the vibrational Schrödinger equation in appropriate vibrational coordinates (SPF in the present case). The dynamic approach is, on the other hand, based on performing BOMD simulation and subsequent construction and analysis of the partial autocorrelation functions corresponding to the O-H stretching normal modes in the two studied conformers. All calculations were carried out at sufficiently high level of theory (MP2/6-311+G(3df,3pd)). The agreement between theory and experiment was found to be excellent, the relative errors in predicted parameters being often less than few percents. Dynamical calculations have led to results which are rather close to the static ones, indicating that even carried out at 10 K, BOMD simulations have already sampled rather satisfactorily the relevant (anharmonic) part of the O-H stretching potential in both cases. However, such sampling is obviously better in the case of the static approach, as can be seen from the significantly better agreement of the vibrational frequency shifts with the experimental data obtained with this approach. We finally address the computational efforts related to the present work. Though the studied system is rather small, just to illustrate the provisional computational cost, we mention that *e.g.* computation of a single BOMD trajectory at the present level of theory took approximately 600 core hours. Essentially all of the resource-intensive jobs have been run utilizing 12-core nodes within the available HPC systems.

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