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Antoine Aerts, Philippe Carbonnière, Falk Richter, Alex Brown. Vibrational states of deuterated trans - and cis -formic acid: DCOOH, HCOOD, and DCOOD. *The Journal of Chemical Physics*, 2020, 152 (2), pp.024305. 10.1063/1.5135571 . hal-02464246

HAL Id: hal-02464246

<https://hal.science/hal-02464246>

Submitted on 26 Aug 2020

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Vibrational states of deuterated trans- and cis-formic acid: DCOOH, HCOOD, and DCOOD

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Abstract

The vibrational eigenenergies of the deuterated forms of formic acid (DCOOD, HCOOD, and DCOOH) have been computed using the block-improved relaxation method as implemented in the Heidelberg multi-configuration time-dependent Hartree package on a previously published potential energy surface [J. Chem. Phys. 148, 064303 (2018)] generated at the CCSD(T)-F12a/aug-cc-pVTZ-F12 level of theory. Fundamental, combination band, and overtone transition frequencies of the trans isomer were computed up to ~ 3000 cm^{-1} with respect to the zero point energy and assignments were determined by visualisation of the reduced densities. Root mean square deviation of computed fundamental transition frequencies with experimentally available gas-phase measurements are 8, 7, and 3 cm^{-1} for trans- DCOOD, HCOOD, and DCOOH, respectively. The fundamental transition frequencies are provided for the cis isomer of all deuterated forms; experimental measurements of these frequencies for the deuterated cis isotopologues are not yet available and the present work may guide their identification.

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I. INTRODUCTION

Formic acid (HCOOH) is the simplest carboxylic acid and, hence, serves as a benchmark system for this class of molecules. Moreover, as the smallest carboxylic acid, it provides a test case for *ab initio* studies, including the determination of vibrational state energies. Formic acid is the most abundant organic acid in the atmosphere¹ and, also, is of great astronomical importance especially for its potential role as an organic building block.² Formic acid, which was first detected in the Sg B2 star-forming region in 1971 by Zuckerman *et al.*,³ has also been observed towards hot molecular cores.⁴

Formic acid features two conformational isomers, *i.e.*, trans and cis. Based on a recent full-dimensional anharmonic computational study by Richter and Carbonnière,⁵ the cis-isomer is about 1415 cm⁻¹ higher in energy than the trans-isomer when comparing zero-point-energies. Another computational study on formic acid by Tew and Mizukami⁶ at a similar level of theory predicted this value to be 1412 cm⁻¹. The isomerism enriches the spectra and could manifest as interesting dynamics in the cis-trans isomerization process. However, the trans form is about 800 times more abundant than the other rotameric form at room temperature. Therefore, the observation of the cis form in the gas phase requires a long absorption path (and no band-overlap) or more elaborate techniques such as demonstrated recently by Meyer and Suhm.⁷ Another approach to detecting the cis-form involves using rare-gas matrix isolation, and this has been the primary method used for the experimental study of the cis form. However, this method induces environmental effects on the vibrational spectrum in going from the gas phase to the matrix. Moreover, the observed shifts in peak positions are dependent on the vibrational state and, thus, do not permit a systematic comparison to gas-phase theoretical results as shown by Meyer and Suhm.⁷ Therefore, if one wishes to benchmark theoretical approaches for obtaining vibrational energies, gas-phase measurements must be conducted directly for both isomers and their isotopologues. Experimental data on the cis form are scarce⁷⁻¹⁰, especially for the deuterated species, and, to the best of our knowledge, results for the deuterated forms are available only from rare-gas matrices isolation measurements;^{11,12} however, new gas phase measurements are being undertaken.¹³

In the present work, we focus on the computation of fundamental vibrational states as well as combination bands and overtones of the deuterated forms of trans-formic acid, *i.e.*,

HCOOD, DCOOH, and DCOOD. We also report the fundamental transition frequencies of the deuterated forms of cis-formic acid. Although the interest in the deuterated forms of formic acid results from the astrophysical interest in the non-deuterated species, spectroscopic evidence of HCOOD and DCOOH in the interstellar medium has been reported.^{14,15} Although the doubly-deuterated form, *i.e.*, DCOOD, is less-likely to be observed, doubly deuterated molecules have been observed in the interstellar medium, *e.g.*, water (D₂O),¹⁶ ammonia (ND₂H),^{17,18} D₂S,¹⁹ and formaldehyde (D₂CO).²⁰ Moreover, even triply deuterated species have been detected, *e.g.*, ammonia (ND₃).²¹

The vibrational states of formic acid (HCOOH) were determined in a number of theoretical studies.^{5-7,11,12,22-28} Tew and Mizukami⁶ computed vibrational eigenstates using vibrational configuration interaction on a global potential energy surface (PES) constructed with 17076 CCSD(T)(F12*)/cc-pVTZ-F12 energies valid up to 15 000 cm⁻¹. Their theoretical trans fundamental energies have a root mean square deviation of 3.0 cm⁻¹ with respect to the gas phase measurements. Maçôas *et al.*¹¹ assigned the overtone spectra of HCOOH and DCOOH using a correlation corrected vibrational self-consistent field technique on a PES constructed with 30816 points at the MP2/6-311++G(2d,2p) level of theory. Demaison *et al.*²³ computed a semidiagonal quartic force field for both isomers at the CCSD(T)/cc-pVTZ level of theory, derived semiexperimental equilibrium structures of HCOOH, and analysed some of its resonance polyads. Other studies provided equilibrium structures and the anharmonic ν_{OH} stretching frequency using the MP2/6-311++G(3df,3pd) level of theory²⁴ as well as ν_{OD} using the density functional tight binding formalism (DFTB).²⁵ The ν_{OH} overtones were studied using a 1D potential computed at the MP2/cc-pVTZ level²⁶ and fundamentals, combination bands, and overtones were computed with vibrational self-consistent field (CC-VSCF) using second-order perturbation correction at the MP2/6-311++G(2d,2p) level for HCOOD.¹² The computational benchmark of Meyer and Suhm⁷ with systematic comparison of band positions with the gas-phase measurements showed the limitation of density functional theory based methods while suggesting the double hybrid B2PLYP-D3(BJ)/aug-cc-pVQZ and MP2/aug-cc-pVQZ methods using second order vibrational perturbation theory (VPT2) to obtain the vibrational energies as a good compromise between cost and accuracy. Going beyond VPT2, most recently, Richter and Carbonnière⁵ computed the vibrational eigenstates of formic acid using the block improved relaxation method²⁹⁻³³ in the Heidelberg Multi Configuration Time Dependent Hartree (MCTDH) method^{29,32,34-37} on a

PES constructed based on CCSD(T)-F12a/aug-cc-pVTZ-F12 energies.

In the present work, methods of quantum dynamics coupled to a PES fit to quantum chemistry calculations are used to produce vibrational eigenstates for deuterated forms of formic acid using the Heidelberg implementation of the MCTDH method.^{29,32,34-37} We use the same method as Richter and Carbonnière⁵, their PES, and the (block-) improved relaxation method²⁹⁻³³ implemented in the MCTDH Heidelberg package which proved to be successful in assigning vibrational states for formic acid (HCOOH),⁵ including the recently confirmed re-assignment of the Fermi-coupled ν_5 and $2\nu_9$ states.³⁸

II. METHODS

We compute the vibrational eigenstate energies of the deuterated forms of formic acid, HCOOD, DCOOH, and DCOOD, using the PES of Richter and Carbonnière⁵ (referred to as the RC-PES) with the (block-) improved relaxation method²⁹⁻³³ in the Heidelberg MCTDH software package.^{29,32,34-37} The PES, valid up to about 6000 cm^{-1} above the zero point energy of the trans isomer, was generated in internal valence coordinates using the AGAPES method^{39,40} and was based upon fitting of CCSD(T)-F12a/aug-cc-pVTZ-F12 *ab initio* energies. The PES has been converged to yield approximately a.5 cm^{-1} threshold for the average vibrational error for levels up to 6000 cm^{-1} above the trans-isomer zero point energy for HCOOH. The kinetic energy operator was generated using the TANA program.^{41,42} The exploitation of the efficiency of MCTDH requires the Hamiltonian, *i.e.*, the kinetic energy operator (KEO) and PES, to be in sum of product (SOP) form. Both the KEO and PES are constructed in SOP form by design. General details of the methods have been provided previously,³⁹⁻⁴² while specific details for formic acid, are given in the vibrational study of HCOOH by Richter and Carbonnière.⁵

The valence coordinates, used for the PES and vibrational state computations are depicted in Figure 1, where the hydrogen isotopes Deuterium (D) or Hydrogen (H) are represented by ^xH . The grids, mode combinations, number and type of primitive functions, as well as the number of single particle functions (SPFs) used in the block improved relaxation computations within MCTDH are given in Table I. In comparison with the previous study of HCOOH,⁵ we used the full torsional τ_2 grid and an increased number of SPFs. Assignments of the vibrational eigenstate energies to the fundamental, overtone, or combinational bands

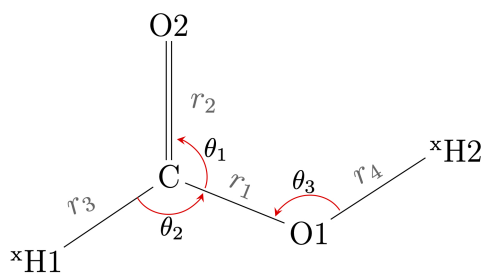


FIG. 1: Valence coordinates used to describe formic acid; the torsional angles τ_1 and τ_2 are respectively the ${}^x\text{H1}$ and ${}^x\text{H2}$ (or D1/D2 depending on deuterium substitution) out of plane motions relative to the O2CO1 body.

Mode combinations	$(r_1, -\cos(\pi - \theta_3))$	(r_2, r_3, r_4)	$(\cos(\theta_1), \cos(\theta_2))$	(τ_1, τ_2)
Number of SPFs	37	35	37	45
Grid size	(30,30)	(30,30,30)	(40,30)	(35,70)
Type	HO	HO	HO	HO
Lower-Upper limits	$([2.122, 3.301],$ $[-0.980, 0.401])$	$([1.943, 2.854],$ $[1.455, 3.900],$ $[1.315, 3.253])$	$([-0.900, -0.1587],$ $[-0.868, 0.292])$	$([-4.218, -2.064],$ $[-1.58, 4.71])$

TABLE I: Specifications of the parameters used for the MCTDH (block-)improved relaxation computations. HO refers to the harmonic oscillator basis. Bond distances are given in Bohr and the dihedral angles are given in radians.

were determined by visualisation of the reduced densities.

In addition to the MCTDH computations, we carried out density functional theory (DFT) B3LYP^{43,44}/aug-cc-pVTZ^{45,46} VPT2⁴⁷ computations as implemented in Gaussian 16⁴⁸ for fundamental transition frequencies of both isomers of all considered species; a smaller number of overtones and combination bands are also reported. Although showing limitations in the predictions, especially in the case of resonant states and at higher transition energies, the functional proved to be in reasonable agreement with the gas-phase measurements with a maximal deviation of 49 cm^{-1} but a RMSD of 25 cm^{-1} for the (anharmonic) fundamental frequencies of trans-HCOOH. Since the goal of the present work is not to test functionals for accurate prediction of vibrational frequencies of formic acid, as has been done previously,⁷ but rather to provide accurate prediction based on a full dimensional PES, a diversity of functionals has not been considered.

III. RESULTS AND DISCUSSION

The accuracy of the RC-PES⁵ for the computation of fundamental, overtone, and combination vibrational bands of trans-HCOOH was assessed in the original work with the computed fundamental transition frequencies deviating by less than 5 cm⁻¹ from known gas-phase experimental transition frequencies. Further gas-phase experimental measurements for the cis-isomer fundamentals reported by Meyer and Suhm⁷ showed a deviation of 8 cm⁻¹ at most with the reported theoretical values from the RC-PES. In comparison, the environmental effect from the gas phase to the matrix is inconsistent, *i.e.*, the frequency shift depends on the vibrational state, and is observed to be as large as 27 cm⁻¹, which is of similar order of magnitude as the difference between cis and trans fundamental transition frequencies stressing the need for accurate gas-phase measurements, including of the deuterated species.

Our theoretical results include fundamental, overtone, and combination vibrational band energies along with experimental results when available for all the deuterated trans-formic acid species: DCOOD, HCOOD, and DCOOH. For comparison, anharmonic vibrational energies computed at the B3LYP/aug-cc-pVTZ level of theory are presented. We also provide the harmonic frequencies and optimized geometries in the Supplemental Material in Tables S1 and S2. Meyer and Suhm⁷ tested a number of functionals and basis sets for HCOOH and their best results, as compared to experiment, used a higher level of theory B2PLYP-D3(BJ)/aug-cc-PVQZ^{45,46,49} which involves a double hybrid functional with Grimme's dispersion correction (D3) in combination with Becke-Johnson (BJ) damping⁵⁰. The method of our choice deviates at most by 5 cm⁻¹ from the theoretical results of Meyer and Suhm⁷ for trans-HCOOH. In general, the vibrational energies from the anharmonic vibrational perturbation theory computations (VPT2) are mostly in good agreement with experimental data although the maximal deviation is of 46 cm⁻¹ for the ν_2 (ν_{CD}) stretching of DCOOD; the good agreement for the relatively low-energy states could be attributed to the small size of the formic acid molecule and its relatively high rigidity. In the following sections, we discuss the vibrational states for each isotopologue, where cis-formic acid fundamental transition frequencies are given at the end; we do not discuss overtones and combination bands for the cis-isomer as experimental measurements are not yet available, while the fundamental frequencies should be available in the near future.¹³

Assignment	Mode	Gas phase ^a	MCTDH	VPT2
τ_{COD}	ν_9	493.2254252(35) ⁵⁷	489.4	492.3
τ_{DCO}	ν_8	873.0 ⁵⁴	871.5	872.8
OCO-COD def.	ν_7	554.4394726(50) ⁵⁷	552.0	549.8
δ_{COD}	ν_6	945.0 ⁵⁴	943.7	939.2
γ_{CD}	ν_5	1042 ⁵²	1035.1	1041.4
$\nu_{\text{C-O}}$	ν_4	1170.79980(2) ⁵⁶	1170.4	1150.8
$\nu_{\text{C=O}}$	ν_3	1742.0 ⁵⁴	1759.0	1762.9
ν_{CD}	ν_2	2213.0 ⁵⁴	2228.1	2167.1
ν_{OD}	ν_1	2631.87379(43) ⁵⁵	2629.4	2602.7, 2569.9 ^b
RMSD			8	21

^aError on the last digit(s) is indicated in brackets when published.

^bDFTB²⁵

TABLE II: For fully-deuterated trans-formic acid (trans-DCOOD), fundamental vibrational energies (in cm^{-1}) with respect to the ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Mode assignment is given as ν =stretching, δ =bending, γ =rocking, def.=deformation.

A. Trans-DCOOD

All experimental fundamental band centers of trans-DCOOD measured in the gas phase have been reported,^{51–57} and the most recent results are provided in Table II. Experimental analysis including rotation has been completed for the ν_1 and ν_4 fundamentals,^{55,56} *i.e.*, the OD and C-O stretches, respectively. Two high-energy overtone and combination bands were also reported.⁵⁸ The higher energy stretching overtone $2\nu_1$ ($2\nu_{\text{OD}}$) energy was obtained using the improved relaxation procedure; the theoretical value of 5173.0 cm^{-1} is in good agreement with the experimental value⁵⁸ of 5181 cm^{-1} and supports the validity of the PES at relatively high energy. The $\nu_2 + \nu_3$ combination band ($\nu_{\text{CD}} + \nu_{\text{C=O}}$)⁵⁸ observed at 3981 cm^{-1} could not be converged in the present work due to the high density of states in that energy region and the mixed nature of the state (which is a function of the choice of coordinate system). Furthermore, molecular geometrical changes observed⁵⁹ in HCOOH following the multiple excitation of the ν_1 mode (ν_{OD}) could not be studied in this work due to the limited energy range validity of the PES used.

Theoretical results compared to experimental measurement for the fundamental bands are gathered in Table II with a root mean square deviation (RMSD) of 8 cm^{-1} and largest deviation of 17 cm^{-1} for the $\nu_{\text{C=O}}$ and 15 cm^{-1} for the ν_{CD} modes. However, we point out the

Assignment	Mode	Gas phase ^a	MCTDH	VPT2
τ_{COD}	ν_9	508.1320569(45) ⁵⁷	505.2	508.7
τ_{HCO}	ν_8	1010.8 ^{72b}	1029.4	1029.9
OCO-COD def.	ν_7	558.2722502(62) ⁵⁷	555.8	553.7
δ_{COD}	ν_6	972.8520(1) ^{65,66}	968.6	968.1
$\nu_{\text{C-O}}$	ν_5	1177.09378(2) ⁶⁹	1179.1	1156.6
γ_{CH}	ν_4	1366.48430(39) ⁶⁸	1361.9	1360.5
$\nu_{\text{C=O}}$	ν_3	1772.119(24) ⁶⁷	1770.5	1775.2
ν_{OD}	ν_2	2631.63835(17) ⁶²	2629.4	2602.8
ν_{CH}	ν_1	2938-2942 ⁶⁰	2934.4	2901.3
RMSD			7	18

^aError on the last digit(s) is indicated in brackets when published.

^bValue reported in⁶⁰, original paper unavailable (1973)

TABLE III: For half-deuterated trans-formic acid (trans-HCOOD), fundamental vibrational energies (in cm^{-1}) with respect to the respective ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

older nature of the concerned experimental results (from 1969) which perhaps could benefit from updated measurements. As expected, the anharmonic vibrational perturbation theory results behave more poorly at higher energy due to anharmonicity, but show an RMSD of 21 cm^{-1} with measured fundamental transition frequencies and a stunningly good agreement for the five lowest energy fundamentals. The relatively good agreement for the OD stretching (ν_1) with a deviation of 29 cm^{-1} in comparison to the maximal deviation of 46 cm^{-1} of the CD stretching (ν_2) could be attributed to the “local” character of the ν_1 mode.²⁶ All other assigned overtones and combination bands are given in the Supplementary Material in Tables S3 and S4.

B. Trans-HCOOD

All fundamental bands were recorded in the gas phase for trans-HCOOD^{51,53,54,60-62} and in rare-gas matrices;^{63,64} they are provided in Table III and matrix shifts with respect to the gas phase measurements are given in Table IV. We stress in this case that the ν_1 and ν_2 fundamental modes are “switched” compared to the HCOOH case, *i.e.*, they represent the CH and OD stretching in HCOOD, respectively. For this reason, the equivalent movement is assigned alongside the mode number throughout this paper. The available experimental

Assignment	Mode	Gas phase ^a	Ne ⁶³	Ar ⁶³	Kr ⁶³	Xe ⁶³
τ_{COD}	ν_9	508.1320569(45) ⁵⁷	-1.2	-1.4/-2.9	-1.1/-3.4/-4.5	-3.0/-5.6
τ_{HCO}	ν_8	1010.8 ⁷²	+26.6 ⁶⁴	+25.6/+24.3	+22.8	+19.6
OCO-COD def.	ν_7	558.2722502(62) ⁵⁷	-0.4	+1.4/+0.4	+1.1/-0.1	+0.0/-1.2
δ_{COD}	ν_6	972.8520(1) ^{65,66}	-1.7	-1.8	-1.2/-4.7/-5.4	-4.1/-8.1
$\nu_{\text{C-O}}$	ν_5	1177.09378(2) ⁶⁹	-0.2	+4.8	+9.1/+2.7	-0.8/-1.2
γ_{CH}	ν_4	1366.48430(39) ⁶⁸	+1.6 ⁶⁴	+7.8/+4.6	+1.9	-1.7
$\nu_{\text{C=O}}$	ν_3	1772.119(24) ⁶⁷	-1.1	-4.9/-6.5	-9.9	-16.4/-15.7
ν_{OD}	ν_2	2631.63835(17) ⁶²	-0.1	-12.1/-13.6	-21.6/-26.8	-31.9/-38.3
ν_{CH}	ν_1	2938~2942 ⁶⁰	+9.5~+13.5	+19.2~+23.2	+11.8~+15.8	+3.6~-0.4

^aError on the last digit(s) is indicated in brackets when published.

TABLE IV: Half-deuterated trans-formic acid (trans-HCOOD) fundamental vibrational energies (in cm^{-1}) compared to matrix isolation values in different rare gas (RG) matrices; values given as $\delta\nu_i = \nu_i^{\text{gas-phase}} - \nu_i^{\text{RG}}$. Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

data for overtone or combination bands is very limited in the gas phase^{58,65-67}, see Table V, but more significant in rare-gas matrices thanks to Marushkevich *et al.*,¹² see Table S5 in the Supplementary Material. From gas-phase measurements, the rotational structure of the ν_3 , ν_4 , ν_5 , ν_6 , ν_7 , and ν_9 fundamentals have been studied^{57,65-71} as well as in the $2\nu_9$ overtone band.⁶⁵

Theoretical results compared to gas phase experimental and B3LYP/aug-cc-pVTZ VPT2 anharmonic computations are gathered in Table III for the fundamental transition frequencies. For the fundamentals, the RMSD is 7 cm^{-1} and the maximum deviation is 19 cm^{-1} for ν_8 but as has already been pointed out in the DCOOD case, the concerned experimental results were obtained a relatively long time ago. Therefore, given the experimental advances in high resolution spectroscopy, these could benefit from being remeasured. Again, the anharmonic vibrational perturbation results behave more poorly at higher energy but show an RMSD of 18 cm^{-1} with measured fundamental transition frequencies.

In Table IV, we gather the gas-phase fundamental transition frequencies alongside the rare-gas, *i.e.*, Ne, Ar, Kr, and Xe, matrices measurements of Domanskaya *et al.*⁶³ in terms of spectral shift from the gas phase transition frequencies. The corresponding absolute values are repeated in the Supplementary Material in Table S6. In general, the shifts between the gas phase to the matrix seem to be consistent, *i.e.*, the same direction and similar magnitude, for the various rare gases given a single vibrational mode; however there are some notable exceptions, *e.g.*, $\nu_{\text{C-O}}$ where Ne and Xe lead to small negative shifts while

Assignment	Mode	Gas phase ^a	MCTDH	VPT2
$2\tau_{\text{COD}}$	$2\nu_9$	1011.6766(1) ^{65,66}	1006.2	1006.2
$\nu_{\text{C-O}}+\tau_{\text{COD}}$	$\nu_5 + \nu_9$	1680.962939(64) ⁶⁷	1681.4	1662.7
$\nu_{\text{C-O}}+\text{OCO-COD def.}$	$\nu_5 + \nu_7$	1732.084(24) ⁶⁷	1729.9	1705.7
$\nu_{\text{OD}}+\nu_{\text{C=O}}$	$\nu_2 + \nu_3$	4404 ⁵⁸	4397.3	4376.0, 4345.8 ^b
$\nu_{\text{CH}}+\nu_{\text{C=O}}$	$\nu_1 + \nu_3$	4702-4736 ⁵⁸	4715.3	4670.5, 4704.3 ^b
$2\nu_{\text{OD}}$	$2\nu_2$	5181 ⁵⁸	5169.7	5118.1, 5163.6 ^b

^aError on the last digit(s) is indicated in brackets when published.

^bCC-VSCF¹¹ based on MP2/6-311++G (2d,2dp)

TABLE V: For half-deuterated trans-formic acid (trans-HCOOD), overtone and combination bands energies (in cm^{-1}) with respect to the respective ground state energy as determined using block-improved relation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2) and CC-VSCF results of Maçôas *et al.*¹¹ Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

Ar and Kr have larger positive shifts. This analysis emphasizes the need for benchmark gas-phase measurements to compare with theoretical predictions, *e.g.*, for the cis-isomer discussed in Section III D. Most rare gas matrix measurements overestimate the gas phase frequencies for the modes ν_1 (ν_{CH}), ν_4 (γ_{CH}), and ν_8 (τ_{HCO}) and underestimate for modes ν_2 (ν_{OD}), ν_3 ($\nu_{\text{C=O}}$), ν_6 (δ_{COD}), and ν_9 (τ_{COD}). The effect of the environment in matrix isolation for the ν_7 (OCO-COD def.) mode seems to be the weakest with a spectral shift with the gas-phase of +1.4 and -1.2 cm^{-1} at maximum for Ar and Xe, respectively.

The reported gas-phase combination and overtone band frequencies within the scope of this study are given in Table V. Our theoretical results agree with the measurements at lower frequencies of $2\nu_9$ ($2\tau_{\text{COD}}$), $\nu_5 + \nu_9$ ($\nu_{\text{C-O}}+\tau_{\text{COD}}$), and $\nu_5 + \nu_7$ ($\nu_{\text{C-O}}+\text{OCO-COD def.}$) with a maximum deviation of about 8 cm^{-1} for the $\nu_5 + \nu_7$ combination band. At higher frequencies, theoretical results for $\nu_2 + \nu_3$ ($\nu_{\text{OD}}+\nu_{\text{C=O}}$), $\nu_1 + \nu_3$ ($\nu_{\text{CH}}+\nu_{\text{C=O}}$), and $2\nu_2$ ($2\nu_{\text{OD}}$) behave more poorly although the agreement with experiment is still fairly good with a maximum deviation of about 11 cm^{-1} for $2\nu_2$. However, the reported measurements⁵⁸ at higher transition ($>4400 \text{ cm}^{-1}$) frequencies might have a large uncertainty and could benefit from updated measurements. Reported transitions in matrices are given in the Supplementary Material in Table S5 and all other assigned overtones and combination bands are given in the Supplementary Material in Tables S7 to S9.

Assignment	Mode	Gas phase ^a	Ar ¹¹	MCTDH	VPT2
τ_{COH}	ν_9	631.5437158(56) ⁷⁵	-5.1/-5.6	627.7	629.0
τ_{DCO}	ν_8	870 ⁷⁴	+4.8/+5.0	871.9	872.9
OCO-COH def.	ν_7	620.5683857(57) ⁷⁵	+1.7/+2.9	617.3	616.2
δ_{COH}	ν_6	-	-	1294.1	1283.5
$\nu_{\text{C-O}}$	ν_5	1142.31075(2) ⁷⁷	-0.2/+2.1/-0.6	1139.3	1125.4
γ_{CD}	ν_4	970 ⁶⁰	+6.2/+4.9/+4.1	970.9	965.7
$\nu_{\text{C=O}}$	ν_3	1725.874974(34) ⁷³	-2/-3	1722.8	1763.8
ν_{CD}	ν_2	2219.6896(2) ⁷⁹	+5.5	2216.5	2183.0
ν_{OH}	ν_1	3566 ⁶⁰	-3.5/-16/-18/-5.1/-14	3567.8	3531.4
RMSD				3	23

^aError on the last digit(s) is indicated in brackets when published.

TABLE VI: For half-deuterated trans-formic acid (trans-DCOOH), fundamental vibrational energies (in cm^{-1}) with respect to the ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computing using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Gas phase and matrix (Ar) isolation measurements are given for comparison. Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

C. Trans-DCOOH

All fundamental bands were recorded in the gas phase for DCOOH^{51,53,54,60,73,74} and some have also been reported in rare-gas matrices;^{11,64} the gas phase measurements and matrix shifts with respect to the gas phase measurements are given in Table VI. Two overtones were also reported: $2\nu_2$ ($2\nu_{\text{CD}}$) at $\approx 4360 \text{ cm}^{-1}$,⁵⁸ where the MCTDH theoretical value is 4385.0 cm^{-1} and $2\nu_5$ ($2\nu_{\text{C-O}}$) at $2254.244 \pm 0.011 \text{ cm}^{-1}$,⁷⁵ with a computed value of 2272.1 cm^{-1} . From gas-phase measurements, the rotational structures of the ν_2 , ν_3 , ν_5 , ν_6 , ν_7 , ν_8 , and ν_9 fundamental bands as well as the $2\nu_5$ overtone have been studied.^{73,75-79} Theoretical results compared to gas phase experimental measurements and B3LYP/aug-cc-pVTZ anharmonic computations are gathered in Table VI. For the fundamentals, the MCTDH results have an RMSD of 3 cm^{-1} with a maximum deviation of about 4 cm^{-1} for mode ν_9 . As already pointed out for other isotopologues, the anharmonic vibrational perturbation theory results behave more poorly at higher energy and, show an RMSD of 23 cm^{-1} when compared with measured fundamental transition frequencies.

In Table VI, we gather the gas-phase fundamental transition frequencies alongside the rare-gas (Ar) matrix measurements of Maçôas *et al.*¹¹ in terms of spectral shift with the gas phase measurements. The absolute values are repeated in the Supplementary Material in

Table S10. Shifts between the gas phase to the matrix follow the same trends as for the modes in HCOOD only for the γ_{CH} (or γ_{CD}) rocking and ν_{OD} (or ν_{OH}) stretching modes. These observations stress again⁷ the need for gas phase measurements to compare to theoretical values which are typically computed in the gas phase. A Fermi resonance between the ν_3 stretch ($\nu_{\text{C=O}}$) and the $2\nu_8$ ($2\tau_{\text{DCO}}$) overtone in rare-gas matrices was reported by Maçôas *et al.*¹¹ for trans-DCOOH around 1723 and 1760 cm^{-1} , all values are given in Table S10. The Fermi resonance was captured in our computations as it can clearly be seen from the reduced density functions given in Figure 2, where the corresponding energies of the vibrational bands are 1722.8 and 1760.9 cm^{-1} , respectively. We assigned the fundamental ν_3 ($\nu_{\text{C=O}}$) at 1722.8 cm^{-1} given the experimental $\nu_{\text{C=O}}$ stretch value reported⁷³ at 1725.874974(34) cm^{-1} . All other assigned overtones and combination bands are given in the Supplementary Material in Tables S11 and S12.

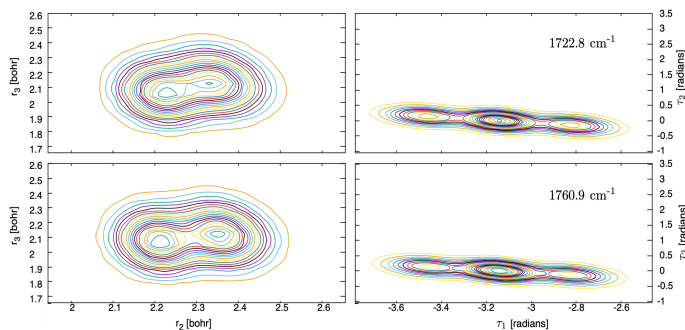


FIG. 2: Contour plot of the reduced density functions in the $\{r_2, r_3\}$ and $\{\tau_1, \tau_2\}$ planes of the ν_3 ($\nu_{\text{C=O}}$), $2\nu_8$ ($2\tau_{\text{HCO}}$) Fermi resonance for trans-DCOOH.

D. Cis isomer

Formic acid is one of the simplest systems that exhibits cis-trans isomerism. The first observation of the thermally less abundant cis form was achieved with rotational spectroscopy by Hocking.⁸ Gas-phase infrared spectra of the cis form of formic acid are scarce,⁷⁻¹⁰ and to the best of our knowledge, not published for its deuterated forms. However, the cis isomer was isolated in rare-gas matrices in experimental studies on HCOOD^{12,63} and DCOOH.^{11,64} The block improved relaxation method implemented in MCTDH, coupled to the RC-PES proved again⁵ to be successful in the estimation of vibrational frequencies of formic acid in

the case of its trans deuterated forms in this work. For this reason, we provide our theoretical values for the cis isomer using MCTDH on the RC-PES as well as anharmonic vibrational energies at the B3LYP/aug-cc-pVTZ level of theory in Tables VII, VIII, and IX for the fundamental vibrational frequencies of DCOOD, HCOOD, and DCOOH, respectively. We note that the vibrational frequencies reported by Tew and Mizukami⁶ for the undeuterated HCOOH cis-isomer differed quite significantly from those determined using MCTDH on the RC-PES.⁵ However, careful analysis by Richter and Carbonnière, see Section III.B.2 of Ref. 5, suggested that the source of this discrepancy was not found in the underlying PESs nor the level of ab initio theory upon which they were based, but rather due to shortcomings in the VCI procedure at the high energies needed to obtain the cis vibrational states.

Assignment	Mode	MCTDH	VPT2
	ν_0	1429.518 ^a	
τ_{COD}	ν_9	369.8	376.0
τ_{DCO}	ν_8	859.7	863.7
OCO-COD def.	ν_7	615.1	616.9
δ_{COD}	ν_6	883.8	872.4
γ_{CD}	ν_5	1029.4	1023.1
$\nu_{\text{C-O}}$	ν_4	1159.5	1141.8
$\nu_{\text{C=O}}$	ν_3	1782.0	1792.5
ν_{CD}	ν_2	2142.6	2111.1
ν_{OD}	ν_1	2682.7	2657.6, 2605.9 ^b

^awith respect to the trans ground state energy

^bDFTB²⁵

TABLE VII: For fully-deuterated cis-formic acid (cis-DCOOD), fundamental vibrational energies (in cm^{-1}) with respect to the (cis) ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

Available rare-gas matrices measurements for the cis isomer agree with the theoretical results within the maximum spectral shifts in comparison with the gas-phase measurements observed in the case of trans-formic acid; the matrix-induced shifts for trans-formic acid are given in Tables IV and VI. The present MCTDH prediction for the ν_9 fundamental of HCOOD (374.8 cm^{-1}) is in very good agreement with the value (378.9 cm^{-1}) predicted recently using a 1-dimensional torsional potential computed at the CCSD(T) level of theory extrapolated to the complete basis set limit.³⁸ A Fermi resonance between the $\nu_{\text{C=O}}$ stretch and the $2\tau_{\text{DCO}}$ overtone in rare-gas matrices was reported by Maçôas *et al.*¹¹ for cis-DCOOH

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Assignment	Mode	Ne ⁶³	Ar ⁶³	Kr ⁶³	Xe ⁶³	MCTDH	VPT2
	ν_0	-	-	-	-	1412.023 ^a	
τ_{COD}	ν_9	-	-	-	-	374.8	381.7
τ_{HCO}	ν_8	1039.3	1041	-	-	1013.3	1017.3
OCO-COD def.	ν_7	629.4	633.0	633.0	632.2	622.5	624.4
					631.6		
δ_{COD}	ν_6	906.8	911.2	911.7	911.6	905.3	892.1
			910.5	909.0	909.2		
$\nu_{\text{C-O}}$	ν_5	1159.0	1164.0	1163.3	1159.8	1161.8	1137.3
γ_{CH}	ν_4	1388.0	1395.4	1388.6	1385.1	1382.7	1381.2
		1394.5	1391.0				
$\nu_{\text{C=O}}$	ν_3	1818.2	1821.0	1821.1	1819.6	1814.8	1823.5
		1798.9	1799.3	1796.4	1791.1		
		1781.2	1788.9	1785.8	1781.3		
ν_{OD}	ν_2	2872.7	2895.3	2888.4	2876.2	2869.5	2849.3
ν_{CH}	ν_1	2685.5	2668.7	2656.7	2641.3	2683.4	2657.6

^awith respect to the trans ground state energy

TABLE VIII: For half-deuterated cis-formic acid (cis-HCOOD), fundamental vibrational energies (in cm^{-1}) with respect to the (cis) ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Experimental values obtained from rare-gas matrix isolation are distinguished by the rare-gas used, Ne, Ar, Kr, and Xe; some bands split into several peaks so more than 1 value is provided. Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

around 1720 and 1777 cm^{-1} . That Fermi resonance was not observed in our gas-phase computations, nor was it detected in the MP2 computations of Maçôas *et al.*¹¹

However, as stressed in the preceding sections and by Meyer and Suhm,⁷ theoretical estimations of the band positions need to be compared to gas-phase measurements due to inconsistency of the spectral shifts induced by the rare-gas matrix. For this reason, we provide the theoretical results in the hope that it will help the experimentalists in the location and assignment of fundamental vibrational modes belonging to half and fully deuterated cis-isomers. Since gas-phase measurements on the cis isomer are challenging⁷ and as such no direct comparison between theory and experiment can yet be made, we have not provided extensive lists of overtone and combination bands for the cis-isomer.

Assignment	Mode	Ar ¹¹	MCTDH	VPT2
	ν_0	-	1415.469 ^a	
τ_{COH}	ν_9	500.7-498.1	490.9	493.0
τ_{DCO}	ν_8	-	861.0	864.6
OCO-COH def.	ν_7	655.2	652.0	647.3
δ_{COH}	ν_6	1248.9/1234.0/1229.2/1239.4	1234.7	1119.9
$\nu_{\text{C-O}}$	ν_5	1143.4	1130.0	1216.8
γ_{CD}	ν_4	961.9/962.9	985.6	965.1
$\nu_{\text{C=O}}^b$	ν_3	1777.2/1777.4/1778.7	1781.0	1792.3
		1721.5/1720.9		
ν_{CD}	ν_2	2183.5/2179.7	2166.9	2138.8
ν_{OH}	ν_1	3615.4/3617.4	3624.8	3599.7

^awith respect to the trans ground state energy.

^bIn Fermi resonance with a DCO wagging mode.

TABLE IX: For half-deuterated cis-formic acid (cis-DCOOH), fundamental vibrational energies (in cm^{-1}) with respect to the respective (cis) ground state energy as determined using block-improved relaxation within MCTDH on the RC-PES (MCTDH) as well as those computed using VPT2 at the B3LYP/aug-cc-pVTZ level of theory (VPT2). Experimental values were obtained from rare-gas matrix isolation using Ar. Mode assignment is given as ν =stretching, δ =bending, γ =rocking, and def.=deformation.

IV. CONCLUSIONS

The PES of Richter and Carbonnière⁵ coupled to the block improved relaxation method implemented in the MCTDH software package was used to determine vibrational eigenenergies of both trans and cis deuterated formic acid. All fundamental vibrational energies as well as overtones and combination bands were computed up to approximately 3000 cm^{-1} (relative to their respective ZPE) for trans- DCOOD, HCOOD, and DCOOH. We report an RMSD of 8, 7, and 3 cm^{-1} from estimations using MCTDH with the fundamental transition frequencies measured in gas-phase experiments for DCOOD, HCOOD, and DCOOH, respectively. Perhaps then, not surprisingly, excellent agreement is obtained between theory and experiment for the limited number of overtone and combination bands for the trans-isomers. For some states with the largest discrepancies, we suggest that new experimental measurements may be warranted. Moreover, the present comparisons reinforce the conclusion⁷ that for benchmarking theoretically determined results must be compared to gas-phase measurements rather than those from rare-gas matrices as shifts are strongly vibrational state dependent. Fundamental vibrational eigenenergies for all deuterated forms of the cis isomer are provided in the hope that they will spur the first experimental gas phase measurements

and help the experimentalists with assignments.

V. SUPPLEMENTARY MATERIAL

See Supplementary Material for the B3LYP/aug-cc-pVTZ harmonic fundamental transition frequencies of the deuterated cis- and trans-isomers of formic acid (DCOOD, HCOOD, and DCOOH); optimized B3LYP/aug-cc-pVTZ equilibrium geometries of the trans- and cis-isomers; MCTDH overtone and combination band energies for fully-deuterated trans-formic acid (trans-DCOOD); experimental (in Ne and Ar), MCTDH, and CC-VSCF overtone and combination band energies for half-deuterated trans-formic acid (trans-HCOOD); fundamental vibrational transition frequencies of half deuterated trans-formic acid (trans-HCOOD) as measured in the gas-phase and using rare-gas matrix isolation (Ne, Ar, Kr, and Xe); MCTDH overtone and combination band energies for half-deuterated trans-formic acid (trans-HCOOD); fundamental vibrational transition frequencies of half deuterated trans-formic acid (trans-DCOOH) as measured in the gas-phase and using rare-gas matrix isolation (Ar); MCTDH overtone and combination band energies for half-deuterated trans-formic acid (trans-DCOOH).

Acknowledgments

The research was partly funded by the Natural Sciences and Engineering Research Council of Canada (NSERC Discovery Grant to A.B.). A.A. acknowledges the financial support of the Commission de Classement des Crédits Internationaux (CCCI) from ULB and the Lucia DeBrouckere fund from the chemistry department of ULB. Most of the computational resources have been provided by the Shared ICT Services Centre, Université Libre de Bruxelles. Test runs were performed on the computers of the Consortium des Équipements de Calcul Intensif (CECI) on Vega (ULB) and Dragon2 (UMons).

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