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Author(s): Marushkevich, Kseniya; Khriachtchev, Leonid; Räsänen, Markku; Melavuori, Mia; Lundell, Jan

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Dimers of the Higher-Energy Conformer of Formic Acid: Experimental Observation

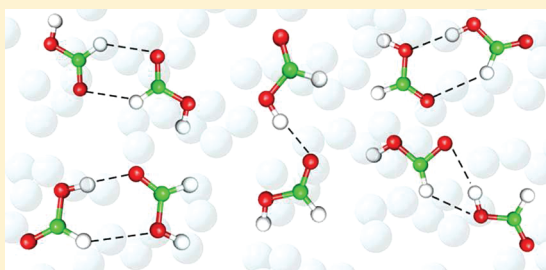
Kseniya Marushkevich,[†] Leonid Khriachtchev,^{*,†} Markku Räsänen,[†] Mia Melavuori,[†] and Jan Lundell[‡]

[†]Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Finland

[‡]Department of Chemistry, University of Jyväskylä, PL 35, FIN-40014 Finland

S Supporting Information

ABSTRACT: We report on the first experimental observation of formic acid dimers composed of two molecules of the higher-energy *cis* conformer. The *cis*–*cis* formic acid dimers are prepared in an argon matrix by selective vibrational excitation of the ground state *trans* conformer (deuterated form HCOOD) combined with thermal annealing of the matrix at about 30 K. Five *cis*–*cis* formic acid dimers are predicted by *ab initio* calculations (interaction energies from -16.9 to -27.2 kJ mol⁻¹), and these structures are used for the assignment of the experimental spectra. Selective vibrational excitation of the obtained *cis*–*cis* dimers leads to the formation of several *trans*–*cis* dimers, which supports the proposed assignments.



INTRODUCTION

Formic acid (HCOOH, FA) is the simplest organic acid attracting significant research and industrial interest. This species has been found in the interstellar medium^{1,2} and in the coma of the Hale-Bopp comet.³ It has been suggested that it may be a key compound in the formation of glycine (NH₂CH₂COOH) in the interstellar medium.⁴ Formic acid may be considered as a building block of biomolecules, and it also serves as a model for the properties of amino acids.^{5,6} Atmospheric FA influences pH-dependent chemical reactions in the Earth clouds and it is the major acidic component of rain.⁷ FA is an important oxygenated volatile organic compound.⁸ The identified FA sources include biomass burning, biogenic emissions from vegetation and soils, secondary production from organic precursors, and emissions from motor vehicles.⁹

Two possible conformers of FA (*trans* and *cis*) differ by the orientation of the hydroxyl group (–OH). The *trans* conformer is lower in energy by ca. 1365 cm⁻¹ than the *cis* form,¹⁰ which yields the Boltzmann population ratio N_{cis}/N_{trans} of 1.4×10^{-3} at room temperature. The higher-energy *cis* form can be efficiently prepared in rare-gas matrices by selective vibrational excitation of *trans*-FA.^{11,12} The higher-energy conformer decays back to the ground-state form via tunneling of the –OH hydrogen atom.^{12,13} The lifetime of the higher-energy *cis* conformer strongly depends on the surrounding, changing from 6.25 h in a nitrogen matrix¹⁴ to 75 min in a xenon matrix¹³ and to 5 s in a neon matrix.¹⁵ The higher-energy conformer of deuterated FA (HCOOD) is very stable compared to *cis*-HCOOH.^{13,16}

The FA molecules can form a number of dimers stabilized by intermolecular hydrogen bonding. The *trans*–*trans* dimers have been extensively studied theoretically.^{17–23} Several such dimers

have been observed experimentally in the gas phase,^{24–26} rare-gas matrices^{17,20,27–31} and helium nanodroplets.³² A number of mixed *trans*–*cis* dimeric structures were also predicted^{17,23,33} and observed experimentally.^{17,30,31} Most of the predicted *trans*–*trans* and *trans*–*cis* dimers have been prepared and identified in our matrix-isolation experiments.^{17,30,31} The information on the *cis*–*cis* dimers is sparse. To our knowledge, only two *cis*–*cis* dimeric structures of FA have been calculated by Roszak et al.²¹ and no direct experimental observation of these structures has been reported. Shimizu and Goncharov et al. have tentatively suggested that high-pressure FA solid may consist of infinite chains of hydrogen bonded molecules in the *cis* conformation.^{34,35} Recently, a solid constituted of the higher-energy conformer of FA has been studied.³⁶

In the present work, we report on the first experimental observation of dimers composed of the higher-energy FA conformer. The experiments are performed in argon matrices. In order to prepare the *cis*–*cis* dimers, we combine selective vibrational excitation to promote the *trans*-to-*cis* conformational change and thermal annealing to produce dimers. The identification of novel structures is based on *ab initio* calculations and selective vibrational excitation of the *cis*–*cis* dimers.

COMPUTATIONAL METHODS AND RESULTS

The equilibrium geometry and harmonic vibrational frequencies of *trans*- and *cis*-FA monomers, *trans*–*trans*, *trans*–*cis*, and *cis*–*cis* dimers, and complexes of *trans*- and *cis*-HCOOD with D₂O (tFAW and cFAW) were calculated using the second-

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order Møller–Plesset perturbation (MP2) method with the 6-311++G(2d,2p) basis set. This level of theory is known to reproduce well the experimental vibrational properties of trans–trans and trans–cis FA dimers.¹⁷ All calculations were performed using Gaussian 03 package.³⁷ The counterpoise method was used to account for the basis set superposition error (BSSE),³⁸ and the zero-point energies (ZPE) were included. Six trans–trans and five trans–cis structures were studied earlier by the same theoretical method (Figure S1a and S1b).¹⁷ In the present work, an additional trans–cis dimer tc6 is found (Figure S1c) which was not reported in ref 17. The tFAW and cFAW geometries are taken from ref 39.

Five stable cis–cis dimeric structures are found on the potential energy surface (PES) (Figure 1). Four cis–cis dimers

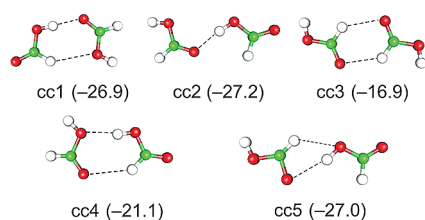


Figure 1. Calculated structures of the cis–cis formic acid dimers. The interaction energies (in kJ mol^{-1}) are given in parentheses (ZPE and BSSE corrected). The structures of the trans–trans and trans–cis dimers are presented in the Supporting Information. The notation of cis and trans conformers of formic acid follows ref 10 although the opposite notation can also be found in the literature.

have two hydrogen bonds (cc1, cc3, cc4, and cc5) and one structure has a single O–H \cdots O hydrogen bond (cc2). Three structures (cc1, cc2, and cc5) have similar interaction energies (-26.9 , -27.2 , and -27.0 kJ mol^{-1} , respectively). These

systems have the O–H \cdots O hydrogen bonds to the terminal oxygen. The O–H \cdots O hydrogen bond is significantly longer in cc5 than in cc2 (by 0.45 Å); nevertheless, this does not make a difference in the interaction energies because of the stabilization by the second C–H \cdots O bond in cc5. The cc1 dimer has two hydrogen bonds [1.867 Å (O–H \cdots O) and 2.765 Å (C–H \cdots O)] and interaction energy -26.9 kJ mol^{-1} . The symmetrical dimer cc3 with two C–H \cdots O hydrogen bonds (2.37 Å) is the weakest structure (interaction energy -16.9 kJ mol^{-1}). The geometries of FA molecules are not changed significantly in the dimers. For example, the O–H bond elongates by ca. 0.1 Å in cc1, cc2, and cc3 compared to the *cis*-FA monomer, and the C=O bond involved in the hydrogen bond slightly elongates from 1.197 to 1.200 Å. Practically the same changes in the bond lengths are found for the dimers of *cis*-HCOOD.

Table 1 shows the calculated vibrational spectra of the cis–cis dimers of deuterated FA (HCOOD). We discuss the vibrational spectra for HCOOD in detail because this species is used in the present experiments. The calculated frequencies of the *trans*- and *cis*-FA monomers (HCOOH and HCOOD) are given in the Supporting Information (Table S1). For cc1, cc2, and cc5, where the O–D bonds are involved in intermolecular interaction, the O–D stretching (νOD) and torsional (τCOD) modes are the most sensitive to the complexation. A large red shift of νOD is predicted for these dimers (from ca. -130 to -185 cm^{-1}). The cc4 dimer is characterized by a smaller red shift of ca. -50 cm^{-1} for the bonded OD stretching mode. The shifts for the uncomplexed νOD mode are less than 10 cm^{-1} . For all dimers except cc4, the torsional modes exhibit blue shifts (up to $+186.7$ cm^{-1} in cc5). The νCH modes involved in hydrogen bonding (cc1, cc3, cc4, and cc5) are blue-shifted from $+34.7$ (cc5) to $+45.7$ (cc1) cm^{-1} . For the cc3 and cc4 dimers,

Table 1. Calculated Characteristic Frequencies (in cm^{-1}), Intensities (in km mol^{-1} , in Parentheses), and Complexation-Induced Shifts (in cm^{-1}) of the cis–cis HCOOD Dimers

assignment	cc1	cc2	cc3	cc4	cc5
νCH	3091.7 (41.1)	3090.6 (42.24)	3092.4 (0.0)	3083.4 (41.7)	3080.6 (26.4)
	+45.7	+44.6	+46.5	+37.5	+34.7
	3050.3 (56.8)	3041.7 (63.5)	3090.9 (25.4)	3074.5 (35.1)	3044.5 (59.0)
	+4.4	-4.2	+45.0	+28.6	-1.4
νOD	2797.2 (68.8)	2798.9 (70.3)	2801.9 (0.0)	2797.5 (65.0)	2799.1 (70.4)
	-6.5	-4.8	-1.8	-6.2	-4.6
	2675.2 (371.3)	2665.8 (448.9)	2801.6 (116.6)	2754.0 (225.1)	2620.3 (461.6)
	-128.5	-137.9	-2.1	-49.7	-183.4
$\nu\text{C=O}$	1810.4 (329.5)	1809.6 (46.6)	1808.0 (550.8)	1818.3 (290.5)	1808.2 (155.9)
	-11.0	-11.7	-13.4	-3.1	-13.2
	1795.3 (368.6)	1796.2 (757.8)	1787.4 (0.0)	1805.0 (302.9)	1791.9 (618.5)
	-26.1	-25.2	-34.4	-16.4	-29.5
$\nu\text{C-O}$	1220.7 (483.3)	1217.6 (532.3)	1193.8 (0.0)	1195.9 (358.5)	1231.1 (61.5)
	+44.6	+41.5	+17.7	+19.8	+55.0
	1195.8 (26.6)	1212.1 (57.7)	1172.2 (771.2)	1157.6 (175.6)	1197.8 (680.2)
	+19.7	+36.0	-3.9	-18.5	+21.7
OCO–CODdef.	664.3 (6.0)	665.2 (4.1)	642.1 (16.8)	661.2 (14.9)	678.8 (7.0)
	+30.5	+31.4	+8.3	+27.4	+45.0
	642.7 (12.1)	642.5 (19.7)	634.7 (0)	634.6 (5.1)	649.3 (9.2)
	+8.9	+8.7	+0.9	+0.8	+15.5
τCOD	580.0 (40.1)	588.4 (39.1)	417.9 (63.8)	500.8 (29.0)	590.3 (36.0)
	+176.4	+184.8	+14.3	+97.8	+186.7
	416.1 (36.1)	420.1 (36.1)	417.4 (0.0)	375.6 (33.1)	423.2 (33.9)
	+12.5	+16.5	+13.8	-28.0	+19.6

the $\nu\text{C}=\text{O}$ frequencies are blue-shifted (up to $+19.8\text{ cm}^{-1}$ in cc4) for one molecule and red-shifted for the other molecule (up to -18.5 cm^{-1} in cc4). For the cc1, cc2, and cc5 dimers, both $\nu\text{C}=\text{O}$ stretching vibrations are blue-shifted (up to $+55.0\text{ cm}^{-1}$ in cc5). The intensities of bonded νOD for all the structures are predicted to be much higher than that for free νOD , which is a normal effect for red-shifted hydrogen bonds. Similar spectral trends are observed for the cis–cis dimers of HCOOH (see Table S2). The calculated spectra for the trans–trans and trans–cis dimers of HCOOH are presented in Tables S3 and S4.

Two cis–cis dimers were previously calculated by Roszak et al.²¹ In their calculations (MP2/aug-cc-pVTZ), the FAD4 structure with an interaction energy of -30.9 kJ mol^{-1} corresponds to the cc1 dimer with an interaction energy -26.9 kJ mol^{-1} in our notation. The second reported cis–cis dimer FAD5 (-24.4 kJ mol^{-1}) is structurally similar to cc4 in our notation (-21.1 kJ mol^{-1}). To the best of our knowledge, the other structures found in the present work (cc2, cc3, and cc5) have not previously been calculated.

EXPERIMENTAL DETAILS

The gaseous samples were prepared by mixing deuterated formic acid HCOOD (IT Isotop, 95–98%), with argon (AGA, 99.9999%), typically in the 1:800 proportion. The matrices were deposited onto a CsI substrate at 12–25 K in a closed cycle helium cryostat (Sumitomo Heavy Industries). The achieved degree of deuteration of FA in matrices exceeded 80%. The IR absorption spectra were measured with a Nicolet SX-60 FTIR spectrometer at 4.3 K using a liquid-nitrogen-cooled MCT detector and a KBr beam splitter (resolution of 0.25 cm^{-1}). Typically 500 interferograms were coadded. Pulsed IR light (ca. 5 ns, 10 Hz) from an optical parametric oscillator (OPO Sunlite with IR extension, Continuum) was used to convert the trans conformer to the cis form by exciting the $\nu\text{OD}+\nu\text{C}=\text{O}$ combination mode at 4382 cm^{-1} .⁴⁰

EXPERIMENTAL RESULTS AND DISCUSSION

trans–trans Dimers. The known bands of trans-HCOOD monomer dominate in the spectra after deposition (Figure 2,

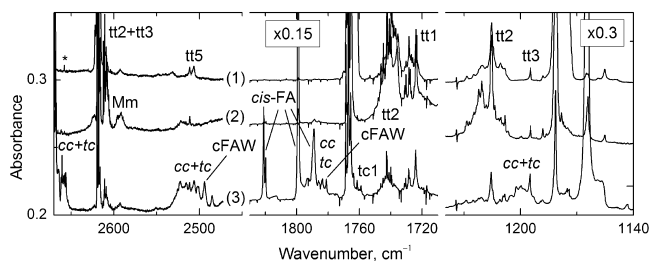


Figure 2. OD, C=O, and C–O stretching bands of HCOOD in an argon matrix. Shown are the results of deposition [trace 1], annealing at 34 K of matrices containing trans-FA [trace 2] and cis-FA [trace 3]. Mm marks the band of higher HCOOD multimers, cc and tc denote various cis–cis and trans–cis dimers, cFAW stands for the cis-HCOOD...D₂O complex. The spectra were measured at 4.3 K. Water impurity (D₂O) band is marked with asterisk.

trace 1 and Table S1).^{16,28,40} In addition, absorptions of several trans–trans dimers (tt1, tt2, tt3, and tt5) are observed (Table 2 and Table S3). The assignment of these trans–trans dimers of HCOOH is done by analogy with the trans–trans dimers of HCOOH.^{17,31}

Upon annealing above 27 K, the bands of the trans-HCOOD monomer and tt5 dimer decrease in intensity and the bands of the tt1 and tt2 dimers grow (Figure 2, trace 2), similar to the case of HCOOH.^{17,20,27,31} Annealing at 34 K vanishes the tt5 band at 2506.4 cm^{-1} completely, indicating the conversion of tt5 to more stable trans–trans structures. The weak broad absorption at ca. 2595 cm^{-1} probably belongs to FA trimers and/or higher aggregates as it grows up at higher FA concentrations and higher annealing temperatures. Upon annealing at 34 K, the νOD and $\nu\text{C}=\text{O}$ bands of tt2 are shifted from 2610.0 and 1739.4 cm^{-1} to 2612.1 and 1742.6 cm^{-1} , respectively. A band at 2511 cm^{-1} usually appears close to the tt5 band at 2506.4 cm^{-1} after deposition, and it does not change much upon annealing. This band seems to originate from a complex of trans-FA but we have no definite assignment for this band. This band may originate from the tt5 dimer in a stable matrix configuration or tt4 dimer; however, this is not supported in other spectral regions. In any case, the 2511 cm^{-1} band is not connected with the cis-FA dimers that are the subject of the present work.

Dimers Containing the Higher-Energy Conformer.

Vibrational excitation of the trans-HCOOD monomer at 4382 cm^{-1} ($\nu\text{OD}+\nu\text{C}=\text{O}$ combination mode) efficiently produces cis-HCOOD (conversion up to $>90\%$). Upon annealing above 27 K, dimerization involves cis-FA and new bands appear in the spectrum as compared to the matrices containing entirely trans-FA (Figure 2, trace 3). In the OD stretching region, the annealing produces new bands in the $2662\text{--}2656\text{ cm}^{-1}$ (close to the cis monomer) and $2525\text{--}2485\text{ cm}^{-1}$ spectral regions. In addition, a band at 2494 cm^{-1} increases in intensity, which seems to correlate with the presence of water in the matrix (D₂O).

The bands at $2662\text{--}2656\text{ cm}^{-1}$ are red-shifted from νOD of the cis-FA monomer by ca. -7 to -13 cm^{-1} ; that is, they originate from the free OD stretching modes of the cis subunits in the dimers. The bands at $2525\text{--}2485\text{ cm}^{-1}$ are substantially red-shifted relative to the cis- and trans-FA monomers, showing that these bands are from the hydrogen-bonded OD modes. These large red shifts are from ca. -144 to -184 cm^{-1} and from -93 to -133 cm^{-1} as counted from the cis- and trans-FA monomers, respectively. In different experiments, the relative intensities of these bands vary but their positions are unchanged. The bands associated with the presence of cis-FA are suitable for a number of cis–cis and trans–cis dimers. The theory predicts spectral shifts from -4.6 to -6.5 cm^{-1} for free and from -128.5 to -183.4 cm^{-1} for the bonded OD stretching mode in the cc1, cc2, and cc5 dimers (Table 1), the most strongly bound cis–cis structures, which is in agreement with the experimental values. The cc3 and cc4 dimers have relatively small shifts (-1.8 – -2.1 and -6.2 – -49.7 cm^{-1} , respectively) and cannot produce the strongly shifted bands at $2525\text{--}2485\text{ cm}^{-1}$. For the trans–cis dimers, structures tc1, tc4, and tc5 are predicted to have absorptions slightly shifted from cis-FA monomer (from -0.6 to -3.3 cm^{-1}). The tc1 and tc4 structures are not suitable for bands observed at $2485\text{--}2525\text{ cm}^{-1}$ in the bonded νOD region due to the calculated shifts for the trans unit: -259.5 and -4.1 cm^{-1} , respectively (Table S4). The other trans–cis dimers (tc2, tc3, and tc5) can absorb at about 2500 cm^{-1} based on the ab initio calculations (Table S4) and experiments with HCOOH.³¹ A broad band at 2425.4 cm^{-1} shifted from the cis-FA frequency by -243.3 cm^{-1} may be the second OD stretching mode of dimer tc2. A broad band at $\sim 2340\text{ cm}^{-1}$ suggests the presence of the

Table 2. Experimental Characteristic Frequencies and Experimental and Calculated Complexation-Induced Shifts (in cm^{-1}) of the HCOOD and HCOOH trans–trans (tt1, tt2, tt3, and tt5) and trans–cis (tc1, tc2, tc3, and tc5) Dimers in an Argon Matrix^a

dimer	assignment	HCOOD			HCOOH		
		calculated	experiment		calculated ^b	experiment ^c	
		shift	frequency	shift	shift	frequency	shift
tt1	$\nu\text{OD}/\nu\text{OH}$	−333.6	2271.8	−346.2	−462.8	3072	−478
			2259.4	−358.6			
	$\nu\text{C}=\text{O}$	−22.1	1724.1	−43.1	−21.7	1728	−39
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+96.1	1265.3	+84.3	+133.8	1224	+120
	$\tau\text{COD}/\tau\text{COH}$	+144.6	660.0	+153.3	+338.9	1225	+121
tt2	$\nu\text{OD}/\nu\text{OH}$	+144.6	660.0	+153.3	+338.9	947	+312
		−5.6	2612.1	−5.9	−7.7	3540	−10
		−237.8	2610.0	−8.0	−332.9	3184	−366
			2365.7	−252.3		3168	−382
			2355.7	−262.3		3154	−396
		2348.9	−269.1		3142	−408	
					3101	−449	
	$\nu\text{C}=\text{O}$	−16.3	1739.4	−27.8	−15.0	1748	−19
		−53.1	1742.6	−24.6			
			1705.9	−61.3			
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+53.9	1228.0	+46.3	+82.0	1180	+76
	$\tau\text{COD}/\tau\text{COH}$	+38.0	1215.4	+33.7	+32.8	1131	+27
		+20.4	524.0	+17.3	+259.5	868	+233
					+22.4	658	+23
tt3	$\nu\text{OD}/\nu\text{OH}$	−1.8	2608.4	−9.6	−2.4	3537	−13
		−3.4			−4.5		
	$\nu\text{C}=\text{O}$	−5.0			−4.1	1765	−2
		−12.9			−12.8		
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+9	1193.7	+12	+6.2	1114.6	+11
				+8.0			
	$\tau\text{COD}/\tau\text{COH}$			−19.6			
				+8.0	661	+26	
				−40.4	667	+32	
tt5	$\nu\text{OD}/\nu\text{OH}$	−107.0	2506.4	−111.6	−4.4	3544	−6
					−149.1	3387	−163
	$\nu\text{C}=\text{O}$	+5.3	1770.7	+3.5	+6.3	1774	+7
		−18.1	1753.4	−13.8	−16.1	1750	−17
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+37.0	1210.9	+29.2	+58.0	1154	+51
				−44.5	1074	−29	
tc1	$\nu\text{OD}/\nu\text{OH}$	−3.3	2661.7	−7.0	−4.6	3604	−12
		−259.5	2346.8	−271.2		3115	−435
			2341.8	−276.2		3081	−469
			2332.1	−285.9	−363.5	3074	−476
	$\nu\text{C}=\text{O}$	−40.1	1758.4	−40.9 ^d	−32.8	1767	−41
		−43.8	1718.0	−49.2			
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+40.5	1199.7	+35.7	+13.8	1259	+10
		+59.7			+89.3	1186	+82
				+40.1	1143	+35.3	
	$\tau\text{COD}/\tau\text{COH}$	+176.0	659.2	+152.5	+269.0	875	+240
				+36.1	550	+45	
tc2	$\nu\text{OD}/\nu\text{OH}$	−92.4	2522.1	−95.9	−128.7	3411	−139
		−198.1	2425.4	−243.3	−279.1		
	$\nu\text{C}=\text{O}$	−9.8	1782.3	−17.0 ^d	−9.3	1793	−14
		−38.0	1717.0	−50.2	−31.9		
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+54.9	1224.8	+43.8	+18.4	1241	−2
	+9.1	1196.8	+32.8	+63.6	1155	+52	
tc3	$\nu\text{OD}/\nu\text{OH}$	−6.7	2607.6	−10.4	−9.4	3363	−253
		−168.8	2492.0	−176.7	−236.0		
	$\nu\text{C}=\text{O}$	−14.3	1782.1	−17.2 ^d	−11.0	1787	−20
		−24.4	1734.5	−32.7	−23.3		
	$\nu\text{C}-\text{O}/$ CO–COHdef.	+50.0	1217.7	+36.0	+109.3	1338	+95
	+30.6	1193.2	+29.2	+51.1	1151	+48	

Table 2. continued

dimer	assignment	HCOOD			HCOOH		
		calculated	experiment		calculated ^b	experiment ^c	
		shift	frequency	shift	shift	frequency	shift
tc5	$\nu\text{OD}/\nu\text{OH}$	-3.1	2656.1	-12.6	+36.3		
		-141.1	2525.5	-92.5	-197.6	3406	-144
			2523.6	-94.4			
			2515.2	-102.8			
			2512.0	-106.0			
	$\nu\text{C}=\text{O}$	-13.2	1784.0	-15.3 ^d	-14.2	1797	-10
		-12.0	1743.2	-24.0	-12.4	1726	-41
	$\nu\text{C}-\text{O}/$ CO-COHdef.	+28.5	1202.5	+20.8	+3.2	1254	+11
					+50.4	1158	+55

^aThe data for the cis subunit of the dimer are in italics. ^bFrom ref 17. ^cFrom refs 17 and 31. ^dSpectral shift is calculated for the strongest Fermi resonance component of the cis conformer (1799.3 cm⁻¹).

tc1 dimer. This band overlaps with the absorption of CO₂ present as an impurity. On the basis of the experiments with different amounts of water in the matrix, the 2494 cm⁻¹ band observed in the bonded νOD region is assigned to the *cis*-HCOOD...D₂O complex (Table 4).

In the $\nu\text{C}=\text{O}$ region, the bands connected with the presence of *cis*-FA are at 1786.1, 1785.6, 1784.0, 1778.7, 1759.0, and 1758.4 cm⁻¹. The bands at 1786.1, 1785.6, 1784.0, and 1778.7 cm⁻¹ (shifts -13.2, -13.7, -15.8, and -20.6 cm⁻¹ from *cis*-FA monomer) can in principle belong to various *trans*-*cis* and *cis*-*cis* dimers. The calculations predict shifts from -11.0 to -13.2 cm⁻¹ for the *cis*-*cis* dimers cc1, cc2, and cc5 and from -9.8 to -14.3 cm⁻¹ for the *trans*-*cis* dimers tc2, tc3, and tc5 (Table 1 and S4). The doublet at 1759.0 and 1758.4 cm⁻¹ shifted by -40.9 and -40.3 cm⁻¹ and by -8.2 and -8.8 cm⁻¹ from *cis*-HCOOD and *trans*-HCOOD may correspond to the most stable *cis*-*cis* structures cc1 and cc2 and to the tc1 dimer (Table 1 and Table S4). The calculated spectral shifts of the *trans*-FA subunit are -38.0, -24.4, and -12.0, cm⁻¹ for the tc2, tc3, and tc5 structures, respectively. Thus, the observed doublet may also belong to the *trans*-FA subunit of the tc5 dimer whereas its origin from tc2 and tc3 is less probable. A band at 1781.0 cm⁻¹ observed in this region is most probably due to the *cis*-HCOOD...D₂O complex (Table 4).

In the $\nu\text{C}-\text{O}$ region, the bands connected with the presence of *cis*-FA are at 1193.2, 1196.8, 1200.5, 1202.5, 1205.5, 1207.5, 1217.7, and 1224.8 cm⁻¹. These bands fit the *cis*-*cis* (cc1, cc2, and cc5) and *trans*-*cis* (tc2, tc3, and tc5) dimers. The bands of the tc2, tc3, and tc5 structures are blue-shifted by +9.1, +30.6, and +28.4 cm⁻¹ from *cis*-FA and by +54.9, +50.0, and +28.5 cm⁻¹ from *trans*-FA by theory. The tc1 dimer absorbs at 1199.7 cm⁻¹ (see below). No definite bands of the new absorbers are observed in the torsional region, despite the relatively high absorption intensities predicted by theory.

At this stage, we can conclude that the new bands observed in the $\nu\text{C}=\text{O}$ and free νOD regions indicate that *cis*-FA participates in the corresponding absorbers because the *trans*-*trans* FA dimers cannot absorb at these frequencies. However, a number of assignments to *cis*-*cis* and *trans*-*cis* dimers are possible.

Discrimination of *cis*-*cis* and *trans*-*cis* Dimers. The discrimination of *cis*-*cis* and *trans*-*cis* dimers can be done by using experiments with different proportions of the *trans* and *cis* conformers. As mentioned above, the *trans*-*trans* dimers dominate after annealing at 34 K of matrices containing entirely

trans-FA (see Figure 3, trace 1). When *cis*-FA molecules are present (amount ~25%), the 2661.7, 2522, and 2515.2 cm⁻¹

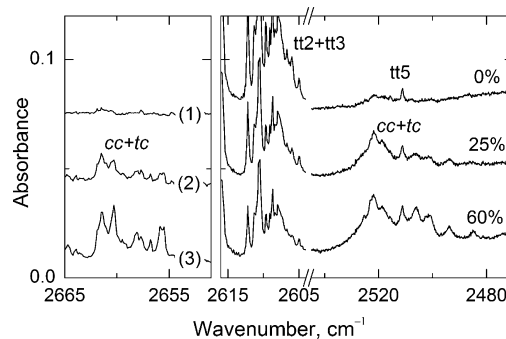


Figure 3. Annealing at 34 K of an argon matrices with different relative amounts of *cis*-HCOOD. cc and tc denote various *cis*-*cis* and *trans*-*cis* dimers. The spectra were measured at 4.3 K. The proportion of *cis*-HCOOD was measured after irradiation and annealing at 34 K.

bands are most pronounced in the OD stretching region, the intensities of the tt1 and tt2 bands (2271.8 and 2610.0 cm⁻¹) decrease, and weak bands at 2500–2511 and 2585.3 cm⁻¹ are detected (Figure 3, trace 2). For the higher *cis*-HCOOD proportion (~60%), the bands at 2659.7, 2660.7, 2657.0, 2511.1, 2506.4, 2505.5, 2502.4, 2500.6, and 2485.3 cm⁻¹ are relatively enhanced compared to the previously mentioned bands (Figure 3, trace 3). The bands enhanced at higher *cis*-HCOOD proportions seem to belong to the *cis*-*cis* dimers (Table 3).

However, a more specific assignment of the observed bands to different *cis*-*cis* and *trans*-*cis* dimers is difficult based only on ab initio calculations because the computed characteristic frequencies are close for the different *cis*-*cis* (cc1, cc2, and cc5) and *trans*-*cis* (tc1, tc2, tc3, and tc5) structures. Among the *cis*-*cis* dimers, a substantial difference is predicted only for the bonded OD stretching mode of cc5 as compared to cc1 and cc2 (~40 cm⁻¹). It follows that the strongly red-shifted OD stretching band at 2485.3 cm⁻¹ most probably belongs to cc5. The most shifted broad band at 2425.4 cm⁻¹ (shift -243.3 cm⁻¹) seems to be characteristic for the tc2 dimer partially overlapped with a broad *trans*-HCOOD...D₂O absorption at 2412 cm⁻¹ (Table 4). The other spectral features do not shed much light on the dimer structures.

Table 3. Experimental Characteristic Frequencies and Experimental and Calculated Complexation-Induced Shifts (in cm^{-1}) of the Observed *cis*–*cis* HCOOD Dimers

dimer	assignment	calculated		experiment	
		shift	frequency	shift	frequency
cc1/cc2	νOD	−4.8 (cc2)	2660.7	−8.0	
		−6.5 (cc1)	2659.7	−9.0	
		−128.5 (cc1)	2511.1	−157.6	
		−137.9 (cc2)	2506.4	−162.3	
			2505.5	−163.2	
		2502.4	−166.3		
		2500.6	−168.1		
	$\nu\text{C}=\text{O}^a$	−11.0 (cc1)	1786.1	−13.2	
		−11.7 (cc2)	1785.6	−13.7	
		−26.1 (cc1)	1785.2	−14.1	
−25.2 (cc2)					
$\nu\text{C}-\text{O}$	+44.6 (cc1)	1205.5	+41.5		
	+19.7 (cc1)	1200.5	+37.5		
	+41.5 (cc2)				
	+36.0 (cc2)				
cc5	νOD	−4.6	2657.0	−11.7	
		−183.4	2485.3	−183.4	
	$\nu\text{C}=\text{O}^a$	−13.2	1778.7	−20.6	
		−29.5			
	$\nu\text{C}-\text{O}$	+55.0	1207.5	+43.5	
		+21.7			

^aExperimental spectral shift is calculated for the strongest Fermi resonance component of the *cis* conformer (1799.3 cm^{-1}).

Selective Vibrational Excitation. More information to assign the *cis*–*cis* and *trans*–*cis* dimers is provided by selective vibrational excitation of these species. It is known that narrow-band excitation of individual vibrational transitions is efficient to promote selective conformational changes in cryogenic matrices.¹² Figure 4 presents the results of selective excitations of the annealing-produced structures at frequencies that correspond to the first OD stretching overtones (free vibrations) of the probable *cis*–*cis* dimers.

Excitation at $5221\text{--}5222\text{ cm}^{-1}$ approximately corresponds to the first overtone of the free OD stretching mode absorbing at $\sim 2656\text{ cm}^{-1}$. Upon this vibrational excitation, two sets of annealing-induced bands decrease in intensity. Different behavior of the bands under selective irradiation allows distinguishing absorptions from two species. One species absorbs at 2657.0 (shift -11.7 cm^{-1}), 2485.3 (-183.4 cm^{-1}), 1778.7 (-20.6 cm^{-1}), and 1207.5 ($+43.5\text{ cm}^{-1}$) cm^{-1} , and the calculated spectral shifts strongly suggest that these bands originate from the cc5 dimer (Table 3). The second set includes bands at 2656.1 , 2525.5 , 2523.6 , 2515.2 , 2512.0 , 1784.0 , 1743.2 , and 1202.5 cm^{-1} , i.e. shifted by ca. -13 and

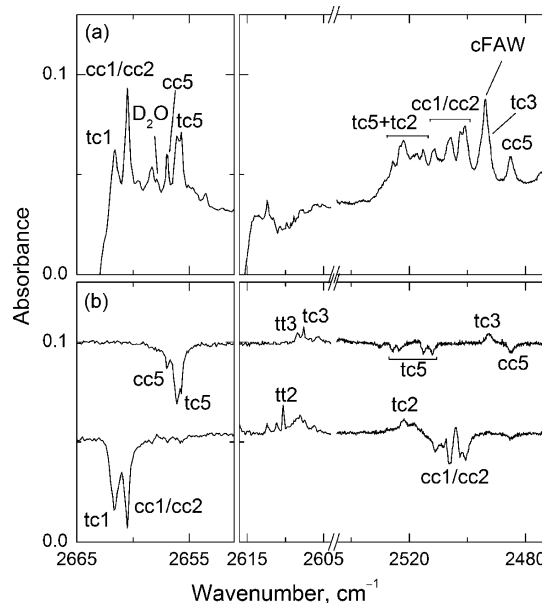


Figure 4. (a) Difference spectrum showing the result of annealing at 34 K of an argon matrix containing *cis*-HCOOD. (b) Difference spectra showing the results of excitations at 5221 and 5231 cm^{-1} (upper and lower traces, respectively). The wavenumber scales are different in the three spectral regions. cFAW stands for the *cis*-HCOOD...D₂O complex. The spectra were measured at 4.3 K.

-100 cm^{-1} for νOD (counted from *cis*-FA and *trans*-FA, respectively), by -15.5 and -25 cm^{-1} for $\nu\text{C}=\text{O}$ (counted from *cis*-FA and *trans*-FA, respectively), and by $+20.8\text{ cm}^{-1}$ for $\nu\text{C}-\text{O}$ (from *trans*-FA), and this is assigned to the tc5 structure (Table 2).

Excitation at 5231 cm^{-1} approximately corresponds to the first overtone of the free OD stretching mode at $\sim 2660\text{ cm}^{-1}$. Upon this vibrational excitation, a number of bands decrease in intensity, including the OD stretching band at 2660.7 , 2659.7 , 2511.1 , 2506.4 , 2505.5 , 2502.4 , and 2500.6 cm^{-1} , the C=O stretching bands at 1786.1 , 1785.6 , and 1785.2 cm^{-1} , and the C–O stretching bands at 1205.5 and 1200.5 cm^{-1} . Thus, the experimental OD and C=O stretching bands are red-shifted by -8.0 and -9.0 (free νOD), -157.6 , -162.3 , -163.2 , -166.3 , and -168.1 (bonded νOD), and -13.2 , -13.7 , and -14.1 ($\nu\text{C}=\text{O}$) cm^{-1} whereas the computational shifts of the cc1 and cc2 dimer are -6.5 (cc1) and -4.8 (cc2) for free νOD , -128.5 (cc1) and -137.9 (cc2) cm^{-1} for bonded νOD , and -11.0 (cc1), -11.7 (cc2), -26.1 (cc1), and -25.2 (cc2) cm^{-1} for the C=O stretching modes. For the C–O stretching mode, the calculations predict blue shifts $+44.6$ (cc1), $+19.7$ (cc1), $+41.5$ (cc2), and $+36.0$ (cc2) cm^{-1} whereas the experimental values are $+41.5$ and $+37.5\text{ cm}^{-1}$. All shifts are counted from the *cis*-

Table 4. Experimental Characteristic Frequencies and Experimental and Calculated Complexation-Induced Shifts (in cm^{-1}) of the HCOOD...D₂O and HCOOH...H₂O Complexes

mode	<i>trans</i> -HCOOD...D ₂ O			<i>trans</i> -HCOOH...H ₂ O ^a			<i>cis</i> -HCOOD...D ₂ O			<i>cis</i> -HCOOH...H ₂ O ^a		
	freq. exp.	shift exp.	shift calc.	freq. exp.	shift exp.	shift calc.	freq. exp.	shift exp.	shift calc.	freq. exp.	shift exp.	shift calc.
$\nu\text{OD}/\nu\text{OH}$	2412	−206	−196.6	3212	−339	−357	2494	−147.7	−136.4	3386	−230	−236
$\nu\text{C}=\text{O}$	1730	−37.2	−36.5	1737	−9	−3	1781.0	−18.3	−20.1	1786	−21	−21
$\nu\text{C}-\text{O}/$			+48.4	1172	+69	+86			+28.1	1342	+93	+90
def.										1189	+34	+54

^aFrom ref 43.

FA conformer. As suggested above, these bands could belong to the cc1 and/or cc2 dimers. The discrimination of these two structures is very conditional and may be confused because all characteristic bands are very close. The second plausible explanation is that the observed bands are different matrix sites of one of these cis–cis structures. Excitation at 5231 cm^{-1} also affects the bands of the tc1 dimer at 2661.7 , 1758.4 , and 1199.7 cm^{-1} (see below). The fundamental νOD band of the cc1/cc2 dimer is very close to that of tc1 and excitation at the first νOD overtone affects the cis-FA units in both dimers.

A band at 2658.0 cm^{-1} remains unassigned. It does not change much upon annealing and irradiations. This absorption seems to originate from a complex or dimer of cis-FA but we have no definite candidates for it.

Due to the high stability of cis-HCOOD,¹⁶ some amount of this species is formed during the FTIR measurements. Hence, traces of the tc1 dimer could be found in the spectra after annealing at 34 K even in experiments without selective vibrational excitation of trans-FA.

Light-Induced Conformational Changes. A number of light-induced conformational changes were observed providing further information on different dimeric structures and supporting our assignments. First, we excited the tt2 dimer at $5134\text{--}5136\text{ cm}^{-1}$, which approximately corresponds to the free νOD overtone of tt2 with the fundamental absorption at 2612.1 cm^{-1} . Upon this excitation, the tt2 concentration decreases and a number of bands rise (2661.7 , ~ 2340 , 1758.4 , 1718.0 , and 1199.7 cm^{-1}). Analysis shows that the rising bands belong to the tc1 dimer (Table 2). A similar tt2-to-tc1 conversion was previously achieved for HCOOH by vibrational excitation at 3540 cm^{-1} , which is free νOH of the tt2 dimer.^{17,30}

The IR-induced decomposition of the cis–cis dimers is accompanied by the appearance of various trans–cis dimers. The bands growing upon excitation of cc5 at 5221 cm^{-1} probably belong to the tc3 dimer previously assigned for HCOOH (Table 2),³¹ which suggests a light-induced conformational change from cc5 to tc3 (Figure 5a). These

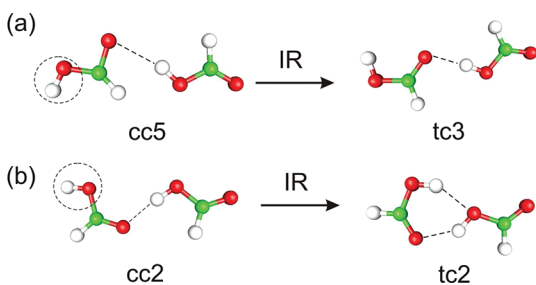


Figure 5. Most probable IR-induced processes for the cis–cis HCOOD dimers. The excitations are created at the first overtones of the free OD stretching modes (marked by circles).

two dimers differ mainly by orientation of the free D atom with respect to the C–O bond, which makes this process very reasonable. Thus, the observed light-induced process supports our assignment for the cc5 and tc3 dimers.

In addition, bands at 2608.4 and 1193.7 cm^{-1} rise upon excitation at 5221 cm^{-1} , and they are assigned to the tc3 dimer. For the tc3 dimer, the complexation-induced shifts of the C–O stretching mode are $+9$ (calculation) and $+12\text{ cm}^{-1}$ (experiment). The experimental shift of the OD stretching mode of tc3 (-9.6 cm^{-1}) agrees well with the corresponding value for HCOOH (-13 cm^{-1}).¹⁷ The calculations give no alternative

candidates for these experimental absorptions. The C=O stretching mode of the tc3 structure is not observed probably due to overlapping with the strong $\nu\text{C=O}$ band of trans-FA monomer; indeed, for the tc3 dimer of HCOOH it is red-shifted by -2 cm^{-1} .¹⁷ The $\nu\text{C=O}$ band rising upon excitation at 5221 cm^{-1} and red-shifted from trans-HCOOD monomer by ca. -30 cm^{-1} (1735 cm^{-1}) is difficult to assign to the tc3 based on the calculations because the computational shift for the tc3 dimer is -13 cm^{-1} ; hence, the assignment of this band is an open question. The tc3 dimer is probably formed from tc5 excited at 5221 cm^{-1} .

Upon excitation at 5231 cm^{-1} , the most probable product of cc2 is the tc2 dimer because the main difference between these two structures is in the orientation of the excited OD group (Figure 5b). Most of the observed tc2 bands fit well the theoretical results. Two bands at 2522.1 (shift -95.9 from trans-FA) and 2425.4 (-243.3 from cis-FA) cm^{-1} rise in the bonded νOD region (Table 2). Two blue-shifted bands at 1196.8 ($+32.8$ from cis-FA) and 1224.8 ($+43.8$ from trans-FA) cm^{-1} rise synchronously in the $\nu\text{C–O}$ region. In the $\nu\text{C=O}$ region, the rising bands at 1782.3 and 1717.0 cm^{-1} are shifted by -17.0 cm^{-1} from cis-FA and by -50.2 cm^{-1} from trans-FA. The formation of the tc2 dimer in this IR-induced process suggests that the initial species is most probably cc2.

CONCLUSIONS

The present work has been focused on the preparation and identification of dimers composed of the higher-energy cis conformer of formic acid. Five stable cis–cis FA dimeric structures, their interaction energies, and vibrational spectra are obtained at the MP2/6-311++(2d,2p) level of theory (Figure 1 and Table 1). Three of them (cc2, cc3, cc5) are calculated for the first time.

The cis–cis dimers are prepared in argon matrices by a combination of vibrational excitation of trans-HCOOD (deuterated form) and thermal annealing. The experimental spectral shifts upon dimerization are in agreement with the ab initio calculations (Tables 2 and 3). This is the first report on the experimental identification of dimers consisting of two higher-energy cis conformers of formic acid. In addition to the new cis–cis dimers (cc1/cc2 and cc5), we observe the formation of four trans–cis (tc1, tc2, tc3, and tc5) dimers and four trans–trans (tt1, tt2, tt3, and tt5) dimers previously identified for HCOOH.^{17,31} The excitation of the first OD stretching overtone of the cis–cis dimers leads to the cis-to-trans conformational changes, yielding the trans–cis dimers tc2 and tc3 (Table 2 and Figure 5).

Six trans–trans, six trans–cis (with the new structure obtained in the present work), and five cis–cis structures have been theoretically predicted so far for formic acid. Before our first work on this subject³⁰ only two trans–trans dimers were experimentally known (tt1 and tt2).²⁷ In ref 30, we reported the first trans–cis dimer (tc1). Later, we have additionally identified two trans–trans dimers (tt3 and tt6) and one trans–cis dimer (tc4),¹⁷ and very recently we have added tc2, tc3, tc5, tt4, and tt5.³¹ In the present work, we report several cis–cis (cc1/cc2 and cc5) dimers. Thus, six trans–trans dimers, five trans–cis dimers, and at least two (or three) cis–cis FA dimers have been experimentally found. The only structures which have not been experimentally observed are one trans–cis (tc6) and two cis–cis (cc3 and cc4) dimers. Thus, the majority of the predicted formic acid dimers have been experimentally

characterized and the identification of all possible dimers of formic acid can be finished soon.

It should be finally noted that the structural assignments are not unambiguous in the case of FA dimers in matrices, and the most probable assignments are always proposed. Most importantly, the matrix effect on structure and spectra of the dimers can be substantial because the interaction potential is rather flat. In other words, the observed matrix-isolated dimers and their vibrational spectra probably differ from the species predicted in vacuum. For example, all predicted so far FA dimers are planar in vacuum; however, this is probably changed by a solid matrix. No theoretical estimations of this effect have been done, and this is a challenge for computational science. Another interesting question concerns the effect of anharmonicity on the vibrational spectra taking into account that the vast majority of calculations are done within the harmonic approximation.

■ ASSOCIATED CONTENT

■ Supporting Information

Calculated structures and interaction energies of trans–trans and trans–cis HCOOD dimers, experimental and calculated spectra of trans- and cis-HCOOD, calculated spectra of the cis–cis HCOOH dimers, trans–trans HCOOD dimers, and trans–cis HCOOD dimers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: leonid.khriachtchev@helsinki.fi.

Notes

The authors declare no competing financial interest.

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