Electronic Supplementary Information for

Shifting Formic Acid Dimers into Perspective: Vibrational Scrutiny in Helium Nanodroplets

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1 Harmonic Vibrational Frequency Calculations

In Table S1, hydrogen bond lengths of the F_cF dimer at various levels of theory are compared to the predicted downshift $\Delta\tilde{\nu}$ of the hydrogen bonded OH stretching band of F_cF ($\tilde{\nu}_D$) with respect to the OH stretching vibration of the formic acid monomer $\tilde{\nu}_M$. These harmonic frequency calculations are scaled to $\tilde{\nu}_M$ at $3570\,\mathrm{cm}^{-1}$. The scaling factors are listed in the second column of Table S1. The methods that tend to underestimate the downshift of the bound OH stretching vibration (cf. Figure 3) predict longer hydrogen bonds than methods that tend to overestimate the downshift, whereas those of M06-2X, MP2, and B2PLYP-D3(BJ) are near-identical. In other words, the SCS-MP2 and PBEh-3c methods underestimate the hydrogen bond strength and this is reflected in smaller downshifts than experimentally observed.

Table S1: Predicted hydrogen bond length (in Å) and downshifts $\Delta\tilde{\nu}$ (in cm^{-1}) of the bound OH stretching vibration of the F_cF dimer $\tilde{\nu}_D$ with respect to the free OH stretching vibration of the monomer $\tilde{\nu}_M$ determined from scaled harmonic band positions

method	**scaling factor**	**hydrogen bond length**	$\tilde{\nu}_M$	$\tilde{\nu}_D$	$\Delta\tilde{\nu}$
SCS-MP2	0.9511	1.798	3570	3286	284
PBEh-3c	0.9283	1.789		3262	308
MP2	0.9543	1.755		3225	345
B2PLYP-D3(BJ)	0.9564	1.756		3209	361
M06-2X	0.9412	1.754		3196	374
B3LYP-D3(BJ)	0.9607	1.747		3181	389

2 Anharmonic Vibrational Frequency Calculations

2.1 VPT2 Calculations with Intermolecular Vibrations

The vibrational motion of the six intermolecular modes, whose contributions are omitted for the VPT2 analysis in the main text (Figure 5), is shown in Figure S1. The harmonically and anharmonically (VPT2) calculated band positions of these modes averaged over two DFT integration grids (*ultrafine* and *superfine*), two optimisation settings (Gaussian 09 keywords *tight* and *very tight*), and two symmetries (C_1 and C_s) are listed in Table S2 alongside standard deviations $\geq 0.5\,\mathrm{cm}^{-1}$.

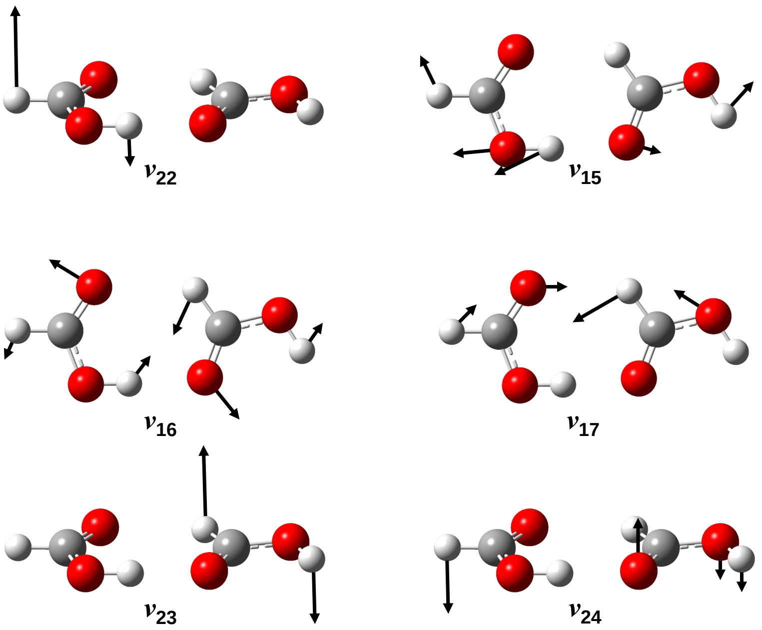

Fig. S1: Intermolecular modes of the higher-energy formic acid dimer F$_c$F. The bands are labelled according to the Herzberg nomenclature.

Table S2: Calculated band positions (in cm^{-1}) for the harmonic (ω) as well as anharmonic ($\tilde{\nu}$, VPT2) vibrational frequencies of the six intermolecular modes (see Figure S1) of the higher-energy formic acid dimer F$_c$F. The bands are labelled according to the Herzberg nomenclature. The methods used are B3LYP-D3(BJ)/aVTZ, B2PLYP-D3(BJ)/aVTZ, MP2/aVTZ, and M06-2X/aVTZ. The calculated band positions are averaged over two DFT integration grids (*ultrafine* and *superfine*), two symmetries (C_1 and C_s), as well as over two optimisation settings (*tight* and *very tight*). Standard deviations $\geq 0.5\,\text{cm}^{-1}$ are displayed in parentheses

ν_i	B3LYP-D3(BJ)		B2PLYP-D3(BJ)		MP2		M06-2X	
	ω	$\tilde{\nu}$	ω	$\tilde{\nu}$	ω	$\tilde{\nu}$	ω	$\tilde{\nu}$
ν_{22}	205	189(5)	202	187(3)	199	188(4)	194	162(21)
ν_{15}	200	182(5)	196	180(2)	194	175(2)	185(2)	165(20)
ν_{16}	153	144(8)	150	142(4)	146	138(1)	144	139(8)
ν_{17}	115	101(7)	115	102(8)	115	106(2)	127(1)	99(29)
ν_{23}	108	103(13)	106	98(9)	103	93(3)	98(6)	208(151)
ν_{24}	63	61(13)	62	67(3)	58	56(2)	61	41(14)

Figure S2 shows the contribution of intermolecular modes to the coupling pattern of the F_cF dimer. The calculated band positions (B3LYP-D3(BJ)/aVTZ VPT2 level) of three high intensity combination bands that contain intermolecular modes are additionally listed in Table S3 and the vibrational motion of these modes is shown in Figures S3. The high intensity band labelled F_cF^{int} in Figure S2 is the $(\nu_3 + \nu_{15})$ combination band.

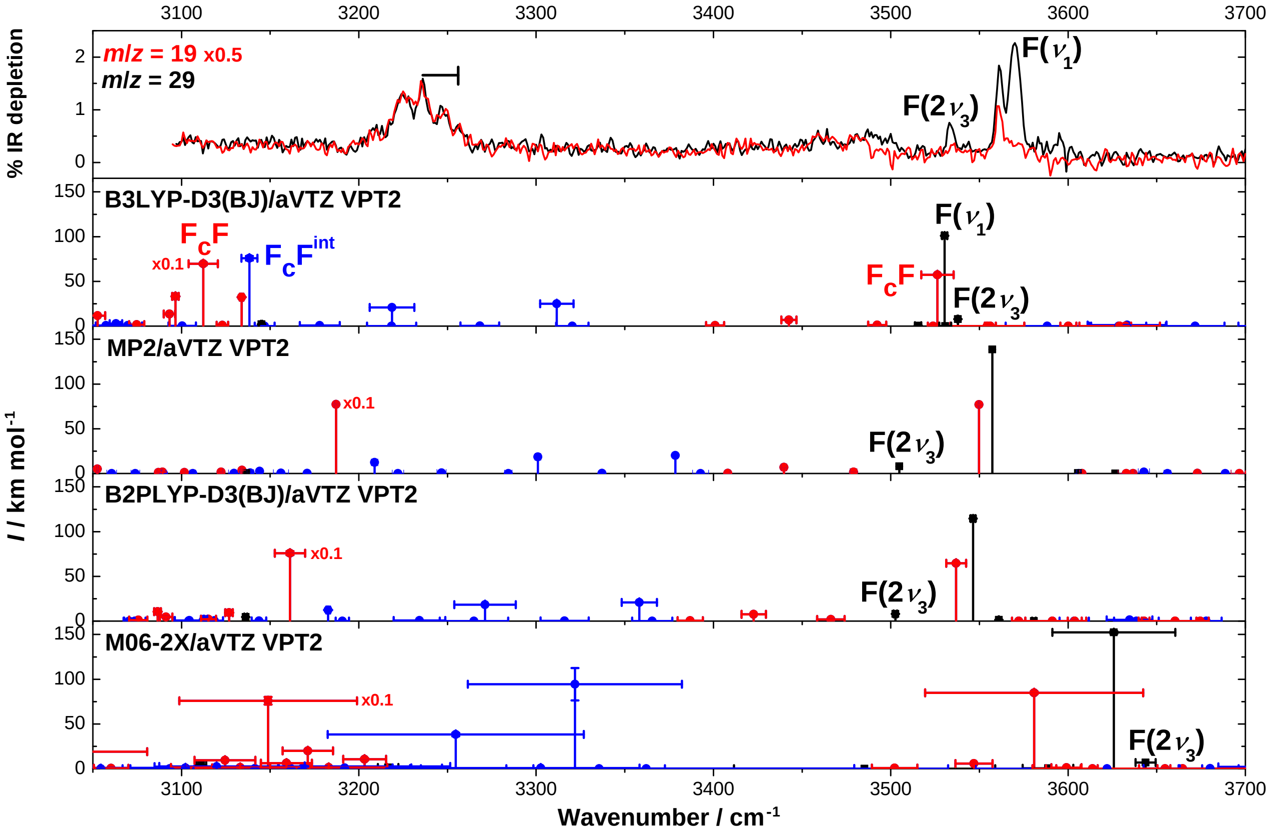

Fig. S2: Infrared depletion spectra (top panel) recorded at m/z 19 and 29 and a dopant partial pressure of 4×10^{-6} mbar. As an estimate of the gas phase band position, an error bar of $+20\,\text{cm}^{-1}$ is shown above the band of the bound OH stretching vibration. The intensity of the spectrum at m/z 19 is scaled by 0.5. $F(\nu_1)$ and $F(2\nu_3)$ mark the band positions of the OH stretching vibration and the overtone of the C=O stretching vibration of the formic acid monomer, respectively. Below the spectra, anharmonic (VPT2) band positions of the formic acid monomer F (black squares) and metastable dimer F_cF (red circles) calculated at the B3LYP-D3(BJ)/aVTZ, MP2/aVTZ, B2PLYP-D3(BJ)/aVTZ, and the M06-2X/aVTZ levels are shown. The optimisation criteria (*tight* and *very tight*), the DFT integration grid (*ultrafine* and *superfine*), and symmetry (C_1 and C_s) have been varied. The standard deviations upon changing the settings are displayed as error bars. The contributions of intermolecular modes of the F_cF dimer are shown in blue.

Table S3: Anharmonically (VPT2) calculated band positions (in cm^{-1}) of three combination vibrations of the $\mathrm{F_cF}$ dimer involving intermolecular modes with particularly high intensity, as seen in Figure S2. Additionally, the band positons of the corresponding fundamentals are listed, which are labelled in Herzberg nomenclature and displayed in Figure S3. The calculations have been performed at the B3LYP-D3(BJ)/aVTZ level

$\nu_i + \nu_j$		ν_i	
$\nu_2 + \nu_{15}$	3312(10)	ν_2	3112(9)
$\nu_2 + \nu_{17}$	3219(13)	ν_3	2952(2)
$\nu_3 + \nu_{15}$	3138(5)	ν_{15}	182(5)
		ν_{17}	101(7)

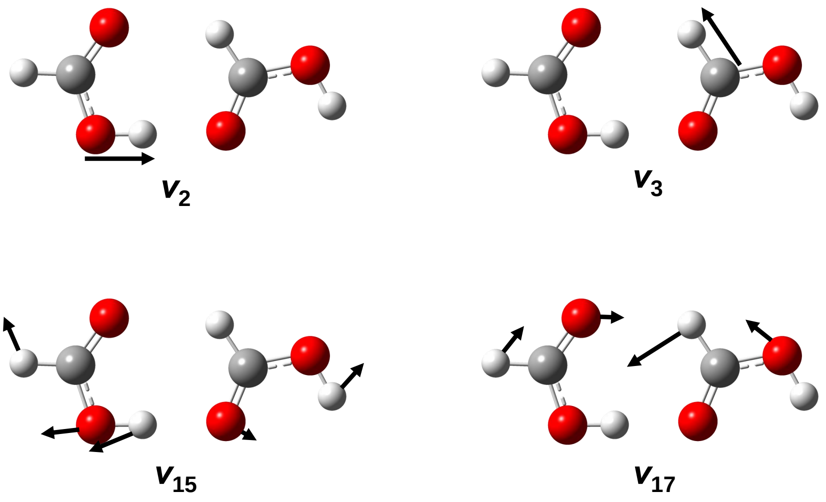

Fig. S3: OH (ν_2) and CH stretching vibrations (ν_3) and intermolecular modes (ν_{17} and ν_{15}) of the higher-energy $\mathrm{F_cF}$ dimer of formic acid.

2.2 VPT2 Calculations Without Intermolecular Vibrations

2.2.1 Sensitivity of VPT2 Calculations

In Figure 5 (main text), VPT2 calculations of the formic acid monomer F and the higher-energy F_cF dimer using B3LYP-D3(BJ)/aVTZ, B2PLYP-D3(BJ)/aVTZ, MP2/aVTZ, and M06-2X/aVTZ were shown, which have been averaged over two DFT integration grids (*ultrafine* and *superfine*), two optimisation criteria (*tight* and *very tight*), as well as two symmetry settings (C_1 and C_s). In Figures S4 – S7, the results for the individual settings are displayed.

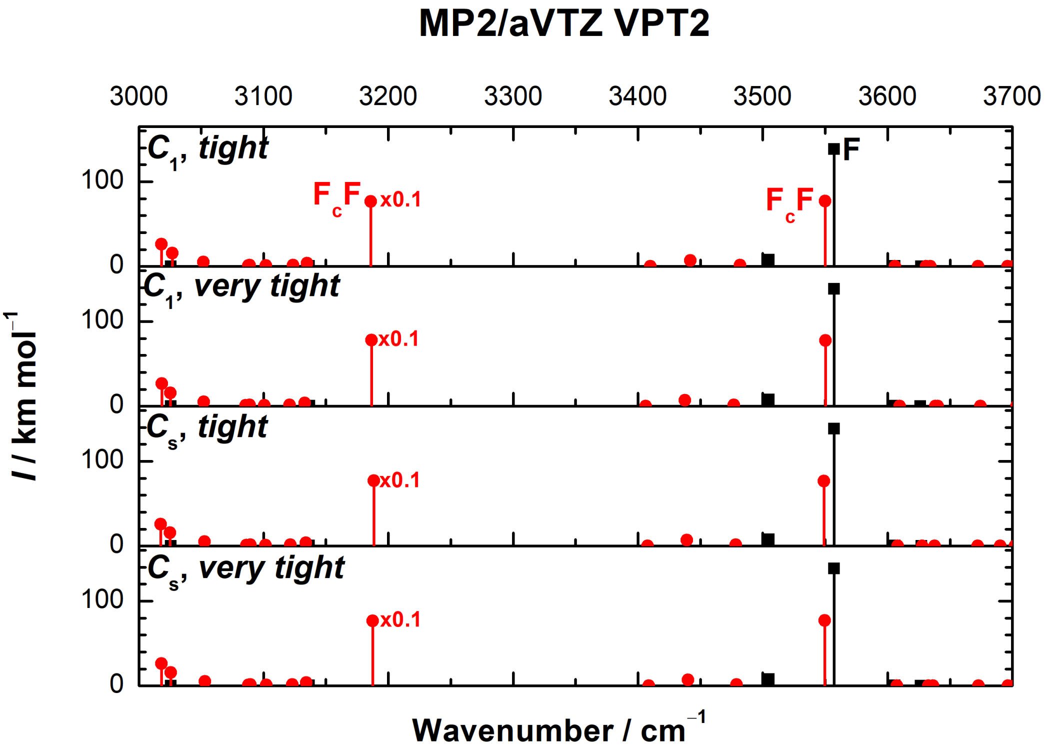

Fig. S4: Anharmonic (VPT2) band positions of the formic acid monomer (black squares) and metastable dimer F_cF (red circles) calculated at the MP2/aVTZ level. The optimisation criteria (*tight* and *very tight*) and symmetry (C_1 and C_s) have been varied.

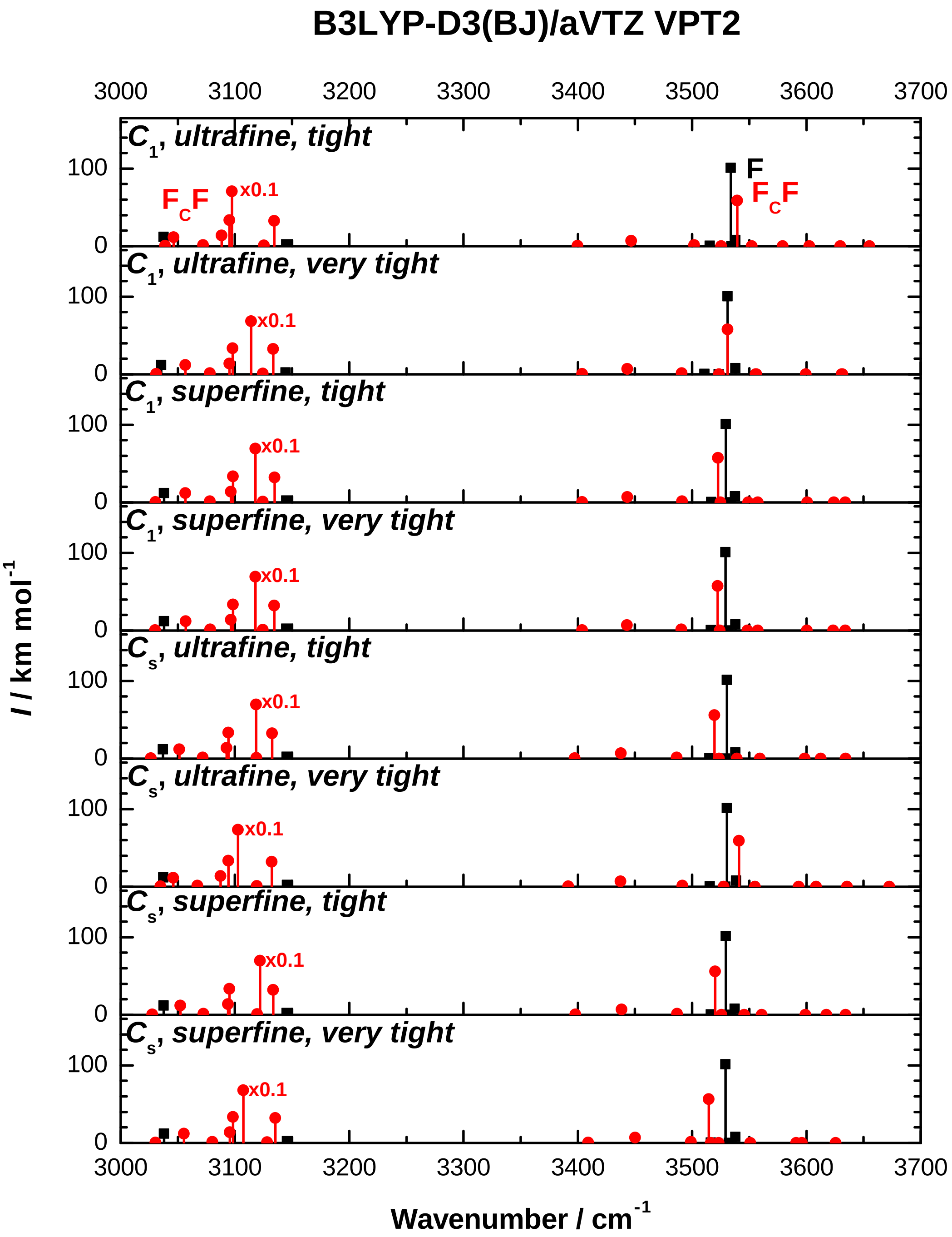

Fig. S5: Anharmonic (VPT2) band positions of the formic acid monomer (black squares) and metastable dimer F_cF (red circles) calculated at the B3LYP-D3(BJ)/aVTZ level. The optimisation criteria (*tight* and *very tight*), the DFT integration grid (*ultrafine* and *superfine*), as well as symmetry (C_1 and C_s) have been varied.

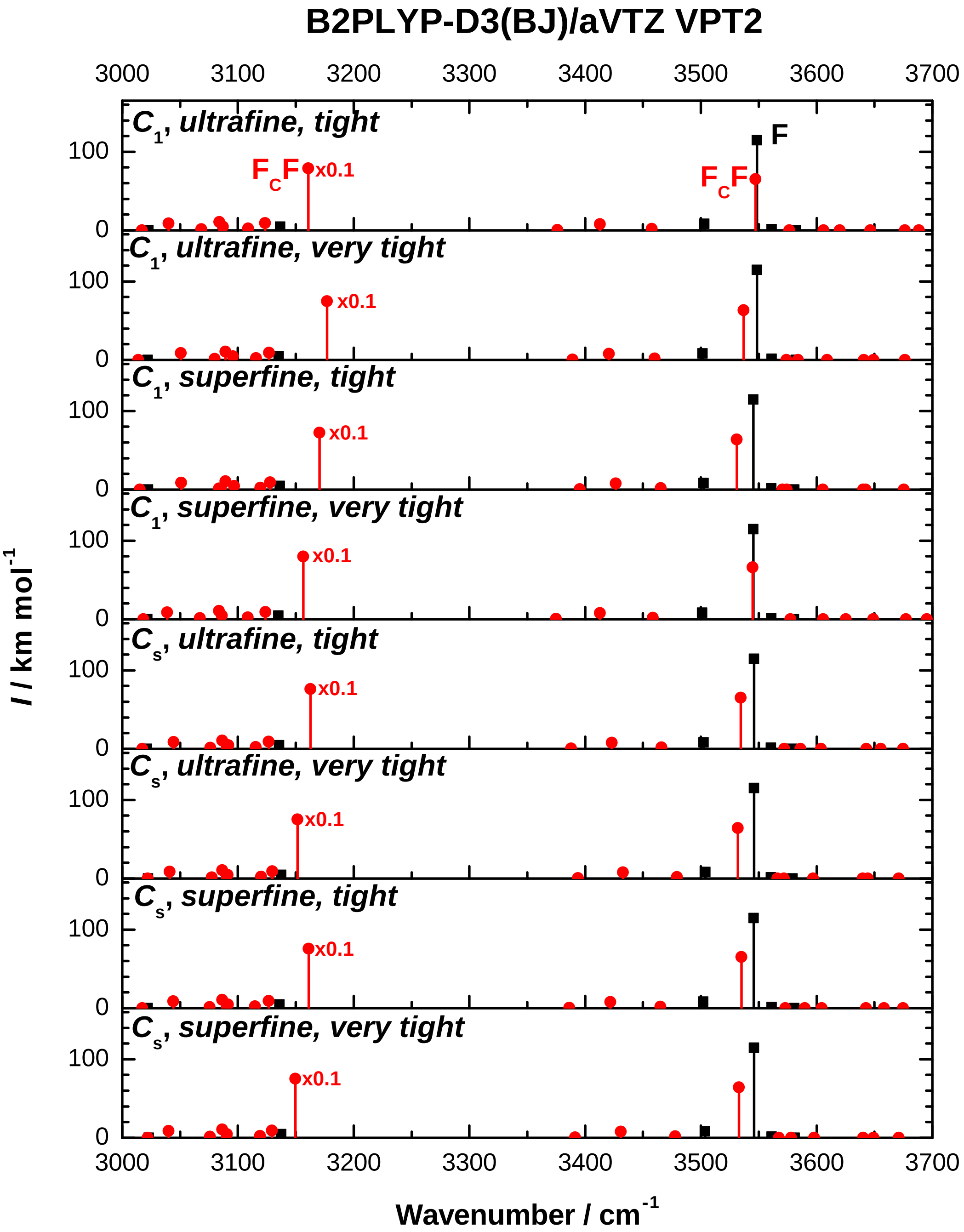

Fig. S6: Anharmonic (VPT2) band positions of the formic acid monomer (black squares) and metastable dimer $\mathrm{F_cF}$ (red circles) calculated at the B2PLYP-D3(BJ)/aVTZ level. The optimisation criteria (*tight* and *very tight*), the DFT integration grid (*ultrafine* and *superfine*), as well as symmetry (C_1 and C_s) have been varied.

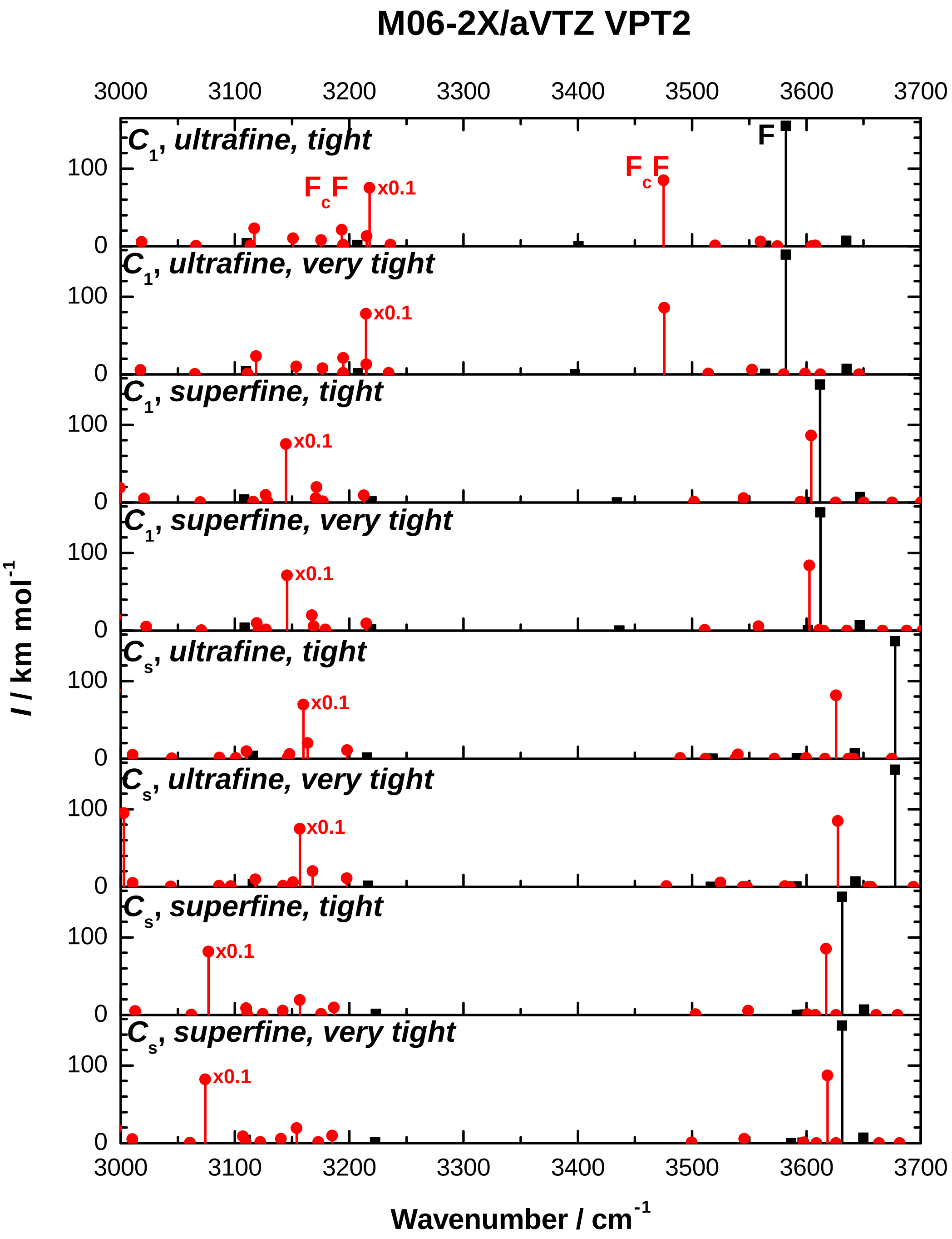

Fig. S7: Anharmonic (VPT2) band positions of the formic acid monomer (black squares) and metastable dimer F_cF (red circles) calculated at the M06-2X/aVTZ level. The optimisation criteria (*tight* and *very tight*), the DFT integration grid (*ultrafine* and *superfine*), as well as symmetry (C_1 and C_s) have been varied.

2.2.2 Combination Vibrations of the F_cF dimer

The calculated band position of the four framework combination vibrations predicted with a non-zero intensity around the bound OH stretching fundamental of the F_cF dimer by the B3LYP-D3(BJ)/aVTZ VPT2 calculations (Figure 5 of the main text) are listed in Table S4. The vibrational motion in these modes is shown in Figure S8.

Table S4: Anharmonically (VPT2) calculated band positions (in cm^{-1}) of combination vibrations and the corresponding fundamentals of the F_cF dimer. The fundamentals are labelled in Herzberg nomenclature. The calculations have been performed at the B3LYP-D3(BJ)/aVTZ level

$\nu_i + \nu_j$		ν_i	
$\nu_5 + \nu_7$	3134(1)	ν_5	1751(3)
$\nu_5 + \nu_9$	3097(2)	ν_6	1706(3)
$\nu_6 + \nu_7$	3093(4)	ν_7	1389(2)
$\nu_6 + \nu_9$	3053(5)	ν_9	1342(5)

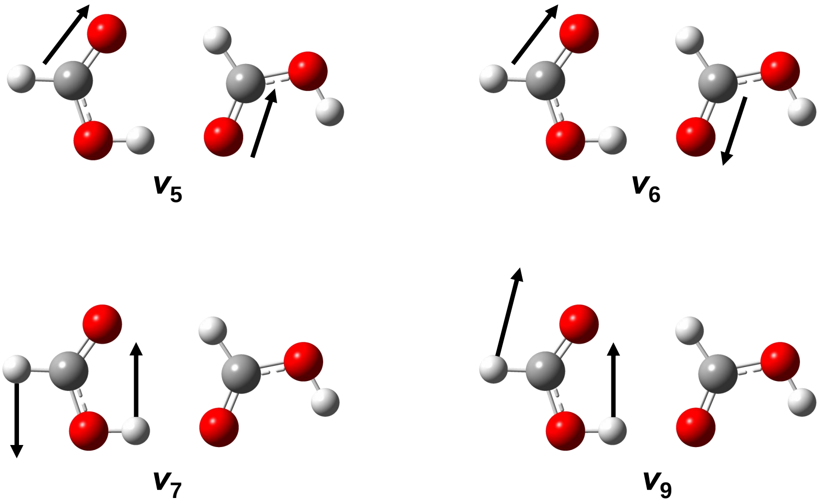

Fig. S8: C=O stretching (ν_5 and ν_6) and C−H in-plane bending vibrations (ν_7 and ν_9) of the higher-energy F_cF dimer of formic acid.