

Supporting Information

Theoretical Study of Vibrationally Averaged Dipole Moments for the Ground and Excited C=O Stretching States of *trans*-Formic Acid

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S1. Experimental

The experimental apparatus and sample preparation technique used to synthesize FA doped pH₂ crystals has been reported recently.¹ Briefly, millimeters thick FA doped pH₂ solids are prepared by “rapid vapor deposition”^{2,3} onto a BaF₂ substrate cooled to approximately 2K in a liquid helium bath cryostat. The samples are characterized using transmission FTIR spectroscopy (0.02 cm⁻¹ resolution) along the substrate surface normal. The FA concentration is estimated using the quotient of inlet quantities of FA and pH₂ measured in separate gas handling manifolds. The thickness of the crystal is measured using empirical correlations based on the integrated intensity of the Q₁(0)+S₀(0) and S₁(0)+S₀(0) double transitions of solid pH₂.⁴ The oH₂ concentration is calculated from the rotational partition function of H₂ assuming full thermal equilibration of nuclear spin states at the temperature at which the ortho/para converter is operated during deposition. The reported molar extinction coefficients for FA isolated in solid pH₂ are determined using the following equation,

$$\varepsilon = \frac{2.303 \int \log_{10}(I_0 / I) d\tilde{\nu}}{[\text{FA}]d} \quad (\text{S1})$$

where d is the thickness of the crystal, and $[\text{FA}]$ is the concentration of FA in the sample. The FA concentration is calculated using the measured ppm concentration and the density of solid pH₂ (2.6×10^{22} molecules cm⁻³) at liquid helium temperatures.⁵ For the intensity data presented here we used two different FA doped crystals; the first crystal had a FA concentration of a 3 ppm, was 3.1 ± 0.2 mm thick, and had a residual oH₂ concentration estimated to be 45 ppm. The second crystal had a FA concentration of 20 ppm, is 2.3 ± 0.2 mm thick, and had a residual oH₂ concentration of 70 ppm. The largest error in ε is likely due to the estimated FA concentration. In the best case of gaseous dopants, systematic errors lead to $\pm 40\%$ errors in the true dopant concentration. However, since FA is a liquid at room temperature, condensation in the dopant manifold and/or in the 1 m long tube that connects the dopant manifold to the cryostat can result in additional errors in the reported FA concentration. Analysis of the two samples reported here using eqn. (1) indicates this is likely the case. Thus, we estimate that the absolute intensities are only good to within an order of magnitude, but the relative intensities are good to within the reported uncertainties based on repeated measurements for a given sample.

S2. Optimized Geometries

Optimized structural parameters for *trans*-FA (**Table S1**) are in overall good agreement with experiment,⁶⁻⁸ especially for the B3LYP post-HF calculations. The BPW91 functional tends to overestimate bond distances. Larger basis sets improve the results; in particular the B3LYP and post-HF bond lengths with diffuse, triple- ζ basis sets are in excellent agreement with experiment. The variation in the bond angles is comparatively smaller. By all methods, the H-C-O bond angle is systematically computed $\sim 2^\circ$ greater than measured experimentally.

Table S1. Optimized structural parameters for *trans*-FA.

Level	Bond distance				Bond angle			
	R _{C-H} (Å)	R _{C-O} (Å)	R _{O-H} (Å)	R _{C=O} (Å)	$\Theta_{\text{HCO(-H)}}$ ($^\circ$)	Θ_{COH} ($^\circ$)	Θ_{HCO} ($^\circ$)	Θ_{OCO} ($^\circ$)
B3LYP/6-31G(d,p)	1.100	1.346	0.974	1.205	109.5	106.6	125.4	125.1
B3LYP/6-31+G(d,p)	1.098	1.384	0.974	1.207	109.9	107.8	125.2	125.0
B3LYP/6-311++G(d,p)	1.098	1.346	0.971	1.199	109.5	107.9	125.3	125.1
B3LYP/cc-pVDZ	1.110	1.347	0.977	1.203	109.1	106.4	125.8	125.1
B3LYP/cc-pVTZ	1.097	1.345	0.970	1.197	109.5	107.5	125.3	125.2
B3LYP/aug-cc-pVDZ	1.103	1.349	0.973	1.205	109.8	107.5	125.1	125.0
B3LYP/aug-cc-pVTZ	1.096	1.345	0.970	1.198	109.7	107.8	125.2	125.1
BPW91/6-31G(d,p)	1.108	1.358	0.982	1.215	109.0	105.7	125.7	125.3
BPW91/6-31+G(d,p)	1.106	1.359	0.982	1.217	109.4	106.8	125.4	125.2
BPW91/6-311++G(d,p)	1.106	1.357	0.979	1.209	109.2	106.8	125.5	125.3
BPW91/cc-pVDZ	1.117	1.358	0.986	1.213	108.7	105.3	126.1	125.3
BPW91/cc-pVTZ	1.105	1.356	0.979	1.207	109.1	106.4	125.5	125.4
BPW91/aug-cc-pVDZ	1.111	1.361	0.982	1.215	109.4	106.4	125.4	125.2
BPW91/aug-cc-pVTZ	1.104	1.357	0.979	1.208	109.3	106.7	125.4	125.3
MP2/6-311++G(d,p)	1.096	1.347	0.969	1.205	109.5	106.4	125.3	125.2
MP2/cc-pVDZ	1.107	1.350	0.975	1.209	109.1	105.1	125.6	125.3
MP2/cc-pVTZ	1.087	1.342	0.968	1.200	109.6	106.2	125.2	125.2
MP2/aug-cc-pVDZ	1.102	1.357	0.975	1.215	109.6	106.4	125.3	125.1
MP2/aug-cc-pVTZ	1.092	1.347	0.971	1.205	109.7	106.5	125.2	125.1
CCSD(T)/6-311++G(d,p)	1.099	1.351	0.969	1.205	109.7	106.3	125.3	125.0
CCSD(T)/aug-cc-pVDZ	1.106	1.361	0.975	1.214	109.8	106.4	125.2	125.0
CCSD(T)/aug-cc-pVTZ	1.095	1.348	0.970	1.204	109.9	106.6	125.1	125.0
BPW91/cc-pVDZ/CPCM (Ar)	1.118	1.355	0.992	1.215	108.8	105.8	125.8	125.4
BPW91/cc-pVDZ/CPCM (pH ₂)	1.118	1.356	0.990	1.214	108.8	105.7	125.9	125.4
Experiment ^a	1.097	1.342	0.972	1.203	109.1 ^b	106.3	123.2	124.8

^a Refs 6-8

^b 111.97 $^\circ$ also reported

The Ar and pH₂ matrices (simulated by the CPCM implicit solvent model at BPW91/cc-pVDZ level) cause similar changes in structure, quantitatively greater for the Ar matrix as expected due to the higher Ar dielectric constant. The most pronounced is the lengthening of the O-H bond, compared to the gas phase, while the C-O bond is shorter. The C=O bonds are only slightly longer and valence bond angles are essentially unaffected by the matrix.

The anharmonic vibrationally averaged bond distances (**Table S2**) are greater than the equilibrium values, most notably the C-H and C-O by ~ 0.1 Å. The C=O bond is only slightly longer, while the O-H becomes somewhat shorter. From the bond angles, only the C-O-H exhibits a systematic change, becoming $\sim 1^\circ$ greater.

Table S2. Ground State Vibrationally Averaged Structural Parameters for *trans*-FA obtained from VCI theory.

Level	R _{C-H} (Å)	R _{C-O} (Å)	R _{O-H} (Å)	R _{C=O} (Å)	Θ _{HCO(-H)} (°)	Θ _{COH} (°)	Θ _{HCO} (°)	Θ _{OCO} (°)
B3LYP/6-311++G(d,p)	1.128	1.367	0.983	1.216	108.6	106.0	126.0	125.4
BPW91/cc-pVDZ	1.108	1.355	0.964	1.202	109.5	109.0	125.3	125.2
MP2/6-311++G(d,p)	1.104	1.359	0.957	1.206	109.3	107.7	125.5	125.2
CCSD(T)/6-311++G(d,p)	1.109	1.360	0.962	1.208	109.6	107.1	125.3	125.1
BPW91/cc-pVDZ/CPCM (Ar)	1.129	1.364	0.994	1.218	108.8	106.1	125.9	125.3
BPW91/cc-pVDZ/CPCM (pH ₂)	1.129	1.365	0.989	1.217	108.7	106.3	125.9	125.4
Experiment ^a	1.097	1.342	0.972	1.203	109.1 ^b	106.3	123.2	124.8

^a Refs. 6-8

^b 111.97° also reported

S3. Single Mode Potential Energy Surfaces and Dipole Moment Functions

At all levels of theory, the potential energy as well as the dipole moment functions along the ν_3 normal mode coordinate (**Fig. S1**) are stable up to 1 Å displacement from equilibrium. The possible exception is the CCSD(T) method, where the dipole moment values exhibit a sudden drop around 0.9 Å. This, however, does not affect the calculated vibrational properties, as the maximum span of the anharmonic wavefunction (for $\nu = 4$) is approximately -0.2 to $+0.25$ Å (**Fig.1** of the main text) and the portion of the surface (and the dipole moment function) used for the single mode calculations was from -0.3 to $+0.5$ Å (Methods).

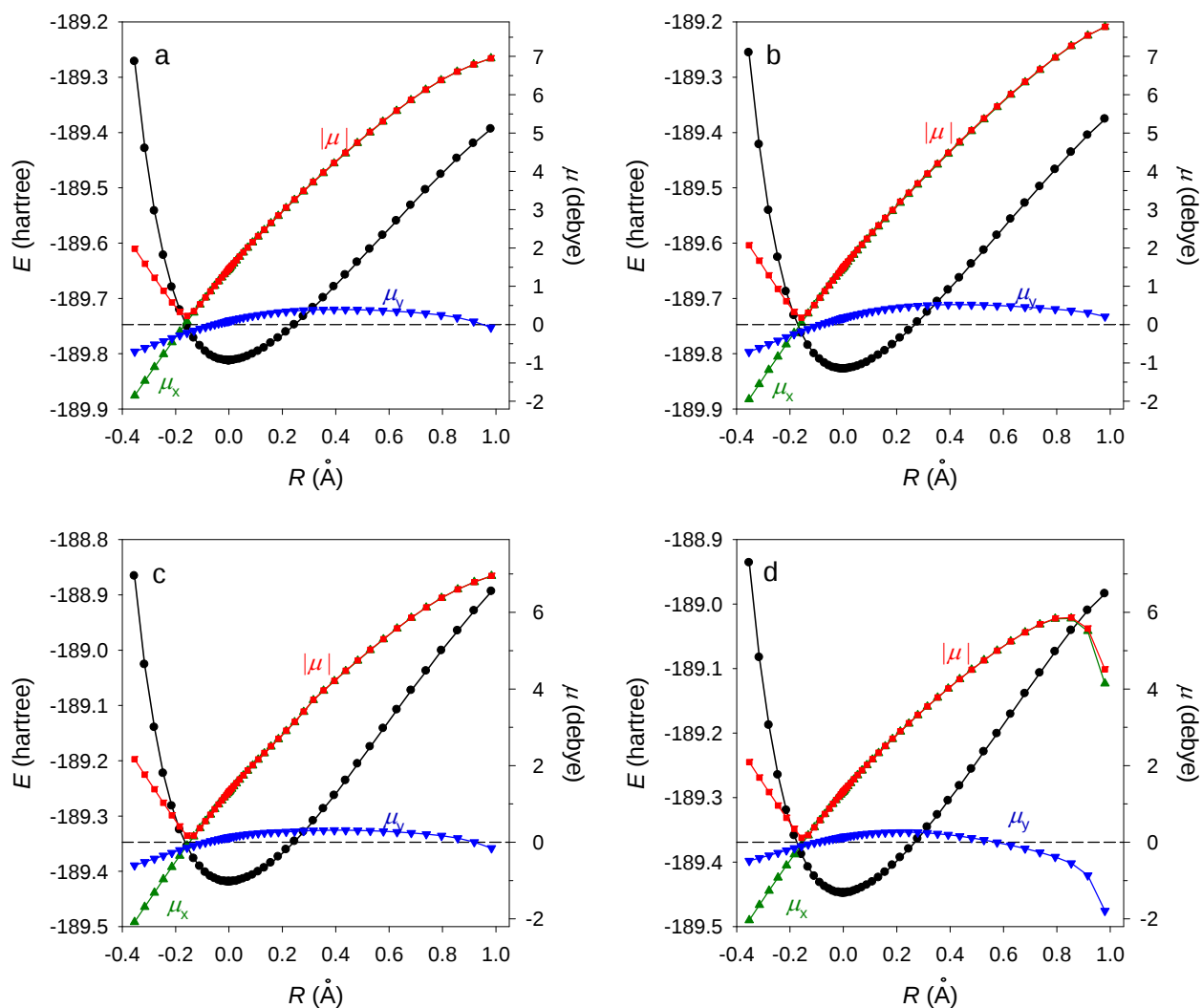


Figure S1. One-dimensional single mode representation of the C=O stretching vibration in *trans*-FA. Potential energy (black circles), the dipole moment components (x-green, y-blue triangles) and magnitude (red squares) as functions of the ν_3 normal mode coordinate (R) calculated at a) B3LYP/6-311++G(d,p), b) BPW91/6-311++G(d,p), c) MP2/6-311++G(d,p) and d) CCSD(T)/6-311++G(d,p) level as functions of the ν_3 normal mode coordinate (R). Molecular orientation is the same as in Fig. 1 of the main text.

S4. Convergence of VCI Dipole Moment Calculations with the Size of the Harmonic Basis

Tests of the VCI harmonic basis (**Table S3**) show that the basis limited to the ground and five excited states ($N_{\text{MAX}} = 5$) can be considered reliable for dipole moment calculations up to the $\nu = 3$ vibrational state. The $\nu = 4$ values, as might be expected, are most sensitive to the inclusion of additional harmonic basis functions. In addition, with a larger harmonic basis ($N_{\text{MAX}} = 6, 7$) the contribution of the ν_3 normal mode to the anharmonic wavefunction becomes significantly smaller (27% for $N_{\text{MAX}} = 7$).

Table S3. Dipole moments (in debye) for the ν_3 vibrational states in *trans*-FA computed at BPW91/cc-pVDZ level by VCI anharmonic theory with the harmonic basis limited to a different number of vibrationally excited states (N_{MAX}).

N_{MAX}	(total number of states)	Vibrational state				
		$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
4	(715)	1.3765	1.3948	1.4027	1.4025	1.0725
5	INT ^a (1876)	1.3786	1.3883	1.4073	1.4156	1.3618
5	(2002)	1.3779	1.3884	1.4059	1.4158	1.3623
6	(5005)	1.3820	1.3979	1.4046	1.4048	1.3938
7	(11440) ^b	1.3738	1.3931	1.4020	1.4104	1.3984

^a Only states interacting directly with ground and fundamentals taken

^b For $\nu = 4$ pure C=O stretch is contained in the VCI state by 27% only

S5. Dipole Moments for ν_1 - ν_9 Vibrational Modes

Single mode BPW91/cc-pVDZ anharmonic calculations for all nine *trans*-FA vibrational modes were used to test the anharmonic ground state (ZPE) contribution of the remaining modes to the ν_3 dipole moments (eqns. 13-16 of the main text). The resulting dipole moments for the ground and first excited vibrational states are shown in **Table S4**, along with the corresponding ZPE corrected values. The dipole moments for singly excited states of the nine *trans*-FA vibrational modes obtained with a multidimensional VCI approach are shown in **Table S5**.

Table S4. Dipole moments (in debye) in the ground and singly excited vibrational states calculated in a single mode approximation at the BPW91/cc-pVDZ level including correction (ZPE) for contribution of all vibrational modes.

	$\nu_1(\text{A}')$	$\nu_2(\text{A}')$	$\nu_3(\text{A}')$	$\nu_4(\text{A}')$	$\nu_5(\text{A}')$	$\nu_6(\text{A}')$	$\nu_8(\text{A}'')$	$\nu_9(\text{A}'')$	$\nu_7(\text{A}')$
$\nu = 0$ single mode	1.3993	1.4011	1.4231	1.4013	1.3994	1.3850	1.4001	1.4049	1.3995
$\nu = 0$ ZPE corrected					1.3935				
$\nu = 1$ single mode	1.3905	1.4055	1.4645	1.3988	1.3933	1.3532	1.3958	1.4090	1.3941
$\nu = 1$ ZPE corrected	1.3852	1.3934	1.4349	1.3914	1.3872	1.3614	1.3893	1.3977	1.3886

Table S5. Dipole moments (in debye) in singly excited vibrational states obtained by VCI theory

Level	$\nu_1(A')$	$\nu_2(A')$	$\nu_3(A')$	$\nu_4(A')$	$\nu_5(A')$	$\nu_6(A')$	$\nu_8(A'')$	$\nu_9(A'')$	$\nu_7(A')$
B3LYP/6-311++G(d,p)	1.4683	1.4737	1.5044	1.4628	1.4651	1.4405	1.4600	1.4764	1.4800
BPW91/cc-pVDZ	1.3353	1.3865	1.3884	1.3624	1.3614	1.3374	1.3617	1.3752	1.3792
MP2/6-311++G(d,p)	1.2745	1.2869	1.2952	1.2739	1.2762	1.2540	1.2688	1.2825	1.2892
CCSD(T)/6-311++G(d,p) ^a	1.3148	1.3236	1.3567	1.3166	1.3185	1.2902	1.3057	1.3194	1.3268
BPW91/cc-pVDZ/CPCM(Ar)	1.5208	1.5476	1.5579	1.5252	1.5255	1.4981	1.5253	1.5390	1.5434
BPW91/cc-pVDZ/CPCM(pH ₂)	1.4674	1.5014	1.5103	1.4779	1.4780	1.4500	1.4778	1.4904	1.4958

^aMolecular dipole moments calculated at CCD/6-311++G(d,p) level.

S6. Spectral Frequencies and IR Intensities for the fundamental and overtone ν_3 transitions

Frequencies of the anharmonic spectral transitions are calculated from the energy eigenvalues of the single-mode (eqn. 1 of the main text) or multidimensional VCI (eqn. 7) Hamiltonians. The transition dipole moments for the fundamental and overtone transitions are obtained from the resulting eigenfunctions:

$$\mu_{v \rightarrow v'} = \langle \psi_{v'}(Q) | \mu(Q) | \psi_v(Q) \rangle = \sum_{i=1}^{N_{grid}} \psi_{v'}(r_i) \mu(r_i) \psi_v(r_i) \quad (S2)$$

and converted to molar extinction coefficients:⁹

$$\varepsilon = 2.506639488 \left| \mu_{v \rightarrow v'} \right|^2 \tilde{\nu} \quad (S3)$$

where ε is the integrated molar absorption coefficient in km.mol^{-1} , $\mu_{v \rightarrow v'}$ is in debye and $\tilde{\nu}$ is the vibrational frequency in cm^{-1} .

Single mode calculations. The most obvious trends in the single mode anharmonic frequencies (**Table S6**) are the decrease with increasing basis set size, and BPW91 frequencies with all basis sets that stand out as systematically lower, compared to the other methods. While the B3LYP and post-HF methods, with the exception of MP2/aug-cc-pVDZ, uniformly yield higher C=O stretch frequencies than observed,^{1,10-15} with augmented correlation consistent basis sets they approach the experimental values quite closely. These trends are very similar for the fundamental and overtone frequencies, with the error increasing the higher the overtone. (The first overtone has not been observed in the gas phase and the computed frequency is compared to the He droplet experimental value,¹³ which might be somewhat lower than the gas phase). The best agreement with experiment for a B3LYP calculation was obtained with the aug-cc-pVDZ basis set, which also gave the best agreement of the MP2 and CCSD(T) calculations with the overtone frequencies, while MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ yielded the most accurate fundamental frequency. The BPW91 frequencies are mostly too low, except for cc-pVDZ basis

set, which yields the exact fundamental vibrational frequency, the first overtone (compared to *trans*-FA in He¹³) only 8 cm⁻¹ higher and the second overtone 47 cm⁻¹ higher than experiment. While some other methods give better agreement for the second overtone, overall the BPW91/cc-pVDZ level appears to perform the best out of all tested methods.

Table S6. Vibrational frequencies (in cm⁻¹) of the ν_3 mode (C=O stretch) in *trans*-FA and its overtones in the single mode approximation.

Level	harmonic	fundamental	1 st overtone	2 nd overtone	3 rd overtone
B3LYP/6-31G(d,p)	1852	1834	3655	5466	7265
B3LYP/6-31+G(d,p)	1820	1812	3611	5397	7171
B3LYP/6-311++G(d,p)	1815	1803	3591	5365	7126
B3LYP/cc-pVDZ	1846	1829	3647	5453	7247
B3LYP/cc-pVTZ	1826	1810	3606	5389	7159
B3LYP/aug-cc-pVDZ	1804	1786	3559	5320	7068
B3LYP/aug-cc-pVTZ	1810	1798	3581	5352	7109
BPW91/6-31G(d,p)	1793	1778	3545	5300	7043
BPW91/6-31+G(d,p)	1764	1753	3492	5219	6932
BPW91/6-311++G(d,p)	1761	1756	3497	5224	6937
BPW91/cc-pVDZ	1787	1777	3541	5294	7036
BPW91/cc-pVTZ	1769	1752	3491	5216	6929
BPW91/aug-cc-pVDZ	1750	1732	3450	5156	6848
BPW91/aug-cc-pVTZ	1755	1733	3453	5158	6851
MP2/6-311++G(d,p)	1810	1802	3595	5378	7153
MP2/cc-pVDZ	1846	1838	3668	5490	7305
MP2/cc-pVTZ	1829	1820	3631	5434	7228
MP2/aug-cc-pVDZ	1774	1766	3522	5270	7008
MP2/aug-cc-pVTZ	1794	1782	3554	5316	7068
CCSD(T)/6-311++G(d,p)	1810	1793	3574	5345	7103
CCSD(T)/aug-cc-pVDZ	1776	1764	3515	5255	6983
CCSD(T)/aug-cc-pVTZ	1803	1788	3563	5324	7073
BPW91/cc-pVDZ/CPCM (Ar)	1775	1766	3520	5262	6993
BPW91/cc-pVDZ/CPCM (pH ₂)	1778	1771	3530	5277	7113
Experiment (gas) ^a	-	1777		5274	
Experiment (He droplets) ^b			3533		
Experiment (Ar) ^c		1768	3517		
Experiment (pH ₂) ^d		1769	3518		
Experiment (nH ₂) ^e		1766			

^a Ref. 12

^b Ref. 13

^c Ref. 11 and 14. (Note: several values were reported, average is used.)

^d Ref. 1

^e Ref. 15

In Ar and pH₂ matrices, simulated by the CPCM model, a decrease in the C=O stretching frequencies is computed for all transitions. Both fundamental and first overtone frequencies computed in the Ar matrix are in a remarkable agreement with experiment. The frequencies computed for the pH₂ matrix are closer to the gas phase values, as expected. However, the experimental frequency differences in the two matrices are smaller than computed. In particular, the same frequency is reported for the fundamental transition in both Ar and pH₂. In normal H₂ (nH₂),¹⁵ which is a mixture of pH₂ and oH₂, the ν_3 frequency is even slightly lower, which is consistent with the shifts observed due to oH₂ clustering. The first overtone in pH₂ experiments is higher than in Ar, consistently with the calculations, which predict the differences between the two matrices increasing with the order of the transition.

The IR absorption intensities calculated in the single-mode approximation are summarized in **Table S7**. The only available experimental value for the absolute absorption intensity in the gas phase, to our best knowledge, is an estimate of Yokoyama et al.¹⁶ for the fundamental ν_3 transition based on the experimental data of Maréchal.¹⁷ Compared to this value of 231 km.mol⁻¹, all computed fundamental intensities are generally higher, by 50 to 150 km.mol⁻¹, reflecting the general tendency of the *ab initio* calculations to yield too high absolute IR intensities. Overall, considering the difficulties in both calculations¹⁸ and measurements of absolute IR intensities, our results are very satisfactory. In particular, BPW91 and MP2 with cc-pVDZ and cc-pVTZ basis sets yield the fundamental IR intensities in a very good agreement with experiment. Interestingly, the trends in the IR intensities do not correlate with the predictions of the dipole moments (**Table I** of the main text); while the experimental intensities are very well reproduced at MP2/cc-pVDZ and BPW91/cc-pVTZ levels, the MP2/cc-pVDZ yielded the worst underestimation of the vibrationally averaged dipole moments and BPW91/cc-pVTZ dipoles are significantly higher than experiment.

All levels of theory yield relatively consistent values for the overtone intensities, except for the third overtone, where B3LYP/6-31G(d,p) yields noticeably larger and the MP2 methods substantially smaller values than the rest of the calculations. Comparison of the overtone intensities with experiment is problematic as the first overtone was not observed in the gas phase, and the second overtone intensity was estimated from the fundamental ν_3 absolute intensity and relative intensities of the other measured transitions reported by Freytes et al.,¹² yielding 2.08 km.mol⁻¹. This value is more than two orders of magnitude greater than all the calculated intensities, which are generally on the order of 10⁻² km.mol⁻¹. As pointed out by Freytes et al.,¹² this value is a “very rough” estimate from the maximum transmittance values of rotationally-resolved branches merged together from different sets of experimental data. It is further brought into question by comparing the first ν_3 overtone intensities measured in the Ar and pH₂ matrices, which are of the same order as the third gas phase overtone and in a much better agreement with calculations.

Table S7: Infrared absorption intensities (in km.mol⁻¹) of the ν_3 mode (C=O stretch) in *trans*-FA and its overtones in the single mode approximation.

Level	fundamental	1 st overtone	2 nd overtone	3 rd overtone
B3LYP/6-31G(d,p)	355	6.20	15.4×10^{-2}	3.89×10^{-3}
B3LYP/6-31+G(d,p)	394	4.08	7.72×10^{-2}	1.64×10^{-3}
B3LYP/6-311++G(d,p)	389	4.21	7.60×10^{-2}	1.47×10^{-3}
B3LYP/cc-pVDZ	313	3.62	6.36×10^{-2}	1.28×10^{-3}
B3LYP/cc-pVTZ	327	3.73	6.68×10^{-2}	1.29×10^{-3}
B3LYP/aug-cc-pVDZ	362	3.68	6.79×10^{-2}	1.36×10^{-3}
B3LYP/aug-cc-pVTZ	366	3.87	7.07×10^{-2}	1.46×10^{-3}
BPW91/6-31G(d,p)	267	3.36	6.82×10^{-2}	1.48×10^{-3}
BPW91/6-31+G(d,p)	345	3.96	7.92×10^{-2}	1.68×10^{-3}
BPW91/6-311++G(d,p)	350	4.24	7.97×10^{-2}	1.61×10^{-3}
BPW91/cc-pVDZ	279	3.57	6.59×10^{-2}	1.28×10^{-3}
BPW91/cc-pVTZ	295	3.62	6.77×10^{-2}	1.29×10^{-3}
BPW91/aug-cc-pVDZ	318	3.62	6.91×10^{-2}	1.43×10^{-3}
BPW91/aug-cc-pVTZ	320	3.71	6.98×10^{-2}	1.44×10^{-3}
MP2/6-311++G(d,p)	348	4.38	7.88×10^{-2}	0.74×10^{-3}
MP2/cc-pVDZ	258	4.08	6.26×10^{-2}	0.54×10^{-3}
MP2/cc-pVTZ	295	3.98	6.77×10^{-2}	0.72×10^{-3}
MP2/aug-cc-pVDZ	322	4.05	7.69×10^{-2}	0.77×10^{-3}
MP2/aug-cc-pVTZ	325	4.05	7.46×10^{-2}	0.85×10^{-3}
CCSD(T)/6-311++G(d,p)	356	4.05	7.13×10^{-2}	1.36×10^{-3}
CCSD(T)/aug-cc-pVDZ	328	3.79	6.95×10^{-2}	1.43×10^{-3}
CCSD(T)/aug-cc-pVTZ	323	3.81	7.22×10^{-2}	1.49×10^{-3}
BPW91/cc-pVDZ/CPCM (Ar) ^a	322 (100%)	3.96 (1.2%)	7.25×10^{-2}	1.29×10^{-3}
BPW91/cc-pVDZ/CPCM (pH ₂)	309 (100%)	3.85 (1.2%)	7.07×10^{-2}	1.39×10^{-3}
Experiment (gas phase) ^b	231 (100%)		2.08 (0.9%)	
Experiment (Ar) ^c	100%	1.4%		
Experiment (pH ₂)	280±20 (100%)	3±2 (1%)		

^a Relative intensities (with respect to the fundamental) shown for easier comparison with experiment.

^b Fundamental from Refs. 16 and 17, 2nd overtone calculated from the relative intensity (shown in parentheses) according to Ref. 12

^c Ref. 14, only relative intensities available

In the solid state matrices an increase in the IR intensity is predicted, an expected effect of the reaction field.^{19,20} For both the Ar and pH₂ matrices the BPW91/cc-pVDZ/CPCM intensities are in excellent agreement with experiment. Although only relative values are available for the Ar matrix, absolute intensities could be determined in the pH₂, albeit with a considerable error due to the uncertainties in the FA concentration and exact optical path (see Experimental). Nevertheless, the calculated absolute intensities for both the ν_3 fundamental and the first overtone are essentially within the experimental error of the measured values, with the fundamental only slightly greater.

VCI calculations. The VCI ν_3 fundamental and overtone frequencies (**Table S8**) are systematically lower than the single mode ones for the fundamental and the first overtone. The B3LYP/6-311++G(d,p) VCI calculation also yields the second overtone frequency lower than the single mode treatment, while the opposite is true for all the other levels. The third overtone is uniformly higher in all VCI calculations. The relative trends essentially parallel the single mode calculations (**Table S6**). The BPW91/cc-pVDZ again predicts lower frequencies than the other methods. Compared to experiment, CCSD(T)/6-311++G(d,p) is in the best agreement with the fundamental frequency, while BPW91/cc-pVDZ comes closest to first and second overtone values. In the Ar and pH₂ matrices the C=O stretch overtone frequency is computed to decrease, by ~ 30 and ~ 20 cm⁻¹ respectively, in very good agreement with the experimental 15 cm⁻¹ (compared to He droplet data). No experimental data are available for the higher overtones.

Table S8: VCI frequencies (in cm⁻¹) for the ν_3 mode (C=O stretch) in *trans*-FA and its overtones.

Level	fundamental	1 st overtone	2 nd overtone	3 rd overtone
B3LYP/6-311++G(d,p)	1795	3586	5442	7289
BPW91/cc-pVDZ	1754	3522	5341	7160
MP2/6-311++G(d,p)	1788	3581	5435	7276
CCSD(T)/6-311++G(d,p)	1784	3574	5428	7267
BPW91/cc-pVDZ/ CPCM(Ar)	1743	3495	5300	7106
BPW91/cc-pVDZ/CPCM(pH ₂)	1744	3501	5309	7117
Experiment (gas) ^a	1777		5274	
Experiment (He droplets) ^b		3533		
Experiment (Ar) ^c	1768	3517		
Experiment (pH ₂) ^d	1769	3518		
Experiment (nH ₂) ^e	1766			

^a Ref. 12

^b Ref. 13

^c Ref. 11 and 14 (Note: several values are reported, average is used)

^d Ref. 1

^e Ref. 15

The VCI computed IR intensities (**Table S9**) for the ν_3 fundamental and the first two overtones are weaker than in the single mode approximation (**Table S7**). The difference is most pronounced in the second overtone, whose intensity is ~ 50 % lower for all methods compared to the single mode approximation. By contrast, the third overtone VCI intensities are calculated much higher than in the single mode treatment, again quite significantly by $\sim 50\%$. The much greater gas phase experimental intensity, by roughly two orders of magnitude, is likely an artifact of the experiment, as already discussed above. In the solid state matrices, the fundamental ν_3 intensity is predicted to increase, while the first overtone intensity shows a slight decrease from the gas phase values. This is qualitatively different from the single mode results, where all the overtone intensities were calculated to increase in both matrices, although on the absolute scale the differences are quite small. As a consequence, the agreement of the VCI BPW91/cc-pVDZ/CPCM results with the Ar and pH₂ matrix data is again excellent. The second overtone intensities again exhibit considerable

increase with respect to the gas phase, even greater than those calculated in the single mode approximation. The third overtone intensity is predicted to increase in the Ar matrix, but decrease in pH₂, while in the single mode treatment a slight increase was predicted for both matrices.

Table S9: VCI IR absorption intensities (in km.mol⁻¹) of the ν_3 mode (C=O stretch) in *trans*-FA and its overtones.

Level	fundamental	1 st overtone	2 nd overtone	3 rd overtone
B3LYP/6-311++G(d,p)	307	4.17	4.68x10 ⁻²	2.52x10 ⁻³
BPW91/cc-pVDZ	216	3.24	3.72x10 ⁻²	2.90x10 ⁻³
MP2/6-311++G(d,p)	240	2.16	2.75x10 ⁻²	1.69x10 ⁻³
CCSD(T)/6-311++G(d,p) ^a	337	2.86	3.32x10 ⁻²	3.45x10 ^{-3 a}
Experiment (gas phase) ^b	231 (100%)		2.08 (0.9%)	
BPW91/cc-pVDZ/CPCM(Ar) ^c	279 (100%)	3.20 (1.1%)	7.19 x10 ⁻²	3.33x10 ⁻³
Experiment (Ar) ^d	100%	1.4%		
BPW91/cc-pVDZ/CPCM(pH ₂) ^c	266 (100%)	3.17 (1.2%)	7.52 x10 ⁻²	2.33 x10 ⁻³
Experiment (pH ₂)	280±20 (100%)	3±2 (1%)		

^a Molecular dipole moments calculated at CCD/6-311++G(d,p) level.

^b Fundamental from Refs. 16 and 17, 2nd overtone calculated from the relative intensity (shown in parentheses) according to Ref. 12

^c Relative intensities (with respect to the fundamental) shown for easier comparison with experiment.

^d Ref. 14, only relative intensity values are available

S7. Spectral Frequencies and IR Intensities for the ν_1 - ν_9 fundamental transitions

The single mode BPW91/cc-pVDZ ν_1 - ν_9 fundamental frequencies (**Table S10**) are generally predicted lower than the experimental values, with the exception of ν_3 and ν_8 , which exactly reproduce the experimental data. The most significantly underestimated are the frequencies for ν_1 and ν_2 vibrations. The corresponding IR absorption intensities are shown in **Table S11**, including the corrected values for the anharmonic ZPE contribution of the remaining vibrational modes. The gas phase experimental values are estimated from relative intensities¹² as discussed in above and in the main text. The ZPE correction can have a significant effect, especially on the ν_3 intensity, which is nevertheless calculated much too low, as also seen in the VCI result (**Table S13** below). The ν_3 , ν_4 , ν_6 and ν_9 fundamental intensities are in a reasonably good agreement with the experiment, but for the remaining modes the predictions underestimate the experimental values.

Table S10. Harmonic and anharmonic frequencies (in cm^{-1}) for nine fundamental transitions of *trans*-FA computed in the single mode approximation at the BPW91/cc-pVDZ level.

	$\nu_1(\text{A}')$	$\nu_2(\text{A}')$	$\nu_3(\text{A}')$	$\nu_4(\text{A}')$	$\nu_5(\text{A}')$	$\nu_6(\text{A}')$	$\nu_8(\text{A}'')$	$\nu_9(\text{A}'')$	$\nu_7(\text{A}')$
Harmonic	3559	2958	1787	1353	1270	1090	1003	700	603
Fundamental	3387	2840	1777	1359	1265	1085	1033	835	610
Experiment (gas phase) ^a	3570	2943	1777	1387	1223	1105	1033	642	625

^a Ref. 12

Table S11. Infrared intensities (in km.mol^{-1}) for the nine fundamental transitions of *trans*-FA calculated in the single mode approximation at the BPW91/cc-pVDZ level including correction for contribution of the ZPE states of remaining vibrational modes.

	$\nu_1(\text{A}')$	$\nu_2(\text{A}')$	$\nu_3(\text{A}')$	$\nu_4(\text{A}')$	$\nu_5(\text{A}')$	$\nu_6(\text{A}')$	$\nu_8(\text{A}'')$	$\nu_9(\text{A}'')$	$\nu_7(\text{A}')$
Harmonic	31.1	62.3	288	2.5	7.4	205	3.49	122	42.0
Fundamental	23.8	74.3	279	1.1	10.6	201	3.73	117	39.6
Fundamental (ZPE corrected)	55.4	77.9	209	3.0	13.9	168	5.63	120	30.8
Experiment (gas phase) ^a	189	162	231	2.31	73.9	208	20.8	171	115
	(82%)	(70%)	(100%)	(10%)	(32%)	(90%)	(9%)	(74%)	(50%)

^a Absolute intensity for ν_3 from Refs. 16 and 17, for the remaining modes calculated from the relative intensities (in parentheses) according to Ref. 12 (also see **Table S7**)

VCI calculations. The VCI anharmonic frequencies (**Table S12**) obtained by post-HF methods outperform the DFT, in particular the BPW91. The frequency shift due to anharmonic corrections is systematically greater in the VCI treatment than in the single mode approximation (**Table S3** above), where the experimental C=O stretching frequency was exactly reproduced by BPW91/cc-pVDZ, but overestimated by all other methods that were used for VCI calculations. In the solid matrices the BPW91/cc-pVDZ predict a significant drop in the OH stretching frequency with respect to the gas phase (150 cm^{-1} in Ar, 110 cm^{-1} in pH_2) compared to a much smaller $\sim 20 \text{ cm}^{-1}$ experimental decrease in both media. The change in the ν_2 vibrational frequency is calculated even qualitatively wrong. The trends for the remaining modes are approximately correct, although the matrix effects are also very small and thus comparable with computational errors.

The trends in the VCI computed intensities (**Table S13**) are very similar to those observed for the single mode BPW91/cc-pVDZ calculations (**Table S11** above). The VCI BPW91/cc-pVDZ intensities agree very well with the ZPE corrected single mode results. In Ar and pH_2 the BPW91/cc-pVDZ/CPCM predicts a significant increase in all fundamental intensities, except ν_2 , which decreases by $\sim 10 \text{ km.mol}^{-1}$ with respect to the gas phase. Compared to the experimental data, the OH stretch intensity is lower than experiment in both cases by about a factor of 2. By contrast, the ν_2 intensity is computed too high, also approximately two-fold, which indicates that its value is likely significantly overestimated even for the gas phase FA. For the remaining modes ($\nu_3 - \nu_9$), the predicted intensities are in a very good agreement with the matrix isolation experimental data. In particular, the correspondence of the absolute intensity values computed and measured in the pH_2 matrix is remarkable.

Table S12: VCI vibrational frequencies (in cm^{-1}) of the nine fundamental transitions in *trans*-FA.

Level	$\nu_1(\text{A}')$	$\nu_2(\text{A}')$	$\nu_3(\text{A}')$	$\nu_4(\text{A}')$	$\nu_5(\text{A}')$	$\nu_6(\text{A}')$	$\nu_8(\text{A}'')$	$\nu_9(\text{A}'')$	$\nu_7(\text{A}')$
B3LYP/6-311++G(d,p)	3581	2913	1793	1372	1244	1082	1026	424	611
BPW91/cc-pVDZ	3364	2807	1754	1317	1229	1060	976	500	582
MP2/6-311++G(d,p)	3652	2996	1781	1396	1261	1100	1037	423	616
CCSD(T)/6-311++G(d,p)	3637	2946	1784	1388	1275	1099	1031	410	613
Experiment (gas phase) ^a	3570	2943	1777	1387	1223	1105	1033	642	625
BPW91/cc-pVDZ/CPCM(Ar)	3213	2784	1741	1315	1229	1059	979	500	583
Experiment (Ar) ^b	3548	2955	1768	1382	1215	1104	1038	635	629
BPW91/cc-pVDZ/ CPCM(pH ₂)	3250	2791	1744	1315	1230	1059	979	503	582
Experiment (pH ₂) ^c	3554	2942	1769	1381	1218 ^d	1107	1035	-	-

^a Ref. 12^b Ref. 11 and 14 (Note: several values are reported, average is used)^c Ref. 1^d nH₂ value, Ref. 15**Table S13:** VCI IR absorption intensities (in km.mol^{-1}) of the nine fundamental transitions in *trans*-FA.

Level	$\nu_1(\text{A}')$	$\nu_2(\text{A}')$	$\nu_3(\text{A}')$	$\nu_4(\text{A}')$	$\nu_5(\text{A}')$	$\nu_6(\text{A}')$	$\nu_8(\text{A}'')$	$\nu_9(\text{A}'')$	$\nu_7(\text{A}')$
B3LYP/6-311++G(d,p)	24	43.3	307	1.92	22.8	264	1.13	135	46.0
BPW91/cc-pVDZ	9.56	61.2	216	2.03	13.3	151	1.81	111	44.7
MP2/6-311++G(d,p)	59.7	37.8	240	1.13	20.4	272	1.82	131	44.3
CCSD(T)/6-311++G(d,p) ^a	53.0	32.8	337	3.50	13.3	285	0.636	133	64.3
Experiment (gas phase) ^b	189	162	231	2.31	73.9	208	20.8	171	115
	(82%)	(70%)	(100%)	(10%)	(32%)	(90%)	(9%)	(74%)	(50%)
BPW91/cc-pVDZ/CPCM(Ar) ^c	45.1	52.4	279	2.4	16.6	192	2.4	126	53.6
	(16%)	(19%)	(100%)	(1%)	(6%)	(69%)	(1%)	(45%)	(19%)
Experiment (Ar) ^d	32%	8%	100%	1.9%	5.3%	76%	1.1%	50%	17%
BPW91/cc-pVDZ/CPCM(pH ₂) ^c	32.2	54.8	266	2.31	14.9	176	2.24	122	51.3
	(12%)	(20%)	(100%)	(1%)	(6%)	(66%)	(0.8%)	(46%)	(19%)
Experiment (pH ₂) ^c	50±13	20±7	280±20	3±2		170±10	1±1		
	(18%)	(7%)	(100%)	(1%)		(61%)	(0.4%)		

^a Molecular dipole moments calculated at CCD/6-311++G(d,p) level.^b Absolute intensity for ν_3 from Refs. 16 and 17, for the remaining modes calculated from the relative intensities (in parentheses) according to Ref. 12 (also see **Table S11**)^c Relative intensities (with respect to the ν_3) shown for easier comparison with experiment.^d Ref. 14, only relative intensity values are available

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