Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Infrared Action Spectroscopy of the Deprotonated Formic Acid Trimer, Trapped in Helium Nanodroplets

Martín I. Taccone,[a] Daniel Thomas,[a,b] Katja Ober,[a] Sandy Gewinner,[a] Wieland Schollkopf,[a] Gerard Meijer,[a] and Gert von Helden,*[a]

[a] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany; E-mail:helden@fhi-berlin.mpg.de

[b] Department of Chemistry, University of Rhode Island, 140 Flagg Rd., Kingston, Rhode Island 02881, United States

Table S1: Relative energies with zero-point energies correction (EE+ZPE) of the seven lowest energy conformers of deprotonated FA trimer calculated at CCSD(T)/aug-cc-pVTZ, MP2/aug-cc-pVTZ, DSDPBEP86/aug-cc-pVTZ and B3LYP-D3(BJ)/aug-cc-pVTZ levels of theory. In the case of conformers a), b) and c), energies at the MP2 level were also computed using the Complete Basis Set extrapolation scheme (CBS) with MP2/aug-cc-pVnZ (n = 3, 4 and 5) and a correction for the difference in correlation energy between CCSD(T) and MP2, with the aug-cc-pVTZ basis set. In the case of CCSD(T) and MP2/CBS, the zero-point energy corrections at the MP2/aug-cc-pVTZ level were used. All values presented are in kJ/mol.

Conformer	CCSD(T)+ZPE$_{MP2}$	MP2/CBS (ΔCCSD(T)-MP2) +ZPE$_{MP2}$	MP2	DSDPBEP86	B3LYP-D3
a	0.00	0.00	0.00	0.00	0.00
b	2.38	2.49	2.21	2.10	1.88
c	5.16	4.01	4.10	4.04	3.07
d	10.27	-	11.01	11.75	11.64
e	11.38	-	11.93	11.51	11.80
f	17.66	-	17.48	17.61	16.87
g	30.43	-	29.26	29.34	27.62

Table S2: Dipole moments of the *cis* and *trans* rotamers of the FA molecule calculated at CCSD/aug-cc-pVTZ, MP2/aug-cc-pVTZ, DSDPBEP86/aug-cc-pVTZ and B3LYP-D3(BJ)/aug-cc-pVTZ. Values from literature are also shown for comparison.

FA rotamer	CCSD	MP2	DSDPBEP86	B3LYP-D3(BJ)	Literature[1]
Cis	3.97	3.88	4.22	3.91	3.79
Trans	1.49	1.43	1.65	1.54	1.42

Table S3: Comparison between relative energies of the three lowest energy conformers of the deprotonated formic acid trimer with BSSE corrections at B3LYP-D3(BJ)/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory. All energies are in kJ/mol and corrected by the zero-point energy.

Conformer	B3LYP	B3LYP+BSSE	MP2	MP2+BSSE
a	0.00	0.00	0.00	0.00
b	1.88	1.95	2.21	3.33
c	3.07	3.07	4.10	4.11

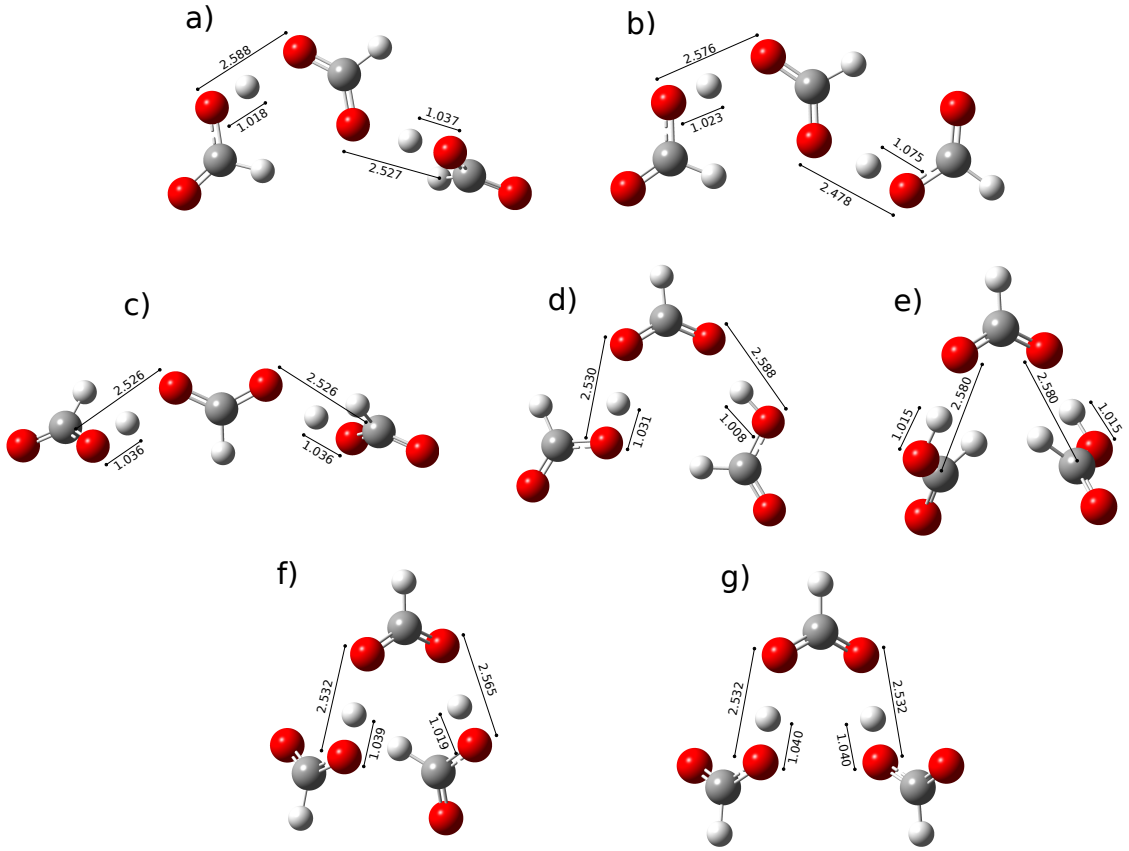

Figure S1: The lowest energy conformers of the FA trimer anion calculated at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory. The O−H bond length of the FAs and the donor-aceptor O−O distance between the FAs and the formate are shown in each structure. All values are in Å.

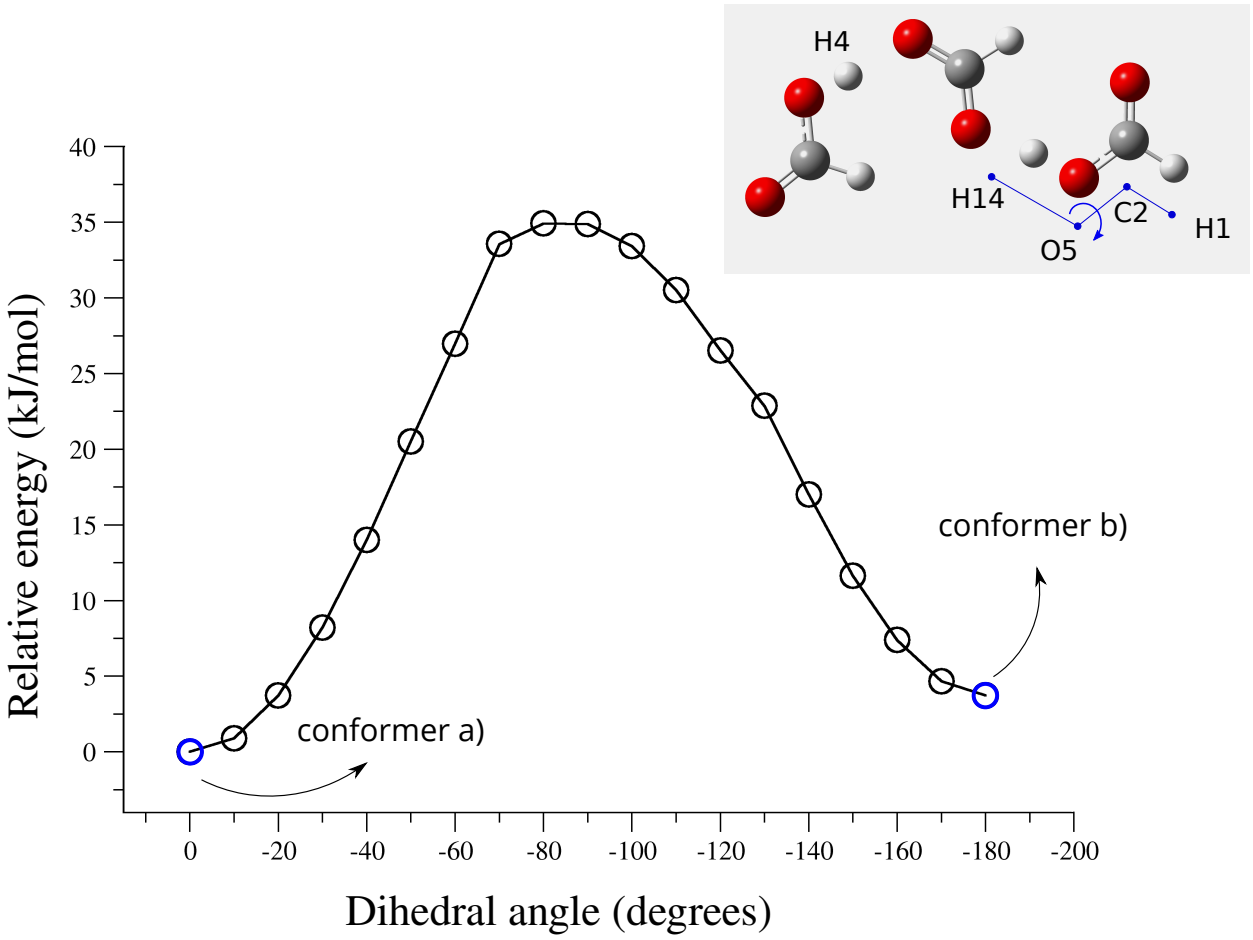

Figure S2: Relaxed potential energy curve (PEC) along the ∠(H1-C2-O5-H14) dihedral coordinate for interconversion of conformer b) to conformer a) at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory. The structures shown in the figure correspond to the blue circles marked in the PEC.

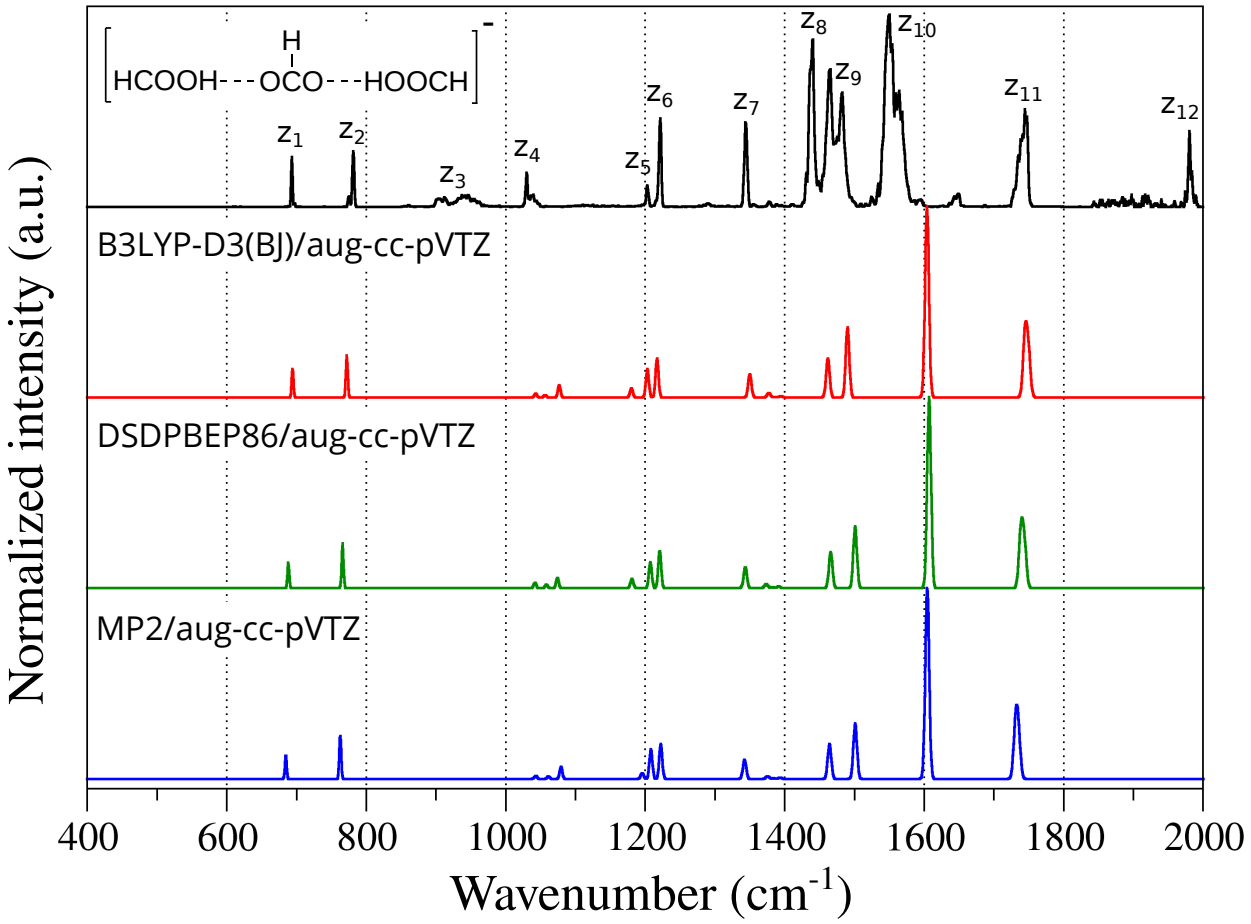

Figure S3: Comparison between experimental spectrum of the deprotonated FA trimer and the theoretical spectra of conformer a) at B3LYP-D3(BJ)/aug-cc-pvVTZ, DSDPBE0PB86/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory.

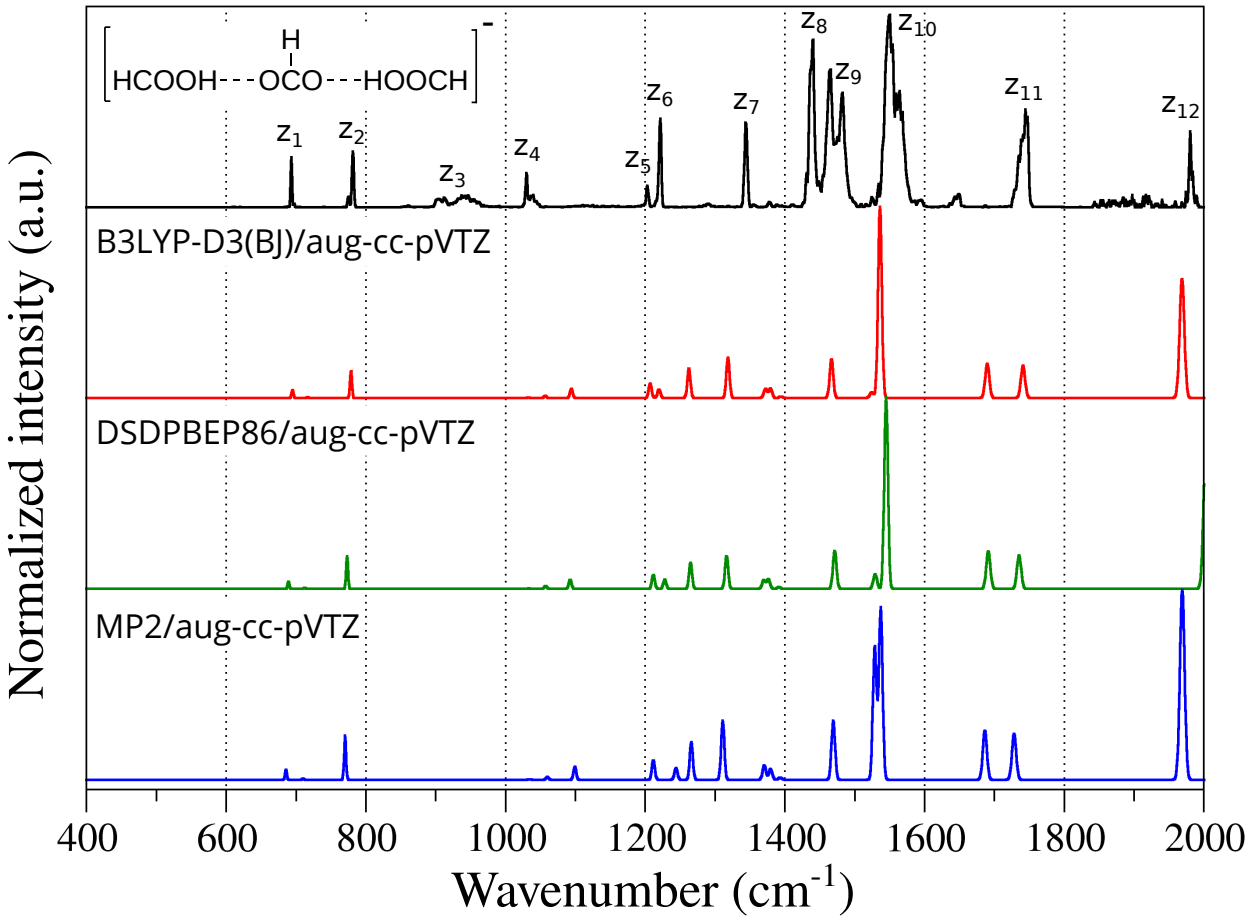

Figure S4: Comparison between experimental spectrum of the deprotonated FA trimer and the theoretical spectra of conformer b) at B3LYP-D3(BJ)/aug-cc-pvVTZ, DSDPBE0PB86/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory.

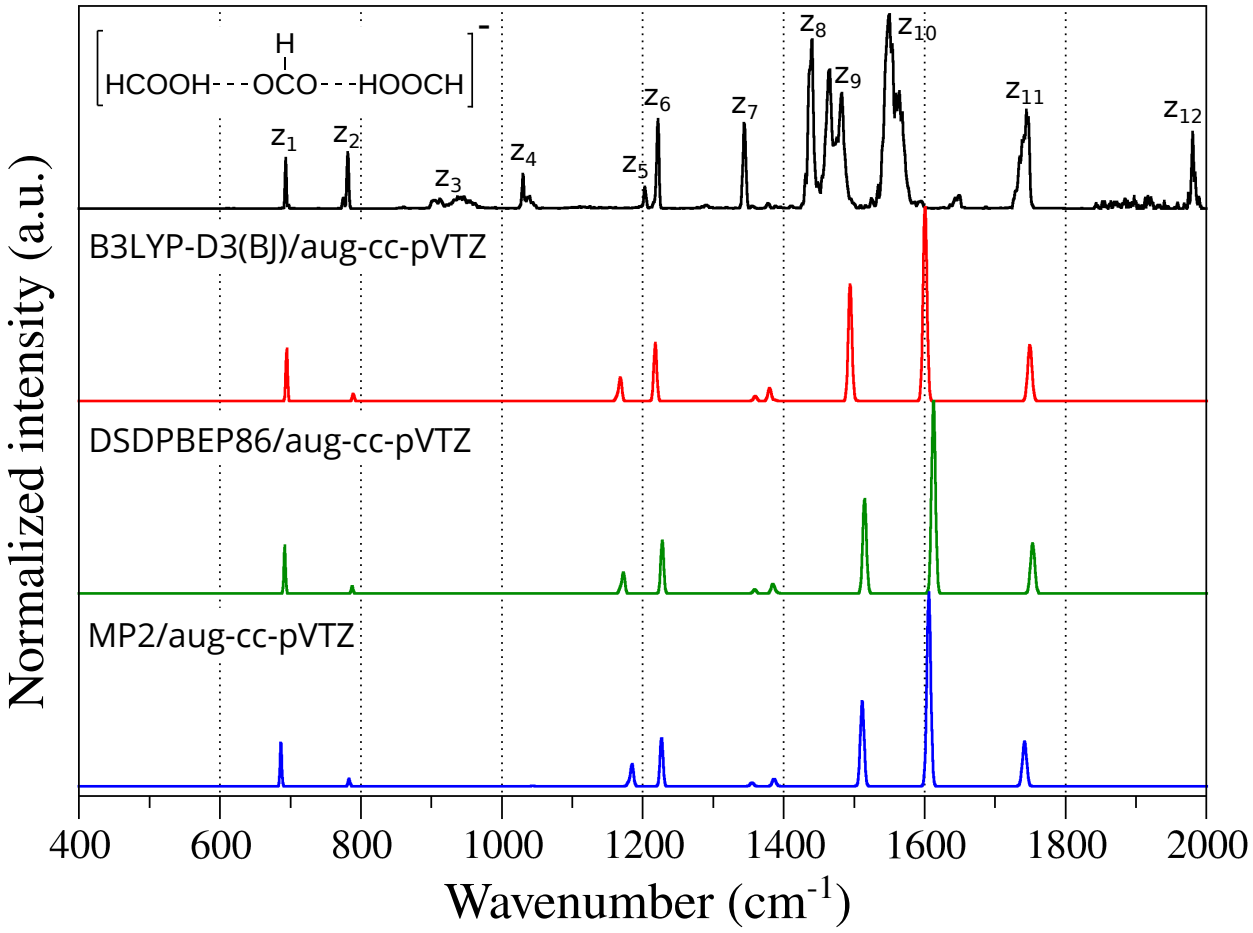

Figure S5: Comparison between experimental spectrum of the deprotonated FA trimer and the theoretical spectra of conformer c) at B3LYP-D3(BJ)/aug-cc-pvVTZ, DSDPBE0PB86/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory.

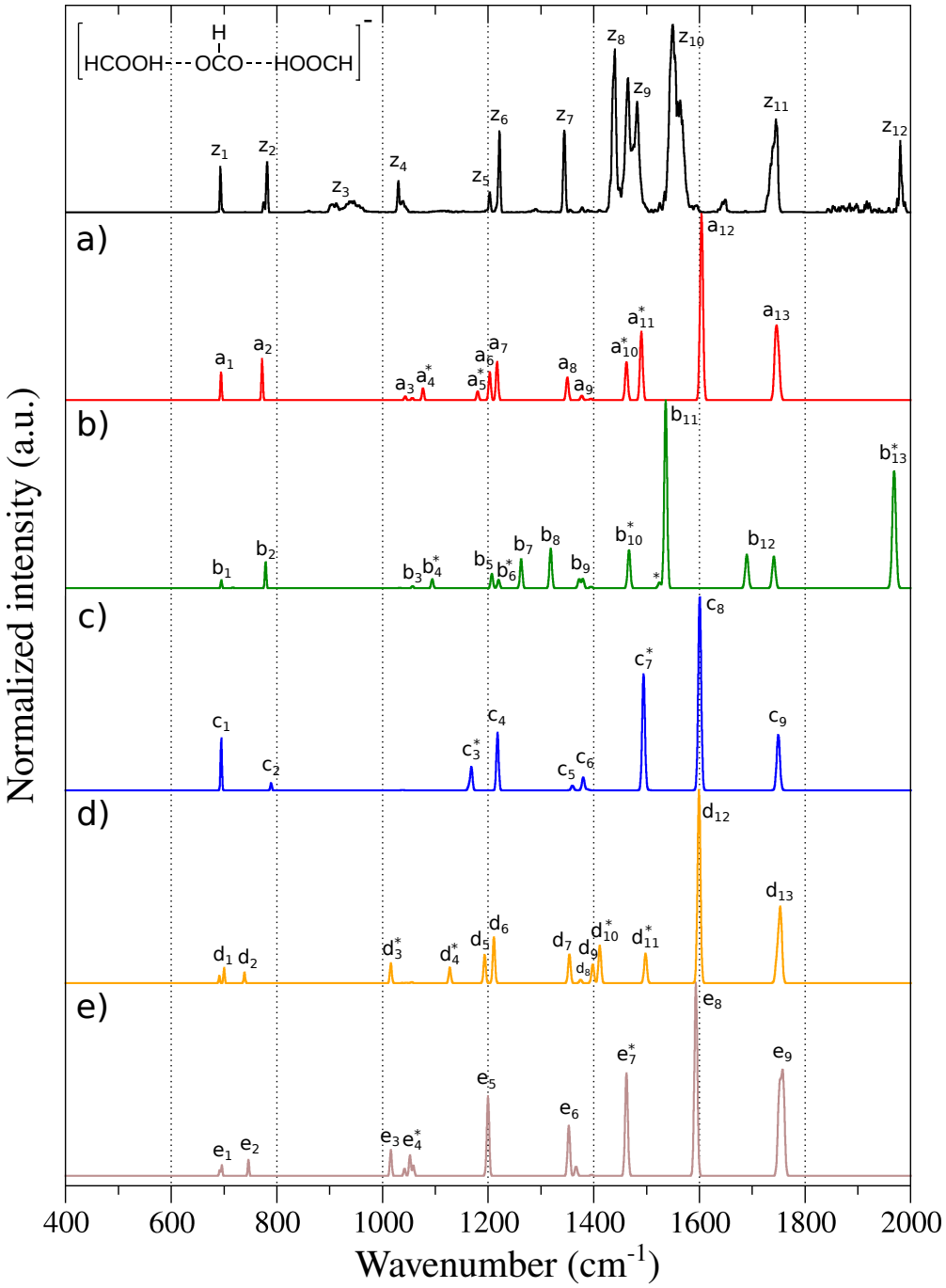

Figure S6: Experimental IR spectra of the $[FAc_3]^-$ (black) in comparison with theoretical harmonic IR spectra of conformers a) to e) calculated at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory. The label in the upper-left corner of each graph corresponds to the structures a) to e) from Figure S1. For discussion purposes, relevant features are marked with numbered letters in each graph. Vibrational modes related to the exchangeable protons displacement are also marked with an asterisk.

Table S4: Vibrational assignment of computed frequencies at B3LYP/aug-cc-pVTZ level of theory, for all structures considered in this work. All values are in cm^{-1}

Vibrational mode	Conformer				
	a)	b)	c)	d)	e)
ν(CH)	2927	2928	2875	2937	2910
	2874	2889	2874	2879	2910
	2817	2863	2801	2790	2834
ν(OH)	2739	2670	2481	2910	2774
	2428	1968	2408	2519	2747
ν(C=O)	1749	1741	1750	1753	1753
	1745	1690	1749	1747	1751
$\nu_{as}(COO^-)$	1604	1536	1600	1599	1593
δ_{ip}(OH)	1490	1524	1502	1498	1463
	1461	1467	1494	1411	1461
δ_{oop}(CH)	1395	1395	1388	1398	1396
	1387	1379	1387	1387	1395
	1377	1372	1380	1375	1366
$\nu_{sym}(COO^-)$	1349	1318	1359	1354	1353
ν(C−OH)	1217	1262	1218	1211	1200
	1204	1207	1217	1193	1197
δ_{oop}(OH)	1180	1220	1168	1127	1058
	1176	1094	1164	1016	1052
δ_{oop}(CH)	1056	1065	1050	1055	1044
	1043	1057	1038	1045	1042
	1038	1032	1038	1038	1016
$\delta(COO^-)$	772	789	789	739	746
δ(COOH)	694	717	695	700	696
	694	695	693	691	692

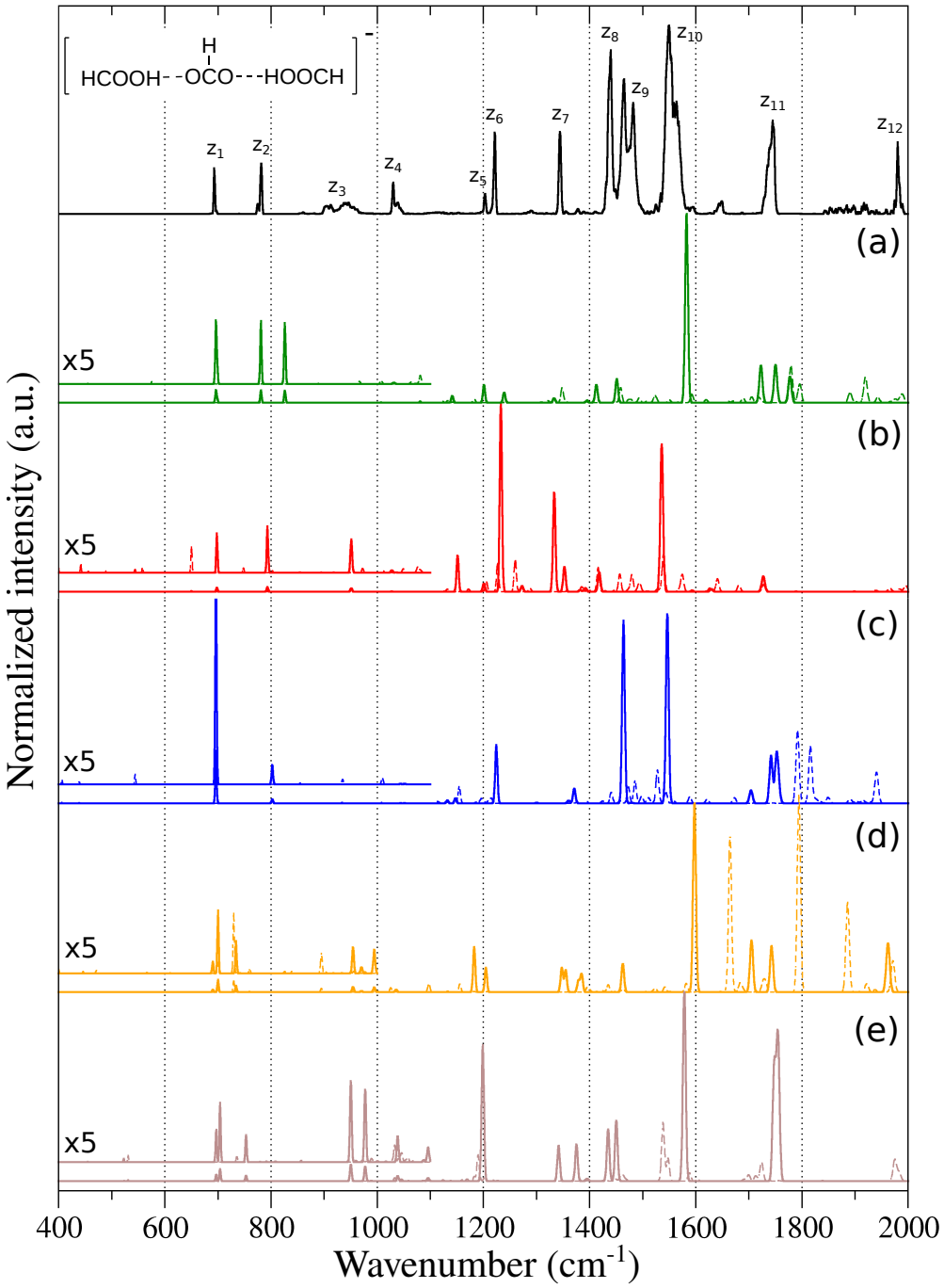

Figure S7: Experimental IR spectra of the $[FAc_3]^-$ (black) in comparison with theoretical anharmonic (VPT2) IR spectra for conformers a) to e), at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory. The label in the upper-right corner of each graph correspond structures a) to e) from Figure S1. Fundamentals bands are plot as solid lines, while combinations and overtones bands are plot as dashed lines.

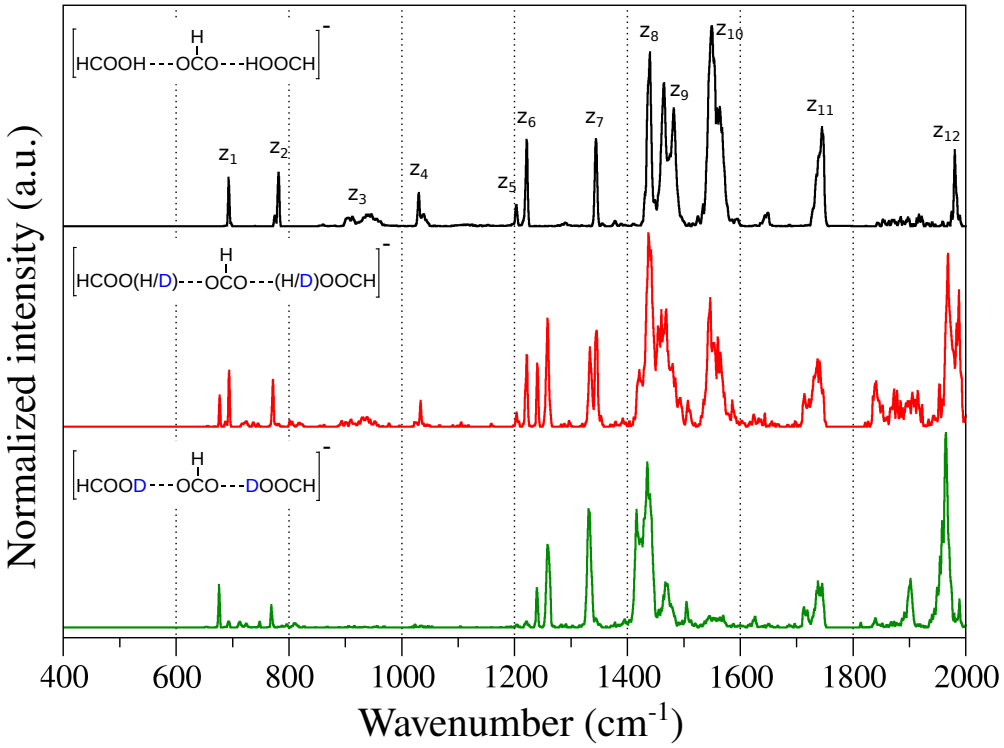

Figure S8: Experimental IR spectra of the $[FAc_3]^-$ with deuterium isotopic exchange, in the 400 - 2000 cm^{-1} spectral region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the exchangeable proton displacement are also marked with an asterisk.

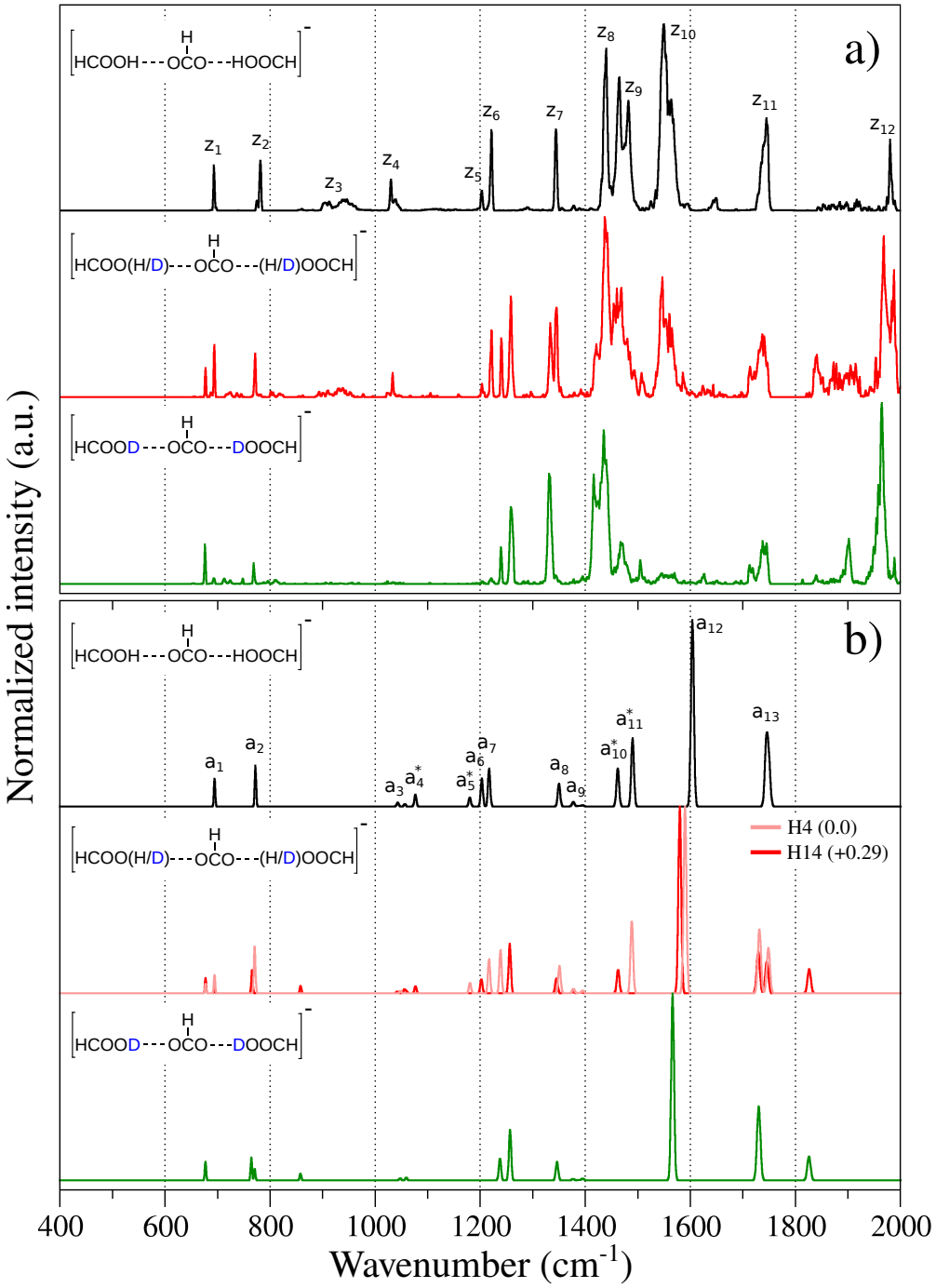

Figure S9: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Black, red, light red and green traces correspond to the theoretical spectra of conformer a) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. Vibrational modes related to the acid protons displacements are marked with a black asterisk. Blue asterisks mark strongly coupled ν(OD)/δ(OCH) vibrational modes. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

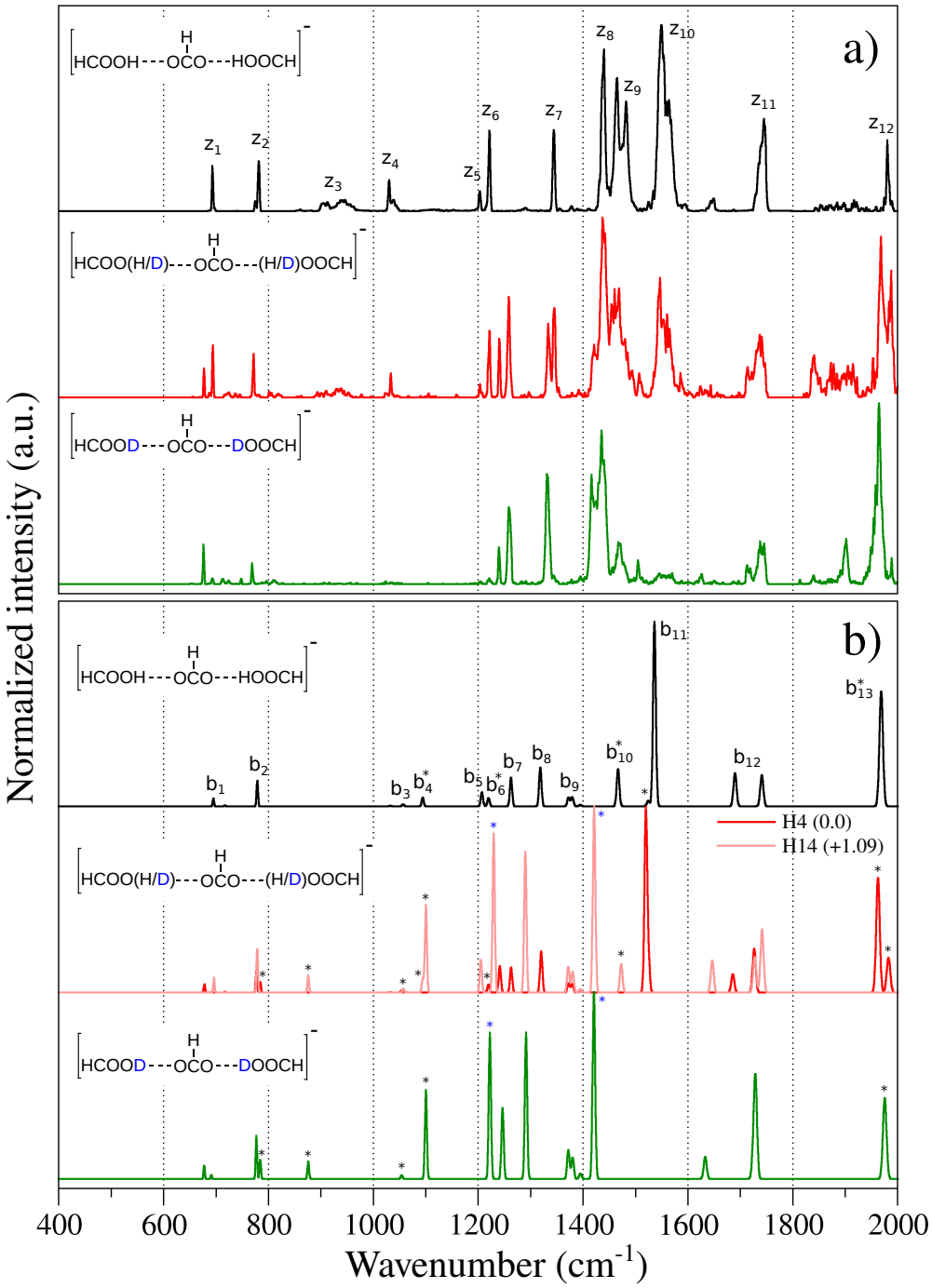

Figure S10: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Black, red, light red and green traces correspond to the theoretical spectra of conformer b) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

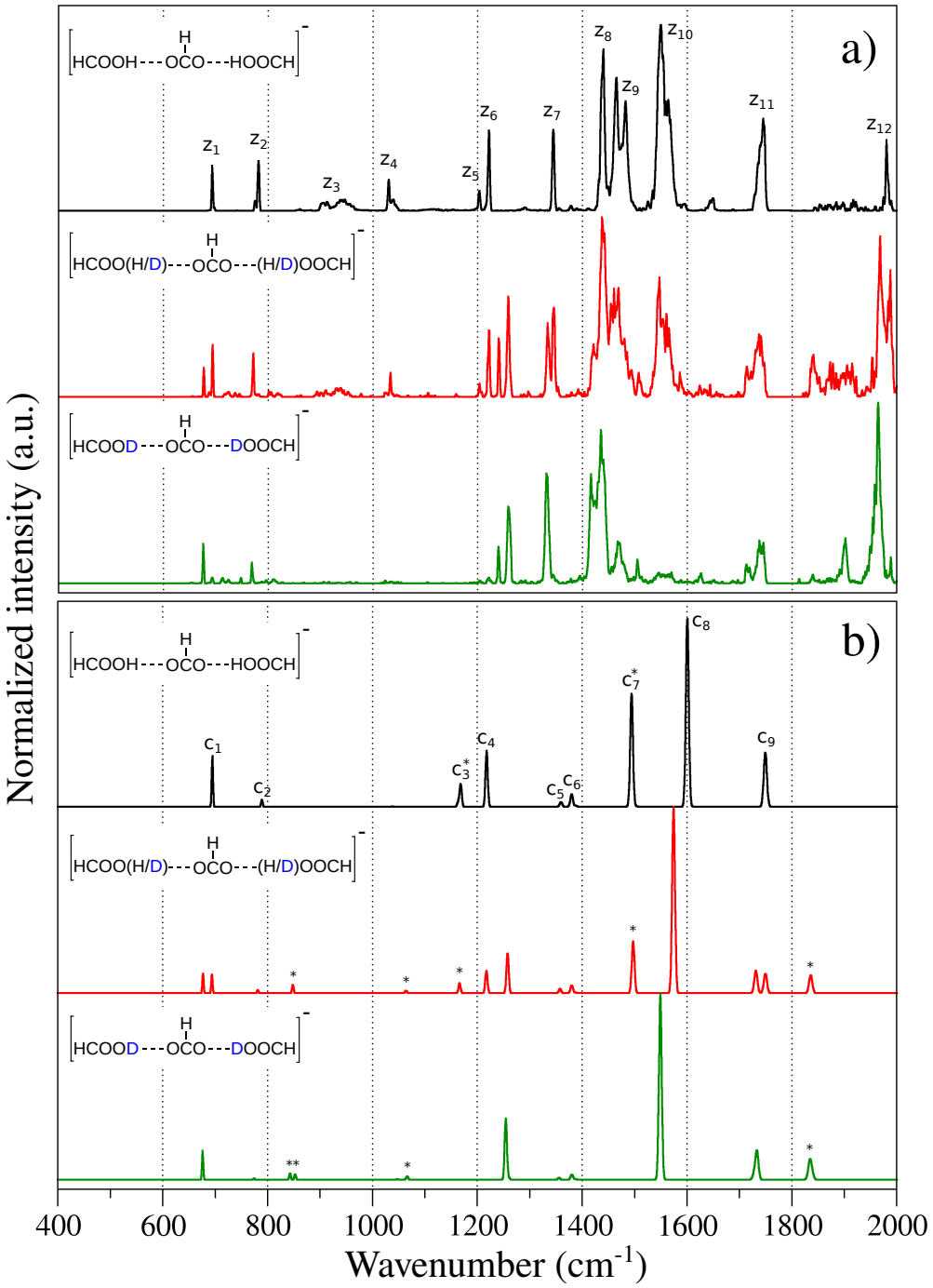

Figure S11: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Black, red, light red and green traces correspond to the theoretical spectra of conformer c) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

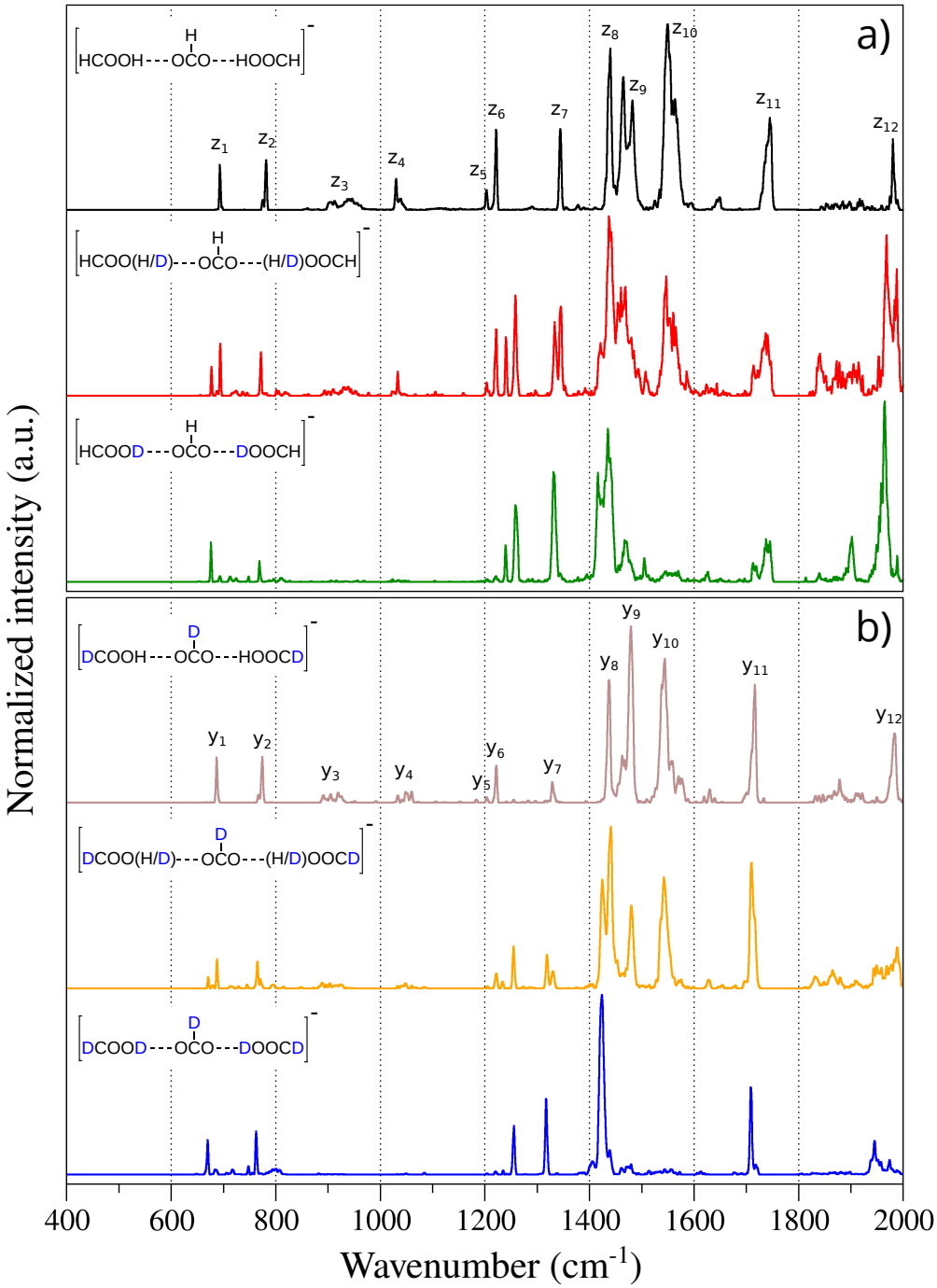

Figure S12: Experimental IR spectra of the $[FAc_3]^-$ and $[^2H\text{-}FAc_3]^-$ with its deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Brown, orange and blue traces correspond to the experimental spectra of $[^2H\text{-}FAc_3]^-$, $[^2H\text{-}FAc_3]^-$ with one deuteron and $[^2H\text{-}FAc_3]^-$ with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph.

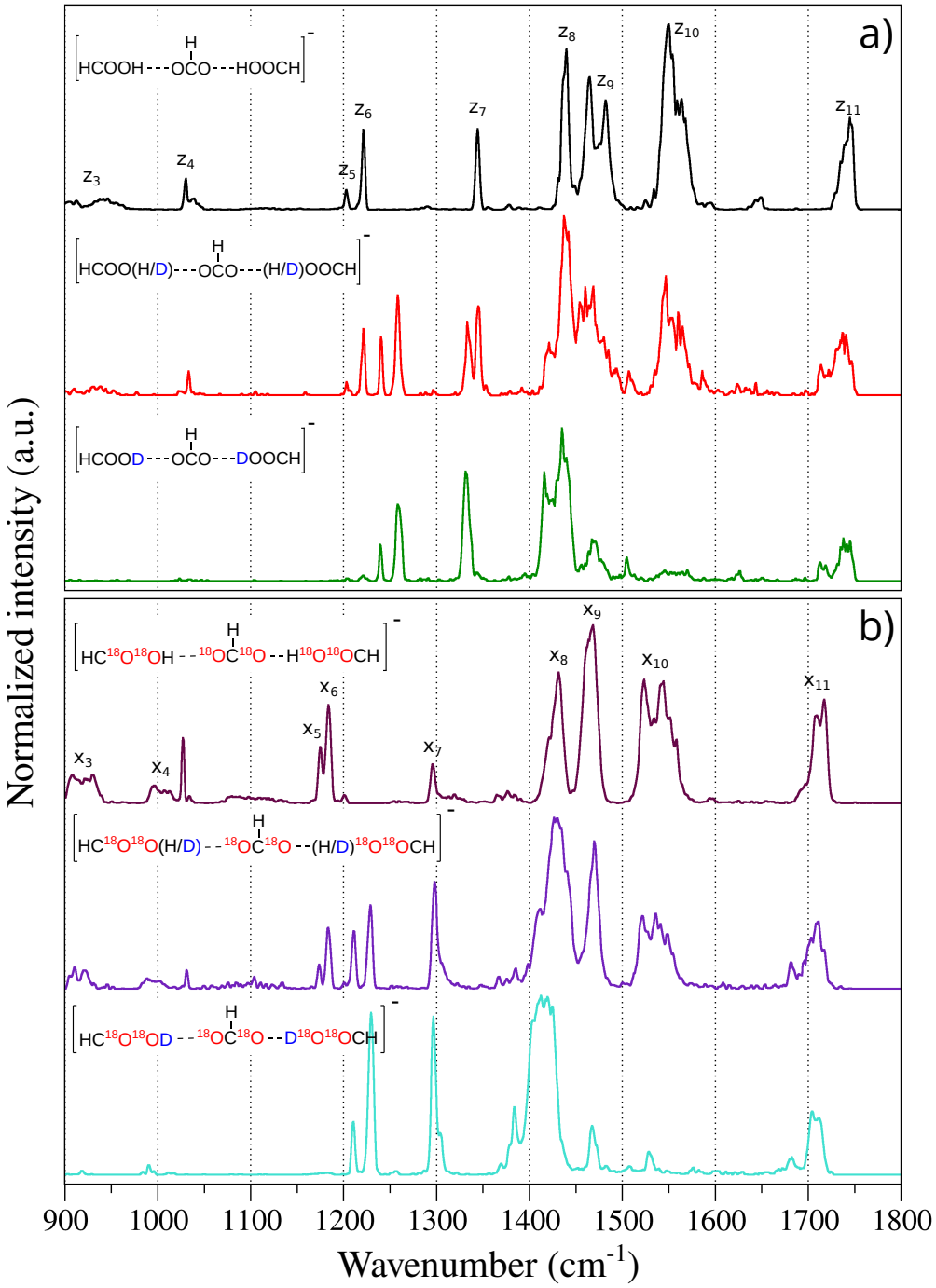

Figure S13: Experimental IR spectra of the $[FAc_3]^-$ and $[^{18}O\text{-}FAc_3]^-$ with its deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Black, red and green traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Maroon, violet and light blue traces correspond to the experimental spectra of $[^{18}O\text{-}FAc_3]^-$, $[^{18}O\text{-}FAc_3]^-$ with one deuteron and $[^{18}O\text{-}FAc_3]^-$ with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph.

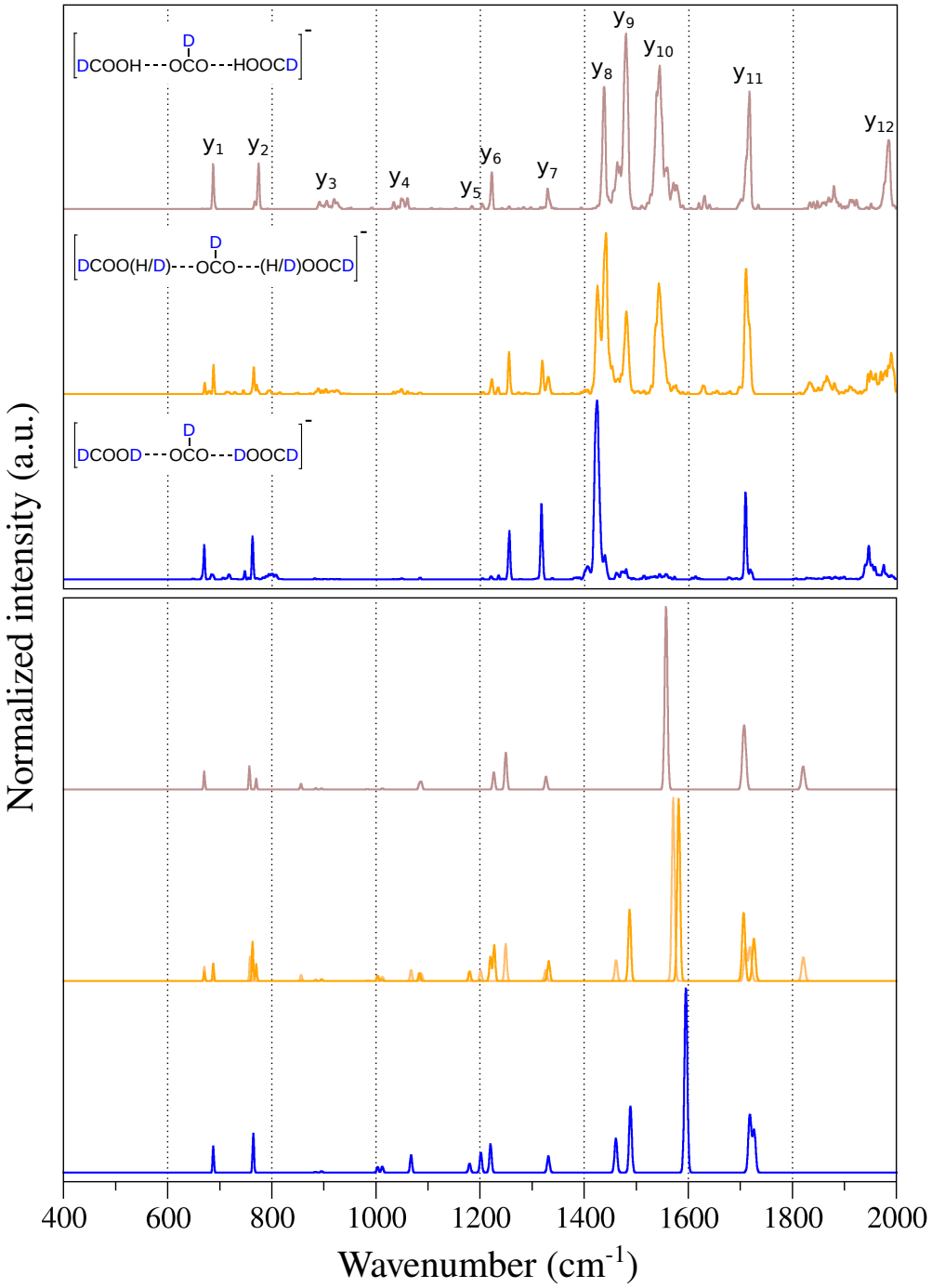

Figure S14: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Brown, orange and blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Brown, orange, light orange and blue traces correspond to the theoretical spectra of conformer a) from Figure 2 in the Manuscript, with one deuteron at H4 position, with one deuteron at H14 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

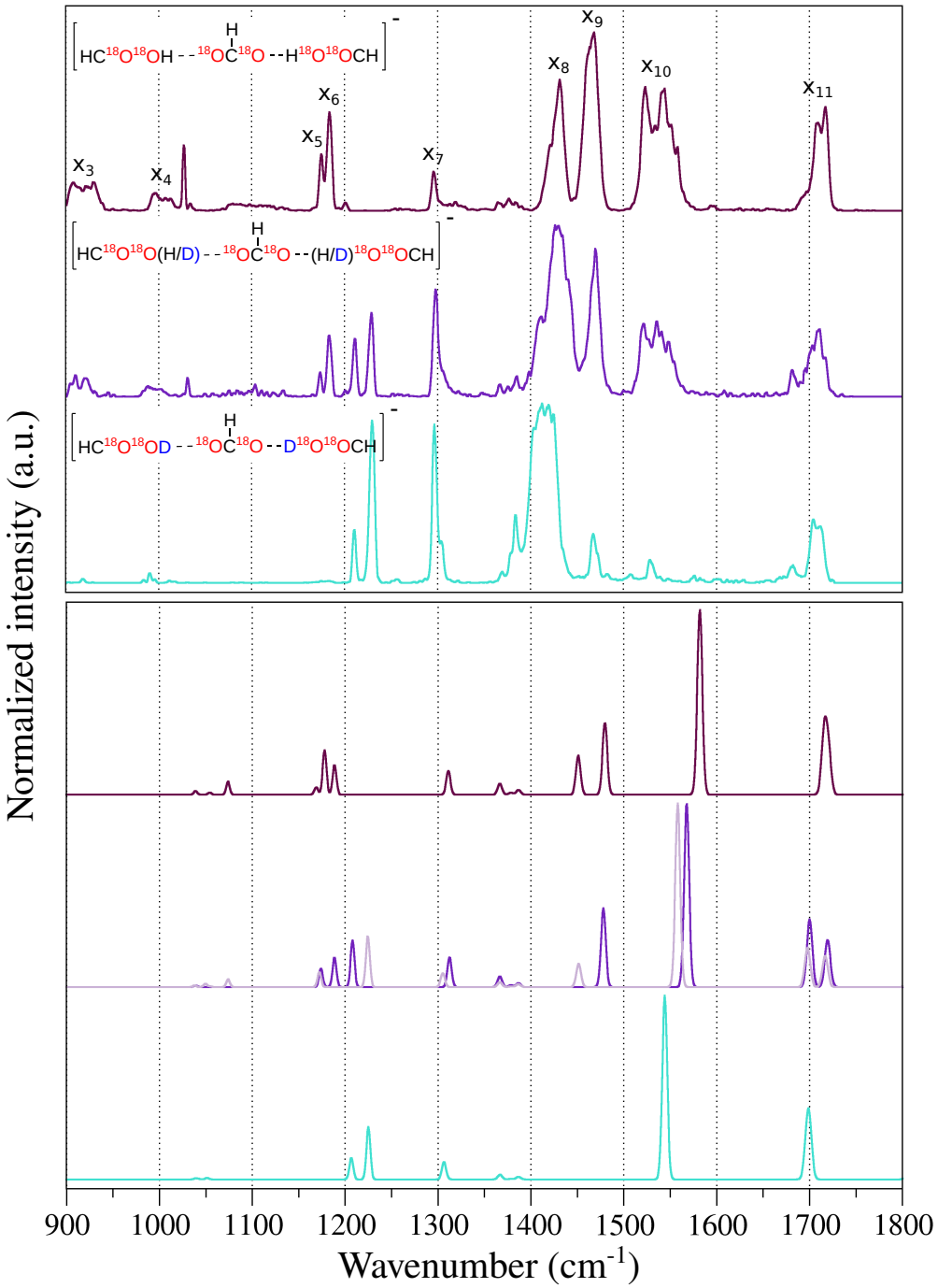

Figure S15: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Maroon, violet and light blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Maroon, violet, light violet and light blue traces correspond to the theoretical spectra of conformer a) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

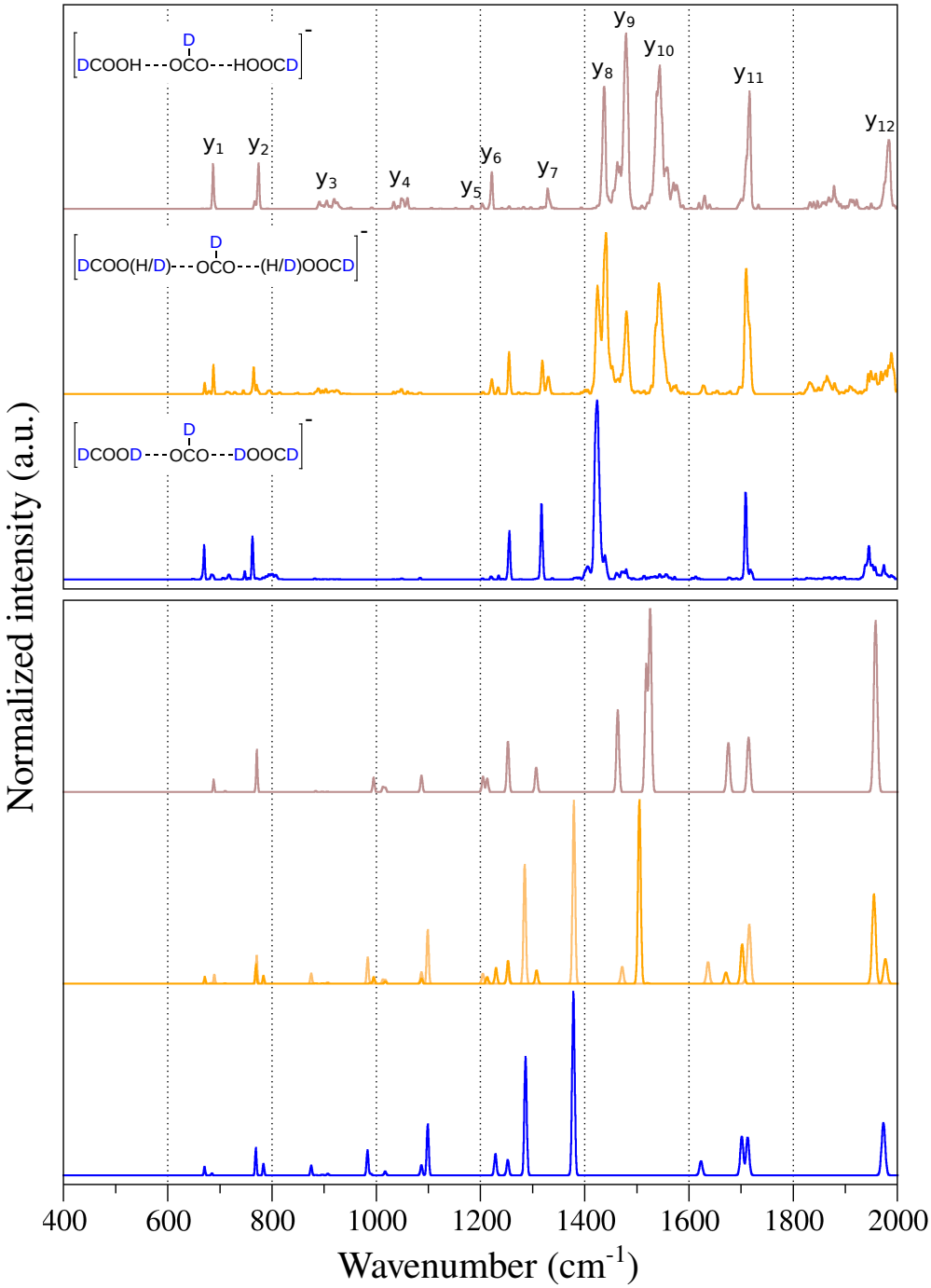

Figure S16: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Brown, orange and blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Brown, orange, light orange and blue traces correspond to the theoretical spectra of conformer b) from Figure 2 in the Manuscript, with one deuteron at H4 position, with one deuteron at H14 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

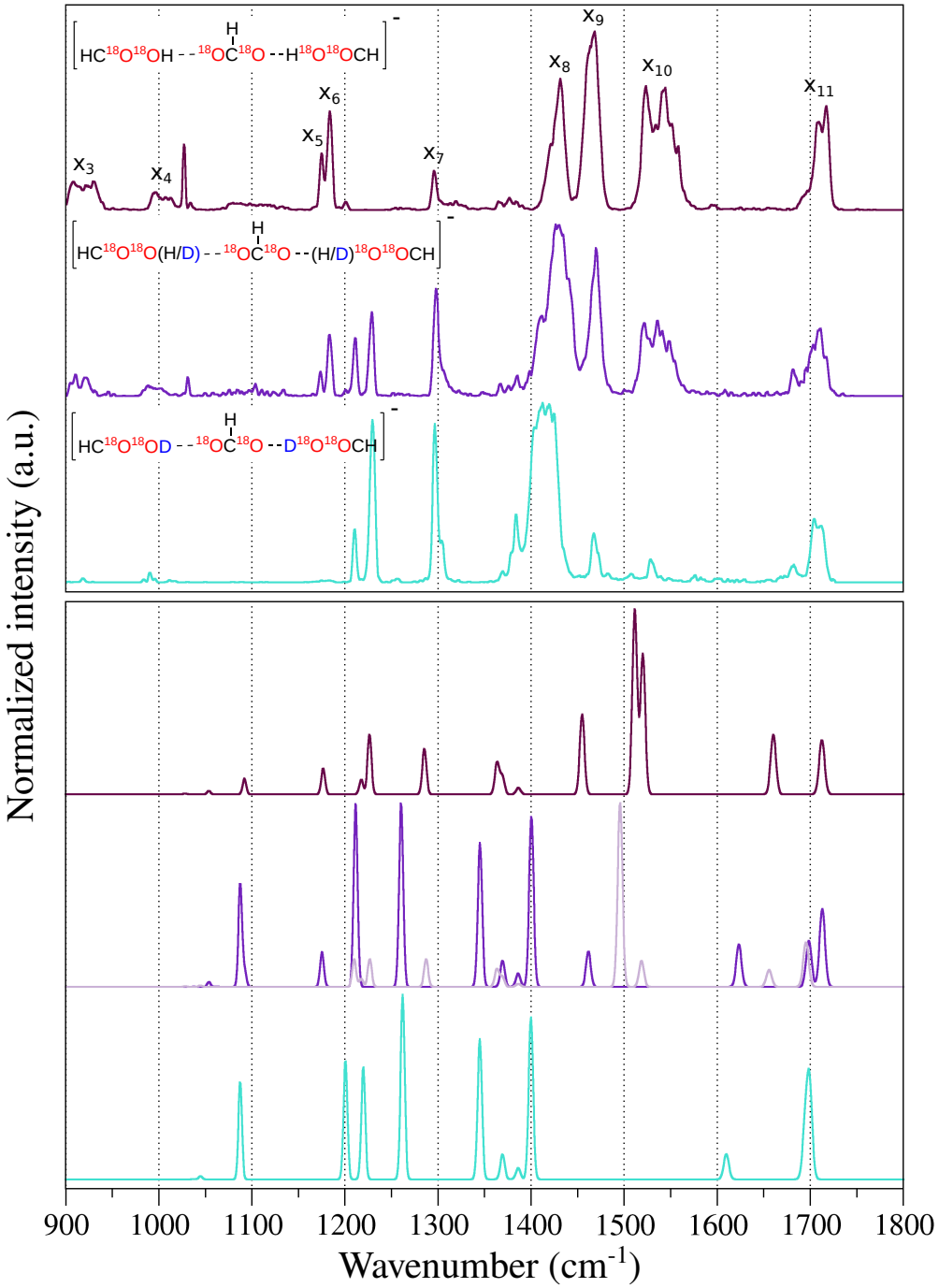

Figure S17: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Maroon, violet and light blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Maroon, violet, light violet and light blue traces correspond to the theoretical spectra of conformer b) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

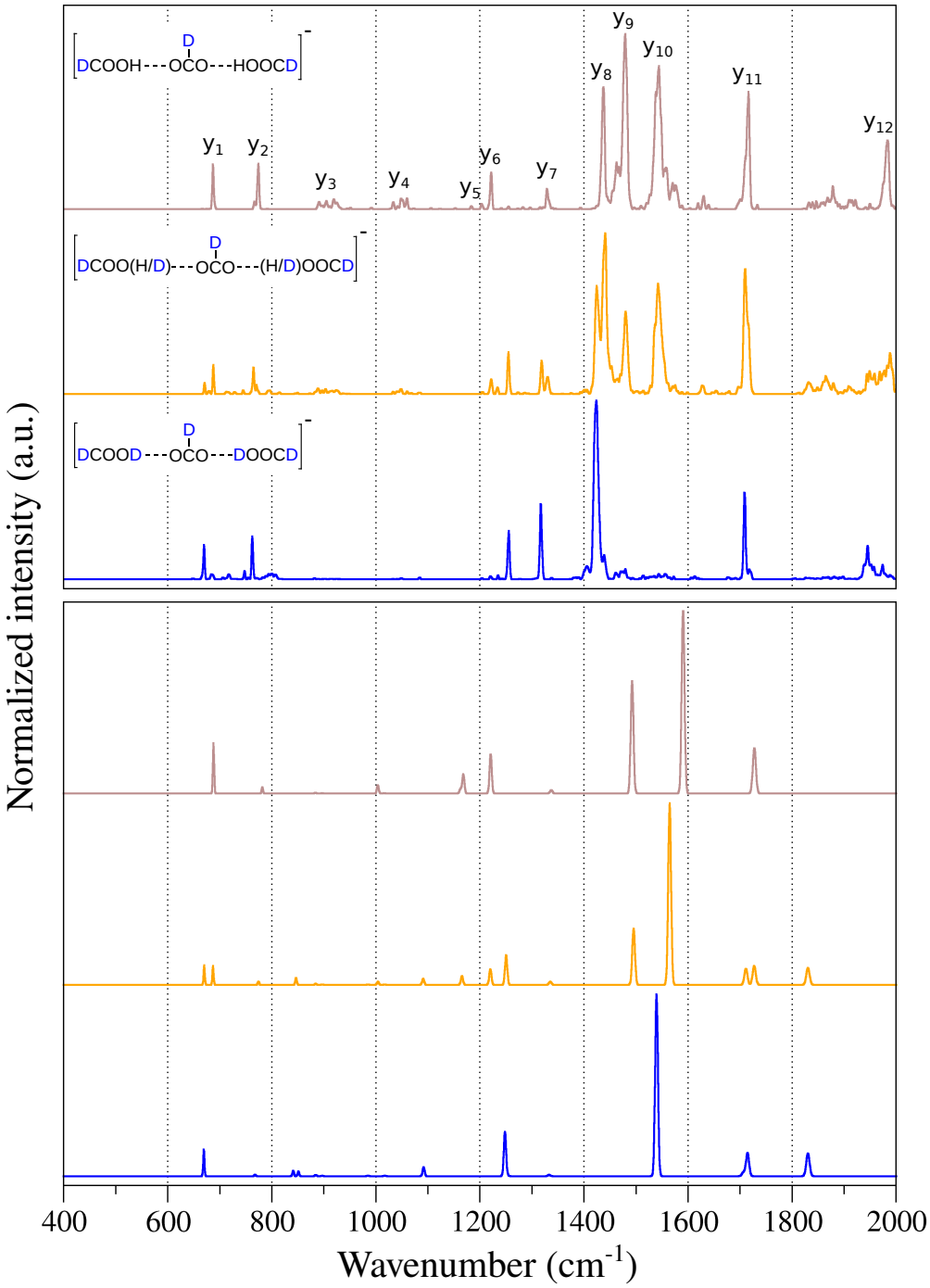

Figure S18: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Brown, orange and blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Brown, orange, light orange and blue traces correspond to the theoretical spectra of conformer c) from Figure 2 in the Manuscript, with one deuteron at H4 position, with one deuteron at H14 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

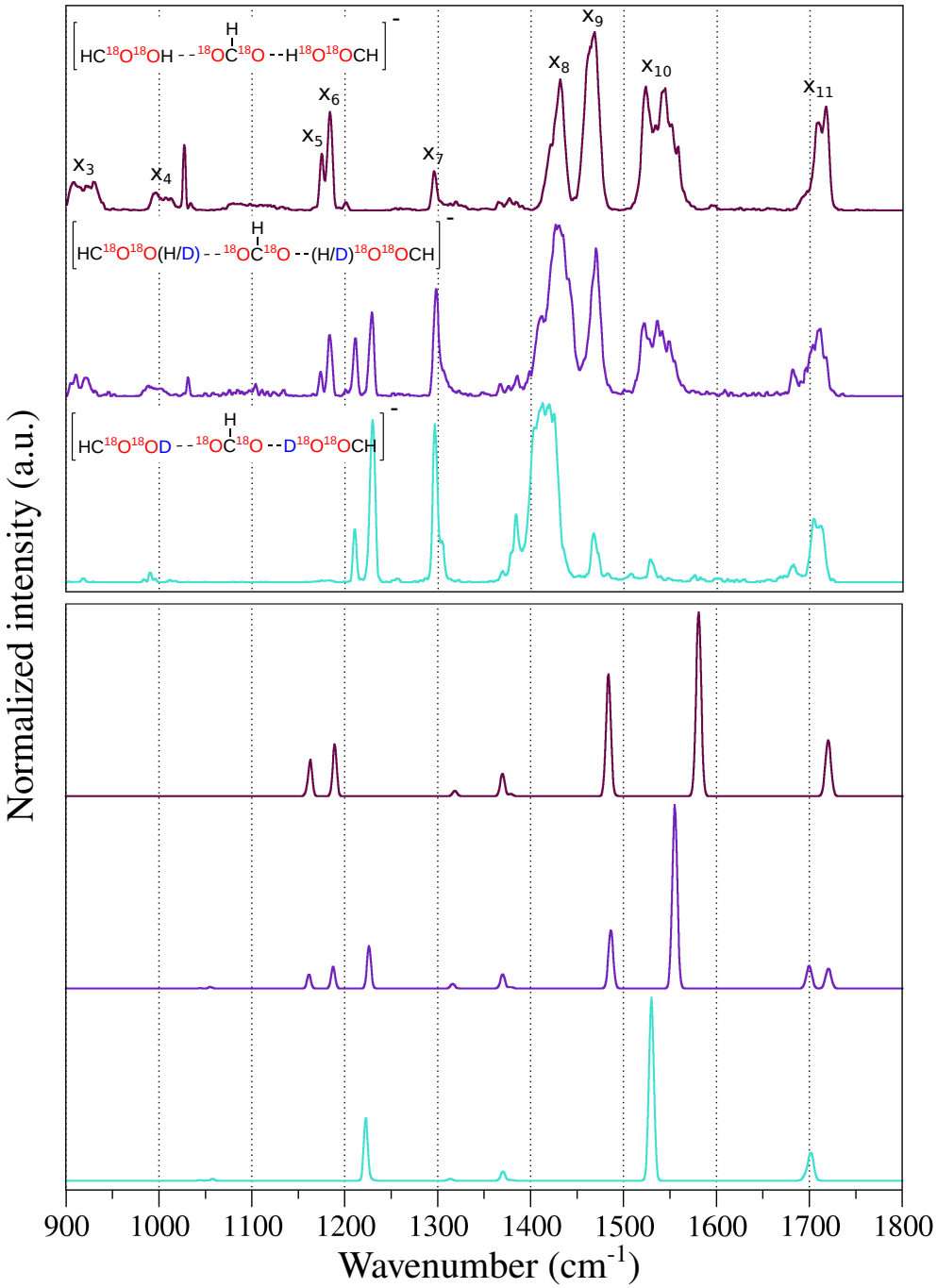

Figure S19: Experimental and theoretical IR spectra of the $[FAc_3]^-$ and deuterium isotopic exchange spectra in the 400 - 2000 cm^{-1} region. (a) Maroon, violet and light blue traces correspond to the experimental spectra of $[FAc_3]^-$, $[FAc_3]^-$ with one deuteron and $[FAc_3]^-$ with two deuterons, respectively. (b) Maroon, violet, light violet and light blue traces correspond to the theoretical spectra of conformer c) from Figure 2 in the Manuscript, with one deuteron at H14 position, with one deuteron at H4 position and with two deuterons, respectively. In the upper-left corner of each spectrum a scheme shows in blue the hydrogens that were exchanged by deuterons. For discussion purposes, relevant features are marked with numbered letter in each graph. Vibrational modes related to the acid proton displacement are also marked with a black asterisk. Theoretical spectra were computed at B3LYP-D3(BJ)/aug-cc-pVTZ level of theory and scaled by a factor of 0.98.

References

[1] W. H. Hocking, *Zeitschrift für Naturforschung A* **1976**, *31*, 1113–1121.