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

The stepwise hydration of $[CH_3COOMg]^+$ studied by cold ion trap infrared spectroscopy: insights into interactions in the magnesium channel selection filters

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Supporting information

S1. Experimental setup

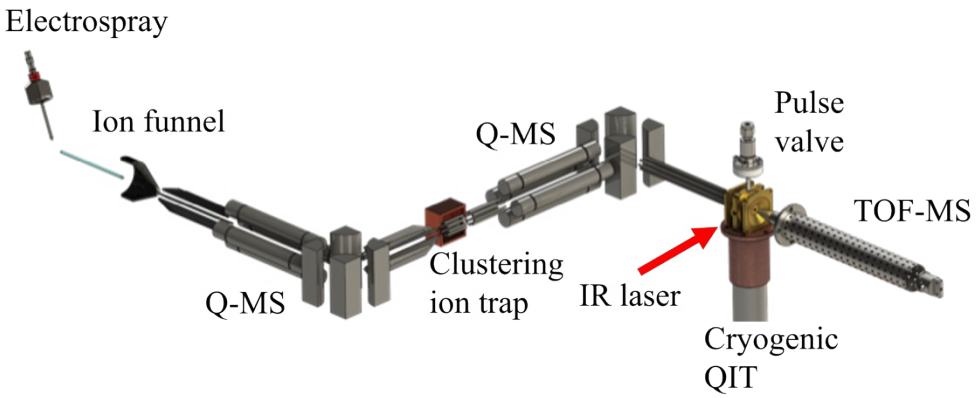

Figure S1 Experimental setup

S2. Gibbs energies of the $(CH_3COOMg)^+ \cdot (H_2O)_n$ clusters for n = 10 and 14.

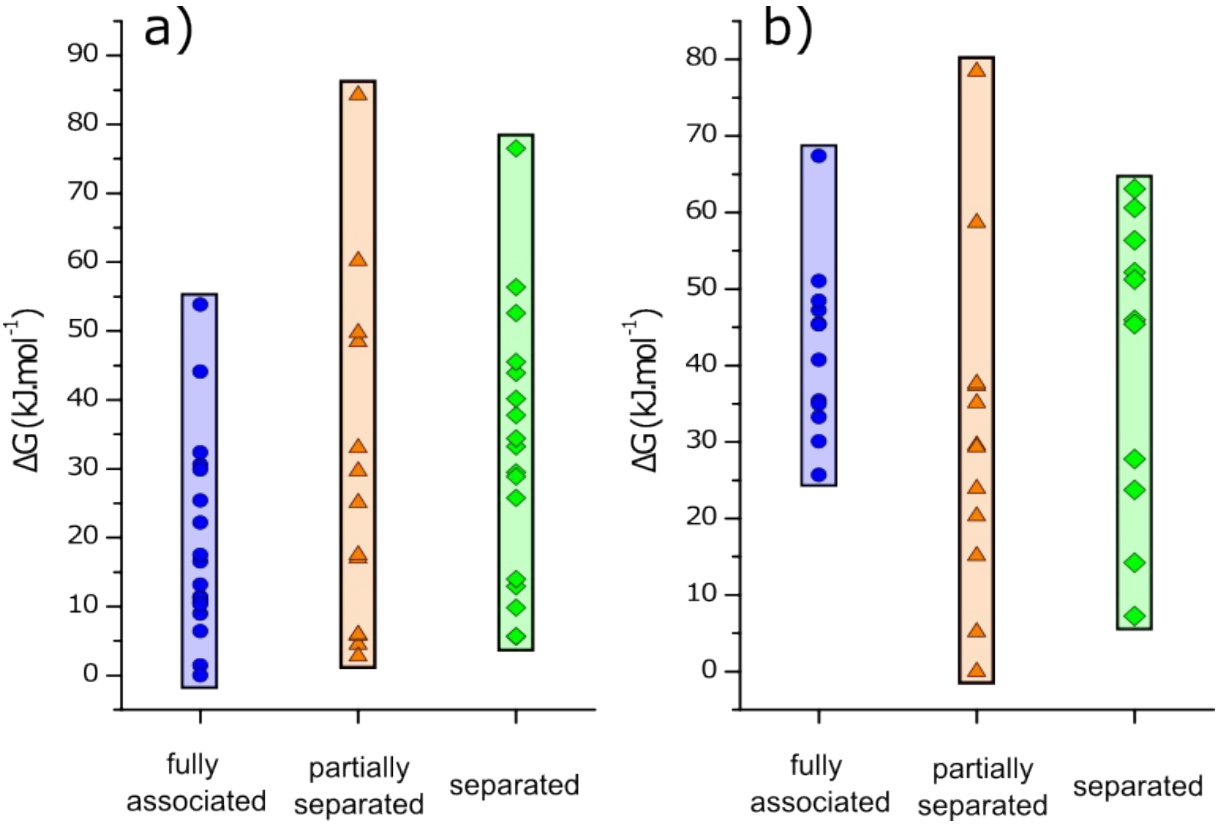

Figure S2 Gibbs energy at 130 K of $(CH_3COOMg)^+ \cdot (H_2O)_n$ clusters with n = 10 (a) and n = 14 (b) sorted according to the type of ion pairing: fully associated (blue), partially separated (orange) and separated (green).

S3. Frequency and intensity calculations

Cluster selection benefited from previous works about alkali acetate ion pairs[1] where it was determined that the carboxylate stretch frequencies are in the first place sensitive to the number and nature (cation or water molecules) of the ligands around each oxygen atom of the carboxylate group, each case defining a family of clusters sharing a common vibrational signature. For $[CH_3COOMg]^+(H_2O)_n$ clusters (n=10 and n=14), the PES is made of several low-energy minima, which cannot be exhaustively calculated with enough accuracy on their energetics to unambiguously identify which clusters populate the experiment at 130 K. Instead, we used a strategy targeting the theoretical vibrational signature of each cluster family, where the complete and exact knowledge of the PES in not required. In this context, the important points were:

- to choose a level of calculation, i.e. RI-B97-D3/dhf-TZVPP, providing quantitative frequencies in order to compare them with experiment.

- to select clusters in order (i) to get members of all the possible families and (ii) in each family, to get sufficiently different clusters (3 to 5) to simulate *a minima* the variety of the environment (made of water molecules) around the above-mentioned ligands.

- Fully associated $(CH_3COOMg)^+\cdot(H_2O)_{10}$

	ΔG (kJ mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_1^{FA}$	22	1382	2	1454	207	1464	151	1502	83	1538	463
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_2^{FA}$	31	1377	37	1440	296	1464	100	1489	13	1555	427
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_3^{FA}$	54	1381	10	1447	287	1463	110	1500	82	1539	440
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_4^{FA}$	17	1385	8	1444	268	1468	93	1503	45	1545	504
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_5^{FA}$	30	1385	4	1451	247	1467	106	1506	55	1546	561
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_6^{FA}$	25	1380	25	1437	281	1467	73	1494	31	1564	460
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_7^{FA}$	32	1380	22	1450	224	1464	182	1488	18	1548	423
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_8^{FA}$	11	1381	3	1448	209	1464	173	1497	52	1536	517
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_9^{FA}$	9	1382	5	1447	195	1475	197	1493	55	1537	538
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{10}^{FA}$	6	1383	3	1442	219	1479	134	1496	77	1536	563
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{11}^{FA}$	11	1381	17	1451	184	1470	192	1488	11	1552	422
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{12}^{FA}$	44	1385	19	1452	166	1470	291	1487	13	1542	428
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{13}^{FA}$	11	1384	3	1455	170	1470	156	1503	86	1542	471
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{14}^{FA}$	13	1382	4	1458	145	1471	146	1501	79	1553	500
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{15}^{FA}$	17	1384	4	1449	202	1484	128	1487	101	1546	520
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{16}^{FA}$	1	1383	1	1458	205	1462	157	1502	72	1544	647
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{17}^{FA}$	0	1384	1	1449	281	1484	78	1487	87	1546	598
$\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_{18}^{FA}$	10	1382	14	1440	325	1469	66	1502	50	1552	496
energy-weighted average		**1383**	**6**	**1449**	**220**	**1472**	**138**	**1496**	**64**	**1544**	**524**

Table S1 Mode-dependent scaled harmonic frequency (f in Hz) and intensities (I in kJ.mol^{-1}) calculations for $\left[(AcOMg)^+\cdot(H_2O)_{10}\right]_m^{FA}$ clusters where FA means fully associated and m is the incremental index of conformations.

$\nu_1, \nu_2, \nu_3, \nu_4$ correspond to COO^-_s or CO stretching modes coupled to CH bending modes and ν_5 refers to the vibration mode of COO^-_a stretching modes. The calculations of the energy-weighted average of the frequencies and intensities are explained further in section S4.

- Partially separated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$

	ΔG (kJ.mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_1^{PS}$	27	1375	17	1436	266	1471	74	1497	23	1578	526
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_2^{PS}$	46	1366	95	1412	228	1476	33	1489	11	1583	526
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_3^{PS}$	14	1379	7	1434	275	1483	115	1491	9	1571	411
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_4^{PS}$	22	1379	9	1437	279	1467	72	1498	29	1570	503
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_5^{PS}$	47	1378	14	1437	295	1470	88	1495	29	1566	454
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_6^{PS}$	30	1368	109	1415	222	1473	62	1493	10	1599	539
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_7^{PS}$	82	1351	234	1401	111	1487	26	1504	9	1604	330
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_8^{PS}$	2	1375	13	1430	240	1467	97	1499	23	1541	559
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_9^{PS}$	15	1372	28	1429	225	1469	81	1495	17	1567	442
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{10}^{PS}$	3	1374	19	1425	243	1467	76	1500	21	1554	566
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{11}^{PS}$	57	1373	83	1422	222	1473	72	1492	8	1587	471
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{12}^{PS}$	0	1375	21	1429	207	1476	115	1494	9	1572	530
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{13}^{PS}$	3	1374	16	1425	289	1474	51	1497	25	1584	448
energy-weighted average		**1375**	**17**	**1429**	**248**	**1472**	**87**	**1496**	**18**	**1565**	**498**

Table S2 Same legend as Table S1 for $\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_m^{PS}$ clusters where PS means partially separated.

- Separated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$

	ΔG (kJ.mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_1^S$	47	1375	27	1425	276	1475	177	1490	11	1544	537
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_2^S$	71	1380	32	1429	296	1468	184	1489	22	1533	466
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_3^S$	7	1378	42	1431	323	1459	166	1493	30	1531	419
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_4^S$	28	1386	36	1421	411	1484	74	1495	48	1528	625
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_5^S$	24	1378	38	1414	308	1485	91	1494	34	1533	542
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_6^S$	29	1373	56	1408	339	1484	95	1487	22	1539	534
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_7^S$	32	1376	61	1415	292	1469	102	1493	20	1544	563
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_8^S$	35	1369	69	1418	288	1470	111	1491	7	1558	468
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_9^S$	23	1375	33	1428	252	1462	105	1501	26	1550	607
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{10}^S$	38	1371	86	1419	320	1465	102	1494	20	1551	552
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{11}^S$	51	1376	14	1414	305	1481	243	1494	38	1532	674
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{12}^S$	8	1375	17	1434	271	1468	123	1496	33	1546	625
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{13}^S$	20	1369	93	1418	327	1461	151	1487	10	1538	348
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{14}^S$	0	1375	20	1424	310	1476	115	1496	29	1540	673
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{15}^S$	4	1372	54	1418	351	1456	171	1494	29	1520	396
$\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_{16}^S$	0	1367	154	1407	316	1466	73	1494	20	1549	412
energy-weighted average		**1383**	**6**	**1449**	**220**	**1472**	**138**	**1496**	**64**	**1544**	**524**

Table S3 Same legend as Table S1 for $\left[(AcOMg)^+ \cdot (H_2O)_{10}\right]_m^S$ clusters where S means separated.

- Fully associated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$

	ΔG (kJ.mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_1^{FA}$	8	1383	22	1446	273	1471	93	1500	50	1555	496
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_2^{FA}$	22	1383	38	1449	288	1469	131	1494	12	1559	458
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_3^{FA}$	10	1380	39	1451	313	1466	136	1488	17	1565	517
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_4^{FA}$	20	1377	63	1438	317	1468	76	1492	12	1571	438
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_5^{FA}$	9	1382	0	1446	207	1476	79	1503	91	1548	494
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_6^{FA}$	42	1387	6	1438	264	1481	55	1507	49	1548	431
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_7^{FA}$	15	1375	6	1458	176	1470	146	1497	72	1551	420
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_8^{FA}$	23	1372	47	1434	307	1469	90	1489	25	1561	388
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_9^{FA}$	25	1372	51	1430	263	1470	53	1491	13	1586	381
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{10}^{FA}$	0	1377	3	1448	241	1469	116	1502	54	1548	602
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{11}^{FA}$	4	1377	10	1448	266	1466	91	1498	58	1552	431
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{12}^{FA}$	20	1375	42	1429	319	1471	50	1497	33	1568	459
energy-weighted average		**1378**	**22**	**1446**	**262**	**1470**	**102**	**1497**	**47**	**1557**	**480**

Table S4 Same legend as Table S1 for $\left[(AcOMg)^+ \cdot (H_2$ clusters.

- Partially separated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$

	ΔG (kJ.mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_1^{PS}$	24	1375	89	1419	254	1474	54	1497	18	1593	626
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_2^{PS}$	37	1355	219	1410	131	1476	78	1501	11	1602	600
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_3^{PS}$	30	1379	35	1412	294	1483	40	1498	25	1563	466
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_4^{PS}$	0	1383	2	1435	230	1478	89	1500	41	1546	524
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_5^{PS}$	78	1335	241	1399	111	1477	51	1495	10	1594	434
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_6^{PS}$	38	1358	183	1403	190	1481	43	1505	8	1605	437
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_7^{PS}$	20	1381	33	1435	251	1476	91	1498	28	1573	654
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_8^{PS}$	59	1364	155	1408	193	1493	50	1506	15	1597	373
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_9^{PS}$	29	1380	47	1425	211	1478	108	1497	20	1571	464
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{10}^{PS}$	5	1376	67	1422	237	1473	92	1499	23	1577	581
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{11}^{PS}$	15	1353	182	1396	174	1472	25	1502	11	1598	524
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{12}^{PS}$	35	1379	50	1432	241	1480	88	1499	18	1585	588
energy-weighted average		**1373**	**71**	**1421**	**225**	**1475**	**73**	**1499**	**25**	**1573**	**563**

Table S5 Same legend as Table S1 for $\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_m^{PS}$ clusters.

- Separated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$

	ΔG (kJ.mol^{-1})	ν_1		ν_2		ν_3		ν_4		ν_5	
		f	I	f	I	f	I	f	I	f	I
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_1^S$	39	1375	47	1431	322	1468	173	1488	10	1544	483
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_2^S$	38	1375	48	1431	345	1465	158	1490	23	1544	488
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_3^S$	45	1380	21	1421	296	1472	130	1497	43	1535	578
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_4^S$	56	1369	111	1414	287	1469	106	1491	16	1552	504
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_5^S$	7	1368	23	1418	253	1467	94	1498	24	1540	460
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_6^S$	49	1372	26	1412	292	1483	107	1493	8	1542	554
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_7^S$	53	1374	70	1413	437	1476	78	1495	34	1524	479
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_8^S$	44	1369	96	1418	291	1467	128	1488	8	1559	596
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_9^S$	16	1374	45	1418	351	1474	73	1500	27	1539	576
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{10}^S$	0	1372	55	1413	285	1474	56	1499	21	1556	556
$\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_{11}^S$	21	1375	29	1426	312	1468	122	1496	29	1541	582
energy-weighted average		**1372**	**39**	**1418**	**294**	**1471**	**82**	**1498**	**24**	**1545**	**535**

Table S6 Same legend as Table S1 for $\left[(AcOMg)^+ \cdot (H_2O)_{14}\right]_m^S$ clusters.

S4. Averaging procedure for theoretical spectra

First, each calculated frequency f_0 was scaled with mode-dependent semi-empirical scaling factors in the aim to determine the theoretical frequencies f that can be compared to experimental results:

- For $\alpha\nu^{COO^-}_s / \nu^{CO} + \beta\delta^{CH}$: $f = 1.1431 \times f_0 - 164.3\ cm^{-1}$
- For $\nu^{COO^-}_a$: $f = 0.9272 \times f_0 + 37.9\ cm^{-1}$
- For δ^{H_2O} : $f = 0.81037 \times f_0 + 93.3\ cm^{-1}$

Despite the high level of calculation and the experimental efforts to produce and characterize low-energy structures, one needs to consider calculated energies with care and interpret datasets accordingly. First, the error bar on the energy is not known and largely comes from empirical knowledge. The generally admitted value for quantum chemical accuracy (~5 kJ.mol^{-1}) should be seen as the minimum error that the RI-B97-D3/dhf-TZVPP level can reach. Secondly, experiment produces a distribution of structures that should correspond to that of a thermal equilibrium at 130 K. Thus, several low-energy structures may contribute to the IR spectra recorded. For these reasons, one estimates that all the structures in the 0-10 kJ.mol^{-1} energy window must be taken into account to interpret experiments.

In addition, IRPD spectra (Fig. 3) suggest the presence of at least two types of vibrational signatures, which reflect two very different environments of the carboxylate group. For this reason, structures were sorted into several types according to the location of the magnesium cation relative to carboxylate (bidentate or monodentate CIPs, or SIPs), which is the primary change of environment influencing the carboxylate probe in these systems.

Finally, taking into account that the knowledge of all the minima of the potential energy surface is out of reach for these clusters, we used an approach aiming at revealing the typical spectroscopic signature of each type of ion pair. For this purpose, we built the theoretical spectrum of each type as a weighted average of the spectra of lowest-energy structures. In order to take into account the energy distribution of the different structures **i** in the same family, the weight $\mathbf{w_i}$ of each one was calculated with the following formula:

$$w_i = \frac{1 - signe(\Delta G_i - \Delta G_c) \times \mathrm{erf}\left(|\Delta G_i - \Delta G_c| \times \beta\right)}{2 \times \alpha}$$

Where erf is the error function, $\mathbf{\Delta G_i}$ is the free energy of the considered structure at 130 K, $\mathbf{\Delta G_c}$ is the cutoff energy, $\boldsymbol{\beta}$ is the bending coefficient and $\boldsymbol{\alpha}$ is the correcting coefficient. The parameters have been chosen so that the structures below 10 kJ.mol^{-1} have a weight close to 1 and the structures beyond 20 kJ.mol^{-1} are strongly penalized by a much lower weight (< 0.5).

An example of plotted weight against Gibbs energy for all the structures of the fully associated $(AcOMg)^+ \cdot (H_2O)_{10}$ is shown in Fig. S3.

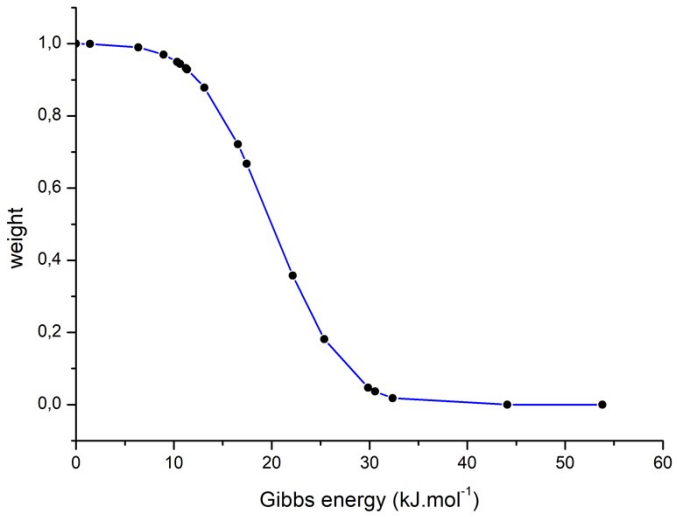

Figure S3 Plot of weight **w** against Gibbs energy with ΔG_c = 20 kJ.mol^{-1} and β = 1.2 (blue curve) and the example of the fully associated $(AcOMg)^{+}\cdot(H_2O)_{10}$ clusters (black dots).

The energy-weighted average of each frequency f and associated intensity I in a family were determined according to the following equation and are presented in Table S1-6.

$$f = \sum_i w_i f_i \quad \text{and} \quad I = \sum_i w_i I_i$$

An arbitrary spectral width of 6 cm^{-1} was chosen in order to model each vibrational transition by a Gaussian function, and present their sums as full theoretical spectra for comparison with the experimental ones (Fig. 4 and S4).

S5. Averaged theoretical spectra

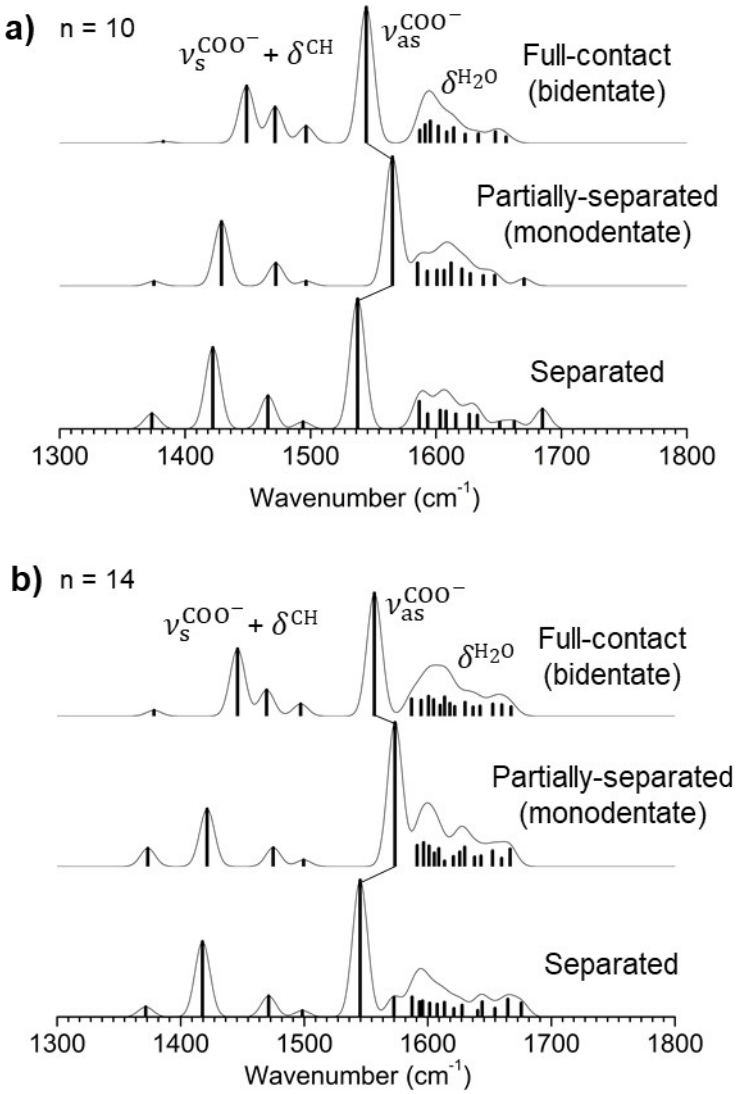

Figure S4 Averaged RI-B97-D3/dhf-TZVPP mode-dependent scaled harmonic vibrational spectra for n = 10 (a) and n = 14 (b)

S6. Structures

Theoretical structures of the most stable clusters in each family and their schematic representations.

- Fully associated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$

C	-0.57500	2.86300	-0.21600
C	-0.28700	1.37200	-0.18400
H	-1.61300	3.06000	-0.48900
H	-0.35700	3.30300	0.76400
O	0.90100	1.02100	0.14700
O	-1.20400	0.55900	-0.47300
Mg	1.75000	-0.60800	1.11600
H	0.08600	3.34300	-0.94600
O	0.16500	-1.54700	2.04000
H	-0.25400	-1.03500	2.75800
H	-0.58900	-2.04900	1.61200
H	-1.68800	0.52900	2.99700
H	-1.26500	0.47000	4.49900
O	-0.91100	0.50600	3.60400
O	3.66200	0.12500	0.46200
H	4.43300	-0.26200	0.89400
H	3.73300	1.09900	0.56000
O	3.07500	-2.02800	2.19500
H	3.03000	-1.91200	3.15300
H	2.81900	-2.94500	2.03000
O	-1.97700	-2.69700	0.98000
H	-1.82200	-2.66600	0.02100
H	-2.62900	-2.00000	1.15500
H	0.97600	0.80500	3.25600
O	1.86400	0.62700	2.89000
H	2.25400	1.49500	2.68800
H	-3.73600	0.55900	1.63600
H	-2.42100	0.38200	0.81500
O	-2.86700	0.14200	1.65900
H	0.88800	-2.05500	-0.94600
O	1.75600	-1.99400	-0.45800
H	2.44000	-1.87700	-1.12800
H	-0.94500	-1.90000	-2.39100
O	-0.70700	-1.85700	-1.45800
H	-0.89700	-0.92500	-1.14700
H	3.00700	3.55900	0.85500
O	2.84100	2.64200	1.09900
H	2.04200	2.33000	0.60900
C	-0.57500	2.86300	-0.21600

- Partially separated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$

C	-0.57500	2.86300	-0.21600
C	-0.28700	1.37200	-0.18400
H	-1.61300	3.06000	-0.48900
H	-0.35700	3.30300	0.76400
O	0.90100	1.02100	0.14700
O	-1.20400	0.55900	-0.47300
Mg	1.75000	-0.60800	1.11600
H	0.08600	3.34300	-0.94600
O	0.16500	-1.54700	2.04000
H	-0.25400	-1.03500	2.75800
H	-0.58900	-2.04900	1.61200
H	-1.68800	0.52900	2.99700
H	-1.26500	0.47000	4.49900
O	-0.91100	0.50600	3.60400
O	3.66200	0.12500	0.46200
H	4.43300	-0.26200	0.89400
H	3.73300	1.09900	0.56000
O	3.07500	-2.02800	2.19500
H	3.03000	-1.91200	3.15300
H	2.81900	-2.94500	2.03000
O	-1.97700	-2.69700	0.98000
H	-1.82200	-2.66600	0.02100
H	-2.62900	-2.00000	1.15500
H	0.97600	0.80500	3.25600
O	1.86400	0.62700	2.89000
H	2.25400	1.49500	2.68800
H	-3.73600	0.55900	1.63600
H	-2.42100	0.38200	0.81500
O	-2.86700	0.14200	1.65900
H	0.88800	-2.05500	-0.94600
O	1.75600	-1.99400	-0.45800
H	2.44000	-1.87700	-1.12800
H	-0.94500	-1.90000	-2.39100
O	-0.70700	-1.85700	-1.45800
H	-0.89700	-0.92500	-1.14700
H	3.00700	3.55900	0.85500
O	2.84100	2.64200	1.09900
H	2.04200	2.33000	0.60900

- Separated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$

H	-1.91100	-0.53000	0.30300
Mg	0.16700	-1.92900	1.18600
O	-0.31100	-3.95800	0.63400
H	-0.12300	-4.70900	1.22100
H	-0.04000	-4.19600	-0.26100
O	-1.79700	-1.39700	0.84900
H	-0.18100	0.63400	2.06700
H	-2.41000	-2.04000	0.47800
O	-1.43100	1.80600	2.13200
H	-1.94900	1.61300	1.32200
H	-2.06500	1.95900	2.84000
O	0.56200	0.01200	1.85300
H	1.18200	0.53800	1.31000
O	2.22900	-2.41500	1.55800
H	2.84200	-2.01100	0.89600
H	2.53300	-2.11900	2.42400
O	2.15900	1.25800	-0.17700
H	1.37600	1.22800	-0.79500
H	2.49500	2.16100	-0.18800
O	3.44700	-1.12700	-0.49200
H	3.19500	-0.17500	-0.44200
H	4.31100	-1.18100	-0.91400
O	-0.15200	-2.59500	3.21000
H	-0.24700	-3.55000	3.38000
H	-0.80200	-2.13800	3.75500
O	-0.08000	-5.45300	3.06400
H	-0.79500	-6.05600	3.30300
H	0.72900	-5.86600	3.39300
O	0.61800	-1.67100	-0.83000
H	0.23200	-0.78600	-1.14800
H	1.54800	-1.65600	-1.10300
C	-1.14300	1.34900	-1.07800
C	-1.29700	2.81100	-1.45600
O	-2.05600	0.83200	-0.36400
O	-0.09900	0.73100	-1.46900
H	-2.31800	3.00100	-1.79700
H	-1.13800	3.42200	-0.55800
H	-0.58000	3.10300	-2.22500

- Fully associated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$

O	-2.90000	-2.80500	-3.84300
H	-3.66500	-3.27200	-4.19400
H	-2.20200	-3.48300	-3.60400
C	0.09300	1.16900	-1.12400
C	0.85400	1.63800	0.08900
O	0.47400	0.11800	-1.75100
O	-0.89200	1.83600	-1.56900
H	0.22300	2.24700	0.73900
H	1.27100	0.79400	0.64400
H	1.68500	2.26000	-0.26800
Mg	-1.00800	0.47500	-3.36500
O	1.07100	-2.89700	-5.05600
H	1.80500	-2.85200	-4.38200
H	1.46900	-3.16200	-5.89100
O	2.62700	2.37700	-2.97600
H	3.09600	1.56300	-2.70300
H	3.28300	2.94200	-3.39900
O	-2.57700	1.60200	-4.20000
H	-2.31000	2.43300	-4.65100
H	-3.26400	1.83700	-3.55600
O	0.41000	1.61700	-4.36800
H	1.23600	1.91700	-3.91500
H	0.07000	2.38300	-4.86600
O	0.52900	-2.72800	-1.15700
H	0.34000	-1.77500	-1.23400
H	0.34100	-2.97000	-0.24300
O	-1.21500	3.79000	-5.12100
H	-1.03800	4.26300	-4.27100
H	-1.30400	4.44700	-5.81900
O	3.22000	-0.16300	-1.94600
H	2.26100	-0.15400	-1.72100
H	3.69700	-0.22200	-1.11000
O	-0.60000	4.49700	-2.58600
H	-0.68100	3.65300	-2.10100
H	-0.97100	5.17700	-2.01500
O	-0.78100	-4.26700	-3.26000
H	-0.15400	-4.06600	-3.97900
H	-0.38500	-3.84300	-2.47700
O	-3.75200	1.76500	-1.57400
H	-4.42700	2.13300	-0.99300
H	-2.88900	2.03000	-1.21400
O	-0.90100	-1.07100	-4.70400
H	-0.11000	-1.62200	-4.92000
H	-1.65700	-1.69200	-4.68700
O	-2.44400	-0.64700	-2.27500
H	-2.81200	-1.44500	-2.72000
H	-3.18000	-0.13000	-1.91000
O	2.80600	-2.83600	-3.02700
H	2.22600	-3.02300	-2.27100
H	3.17500	-1.96000	-2.82100

- Partially separated $(CH_3COOMg)^{+}\cdot(H_2O)_{14}$

C	0.23200	1.41800	-0.25300
C	-0.62100	2.05500	-1.32900
O	1.49500	1.53500	-0.34200
O	-0.34500	0.81100	0.71000
H	-1.65900	1.72000	-1.27600
H	-0.20600	1.82500	-2.31400
H	-0.58100	3.14300	-1.20100
Mg	0.42800	-0.33700	2.31500
O	2.41500	-0.08500	1.51700
H	2.21200	0.58800	0.79500
H	2.74900	-0.86600	1.03600
O	2.81400	-0.23700	5.81400
H	2.05500	0.21000	6.24000
H	3.31400	-0.67400	6.51300
O	0.24100	-2.10400	1.14600
H	0.95500	-2.29000	0.49400
H	-0.60100	-2.30300	0.72500
O	-1.54700	-0.60700	2.98800
H	-2.17100	0.11900	2.78500
H	-1.67400	-0.88100	3.91900
O	-2.64600	1.65700	1.81900
H	-3.47500	1.71100	1.33200
H	-1.94700	1.37800	1.17900
O	-0.56300	3.55500	2.72200
H	-0.08100	3.93100	1.95500
H	-1.42500	3.25600	2.38800
O	2.50600	-2.18600	-0.37300
H	3.03800	-2.96000	-0.58600
H	2.49200	-1.60300	-1.17600
O	-1.16400	-1.41300	5.59900
H	-1.69200	-1.88700	6.25000
H	-0.80700	-0.60700	6.03200
O	0.71200	1.41500	3.50700
H	0.23300	2.25200	3.19500
H	1.68600	1.63600	3.56300
O	0.26300	0.89600	6.14100
H	0.33500	1.17600	5.18900
H	-0.00200	1.68000	6.63600
O	1.00900	4.36700	0.53200
H	1.60700	5.11700	0.62100
H	1.54400	3.62900	0.20200
O	2.27100	-0.30600	-2.29900
H	2.90600	-0.09300	-2.99200
H	2.13800	0.51300	-1.78000
O	1.16400	-1.50800	3.92400
H	1.85500	-1.16100	4.52600
H	0.47300	-1.85500	4.51300
O	3.37400	1.62500	3.63100
H	3.48800	0.99700	2.89800
H	3.55100	1.10300	4.43200

- Separated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$

O	-3.02000	-1.90700	2.46000
H	-3.87300	-2.34700	2.36900
H	-2.56700	-1.95700	1.58400
C	0.04700	1.06100	-0.75300
C	0.05700	2.57700	-0.84600
O	-1.04400	0.49300	-0.47200
O	1.15600	0.44100	-0.93900
H	0.09500	2.98600	0.17300
H	0.92400	2.93600	-1.40400
H	-0.86900	2.93400	-1.30300
Mg	0.50100	-2.37500	1.72200
O	0.12700	-4.32300	1.13100
H	0.50500	-5.14300	1.53400
H	-0.00700	-4.46100	0.17900
O	-1.16200	-1.89300	0.47500
H	-1.09000	-0.96800	0.04500
H	-1.19600	-2.53300	-0.27400
O	-1.83400	0.89500	2.18600
H	-1.85200	0.96700	1.21200
H	-2.55300	0.28400	2.40900
O	1.06400	-4.60700	4.75700
H	0.24100	-4.12500	4.55700
H	1.04100	-4.81400	5.69900
O	0.50100	-0.38700	2.46900
H	-0.34500	0.13800	2.39400
H	1.22800	0.21000	2.21400
O	2.19300	-2.86300	2.84700
H	2.21000	-3.38700	3.66300
H	3.04000	-2.40100	2.70300
O	2.69700	1.05200	1.23800
H	2.29100	0.99500	0.33800
H	2.96300	1.96900	1.36600
O	0.50800	-1.68200	-2.96500
H	0.74300	-0.92500	-2.39900
H	1.27000	-1.82000	-3.53800
O	-0.69800	-2.66700	3.57400
H	-1.65700	-2.56400	3.33900
H	-0.48500	-1.87100	4.08200
O	1.03700	-6.43000	2.53800
H	1.85800	-6.89700	2.34700
H	1.15200	-6.02600	3.41700
O	1.76300	-1.91200	0.13400
H	1.51000	-1.06000	-0.32300
H	2.71300	-1.86000	0.32200
O	-0.67900	-3.67800	-1.53600
H	-0.16300	-3.04200	-2.09400
H	-1.34100	-4.06500	-2.11800
O	4.13300	-1.28900	1.66800
H	3.83400	-0.35800	1.59200
H	5.09200	-1.28800	1.58800

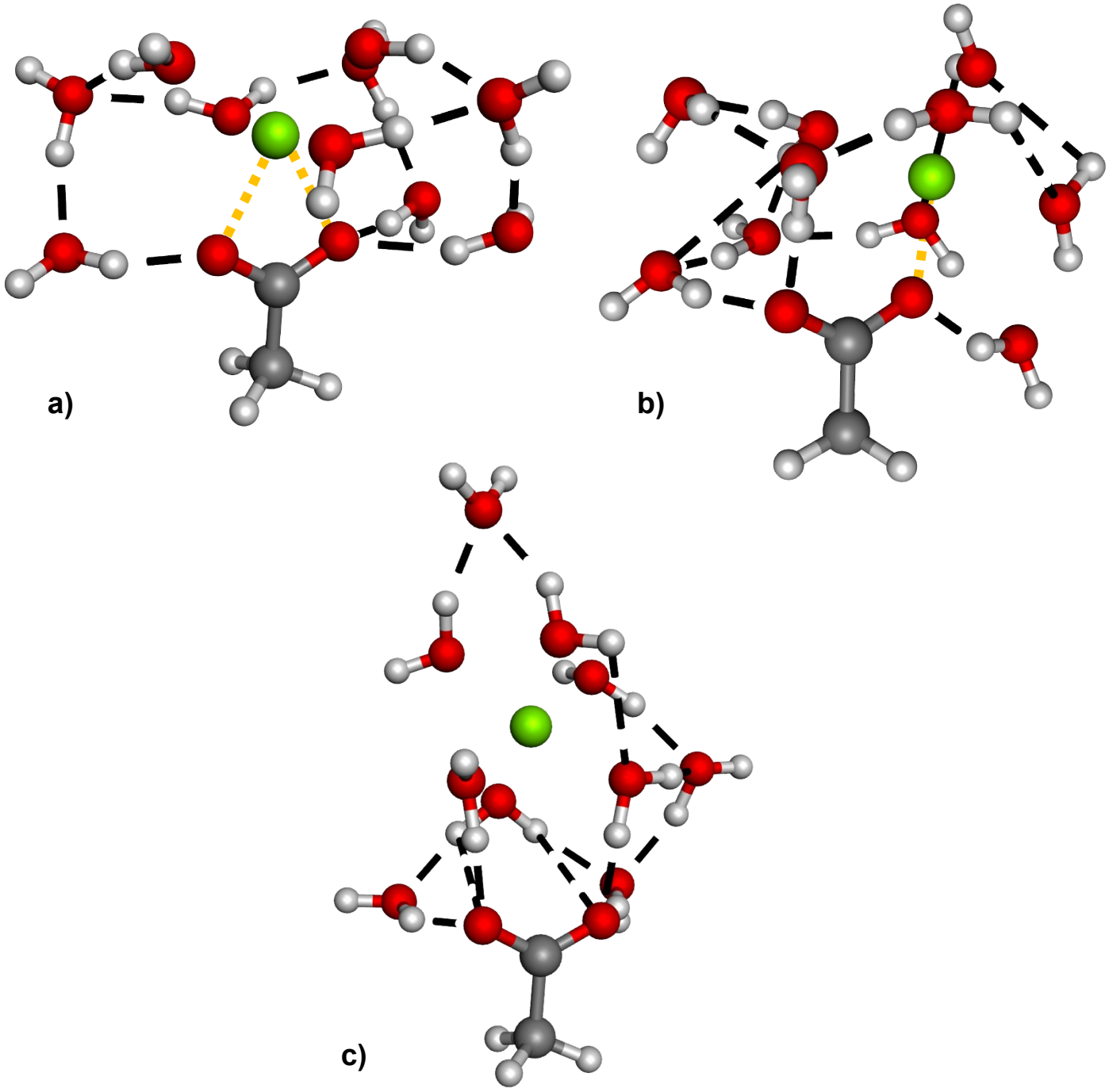

Figure S5 Schematic representation of the most stable structures of a) fully associated, b) partially separated and c) separated $(CH_3COOMg)^+ \cdot (H_2O)_{10}$ clusters

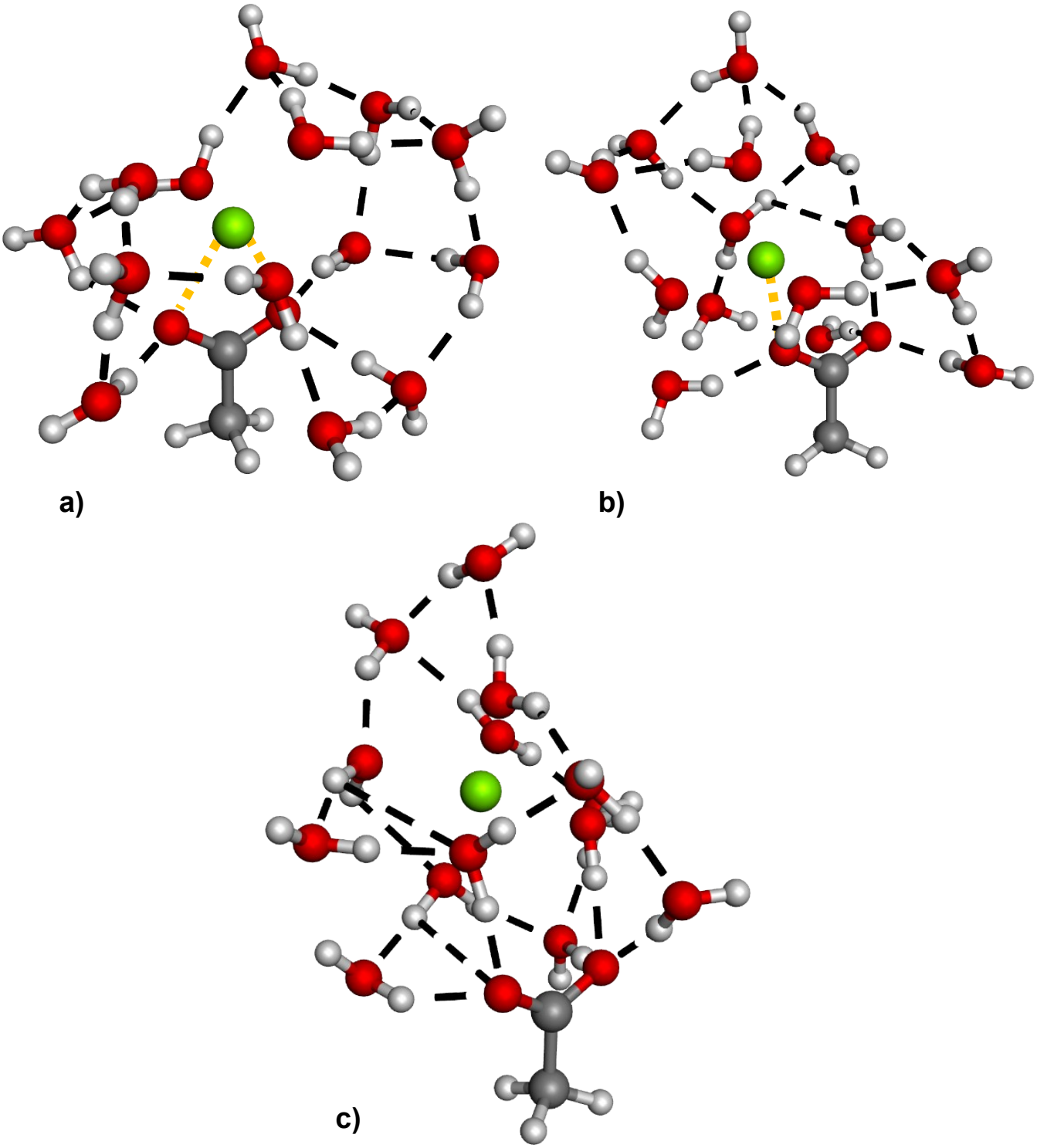

Figure S6 Schematic representation of the most stable structures of a) fully associated, b) partially separated and c) separated $(CH_3COOMg)^+ \cdot (H_2O)_{14}$ clusters

S7. Reference

1. J. Donon, J.-X. Bardaud, V. Brenner, S. Ishiuchi, M. Fujii and E. Gloaguen, *Phys. Chem. Chem. Phys.*, 2022, **24**, 12121-12125.