Supporting Information: Impact of Small Adsorbates in the Vibrational Spectra of Mg- and Zn-MOF-74 Revealed by First-Principles Calculations

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S1 Further structural parameters

In this section, we provide additional structural data of Mg-MOF-74 and Zn-MOF-74 collected in Tables S1 and S2. These data supplement those presented in Table 1 of the main text. In particular, we include other results obtained in previous DFT calculations with similar methodologies. In addition, we present the original lattice constants of the primitive rhombohedral cells. This cell can be unequivocally defined through the lattice constant a_r and the angle α, while the conventional hexagonal cell, which is defined by two lattice parameters a and c. These two sets of crystallographic parameters are related to each other by the following expressions[S1]

$$a = a_r\sqrt{2-2\cos\alpha}, \quad (1)$$

$$c = a_r\sqrt{3+6\cos\alpha}. \quad (2)$$

Table S1: Structural parameters of the unit cells. In each case we present the original results associated to the primitive rhombohedral cell and the corresponding parameters in the conventional hexagonal cell. We compare our results with other calculations and experimental estimations reported in the literature, whenever possible.

		rhombohedral		hexagonal			
Metal	Adsorbate	a_r (Å)	α (°)	a (Å)	c (Å)	Method	ref.
Mg	Empty	15.160	117.8	25.962	6.807	PBE+D3	This work
	Empty			25.921	6.8625	NPD at 20 K	S2
	Empty			25.892	6.874	XRD	S3
	Empty			26.05	6.91	vdW-DF2	S4
	Empty			26.12	6.93	PBE+D2	S5
	Empty			26.084	6.863	vdW-DF	S6
	Empty			26.236	6.992	B3LYP+D	S7
	Empty			25.92	6.86	NPD at 10 K	S8
	Empty			26.04	6.92	PBE+D3	S8
	Empty			25.881	6.879	NPD	S9
	Ar	15.091	117.8	25.844	6.779	PBE+D3	This work
	CO_2	15.043	117.8	25.762	6.749	PBE+D3	This work
	CO_2 (0.75)			25.847	6.8788	NPD at 20 K	S2
	CO_2			25.824	6.8904	NPD at 20 K	S2
	CO_2			25.944	6.852	vdW-DF	S6
	CO_2			26.236	6.992	B3LYP+D	S7
	CO_2 (0.64)			25.854	6.889	NPD	S9
	H_2O	15.005	117.7	25.689	6.823	PBE+D3	This work
	H_2O			25.943	6.870	vdW-DF	S6
	NH_3	15.022	117.7	25.717	6.843	PBE+D3	This work
Zn	Empty	15.100	117.9	25.874	6.616	PBE+D3	This work
	Empty			25.866	6.808	XRD	S3
	Empty			26.20	6.92	vdW-DF2	S4
	Empty			26.17	6.92	PBE+D2	S5
	Empty			26.142	6.875	vdW-DF	S6
	Empty			26.299	6.914	B3LYP+D	S7
	Empty			25.89	6.82	NPD at 10 K	S8
	Empty			26.05	6.98	PBE+D3	S8
	Ar	15.013	117.9	25.724	6.581	PBE+D3	This work
	CO_2	14.911	117.9	25.548	6.549	PBE+D3	This work
	CO_2			26.159	6.570	vdW-DF	S6
	CO_2			26.299	6.914	B3LYP+D	S7
	CO_2 (1.50)			25.850	6.8072	NPD at 10 K	S10
	H_2O	15.080	118.1	25.862	6.331	PBE+D3	This work
	H_2O			26.769	5.841	vdW-DF	S6
	NH_3	15.054	117.8	25.777	6.798	PBE+D3	This work

Table S2: Structural parameters involving the coordination complexes and the ligand. In each case we present the M–O distances (the average of the four planar ligands and the apical one) together with metal-metal distance and the bond length with the adsorbate M–A. We compare our results with other calculations and experimental estimations reported in the literature, whenever possible.

Metal	Adsorbate	$\langle$M–O$\rangle_{pl}$ (Å)	M–O_{ap} (Å)	M–M (Å)	M–A (Å)	Method	ref.
Mg	Empty	2.02	2.06	2.92	**	PBE+D3	This work
	Empty	2.01	2.08		**	NPD at 20 K	S2
	Empty	2.02	2.04	2.93	**	vdW-DF2	S4
	Empty	2.04	2.09		**	vdW-DF1	S5
	Empty	2.01	2.08		**	NPD at 10 K	S8
	Empty	2.02	2.04		**	PBE+D3	S8
	Ar	2.02	2.06	2.92	3.22	PBE+D3	This work
	CO_2	2.02	2.06	2.95	2.33	PBE+D3	This work
	CO_2	2.01	2.10	2.94	2.28-2.30	NPD at 20 K	S2
	CO_2				2.392	vdW-DF1	S5
	CO_2				2.398	vdW-DF1	S6
	CO_2				2.411	PBE+D3	S8
	H_2O	2.04	2.09	3.02	2.18	PBE+D3	This work
	H_2O				2.232	vdW-DF1	S6
	H_2O				2.135	PBE+D3	S8
	NH_3	2.05	2.09	3.02	2.22	PBE+D3	This work
Zn	Empty	2.03	2.23	2.94	**	PBE+D3	This work
	Empty	2.03	2.08	2.98	**	vdW-DF2	S4
	Empty	2.06	2.20		**	vdW-DF1	S5
	Empty	2.05	2.08		**	NPD at 10 K	S8
	Empty	2.03	2.08		**	PBE+D3	S8
	Ar	2.03	2.23	2.94	3.47	PBE+D3	This work
	CO_2	2.03	2.28	2.96	2.82	PBE+D3	This work
	CO_2	2.01	2.15	3.00	2.43	NPD at 20 K	S10
	CO_2				2.867	vdW-DF1	S5
	CO_2				2.826	vdW-DF1	S6
	CO_2				2.837	PBE+D3	S8
	H_2O	2.04	**	3.26	2.24	PBE+D3	This work
	H_2O				2.228	vdW-DF1	S6
	H_2O				2.224	PBE+D3	S8
	NH_3	2.09	2.20	3.12	2.16	PBE+D3	This work

S2 Complete spectra of loaded MOFs

In the main text we have presented only partial regions of the vibrational spectra of loaded MOFs with Ar, CO_2, H_2O and NH_3. For this reason, we include here in Figs. S1 and S2 the vibrational spectra over the whole wavenumber range. We have omitted the region between 1700 cm^{-1} and 2300 cm^{-1} since there is no relevant IR/Raman signal in that region.

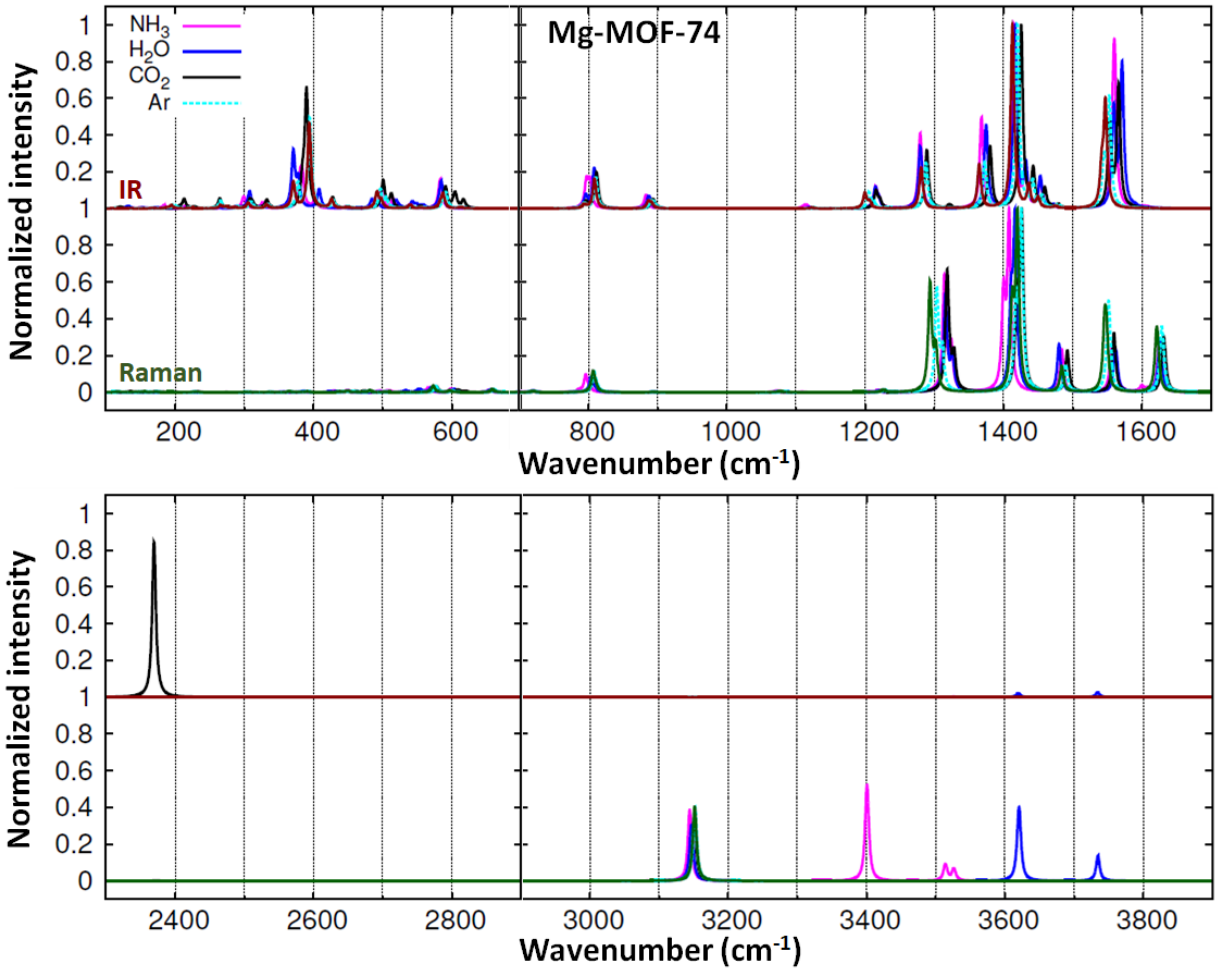

Figure S1: Calculated Raman and IR spectra for Mg-MOF-74 hosting for adsorbates: Ar, CO_2, H_2O and NH_3. The IR and Raman spectra of the bare Mg-MOF-74 are plotted in red and green solid lines respectively, while spectra of loaded MOFs are plotted as indicated in the legend.

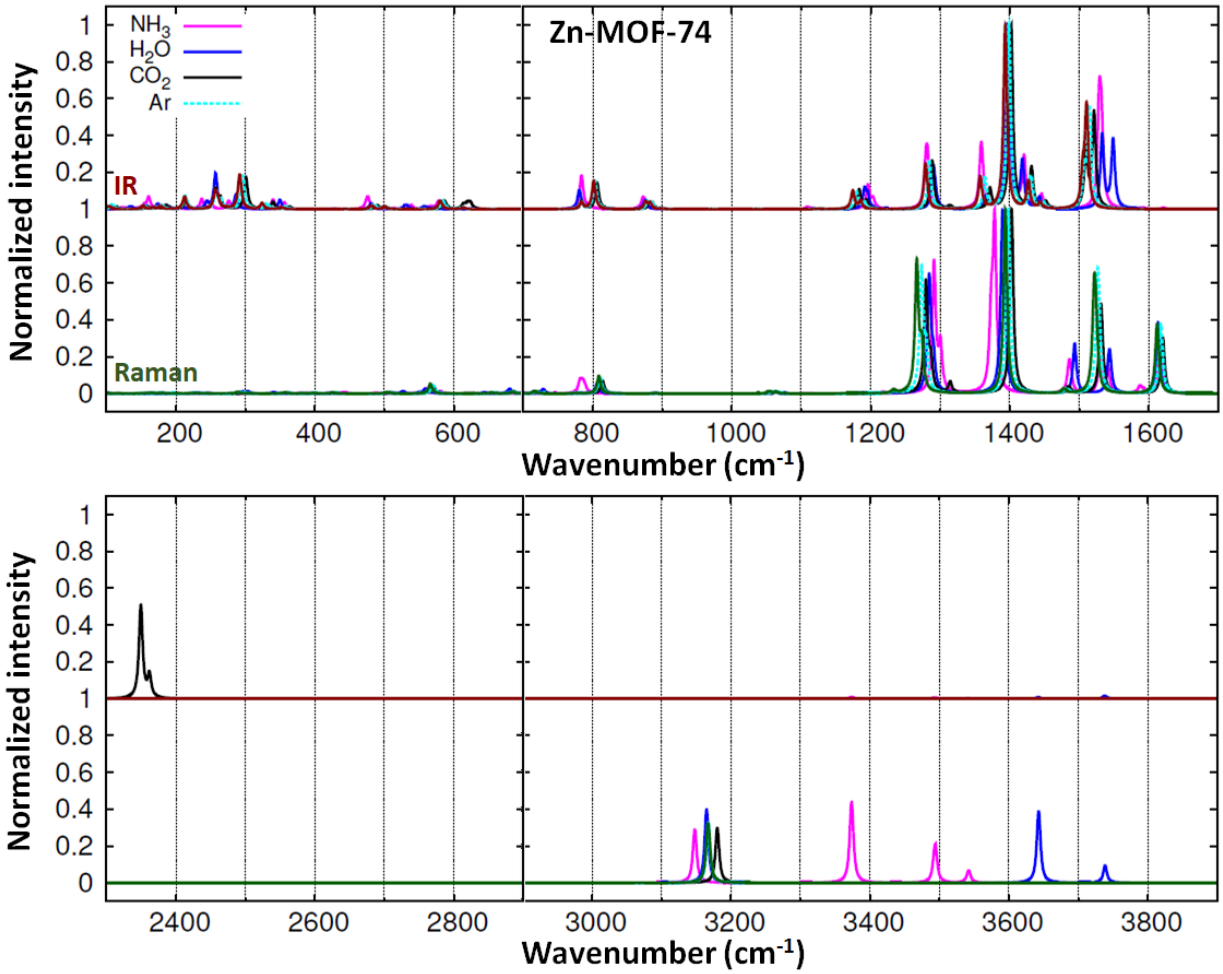

Figure S2: Calculated Raman and IR spectra for Zn-MOF-74 hosting for adsorbates: Ar, CO_2, H_2O and NH_3. The IR and Raman spectra of the bare Zn-MOF-74 are plotted in red and green solid lines respectively, while spectra of loaded MOFs are plotted as indicated in the legend.

S3 Vibrational spectra of isolated adsorbates

In this section we include the vibrational spectra of the isolate gas phase adsorbates in Figs. S3, S4 and S5. Notice that we have used the nomenclature established by Herzberg[S11] to denote the vibrational normal modes. The normal modes of the isolated adsorbates serve as a reference to track their evolution when adsorbed on the metal open sites of MOF-74.

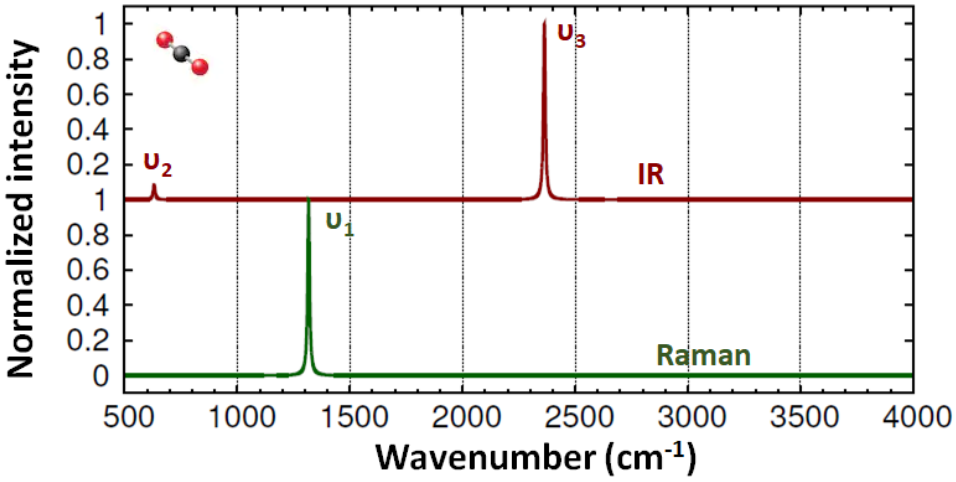

Figure S3: Calculated Raman and IR spectra of the gas phase CO_2 molecule. Normal mode assignment: $\upsilon_3 = 2363$ cm^{-1} (C=O asymmetric stretching); $\upsilon_1 = 1316$ cm^{-1} (C=O symmetric stretching); $\upsilon_{2(1)} = 632$ cm^{-1} and $\upsilon_{2(2)} = 630$ cm^{-1} (O=C=O bending, degenerated).

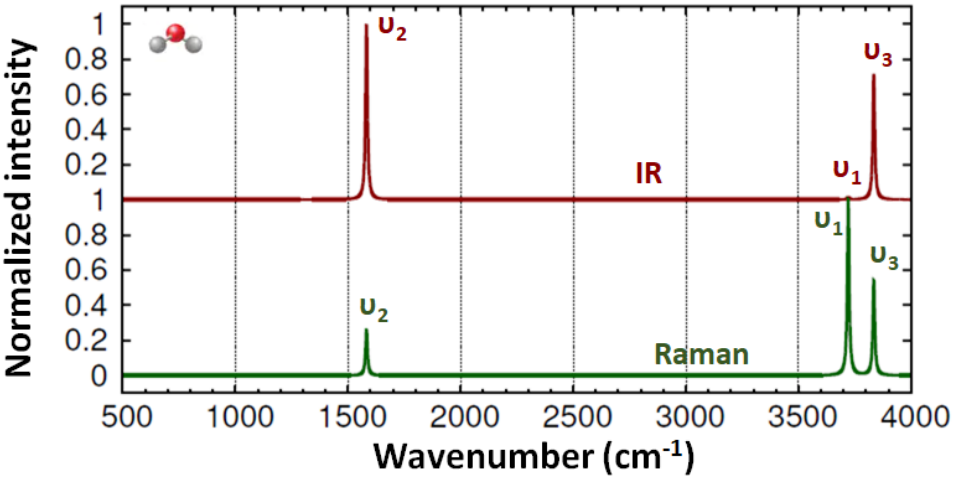

Figure S4: Calculated Raman and IR spectra of the gas phase H_2O molecule. Normal mode assignment: $\upsilon_3 = 3834$ cm^{-1} (O–H symmetric stretching); $\upsilon_1 = 3721$ cm^{-1} (O–H asymmetric stretching); $\upsilon_2 = 1582$ cm^{-1} (H–O–H bending).

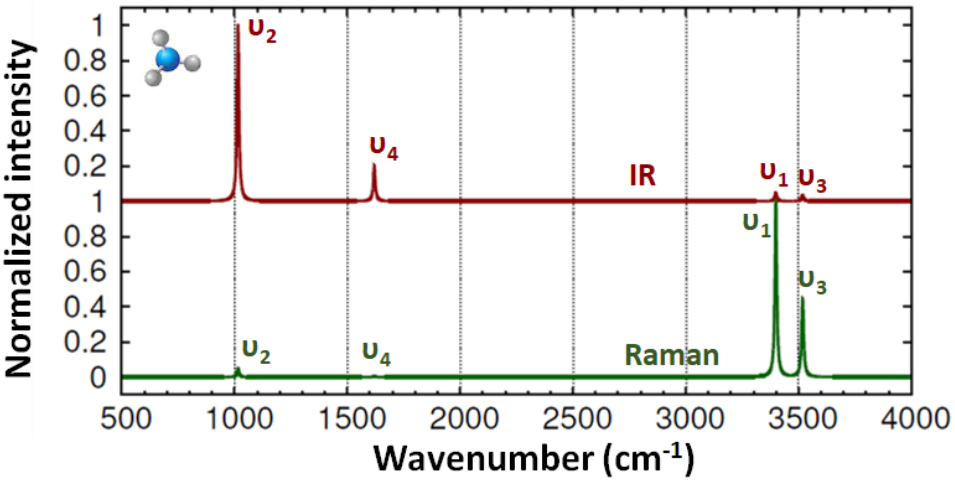

Figure S5: Calculated Raman and IR spectra of the gas phase NH_3 molecule. Normal mode assignment: $\upsilon_{3(1)} = 3519$ cm^{-1} and $\upsilon_{3(2)} = 3516$ cm^{-1} (N–H asymmetric stretching, degenerated); $\upsilon_1 = 3399$ cm^{-1} (N–H symmetric stretching); $\upsilon_{4(1)} = 1620$ cm^{-1} and $\upsilon_{4(2)} = 1619$ cm^{-1} (H–N–H scissoring, degenerated); $\upsilon_2 = 1015$ cm^{-1} (N–H wagging).

S4 Frequency shifts of adsorbed molecules

In this section, we present Tables S3, S4 and S5 where we have collected the evolution of the vibrational modes associates to the adsorbed molecules. For each adsorbate, we take as reference their IR/Raman signals in gas phase and we study the evolution of these signals when adsorbed on MOF-74.

Table S3: Positions of the bands (in cm^{-1}) of the IR and Raman spectra of CO_2 in gas phase and adsorbed on Mg-MOF-74 and Zn-MOF-74. The experimental values for the gas phase molecules are taken from ref. S11, while those on MOF-74 from ref. S12. Notice that the Raman signal of υ_1, denoted with an asterisk, could not be determined in experiments since it might be overlapped with other MOF signals. Notice that for Co-MOF-74 and Ni-MOF-74 this signal does appear at 1380 and 1382 cm^{-1}.

		υ_2	υ_1	υ_3
gas phase (exp.)	IR	667	Inactive	2349
	Raman	Inactive	1333	Inactive
On Mg-MOF-74 (exp.)	IR	658	–	2352
	Raman	–	*	–
On Zn-MOF-74 (exp.)	IR	658	–	2338
	Raman	–	*	–
gas phase	IR	630/632	Inactive	2363
	Raman	Inactive	1316	Inactive
On Mg-MOF-74	IR	604/616	1322	2368
	Raman	608/618	1318	2369/2374
On Zn-MOF-74	IR	615/623	1313	2349/2361
	Raman	619/626	1314	2356

Table S4: Positions of the bands (in cm^{-1}) of the IR and Raman spectra of H_2O in gas phase and adsorbed on Mg-MOF-74 and Zn-MOF-74. The experimental values for the gas phase molecules are taken from ref. S13, while those for the molecule adsorbed on Mg-MOF-74 from ref. S14. Notice that the Raman signal of υ_2, denoted with an asterisk, could not be determined in our calculations since it might be overlapped with other MOF signals.

		υ_2	υ_1	υ_3
gas phase (exp.)	IR	1595	3657	3756
On Mg-MOF-74 (exp.)	IR	1610	3576	3663
gas phase	IR	1582	3721	3834
On Mg-MOF-74	IR	*	3619	3734
	Raman	*	3620	3734
On Zn-MOF-74	IR	1578	3642	3738
	Raman	1578	3643	3738

Table S5: Positions of the bands (in cm^{-1}) of the IR and Raman spectra of NH_3 in gas phase and adsorbed on Mg-MOF-74 and Zn-MOF-74. The experimental values for the gas phase molecules are taken from ref. S11, while those on Mg-MOF-74 from ref. S15.

		υ_2	υ_4	υ_1	υ_3
gas phase (exp.)	IR	950	1627	3337	3414
On Mg-MOF-74 (exp.)	IR	1114	–	–	–
gas phase	IR	1015	1619/1620	3399	3516/3519
On Mg-MOF-74	IR	1109	1602/1607	3401	3514/3525
	Raman	1109	1600/1608	3400	3514/3526
On Zn-MOF-74	IR	1109	1591/1621	3373	3493/3540
	Raman	1109	1587/1591	3373	3492/3542

S5 Frequency shifts of loaded MOFs

Here, we use Tables S6, S8, S7 and S9 to make a systematic comparison of the frequency shifts experimented in the vibrational spectra of MOF-74 hosting different adsorbates.

Table S6: Bands and frequency shifts (both in cm^{-1}) in the IR spectra of Mg-MOF-74 after the incorporation of four adsorbates: H_2O, NH_3, CO_2 and Ar. The frequency shifts are calculated as ν(MOF+ads)$-\nu$(MOF). The superscript s denotes a shoulder while c indicates the coalescence of two originally separated peaks. The question mark remarks some uncertainty in the assignment.

bare	H_2O		NH_3		CO_2		Ar	
band	band	shift	band	shift	band	shift	band	shift
3150.5	3145.5	−5	3143	−7.5	3149.5	−1	3151	0.5
1547	1571	24	1560	13	1566	19	1553	6
1541^s	1559	18	1560	19	1553	12	1545	4
1449.5	1453	3.5	1453	3.5	1459.5	10	1455	5.5
1436.5	1432	−4.5	1431.5	−5	1442.5	6	1442	5.5
1413	1417	4	1415	2	1425	12	1420	7
1365	1374.5	9.5	1368	3	1380.5	15.5	1373	8
1281	1279.5	−1.5	1279	−2	1289	8	1287	6
1206	1218.5^s	12.5	1218.5^s	12.5	1220^s	14	1212	6
1199.5	1215	15.5	1215.5	16	1215	15.5	1205.5	6
890	887^c	−3	883	−7	894	4	893.5	3.5
887	887^c	0	883	−4	892.5	5.5	890.5	3.5
808.5	808.5	0	802	−6.5	812	3.5	810.5	2
794	796.5	2.5	797	3	796.5	2.5	794	0
587	584	−3	583	−4	590.5	3.5	591	4
555.5	557	1.5	–	–	554	−1.5	558.5	3
539.5	543	3.5	540	0.5	536	−3.5	541.5	2
497	494	−3	514	17	512.5	15.5	504.5	7.5
492	484.5	−7.5	498	6	500.5	8.5	496.5	4.5
426	408	−18	402.5?	−23.5	427.5	1.5	429	3
394	370?	−24	383?	−11	390?	−4	395	1
370.5	377?	6.5	380?	9.5	384^s?	13.5	377	6.5

Table S7: Bands and frequency shifts (both in cm^{-1}) in the IR spectra of Zn-MOF-74 after the incorporation of four adsorbates: H_2O, NH_3, CO_2 and Ar. The frequency shifts are calculated as ν(MOF+ads)$-\nu$(MOF). The superscript c indicates the coalescence of two originally separated peaks. The question mark denotes some uncertainty in the assignment.

bare	H_2O		NH_3		CO_2		Ar	
band	band	shift	band	shift	band	shift	band	shift
3165.5	3163	−2.5	3146.5	−19	3179	13.5	3166.5	7
1510.5	1533	22.5	1529.5^c	19	1521	10.5	1514.5	4
1505.5	1548.5	43	1529.5^c	14	1510	4.5	1507.5	2
1444	1442.5	−1.5	1445	1	1451.5	7.5	1448	4
1427	1418	−9	1420.5	−6.5	1431.5	4.5	1430.5	3.5
1393.5	1397.5	4	1401	7.5	1402	8.5	1398.5	5
1357.5	1364	6.5	1359	1.5	1371.5	14	1364	6.5
1279	1290	11	1280.5	1.5	1289	10	1284	5
1185	1194.5	9.5	1202.3	17.3	1193.5	8.5	1189.5	4.5
1174	1191.5	17.5	1196	22	1183.5	9.5	1178.5	4.5
882	–	–	875.5	−6.5	884.5	2.5	884.5	2.5
876	875	−1	872.5	−3.5	882	6	879	3
801	802.5	1.5	783.5?	−17.5	806	5	803	2
783.5	780.5	−3	795?	11.5	783.5	0	783.5	0
580	–		578	−2	586	6	583.5	3.5
481	480.5	−0.5	478	−3	489	8	485	4
324	–	–	339.5?	15.5	339	15	330	6
291.5	286	−5.5	–	–	300.5	9	296	4.5
256.5	257	0.5	–	–	257	0.5	257.5	1
212	209.5	−2.5	–	–	214.5	2.5	213	1

Table S8: Bands and frequency shifts (both in cm^{-1}) in the Raman spectra of Mg-MOF-74 after the incorporation of four adsorbates: H_2O, NH_3, CO_2 and Ar. The frequency shifts are calculated as ν(MOF+ads)$-\nu$(MOF). The question mark denotes some uncertainty in the assignment.

bare	H_2O		NH_3		CO_2		Ar	
band	band	shift	band	shift	band	shift	band	shift
3151	3147	−4	3144	−7	3150	−1	3151	7
1621.5	1626.5	5	1625	3.5	1631	9.5	1628.5	7
1547	1562	15	1558	11	1559.5	12.5	1552	5
1484	1480	−4	1484	0	1492	8	1490	6
1420	1416.5	−3.5	1407	−13	1426	6	1427	7
1413	1411.5	−1.5	1400	−13	1420	7	1418	5
1302	1326	24	1324	22	1328	26	1311	9
1294	1316	22	1314	20	1318.5	24.5	1304	10
1226.5	1219.5	−7	1218	−8.5	1223	−3.5	1227.5	1
1077.5	1078	0.5	1075	−2.5	1086.5	9	1083.5	6
1071.5	1075?	3	1072?	0.5	–	–	1077.5	6
807	804	−3	796	−11	808	1	808	1
658.5	655.5	−3	654	−4.5	660	1.5	660.5	2
597	602.5	5.5	598.5	1.5	–	–	600	3
573	570	−3	565.5	−7.5	578	5	576.5	3.5
502.5	–	–	508.5	6	506	3.5	505.5	3

Table S9: Bands and frequency shifts (both in cm^{-1}) in the Raman spectra of Zn-MOF-74 after the incorporation of four adsorbates: H_2O, NH_3, CO_2 and Ar. The frequency shifts are calculated as ν(MOF+ads)$-\nu$(MOF). The superscript d stands for a splitting in two bands. The question mark denotes some uncertainty in the assignment.

bare	H_2O		NH_3		CO_2		Ar	
band	band	shift	band	shift	band	shift	band	shift
3167	3165	−2	3147.5	−19.5	3180	13	3167.5	7
1612	1613.5	1.5	1615	3	1620	8	1617.5	5.5
1522	1543.5?	21.5	$1529.5/541^d$	7.5/19	1531	9	1527	5
1478	1493?	15	1486	8	1484.5	6.5	1481.5	3.5
1393.5	1390	−3.5	$1378/1373^d$		1402.5	9	1397.5	4
1272.5	1289	16.5	1300	27.5	1285	12.5	1278.5	6
1266.5	1284	17.5	1291	24.5	1279	12.5	1273	6.5
1063	1064.5	1.5	1066	3	1071	8	1067	4
1053.5	1061	7.5	1062	8.5	1063.5	10	1058.5	5
808.5	806	−2.5	$784/782^d$	$-24.5/-26.5$	813.5	5	810	1.5
716	728.5	12.5	–	–	719.5	3.5	717	1
684.5	680	−4.5	–	–	685	0.5	685	0.5
654.5	643.5	−11	647.5	−7	659	4.5	656.5	2
566	559	−7	$580/600^d$	14/34	570.5	4.5	569	3

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