

Coordination structure and charge transfer in microsolvated transition metal hydroxide clusters $[\text{MOH}]^+(\text{H}_2\text{O})_{1-4}$

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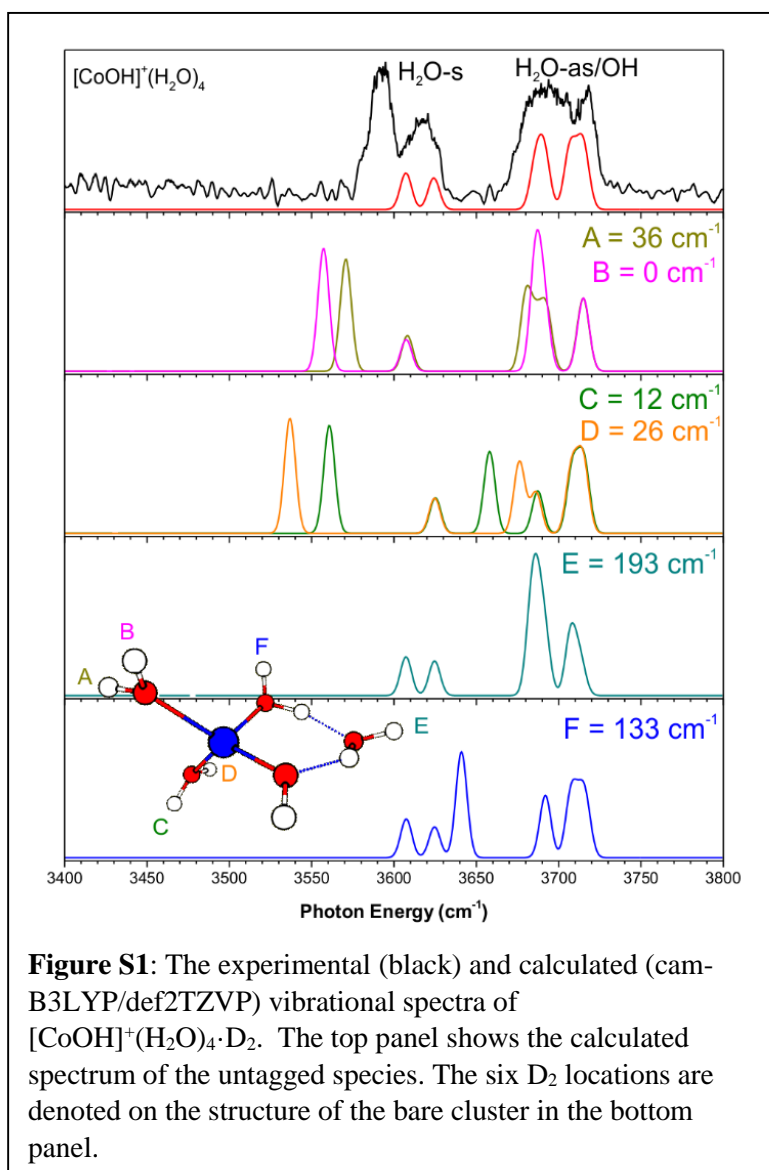
Electronic Supplementary Information

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A) D₂ perturbation in the experimental spectra

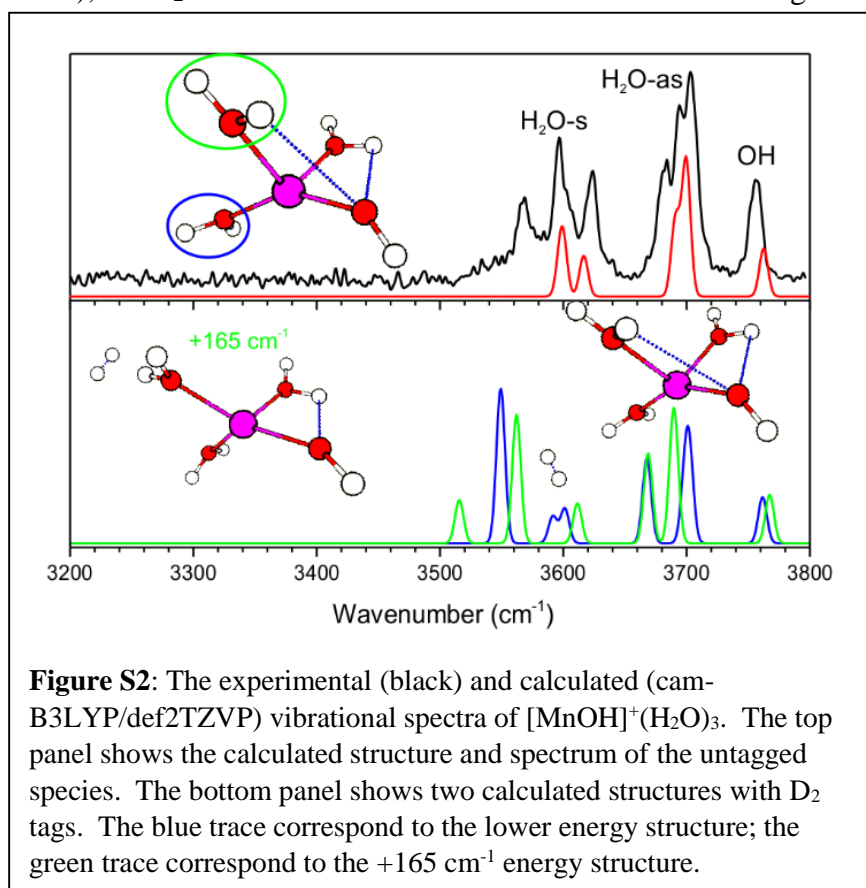
A typical example of the calculation results including the D₂ tag is illustrated in Figure S1, which shows the calculated IR spectra of [CoOH]⁺(H₂O)₄·D₂ isomers. For comparison, the calculated spectrum of the bare cluster is shown in red in the top panel. The six available binding sites for D₂ are indicated as A-F. The four sites on the two free waters (A-D) are within 40 cm⁻¹ of each other, with B being the lowest in energy. The calculated spectra of isomers A/B are in good agreement with the experiment, both erring in the overestimation of the D₂-H₂O interaction. For these tag isomers, the hydroxide stretch is overlapped with the free H₂O-as of the AD water at the calculated frequency of 3715 cm⁻¹. Isomers C/D yield a slightly blueshifted H₂O-s for the free water, and may contribute to the non-Gaussian shape of the experimental feature. The broader calculated 3712 cm⁻¹ band of these isomers consists of the stretch of the AD water, the H₂O-as of the free water, as well as the hydroxide. Note that the distinctive 3658 cm⁻¹ vibration in isomer C is the H₂O-as of the D₂ perturbed water, and its calculated frequency is likely to have a larger error (i.e. the s/as coupling of the D₂ tagged water is affected). The tag isomers E/F have higher energies, at 193 cm⁻¹ and 133 cm⁻¹, respectively. Isomer F can be eliminated on the basis of the D₂-perturbed H₂O-s at 3641 cm⁻¹. Considering that this frequency is typically underestimated, this vibration would likely lie ~3670 cm⁻¹. Such a feature is clearly not present



between the experimental H₂O-s and H₂O-as bands. Isomer E has essentially the same appearance as the bare cluster, and its presence in the experimental spectrum cannot be eliminated. All of these tag isomers are very close energetically, and have similar appearances when taking into account the error in the D₂-H₂O interaction. Determining exactly which tag isomers are present is difficult, and it does not provide any significant new information to the analysis of the experimental spectrum. From the calculated spectrum of the bare cluster, one can already see that the 3592 cm⁻¹ feature is the D₂ perturbed H₂O-s feature.

For an example of further complications that can arise from calculating D₂ tagged clusters, Figure S2 shows the calculated results for [MnOH]⁺(H₂O)₃. Two tagging isomers are shown, with D₂ located on two different water ligands. These two isomers have a calculated energy difference of only 165 cm⁻¹. The untagged structure shows two types of water: a free water and two that are weakly interacting with hydroxide, giving rise to two distinct H₂O-s vibrations. In the lower energy isomer (right structure, blue spectrum), the D₂ is interacting with the free water, and the corresponding H₂O-s stretch redshifts from 3616 cm⁻¹ to 3549 cm⁻¹. In the other structure (green spectrum), the D₂ interaction removes one waters from interacting with the hydroxide ligand,

giving rise to three types of water (i.e. D₂ bound, hydroxide bound, and free). The H₂O-s stretch region now splits into three features, with the lowest frequency band corresponding to HO-H₂O interaction and the middle feature corresponding to the D₂-perturbed H₂O-s. Neither calculated spectrum fits the experiment. The higher energy isomer offers a



better fit in terms of the overall shape of the spectrum, although it appears that the strength of both the D₂-H₂O and HO-H₂O interactions are overestimated. Comparison with the n=4 experimental spectrum shows that the middle peak in the experimental spectrum is likely the D₂ perturbed H₂O-s stretch, in agreement with the higher energy isomer. For most of the other species studied here, the D₂ induced features are easier to pinpoint because addition of the tag induces minimal structural changes, as is in the case for the n=4 cluster.

B) Isomers of [MnOH]⁺(H₂O)₄

Figure S3 shows various isomers of [MnOH]⁺(H₂O)₄. The two isomers responsible for

the experimental spectrum are shown in the top panel.

The next two isomers have all four water in the first shell, and the highest energy isomer here has the second shell water in an

AA configuration. The isomer with $\Delta E = +764 \text{ cm}^{-1}$

can be eliminated because it has a hydroxide stretch

that is higher in frequency than the lowest energy isomer and there is not an obvious feature at higher

frequency in the experimental spectrum.

The $\Delta E = +816 \text{ cm}^{-1}$ and

$\Delta E = +838 \text{ cm}^{-1}$ isomers

both have intensities in the 3400-3500 cm^{-1} region,

where the experimental

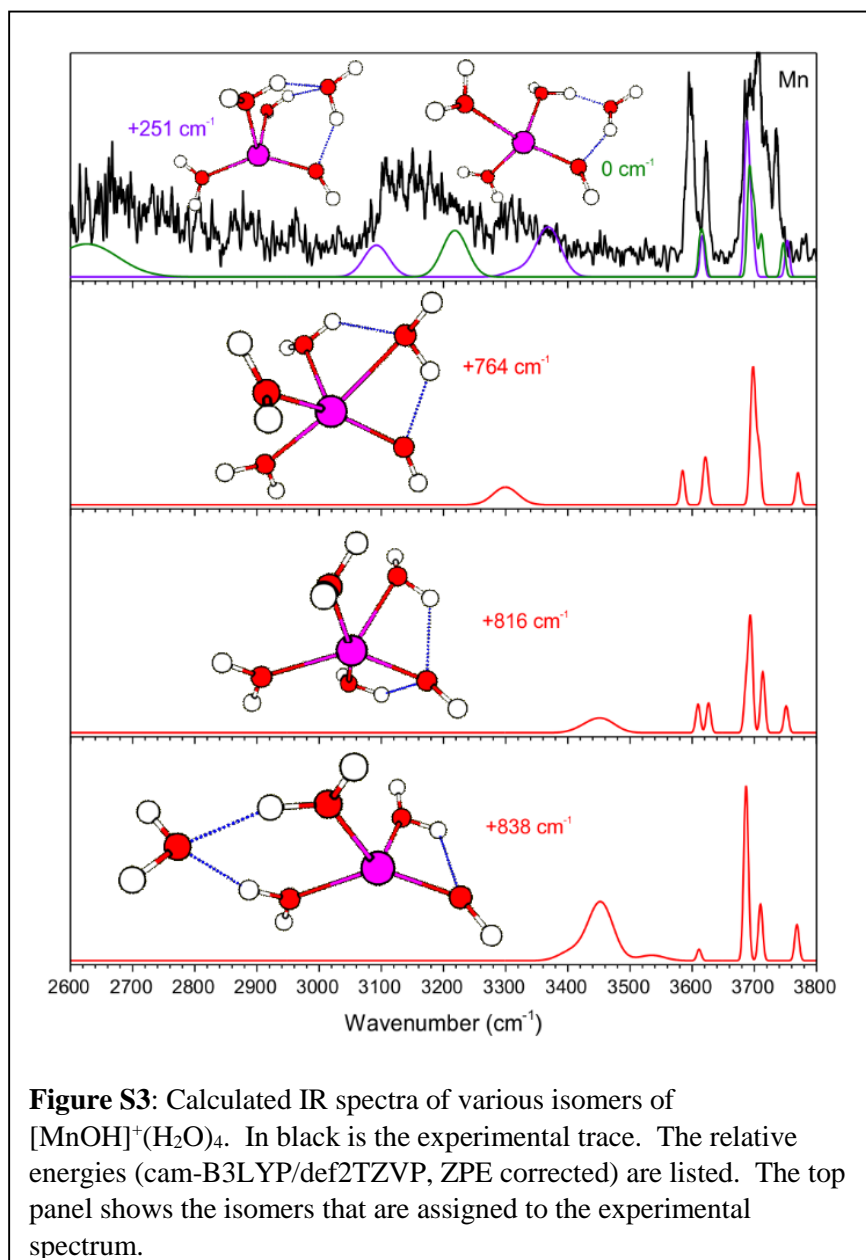


Figure S3: Calculated IR spectra of various isomers of [MnOH]⁺(H₂O)₄. In black is the experimental trace. The relative energies (cam-B3LYP/def2TZVP, ZPE corrected) are listed. The top panel shows the isomers that are assigned to the experimental spectrum.

spectrum shows minimal intensity. Considering all these calculated spectra, the two lowest energy isomers fit the experiment the best. Note that only the lowest energy isomer has a vibration that accounts for the broad feature below 3000 cm^{-1} .

C) Isomers of $[\text{FeOH}]^+(\text{H}_2\text{O})_4$

Figure S4 shows the calculated IR spectra for the different isomers of $[\text{FeOH}]^+(\text{H}_2\text{O})_4$. The experimental spectrum of the $n=4$ cluster shows two distinct features in the hydroxide stretch region, with approximately similar intensities. This indicates the equal presence of two isomers with different hydroxide interactions. The lowest energy isomer with the second shell water in an AAD configuration (green trace) accounts for the intensities in the 3200-3400 cm^{-1} region as well as the 3734 cm^{-1} hydroxide peak. The $\Delta E = +768 \text{ cm}^{-1}$ isomer with the AA motif has a hydroxide stretch that is higher frequency than the lowest energy isomer, accounting for the 3751 cm^{-1} feature. This isomer also accounts for the additional intensities around 3500 cm^{-1} region. The lack of any intensity at $\sim 2700 \text{ cm}^{-1}$ in the experimental spectrum indicates that the $\Delta E = +257 \text{ cm}^{-1}$ isomer, with AD motif, is not present in the experiment. An additional $\Delta E = +706 \text{ cm}^{-1}$ isomer was found, where all four water

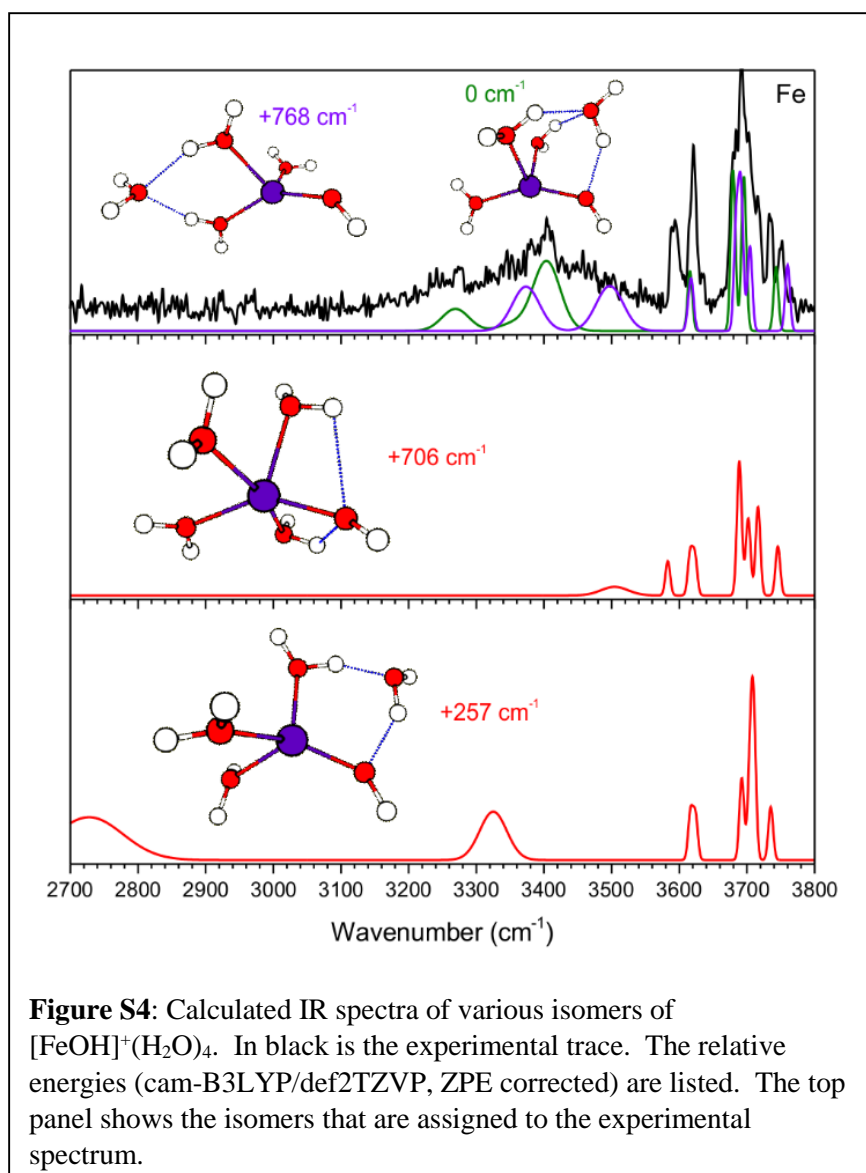
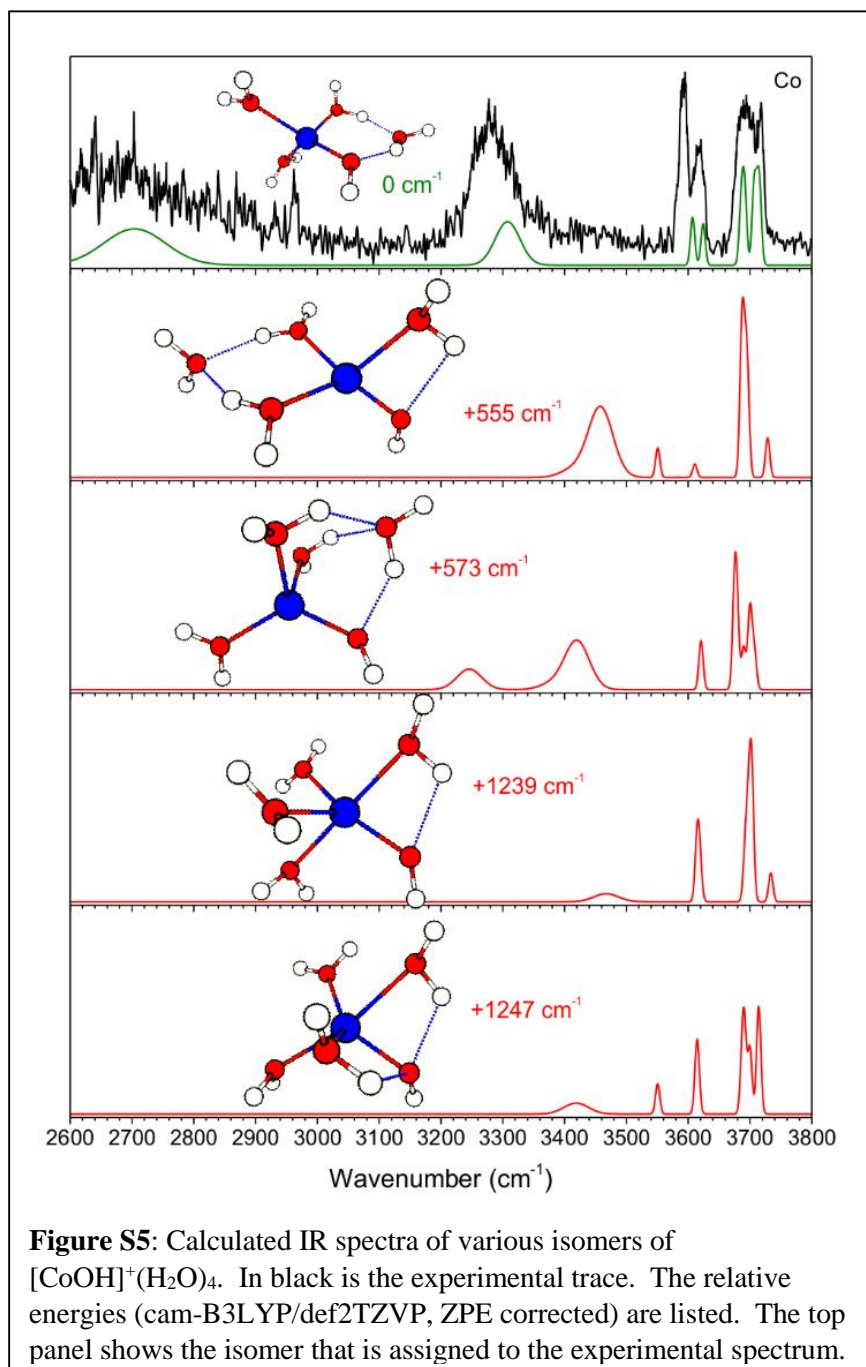


Figure S4: Calculated IR spectra of various isomers of $[\text{FeOH}]^+(\text{H}_2\text{O})_4$. In black is the experimental trace. The relative energies (cam-B3LYP/def2TZVP, ZPE corrected) are listed. The top panel shows the isomers that are assigned to the experimental spectrum.

molecules are in the first solvation shell. Its hydroxide stretch is at a similar frequency as that of the lowest energy isomer and it only has weak intensity in the 3500 cm^{-1} region. Its presence as a minor contribution to the experimental spectrum cannot be ruled out. However, comparisons of the calculated IR spectra with the experimental spectrum indicates that the dominant isomers are those two with the fourth water in the AAD and AA configurations.

D) Isomers of $[\text{CoOH}]^+(\text{H}_2\text{O})_4$

Figure S5 shows various isomers of $[\text{CoOH}]^+(\text{H}_2\text{O})_4$. The lowest energy isomer assigned to the experimental spectrum is shown in the top panel. The next two isomers, $\Delta E = +555\text{ cm}^{-1}$ and $\Delta E = +573\text{ cm}^{-1}$ have the fourth water in the second solvation shell in the AA and AAD configuration. The $\Delta E = +573\text{ cm}^{-1}$ isomer may be present in minor quantities in the experimental spectrum, since there are weak intensities at $\sim 3450\text{ cm}^{-1}$. However, it should be noted that anharmonic effects that give rise to the broad width of the 3280 cm^{-1} feature can also give



rise to additional intensities in this region. The $\Delta E = +555 \text{ cm}^{-1}$ isomer has a higher frequency hydroxide stretch and a vibration at 3550 cm^{-1} , both of which not observed in the experimental spectrum. The two other isomers have all four waters in the first solvation shell. They are calculated to be much higher in energy and are not likely to contribute to the experimental spectrum.

E) Isomers of $[\text{NiOH}]^+(\text{H}_2\text{O})_4$

Figure S6 shows various isomers of $[\text{NiOH}]^+(\text{H}_2\text{O})_4$. The lowest energy isomer assigned to the experimental spectrum is shown in the top panel.

The presence of the two isomers with the fourth water in the second solvation shell ($\Delta E = +421 \text{ cm}^{-1}$ and $\Delta E = +781 \text{ cm}^{-1}$) can be eliminated because the experimental spectrum does not have intense broad features in the $2500\text{-}3500 \text{ cm}^{-1}$ region. The $\Delta E = +469 \text{ cm}^{-1}$ isomer is another way to arrange five ligands in an octahedral geometry. It has doublets in the 3370 cm^{-1} and 3610 cm^{-1} region which are not experimentally observed. However, it should be noted that both of these experimental features are

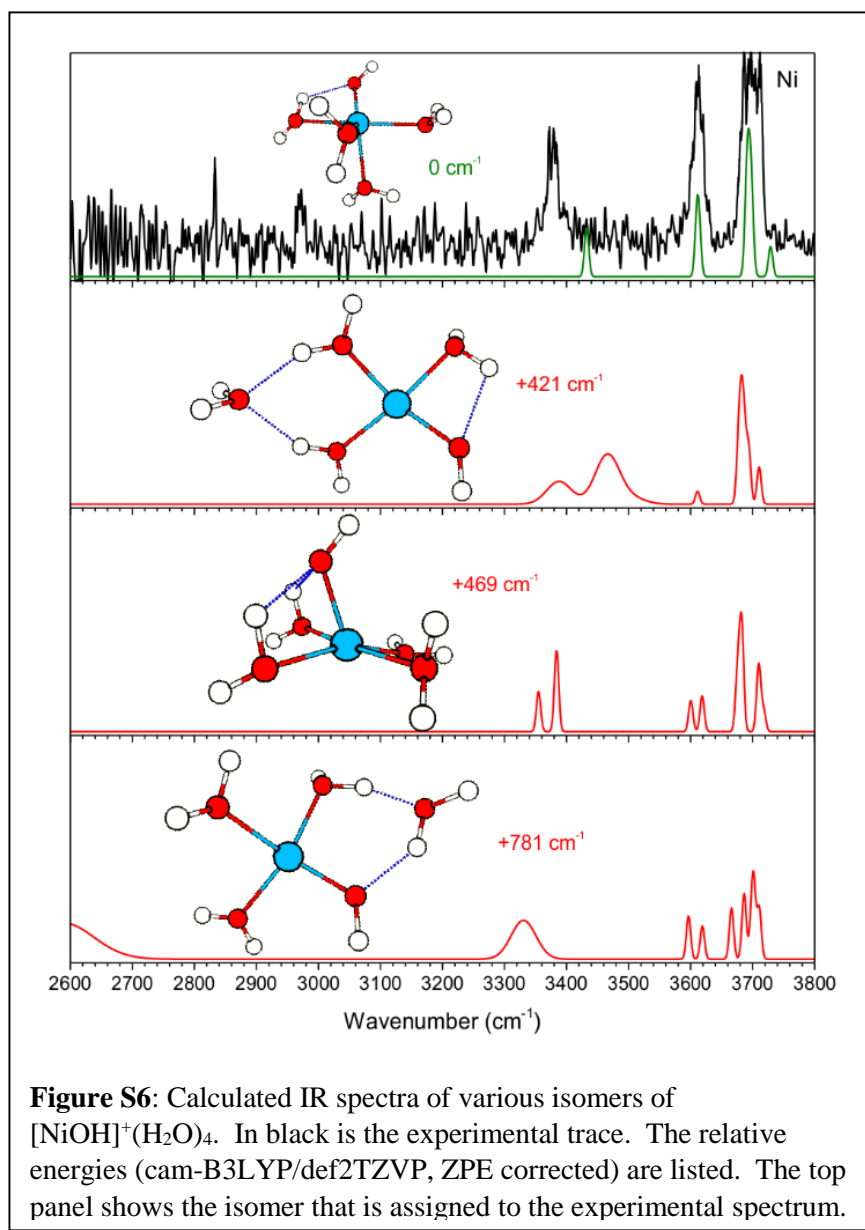


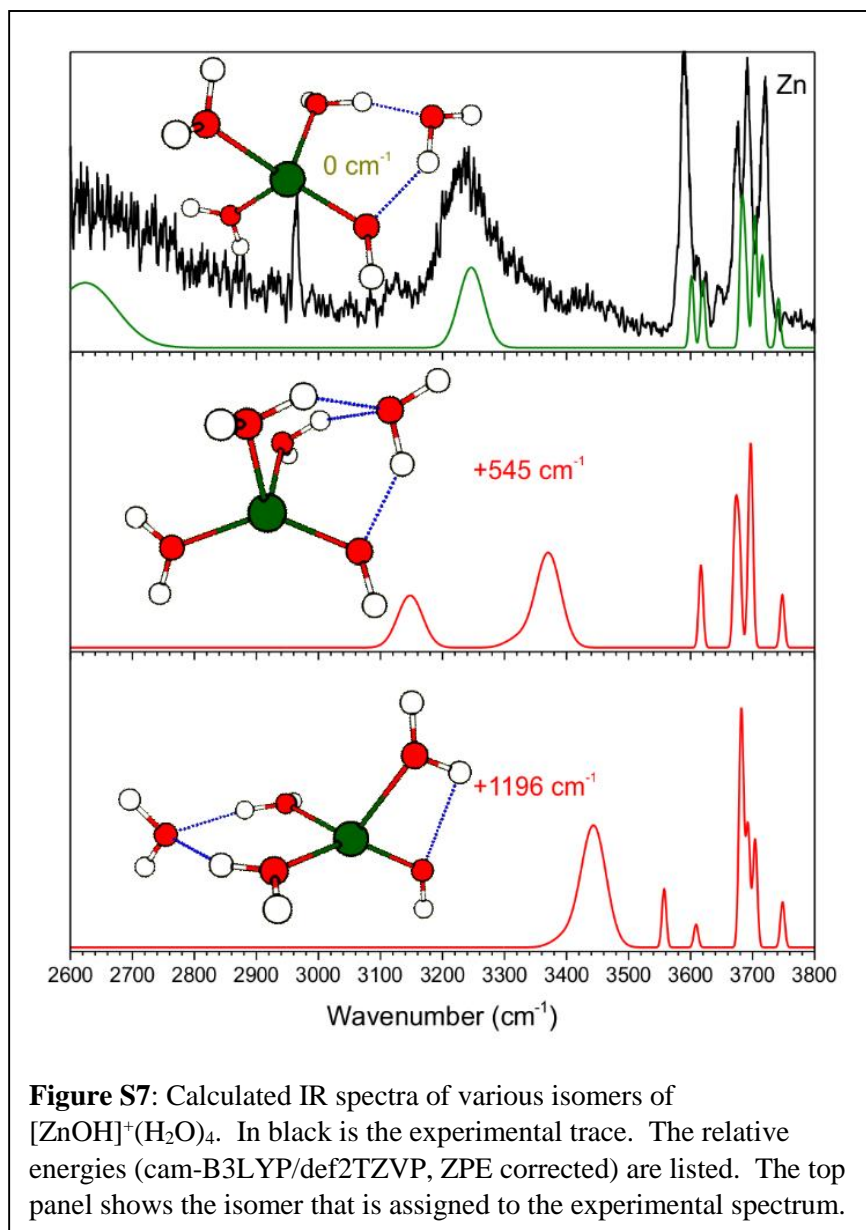
Figure S6: Calculated IR spectra of various isomers of $[\text{NiOH}]^+(\text{H}_2\text{O})_4$. In black is the experimental trace. The relative energies (cam-B3LYP/def2TZVP, ZPE corrected) are listed. The top panel shows the isomer that is assigned to the experimental spectrum.

slightly broad, and therefore the presence of this isomer cannot be completely ruled out.

F) Isomers of $[\text{ZnOH}]^+(\text{H}_2\text{O})_4$

Figure S7 shows various isomers of $[\text{ZnOH}]^+(\text{H}_2\text{O})_4$. The lowest energy isomer assigned to the experimental spectrum is shown in the top panel. No stable isomers were found where all four ligands are in the first solvation shell. The $\Delta E = +545 \text{ cm}^{-1}$ isomer with the fourth water in the AAD configuration may be present in minor quantities in the experimental

spectrum. Particularly, it may be responsible for the shoulder at $\sim 3420 \text{ cm}^{-1}$ and $\sim 3120 \text{ cm}^{-1}$. The isomer with water in the AA configuration is found to be 1196 cm^{-1} higher in energy, and it has a vibration at 3558 cm^{-1} , not observed in the experimental spectrum.



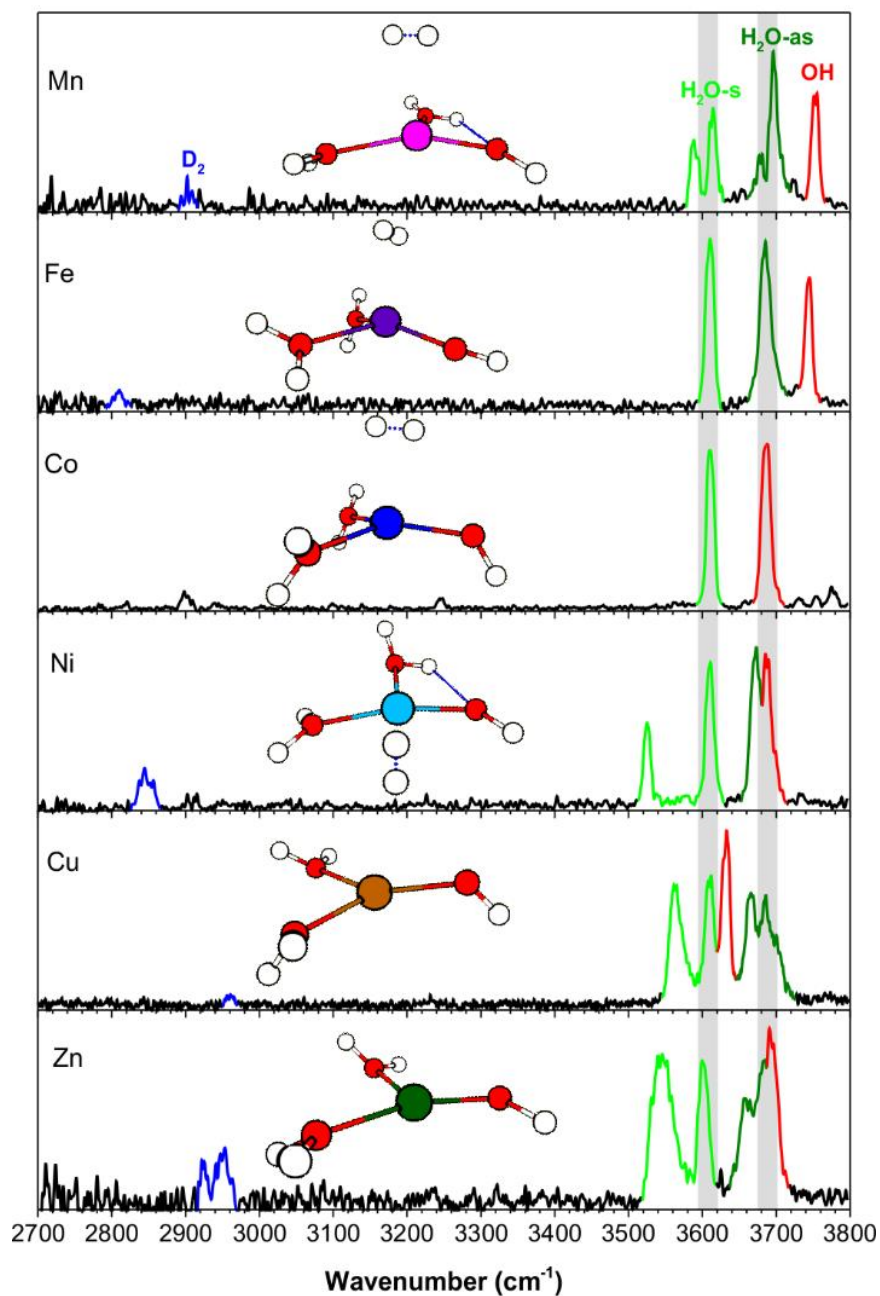


Figure S8: The assigned experimental spectra of $[\text{MOH}]^+(\text{H}_2\text{O})_2$. Highlighted in blue is the D_2 stretch, in green are the $\text{H}_2\text{O-s}$ and $\text{H}_2\text{O-as}$ stretches, and in red is the hydroxide stretch. The grey bars allow for comparison of the $\text{H}_2\text{O-s}$ and $\text{H}_2\text{O-as}$ bands for different metals (highlighting the higher frequency edge of the bands).

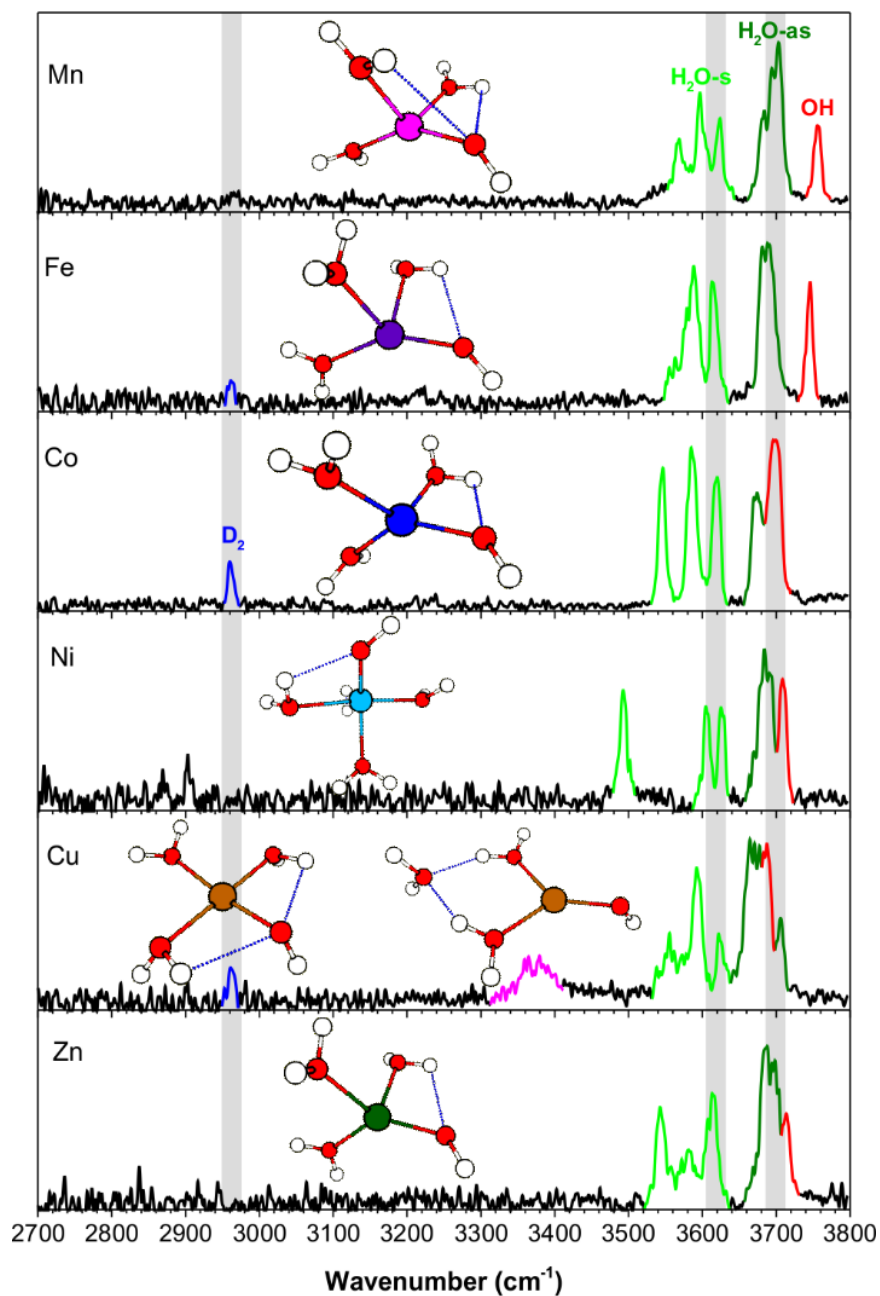


Figure S9: The assigned experimental spectra of $[\text{MOH}]^+(\text{H}_2\text{O})_3$. Highlighted in blue is the D_2 stretch, in green are the $\text{H}_2\text{O-s}$ and $\text{H}_2\text{O-as}$ stretches, in red is the hydroxide stretch, and in magenta are the H-bonded OH stretch involving the second shell water. The grey bars allow for comparison of the D_2 , $\text{H}_2\text{O-s}$ and $\text{H}_2\text{O-as}$ bands for different metals (highlighting the higher frequency edge of the bands).

Table S1: Calculated sequential H₂O binding energies (eV) of the untagged clusters. The geometry is optimized at the DFT level (cam-B3LYP/def2TZVP). The MP2 (MP2/aug-cc-pVTZ) and CCSD (CCSD/def2TZVP) calculations are single point calculations. The ZPE corrections are derived from the DFT calculation.

	n=2			n=3			n=4		
	DFT	MP2	CCSD	DFT	MP2	CCSD	DFT	MP2	CCSD
MnOH	1.246	1.253	1.259	1.043	1.047	1.071	0.854	0.810	0.781
FeOH	2.088	1.302	1.309	1.053	1.041	1.048	0.835	0.810	0.760
CoOH	1.383	1.145	-	1.168	2.105	-	0.835	0.801	0.767
NiOH	1.308	1.515	1.371	1.067	1.058	1.068	0.856	0.948	0.939
CuOH	1.225	1.606	1.319	0.920	1.120	1.006	0.799	0.773	0.746
ZnOH	1.346	1.275	1.347	1.085	1.027	1.094	0.931	0.831	0.818