

Supporting information

” Why does the IR spectrum of hydroxide stretching vibration weaken with increase in hydration?”

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Contents

- **Summary on the convergence of quantum chemistry methods, the definition of dipole moment for charged species, and the Raman intensities. Full reference for reference 41 and 42 is also given.**

- 1) **Table S1: Vibrational calculation results with MP2**
- 2) **Figure S2: Dipole moment function calculated by QCISD(T) and MP2**
- 3) **Table S2: Raman scattering intensity**

Accuracy and convergence of quantum chemistry methods:

For OH⁻ and OH radical, we confirmed the accuracy of the single reference methods by comparing the vibrational calculation results obtained from potential energy curve and dipole moment function calculated by full valance internally contracted multireference configuration interaction^{1,2,3} (MRCI) using the 6-311++G(3df,3pd) basis^{4,5,6,7}. We obtained fundamental peak positions of 3570 and 3592 cm⁻¹ for OH⁻ and OH radical, respectively. These values are in close agreement with the QCISD(T) peak positions of 3578 and 3597 cm⁻¹ and the B3LYP values of 3578 and 3547 cm⁻¹. All these values are within 20 cm⁻¹ of the experimental values of OH⁸ and OH⁹, given in Table 1 of the text and Table S1. Furthermore, MRCI calculation gave intensities of 86.7 and 6.7 km/mol for OH⁻ and OH radical respectively. These values are also consistent with the QCISD(T) results of 127 and 7.7 km/mol as well as the B3LYP results of 86.9 and 9.5 km/mol, given in Table 1 of the text.

In Table S1 we present the results obtained by MP2/6-311++G(3df,3pd). The peak positions are blue shifted by ~140 cm⁻¹ for both OH⁻ and OH radical compared to the experimental values signifying that this method may not be a good choice to use for hydroxide systems when considering the absolute peak position in comparison with experiment. Indeed the values for the mono- and di-hydrate are also blue shifted by 80 cm⁻¹ compared to the experimental values by Johnson and coworkers¹⁰. However, MP2 results show the general trend that the peak position blue shifts and the intensity greatly decreases with increase in *n*.

Table S1: Peak position (cm⁻¹) and absorption intensity (km/mol) of OH⁻(H₂O)_{*n*} *n*=0-5 and OH calculated using the local mode model with MP2/6-311++G(3df,3pd), as well as the experimental values.

	MP2			Exp
	peak position	intensity		peak position
OH ⁻	3695	6.10E+01	3695	3555.6 ^a
OH ⁻ (H ₂ O)	3731	1.07E+01	3731	3653.0 ^b
OH ⁻ (H ₂ O) ₂	3744	3.16E+00	3744	3660.0 ^b
OH ⁻ (H ₂ O) ₃	3757	7.52E-02	3757	
OH ⁻ (H ₂ O) ₄	3757	1.65E-01	3757	
OH ⁻ (H ₂ O) ₅	3727	2.67E+00	3727	
OH	3708	2.13E+01		3570.0 ^c

a: Experimental results from ref 9, b: Experimental results from ref 10; c: Experimental results from ref 8.

In Figure S1, we compare the variance of the dipole moment function calculated by QCISD(T) and MP2 with the 6-311++G(3df,3pd) basis. As can be seen below the general trend is similar to those obtained using B3LYP/6-31+G(d,p) given in Fig. 2 (a) of the text.

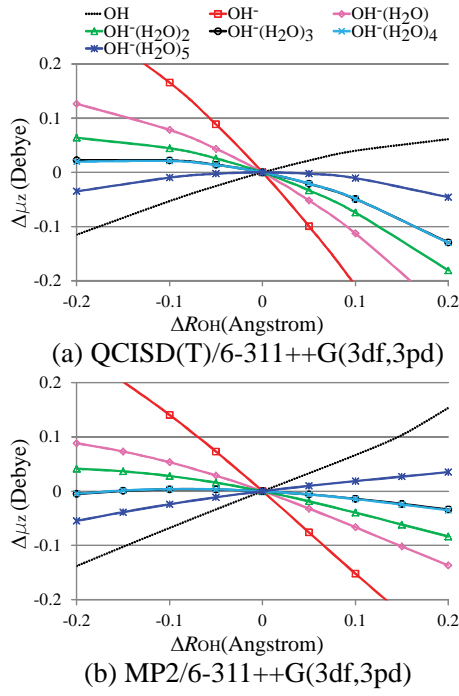


Figure S1: Dipole moment function of $\text{OH}^-(\text{H}_2\text{O})_n$, $n=0-5$ and OH radical calculated using (a) QCISD(T)/6-311++G(3df,3pd), (b) MP2/6-311++G(3df,3pd). The equilibrium dipole moment value is set to zero. Curves for OH, OH^- , $\text{OH}^-(\text{H}_2\text{O})$, $\text{OH}^-(\text{H}_2\text{O})_2$, $\text{OH}^-(\text{H}_2\text{O})_3$, $\text{OH}^-(\text{H}_2\text{O})_4$, and $\text{OH}^-(\text{H}_2\text{O})_5$ are given in black lines, red square, pink rhombus, green triangle, black circle, light blue cross, and blue star, respectively.

Origin of the dipole moment for charged species:

When one defines a dipole moment in charged species one must define it with respect to some reference coordinate origin so the dipole moment for a given geometry in the Cartesian coordinate is given as

$$\begin{aligned}
 \vec{\mu} &= \sum_{\alpha}^{N_{\text{atom}}} Q_{\alpha} (\vec{R}_{\alpha} - \vec{R}_{REF}) - \int_{\text{allspace}} \rho(\vec{r}) (\vec{r} - \vec{R}_{REF}) d\vec{r} \\
 &= \sum_{\alpha}^{N_{\text{atom}}} Q_{\alpha} (\vec{R}_{\alpha}) - \vec{R}_{REF} \sum_{\alpha}^{N_{\text{atom}}} Q_{\alpha} - \int_{\text{allspace}} \rho(\vec{r}) (\vec{r}) d\vec{r} + \vec{R}_{REF} \int_{\text{allspace}} \rho(\vec{r}) d\vec{r} \\
 &= \sum_{\alpha}^{N_{\text{atom}}} Q_{\alpha} (\vec{R}_{\alpha}) - \int_{\text{allspace}} \rho(\vec{r}) (\vec{r}) d\vec{r} - \vec{R}_{REF} Q
 \end{aligned}$$

where, \vec{R}_{α} , \vec{R}_{REF} , and \vec{r} are the position vectors of atom α , the reference point, and the electron, respectively. Here Q is the total charge of the system and for our present $\text{OH}^-(\text{H}_2\text{O})_n$ $n=0-5$ clusters, $Q=-1$. Following the customary definition, we define the center of mass as the reference point. This is equivalent to taking the center of mass as the coordinate origin and calculating the dipole moment. Considering the large discrepancy between the masses of the electron and nuclei we take the center of mass of the nuclei as the reference in our calculation. In the analysis using the AIM method, we place the origin at the oxygen atom and derive the dipole moment, but when we calculate the intensity we add in the correction for this center of mass term. These center of mass reference dipole moment functions are plotted in Fig. 2 of the text, and Fig. S1 in this supplementary material.

Raman intensities:

As shown in Table S2, the increase in the number of water molecules in the first hydration shell does not cause large variations toward the Raman activity for the OH⁻ stretching fundamental compared to the massive decrease in the IR absorption intensity discussed in the text and given in Table 2. We note here that the calculated results are based on the harmonic approximation using the normal mode that corresponds to the hydroxide stretching vibration. Using the keyword “Freq=internal” in the Gaussian09 program, we confirmed that this normal mode consists of 99% hydroxide stretching motion so it is separated from all other motion of the solvating water molecules. It is important to note that the absolute value of the Raman activity increases greatly when using a bigger basis set 6-311++G(3df,3pd), thus showing large basis set dependence. However when comparing the calculation done for a given basis set, the Raman activity does not show a massive variance with the number of water molecules in the first solvation shell. As a conclusion we do not see orders of magnitude difference in the Raman intensity with addition of solvating water molecules.

Table S2: The Raman activity, in Å⁴ amu⁻¹, of OH⁻(H₂O)_n, n=0-5 and OH radical calculated by B3LYP/6-31+G(d,p) and 6-311++G(3df,3pd) for the hydroxide stretching vibration using the harmonic approximation.

Species	Raman activity	Raman activity
	6-31+G(d,p)	6-311++G(3df,3pd)
OH ⁻	120.9	172.6
OH ⁻ (H ₂ O)	92.0	119.0
OH ⁻ (H ₂ O) ₂	93.3	139.3
OH ⁻ (H ₂ O) ₃	91.3	121.9
OH ⁻ (H ₂ O) ₄	109.4	116.9
OH ⁻ (H ₂ O) ₅	82.7	100.2
OH	59.0	57.1
H ₂ O	80.9 ^a , 37.9 ^b	92.9 ^a , 27.6 ^b

a: antisymmetric stretch b: symmetric stretch

Full Reference 41 and 42

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