

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

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Due to the wide interest in acid base chemistry, the local hydration structure of aqueous hydroxide has been studied using many different techniques such as X-ray and neutron scattering, X-ray absorption, Raman scattering, and infrared (IR) absorption methods. Many theoretical molecular dynamics simulations based on polarizable force fields as well as density functional theory have been performed to provide the molecular level understanding on hydroxide hydration. The present consensus is that there are on average four water molecules strongly hydrogen bonded on the oxygen end of hydroxide and this number thermally fluctuates between three to five in the aqueous phase. An interesting feature for the solvated hydroxide is its IR intensity. The stretching vibration spectra of the gas phase hydroxide have been observed and calculated to have a stronger intensity compared to the OH stretching vibration of the gas phase H₂O molecule. However, the IR spectra of concentrated aqueous OH⁻ only show a small hump for the hydroxide stretching vibration. The understanding of the hydroxide ion water clusters, OH⁻(H₂O)_n, provides useful insight and fundamental knowledge to this problem. Indeed, the experimental vibrational spectra with argon predissociation spectroscopy for OH⁻(H₂O)_n·Ar (*n*=1-5) showed a decrease in the intensity of the OH⁻ stretching peak as *n* is increased. By *n*=3 it was not observable in the argon predissociation spectra. In this theoretical study we systematically examine the consequence of hydration toward the hydroxide stretching vibration for the hydrated hydroxide cluster as a function of water molecules in the first solvation shell for OH⁻(H₂O)_n *n*=0-5 and compare it with the OH radical.

Using the solvation structure for OH⁻(H₂O)_n (*n*=1-5) with water molecules attached to the oxygen edge, we calculated the hydroxide stretching vibration peak position and absorption intensity using the local mode model.

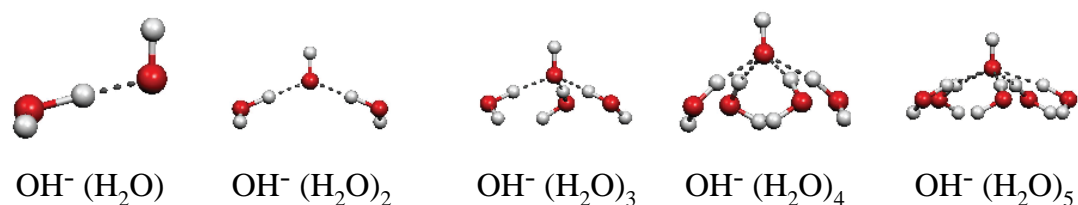


Figure 1: The structures of OH⁻(H₂O)_n: *n*=1-5 considered in this study

As given in Table 1 below, our calculations reproduce the available experimental peak positions to within 20 cm⁻¹. Furthermore, while the bare hydroxide has very strong absorption which is more than an order larger than the OH radical, addition of solvating water causes the intensity to decrease greatly. By *n*=3, the absorption intensity is an order smaller than the bare case. This is consistent with the disappearance of the OH⁻ peak starting from *n*=3 in the aforementioned argon predissociation cluster

experiments.

Table 1: Peak position (cm^{-1}) and absorption intensity (km/mol) of $\text{OH}^-(\text{H}_2\text{O})_n$, $n=0-5$ and OH calculated using the local mode model with QCISD(T)/6-311++G(3df,3pd) and B3LYP/6-31+G(d,p).

	QCISD(T)		B3LYP		Exp
	peak position	intensity	peak position	intensity	peak position
OH^-	3578.5	173.0	3578.2	125.4	3555.6 ^a
$\text{OH}^-(\text{H}_2\text{O})$	3648.4	48.2	3651.7	25.6	3653.0 ^b
$\text{OH}^-(\text{H}_2\text{O})_2$	3675.7	20.1	3686.6	8.5	3660.0 ^b
$\text{OH}^-(\text{H}_2\text{O})_3$	3702.9	8.2	3695.0	0.5	
$\text{OH}^-(\text{H}_2\text{O})_4$	3716.6	8.1	3710.3	0.3	
$\text{OH}^-(\text{H}_2\text{O})_5$	3684.4	0.2	3685.9	0.5	
OH	3597.6	7.7	3546.7	9.5	3570.0 ^c

a: J. C. Owrutsky et al. *J Chem Phys* **1985**, 83, 5338–5339. b: W. H. Robertson et al. *Science* **2003**, 299, 1367–1372. c: P. J. Linstrom et al. NIST Chemistry WebBook, NIST Standard Reference Database Number 69: NIST Chemistry WebBook, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>

The above trend for the intensity is due to the interesting characteristic in the hydroxide dipole moment function (DMF) which is responsible for the vibrational

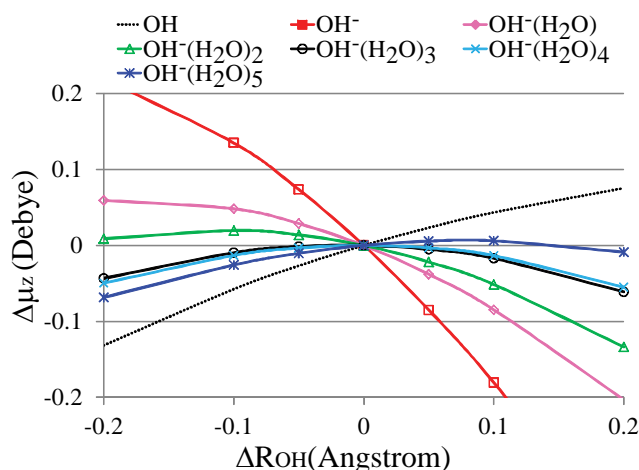


Figure 2: Dipole moment function calculated for solvated hydroxide clusters using B3LYP/6-31+G(d,p). The value of the equilibrium is set to zero.

transition moment. As seen in Figure 2, the DMF of OH^- greatly decreases as the bond is elongated accounting for the strong intensity. One can easily notice that the sign of the gradient at the equilibrium bond length is opposite for OH^- and OH. Furthermore, it is obvious that an increase in n causes the absolute value of the negative DMF gradient at the equilibrium to become smaller. In fact, $n=3-5$, their values are close to zero, thus resulting in weak IR intensities.

This n dependence of the DMF is due to the directional hydrogen bonding of the solvating water molecules. At the meeting we will present detailed analysis on the electronic charge migration associated with the hydroxide stretching vibration which leads to this change in the trend of the DMF.

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