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Research paper

(Li, Na, K)OH hydration bonding thermodynamics: Solution self-heating

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ABSTRACT

The resultant energy of solvent H–O bond exothermic elongation by O:⇔:O repulsion, featured at <3100 cm^{-1}, and the solute H–O bond endothermic contraction by bond-order-deficiency, at 3610 cm^{-1}, heats up the (Li, Na, K)OH solutions. The solution temperature increases linearly with the number fraction of the ordinary O:H–O bonds transiting into their hydration states. The elongated H–O bond emits >150% the O:H cohesive energy of 0.095 eV that caps the energy dissipating by molecular motion, thermal fluctuation, diffusion, and even evaporation. Therefore, the intramolecular H–O bond relaxation dictates the OH^- solvation bonding thermodynamics and the performance of basic solutions.

1. Introduction

Exothermic and endothermic reactions are of great importance to both basic and engineering sciences [1–3], as well as efficiency of drug functioning [4]. However, why the OH^- hydration heats up its solution remains to be resolved. A comprehensive discussion [5] on the thermodynamic chemistry occurred in liquids, solids, and semiconductor materials suggested that the concurrent understandings are mainly within the framework of classical thermodynamics in terms of enthalpy [6,7] and Gibbs energy [8]. The heat generation at reaction is mainly attributed to the solute-solvent electron transportation [5,9] and molecular interactions [10], water molecular motion dynamics [11], H–O correlation [12]. Inter- and intra-molecular cooperative interactions govern the path, ultimate outcome, and efficiency of aqueous solvation [13].

The pump-probe ultrafast infrared absorption spectroscopy investigation [14] suggests that the spectral signal for the OH^- solvation decays its intensity in 200 fs and this process is followed by a thermalization that becomes slower with increasing the solute concentration. The molecular thermalization proceeded by water molecular rotation, reorientation, and diffusion is suggested to be responsible for the solvation thermodynamics [15]. Two processes of molecular motion relaxations occur upon NaOH hydration in bulk water [16] and in water clusters [17]. One is the slow process on 200 ± 50 fs time scales and the other faster dynamics on 1–2 ps scales. Density functional theory calculations suggest that the OH^- hydration shall contains OH^- – $3H_2O$ molecules [3] and the hydrating molecular structure undergoes evolution by reorientation at heating [18]. However, quantitative information and atomistic insight into the solvation intramolecular bonding and intermolecular nonbonding thermodynamics and their cooperativity still open for examination.

Extending our recent findings on the YOH(Y = Li, Na, K) solvation Raman spectroscopy [19], we show herewith quantitatively that the energy difference between the solvent H–O bond elongation by O:⇔:O compression and the solute H–O bond contraction due to HO^- bond-order deficiency heats up the YOH solutions. The solution temperature T(C) varies linearly with the fraction number $\Delta f(C)$ of the H–O bonds transiting from the mode of ordinary water to the elongated and contracted states upon the YOH being hydrated.

2. Principles

2.1. YOH solvation phonon spectrometrics

The YOH solvation proceeds as follows [19] with involvement of possible bonding thermodynamics, as listed in Table 1:

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Table 1
Bonding thermodynamics of YOH solvation.

Energy absorption Q_a	Solvent H–O bond thermal contraction by temperature raising	significant
	solute H–O contraction by bond-order-deficiency [22]	significant
	hydrating H–O bond contraction by Y^+ polarization [23]	Negligible because YX solvation and polarization change little the solution temperatures
Energy emission Q_e	YOH dissolution into Y^+ and OH^- [19]	
	solvent H–O elongation by O:⇔:O repulsion [19]	significant
	O:H elongation by Y^+ polarization [23]	Negligible due to tiny O:H energy
Energy dissipation Q_{dis}	molecular motion and structure fluctuation	With little contribution to energy absorption or emission
	heat loss due to the non-isothermal calorimetric detection	Cause error tolerance

$$\begin{aligned} & YOH + 4H_2O \rightarrow Y^+ \\ & \quad + OH^- \text{ (H - O contraction due to bond order loss,} \\ & OH^- \text{ has one H - O bond loss from } H_2O) \\ & \quad + 3H_2O + H_2O\text{(H - O contraction by compression)} + (\text{heat} \uparrow) \end{aligned}$$

Solvation in water dissolves the YOH into a Y^+ ion and an OH^- hydroxide. The Y^+ leaves one of its electron behind the OH^- that keeps its sp^3-orbital hybridization with three lone pairs ":" on it. This process adds three ":" and one H^+ into the solvent consisting N value of H_2O molecules and turns the initial 2 N protons into 2 N + 1 and the ":" from 2 N to 2 N + 3. The excessive two ":" forms uniquely the O:⇔:O repulsive nonbond, called super-HB, for convenience, as Fig. 1a inset illustrated. The stronger O:⇔:O repulsion compresses its neighboring O:H–O bond. Mechanical compression shortens the O:H and lengthens the H–O cooperatively [20], see Fig. 1b inset. On the other hand, the OH^- solute is subject to bond order-deficiency, which shortens its due H–O bond [21].

Fig. 1a and b display the full-frequency Raman spectra for YOH solutions [19], which agrees with those probed with infrared spectra from YOH and YOD solutions [17,24,25]. Solvation broadens and flattens the H–O vibration peak towards lower frequencies. The peak position corresponds to the bond stiffness $(\omega_x)^2 \propto (E/d^2)_x$ of the x segment of the O:H–O bond (x = L and H for the O:H and the H–O, respectively). The E_x is the bond energy and d_x the bond length. The O:H–O bond consists the weaker O:H (~0.1 eV, ~200 cm^{-1}) intermolecular van der Waals bond (vdW) and the stronger H–O (~4.0 eV; 3200 cm^{-1}) intramolecular covalent bond, which are coupled by the Coulomb repulsion between electron lone pairs on adjacent oxygen ions [22]. At 4 °C temperature, d_L = 1.70 and d_H = 1.0 Å. If a specific bond becomes shorter and it turns to be stiffer, a blue shift of its vibration peak occurs, and vice versus. One can thus judge how the bond length and energy change from the phonon band frequency shift and how the O:H and the H–O segment cooperate. The rest bond bending vibration modes are out of immediate concern.

It has been extensively affirmed that the O:H–O bond disparity and the O-O repulsivity dictate the extraordinary adaptivity, sensitivity, recoverability of water and ice subjecting to stimulation

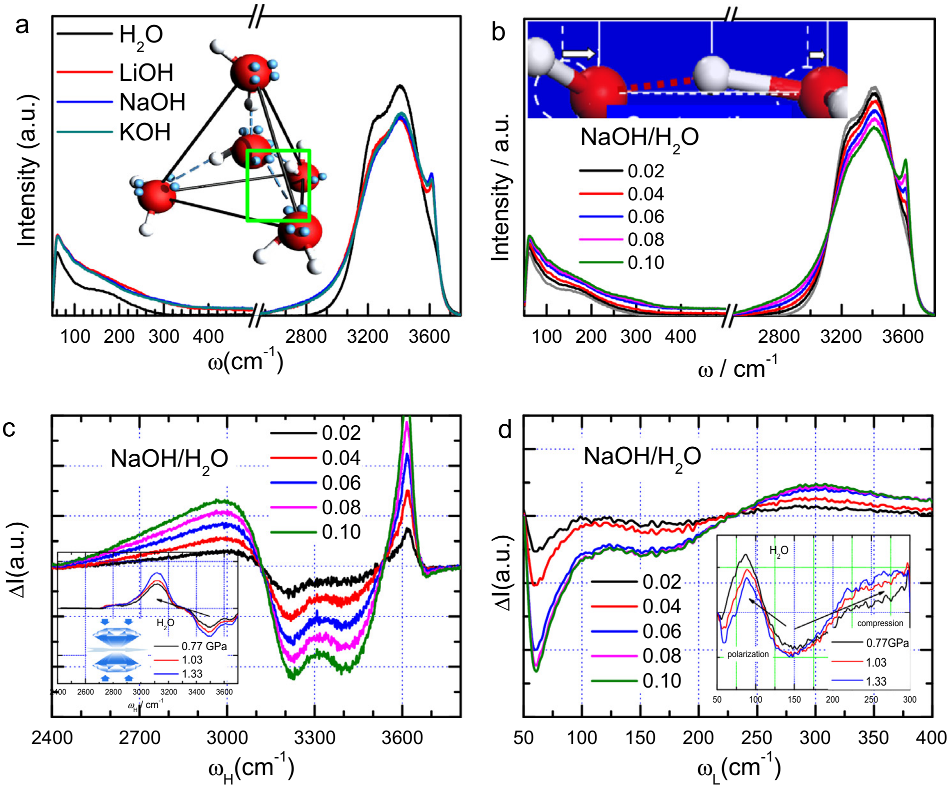

Fig. 1. Full-frequency Raman spectroscopy for (a) YOH/H_2O of the same concentration and (b) concentrated NaOH/H_2O solutions and (c, d) the DPS profiles [19]. Inset **a** illustrates the central HO^- replacement of the $2H_2O$ unit cell, which derives an O:⇔:O bond as framed. Inset **b** shows the O:H–O bond cooperative relaxation under O:⇔:O compression, which has the same effect of pressure on the O:H–O bonds DPS as insets c and d demonstrated [19]. The O:H–O bond compression proceeds by O:H contraction and H–O elongation [22].