Polyborates in aqueous borate solution: A Raman and DFT theory investigation

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ABSTRACT

The geometries, energies and vibrational frequencies of various polyborates in both gaseous and aqueous phase were calculated at the B3LYP/aug-cc-pVDZ level. The calculated total symmetrical stretching Raman shifts of $B(OH)_3$, $B(OH)_4^-$, $B_2O(OH)_4$, $B_2O(OH)_5^-$, $B_2O(OH)_6^{2-}$, $B_3O_3(OH)_3$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_3O_3(OH)_6^{3-}$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ were assigned to 877.40, 735.33, 785.22, 792.90, 696.79, 587.72, 599.06, 740.16, 705.01, 551.67 and 521.04 cm^{-1}, respectively. The results can be used as the characteristic frequency for polyborates in aqueous phase at room temperature. At least six types of polyborates $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$, occur in aqueous solutions at ambient temperature. The chemical species distribution and the relevant interaction mechanisms among polyborates in the solutions were also suggested.

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1. Introduction

Dozens of polyborates exist in aqueous borate solutions under common condition. The existing forms and their interactions among these different polyborates mainly depend on pH, temperature, concentration of total boron and counter-ion in the solution [1,2]. Therefore, hydroxyl-hydrated borate solutions are more complicated than other salts. Many studies have been done in this field, including conductometric, potentiometric titration [3,4], ^{11}B NMR [5–7], vibrational spectrum [8–11], MS [12], X-ray scattering [13] *etc*. Unfortunately, the more studies are performed on the borate, the more controversial issues are founded.

Vibrational spectrum has been effectively used to identify and characterize the solid hydrated borates. Li et al. [14] studied the FT-IR and Raman spectra of about 30 hydrated borates and gave a few tentative assignments. FT-IR difference spectroscopy and Raman spectra have been used to study the aqueous solution structure of borates of high boron-concentration [8,15,16]. It is noteworthy that the characteristic frequencies of ions can be only obtained when the borates have the large solubility. A detailed theoretical study of the infrared vibrational spectra of boric acid using DFT method with a large variety of exchange correlation functions concluded that B3LYP is a suitable method to the study of this system [17]. Other computational studies have examined the hydration, acidity and NMR shifts of boric acid [18,19]. To our knowledge, we are not

aware of any detailed *ab initio* studies on the structure optimization and Raman frequency of other polyborates in aqueous solution.

In the present work, we studied the Raman spectra of solid hydrated borates and their concentrated aqueous solutions. In order to assignment Raman shifts of aqueous borate solutions deliberatively, we calculated the optimization structure and Raman vibrational frequencies of polyborates at the B3LYP/aug-cc-pVDZ level. The characteristic frequencies of polyborates in aqueous phase were summed, compared with the experimental Raman spectra. The chemical species distribution in borate solutions and the relevant interaction mechanisms among polyborates have also been proposed.

2. Experimental and calculated methodologies

H_3BO_3, $Na_2B_4O_7 \cdot 10H_2O$, $NaBO_2 \cdot 4H_2O$ and KOH (all were analytic grade reagent) were commercially available and recrystallized twice from distilled water. $K_2B_4O_7 \cdot 4H_2O$ and $NaB_5O_8 \cdot 5H_2O$ were synthesized according to the phase diagram in the ternary system $K_2O–B_2O_3–H_2O$ [20] and $Na_2O–B_2O_3–H_2O$ [21], and verified by both element analysis and X-ray powder diffraction, respectively. The sample solutions were prepared by weighting with double-distilled water ($\kappa < 1.00\,\mu S\,cm^{-1}$) and the overall relative uncertainty of the solution preparation was 0.1%. The sample solutions were carefully protected from atmospheric CO_2 and could be used for about one week without changes of concentration. Acidity of all the solutions was measured using an Orion 310P-01 pH meter (Thermo, USA) with a reproducibility of 0.5%. In all the pH measurements a thermostat (GDH-1015 W, Sayfo analytical instrument factory, Jintan Jiangsu, China) was used to maintain the temperature

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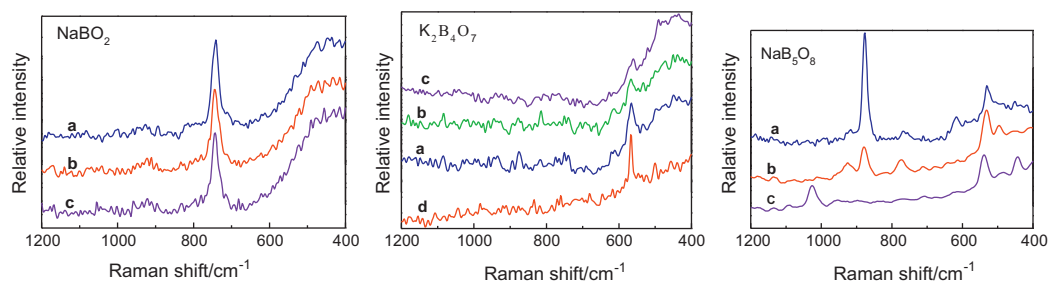*E-mail addresses:* yongqzhou@163.com (Y. Zhou), fangch@isl.ac.cn (C. Fang), fangy8@isl.ac.cn (Y. Fang).

Fig. 1. Raman spectra of NaBO$_2$ (a, 4.19 mol L^{-1}; b, 4.58 mol L^{-1}; c, 4.98 mol L^{-1}; d, microcrystals), K$_2$B$_4$O$_7$ (a, 1.64 mol L^{-1}; b, 1.51 mol L^{-1}; c, 1.38 mol L^{-1}; d, microcrystals) and NaB$_5$O$_8$ (a, 1.39 mol L^{-1}; b, 0.79 mol L^{-1}; c, microcrystals) solution.
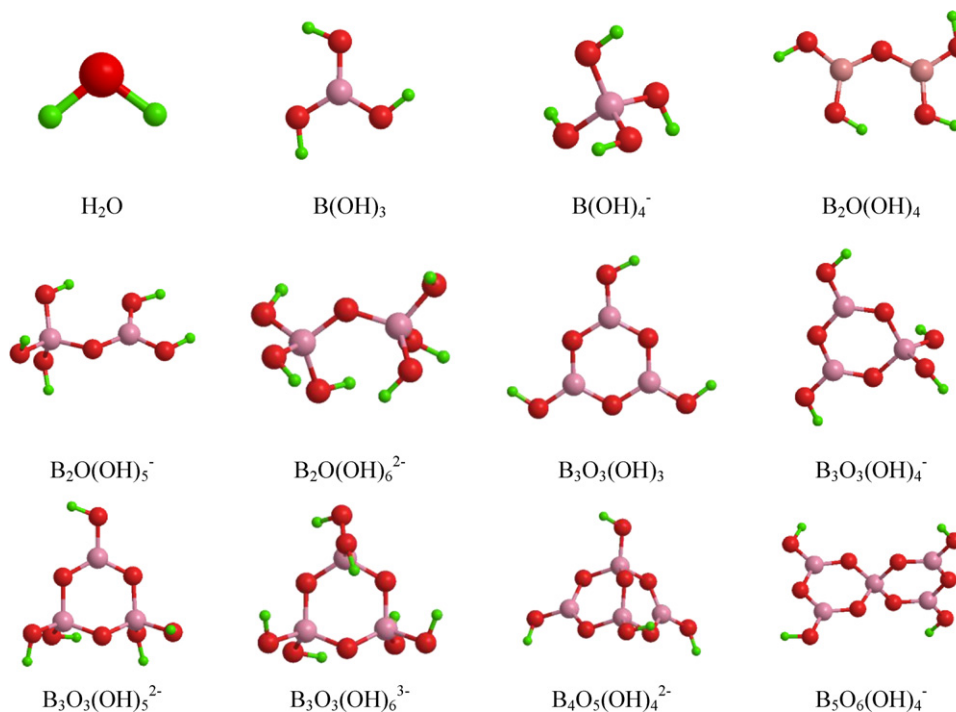

Fig. 2. Optimized configurations of polyborates and water molecule at the B3LYP/aug-cc-pVDZ level in aqueous phase.

at 298.15 ± 0.01 K. Raman spectra of solid and liquid samples were recorded in the ranges of 300–4000 cm^{-1}, respectively, with a Nicolet Almega Dispersive Raman spectrometer at room temperature. The laser wavelength is 532 nm and exposure time 8 s. The solid samples were put in the microscope slide with the number of exposures of 1 time, and the liquid samples in a quartz glass tube with that of 32 times, respectively.

In this work, the structure and Raman shift of common polyborates were investigated using the B3LYP method. To make a search for the local minimum energy and the characteristic frequencies of polyborates in aqueous phase, Dunning's aug-cc-pVDZ correlation consistent basis sets [22] were employed for all the atoms. In order to consider the long-range electrostatic effect of solvent, we employed a single-point polarized continuum model (PCM) in the calculation for all the polyborates. Geometry optimization of the various possible configurations of polyborates were done at B3LYP/6-31G(d) level. Then the lowest energy structures were considered for further geometry optimizations and Raman frequency calculations at the B3LYP/aug-cc-pVDZ level. The vibrational frequency was calculated at the same level in order to ascertaining the nature of the stationary points (no virtual frequency). The calculated vibration frequency can be adjusted through multiplying by a fixed factor $f = 1.0233$ below 1500 cm^{-1} [23]. Z-matrix

coordinates constrained to the appropriate symmetry were used to speed up the optimizations. All the geometry optimization and frequency analysis were performed with the Gaussian 03 software package [24].

3. Results and discussions

3.1. Experimental FT–Raman spectra

FT–Raman spectra of concentrated aqueous NaBO$_2$, K$_2$B$_4$O$_7$ and NaB$_5$O$_8$ solutions and their corresponding microcrystal were recorded and displayed in Fig. 1.

The range of 400–1200 cm^{-1} is the most favorable zone for the investigation of borate solution, which is considered as the characteristic absorption bands of polyborates [8,10,25,26]. The only obvious band near 740 cm^{-1} in Raman spectra is the characteristic peak of B(OH)$_4^-$ in aqueous NaBO$_2$ solutions. In K$_2$B$_4$O$_7$ solution, three obvious bands can be assigned to the characteristic vibrations of B$_4$O$_5$(OH)$_4^{2-}$ (566 cm^{-1}), B$_3$O$_3$(OH)$_4^-$ (614 cm^{-1}) and B(OH)$_4^-$ (741 cm^{-1}), respectively.

The higher solubility and the suitable pH of aqueous NaB$_5$O$_8$ solution in favor of polyborate formation make it a typical sample for vibrational spectrum study. The Raman shifts close to 613, 565