

Molecular structure of NaOH solutions at high P and T : Insights from *in situ* Raman spectroscopy and *ab initio* molecular dynamics simulations

JOHANNES STEFANSKI^{1,2}, CHRISTIAN SCHMIDT² AND SANDRO JAHN^{2,3}

¹Freie Universität Berlin, Institut für Geologische Wissenschaften, Arbeitsbereich Mineralogie-Petrologie, Malteserstraße 74-100, 12249 Berlin, Germany

²Deutsches GeoForschungsZentrum GFZ, Sektion 3.3, Telegrafenberg, 14473 Potsdam, Germany

³Institut für Geologie und Mineralogie, Universität zu Köln, Greinstr. 4-6, 50939 Köln, Germany

Sodium rich peralkaline fluids occur in several processes in the Earth's crust, e.g. late stage hydrothermal reactions in peralkaline agpaitic igneous rocks involve NaOH as an essential component [1]. Moreover, aqueous NaOH solutions at elevated temperature are indispensable in today's chemical industry, e.g. in the aluminium production (Bayer process). Addition of NaOH causes substantial changes in the water structure, which are reflected in the Raman spectrum [2] but are not completely understood, particularly at high pressure, P , and temperature, T . Here, we investigated structural and vibrational properties of 5.5 and 27 molal sodium hydroxide solutions. The solutions were contained in a hydrothermal diamond anvil cell and analysed by *in situ* Raman spectroscopy from ambient conditions up to 0.8 GPa and 700 °C. *Ab initio* molecular dynamics simulations were used for the interpretation of the experimental spectra. From the simulations, power spectra of the hydrogen velocity auto-correlation function and *ab initio* Raman spectra [3] were derived. The mode-projection approach [4] was employed to decompose normal modes of water and the stretching mode of hydroxide ion. The simulated frequency spectra agree with the experimentally obtained Raman spectra and show the same changes with P and T . At near ambient conditions, addition of NaOH results in rapid destruction of the water network, which confirms earlier studies [5]. At high T , the H_3O_2^- concentration has by far the largest impact on the Raman spectra. The hydrogen bonding distance decreases with increasing P and T because of the proton-transfer between water and the hydroxide ion, which is crucial for Raman spectroscopic analyses using the O–H stretching band as standard. Further observed structural changes with P and T include increasing coordination of Na^+ and changes in the connectivity.

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