A Raman Study of Aqueous KOH Solution in Glassy State

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Synopsis. Raman spectra of an aqueous KOH solution were measured in the OH stretching region and in the low frequency region (<700 cm^{-1}). Contrary to the results reported by Sharma and Kashyap,[5] only one Raman band specific to an aqueous KOH solution was observed at ≈285 cm^{-1} in the low frequency Raman spectrum.

Raman spectra of aqueous alkali hydroxide solutions have been investigated in the OH stretching frequency region by a large number of workers.[1-3] One of the notable characteristics of the OH stretching Raman spectrum is the existence of the sharp peak at 3620 cm^{-1}. This is due to the stretching vibrations of the OH$^-$ ions in the solution.

On the other hand, it seems that there have been only two Raman studies[4,5] on the low frequency region of alkali hydroxide solutions. Sharma and Kashyap[5] observed two new bands in the low frequency Raman spectra for aqueous NaOH and KOH solutions, in addition to the two restricted translational Raman bands at ≈60 and ≈170 cm^{-1} which are common to all aqueous solutions.[4,6] However, Walrafen,[4] who measured Raman spectra of many aqueous electrolyte solutions including LiOH, NaOH, and KOH solutions, didn't mention about the new band(s) in his low frequency Raman spectra for the LiOH, NaOH, and KOH solutions.

We have recently shown that vitrification of an aqueous solution reduces the Rayleigh scattering wing in a Raman spectrum of the solution, thus permitting unequivocal detection and characterization of weak Raman bands near the exciting line.[7] Therefore, it would be interesting to see the Raman spectrum of aqueous alkali hydroxide solution in the glassy state to clarify the discrepancy of the two reports. We here report a Raman study of glassy aqueous KOH solution.

The sample solutions were prepared by dissolving the commercially obtained KOH pellets (Wako chemicals, guaranteed grade) into distilled water. Raman measurements were essentially the same as previously reported.[7] The concentration of alkali hydroxide solution was determined by titration using Methyl Orange as an indicator against a standardized 0.1 M HCl (1 M=1 mol dm^{-3}) solution. Here the KOH concentration was denoted by R (=moles of water/moles of KOH).

The obtained Raman spectra for both liquid and glassy states of a KOH solution (R=3.9) are shown in Fig. 1. Contrary to the results by Sharma and Kashyap,[5] we see only one Raman peak specific to the KOH solution in the low frequency Raman spectrum. Judging from the Raman spectra reported by Sharma and Kashyap, they devided the single broad Raman envelope into two components: One at 292 cm^{-1} and the other at 332 cm^{-1}. Depolarization measurements indicate that the band at ≈285 cm^{-1} is polarized. It must be pointed out that Raman spectra for glassy NaOH (or NaOD) solutions also gave similar results: single peak at ≈285 cm^{-1} for a NaOH-H_2O solution and at ≈283 cm^{-1} for a NaOD-D_2O solution (intensity is concentration dependent).[8] The two restricted translational Raman

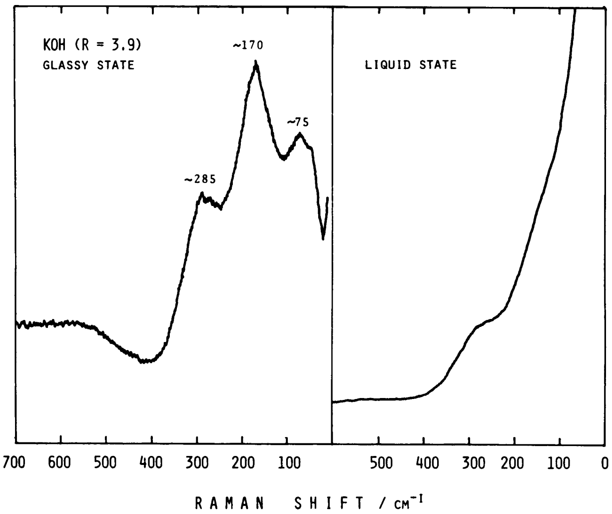

Fig. 1. Raman spectra of aqueous KOH solution (R=3.9) in low frequency region (10∼700 cm^{-1} for the glassy state, 70∼600 cm^{-1} for the liquid state).

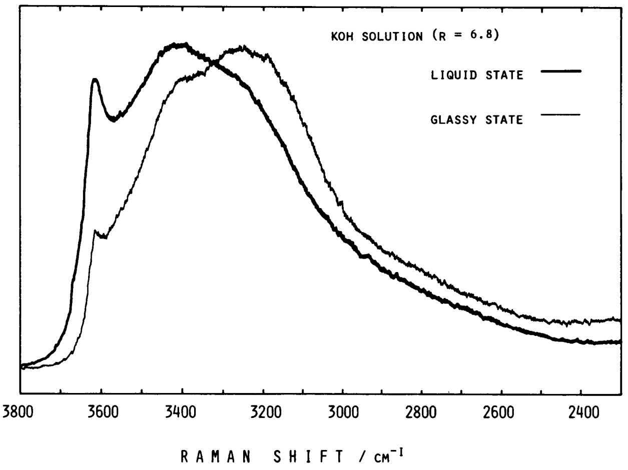

Fig. 2. Raman spectra in the OH stretching vibrational region of aqueous KOH solution (R=6.8).
Thick curve : liquid state at room temperature; thin curve: glassy state at liquid nitrogen temperature.

peaks at ≈170 and ≈75 cm^{-1} are usually assigned to the stretching ($\nu_{OH..O}$) and bending ($\delta_{OH...O}$) vibrations of the hydrogen-bonds between water molecules (and water molecules and anions).[4,6] As the peak at ≈285 cm^{-1} increases in intensity with increasing KOH concentrations and it is observed only in aqueous solutions of alkali hydroxides and ammonia, we come to conclude that it is due to the stretching vibrations of hydrogen-bonds between water molecules and OH$^-$ ions. The fact that its frequency virtually remains unchanged with KOH concentrations also supports the assignment.

The OH stretching Raman spectra for both liquid and glassy states are shown in Fig. 2. It is observed that the relative intensity of the peak at ≈3620 cm^{-1} decreases from a liquid state to a glassy state. This arises from the decrease in ionisation of KOH at low temperatures. The most characteristic feature of the OH stretching Raman spectrum is the continuity of the spectrum down to about 2200 cm^{-1}. A similar continuum is observed in a Raman spectrum of an acid solution.[8-10] It is to be noted that the OH stretching Raman spectrum terminates at about 2900 cm^{-1} in most aqueous electrolyte solutions.[11]

The hydrogen-bonds between oxonium ions and water molecules are very strong.[12,13] Pernoll *et al.*[9] attributed the continua observed in acid solutions to the large polarizability of the hydrogen-bonds caused by protons in the hydrated oxonium ions. A similar interpretation can be invoked to explain the continuum for the KOH solution. Here the OH$^-$ ions play the same role as oxonium ions do in an acid solution. In an aqueous acid solution, protons move around very quickly among water molecules so that each H_3O^+ ion is short-lived scarcely enough to vibrate as a distinct species.[14,15] These rapid proton movements shift and split the energy levels of the OH stretching vibrations, resulting in the continuous distribution of the OH stretching vibrations to lower frequency region.

An interesting point is that the continuum rather increases in intensity in the glassy KOH solution when the intensities are compared by making the peak heights of both states (liquid and glassy states) equal. This is mainly due to the increase in hydrogen-bond strength going from a liquid state to a glassy state, as revealed by the shift of the spectrum peak to a lower frequency side. The intensity increase in the frequency region of 3100—3300 cm^{-1} is a clear indication that strongly hydrogen-bonded structure is recovered to some extent in the glassy state. Liquid water has a strong peak near 3200 cm^{-1} whose intensity grows as the temperature approaches the freezing point of water and this feature is ascribed to the increase of strongly hydrogen-bonded water molecules in the liquid with temperature decrease.[17] The fact that amorphous solid water and polycrystalline ice, where all water molecules are strongly coupled with hydrogen-bonds, have the strongest peak at ≈3100 cm^{-1}[18,19] also substantiates the above interpretation.

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