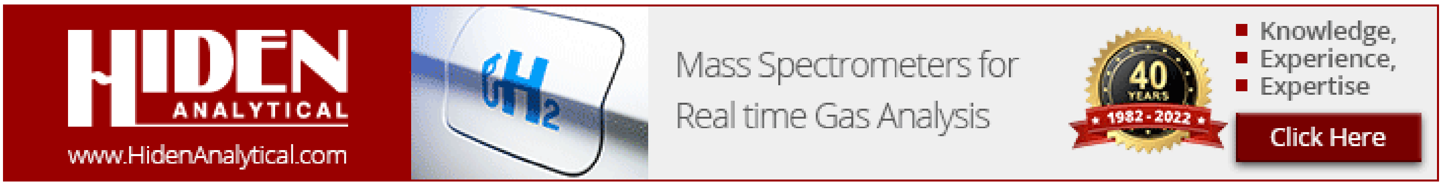

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Different structures give similar vibrational spectra: The case of OH^- in aqueous solution

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We have calculated the anharmonic OH^-(aq) vibrational spectrum in aqueous solution with a "classical Monte Carlo simulation + QM/MM + vibrational" sequential approach. A new interaction model was used in the Monte Carlo simulations: a modified version of the charged-ring hydroxide-water model from the literature. This spectrum is compared with experiment and with a spectrum based on CPMD-generated structures, and the hydration structures and H-bonding for the two models are compared. We find that: (i) the solvent-induced frequency shift as well as the absolute OH^- frequency are in good agreement with experiment using the two models; (ii) the Raman and IR bands are very similar, in agreement with experiment; (iii) the hydration structure and H-bonding around the ion are very different with the two ion-water interaction models (charged-ring and CPMD); (iv) a cancellation effect between different regions of the hydration shell makes the total spectra similar for the two interaction models, although their hydration structures are different; (v) the net OH^- frequency shift is a blueshift of about +80 cm^{-1} with respect to frequency of the gas-phase ion.

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