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# States of Ions in Aqueous Solutions and Stability of Water Molecules Hydrated to Ions Studied by Computational Methods

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Summary

Stability of hydrogen and oxygen atoms of water molecules hydrated to a magnesium ion relative to that in bulk water was studied by molecular orbital (MO) calculations. The theoretical background is that the isotopic reduced partition function ratio (rpfr) is larger for a more stable species.

All MO calculations were made at the HF/6-31G(d) level of theory using Gaussian 98 and 03 program packages. As model species of water hydrated to a magnesium ion, we considered water molecules in $Mg^{2+}(H_2O)_n$ clusters with $n$ up to 90. Structures of the clusters were first optimized and, at the optimized structures, the vibrational analysis was carried out and rpfrs were calculated.

The hydration number in the primary hydration sphere around a magnesium ion was six. Oxygen atoms of some water molecules in the primary hydration sphere had one hydrogen bond while those of other water molecules had no hydrogen bond. The oxygen isotopic rpfr values of the former oxygen atoms were larger than those of the latter, and both were substantially larger than that of bulk water. Oxygen atoms in the primary hydration sphere around a magnesium ion were thus more tightly bound and consequently more stable than that in bulk water. Oxygen atoms with two hydrogen bonds in the secondary hydration sphere had rpfr values nearly equivalent to that in bulk water, which meant that their stability was comparable to that in bulk water. The existence of a magnesium ion thus affected the stability of oxygen atoms only in its primary hydration sphere and not those in secondary and higher hydration spheres.

The influence of a magnesium ion on the stability of hydrogen atoms of water molecules was minimal. Although hydrogen isotopic rpfr values of some hydrogen atoms in the primary sphere were slightly larger and those of other hydrogen atoms were slightly smaller than that of a hydrogen atom in bulk water, rpfr values of hydrogen atoms in the primary hydration sphere were, on an average, equivalent to that in bulk water. The stability of hydrogen atoms in the secondary and higher hydration spheres were also not affected by the existence of a magnesium ion.