D/H and $^{18}O/^{16}O$ Isotopic Reduced Partition Function Ratios of Water Molecules around a Sodium Ion

Takao Oi and Akiko Otsubo

Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan

Reprint requests to T. O.; Fax: +81-3-3238-3361; E-mail: t-ooi@sophia.ac.jp

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With the final goal set at theoretical elucidation of experimentally observed isotope salt effects, molecular orbital calculations were performed to estimate the D/H and $^{18}O/^{16}O$ isotopic reduced partition function ratios (RPFRs) of water molecules around a sodium ion. As model water molecules in the *i*th hydration sphere of the sodium ion in sodium ion-bearing aqueous solution, we considered water molecules in the *i*th hydration sphere that were surrounded by water molecules in the (*i*+1)th hydration sphere in clusters, $Na^+(H_2O)_n$ (*n* up to 100). The calculations indicated that the $^{18}O/^{16}O$ RPFR in the primary hydration sphere is slightly smaller than that of bulk water while the D/H RPFR is practically the same as that of bulk water, and that the influence of the existence of the sodium ion is limited to the primary hydration sphere.

Key words: Reduced Partition Function Ratio; Isotope Salt Effects; Sodium Ion; Hydrogen and Oxygen Isotopes.