Laboratory measurements of spin temperature of water molecules from ice in thermal desorption

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H_2O contains two protons with nuclear spin of I=1/2, and two nuclear-spin modifications exist: the ortho (I=1, triplet, parallel nuclear spin) and the para (I=0, singlet, antiparallel nuclear spin) with statistical weights 2 I + 1. Nuclear-spin temperature (T_{spin}) is defined as the temperature that reproduces a given the ortho-to-para ratio (OPR) if in local thermodynamic equilibrium. The OPR of H_2O is equal to 3 in statistical equilibrium, which is achieved at temperatures above ~50 K.

T_{spin} of H_2O molecules is often observed in comet coma and in star forming regions to investigate these molecules' physical and chemical histories. In cometary coma, T_{spin} of H_2O molecules has been derived to be ~30 K [1]. These values have been implicated as the temperature of cold grains at molecular condensation or formation in a molecular cloud, or in the solar nebula [2]. However, the real meaning of the observed T_{spin} remains a topic of continuing debate.

The present study experimentally measured the T_{spin} of H_2O thermally desorbed from amorphous solid water (ASW) deposited at 8 K. The experiment was performed with the RASCAL apparatus at Inst. of Low Temp. Sci., which consists of a vacuum sample chamber, and a laser system. ASW was prepared on a Al substrate at 8 K by vapor-deposition in the vacuum chamber, and then heated to 150 K to sublime H_2O. The thermally desorbed H_2O molecules were analyzed ro-vibrationally by the resonance enhanced multiphoton ionization (REMPI) method [3]. We also produced ASW at 8 K by photolysis of a CH_4/O_2 mixture (photoproduced ASW) for the idea that T_{spin} of H_2O molecules may relate to formation processes on cold dust grains. Figure 1 shows the REMPI spectrum of desorbed H_2O for the vapor-deposited ASW. The spectrum was best reproduced by the simulation with T_{rot} = T_{spin} = 150 K, where T_{rot} represents rotational temperature. Thermally desorbed H_2O molecules from the both ice samples showed T_{spin} almost at the statistical high-temperature limit. These results suggest that the T_{spin} of gaseous H_2O molecules thermally desorbed from ice does not necessarily reflect the surface temperature at which H_2O molecules condensed or formed. We discuss the possibility of nuclear-spin conversion of H_2O in water ice [3].

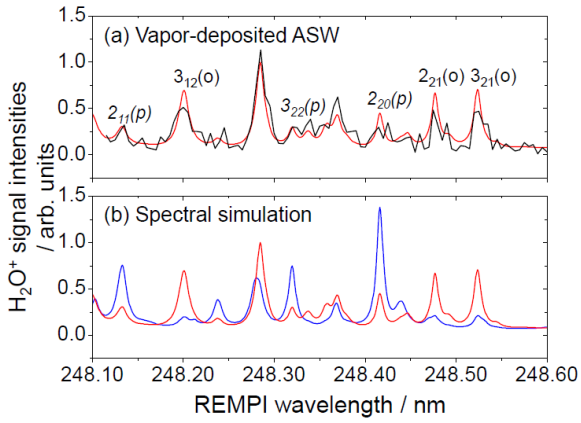

Figure 1. (a) (The black line) 2+1 REMPI spectrum of thermally desorbed H_2O from vapor-deposited ASW. (The red line) The best-fitting simulations with T_{rot} = T_{spin} = 150 K. Indications ($J_{Ka,Kc}$) are rotational assignments in H_2O. H_2O molecules with (K_a + K_c = odd) are ortho, while those with (K_a + K_c = even) are para species (*italic transitions*). (b) Reference simulations with T_{spin} = 150 K (red) and 8 K (blue). T_{rot} is fixed at 150 K.

References

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