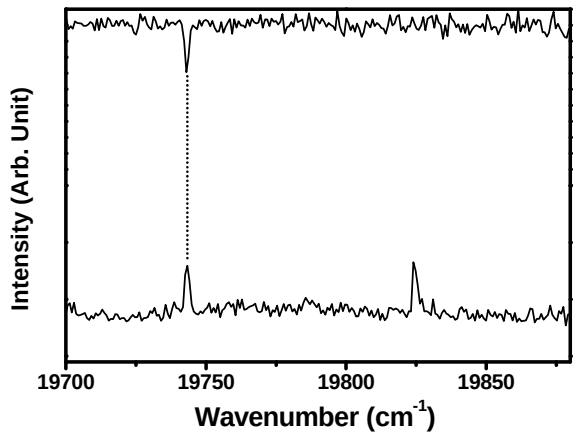
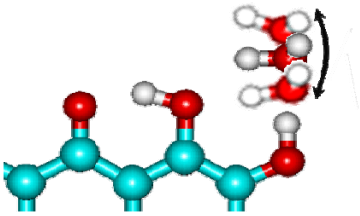
Supporting Infomation

1. Vis-Vis HB spectrum (upper) of $Az(H_2O)_1$ obtained with the HB laser fixed at the frequency of a given conformer (19743cm^{-1}, the origin band of B, in this case), shown against the FE spectrum (lower). Note that the peak at 19825 cm^{-1} in the FE spectrum is not hole-burnt, and therefore must originate from another conformer (conformer C, in this case). We carried out repeated runs of HB and found three conformers.



2. Intermolecular stretching vibration mode of the hydrogen bond between O2−H2 and water in conformer **1** of $Az(H_2O)_1$ with a calculated frequency of 165 cm^{-1}, in good agreement with the experimental value (~150 cm^{-1}) deduced from its vibrational progression in the FE spectrum.



3. Transition energies of the three conformers of $Az(H_2O)_1$ calculated by TDDFT (upper panel) vs. experimental FE spectrum (lower panel). The theoretical energies were scaled by an arbitrary constant to make the 0-0 band of **1** match the origin band of A at 18792cm^{-1}.