ELUCIDATION OF THE LOCAL BINDING MOTIFS OF ELECTRONS TRAPPED ON WATER

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When electrons interact with water the hydrogen bonding networks deform so as to localize the excess charge until a self-consistent configuration is obtained. Photoelectron spectroscopy of negatively charged water clusters has established that multiple isomers are almost always created in this process, and it is likely that these isomers reflect local mimina in this rearrangement pathway. By capitalizing on recent advances in argon nanomatrix vibrational spectroscopy, the structures of the dominant isomers in the small negatively charged water clusters have been elucidated and determined to be dominated by one water molecule's interaction with the excess electron. Here we report the structure of the more weakly electron binding isomer of the hexamer anion in order to explore a competing electron accommodation pathway. It has been difficult to isolate the spectroscopic signatures of co-existing isomers because the OH stretching region is typically well above the electron binding energy of the less stable forms, leading to severe line broadening by fast autodetachment. We overcome this problem by focusing on the low energy bending modes of the perdeutero water hexamer anion, and indeed recover sharp spectroscopic signatures for both isomers. The resulting bands are heavily overlapped, but we unravel their independent contributions by systematically controlling the relative populations of each form by increasing the number of attached argon atoms. The isolated band patterns establish that the weaker binding isomer does not display the characteristic electron binding motif common to the more strongly bound isomer class, where a single water molecule points toward the electron cloud with both of its hydrogen atoms. Rather, it structurally resembles the "Book" isomer of the neutral water hexamer, which has been identified as a precursor leading to production of the high binding isomer.