

SIZE-SELECTED SPECTRA OF WATER CLUSTERS USING ISOTOPE DILUTION

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Molecular rotational spectroscopy is a powerful for determining the structures of molecular clusters. A key feature of the technique is the high spectral resolution that makes it possible to record the spectra of the large number of isomers generated in the pulsed jet expansion without significant spectral overlap. However, when many clusters are produced the spectral line density can make it difficult to identify individual spectra. This work explores the potential to assign a cluster size for each transition in the spectrum of water clusters using isotopic dilution. Previous work on the structures of water clusters used ^{18}O water “spiking” to obtain the oxygen atom framework geometry from the analysis of the set of isotopomers coming from single H_2^{18}O incorporation into the water cluster. That work showed that, to a good approximation, the H_2^{18}O substitutes into the geometry according to simple statistics. This observation suggests that the water cluster size for each transition in the spectrum can be determined by the reduction in the signal intensity when a known percentage of H_2^{18}O is spiked into the water sample. The success of this isotope dilution approach to generating size-selected cluster spectra is illustrated using the known assignments of water cluster spectra. The analysis method is then used to identify a weak spectrum for the water heptamer that was previously unassigned. On the large water cluster size limit, the method led to the successful identification of four hydrogen bond network isomers of $(\text{H}_2\text{O})_{14}$ and a polar isomer of $(\text{H}_2\text{O})_{16}$. Many transitions are left unassigned including many in the $N=8-10$ size range based on their isotope dilution behavior.