I. Experiment

For the IR excitation of the clusters we used a tuneable solid state IR laser (LaserVision). Subsequent photionization was carried out at 80 ns delay with an excimer laser (Lambda PhysicsLPX200i) pumped dye laser (Lambda Physics LPD3000) at 388 nm (standard). A few scans were recorded at 360 nm. We could not observe an effect of the photoionization energy on the recorded IR action spectra. The spectra were recorded with 5 (around 3700 cm^{-1}, free OH stretch) and 10 cm^{-1} stepwidth and the frequencies were aligned by comparison with spectra of polystyrol and polyethylene foils. The IR spectra depicted in Figs. 2,3 are averaged single scan spectra (six scans for the Ne, four scans for the Ar seeded expansions, see Fig. S3). The signal intensity for a given IR photon energy was measured as the ratio of the ion yield at each mass with the IR laser on (IR + UV laser) vs. off (UV laser alone). For each IR photon energy, 1000 time of flight mass spectra were averaged in both operation modes.

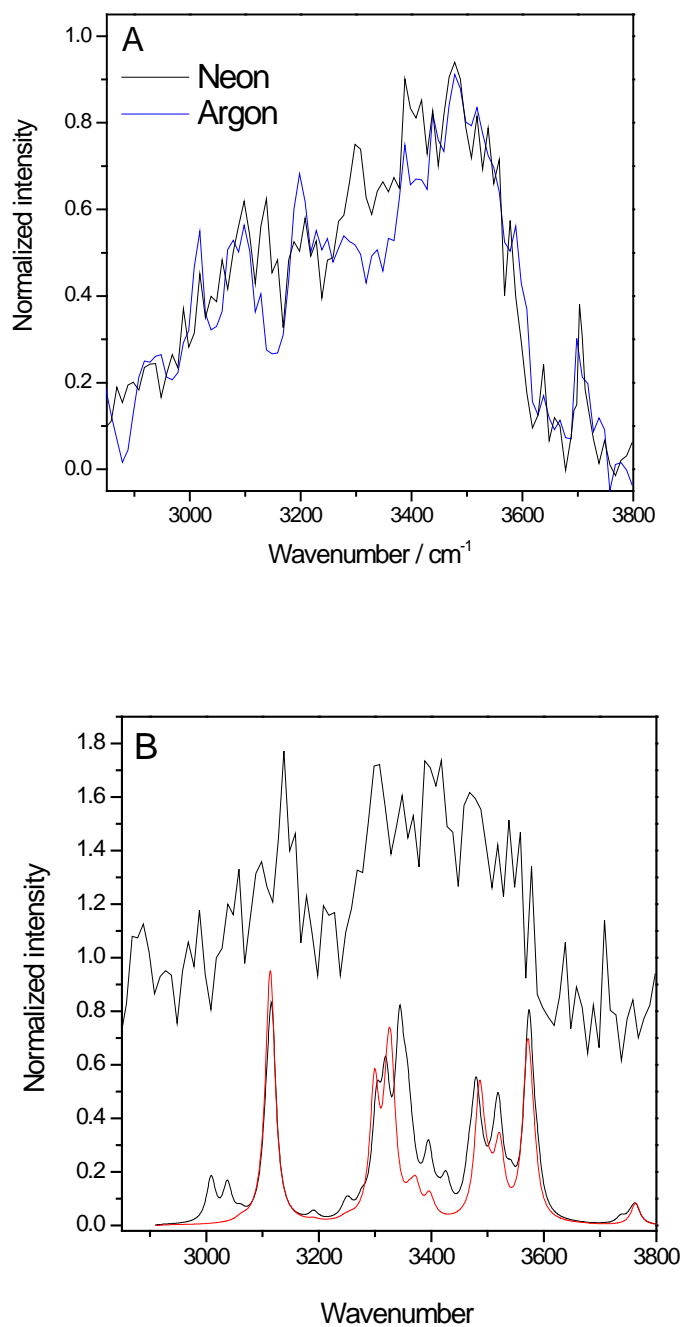## II. Effect of the sodium tag in experimental and simulated spectra

Figure S1, panel A: Maximum intensity normalized spectra of six scans using Ne (black line, Fig. 3) and four scans using Ar (blue line, Fig. 3) as seed gas plotted together. This comparison shows that the characteristic features of isomer A at 3140 cm^{-1} and around 3300 cm^{-1} are missing in the Ar experiment.

Panel B: Difference IR spectrum of the scans shown in A (Neon expansion - Argon expansion, offset 0.8) compared with harmonically predicted spectra of isomer A (B3LYP/6-31+G** level of theory, scaling factor 0.965, Gaussian 09 software package). The red trace

belongs to $(H_2O)_{20}$, the black trace to $Na(H_2O)_{20}$, see Fig. S2. The comparison suggests a limited effect of sodium tagging on the most prominent spectral features, even for a highly symmetric cluster like isomer A. The predicted absorption pattern of $Na(H_2O)_{20}$ agrees well with the difference spectrum and explains the satellite peaks around the major DAA peak at ~3140 cm^{-1} and the presence of the satellite free OH stretch feature around 3650 cm^{-1}.
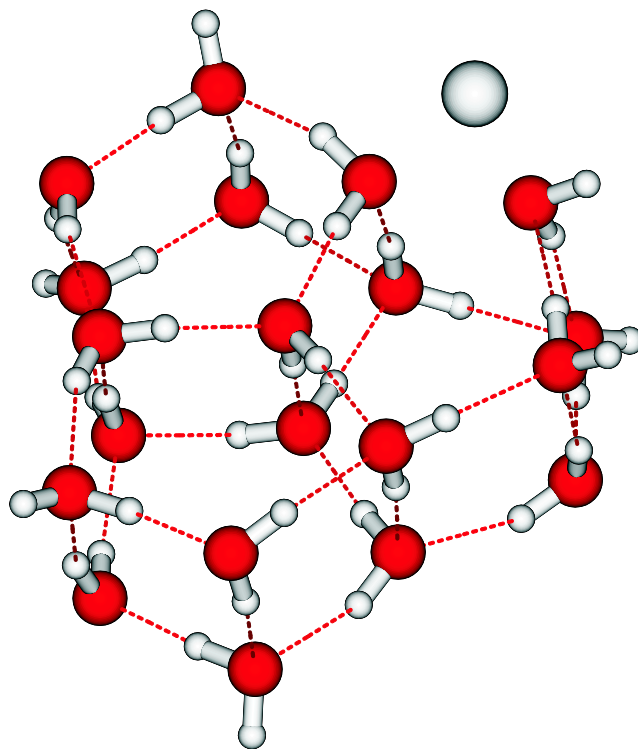
Sodium tagged isomer A

Figure S2. Most stable topology of sodium atom tagged isomer A, result of an exploratory study. Various starting configurations with the sodium atom attached to the surface of isomer A were tested. The energy optimization of isomer A and sodium tagged isomer A clusters was performed on the B3LYP/6-31+G** level of theory using the Gaussian 09 software package.
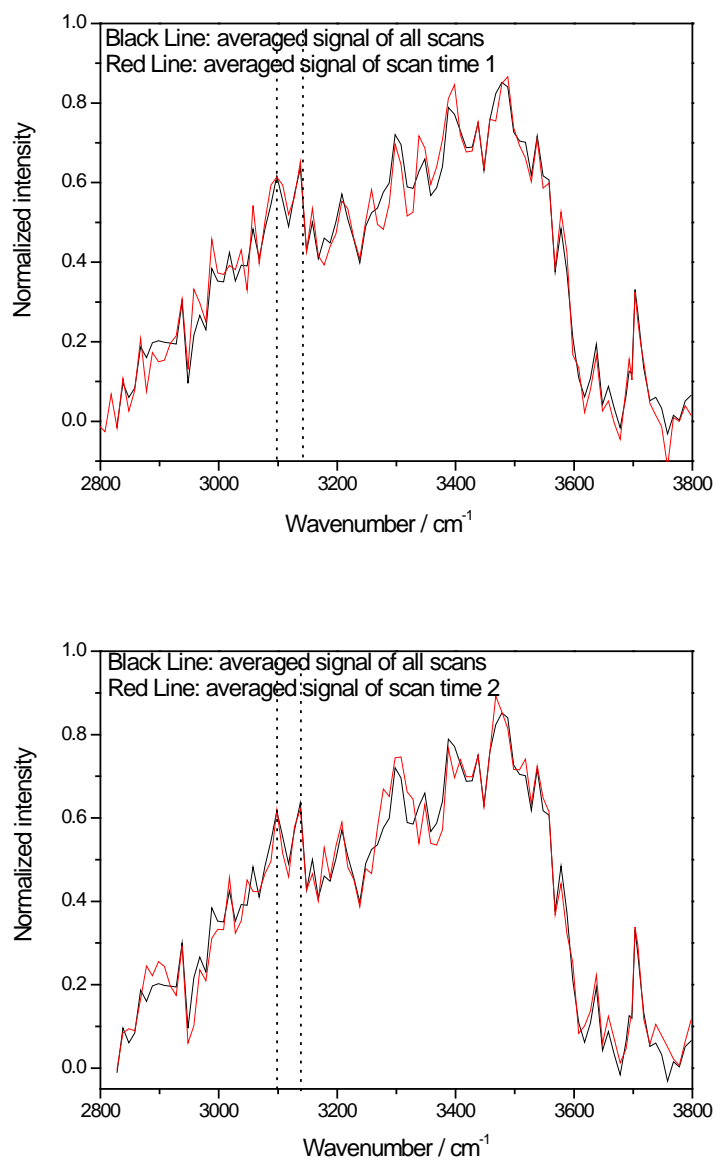
III. Reproducibility of experiments

Figure S3. The two panels of this figure indicate the statistical noise in the presented IR spectra of $Na(H_2O)_{20}$ generated in Ne seeded expansions. The averaged IR spectrum of the complete campaign is compared with spectra from two not overlapping scan times. The comparison shows the reproducibility of the characteristic features of isomers A and B in the region of DAA oscillators.
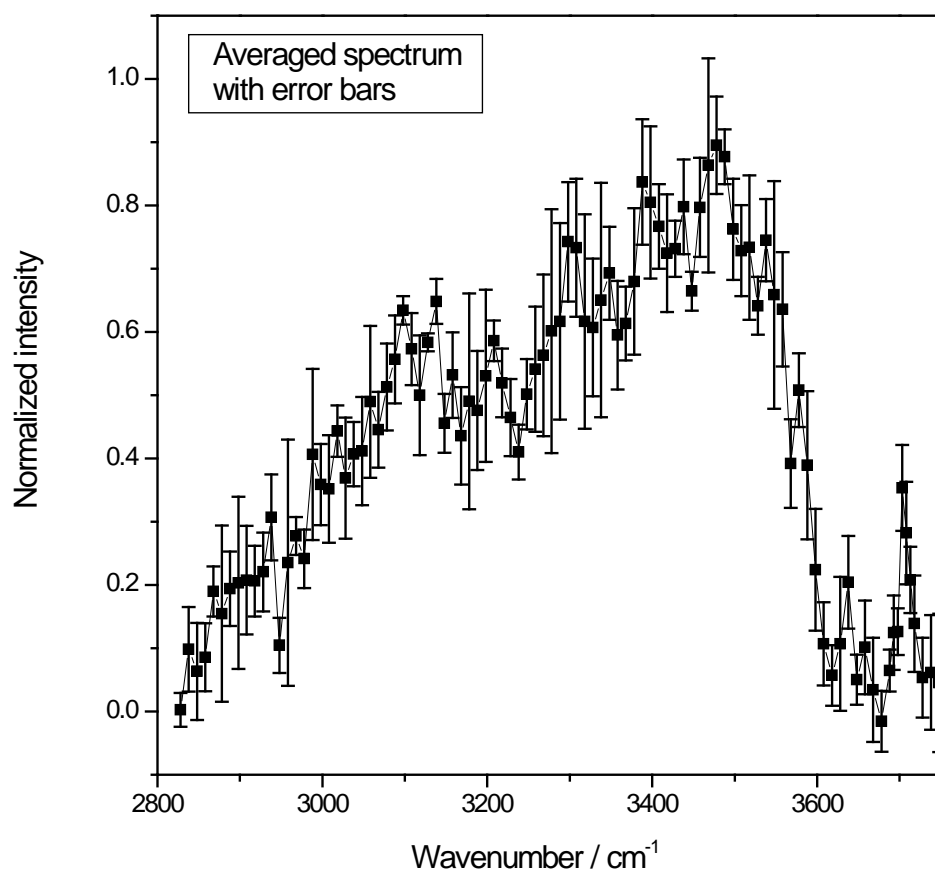
Figure S4. This figure shows the averaged spectrum of the seven days scanning time with error bars representing a confidence level of 80 % for individual points. This illustrates the robustness of the main features (3140 and 3310 cm^{-1} for isomer A and 3090 cm^{-1} for isomer B) and the overall absorption pattern used to assign the spectra to isomers A and B. Minor features are much less reliable due to remaining noise level. A significant fraction of the noise is probably caused by baseline fluctuations during one IR Laser scan, which have a minor effect on the absorption pattern. This noise component is largely reduced in spectra averaged over three or more days scanning time.
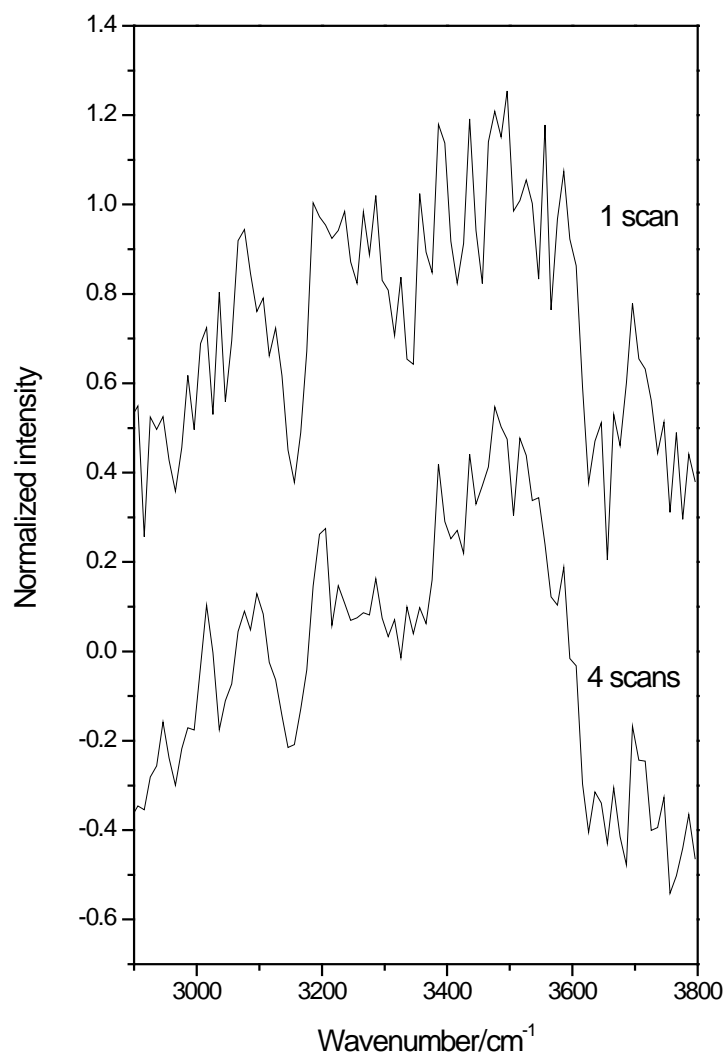
Figure S6. This figure shows the reduction in noise from a single scan (1 day scan time) to 4 days scan time for the IR spectra of Na(H$_2$O)$_{20}$ taken in the Ar seeded expansions.
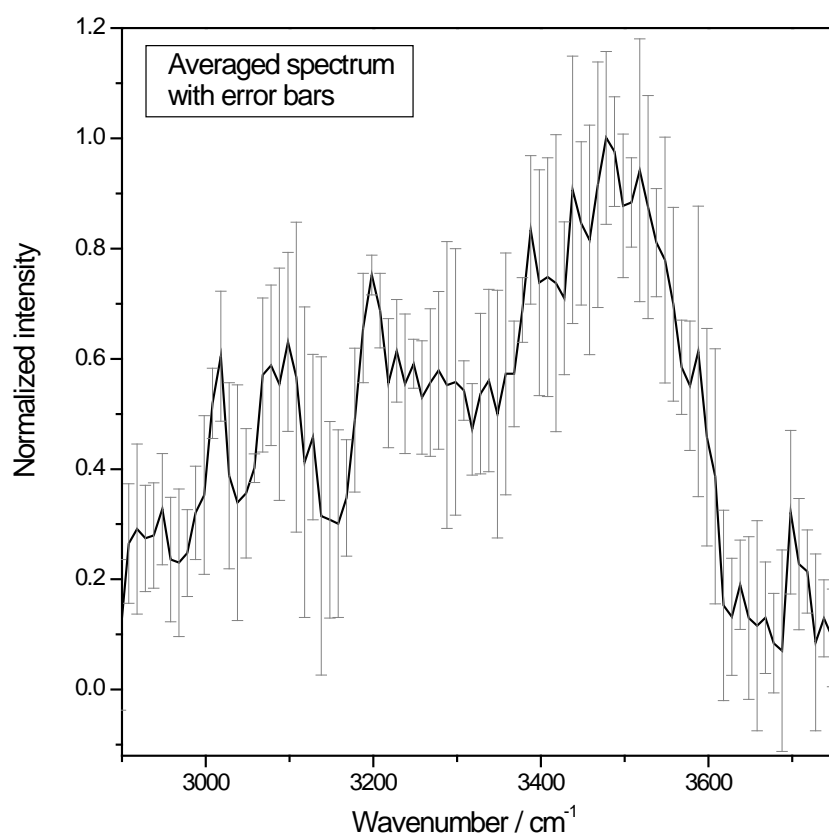
Figure S7. This figure shows the averaged spectrum of four days scanning time with error bars representing a confidence level of 68 % for individual points. Again main features and overall absorption pattern are robust while minor features are much less reliable. The comparison with figure S6 indicates that baseline shifts of interconnected data points significantly contribute to the relatively high noise level. However, these have minor effects on the absorption pattern.
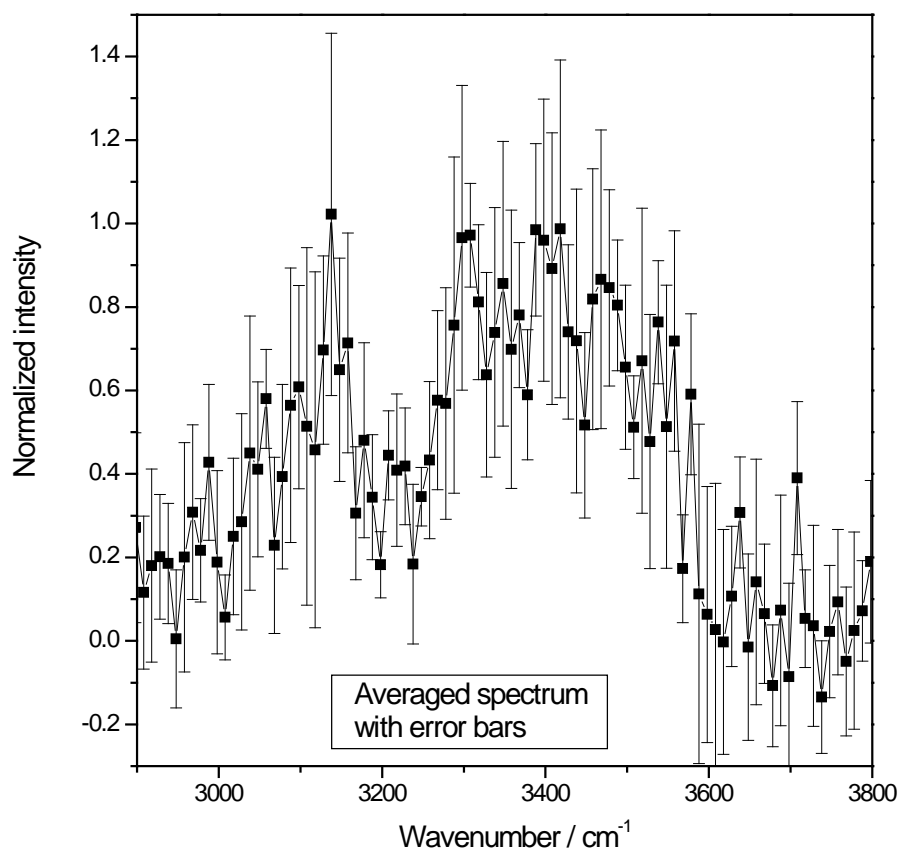
Figure S8. This figure shows the difference spectrum between the averaged spectra taken in neon and argon seeded expansions with error bars representing a confidence level of 80 % for individual points. The characteristic features of isomer A, the peak at 3140 cm^{-1} and the absorption gap from 3150 and 3280 cm^{-1} are of high significance.