

Supplementary information

Simulation of IR spectra with admixing of isomers

To account for the presence of other isomers as the most stable ones we simulated IR action spectra by empirically admixing small fractions of slightly less stable representative isomers. Here harmonic frequencies are corrected using binding motif specific scaling factors (see Ref. 33 in the paper). They are depicted in Table S1. One effect is that some DA/DC oscillators are slightly less red shifted compared to shifting them by 150 cm^{-1} . This slightly improves the match of predictions for DA features in chain type structures. The other effect is that the low lying eAC motif accepting two H atoms is slightly more red shifted. However, it is clear that reliable anharmonic frequency calculations must be provided in future for making such spectra simulations more robust.

Table S1 Binding motif specific scaling factors for predicted harmonic OH oscillator frequencies.

DA,DC	eC, eAC single interaction	eC, eAC double interaction	CH,DAA,DAC
0.968	0.99	0.98	0.95

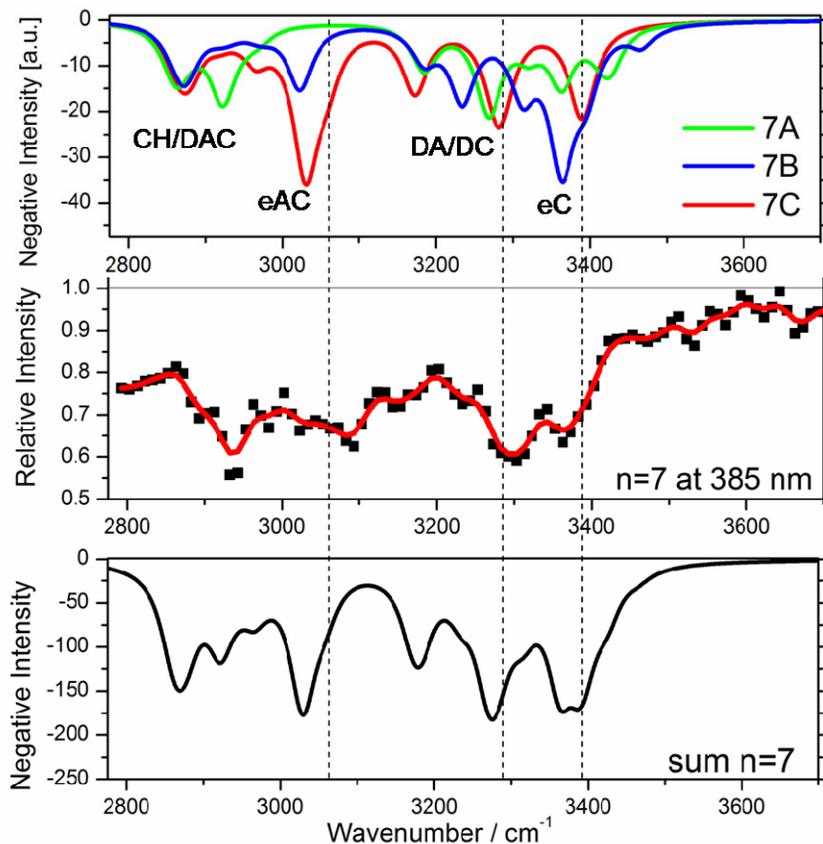
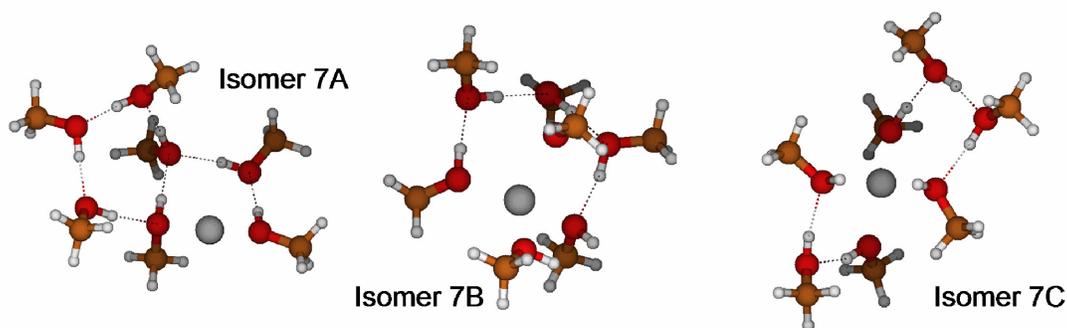


Fig. S1 Upper panel: Predicted IR spectra of Isomers 7A, 7B and 7C. Middle panel: Experimental IR action spectrum for n=7 at 360 nm. Lower panel: Predicted IR spectrum for a mixture of 40 % Isomer A, 20 % isomer B and 40 % isomer C.



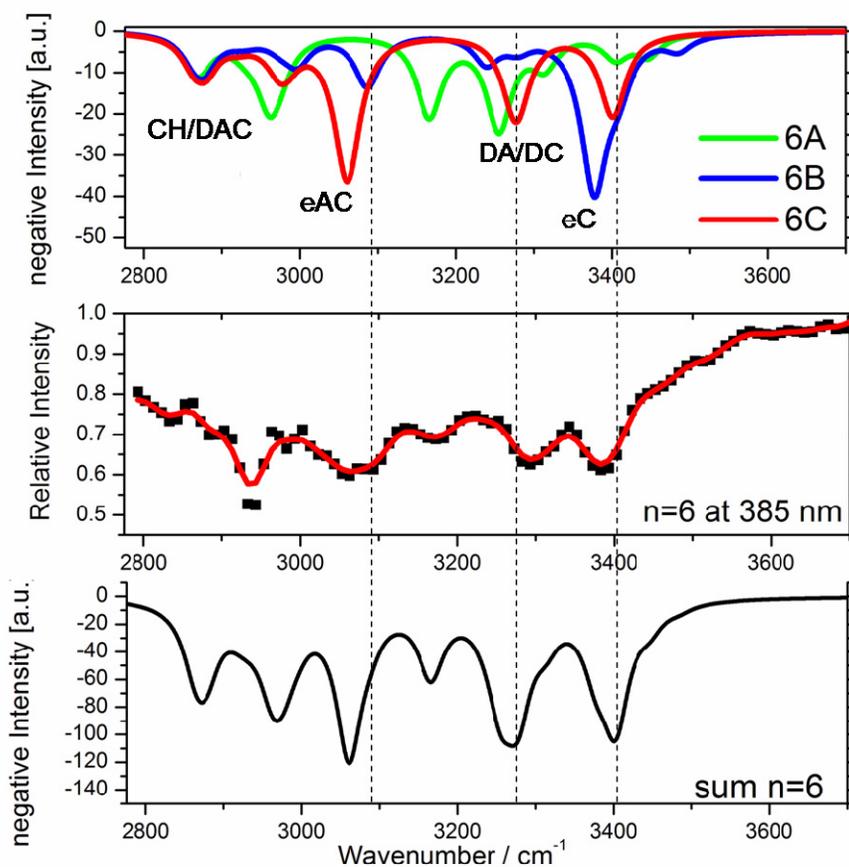
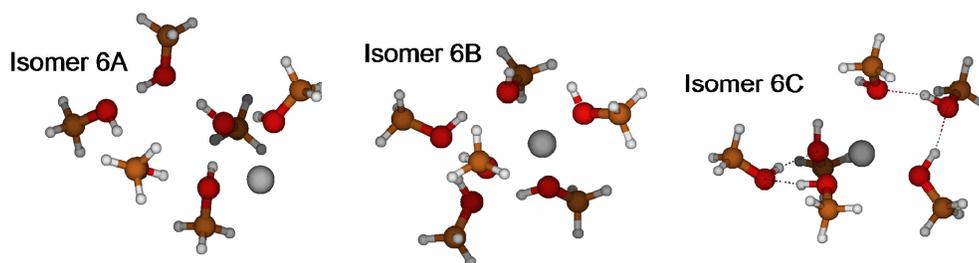


Fig. S2 Upper panel: Predicted IR spectra of Isomers 6A, 6B and 6C. Middle panel: Experimental IR action spectrum for $n=6$ at 385 nm. Lower panel: Predicted IR spectrum for a mixture of 35 % Isomer A, 15 % isomer B and 50 % isomer C.



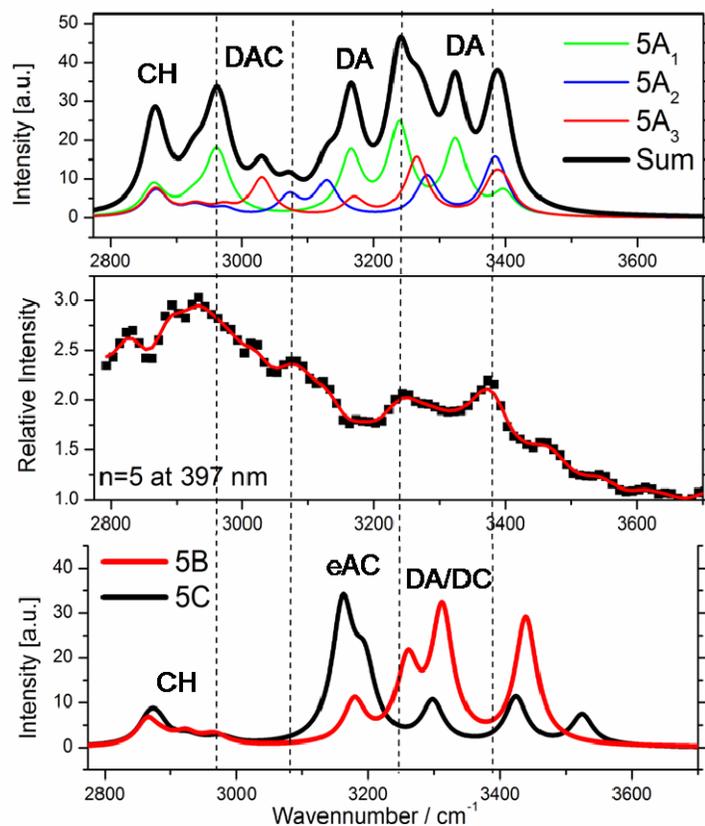
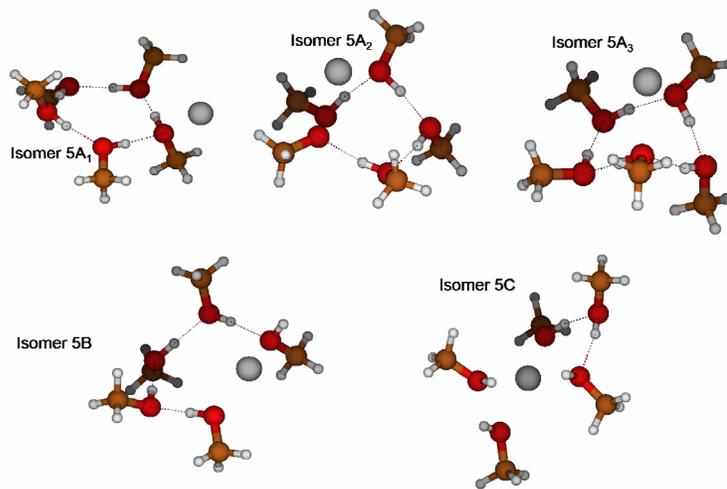


Fig. S3 Upper panel: Predicted IR spectra for individual isomers and the sum of A_{1-3} , Middle panel: Experimental IR action spectrum for $n=5$ at 397 nm. Lower panel: Predicted IR spectrum for isomers 5B and 5C.



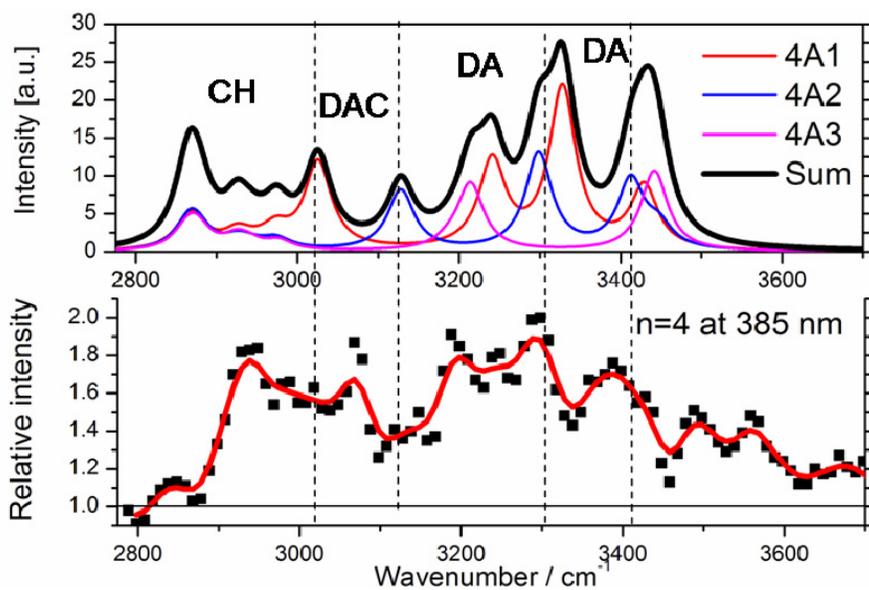
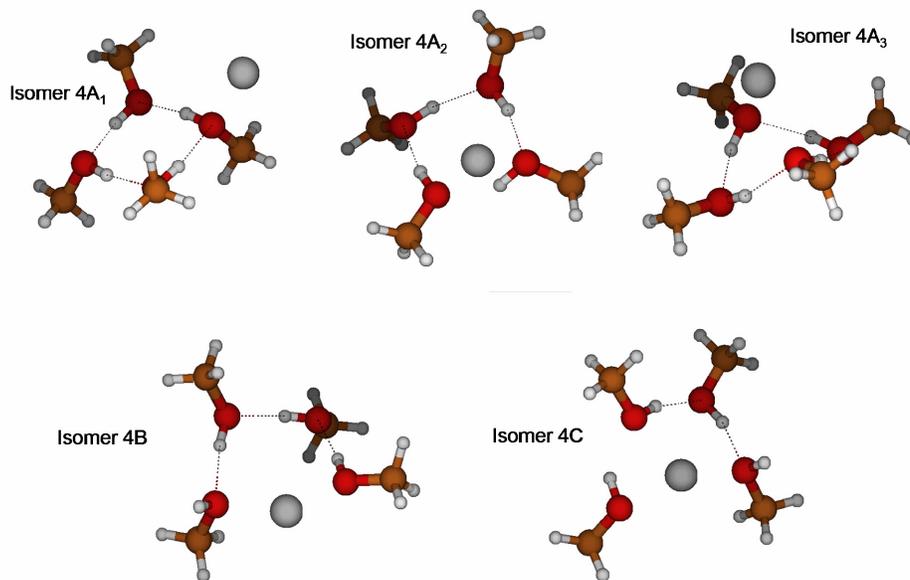


Fig. S4 Upper panel: Predicted IR spectra for individual isomers 4A₁₋₃, and their sum. Lower panel: Experimental IR action spectrum for n=4 at 385 nm and cold expansion conditions.



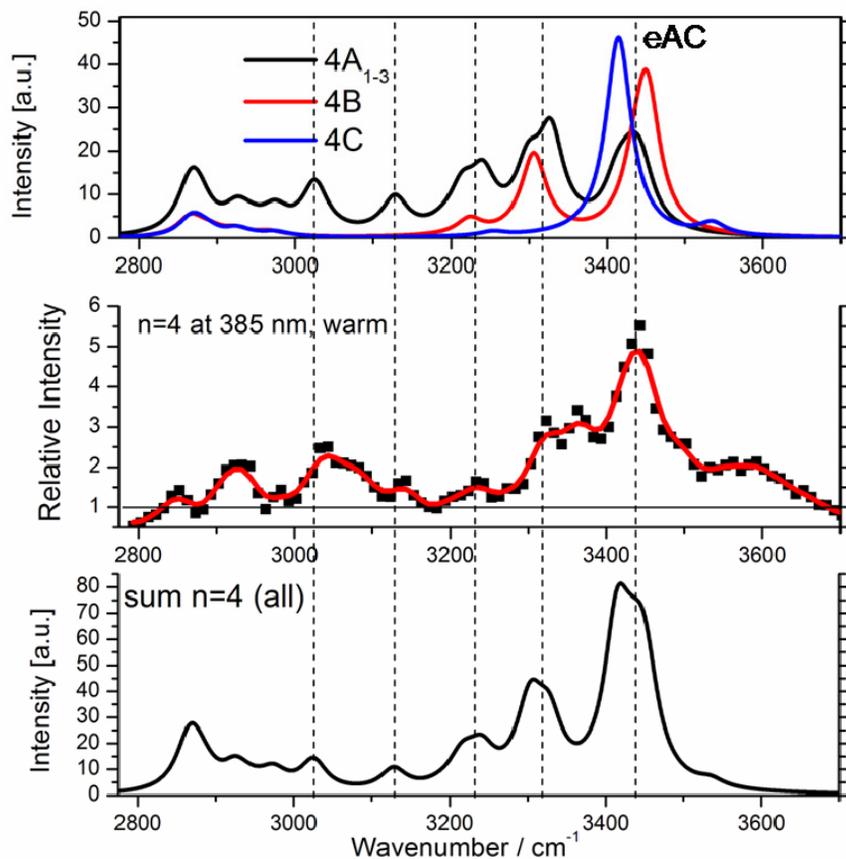
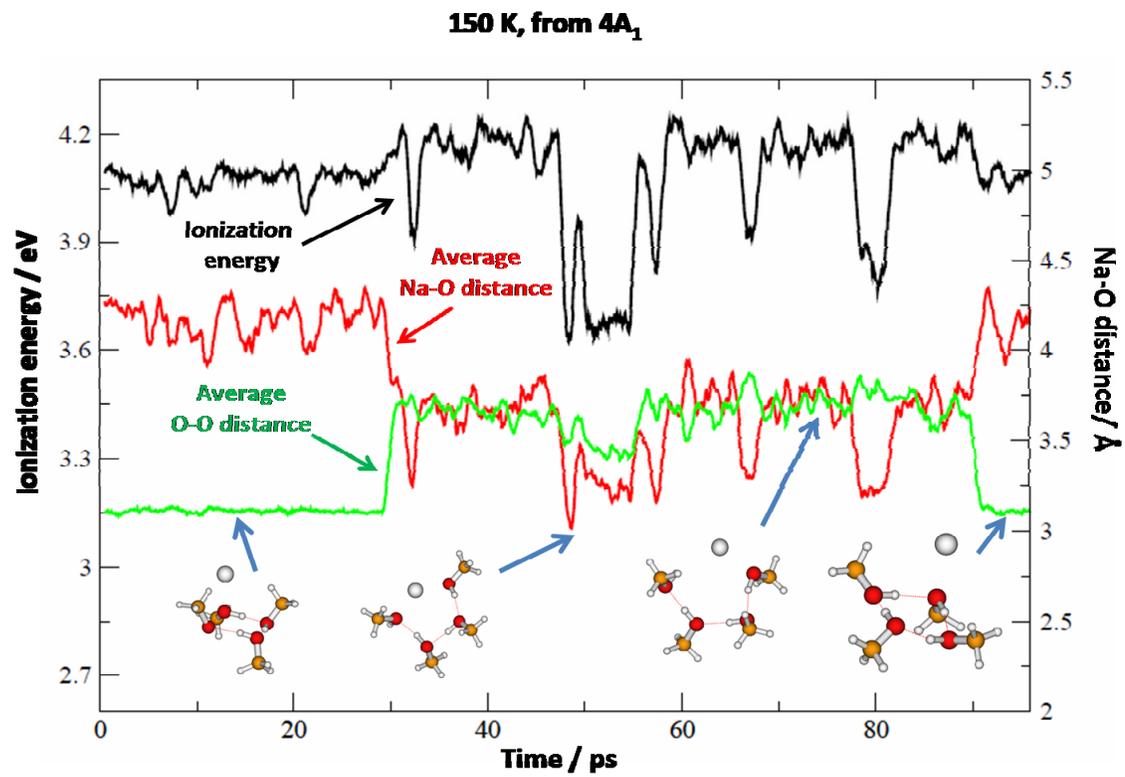
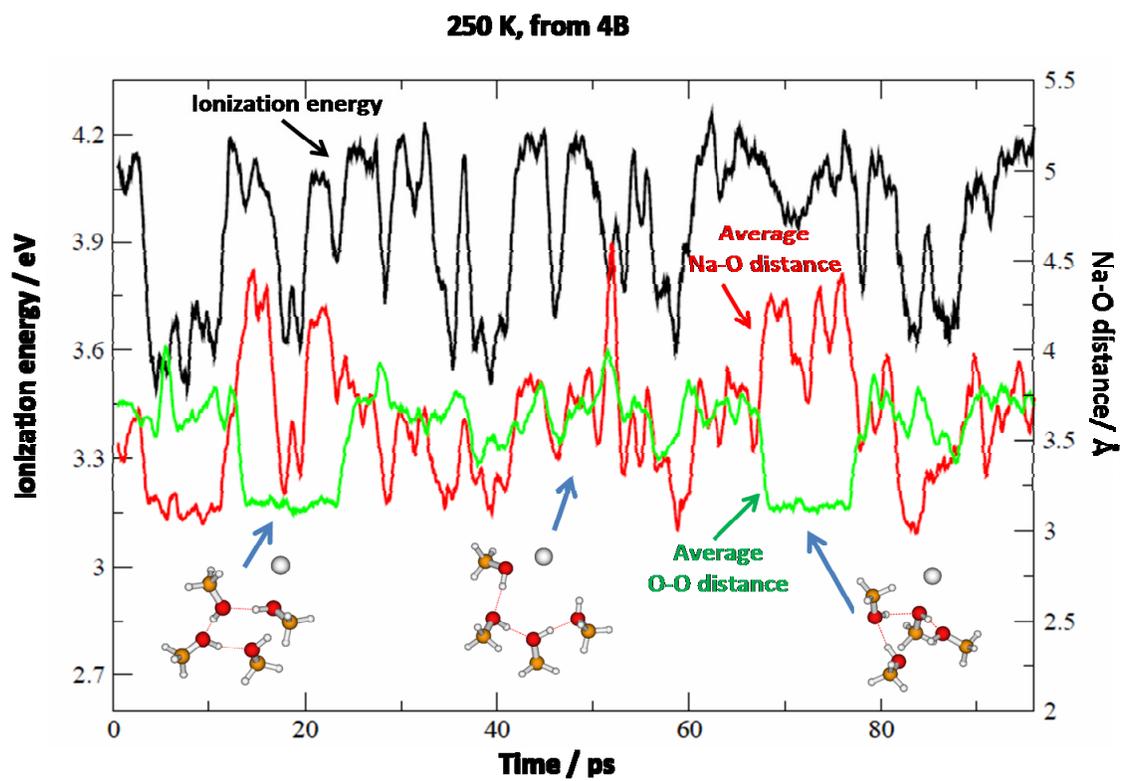


Fig. S5 Upper panel: Predicted IR spectra for individual isomers 4B,C and the sum of 4A₁₋₃, Middle panel: Experimental IR action spectrum for n=4 at 385 nm and warm expansion conditions. Lower panel: Predicted IR spectrum for the equal weighted sum of isomers 4A₁₋₃ and 4B,C.

S6 (a)



S6 (b)



S6 (c)

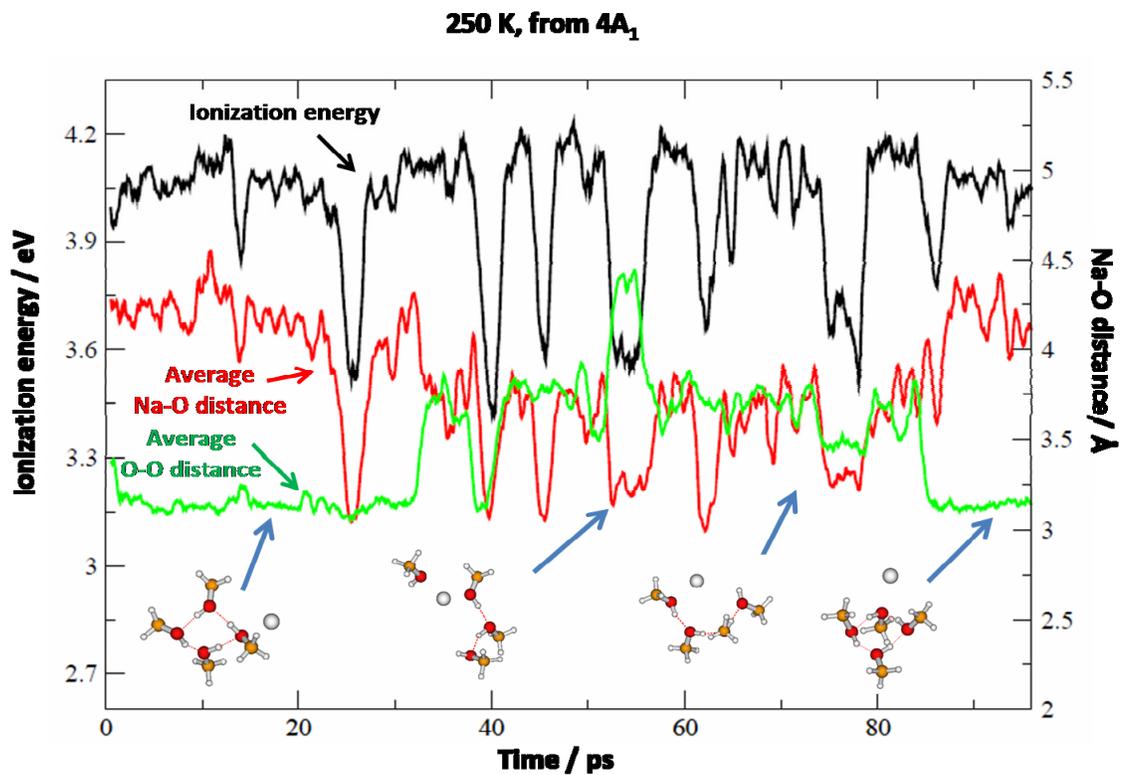


Fig. S6 (a-c) Predicted evolutions of the ionisation energy and average Na-O and O-O distances along several molecular dynamics simulations of the Na(CH₃OH)₄ cluster. Short O-O distances indicate fully hydrogen bonded structures similar to $4A_{1-3}$.

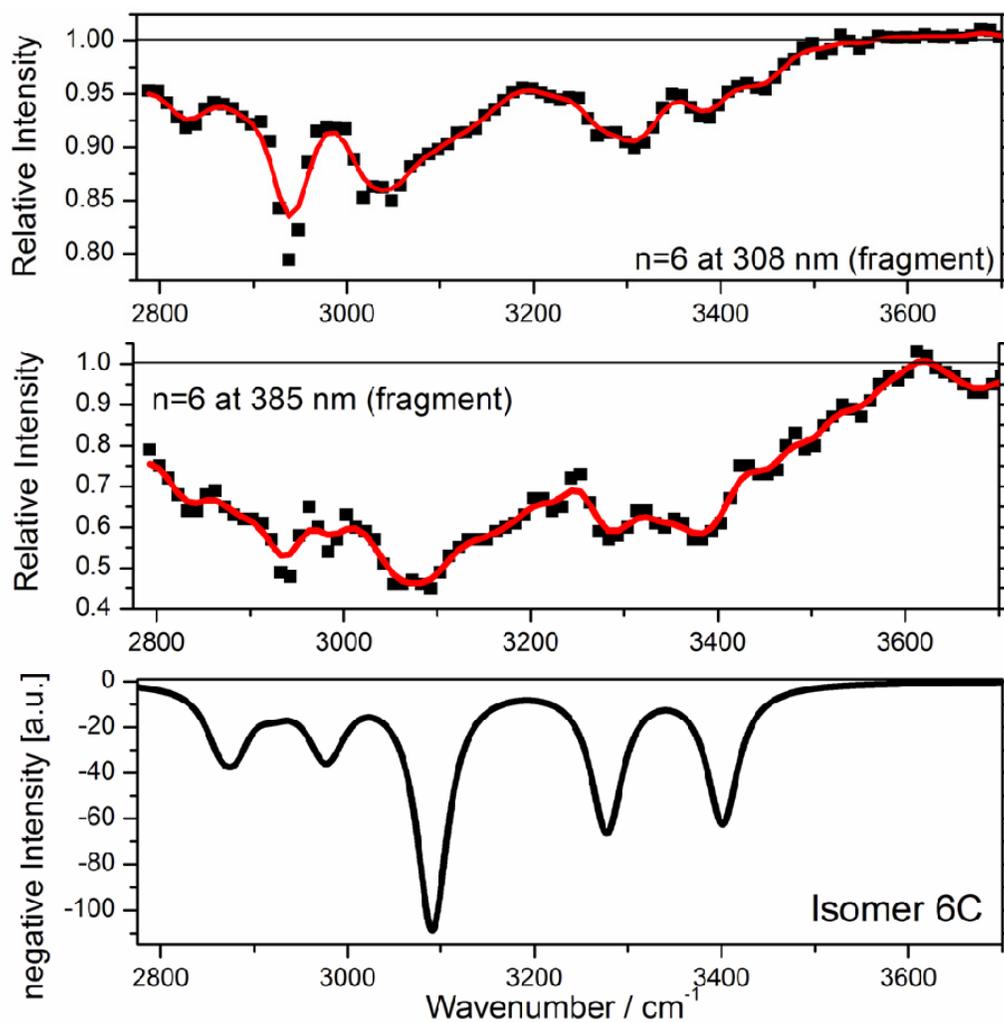


Fig. S7 Upper panels: Experimental IR action spectra for fragments of $n=6$ at 308 and 385 nm (expansion conditions: 40 % methanol in He at 2 bar for 308 nm and 60 % methanol in He at 1.4 bar for 385 nm). Lower panel: Predicted IR spectrum for isomer 6C.