Thin Film Infrared Spectroscopy on Planar Silver Halide: A New Technology for Water and Other Liquids in the Mesoscopic Domain -Supplemental Material

Edward M. Kosower and Galina Borz
School of Chemistry, Tel Aviv University, Tel Aviv 69978 Israel
e-mail: kosower@post.tau.ac.il Fax: 972-3-6409293 Tel: 972-3-6408556

Prologue (Supplement)

In this prologue supplement are given comparisons of spectra measured in the "classical" manner with those measured with a short acquisition time. The signal energies for the "classical" spectra were either the same as those used for our "novel" spectroscopy (Sg 100, or are relatively low (Sg 500) compared to those commonly used (Sg > 8,000). We present here comparisons for ethanol (1), acetonitrile (2) and N-methylformamide (3). In each case, it is clear that the "classical" spectra are smoothed out (averaged) versions of the "novel" spectra. The novel spectra contain a lot of amazing detail while the "classical" spectra contain the expected averaged peaks, suitable for identification but not for detailed analysis. It is also obvious that the spectra are all of *liquids*. In all cases, gas phase spectra of the same compounds would be substantially weaker to say nothing of being quite difficult to obtain in the case of N-methylformamide, b.p. 182 ^{o}C. **The key points in all these examples are that the polar surface restricts the motion of the molecules on the surface and lowers the rate of evaporation, the low phonon energy (low signal) does not augment thermal motion of the surface molecules, and the short time scan minimizes the number of trajectories for averaging over motions of the molecules.** The results are much closer to the intrinsic spectroscopic properties of the molecules.

(1) Ethanol

The mid infrared spectrum of ethanol contains five main regions, OH stretch, methyl C-H stretching, CH_2-O-H bending, C-C stretching and librations. Figure S1 displays the comparison of a "classical" ethanol spectrum (averaged over 300 s) with a "novel" spectrum (0.1 s). On expansion, the "novel" spectrum reveals ethanol peaks like those that are described in the article for water, peaks that have not yet been analyzed. The fluctuations represent oligomer formation on breaks in H-bonded chains followed since they become frequent at phonon energies comparable to H-bond strengths. The two spectra are clearly related and refer to the same entity, *liquid* ethanol. Plots of ROH signals versus time show that the time for complete evaporation varies with R, from 5 min for methanol to 19 min for 1-propanol, as would be expected for liquid samples. (not shown)

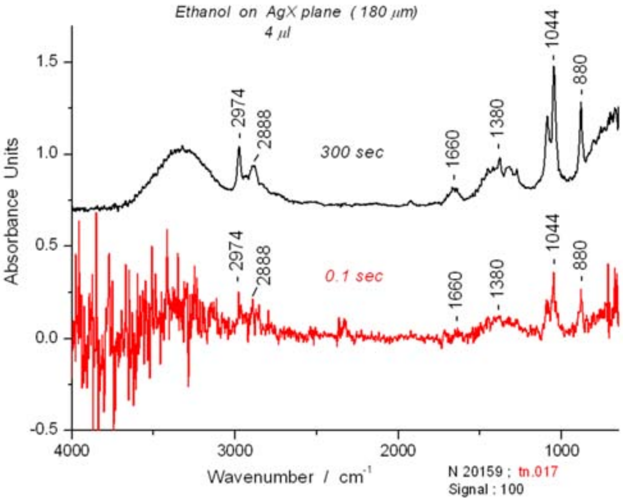

Fig. S1. Comparison of two spectra of ethanol for a 4 μL sample on AgX fiber. The upper spectrum was averaged over 300 s. The lower spectrum was taken with a single 0.1 s scan.

(2) Acetonitrile

The mid infrared spectrum of acetonitrile contains six main regions, methyl C-H stretching, CN stretching, C-C stretching, CN bending and librations. Figure S2 displays the comparison of a "classical" acetonitrile spectrum (averaged over 300 s) with a "novel" spectrum (0.25 s). On expansion, the "novel" spectrum reveals peaks like those that are described in the article for water but have not yet been analyzed. The two spectra are clearly related and refer to the same entity, *liquid* acetonirile.

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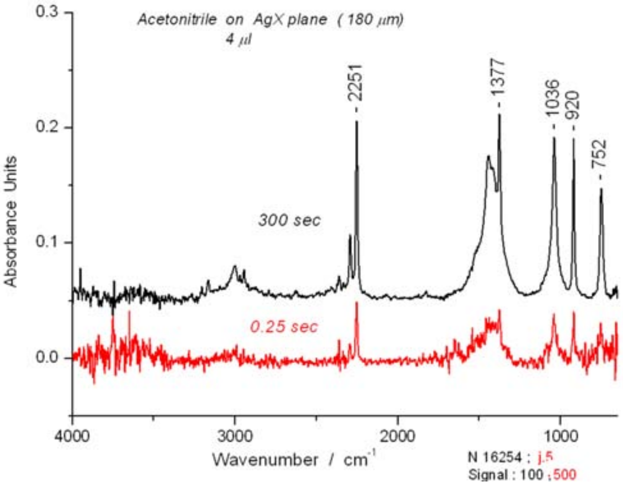


Fig. S2. Comparison of two spectra of acetonitrile for a 4 μL sample on AgX fiber. The upper spectrum was averaged over 300 s. The lower spectrum was taken with a single 0.25 s scan at Sg 500.

(3) N-Methylformamide

The mid infrared spectrum of N-methylformamide contains six main regions, NH stretching, methyl C-H stretching, amide stretching, C-N stretching, CN bending and librations. Figure S3 displays the comparison of a “classical” N-methylformamide spectrum (averaged over 300 s) with a “novel” spectrum (0.1 s). On expansion, the “novel” spectrum reveals peaks like those that are described in the article for water and have been analyzed to some extent. As in the case of ethanol, the fluctuations represent oligomer formation on breaks in H-bonded chains since they become frequent at phonon energies comparable to H-bond strengths.The two spectra are clearly related and refer to the same entity, *liquid* N-methylformamide

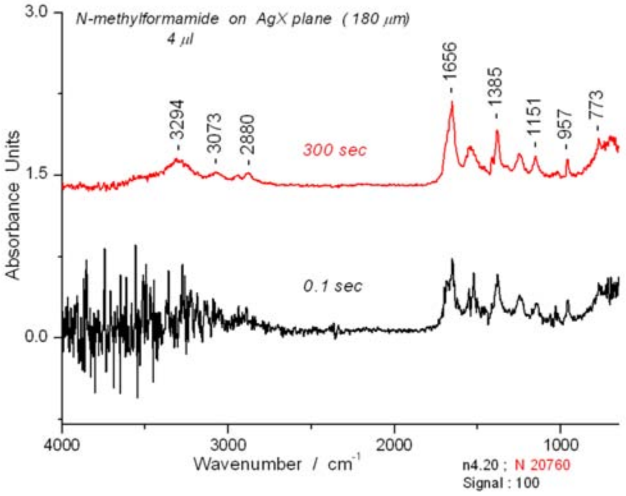


Fig. S3. Comparison of two spectra of N-methylformamide for a 4 mL sample on AgX fiber. The upper spectrum was averaged over 300 s. The lower spectrum was taken with a single 0.1 s scan.

High resolution spectra of liquid water

The primary results of measurements of liquid water by thin film spectroscopic techniques are high resolution spectra. To illustrate the richness of the spectra we show one of the spectra (for 4.0 μL) that is divided into five ranges of 700 cm^{-1} each as follows: (S4) 4100 – 3400 cm^{-1} (S5) 3400 – 2700 cm^{-1} (S7) 2700 – 2000 cm^{-1} (S6) 2000 – 1300 cm^{-1} (S8) 1300 – 600 cm^{-1}. In the O-H stretching region (S4 and S5) there are at least 125 distinct peaks, of which we have labeled 42. The reason for labeling so many peaks is to facilitate their use in comparisons. The partial spectra displayed in S4-S8 represent the first spectrum that reached maximum height in the early part of one experiment.

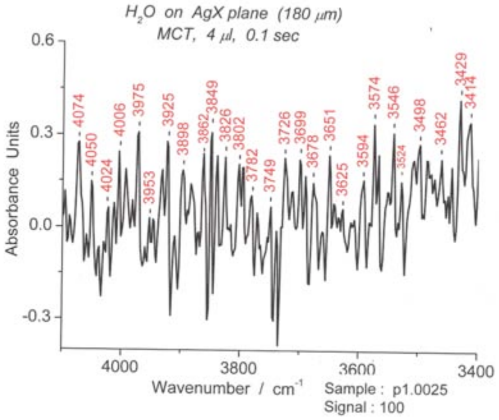


Fig. S4. A portion of the spectrum of water on AgX over the range from 4100 cm^{-1} to 3400 cm^{-1}

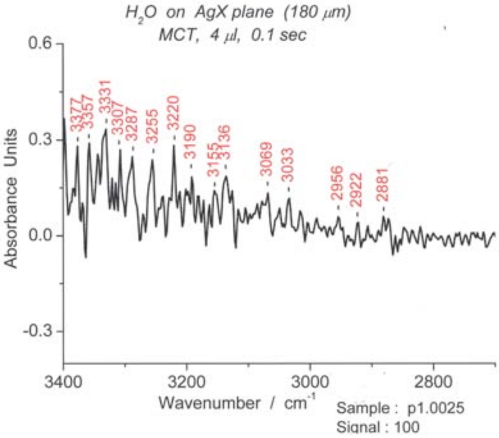


Fig. S5. A portion of the spectrum of water on AgX over the range from 3400 cm^{-1} to 2700 cm-^{1}

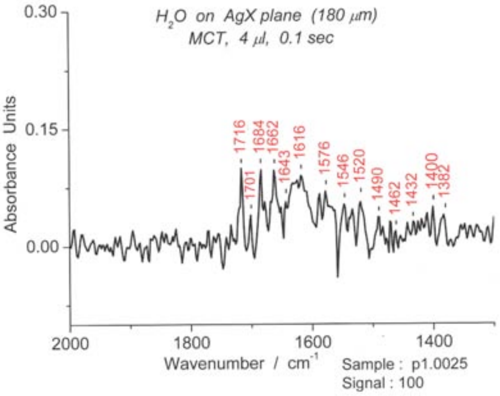


Fig. S6. The bending and deformation region of the spectrum of water over the range 2000 -1300 cm^{-1}

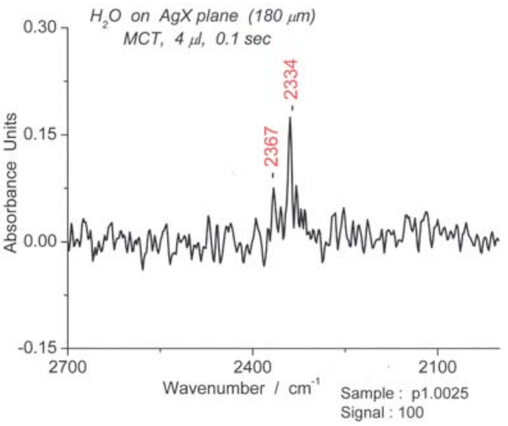


Fig. S7. Spectrum of water from 2700 to 2000 cm^{-1}. Note the multiple CO_2 bands and the "2100 band" of water.

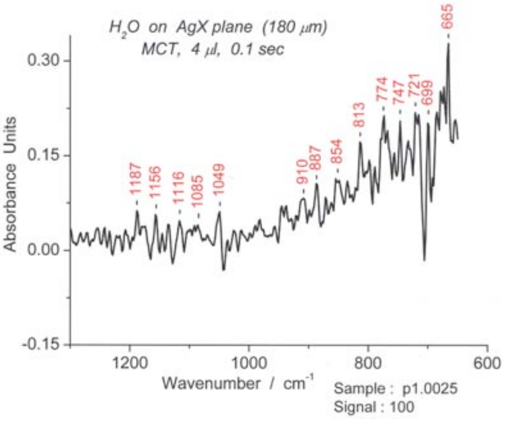


Fig. S8. Spectrum of water from 1300 to 650 cm^{-1}. The peaks are mostly L_1 and L_2 librations, except for the CO_2 absorption at 665 cm^{-1}.

Specific oligomers that are wholly water

We used Abs vs t (time) plots to find the highest peaks for one oligomer that coincided with the lowest peaks for another. In that way, we could select spectra that had a preponderance of one oligomer. Focusing on the 1541 peak, we then search for a "clean" spectrum in the set, usually one of those with the highest absorbance and lacking other prominent peaks. By plotting absorbance at 1541 cm^{-1} versus time, we can locate specific spectra with high absorbance. Since we surmised that the 1558 cm^{-1} was also a cyclic hexamer we also searched for a spectrum with minimal absorbance at 1558 cm^{-1}. (S9)

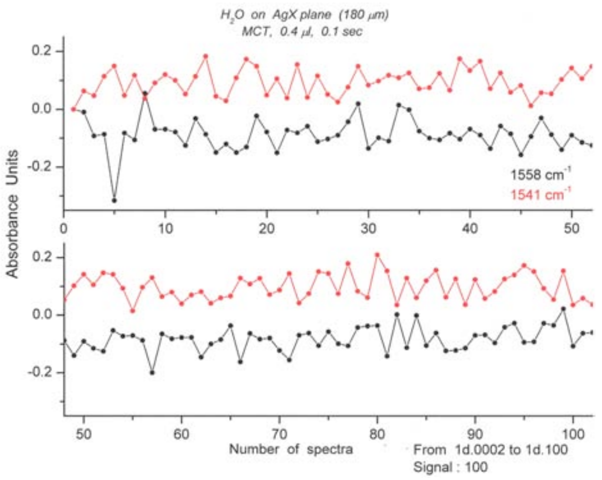


Fig. S9. Absorbance vs spectrum number (i.e., time, 10 spectra = 1 s) for ~100 spectra of 0.4 µL of water for 1541 and 1558 cm^{-1} in the bending region

For spectrum #95, the shorter wavelength region (3600 – 3900 cm^{-1}) is segmented somewhat less obviously into three groups, each of which seems to have two parts, i.e. 6 groups in toto. The group limits are given in the caption for S10. The last portion of the long wavelength region (3500 -3605 cm^{-1}) is included as an "anchor". A set of isomotomers for a water hexamer falls naturally into six groups (illustrated in S11) in contrast to the five groups found for the cyclic pentamer.

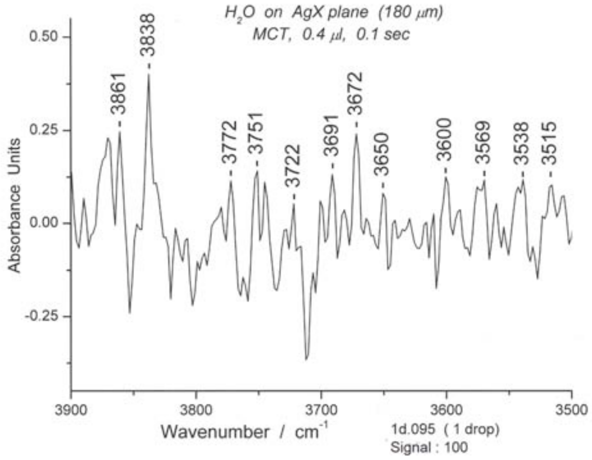


Fig. S10 Spectrum #95 of water in part of the OH stretching region, 3500-3900 cm^{-1}, including the three groups, 3605- 3715 cm^{-1}, 3715- 3800 cm^{-1} and 3800-3895 cm^{-1} with each group consisting of two parts.

5.2 Cyclic Hexamer (boat form)

It was reasonable to assume that the tagged deformation peak at 1558 cm^{-1}, close to the peak of the chair form at 1541 cm^{-1}, was a marker for the boat form of the cyclic hexamer. In S12 the intensity of the 1558 cm^{-1} peak increased markedly in a composite 0.8 µL spectrum over that for 0.4 µL (Figure 20).

We selected spectrum #815 in a spectroscopic series for 0.8 µL

(S12) displaying a strong 1558 cm^{-1} peak. A spectrum for the range for 3630-3900 cm^{-1}, with three apparent groups, each split into two, giving six groups in total. (S13)

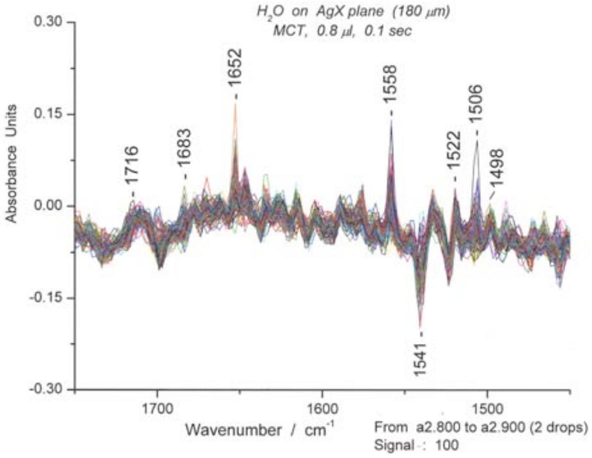


Fig. S12. A composite set of ~100 spectra for 0.8 μL of water for the bending region

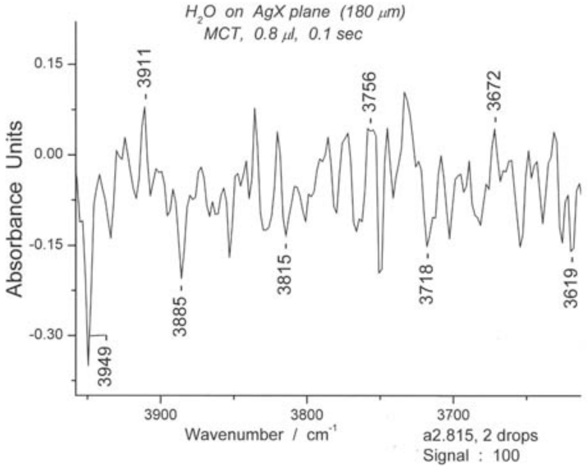


Fig. S13. The "asymmetric" portion (OH stretching) of the water spectrum #815 from 3600-3960 cm^{-1}.

5.3 Book 1

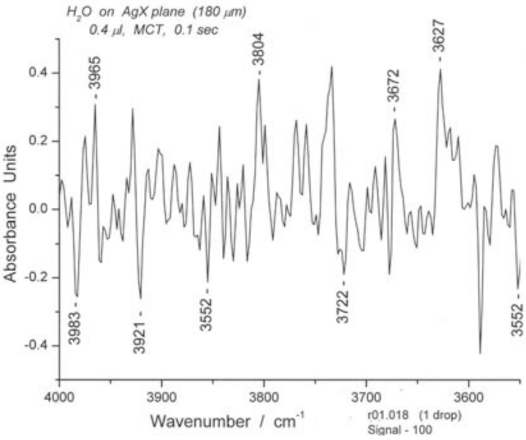


Fig. S14. Spectrum *18 of water in the "asymmetric" region

Strong evidence that Book 1 is a metastable species of unique geometry rests on the OH stretching bands seen in a comparison of spectra #s 17/18 and #s 19/20 in which one observes the close parallelism between the many peaks (~ 60) of these pairs. This implies that we are looking at the buildup of spectrum #18 and the beginning of its disappearance. These spectra show that the lifetime of book 1 is > 0.4 s. In fact, at least two spectra before and two spectra after those shown are also very similar so that the lifetime is at least 0.8 s. This point is illustrated with a set of spectra (#s 15-21) in S15 (over a restricted range for clarity) in which there are a large number of tagged peaks.

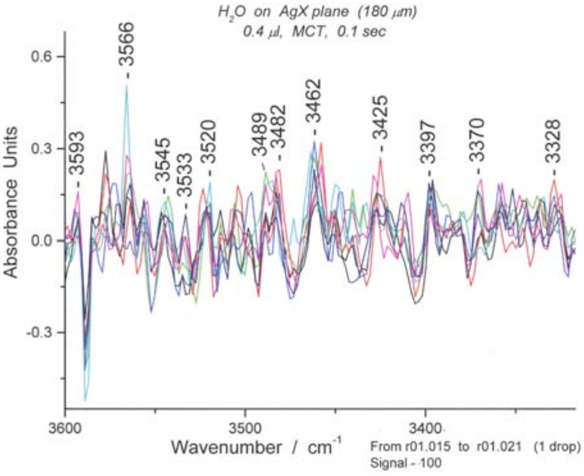


Fig. S15. A set of seven spectra (#15-21) for the "symmetric" portion of the OH stretching region over the range from 3300 to 3600 cm^{-1}

5.4 Book 2

Another tagged peak in various spectral sets was that at 1520 cm^{-1}. We searched for spectra in which the 1520 cm^{-1} peak was prominent. In practice, one needs to include 1519-1522 cm^{-1} in the search. We found two that had a peak with an absorbance of 0.11 (#s753, 913). A 100 spectrum set of the results for #s 700-800 is shown in S16. (The set for #s 900-1000 was similar and is not shown).

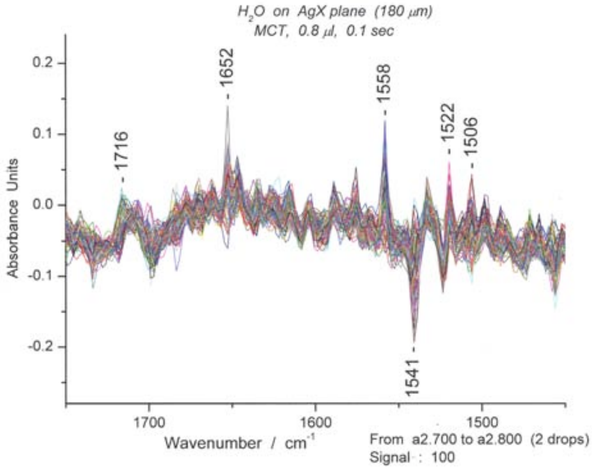


Fig. S16 A composite set of 100 water spectra for the region between 1450 and 1750 cm^{-1}.

We selected spectrum #753 to define the spectrum of what is assigned the structure of book 2, based on the proximity of the bending maximum to that of book 1. S17 is the spectrum for the “asymmetric” OH stretching region.

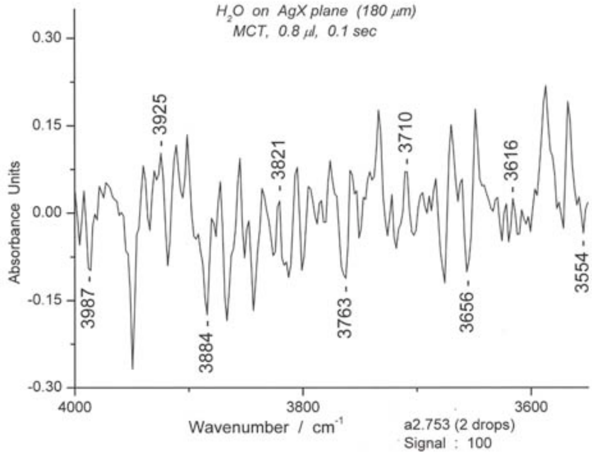


Fig. S17. The “asymmetric” OH stretching region (3550-4000 cm^{-1}) of the water spectrum #753.

The excellent correlations displayed in Figure 30 for spectra measured in the sequence (1000 spectra, 100 s) demonstrate that the oligomer compositions are recreated at various times. Note that the spectra are from widely separated parts of the experiment, ranging from #105 to #990. The concidence of oligomer compositions is illustrated in S18 for the bending region. This figure shows that the environment is similar for all the points on the line.

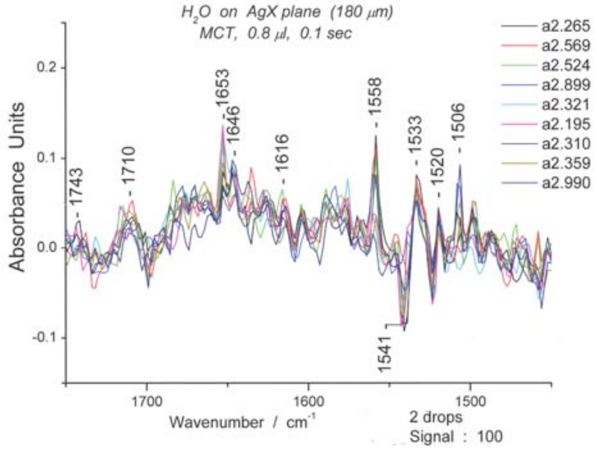


Fig. S18. The bending regions of the spectra that belong to the points shown for line 1 in Figure 39.

In a corresponding correlation for Book 1, we plotted the intensities for the 1506 cm^{-1} peak against the intensities of the libration at 1028 cm^{-1}. The results are shown in S19. An apparent scatter appeared with the use of >30 data points. The straight lines seen in S19 served as a guide for drawing six lines. The spectra belonging to each line suggest that the oligomer composition is similar for all of the points of a particular line, but varies from line to line.

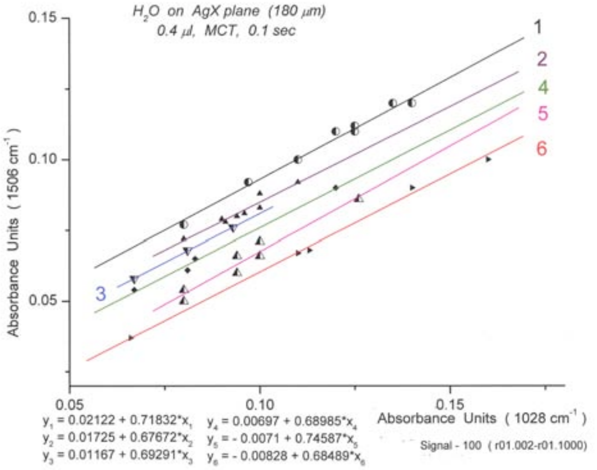
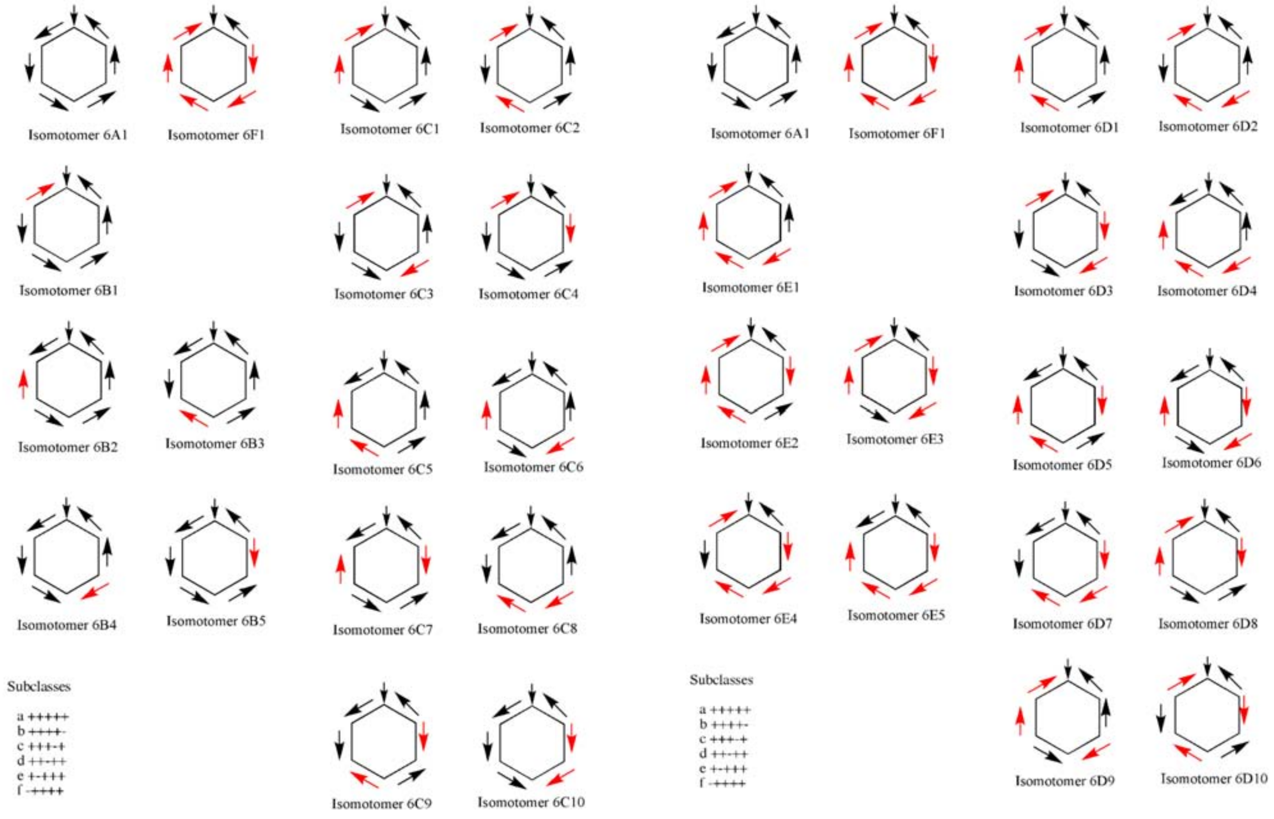


Fig. S19. Plots of absorbances of the bending peak of Book 1 (1506 cm^{-1}) versus the absorbances of the H-bonding libration peak (1028 cm^{-1}) The six lines result from different oligomer compositions



S11 Isomotomers of the cyclic hexamer of water. The black arrow in the ring near the oxygen (O) at the top represents the direction of motion of the H in the hydrogen bond to the next oxygen. The black arrows around the rings indicate motion in the same direction. The red arrows are directed in the opposite direction from the black arrows. The motions of the hydrogens external to the ring are labelled (+) in one direction and (-) depending on their relation to the H external to the ring. The primary vibration is that of water at the top. Its energy varies according to its interaction with the all of the other motions. A complete set falls naturally into six groups (number of variants), A (1), B (5), C (10), D (10), E (5) and F (1).

Both parts of the figure include the first and last isomotomers, A and F. The left hand side also has the B and C groups, while the right hand side also contains the D and E groups. The pattern of the spectroscopic groups reflects the pattern of the isomotomers but must include contributions from other oligomers, especially on the shorter wavelength side.