

Supplementary information

Femtosecond Soft–X–Ray Absorption Spectroscopy of Liquids with a Water–Window High–Harmonic Source

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1. SXR probe and optical pump beams characterization

The SXR probe beam size was estimated by transmitting the XUV beam (>90% transmission) through a laser-drilled pinhole.

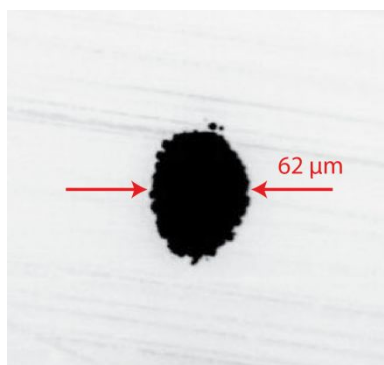


Fig. S1. Pump laser-drilled pinhole used for the SXR probe beam spot measurement.

The pump beam ($\lambda=400$ nm) spot-size measurement was carried out using a beam profiler camera. The image was then normalized using the pump pulse energy (220 μ J) and pulse duration ($\tau = 30$ fs) in order to estimate the peak intensity.

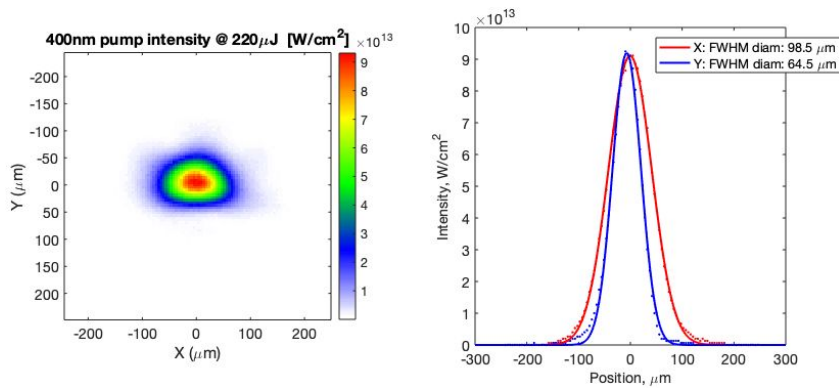


Fig. S2. Measured pump beam profile and intensity estimation.

The pump-probe beam crossing angle was estimated to be 0.5 deg (8 mm beam separation at 900 mm from the focus). At 62 μm probe beam diameter, this corresponds to a temporal smearing of 1.7 fs.

2. SXR spectrometer description and resolution analysis

The spectral resolution of the SXR spectrometer was estimated to be 0.4 eV at the carbon K-edge, see Fig. S3

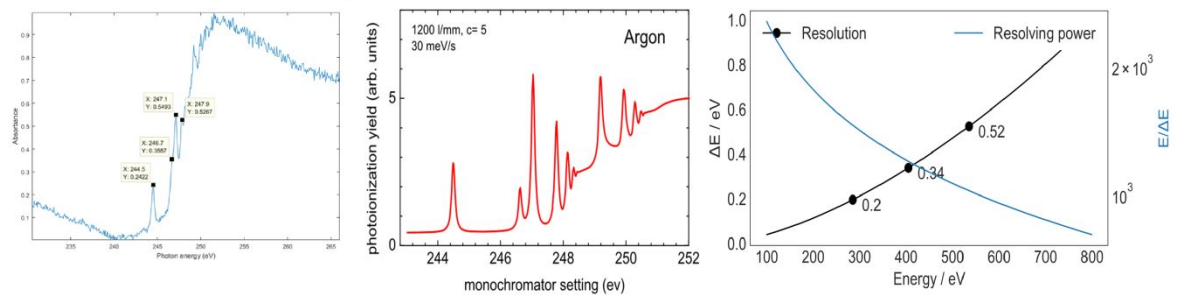


Fig. S3. Determination of the SXR spectrometer resolution. Left panel: measurement of an argon absorption spectrum realized by filling the interaction chamber with 0.1 mbar of argon. Center panel: comparison to the spectrum measured at a synchrotron (adapted from Ref [S1]). Right panel: spectral resolution limit and resolving power estimated from the detector spatial resolution (26 μm) and the SXR source spot size (70 μm) considering the measured slope error of 2.2 arc sec rms from Ref [S2].

3. Theoretical Simulations

Methanol monomer

Initial monomer coordinates from Ref. [S3]

C	0.66636000	-0.02007900	0.00000000
H	1.08402800	0.98580400	-0.00000100
H	1.03171200	-0.54359100	-0.89121300
H	1.03171200	-0.54359000	0.89121400
O	-0.74983700	0.12206000	0.00000000
H	-1.14691400	-0.75463300	0.00000000

A comparison between calculated and experimental spectrum of methanol monomer is shown in Fig. S4.

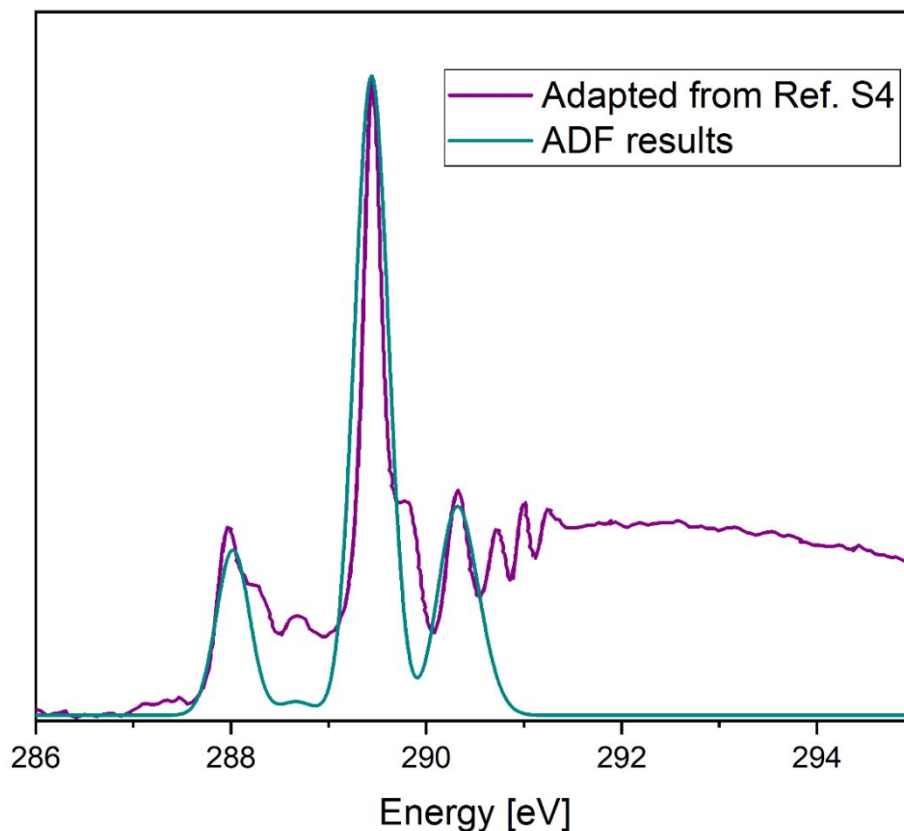


Figure S4: Comparison between the calculated XAS spectra with experimental data adapted from Ref [S4]. The calculated spectrum has been shifted by -2.48 eV over the experimental spectrum in order to facilitate the comparison. As can be seen, the main absorption features and intensities are reproduced. This suggests that the computational method is sufficiently accurate to provide a reasonable agreement with the experimental data. In the calculation, the higher Rydberg states are missing because of the limited size of the ET-QZ3P-3DIFFUSE basis set.

Methanol dimer

Dimer initial coordinates from Ref. [S3]

C	2.26787400	0.10798800	0.37128600
H	3.22136000	-0.38607000	0.18115800
H	1.97592600	-0.10564700	1.40771700
H	2.42190000	1.19062800	0.27552100
O	1.33425700	-0.39111500	-0.57013400
H	0.47630500	0.03699600	-0.41646100
O	-1.28532800	0.64678200	-0.06904400
H	-1.68195200	1.23866900	-0.71669800
C	-2.19424300	-0.42293800	0.21018700
H	-3.12013800	-0.05272200	0.65984100
H	-2.43075300	-0.99980500	-0.68857100
H	-1.69586700	-1.07768300	0.92208300

In Fig. S5 the dimer configurations as a snapshot of the AIMD trajectory between 0 fs (time of ionization) and 100 fs are illustrated. The proton dynamics is clearly observed in the early tens of femtoseconds in agreement with a previous study.
S5

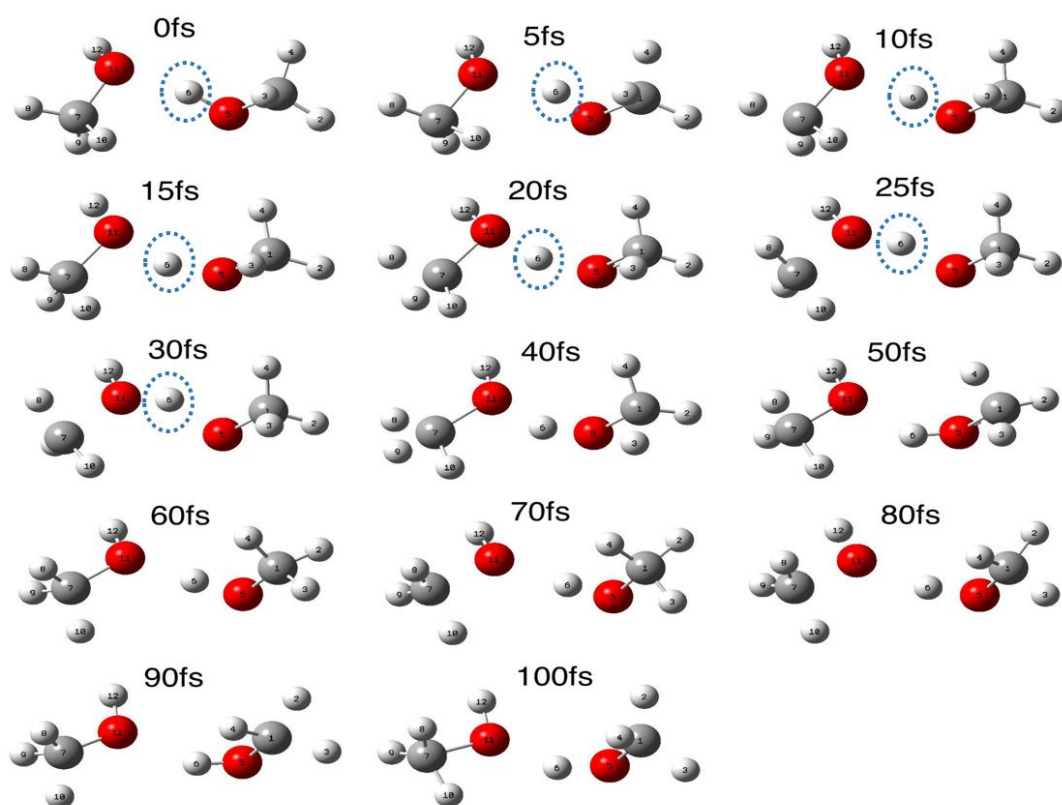


Figure S5: Snapshots of the methanol dimer configuration in the period comprised between 0 fs and 100 fs in 5 fs steps. The snapshots clearly show the transfer of the proton H6 (blue circled) from the oxygen of the H-bond donor (O5) and the oxygen of the H-bond acceptor (O11) during the considered period of time.

Figure S6 shows the bond length variation for the calculated trajectories for different O-H moieties involved in the proton dynamics. With respect to the labeling of figure S5, panel A refers to the variation of the O5-H6 bond length while panel B refers to the variation of the O11-H6 bond length. A very fast proton exchange takes place between 0 and 50 fs as H6 is exchanged between O11 and O5. This is evidenced by the O5-H6 bond length increase (panel A) concomitant with a sharp decrease of the O11-H6 bond length (panel B). A similar behavior is observed between 100fs and 160fs, where H6 is transferred from O5 to O11. Panel C illustrates the O11-H12 bond length variation. This panel shows that, unlike H6, H12 doesn't take part in exchange or transfer processes.

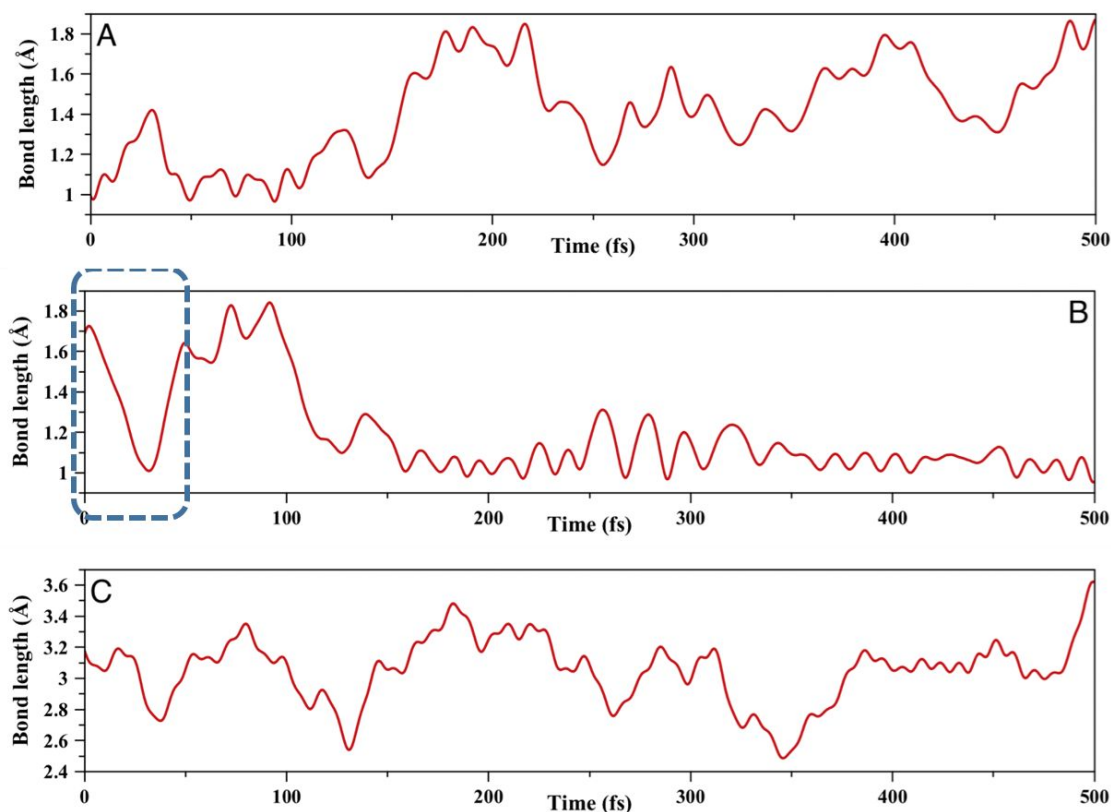


Figure S6: O-H bond length variation during the 500fs calculated trajectory for 05-H6 (A), O11-H6 (B) and H12-O5 (C) according to the labeling in S5.

4. References

- [S1] Follath, R.; Schmidt, J.; Weigand, M.; Fauth, K. The X-ray microscopy beamline UE46-PGM2 at BESSY. *AIP conference proceedings* **2010**, 1234, 323–326.
- [S2] Yin, Z.; Peters, H. B.; Hahn, U.; Ag^oaker, M.; Hage, A.; Reininger, R.; Siewert, F.; Nordgren, J.; Viefhaus, J.; Techert, S. A new compact soft x-ray spectrometer for resonant inelastic x-ray scattering studies at PETRA III. *Review of Scientific Instruments*. **2015**, 86, 093109, 1-5.
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