Supplementary Information

”Site-specific X-ray induced dynamics in liquid methanol”

Supplementary Methods

ESI-Figure 1: C 1s and O 1s core level spectra of liquid methanol. The raw data is shown as red open circles. The black solid line indicates the total fit function and the red traces show the individual Voigt functions used. The residual of the fit is shown in blue.

To determine the additional broadening of the liquid phase due to polarisation screening the gas and liquid phase O 1s XPS peaks are fitted. The XPS spectrum was fitted using a single peak for the liquid phase and a vibrational progression of peaks. The relative energy and intensity values of the vibrational progression were taken from the work of Wiklund et al.[1] and Sankari et al.[2] For the O1s vibrational progression values for water were used as, to the best of our knowledge, no such gasphase values have been reported for methanol O1s. Since it is argued in this work and in previous PTM-CS studies of water[3] that the 1s$^{-1}$ state is dissociative, we believe that not using a vibrational progression to fit the
liquid phase peak best represents the predicted composition of the experimental trace. The resulting fit is shown in ESI-Figure 1. We compared this result with fit functions containing more or fewer peaks, and the results obtained qualitatively reproduce what we present in the main text.

The FWHM of the gas and liquid phase peak is then used to extract the additional broadening factor via \( f_{b,XPS} = \sqrt{FWHM_l^2 - FWHM_g^2} \). The gas phase Auger spectrum was then convoluted with a gaussian function of a full-width-at-half-maximum (FWHM) that is determined by the additional XPS broadening factor \( (f_{b,Auger} = 3 \times f_{b,XPS}) \). In our experiments the additional broadening factor \( f_{b,XPS} \) and corresponding FWHM of the broadening-function are determined to be 0.82 / 2.46 eV in the case of the carbon site and 1.09 / 3.27 eV for the oxygen site.

References

