

Investigation of excited states of WO₃ in picoseconds by L₁-edge XANES

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Tungsten trioxide (WO₃) has attracted much attention as a photocatalyst for decomposition of water by sunlight since its band gap is small enough to absorb visible light and the highest valence band potential is located lower than the redox potential of water oxidation.^[1] In particular, combination of WO₃ with TaON can promote effectively the generation of hydrogen (H₂) and oxygen (O₂) from water.^[2] Recently, we have reported pump-probe X-ray absorption near edge structure (XANES) results at W L₃-edge in WO₃ measured in SPring-8 Angstrom Compact Free Electron Laser (SACLA).^[3] A fast transient process with the local electronic and geometric structures changing was found within 200 ps in addition to the initial photoexcitation (<500 fs). Although the transient L₃-edge XANES measurement is a powerful tool to elucidate the local electronic changes, detailed geometric structure in the excited states is still not clearly understood. W L₁-edge XANES can yield more information on the local geometry around W atoms.^[4] In this study, we performed transient W L₁-edge XAFS experiments and analyzed the obtained results with theoretical calculations to understand the characteristics of the initial and the metastable states of the photoexcited WO₃.

The pump-probe W L₁-edge XANES measurements were performed at SACLA in a similar way to Ref. 3. Fig. 1(a) shows a W L₁-edge XANES spectrum of WO₃ in the ground state, and difference spectra of various delay times between the probe X-ray and the 400 nm excitation laser pulses. The observed ground state spectrum reproduced a static XANES spectrum.^[4] The pre-edge shoulder structure at 12105 eV in the XANES spectrum (dots) is largely influenced by the local structure around the absorbing atom.^[4] Remarkably, a peak at 12103 eV in the difference spectra grows as the delay time increases up to about 200 ps. The timescale of the spectral changes is consistent with the previous L₃-edge XANES measurements.^[3] To investigate the structural transformation, we calculated spectra for various structural models using the Full potential multiple scattering (FPMS) code.^[5] We can recognize how the structural changes modify W L₁ XANES and find the most plausible model by the calculations. Fig. 1(b) shows calculated difference spectra with respect to the calculated ones for the ground state of WO₃. In all the calculated spectra for the excited state,

the energy positions were shifted by -1 eV before subtraction. The calculated result without any structural change (red line) grasps the observed features at 3 ps. The observed difference spectrum at 3 ps is thus ascribed to the charge transfer from O 2p bands to W 5d bands (resultant W ions are pentavalent) due to the photoexcitation, while the local structure may not significantly change within a few ps.

The peak intensity at 12103 eV in the difference spectrum at 193 ps is greater than that at 3 ps. This is a specific feature of the ~ 200 ps spectrum, which cannot be explained by the edge energy shift only. The calculated difference spectra (blue lines) exhibit the observed feature at 200 ps, in case that O1 or O2 [see inset of Fig. 1(b)] is pushed to W with O6 or O5 pulled from W, respectively. For example, when O1 moves towards W by 0.05 Å and O6 away by 0.05 Å in our model, the peak intensity at 12103 eV in the difference spectrum becomes greater. This deviation increases the local distortion from a regular octahedron around W. Therefore, an anisotropic structural change in the a -axis (O2 and O5) or the c -axis (O1 and O6) may occur in the metastable state at 200 ps. These changes are also in good agreement with the results found in W L_3 -edge EXAFS at 150 ps. Further information on the excited states could be extracted on the basis of the obtained structures.

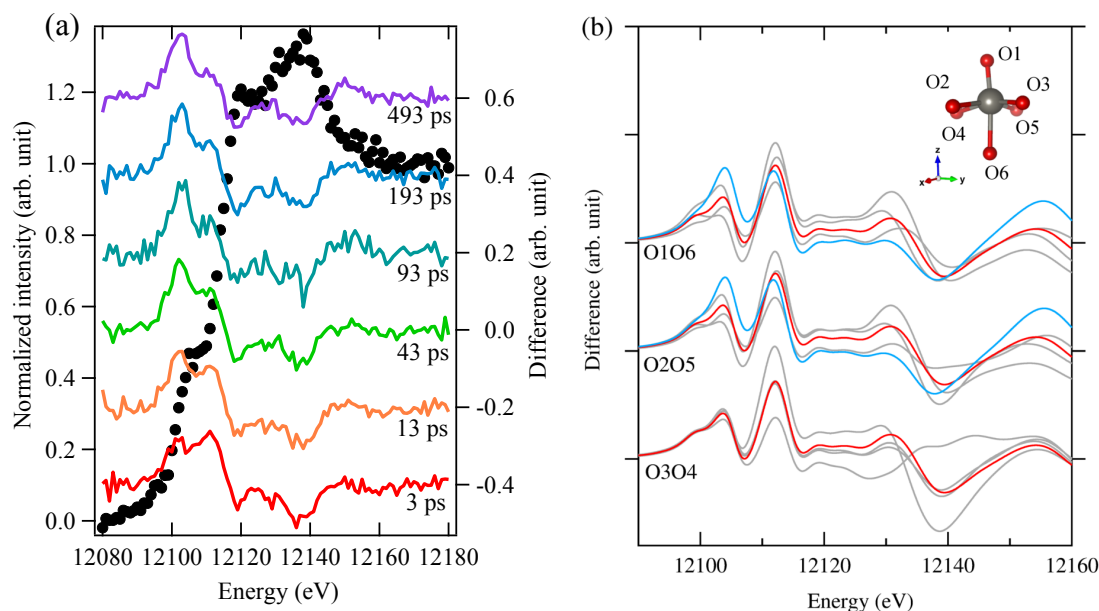


Figure 1. a) Observed WO_3 W L_1 -edge XANES (dots) and difference spectra at various delay times (solid line). b) Calculated different spectra for several structural models where two W-O bond distances are deviated. The difference spectra without the structural change are depicted by red lines for comparison. The calculated spectra that show a similar tendency to the observed one at 193 ps are highlighted by blue lines.

References:

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