Supporting Information:

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1. The Pump-laser intensity dependence of the intensity of $\Delta\mu$

Fig. S1 shows the Pump-laser intensity dependence of the intensity of $\Delta\mu$(difference spectra). We found a linear relationship when the pump-laser intensity was less than 200 mJ cm^2. Thus we set the pump laser intensity to be 200 mJ/cm^2.

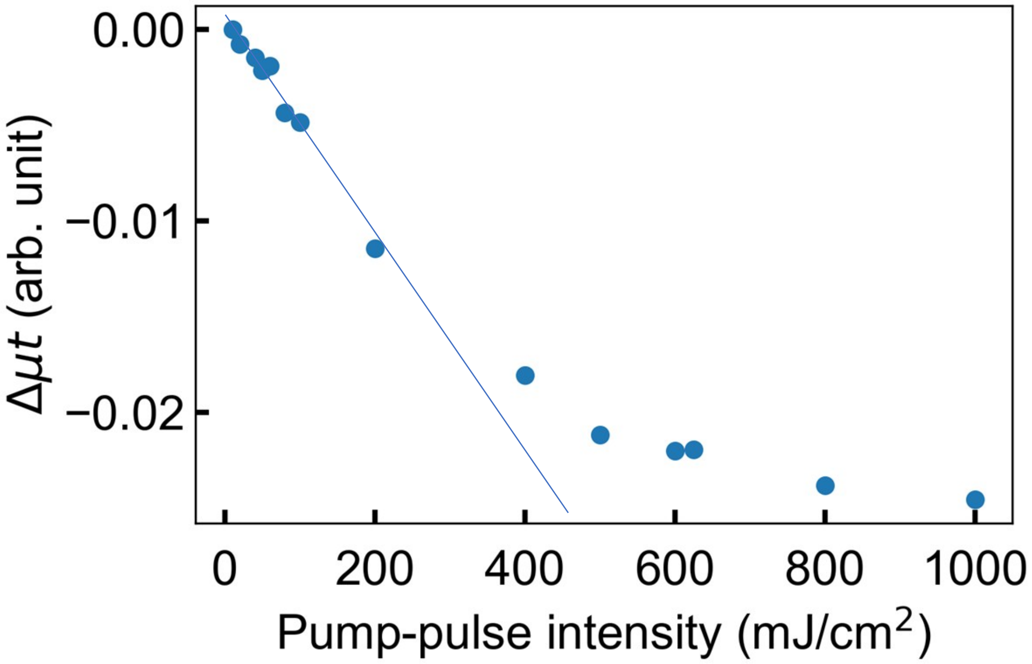
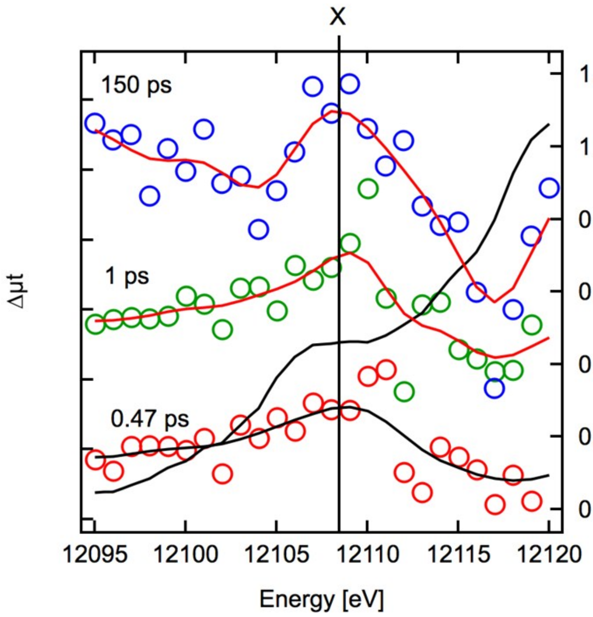


Figure S 1 The laser fluence dependence of the difference spectrum of W L3 edge XANES of WO_3.

2. The difference between the photoexcited state spectrum and the energy-shifted ground state spectrum

The differences between the photoexcited state spectrum and the energy-shifted ground state spectrum are displayed in Fig. S2a. The intensity around peak X gradually increased upto 150 ps. The result indicates that the local structure of WO_3 changes in the early stage of the photoexcitation. It should be noted that no further energy shift was not taken into account. Figure S2b shows the difference spectra between the calculated W L_1 spectrum with the position shift of the W atom in each crystal axis direction and the calculated spectrum for no position shift of W atom.



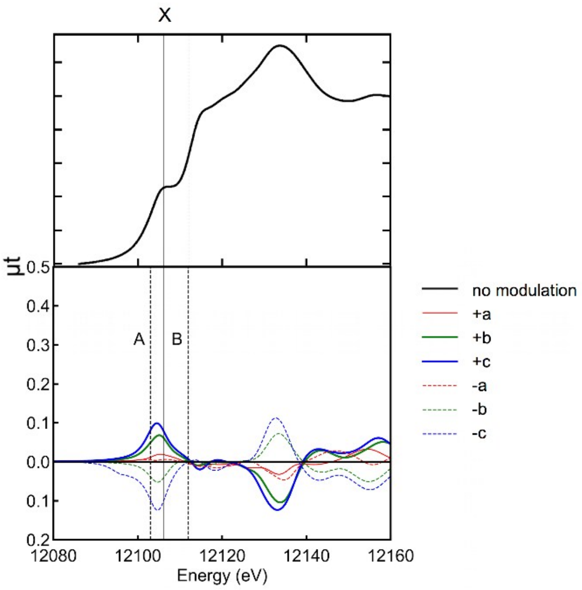


Figure S 2a The differences between the W L_1 XANES spectrum of the photoexcited state and the XANES spectrum energy-shifted by -1 eV of the ground state.

Figure S 2b The differences between the calculated W L_1 XANES spectrum with the position shift of W in each crystal axis and the calculated W L_1 XANES spectrum of the original position. Topmost spectrum is calculated WL1 edge spectrum of WO3. All spectrum features were reproduced well in the FPMS calculation.

3. Kinetic trace of W L_1 XANES in the vicinity of time 0

Figure S 3 shows the kinetic traces of A and B around the delay time 0. The time resolution of the experiments was about 0.5 ps. The convolution line shown as the black solid line follows well both the kinetic traces. This implies that the initial photoexcited state is formed within 0.5 ps.

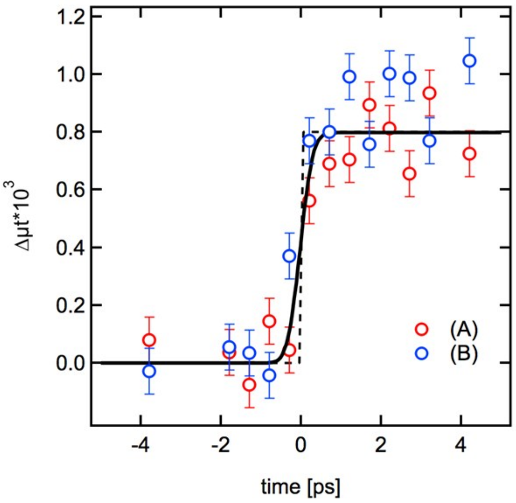


Figure S 3 The kinetic traces of W L_1 edge near the delay time 0 ps. The black solid line is a convolution curve of a step function (shown as the dashed line) and a Gaussian function.

4. Calculated difference spectra of W L1 edge XANES for various position movements of the absorbing W atom.

Figure S 4-a - d show calculated difference spectra of W L_1 edge XANES for various position movements of the absorbing W atom. The difference spectra were obtained by the subtraction of the calculated spectrum without the W movements and energy shift from the calculated spectra with the W movements and energy shift of -1 eV. The W movements was defined by the direction of the crystal axes. For example, the postion shift (+a, +b) describes that the W atom is moved by the translation vector (+0.1 Å, +0.1 Å, 0.0 Å) where each component is along to the a, b and c axes, respectively. The difference spectra for one direction movements, such as the direction of +a axis, were already shown in the main text. Figures S1(a), (b) and (c) shows the difference spectra for the W movement directions between two crystal axes. The W position shifts are schematically shown by the insets in each spectra. Figure S3(d) shows the spectra for the directions among all the crystal axes. The directions of the W position shifts are schematically shown by using a cube and arrows. As a result, all the difference spectra which has a larger peak at 12103 than at 12112 eV involve the direction of +b or +c axes. Although the direction of a axis seems to influence the peak intensity of (-a, +b) and (-a, +c) in Figure S3(a) and S3(c), the peaks have the close intensity to the ones of the peaks for the direction of +b and +c axes in

Figure 1(a) in the main text, respectively.

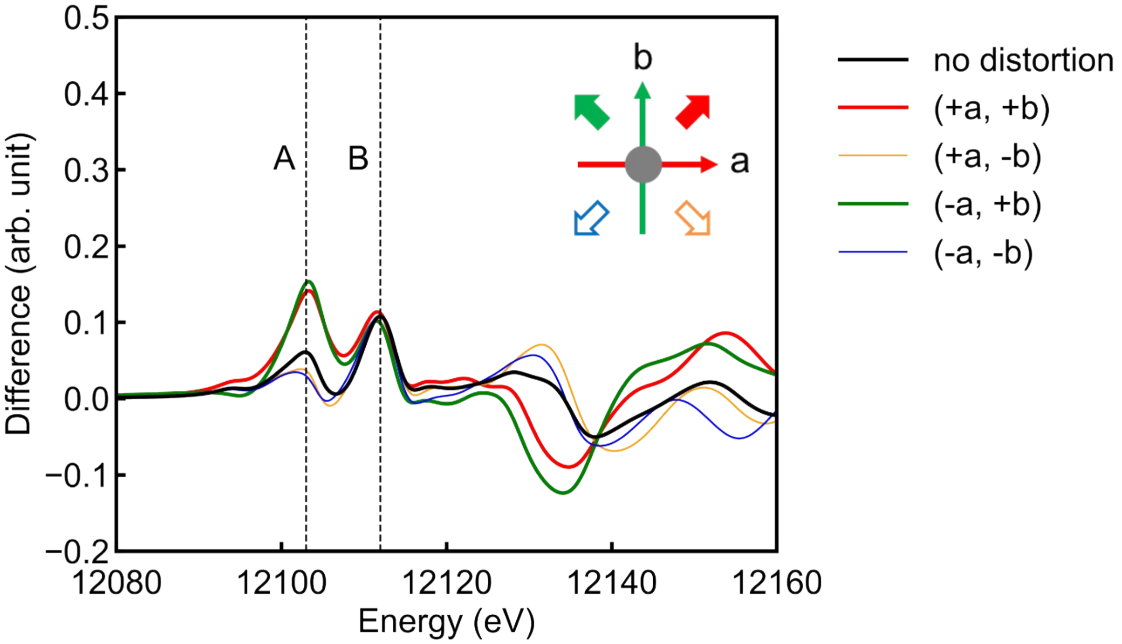


Figure S 4-a Calculated difference spectra of W L_1 edge XANES for the W position shift in the direction between a and b axes.

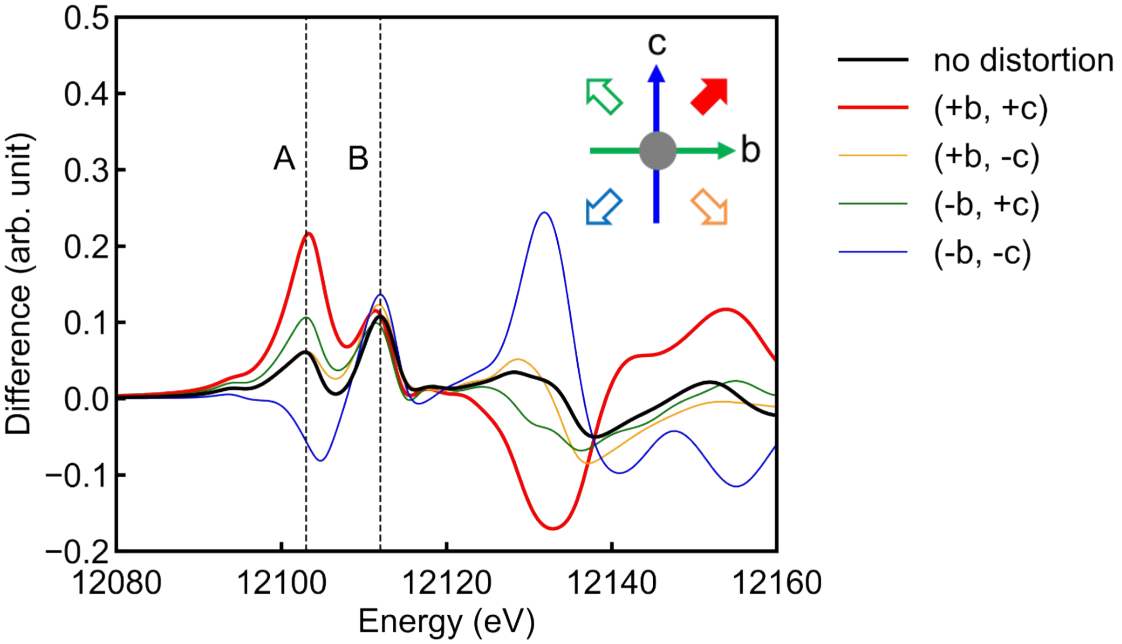


Figure S 4-b Calculated difference spectra of W L_1 edge XANES for the W position shift in the direction between b and c axes.

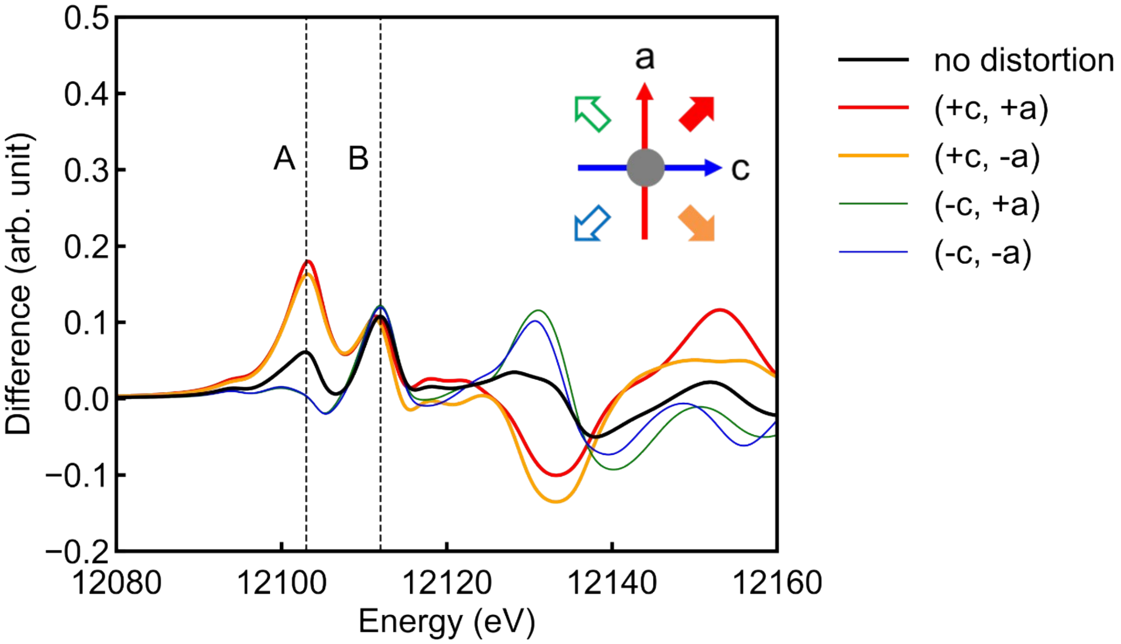


Figure S 4-c Calculated difference spectra of W L_1 edge XANES for the W position shift in the direction between a and c axes.

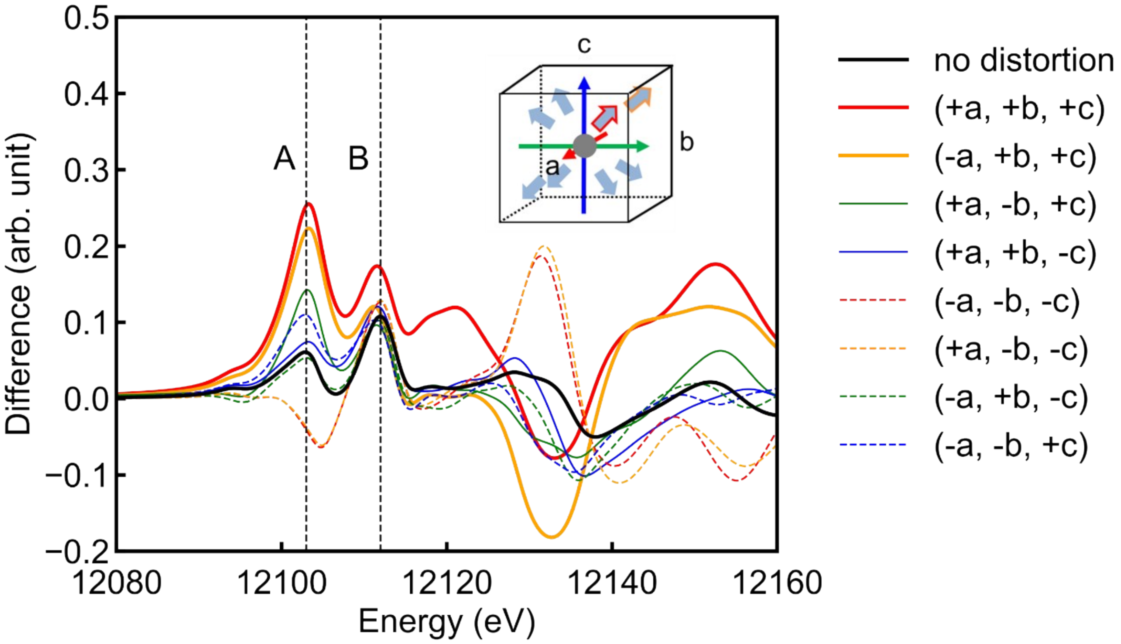


Figure S 4-d Calculated difference spectra of W L_1 edge XANES for the W position shift in the direction among a, b and c axes.

5. Calculated XANES spectra for higher-symmetry structural model.

To check a possibility of a local structural change toward a local higher-symmetry structure, we calculated XANES spectra for various structural models including an orthorhombic one. In a cubic model, each WO_6 unit takes a virtual regular octahedral structure and all W-O bonds have same distance. The bondlength is obtained by the averaged bondlength of monoclinic WO_3 to reduce effects of the bondlengths on XANES. An orthorhombic model (abc) is similar to the cubic model but average of bondlenth of WO_3 is individually taken in each crystal axis. Therefore, the lattice constants of the orthorhombic model (abc) are different each other. In orthorhombic models including W-O bond alternation, here we call them alternation models, oxygen atoms in W-O bonds along to a designated axis uniformly shift toward neighboring W atoms to make the bond alternation. For example, W-O bondlengths along to b axis in an alternation model (b) have two different distances. The two distances were obtained by averaging the shorter and longer bondlengths along to b axis in the monoclinic WO_3, respectively. The other W-O bondlengths are same as the ones in the orthorhombic model (abc). Alternation models (c) and (bc) are defined in the same way of the alternation model (b). The boldlenths in all the models are shown in Table S3. It should be noted that we did not check an alternation model (a) because bond alternation of about 0.02 Å along to a axis is quite smaller than the ones of about 0.3 Å along to the other axes.

Figure S 5-a shows calculated XANES spectra for the model structures. For comparison, the spectrum for the monoclinic structure is shown. The spectra for the cubic, orthorhombic (abc) models have no pre-edge peak in the energy range between A and B (see Figure S 5-a) due to either the regular or almost regular octahedral structure around the absorbing W atom. Since difference of the bondlengths between the structural models, the two spectra are not so different. On the other hand, the pre-edge peak appears in the alternation models because of the local octahedral structure distorted by the bond alternation. However, the distortion of the local structure and the intensity of the pre-edge peak in the alternation models are less pronounced than those in the monoclinic structure. The less pronounced pre-edge peak feature is also shown more clearly at a peak A in Figure S 5-b. The difference spectra in Figure S 5-b are obtained by subtraction of the XANES spectrum for the monoclinic structure without energy shift from the XANES spectra with energy shift of -1 eV. The smaller peak A than that of the monoclinic structure indicates that the local structural in the photoexiced state does not change toward an orthorhombic structure.

Table 5-1

The bondlengths between W and O atoms in various structural models used for calculations. The bondlengths are shown in Å.

	a	b	c
cubic	1.929	1.929	1.929
orthorhombic (abc)	1.899	1.933	1.956
alternation (b)	1.899	1.767 2.098	1.956
alternation (c)	1.899	1.933	1.767 2.098
alternation (bc)	1.899	1.767 2.098	1.767 2.098

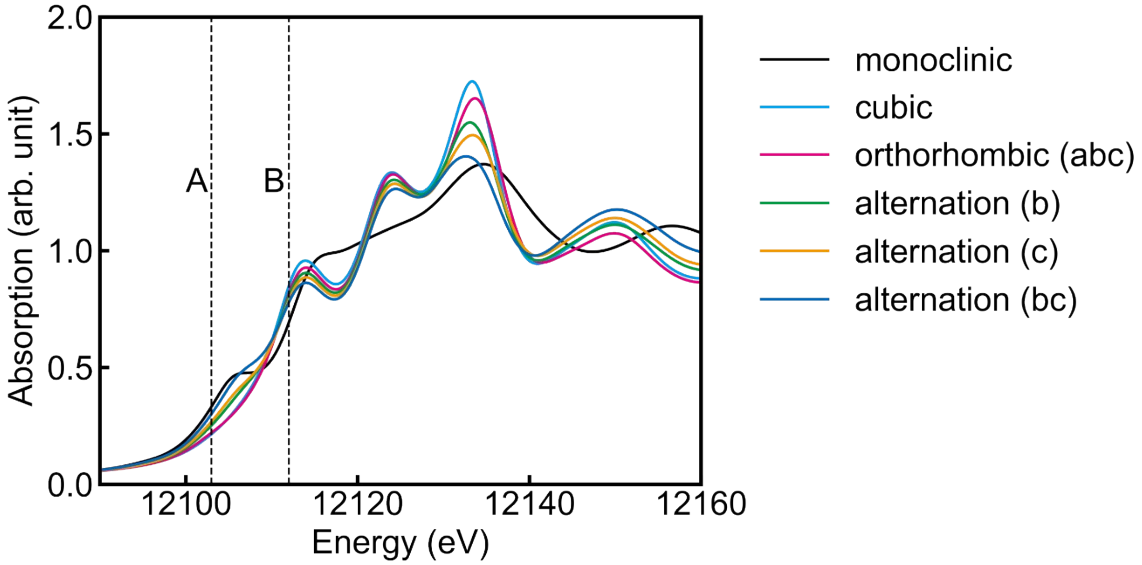


Figure S 5-a Calculated XANES spectra for various structural models including orthorhombic ones.

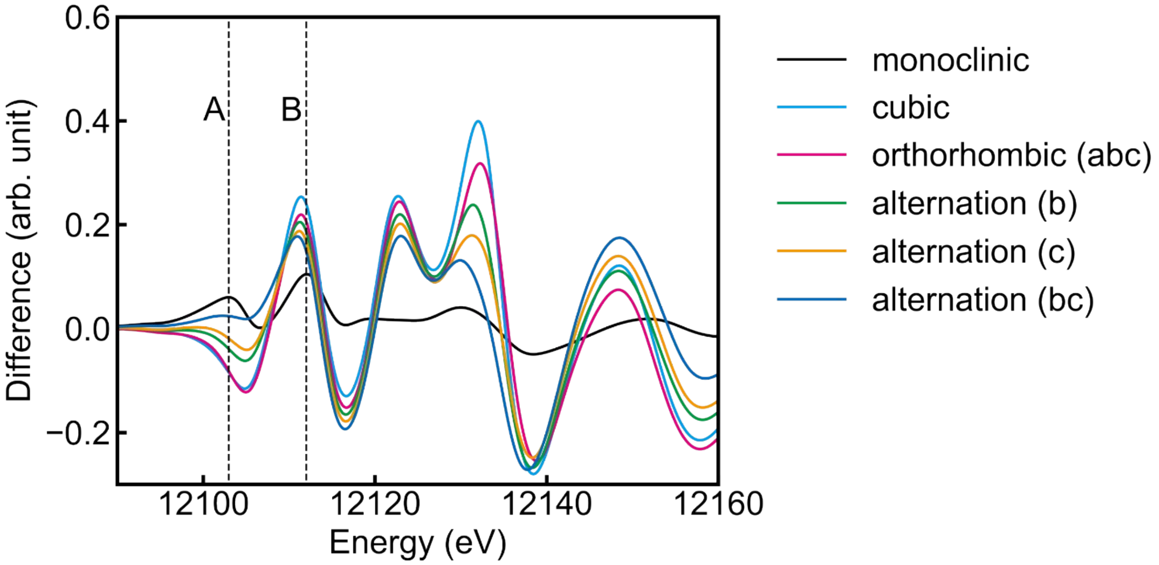


Figure S 5-b Calculated difference spectra for various structural models including orthorhombic ones.