Thorough search analysis on time resolved EXAFS of WO_3 structural change

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WO_3 is a photocatalyst. It is important to follow the photoabsorption process to understand the mechanism. There are many time resolved spectroscopic results about the photoabsorption process using the visible light and the infrared but it is not sensitive to the local structure. We have applied ultrafast XAFS spectroscopy to the system and successfully got the spectra. However, it is impossible to analyze the EXAFS data because of too many fitting parameters to give the local minimum and we need to develop the new analysis technique to analyze the complex system. We now propose a "Thorough Search" method and successfully obtain the local structure of metastable WO_3 state after 100 ps.[1]

The "Thorough Search" method is referred to the search through the parameters completely with a certain precision. And we have searched 1.48 million points in the parameter space representing the model structures. The model structures were evaluated using R-factor defined as following,

$$\text{R-factor} = \frac{\sum\{\Delta\chi(k_i)_{Data} - \Delta\chi(k_i)_{Calculated}\}^2}{\sum \Delta\chi(k_i)_{Data}^{\ 2}}$$

where, $\Delta\chi(k)$ is difference between EXAFS oscillation after and before the photoabsorption. The subscript "*Data*" and "*Calucalted*" are the observed and calculated $\Delta\chi(k)$, respectively. As a result, we got a structural model for the metastable WO_3 state which fits well as shown in Fig.1. We adopted several calculated results with R-factor < 0.01. Fig.2 shows the histogram of bond distance distribution of all model structures with R-factor < 0.01. The histogram indicates the contraction of the shortest bond and elongation of the longest bond. We are now refining the structure model.

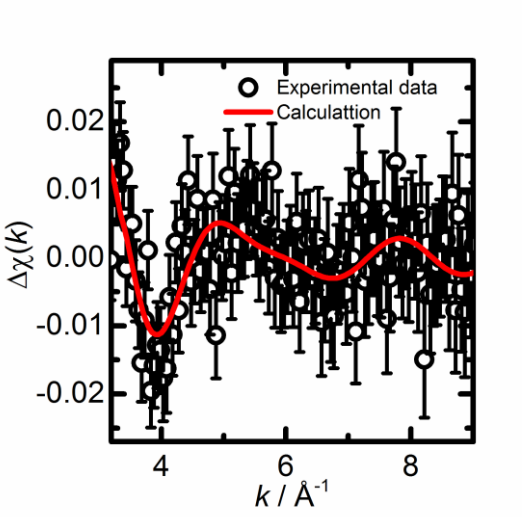

Fig.1 Change of EXAFS oscillation due to the photoabsorption. Black dots show experimental data and red line is calculated one.

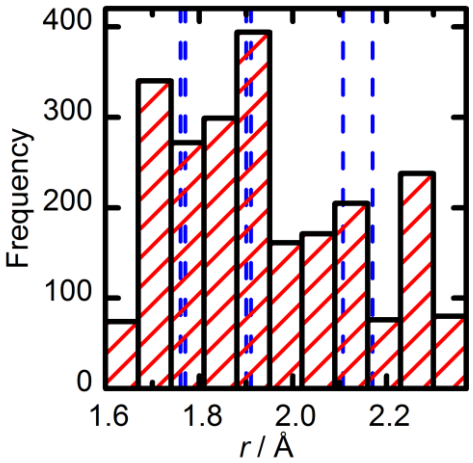

Fig. 2 histogram of bond length which are structural models satisfied R-factor<0.01

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