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Metastable structure of photoexcited WO₃ determined by the pump-probe extended X-ray absorption fine structure spectroscopy and constrained thorough search analysis

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1 The local structure of WO₃ photocatalyst in the
2 photoexcited metastable state created 150 ps after laser
3 irradiation have been determined by the pump-probe L₃-
4 edge EXAFS and the constrained thorough search analysis.
5 A highly distorted octahedral local structure was found
6 where one of the shortest W-O bonds was further shortened
7 to 1.66 Å while the other five bonds were rather elongated
8 even though theoretical calculations predicted the reverse
9 change. We discuss this contradiction and propose a
10 possible structure for the metastable state.

11 **Keywords:** Photocatalyst, Pump-probe EXAFS,
12 **Thorough search method**

13 Photocatalysts are paid attention to harvest sunlight to
14 split water into H₂ and O₂.¹ Many kinds of researches have
15 been carried out to improve the efficiency of photocatalyst
16 such as impurity doping, Z-scheme method, and so on.
17 Usually, these processes are understood in the energy band
18 model. In the energy band model, the positions of Fermi
19 level, minimum of the conduction band, and maximum of
20 valence band are important against the reduction and
21 oxidation potentials for H₂/H₂O and O₂/H₂O. The local
22 structure and electronic state of the photoexcited state need
23 to be elucidated to understand the photocatalysis of water
24 splitting and to improve the performance of water-splitting
25 photocatalysts.

26 A pump-probe (PP) X-ray absorption fine structure
27 (XAFS) investigation of the photocatalysts using pulsed X-
28 rays emitted from an X-ray free electron laser (XFEL) and
29 synchrotron radiation (SR) has revealed element-specific
30 local electronic and geometrical structures, thereby
31 providing new scientific knowledge about photocatalysis
32 that cannot be obtained by other techniques.² WO₃ is used as
33 a Z-scheme water-splitting photocatalyst that is sensitive to
34 visible light, which is the main component of sunlight.³ We
35 have acquired PP X-ray absorption near edge structure (PP-
36 XANES) spectra of WO₃ after pulsed laser irradiation and
37 have found that the valence change of W ion just after laser
38 irradiation (<500 fs) then the metastable state (MS) was
39 created within 150 ps followed by relaxation to the ground
40 state (GS) with a time constant of 2 ns.⁴⁻⁷ We proposed that
41 the photoelectrons were trapped at distorted stoichiometric
42 W sites in the crystal lattice, similar to the trapping of
43 polarons, instead of at surface or bulk defects.⁶ The
44 formation time for the MS, 150 ps, was longer than that for
45 the other oxides such as TiO₂ and Fe₂O₃, consistent with

46 previously-reported optical measurement results.⁸ It is
47 desirable to acquire the PP extended X-ray absorption fine
48 structure (PP-EXAFS) spectrum to confirm the structure
49 change because EXAFS is sensitive to local structural
50 features such as bond lengths.⁹ However, PP-EXAFS
51 spectral measurements are much more difficult than PP-
52 XANES measurements⁶ because of the lower PP-EXAFS
53 signal intensity. In addition, compounds with a complex
54 structure, such as WO₃, require a multishell fitting which is
55 inherently challenging. We addressed these two difficulties
56 by taking the difference spectra between before and after
57 photoabsorption to obtain the EXAFS spectrum of MS WO₃.
58 The difference spectra were accumulated and then analyzed
59 using the constrained thorough search (CTS) method to
60 elucidate the bond lengths in MS WO₃.^{10, 11}

61 In the present paper, we report the PP-EXAFS results
62 for the structure of the MS WO₃ state to clarify the local
63 structure change and to attempt to explain the long
64 formation time for MS WO₃.

65 The WO₃ was purchased from Wako Chemicals, and
66 50–200 nm WO₃ particles were dispersed in ultrapure water.
67 The concentration of WO₃ was 2.5 mmol L⁻¹. The WO₃ jet
68 was supplied to the cross point of the laser used for
69 photoexcitation (Ti-sapphire with a 1 ps pulse width, 945
70 Hz repetition rate, and 400 nm wavelength) and the X-ray
71 beam emitted from the Photon Factory Advanced Ring (PF-
72 AR, 6.5 GeV, 60 mA, single bunch operation with pulse
73 width of 100 ps, and pulse interval of 1.26 μs). The
74 fluorescence X-rays were monitored using a scintillation
75 counter with a Cu filter to attenuate the elastic X-rays.
76 Details of the experimental setup are available elsewhere.⁴

77 The difference spectrum before and after the
78 photoirradiation, $\Delta\mu(=\mu_{\text{API}} - \mu_{\text{BPI}})$, was accumulated, thereby
79 reducing the possible fluctuations. The μ_{API} and μ_{BPI} were
80 the spectra recorded after and before the photoirradiation,
81 respectively. The spectrum of the MS WO₃, μ_{MS} , was
82 obtained by assuming that μ_{API} was a linear combination of
83 the spectrum of the ground state (GS), μ_{GS} , and μ_{MS} . $\mu_{\text{API}} =$
84 $\alpha\mu_{\text{MS}} + (1 - \alpha)\mu_{\text{GS}}$, where α , the fraction of MS WO₃, was
85 obtained from the XANES spectrum, as shown in Figure S1
86 in the supporting information (SI-1). μ_{BPI} was equal to that
87 of the ground state, μ_{GS} . Therefore, μ_{MS} is obtained from
88 $\mu_{\text{MS}} = \Delta\mu/\alpha + \mu_{\text{GS}}$, which was then processed and analyzed
89 using the EXAFS analysis programs REX2000¹² and
90 LARCH¹³, as described in SI-2. The Fourier transformation

1 ranges of Δk and Δr were $5 (= 8 - 3) \text{ \AA}^{-1}$ and $1 (= 2 - 1) \text{ \AA}$,
 2 respectively, so that the amount of information, M , was
 3 approximately 5 ($M = 2\Delta k \cdot \Delta r / \pi + 2$).¹⁴ The inversely
 4 Fourier transformed data were first analyzed by a curve-
 5 fitting method using the LARCH package.¹³ Further details
 6 of the structure, including bond lengths, were derived from
 7 the EXAFS spectra using the CTS method, as explained in
 8 SI-4.^{10,11,15}

9 Figure. 1 shows the EXAFS oscillation of the MS WO_3 ,

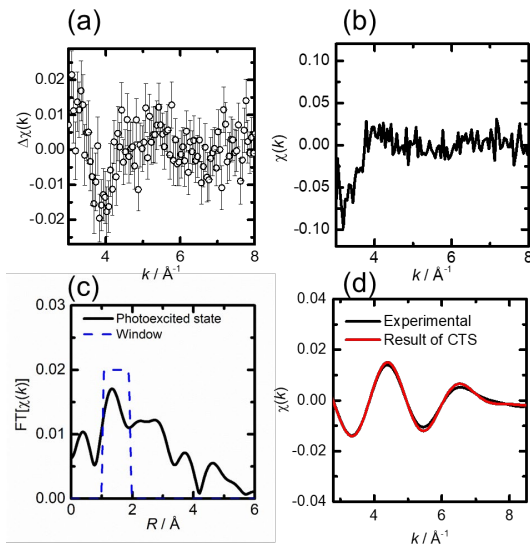


Figure 1. (a) $\Delta\chi(k)$ for W L_3 -edge EXAFS spectra between before and 150 ps after the irradiation. (b) $\chi_{MS}(k)$ for the MS WO_3 . (c) The Fourier transform of $\chi_{MS}(k)$. The broken line shows the range of Fourier filtering. (d) Inversely Fourier transformed data (black line) for the MS WO_3 with the results of CTS (red line). The enlarged one is available in Fig. S4

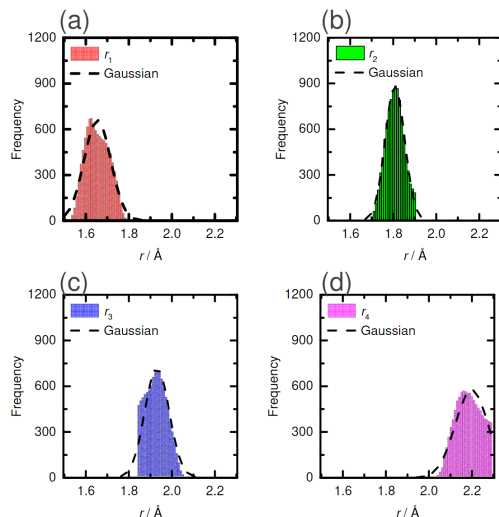


Figure 2. (a)-(d) Distribution of bond lengths that satisfy R-factor < 0.10 for the structure parameters for the MS WO_3 . Dashed lines show the fitting results obtained using a Gaussian function.

10 $\chi(k)_{MS}$, and its Fourier transform. The main peak at 1.4 \AA
 11 was inversely Fourier transformed to the k -space, and the
 12 data were analyzed by one-shell curve fitting. The one-shell
 13 curve fitting results are shown in Figure S2 and Table S1 in
 14 SI-3. We conducted the analysis using two methods. In the
 15 first method, the Debye-Waller (DW) factor was adjusted
 16 freely; in the second method, the DW factor was constrained
 17 as a function of the bond length given by Eq S5 in SI-4.
 18 Both results indicated that the bond length contracted in the
 19 MS WO_3 ; however, details of the structure were unclear.

20 We carried out the CTS analysis based on the uniform
 21 prior probability principle.¹¹ CTS analysis can visualize the
 22 correlations of parameters from the multi-dimensional
 23 parameter space. Especially, CTS analysis can be all
 24 candidates which reproduce the experimental data well and
 25 reject the possibility of other structures in the searched
 26 parameter space. CTS analysis was applied to extract the
 27 convincing information. We assumed the followings:

- 28 1. MS WO_3 has distorted octahedra, similar to GS WO_3 .
- 29 2. DW factors are functions of the bond length in Eq S5 in
 30 SI-4.¹⁶ A greater length corresponds to a larger DW factor.
- 31 3. EXAFS spectroscopy is sensitive to short bonds because
 32 of the $\exp(-2r/\lambda - 2\sigma^2 k^2)/r^2$ term.

33 The structural parameters were limited to the value of
 34 $M (\approx 5)$. The GS WO_3 has a monoclinic structure in which
 35 two distorted octahedral sites are present, as shown in Table
 36 S3.¹⁷ The bond lengths in GS WO_3 have 12 different values.
 37 Two sites have a similar local structure; the corresponding
 38 W-O distances are therefore denoted as $r_1''', r_2''', r_3''', r_4'''$,
 39 r_5''' , and r_6''' in Table S3 in SI-4. We intended to
 40 demonstrate that $r_1''' \neq r_2'''$ in the MS WO_3 , as predicted
 41 from the W L_1 -edge XANES results.⁶ According to
 42 assumption (3) (i.e., that shorter bonds (r_1''' , r_2''') have
 43 greater contributions to the EXAFS spectra), we assumed that
 44 that r_1''' and r_2''' were independently optimized and we
 45 constrained $r_3''' = r_4''' = r_3$ and $r_5''' = r_6''' = r_4$, as shown in
 46 Table S3. The CTS was carried out for the four parameters
 47 $r_1 (= r_1''')$, $r_2 (= r_2''')$, r_3 , and r_4 with the corresponding
 48 coordination numbers, $N_1 = N_2 = 1$ and $N_3 = N_4 = 2$, as shown in
 49 Table S2 and Table S3 in SI-4. Table 1 shows the CTS
 50 results that reproduced the crystal data given in Table S3 in
 51 SI-4 for the GS WO_3 . Note that r_1 and r_2 are approximately
 52 the same as shown in Table 1 even if the two parameters are
 53 independently changed. Figure S5 shows the occurrence
 54 histograms. We found that the histograms for r_1 and r_2 have
 55 similar distributions and the same peak positions.
 56 Consequently, for the GS WO_3 , we conclude that r_1 and r_2
 57 agreed with each other within the error.

58 Table 1 shows the CTS results for the MS WO_3 .
 59 Figure S4 shows a comparison between the Fourier filtered
 60 $\chi(k)_{MS}$ and the calculated one. The observed data were well
 61 reproduced by the parameters determined by the CTS
 62 method. The R-factor (Eq S3) was 0.02. In the case of the
 63 MS WO_3 , we found that r_1 and r_2 were not equal and that r_1
 64 was 0.11 \AA shorter than that for the GS WO_3 .

Table 1. Results of constrained thorough search analysis for the W L₃-edge EXAFS spectra of GS and MS WO₃. "Crystal" indicates crystallographic data.¹⁷

Sample	$r_1 / \text{\AA}$	$r_2 / \text{\AA}$	$r_3 / \text{\AA}$	$r_4 / \text{\AA}$	R-factor
GS	1.77 ±0.08	1.77 ±0.08	1.91 ±0.04	2.17 ±0.09	0.049
Crystal	(1.75	1.77	1.90	2.13)	
MS	1.66 ±0.06	1.81 ±0.04	1.93 ±0.06	2.19 ±0.07	0.012

1
2 The histograms of r_1 and r_2 show different peak positions
3 (Figure 2). The 2 dimensional frequency plot in Figure S6
4 clearly shows the different peak position at $r_1 \neq r_2$. Bonds
5 other than r_1 in the MS WO₃ were longer than the
6 corresponding bonds in the GS WO₃, in good agreement
7 with previously reported WO₃ L₁-edge XANES results.⁶ The
8 photoexcited MS WO₃ exhibited a further distorted structure.

9 The CTS analysis showed that the MS WO₃ exhibited
10 a further distorted structure, where the shortest W=O bond
11 was further shortened from 1.77 Å to 1.66 Å. This structure
12 change was interpreted as follows in a previous paper.⁶ The
13 photoelectron excited by the pulsed laser would occupy the
14 d_{xy} orbital of W, which was on a plane perpendicular to the
15 shortest W=O bond. The orbital was located at the bottom of
16 the conduction band in energy scale, forming a π^*
17 antibonding orbital with $2p_x$ and $2p_y$ for oxygen atoms in the
18 xy plane. Thus, the W-O bonds in the xy plane were
19 elongated, pushing up the W atom in the direction of the
20 shortest W=O bond.⁶ As described later and in SI-8 and in
21 SI-9, this previous interpretation is not consistent with the
22 results of the density functional theory (DFT) and quantum
23 mechanics/molecular mechanics (QM/MM) calculations.
24 This discrepancy will be discussed below.

25 In the literature, the MS WO₃ was assumed to be
26 located in bulk or surface defect sites.¹⁸⁻²⁰ However, we
27 disproved these possibilities because the amount of MS
28 states was much larger than the amount of defects.
29 Yamakata et al. recently reported that introducing defects by
30 reducing WO₃ decreased the lifetime of the MS WO₃.²¹
31 Surface defects might be less likely because the surrounding
32 environment did not affect the lifetime of the MS WO₃, as
33 shown in SI-7. We proposed the MS WO₃ should be located
34 at the normal lattice sites in the bulk stoichiometric WO₃
35 and be distorted from the structure of the GS WO₃. Such
36 distortion would stabilize the MS WO₃, similar to the
37 stabilization of polarons.

38 However, we still faced two problems. First, the DFT
39 and QM/MM calculations for the MS WO₃ local structure
40 indicated that the less-distorted structure was stable, with
41 the shortest W=O bond being elongated as shown in Table
42 S5 in SI-8. Second, it was unclear why the formation of the
43 MS WO₃ structure took 150 ps. The vibration frequencies of
44 W-O are on the order of 100 cm⁻¹ or 3 THz or 0.3 ps. Fe₂O₃
45 hematite and CuWO₄ took less than 1 ps to produce a
46 polaronic MS.^{22, 23} Thus, the simple isolated distorted MS
47 structure should form much faster. According to the L₃-edge
48 XANES result obtained from femtosecond time resolved

49 measurement, the W⁵⁺ was formed and was gradually
50 changed to the MS structure.⁵ Such a long time scale might
51 be related to the collective structure change. If the single
52 distorted structure of the MS WO₃ was located in the GS
53 WO₃, it should have a greater distortion energy between the
54 surrounding GS WO₃. Thus, the theoretical calculation
55 suggested a less distorted structure. If the two distorted MS
56 along which the shortest W=O bonds were assumed to be
57 headed, the distortion energy should be released.
58 Consequently, the formation of the well-ordered distorted
59 MS WO₃ cluster shown in Figure 3 should require a long
60 time.

61 The problem with the well-ordered MS WO₃ clusters is
62 the charge balance, which should show a large negative
63 charge. To compensate for the negative charge, holes should
64 combine with photoexcited electrons in the well-ordered MS
65 WO₃ cluster. In this case, the recombination of photoexcited
66 electrons and holes might be enhanced. If the spins of the
67 hole and the photoexcited electron near the hole were
68 parallel or in a triplet state, the well-ordered distorted MS
69 cluster should be stabilized and had a finite lifetime. The
70 large-scale DFT calculations of the MS excited state with a
71 large cluster size or time-resolved micro X-ray Magnetic
72 Circular Dichroism (XMCD) of O and W could support our
73 hypothesis for the formation of such a well-defined distorted
74 MS WO₃ cluster, which will be the future challenge.

75 Picosecond time-resolved W L₃-edge EXAFS
76 spectroscopy was conducted to characterize the structural
77 change in MS WO₃ in detail. We applied the CTS method to

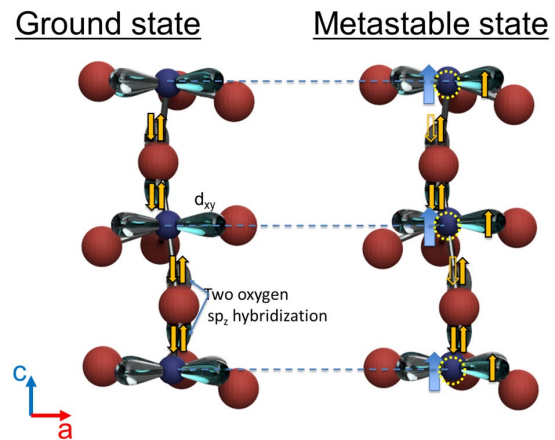


Figure 3: The local structure change in the GS WO₃ (left panel) and the MS WO₃ (right panel). Large red and small blue circles represent O and W atoms, respectively. Yellow broken circles indicate the position of W in GS. Thick blue arrows show the movement of W atoms in the MS WO₃. W atoms along the c-axis move in the direction corresponding to W=O contraction. Orange filled and empty arrows in the orbitals correspond to electrons with spin and holes, respectively. Grey filled circles indicate holes. The unpaired electron spins are all parallel in the polaron cluster.

1 analyze the EXAFS data for the MS WO₃, where one of the
 2 shortest bonds was further shortened by 0.11 Å from its
 3 original bond length, consistent with the structure proposed
 4 on the basis of W L₁-edge XANES spectroscopy. This
 5 structural change in the MS WO₃ led the distorted MS
 6 structure, which should be stabilized, to form well-ordered
 7 distorted clusters in conjunction with the formation of the
 8 triplet state.

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 20 2013G166, 2015G541, 2015G542).

21
 22 Supporting Information is available on
 23 http://dx.doi.org/10.1246/cl.*****.

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NOTE The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge.

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You are requested to put a brief abstract (50-60 words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand what the graphic shows.

Graphical Abstract	
Textual Information	
A brief abstract (required)	The local structure of WO_3 photocatalyst in the photoexcited metastable state created 150 ps after laser irradiation have been determined by the pump-probe L_3 -edge EXAFS and the constrained thorough search analysis. A highly distorted octahedral local structure was found whose one of the shortest W-O bonds being further shortened to 1.66 Å while the other five bonds were elongated even though theoretical calculations predicted the reverse change. We discuss this contradiction and propose a possible structure for the metastable state.
Title(required)	Metastable structure of photoexcited WO_3 determined by the pump-probe extended X-ray absorption fine structure spectroscopy and constrained thorough search analysis
Authors' Names(required)	Daiki Kido, Yohei Uemura, Yuki Wakisaka, Akihiro Koide, Hiromitsu Uehara, Yasuhiro Niwa, Shunsuke Nozawa, Kohei Ichiyangagi, Ryo Fukaya, Shin-ichi Adachi, Tokushi Sato, Harry Jenkins, Toshihiko Yokoyama, Satoru Takakusagi, Jun-ya Hasegawa, and Kiyotaka Asakura
Graphical Information	
<p>The graphical information consists of two parts. On the left, a 3D ball-and-stick model of a distorted octahedral structure is shown, with a yellow box labeled 'Metastable state' highlighting it. On the right, a schematic diagram illustrates the experimental setup for pump-probe EXAFS. A Ti:sapphire laser (Pump) is shown as a purple block with a red laser beam passing through a lens and hitting a sample. An X-ray (Probe) source is shown as a blue beam passing through a lens and hitting the same sample. The sample is a small brown rectangular block.</p>	