



Title	Evidence for Multi-Atom Resonance X-ray Raman Spectroscopy : An in situ Low Z-element and Bond-specific X-ray Spectroscopy
Author(s)	Sirisit, Natee; Kido, Daiki; Wakisaka, Yuki et al.
Citation	e-Journal of Surface Science and Nanotechnology, 16, 387-390 <a href="https://doi.org/10.1380/ejsnt.2018.387">https://doi.org/10.1380/ejsnt.2018.387</a>
Issue Date	2018
Doc URL	<a href="https://hdl.handle.net/2115/71471">https://hdl.handle.net/2115/71471</a>
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Type	journal article
File Information	16_387.pdf



# Evidence for Multi-Atom Resonance X-ray Raman Spectroscopy—An *in situ* Low $Z$ -element and Bond-specific X-ray Spectroscopy

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(Received 2 July 2018; Accepted 26 August 2018; Published 1 September 2018)

We have shown a possibility of multi-atom resonant X-ray Raman (MARX-Raman) spectroscopy by measuring the N K-edge loss spectrum of TaN at Ta  $L_3$ -edge and C K-edge loss spectrum of  $\text{Er}(\text{C}_5\text{H}_5)_3$  at Er  $L_1$ -edge. When the excitation X-ray energy was tuned to the Ta  $L_3$ -edge and inelastic scattering spectra were recorded around 400 eV loss corresponding to the N K-edge Raman region, we found a clear enhancement of emission spectrum. The same enhancement was observed in C K-edge Raman region in  $\text{Er}(\text{C}_5\text{H}_5)_3$ . These experimental results have indicated the possibility of MARX-Raman phenomenon which may lead to a new *in situ* and bond-specific XAFS spectroscopy for low  $Z$  elements. [DOI: 10.1380/ejssnt.2018.387]

Keywords: X-ray absorption fine structure; XAFS; Multi-atom resonance; *In situ*; Synchrotron radiation

## I. INTRODUCTION

X-ray absorption fine structure (XAFS), appearing 100–1000 eV above the X-ray absorption edge [1], provides bond distances and coordination numbers around the X-ray absorbing atom. Since the X-ray has a large penetration ability, it is possible to carry out an *in situ* measurement of catalysts and electrodes under reaction conditions. However, when applied to low  $Z$  elements, which have an X-ray absorption edge in the soft X-ray regime (less than 1000 eV), it is quite difficult to observe the XAFS under the reaction conditions because the soft X-ray has a small penetration ability (for example, the transmittance of an X-ray with 500 eV is just 0.1 for a 1 mm-thick  $\text{N}_2$  gas layer at 1 bar atmosphere). On the other hand, X-ray Raman spectroscopy can provide *in situ* XAFS measurements on low  $Z$  elements because the X-ray Raman spectroscopy uses hard X-rays and provides the low  $Z$  element XAFS as the X-ray energy loss spectrum [2, 3]. However, the X-ray Raman intensity is quite low. Moreover, when X-ray Raman spectroscopy is applied to a real system which is composed of many species having the same X-ray absorbing atoms, it is impossible to obtain the local structure around a specific compound. For example, it is difficult to measure the XAFS of O on Pt nanoparticle in the water environment.

Under visible light, a resonant Raman scattering enhances the sensitivity and selectivity by tuning the incident visible light energy to the electronic transition of the specific compound. In the X-ray region, resonant X-ray Raman scattering is observed [4] and enhances the Raman sensitivity [5]. In this resonant X-ray Raman scattering, the X-ray is tuned to the absorption edge and the Raman signal of the same X-ray absorbing atom is detected. Therefore, the X-ray absorption and Raman emission occur at a single atom. If one uses an absorption edge of the

central metal in a metal complex to which low  $Z$  atoms are directly coordinated and if the excitation energy transfer occurs from the X-ray absorbing atom to the coordinating low  $Z$  atoms, one can obtain the X-ray Raman spectrum of the directly bonded low  $Z$  atoms, which is enhanced through the X-ray absorption of the central atom. To the best of our knowledge, nobody has previously estimated the probability of such a process experimentally or theoretically. In this paper we measured the interatomic resonant Raman signal. The X-ray tuned to the excitations of Ta  $L_3$ -edge and Er  $L_1$ -edge with the detection of Raman emission of N K-edge and C K-edge, respectively, in order to see such an enhancement occurs or not, qualitatively. In this preliminary work we found some possibility of the occurrence of this new type of interatomic resonant X-ray Raman.

## II. EXPERIMENTAL

X-ray Raman measurements were carried out in the beam line, BL36XU of SPring-8 [6]. The SPring-8 was operated in a top-up mode of the current of 100 mA and the ring energy 8 GeV. The X-ray emitted from tapered undulator was monochromatized with a Si(220) double crystal. The first sample was 10 wt% tantalum nitride (TaN) diluted with  $\text{SiO}_2$ . The mixture was pressed to 10 mm disk. The sample content was 100 mg. The second sample was tris(cyclopentadienyl)erbium(III) [ $\text{Er}(\text{C}_5\text{H}_5)_3$ ] which was put under an inert atmosphere in a home-made airtight cell with windows. The emitted X-rays were analyzed by Johan type 4 Ge(660) monochromator located at 820 mm from the sample. The monochromator was in the plastic case filled with He gas. Since the emission analyzer was designed to study the Pt catalyst by high energy resolution fluorescence detection X-ray spectroscopy, the detectable range of emission energy was limited to  $9440 \pm 50$  eV which covered the energy regions of loss spectra for N K-edge at Ta  $L_3$ -edge and for C K-edge Er  $L_1$ -edge, respectively. Emission intensities were

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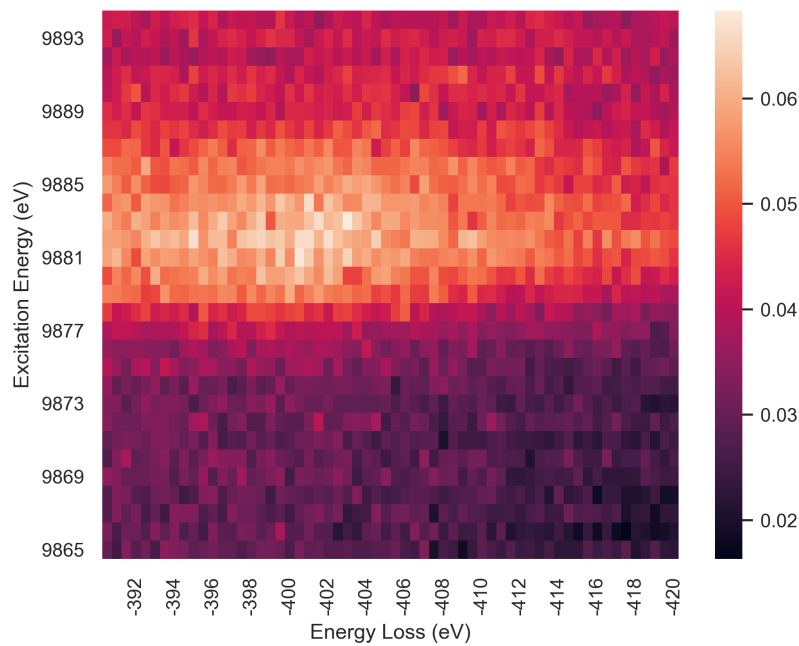


FIG. 1. Color mapping of the scattering X-ray intensity against excitation energy and energy loss.

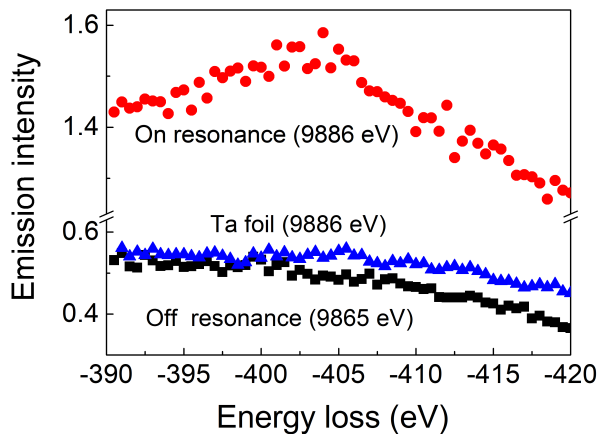


FIG. 2. Raman spectra of TaN excited at 9865 eV (a line formed by black squares) and 9886 eV (by red circles). A line by blue triangles shows the emission spectrum of Ta foil.

plotted against both excitation and loss energies in a two-dimensional way. The energy step and spectrum range of the excitation X-ray were 1 eV and 30 eV, respectively. Those of emission X-ray were 0.5 eV and 30 eV, respectively. Accumulation time was 10 s per point. Then the incident X-ray energy was fixed at 9865 eV (before the edge) and 9886 eV (just on the resonance) for Ta  $L_3$ -edge and fixed at 9752 eV for Er  $L_1$ -edge. Incident X-ray ( $I_0$ ) was detected by an ionization chamber and emitted X-rays from a sample were detected by a two-dimensional pixel array detector with 512 by 512 pixels (Medipix3RX; Merlin). We found that the intensity of the  $I_0$  was almost constant because of the top-up mode.

### III. RESULTS

Figure 1 shows the two-dimensional mapping of emitted x-ray, where we found the higher intensity range (bright region) around 9881–9885 eV in the excitation energy

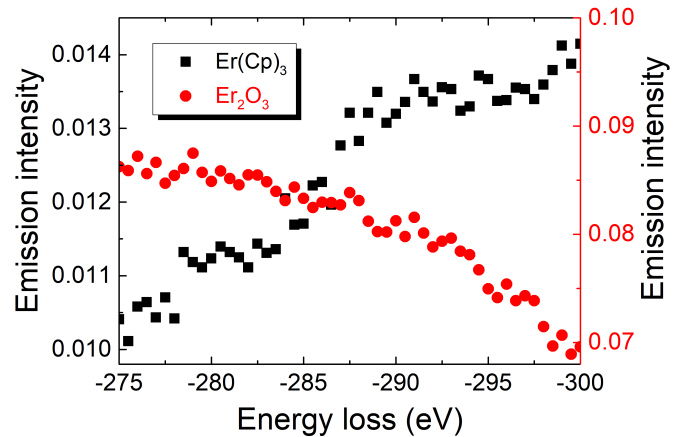


FIG. 3. Raman spectra at 9752 eV of  $\text{Er}(\text{C}_5\text{H}_5)_3$  (a line formed by black squares) and  $\text{Er}_2\text{O}_3$  (by red circles).

axis and  $-396$ – $-404$  eV in the loss energy axis. Note that Ta  $L_3$  absorption edge energy was 9881 eV and N K-edge appears at 401 eV [7]. The high intensity region appeared at the Ta  $L_3$  absorption edge in the excitation energy and N K-edge in the loss spectrum.

Figure 2 shows the TaN Raman spectra excited at 9865 eV (smaller than Ta  $L_3$ -edge) and 9886 eV (a little larger than Ta  $L_3$ -edge), respectively. The emission intensities were clearly changed at the N K-edge position when the sample was excited at 9886 eV. We did not find a peak in the Ta foil emission spectra excited at 9886 eV as shown in Fig. 2. Figures 1 and 2 are the evidence of the possibility of enhancement effect on the N Raman signal by the neighboring Ta  $L_3$  absorption though the S/N ratio was not so good as the N K-edge spectrum of TaN available in the literature [8].

Figure 3 shows the C K-edge Raman spectra tuned at 9752 eV just above the Er  $L_1$ -edge of  $\text{Er}(\text{C}_5\text{H}_5)_3$ . There was a sudden change in the emission intensities around  $-287$  eV, the energy of which corresponded to the C K-

edge loss energy. We did not find a change at corresponding loss energy around  $-287$  eV in the  $\text{Er}_2\text{O}_3$  emission spectrum for reference in the same region as shown in Fig. 3.

#### IV. DISCUSSION

There is a possibility to observe the peak emission line involving the transition of the electrons in the same absorbing atom. Actually, a weak  $\text{N}_3\text{L}_3$  transition is found in the literature at  $9474$  eV, corresponding to  $-412$  eV in term of energy loss in Fig. 2 [7]. In the present case, we found the peak at  $-405$  eV in term of energy loss or  $9481$  eV in term of emission energy. However, we did not find a change in the emission spectrum of Ta foil which should also have shown the emission line if it had been the  $\text{N}_3\text{L}_3$  transition. It indicates that  $\text{N}_3\text{L}_3$  transition intensity might be tiny.

In addition, we carried out the experiment of  $\text{Er}(\text{C}_5\text{H}_5)_3$ . We excited Er  $\text{L}_1$ -edge and detected the C K-edge Raman. We observed the change at  $-286$  eV loss position but we did not observe a clear change at C K-edge energy in the emission spectrum of  $\text{Er}_2\text{O}_3$ . Therefore, both spectra indicate the most probable assumption is multi-atom resonance X-ray Raman process.

Multi-atom resonance X-ray Raman process is similar to MARPE (multi-atom resonant photoemission) which was first demonstrated experimentally by Kay [9–11] in 2000 and theoretically by Arai in 2003 [12]. In the MARPE, the total excitation energy was transferred to the photoelectron's kinetic energy. In our process, the imperfect energy transfer occurs, and the radiated X-ray signals reflect the energy loss spectrum or Raman spectrum of N (C) K-edge similar to a radiative Auger process which was demonstrated experimentally by Kawai late 1990's [13, 14] and theoretically by Fujikawa [15] though their processes were in the same atom or intra-atomic processes. The multi-atom X-ray emission was observed in the  $K\beta''$  transition where the electron in the bonding orbital directly fills the core hole [16]. In our case, the enhancement of N (C) K-edge X-ray Raman occurs using

Ta (Er)  $\text{L}_3$ - ( $\text{L}_1$ -) edge when the resonant conditions are satisfied where the electron at the antibonding being relaxed to core hole produces the radiative Auger. There is also a criticism why a fine structure does not appear like XANES (X-ray absorption near edge structure). We are thinking that the low S/N may make the fine structure unclear.

Although the further studies must be necessary to establish the process, this Raman process leads to a new characterization method if it is true. In this Raman spectroscopy, we can use hard X-rays to obtain the N X-ray absorption spectra. Thus, it will be a new way to perform an *in situ* measurement for low  $Z$ -element. In addition, it is a bond-specific method. Only N which has a bond to Ta is enhanced even if the other N is present. This is important when the method is applied to the real system. For example, Raman spectra of C or O adsorbed on Pt surfaces of nanoparticles can selectively be measured even if the Pt is present on graphite (C) in the water ( $\text{H}_2\text{O}$ ) atmosphere like fuel cell electrodes. Since the incident X-ray energy can be fixed to a certain energy, X-ray free electron laser (XFEL) may be a good X-ray source. It will provide a high time resolution technique using the pump-probe measurement [17, 18] and the Von Hamos type energy analyzer [19]. The new X-ray Raman spectroscopy is coined as multi-atom resonant X-ray Raman (MARX-Raman) though we need many further studies such as improvement of the S/N ratio of the spectrum and the applicability to other elements as well as theoretical justifications.

#### ACKNOWLEDGMENTS

The authors would like to express our thanks to Grant-in-Aids for Exploratory Research from JSPS (No. 26620110) and NEDO PMFC project for their financial support. The work at SPring-8 was carried out under the proposal No. 2016A7903. N. S. acknowledges financial support from the Royal Thai Government. 2D spectrum is plotted by seaborn library [20].

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