Application of an Augmentation Method to MCR-ALS Analysis for XAFS and Raman Data Matrices in the Structural Change of Isopolymolybdates

Morihisa SAEKI,*1† Takumi YOMOGIDA,*2† Daiju MATSUMURA,*3 Takumi SAIITO,*4 Ryuzo NAKANISHI,*1 Takuya TSUIJI,*3 and Hironori OHBA*1

*1 Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology, 2-4 Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan
*2 Sector of Nuclear Science Research, Japan Atomic Energy Agency, 2-4 Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan
*3 Sector of Nuclear Science Research, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo, Hyogo 679-5148, Japan
*4 Nuclear Professional School, School of Engineering, The University of Tokyo, 2-22 Shirakata Shirane, Tokai-mura, Ibaraki 319-1188, Japan

We measured X-ray absorption fine structure (XAFS) and Raman spectra of isopolymolybdates(VI) in highly concentrated HNO₃ solution (0.15 – 4.0 M), which change their geometries depending on the acid concentration, and performed the simultaneous resolution of the XAFS and Raman data using a multivariate curve resolution by alternating least-squares (MCR-ALS) analysis. In iterative ALS optimization, initial data matrices were prepared by two different methods. For low sensitivity of the XAFS spectra to the geometrical change of the isopolymolybdates, the MCR-ALS result of single XAFS data matrix shows a large dependence on the preparation method of the initial data matrices. This problem is improved by the simultaneous resolution of the XAFS and Raman data: the MCR-ALS result of an augmented matrix of these data has little dependence on the initial data matrices. This indicates that the augmentation method effectively improves the rotation ambiguities in the MCR-ALS analysis of the XAFS data.

Keywords XAFS, Raman spectroscopy, MCR-ALS analysis, augmentation method, isopolymolybdates

(Received April 28, 2020; Accepted July 7, 2020; Advance Publication Released Online by J-STAGE July 10, 2020)

Introduction

X-ray absorption fine structure (XAFS) spectroscopy is available to investigate the electronic and geometrical structures of a metal ion complex in a solution.¹ The XAFS data is divided into the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) based on the region of the absorption energy. XANES is the spectral profile near the absorption edge that gives information on the ionic valency of the metal ion, while EXAFS is the oscillation appearing in the energy region above the absorption edge, giving information about the bond length between the metal ion and the ligands. Especially, the EXAFS data is valuable to investigate the geometrical structure of the metal ion complex, because an in-situ observation of the bond length in the solution is difficult with other spectroscopic techniques.

XAFS spectroscopy is often used to study structural changes of the metal ion complex caused by environmental factors, such as the acidity, ion concentration, and chemical reaction. When the chemical system is composed of only the initial and final complexes, the XAFS data is analyzed by linear combinations of their spectra. On the other hand, in a chemical system having an intermediate complex (initial → intermediate → final), the analysis needs the XAFS spectrum of the intermediate. However, there is often difficulty to obtain the XAFS spectrum of the isolated intermediate complex. To overcome this difficulty, researchers have designed to analyze the XAFS spectra using a multivariate curve resolution by alternating least-squares (MCR-ALS) chemometrics method.²–15 The MCR-ALS method can separate the pure XAFS spectrum of the intermediate from those of the initial and final complexes without additional information.

Analysis using the MCR-ALS method is started from preparing a data matrix D. For example, suppose that the XAFS spectra of the metal ion complex are recorded in the 1 – 4 M HNO₃ solution. When the digitized XAFS spectrum against the absorption energy in the xM HNO₃ solution is Dₓ, the arrangement of the Dₓ matrix in the sequence of the HNO₃ concentration, x = 1 – 4 M, yields the D matrix,

\[
D = \begin{bmatrix}
D_{10} & D_{11} & D_{12} & \cdots & D_{1n} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
D_{40} & D_{41} & D_{42} & \cdots & D_{4n}
\end{bmatrix}
\]
The \( D \) matrix is decomposed into the concentration profile matrix \( C \) and the pure spectrum matrix \( S \) by iteratively solving the equation

\[
D = CS^T + E, \tag{1}
\]

to minimize the Frobenius norm, \( \| D - CS^T \|_F \). Here, \( S^T \) is a transposed matrix of \( S \), and \( E \) is a matrix of the residuals.

The decomposition procedure in MCR-ALS has rotation ambiguities in the solving procedure.\(^{16–19} \) In obtaining one set of \( C_{\text{new}} \) and \( S_{\text{new}} \) that satisfy Eq. (1), we can prepare another set of \( C_{\text{new}} \) and \( S_{\text{new}} \) by the operation

\[
D = CS^T = CT^{-1}TS^T = C_{\text{new}}S_{\text{new}}^T. \tag{2}
\]

Here, \( T \) is an arbitrary rotation matrix. Equation (2) means that there are innumerable sets of \( C_{\text{new}} \) and \( S_{\text{new}} \) in the MCR-ALS solution. A decrease of the rotation ambiguities is the main issue in the development of the MCR-ALS. One way to decrease the rotation ambiguities is the application of numerical constraints, such as non-negativity, unimodality and closure.\(^{20,21} \) Especially, the non-negativity obliges the concentration profiles and the pure spectra to be positive under any condition, and it is crucial to obtain a plausible \( C \) and \( S \) matrix.

In addition to the above constraints, multiple data set analysis also decreases the rotation ambiguities.\(^{3,16,19} \) For example, the structural change of the metal ion complex, depending on the acidity, is investigated by the XAFS and Raman spectroscopies. In the analysis using the multiple data set, which is called the data augmentation method, the rotation ambiguities also decreases the rotation ambiguities.\(^{3,16,19} \) For example, the non-negativity obliges the concentration profiles and the pure spectra to be positive under any condition, and it is crucial to obtain a plausible \( C \) and \( S \) matrix.

Here, we refer to a comparison of the MCR-ALS analysis with principal component analysis (PCA), which is also employed as in a chemometrics analysis of the XAFS spectra.\(^{22,23} \) The PCA analysis is useful to investigate the number of pure components in the chemical system, though pure XAFS spectra obtained by the analysis does not reproduce the actual spectra of the pure components. In the MCR-ALS analysis, we can make an effort to approach the pure XAFS spectra to the actual ones by applying the multiple data set analysis and the numerical constraints, which reflect the requirements based on the physical properties of the spectroscopic techniques without restricting the underlying chemistry, and discuss the pure XAFS spectra without any further modification. This is an advantage of the MCR-ALS analysis.

The MCR-ALS analysis using the augmented data matrix is a promising method to extract the pure spectrum of the intermediate complex. Although there were several reports on the XAFS study combined with Raman spectroscopy, they have analyzed the XAFS data matrix separately from the Raman one.\(^{12–14} \) In this paper, picking up the structural change of isopolyomolybdate(VI), \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) in highly concentrated \( \text{HNO}_3 \) solutions (0.15 – 4.0 M), we apply the MCR-ALS analysis to the augmented matrix of the XAFS and Raman data. It is well known that the \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) species drastically changes its chemical formula in an aqueous solution with increasing acid concentration (Fig. 1).\(^{24,25} \) The \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) exists as a \([\text{MoO}_3]^{6–} \) species in low-concentration acids (pH 5 – 6),\(^{24–26} \) grows up to larger Mo polymers with increasing the acidity, and forms a \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) species at around pH 1.\(^{24,25,31} \) In the region below pH 1, it is believed that the \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) species (initial complex) is decomposed into \([\text{MoO}_3 (\text{H}_2 \text{O})]^{2–} \), \([\text{Mo}_2 \text{O}_7 (\text{H}_2 \text{O})]^{2–} \) or \([\text{H Moor}_3 (\text{H}_2 \text{O})]^{3–} \) species (Fig. 1).\(^{24,25,31} \) Though the intermediate and final complexes change depending on the type of acids. We measured the XAFS and Raman spectra of the \([\text{Mo}_{30} \text{O}_{74} (\text{H}_2 \text{O})_{16}]^{8–} \) species with changing the \( \text{HNO}_3 \) concentration from 0.15 to 4.0 M, applied the MCR-ALS analysis to the \([D_{\text{XAFS}}D_{\text{Raman}}] \) matrix, and investigated the effect of the augmentation method on the analysis of the XAFS data.

### Experimental and Analysis

**Preparation of sample solutions**

A stock solution of 0.15 M \([\text{MoO}_3]^{6–} \) was prepared by
dissolving (NH₄)₂MoO₄·4H₂O (Wako Chemical, >99.0%) into distilled water. The HNO₃ solutions of 0.03 M [MoO₂]₆⁻ were prepared by the addition of a HNO₃ solution (Kanto Chemical, special grade) to the stock solution. The acidity of the sample solution was arranged within the range of 0.15 to 4.0 M. The conditions of the sample preparation are listed in Table S1 (Supporting Information). The HNO₃ concentration does not directly correspond to the pH of the sample solution, because the dehydration reaction in the formation of the [MomOy(H₂O)z]p species consumes the H⁺ ions. The concentration of Mo was kept at 0.21 M in every measurement. In some sample solutions, a white precipitate was formed about 1 h after sample preparation at room temperature. Thus, XAFS and Raman measurements were started as soon as we completed the preparation of the sample solution.

Mo K-edge X-ray absorption measurement
X-ray absorption spectroscopy was performed at beamline BL14B1 of SPring-8 (Harima, Japan) by using an electron energy of 8.0 GeV with an average current of 100 mA. A Si(311) double-crystal monochromator was employed to monochromatize the white X-ray beam from the synchrotron. The intensities of the incident X-rays (I₀) and the transmitted X-rays (I₁) were monitored using ionization chambers (17 cm long for I₀ and 31 cm long for I₁) filled with 100% Ar gas. A capped quartz cuvette (30 × 12 × 40 mm) containing 6 ml of the sample solution was placed in the X-ray beamline. The X-ray absorption spectrum at the Mo K-edge (20 keV) was measured in the transmission mode at room temperature. The data were collected in k-steps of less than 0.05 Å⁻¹ across an EXAFS region. The XAFS data were analyzed using the Athena and Artemis programs.¹²

Model fitting of EXAFS oscillations for [MoO₂O₄(H₂O)]₆⁻
Analysis of the EXAFS oscillations, χ(k), of the [MoO₂O₄(H₂O)]₆⁻ species was performed by a least-squares k¹χ(k) model fitting. The χ(k) function,

\[
\chi(k) = S_o \sum_i N_i \frac{k R_i^2}{k R_i^2 + f_{ii}(k)} \exp(-2k^2 \sigma_i^2) \exp \left[-2R \left(\frac{\lambda(k)}{\lambda(k)}\right)^2\right] \sin[2kR + \phi_i(k)],
\]

was obtained from an ab initio calculation of the amplitude, \(f_{ii}(k)\), the phase shift, \(\phi_i(k)\), and the mean free path, \(\lambda(k)\), by using the FEFF 6.01 program. The structural parameters were refined by fitting the k¹-weighted theoretical model function, χ(k), to the experimental EXAFS oscillations. The model fitting of the EXAFS oscillation gives information on the amplitude reduction factor (\(S_o^2\)), coordination number (CN), Debye–Waller factors (\(\sigma^2\)) and distance of each chemical bond (r). In this study, \(S_o^2\) was fixed to 0.9, the value of which was obtained from a model fitting of the EXAFS oscillation in the NaN₅MoO₄·2H₂O crystal.

Raman measurement
The Raman spectra of the sample solutions were measured with a Raman analyzer (Enhanced Spectrometry R532). The wavelength and power of the laser were 532 nm and 50 mW, respectively. The scattered light from the sample solutions was collected and focused onto the slit of a single spectrograph (1800 grooves/mm grating) equipped with a notch filter and a linear CCD array. The spectra were typically acquired by accumulating 50 measurements, each of which was obtained by an exposure time of 800 ms. The observed Raman spectra were scaled based on a calibration curve of the \(v_1\) band of NO₃⁻ (1046 cm⁻¹).

MCR-ALS analysis
MCR-ALS was performed using MCR-ALS GUI programs for MATLAB versions. The preparation of a row-wise augmented data matrix, \([D_{XAFS}D_{Raman}]\), follows the recipe reported by Jalalvand et al. To meet the requirement that normalizations of the XAFS and Raman data have similar weights on the iterative ALS optimization, we divided the \(D_{XAFS}\) and \(D_{Raman}\) matrix to its maximum value in the preparation. For the iterative solution of Eq. (1), initial C and S matrices were prepared by evolving factor analysis (EFA) and the purest variable detection method against the spectra (PureS). Equation (1) was iteratively solved by an ALS algorithm described by Jaumot et al. As constraints, we applied non-negativity, unimodality and closure to the C matrix and only non-negatively to the \([S_{XAFS}S_{Raman}]\) matrix.

Ab initio MO calculation
To analyze the pure EXAFS oscillations obtained by the MCR-ALS analysis, we prepared the model structures of the [MoO₂O₄(H₂O)]₆⁻ species by geometrical optimization in a MP2/cc-pVDZ calculation. The stability of the optimized geometries was checked by frequency analysis. All calculations were carried out by the Gaussian16 program.

Results and Discussion
XANES spectra, EXAFS oscillations and Raman spectra of [MoO₂O₄(H₂O)]₆⁻
We measured the Mo K-edge XAFS spectra of the [MoO₂O₄(H₂O)]₆⁻ species in the region of 19.7 - 21.3 keV. Figures 2a and 2b are the normalized XANES spectra and the \(k^2\)-weighted EXAFS oscillations of the [MoO₂O₄(H₂O)]₆⁻ species in the 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0 and 4.0 M HNO₃ solutions. The original normalized XAFS spectra are shown in Fig. S1 (Supporting Information). The features of the XANES spectra have a little dependence on the HNO₃ concentration. The pre-edge peak (20.005 keV), which is an electronic transition from the 1s Mo orbital to the p-d Mo hybrid orbital, keeps its intensity and position. This indicates that there is no change of the ionic valency in all Mo(VI) atoms of the [MoO₂O₄(H₂O)]₆⁻ by the acidification. On the other hand, the EXAFS oscillations change with increasing the HNO₃ concentration. Especially, the oscillations in the region of \(k = 3 - 9\) Å⁻¹ show drastic change. This means that the acidification changes the geometries of the [MoO₂O₄(H₂O)]₆⁻, as explained in Fig. 1.

Figure 2c is the normalized Raman spectra of the [MoO₂O₄(H₂O)]₆⁻ species in the region of 750 - 1030 cm⁻¹, where the vibrational bands of Mo-O stretching are observed. Parts of the observed spectra of the [MoO₂O₄(H₂O)]₆⁻ reproduce those of previous works. The main Mo-O band is red-shifted from 954 to 950 cm⁻¹ in the 0.2 - 0.8 M HNO₃ and is blue-shifted from 950 to 954 cm⁻¹ in the 0.8 - 4.0 M HNO₃. These spectral shifts indicate the existence of at least three [MoO₂O₄(H₂O)]₆⁻ species.

Determination of number of pure components
In the MCR-ALS analysis, we prepared the \(D_{XAFS}\) and \(D_{Raman}\) matrices from the spectra of the [MoO₂O₄(H₂O)]₆⁻ species in 16 kinds of the HNO₃ concentrations: 0.15, 0.16, 0.18, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 3.0 and 4.0 M (Table S1). The number of species composing the chemical system is
estimated by singular value decomposition (SVD) of the data matrix. Figure 3a shows the dependence of the singular value (SV) on the number of components, \( n \), which is obtained by the SVD of the \([D_{\text{XAFS}}], [D_{\text{Raman}}]\) and \([D_{\text{XAFS}}D_{\text{Raman}}]\) matrices. Nearly zero SV means that the component is attributed to a noise or a minor species. Figure 3a shows that the SVs are nearly zero above \( n = 2 \) in the \([D_{\text{XAFS}}]\) and non-zero from \( n = 1 \) to 3 in the \([D_{\text{Raman}}]\). The difference is attributed to a lower sensitivity of the XAFS spectra than the Raman spectra to a geometrical change of the \([\text{Mo}_n\text{O}_y(\text{H}_2\text{O})_z]\) species.

Based on the SVD result in the \([D_{\text{XAFS}}D_{\text{Raman}}]\) matrix, we concluded that consideration of 3 components is sufficient to analyze the experimental data. This idea is supported by residual maps, which were obtained from the \( E \) matrix in the MCR analysis of the \([D_{\text{XAFS}}]\) and \([D_{\text{XAFS}}D_{\text{Raman}}]\) matrices using the EFA and PureS methods.

Comparison of fraction profiles between \([D_{\text{XAFS}}]\) and \([D_{\text{XAFS}}D_{\text{Raman}}]\). Figure 3b is fraction profiles of the 3 components of the \([D_{\text{XAFS}}]\) and \([D_{\text{XAFS}}D_{\text{Raman}}]\) matrices in preparing the initial \( C \) and \( S \) matrices by the EFA and PureS methods. The fraction profiles obtained from the \([D_{\text{XAFS}}]\) matrix are largely dependent on the EFA and PureS methods: for instance, the fraction of component 3 in 4 M \( \text{HNO}_3 \) is 1.0 in the EFA method and decreases to 0.8 in the PureS. Moreover, the fraction changes of components 2 and 3 are not smooth around 1 M. The large dependence on the initial matrices is attributed to the low sensitivity of the XAFS spectra to a geometrical change of the \([\text{Mo}_n\text{O}_y(\text{H}_2\text{O})_z]\) species.
and suggests that the rotation ambiguities is large in the MCR analysis of single \([\text{D}XAFS]\) matrix. On the other hand, the fraction profiles obtained from the \([\text{D}XAFS\text{D}Raman]\) matrix show little dependence on the EFA and PureS methods and smooth fraction change in every component. The comparison between the \([\text{D}XAFS]\) and \([\text{D}XAFS\text{D}Raman]\) matrices confirms that the augmentation method effectively improves the sensitivity of the XAFS spectra to the geometrical change. We assume that the small dependence on the preparation method of the initial matrix indicates a decrease of the rotation ambiguities in the MCR-ALS analysis of the XAFS data.

For a comparison, we also calculated the fraction profiles of the 3 components from the single \([\text{D}Raman]\) matrix (Fig. S3). The fraction profiles obtained from the \([\text{D}XAFS\text{D}Raman]\) agree with those from the \([\text{D}XAFS]\) matrix, which indicates that our preparation of the augmented \([\text{D}XAFS\text{D}Raman]\) matrix works well.

**Pure XANES, EXAFS and Raman spectra in MCR-ALS analysis of \([\text{D}XAFS\text{D}Raman]\)**

Figure 4 shows pure XANES, \(k^3\)-weighted EXAFS oscillations, Fourier transforms (FTs) of the EXAFS oscillations and Raman spectra of components 1 – 3, which were obtained by the MCR-ALS analysis of the \([\text{D}XAFS\text{D}Raman]\) matrix using the EFA method. The dashed lines in the EXAFS oscillations (b) are simulated curve of component 1 by \([\text{Mo}_3\text{O}_7\text{H}_2\text{O}_6]^{2+}\), that of component 2 by \([\text{Mo}_2\text{O}_5\text{H}_2\text{O}_6]^{2+}\) and that of component 3 by \([\text{Mo}_3\text{O}_7\text{H}_2\text{O}_6]^{2+}\) and \([\text{HMo}_3\text{O}_7\text{H}_2\text{O}_6]^{2+}\). The Mo–Mo band of component 2 is indicated by an asterisk in (c). Raman spectrum of a \((\text{NH}_4)_8\text{Mo}_{36}\text{O}_{112}\) crystal, which is reprinted with permission from Ref. 28 by the Chemical Society of Japan (Copyright 1997), is also shown in (d).

![Figure 4](image)

Features of the XANES spectra have a small dependence on the components (Fig. 4a), the EXAFS oscillation of component 1 is evidently different from those of components 2 and 3 (Fig. 4b). The difference between components 2 and 3 is subtle, but present: it is observed as an increase of the band intensity at \(r - \alpha = 1.7\ \text{Å}\) from components 2 to 3 in the FTs (Fig. 4c). The FTs of component 1 show the appearance of the Mo–Mo band (2.5 – 3.5 Å), which is slightly observed in components 2 and 3.

Figure 4d is the pure Raman spectra of components 1 – 3. For a comparison, the Raman spectrum of a \((\text{NH}_4)_8\text{Mo}_{36}\text{O}_{112}\) crystal is also shown.\(^28\) The feature of the Raman spectrum of component 1 agrees with that of the \((\text{NH}_4)_8\text{Mo}_{36}\text{O}_{112}\) crystal. Thus, we assign components 1 to the \([\text{Mo}_3\text{O}_7\text{H}_2\text{O}_6]^{2+}\) species. The Raman spectra of components 2 and 3 show similar vibrational bands, except for the blue shift of the main band. This suggests that components 2 and 3 have similar geometries, which is consistent with results in the EXAFS oscillations (Figs. 4b and 4c).

**Model fitting of pure EXAFS oscillation of component 1**

We performed a model fitting of the EXAFS oscillation of component 1 (Fig. 4b) based on the crystal structure of \(\text{K}_8[\text{Mo}_{36}\text{O}_{112}\text{H}_2\text{O}_6]\), where 32 MoO\(_6\) octahedra and 4 MoO\(_7\) units were combined by sharing their edges or corners.\(^39\) Based on the Mo–O and Mo–Mo distances reported in the \(\text{K}_8[\text{Mo}_{36}\text{O}_{112}\text{H}_2\text{O}_6]\) crystal,\(^39\) we classified the Mo–O distances as follows:
into four types and the Mo–Mo distances into two types depending on their lengths, as shown in Table 1. The CN values calculated from the crystal structure are also listed.

We applied model fitting to the EXAFS oscillation of component 1 in the $k$-range of 3.0 – 17.8 Å⁻¹ while fixing the CN to the values in Table 1. The simulated curve using Eq. (4) reproduces the pure EXAFS oscillation of the [Mo₃₆O₁₁₂(H₂O)₁₆]⁸⁻ species (Fig. 4b). The obtained $r$ and $\sigma^2$ values and R factors are listed in Table 2.

**Model fitting of pure EXAFS oscillation of components 2 and 3**

As summarized in Fig. 1, previous works on the [MomOy(H₂O)z]p species in highly concentrated acid solutions suggest that components 2 and 3 are attributed to the [Mo₂O₅(H₂O)₆]²⁺, [MoO₂(H₂O)₄]²⁺ or [HMoO₃(H₂O)₃]⁺ species. Assuming that the large [Mo mOy(H₂O)z]p species is decomposed into small species with increasing the acidity, we can attribute changes of the EXAFS oscillations in component 2 to that of [Mo₂O₅(H₂O)₆]²⁺ → [MoO₂(H₂O)₄]²⁺ or [Mo₂O₅(H₂O)₆]²⁺ → [HMoO₃(H₂O)₃]⁺.

Figures 5a – 5c are the optimized geometries of the [Mo₂O₅(H₂O)₆]²⁺, [MoO₂(H₂O)₄]²⁺ and [HMoO₃(H₂O)₃]⁺ species in the MP2/cc-pVDZ calculation. The geometrical parameters are listed in Table 3, which suggests that the Mo–O bonds are classified into short bonds (1.7 – 1.8 Å), medium bonds (1.9 – 2.0 Å) and long bonds (2.1 – 2.4 Å). Comparison of the Mo–O bonds among three species reveals the absence of the medium bond.

---

### Table 1

| Classification of Mo–O and Mo–Mo distances in the K₈[Mo₃₆O₁₁₂(H₂O)₁₆] crystal (The CN values calculated from the crystal structure are also listed) |
|---|---|---|
| Length/Å | CN |
| Mo=O (1) | 1.6 – 1.8 | 1.89 |
| Mo–O (2) | 1.8 – 2.0 | 1.67 |
| Mo–O (3) | 2.0 – 2.2 | 1.22 |
| Mo–O (4) | 2.2 – 2.4 | 1.33 |
| Mo–Mo (1) | 3.2 – 3.5 | 2.22 |
| Mo–Mo (2) | 3.7 – 4.1 | 2.44 |

### Table 2

| The $r$ and $\sigma^2$ values obtained by a model fitting of the pure EXAFS oscillation for component 1 (Fig. 4b) based on the crystal structure of K₈[Mo₃₆O₁₁₂(H₂O)₁₆] (The values in parenthesis are the errors in the fitting) |
|---|---|---|---|---|
| | $r$/Å | $\sigma^2$/Å² | $\Delta E$ | R-factor |
| Mo=O (1) | 1.718 (0.006) | 0.002 (0.000) | −0.9 (2.9) | 3.7% |
| Mo–O (2) | 1.975 (0.029) | 0.008 (0.003) | 2.151 Å (1) | 1.751 Å (1) |
| Mo–O (3) | 2.212 (0.053) | 0.005 (0.004) | 2.212 Å (1) | 1.971 Å (m) |
| Mo–O (4) | 2.334 (0.055) | 0.012 (0.011) | 2.334 Å (1) | 1.971 Å (m) |
| Mo–Mo (1) | 3.353 (0.040) | 0.010 (0.004) | 3.353 Å (1) | 1.971 Å (m) |
| Mo–Mo (2) | 3.544 Å (1) | 0.007 (0.005) | 3.544 Å (1) | 1.971 Å (m) |
| Mo–Mo (3) | 3.508 (0.026) | 0.009 (0.002) | 3.508 Å (1) | 1.971 Å (m) |

### Table 3

| Geometrical parameters of the [Mo₂O₅(H₂O)₆]²⁺, [MoO₂(H₂O)₄]²⁺ and [HMoO₃(H₂O)₃]⁺ species, which were optimized in an MP2/cc-pVDZ calculation |
|---|---|---|---|---|
| | [Mo₂O₅(H₂O)₆]²⁺ | [MoO₂(H₂O)₄]²⁺ | [HMoO₃(H₂O)₃]⁺ |
| Mo1–O1 (Mo2–O6) | 1.740 Å (s) | 1.714 Å (s) | 1.727 Å (s) |
| Mo1–O2 (Mo2–O2) | 1.916 Å (m) | 2.151 Å (l) | 1.751 Å (s) |
| Mo1–O3 (Mo2–O7) | 2.262 Å (l) | 2.321 Å (l) | 1.971 Å (m) |
| Mo1–O4 (Mo2–O8) | 2.347 Å (l) | 2.361 Å (l) | 2.184 Å (l) |
| Mo1–O5 (Mo2–O9) | 2.393 Å (l) | 2.360 Å (l) | 2.360 Å (l) |
| Mo1–Mo2 | 3.353 Å (1) | 3.544 Å (1) | 3.544 Å (1) |

---

### Table 4

| The $r$ and $\sigma^2$ values obtained by the model fitting of the pure EXAFS oscillation for component 2 based on the [Mo₂O₅(H₂O)₆]²⁺ geometry and that for component 3 based on the [MoO₂(H₂O)₄]²⁺ and [HMoO₃(H₂O)₃]⁺ geometries |
|---|---|---|---|---|
| CN | $r$/Å | $\sigma^2$/Å² | $\Delta E$ | R-factor |
| Component 2 ([Mo₂O₅(H₂O)₆]²⁺) | | | | |
| Mo1–O1 | 1.714 (0.007) | 0.002 (0.000) | −0.9 (2.9) | 3.5% |
| Mo1–O2 | 1.893 (0.029) | 0.007 (0.004) | 2.151 Å (1) | 1.751 Å (1) |
| Mo1–O3 | 2.212 (0.053) | 0.005 (0.004) | 2.212 Å (1) | 1.971 Å (m) |
| Mo1–O4 | 2.334 (0.055) | 0.012 (0.011) | 2.334 Å (1) | 1.971 Å (m) |
| Mo1–Mo2 | 3.353 (0.040) | 0.010 (0.004) | 3.353 Å (1) | 1.971 Å (m) |
| Component 3 ([MoO₂(H₂O)₄]²⁺) | | | | |
| Mo1–O1 | 1.700 (0.006) | 0.002 (0.000) | −8.4 (2.6) | 6.0% |
| Mo1–O2 | 2.215 (0.031) | 0.006 (0.003) | 2.215 Å (1) | 1.971 Å (m) |
| Mo1–O3 | 2.368 (0.106) | 0.018 (0.018) | 2.368 Å (1) | 1.971 Å (m) |
| Component 3 ([HMoO₃(H₂O)₃]⁺) | | | | |
| Mo1–O1 | 1.711 (0.006) | 0.001 (0.000) | −2.2 (2.5) | 3.7% |
| Mo1–O2 | 1.897 (0.016) | 0.004 (0.002) | 2.215 Å (1) | 1.971 Å (m) |
| Mo1–O3 | 2.228 (0.029) | 0.007 (0.003) | 2.368 Å (1) | 1.971 Å (m) |
| Mo1–O4 | 2.392 (0.080) | 0.009 (0.011) | 3.353 Å (1) | 1.971 Å (m) |

In the [Mo₂O₅(H₂O)₆]²⁺, only parameters involving the Mo1 atom are listed, because the arrangement of the O atoms around the Mo atom is almost the same between Mo1 and Mo2. The CNs were fixed to the calculated values from the model structures. The values in parenthesis indicate the error in the fitting. $S_0^2$ is kept at 0.9.

---

**Fig. 5** Optimized geometries of the [Mo₂O₅(H₂O)₆]²⁺, [MoO₂(H₂O)₄]²⁺ and [HMoO₃(H₂O)₃]⁺ species in the MP2/cc-pVDZ calculation. The geometrical parameters are listed in Table 3.
bond in the [MoO₂(H₂O)₄]²⁺.

Using the optimized geometries of the [Mo₂O₅(H₂O)₆]²⁺, [MoO₃(OH)₃]⁺, and [HMoo₄(H₂O)]⁺ species, we performed model fitting of the EXAFS oscillations of component 2 by the [Mo₂O₅(H₂O)₆]²⁺ geometry and component 3 by the [MoO₃(OH)₃]⁺ and [HMoo₄(H₂O)]⁺ geometries in the k-range of 3.0 - 17.8 Å⁻¹. Figure 4b shows that the simulated curve using the [Mo₂O₅(H₂O)₆]²⁺ geometry reproduces the pure EXAFS oscillations of component 2. Table 4 shows the r, σ² and ΔE values and R-factors in the model fitting. The ΔE value in the fitting of component 3 by the [HMoo₄(H₂O)]⁺ (~2.2 eV) agrees with that in the fitting of component 2 by the [MoO₃(OH)₃]⁺ (~0.9 eV) within the analytical error (2.5 - 2.9 eV), while the E value in the fitting of component 3 by the [MoO₃(OH)₃]⁺ (~8.4 eV) is too negative. Moreover, the R-factor in the fitting of component 3 by the [Mo₂O₅(H₂O)₆]²⁺ (6.0%) is larger than those in other fittings (3.5 - 3.7%). Thus, we attribute the change of component 2 to that of the [Mo₂O₅(H₂O)₆]²⁺ → [HMoo₄(H₂O)]⁺ species in the HNO₃ solution.

Conclusions

We measured the XAFS and Raman spectra of the [Mo₂O₅(H₂O)₆]²⁺ species in a highly concentrated HNO₃ solution, and applied the MCR-ALS analysis to the augmented matrix of the XAFS and Raman data. In iterative ALS optimization, initial data matrices were prepared by the EFA and PureS methods. The pure fraction profiles of the [Mo₂O₅(H₂O)₆]²⁺ are largely different between the EFA and PureS methods in the MCR-ALS analysis of single [DₓAFS] matrix. The large dependence of the MCR-ALS result on the preparation methods of the initial matrices suggests the large rotation ambiguities in the analysis of single XAFS data matrix, which come from the low sensitivity of the XAFS spectra to geometrical change of the [Mo₂O₅(H₂O)₆]²⁺ species. The augmentation method improves the dependence on the preparation methods: the MCR analysis of the [DₓAFS] gives the pure fraction profiles that are identical between the EFA and PureS methods. Thus, we concluded that the augmentation method effectively improves the rotation ambiguities in the MCR-ALS analysis of the XAFS data.

The MCR-ALS analysis of the [DₓAFS] matrix showed the existence of three kinds of the [Mo₂O₅(H₂O)₆]²⁺ species in the 0.15 - 4.0 M HNO₃ solutions. Based on model fitting of the pure EXAFS oscillations, we attribute the change of component 1 → 2 → 3 to that of [Mo₂O₅(H₂O)₆]²⁺ → [MoO₃(OH)₃]⁺ → [HMoo₄(H₂O)]⁺ in the highly concentrated HNO₃ solution.

Acknowledgements

The present experiment was performed under the approval of Japan Synchrotron Radiation Research Institute. (Proposal No. 2016A3609, 2017A3609). The computations were performed using Research Center for Computational Science, Okazaki, Japan. We are thankful to Dr. Yoshihiro Okamoto (JAERI) for his advice about the synchrotron-radiation experiment.

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References

1. Y. Iwasawa, K. Asakura, and M. Tada, “XAFS Techniques for Catalysis, Nanomaterials, and Surfaces”, 2017, Springer, Switzerland.
2. D. Muller-Bouvet, N. Emery, N. Tassali, E. Panabière, S. Bach, O. Crosnier, T. Brousse, C. Cénac-Morthe, A. Michalowicz, and J. P. Pereira-Ramos, Phys. Chem. Chem. Phys., 2017, 19, 27024.
3. A. Rochet, B. Baubet, V. Moizan, E. Devers, A. Hugon, C. Pichon, E. Payen, and V. Briois, J. Phys. Chem. C, 2015, 119, 23928.
4. J. Hong, E. Marceau, A. Y. Khodakov, L. Gaberová, A. Griboval-Constant, J.-S. Girardon, C. L. Fontaine, and V. Briois, ACS Catal., 2015, 5, 1273.
5. A. Voronov, A. Urakawa, W. v. Beek, N. E. Tsakoumis, H. Emerich, and M. Rønning, Anal. Chim. Acta, 2014, 840, 20.
6. M. Staniuk, O. Hirsch, N. Kränzlin, R. Böhlen, W. van Beek, P. M. Abdala, and D. Koziej, Chem. Mater., 2014, 26, 2086.
7. W. H. Cassinelli, L. Martins, A. R. Passos, S. H. Pulcinelli, C. V. Santillti, A. Rochet, and V. Briois, Catal. Today, 2014, 229, 114.
8. H. W. P. Carvalho, S. H. Pulcinelli, C. V. Santillti, F. Leroux, F. Meneau, and V. Briois, Chem. Mater., 2013, 25, 2855.
9. C. A. Nunes, E. C. Resende, I. R. Guimarães, A. S. Anastácio, and M. C. Guerreiro, Appl. Spectroscopy., 2011, 65, 692.
10. P. Conti, S. Zamponi, M. Giorgetti, M. Berrettoni, and W. H. Smyrl, Anal. Chem., 2010, 82, 3629.
11. V. Girard, D. Chiche, A. Baudot, D. Bazer-Bachi, L. Lemaître, V. Moizan-Basle, A. Rochet, V. Briois, and C. Geantet, Phys. Chem. Chem. Phys., 2019, 21, 8569.
12. A. Rochet, A. Ribeiro Passos, C. Legens, and V. Briois, Catal. Struct. React., 2017, 3, 33.
13. A. Rochet, B. Baubet, V. Moizan, E. Devers, A. Hugon, C. Pichon, E. Payen, and V. Briois, J. Phys. Chem. C, 2017, 121, 18544.
14. A. Rochet, B. Baubet, V. Moizan, C. Pichon, and V. Briois, C. R. Chim., 2016, 19, 1337.
15. B. L. Caetano, V. Briois, S. H. Pulcinelli, F. Meneau, and C. V. Santillti, J. Phys. Chem. C, 2017, 121, 886.
16. C. Ruckebusch and L. Blanchet, Anal. Chim. Acta, 2013, 765, 28.
17. R. Tauler, J. Chemom., 2001, 15, 627.
18. J.-H. Jiang and Y. Ozaki, Appl. Spectroscopic Rev., 2002, 37, 321.
19. A. de Juan and R. Tauler, Anal. Chim. Acta, 2003, 500, 195.
20. M. Garrido, F. X. Rius, and M. S. Larrrechi, Anal. Bioanal. Chem., 2008, 390, 2059.
21. A. de Juan and R. Tauler, Crit. Rev. Anal. Chem., 2006, 36, 163.
22. S. R. Wasserman, P. G. Allen, D. K. Shuh, J. J. Bucber, and N. M. Edelstein, J. Synchrotron Radiat., 1999, 6, 284.
23. A. Manceau, M. Marcus, and T. Lenoir, J. Synchrotron Radiat., 2014, 21, 1140.
24. M. T. Pope, “Heteropoly and Isopoly Oxometalates”, 1983, Chap. 6.2.5, Springer, Berlin, 15.
25. K.-H. Tityko and O. Glemser, “Advances in Inorganic Chemistry and Radiochemistry”, ed. H. J. Emeléus and A. G. Sharpe, 1976, Vol. 19, Academic Press, 239.
26. F. A. Cotton, G. Willkinson, C. A. Murillo, and M. Bochmann, “Advanced Inorganic Chemistry”, 1999, Chap.
27. K. H. Tytko, G. Baethe, and J. J. Cruywagen, Inorg. Chem., 1985, 24, 3132.

28. S. Himeno, H. Niiya, and T. Ueda, Bull. Chem. Soc. Jpn., 1997, 70, 631.

29. S. Himeno and M. Hasegawa, Inorg. Chim. Acta., 1984, 83, L5.

30. J. M. Coddington and M. J. Taylor, J. Chem. Soc., Dalton Trans., 1990, 41.

31. D. T. Richens, “The Chemistry of Aqua Ions”, 1997, Chap. 6.2.5, John Wiley & Sons, New York, 327.

32. B. Ravel and M. Newville, J. Synchrotron Radiat., 2005, 12, 537.

33. J. Jaumot, R. Gargallo, A. de Juan, and R. Tauler, Chemom. Intell. Lab. Syst., 2005, 76, 101.

34. J. Jaumot, A. de Juan, and R. Tauler, Chemom. Intell. Lab. Syst., 2015, 140, 1.

35. A. R. Jalalvand, S. Ghobadi, H. C. Goicoechea, E. Faramarzi, and M. Mahmoudi, Helion, 2019, 5, e02153.

36. M. Maeder, Anal. Chem., 1987, 59, 527.

37. W. Windig and D. A. Stephenson, Anal. Chem., 1992, 64, 2735.

38. M. J. Frisch et al., “Gaussian 16 Revision A.03”, 2016, Gaussian, Inc., Wallingford, CT.

39. B. Krebs and I. Paulat-Boschen, Acta Crystallogr., Sect. B, 1982, 38, 1710.