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Multielectron Excitation Structures in X-Ray Absorption Fine Structure Spectra of Bromide Ion in Tetra-*n*-Propylammonium Salt and Solutions

Hajime TANIDA, Hideto SAKANE, Iwao WATANABE,* and Yu YOKOYAMA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

Strong multielectron excitation structures (MEES) in the extended X-ray absorption fine structure (EXAFS) region have been observed in Br *K*-edge absorption spectra of tetra-*n*-propylammonium bromide and bromide ion in aqueous and acetonitrile solutions. The MEES were extracted from the background of EXAFS spectra. The positions of steps due to MEES are well predicted by the *Z*+1 approximation.

Multielectron excitation structures (MEES) in the extended X-ray absorption fine structure (EXAFS) region have attracted few people except for theorists because they appear only in the spectra of gaseous samples[1,2)] or they can be identified only by elaborate procedures with extremely high quality data.[3,4)] Thus, the MEES have not been paid attention by most of the EXAFS users. However, we have found that EXAFS analyses can not be performed at all unless the MEES are removed in the case of bromide in organic salt or in solution. The present paper reports the most pronounced MEES ever known other than those found for inert gases, and it advises that we must be aware of the MEES present more or less in the EXAFS spectra.

The measurements were performed at BL-6B and 10B of Photon Factory of the National Laboratory for High Energy Physics in Tsukuba. The 0.1 mol dm^{-3} Br^- solutions were prepared by dissolving tetra-*n*-butylammonium salt into distilled water and acetonitrile, and absorption spectra were obtained with the cell length of 1 cm. Powder sample of tetra-*n*-propylammonium bromide (TPAB) was diluted with boron nitride. Acetonitrile, tetra-*n*-butylammonium bromide and TPAB were purchased from nacalai tesque, Inc., Kyoto. Acetonitrile was purified according to the standard procedures.[5] The water content in acetonitrile solution was determined to be about 40 mmol dm^{-3} by Karl–Fischer titration. The titrations were performed at Osaka University a few days after the EXAFS measurements.

Normalized EXAFS interference function χ in k space is defined as

$$\chi = \frac{\mu - \mu_b - \mu_0}{\mu_0} , \qquad k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} ,$$

where k is the photoelectron wave vector, m is the electron mass, E is the incident X–ray energy and E_0 is the energy threshold which is chosen to be the midpoint of the edge jump.

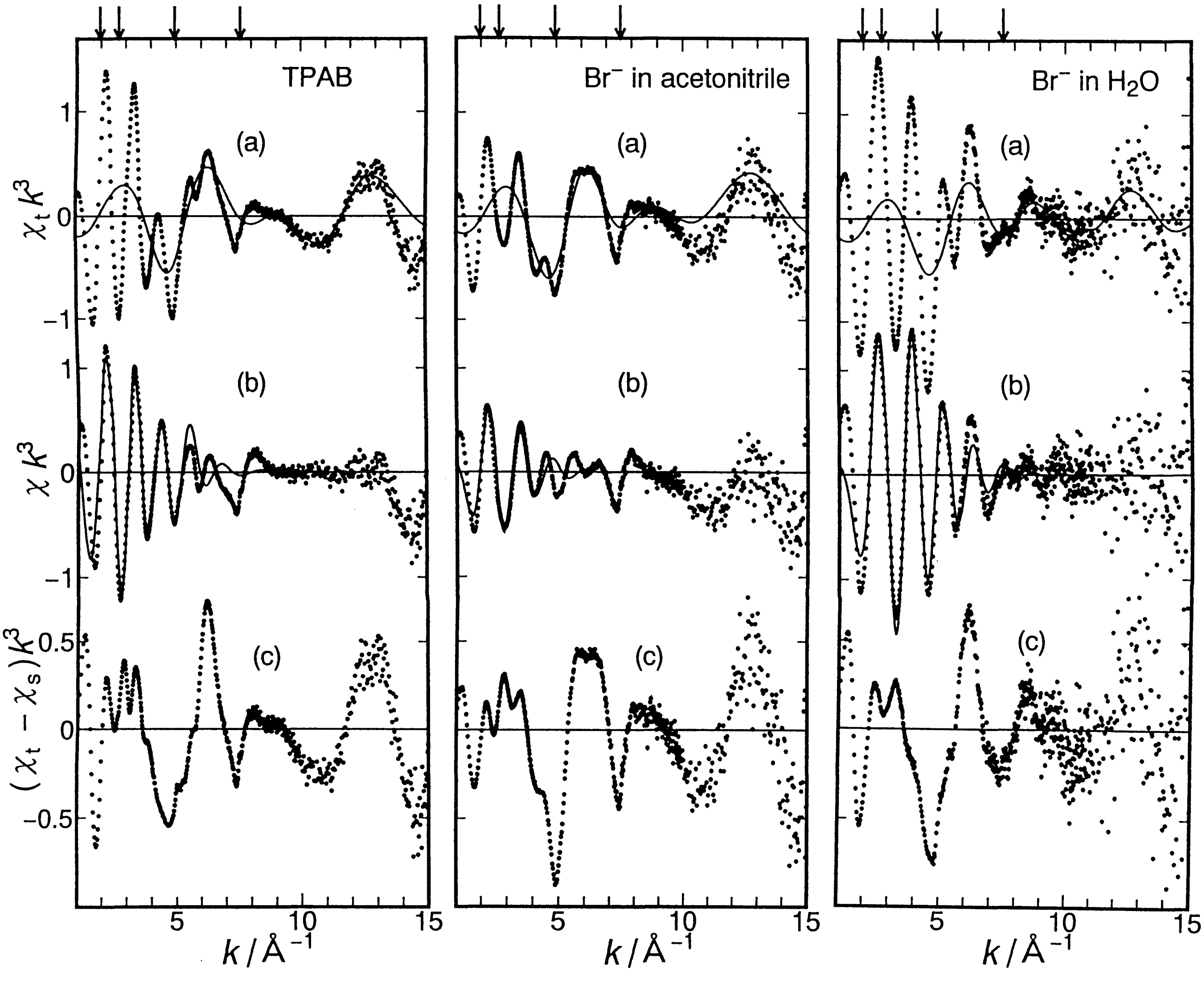

Fig. 1. The EXAFS spectra of TPAB, Br^- in acetonitrile and H_2O. For details see the text.

μ is the total absorption coefficient, μ_0 is the K absorption of the hypothetical isolated absorbing atom, and μ_b is the background absorption. μ_b is obtained by a least–square fitting with the formula, $AE^{-3} + BE^{-4} + C$.

The curves with dots in Fig. 1(a)s are the tentative EXAFS oscillation spectra, $\chi_t{\cdot}k^3$, given by using a simple base line obtained with a sixth–order polynominal least–square calculation. One may easily notice that negative peaks at around 5 and 7.5 Å^{-1} are abnormal in the spectra of TPAB and Br$^-$ in acetonitrile. They are too strong in magnitude to be a part of EXAFS oscillation and the peaks at 7.5 Å^{-1} are acute. The Br K–edge absorption is known to accompany simultaneous outershell electron excitations, so–called shake–up, which energies correspond to the binding energies E_b for Kr in the Z+1 approximation.[2,4] The E_b values for Kr are given in Table 1, and their positions are indicated by the arrows in Fig. 1. In Fig. 1(a)s are also shown the baselines μ_0 as thin solid curves obtained from $\chi_t{\cdot}k^3$ by the method described elsewhere.[6] The use of the baselines gives $\chi{\cdot}k^3$ spectra as the dotted curves in Fig. 1(b)s. EXAFS oscillations appear only in the low k region in the present samples. Such quick reduction in EXAFS amplitude makes the MEES very distinct.

Table 1. Binding energies E_b for Kr[7] and their corresponding k values and the MEES onset energies observed in Fig. 1 for TPAB, Br$^-$ in acetonitrile and H_2O

	E_b/eV	k/Å^{-1}	Onset energies/eV		
			TPAB	CH_3CN	H_2O
$4p_{3/2}$	14.0	1.90	12.1	12.0	13.3
$4p_{1/2}$	14.7	1.96			
$4s$	27.5	2.69	24.1	23.4	29.4
$3d_{5/2}$	93.8	4.96	83.3	90.2	87.0
$3d_{3/2}$	95.0	4.99			
$3p_{3/2}$	214.4	7.50	207.3	207.4	208.1
$3p_{1/2}$	222.2	7.64			
$3s$	292.8	8.77			

The EXAFS spectra $\chi{\cdot}k^3$ were further treated with fitting calculation using a following equation,

$$\chi\cdot k^3 = k^3\sum_j \frac{B_jF(k')}{k'r_j^2}\exp(-2\sigma_j^2k'^2)\sin\left(2k'r_j+\phi(k')-C_{3,j}k'^3\right), \qquad k'=\sqrt{k^2-\frac{2m}{\hbar^2}\Delta E_0}\,.$$

The variable parameters of the curve–fitting calculation are the interatomic distance r (except for TPAB, since its structure is known), the amplitude factor B, the Debye–Waller factor

σ, the third order coefficient C_3 and the correction in threshold energy ΔE_0. C_3 contains the information about asymmetrical distribution and anharmonic potential of surrounding atoms. j is the shell number; five shells are used for TPAB and one for the others. The backscattering atoms are C for acetonitrile and O for aqueous solution. The backscattering amplitudes $F(k)$ and the phase shifts $\phi(k)$ are taken from the tables of Teo and Lee or McKale *et al.*$^{8)}$ The thin solid curves in Fig. 1(b)s are the results of the fitting calculations and are noted as χ_s.

Now we can extract the MEES more exactly by subtracting χ_s from χ_t as shown in Fig. 1(c)s. Four onset energies are easily determined and are listed in Table 1. They are found to be correlating very well with the E_b values for Kr. There seems to be an additional structure at k = 11 Å^{-1} though its origin is not known. This study clearly indicates that we must take into account of MEES in studying the sample whose EXAFS oscillation is weak.

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