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Size distribution of sulfur species in fine and ultrafine aerosol particles using sulfur *K*-edge XANES*

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Abstract The sulfur species existing in different size aerosol particles were determined based on the 'white line' energy shift and the features of post edge structure of sulfur *K*-edge XANES (X-ray Absorption Near Edge Structure). The results indicated that sulfates were dominant sulfur species in aerosol particles. However, small amount of reductive sulfur species were also found in the ultrafine aerosol particles(<0.1 μm). Sulfates in aerosols mostly exhibited as $(NH_4)_2SO_4$ and gypsum. Most $(NH_4)_2SO_4$ distributed in aerosol particles finer than 0.952 μm, while gypsum was the dominant sulfate in coarse aerosols.

Key words sulfur species, aerosol, size distribution, XANES

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1 Introduction

It is well known that sulfur is an important hazardous element in air pollutants. Sulfur containing compounds in aerosol particles not only cause various environment problems, such as radioactive force[1, 2] and acidification deposition[3, 4], but also do harm to human health[5, 6]. Hence, the sulfur species in aerosol particles are of great interest in recent years. On the other hand, fine and ultrafine aerosols may have more adverse toxicological effects than coarse aerosols[7]. So it is necessary to clarify the sulfur species in size-fractionated aerosol particles.

XANES has been widely used for species identification in various fields, such as geochemistry, biology and environmental sciences[8, 9]. It was also applied to sulfur species studies in aerosol particles in recent years[10, 11]. The sulfur *K*-edge XANES is capable of identifying oxidation states of sulfur by the energy shift of 'white line', as well as species identification by the features of post edge (called 'shape resonance'[12, 13]).

In this paper, oxidation states and species of sulfur in fine and ultrafine aerosol particles were analyzed using XANES. The results were expected to be useful for clarifying the size dependence of sulfur compounds in atmospheric chemical reactions.

2 Experimental

2.1 Sampling

The study area was located at the Shanghai Institute of Applied Physics (SINAP, 31°24′N, 121°17′E), a suburb of Shanghai, China. Size separated aerosol particles were collected using an Electrical Low Pressure Impactor (ELPI, DEKATI Corp.). It was set up on the roof of a building with 18 m high in the SINAP. The impactor stages allowed collecting aerosol particles in 13 sizes, i.e. 0.0287, 0.0571, 0.0947, 0.157, 0.264, 0.384, 0.616, 0.952, 1.61, 2.40, 4.01, 6.71 and 9.95 μm, respectively. No-hole polycarbonate filters (25 mm in diameter, Whatman Corp.) were used for all impactor stages, and the flow rate was set at 9.93 $L\cdot min^{-1}$. A 24 hours sampling was taken on 28 July,

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2.2 Sulfur *K*-edge XANES

Sulfur *K*-edge XANES spectra were measured at Beamline 4B7A of the Beijing Synchrotron Radiation Facility (BSRF), Beijing, China[14, 15]. The aerosol particles were exposed to the incident X-ray beam with incident angle 45°. The beam path and the samples were placed in vacuum to suppress X-ray scattering and absorption by air. The emitted fluorescence X-ray was measured using a solid state detector (ORTEC Corp.). The XANES spectra were recorded with a 0.3 eV step length (3—6 s for each point). The blank filter was also measured for comparison, and the sulfur absorption was negligible.

3 Results and discussion

For sulfur, the intense 'white line' originates from the $s \rightarrow p$ electric transition. The energy position of 'white line' varies between 2469 and 2480 eV, depending on the oxidation state of sulfur atom. Higher oxidation state shifts its absorption edge to higher energy. The relationship between the edge shift and the oxidation state is shown in Fig. 1. A strong linear correlation between the oxidation states of sulfur and the position of 'white line' was observed, where the solid circles were measured at BSRF.

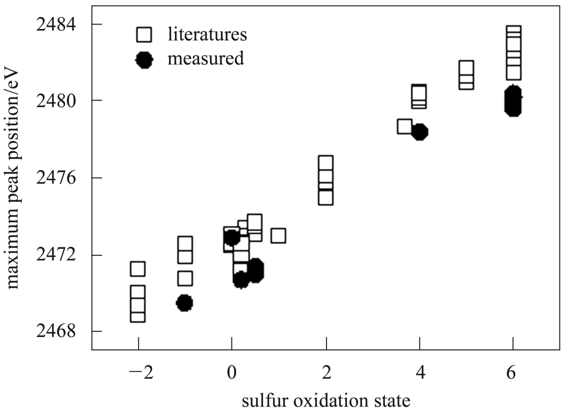

Fig. 1. Relation between the oxidation state of S atom and the peak energy of white lines in XANES.The data marked as □ were summarized from Refs. [16—25], and the data marked as • were measured at BSRF.

The XANES spectrum can be deconvolved into a group of Gaussian shape curves[19] and two arc tangent curves for the steps of reduced sulfur and oxidized sulfur (2473.1 eV and 2477.5 eV, respectively). The result of Stage 1 (0.0287 μm) is shown in Fig. 2. The sulfur oxidation states were identified by comparing the 'white line' energy shift with the reference samples as summarized in Fig. 1.

In Fig. 2, sulfates (G3) were the dominant species in aerosol particles. However, small amounts of reductive sulfur compounds (G1 and G2) were also found.

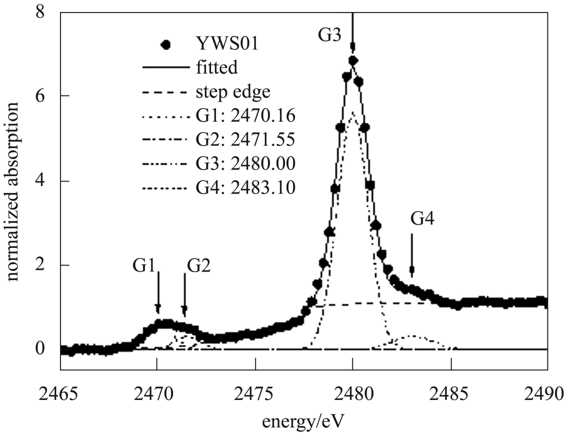

Fig. 2. Deconvolution of XANES spectrum into three gaussian and arc tangent peaks to obtain the information of oxidation states in the ultrafine aerosol particles (stage 01, $D_{\mathrm{m}} = 0.0287$ μm).

The percentage of reductive and oxidation sulfur in different size aerosol particles is shown in Fig. 3. The reductive sulfur compounds increased with the decrease of particle size below 0.1 μm. In the particle size between 0.1—1.0 μm, the percentage of sulfates was higher than in other sizes. The difference of oxidation state in various sizes implied that the atmospheric chemistry reactions in aerosol particles were not uniform in different sizes.

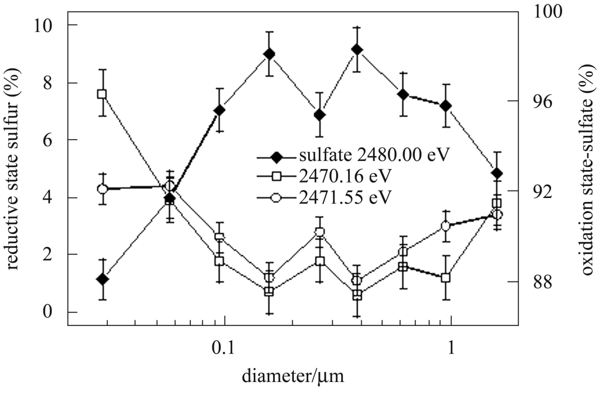

Fig. 3. Size distribution of reductive and oxidative state sulfur in aerosol particles.

It is difficult to distinguish various sulfates since the difference of 'white line' positions are usualy less than ±0.5 eV.

Fortunately, the post edge of sulfur *K*-edge XANES provided a clue to distinguish various sulfates. As Pingitore[12] and Solomon[13] studied, the post edge was sensitive to the ligands around the central atom in sulfate compounds. So the subsequent structure in the post edge region after 'white line' was called 'shape resonance'. For sulfates, the shape resonance region located between 2482 eV and 2450 eV.

Many researches suggested that $(NH_4)_2SO_4$ and gypsum ($CaSO_4 \cdot 2H_2O$) are the main sulfate compounds in aerosols by chromatography analysis[26, 27]. However, the size fractionated features of sulfates in fine and ultrafine aerosols were seldom studied.

The K-edge sulfur XANES spectra of reference compounds ($(NH_4)_2SO_4$ and gypsum) and size fractionated aerosol particles are illustrated in Fig. 4.

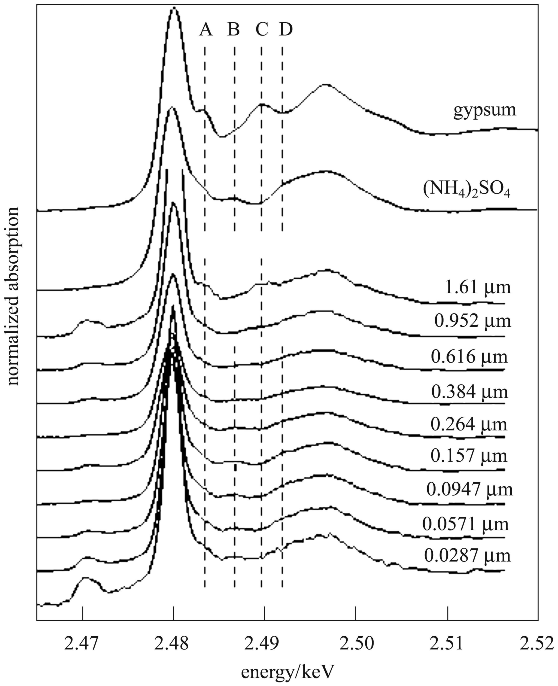

Fig. 4. Sulfur K-edge XANES for the sulfate species in different sizes. The spectra for gypsum, $(NH_4)_2SO_4$ are shown for comparison.

In Fig. 4, the shape resonance features of gypsum and $(NH_4)_2SO_4$ are marked by dash lines (A, B, C and D). For gypsum, the spectrum exhibited a stronger shoulder peak at "A", and had another obvious peak at "C", whereas the peaks at "B" and "D" were the features of $(NH_4)_2SO_4$.

By comparing the XANES spectra of aerosol particles and the references, gypsum was the main sulfate species in aerosol particles larger than 0.952 μm, while $(NH_4)_2SO_4$ mainly existed in finer particles, especially in ultrafine particles.

The results were consistent with previous studies[10]. The $(NH_4)_2SO_4$ in the ultrafine aerosols mainly originated from the reactions of ammonia and H_2SO_4 in air or in the water phase in aerosols[28]. Gypsum might be formed by the reaction of $CaCO_3$ and sulfate ions in aerosols during transportation[29]. Since the $CaCO_3$ mostly came from crustal dust, it was not strange that gypsum was recognized mainly in coarse aerosol particles.

4 Conclusion

XANES provides a new merit tool for sulfur species identification in aerosol particles for its high sensitivity to valence state and chemical species. Size distribution of sulfur bearing species in aerosol samples was studied using XANES. The results indicated that sulfate compounds were the dominant components in aerosols and distributed variously in different particle sizes. Higher percentage of sulfates was found in the aerosols ranging from 0.1—1.0 μm. Based on the features of post edge XANES, $(NH_4)_2SO_4$ was the dominant sulfur species in finer aerosols, while gypsum mainly distributed in coarse aerosols.

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