

Using X-ray absorption to probe sulfur oxidation states in complex molecules

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Abstract

X-ray absorption near-edge structure (XANES) spectroscopy offers an important non-destructive tool for determining oxidation states and for characterizing chemical speciation. The technique was used to experimentally verify the oxidation states of sulfur in different types of complex molecules because there are irregularities and uncertainties in assigning the values traditionally. The usual practice of determining oxidation states involves using a set of conventional rules. The oxidation state is an important control in the chemical speciation of sulfur, ranging from -2 to $+6$ in its different compounds. Experimental oxidation-state values for various types of sulfur compounds, using their XANES peak-energy positions, were assigned from a scale in which elemental sulfur and sulfate are designated as 0 and $+6$, respectively. Because these XANES-based values differed considerably from conventionally determined oxidation states for most sulfur compounds, a new term ‘oxidation index’ was coined to describe them. The experimental values were closer to those conventional values obtained by assigning shared electrons to the more electronegative atoms than to those based on other customary rules for assigning them. Because the oxidation index is distinct and characteristic for each different type of sulfur functionality, it becomes an important parameter for characterizing sulfur species, and for experimentally verifying uncertain oxidation states. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: X-ray absorption; XANES; Sulfur; Oxidation state; Oxidation index

1. Introduction

Geochemical, biogeochemical, and environmental studies of sulfur have proliferated recently because of the recognition of its role in many important processes on the earth’s various ecosystems. For example, the sulfur gases (e.g. sulfur

dioxide, dimethyl sulfide) affect the atmospheric sulfate-aerosol burden, and hence, play a significant part in changing the radiation balance of the atmosphere [1,2]. Sulfur is intimately intertwined with the diagenesis of organic matter in sediments, and is a crucial factor in the cycling of several other elements, including iron [3]. Thus, there is widespread interest in understanding the occurrence of the different types of sulfur compounds and their transformations in environmen-

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tal and geochemical systems. Most of these transformations involve changes in oxidation states, which range from -2 to $+6$ in the various organic and inorganic compounds of sulfur. Hence, the oxidation state is viewed as an important criterion in characterizing the various types of chemical species of sulfur, i.e. its speciation. The ability of sulfur to catenate, i.e. to form multiple sulfur–sulfur linkages, and thereby form mixed oxidation-state species, generates a variety of organic and inorganic compounds, and adds to the complexity of its speciation. Although the oxidation state is particularly important in controlling sulfur's speciation, there are irregularities and uncertainties in assigning the values, particularly in complex organic molecules, because the practice involves using a set of certain rules, the choice of which is arbitrary.

In this study, X-ray absorption near-edge structure (XANES) spectroscopy was used to experimentally verify anomalies in the oxidation states of sulfur in complex organic molecules obtained by the conventional approach, and to better assign the oxidation values. Conventionally, the oxidation state of elements in complex covalent compounds is derived either by assigning the shared electrons to the more electronegative atoms, or by drawing analogies with similar structures. Although the XANES method was used earlier for studying organic sulfur speciation in various geochemical and environmental samples, including sediment, petroleum, and coal samples [4–7], its use in understanding the oxidation state of organically bound sulfur was very limited. In this study, oxidation values were obtained for various types of sulfur compounds using their XANES peak-energy positions, assigning them from a scale in which elemental sulfur and sulfate are designated as 0 and $+6$, respectively. A comparison of such experimental values with empirically determined oxidation states showed serious discrepancy for several sulfur compounds. Because the experimental oxidation state value from XANES data is inconsistent with the traditional oxidation state formalism, a new term 'oxidation index' is introduced for the experimental quantity. The use of this quantity for characterizing unknown sulfur species from a samples' XANES spectrum is illustrated.

2. Oxidation state: significance and conventional assignment

Traditionally, the concept of oxidation state describes the status of combination of an element in a compound in terms of the number of valence electrons gained or lost from that of a neutral atom by assigning the electrons in a conventional way. Thus, it gives a simple approach for describing the relative changes in electronic charges (hence, the effective nuclear charges) on atoms without considering their electronic structure in detail. Nonetheless, it is an important and useful concept because it provides a way for: (1) identifying and recognizing a particular species; (2) classifying and grouping the different molecular species of an element; and (3) understanding electron transfers during transformations. An important illustration of the third point stems from the assignment of new values for the oxidation state of sulfur in thiosulfate using XANES spectroscopy [8]. From a calibration of peak energy versus oxidation state for the inorganic sulfur species, FeS, S^0 , SO_3^{2-} , and SO_4^{2-} whose assigned oxidation states are unambiguous, the oxidation states were established for the outer and inner sulfur atoms of thiosulfate as -1 and $+5$, respectively. The revised values give a far better understanding of the role of thiosulfate as an energy substrate for bacteria because intra-molecular electron transfer, which generates metabolic energy with the production of sulfide and sulfate, cannot be envisaged with the previous view that the oxidation states were -2 and $+6$ for the outer and inner sulfur atoms of thiosulfate [9,10].

Although the conventional rules for assigning oxidation states are given in general chemistry texts, the treatment is often inadequate. To put the subsequent discussion in the proper perspective, the rules are described below, which are based mainly on discussions by Pauling, Jørgensen, and Hilderbrand & Powell [11–13]. Rule 1: The oxidation state is zero for any element in its free state. Rule 2: The sum of the oxidation states of all the atoms in a species must be equal to the net charge on the species. Rule 3: The oxidation state of an element in a compound of uncertain structure can be calculated from a

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