

Chemical Bonding in Restacked Single-Layer MoS₂ by X-ray Absorption Spectroscopy

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Restacked single-layer MoS₂ films have been studied by polarized X-ray absorption spectroscopy at the S K and Mo L_{III} edges. These restacked single-layer MoS₂ films were obtained by exfoliation of MoS₂ powder and subsequent collection of the single molecular layer of MoS₂ onto a glass substrate. Films with and without tetrachloroethylene (TCE) included between the layers were obtained. The interlayer spacing of the film without tetrachloroethylene is 6.2 Å, and there is a 4.0-Å interlayer expansion on introducing TCE molecules between layers of MoS₂. The S K-edge X-ray absorption spectra of restacked single-layer MoS₂ films with and without TCE included between the layers have been compared with that of MoS₂ powder. A few percent of sulfate anion was found in the restacked single-layer MoS₂ films; it may originate from the partial decomposition of the molybdenum disulfide. Apart from that, the S K-edge absorption spectra of restacked single-layer MoS₂ films with and without TCE are similar to that of MoS₂ powder. This suggests that the chemical bonding of the S atom in the restacked MoS₂ films is identical with that found in crystalline MoS₂. In particular, we found no evidence for the presence of a new axial ligand on the S atom that should have manifest itself by introducing a new absorption band below the ionization threshold. Also, no difference was observed at the Mo L_{III} edge between the restacked single-layer MoS₂ films and the MoS₂ powder.

Introduction

The idea of incorporating a guest atom or molecule between the planes of the layered host material (intercalation) is a particularly appealing one, since the resulting structure can possess novel electrical, structural and mechanical properties. This class of materials has been recently referred to as "nanocomposite",¹ since the host matrix and guest molecules are mixed on the molecular level. Much excitement has been generated from the use of these nanocomposite materials in a variety of technological applications, e.g., in energy storage, electrochromic and ferroelectric devices, reversible batteries, nonlinear optical and quantum size devices, and catalysis.²

Recently, novel materials have been obtained by restacking single-layer molybdenum disulfide with organic molecules included between the layers.^{3,4} Molybdenum disulfide is a compound semiconductor, consisting of

S-Mo-S sandwich layers.⁵ In crystalline 2H-MoS₂, each Mo atom is coordinated by six S atoms in a trigonal prismatic arrangement. The nearest layers are connected with van der Waals bonds that are very easy to break by simply "pulling off" the layers. A large variety of organic molecules can be included between the layers of MoS₂. The interlayer distance of the reconstructed system varies with the nature of the guest molecule, the expansion being similar to the van der Waals dimension of the organic molecules. It is therefore possible to precisely control the interlayer separation distance. Although much effort has been made to characterize these reconstructed layers, the question of the S and Mo chemical bonding in the reconstructed film is still an open one and will be addressed here by X-ray absorption spectroscopy.

High-quality X-ray absorption spectroscopy data can be obtained by using synchrotron radiation.⁶ X-ray photoabsorption by an atom involves the promotion of a

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core electron to a bound or continuum state. The absorption process thus reveals information about the electronic structure of the absorbing atom and its local environment. With oriented samples, the identification and assignment of the various features of the absorption spectrum can be greatly facilitated by performing polarization-dependent X-ray absorption spectroscopy. This type of measurement takes advantage of the plane polarization of the synchrotron radiation to get information about the symmetry of the empty molecular orbitals and available continuum states. Polarized studies provide a method of resolving and orientationally selecting specific edge features which are frequently unresolved or appear to have a low intensity in the spectra of unoriented samples.

In this paper, the question of the S and Mo chemical bonding in restacked single-layer molybdenum sulfide (MoS₂) films is addressed by polarized X-ray absorption spectroscopy at the S K and Mo L_{III} edges. Restacked single-layer MoS₂ films with tetrachloroethylene (TCE) included between the layers (layer expansion of 4.0 Å) were compared to restacked single-layer MoS₂ films without the organic molecule included between the layers and to commercial MoS₂ powder. This study will demonstrate that the chemical procedure used to prepare restacked single-layer MoS₂ films (with and without organic molecules included between the molecular planes) does not modify significantly the characteristic chemical bonding of the S and Mo atoms found in crystalline MoS₂.

Experimental Methods

Sample Preparation and Characterization. The film preparation starts with exfoliation of MoS₂ powder (Johnson Matthey Inc.) following Joensen et al.⁷ MoS₂ is intercalated with lithium, and the lithiated MoS₂ is reacted with water. The evolving H₂ gas "blows" apart the MoS₂ crystals into its constituent single molecular layers. The single molecular layers are washed with water several times with centrifuging to obtain a neutral suspension. The next step is to introduce a water-immiscible liquid (usually an organic solvent) over the aqueous suspension of monomolecular layers of MoS₂ and shake the mixture. With sufficient shaking the layers in suspension collect at the water/organic (w/o) interface. Once collected at the w/o interface, the layers spontaneously spread up the walls of the glass container in which the mixture is held. At this point, when a microscope glass slide wet with water is brought in contact with the w/o interface, a thin film of MoS₂ with organic solvent molecules included between the layers spontaneously spreads on the slide. The details of the experimental method are described elsewhere.^{3,8}

A few milliliters of a suspension of single molecular layers of MoS₂ in water (concentration of about 2 mg cm⁻³) was used with an equal amount of reagent grade tetrachloroethylene (TCE) to prepare TCE-included MoS₂ films on microscope glass slides. Films with area as large as 1 × 2 cm were obtained. The films were made almost a month before the X-ray absorption measurements and stored in air prior to the experiment. No attempt has been made to characterize freshly prepared films.

The film thickness was measured with an optical interference microscope and was found to be about 500 Å. X-ray diffraction patterns for films spread on glass substrate were obtained with a Philips diffractometer using nickel-filtered Cu K α radiation.

Theoretically, the maximum TCE content in the lattice in the form of a monolayer is about 0.25. This is estimated by the molecular size of the molecule. Early attempts to measure it by

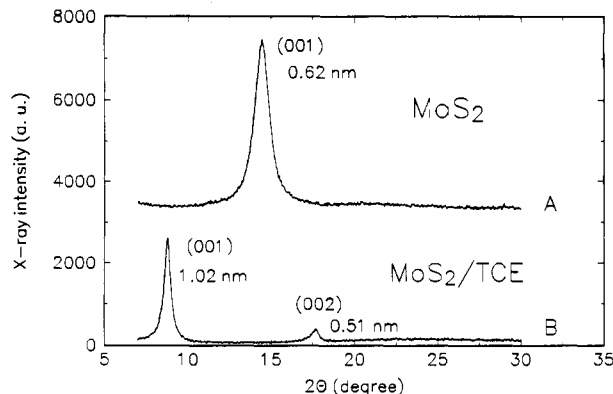


Figure 1. X-ray diffractograms of (A) a restacked film of single layer MoS₂ and (B) a TCE-included-MoS₂ film

determining the chlorine atomic percentage in thin films using X-ray fluorescence did not succeed. In view of the lack of experimental data to support this number, it should be considered only as an upper limit.

Synchrotron Source Characteristics and Beam Line Specifics. The polarized X-ray absorption experiments were realized using the double-crystal monochromator of the Canadian synchrotron radiation facility located at the Aladdin source of the Synchrotron Radiation Center, University of Wisconsin, Madison, WI. During the experiments, the storage ring was operated at 800 MeV, with current up to 180 mA. The beam size was 3 × 1 mm.

Data Collection, Calibration, and Analysis. The sample being large enough, the whole cross section of the beam was used. All the data were obtained in the total electron yield mode. The samples did not show any charging effect.

The energy calibration was done by assigning an energy of 2474.5 eV to the first inflexion point of a powdered sample of CuSO₄·5H₂O. This calibration sample was run at intervals during the experiment.

The samples were mounted vertically on the sample holder. The azimuthal angle ϕ was changed by rotating the sample along the vertical axis. The angle θ between the direction of travel of the incoming beam and the plane containing the substrate surface was used to annotate the sample orientation, so that $\theta = 0$ corresponds to grazing incidence. Keeping in mind that \vec{E} is located in the plane of the storage ring and perpendicular to the travel direction, the grazing and normal incidence angles correspond to configurations where \vec{E} is respectively nearly normal and parallel to the substrate surface. Due to the very good signal-to-noise ratio, only two scans were averaged for each orientation. A first-order polynomial equation was fitted to the preedge region of the spectrum and subtracted from the entire spectrum. All the spectra were normalized to unity in the postedge region.

The X-ray absorption spectra of a number of powdered reference samples (MoS₂, MoO₂, MoO₃) were also recorded. Commercially available powders were used in all cases. They were finely crushed in an agate mortar and pressed on a sticking tape. This tape did not show any absorption features in the energy range where the S K and Mo L_{III} edges are located.

Results and Discussion

X-ray Diffraction. Figure 1 shows the X-ray diffractograms of (A) a restacked film of single-layer MoS₂ and (B) a TCE-included restacked single-layer MoS₂ film. A restacked film of single-layer MoS₂ (without any organic inclusions) yields an X-ray diffraction pattern that can be indexed using an interlayer spacing of 6.2 Å. The TCE-included restacked single-layer MoS₂ films have an interlayer spacing of 10.2 Å, indicating an expansion of 4.0 Å. The van der Waals "thickness" of the TCE molecule

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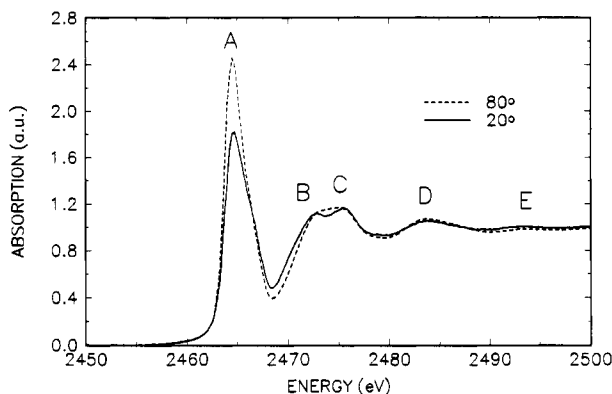


Figure 2. Polarized S K edge X-ray absorption spectra of powdered MoS₂. The incidence angle θ is displayed on the graph.

is about 4.0 Å (that of a methylene group⁹), indicating that the molecule is oriented between the layers of MoS₂ with its molecular axis parallel to the basal planes of the host. Lack of mixed X-ray reflections and the presence of a sharp multiple (001) line in the diffraction pattern of these materials indicate that they are highly oriented, with the basal MoS₂ planes parallel to the substrate. All these results have been presented and discussed in more detail elsewhere,^{3,10,11} and the interested reader should refer to these papers for more information. X-ray diffractograms of TCE-MoS₂ films before and after X-ray absorption spectroscopy measurements were identical, indicating that the TCE molecules were always present in the film.

Sulfur K-Edge X-ray Absorption. Figure 2 shows the S K-edge X-ray absorption spectra of MoS₂ powder at two different orientations. Unfortunately, at the time of the experiment, we did not have single-crystal MoS₂ at hand. However, MoS₂ powder is well-known for its lubricant properties and its tendency to orient under shear constraint. Therefore, MoS₂ was oriented by pressing it onto a sticking tape. Five features are observed in Figure 2, labeled A-E. Feature A displays the most prominent orientational dependence and we will discuss it now. Its intensity is reduced when θ is varied from 80° to 20°, with a hint of a shoulder on the high-energy side of the peak. This strong orientational dependence of the first absorption feature clearly points to the fact that we were at least partially successful in orienting the MoS₂ powder by pressing it. In the following, the usual convention of taking the z axis normal to the plane of the layered structure will be followed. If we assume that the MoS₂ powder is perfectly oriented, the z axis of the layered structure is perpendicular to the substrate surface. So, at normal incidence, the electric field vector of the X-ray photon is perpendicular to the z axis, and the X-ray absorption event causes the excitation of a core electron to S p_x and p_y states. In contrast, at grazing incidence, the electric field vector is parallel to the z axis, and X-ray absorption causes the excitation of a core electron to S p_z states.

Assignment of feature A can be made on the basis of the MoS₂ band structure calculations performed by Mattheiss.¹² 2H-MoS₂ has the same two-dimensional crystal

structure as the group-VB 2H compounds and the band structures for these two groups are similar. The band structure of 2H-MoS₂ (Figure 8 of ref 12) shows a lowest group of 12 bands evolving from S-atom p orbitals. Above these, we find the 10 Mo d orbitals, which are splitted into a lower pair of d subbands and a group of eight d bands at higher energies. Density-of-states curves for 2H-MoS₂ are also given in that paper (Figure 11 of ref 12). Linear combination of atomic orbitals (LCAO) results for 2H-MoS₂ with hybridization effects and interlayer interactions included results in the formation of a narrow d subband whose center is located at about 0.32 Ry (Figure 11c of ref 12). This subband is entirely filled, the Fermi level of the semiconducting 2H-MoS₂ being located at 0.42 Ry (Figure 11a of ref 12).

From Mattheiss calculations,¹² we can also compare the relative energy at the S site of the p_x , p_y , and p_z orbitals that are located above the Fermi level. In the band structure model of the X-ray absorption phenomenon, these are the bands of interest, since they are empty. Table V of ref 12 gives the symmetry properties of Bloch sums from s , p , and d orbitals at the metal and sulfur sites of 2H-MoS₂. The symmetry property of S p_z and S p_x and p_y orbitals have much in common at four (M , K , L , and H in Table V of ref 12) out of the six symmetry points in the Brillouin zone. For these symmetry points, there is little separation in energy between the empty S p_x and p_y bands and those with p_z character. However, at symmetry points Γ and A , the symmetry properties of the S p_z and S p_x and p_y are totally different. This yields to an energy difference of more than 0.3 Ry in the position of the lowest energy empty S p_z and S p_x and p_y orbitals (Figure 8 of ref 12). So, at grazing incidence, the energy position of the first absorption feature is expected to move to higher energy compared to that observed at normal incidence. This is in agreement with the appearance of a shoulder on the high energy side of peak A at grazing incidence (Figure 2). A similar effect has also been observed by Heald and Stern,¹³ who found an anisotropy effect in the Se K-edge X-ray absorption spectrum of 2H-WSe₂, a material isostructural to 2H-MoS₂. In this case also, they observed that the strength and position of the first absorption feature varies with the polarization direction, being more intense and occurring at a slightly lower energy at normal incidence.

Assignment of absorption features by comparison with band structure calculations are adequate as long as these calculations have been or can be performed. This is not always the case. In fact, in most contemporary X-ray absorption studies, the structure (and composition) of the material under investigation is unknown and band structure calculations cannot be performed. Other ways of assigning absorption features need to be found. For example, Tyson et al.¹⁴ have studied the polarized sulfur and chlorine X-ray K-edge absorption spectra of a number of S and Cl oxyanions. By comparing their experimental measurements with extended continuum multiple-scattering X_α computations (EC-MS- X_α), they were able to identify features in the absorption spectra both by symmetry and final-state type.

Features appearing in the K-edge X-ray absorption spectrum of a given element can be divided in two

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categories. In the first one, features appearing below the ionization threshold are associated with the transition of the 1s core electron to the final bound state. In the second one, features located above the ionization threshold arise as a consequence of a transition of the 1s core electron to final continuum states.¹⁴ Assignment of absorption peaks falling in this latter category is more difficult to do, since the peak energy position can depend on both the first and second shell of neighbors. In contrast, assignment of absorption peaks in the first region is more easy to realize, owing to the localized nature of the final state involved in the transition. Let us consider the polarized K-edge absorption spectrum of chlorate (potassium chlorate) and thiosulfate (magnesium thiosulfate) to determine the modifications occurring in the X-ray absorption spectrum as a result of a change in coordination geometry.

In KClO₃, the chlorine is bound to three O atoms, with a Cl–O bond length of 1.418 Å and a O–Cl–O bond angle of 106.4°.¹⁵ The point group symmetry is C_{3v} and the first shell of atoms doesn't completely surround the chlorine atom. This is analogous to the first coordination sphere of the S atom in bulk MoS₂. The polarized Cl K-edge absorption spectrum of the KClO₃ single crystal shows appreciable orientational dependence.¹⁴ If the electric-field vector is oriented parallel to the C₃, only one absorption feature is observed below the ionization threshold. This absorption feature is located at 2833.0 eV. On the other hand, if the electric-field vector is oriented perpendicular to the C₃ axis, the first absorption feature is more intense than in the previous case and occurs at lower energy (2831.8 eV).

In MgS₂O₃·6H₂O crystal, the point-group symmetry of the thiosulfate anion is also C_{3v}. In that case however, the first coordination sphere of the central S atom is made of three oxygen and one sulfur atoms. As for the case of ClO₃⁻ anion, the C₃ axis is perpendicular to the plane defined by the oxygen atoms and parallel to the S–S bond. Only one transition of the 1s core electron to a bound state is observed when the electric-field vector is perpendicular to the C₃ axis. Yet, when the electric-field vector is oriented parallel to the C₃ axis, two transitions are observed below the ionization energy. The shape of this absorption spectrum in the vicinity of the absorption edge is different from that observed previously. It reflects the difference in chemical bonding between the central S atom and the O or S atoms of the first coordination shell and can thus be used to track any variation in the chemical bonding of the absorbing element.

The orientational dependence of the first absorption feature observed in the absorption spectrum of MoS₂ powder is similar to that of the ClO₃⁻ anion. In MoS₂, the first coordination shell of the S atom is made of three Mo atoms at 2.35 Å. These Mo atoms are located at the corners of a right equilateral trigonal prism, so as to give a 3-fold axis of symmetry (C₃) to the first coordination shell surrounding the S atom. This 3-fold axis is parallel to the c axis of the crystalline structure and perpendicular to the plane of the layer. So, the atomic spatial arrangement around the S absorbing atom is similar to that found for the Cl atom in the chlorate anion and similar spectra are expected below the ionization threshold. In the dry restacked single-layer MoS₂ film, any new axial ligand on the S atom should manifest itself by introducing a new

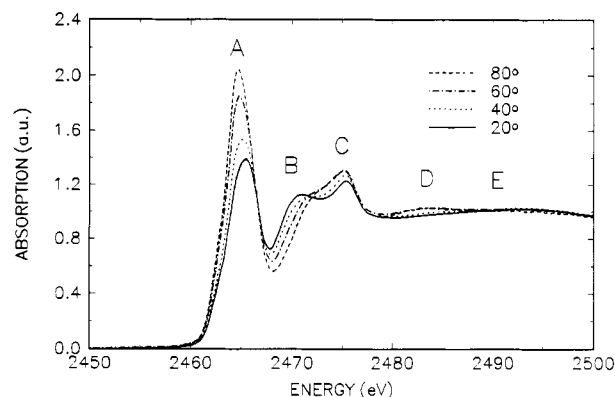


Figure 3. Polarized S K edge X-ray absorption spectra of dry and aged reconstructed MoS₂ layer. The incidence angle θ is displayed on the graph.

Table 1. Energy Peak Position of the S K-Edge X-ray Absorption Spectrum of Restacked Single-Layer MoS₂ Films as a Function of the Incidence Angle θ ^a

feature	$\theta = 80^\circ$ (eV)	$\theta = 20^\circ$ (eV)
A	2464.9	2465.4
B	2470.5	2470.2
C	2475.3	2475.1
D	2483.0	
E	2491.8	2491.8

^a An arctan step function was used to model the continuum step at the absorption edge:

$$\left[f(E) = A \left(\frac{1}{2} + (1/\pi) \arctan \left(\frac{2.3548(E - E_0)}{w/2} \right) \right) \times \exp(-B(E - E_0)) \right], \text{ with } E_0 = 2471.3 \text{ eV}, A = 0.974, W = 2.44, B = 1.08 \times 10^{-4}]$$

absorption band below the ionization threshold, which should be readily detectable when the electric-field vector is oriented perpendicular to the plane of the reconstructed layer by analogy with Mg₂S₂O₃.

Figure 3 shows the polarized S K-edge X-ray absorption spectrum of the dry restacked single-layer MoS₂ film without tetrachloroethylene. Absorption spectra have been recorded at four different orientations of the sample relative to the X-ray beam. Five features are observed in the spectra, labeled A–E in Figure 3, whose intensity (and energy position) vary with the orientation of the sample. A line-fitting program has been used to deconvolute the various absorption features of Figure 3. An arctan step function (with $E_0 = 2471.3$ eV) was used to model the continuum step at the absorption edge with Gaussian line shapes to fit the various peaks. The energy position of the Gaussian line shapes that best fit the spectrum of Figure 3 are listed in Table 1. The intensity of feature A, given by the area under the peak, shows the most pronounced dependence on the incidence angle and Figure 4 gives a plot of its normalized area with respect to $\cos^2 \theta$. The data are consistent with a linear dependence in $\cos^2 \theta$. The peak area at grazing incidence is about 80% of its value at normal incidence.

Several observations are worthy of note from the previous figures. Feature A of Figure 3 shows the same polarization dependence as that observed in Figure 2, viz., its intensity is reduced when θ is varied from 80° to 20°, with a hint of a new shoulder on the high-energy side of the peak. This is consistent with the previous X-ray

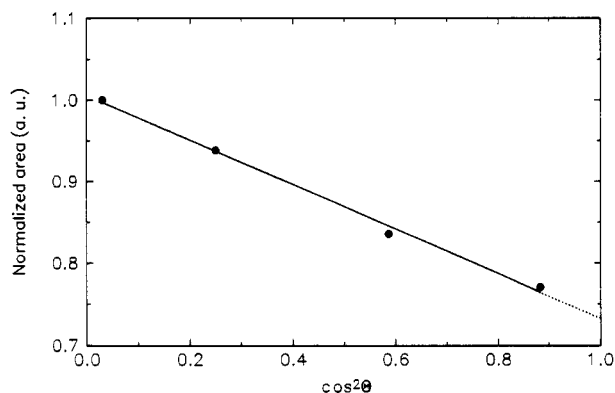


Figure 4. Variation of the normalized area of feature A with respect to $\cos^2 \theta$.

diffraction measurements, which have shown that dry restacked single-layer MoS_2 films are highly oriented, with the basal plane of the MoS_2 layer lying flat on the substrate surface. Below the ionization threshold, there is no appearance of a new absorption band beside that already found in bulk MoS_2 which would indicate the presence of an extra axial ligand on the S atom of the reconstructed layer. The fact that feature A occurs at the same energy position in both Figures 2 and 3 suggests that the electronic structure and chemical bonding in the MoS_2 powder and dry restacked MoS_2 films are similar. Other evidences suggest that it is indeed the case.

It is known from extended X-ray absorption fine structure (EXAFS) structural studies at the Mo K edge that single layers of MoS_2 in aqueous suspension have two nearest Mo-Mo distances at 2.8 and 3.8 Å, while the bulk value is 3.16 Å. However, when such single layers are reassembled (restacked MoS_2 film) and dry, the bulk Mo-Mo distance is recovered.¹⁶ The same conclusion has also been reached, using X-ray diffraction line shape analysis¹¹ and Raman scattering spectroscopy.^{11,17} In that case, they have been able to demonstrate that, in a suspension of freshly prepared single molecular layers of MoS_2 , the Mo atoms are octahedrally coordinated, in contrast to the trigonal prismatic coordination of Mo in bulk MoS_2 . For a restacked film however, the octahedral coordination of MoS_2 appears to be a metastable structure, since on heating or aging, it transforms back to the trigonal prismatic coordination, with an interlayer spacing identical to that of the bulk MoS_2 powder. All the restacked MoS_2 films we have studied have been prepared a month before the experiment and should correspond to what was previously called an aged sample. The similarity observed between the S K-edge X-ray absorption spectra of dry restacked MoS_2 film and bulk MoS_2 is therefore totally consistent with the results found by other authors.^{11,16,17} Comparison between Figures 2 and 3 nevertheless shows that the variation of the intensity of feature A and B is more pronounced for the dry restacked film than it is for the MoS_2 powder. This difference is most probably related to the fact that the MoS_2 powder is not totally oriented. Also, feature C is more intense in Figure 3 than it is in Figure 2. This will be discussed shortly.

Figure 5 shows the polarization-dependent S K-edge X-ray absorption spectra of exfoliated and restacked

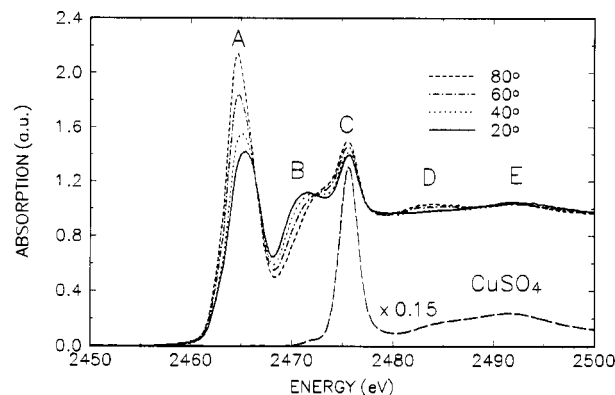


Figure 5. Polarized S K-edge X-ray absorption spectra of reconstructed MoS_2 with tetrachloroethylene included between the layers. The incidence angle θ is displayed on the graph. The absorption spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is also displayed.

single-layer MoS_2 film with tetrachloroethylene (TCE) included between the layers. Again, the absorption spectra have been recorded at four different orientations of the sample relative to the X-ray beam. These spectra show considerable resemblance with those of restacked single-layer MoS_2 films without TCE (Figure 3). Below the ionization energy threshold, feature A falls exactly at the same energy position and displays the same dependence on the polarization direction as that observed in Figure 3. This is consistent with the fact that the orientation of MoS_2 films that include TCE is identical to that of films without organic molecules. Again, there is no appearance of a new absorption band beside that already found in bulk MoS_2 that would indicate the presence of an extra axial ligand on the S atom of the reconstructed layer. In fact, these spectra differ only by the intensity of feature C, which is probably related to the presence of some sulfate (SO_4^{2-}) anions in the film. For comparison, the absorption spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is also given in Figure 5. The S K-edge absorption spectrum of that compound shows a very intense absorption peak (called "white line") that greatly facilitates its identification. This peak is located at 2475.2 eV and is shifted by more than 10 eV with respect to feature A of MoS_2 . A similar energy shift has been observed between SO_4^{2-} and the S ligand of $\text{S}_2\text{O}_3^{2-}$ anion.¹⁴ This reflects the very large difference of electronegativity between both environments, which modifies the energy position of the S 1s core level. The intensity of feature C does not show any strong orientational dependence, a fact consistent with its assignment to the SO_4^{2-} anion, since it has a T_d symmetry.¹⁴ A rough estimate of the amount of SO_4^{2-} can be made on the basis of the intensity of that peak. Values of 5% and 10% are found for exfoliated MoS_2 without and with TCE included in between the molecular planes, respectively. As far as we can tell, the amount of SO_4^{2-} present in the restacked film does not depend on the pH of the water solution used to rinse the single molecular layer. Sulfate ion is the common decomposition product of transition metal sulfides and it has been observed to occur (to various extent) upon exposure of sulfides to oxidizing agent.¹⁸

Molybdenum L-Edge X-ray Absorption. X-ray absorption near edge structure spectroscopy at the Mo L_{III} edge (2520 eV) offers some unique advantages over spectroscopy at the K edge (20 keV). At the Mo K edge,

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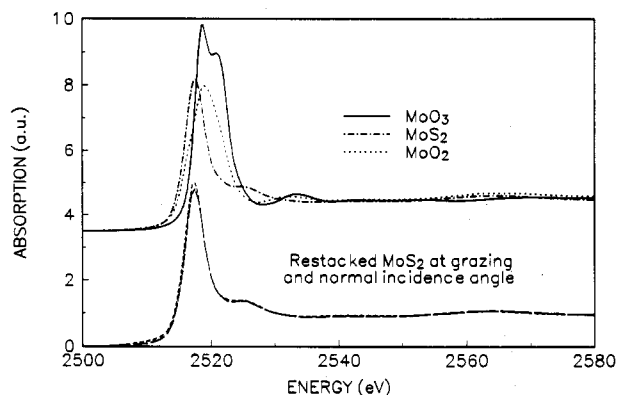


Figure 6. Mo L_{III}-edge X-ray absorption spectra of MoO₃, MoO₂ and MoS₂ (upper portion). Also shown in that figure (lower portion) is the absorption spectrum of restacked MoS₂ (without TCE) at grazing and normal incidence. The spectra of TCE-included restacked MoS₂ (not shown) are identical to that of restacked MoS₂ without TCE.

the effective resolution is limited by the natural line width of 6 eV of the core hole¹⁹ which tends to blur the displacement of the absorption edge of the element following a modification of its oxidation state. A much improved resolution can be obtained at the Mo L_{III} edge, because of both a smaller natural line width and higher resolution of the monochromator. In addition, XANES at the L_{III} edge probes orbitals of d character which are the primary orbitals involved in bonding.

Figure 6 shows the Mo L_{III} edge of MoO₃, MoO₂, and MoS₂ bulk reference compounds. Although MoS₂ and MoO₂ have the same formal oxidation potential (+4), the strong white line observed just at the absorption edge of MoO₂ is located at higher energy than that found in MoS₂. This is due to the fact that the electronegativity of the O atom is larger than that of S. The spectrum of MoS₂ shows a single white line peak. This is consistent with the band structure calculation of MoS₂, which shows that the d bands are split into two subbands. Since 2H-MoS₂ is a semiconductor, the Fermi level falls between the two subbands, and transitions of the core electron to the upper band are the only one expected. For reference, the Mo L_{III} edge of MoO₃ is also included in this figure, with its characteristic split maximum which arises as a consequence of the ligand field splitting of the d orbitals. So, the energy position of the Mo L_{III} edge is a sensitive probe to determine

whether or not the chemical bonding in the reconstructed MoS₂ layer has evolved during the chemical procedure used to form the film.

We have recorded the Mo L_{III} edge of reconstructed MoS₂ layer with and without TCE included between the layers. Firstly, as shown in Figure 6, there is no orientational dependence at the Mo L_{III} edge. This result was expected from previous measurement at the tungsten L_{III} edge of 2H-WSe₂, a compound which is isostructural with 2H-MoS₂. The reason for the absence of a polarization dependence effect is not clear yet but should be related to the site symmetry of the Mo. Second, the Mo L_{III} edge of the reconstructed films does not show any significant difference to that of the bulk MoS₂ powder. This means that the chemical bonding of the Mo atoms in the restacked single-layer MoS₂ films is identical to that found in MoS₂ powder.

Conclusion

Restacked single-layer MoS₂ films with variable interlayer spacing have been studied by X-ray absorption spectroscopy, in search of evidence for the existence of an interaction between the S atom and the organic molecule located between the layers. No such evidence has been found, suggesting that the assembly is held together by weak van der Waals bonds. In a sense, this is rather reassuring, since it explains why so large a variety of organic molecules can be included between layers of MoS₂ and other transition-metal dichalcogenides.³ Also, it is clear from the above results that the electronic structure of restacked single-layer MoS₂ films is similar to that of MoS₂ powder. It is expected that restacked single-layer MoS₂ films with variable interlayer spacing may find applications in the Li/MoS₂ rechargeable batteries as electrode materials with improved diffusivity of the Li species in the molybdenum disulfide. This should help to improve the performance of the electrode. Work along these lines is currently underway in our laboratories.

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