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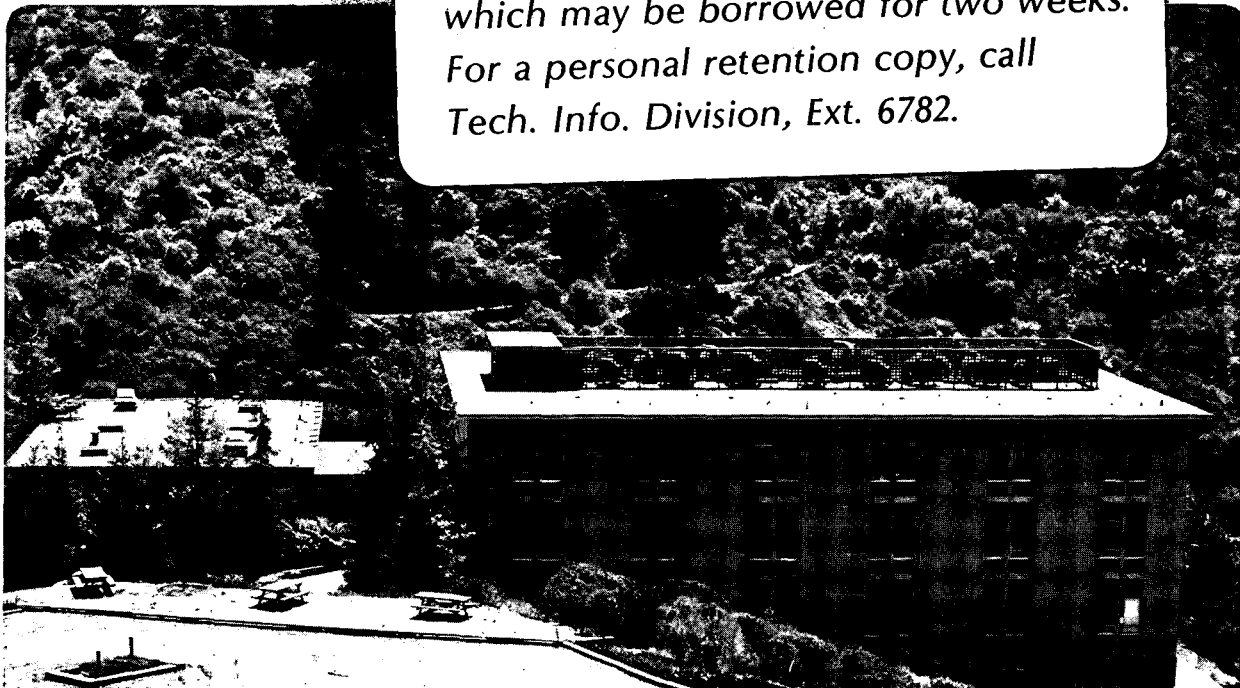
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M.H. Farias, A.J. Gellman, G.A. Somorjai,
R.R. Chianelli, and K.S. Liang

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THE CO-ADSORPTION AND REACTIONS OF SULFUR, HYDROGEN AND OXYGEN
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ABSTRACT

The chemisorption and reactivity of O₂ and H₂ with the sulfided Mo(100) surface and the basal (0001) plane of MoS₂ have been studied by means of Thermal Desorption Spectroscopy (TDS); Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). These studies have been carried out at both low (10⁻⁸-10⁻⁵ torr) and high (1 atm) pressures of O₂ and H₂. Sulfur desorbs from Mo(100) both as an atom and as a diatomic molecule. Sulfur adsorbed on Mo(100) blocks sites of hydrogen adsorption without noticeably changing the hydrogen desorption energies.

TDS of ¹⁸O co-adsorbed with sulfur on the Mo(100) surfaces produced the desorption of SO at 1150 K, and of S, S₂ and O, but not SO₂. A pressure of 1 x 10⁻⁷ torr of O₂ was sufficient to remove sulfur from Mo(100) at temperatures over 1100 K. The basal plane of MoS₂ was

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unreactive in the presence of 1 atm of O_2 at temperatures of 520 K.

Sputtering of the MoS_2 produced a marked uptake of oxygen and the removal of sulfur under the same conditions.

1. INTRODUCTION

Molybdenum compounds have many important applications as catalysts in the chemical industry. The catalytically active molybdates and molybdenum oxides are widely used for hydrodesulfurization, selective oxidation and oxidative dehydrogenation, and it is believed that they will play an important role in coal liquefaction [1].

The surface chemistry of molybdenum has been the topic of a number of recent investigations [2-15]. Among them, there are several studies of the adsorption of gases on molybdenum single crystal surfaces that have been modified by carbon and oxygen [2-7]. Both carbon and oxygen have been found to decrease the reactivity and the tendency to dissociate coadsorbed molecules.

Although some attention has been paid to the chemisorption of sulfur on molybdenum single crystal surfaces [8,9], little is known about the effects of monolayer and submonolayer amounts of sulfur adlayers on the chemistry of gases coadsorbed on molybdenum single crystals [10,11].

Here we report the results of a study of the effects of sulfur on the chemisorption of hydrogen and oxygen on Mo(100). We have also studied the reactivity of the sulfided Mo(100) and of MoS₂ with oxygen and hydrogen at both low (5×10^{-9} torr) and high (1 atmosphere) pressures.

2. EXPERIMENTAL

The experiments were performed in two separate ultra high vacuum (UHV) chambers. The experimental apparatus has been described in detail elsewhere [11]. The Mo single crystals used were obtained from the Materials Research Corporation and were cut and polished to within $\pm 1^\circ$ of the (100) face. The thermal desorption spectra were obtained with a UTI mass spectrometer interfaced to a PET/Commodore microcomputer. Before each experiment, the sample was flashed and the surface cleanliness was checked by Auger electron spectroscopy (AES) and Low Energy Electron Diffraction (LEED). The background pressure of the chambers was in the 10^{-10} torr range. The thermal desorption measurements utilized a constant heating rate of 20 K-s^{-1} . Oxygen and hydrogen exposures were usually performed at 5×10^{-9} torr. To avoid contamination due to background hydrogen, high purity deuterium (D_2) was used. The ^{18}O oxygen isotope was used in the thermal desorption measurements to avoid mass number mixing between atomic sulfur and molecular oxygen. A needle doser positioned in front of the crystal was utilized for depositing both gases. Molecular sulfur was deposited on the Mo(100) samples by means of a solid state (Pt/Ag₂S/AgI/Ag) electrochemical cell [16-20]. We achieved a uniform distribution of sulfur across the surface by using a source with a wide (7 mm) aperture.

Auger calibrations of sulfur and oxygen were made by using the Mo 221 eV, the S 152 eV, and the O 510 eV peaks. Desorption of the adsorbed sulfur was observed for electron beam currents of the Auger spectrometer of about 2 μA . This effect is depicted in Fig. 1, where we show the variation in the Auger peak height ratio $I_{\text{S}(152\text{eV})}/I_{\text{Mo}(221\text{eV})}$

as a function of time during a continuous electron beam exposure ($I = 1 \mu\text{A}$, $E = 3 \text{ keV}$). The sample was cooled to about 270 K during adsorption and dosing. The electron beam stimulated desorption was very noticeable for an Auger peak $[I_{\text{S}(152\text{eV})}/I_{\text{Mo}(221\text{eV})}]$ ratio greater than about 4:1. Defocusing of the electron beam and lower currents were used to reduce this electron beam stimulated desorption to a level that was undetectable during the time needed to take the Auger spectrum (3-5 min). The following parameters were used to obtain the Auger spectra: cylindrical mirror Analyzer (CMA): $E_0 = 2 \text{ keV}$, $V_m = 3 V_{\text{pp}}$, $v_{\text{sc}} = 4 \text{ eV s}^{-1}$, $\omega_0 = 4.6 \text{ kHz}$, $\tau = 0.1 \text{ s}$. Retarding field analyzer (RFA): $E_0 = 2 \text{ keV}$, $V_m = 7 V_{\text{pp}}$, $v_{\text{sc}} = 5 \text{ eV s}^{-1}$, $\omega_0 = 2.5 \text{ kHz}$, $\tau = 0.3 \text{ s}$.

The experiments at high pressure (1 atm) were carried out in a UHV chamber equipped with a high-pressure isolation cell [21]. One can carry out in situ surface characterization before and after treating the sample at high pressure. The AES measurements were made using the RFA described above and a glancing incidence electron gun. The exposures of the surface of Mo(100) precovered with 0.5 and 1 monolayer of sulfur and of the basal (0001) plane of MoS_2 were carried out separately at 1 atm of H_2 and O_2 for 10 min. at a temperature of 520K. Sputtering of the basal plane of MoS_2 was performed using He^+ ions for 10 min. with a current of $10 \mu\text{A}$ and a voltage of 500V.

3. RESULTS

3.1. The Adsorption-Desorption Behavior of S on Mo(100). Quantitative Determination of the S Coverage

In Fig. 2 we show the Auger peak height ratio $I_{S(152eV)}$ to $I_{Mo(221eV)}$ for two initial sulfur coverages after heating to increasing temperatures. The Mo(100) crystal was heated for 20 seconds to increasingly higher temperatures after sulfur deposition at about 220K. This figure shows two experiments with different initial doses of sulfur. The initial Auger peak ratios were 2.7 and 5.2 respectively, as measured using a CMA. In one of the experiments, heating was continued until the sulfur was completely desorbed at about 1900K. Both experiments show an abrupt decrease in the Auger peak ratio in the temperature region below 400K, indicating desorption at these temperatures. Between 400K and 1000K, the Auger ratio remains constant at 2.2 ± 0.1 . Between 1000K and 1900K, the ratio decreases continuously indicating desorption in this temperature range. Ordered LEED patterns observed in these experiments are shown in Fig. 3. The different LEED patterns that were seen in the various ranges of Auger peak ratios and temperatures are listed in Table 1. Below 350K and for Auger peak ratios over 2.3, we observed only the LEED spots corresponding to the Mo(100) with a high background. A faint $c(4 \times 4)$ surface structure was observed in some of the experiments for Auger peak ratios of ~ 0.2 . These results were complemented with thermal desorption spectroscopy (TDS) measurements of sulfur deposited on Mo(100), shown in Fig. 4. For small coverages (θ_s , defined later), sulfur desorbs atomically at about 1800K. A shoulder appears at about 1550K for $\theta_s > 0.5$ and shifts down in temperature to about 1250K for θ_s

≥ 1 . Molecular sulfur, S_2 , (not shown here) desorbs showing a small peak that grows with increasing coverage and moves from 1400K to 1300K. S_2 desorbs also for coverages greater than about 1, showing one peak at 1000-1100K, and several peaks below 400K. This molecular sulfur contributes to the atomic sulfur desorption spectra due to cracking of the molecule in the ionizer of the mass spectrometer. It has been suggested that the molecular sulfur peak at 1000-1100K originates from sulfur adsorbed in the neighborhood of adsorbed oxygen atoms [22]. As will be discussed in Sec. 3.3, we do not believe this to be the case. The desorption spectra of S on Mo(100) appears to be quite similar to that observed for S on W(100) [22]. Assuming first-order kinetics in the desorption process of S, and a rate constant of 10^{13} s^{-1} , the desorption energies for the peaks at 1800K, and in the range of 1550-1200K, are 110 Kcal mol $^{-1}$, and 95-70 Kcal mol $^{-1}$, respectively.

Our results agree in part with previously reported overlayer structures of sulfur on Mo(100) [8,9,12,13], and of TDS measurements after molecular sulfur and H_2S adsorption on Mo(100) [9]. Some of the differences in the observed LEED patterns could be the result of contamination by small amounts of oxygen, which can generate several LEED patterns, as has been discussed by Salmeron et al [9]. We did not observe the $(\sqrt{5} \times \sqrt{5}) R\bar{1}27^\circ$ LEED pattern seen by Clark [8], and in contrast with Salmeron et al [9] we saw the $p(2 \times 1)$ pattern at higher sulfur coverage than the sulfur coverage at which the $c(2 \times 4)$ and $\begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix}$ patterns appear.

We define the monolayer of sulfur ($\theta_s = 1$) for a $I_S(152\text{eV})$ to $I_{Mo}(221\text{eV})$ ratio of 2.2 based on the results shown in Fig. 2 and the assignment of the $p(2 \times 1)$ structure to the monolayer. There is a large

change in the sulfur to molybdenum Auger peak ratio for small changes in temperature in the region of 200-500K. This change comes from an abrupt decrease in the sulfur Auger peak as well as a correspondingly large increase in the molybdenum Auger peak. Between 400K and 1000K both peaks stay at a constant amplitude with a ratio of 2.2 ± 0.1 and the $p(2 \times 1)$ LEED pattern appears. We interpret the region where the abrupt change in the Auger ratio was observed as the region where the multilayers of sulfur desorb. We believe that the sulfur monolayer exists in the temperature range 400-1000 K where the Auger ratio is 2.2 ± 0.1 and the $p(2 \times 1)$ structure exists. This definition agrees with that of Clark [8]. To explain the observed LEED patterns, Clark [8] proposed real space structures with two different adsorption sites (four-fold and bridged), for the $p(2 \times 1)$, $c(4 \times 2)$, $\begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix}$ and $(\sqrt{5} \times \sqrt{5})R \pm 27^\circ$ structures, and only one site (four-fold) for the $c(2 \times 2)$ and $c(4 \times 4)$ structures. Salmeron et al [9], considered sulfur adsorption only at the four-fold sites of the Mo(100) surface for all the observed structures [37]. It is known that in the presence of hydrogen, the Mo(100) surface undergoes phase transformations [14] and it is accepted, although not well understood, that oxygen causes reconstruction of the Mo(100) surface. With this evidence, the possibility of sulfur induced reconstruction of the Mo(100) surface can not be disregarded. Our results cannot identify whether the formation of any of the ordered sulfur surface structures on the Mo(100) crystal face is accompanied by reconstruction of the metal surface. Intensity analysis and surface crystallography calculations are needed to answer the question of possible Mo reconstruction during sulfur adsorption.

3.2 The Adsorption-desorption behavior of D_2 on sulfided Mo(100) surfaces

The adsorption of hydrogen on the clean and sulfided Mo(100) surfaces was studied using TDS. The effect of ordering the S atoms on the sulfided Mo(100) surface was monitored. High purity deuterium (D_2) gas was used for these experiments. A clean Mo(100) surface was exposed to D_2 at a pressure of 5×10^{-9} torr for 200 s at 140 K. This exposure of 1L ($1L = 10^{-6}$ torr s) was enough to give a saturation dose of D_2 on the Mo(100). The desorption spectrum obtained after this exposure is shown in the upper curve of Fig. 5. This curve shows three desorption peaks at 300, 340, and 430K. There is a very good agreement of the temperature of the peak maxima and the relative peak amplitudes of the various states with previously reported results [6,23].

The ability of the Mo(100) surface to chemisorb D_2 was strongly modified by the addition of fractions of a monolayer of sulfur. This effect for the case of disordered S is depicted in the same figure for five different sulfur coverages (0.25, 0.5, 0.75, 0.85, and 0.97). In these experiments, sulfur was deposited on the surface at 140K (the sulfur layer remained disordered under these conditions) and the crystal was subsequently exposed to 1L of D_2 . The Mo(100) surface was cleaned after each experiment. The amount of D_2 desorbed was monitored and was seen to diminish significantly with increasing sulfur coverage. However, sulfur causes no noticeable shift in the temperature of the desorption maxima (TDM). These results agree with those of Han and Schmidt [23] who, by assuming second-order kinetics for desorption peaks at 340K and 430K, and first-order kinetics for the desorption peak at

300K, calculated the desorption energies of hydrogen from clean Mo(100) to be 20 ± 2 Kcal mol⁻¹, 27 ± 2 Kcal mol⁻¹ and 16 ± 2 Kcal mol⁻¹, respectively. The relative areas under the curves of Fig. 5 are shown in Fig. 6. One can see a marked decrease in the relative area as a function of sulfur coverage. In that figure we also show results for the case where the sulfur atoms were ordered (as detected by LEED) on the Mo(100) surface before depositing D₂. A sulfur coverage of 0.25 showing a C(2x2) LEED pattern was enough to block almost completely, with no noticeable shift in TDM, the chemisorption of D₂. Surfaces with one monolayer or more of sulfur did not show any D₂ desorption peaks after exposures at low D₂ pressures.

3.3 The Adsorption-Desorption behavior of O₂ on sulfided Mo(100) surfaces

The adsorption of O₂ on clean and sulfided Mo(100) surfaces was studied at a pressure of 5×10^{-9} torr and an adsorption temperature of 140K.

In Fig. 7 we show the Auger peak ratio $I_{O(510eV)}$ to $I_{Mo(221eV)}$ as a function of sulfur coverage for a disordered as well as for an ordered sulfur layer. In order to reduce the adsorption of background gases on the sample during the experiment, the adsorption of sulfur was started during cooling when the sample was below 200K. In these measurements, a constant dose of 1.2L of O₂ was used. There is a continuous decrease in the amount of O₂ adsorbed with increasing sulfur coverage. This decrease is faster when the sulfur atoms are ordered. No adsorption of O₂ was detected by Auger or Thermal Desorption measurements for $\theta_s \geq 1$

indicating that the amount of adsorbed oxygen was reduced by at least one order of magnitude by the presence of sulfur.

TDS measurements obtained after the adsorption of the ^{18}O oxygen isotope on sulfided Mo(100) surfaces show desorption of S, S_2 and S^{18}O , indicating that reaction between S and ^{18}O occurred, causing desorption of S^{18}O as a product. Results for $m/e = 32(\text{S})$, $50(\text{S}^{18}\text{O})$, and $64(\text{S}_2)$ are depicted in Figs. 8a, 8b, and 8c, respectively. In these measurements the S atoms were not ordered before dosing with $^{18}\text{O}_2$. Qualitatively similar results were obtained when the sulfur was ordered. For $\theta_s < 0.5$ the desorption peak at 1550K in Fig. 8a is predominant over that at 1800K, indicating that there is a displacement of S by ^{18}O from the higher energy state at 1800K, to the lower at 1550K. For higher coverages ($\theta_s > 0.5$) and for the rest of the desorption peaks in Fig. 8a, there is a high degree of similarity with the desorption peaks of S shown in Fig. 4, obtained from S adsorbed on Mo(100). As in that case, the peaks at 200-400K and at 1150K are due to cracking of sulfur molecules (see Fig. 8c) in the ionizer of the mass spectrometer. In Fig. 8b, we can see three S^{18}O desorption peaks for $\theta_s = 0.1$ at 1200K, 1400K, and 1550K. Two of those desorption peaks at 1200K and 1400K decrease rapidly with sulfur coverage and disappear for $\theta_s \approx 0.3$, and $\theta_s \approx 0.5$, respectively. The third desorption peak at 1550K for $\theta_s = 0.1$ looks symmetric and moves down in temperature with increasing θ_s , characteristic of a second order desorption process. For this peak, we find an activation energy for desorption of $64 \pm 4 \text{ Kcal mol}^{-1}$ and a preexponential factor of 10^9 s^{-1} . In Fig. 8c, we show the desorption spectra of S_2 molecules for $\theta_s > 0.5$. As described before, the desorp-

tion peaks at 200-400K are due to the multilayer of sulfur. The desorption peak at 1150K, that appears to have zero order desorption kinetics, has been attributed to S atoms in the neighborhood of adsorbed O atoms, which weakens the bonding of sulfur [22]. Examination of Fig. 8a shows that surfaces that have been both sulfided and exposed to oxygen do not show this desorption feature. Thus, it would seem that the sulfur desorption peak at 1150K is not related to oxygen contamination. The other desorption peak in Fig. 8c shifts to lower temperatures with increasing coverage and is fairly symmetric, indicative of second order desorption. The desorption energy is 79 ± 8 Kcal mol⁻¹, and the preexponential factor is 10^{12} s⁻¹. In table II, we list the temperature of maximum desorption rate and the heats of desorption for sulfur and oxygen from their various binding states on the Mo(100) crystal surface.

The sulfided Mo(100) surface was exposed to a partial pressure of oxygen of 1×10^{-7} torr, and was heated to increasingly higher temperatures. Auger measurements obtained during oxygen dosing showed a gradual decrease of the sulfur peak with a corresponding increase in the oxygen peak from 1100K to 1300K, indicating that sulfur was displaced from the Mo(100) surface by oxygen in this temperature range. The oxygen AES peaks observed for temperatures below 1100K at various sulfur coverages correspond to those depicted in Fig. 7.

3.4 Exposure of the Sulfided Mo(100) Surface and the Basal Plane of MoS₂ to High Pressures of H₂ and O₂.

The chemical behavior of sulfur precovered Mo(100) and of the basal plane of MoS₂ surfaces upon exposure to atmospheric pressures of H₂ and

O_2 was studied. Each surface was exposed separately to each gas (1 atm.) for 10 min. The temperature of the sample during the experiment was 520K. Sulfur precovered Mo(100) surfaces with $\theta_s = 1$ and $\theta_s = 0.5$ exposed to oxygen showed removal of sulfur and a significant uptake of oxygen, as detected by Auger spectroscopy. The basal plane of MoS_2 was inert to O_2 exposures under these experimental conditions. Exposure to H_2 did not remove sulfur from either the MoS_2 or the sulfided Mo(100) surfaces with $\theta_s = 1$ and $\theta_s = 0.5$.

The adsorption behavior of MoS_2 changed drastically after sputtering the sample with He ions ($I = 10 \mu A$, $V = 500$ volts) for 10 min. This treatment was observed to destroy the hexagonal LEED pattern observed for the ordered basal plane of MoS_2 but not to change the $I_{S(152eV)}/I_{Mo(221eV)}$ Auger peak ratios (12 = 1). It appears that while sputtering produces defects on the surface it does not selectively remove sulfur. Subsequent annealing to $\sim 1100K$ regenerated the hexagonal LEED pattern. After sputtering and subsequent exposure to O_2 (1 atm), the basal plane of MoS_2 showed a marked uptake of oxygen presumably due to chemisorption at defects introduced into the surface by sputtering. There was also a marked decrease in the $I_{S(152eV)}/I_{Mo(221eV)}$ Auger peak ratio from $\sim 12:1$ to $\sim 2:1$. Upon heating this surface, the evolution of SO and either SO_2 or S_2 was detected by the mass spectrometer. In this case it was not possible to distinguish between S_2 and SO_2 because the exposure was made using $^{16}O_2$.

4. DISCUSSION

The chemisorption of hydrogen was strongly inhibited by the presence of preadsorbed sulfur on Mo(100). Ordering of the S overlayers caused even stronger inhibition of chemisorption. This is consistent with recent reports of the effect of sulfur on other metals. An attenuation of the H_2 desorption peaks as a function of S coverage has been observed on Pt(111) [24]. The surfaces studied were clean Pt(111), Pt(111) - (2 x 2)S, and Pt(111) - ($\sqrt{3} \times \sqrt{3}$)R30°S. The decrease in the amplitude of the H_2 desorption peaks was greater for the higher temperature peaks. On Ni(100) [25] a strong reduction of hydrogen uptake and a shift of the TDS maxima to a lower temperature have been found to be due to the presence of preadsorbed S. The sticking coefficient of H_2 was reduced by one order of magnitude from that on clean surface by the presence of a sulfur coverage of $\theta_s = 0.25$. These effects were explained in terms of changes in the surface electron density in the presence of the electron acceptor adsorbate, showing the important role of the electronic effect. Adlayers of sulfur on Fe(100) were found [26] to reduce hydrogen adsorption drastically. No hydrogen adsorption was observed on an Fe(100) - c(2 x 2) S surface at 200K for exposures up to 2000L H_2 .

The effect of disordered sulfur on the adsorption of hydrogen on Mo(100) is not as drastic as in the cases of Pt(111), Ni(100) or Fe(100). It is possible that sulfur adsorbs molecularly as S_2 leaving some available sites for adsorption of hydrogen. Upon ordering the S becomes more evenly distributed making it more efficient for blocking of adsorption sites. We detect some hydrogen adsorption for high coverages

of sulfur ($0.5 < \theta_s < 1$) when unordered but none for ordered overlayers in this coverage range. Fig. 6 shows the dependence of the D_2 desorption peak area on sulfur coverage for ordered and disordered layers. The broken curve is calculated from the theoretical expression for the sticking coefficient as a function of sulfur coverage, $S(\theta)$, for dissociative chemisorption of a homonuclear diatomic molecule involving pairs of adjacent unoccupied sites, $S(\theta)/S_0 = (1 - n\theta)^2$, where we have used $n = 1$. This is based on an adsorption model that assumes that one sulfur atom blocks one hydrogen adsorption site. The fit with the experimental points for disordered sulfur is good, indicating that the effect of disordered layers of S on the adsorption of hydrogen on Mo(100) is blockage of adsorption sites. For the case of ordered layers of S, the strong decrease in the amount of the adsorbed hydrogen for $\theta_s = 0.25$ seems to indicate that each sulfur atom blocks about 4 hydrogen adsorption sites. More detailed measurements are in progress to clarify this point. There are no appreciable changes in the desorption temperature maxima, indicating that any electronic effect that may change the binding energy of hydrogen atoms to the Mo surface atoms is negligible. Lowering of the amount of D_2 adsorbed with sulfur must reduce the hydrogenation ability of Mo.

We observe desorption of SO as well as S, S_2 and O, but not of SO_2 in the TDS spectra upon adsorption of oxygen on Mo(100) with ordered or disordered sulfur layers. Sulfur-oxygen reactions have been studied before on other metals. Bonzel [27] observed the evolution of SO_2 upon adsorption of H_2S and O_2 on Cu(110). Holloway and Hudson [28] exposed sulfur covered Ni(111) surfaces to oxygen gas, resulting in the removal

of sulfur as SO_2 at temperatures near ambient at a rate proportional to the gas-phase oxygen pressure. Ku and Wynblatt [29] estimated that the heat of desorption of SO_2 (or of its dissociation products) from Rh(110) and Pt(110) is greater than 54 Kcal mol^{-1} , indicating strong adsorption of SO_2 on both surfaces. Bonzel and Ku [30] observed SO_2 as the product of a reaction between oxygen and sulfur precovered Pt(110) surfaces that obeyed the Langmuir-Hinshelwood mechanism. Kohler and Wassmuth [31] found molecular desorption of SO_2 adsorbed on Pt(111). Astegger and Bechtold [32] reported desorption of SO_2 from both coadsorbed sulfur and oxygen on Pt(111) and adsorbed SO_2 on Pt(111), while adsorption of SO_2 on oxygen precovered Pt(111) surfaces gave small amounts of SO_3 . On polycrystalline foils of W and Pt, Wu and Burns [33] found that the decomposition of SO_2 ($0 < \theta < 0.5$) oxidized the clean W surface, produced a tungsten oxide that was stable up to temperatures of 1400K and yielded elemental and molecular sulfur during the desorption process. Golub and Fedak [34] noted that SO_2 adsorbed on a polycrystalline tungsten filament gives desorption of atomic sulfur at 1650K, and of oxygen in the form of volatile tungsten oxides WO , WO_2 , WO_3 in the temperature range 1700-2000K. All these results seem to indicate that the weaker the sulfur-metal and oxygen-metal bonds, the easier it is to obtain SO_2 as the product of sulfur-oxygen surface reactions on metals. Our observations of desorption of SO , S , S_2 and O but not of SO_2 from sulfur-oxygen reactions on Mo(100) fit well with this observation because the heats of adsorption of sulfur and oxygen on molybdenum are slightly lower than on tungsten, where only elemental sulfur and tungsten oxides are observed to desorb, but greater than on Cu, Ni, Pt or Rh, where SO_2 is seen as the primary desorption product.

The results of our study of oxygen adsorbed on the sulfided Mo(100) surface indicate that sulfur blocks the adsorption of oxygen at low temperatures and pressures. At pressures of 10^{-7} torr of oxygen, temperatures of 1100-1300K were needed to displace the sulfur. In the case of MoS_2 , exposures to 1 atm of O_2 at 520K were insufficient to remove sulfur. Introduction of defects into the surface by sputtering produced a drastic increase in the rate of oxidation of the surface and in the removal of sulfur. Tauster and Pecoraro have associated the chemisorption of oxygen on Mo-S catalysts with hydrodesulfurization (HDS) activity [36]. Furthermore, HDS has long been thought to occur at the edge or defect sites of MoS_2 crystallites in these catalysts. We have shown that oxygen chemisorption is undoubtedly associated with defect sites in MoS_2 and not with the ordered basal plane. It will be interesting to study the HDS activity of the ordered basal plane of MoS_2 as compared to the activity of the sputtered surface.

5. SUMMARY

1. Sulfur adsorbed on the Mo(100) surface desorbs both atomically and molecularly with the major atomic desorption peak at 1800K.
2. The major effect of ordered or disordered sulfur adsorbed on Mo(100) surfaces on the chemisorption of hydrogen is to block adsorption sites without causing appreciable changes in the desorption energies. Site blockage is more effective when the sulfur layer is ordered.
3. A reaction was observed between the ^{18}O oxygen isotope and sulfur adsorbed on the Mo(100) surface, producing S^{18}O in the desorption spectra at 1150K. S , S_2 and ^{18}O were also seen to desorb but no SO_2 was found.
4. In the presence of 1×10^{-7} torr of O_2 , the overlayer of sulfur on Mo(100) was readily removed at temperatures over 1100K.
5. The ordered basal plane of MoS_2 was inert to the presence of 1 atm of O_2 at temperatures of 520K. However, sputtering of the MoS_2 produced a marked uptake of oxygen and a removal of sulfur under the same conditions.

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Table 1. LEED patterns observed for various ranges of Auger Peak ratios and temperatures.

Structure	$I_{S(152eV)}/I_{Mo(221eV)}$	Sulfur Coverage Range (Monolayers)	Temperature Range (K)
p(2 x 1)	2.3 - 2.15	1.05 - 0.99	400 - 850
c(4 x 2)	2 - 1.6	0.9 - 0.75	1100 - 1320
(2,-1,1,1)	1.45 - 1.3	0.7 - 0.65	1360 - 1410
c(2 x 2)	1.1 - 0.25	0.55 - 0.15	1450 - 1800

Table 2. Temperature of maximum desorption rate and heats of desorption for sulfur and oxygen on Mo(100).

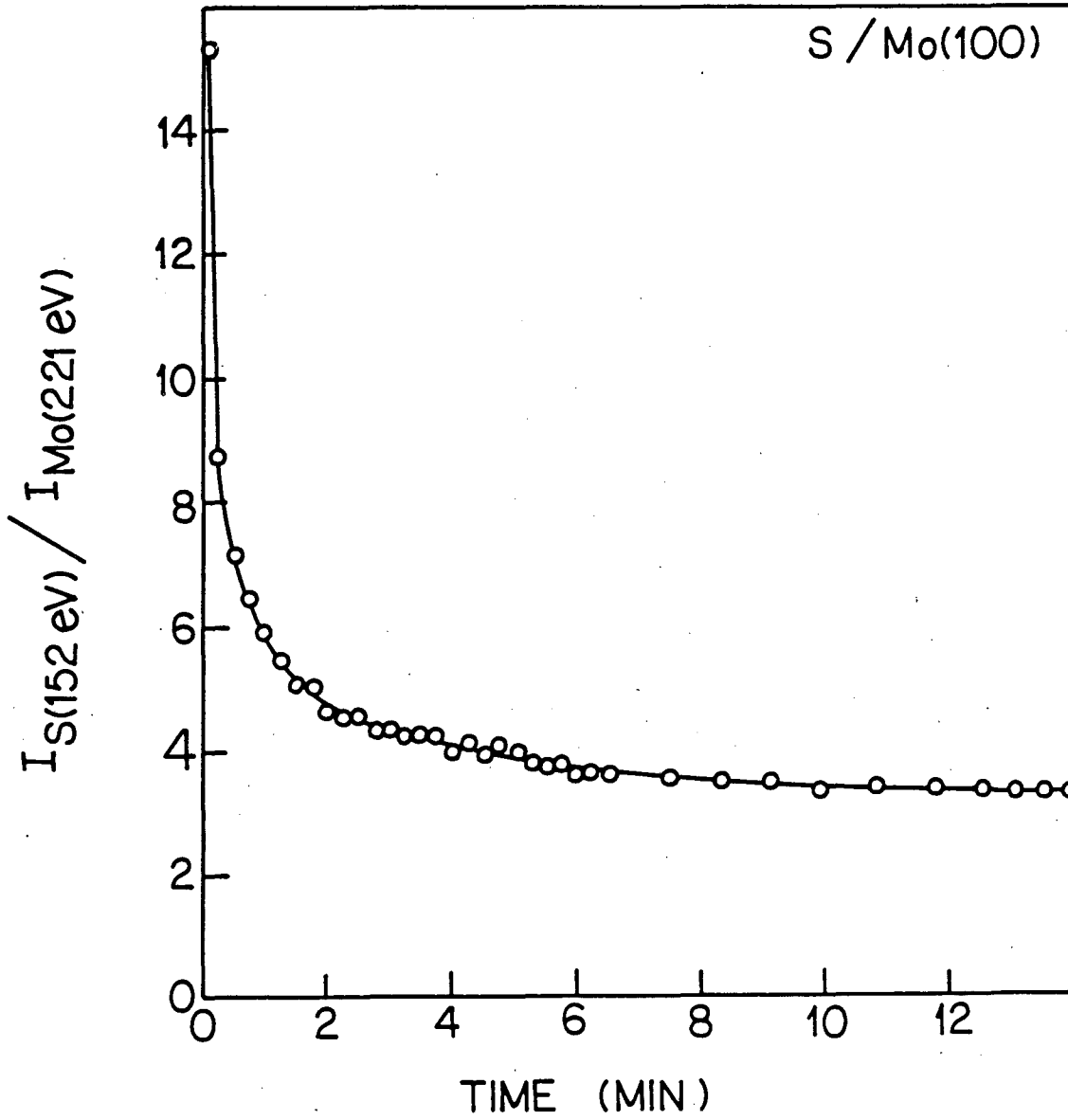
	Temperature of maximum desorption rate (K)	Heats of desorption (K cal mol ⁻¹)
S	1800 1550-1200	110 95-70
O	1800	110

FIGURE CAPTIONS

- Fig. 1. Variation in the Auger peak height ratio $I_{S(152eV)}/I_{Mo(221eV)}$ as a function of time during a continuous electron beam exposure ($I = 1\mu A$, $E = 3KeV$). The sample was cooled to about 270K during adsorption and electron beam exposure.
- Fig. 2. Variation in the Auger peak height ratio $I_{S(152eV)}/I_{Mo(221eV)}$ for two different initial sulfur coverages as a function of crystal temperature. Annealing time 20 s.
- Fig. 3. Ordered LEED patterns of sulfur on Mo(100). a) $p(2 \times 1)$, $E = 129$ eV; b) $c(2 \times 4)$, $E = 152$ eV; c) $(2, -1, 1, 1)$, $E = 97$ eV; d) $c(2 \times 2)$, $E = 91$ eV; e) clean Mo(100), $E = 84$ eV.
- Fig. 4. Thermal desorption spectra of atomic sulfur on Mo(100). Rate of temperature rise $20Ks^{-1}$.
- Fig. 5. Thermal desorption spectra of deuterium after 1 L exposure as a function of sulfur coverage on Mo(100). Rate of temperature rise $20 K s^{-1}$.
- Fig. 6. The evolution of the areas of the deuterium desorption peaks after 1L exposure as a function of sulfur coverage on Mo(100). Sulfur layer disordered (O), sulfur layer ordered (X). The broken line corresponds to the expression $S(\theta)/S_0 = (1 - \theta)^2$ (see the text).
- Fig. 7. Auger peak ratio $I_{O(510eV)}/I_{Mo(221eV)}$ after an exposure of 1.2L of oxygen as a function of sulfur coverage on Mo(100). Sulfur layer disordered (O), sulfur layer ordered (X).

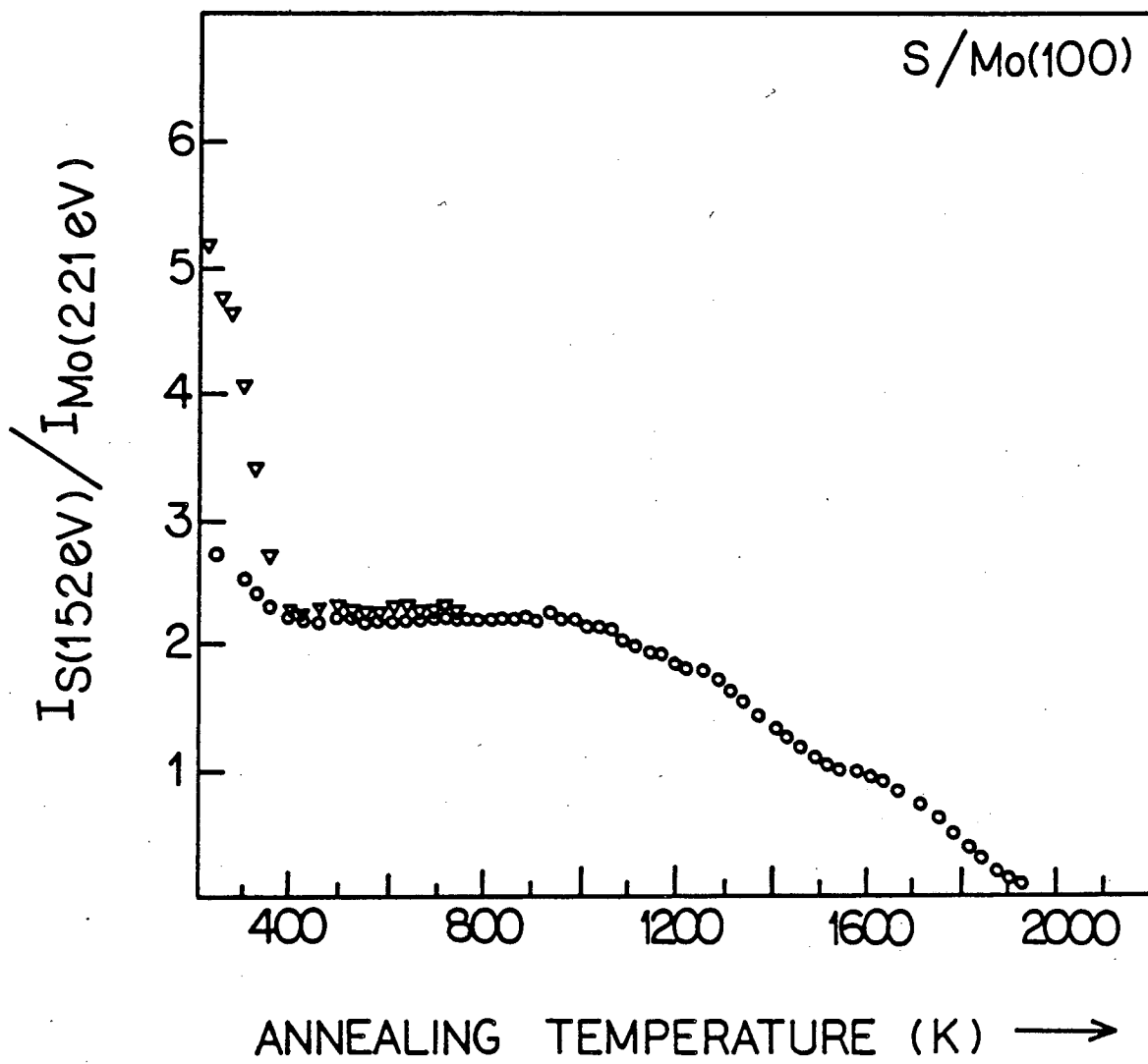
Fig. 8. Thermal desorption spectra of a) atomic sulfur, b) sulfur monoxide, and c) molecular sulfur, after an exposure of 1.2L of oxygen at 150K as a function of sulfur coverage on Mo(100).

Rate of temperature rise 20 Ks^{-1}



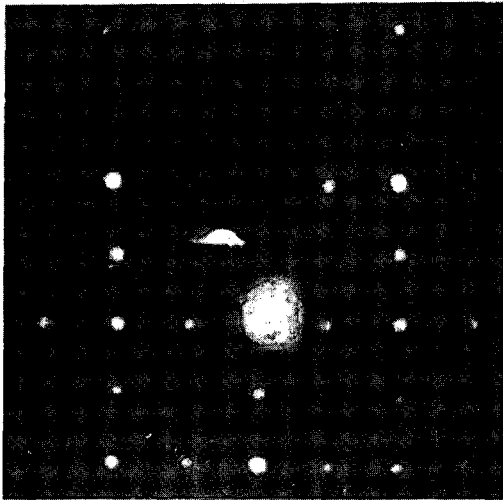
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Fig. 1

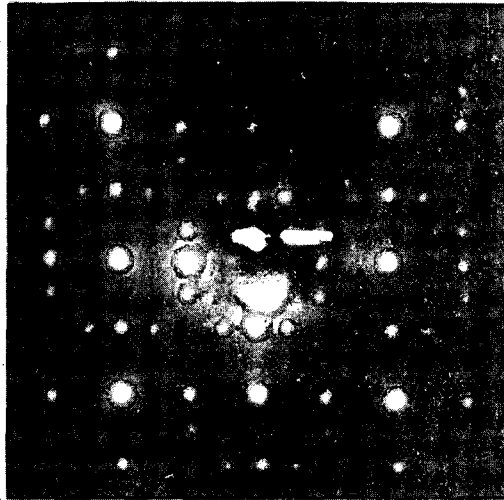


XBL 837-10686

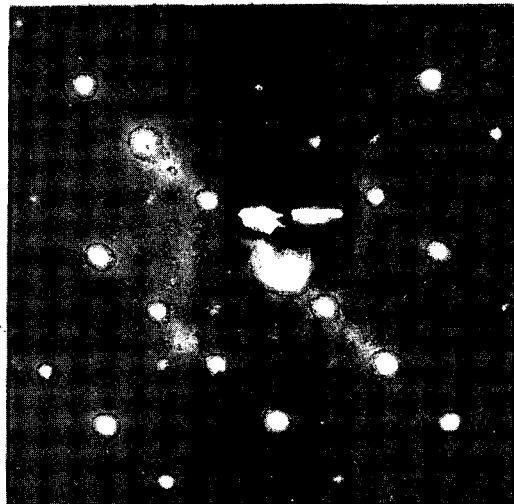
Fig. 2



a



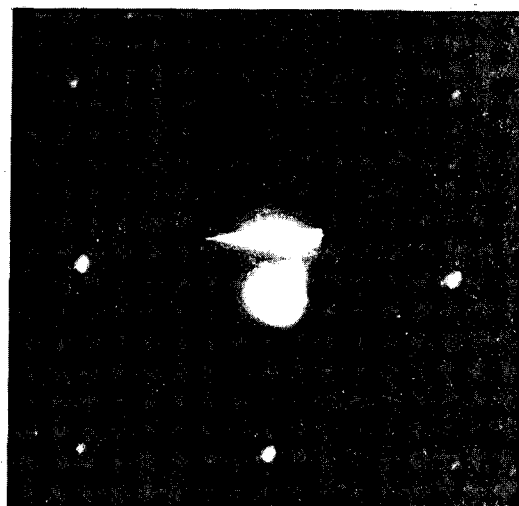
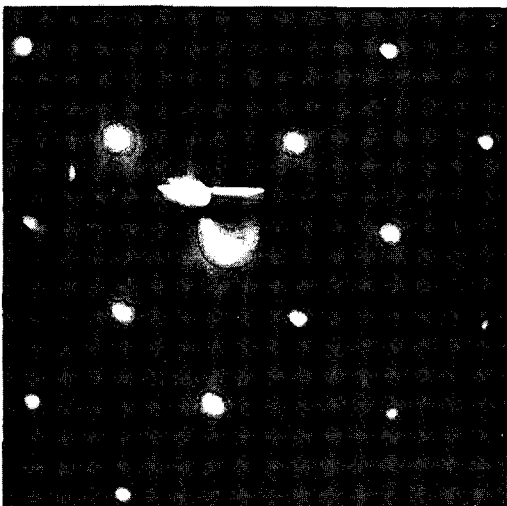
b



c

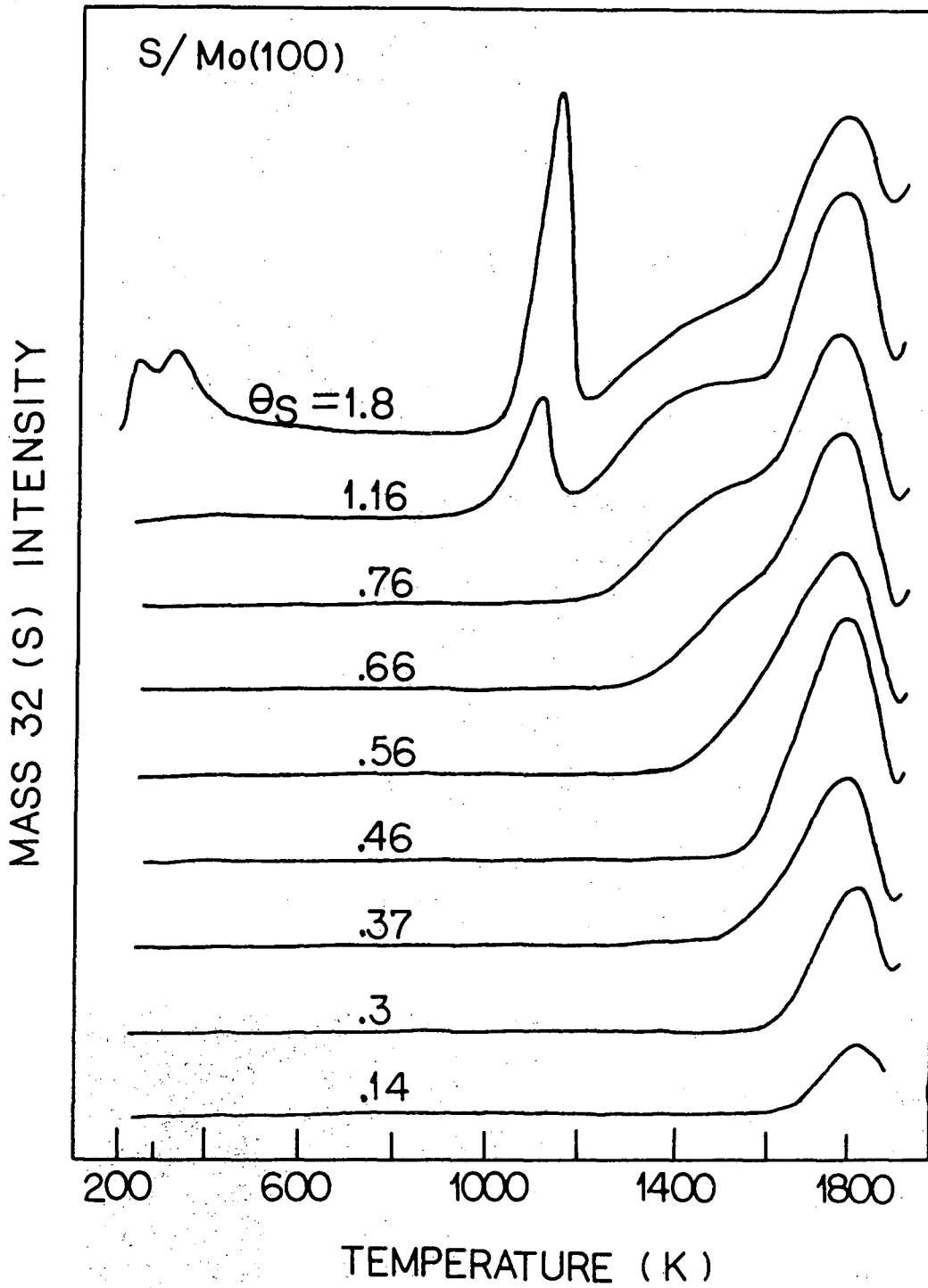
d

e



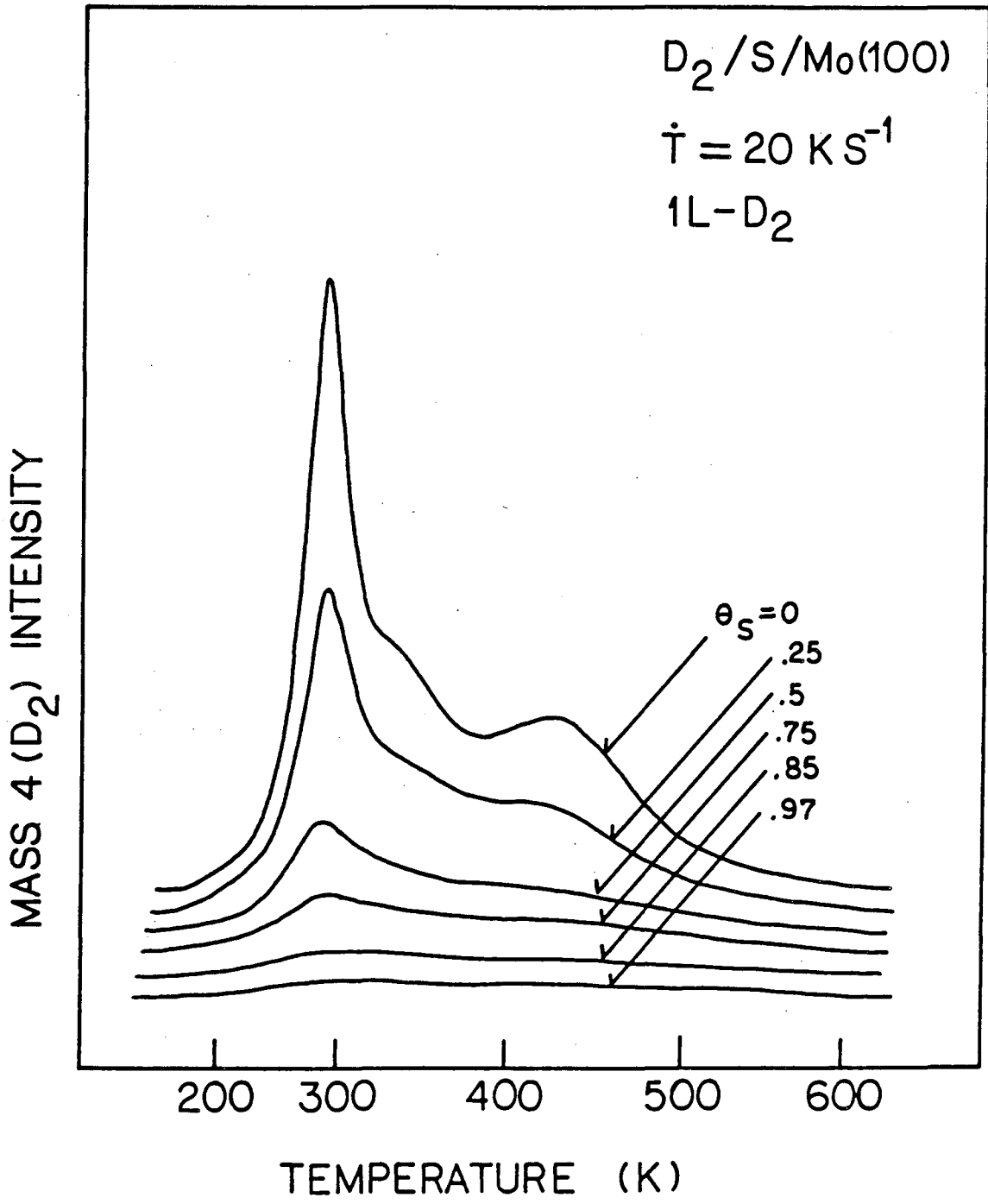
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Fig. 3



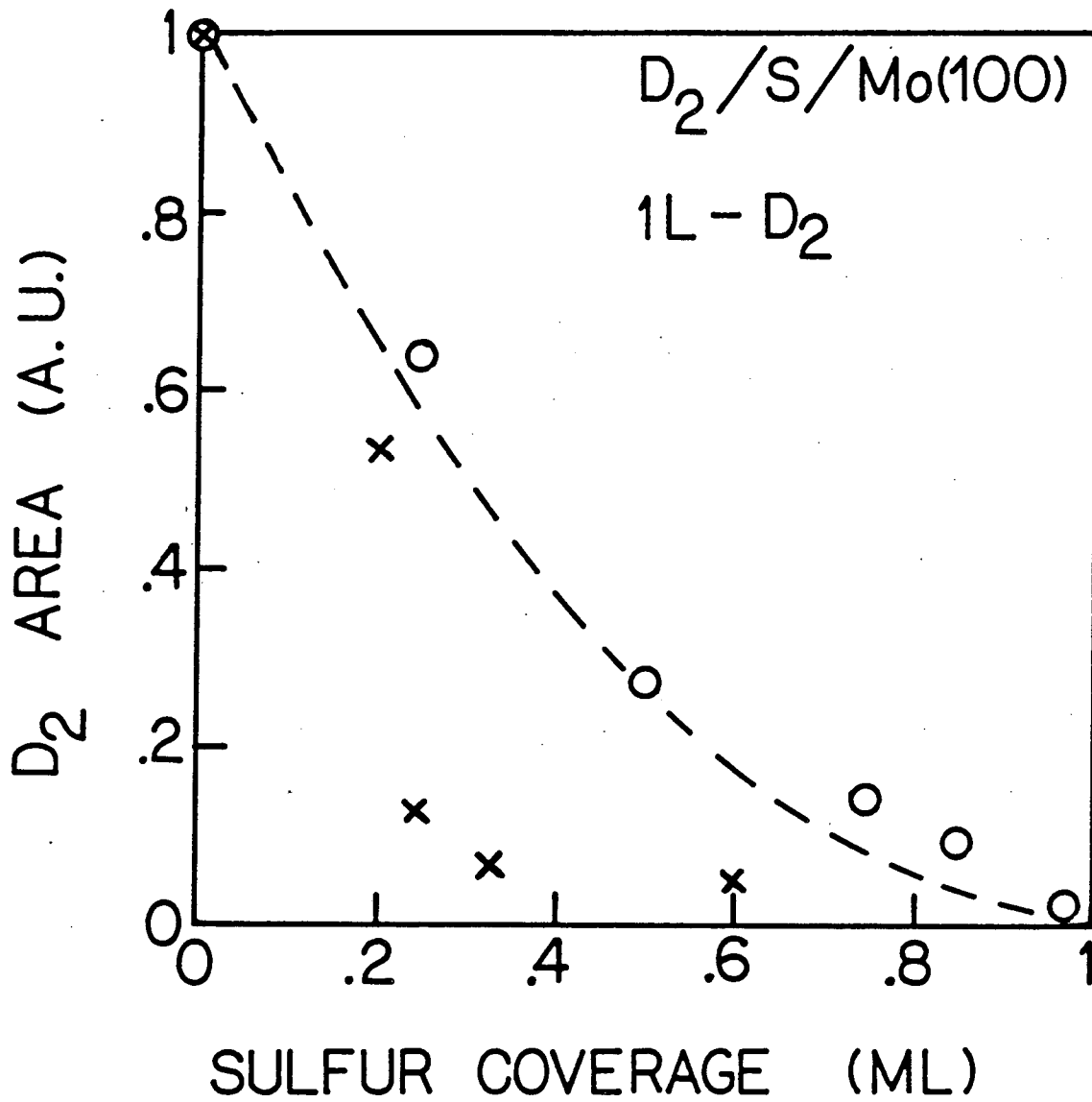
XBL 837-10687

Fig. 4



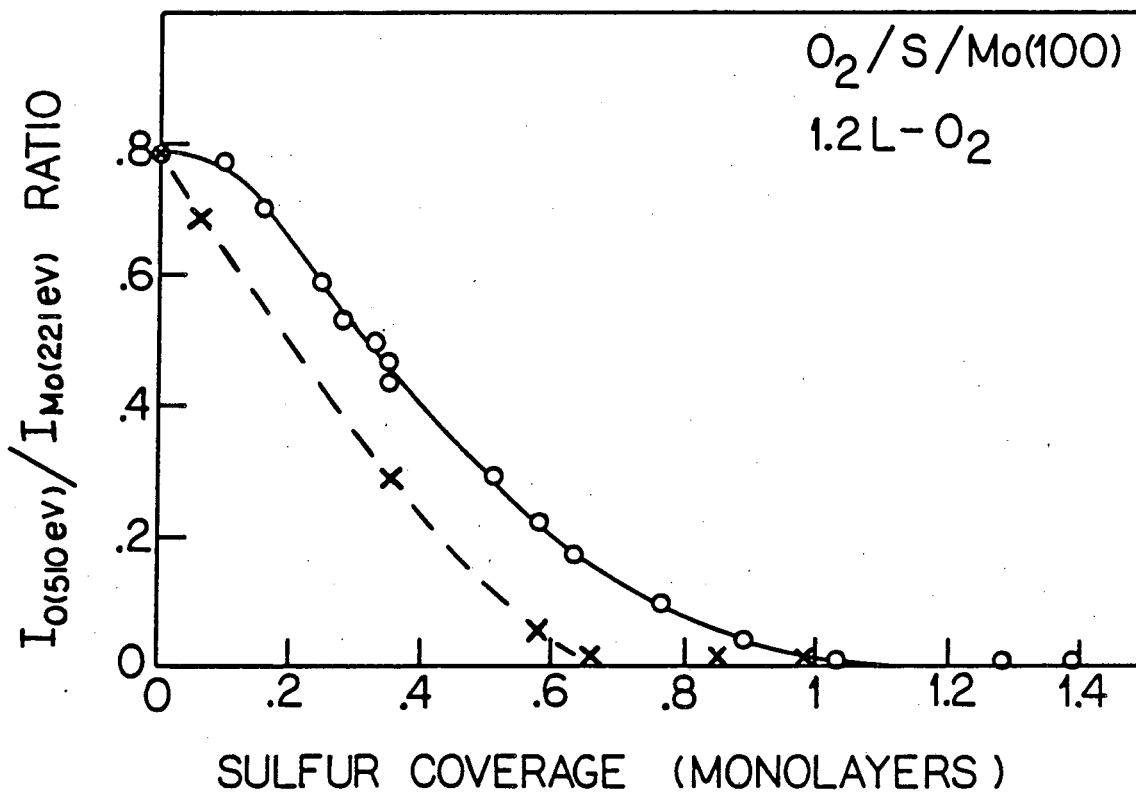
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Fig. 5



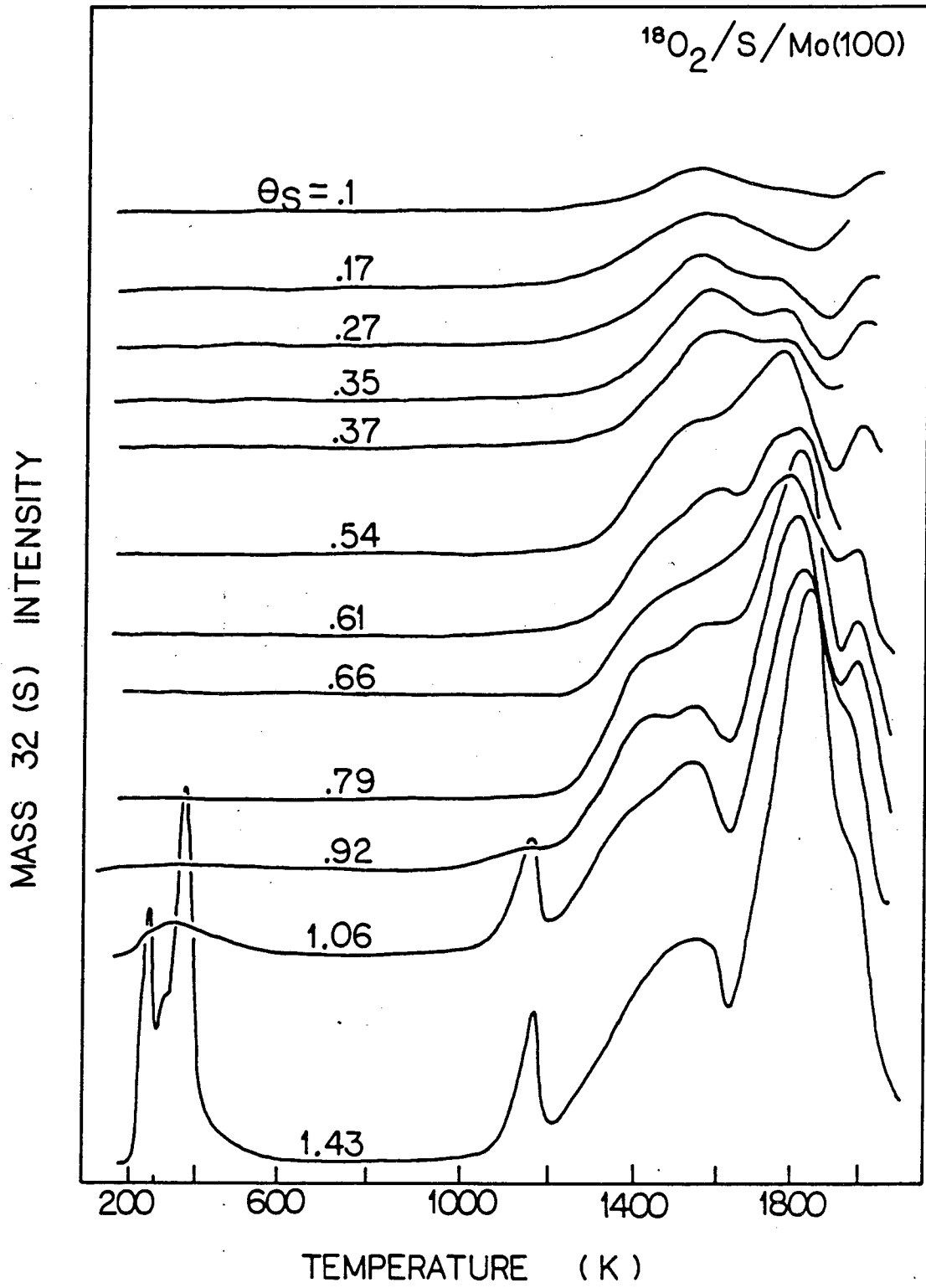
XBL 837-10689

Fig. 6



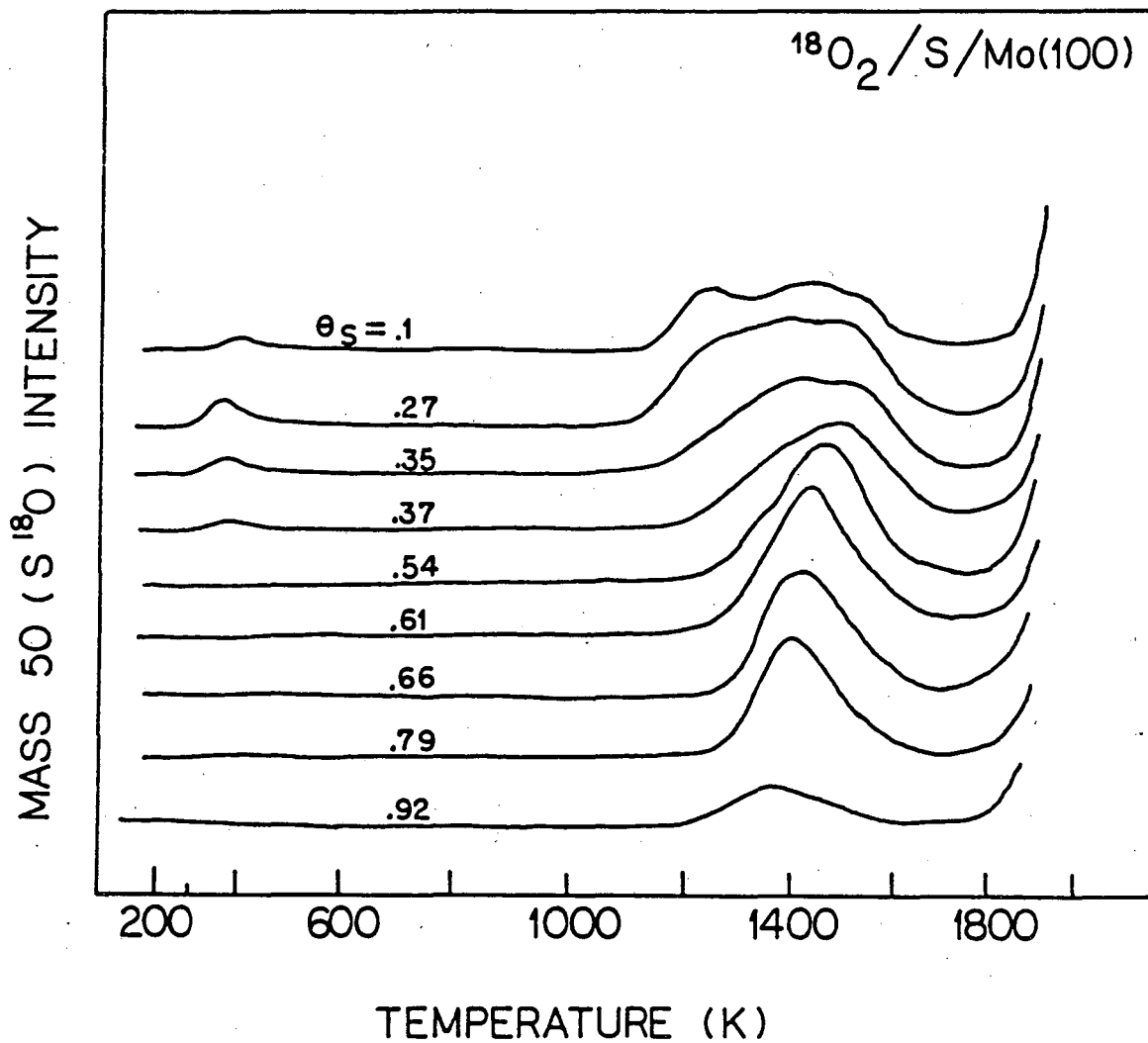
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Fig. 7



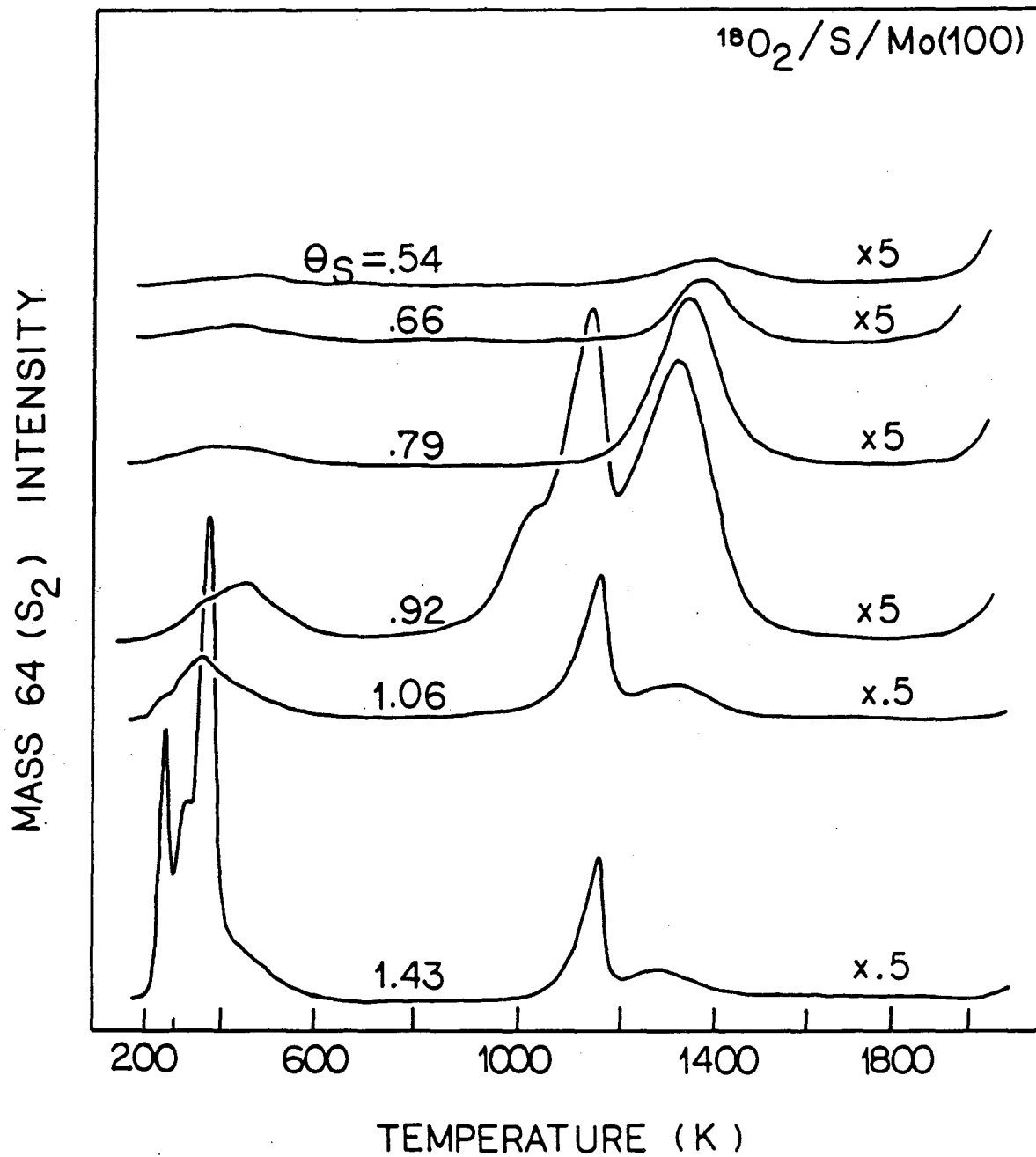
XBL 837-10691

Fig. 8a



XBL 837-10692

Fig. 8b



XBL 837-10725

Fig. 8c

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