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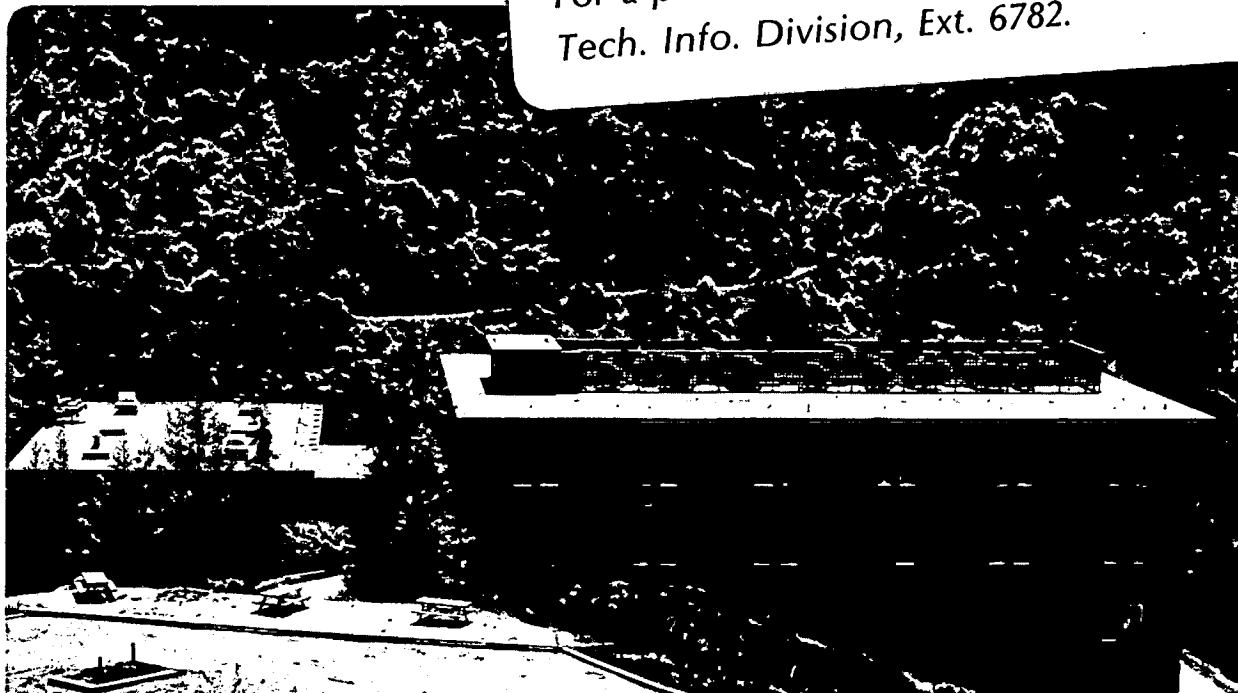
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Title: A Thermal Desorption Study of Thiophene Adsorbed on the
Clean and Sulfided Mo(100) Crystal Face

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A Thermal Desorption Study of Thiophene Adsorbed on the
Clean and Sulfided Mo(100) Crystal Face

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ABSTRACT

The adsorption of thiophene (C_4H_4S) on the clean and sulfided Mo(100) crystal surface has been studied. A fraction of the adsorbed thiophene desorbs molecularly while the remainder decomposes upon heating, evolving H_2 and leaving carbon and sulfur deposits on the surface. The reversibly adsorbed thiophene exhibits three distinct desorption peaks at $370^\circ K$, $240^\circ K$ – $300^\circ K$ and $150^\circ K$ – $180^\circ K$, corresponding to binding energies of 22 kcal/mole, 13–16 kcal/mole and 7–9 kcal/mole respectively. Sulfur on the Mo(100) surface preferentially blocks the highest energy binding site and causes an increase in the amount of thiophene bound in the low binding energy, multilayer state. The thiophene decomposition reactions yield H_2 desorption peaks in the temperature range $300^\circ K$ – $700^\circ K$. We estimate that 50%–66% of the thiophene adsorbed to the clean Mo(100) decomposes. The decomposition reaction is blocked by the presence of $c(2 \times 2)$ islands of sulfur and is blocked completely at $\theta_S=0.5$, at which point thiophene adsorption is entirely reversible.

1. INTRODUCTION

The molybdenum sulfides are widely used to catalyze the hydrodesulfurization (HDS) reactions of sulfur containing molecules. A prototype reaction of this class is the removal of sulfur from thiophene (C_4H_4S). Recent review papers summarize the large body of chemical and catalytic information available on the sulfides and oxides of group VI metals.⁽¹⁻²⁾ It is generally thought that the active component of these HDS catalysts is MoS_2 , and that the active sites for C-S bond breaking are at the edge sites of the basal plane of this layered compound. At these sites the molybdenum ions can exist in a number of different oxidation states.⁽¹⁻⁴⁾

In spite of the large effort devoted to the HDS chemistry of molybdenum sulfides and cobalt-molybdenum sulfides, very little use has been made of surface science techniques in these studies. Therefore, we undertook the detailed investigation of the chemisorption and structural properties of well defined Mo-S ensembles, under ultra-high vacuum conditions, using the surface sensitive techniques of Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Thermal Desorption Spectroscopy (TDS). First, we investigated the adsorption properties of various organic and sulfur containing molecules on the basal plane of a MoS_2 single crystal (6), and found only weak binding. It is not possible to prepare well defined MoS_2 crystal surfaces with large numbers of edge and defect sites. Instead, we have prepared Mo-S ensembles of different geometries by depositing various amounts of sulfur on Mo(100) single crystal surfaces (7).

Several ordered surface structures form as the sulfur coverage increases and it was thought that these structures may act as models for some of the sites present on the molybdenum sulfide catalysts.

In this paper we report the adsorption behavior of the Mo(100) crystal surface when clean and when covered with various amounts of sulfur. Thiophene was used as the adsorbate and thermal desorption was utilized to determine its various binding energies on the Mo(100)-S surfaces. The desorption yielded molecular thiophene and hydrogen that is produced from thiophene decomposition. The increase of the molecular thiophene to hydrogen ratio with increasing sulfur coverage indicates that sulfur blocks the sites where thiophene decomposition occurs. The presence of sulfur on the Mo(100) crystal surface does not change the heats of adsorption of molecular thiophene from those of thiophene bound to the clean surface.

2. EXPERIMENTAL

This study was carried out in two separate ultra-high vacuum chambers, each pumped with both ion and oil diffusion pumps and having a base pressure of 1×10^{-9} torr. Each chamber was equipped with a Low Energy Electron Diffraction (LEED) optics assembly and was capable of performing Auger Electron Spectroscopic (AES) analysis of the surface. Analysis of residual gases and of desorbing species during Thermal Desorption Spectroscopy (TDS) experiments was performed with a UTI quadrupole mass spectrometer.

One chamber was used for the study of reversible thiophene adsorption on the clean Mo(100) surface at low exposures ($\leq 4L$), and for the study of the reversible adsorption of thiophene to the partially sulfided Mo(100) surface. This chamber was equipped with a cylindrical mirror analyzer (CMA) for AES and a doser for the deposition of thiophene. The Mo(100) crystal was spot-welded between two Ta rods and heated resistively. These rods were connected to two copper blocks cooled with liquid nitrogen, thus achieving a temperature range of $150^\circ K$ – $2100^\circ K$. The temperature was measured with a W-5%Re/W-26%Re thermocouple spot-welded to the edge of the crystal.

The other chamber was used to study the reversible adsorption of thiophene to Mo(100) at high exposures ($> 4L$), and the irreversible adsorption of thiophene to both the clean and partially sulfided Mo(100) surface. In this chamber the LEED optics were used in the retarding field mode (RFA) for AES analysis.

Deposition of thiophene was accomplished by introduction into the chamber via a leak valve. The crystal was mounted by spot-welding a Ta wire around its edge. This Ta wire was attached to two copper blocks, again cooled by liquid nitrogen, allowing a temperature range of 110°K–1500°K. The temperature was measured with a Cr–Al thermocouple, spot-welded to the edge of the crystal but away from the Ta heating wire.

Sulfiding of the surface was accomplished primarily by a flux of S₂ molecules (0.2 monolayers/min) produced in an electro-chemical cell.⁽⁵⁾ Other methods included the use of H₂S and the deposition of sulfur via the decomposition of thiophene. In this last case, however, care must be taken to remove the carbon deposited by the process. This can be carried out by heating the sample until carbon dissolves into the bulk of the crystal or by low pressure ($\sim 5 \times 10^{-8}$ torr) O₂ treatment at $\sim 800^\circ\text{K}$.

Calibration of the surface sulfur coverage, θ_s , has been carried out using AES and LEED. We have observed the $c(2 \times 2)$, $\begin{pmatrix} 2\bar{1} \\ 11 \end{pmatrix}$, $c(2 \times 4)$ and $p(2 \times 1)$ structures of sulfur on Mo(100) with increasing coverage, θ_s .⁽⁶⁾ The $p(2 \times 1)$ structure has been defined as the monolayer structure ($\theta_s=1$) corresponding to one sulfur atom per Mo surface atom. We have calibrated θ_s using the S_{150eV}:Mo_{221eV} AES peak height ratios as described in a previous publication⁽⁷⁾. Corrections have been made for the differences observed due to the use of a CMA in one chamber and an RFA in the other for the determination of the AES peak height ratios.

Special procedures were necessary for the introduction of thiophene vapor into the chamber. The compound was frozen, with liquid nitrogen, in a glass bulb. The bulb was evacuated with a mechanical pump and then allowed to warm to room temperature. The bulb was then re-evacuated until the liquid began to boil, thus removing any dissolved gases.

Exposures reported in this paper are in Langmuirs ($1L = 10^{-6}$ torr sec), measured by multiplying the reading of the ionization pressure gauge by the time of exposure to thiophene. This point is important because the ionization gauge sensitivity correction factor for organic molecules differs significantly from unity. A correction has been made for the exposures of thiophene made with the doser so that they correspond to the exposures made using the leak valve.

3. RESULTS

3.1 Reversible Adsorption of Molecular C₄H₄S on Clean Mo(100)

The desorption spectra of thiophene from Mo(100) show contributions from molecularly adsorbed thiophene, and from H₂ produced by the decomposition of irreversibly adsorbed thiophene. Figure 1 shows the desorption spectra of molecular thiophene, deposited on Mo(100) at exposures in the range 0.1L to 15L. These spectra were obtained by monitoring the mass 84 peak, which is the parent peak of the thiophene fragmentation pattern. The spectra show three distinct peaks, two high temperature peaks at 370°K and 240°K-300°K and a low temperature peak that starts at 180°K for exposures of ~4L and drops to 150°K at higher exposures. This indicates several binding sites for molecular thiophene, having different heats of adsorption.

Figure 2 shows the areas under the peaks at 370°K and 240°K-300°K and the total area under the desorption spectrum for exposures up to 4L. It is interesting to note that both the 370°K peak and the 240°K-300°K peak grow simultaneously with increasing exposure, rather than having the high temperature peak, corresponding to the most strongly bound molecular thiophene, saturate before the appearance of the peak at lower temperature. This could be explained by assuming a low mobility of adsorbed thiophene on the surface, and thus little exchange between the high and low energy binding sites. A final point to note about these two peaks is that while the 370°K desorption peak remains at that temperature during increasing thiophene exposure, the

lower temperature desorption peak moves from 300°K at low exposure down to 240°K at 3L exposure.

The lowest temperature desorption peak at <180°K only appears at exposures greater than 4L. At higher exposures this low temperature feature shows desorption peaks shifting to 164°K, 157°K and finally to 153°K at the 15L exposure. The peak at 153°K continues to grow throughout the range of exposures investigated. This peak is due to desorption of condensed thiophene from second and multilayers of the adsorbate.

3.2 Reversible Adsorption of Molecular C₄H₄S on Sulfided Mo(100)

Figure 3 displays the thermal desorption spectra of molecular thiophene from the partially sulfided Mo(100) surface. In these experiments the thiophene exposure was fixed at 1L while the surface sulfur concentration was varied from $\theta_s=0$ through $\theta_s=1.8$. The desorption spectra show the same three peaks characteristic of thiophene desorption from the clean Mo(100) surface.

Figure 4 depicts the areas under the three desorption peaks as a function of sulfur coverage. The peak at 370°K, corresponding to the highest energy binding site, is sharply attenuated by the presence of sulfur. The thiophene desorption peak at 280°K is only attenuated at high surface sulfur coverages. The area under the lowest temperature peak is greatly increased by the presence of sulfur, as is the total area under the desorption spectrum. As will be discussed in Section 3.3, this is due, in part, to the fact that thiophene does not decompose as readily on the sulfided surface as on the clean metal

surface. However, the area of the low temperature desorption peak continues to increase with increasing θ_s beyond the coverage of $\theta_s=0.5$, at which thiophene decomposition is completely blocked. This would seem to indicate that the presence of sulfur on the surface actually enhances the sticking probability of thiophene.

3.3 Irreversible Adsorption of Thiophene on Clean and Sulfided Mo(100) Surfaces

A fraction of the thiophene deposited on the clean Mo(100) is adsorbed irreversibly. Heating of the crystal past the high temperature molecular desorption peak at 370°K results in the sequential evolution of H₂ from the surface and the formation of strongly bound deposits of carbon and sulfur. The coverage of sulfur left on the initially clean surface after the adsorption and subsequent desorption of thiophene (1L) corresponds to $\theta_s=0.15$. As will be discussed in section 4.3 this indicates that a large fraction of the thiophene is adsorbed irreversibly.

Figure 5 shows the desorption spectrum of H₂ from a Mo(100) surface that has been sulfided to varying degrees and then exposed to 1.L of thiophene. The spectrum is characterized by peaks at 340°K, 590°K and 650°K for small θ_s . Two shoulders at 400°K and 530°K are also present and become dominant features as θ_s is increased. The effect of pre-adsorbed sulfur is to reduce the intensity of the peaks at 340°K, 590°K and 650°K until they are no longer observable at $\theta_s=0.5$. The peaks at 400°K and 530°K become negligible at sulfur coverages of $\theta_s=0.7$.

For the purposes of discussion, the peaks have been divided into two regions, grouping the peaks between 300°K and 500°K, and those between 500°K and 750°K. Figure 6 plots two quantities, the peak area in the region between 500°K and 750°K and the increase in sulfur coverage, $\Delta\theta_s$, after each thermal desorption, each as function of initial sulfur coverage. The amount of H_2 evolved in the temperature range 500°K-750°K declines with θ_s in the same way as $\Delta\theta_s$, the amount of sulfur deposited by the decomposition of thiophene. The desorption spectrum of H_2 from the clean Mo(100) surface shows peaks in the temperature range of 300°K-500°K.⁽⁸⁾ It is possible that the peaks in this range in Fig. 5 are due to H-H recombination processes and are in fact caused by contamination by background H_2 during the experiment.

4. DISCUSSION

4.1 Reversible Adsorption of Molecular C₄H₄S on Clean Mo(100)

The desorption spectra of molecular thiophene from clean Mo(100) show three peaks. The high temperature peak appears at 370°K. A lower temperature peak that appears at 300°K for low coverages and shifts to 240°K for high coverages. We have noted that the two binding sites associated with these peaks are populated simultaneously during exposure to thiophene. We attribute this to a low degree of mobility of thiophene on the surface, hindering exchange of molecules between the two binding sites.

The peak at 370°K remains at that temperature throughout the range of coverages investigated, indicating first order desorption kinetics.⁽⁹⁾ With this information and assuming a desorption pre-exponential factor of 10^{13} sec^{-1} we can calculate a desorption energy of 22 kcal/mole.

The second peak moves from a temperature of 300°K at low exposures down to 240°K at an exposure of 3L. This type of behavior can be attributed to either second order desorption kinetics or to a binding energy that is coverage dependent. A plot of $\ln[\sigma T_p^2]$ vs. T_p^{-2} (σ -coverage, T_p -peak temperature) yields a fairly straight line, also characteristic of second order desorption.⁽⁹⁾ However, in view of the fact that this thiophene is probably adsorbed molecularly, and further that we have argued that it has low mobility on the surface, it seems unlikely that desorption is second order. Instead, we suggest that it is a first order process having a coverage dependent desorption

energy. If we assume a pre-exponential factor of 10^{13} sec^{-1} we find a desorption energy of 16 kcal/mole in the limit of low coverage. For the monolayer coverage, which we believe to occur at exposures of 3L, the desorption energy has dropped to 13 kcal/mole.

At exposures of 3L we see the appearance of a third peak at 180°K which shifts down in temperature and grows indefinitely with increasing exposure. The low temperature limit of this peak is 153°K. We assign this feature to the growth of multi-layers of thiophene, until, at very high exposures, bulk thiophene condenses onto the crystal. Using the Clausius-Clapeyron equation and values for the heats of melting and vaporization⁽¹⁰⁾ an approximate thiophene vapor pressure of 10^{-8} torr is obtained at a temperature of 124°K. These two values are within our adsorption conditions and hence the formation of multilayers is possible.

4.2 Reversible Adsorption of Molecular C_4H_4S on Sulfided Mo(100)

The desorption of molecular thiophene from the sulfided Mo(100) surface shows the same three peaks for small θ_s as from the clean surface, but with different relative magnitudes. The high temperature peak at 370°K is clearly attenuated with increasing θ_s indicating a blocking of the high energy molecular binding site. It appears from Fig. 4 that the lower energy binding site, with a desorption peak at ~240°K, is less strongly blocked by small sulfur coverages. This trend of preferential blocking, by sulfur, of the high energy thiophene binding site was observed in other repetitions of the experiment.

The desorption peak at 180°K grows rapidly with increasing θ_S , in spite of the fact that the thiophene exposure remains constant. The increase in the area of this peak is far greater than the corresponding decrease in the area of the 370°K desorption peak, indicating that there is not just simply an exchange of thiophene between these two binding sites. The increase can be attributed in part to a decrease in the amount of thiophene decomposed on the surface. This can be seen from the complementary decrease in the area of the H₂ desorption peak arising from thiophene decomposition. However, the increase in the area of the 180°K thiophene desorption peak continues for sulfur coverages greater than that at which decomposition is completely blocked ($\theta_S=0.5$). This would seem to indicate that the presence of sulfur on the Mo(100) tends to increase the thiophene sticking probability.

It is worth noting that the temperature of this peak is the same as that of the multi-layer desorption peak of thiophene from the clean Mo(100). This may mean that thiophene on the sulfided surface forms aggregates or islands and thus has the same desorption characteristics as the multilayer. If the presence of sulfur facilitates the formation of these islands this could explain the apparent increase in the thiophene sticking coefficient with θ_S .

4.3 Irreversible Adsorption of C₄H₄S on Mo(100)

We have shown in the experimental section that for sulfur coverages below $\theta_S=0.5$ a fraction of the thiophene cannot desorb intact upon heating to 300°K. Instead a series of decomposition reactions take place, resulting in the evolution of H₂ and the formation of sulfur

and carbon containing deposits. The desorption spectrum of H_2 from clean Mo(100) shows peaks at temperatures below $500^\circ K$,⁽⁸⁾ and so it is possible that the desorption peaks at $340^\circ K$ and $400^\circ K$ in Figure 5 are due to H_2 adsorbed from the background. The desorption spectra of H_2 from H_2S on the Mo(100) surface⁽⁶⁾ can be compared to those in Figure 5 to show that S-H bond breaking processes are not rate determining. Most probably, the rate determining steps include C-H, C-C and C-S bond breaking reactions. In experiments in which the sample was annealed after deposition of thiophene the carbon AES peak at 273 eV was observed to change from the "graphitic" form to the "carbide" form in the temperature range $600^\circ K$ - $700^\circ K$. This is the same range in which H_2 desorption is observed.

As can be seen in Figure 6 the amount of sulfur deposited on the surface and the amount of H_2 evolved in the temperature range $500^\circ K$ - $750^\circ K$ due to thiophene decomposition, both decrease linearly as the amount of sulfur initially present on the surface increases. At $\theta_s=0.5$ both go to zero and for higher θ_s the thiophene is desorbed molecularly. Since, for $\theta_s < 0.5$ sulfur is present on the surface in islands having $c(2 \times 2)$ structure we can discuss the desorption of thiophene in terms of two distinct regions of the surface. Desorption from the regions covered by $c(2 \times 2)$ islands of sulfur will be entirely molecular. Desorption from the sulfur free regions will be identical to the desorption from the clean Mo(100) surface.

We can estimate the fraction of the adsorbed thiophene that is decomposed during desorption. This can be done by calculating the amount of thiophene that can be packed onto the surface and comparing

this to the amount of excess sulfur that is left after decomposition. Thiophene is a pentagonal shaped planar molecule. Its dimensions, calculated using gas phase bond lengths and the Van der Waals radii of its various components atoms are: 6.8\AA and $6.1\text{\AA}^{(11)}$ for the maximum and minimum diameters (perpendicular and parallel respectively to the symmetry axis). The thickness is approximately 3.4\AA . For molecules π -bonded parallel to the surface with free rotation about the vertical axis the maximum coverage is 0.25 monolayers, or one thiophene molecule per four surface Mo atoms. Thiophene bonded vertically through the S atom, with rotational disorder can have a coverage of 0.30 monolayers. Since the maximum amount of sulfur left on the clean surface after the decomposition of thiophene corresponds to $\theta_s=0.15$ we can estimate a cracking fraction of 0.50-0.66. Since the decomposition of thiophene requires a fairly large ensemble of Mo atoms this cracking fraction must drop linearly with sulfur coverage to a value of zero at $\theta_s=0.5$, at which point the surface is entirely covered by sulfur in the $c(2 \times 2)$ structure.

5. CONCLUSIONS

Thiophene adsorbed to the clean and partially sulfided Mo(100) crystal face shows three distinct molecular binding states and at least one irreversible, dissociative binding state. The effect of sulfur on the surface is to block the irreversible binding site for $\theta_s > 0.5$ and to preferentially block the highest energy molecular binding site. The lowest energy binding site is common to all surfaces for high thiophene exposures and is probably due to multi-layer growth of thiophene.

These results can be viewed in light of the experimental evidence that hydrodesulfurization takes place at the edge sites of MoS_2 . Completely sulfided Mo(100) does not dissociate thiophene and adsorb it molecularly in a weakly bound state. It is only the partially sulfided surface, having ensembles of bare Mo atoms that is able to dissociate thiophene.

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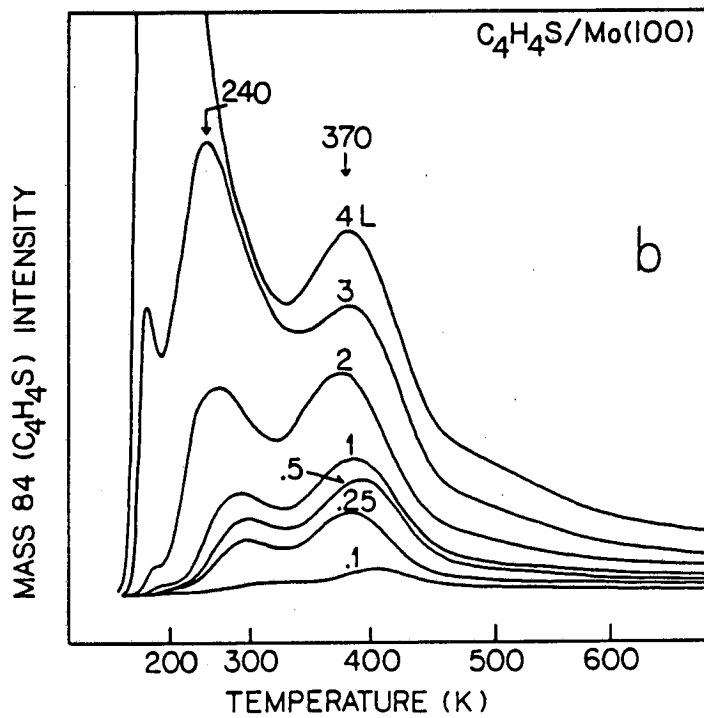
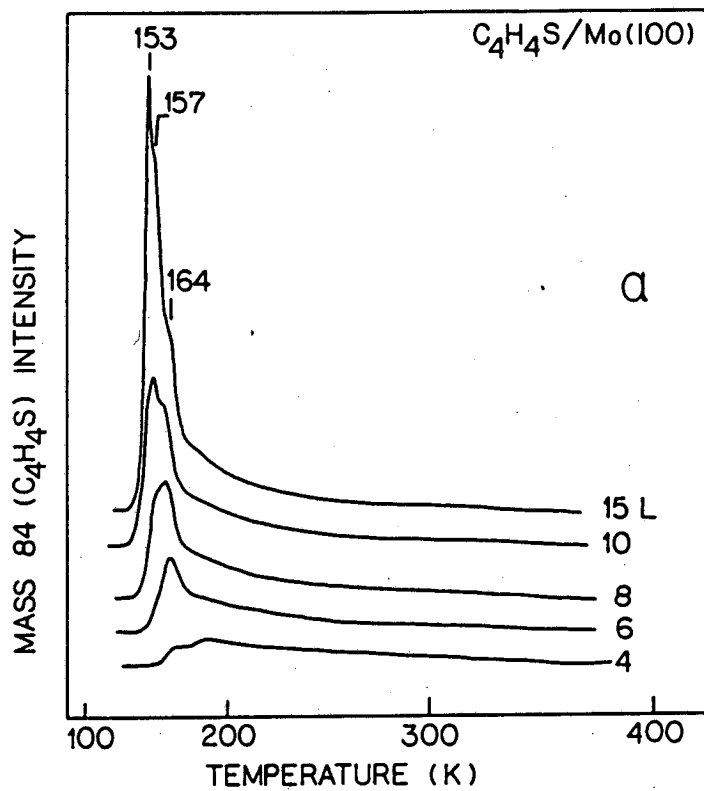
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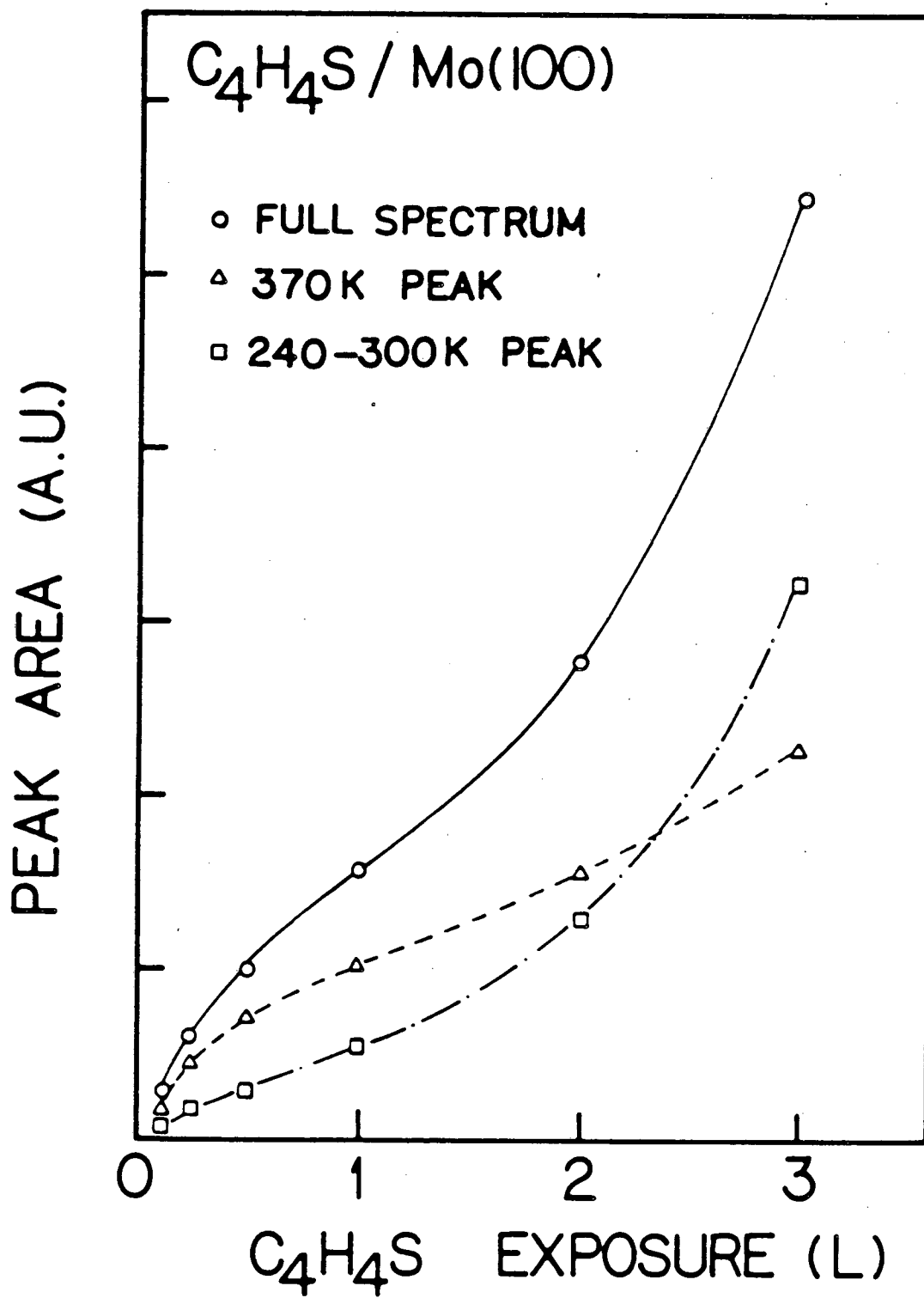
FIGURE LEGENDS

- Figure 1. Thermal desorption spectra of molecular C_4H_4S adsorbed on clean Mo(100). The exposure in Langmuir's is shown with each curve.
- Figure 2. The evolution of the areas of the C_4H_4S desorption peaks from clean Mo(100) as a function of C_4H_4S exposure. The areas are shown for the peaks at $370^\circ K$ and $240^\circ-300^\circ K$, and for the area under the full spectrum.
- Figure 3. Thermal desorption spectra of C_4H_4S from the Mo(100) surface that has been sulfided to varying degrees. The C_4H_4S exposure was always 3L. The sulfur coverage is shown at the right hand side of each spectrum.
- Figure 4. The areas under the three desorption peaks of molecular C_4H_4S are depicted as a function of the initial sulfur coverage of the Mo(100).
- Figure 5. H_2 thermal desorption spectra from the thermal decomposition of C_4H_4S adsorbed on Mo(100). The initial sulfur coverage of the surface is shown to the left of each spectrum. In each case the exposure was 1. L.
- Figure 6. The peak area in the range $500^\circ K-750^\circ K$ in the thermal desorption of H_2 shown in Fig. 5, as a function of the initial sulfur coverage. In the same figure we show the increment of the sulfur coverage due to C_4H_4S decomposition.



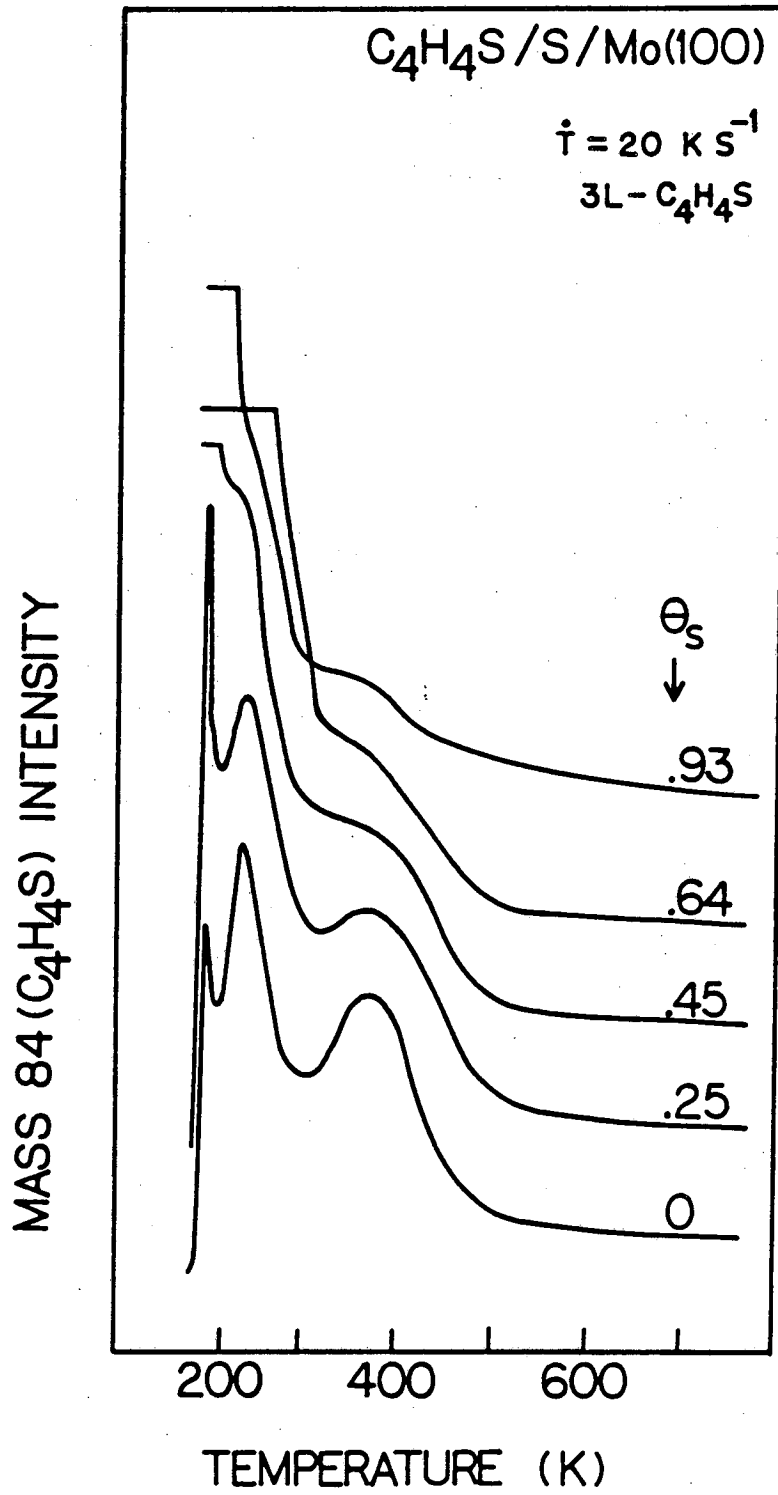
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Fig. 1



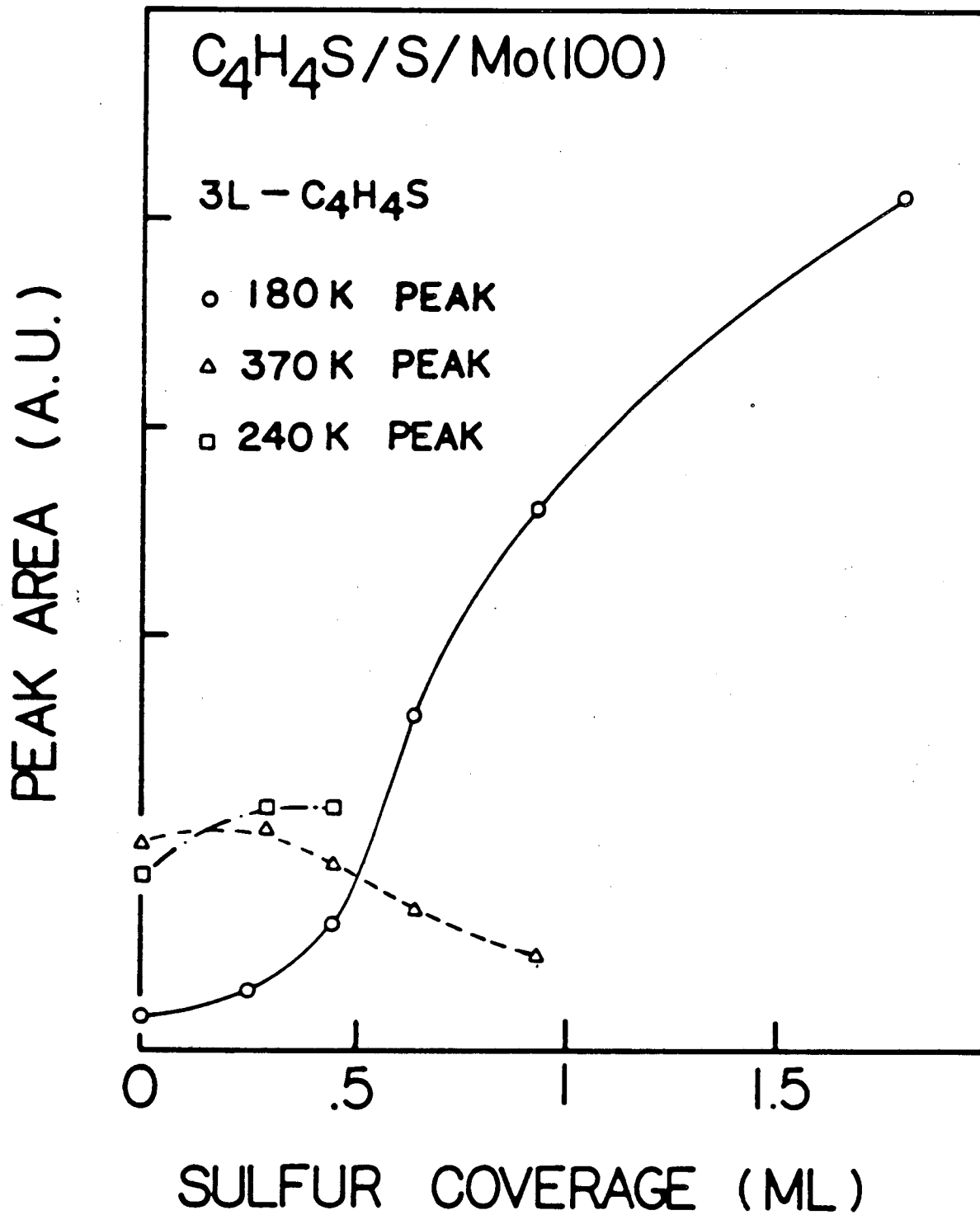
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Fig. 2



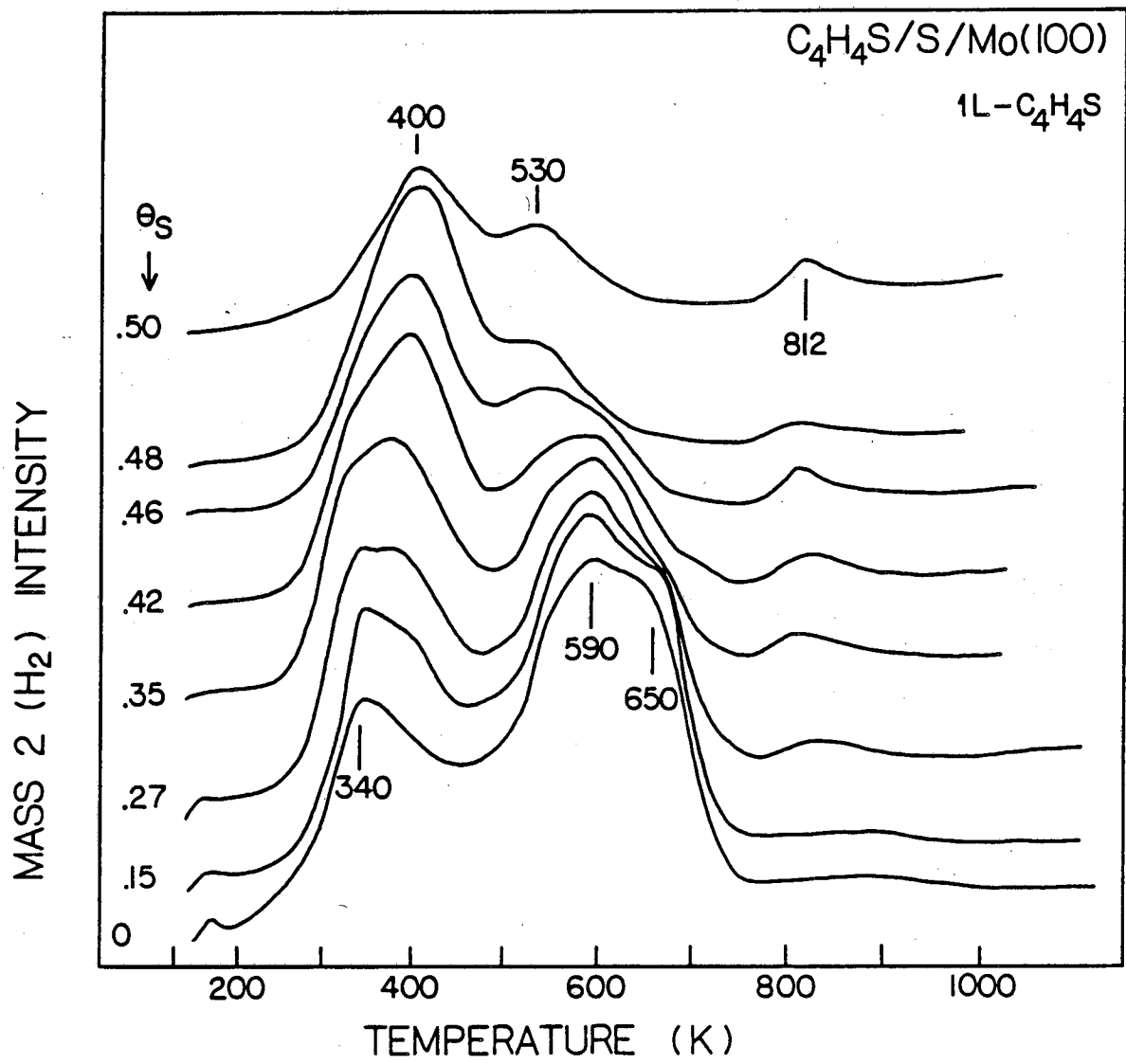
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Fig. 3



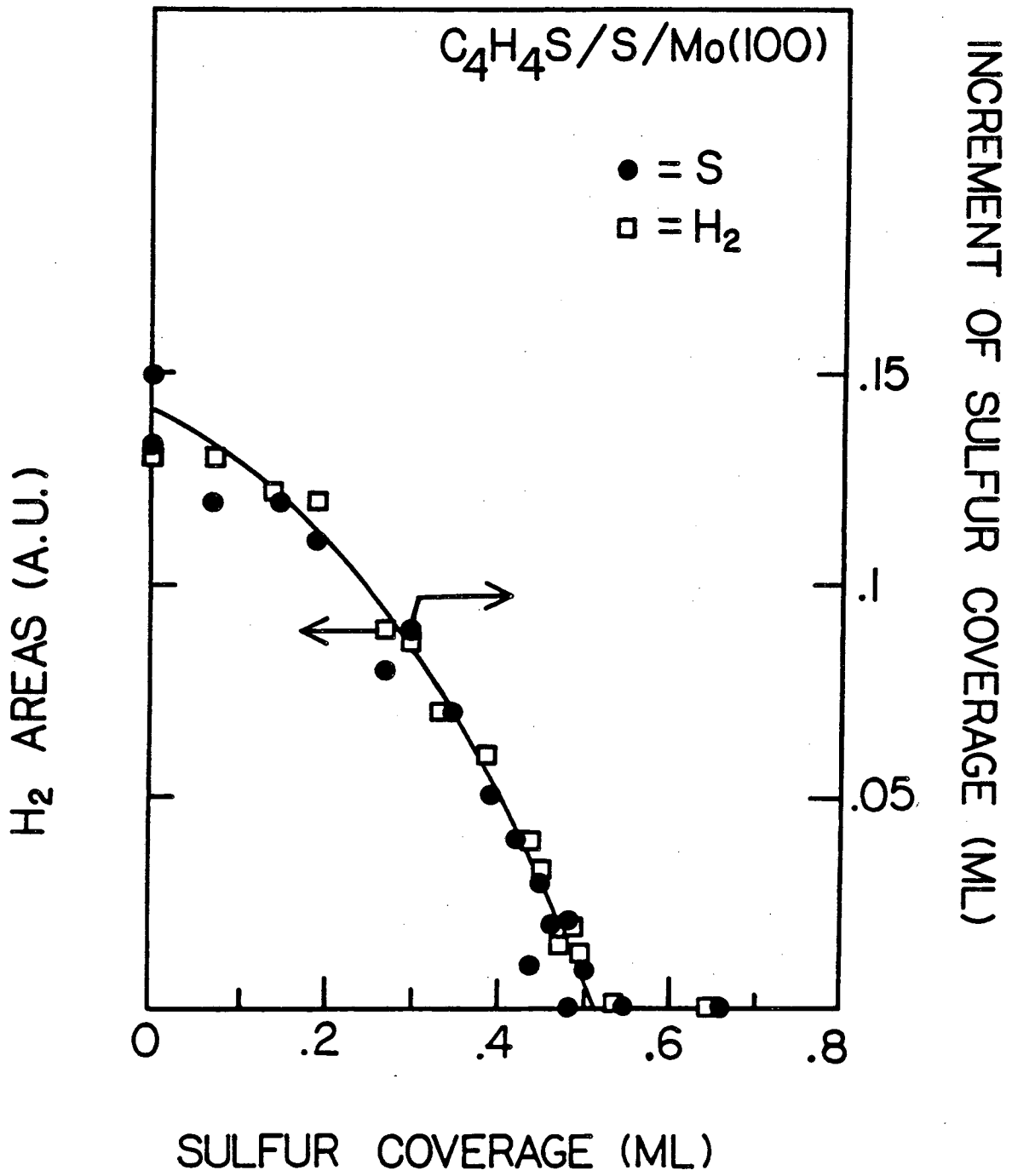
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Fig. 4



XBL 835-9510

Fig. 5



XBL 835-9509

Fig. 6

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