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SURFACE EXTENDED X-RAY ABSORPTION FINE STRUCTURE OF LOW-Z
ADSORBATES USING FLUORESCENCE DETECTION

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Abstract

Comparison of X-ray fluorescence yield (FY) and electron yield surface extended X-ray absorption fine structure spectra above the S K-edge for c(2x2) S on Ni(100) reveals an order of magnitude higher sensitivity of the FY technique. Using FY detection thiophene (C₄H₄S) chemisorption on Ni(100) is studied with S coverages down to 0.08 monolayer. The molecule dissociates at temperatures as low as 100K by interaction with fourfold hollow Ni sites. Blocking of these sites by oxygen leaves the molecule intact.

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Surface extended x-ray absorption fine structure (SEXAFS) and near edge x-ray absorption fine structure (NEXAFS) studies of chemisorbed species on surfaces are usually carried out by means of electron yield (EY) detection¹. Owing to the convenient ultra-high-vacuum (UHV) compatibility of electron detectors and the inherent surface sensitivity of electron detection techniques little effort has been made to use other schemes for measuring the surface absorption coefficient².

In principle, it is well known that the detection of the X-ray fluorescence signal associated with the inner shell excitation of atoms diluted in solids or liquids is a powerful method to obtain their local structure by means of EXAFS³. Recently, fluorescence yield (FY) EXAFS has also been demonstrated to be a useful probe for certain surface problems, i.e. the structure of high-Z adsorbates (e.g. Au) on low-Z substrates (e.g. Si)⁴. However, since the FY strongly decreases with decreasing atomic number Z ⁵, FY detection has been thought to be ill suited for obtaining the SEXAFS of low-Z adsorbates on high-Z substrates. This case is of extreme importance because the interaction of low-Z molecules with metal surfaces is the heart of heterogeneous catalysis. It is clear that FY EXAFS studies on such systems, if possible, could revolutionize traditional surface science in that they would allow the study of samples under UHV as well as "real" non-vacuum conditions.

Here we report SEXAFS and NEXAFS studies by means of FY detection above the K absorption edge (2,470eV) of sulfur⁶, chemisorbed at submonolayer coverage as atoms or in thiophene (C_4H_4S) molecules on Ni(100). We find that FY detection is not only feasible but, surprisingly, offers an order of magnitude higher sensitivity than any EY detection mode, including Auger

electron yield (AY) detection which had previously proven to be particularly suitable for the S on Ni system⁸. We also find a significantly reduced background in our soft x-ray FY studies as compared to previous FY studies at higher x-ray energies^{3,4}. It is therefore unnecessary to utilize grazing x-ray incidence schemes⁴. NEXAFS and SEXAFS spectra obtained by FY detection are used to study the dissociation of thiophene on Ni(100). We find that the four-fold hollow (FFH) Ni(100) site is responsible for breaking the S-C bond in the thiophene ring at temperatures as low as 100K. Blocking of these sites by O atoms leaves the heterocyclic ring intact upon chemisorption.

Experiments were performed at the Stanford Synchrotron Radiation Laboratory using the "Jumbo" monochromator⁹. With Ge(111) monochromator crystals and storage ring currents of 50mA, we obtained a flux of about 2×10^{10} photons/sec at the S K-edge in a 2x4 mm spot (spectral resolution about 1.5eV). The S K (2.3keV) radiation from the sample was recorded with a proportional counter¹⁰ which was mounted in the horizontal plane, perpendicular to the x-ray beam, and collected a solid angle of 10% of 4π sr. A 12.7 μ m thick Be window (40% transmission) of 5cm diameter was used to separate the UHV sample chamber from the P10 (90% argon, 10% methane) detector gas. The energy resolution of our counter was approximately 1keV and a discriminator window was centered on the S K peak. The NEXAFS and SEXAFS spectra were recorded for 20° grazing (\vec{E} vector close to the sample normal) and 90° normal (\vec{E} in the surface plane) x-ray incidence angles. The Ni(100) single crystal was cleaned by Ar⁺ bombardment and oxygen heat treatments to produce a surface free of C, O, and S within the sensitivity limits of Auger electron spectroscopy. To obtain a sharp c(2x2) LEED pattern from atomic S on Ni(100) the clean annealed surface was dosed with 5 Langmuirs (1 Langmuir (L)

corresponds to 10^{-6} torr*sec exposure) H_2S at 100K and then shortly heated to 420K. Thiophene was adsorbed on the clean or oxygen predosed (20L at 300K, c(2x2) LEED pattern) Ni(100) surface at 100K. All spectra was recorded at 100K.

The c(2x2) S on Ni(100) surface, corresponding to half monolayer (ML) coverage, was used to compare AY⁸ and FY detection. Fig. 1 shows SEXAFS spectra recorded with both techniques at grazing x-ray incidence and using the same data acquisition time (10 sweeps, 2 sec/point). Spectra obtained at normal incidence gave similar results with a reduction in count rate by a factor of 2.5 for both detection modes.

Clearly, the AY and FY spectra in Fig. 1 have comparable signal-to-noise (STN) ratios and analysis of the spectra using the Fourier transform method proved their equivalence. However, the STN ratio is the figure of merit only if the noise of the data is purely statistical. With decreasing concentration of the surface species of interest a sensitivity limit will be set by instrumental noise or structures (INS), e.g. arising from normalization problems, which are independent of counting time. In this case, the criterion of merit is no longer the STN but rather the signal-to-background (STB), defined as the ratio of the edge jump over the signal before the edge. Measurability demands that the STB exceeds the INS. Fig. 1 shows that the FY technique offers an eight times larger STB or sensitivity for S. A similar enhancement is observed at 90° x-ray incidence. This surprising result is due to a much reduced background from the substrate relative to all EY techniques. The background is also significantly smaller than in typical FY measurements at higher x-ray energies^{3,4}. Reasons for the enhanced STB are:

1. In contrast to the Auger peak which sits on a significant inelastic electron background', the fluorescence line has almost no background

originating from inelastic scattering events. The cross-section for inelastic scattering of x-rays is small compared to electrons and decreases with decreasing photon energy, thus being more favorable in the soft than hard x-ray range.

2. The x-ray absorption cross section increases with decreasing photon energy. This enhances the excitation probability of the low Z atom on the surface and decreases the sampling depth in the metal substrate, leading a reduced elastically scattered background.
3. At soft x-ray energies, the condition for Bragg scattering is not fulfilled for most crystalline materials such that the Bragg scattered intensity from the substrate is negligible.
4. Even for disorderd substrates, the elastically scattered intensity is reduced at low photon energies because the short wave vector of the incident radiation reduces the accessible volume in reciprocal space.
5. Energy discrimination and windowing of the characteristic fluorescence line does not suffer from similar interference problems as AY detection which for low-Z atoms is often rendered useless by a superposition of Auger and photoemission peaks^{2, 11}.

We have used the high sensitivity of the FY technique to study the interaction of thiophene with Ni(100). Because such studies involved S coverages of less than 0.1 ML (1 layer of thiophene corresponds to 0.1 ML of S) they are presently not feasible with EY detection. Fig. 2 shows NEXAFS spectra for thiophene chemisorbed on clean and 0 predosed (c(2x2) pattern) Ni(100) recorded at normal x-ray incidence. The spectra have been scaled as indicated to reveal the S coverage which is proportional to the edge jump. As a reference for the edge jump we used the c(2x2) S on Ni(100) surface which corresponds to 0.5 ML coverage. For thiophene chemisorption on clean Ni(100)

an exposure of 1L produces a coverage of 0.08 ML. The NEXAFS spectrum (Fig. 2a) is dominated by a threshold peak A and a broader structure C. For thiophene exposures in excess of 2L another peak B appears which is accompanied by a broader structure D. These structures dominate in the 12L spectrum shown in Fig. 2b which corresponds to a thin multilayer. Heating the sample diminishes structures B and D until they vanish around 180K. At higher temperatures ($T < 600\text{K}$) the spectra, including that for a $p(2 \times 2)$ LEED pattern which develops around 540K, look like that shown in Fig. 2c which was recorded after heating to 270K. When scaled to the same size the 1L (Fig. 2a) and 270K (Fig. 2c) spectra are very similar to each other and to that for $c(2 \times 2)$ S on Ni(100). On the other hand, except for peak A, the 12L multilayer spectrum is almost identical to that for gas phase thiophene¹². The same comparison holds for the corresponding spectra recorded at grazing incidence (not shown). When the Ni(100) surface is precovered with a $c(2 \times 2)$ O layer the NEXAFS spectra for 1L and 12L thiophene exposure at 100K are almost identical and consist of peaks B and D only (Figs. 2d and 2e). These peaks which are characteristic of the thiophene molecule¹² disappear after heating to higher temperatures (Fig. 2f).

The NEXAFS results shown in Fig. 2 suggest that on clean Ni(100) thiophene dissociates at temperatures as low as 100K. The dissociation of the S-C bond is suggested by the absence of resonance B in Fig. 2a. This resonance is known to be characteristic of the S-C bond from the multilayer thiophene spectra (Figs. 2b and 2e), gas phase spectra of various molecules with S-C bonds¹² and from $X\alpha$ multiple scattering calculations¹³. Peaks A and C are associated with S-Ni bonds since they are also observed for the $p(2 \times 2)$ and $c(2 \times 2)$ atomic S overlayers on Ni(100)^{8, 10}. For the oxygen preadsorbed surface only resonances B and D are observed. This and the fact that no S

remains on the surface upon heating (Fig. 2f) unambiguously proves that thiophene does not dissociate on the $c(2 \times 2)$ O covered Ni(100) surface.

SEXAFS measurements on the same 1L samples whose NEXAFS spectra are shown in Figs. 2a and 2d provide further information. Fig. 3 shows their respective Fourier transforms and those of $c(2 \times 2)$ S on Ni(100) and multilayer thiophene. The transform for 1L thiophene adsorbed at 100K is dominated by the same peak as that for $c(2 \times 2)$ S on Ni(100), corresponding to the S-Ni nearest neighbor (NN) distance. Analysis of the polarization dependence of the 1L spectrum reveals that S sits in the FFH site with a distance of 2.22 ± 0.02 Å, indistinguishable within experimental error¹⁴ from $p(2 \times 2)$ ¹⁵ and $c(2 \times 2)$ ^{8, 16} S on Ni(100). In contrast, for the oxygen predosed surface a 1L thiophene exposure shows a peak in the Fourier transform at nearly the same position as the thiophene multilayer and (not shown) thiophene gas¹². Using the known S-C bond length $R = 1.714$ Å in the thiophene molecule as a reference we obtain a distance of 1.71 ± 0.02 Å for multilayer thiophene and 1.74 ± 0.04 Å for 1L thiophene on O predosed Ni(100). This clearly demonstrates that for this latter case the molecule remains undissociated upon chemisorption. Furthermore, the absence of a S-C bond related peak around 1.3 Å in Fig. 3b is direct support for our model of dissociated thiophene on the clean Ni(100) surface.

Our FY NEXAFS and SEXAFS studies suggest the existence of a site-dependent desulfurization process. On the clean Ni(100) surface, S is broken out of the thiophene ring by bonding to FFH Ni sites. This occurs already at a remarkably low temperature of 100K. The dissociated thiophene layer passivates the surface such that with increasing coverage, the molecules remain undissociated in the second and higher layers. For the $c(2 \times 2)$ O precovered surface, O atoms are known to occupy the active FFH Ni sites¹⁶. Thus blocking of these sites prevents thiophene dissociation.

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Figure Captions

- Fig. 1. Auger electron yield and x-ray fluorescence yield SEXAFS spectra above the S K edge for c(2x2) S on Ni(100), corresponding to half a S monolayer. Both spectra were recorded at grazing x-ray incidence. Underneath each spectrum the SEXAFS oscillations after background subtraction are shown enlarged.
- Fig. 2. Fluorescence yield NEXAFS spectra for thiophene on clean and oxygen pre-dosed (c(2x2) overlayer) Ni(100) at various exposures and temperatures.
- 1L exposure at 100K on Ni(100).
 - 12L exposure at 100K on Ni(100).
 - Sample in b) heated to 270K.
 - 1L exposure at 100K on c(2x2) O on Ni(100).
 - 12L exposure at 100K on c(2x2) O on Ni(100).
 - Sample in e) heated to 270K.
- Fig. 3 Absolute Fourier transforms of fluorescence yield (S)EXAFS spectra for four selected cases.
- c(2x2) S on Ni(100); 0.5 ML of atomic S.
 - 1L thiophene on Ni(100) at 100K; 0.08 ML of S.
 - A thiophene multilayer (7 layers) condensed on c(2x2) O/Ni(100).
 - 1L thiophene on c(2x2) O on Ni(100) at 100K; 0.08 ML of S.

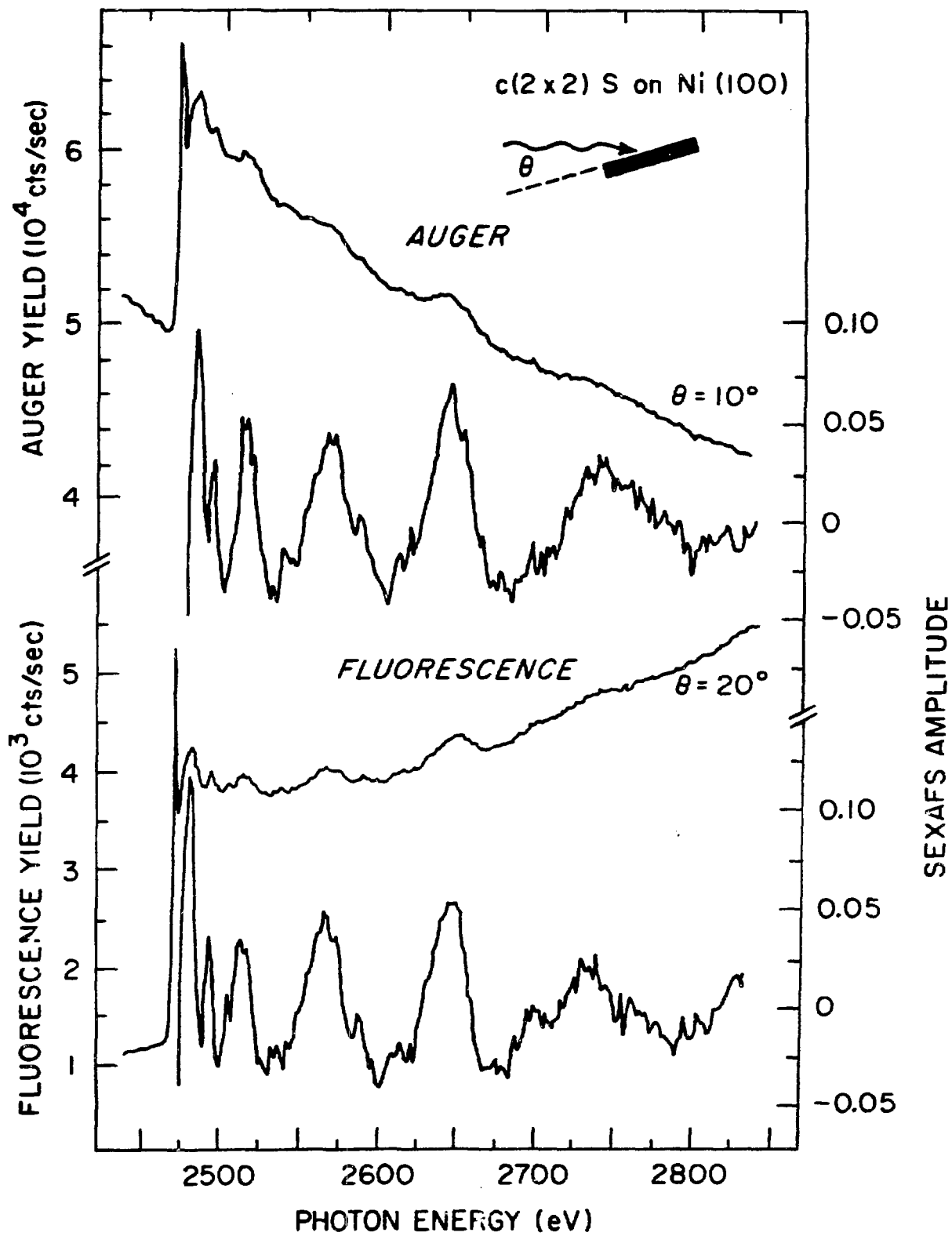


Fig. 1
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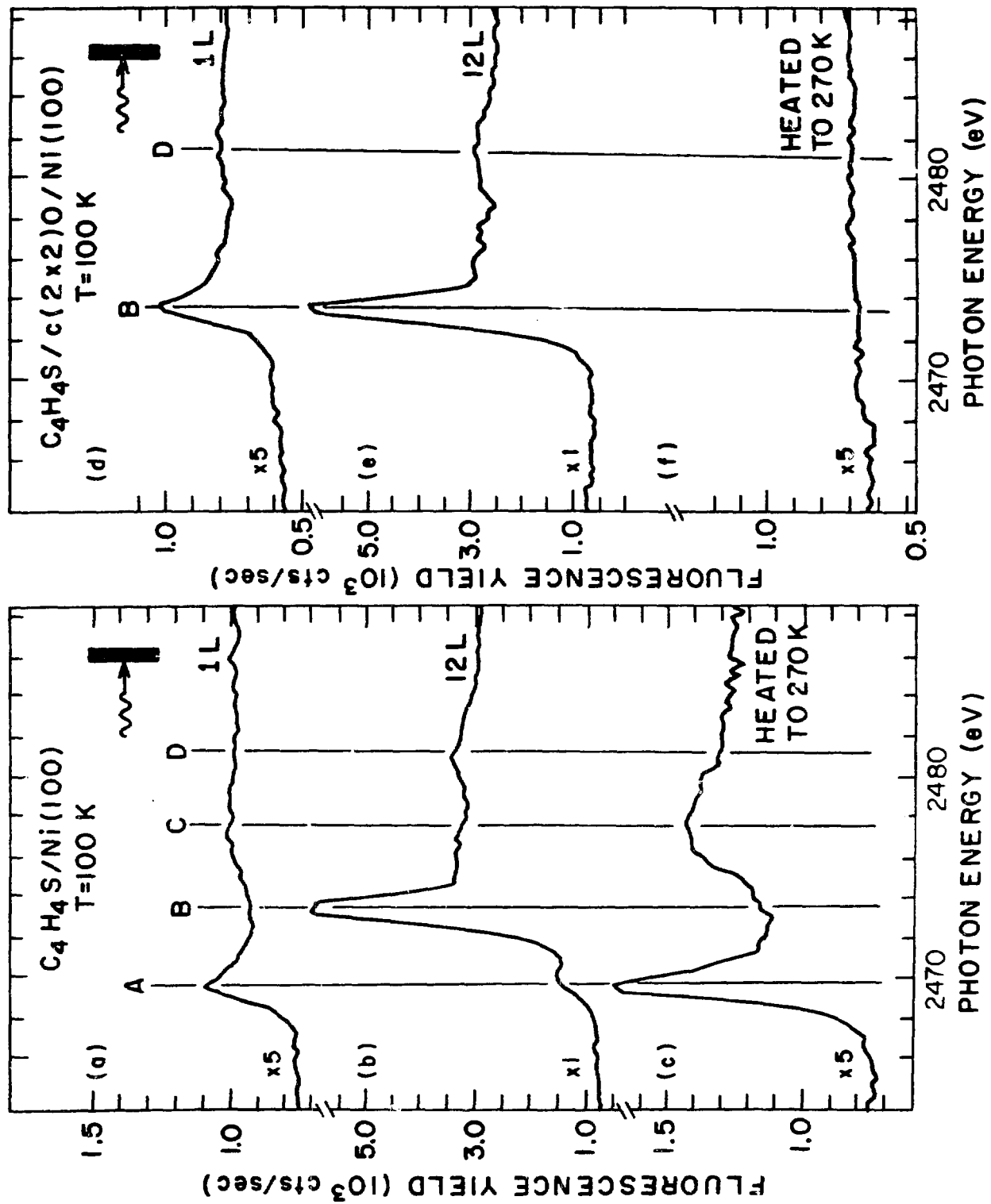


Fig. 2
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