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T. Strunskus, C. Hahn, D. Frankel and M. Grunze

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Degradation of Pyromellitic Dianhydride during XPS analysis

T. Strunskus, C. Hahn, D. Frankel and *M. Grunze

Laboratory for Surface Science & Technology, Sawyer Research Center, University of Maine, Orono, ME 04469 and
*Institut für Angewandte Physikalische Chemie, Universität Heidelberg, INF 253, 6900 Heidelberg, FRG

The degradation of Pyromellitic dianhydride (PMDA) under x-ray exposure has been studied by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Absorption Reflection Spectroscopy (FTIRAS). The data indicate cleavage of the anhydride rings and emission of CO and CO_2 molecules into the vacuum.

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been applied to the study of a wide range of materials under ultra-high vacuum (UHV) conditions. A necessary condition for the unambiguous interpretation of the XPS data is to know if and how the material under investigation is changed during the XPS experiment. Changes can be induced by the x-rays themselves, by secondary electrons emitted from the sample and/or by heat transfer from the x-ray source to the sample.

Pyromellitic dianhydride (PMDA) is an important precursor molecule for the formation of polyimides[1-5] and is known as a strong acceptor molecule in charge transfer complexes[6]. It's high symmetry made it an interesting candidate for ab initio calculations[7-9] and its low hydrogen content for a detailed ^{1}H-NMR analysis[10]. The application of x-ray photoelectron spectroscopy to the investigation of the PMDA molecule has been reported previously[1-5,8]. X-ray induced damage of PMDA has been reported by Kowalczyk et al.[5] for prolonged exposures (> 16 hrs.) to monochromatized Al K_α radiation. In the report at hand we have used a combination of XPS and Fourier transform infrared

absorption reflection spectroscopy (FTIRAS) to analyze the changes of the PMDA molecule during exposure to x-rays.

Figure 1 shows the structural formula for the PMDA molecule which consists of a planar phenyl ring connected to two five membered unsaturated anhydride rings. X-ray structural analysis of crystalline PMDA showed only a slight distortion of the anhydride rings from a planar conformation giving the molecule nearly perfect D_{2h}-symmetry[10].

II. EXPERIMENTAL

For the XPS experiments we have used an Al K_α x-ray source (1486.6 eV) and a hemispherical electron analyzer (Leybold Heraeus EA 11). The measurements were done at an emission angle of 85° with respect to the surface. The x-ray source was run at 10 kV and 20 mA. Data acquisition was done at 100 eV pass energy. Acquisition time was 120 s (2 scans) for each spectrum with the O1s spectra taken first. The binding energy was referenced to the Pt 4f doublet at 70.9 and 73.3 eV.

PMDA (Aldrich Gold Label, zone refined) was loaded into a Knudsen cell (100 μm hole) and kept under vacuum until evaporation. The sample was a Pt(111) single crystal cleaned by cycles of sputtering and heating in O_2 at 1000 K. For evaporation of the PMDA, the sample was cooled to 250 K and the pre-heated (425 K) Knudsen cell was transferred from a side-arm through a gate valve into the main chamber. Evaporation times were 1 and 10 minutes for a "thin" and a "thick film", respectively, during which the pressure rise in the main chamber (base pressure < 2 * 10^{-10} mbar) was in the 10^{-9} range. Using the attenuation of the Pt 4f XPS emission and an electron mean free path of λ=2.9 nm for organic materials at 1400 eV kinetic energy[11], a film thickness of 2 nm is estimated for the thin film, assuming a homogeneous and continuous film. However, island formation of the PMDA on the Pt surface cannot be ruled out, giving rise to a high uncertainty of the thickness of the thin PMDA film. For the thick film the Pt emissions are totally attenuated.

In situ IR measurements were made in a small side chamber connected via CaF_2 windows and grazing incidence optics to a commercial FTIR spectrometer (Mattson Cygnus 100). XPS measurements were done in the main chamber.

III. RESULTS AND DISCUSSION

Figure 2a shows the infrared spectrum (ratioed to the clean surface spectrum) of the thin PMDA film in the 2000 to 800 cm^{-1} region directly after evaporation onto a Pt(111) single crystal. The spectrum in fig. 2b was taken after 3 hours of x-ray exposure. Figure 2c shows the difference spectrum. There are major changes in the IR spectrum after x-ray exposure. The absorption intensity of all bands is decreased and the bandshapes are changed. After X-ray exposure the phenyl ring modes at 1462 cm^{-1}, 1370 cm^{-1}, 1275 cm^{-1} and 1074 cm^{-1} (for mode assignment see ref.1) are hardly distinguishable from the background. The symmetric and asymmetric anhydride ν_{COC} stretches at 1242 cm^{-1} and 934 cm^{-1} respectively, are decreased to about 1/4 of their original intensity and shifted to lower wavenumbers. The decrease in the symmetric anhydride carbonyl stretches between 1870-1844 cm^{-1} and asymmetric carbonyl stretches between 1816-1780 cm^{-1} is less pronounced, but there is a change in the lineshape. Altogether these changes indicate fragmentation in one or both of the anhydride rings of the PMDA molecule. However, some anhydride entities must remain intact since the typical anhydride vibrations are still observed. At least one of the bonds to the central phenyl ring must be broken to account for the decrease in the intensity of the ring modes. However, more drastic changes on the phenyl rings are possible. No additional absorption bands are observed after x-ray exposure, indicating that the fragmented molecule has no new functional groups with strong IR absorption.

The photoelectron spectra for the C1s and O1s emission of the same sample as in fig. 2 are shown in figs. 3 and 4, respectively. The spectra marked with an "a" were taken directly after the infrared measurement (fig. 2a), the "b" spectra were taken after 3 hours X-ray exposure with the sample remaining at the same position. The "a" spectra were

shifted by 0.3 eV to lower binding energy to correct for charging differences and to match up features of the "b" spectra. The "c" spectra are the magnified difference spectra of the "a" and "b" spectra.

The "a" spectra agree very well with XPS spectra for bulk PMDA reported previously[1,3,4]. In the C1s spectrum (fig. 3a) the carbonyl emission appears at 288.7 eV binding energy, the phenyl emission at 284.9 eV. The O1s emission (fig. 4) is also characteristic for bulk PMDA with the broad peak containing contributions from the carbonyl oxygen emission at 531.5 eV and the anhydride oxygen emission at 533 eV. From figs. 3 and 4 it can be seen that there is an overall loss of intensity and broadening of the peaks following x-ray exposure. The intensity loss is predominantly from the carbonyl portions of the carbon and oxygen emissions. This can only be explained by a fragmentation of the PMDA molecule and preferential loss of carbonyl groups either as CO or CO_2 since desorption of the whole molecule should not change relative intensities.

Quantitative analysis of the XPS spectra[4] further supports this conclusion. From the data in Table 1 it can be seen that there is a decrease in the oxygen to carbon ratio from 0.54 to 0.48 compared with the stochiometric ratio of 0.60. Although the absolute error, i.e. comparing experimental with theoretical values, can be quite high (10% to 20%), the relative error, i.e. comparing two experimental values with each other, is found to be too small (about 3% estimated from repeating the integration with different limits and different linear backgrounds) to explain the decrease in the carbon to oxygen ratio. Also the high O/C ratio of 0.95 of the difference spectra indicate an overproportional loss of oxygen compared to simple desorption of PMDA. Analysis of the carbonyl carbon to phenyl carbon ratios again show an overproportional loss of the carbonyl carbon resulting in a decrease of the carbonyl carbon to phenyl carbon ratio.

Under the assumption that the decrease in phenyl carbon intensity is due to desorption of molecular PMDA, the proportional integrals for the carbonyl C1s and total O1s emission can be calculated and subtracted from the total decreases as is done in Table

1. The oxygen to carbon ratio of 1.5 calculated after this subtraction compares to a loss of CO groups (O/C=1.0) or to a loss of CO_2 (O/C=2.0) indicating loss of a mixture of CO and CO_2.

In the fragmentation pattern of PMDA a loss of CO_2 is observed as the first step[12,13]. The signal of the molecular ion (mass 218) is very weak compared to the fragmented molecule (mass 174) indicating the instability of the ionized PMDA molecule. The loss of one CO group should lead to a fragment with mass 190, which is not observed in the mass spectrum[12,13]. Intense signals are also obtained for mass 102 (loss of one CO and two CO_2 molecules) and mass 74 (loss of two CO and two CO_2 molecules).

The decrease in the infrared bands is much more pronounced than the decrease in the XPS carbon and oxygen emissions. Infrared absorbance bands are characteristic of molecular vibrations which are in most cases related to certain functional groups. A decrease in absorbance intensity of an infrared band indicates a depletion of that particular functional group. Breaking a bond in a functional group (in this case in the anhydride ring or in central phenyl ring) is sufficient to reduce the infrared absorption intensity of the characteristic infrared band of this functional group to zero wi' 1out the loss of any material. The XPS emission, however, is characteristic for the amount and distribution of the material within the XPS probing depth. The small decrease in the XPS emissions indicates that most of the organic material remains on the platinum surface. However, the infrared spectra indicate that most of the remaining material has undergone chemical changes and can not be intact PMDA anymore.

The same experiment done for a thick (> 13 nm) PMDA film gave qualitatively the same changes in the IR and XPS spectra and the spectra are not reported here for that reason. However, these results indicate that the changes in the PMDA film are independent of film thickness and are thus not induced by secondary electron emission from the underlying platinum substrate.

CONCLUSIONS

XPS and FTIRAS measurements on vapor deposited thin films of PMDA indicate that PMDA undergoes substantial fragmentation after prolonged x-ray exposure. IR measurements indicate fragmentation of anhydride rings and disruption of bonds connected with the central phenyl ring. Quantitative analysis of the XPS data indicates that this is accompanied by the loss of CO and CO_2 molecules into the vacuum along with a small quantity of sublimated PMDA.

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FIGURE CAPTIONS

Figure 1: Structure formula of PMDA

Figure 2: IR Spectrum of a thin PMDA film on a Pt(111) surface

    a) directly after adsorption at 250 K
    b) after 3 hrs. of X-ray exposure
    c) difference spectrum a-b

Figure 3: C1s photoemission spectrum of a thin PMDA film on a Pt(111) surface

    a) after adsorption at 250 K
    b) after 3 hrs. of X-ray exposure
    c) difference spectrum a-b

Figure 4: O1s photoemission spectrum of a thin PMDA film on a Pt(111) surface

    a) after adsorption at 250 K
    b) after 3 hrs. of X-ray exposure
    c) difference spectrum a-b

Table 1. Integrated Intensities of the XPS Emission Bands[1]

	ΣO	ΣC	O/C	C1s (Ph)	C1s (CO)	C1s(CO)/C1s(Ph)
Theory	6.00	10.00	0.60	6.00	4.00	0.67
Before x-ray exposure	5.37	10.00	0.54	5.89	4.11	0.70
After x-ray exposure	4.23	8.80	0.48	5.49	3.30	0.60
Δ difference spectra	1.14	1.20	0.95	0.40	0.81	2.03
-"PMDA (subl.)"	0.36	0.67	0.54	0.40	0.28	0.70
= emitted fragments	0.78	0.53	1.47	0	0.53	--

[1] quantitative analysis was done as described in [4] and the results are normalized to 10 carbon atoms

PMDA

Fig. 1

FIG. 2

Fig. 5

Binding Energy (eV)

Intensity (arb. units)

a

b

c

x4
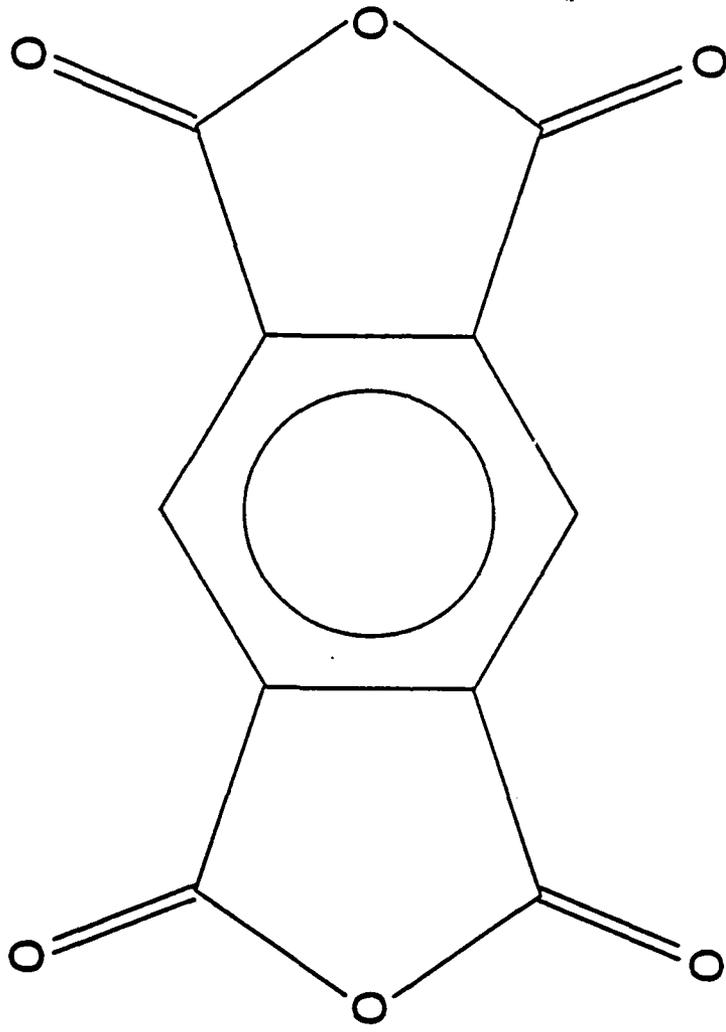
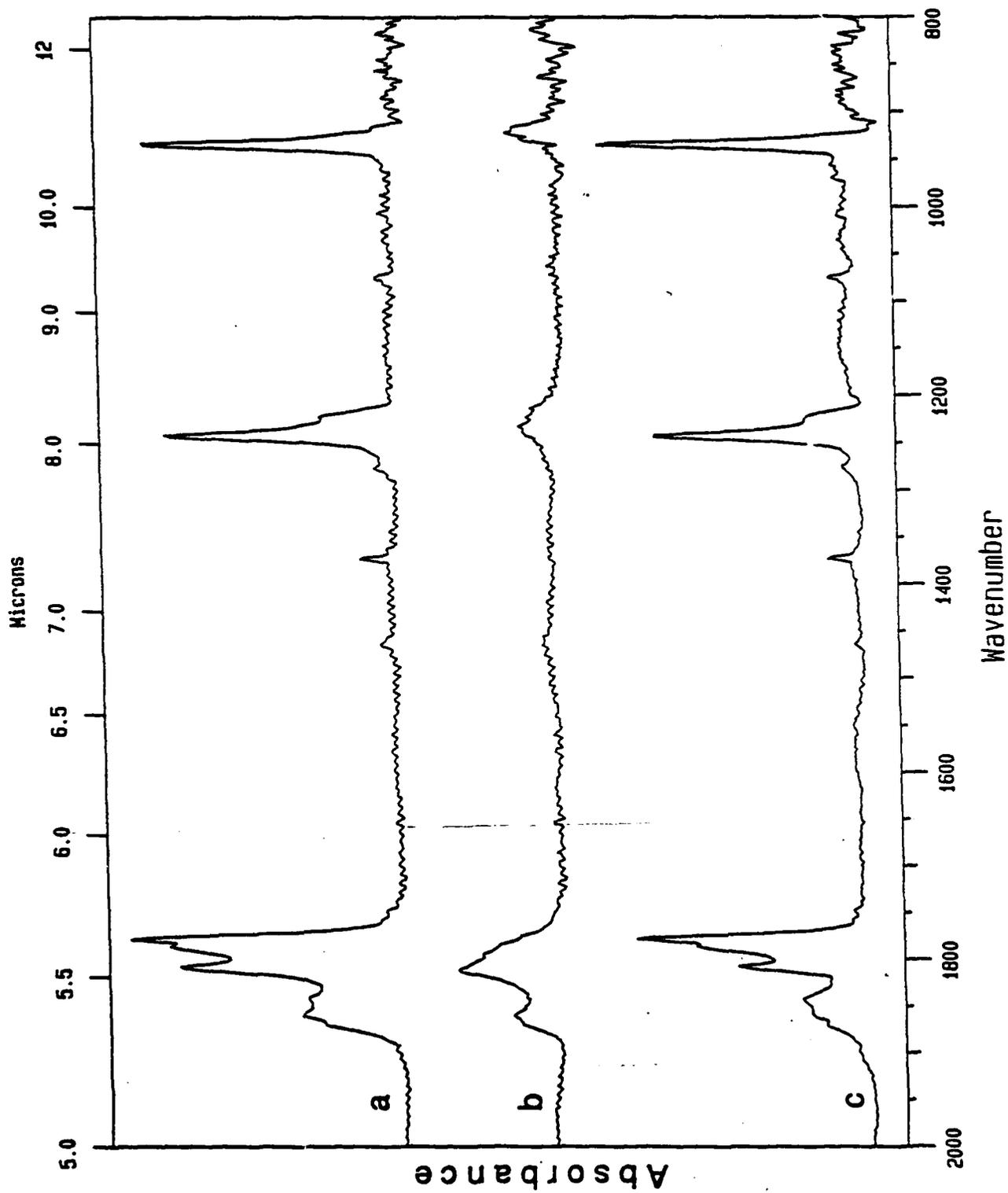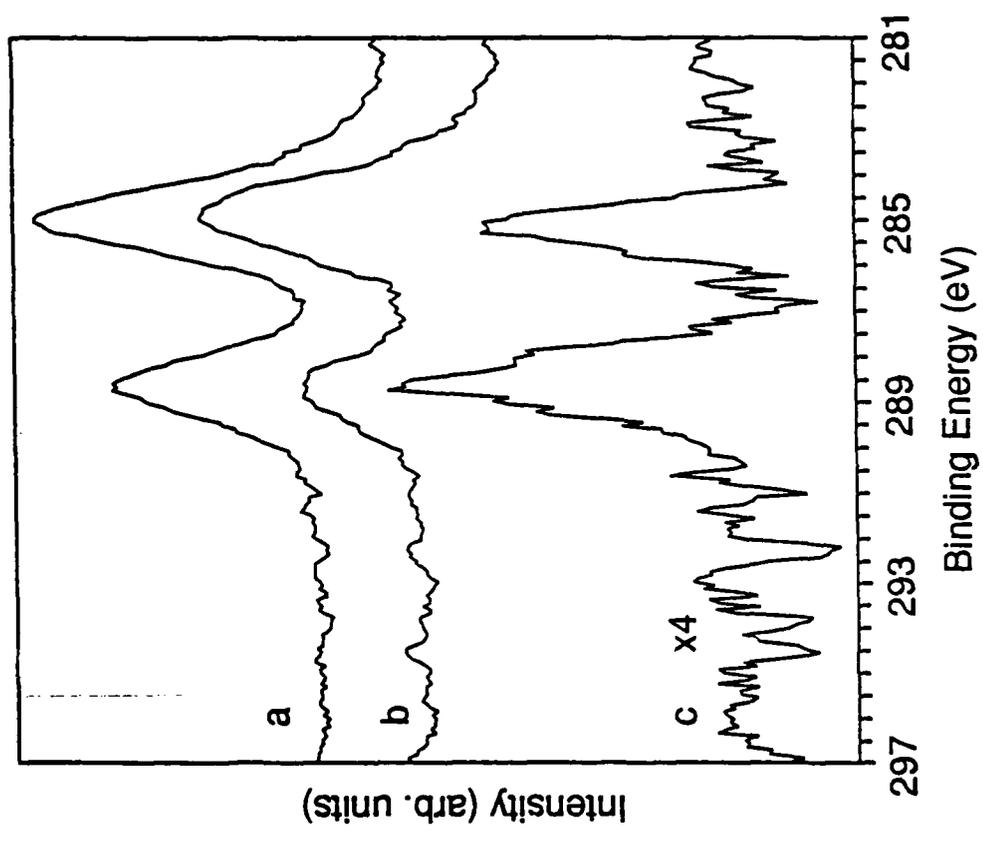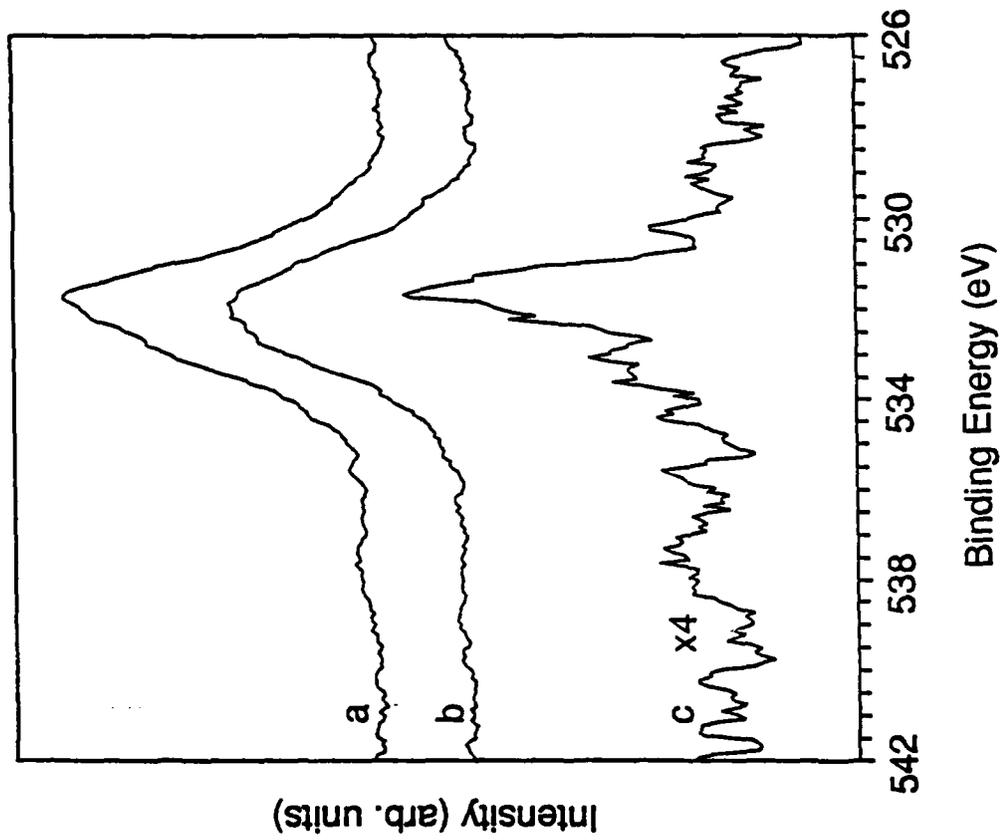## TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

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