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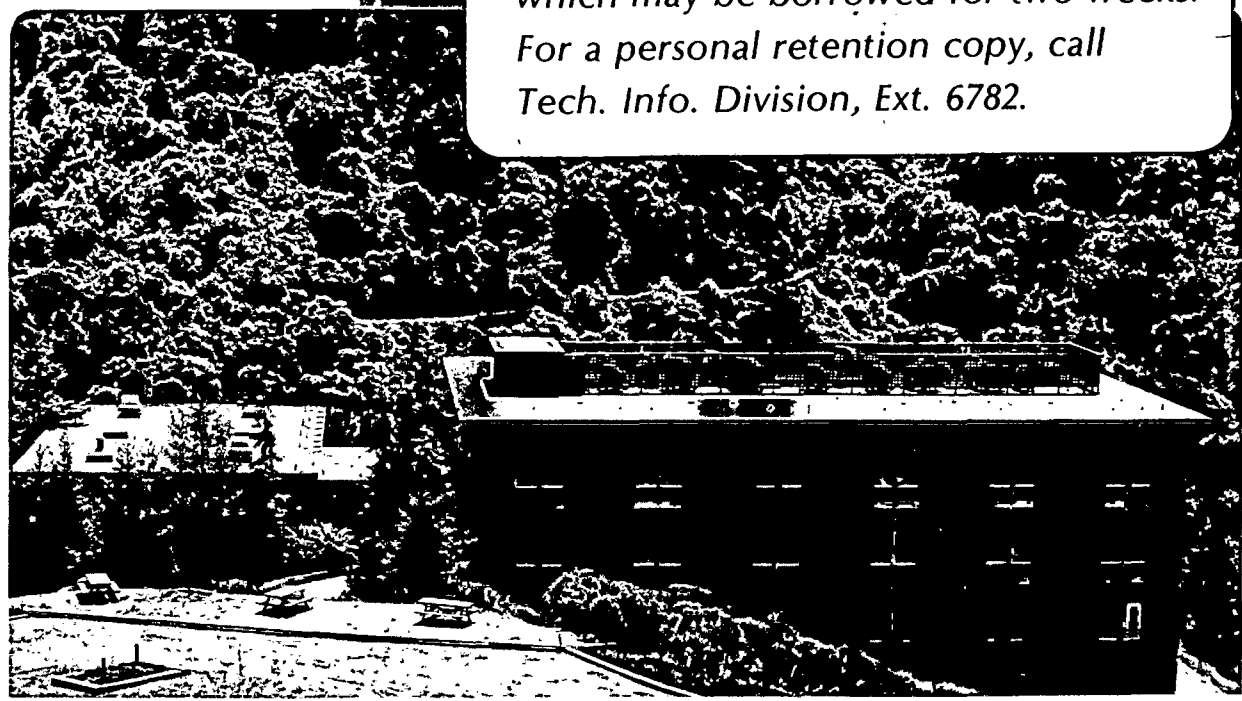
THE INTERACTION OF POTASSIUM WITH π -ELECTRON
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E.L. Garfunkel, J.J. Maj, J.C. Frost, M.H. Farias,
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THE INTERACTION OF POTASSIUM WITH π -ELECTRON
ORBITAL CONTAINING MOLECULES ON Pt(111)

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ABSTRACT

The interaction of co-adsorbed potassium with π -orbital containing molecular adsorbates (benzene, PF₃, NO, C₄H₈, and CH₃CN) on the Pt(111) crystal face was studied by thermal desorption spectroscopy. Co-adsorbed potassium significantly weakened the platinum-benzene bond. More of the benzene desorbed intact upon heating, instead of dissociating to yield H₂ and surface carbon. In contrast, in previous studies it was shown that co-adsorbed potassium substantially increases the platinum-carbon bond strength for adsorbed CO [1]. Adsorbed NO was found to dissociate in an amount proportional to the K concentration, yielding N₂ and N₂O (as well as NO) in the desorption spectra. The adsorption of PF₃, C₄H₈, and CH₃CN was blocked by potassium, and no additional or shifted peaks were observed. A molecular orbital description is given to account for the potassium induced effects. We propose that only adsorbates having molecular orbitals with energy levels located near to E_f can be significantly affected by "electronic promotion" in catalysis.

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INTRODUCTION

The electronic and catalytic effects of alkali metal monolayers have long been observed and documented [2]. On many transition metals and semiconductors, the ability of adsorbed alkalis to lower the work function has led to useful applications [3]. The well known use of alkali metals and oxides as promoters for catalytic reactions [4] such as the ammonia synthesis and the hydrogenation of carbon monoxide has also stimulated many studies of the atomic scale properties of alkali monolayers.

In previous investigations we found that potassium increased the sticking coefficient of oxygen on the Pt(111) crystal face by promoting its dissociation[5]. Carbon monoxide, on the other hand, did not dissociate in the presence of potassium on this surface. Instead, the co-adsorption of potassium caused a 12 kcal/mole increase in the heat of adsorption of CO as well as a decrease in the stretching vibrational frequency to as low as 1400 cm^{-1} [1]. The weakening of the C=O bond can be explained by a potassium induced enhancement in electron backdonation from Pt into the 2π orbital of CO with simultaneous strengthening of the Pt-C bond. On Fe[6,7] and Ni[8] surfaces, potassium has the ability to enhance backdonation to the extent that CO dissociates much more extensively during adsorption at room temperature.

In this paper we report on the interactions of benzene (C_6H_6), phosphorous trifluoride (PF_3), acetonitrile (CH_3CN), 1-butene (C_4H_8), and nitric oxide (NO) with co-adsorbed potassium on the Pt(111) crystal surface. Thermal desorption was the main technique used. We have chosen to study the interactions of these adsorbates with potassium adlayers for insight concerning electronic interactions in chemisorption. For example, Benzene has π electron orbitals which could participate in alkali induced charge variations when chemisorbed.

PF₃ acts as both a σ -donor and a π -acceptor, similar to CO, and thus might exhibit similar changes upon chemisorption with potassium. We find that the presence of potassium on the Pt(111) crystal surface weakens the platinum-benzene bond, while the energy of desorption of PF₃, butene, and acetonitrile remain essentially unchanged with co-adsorbed potassium. Nitric oxide dissociated on potassium adlayers.

EXPERIMENTAL

Experiments were performed in two separate ultrahigh vacuum (UHV) systems with base pressures of 2×10^{-10} torr. Both chambers were equipped with a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) and a UTI quadrupole mass spectrometer, interfaced to a PET/Commodore microcomputer, used for thermal desorption spectroscopy. One chamber contained a 4-grid low energy electron diffraction system.

Platinum single crystals (99.998% purity) cut to the (111) orientation were used in all experiments. Prior to the experiments, impurities were removed by argon ion sputtering, heat cycling to 1000K in 1×10^{-6} torr oxygen, and a final flash to 1400K to desorb any surface oxygen. In the NO experiments, the cleaning procedure used between runs was simply a flash to 1400K. This produced a clean surface as monitored by AES, and exhibited the characteristic hexagonal LEED pattern of Pt(111). In the PF₃ desorption experiments, we observed small amounts of phosphorous (by AES) after desorption. The phosphorous was removed between experiments by treating the crystal at 900-1000K with 10^{-7} torr oxygen, followed by a flash to 1400-1500K to remove excess oxide.

In the experiments with the hydrocarbons a different and effective method of crystal cleaning was used. We found that if we deposited potassium on a carbon contaminated surface, and then exposed it to 5×10^{-7} torr oxygen while

heating the sample to 500K, all traces of carbon were removed. Thus there was no need to oxidize the platinum at high temperatures which often brings impurities to the surface. Potassium dissociates O_2 , and it is this reactive atomic oxygen that readily oxidizes surface carbon. The remaining K_2O was flashed off by heating to 1200K.

Potassium was deposited using a "Saes Getters" source mounted 3 cm from the crystal. Deposition rates were typically 1 monolayer/minute. The potassium monolayer coverage, $\theta_K \cong 1$ corresponds to 5.5×10^{14} K-atoms/cm², or 36% of the density of surface atoms of the Pt(111) crystal face [5].

For each experiment, first potassium was deposited on the platinum surface and the coverage and purity determined by AES [5]. Then the appropriate exposure of a molecular adsorbate was applied via a needle doser. Exposures reported are uncorrected values measured from our ionization gauge. For the TDS experiments, after dosing with the appropriate gas, the sample was resistively heated to 1400K, at a rate of 30 K s^{-1} . The chambers were constructed with the sample mounted 2 cm from the mass spectrometer ionizer such that $\approx 90\%$ of the monitored products come from direct line-of-sight desorption, minimizing the interference of desorption from the chamber walls and pumping speed effects.

RESULTS

1. Benzene (C_6H_6)

The thermal desorption spectra for molecular benzene adsorbed on clean Pt(111) are shown in figure 1a. For higher coverages, these spectra are in relatively good agreement with previously reported results [9], showing two overlapping desorption peaks centered at approximately 375 and 450K. (At lower coverages Tsai and Muetterties [9] show two peaks filling simultaneously; our spectra show the peaks filling sequentially.) Generally, 5-10 L exposures

are required to achieve saturation coverage. The benzene thermal desorption peak shoulder extends to just below room temperature at high CO exposures [9], but cooling was not used in our experiments to detect the desorption behavior in this region.

The benzene thermal desorption spectra for 1 L exposures at several potassium coverages are shown in figure 1b. As potassium pre-coverage is increased, we see a decrease in the temperature of the maximum benzene desorption rate. At first, this decrease is displayed by a broadening on the low temperature side of the peak. Then at moderate K coverages the high temperature edge also shifts to lower energy. At higher coverages, $\theta_K > .4$, benzene could no longer be adsorbed at 300K.

2) Phosphorous Trifluoride (PF₃)

The thermal desorption spectra of PF₃ on clean Pt(111) are shown in Figure 2a. PF₃ exhibits first order desorption kinetics with a peak temperature of ~ 500 K and a FWHM of about 70 K, consistent with results published previously [10]. Figure 2b shows the effect of various potassium coverages on the PF₃ desorption spectra. The amount of adsorbed PF₃ decreases with increasing potassium coverage. The blocking of sites by potassium was such that by $\theta_K = 0.5$ (i.e. 50% of saturation coverage) no more PF₃ could be adsorbed. There also appears to be a slight decrease in the desorption peak temperature (~ 25K), as well as an increase in the FWHM of the peaks from 70 to 130 K with increasing potassium coverage. PF₃ does not appear to adsorb on, or react with, a potassium multilayer. This is indicated both by the negligible amount of PF₃ adsorbed on K multilayers (as evidenced both in AES and TDS) and the K desorption spectra, found to be almost identical to that of clean K overlayers.

3. Acetonitrile (CH_3CN)

CH_3CN desorbed mostly intact from Pt(111) as has been observed in previous studies [11]. Some dissociation occurred upon heating, as was monitored by AES following the thermal desorption cycle. Preadsorbed potassium was found to effectively block sites for acetonitrile adsorption, as was observed for PF_3 and butene, but no shifts in desorption peak temperature or width were detected.

4. Butene (C_4H_8)

The H_2 desorption spectrum (see figure 3), following room temperature adsorption of 1-butene on clean Pt(111), is identical to that of 2-butene [12]. This is thought to be due to the rapid formation of the stable butylidyne species upon adsorption [13]. For a given exposure of 1-butene, much less is adsorbed onto the platinum surface if it is pre-dosed with potassium. This decrease in coverage is not simply proportional to the potassium coverage; small potassium coverages have a large effect. For example a potassium coverage of .5 monolayers (corresponding to an atomic ratio K/Pt of .16) reduces the butene adsorption by a factor of 5 following 10 L exposures. The drop in adsorption is due to physical blocking, not simply a change in sticking coefficient. The second peak in the H_2 TDS curves for the potassium exposed surface appears slightly broadened and shifted to lower temperatures.

5. Nitric oxide (NO)

The NO (mass 30) thermal desorption spectra (see Figure 4a) are in agreement with previous work [14]. Two sequentially filled states at 430 and 340 K are observed in the spectra. In addition, we found that small amounts of N_2 and traces of N_2O were desorbed. The relative distributions of nitrogen containing species which desorb are shown in figure 4b. After each experiment, AES and LEED analysis of the surface showed the presence of small amounts of platinum

oxide [5]. This decomposition of NO is attributable to the presence of defect sites[14] on the (111) surface plane estimated to be $\leq 5\%$ of monolayer coverage. Sharp (2x2) overlayer LEED patterns were observed for NO exposures of > 1 L.

Figures 5a,b and c show the desorption spectra for NO, N₂ and N₂O obtained by varying the initial θ_K and dosing the surface with 1 L NO. The general feature observed with increasing potassium coverage is an increased yield of N₂ and N₂O in the desorption spectra. As θ_K is increased, the intensities of the 340 and 430 K NO desorption peaks rapidly decrease and a broad desorption peak appears between 600 and 700 K. No significant shifts in desorption temperatures of the peaks are noted for the 340 and 430 K desorption states. Figure 5d presents the integrated distributions of N atoms among the NO, N₂ and N₂O species observed desorbing from the surface. The intensity of the NO desorption peak decreasing steadily with increasing θ_K .

Figure 6 shows the integrated distributions of N atoms among the desorbing species for $\theta_K = 0.5$ and NO doses of between 0.1 and 1 L. NO does not become the predominate species desorbing until the initial NO dose is greater than 0.5 L. This coincides with the appearance of the 340 K desorption state in the NO desorption spectra.

DISCUSSION

1. Benzene

A fraction of the benzene adsorbed on clean Pt(111) will desorb intact upon heating, while the remainder dissociates giving off hydrogen. This behavior is also seen on other transition metals and crystallographic faces, but the Pt(111) surface appears unique in its low activity for C-C and C-H bond-breaking[15].

It has been proposed that dissociation of benzene occurs at steps or other defect sites, because of geometric (steric) and/or electronic variations at these sites. We found that all of the adsorbed benzene dissociated upon heating for exposures of up to $\approx .4$ L, and most of the additional benzene desorbed intact up to exposures of 2 L. For exposures greater than 2 L at room temperature the sticking coefficient became zero; presumably the first monolayer was saturated at this point. Thus, our results imply that benzene molecules on the flat Pt(111) surface can readily dissociate upon heating (as well as at step/defect sites) since the amount dissociated is much in excess of the estimated defect site concentration (<5%).

On Pt(111), that fraction of benzene that desorbs molecularly above room temperature yields two peaks in the thermal desorption spectrum at approximately 375 and 450 K. The appearance of these two peaks is not yet fully understood although several interpretations are possible to explain their origin: lateral interactions at high coverages, different surface structures (as revealed by LEED) [16], different sites being occupied (presumably top or threefold) [17], etc.

Much more of the benzene desorbed intact upon heating when the Pt surface was pre-dosed with potassium: this is seen both from the larger thermal desorption peak area as well as the smaller fraction of carbon that remains on the surface (as detected by AES) after heating. In addition, we observed a lower temperature for the benzene desorption rate maximum as potassium is added.

Both the decrease in desorption temperature and the increased amount of molecular desorption imply that the benzene-platinum bond strength is weakened when potassium is present. Several explanations can be proposed. Benzene is thought to be an electron donor in transition metal complexes, with the π -orbital often involved in a symmetric coordination with the metal atom or ion [18].

Thus, one might expect that if the platinum surface is already "electron-rich" due to charge transfer from potassium, the benzene might not be able to donate charge, hence bond, as strongly.

This type of explanation however, is probably too simplistic, and a more complete understanding of the electron energy levels is required to develop even a qualitative model of the potassium induced changes of adsorption. Figure 7 shows the molecular orbital diagram for benzene-chromium [18]. Of interest here are the molecular orbitals involved near the "Fermi level," i.e. the highest occupied and lowest unoccupied molecular orbitals. All of the filled orbitals in the benzene chromium bond are either bonding or non-bonding between the benzene π -ring and chromium d-orbitals. The lowest unoccupied level, however, is "anti-bonding" between the benzene e_{1g} and chromium d-orbitals. Thus, if one electron were added to the system, this electron would fill the $2e$ level, weakening the metal-benzene interaction.

Of course there is quite a difference between a chromium atom and a platinum surface, but we believe that the general character of the bonding is the same: in both cases there is a symmetric coordination to the metal atom(s) and benzene can be considered primarily as an electron donor. For the platinum surface promoted with potassium, the Pt atoms can be considered to increase their electron density in the near surface region as they screen the slightly ionized potassium atoms. This surface polarization also drops the work function, and the platinum should then be able to donate charge more readily to adsorbates. If we assume similar bonding characteristics to the chromium complex, then the lowest unoccupied acceptor level of the benzene-platinum system is anti-bonding between the ring and the metal. Potassium should help populate this level, weakening the metal-ring bond. Another complementary effect would be the inability of benzene to donate charge into the metal if

the population of the 6s Pt level was increased due to the potassium. We feel, however, that this is a minor perturbation in comparison to donation into the anti-bonding level, because the analogous effect of bond weakening was not seen for CO.

2. Phosphorous trifluoride

Adsorbed phosphorous trifluoride was found to desorb intact from both clean and partially potassium covered surfaces at about 500K. The thermal desorption spectra also showed some peak broadening, and a slight decrease in desorption maximum temperature. The lack of a large effect was at first surprising, since we had expected to observe effects similar to those seen for the (K+CO)/Pt(111) system, i.e. a 200K increase in desorption temperature [1].

However, for PF₃ bound to a metal, the σ -donor energy level is located well below E_f at $\approx 8\text{eV}$, while the 2π acceptor level is split into two levels [10], one located 4.5eV below E_f , the other at 4eV above E_f (see figure 8). Thus, the absence of significant potassium induced chemisorption changes in PF₃ could be explained by 1) assuming that the σ donor levels, and the bonding 2π -acceptor levels, are fully occupied prior to potassium coadsorption, and 2) that the nearest unoccupied PF₃ level is too far above E_f to be able to accept electrons from the metal, even upon potassium coadsorption. One explanation for the slight drop in PF₃ desorption temperature is that there could be a decrease in 5σ (PF₃) + s-band (Pt) overlap, resulting from a filling of the 6s Pt band when potassium is adsorbed as mentioned above [10,19].

For CO, which exhibits a large change in bonding when co-adsorbed with potassium, the 2π bonding orbital is located only $\approx 0.6\text{-}2.0\text{ eV}$ below E_f [20]. Here the potassium is able to enhance the d- 2π overlap, which strengthens the M-C bond and weakens the C-O bond (since the 2π level is antibonding

between the C and O atoms)[1]. CO is therefore more sensitive to changes in surface electron density.

3. Acetonitrile

Acetonitrile is known to be σ -bonded to metals via the lone pair orbital of its nitrogen [11]. No accessible back-bonding levels are located near E_f , so there is no possibility of additional charge transfer between the metal and the unoccupied molecular orbitals. Therefore no significant changes in bonding are expected and none were found upon co-adsorption of this molecule with potassium.

4. Butene

The stable structure of alkenes adsorbed on the Pt(111) surface at 300K is thought to be a $R-C \begin{matrix} \nearrow M \\ -M \\ \searrow M \end{matrix}$ species [13]. Thus one does not expect any accessible adsorbate energy levels to exist near E_f since the highest σ -bonded levels are usually 5-15 eV below E_f . The similar shape of the H_2 thermal desorption profiles following butene exposures with and without potassium pre-deposition is therefore to be expected, assuming that metal carbon bonding has an effect on the hydrogen desorption temperature. The changes induced in the second H_2 desorption peak are difficult to interpret and will require more information on the nature of the CH_n fragments believed to be present at these temperatures.

5. Nitric oxide

The general features of non-dissociative NO and CO adsorption on metals are similar. The major difference, for our purposes, is that the gas phase NO molecule has one electron in the $2\pi^*$ antibonding orbital, while CO has none. From other experiments[21], NO was found to react directly with K as observed for NO exposures on K multilayers; hence no K induced NO-Pt changes

could be observed.

Our data indicate, however, that NO was dissociated only in an amount proportional to the potassium coverage on the surface. As seen in Figures 5 and 6, the dissociated NO adsorption state(s) filled first, followed by adsorption into the 340 and 430 K associatively adsorbed states. The undissociated states were not significantly altered in the presence of co-adsorbed potassium as their peak position remained essentially unchanged. On potassium, NO dissociates to N_2 and N_2O , with N_2 dominating [21].

Electron withdrawing additives such as the halogens, sulfur, and oxygen, are also frequently used in catalysis and are being studied by UHV techniques in several laboratories [4,7,22]. Just as potassium and other alkali metals transfer charge to the transition metal which can then backdonate into accessible orbitals of the adsorbed molecules, the withdrawal of charge from the metal by an electron acceptor should also influence the metal-adsorbate bond. However more theoretical and experimental studies are needed to enable accurate predictions of the influence of co-adsorbed electron donors (alkali metals) or electron acceptors (halogens, sulfur, oxygen) on the bonding and thus the reactivity of adsorbed molecules.

CONCLUSION

The bonding of benzene and CO to the platinum (111) surface is markedly altered upon the co-adsorption of potassium. The weakening of the benzene-metal bond and the strengthening of the CO-metal bond by co-adsorbed potassium can be explained by charge transfer into molecular orbitals of the adsorbates with energy levels near the Fermi level, E_f . The absence of significant bonding changes of adsorbed PF_3 , CH_3CN , and C_4H_8 in the presence of potassium is analogously explained by the absence of accessible molecular orbitals for charge transfer within $\approx 2eV$ of E_f .

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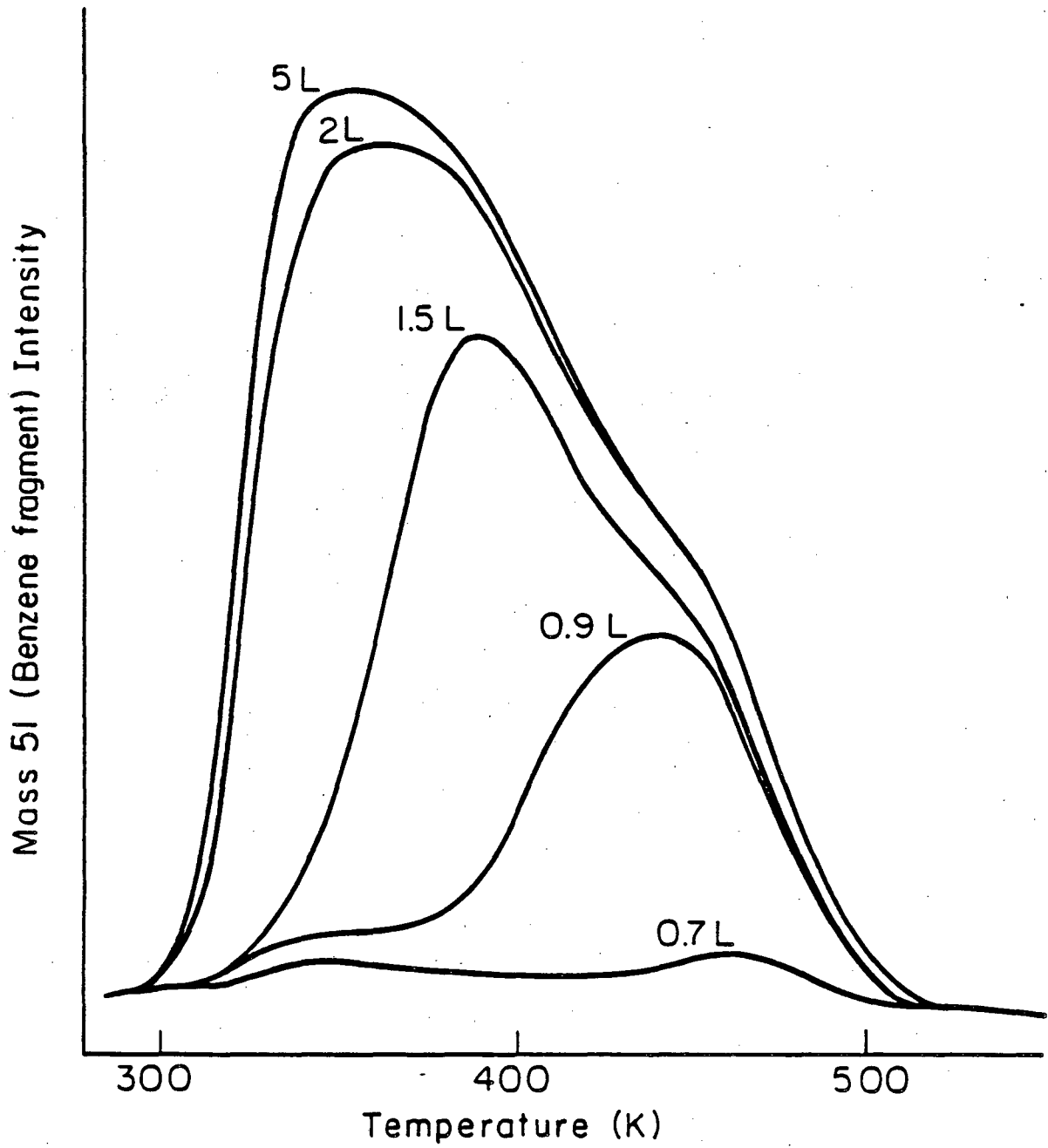
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Figure Captions

- Figure 1: a) Benzene thermal desorption spectra from Pt(111) following several exposures. b) Benzene thermal desorption spectra from Pt(111) following 1 L benzene exposure. (Heating rate \approx 30 K/s). Note that a potassium monolayer (saturation) is defined such that $\Theta_K=1$ and is about 1/3 the atomic density of the platinum surface layer.
- Figure 2: a) The PF₂ (mass 69) thermal desorption spectra for various PF₃ exposures on Pt(111), and b) PF₂ thermal desorption spectra with 1 Langmuir PF₃ exposures on Pt(111) with various coverages of preadsorbed potassium.
- Figure 3: The H₂ thermal desorption spectra following 10 L exposures of butene on Pt(111) with various potassium coverages.
- Figure 4: The NO (a) thermal desorption spectra following various NO exposures on Pt(111). b) The distribution of nitrogen atoms in the desorbing NO, N₂, and N₂O species.
- Figure 5: The NO (a), N₂ (b) and N₂O (c) thermal desorption spectra following 1 Langmuir NO exposures on the Pt(111) surface with various coverages of preadsorbed potassium. d) The distribution of nitrogen atoms in the desorbing NO, N₂, and N₂O species.
- Figure 6: The distribution of nitrogen atoms in the desorbing NO, N₂, and N₂O species for $\Theta_K=0.5$.
- Figure 7: Molecular orbital correlation diagram for dibenzene-chromium.
- Figure 8: Approximate positions of orbital energies for PF₃. Both gas phase and chemisorbed (or complexed) positions are given.

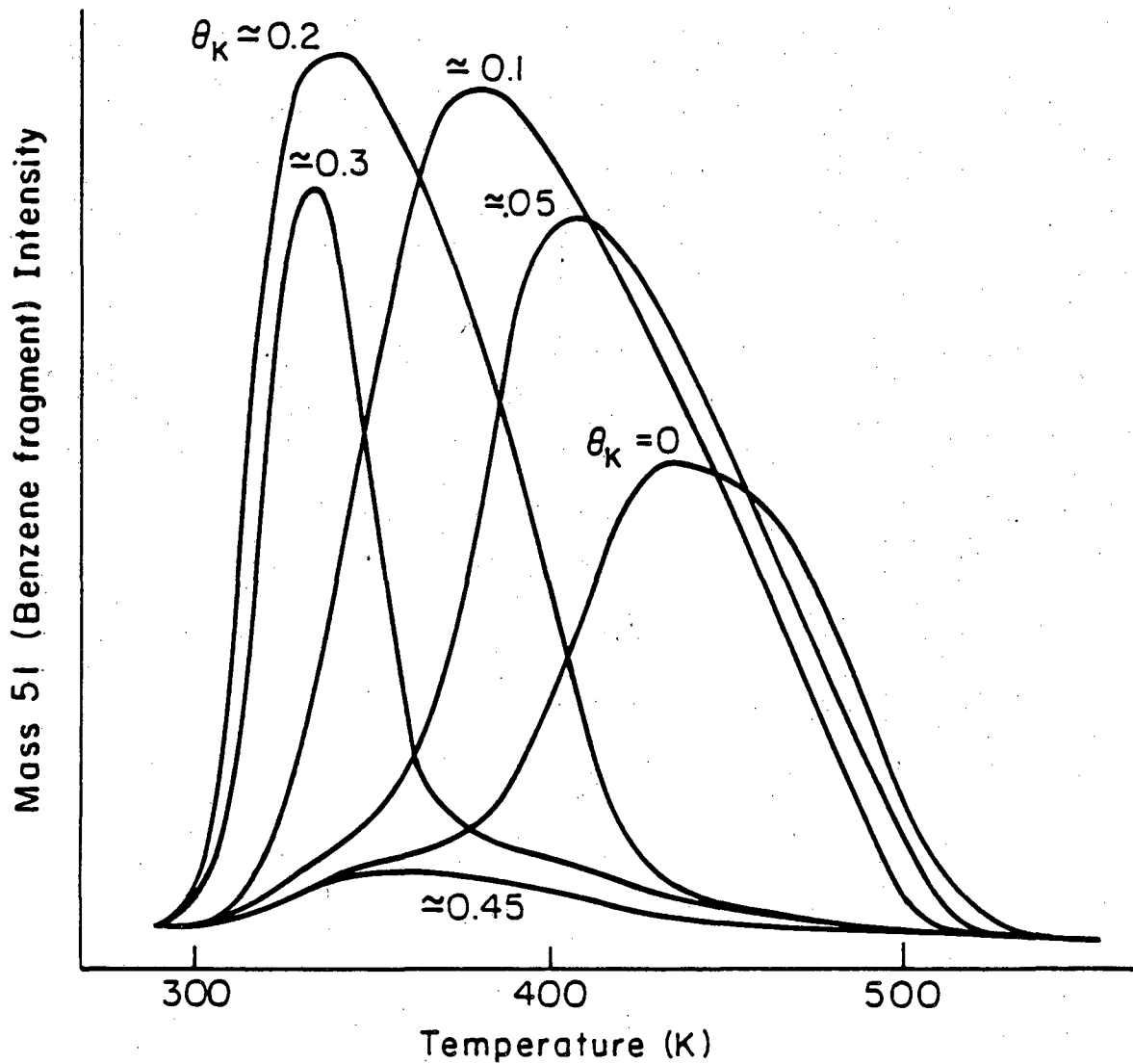
Benzene Thermal Desorption from Pt(III) Following Several Exposures



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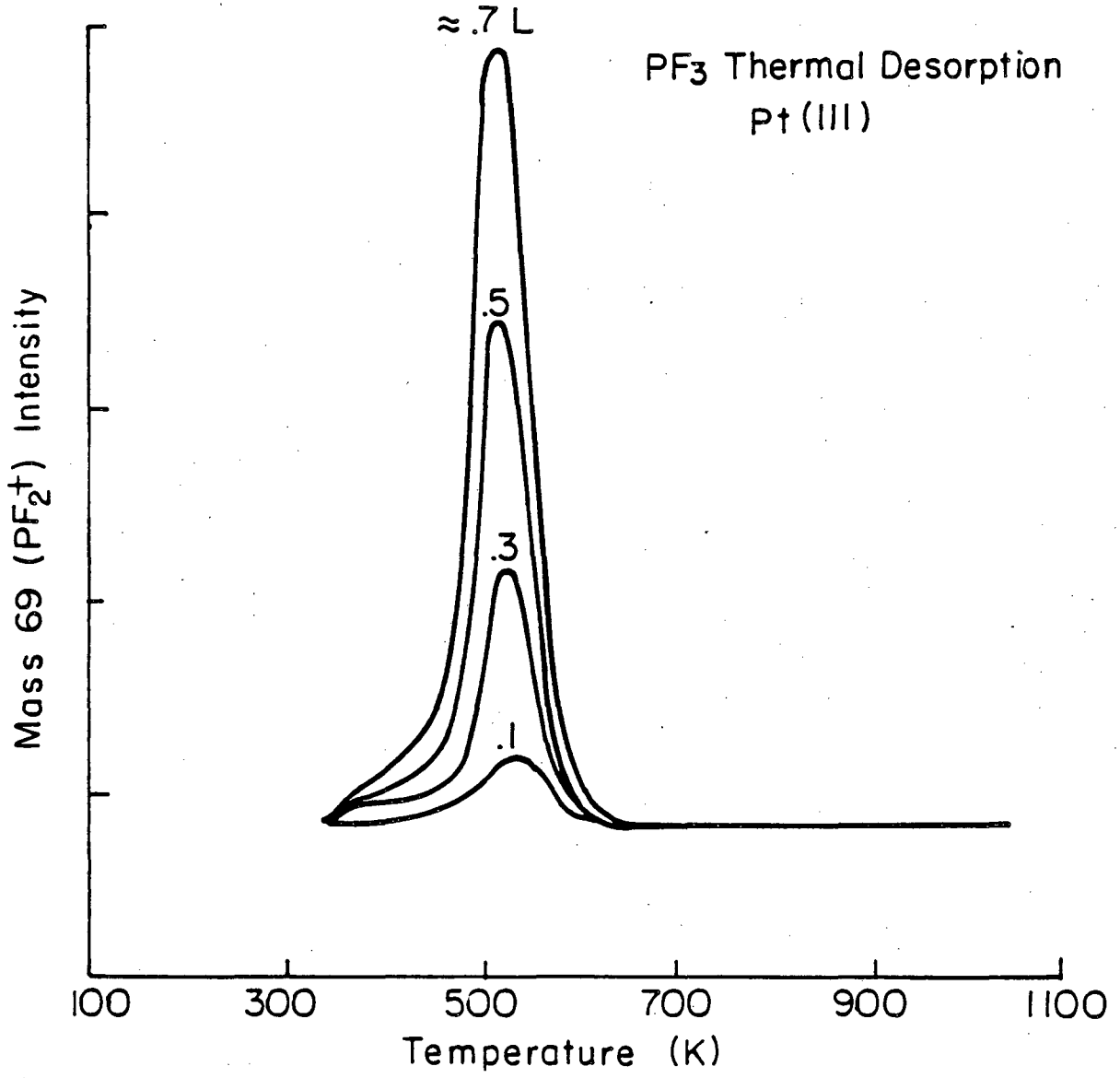
Fig. 1a

Benzene Thermal Desorption
Following 1 L Benzene Exposure on Pt(111) + K



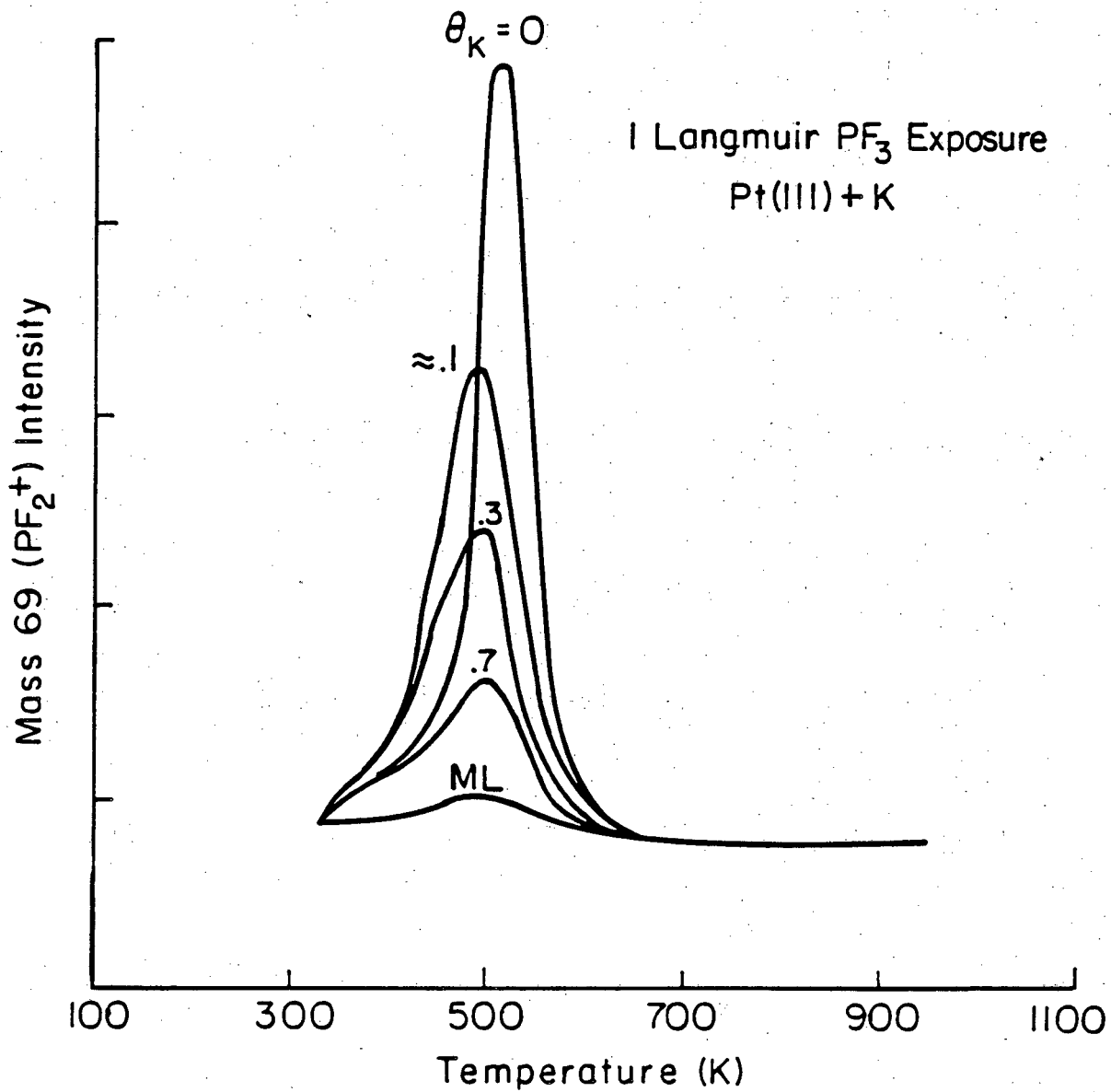
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Fig. 1b



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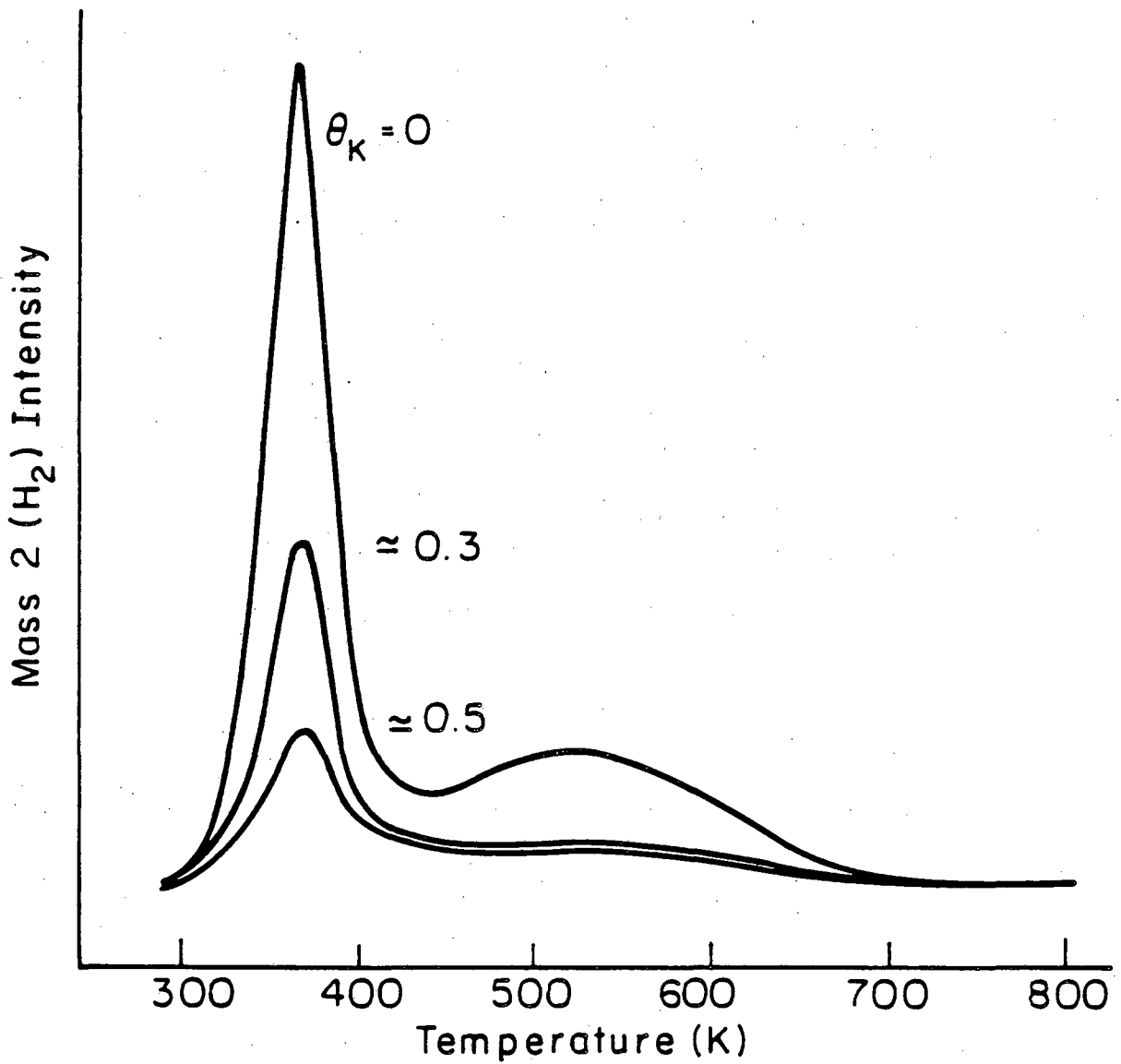
Fig. 2a



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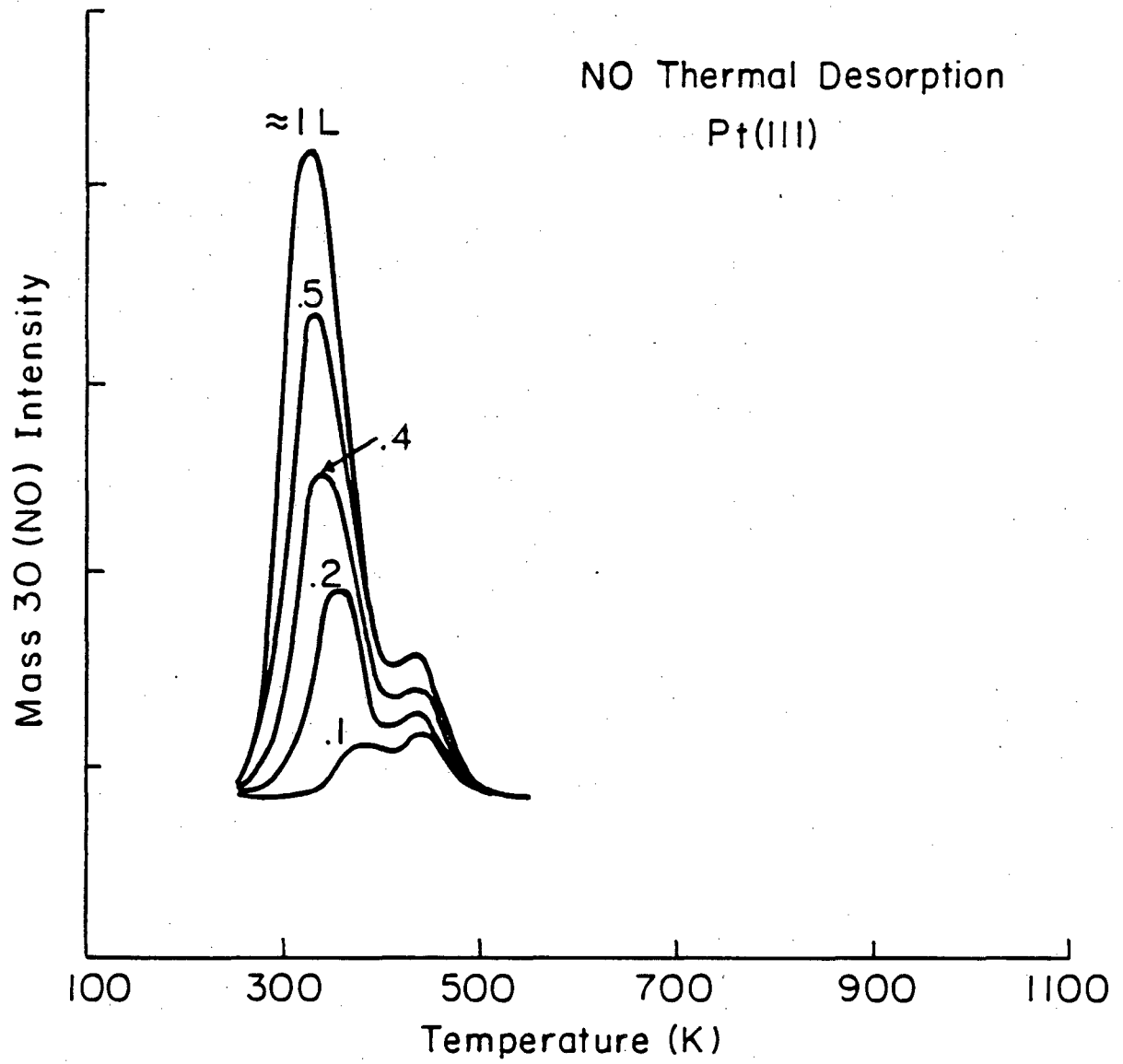
Fig. 2b

Hydrogen Thermal Desorption
Following IOL Butene Exposure on Pt(III)+K



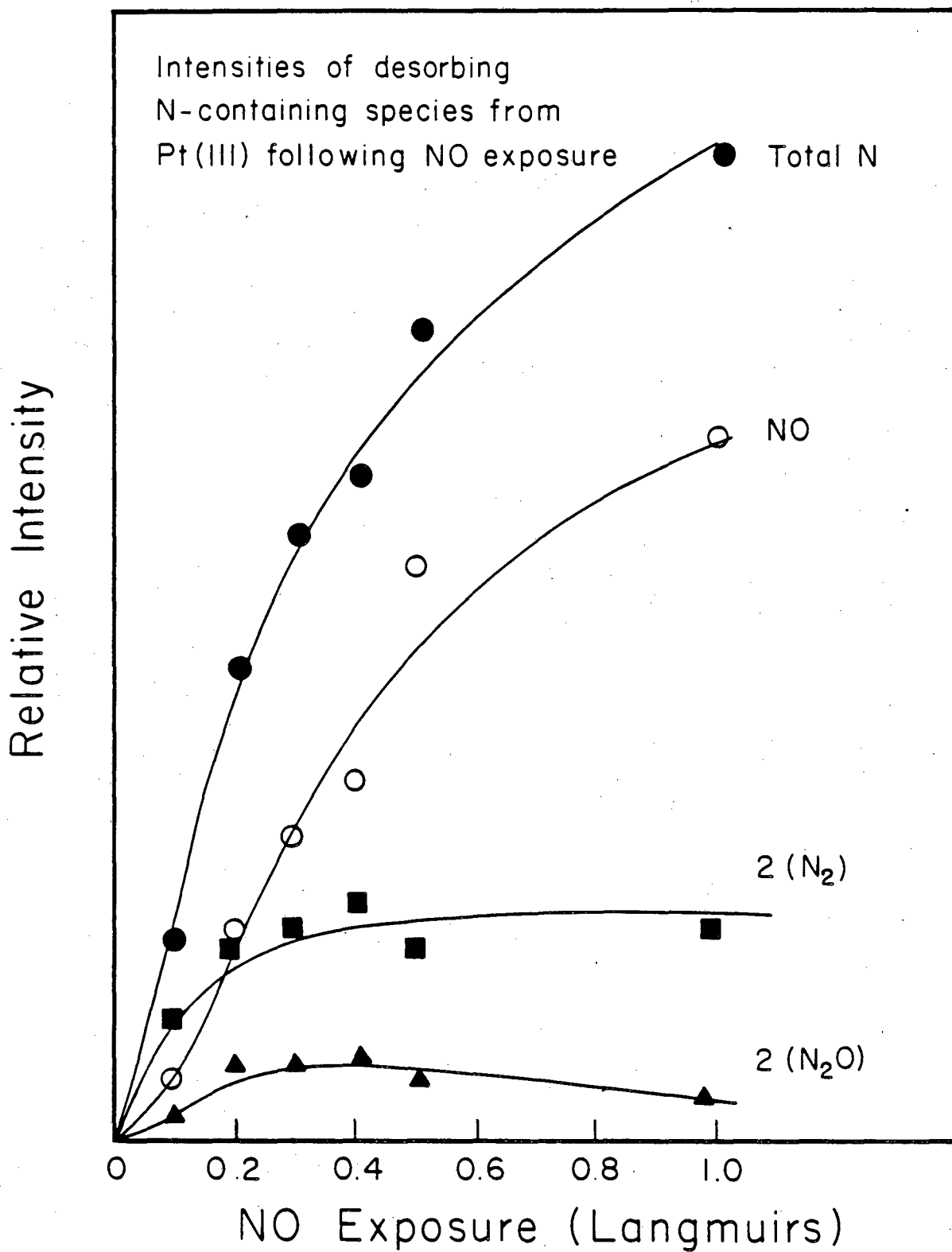
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Fig. 3



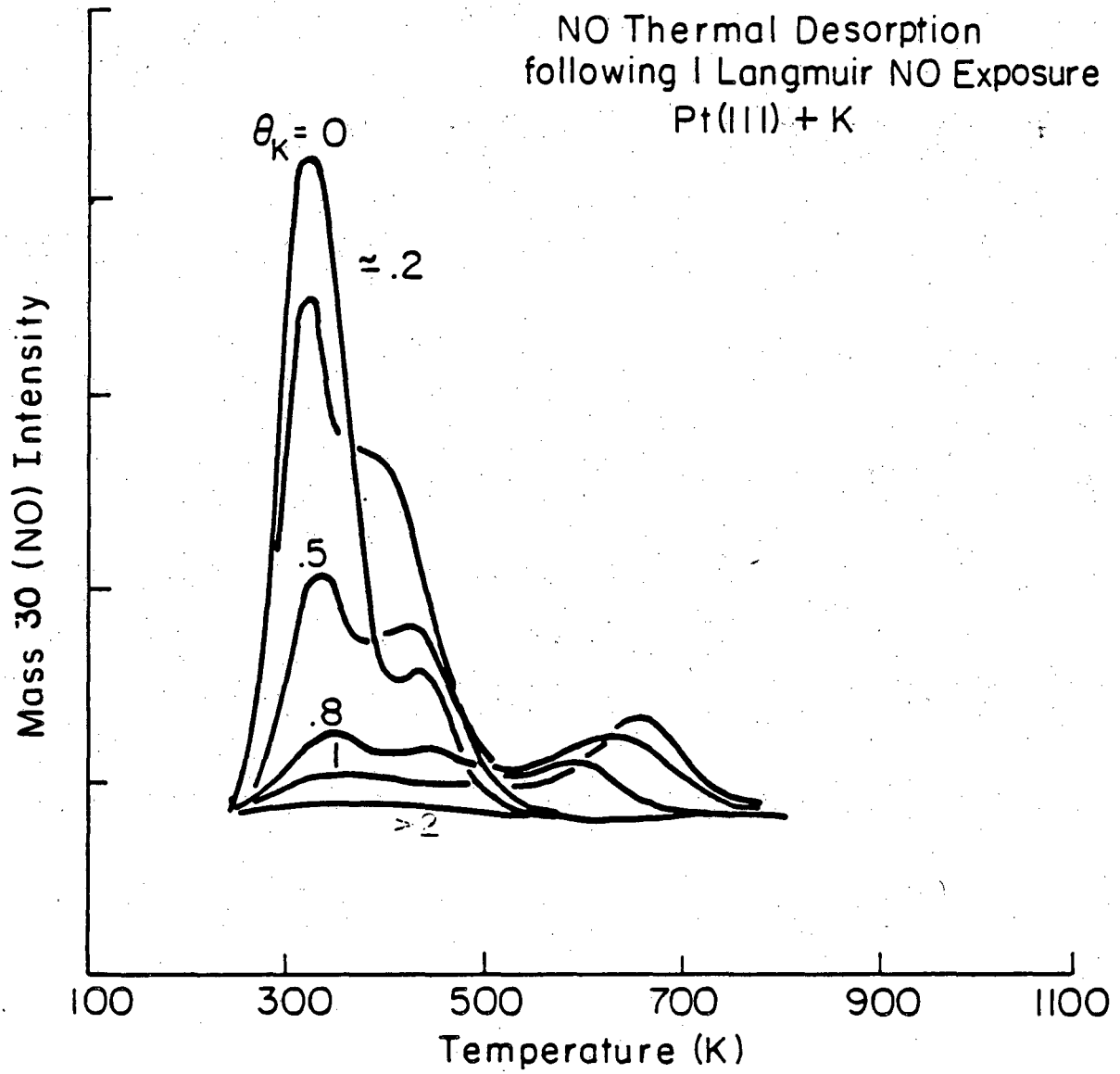
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Fig. 4a



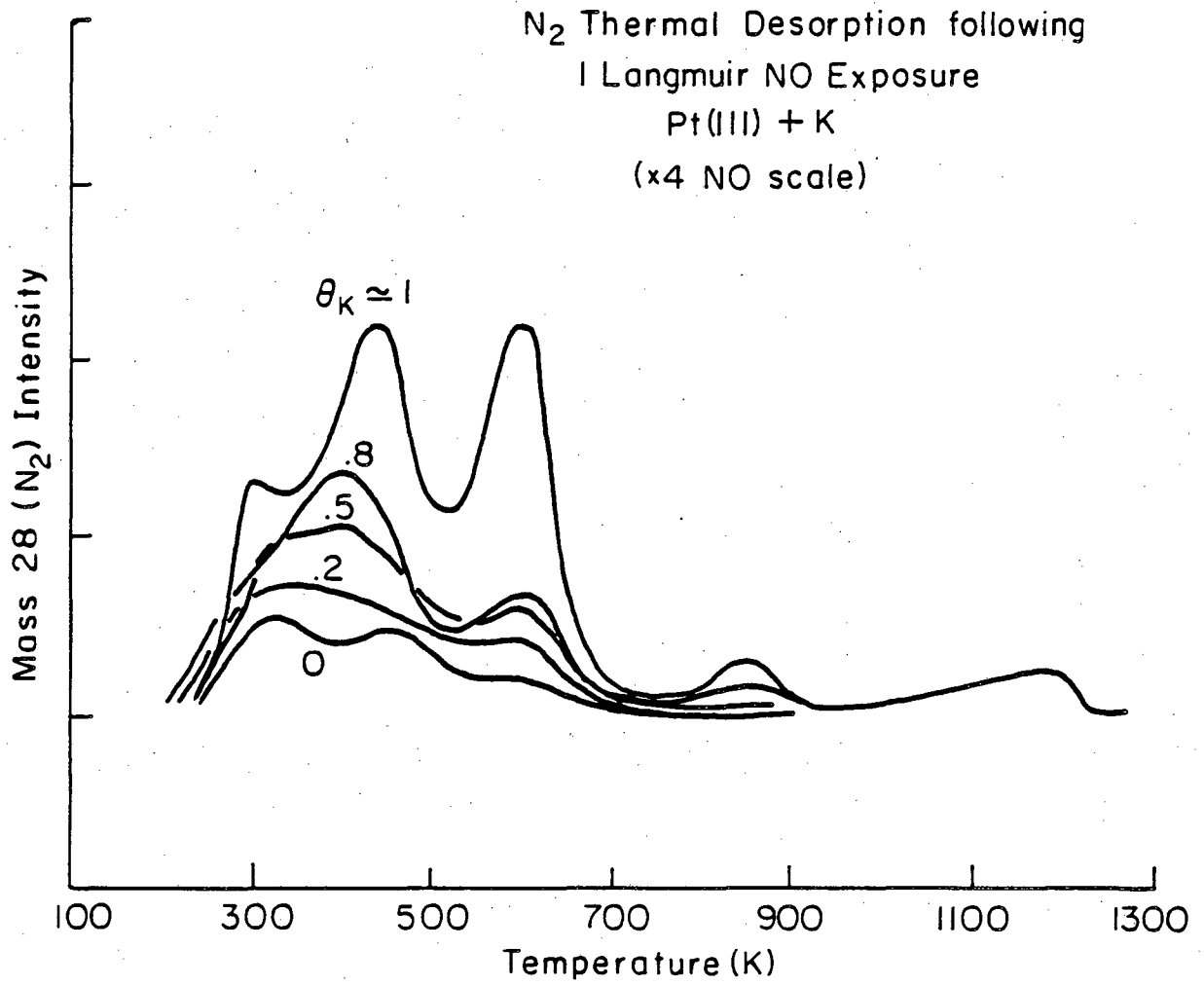
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Fig. 4b



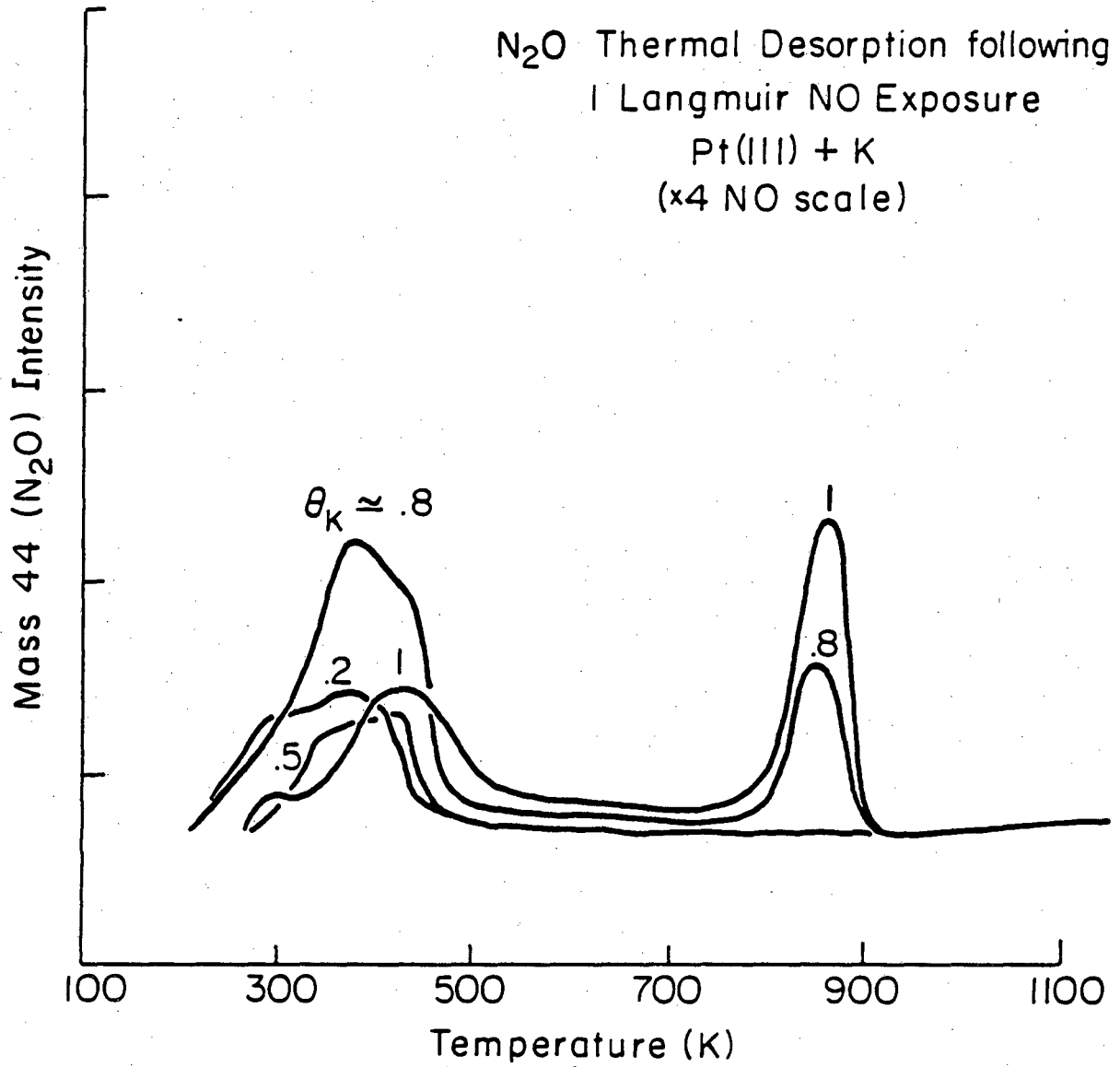
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Fig. 5a



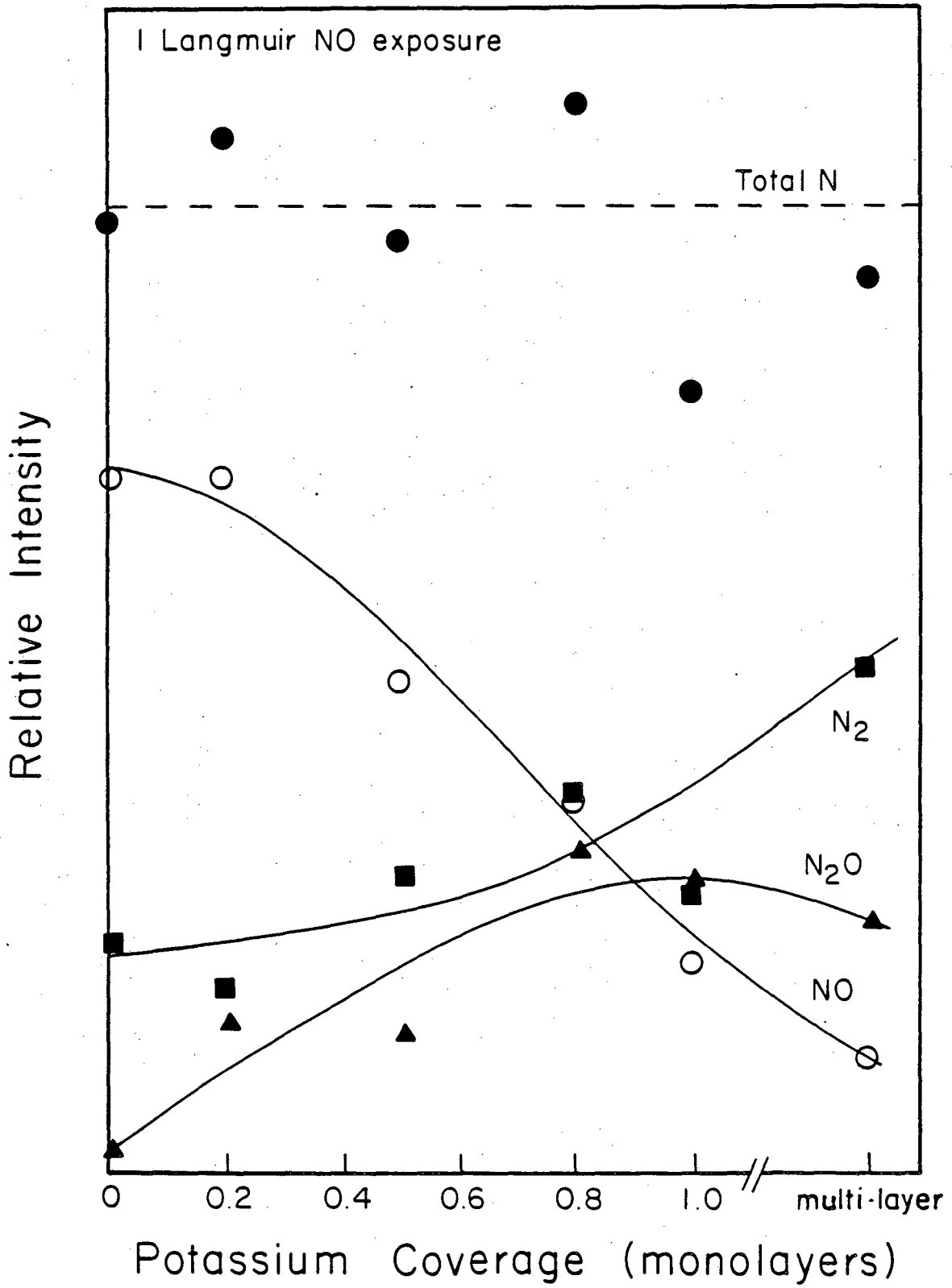
XBL 827-6191

Fig. 5b



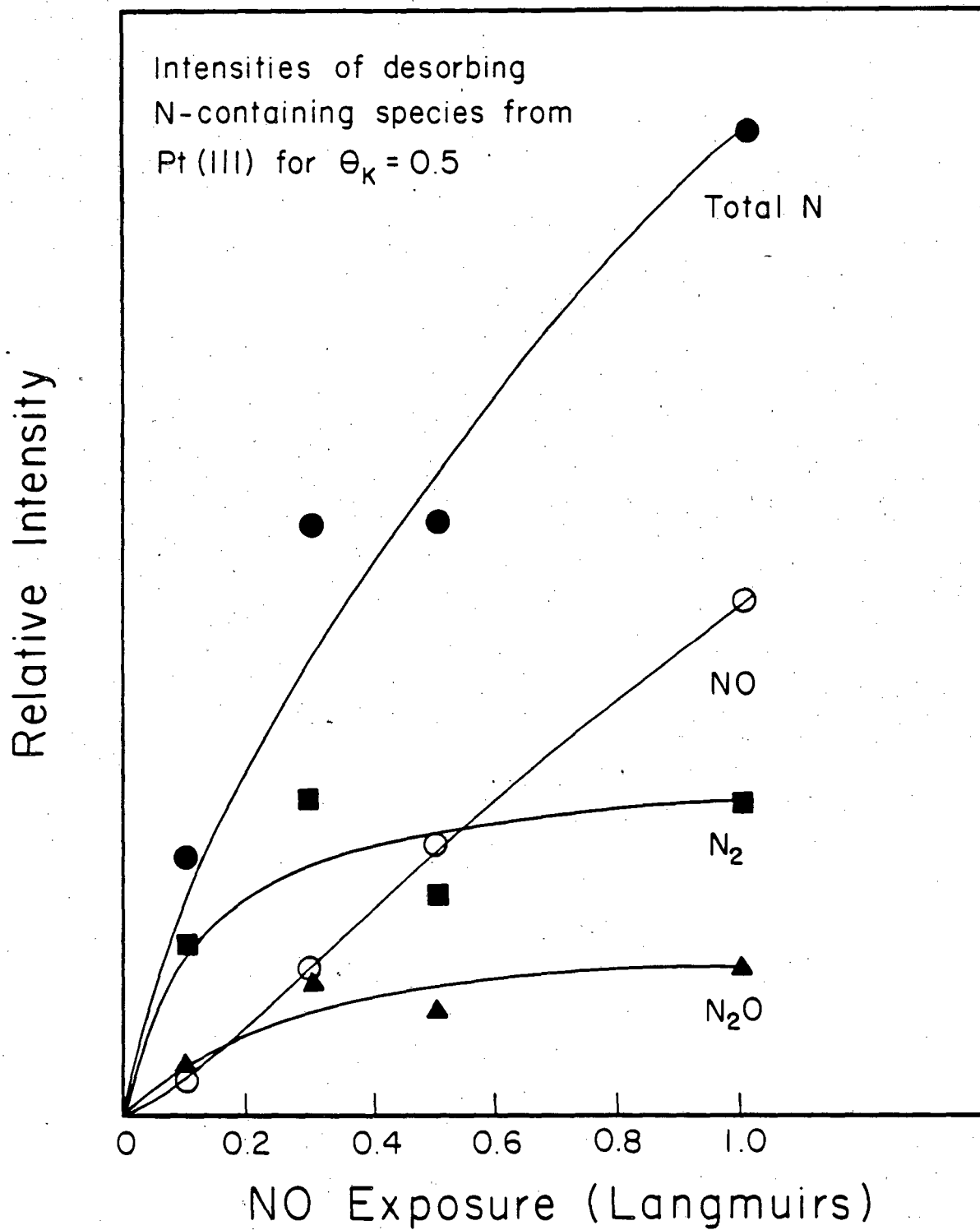
XBL827-6192

Fig. 5c



XBL 828-11088

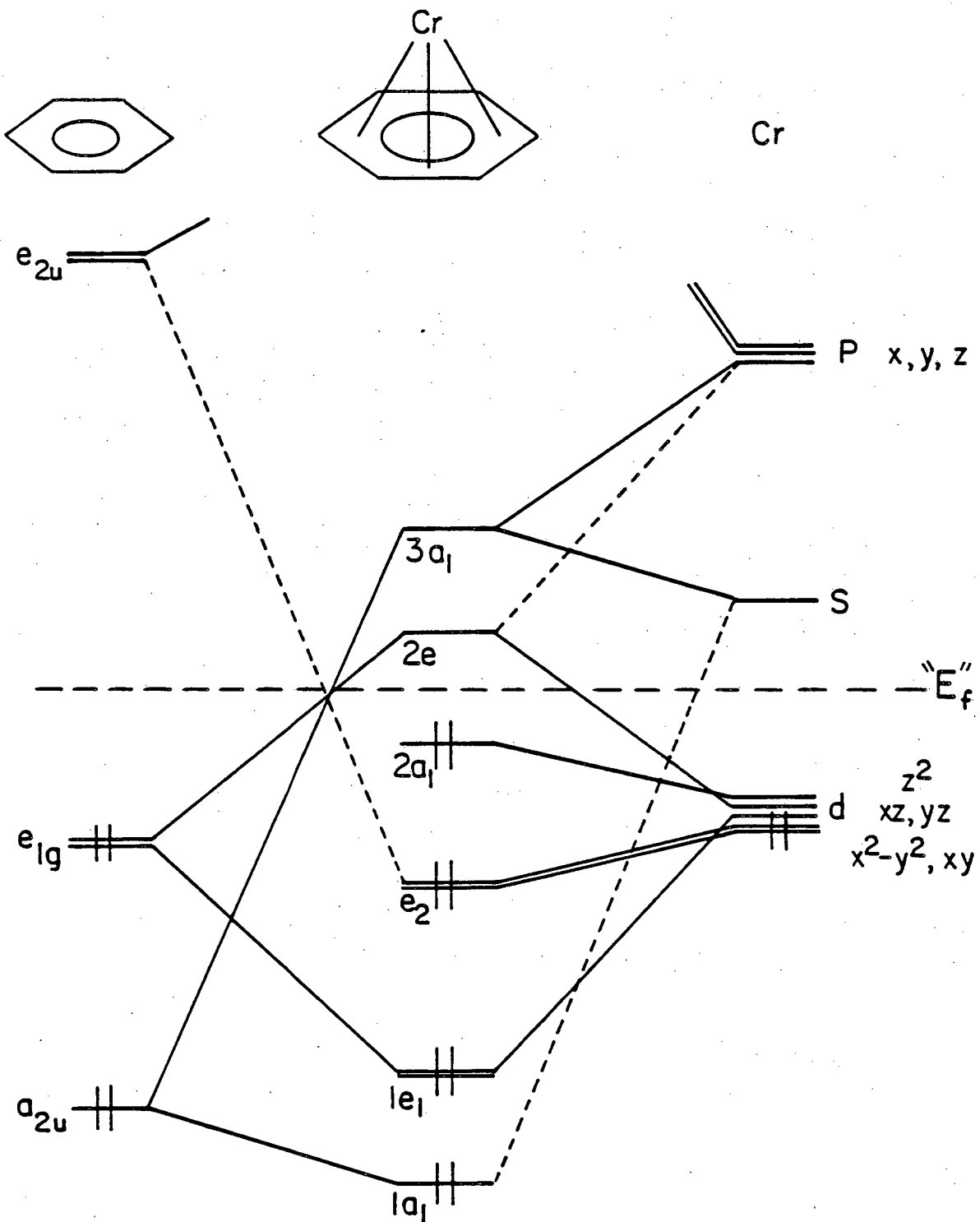
Fig. 5d



NBL 828-11039

Fig. 6

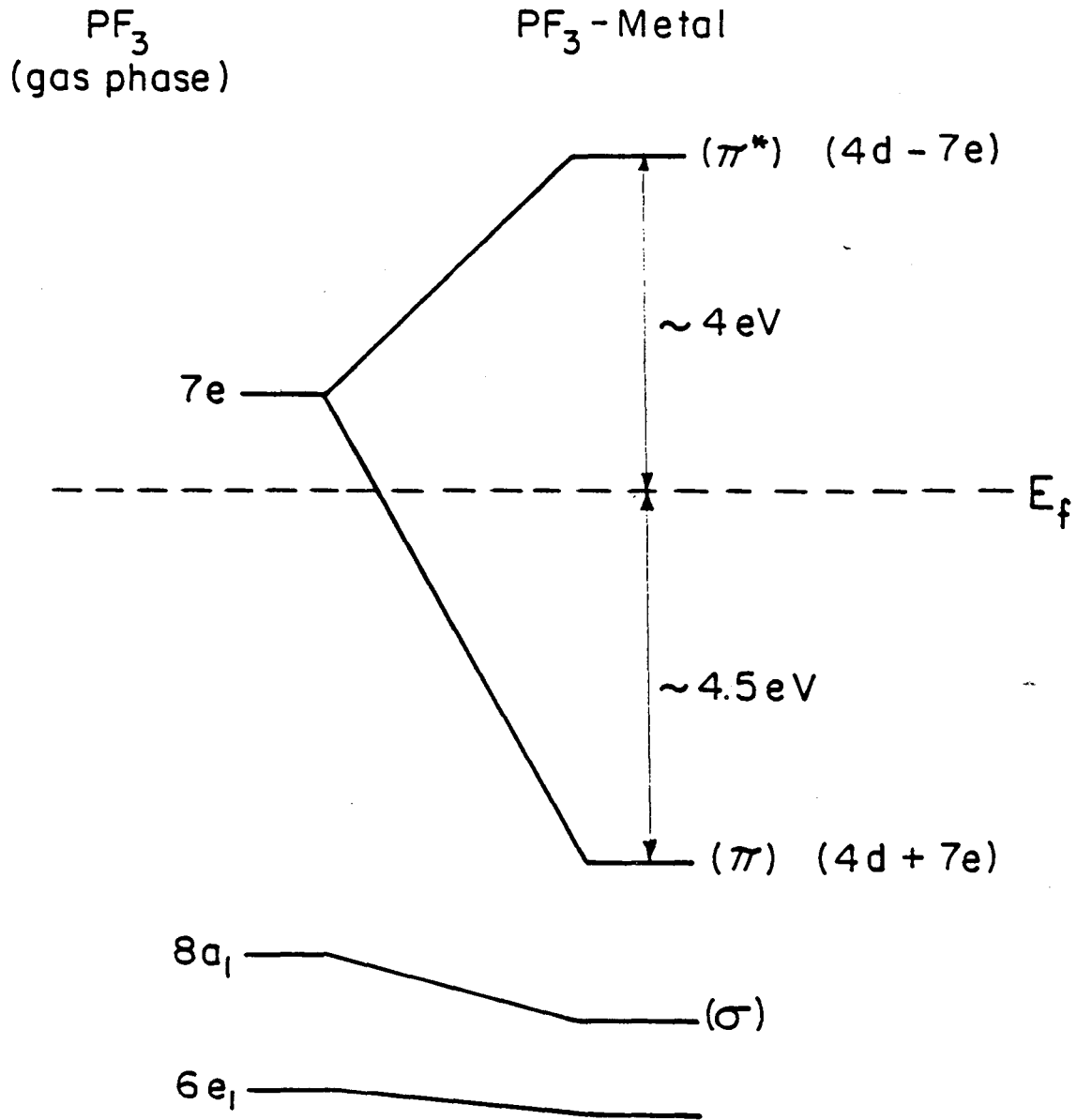
Valence Orbitals of Benzene-Cr: Energy levels are approximate



XBL 8211-6884

Fig. 7

Approximate Energy Levels of PF_3 in the Gas Phase and on a Metal Surface



XBL 82 11-6883

Fig. 8

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