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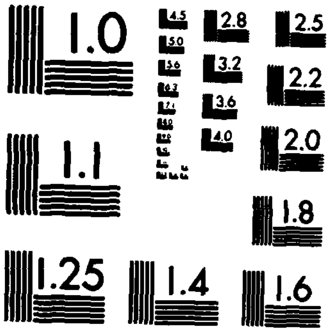
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20. ABSTRACT (continued)

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Abstract

The adsorption of C_2N_2 on Pt(111) results in two desorption states (α,β). The α state, T_{max} = 368K, is due to the desorption of molecularly adsorbed C_2N_2. The β state, T_{max} = 780K, may be due to the recombination of adsorbed CN groups or the decomposition of an extended $(CN)_x$ polymer. Coadsorption of H_2 and C_2N_2 results in a surface nitrene which decomposes to give back H_2 and C_2N_2 at 430K. Decomposition of ethylenediamine results in the same species. Dehydrogenation of ethylene-d_4-diamine shows that the amine hydrogens are removed first in this process followed at 430K by the removal of the hydrogens from the carbons liberating C_2N_2 as the final product.

1. INTRODUCTION

Recently there have been several studies of the bonding and chemistry of organic cyanides on the surfaces of a variety of single crystal metals; CH_3CN (10), CH_3NC (10), HCN (2,3), C_2N_2 (1,2,4-6,10,12-14), and $C_4N_4H_6$ (11) have been the objects of studies on various surfaces of Pt, Ni, and Cu.

The oxidation of C_2N_2 has been studied on Cu(1). The thermal chemistry of C_2N_2 has been studied previously on Pt(100) (4,13, 14), Pt(110) (2,6), Pt(111) (12) and a stepped Pt surface with Pt(111) terraces (5). Only C_2N_2 is observed as a desorption product from Pt surfaces. In all of these cases three desorption states are observed (α, β_1, β_2). The α state desorbs in the temperature range of 370 K (for the Pt(111)) to 460 K (for the Pt(110) surface). The β_1 state desorbs in the range 680 K - 690 K. The β_2 state desorbs in the range 750 K to above 800 K. The present interpretation of the α state is that it is due to molecularly adsorbed cyanogen. Two interpretations of the β states have been put forward. Lambert, et. al. (2) have suggested that the β states are due to the recombination of CN groups, while Netzer, et. al. (4) have proposed the existence of a paracyanogen like overlayer.

In this paper we describe the chemistry of C_2N_2, the coadsorption chemistry of H_2 and C_2N_2, and the decomposition of ethylenediamine on Pt(111).

2. EXPERIMENTAL

All experiments were performed in a stainless steel ultra-high vacuum chamber with a base pressure of less than 1 X 10^{-10} torr. The system is equipped with four-grid LEED optics, a UTI 100C quadrupole mass spectrometer and an argon ion gun. Auger analysis was performed by using the LEED optics as a retarding field analyzer. The mass spectrometer is multiplexed with an IBM Personal Computer, which performs at sufficient speed to allow the monitoring of sixteen separate masses and the crystal temperature every second. The Intel 8087 mathematics coprocessor is used to aid in signal averaging of the mass and temperature signals and in evaluating a fourth order polynomial to correct for non-linearities in the thermocouple voltage. The computer has also been set up to take Auger spectra and to produce hard-copy output on a dot matrix printer of both the Auger and thermal desorption spectra.

The crystal used has approximately 0.5 cm^2 surface area on both sides and is 1.5 mm thick. The crystal is spot-welded to a platinum wire which is attached between two copper rods. The crystal is resistively heated by a dc current through the copper rods and the spot welded Pt wire. The temperature ramp is forced to be linear by a simple feedback circuit which senses the thermocouple voltage and controls the dc power supply.

The crystal temperature is monitored by a chromel-alumel thermocouple spot-welded to the edge of the crystal. The copper rods are also in thermal contact through sapphire washers with a reservoir of liquid nitrogen which allows cooling of the crystal to 100 K.

All gas exposures were performed in the pressure range of 1 X 10^{-9} torr to 5 X 10^{-8} torr. Pressures were read directly from the ion gauge without correction for sensitivity relative to N_2. The reagents in this experiment were used without further purification before introduction to the vacuum system. The ethylenediamine and the ethylene-d_4-diamine, which are liquids at room temperature, were degassed by several freeze-pump-thaw cycles. The sources and stated purities of the reagents were (1) Deuterium, Matheson - purity 99.5%, (2) Cyanogen, Linde - purity 98.5%, (3) ethylenediamine, Fisher - 99.6%, (4) ethylene-d_4-diamine, MSD - purity 99.5% (lot # 1588 - H).

The Pt(111) crystal was cleaned by standard techniques of ion bombardment, annealing and oxygen treatments. Care was taken to avoid any contamination of the crystal by strongly bound oxygen which has been shown to affect the chemistry of some hydrocarbons on platinum (9).

3. RESULTS

3.1 Cyanogen on Pt(111)

When cyanogen was adsorbed on Pt(111) at 285 K only an increase in background was observed in the LEED pattern. Upon slow heating of the sample no ordering was observed.

Thermal desorption spectra (TDS) of C_2N_2 adsorbed at 285 K on Pt(111) as a function of coverage are shown in fig. 1. The a peak (T_{max} = 368 K) desorbs at a lower temperature from the (111) face of Pt than has been seen from Pt(100) (T_{max} = 413 K (4)), Pt(110) (T_{max} = 468 K (2)) and Pt(s)(9(111)x(111)) (T_{max} = 405 K (5)). The β peak (T_{max} = 780 K) at moderate to high coverages is very broad and shows no characteristic differentiation into two peaks (β_1 and β_2). Even at low coverages, where typically β_2 is the predominent peak, only a single peak is seen. In comparison to the peak temperatures for the β peaks on the other Pt surfaces studied the β peak in this experiment is most similar to β_2. On the other hand β_1 is typically the larger of the two peaks with β_2 only showing up at very low coverages or as a shoulder to the β_1 peak at high coverages. No assignment as to β_1 or β_2 is made in this study. This is consistent with the experiments of Hoffmann, et. al. which also do not cleanly resolve β_1 and β_2 states. The ratio of integrated intensity in the α state to the β state is approximately 0.5 at saturation coverage.

Our results are in good agreement with the peak temperature for the α states as reported by Hoffmann, et.al.$^{(12)}$ However, our observed α/β intensity ratio is very different from that reported by these authors.[12] Quantitative measurements of the α intensities in the work of reference 12 may have been hampered by desorption from the crystal suspension, which they mention as an experimental problem. Also the adsorptions of C_2N_2 in this work were done at a slightly lower temperature than the experiments of Hoffmann, et.al.$^{(12)}$ and this may contribute to the enhanced α/β ratio.

The carbon and nitrogen coverages on the surface were followed with Auger electron spectroscopy. The AES spectrum of a saturation coverage layer at 285 K showed a C to Pt intensity ratio (I at 272 to I at 237) of $\sim$0.44. The C to N intensity ratio (I to 272 to I at 381 corrected for the Pt intensity at 381) was 0.7.

3.2 C_2N_2 Coadsorbed with H_2

The coadsorption was performed by first adsorbing, at 285 K, 10 Langmuir of H_2 followed by the cyanogen exposure. Several experiments were also carried out with the opposite adsorption order. After the initial exposure no LEED pattern was observed nor was any observed during a slow heating of the sample.

Several sets of typical TDS data for mass 52 are shown in fig. 2. As can be seen, a new C_2N_2 peak appears when cyanogen is coadsorbed with H_2. This peak (T_{max} = 438 K) is very sharp, and, for low exposures of cyanogen, is the only peak observed for mass 52. Saturation of this new peak occurs at approximately 0.3 L exposure. Fig. 3 shows the hydrogen desorption spectra from a clean (H_2 only adsorbed) and coadsorption experiments. In comparing fig. 2 with fig. 3 it is seen that the H_2 intensity is removed from the normal desorption state and shows up in a new state with T_{max} = 430 K, which is the same temperature as T_{max} for the new cyanogen peak mentioned above. The shifting of the hydrogen intensity to the new state is complete at the coverage of cyanogen which corresponds to the saturation exposure (for the new C_2N_2 peak (0.3L)). Upon increasing exposure of cyanogen the α and β peaks are seen to grow in a manner similar to cyanogen on clean Pt(111). The major difference however, is that the ratio of peak area, α/β, is significantly larger in the case of the coadsorption than on the clean surface (Fig. 4). The ratio of integrated intensity in the α peak (including the new 430 K state) to the β peak is approximately 1.1 as opposed to the value of 0.5 for adsorption on clean Pt(111). This is not the case if H_2 is adsorbed after the C_2N_2. For postadsorbed H_2 the α/β ratio is 0.5, the same as in the absence of H_2. A similar enhancement of the α peak has been observed by Lambert, et. al. (6) in experiments on the coadsorption of C_2N_2 and CO on Pt(110). In an experiment which consisted of an exposure of 10 L of C_2N_2 and 30 L CO only the α peak is seen and the β peak is completely eliminated from the desorption spectra. It should be noted that in our experiments the α peak is somewhat narrower in the presence of H_2 (compare figures 1 and 2). Lambert also coadsorbed 10 L C_2N_2 with 0.3 L H_2 and recorded a significant amount of HCN evolving from the surface of a Pt(110) crystal (6). No H_2 spectrum was reported in that study. We also have noted small amounts of HCN in the desorption spectra. However, a small HCN impurity in the cyanogen makes quantification of the amount of HCN from hydrogenation of surface CN difficult in our experiments. The substitution of D_2 for H_2 in the coadsorption did not resolve this issue since DCN (mass 28) desorbs at the same temperature as CO (mass 28) which is present in small amounts from the background. The amount of HCN produced in our experiments on the Pt(111) surface appears to be much smaller than the amount observed by Lambert, et. al. from the Pt(110) surface. The order in which the H_2 and C_2N_2 were adsorbed on the surface had no effect on the generation of the 430 K state. In either order no displacement of the initial adsorbate was detected in the mass spectrometer during the exposure of the second component.

3.3 Ethylenediamine and Ethylene-d_4-diamine

In order to investigate whether the new peak in the TDS spectrum of the cyanogen coadsorbed with H_2 was possibly due to a hydrogenated cyanogen surface species, the chemistry of ethylenediamine ($NH_2-CH_2-CH_2-NH_2$) was also studied on this surface. The only products seen in the thermal desorptions following exposures at 290 K were H_2, HCN, and C_2N_2 (see Fig. 5).

The broad but well-defined nature of the H_2 desorption spectra suggests the existence of two overlapping H_2 peaks possibly coming from the sequential dehydrogenation of the amine and methylene groups. To resolve this question the ethylenediamine experiments were repeated using the selectively deuterated ethylene-d_4-diamine ($NH_2-CD_2-CD_2-NH_2$). The thermal desorption spectra for the H_2, HD and D_2 are shown in Fig. 6a. It can clearly be seen that the amine groups dehydrogenate at or just above the adsorption temperature and that the methylene groups are dehydrogenated at higher temperatures. The maximum in the rate of dehydrogenation of the methylene groups occurs at the same temperature as the maximum in the 430 K desorption peak of C_2N_2. This phenomenon is discussed below. Fig. 6a also shows a summation of the H_2 + HD + D_2 desorption spectra and this summation is compared to the H_2 desorption spectra from undeuterated ethylenediamine. The agreement is very good.

4. DISCUSSION

4.1 C_2N_2 on Pt(111)

The thermal desorption spectra of cyanogen from Pt(111) in Fig. 1 show a good qualitative agreement with experiments carried out with other Pt surfaces ((100), (110), and stepped (111)). The low temperature α peak exhibits no shift in peak temperature over the exposure range of 0.1 to 10.0 L, which is indicative of a first order kinetic desorption process. Using Edwards relationship between T_{max}, the width of the desorption peak and the activation energy of desorption (7) for first order desorption kinetics, the activation energy of desorption for the α peak, is found to be 10.5 kcal/mole. As we expect, this is slightly less than the value of 12.4 kcal/mole found by Netzer for the α peak of cyanogen from Pt(100) (4). The fact that the α peak is seen to be first order on all the Pt surfaces thus far studied strongly supports the hypothesis that the α peak is the desorption of molecularly adsorbed cyanogen. A complete study of the desorption kinetics of the α state on Pt(111) which will allow an independent measurement of the preexponential and activation energy is now underway in our laboratory.

The β peak as shown in Fig. 1 exhibits a decrease in the peak temperature from T_{max} = 780 K at 0.1 L exposure to T_{max} = 750 K at 1.0 L exposure. Above 1.0 L the peak temperature is seen to increase to T_{max} = 815 K at a saturation exposure of 10.0 L. Lambert's interpretation of the β state as recombination of CN groups would account for the apparent second order nature of the β peak at low coverages. However, the fact the peak temperature rises for exposures greater than 1.0 L precludes the assignment of this peak to simple second order kinetics.

Based on T_{max} for the α peak of cyanogen desorption reported in the literature combined with this work, the order of activity of Pt surfaces is given by:

Pt(111) < Pt(100), Pt(stepped) < Pt(110)

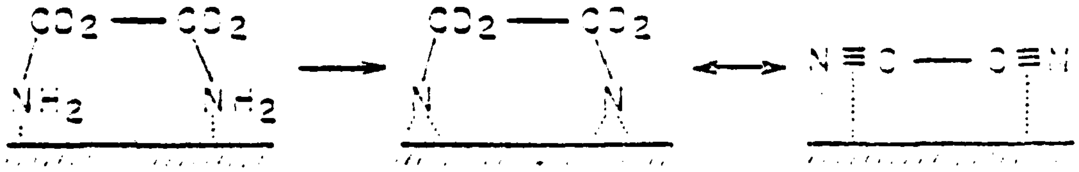
This same order correlates well with the relative areas under the β peaks of cyanogen compared to the α peak at saturation. On clean Pt(111), the integrated intensity of the α peak is ~50% of integrated intensity of the β peak at saturation. On Pt(100) and Pt(stepped) the α state contains roughly 25% of the integrated intensity seen in the β peak. On Pt(110) the α peak is almost nonexistent, with an integrated intensity only 5-10% of the β peaks. This trend can be seen to extend to two, more active, first transition series elements Ni(111)(10), which leads to complete dissociation resulting in N_2 production and Cu(111)(1), where it is seen that cyanogen desorbs exclusively from the β state and the α state shows only weakly at very large exposures. On the other end of the spectrum, cyanogen desorption from Ag(110) (2) shows only the α state. We feel that the relative insensitivity of the β states to the structure of the Pt surface favors the concept of a paracyanogen type structure for the β state as proposed by Netzer. However, the recombination of CN groups can not be ruled out without further spectroscopic studies. Combining our results with previous results in the literature leads us to the more complete order of reactivity of the transition metal surfaces studied to date towards C_2N_2.

Ag(110) < Pt(111) < Pt(100) $\sim$ Pt(stepped) < Pt(110) < Cu(111) < Ni(111).

4.2 H_2/C_2N_2-ethylenediamine on Pt(111)

When 10.0 L of hydrogen is coadsorbed with cyanogen on Pt(111), a new state at 430 K, which we shall designate as γ, is seen in the thermal desorption spectrum of mass 52 (Fig. 2). At low coverages of cyanogen the γ peak is the only one present and reaches saturation at 0.3 L cyanogen. Above this exposure the α and β peaks of cyanogen are seen to grow in a manner similar to cyanogen on clean Pt(111). The hydrogen thermal desorption spectrum develops a new peak at 430 K and the H_2 intensity gradually shifts with increasing cyanogen exposure from the normal peak at 325 K to the new peak at 435 K. All of the hydrogen is seen to desorb from this higher temperature state with cyanogen exposures greater than 0.3 L. This is the same cyanogen exposure which corresponds to the saturation of the γ peak in the mass 52 spectrum. The fact that the hydrogen and cyanogen desorb at the same temperature and that saturation of their respective peaks occurs at the same exposure of cyanogen indicates that this small amount of cyanogen (0.3 L) is binding all of the hydrogen present on the surface until the temperature reaches 430 K, at which point the hydrogen and cyanogen simultaneously desorb. All of the above results are independent of the order of the coadsorption; H_2 first or C_2N_2 first.

The new states for hydrogen and C_2N_2 at 430 K mentioned above are also seen in the thermal dehydrogenation of ethylene-d_4-diamine (see Fig. 6a). The summation of the HD and D_2 desorption spectra (Fig. 6b) has a maxima at 450 K. Clearly then, ethylenediamine decomposes in two steps: (1) the amine groups dehydrogenate at or slightly above the adsorption temperature of 235 K. This leads to H_2 desorption which peaks at 380 K. The resulting surface species is the ethylenedinitrene (2) shown below. (2) the ethylenedinitrene further dehydrogenates at ~430 K to give cyanogen as a reaction limited desorption peak.



(1) (2) (3)

The D atoms liberated from the ethylene-d_4-dinitrene recombine with adsorbed H or D to form the observed HD and D_2 products. It can be seen from figure 6a that at the onset of dehydrogenation of the methylene groups (production of adsorbed atomic D) the concentration of adsorbed H is still high. This leads to an initially large production of HD relative to D_2 and results in the somewhat skewed shape of the D_2 desorption peak to higher temperatures.

The mass 52 peak (C_2N_2) in figure 5 and the sum of the HD + $2D_2$ in figure 6b closely resemble the cyanogen γ state and the H_2 desorptions from the H_2/C_2N_2 coadsorption experiments. This suggests to us that adsorbed cyanogen is hydrogenated to give the dinitrene in the coadsorption experiments. Thus, the ethylenedinitrene - cyanogen transformation appears to be reversible. This process would certainly account for the fact that a small amount of cyanogen is able to bind up all of the hydrogen on the surface when C_2N_2 is coadsorbed with hydrogen.

Conrad, et. al.(13) have studied the reaction of C_2N_2 and H_2 on Pt(100) by UPS. They observe a new feature in the UPS spectrum which they attribute to "an intermediate reaction complex at the surface." The ultimate chemistry of H_2 - C_2N_2 on Pt(100) is significantly different from what we observe on Pt(111). In particular much more HCN is observed from Pt(100). It is possible, however, that the surface complex alluded to by Conrad, et. al. is the ethylenedinitrene which we believe is formed on Pt(111).

Another interesting aspect of the H_2/C_2N_2 coadsorption experiments is that the α/β integrated intensity ratio is significantly larger in the case of H_2 preadsorption. In the H_2 preadsorption experiments this ratio is 1.1, whereas it is 0.5 in both the H_2 postadsorption and the pure C_2N_2 experiments. Thus, while the formation of the ethylenedinitrene species is independent of the order of adsorption of H_2 and C_2N_2 the hydrogen pretreated surface favors the molecular adsorption process. If a model were assumed in which only the α state was populated on adsorption at 235 K and the β state was formed in competition with direct desorption, a branching ratio between direct desorption and formation of the β state would control the α/β ratio. Since the hydrogen surface concentrations were similar in the post- and pre-adsorption experiments we would expect the α/β ratio to be the same in the post and pre-adsorption experiments. Since the α/β ratio is not affected by hydrogen postadsorption but is dramatically affected by preadsorption we are led to the conclusion that the β state is present on the surface at the adsorption temperature of 285 K as opposed to being formed during the temperature ramp of the desorption experiment.

In both the H_2/C_2N_2 coadsorption and ethylenediamine experiments the γ peak in the cyanogen desorption spectrum is extremely narrow with a high temperature shoulder. If this peak is assumed to be first order an activation energy of 45 kcal mole is obtained along with a preexponential factor on the order of 10^{23}. While such large preexponential factors cannot a priori be ruled out in desorption kinetics, we suspect that non-first order kinetic behavior is a more likely explanation. Madix and coworkers (8) have shown, in the decomposition of formic acid, that narrow desorption peaks can be the result of an autocatalytic process. Since the cyanogen from the dehydrogenation of ethylenedinitrene is formed on the surface at temperatures well above the desorption temperature of molecular cyanogen, the peak shape may be the result of a sequential removal of the methylene hydrogens with several intermediate species. To address this question a more detailed kinetic study is currently being conducted in this lab. These studies should shed light on the origin of the unusual kinetic behavior of the γ state.

The dehydrogenation of ethylenediamine also results in the production of modest amounts of HCN. Thus we expect that the decomposition of the ethylenedinitrene is more complex than indicated in the schematic above. The most likely pathway involves sequential removal of hydrogens with a mixture of partially hydrogenated species on the surface. It should be noted that the dehydrogenation of ethylenediamine does not lead to the formation of any of the β state in the cyanogen desorption. We expect that the formation of HCN from ethylenediamine involves another channel of the decomposition of the ethylenedinitrene as opposed to hydrogenation of adsorbed CN groups.

The most likely mode of bonding of the ethylendinitrene species to the surface is through the nitrogens as shown previously in the schematic. The facile dehydrogenation and rehydrogenation of the carbons in this species may then be considered to be unusual since the carbons are not directly interacting with the surface. Recent work on deuterium exchange for hydrogen in the ethylidine (CH_3-C) species on Pt(111) by White and coworkers(15) and Ibach(16) have demonstrated facile H/D exchange for this species which also involves hydrogen exchange on and off a carbon atom not bonded directly to the surface. It is interesting to speculate at this point as to whether or not the facile activation of C-H bonds for carbon atoms which are one atom removed from the surface is indeed a general phenomena.

5. SUMMARY

The coadsorption chemistry of H_2 and C_2N_2 and the dehydrogenation of ethylenediamine on Pt(111) proceed through a common surface intermediate, the ethylenedinitrene. The dehydrogenation of the ethylenedinitrene leads to cyanogen desorption at the elevated temperature of 430 K. Deuterium labeling experiments with ethylene-d_4-diamine indicate that the amine hydrogens are removed at or slightly above the adsorption temperature of 235 K. Further kinetic and spectroscopic measurements on this system are underway to determine the details of the dehydrogenation of ehtylenedinitrene both in terms of specific additional intermediates as well as the kinetics which lead to the sharp desorption of cyanogen at 430 K.

This work has been supported in part by the Office of Naval Research.

Figure Captions

1. Cyanogen (as mass 52) thermal desorption spectra after various exposures of cyanogen on Pt(111). Temperature ramp is 7K/sec. The baselines have been shifted upward for clarity.

2. Cyanogen (as mass 52) thermal desorption spectra following various cyanogen exposures to a H_2 pretreated (10.0L) Pt(111) surface.

3. Hydrogen (as mass 2) thermal desorption spectra following postadsorption of various exposures of cyanogen. In each experiment a 10.0L exposure of H_2 was used.

4. Comparison of the cyanogen (as mass 52) desorption spectrum from a clean and hydrogen pretreated Pt(111) surface.

5. Thermal desorption spectra following exposure of 1.0L ethylenediamine to a clean Pt(111) surface. Top is H_2 as mass 2; center is HCN as mass 27; bottom is cyanogen as mass 52.

6a. H_2, HD, D_2 thermal desorption spectra following exposure of $NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$ and $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$ to a Pt(111) surface. 1) H_2 from $NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$; 2) ($H_2$ + HD + D_2) from $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$; 3) H_2 from $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$; 4) HD from $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$; 5) D_2 from $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$.

6b. H_2 (curve 1) and (HD + $2D_2$) X 1.3 (Curve 2) Signals from $NH_2\text{-}CD_2\text{-}CD_2\text{-}NH_2$ adsorbed on Pt(111).

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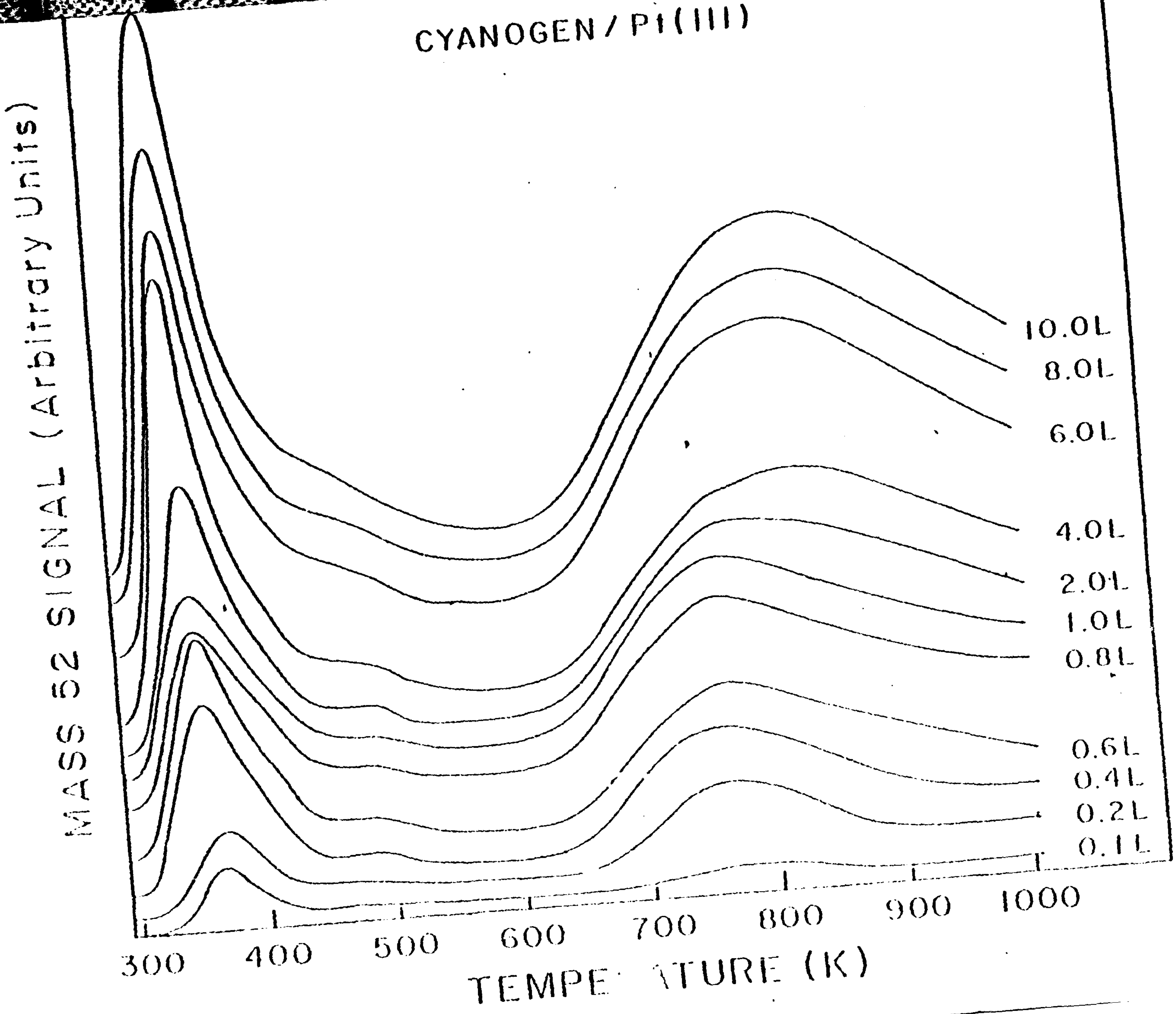
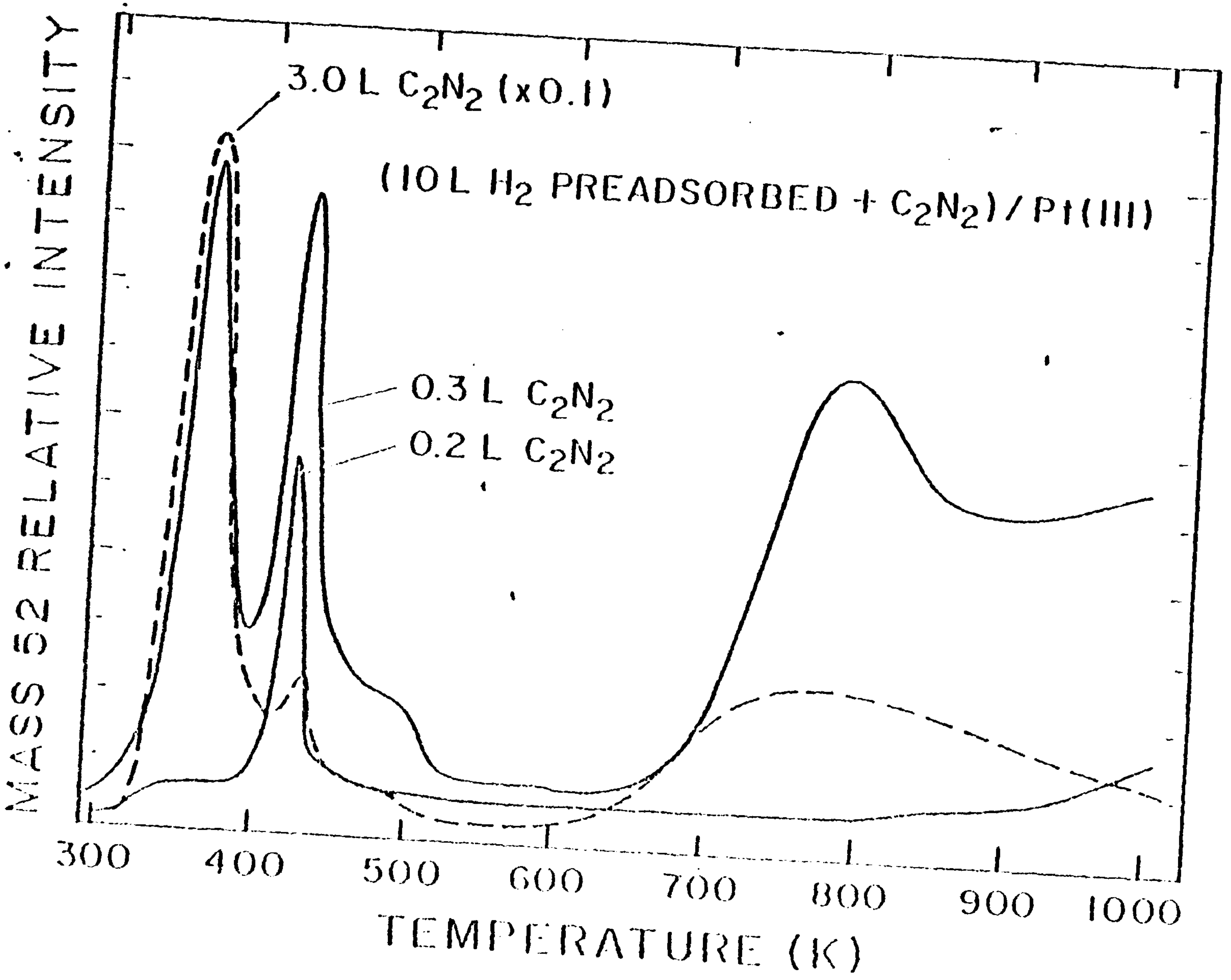
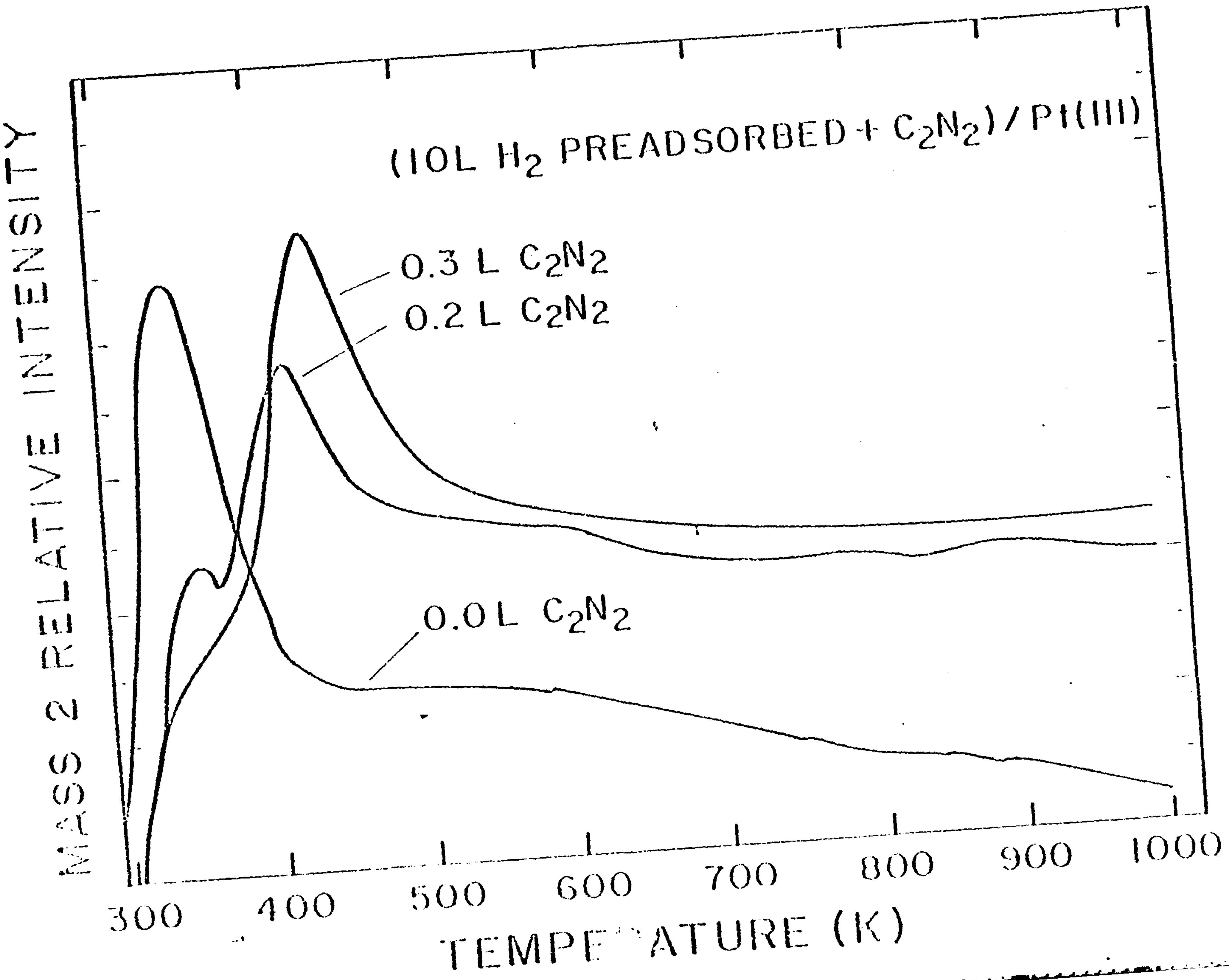
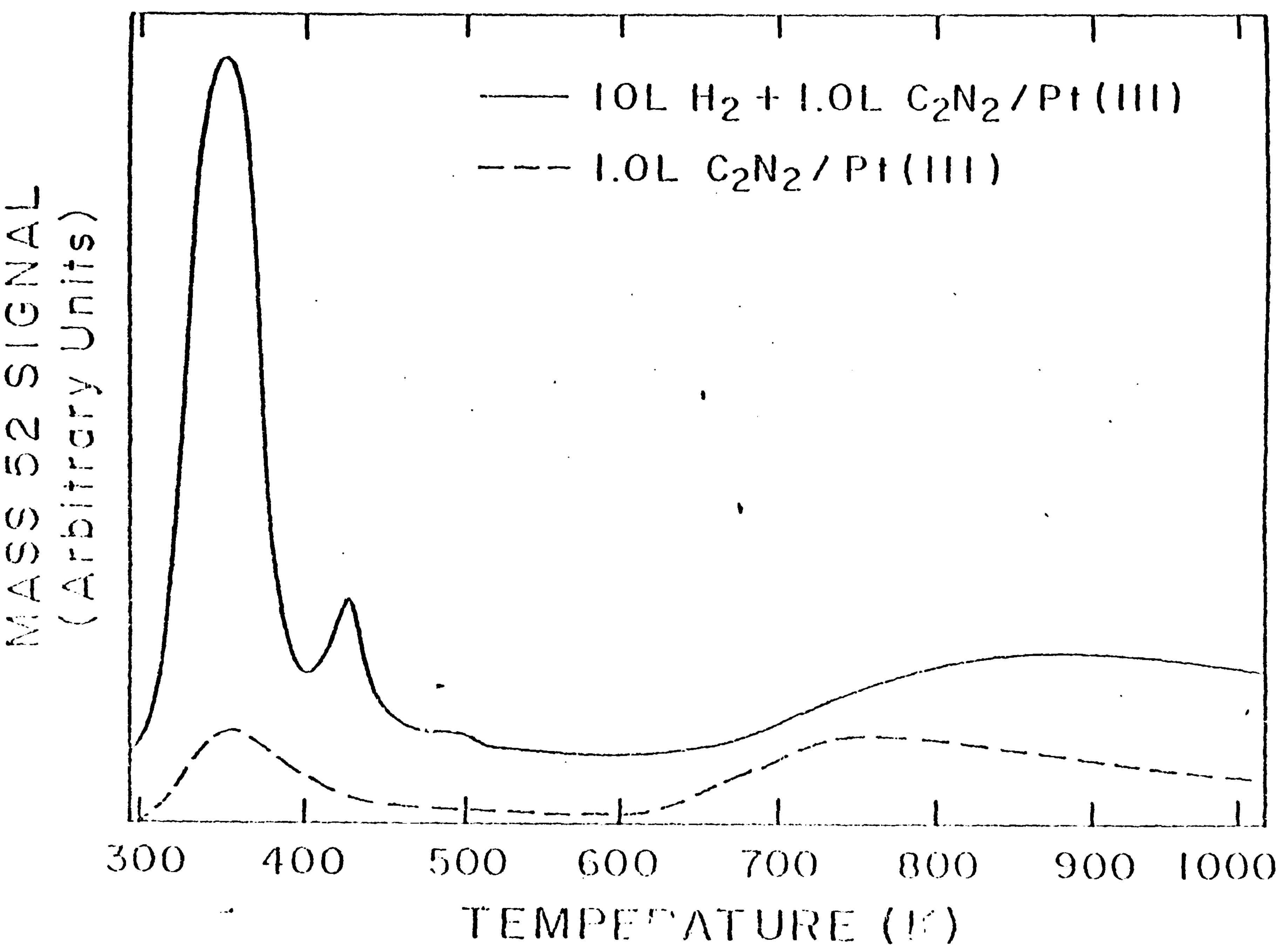

CYANOGEN / Pt(111)
MASS 52 SIGNAL (Arbitrary Units)
10.0L
8.0L
6.0L
4.0L
2.0L
1.0L
0.8L
0.6L
0.4L
0.2L
0.1L
300
400
500
600
700
800
900
1000
TEMPERATURE (K)

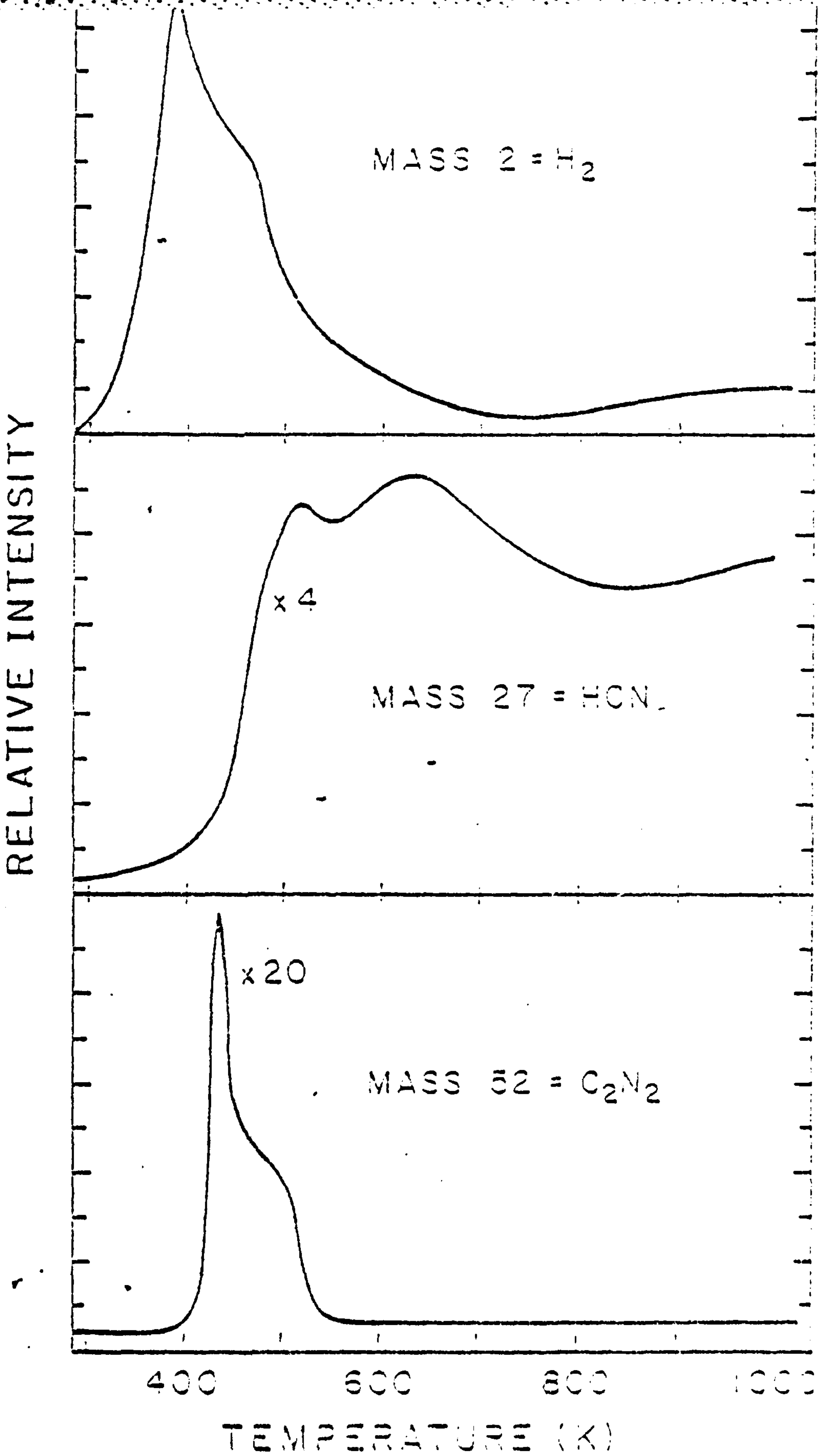


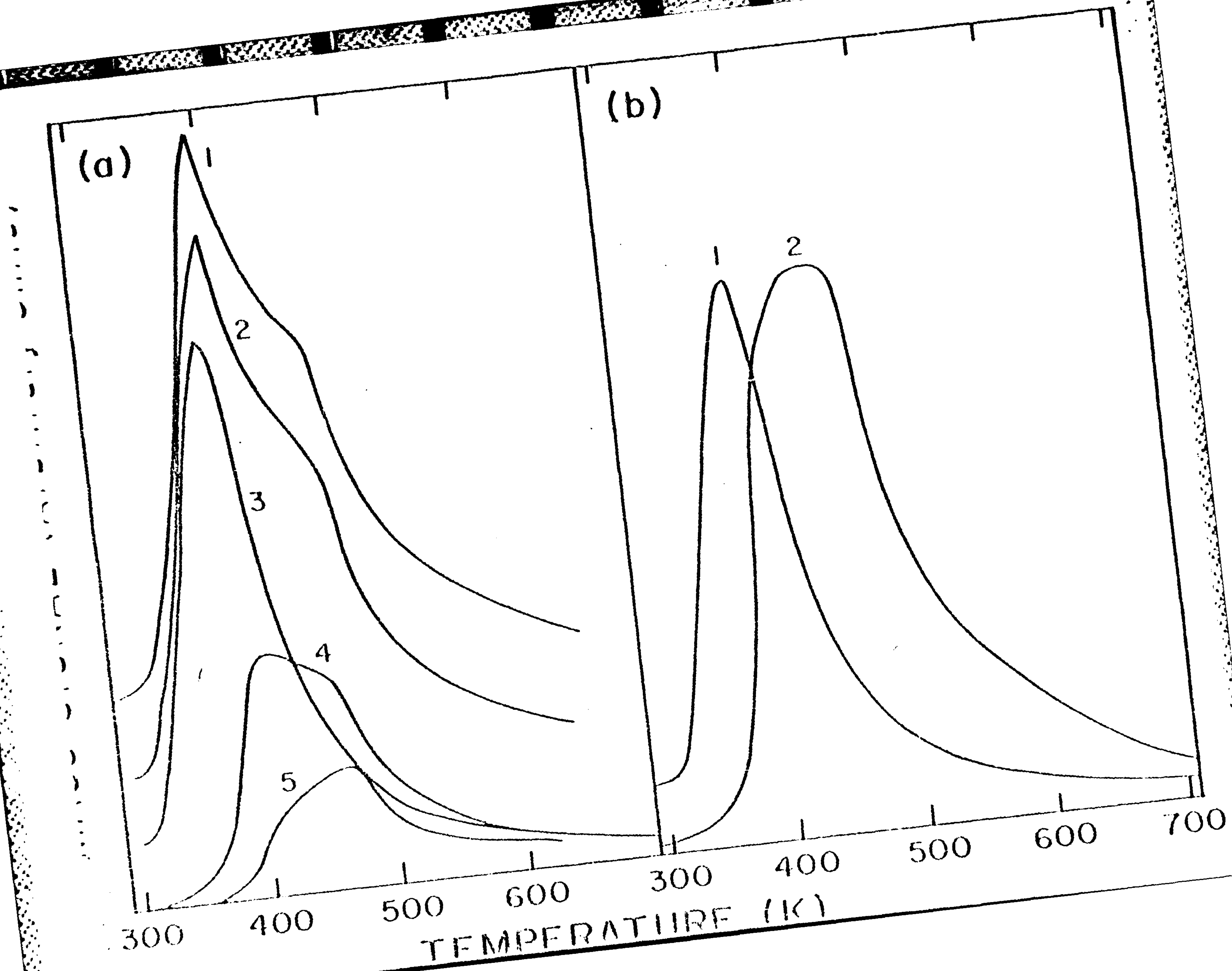
3.0 L C_2N_2 (x0.1)
(10 L H_2 PREADSORBED + C_2N_2)/Pt(111)
0.3 L C_2N_2
0.2 L C_2N_2
MASS 52 RELATIVE INTENSITY
300
400
500
600
700
800
900
1000
TEMPERATURE (K)


(10L H_2 PREADSORBED + C_2N_2) / Pt(111)
0.3 L C_2N_2
0.2 L C_2N_2
0.0 L C_2N_2
MASS 2 RELATIVE INTENSITY
300
400
500
600
700
800
900
1000
TEMPERATURE (K)



10L H_2 + 1.0L C_2N_2/Pt(111)
1.0L C_2N_2/Pt(111)
MASS 52 SIGNAL (Arbitrary Units)
300
400
500
600
700
800
900
1000
TEMPERATURE (K)


RELATIVE INTENSITY
MASS 2 = H_2
x 4
MASS 27 = HCN
x 20
MASS 52 = C_2N_2
400
600
800
1000
TEMPERATURE (K)


(a)
1
2
3
4
5
300
400
500
600
(b)
1
2
300
400
500
600
700
TEMPERATURE (K)

FILMED

02-84