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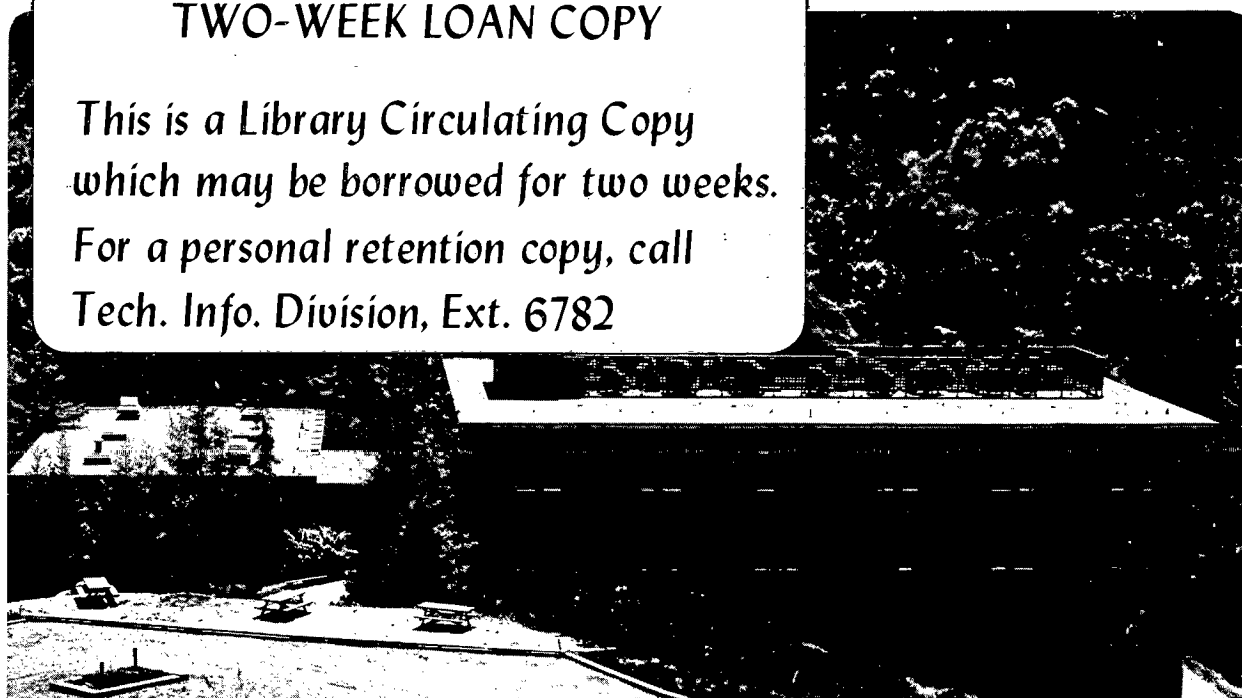
MOLECULAR BEAM SURFACE SCATTERING: THE DECOMPOSITION
OF AMMONIA ON SINGLE CRYSTAL PLATINUM SURFACES

Jonathan Daniel Sokol
(M. S. thesis) ✓

August 1979

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MOLECULAR BEAM SURFACE SCATTERING: THE DECOMPOSITION
OF AMMONIA ON SINGLE CRYSTAL PLATINUM SURFACES

by

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DEDICATION

To My Mother
and My Sister

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I greatly appreciate the support and encouragement my research director Gabor Somorjai has given me, and I am grateful for his introducing me to the field of surface science.

Words cannot describe my debt to Bill Guthrie, my co-worker. His knowledge and understanding of the experimental and theoretical aspects of this work, from the interpretation of the data to the nuts-and-bolts operation of the machine, made this thesis possible. I would especially like to thank Sylvia Ceyer and Fred Wagner for their valuable advice and friendship. I would also like to thank Te-hua Lin, who helped out on the latter portions of this work. I am grateful for the useful discussions I've had with Donald Olander and Miguel Salmeron.

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Don Daniellson, Mark Davis, Roger Carr, and Jeff Lince.

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I. INTRODUCTION

The subject of this work is the interaction of ammonia with single crystal platinum surfaces. The adsorption/desorption processes, as well as the decomposition reaction were investigated by means of molecular beam scattering, and the reaction mechanisms and kinetics have been determined. The surfaces used for these experiments are the Pt(111) and the Pt(557) crystal faces. Also described in this work is a method for measuring system pumping speeds using molecular beams.

Molecular beam-surface scattering is well established as a powerful technique for probing the atomic and molecular interactions at the gas-solid interface. Using well-defined beams and well characterized surfaces in an ultra-high vacuum environment, one can explore the behavior of a molecule colliding with a solid surface. The beam scattering technique allows for the variation of a number of experimental parameters that are fixed or not available in other methods of surface science investigation. The molecular beam can be energetically defined using supersonic nozzles, and even state selected using electromagnetic fields. A beam is by nature spatially defined, which allows one to control the angle at which the impinging molecules strike the surface. By means of a universal mass detector that is rotatable around the interaction zone, angular distributions of scattered or product molecules can be measured, yielding information regarding the accommodation of the reactant at

the surface. As one is detecting only the molecules coming from a single collision with the surface, one can determine, by means of phase-sensitive detection and time-of-flight, surface residence times and product velocity distributions. Of course, as with other methods of surface experimentation, the surface structure, chemical composition, and temperature can be well controlled.

As will be described, the present work takes advantage of many of the techniques molecular beam scattering offers. While some of the information gleaned from these experiments could be inferred using another method (e.g., desorption rate constants can be obtained from flash desorption studies), only the molecular beam scattering technique can give direct, unambiguous, gas-surface interaction kinetics and dynamics. The ammonia/platinum system is particularly difficult to study by flash desorption and Auger electron spectroscopy due to the problems associated with hydrogen adsorption from the background, the coincidence of nitrogen and platinum Auger peaks, and electron beam effects.

II. EXPERIMENTAL

The molecular beam apparatus used for these experiments has been described extensively.^{1,2} A schematic of the machine is shown in Figure 1. Briefly, the ion-pumped ultra-high vacuum chamber, equipped with LEED and retarding field Auger electron spectroscopy guns and optics as well as a sputter-ion gun, is connected via a 1 mm hole to a differentially pumped molecular beam source. A quadrupole mass spectrometer attached to a rotatable feedthrough in the main chamber can rotate around a crystal mounted on a manipulator. The crystal-to-ionizer distance is 3 cm.

A. Modifications

The changes that have been made to the machine since it was last described are as follows..

1) Beam line: the glass manifold that fed the beam has been replaced by an all stainless steel manifold. The new manifold is designed to allow for gas mixing so that two different gases can be regulated separately and fed into the source simultaneously.

2) Source: the ceramic multichannel array was removed from the heatable source tube. The source now consists of a stainless steel tube terminating in a round hole 0.010" in diameter and 0.010" in length. Used at experimental backing pressures (1-50 torr), the source forms a beam somewhat more spatially collimated than an effusive source. Nevertheless, calculations show that the velocity distribution of the beam can adequately be described as thermal.

3) Electron multiplier: the Cu-Be dynode electron multiplier used previously was found to degrade too rapidly under current experimental conditions. Consequently, it was replaced by a high speed off-axis channeltron electron multiplier (Galileo model 4770) used as an analog device. It was found that the channeltron also lost gain during the course of an average experiment, but could be adequately regenerated by baking out the entire main chamber at $\sim 120^{\circ}\text{C}$ overnight. The deflector plate of the multiplier could be used as a Faraday cup to collect ions. This made it possible to estimate the multiplier gain. When making these measurements the deflector plate was biased 20 volts more negative than the ionizer electron energy to prevent collection of electrons, and currents were measured with a picoammeter equipped with current suppression. It proved difficult to find a signal regime in which the channeltron did not saturate and yet ion current was large enough to measure. The multiplier gain varied around 10^5 . Scattered and product signals varied between .01 and 10 nanoamps. This corresponds to count rates of 10^3 - 10^6 counts/second.

B. Materials

The platinum crystals used were wafers ~ 6 mm in diameter and ~ 2 mm thick spark cut from a single crystal rod (MRC MARZ grade). The major bulk impurities in the rod (by MRC analysis) were palladium and silicon (each ~ 20 ppm). The samples were oriented by Laue x-ray back diffraction and polished by standard techniques. Immediately prior to

placement in vacuum, the crystals were etched in warm dilute aqua regia. The surfaces studied, Pt(111) and Pt(557) (or Pt-S[6(111)x(100)]) are shown in Figure 2. Surface impurities most frequently detected by A.E.S. were carbon, calcium, silicon, phosphorus and sulfur. Methods for surface cleaning are described below.

Anhydrous ammonia (Matheson 99.99%) was used without further purification. Deuterated ammonia (99% D) was obtained from Merck, Sharpe and Dohme. The deuterium used was purchased from Liquid Carbonic and was 99.7+% pure in D. Mass spectrometry indicated no impurities in the gases beyond the rated specifications.

C. Crystal Cleaning

The routine cleaning procedure was as follows. The hot crystals ($T \sim 750^\circ\text{C}$) were argon ion sputtered twice with the ion pump gate valve closed at an argon pressure of 5×10^{-5} torr for 20 minutes, the first time at 800 eV ion energy and the second time at 600 eV. 15-20 minutes of oxygen treatment followed in order to remove surface carbon, at a crystal temperature of 525°C and an oxygen pressure of 2×10^{-7} torr. Finally, the crystals were flashed to 950°C for about 5 minutes to anneal and order the surfaces. The cleanliness and structure of the surfaces were confirmed by Auger electron spectroscopy and low energy electron diffraction.

When a new crystal was placed in the chamber, or after the chamber was vented, the surfaces tended to be dirtier, and more vigorous cleaning was required. The Pt(557) crystal

had a considerable amount of calcium in it, and very high temperature ($T \sim 1000^\circ\text{C}$) and high energy (1500 eV) sputtering was required to leech all the calcium out of the bulk. Silicon and phosphorus contaminated the Pt(111) surface. It was found that silicon segregates to the surface at 600°C , so the crystal was left at that temperature for 30 minutes, then sputtered. Repeated cycles of segregation and sputtering successfully cleaned the crystal of surface Si. High energy sputtering, alternated with oxygen treatments got rid of the P.

D. Experimental Method

The process of following a molecular beam scattering experiment by phase-sensitive detection has been described in detail elsewhere.^{1,2,3} The molecular beam source was run with backing pressures between 1 and 30 torr for NH_3 . This corresponds to fluxes at the surface of the order of 10^{13} molecules $\text{NH}_3/(\text{cm}^2\text{-sec})$. Beam intensities were not linear with respect to backing pressure, as shown in Figure 3. Indeed, for ammonia, source pressures greater than 30 torr caused no increase in beam intensity, and in fact the elevated source chamber pressures caused by high backing pressures (>60 torr) resulted in attenuated beam intensities. Under typical operating conditions (backing pressure ≈ 5 torr), chamber pressures were as follows: $P_{\text{source}} = 1.5 \times 10^{-5}$ torr, $P_{\text{buffer chamber}} = 1 \times 10^{-7}$ torr, $P_{\text{main chamber}} = 1.5 \times 10^{-9}$ torr.

The beam was chopped at frequencies between 5 and 200 Hz by a chopping motor in the differential chamber. An Ortholoc 9502 lock-in amplifier used in quadrature mode was employed for detection, referenced to a photodiode-L.E.D. couple at the chopper. Data are in the form of an amplitude and a phase lag, which are derived by a polar coordinate transformation from the two lock-in amplifier signals.

The mass spectrometer ionizer was optimized on the ammonia signal. For an emission current of 2.4 ma, detector operating voltages were as follows: ion energy = +11 V, focusing voltage = -8 V, electron energy = -70 V channeltron voltage = -3 kV, channeltron deflection voltage = -80 V.

Detection of product or the scattered beam was performed by one of two different techniques. A discussion of detector modes is given in Reference 1. For most experiments, the rotatable quadrupole mass spectrometer detector was fixed in a position behind the crystal, out of direct line-of-sight of the direct beam and the molecules scattered from the surface. In this 'background mode' (previously referred to as 'integral mode'), one measures the intensity of the modulated background product signal i.e., the modulated chamber pressure of the detected mass. This detection mode was found to be extremely useful under most reaction conditions where chopping speeds were low and the signal was not significantly demodulated by the pumping speed of the chamber. The modulated chamber background¹ is proportional to $(1+(\omega/S/V)^2)^{-1/2}$, where ω is the chopping frequency, S the system pumping

speed, and V the chamber volume. Background mode detection was also effective in determining the chamber pumping speeds for various gases, as will be discussed below.

The second detection configuration employed was measurement of number densities of molecules directly scattered from the surface by placing the detector at positions facing the crystal. This 'differential mode' was used to obtain scattered molecule angular distributions for He and NH_3 . It was also used for isotope exchange experiments, for which it was found that the signal-to-noise was too small to observe isotopically substituted ammonia in the background mode from a mixed beam of NH_3 and D_2 . This was due to the relatively high background pressure of ammonia, which exchanged readily with the modulated deuterium background in the ionizer. In order to circumvent this problem, liquid nitrogen-filled cooling shields in the main chamber were used to reduce the ammonia background.

An attempt was made to examine hydrogen exchange by employing a mixed beam of NH_3 and ND_3 . This proved unsuccessful, as the ammonia became isotopically scrambled in the steel source gas manifold.

E. Poisoning

Changes in the chemical composition of the surface during the course of an experiment created difficulties in the acquisition of reproducible data. Unlike in other investigations,⁴ no poisoning due to surface carbon buildup was observed and the Auger spectra following an experiment showed no

evidence of surface carbon. There were, however, two major sources of surface poisoning.

1) Bulk calcium - In the early stages of these experiments, allowing the Pt(557) crystal to remain at temperatures above 1250 K for an extended length of time resulted in loss of catalytic activity for ammonia decomposition. Calcium, presumably segregated out of the bulk, was the only surface impurity detected by Auger following such a high temperature poisoning. The calcium was eventually depleted by means of the cleaning procedure described above.

2) Surface nitrogen - The ammonia decomposition reaction is self-poisoning. At a fixed temperature nitrogen and hydrogen production dropped, while the scattered ammonia signal grew as a function of the time the crystal was exposed to the beam. This self-poisoning phenomenon is rapid and at temperatures at which decomposition took place readily (750-800 K) product signals dropped significantly within three minutes of exposure. The activity of the crystal could not be restored by leaving the crystal in vacuo. The surface species causing the poisoning could be removed by flashing the crystal to 1200 K for five minutes. Therefore, in order to obtain accurate, reproducible data, the crystal was flashed following the measuring of each data point. While this poisoning was observed to some extent to all temperatures below 1000 K, it proved to be most troublesome at temperatures where decomposition takes place to a significant extent.

F. Crystal Mounting and Orientation

A standard Varian manipulator head with flip rod through the center was used. Two different crystal holders were used, one equipped with a spring loaded azimuthal rotator and the other capable of holding up to three crystals. Both are described by Gale.¹ Figure 4 shows how the crystals were mounted on the multiple-crystal holder. Small pieces of ceramic tubing were attached to the top and bottom of the crystal by means of spotwelded strips of Ta foil. The crystal was then placed against a Ta foil-covered ceramic block and stainless steel wire was run through the tubes and tied to a small, fiberglass insulated, stainless steel spring that rests on the back of the ceramic block. In this way the crystal was held against the block firmly, without being electrically grounded. The crystal was heated radiatively via the resistive heating of the Ta foil on the ceramic block. Crystal temperatures were determined by a chromel-alumel thermocouple spotwelded to the edge of the crystal.

A sighting cathetometer with calibrated rotatable cross-hairs was used to measure the azimuthal angle of the Pt(557) crystal. The angle of the scope cross-hairs was calibrated against LEED photographs. Absolute determination of the up- and downstairs directions of the steps was accomplished by helium scattering. It has been shown⁵ that helium will scatter specularly from a stepped crystal's microscopic surface, i.e., the terraces. Thus, comparing the maximum in the angular distribution of scattered helium to that expected from the macroscopic surface, the step direction

and, if the resolution is satisfactory, the angle from the low Miller index plane from which the crystal was cut can be determined. Results of such an helium scattering experiment are shown in Figure 5, for the Pt(557) crystal used in the experiments. Plotted against detector angle is the scattered signal divided by the direct beam signal. The crystal was fixed at a polar angle of incidence of 45° with the step edges perpendicular to the beam direction. The crystal temperature was 1110 K and the beam was chopped at a frequency of 100 Hz. As can be seen in Figure 5, the scattering maximum occurs about 20° further out from the incident beam than would be expected from specular scattering off the macroscopic surface. As the scattered angle will reflect twice the angle between macroscopic and microscopic surface normals, this result indicates that the surface terraces are about 10° from the macroscopic surface. This agrees to within the machine's resolving power with the 9.45° angle expected for a Pt(557) surface. That the specular angle is further out from the incident beam than macroscopic specular scattering implies that the beam is incident on the open side of the steps.

Crystal angles are defined as follows: polar angle of incidence (θ) is measured from the crystal's macroscopic surface normal, or the back-reflection of a He-Ne laser beam aimed through the source collimating orifices. The sign of the polar angle has significance only in conjunction with the azimuthal angle. Azimuthal angle (α) is defined as 0° when the step edges lie parallel to the plane defined by

the beam and the detector. When both azimuthal and polar angles are greater than zero the beam impinges on the open side of the steps (see Fig. 6).

An aluminum tube with a small foot at its end was hung from a mini-feedthrough at the top of the chamber, permitting the azimuthal rotation mechanism to be 'kicked' from one side to the other, allowing both positive and negative azimuthal rotation without crystal readjustment. This made available azimuthal rotation $0^\circ < \alpha < 127^\circ$ and $-147^\circ < \alpha < -43^\circ$.

For temperature dependence experiments on the Pt(557), polar angles used were $\theta = 45$ and 55° with $\alpha = +90^\circ$. On the Pt(111), the angle used was $\theta = 45^\circ$ for the temperature dependence runs.

III. EVALUATION OF SYSTEM PUMPING SPEEDS BY THE MODULATED MOLECULAR BEAM METHOD

If absolute quantitative product yields are desired from a background mode experiment, it is imperative that the chamber's pumping speed for each reaction product is known. The background mode measures the modulated background of a species in the reaction chamber. This is a function of the species' residence time in the chamber. That the chamber is pumped by a titanium sublimation pump and occasionally by liquid nitrogen filled cold shields as well as a 400 ℓ /sec ion pump implies that some direct measurement of pumping speeds for the various gases under experimental conditions is required. The modulated molecular beam technique provides a simple and accurate means for such a measurement.⁶

The rate of change of concentration of any gas in a pumped chamber is just the difference between the leak rate of gas into the chamber (or rate at which product desorbs from a surface into the gas phase) and the rate at which the gas is pumped out of the chamber. If the leak rate is time independent, an equilibrium concentration will be reached, provided the leak rate is not too high or the pumping speed too small. If the leak rate is modulated, the number density of gas particles in the chamber will have a time dependence, and will be a function of the chopping frequency. This is the case for a chopped molecular beam or a product desorbing from a surface where the reactant is modulated. The chamber pumping speed can be determined using the analysis technique

developed by Jones et al.³ Where $n(t)$ is the time dependent number density of molecules in the chamber, I_0 is the unmodulated leak rate into the chamber, $g(t)$ is the gating function, S the system pumping speed and V the chamber volume, the rate of change of number density is given by

$$\frac{dn(t)}{dt} = I_0 g(t) - \frac{S}{V} n(t).$$

If S/V is a constant (this will not necessarily be the case in a real system with sublimators and walls capable of pumping), the first Fourier components of $n(t)$ and $g(t)$ can be used to exactly determine the system pumping speed.

$$n(t) = n_0 + n_1 e^{i\omega t}$$

$$g(t) = g_0 + g_1 e^{i\omega t},$$

where n_0 and g_0 are the zeroth order, and n_1 and g_1 are the first order components of the number density and gating function, respectively. ω is the beam modulation frequency. Differentiating and substituting,

$$i\omega n_1 e^{i\omega t} = I_0 (g_0 + g_1 e^{i\omega t}) - \frac{S}{V} (n_0 + n_1 e^{i\omega t}).$$

Equating terms of same order,

$$n_0 = \frac{V}{S} I_0 g_0$$

$$n_1 = \frac{I_0 g_1}{i\omega + S/V}.$$

Focusing on the first order expression, one gets, upon transforming to polar coordinates,

$$r = I_0 g_1 / (\omega^2 + (S/V)^2)^{1/2}$$

$$\tan \phi = \omega / (S/V),$$

where $re^{i\phi}$ is the reaction product vector measured by the lock-in amplifier. If normalized against the leak rate into the chamber,

$$r = 1 / (\omega^2 + (S/V)^2)^{1/2}.$$

In a pumping speed determination experiment, a beam is elastically scattered from some surface in the chamber. The direct beam intensity and the modulated background are measured as a function of chopping frequency. The amplitude and phase lag of the modulated background are referenced to the amplitude and phase lag of the direct beam. Because of experimental conditions (e.g., the detector measures only a fraction of the direct beam, the ionizer volume is different for the background and direct beam measurements), the normalized background amplitude is not equal, but proportional to $1/(\omega^2 + (S/V)^2)^{1/2}$. Given ω , by measuring r and ϕ the effective pumping rate S/V and the proportionality constant can be determined.

The chamber pumping speeds for nitric oxide, water, ammonia, and nitrogen were measured in this way, and the results are shown in Figures 7-10. The beams were scattered off hot Ta foil, the temperature of which was raised until the measured phase lag ceased to change. Further assurance of non-interactive scattering (at least on the time scale of interest) was provided by scattering the beams from the

ceramic crystal holder or a stainless steel retaining screw on the crystal manipulator, and obtaining the same results.

The data was fit to the above described complex functional form by either the BCQNR or the MINUIT minimization programs,⁷ and the best fits are presented along with the data in Figures 7-10. It is clear from the data that while some gases in some pumping situations behave more linearly than others, none of the gases truly fit the simple model. While in all cases the amplitude data can be well modeled, the phase lag, a more sensitive measure of residence times, is invariably a poor fit. The closest fit is for ammonia when the chamber was pumped by the liquid nitrogen cold shields and titanium sublimation pump along with the ion pump. Comparing with the ammonia data for the ion pump only system, it becomes clear that wall effects play a large role in the chamber pumping speed. By this token, one might conclude that a gas with a low sticking probability on the walls should fit the model better. As is seen in Figure 10, nitrogen does indeed behave almost as expected. The nitrogen pumping speed is sufficiently small (50 sec^{-1}) that little information can be drawn from the amplitude data, because even the smallest usable chopping frequencies are on the order of S/V . Thus, for most of the frequency range, $r \propto 1/\omega$, yielding no pumping speed information. With nitric oxide and ammonia in the uncooled chamber the model underestimates the high frequency phase lags. In fact, the NO phase lag becomes greater than 90° . This implies residence times on the order of the chopping frequency in the chamber,

presumably on the chamber walls. With the walls cooled, any condensable molecule that strikes a wall sticks and is permanently (with respect to the modulation frequency) pumped out of the gas phase. A phase lag greater than 90° signifies some sequential process that the molecule undergoes, each step contributing up to 90° of phase lag. In the present circumstance this most probably means that a gas molecule is adsorbing and desorbing on the chamber walls more than once before it is finally pumped away, and its residence time during each wall collision is a large fraction of the shorter chopping periods ($1/\omega$). For almost all gases, the low frequency data are too high. Indeed, most of the plots look as though there will be a finite phase lag at zero frequency. This is an experimental artifact, caused by unsteadiness in the chopper motor when it is run at low frequency.

While comparisons have not been made of this technique with other pumping speed determination methods, the molecular beam method is self-consistent and potentially very powerful. A more sophisticated kinetic scheme could be formulated and pumping speeds as a function of time, chamber temperature, source pressure, and pumping conditions could be determined. Even when applied in the simple manner described above, it can yield reliable and useful information, particularly for molecules with large wall sticking coefficients (where the walls act as pumps) and for molecules with very small sticking coefficients (where there are no wall effects).

IV. AMMONIA ADSORPTION AND DECOMPOSITION ON PLATINUM: A SURVEY OF THE PREVIOUS WORK

The catalytic decomposition of ammonia has been studied since the early part of this century. Primarily of interest in conjunction with ammonia synthesis, this reaction has been thoroughly examined in the torr pressure range and higher on a variety of metal catalysts. The basic reaction kinetics were mapped out by Temkin in 1940,⁸ though other schemes have since been suggested. The general spread of high and ultrahigh vacuum techniques has led, in the past 10-15 years, to a reexamination of the ammonia decomposition reaction under low pressure conditions and with better characterized catalysts. Recently this reaction has been studied in an effort to understand the kinetics involved in the catalyzed decontamination of exhaust gases.

With regard to the present work, which is an examination of the decomposition reaction under ultrahigh vacuum and essentially single collision conditions, the relevance of earlier, high pressure, work is questionable. Little or no information about elementary surface processes can be gained from experiments on dirty surfaces or from experiments in which gas phase interactions are important. More of interest is the work that has been done under conditions similar to those of the present work.

Gland has studied the adsorption and decomposition of ammonia on a Pt-S[12(111) x (111)] surface using LEED, Auger electron spectroscopy and thermal desorption spectroscopy.⁹

Ammonia was adsorbed on this surface at -75°C . The initial sticking coefficient of the NH_3 was found to be approximately unity. Electron beam exposure increased the amount adsorbed. In experiments with minimum electron beam exposure (in order not to perturb the gas/surface system), Gland found the saturation coverage of ammonia to be approximately 1/20th of a monolayer, as determined by nitrogen/platinum Auger peak ratios. Flash desorption showed that about half the adsorbed ammonia decomposed into N_2 and H_2 , while half desorbed as ammonia. No ammonia fragments (NH_2 , NH , H or N) were detected. The ammonia showed two desorption peaks, at 407 K and 315 K, corresponding to desorption energies of approximately 96.3 and 77 kJ/mole, respectively. Peak desorption of N_2 from the flash occurred at 526 K with a shoulder around 625 K. This high temperature shoulder grew with increased exposure of the adsorbed NH_3 to the electron beam. H_2 also showed a shouldered peak, at 378 K. The nitrogen desorption behavior was similar to that from atomic nitrogen which led Gland to believe the nitrogen desorption is from a dissociated state, in spite of the fact that the desorption peak shows first order behavior as a function of coverage.

He also concluded that the hydrogen produced from ammonia is in a dissociated state on the surface. It is generally accepted that hydrogen is dissociatively adsorbed on platinum surfaces.¹⁰ While the fact that increased electron beam exposure of the surface suggests that NH_3 adsorption may be activated, it is proposed by Gland that the electron

beam serves to induce hydrogen desorption from a saturated surface, thus allowing more ammonia to adsorb. This possibility is lent credence by virtue of the fact that the total amount of desorbed hydrogen does not increase proportionately to the amount of desorbed nitrogen.

That the surface hydrogen may occupy sites that could otherwise be available for ammonia adsorption has also been suggested by Frennet.¹¹ As will be mentioned below, it is established at higher pressures that hydrogen acts to inhibit decomposition reaction.

Mummey and Schmidt also used A.E.S. and T.D.S. to look at ammonia adsorption on platinum.⁴ A high purity polycrystalline ribbon was subjected to very small ($\sim 10\text{L}$) and very large (10^9L) room temperature exposures of ammonia. At low exposure, the primary surface species detected by flash desorption was hydrogen (reported surface density ratios $\text{NH}_3 : \text{N}_2 : \text{H}_2$ were 1: 5: 30), though flash desorption from the heavily dosed surface showed nitrogen to be the predominant surface species (density ratios $\text{NH}_3 : \text{N}_2 : \text{H}_2$ were 1: 16.8: 1.6). With the 10L exposure, desorption peaks came at 465 K for NH_3 , 635 K for N_2 and 440 K for H_2 . Peaks shifted to 530 K for NH_3 , 520 K with a high temperature shoulder for N_2 , and 635 K for H_2 . The authors suggest that with low exposures ammonia adsorbs associatively while at high exposures decomposition takes place leaving a considerable amount of nitrogen on the surface. They also postulate the existence of ammonia fragments on the heavily dosed surface.

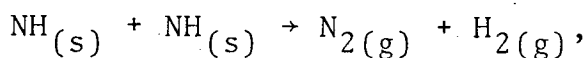
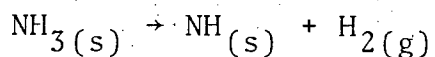
Robertson and Willhoft examined the decomposition reaction on platinum filaments at pressures $\leq 10^{-4}$ torr as a function of temperature and catalyst pretreatment.¹² Filaments that were flashed in vacuo to just below melting temperature before each measurement were found to have a high initial activity which fell to a steady value, for pressures $\sim 10^{-4}$ torr. At these pressures, the reaction probability was fit to an Arrhenius-type expression. From 660-1900 K, the reaction probability could be fit by a pre-exponential factor of 0.05 and an activation energy of 4 kcal/mole. From 440-660 K pre-exponential factors on two different filaments were 7.9×10^4 and 1.3×10^3 and activation energies were 23 and 17 kcal/mole, respectively. The reaction probability as a function of NH_3 pressure between 1.2×10^{-4} and 7×10^{-7} torr was also measured, and an apparent reaction order of 0.63 was determined. The reaction was also run in the presence of hydrogen which, it was found, retarded the decomposition. Robertson and Willhoft also did experiments in an "ultrahigh vacuum" chamber. Reaction pressures are not noted, but a high temperature activation energy of 4.1 kcal/mole and an activation energy of 50-60 kcal/mole below 500 K were determined. Under clean filament conditions (not established by any analytical technique) the reaction probability was found to be monotonic increasing as a function of temperature, but a peak in the reaction probability was found around 900 K if the filament was not flashed between measurements. The

authors attribute this to carburization. Carburized wires also showed activities 20 times greater than 'clean' ones. This increased activity is attributed to carbon dissolved in the filament. The authors found their data to be compatible with earlier, higher pressure studies.

Fogel et al. studied ammonia decomposition at 10^{-4} torr over a .4 mm platinum plate by secondary ion mass spectroscopy.¹³ Using a primary beam of 20 keV argon ions, they followed the reaction as a function of catalyst temperature. On an active surface (i.e., one that has been cleaned of carbon by long oxygen exposures), they found secondary ions of mass 2 fall to a steady number at around 800 K while mass 28 ions rise a factor of 2 between 300 K and 1100 K. At this temperature the mass 28 signal peaks and subsequently falls off at higher temperatures. The secondary ions at masses 17 and 16 are fairly steady over the temperature range, though mass 15 rises sharply at ~800 K. Data obtained by standard gas phase mass spectrometry shows masses 2 and 28 gradually increasing with time while masses 17, 16 and 15 start dropping at around 800 K. The mass 15 signal drop is more gradual than that at mass 17 or 16. In contrast to Robertson and Willhoft's work, Fogel et al.'s S.I.M.S. measurements show virtually no temperature dependence of the S.I.M.S. signals on 'inactive' surfaces presumed to be carbon poisoned.

While it is not completely clear what the significance of the data is, the authors show that the peak in the mass

28 secondary emission can at least in part be attributed to surface carbon monoxide. They also conclude that the decomposition reaction occurs in two stages,



from the rise in the $M/e = 15$ secondary ion signal and the more gradual drop in the gas phase signal at that mass. They finally postulate a strongly bound Pt-NH_3 surface species below 800 K on the basis that 1) there is no detectable decomposition here and 2) the secondary PtN^- and PtN_2^- signals become measureable only below this temperature.

In the course of investigating the oxidation of ammonia on a platinum wire, Hoenig and Tamjidi observed that the adsorption of ammonia caused the exo-electron emission from a 1100 K wire to drop by a factor of 2 below the vacuum level.¹⁴ This increase in the work function suggests either that the adsorbed species acts as an electron acceptor or that there is significant surface reconstruction upon adsorption. Although Gland, using LEED, did not observe any radical reconstruction of his stepped Pt crystal upon NH_3 adsorption,⁹ the polycrystalline filaments used by Hoenig and Tamjidi could have undergone some work function increasing reconstruction. If the adsorbed ammonia acts as an electron acceptor, this could suggest that the surface species is some ammonia fragment.

Melton and Emmett followed the decomposition in the 10^{-4} - 10^{-1} torr range on platinum wires by mass spectrometry.¹⁵ They looked for ions as well as neutrals containing nitrogen and found NH_4^+ , NH , N , N_2 , NH_2 and NH_2^- in the gas phase at 1473 K. N_2 production started at ~600 K and rose sharply and was a linear function of NH_3 pressure around 10^{-4} torr. Using a mixture of NH_3 and D_2 , they detected both NH_3D^+ and NH_4^+ , though only trace amounts of doubly substituted ammonia ions. These data corroborate Kemball's work¹⁶ in the torr pressure range, in which it was proposed that NH_2D is always the initial product in the ammonia-deuterium exchange, with NHD_2 and ND_3 formation taking place in later surface reaction steps.

Among the experiments performed at higher pressures, there are a few experiments that have a bearing on the present work. Loffler and Schmidt showed that in the 10^{-2} - 10^1 torr pressure range between 500 and 1400 K, ammonia decomposition on single crystal wires and various single crystal faces of platinum could be fit to a Langmuir-Hinshelwood unimolecular rate equation.¹⁷ They found the relative activities of the Pt surfaces studied to be as follows: polycrystalline $\approx (210) > (110) > (111) > (100)$. Morrow and Cody used infrared absorption to look at ammonia adsorption on supported platinum.¹⁸ In their experiments, run between room temperature and 500 K, they saw a single adsorbed species, i.e., coordinately bound NH_3 . Addition of small amounts of H_2 to adsorbed ND_3 precipitated rapid H-D exchange without

decomposition of ammonia (at least no infrared peaks that could not be assigned to NH_3 or partially deuterated ammonia). The spectra were essentially the same as those obtained by adsorbing a 1:1 NH_3/ND_3 mixture. No peaks that could be attributed to Pt-H were observed. It is significant, though not completely obvious how exchange can take place without the presence of ammonia fragments.

Interactions of ammonia and other metals besides platinum have also been studied under ultra-high vacuum conditions. Kunimori et al., did a high resolution AES study of ammonia on palladium at room temperature and observed only chemisorbed molecular ammonia.¹⁹ Gasser and Green looked at the temperature dependence of the steady state decomposition on a reduced Re filament.²⁰ They saw no decomposition below ~500 K. Between 600 and 800 K, the probability of decomposition was observed to be a steady 4%. Above 800 K, the authors claim that the decomposition probability rose sharply, but desorption of NH_3 from the chamber's walls prohibited measurements at these temperatures. Ammonia decomposition on W has been studied by several authors.²¹ There is disagreement as to the reaction order at low pressures though there seems to be a correlation between the surface coverage of nitrogenic species and the N_2 production rate.

Several decomposition studies have been carried out on iron.²² Structural sensitivity was observed on single crystal faces and decomposition takes place at temperatures as low as 300 K. Surface intermediates, NH_x ($x=1$ or 2) have been detected on Fe surfaces by photoelectron spectroscopy.

To summarize the previous work, decomposition of ammonia on platinum 'turns on' at ~ 500 K. Below this temperature, it appears that ammonia is associatively adsorbed on platinum, though hydrogen exchange can take place. From isotope experiments there is evidence that exchange takes place one hydrogenic atom at a time. Decomposition rates increase with temperature, though under certain experimental conditions the decomposition peaks or levels off. The more open crystal faces of Pt seem to be most catalytically active. Activation energies for ammonia desorption appear to be on the order of 18-25 kcal/mole.

V. RESULTS

A. Pt(111)

1. Crystal Temperature Dependence of Ammonia Adsorption and Decomposition

The results of the crystal temperature dependence experiments, taken in the background mode, are shown in Figures 11a-d and 12. Measured amplitudes (r) have been divided by the scattered ammonia signal at 1250 K ($r_{1250\text{ K}}$). This 'hot crystal' amplitude was determined to be the same as the amplitude of ammonia scattered from hot tantalum, the ceramic crystal mount, and a stainless steel screw on the crystal mount. It was thus concluded to be the maximum amplitude attainable in the background mode by scattering ammonia in the chamber. On the time scale of these experiments (the chopping frequency $f \leq 150\text{ Hz}$), $r_{1250\text{ K}}$ is independent of gas/surface interaction, and so will be referred to as 'elastic scattering'. Dividing all amplitude measurements by $r_{1250\text{ K}}$ removes the effects of beam fluctuations, pumping speed, and changes in detector gain. It also serves to normalize the data from different experimental runs. The phase data for ammonia is also referenced to elastically scattered ammonia. The plotted phase lags ($\Delta\phi$) are the change in phase lag from the elastically scattered signal ($\Delta\phi = \phi - \phi_{1250\text{ K}}$). This should be a true measure of surface residence time because all non-surface contributions to the phase lag, including the chamber pumping speed, have been

cancelled out. To correct for pumping speed differences, the hydrogen phase lags have been referenced to an elastically scattered hydrogen beam. The product phase lags have been further corrected by subtracting the calculated difference in phase lags due to different chopper-to-crystal transit times for ammonia and hydrogen. Unless otherwise noted, all amplitude and phase data described has been normalized in the above manner.

Data was taken at four modulation frequencies, 5, 20, 50, and 150 Hz. Source pressures were 5 to 15 torr. No other decomposition products besides H_2 and N_2 were detected, though fragmentation in the ionizer prohibited all possible measurement of NH_2 , NH , H , or N . The nitrogen signal was about a factor of 5 smaller than the hydrogen signal, and so was essentially lost in the noise. Because the signals were small, hydrogen production could only be measured at 5 Hz.

The scattered ammonia signal is essentially flat above ~550 K. The normalized amplitude is near unity, and the phase lag is, to within experimental error ($\pm 5^\circ$), 0° . At lower temperatures the amplitude drops sharply. In the high frequency plots it can be seen that the scattered ammonia amplitude levels off at the lowest measured temperatures. In the discussion below it will be shown that this low temperature asymptote in the amplitude is a measure of $1-s$, where s is the initial sticking coefficient of ammonia on the surface.

The ammonia phase lag begins to rise as the amplitude starts to drop. It reaches a maximum of $36 \pm 5^\circ$, independent of chopping frequency, and then drops back down at lower temperatures. This behavior, along with the temperature dependence of the amplitude, is indicative of simple adsorption-desorption kinetics (see below).

The hydrogen amplitude (Fig. 12) rises fairly sharply between 650 K and 775 K. It peaks at 750-800 K, and falls gradually at higher temperatures. The peak temperature hydrogen signal represents between .1 and 1% decomposition of ammonia. This is much smaller than the error in the ammonia amplitude data ($\sim 4\%$), and no drop due to decomposition is detectable in the ammonia signal. There is essentially no hydrogen phase lag above 750 K. Below 750 K the phase lag rises gradually. Below 600 K the measured hydrogen signals are too small to yield reliable phase information. The maximum measured phase lag is about 60° .

2. Beam Pressure Dependence of the Low Temperature Amplitude

In anticipation of the result that the low temperature ammonia amplitude represents 1-s the scattered ammonia amplitude at 375 K was measured at 150 Hz as a function of beam pressure. Plotted in Figure 13 is $1-r_{375\text{ K}}/r_{1250\text{ K}}$ (or s) vs $r_{1250\text{ K}}$. As can be seen, the sticking coefficient drops $\sim 10\%$ as the beam is raised by a factor of three. This small change could be regarded as a weak coverage dependence to the sticking coefficient. Because this effect is so slight,

it will be assumed, for the purpose of model fitting, that the sticking coefficient is coverage independent.

3. Beam Angle of Incidence Dependence of the Low Temperature Amplitude

The 375 K ammonia amplitude was measured as a function of beam angle of incidence. Results are plotted in Figure 14, for a 15 torr beam chopped at 25 Hz. Data could only be taken at angles $\theta \geq 0^\circ$ because of problems inherent in the geometry of the machine, but it is reasonable to assume that angle of incidence data on a Pt(111) surface is symmetrical around normal incidence, $\theta = 0^\circ$. While the data is scattered, the signal is flat to within less than 15% over the range of angles measured. One might argue that $r_{375\text{ K}}$ falls off at the steeper angles. This is possible from the appearance of the data, but the falloff is much more gradual than the cosine behavior that would be expected if there were an activation barrier to adsorption. To within the error of the data however, there is no angle of incidence dependence to $r_{375\text{ K}}$, and hence to the sticking coefficient. If ammonia adsorption on Pt(111) is an activated process, the barrier is below detection limits (less than .5 kcal/mole). A slight falloff of signal at steeper angle of incidence could reflect the coverage dependence of the sticking coefficient: at more grazing angles of incidence, the surface area of the crystal that the beam subtends is greater. Therefore, increasing the angle of incidence is equivalent to decreasing the beam pressure at the surface.

4. Angular Distributions of Scattered Ammonia

Measurements were made of the scattered ammonia angular distributions for two crystal temperatures, 1250 K and 375 K. The modulation frequency used was 100 Hz and the source backing pressure was 15 torr. The unnormalized differential mode amplitudes as a function of detector angle are shown in Figure 15. Arrows on the abscissas indicate the beam angle of incidence. At the high crystal temperature ammonia scattering is broad and cosinelike, peaking at the surface normal (a cosine distribution has been drawn in). At 375 K, however, the peak of the distribution is at the specular angle and the distribution is narrower. This behavior, as will be discussed below, is consistent with linear adsorption and desorption kinetics.

B. Pt(557)

1. Crystal Temperature Dependence of Ammonia Adsorption and Decomposition

The results of the crystal temperature dependence experiments on the Pt(557) surface are shown in Figures 16-18. Chopping frequencies used were 5, 20, and 50 Hz and source pressures were 5 and 15 torr. The data has been normalized in the same way as the Pt(111) data. The nitrogen phase lag data in Figure 18a is referenced to an elastically scattered nitrogen beam. As with Pt(111), no other products of decomposition besides hydrogen and nitrogen were detected.

At all measured chopping frequencies, both H_2 and N_2 amplitudes rise sharply between 650 and 700 K, peak at around 725 K and fall off gradually at higher temperatures. The extent to which decomposition takes place on the Pt(557) surface is much greater than that on the Pt(111). At peak temperatures the hydrogen amplitude is ~15 times greater for the stepped surface than for the (111) surface, (see Figure 19). The amplitudes have not been corrected for differences in pumping speeds and detector transmission factors between ammonia and the products. Hydrogen and nitrogen have smaller chamber pumping speeds than ammonia. Therefore, their background mode amplitudes look artificially large compared to the ammonia signals. Nitrogen data was only taken at 5 Hz because signal-to-noise was poor. The shape of the nitrogen amplitude curve is about the same as that for hydrogen, correcting for the amplitude differences.

At temperatures where decomposition is significant, the scattered ammonia amplitude essentially follows the product signals, falling with the onset of decomposition and slowly rising as decomposition tails off. At temperatures below the decomposition region, the ammonia amplitude looks similar to the ammonia amplitude from the (111) face. The low temperature asymptote is larger for the stepped surface, however. This implies a smaller sticking coefficient on the Pt(557). The phase lag data (Figs. 17) for ammonia are also similar to that on the (111). The maximum phase lag is smaller, however, only $\sim 14^\circ$. The magnitude of this phase lag is independent of

chopping frequency. There also appears to be some structure in the ammonia phase lag between 600 and 800 K, especially in the 5 Hz data. These phase lags are small, however, and the error in phase lag is $\sim 5^\circ$.

The hydrogen phase lags (Figs 18) are similar to those on the (111) surface. There is no phase lag at high temperatures but $\Delta\phi$ rises on the low temperature side of the hydrogen peak. The temperature at which the phase lag begins to rise increases with increasing chopping frequency. The effects of dephasing are always more visible at higher frequencies because at high frequencies the surface residence time represents a larger fraction of the chopping period. The nitrogen phase behavior is different from that of hydrogen. Dephasing occurs $\sim 200^\circ$ higher for nitrogen than for hydrogen at the same chopping frequency. The nitrogen phase lag becomes greater than 90° at ~ 600 K. This indicates sequential elementary processes leading to nitrogen production. There is no evidence for such a series process for hydrogen production.

Figure 20 shows the crystal temperature dependence data for the decomposition of deuterated ammonia, taken with a 5 torr beam at a frequency of 20 Hz. The deuterium amplitude curve is qualitatively similar to, although larger in magnitude than, the corresponding curve for NH_3 . The ND_3 amplitude curve shows more attenuation at the lowest temperatures than does the NH_3 data. As will be discussed below, this implies that ND_3 has a higher probability for adsorption than NH_3 . The ND_3 phase lag data is qualitatively similar to

the NH_3 data, but the low temperature peak is larger, $\sim 29^\circ$. The D_2 phase lag data is shown in Figure 18b along with the 20 Hz H_2 phase lags. They are essentially equivalent.

2. Beam Temperature Dependence of Ammonia Adsorption and Decomposition

With effusive or near effusive beams it is difficult to obtain any real information from beam temperature studies, owing to the significant high temperature tails and large half-widths of thermal energy distributions. Crystal temperature dependence experiments were performed with a beam temperature of 565 K. The results were indistinguishable from results of experiments with a room temperature beam. Thus, within experimental error and within the experimental limit of the apparatus, there is no beam energy dependence to the adsorption or decomposition of ammonia on the Pt(557) surface.

3. Beam Angle of Incidence Dependence of Ammonia Adsorption and Decomposition

Figure 21 shows data for the reaction as a function of θ and α . Hydrogen production was measured at 725 K and ammonia adsorption was measured at 475 K and 725 K. The source pressure was 5 torr and the chopping frequency was 5 Hz. The chamber geometry and crystal mounting made accurate measurement of pure θ and α dependence difficult, so this data was taken by a combination of rotating the crystal azimuthally and varying the polar angle. The combination of rotations was equivalent to keeping α constant at $+90^\circ$ and

varying θ . While the data is sparse, it is clear that there is no significant dependence on angle of incidence, either in the decomposition region or in the low temperature adsorption region. The angle of incidence data corroborates the beam temperature data in demonstrating that, to within experimental error, ammonia adsorption on this surface is not activated. From the angle of incidence data, one can also conclude that adsorption of ammonia is not enhanced by the presence of steps on the surface.

4. Beam Pressure Dependence of Decomposition

Hydrogen and nitrogen production, and scattered ammonia were monitored at 725 K as a function of incident beam pressure. Results are shown in Figure 22. For the purpose of determining reaction order, the amplitude data (Fig. 22a) has been plotted on a logarithmic scale. The ordinate is unnormalized amplitude and the abscissa is the scattered ammonia amplitude at a crystal temperature of 1250 K. The scattered ammonia signal is a better measure of beam pressure than the direct beam intensity because the channeltron saturates with large ion fluxes. The slopes of the product amplitude curves, determined by least squares, yield reaction orders in ammonia as follows: 0.87 for hydrogen and 0.98 for nitrogen. The scattered ammonia data have a slope of 1.05. These are, to within experimental error, the same value. From the amplitude data, then, the reaction is essentially first order in ammonia.

If a reaction is nonlinear, the product phase lag should vary with incident beam pressure. Figure 22b shows hydrogen and nitrogen phase lags as a function of the hot scattered ammonia amplitude. There is no variation in the hydrogen phase lags. Nitrogen, however, shows a slight increase in dephasing at low incident intensities.

Hydrogen production can therefore be considered to be first order in ammonia concentration. Considering the phase lag behavior of nitrogen as a function of beam pressure as well as crystal temperature (Fig. 18a), there may be an extra elementary step in the nitrogen production pathway that is nonlinear in ammonia.

5. $\text{NH}_3 + \text{D}_2$: The Isotope Exchange Reaction.

Results of hydrogenic exchange as a function of crystal temperature for this reaction are shown in Figure 23. A mixed beam (55 torr total, 15 torr NH_3) of ammonia and deuterium was used, modulated at 5 Hz. This gave a beam intensity ratio at the mass spectrometer of 2:1 $\text{D}_2:\text{NH}_3$. For the reasons explained above, this experiment was performed in the differential scattering mode. The detector sat at the surface macroscopic normal. Product amplitudes, $M/e = 18, 19$, and 20 are referenced to the direct beam ammonia intensity. Approximately 10% of the incident ammonia shows some extent of hydrogenic exchange. Production of partially and fully deuterated ammonia peaks between 625 and 675 K. At higher temperatures production declines, presumably because

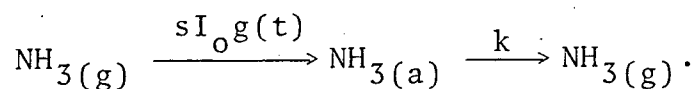
of competition between the exchange and decomposition pathways (see Fig. 24). The amplitude of exchanged ammonia also drops at lower temperatures. Most likely this is a result of the same process (ammonia adsorption/desorption: see below) which demodulates the NH_3 amplitude in the runs without deuterium.

VI. DISCUSSION

A. Pt(111)- Adsorption and Desorption of Ammonia

The extent to which decomposition takes place on the (111) surface is quite small. Less than 1% of the adsorbed ammonia undergoes decomposition under the most reactive conditions ($T \sim 775$ K). Thus (to within experimental error) the decomposition pathways do not perturb significantly the temperature dependence of the ammonia adsorption-desorption kinetics. Therefore, the behavior of the scattered ammonia signal as a function of temperature can be considered independently of any chemical reactions of the adsorbed ammonia molecules.

The temperature dependence data were fit to the simplest possible mechanism for the adsorption and desorption of a molecule from a surface:



Here, I_0 is the unmodulated beam intensity and $g(t)$ is the chopper gating function. The model parameter s will be referred to as the sticking coefficient. In the model it is a constant, independent of temperature, modulation frequency, and surface coverage. It represents the probability that a molecule impinging on the surface will adsorb. In terms of the experiments, s can be thought of as the probability that a molecule will undergo a detectable interaction with the surface. The fastest chopping frequency used in these

experiments is 150 Hz, so with a phase lag uncertainty of 5° (the average error in the phase lag differences), the fastest interaction detectable by a phase lag is about 100 μsec . Within the temperature and frequency range of these experiments, a constant sticking coefficient was found to be adequate in the modeling of the data. The other model parameter, k , is the standard first order Arrhenius form $k \equiv A e^{-E/RT}$. It is the temperature-dependent probability per unit time that an adsorbed molecule will desorb from the surface, and can be compared with previously measured values of the desorption rate constant.

The kinetics for the model in the above equation are worked out using the method of Jones et al.³ The rate of change of the surface concentration of ammonia $n(t)$ is

$$\frac{dn(t)}{dt} = sI_0g(t) - kn.$$

As in the pumping speed calculations above, the time-dependent terms are expanded in a Fourier series to first order, the surface concentration is differentiated and the terms of same order are set equal to each other. The first order terms give:

$$i\omega n_1 = sI_0g_1 - kn_1$$

or

$$n_1 = (sI_0g_1)/(i\omega + k).$$

The detected number density is proportional to the sum of the amount of ammonia desorbed from the surface ($k \cdot n$) and the amount of ammonia that does not adsorb $((1-s)I_0 g_1)$.

This gives the measured reaction product vector

$$re^{i\phi} \propto [ksI_0 g_1 / (i\omega + k)] + (1-s)I_0 g_1.$$

Dividing by the high temperature 'elastically' scattered signal (as described in the results section) cancels out the proportionality factors due to the chamber pumping speed as well as the incident beam parameters:

$$\frac{re^{i\Delta\phi}}{r_{1250K}} = \frac{ks}{i\omega + k} + 1-s,$$

where r/r_{1250K} and $\Delta\phi$ are the scattered amplitude and phase referenced to the elastically scattered signal. Solving for r/r_{1250K} and $\Delta\phi$ (the experimentally derived parameters),

$$\frac{r}{r_{1250K}} = \left[1 + \frac{(s^2 - 2s)}{1 + (k/\omega)^2} \right]^{\frac{1}{2}}$$

$$\tan\Delta\phi = wks / (k^2 + \omega^2(1-s)).$$

At low temperatures (where k is small) and high chopping frequencies, the amplitude approaches $(1-s)$. Only the molecules that have not adsorbed are detected. The residence time of the adsorbed molecules has become sufficiently long that the signal due to them is completely demodulated. At high temperatures the desorption rate becomes so rapid that $r/r_{1250K} \approx 1$.

Differentiation of the expression for $\tan\Delta\phi$ with respect to temperature elucidates the phase lag behavior. The derivatives show that the change in phase lag goes through a maximum when $k = w(1-s)^{\frac{1}{2}}$. At this temperature,

$$\Delta\phi(\phi_{\max}) = \tan^{-1} \frac{s}{2(1-s)^{\frac{1}{2}}}$$

$$r/r_{1250K}(\phi_{\max}) = (1-s)^{\frac{1}{2}}.$$

The magnitude of this phase peak is thus independent of frequency and is a function solely of the sticking coefficient. The physical reason for the phase peak is as follows. The measured phase lag is derived from the vector sum of two terms, the reaction product vector due to molecules desorbing from the surface and the reaction product vector of ammonia that has undergone (immeasurably) rapid scattering from the surface. As the temperature drops, the adsorbed ammonia spends more time at the surface, so the phase lag increases. At the same time, demodulation of the signal occurs. Fewer adsorbed molecules make a contribution to the total measured signal. Thus, a maximum value of the phase lag appears at some surface temperature. With lower temperatures, the non-adsorbing ($\Delta\phi = 0$) ammonia contributes more to the total phase lag so that $\Delta\phi$ returns to 0° .

The Pt(111) ammonia data in Figures 11a-d follow this behavior very closely. A computer least squares fit of the data to the calculated amplitudes and phase lags as a function of temperature and modulation frequency was made using

the MINUIT minimization program.⁷ The best fit to the data gives the following values of the adsorption-desorption parameters:

$$s = 0.74$$

$$k = 2.65 \times 10^{10} e^{-15,500/RT}$$

Amplitude and phase curves, using these values of s and k have been drawn in on Figures 11a-d. The prefactor is in units of sec^{-1} and the activation energy is in units of cal/mole.

The simplicity of the mechanism and the quality of the fit make this model extremely attractive. The angular distributions in Figure 15 provide independent confirmation of the model. The high temperature angular distribution is cosinelike, indicating that adsorption-desorption is taking place even at 1250 K. If the sticking coefficient had a temperature dependence such that at high temperatures no ammonia was adsorbing, one would expect specular scattering at high temperatures. The model predicts that at low temperatures ($r \sim 1-s$) all adsorbed molecules are lost to the detector and only the molecules that have not adsorbed are phase-sensitive detectable. Therefore, one would expect essentially specular scattering at very low temperatures. The angular distribution taken at 375 K peaks very near the specular angle. One might expect the distribution to peak even closer to the normal than it does, considering that the molecules that have not adsorbed on the surface are

not undergoing truly elastic scattering. They are only interacting with the surface for a shorter time than can be detected by phase lags.

The adsorption-desorption mechanism described above does not, of course, completely describe the ammonia/Pt(111) system. Decomposition of ammonia takes place, though at high temperatures where k is large compared to the chopping frequencies used in these experiments. A discussion of the mechanism of ammonia decomposition and some comments on surface poisoning will be given below.

The data in Figure 13 suggest a weak yet measurable dependence of the sticking coefficient on beam pressure. Though it is a good approximation, a constant sticking coefficient cannot account for this pressure dependence. Some functional form, very weakly dependent on surface coverage would more correctly describe s .

1. Comparison of the Data and the Model

With due consideration of the error limits on the data, the quality of the fit is good. At all frequencies the low temperature amplitude demodulation is well described by the model. However, the calculated amplitude curve approaches unity far more rapidly than does the data. Several surface processes could be responsible for this. First, while hydrogen exchange was not studied on the (111) surface, evidence from the experiments on the Pt(557) crystal for low temperature exchange must be considered. If there is some hydrogen exchange occurring, this extra elementary surface

process could demodulate the scattered ammonia signal. Such behavior should be accompanied by a phase lag, which could exist but be lost in the uncertainty in the phase data. Surface poisoning, due to partial decomposition of the ammonia into nonvolatile species would also reduce the scattered ammonia signal. Decomposition to desorbing products should also effect the ammonia signal to some extent. This reaction pathway is so insignificant, however, that the detector's signal-to-noise ratio would have to be improved by about an order of magnitude in order to detect such a change. It is reasonable to conclude that decomposition is taking place only at defect sites on the (111) surface.

The phase lag data is also fit well by the model. As the peaking of the phase lag is so closely tied to the sticking coefficient, a small change in the value of s can significantly alter the shape of the $\Delta\phi$ curve.

2. The Physical Significance of s and k , and Comparison with Previous Measurements

A sticking coefficient of 0.74 compares favorably with previous reports of an ammonia sticking coefficient near unity.⁹ A high value for s would be expected, considering that ammonia has a reasonably large dipole moment for a covalently bonded molecule. A certain fraction of impinging molecules will not have the proper steric or electronic configuration, or energetics needed for adsorption. These molecules will scatter elastically or inelastically, and make the sticking coefficient smaller than unity.

Alternatively, some molecules may impinge on surface sites that are already occupied. This too will reduce the sticking coefficient.

The desorption rate constant does not have expected values. Prefactors for desorption are generally thought to be of the order of the metal-adsorbate bond frequency, $\sim 10^{13} \text{ sec}^{-1}$. If the best-fit pre-exponential factor ($2.65 \times 10^{10} \text{ sec}^{-1}$) is to be believed, this desorption process must be considerably slower than a molecular vibration. Here again, surface processes like hydrogenic exchange can be invoked, as such a surface interaction would slow down the desorption process. Another possibility is that the adsorbed ammonia must undergo some sort of conformational change in order to desorb. An example of this could be inversion. In the gas phase, the ammonia inversion frequency is $\sim 10^6 \text{ sec}^{-1}$. It must also be noted that low prefactors (around 10^9 sec^{-1}) have been reported for other systems, e.g., CO and O_2 on tungsten.²³

Gland's T.D.S. measurement of the ammonia activation energy for desorption from the low energy site (77 kJ/mole = 18.4 kcal/mole) on a Pt-S[(12(111)x(111))] surface was based on a prefactor of 10^{13} . Substituting the prefactor determined here into Gland's data yields an activation energy for desorption of 14.9 kcal/mole, in good agreement with the 15.5 kcal/mole energy derived in this work. While Gland's stepped surface is not the same as a (111) surface, its terrace width is large so that the comparison is reasonable.

B. Adsorption and Decomposition of Ammonia on the Stepped Pt(557) Surface

Decomposition of ammonia on the Pt(557) surface is a significant reaction pathway, and must be considered in a discussion of the mechanism of the ammonia interaction with this surface. At peak temperature (~ 725 K), 10% of the adsorbed ammonia decomposes to produce nitrogen and hydrogen, an effect approximately 15 times greater than decomposition on the (111) surface. Unlike on the (111) surface, the decomposition has a measurable effect on the detected amplitude of scattered ammonia.

The amplitude and phase behavior of reactants and products on the (557) surface is complicated, and any reaction mechanism invoked to explain the system should describe most, if not all aspects of this behavior. An acceptable reaction model must be capable of reflecting the following experimentally determined observations about the surface interaction.

* At low temperature, the amplitude and phase behavior of NH_3 is qualitatively similar to that on the (111) surface. There is no detectable decomposition in this low temperature range ($T \lesssim 550$ K). A model must therefore be able to describe low temperature ammonia interactions in terms of simple adsorption and desorption. The angle of incidence and beam temperature studies imply that adsorption on the (557) surface is not activated, so there should not be a parameter representing a barrier to adsorption.

* Product amplitudes rise rapidly with increasing temperatures. For example, at 5 Hz, the hydrogen amplitude rises a factor of 30 over a 150° range. This sudden 'turning on' of the decomposition pathway is accompanied by a diminution of the hydrogen signal dephasing. At peak hydrogen amplitudes, the H₂ phase lag has dropped to 0°. This rise in product amplitude is also accompanied by a comparable drop in ammonia amplitude.

* At temperatures above ~750 K, the product amplitudes fall again gradually, so that almost no hydrogen is being produced at 1300 K. This implies that at temperatures above 750 K there is a more favorable, non-reactive pathway open to the reactant. A successful reaction model must give adsorbed ammonia an alternative to decomposition that predominates at higher temperatures.

* Hydrogen production is experimentally determined to be first order in ammonia concentration. If there are non-linear steps in the pathway to hydrogen production and desorption, these must be weak enough to give an overall first-order appearance to the reaction. It is possible that the reaction is truly non-linear. If there is substantial adsorption of hydrogen from the background, the surface concentration of hydrogen atoms would be larger than expected simply from ammonia decomposition. This would make the re-combinative desorption of hydrogen appear first-order, even if there are non-linear steps in the decomposition reaction.

* Nitrogen amplitude behavior is similar to that of hydrogen, in that it rises sharply and falls gradually. The phase lag information suggests however, that there may be a step that is not first-order in the nitrogen production mechanism. There should also be a serial step leading to nitrogen desorption, as indicated by the temperature dependence of the phase lag (phase lags $>90^\circ$ imply a series of reaction steps, each contributing a maximum of 90° of phase lag).

* A suitable reaction mechanism should also account for the hydrogen exchange that takes place on the surface. Exchange was observed between 450 and 800 K. Exchange presumably takes place at all temperatures where surface ammonia remains intact for a minimum amount of time. At 700 K, assuming no decomposition, the surface residence time of NH_3 is 200 μsec . Exchange is not detectable below ~ 600 K because demodulation reduces the exchange amplitude below detection limits. There are two possible explanations for the loss of the isotopically exchanged ammonia signal at higher temperatures. First, the surface residence time of molecular NH_3 may be too short for exchange to take place. The other possibility is that exchange takes place at the same sites at which decomposition occurs, and at ~ 700 K exchange followed by ammonia desorption becomes the less favorable competitive pathway. Presumably at high temperatures where decomposition becomes insignificant, desorption is taking place too rapidly to allow exchange.

* Self-poisoning of the reaction takes place to some extent at all temperatures (as evidenced by the time dependence of the ammonia and product signals), but primarily at temperatures where decomposition takes place readily. While the fraction of molecules that actually cause the surface poisoning may be small, this kinetic pathway should be considered in a reaction model.

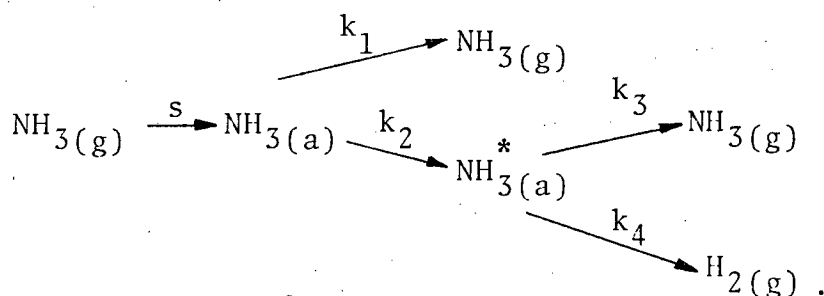
1. Kinetic Models for $\text{NH}_3/\text{Pt}(557)$

In the kinetic models described below, nitrogen production, hydrogen exchange, and surface poisoning have been neglected. For nitrogen production and hydrogen exchange, the detector signal-to-noise ratio was too small to allow precise measurement. No attempt was made to quantify self-poisoning. Some suggestions will be given on possible elementary steps that could account for these observed phenomena.

The data was fit to several variations of a single kinetic model, with differing amounts of success. The MINUIT program was again employed to find the best fits to the kinetic parameters.

a. The Basic Model

The basic model employs a second ammonia desorption step to cause the falloff in hydrogen production:



As in the adsorption-desorption model, s is the temperature, frequency, and coverage independent probability that an incident ammonia molecule adsorbs on the surface, the sticking coefficient. The rate constants (k_1 - k_4) are first-order Arrhenius functions. At low temperatures, k_1 is greater than k_2 and the predominant desorbing species is NH_3 . As the temperature rises, k_2 increases and decomposition becomes more favorable. At very high temperatures, k_3 dominates over k_4 and adsorbing ammonia again desorbs without decomposing. To put a physical interpretation on the mechanism, k_2 represents activation of the adsorbed ammonia, either diffusion to the steps or some configurational change in the molecule. $\text{NH}_3^*_{(a)}$ is transition state ammonia, capable of decomposing or desorbing intact. The decomposition process itself is undifferentiated. It is assumed that all processes leading from the activated species to gas phase hydrogen can be subsumed in one rate constant. The parameter k_4 represents the dissociation of ammonia into atoms and recombinative desorption of hydrogen. The desorption process limited by k_3 is necessary: once k_2 prevails over k_1 , there is no way for k_1 -type desorption to dominate the mechanism.

The analysis of the kinetics is performed as in the (111) case. Where the variables n and n^* are the first Fourier coefficients of the surface concentrations of $\text{NH}_3(a)$ and $\text{NH}_3^*_{(a)}$, respectively, and all other variables are the same as in the (111) analysis,

$$i\omega n = sI_0 g_1 - (k_1 + k_2)n.$$

Rearranging,

$$n = \frac{s I_0 g_1}{i\omega + (k_1 + k_2)}.$$

$$i\omega n^* = k_2 n - (k_3 + k_4) n^*,$$

so

$$n^* = \frac{k_2 n}{i\omega + (k_3 + k_4)} = \frac{k_2 s I_0 g_1}{(i\omega + k_1 + k_2)(i\omega + k_3 + k_4)}.$$

The gas phase time-resolved number density of NH_3 is the detected reaction product vector $\text{re}^{i\phi}_{\text{NH}_3}$. As in the Pt(111) analysis, the reaction product vector is normalized against a scattered beam of ammonia at 1250 K to cancel out incident beam and pumping speed effects.

$$\frac{\text{re}^{i\Delta\phi}}{r_{1250\text{K}}} \text{NH}_3 = \frac{k_1 s}{i\omega + (k_1 + k_2)} + \frac{k_2 k_3 s}{(i\omega + k_1 + k_2)(i\omega + k_3 + k_4)} + 1 - s.$$

The reaction product vector for hydrogen is

$$\frac{\text{re}^{i\Delta\phi}}{r_{1250\text{K}}} \text{H}_2 = \frac{k_2 k_4 s}{(i\omega + k_1 + k_2)(i\omega + k_3 + k_4)}.$$

As was described above, the hydrogen phase lag was referenced to an elastically scattered hydrogen beam.

The hydrogen amplitude was corrected for pumping speed and detection efficiency differences between ammonia and hydrogen by means of an extra fitting parameter in the numerator of the hydrogen reaction product vector. This parameter is the ratio between the observed hydrogen amplitude

and the hydrogen amplitude that would be measured if the pumping speeds and detector efficiencies for ammonia and hydrogen were the same.

The computer calculation was performed in two stages. First the low temperature adsorption and desorption of ammonia was fit to give values for k_1 and s . The low temperature ammonia data ($T \leq 500$ K for 5 Hz, $T \leq 525$ K for 20 Hz, and $T \leq 550$ K for 50 Hz) were fit to the kinetic model employed for the $\text{NH}_3/\text{Pt}(111)$ system. This yielded parameter values as follows:

$$s = 0.49$$

$$k_1 = 7.45 \times 10^7 e^{-13,200/RT}.$$

The remaining parameters were then fit with these values fixed. The results are

$$k_2 = 1.75 \times 10^8 e^{-18,300/RT}$$

$$k_3 = 9.74 \times 10^{15} e^{-31,000/RT}$$

$$k_4 = 6.5 \times 10^9 e^{-5400/RT}.$$

All prefactors are in units of sec^{-1} and all activation energies are in units of cal/mole.

The temperature dependence of this model is shown in Figures 16-18. Several problems are apparent in the fit. First, the ammonia amplitude data, while adequately fit in the low temperature region, is not fit at all in the decomposition region. The calculated curve fails to dip enough

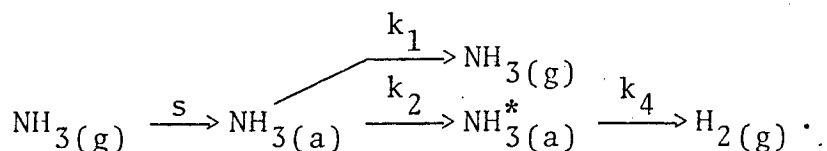
where decomposition is significant. The ammonia phase data is fit well, though the phase peak is a reflection solely of the low temperature parameters. The fit to the hydrogen data is not as acceptable. The calculated low temperature rise is far too slow to fit the data, although the falloff at higher temperatures is modeled well. The calculated temperature dependence of the phase lag, while qualitatively similar to the data, dephases at too low a temperature.

While the mechanism is physically reasonable, the fit to the data is crude. Furthermore, it is not obvious that the values of the rate constants are sensible ones. The adsorption/desorption parameters s and k_1 are similar to those for the (111) surface, and arguments similar to those above can be made in favor of their calculated values. The rate constant k_2 , which is assumed to govern the rate of diffusion of ammonia to surface steps, has a prefactor well within the generally accepted limits for diffusion rate constants.²⁴ Gland's high energy flash desorption peak, reanalyzed using the prefactor determined in this work for k_3 , yields an activation energy of 29.6 kcal/mole. This is virtually identical to the k_3 energy of 31 kcal/mole. In spite of the agreement with Gland's result, the prefactor of k_3 is much greater than the expected value for desorption of 10^{13} sec^{-1} . As the surface processes that k_4 reflects are not obvious, it is not clear how reasonable its calculated values are. Further discussion of these calculated parameters is given below, following a description of the other models that were fit to the data.

An attempt was made to improve the fit by changing the form of k_2 . With the assumption that k_2 is a diffusion step, a 'hopping' model was proposed for this parameter. For this model the rate of diffusion to the steps is governed by the product of an Arrhenius expression and a probability that a molecule will hop from the site it occupies to the nearest step. This is based on an equal probability of an adsorbed molecule hopping from a site to any adjacent site of same symmetry. This model did not significantly improve the fit to the data.

b. Other Models

The next model tried was based on two observations regarding the above models. First, the Arrhenius rate constant k_2 is incapable of 'turning on' rapidly enough to account for the observed sharp rise in product formation. Some functional form other than an Arrhenius function is required to match the data in this temperature region. Second, if k_2 did not continue to increase exponentially with temperature after product formation peaks, the falloff of the hydrogen amplitude could be accounted for by k_1 . This would make the rate constant k_3 superfluous. The following kinetic model was therefore proposed:



The parameters s , k_1 , and k_4 are the same parameters as in the basic model (k_4 could describe different reaction steps,

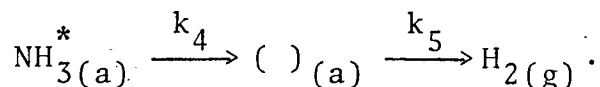
but it still governs the decomposition of activated ammonia and the recombinative desorption of H_2). For this model, however, k_2 governs a sudden surface phenomenon, nominally a surface phase transition. It was assumed that the ammonia/Pt(557) system undergoes a transformation which puts the ammonia molecules in a configuration favorable to decomposition. The rate constant k_2 has the following form:

$$k_2 = A / (1 + e^{-(T - T_0 / \Delta T)}).$$

Here, A , T_0 , and ΔT are parameters to be fit. T_0 determines the temperature at which the rise takes place and ΔT determines the width of the rise. A is a prefactor. The fitting parameter used to correct for pumping speed and detector efficiency differences between ammonia and hydrogen was replaced by an experimentally determined constant. The amplitude data for both ammonia and hydrogen were fit very well by this model. The fit to the hydrogen phase lag data, however, is slightly worse than the original model fit.

The fundamental problem with the above models is their inability to fit the product phase lags. Dephasing occurs in the hydrogen signal at the same temperatures at which the hydrogen amplitude rises sharply. It is possible that the low temperature hydrogen amplitude is demodulated as a consequence of the dephasing. If this is the case, the hydrogen amplitude is in essence showing behavior similar to the low temperature ammonia amplitude. Possibly hydrogen production does not suddenly 'turn on'. Demodulation could just

make it appear to do so. If a kinetic model could describe the dephasing properly, the hydrogen amplitude behavior should be a natural consequence of the kinetics. An extra serial step in the decomposition of activated ammonia could accomplish this:



Here $()_{(a)}$ represents some unknown surface intermediate. This form of the model has yet to be tested.

A model with a temperature dependent sticking coefficient might be invoked. Such a sticking coefficient would cause the falloff of hydrogen production without a second desorption step or an artificial rate constant for k_2 . There are three reasons why this type of model was not tested.

1) The angular distribution of hot scattered ammonia from the Pt(111) surface clearly demonstrated that adsorption was taking place even at high temperatures.

2) A constant sticking coefficient fits the low temperature ammonia behavior excellently.

3) It is not clear what functional form would be physically reasonable for $s(T)$. The function would have to fit both the low temperature and high temperature data.

c. The Unmodeled Observables

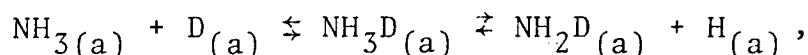
Nitrogen production, hydrogen exchange and surface poisoning have been ignored in the above reaction models. Possible surface processes that account for these observed phenomena are as follows.

Nitrogen production should take place from the same transition state as hydrogen. The basic model will not allow for product phase lags greater than 90° so a series of steps are needed to account for the nitrogen phase behavior.



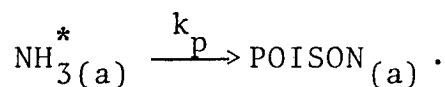
FRAGMENTS represents ammonia fragments on the surface. k_6 could be a nonlinear rate constant.

Hydrogen exchange takes place at temperatures where decomposition is not favored ($T \lesssim 700 \text{ K}$). It is therefore quite possible the adsorbed ammonia rather than the decomposable activated species that undergoes exchange. Presumably the activated species is not present long enough to undergo exchange. For the $\text{NH}_3 + \text{D}_2$ reaction the kinetics are



where there is a steady-state concentration of NH_4 (H represents an H or a D). The short-lived surface complex is implied from the work of Morrow and Cody.¹⁸ Presumably exchange between ammonia molecules takes place either through short-lived NH_2 and NH_4 intermediates or via a concerted mechanism.

While self-poisoning of the reaction was observed at all temperatures below 1000 K, it was most apparent in the decomposition region. It is reasonable to assume that it is the result of a partial decomposition of the activated species into a non-volatile surface fragment:



Poisoning occurs on the (111) surface as well as the (557), though not to the same extent. It must therefore be concluded that a small concentration of non-desorbing fragments can have a significant effect of the remaining reaction pathways.

2. Comparison and Interpretation of the Calculated Reaction Parameters

The low temperature adsorption/desorption parameters were fit independently of decomposition, so they will be discussed separately. The most significant fact that can be seen from a comparison of the (111) and (557) amplitude data is the discrepancy in sticking coefficients. $s_{(111)} (=0.74)$ is greater than $s_{(557)} (=0.49)$. Apparently the surface steps inhibit ammonia adsorption. As there is no angle of incidence effect on adsorption, the electronic configuration of the steps must distort the entire structure such that the terraces no longer behave like (111) planes. This is reasonable considering the terraces are only 6 atoms wide. While the steps inhibit adsorption, they enhance the decomposition process.

The desorption rate constants for the two surfaces are similar: $k_{1(557)} = 7.45 \times 10^7 e^{-13,200/RT}$ and $k_{(111)} = 2.65 \times 10^{10} e^{-15,500/RT}$. The activation energies are almost identical, but the prefactors differ by over two order of magnitude. If more molecules undergo hydrogen exchange on the (557) surface before desorbing, the (557) prefactor would be smaller than the (111) prefactor. The lower value for the

prefactor could also be due to surface diffusion of ammonia before desorption.

As was stated above, the basic model rate constant k_2 is of reasonable value for a diffusion-controlled step (it is unfortunate that it fits the data so poorly). The activation energy of k_3 fits well with Gland's results, but the prefactor (9.74×10^{15}) is three orders of magnitude faster than expected. Large desorption prefactors have been previously reported. If activated ammonia is weakly bound to the surface, the desorption rate constant could be governed by rotational rather than vibrational degrees of freedom. Madix attributes large desorption prefactors to an increase in rotational entropy in the transition state molecule.²⁵ A second desorption process (desorption from the steps?) corroborates Gland's observation of two T.D.S. peaks from his stepped surface.

The kinetic steps represented by k_4 in the basic model have a low activation energy and a low prefactor ($k_4 = 6.5 \times 10^9 e^{-5400/RT}$). As k_4 represents two or more steps, the value of the prefactor may not be unreasonably low. Robertson and Willhoft fit their 'ultrahigh vacuum' decomposition reaction probability with an activation energy of 4.1 kcal/mole for temperatures above 500 K.¹² It is of interest to note that the activation energy of k_4 is also remarkably close to the previously reported energy of hydrogen recombinative desorption on platinum, 4.5-5.2 kcal/mole.²⁶ It is possible, therefore, that hydrogen

recombination is rate-limiting for k_4 . The production of hydrogen from ammonia was, however, determined to be first order. This behavior can be rationalized, as was stated above, if it is assumed that there is adsorption of hydrogen from the ambient.

C. Adsorption and Decomposition of ND_3 on Pt(557)

There is not enough data to properly analyze the reaction of ND_3 on the (557) surface. From the low temperature data, however, a sticking coefficient of $s = 0.70 \pm 0.05$ can be deduced. This is somewhat larger than s for NH_3 . It indicates that the deuterated species has a higher adsorption probability than NH_3 . Furthermore, assuming equal pumping speeds and detector transmission factors, more than twice as much ND_3 is decomposed as NH_3 at peak temperatures. This is very different from the results reported by Shindo *et al.*,²¹ who examined the isotope effect of ammonia decomposition on tungsten. They observed that the rate of nitrogen production from NH_3 was 1.2 times greater than from ND_3 .

The entire surface reaction is shifted about 25 K to higher temperature, compared to the NH_3 data. To draw any conclusions about the mechanism of this isotope effect from the scant ND_3 data would, however, be unwise. Ammonia adsorption and decomposition are nevertheless effected by isotope substitution.

VII. SUMMARY AND CONCLUSIONS

Ammonia adsorbs associatively on the Pt(111) and Pt(557) surfaces. The sticking coefficients are high ($s_{111} = 0.74$, $s_{557} = 0.49$). The probability of adsorption on the stepped surface is 66% smaller than on the flat surface. In spite of this, approximately 15 times more adsorbed ammonia decomposes to produce N_2 and H_2 on the stepped surface. On the stepped surface at peak temperatures (725 K), 10% of the adsorbed ammonia decomposes. Hence the steps enhance decomposition while diminishing the probability of reactant adsorption.

There is essentially no reactant angle of incidence dependence to adsorption on either crystal, nor to decomposition on the (557) surface. The sticking coefficient on the (111) surface was shown to have a weak coverage dependence. The production of hydrogen on the stepped surface was, however first order in ammonia pressure.

Hydrogenic atom exchange between NH_3 and D_2 takes place on the (557) surface at temperatures where there is little or no decomposition ($T \leq 700$ K). Approximately 10% of adsorbed ammonia undergoes exchange. This presumably occurs through a short-lived NH_3D intermediate.

The interaction of NH_3 with Pt(111) can be described by a simple adsorption and desorption model. The best fit parameters for this model are $s = 0.74$, $k = 2.65 \times 10^{10} e^{-15,500/RT}$. Decomposition is not a significant pathway on the (111)

surface and can be assumed to take place only at defect sites on the surface.

Ammonia adsorption and decomposition on Pt(557) is considerably more complicated. No kinetic model tested could adequately match the product phase behavior. Low temperature adsorption and desorption of ammonia was well fit by the following parameters: $s = 0.49$, $k_1 = 7.45 \times 10^7 e^{-13,200/RT}$. In the basic model tested, activation of adsorbed ammonia (surface diffusion to steps) was fit by $k_2 = 1.75 \times 10^8 e^{-18,300/RT}$. A second desorption step was best fit by the rate constant $k_3 = 9.74 \times 10^{15} e^{-31,000/RT}$. The surface reaction (decomposition followed by hydrogen desorption) was found to be governed by the rate constant $k_4 = 6.5 \times 10^9 e^{-5400/RT}$. The value of this rate constant suggests the possibility that recombinative desorption of H_2 is rate limiting. This model fails to fit the sharp low temperature rise in hydrogen production.

A better fit to the amplitude data was found by employing an artificial steplike function (representing a surface phase transformation) for the kinetic step representing ammonia activation. This model showed no improvement to the hydrogen phase lag fit.

It was postulated that the sharp change in hydrogen amplitude at low temperatures may be a demodulation effect.

Finally, deuterated ammonia has higher probabilities of adsorption and decomposition on Pt(557) than does NH_3 .

Clearly there are several experiments that should be performed to further elucidate the ammonia/platinum system. They are as follows:

1) A careful LEED study of the ammonia covered Pt(557) surface, in order to determine if there is indeed a surface phase transformation at ~ 700 K.

2) An examination of the temperature, frequency, and pressure dependence of ND_3 on Pt(557). This would remove the possibility of background adsorption of hydrogen interfering with the reaction. It would also elucidate the isotope effect.

3) An investigation of isotope exchange employing NH_3 and ND_3 on both surfaces. A dosing needle could introduce one of the reactants to the surface to avoid isotope mixing on walls or in the source. Use of deuterated ammonia rather than deuterium would better clarify the mechanism of the interaction, and confirm that exchange takes place without decomposition.

4) A careful examination of the temperature and frequency dependence of nitrogen production on the (557) surface. This would complete the kinetic model and determine the disposition of all the reaction products.

5) A spectroscopic analysis of the reaction. Employment of high resolution electron energy loss spectroscopy could give insight into surface intermediates, elucidate the nature of the self-poisoning process, and clarify the reaction mechanism.

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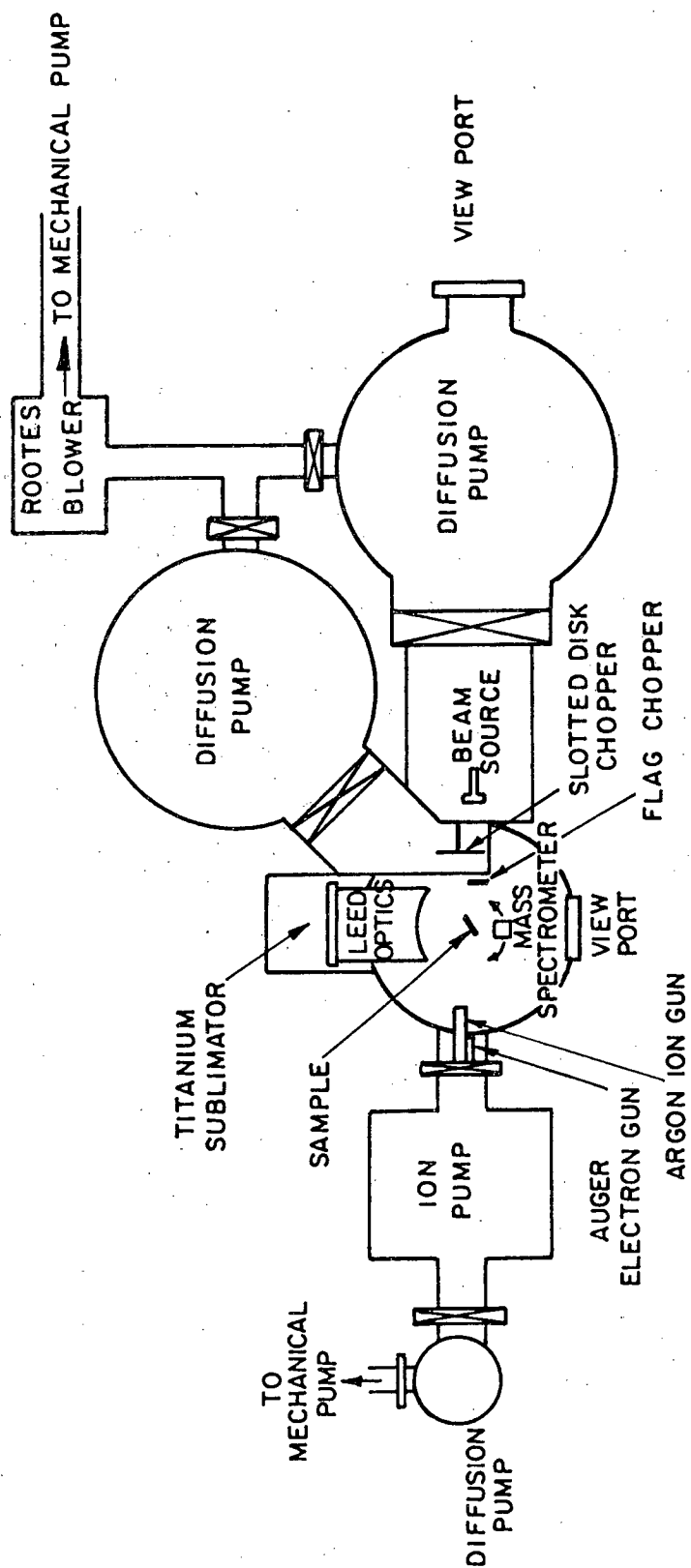
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FIGURE CAPTIONS

1. Schematic of the molecular beam apparatus used in these experiments.
2. Models of the Pt(557) and Pt(111) crystal surfaces.
3. Detected incident ammonia amplitude as a function of source backing pressure.
4. Front and back of multiple-crystal holder, showing two mounted crystals.
5. Angular distribution of helium scattered from Pt(557). Arrow on abscissa indicates beam angle of incidence, $\theta = 45^\circ$, $\alpha = +90^\circ$.
6. Definition of angles on a stepped surface. The right side of the figure is where θ and α are greater than 0° .
7. Normalized amplitudes and phase lags as a function of modulation frequency ($\omega = 2\pi f$) from nitric oxide pumping speed experiments. Curves show functional fits for a pumping speed of 80 sec^{-1} .
8. Normalized amplitudes and phase lags as a function of ω from water pumping speed experiments. Curves show functional fits for a pumping speed of 630 sec^{-1} .
9. Normalized amplitudes and phase lags as a function of ω from ammonia pumping speed experiments. Shown are data and curves for the chamber pumped by the ion pump alone and for the chamber pumped by the ion pump, TSP, and liquid nitrogen shields. Fits are to pumping speeds of 380 sec^{-1} and 595 sec^{-1} , respectively.
10. Normalized amplitudes and phase lags as a function of ω from nitrogen pumping speed experiments. Curves show functional fits for a pumping speed of 50 sec^{-1} .
11. Amplitudes and phase lags of ammonia scattered from the Pt(111) surface as a function of crystal temperature. Curves are best fits to the simple adsorption-desorption model with $s = 0.74$, $k = 2.65 \times 10^{10} e^{-15,500/RT}$.
 - a. $f = 5 \text{ Hz}$. Error in amplitude data is $\pm 4\%$; error in phase data is $\pm 5^\circ$.
 - b. $f = 20 \text{ Hz}$. Error in amplitude data is $\pm 4\%$; error in phase data is $\pm 5^\circ$.
 - c. $f = 50 \text{ Hz}$. Error in amplitude data is $\pm 4\%$; error in phase data is $\pm 5^\circ$.

- d. $f = 150$ Hz. Error in amplitude data is $\pm 7\%$; error in phase data is $\pm 5^\circ$.
12. Hydrogen production from $\text{NH}_3/\text{Pt}(111)$. Shown are normalized amplitudes and phase lags as a function of crystal temperature. Error in amplitude data is ± 0.05 ; error in phase data is $\pm 10^\circ$.
 13. Ammonia sticking coefficient ($1 - r_{375\text{K}}/r_{1250\text{K}}$) on $\text{Pt}(111)$ as a function of beam pressure. Abscissa is the scattered ammonia amplitude for a crystal temperature of 1250 K, $f = 150$ Hz.
 14. Scattered ammonia amplitude from $\text{Pt}(111)$ as a function of beam angle of incidence from surface normal. Crystal temperature is 375 K.
 15. Angular distributions of ammonia scattered from $\text{Pt}(111)$. Arrows indicate beam angle of incidence.
 - a. $T = 1250$ K. Curve is a cosine function.
 - b. $T = 375$ K.
 16. Scattered ammonia and product amplitudes from $\text{NH}_3/\text{Pt}(557)$ as a function of crystal temperature. Curves are best fits to the basic model described in the text (solid lines = NH_3 , dashed lines = H_2). Product amplitudes are not corrected for pumping speed and detector efficiency differences.
 - a. $f = 5$ Hz. Shown is scattered ammonia and product hydrogen and nitrogen. Error in ammonia data is $\pm 3\%$, in hydrogen data ± 0.33 , in nitrogen data ± 0.1 .
 - b. $f = 20$ Hz. Shown is scattered ammonia and product hydrogen. Error in ammonia data is $\pm 3^\circ$, in hydrogen data ± 0.1 .
 - c. $f = 50$ Hz. Shown is scattered ammonia and product hydrogen. Error in ammonia data is $\pm 5\%$, in hydrogen data ± 0.1 .
 17. Ammonia phase lag from $\text{NH}_3/\text{Pt}(557)$ as a function of surface temperature. Error in data is $\pm 5^\circ$. Curves are best fits to the basic model described in the text.
 - a. $f = 5$ Hz.
 - b. $f = 20$ Hz.
 - c. $f = 50$ Hz.

18. Temperature dependence of product phase lags from $\text{NH}_3/\text{Pt}(557)$ and $\text{ND}_3/\text{Pt}(557)$. Error in data is $\pm 10^\circ$. Curves are best fits to the basic kinetic model described in the text for the hydrogen data.
 - a. $f = 5$ Hz. Shown are product hydrogen and nitrogen phase lags.
 - b. $f = 20$ Hz. Shown are product hydrogen and deuterium phase lags.
 - c. $f = 50$ Hz. Shown are product hydrogen phase lags.
19. Comparison of nitrogen and hydrogen production from the (111) and (557) surfaces as a function of crystal temperature. The hydrogen data from the two surfaces are directly comparable. The nitrogen data has not been corrected for pumping speed and detection efficiency differences.
20. ND_3 amplitude and phase lag and product D_2 amplitude from $\text{ND}_3/\text{Pt}(557)$ as a function of crystal temperature. D_2 amplitude has been divided by two and is not corrected for pumping speed and detector efficiency differences. Error in ND_3 amplitude is $\pm 5\%$; in ND_3 phase lag $\pm 5^\circ$; in D_2 amplitude ± 0.1 . $f = 20$ Hz.
21. Beam angle of incidence dependence on ammonia adsorption and decomposition on $\text{Pt}(557)$. Shown are ammonia and hydrogen amplitudes for a crystal temperature of 725 K and ammonia amplitude for a crystal temperature of 470 K. $f = 5$ Hz. $\alpha = +90^\circ$.
22. Ammonia beam pressure dependence of hydrogen and nitrogen production. Plotted are hydrogen, nitrogen, and ammonia signals at $T = 725$ K as a function of the scattered ammonia amplitude at 1250 K. $f = 5$ Hz.
 - a. Signal amplitudes (unnormalized, in arbitrary units). Lines are linear least squares fits to the data.
 - b. Signal phase lags.
23. Amplitudes of isotopically substituted ammonia from $\text{NH}_3 + \text{D}_2$ on $\text{Pt}(557)$. Plotted are differential mode amplitudes of $M/e = 18, 19$, and 20 as a function of crystal temperature. $\theta = 45^\circ$, $\alpha = +90^\circ$. Detector looked at surface normal. Error in data is $\pm 75 \times 10^{-6}$.
24. Temperature dependence of ammonia adsorption, decomposition, and isotope exchange (from $\text{NH}_3 + \text{D}_2$) on $\text{Pt}(557)$. Ordinate is signal amplitude in arbitrary units. Curves have been drawn through the data points to assist the eye.



XBL 785-4948

Figure 1

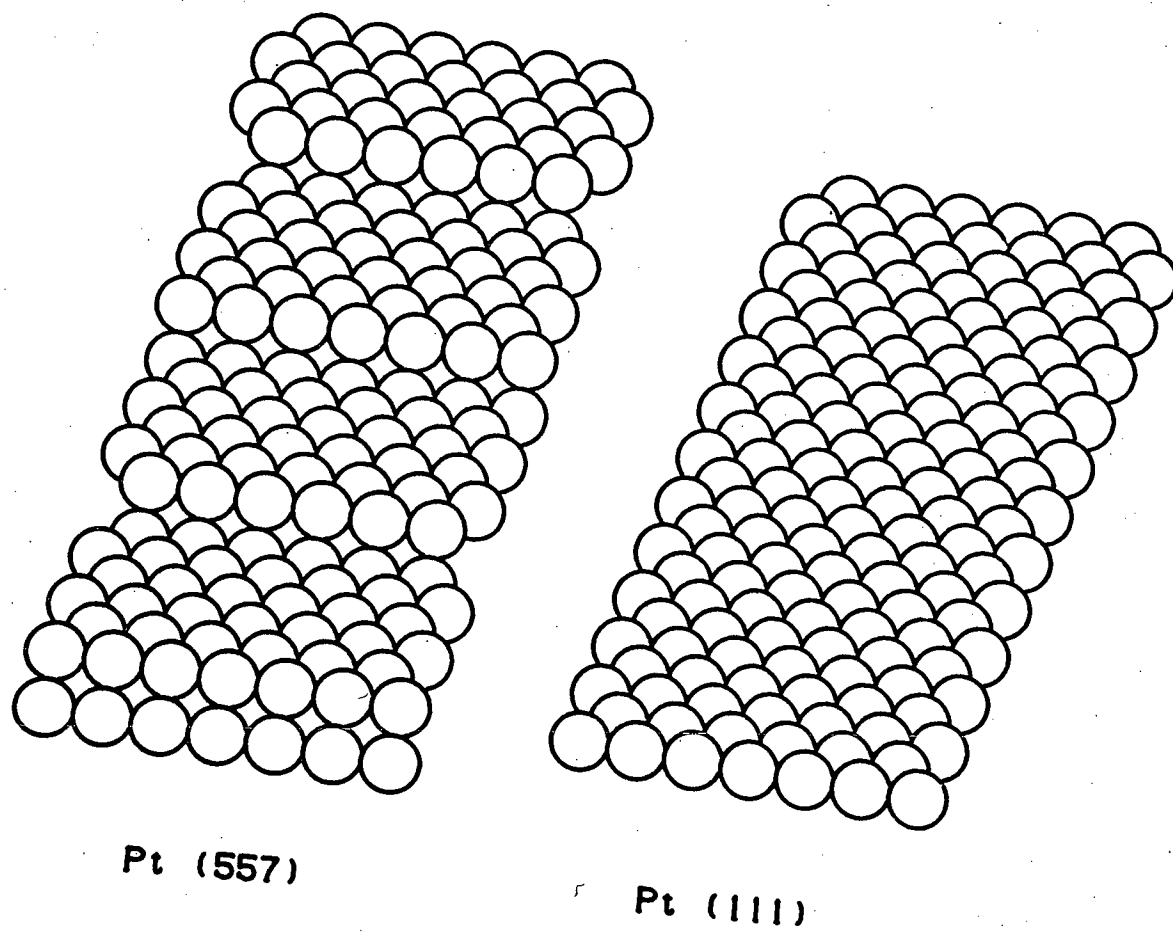


Figure 2

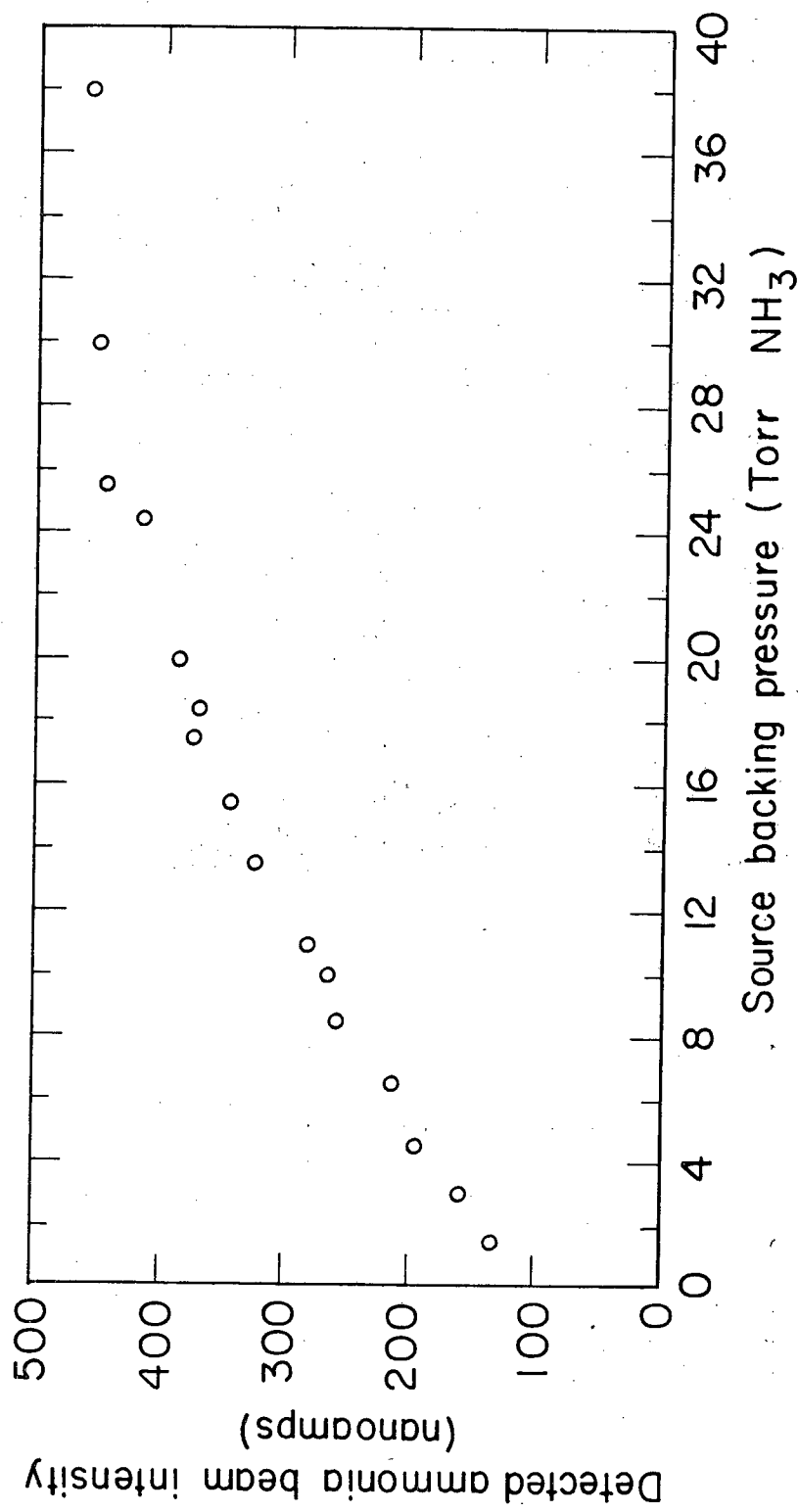
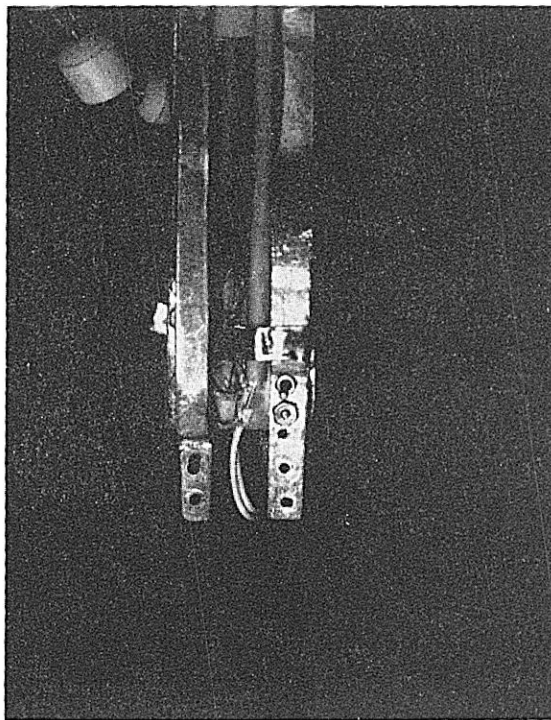
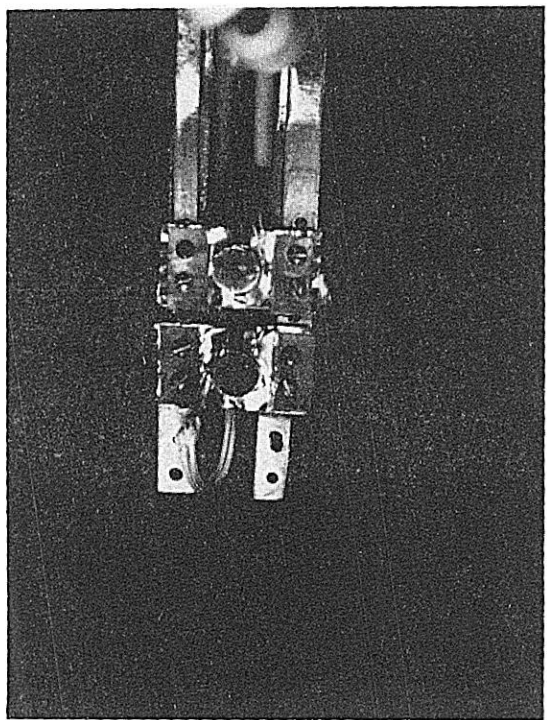


Figure 3

XBL 798-2529



XBB 798 10342

Figure 4

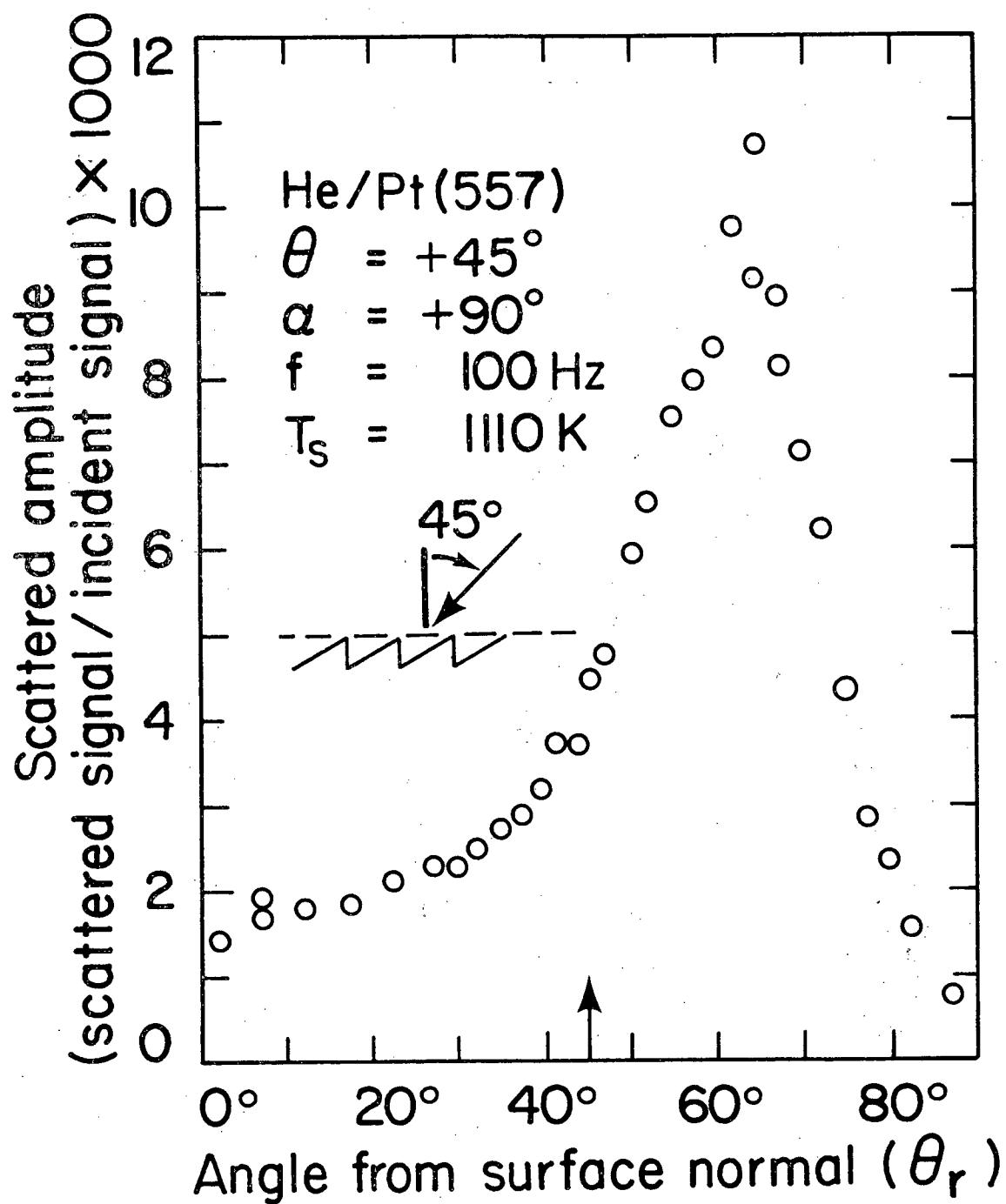


Figure 5

XBL798 - 2525

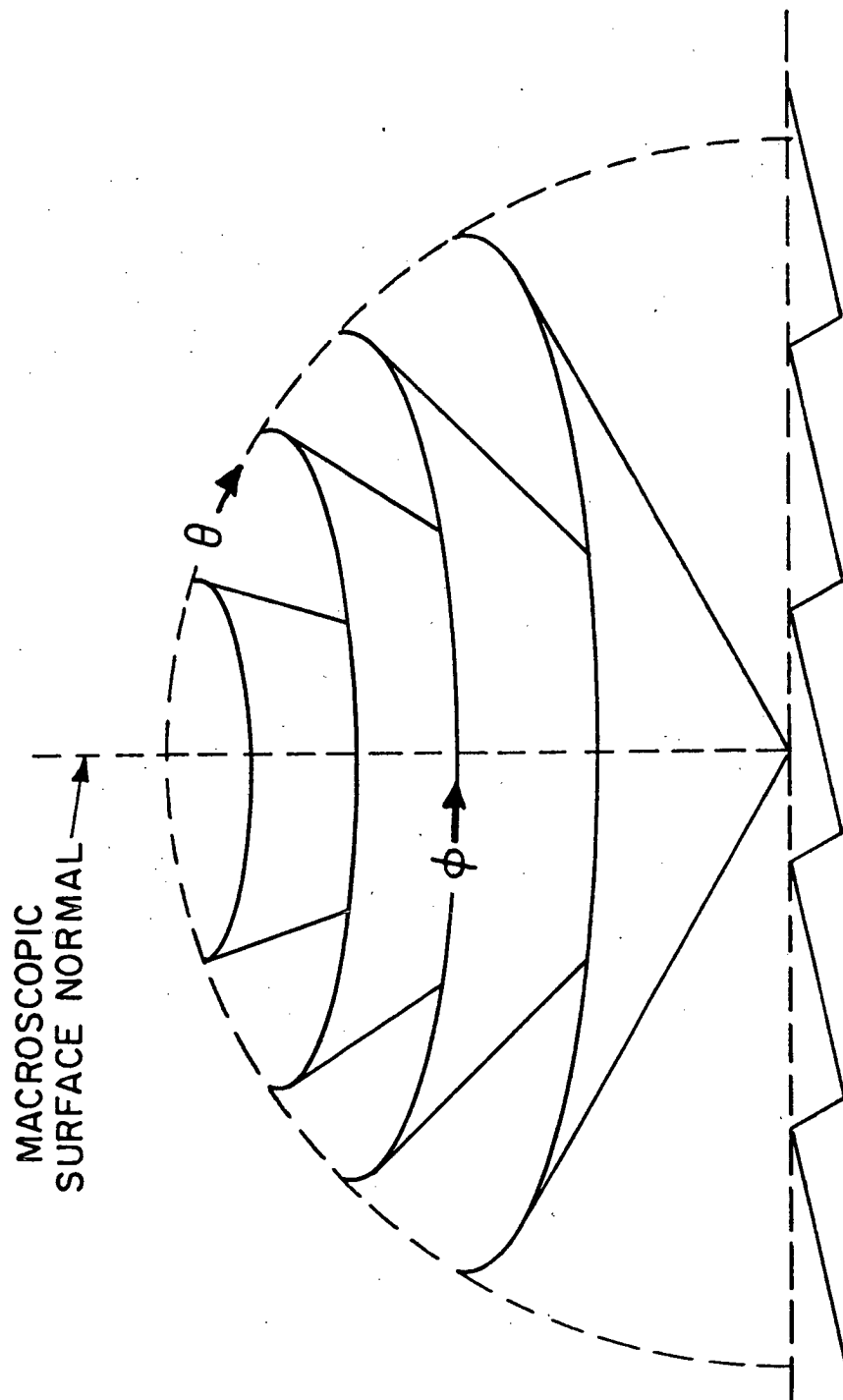


Figure 6

XBL 767-7183

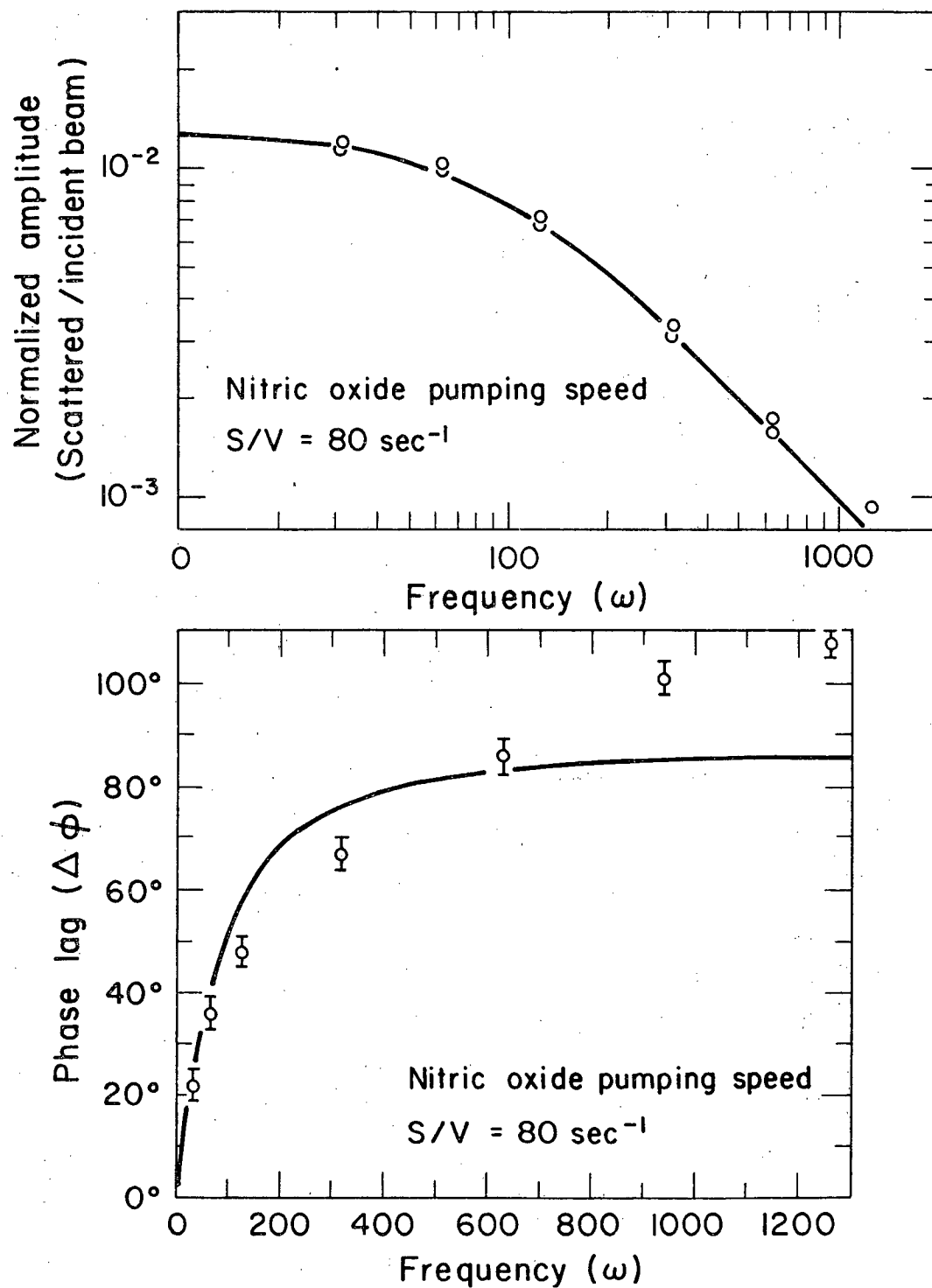


Figure 7 XBL 798 - 2526

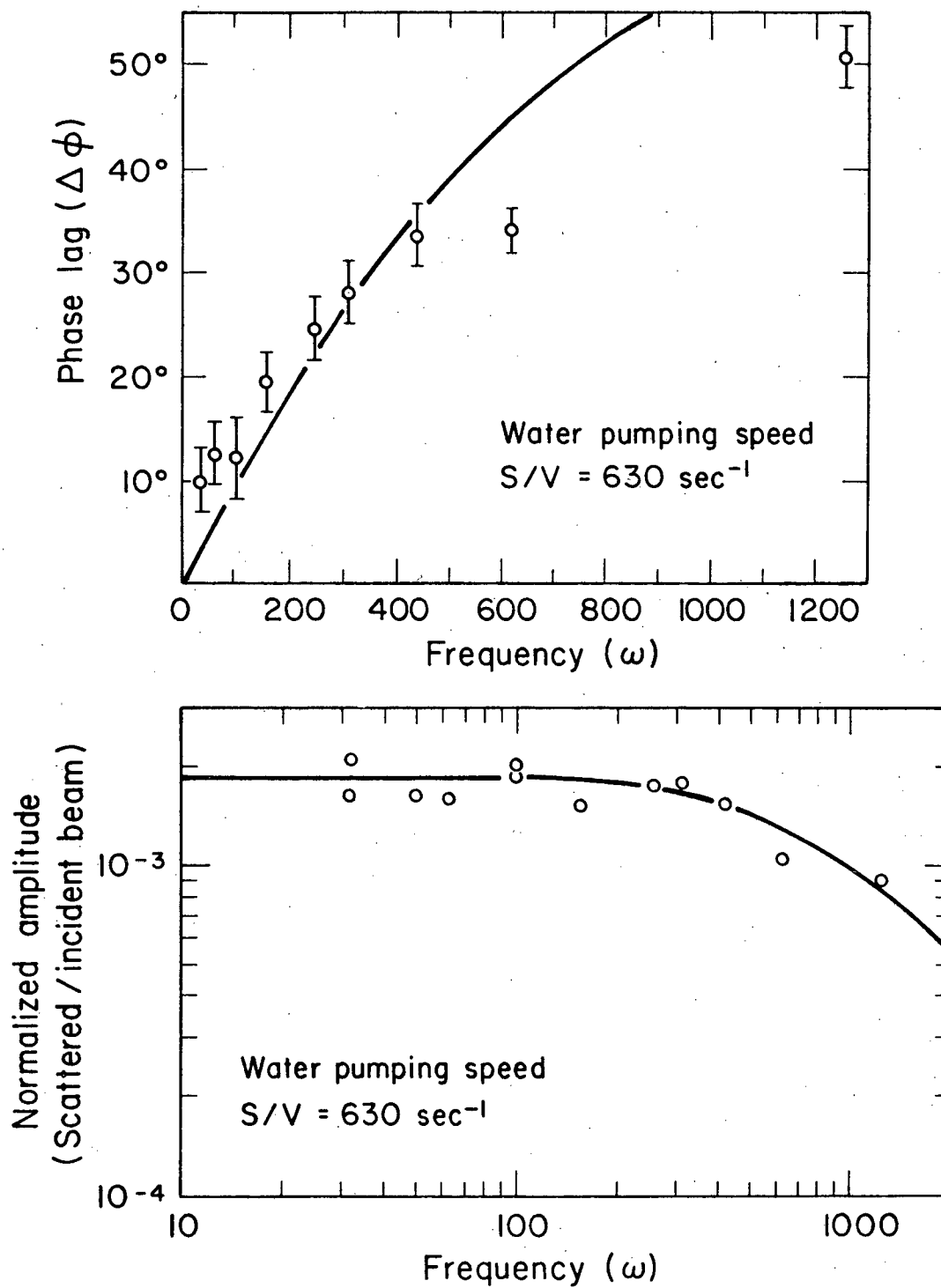
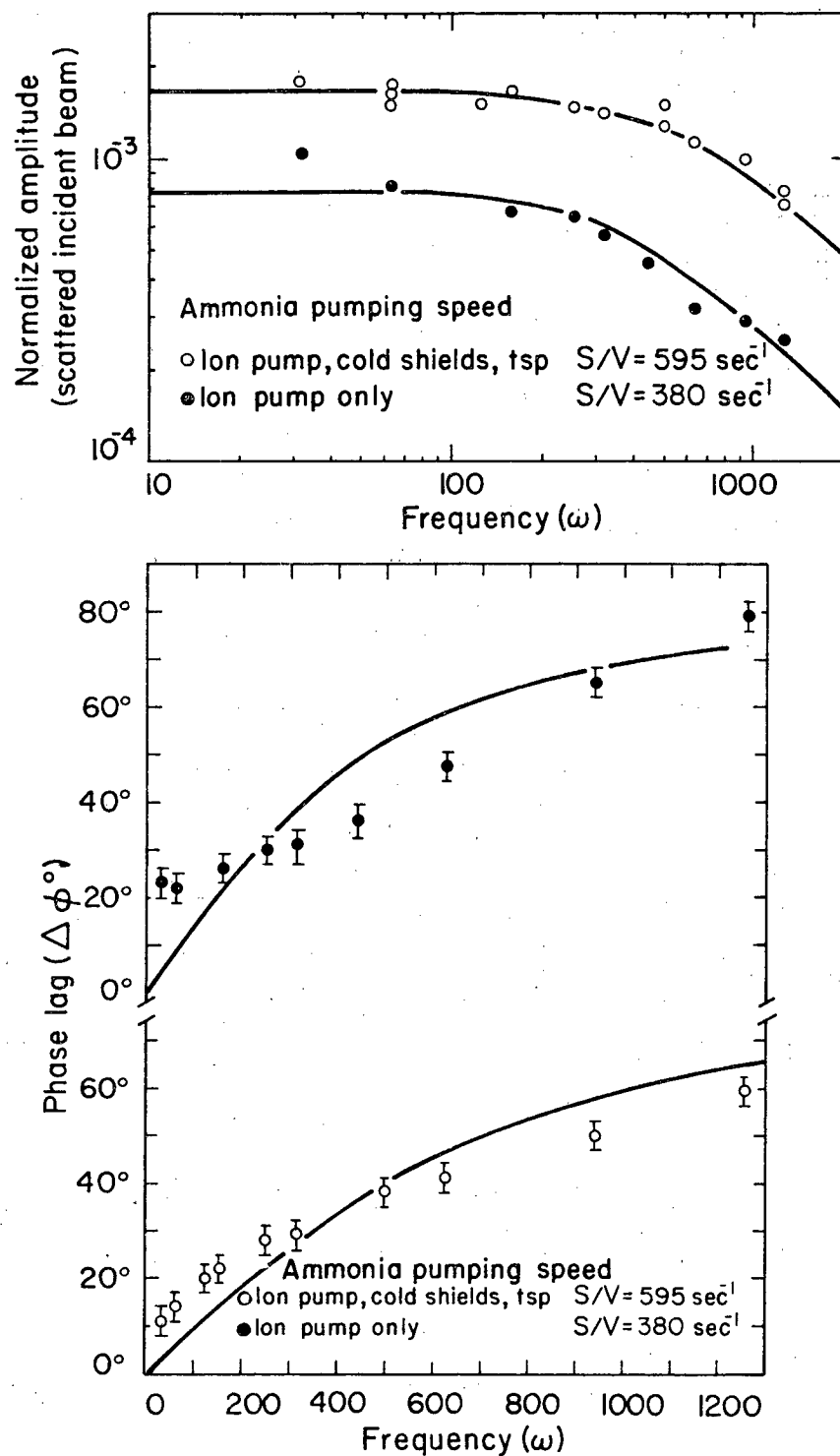


Figure 8

XBL 798-2527



XBL 798-2528

Figure 9

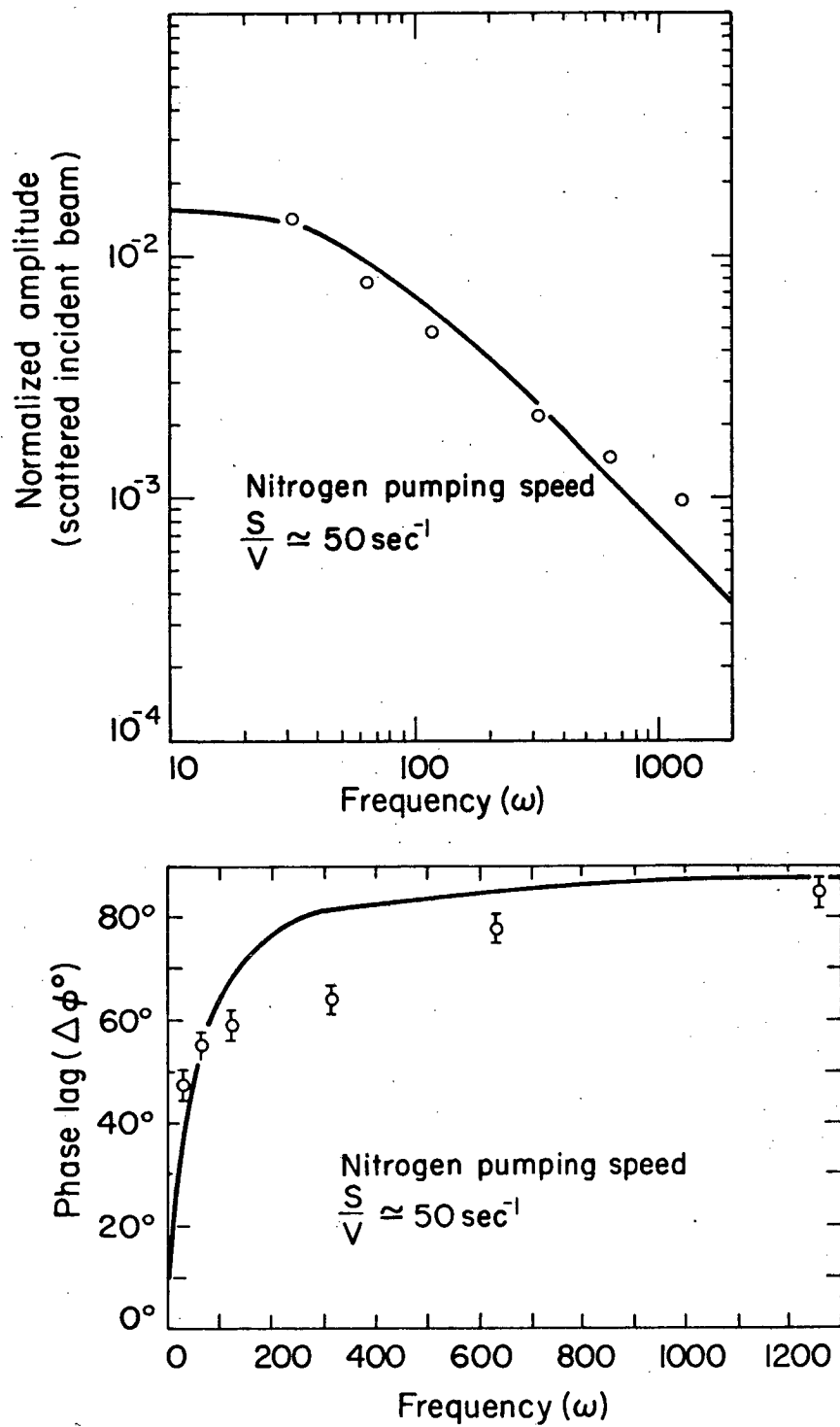


Figure 10

XBL 798-2533

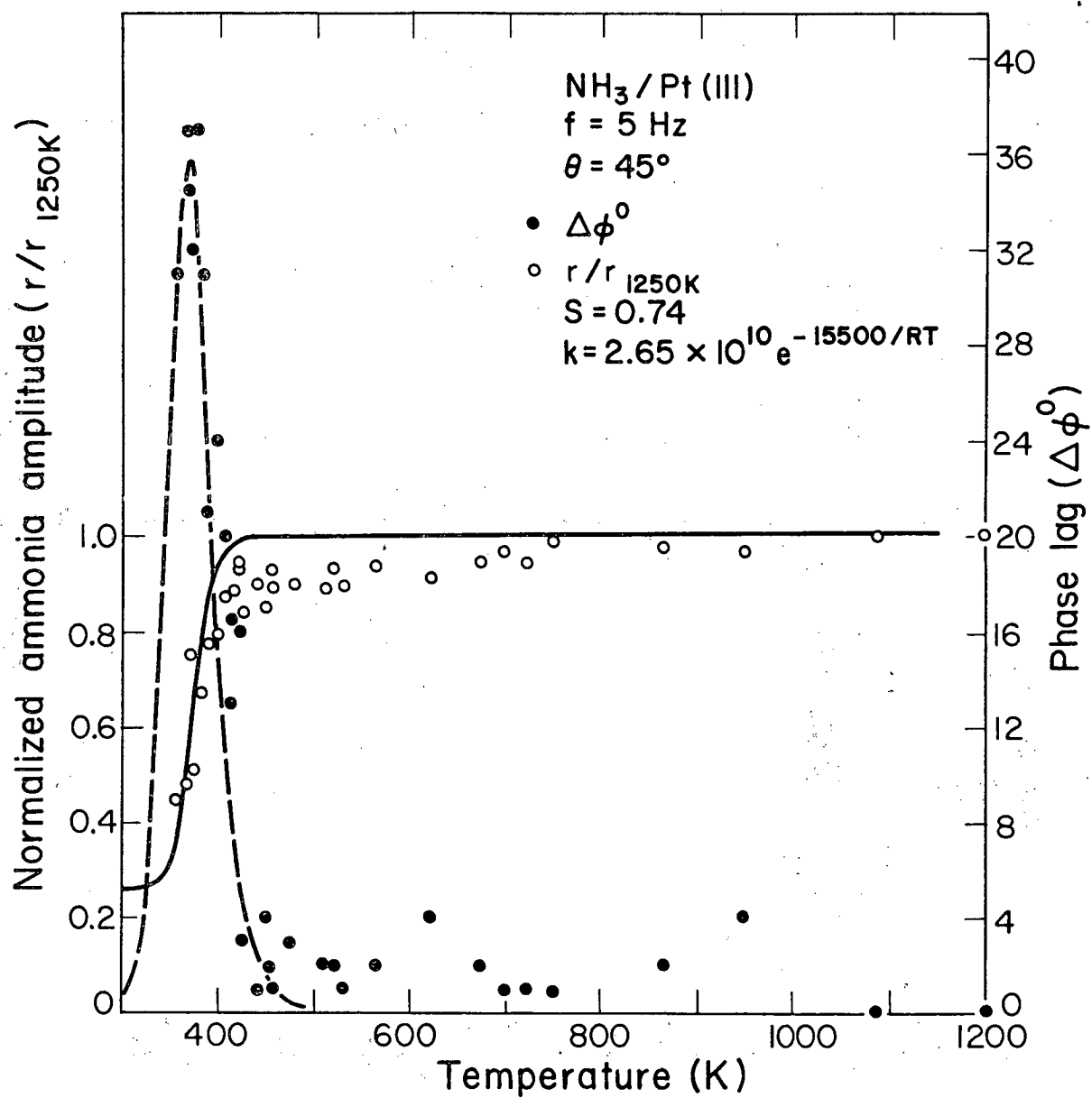


Figure 11a

XBL 798 - 2531

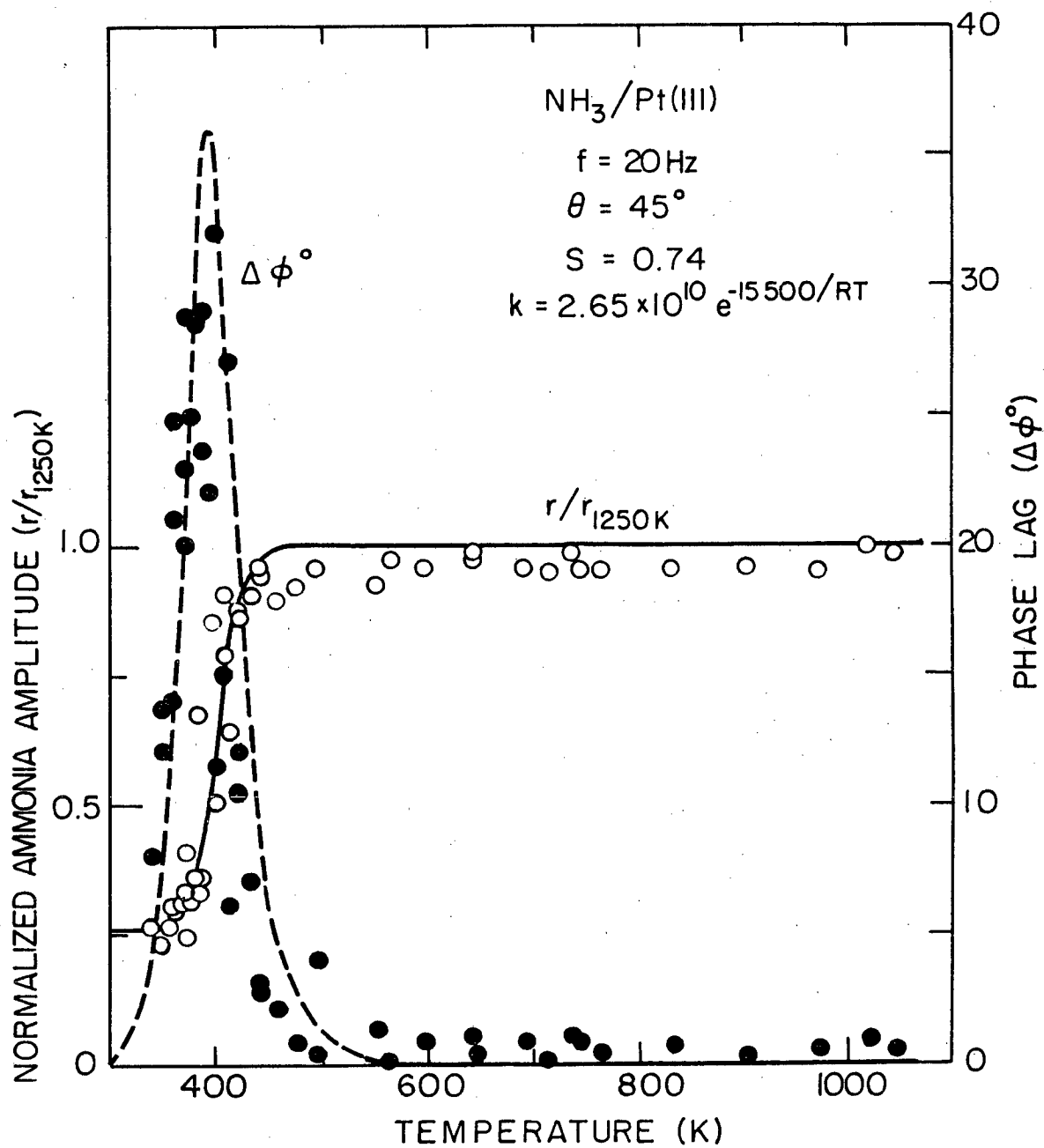


Figure 11b

XBL 798-67 54

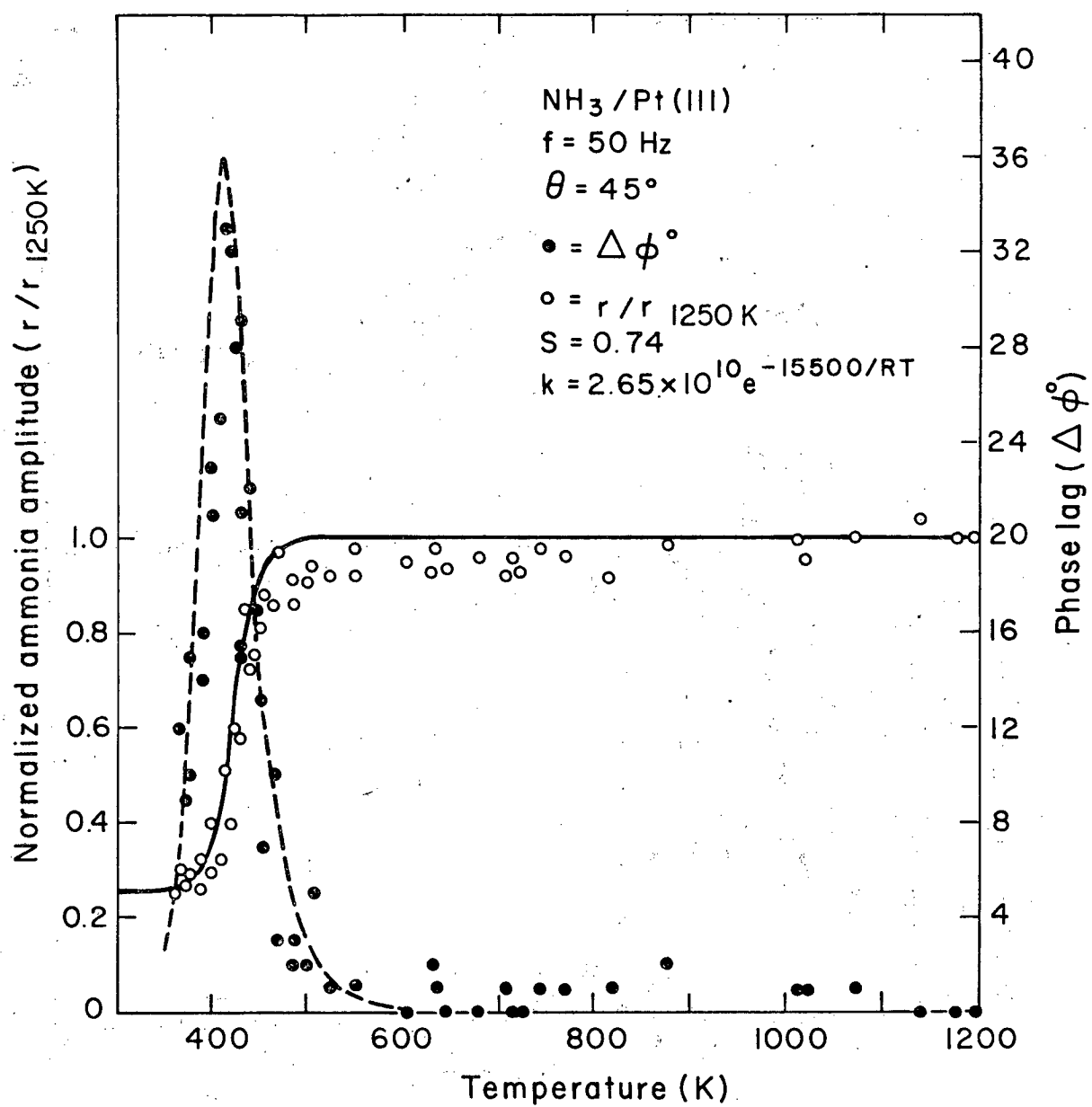


Figure 11c

XBL 798-2524

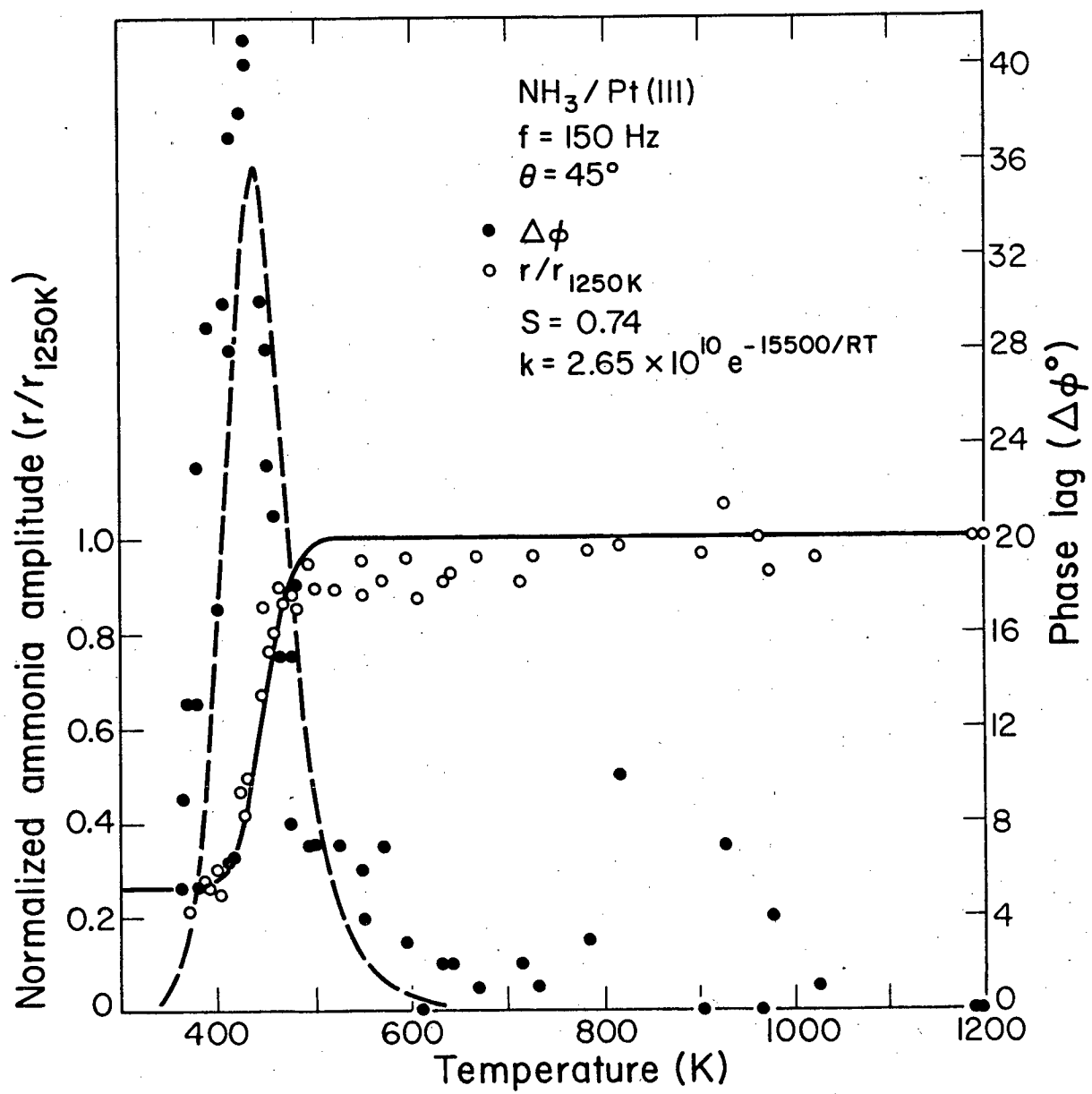
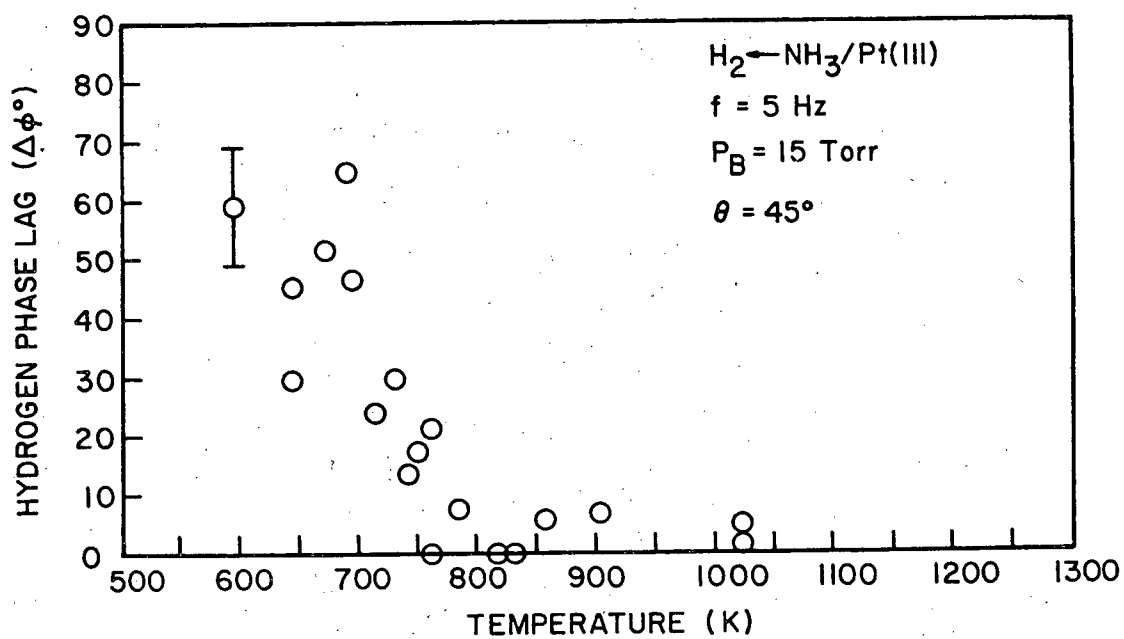
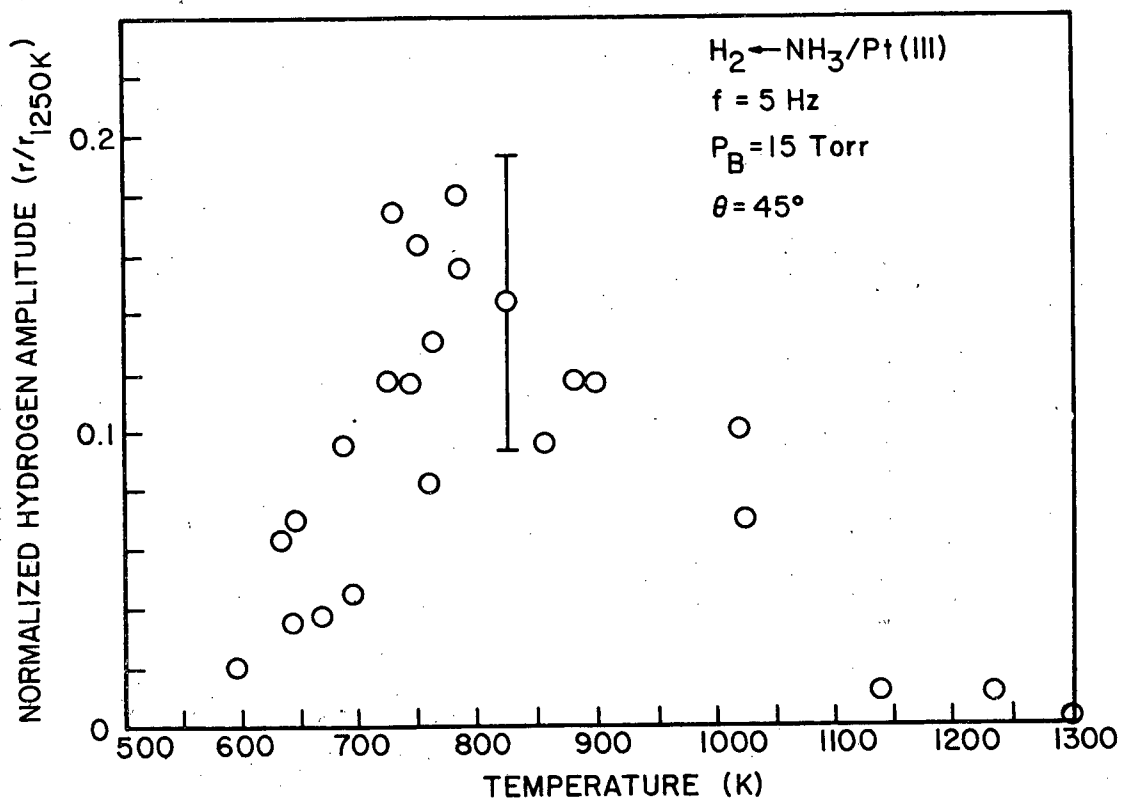


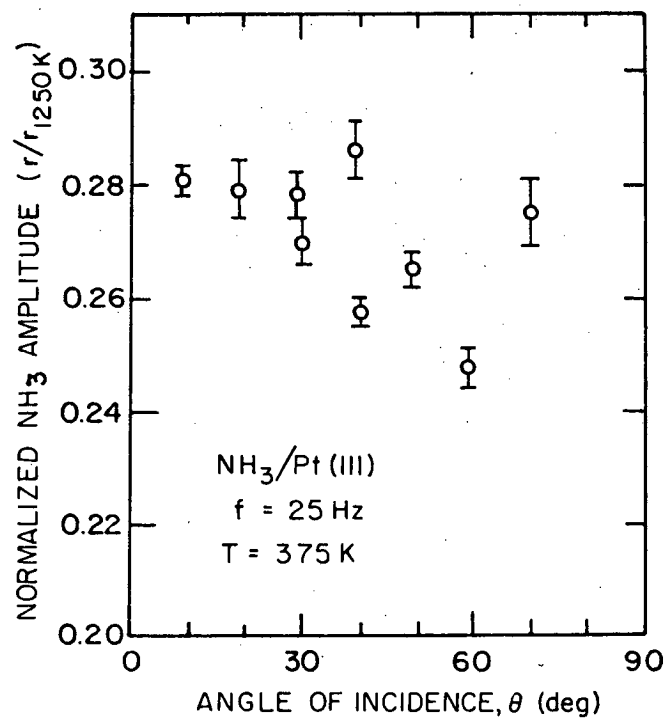
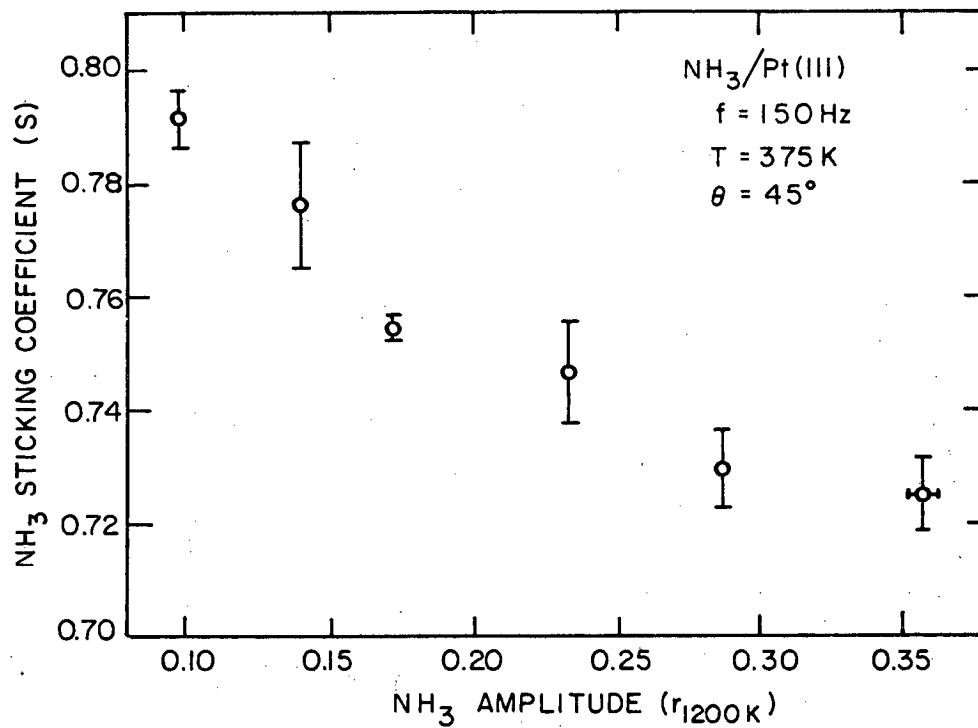
Figure 11d

XBL 798-2535



XBL 798-11049

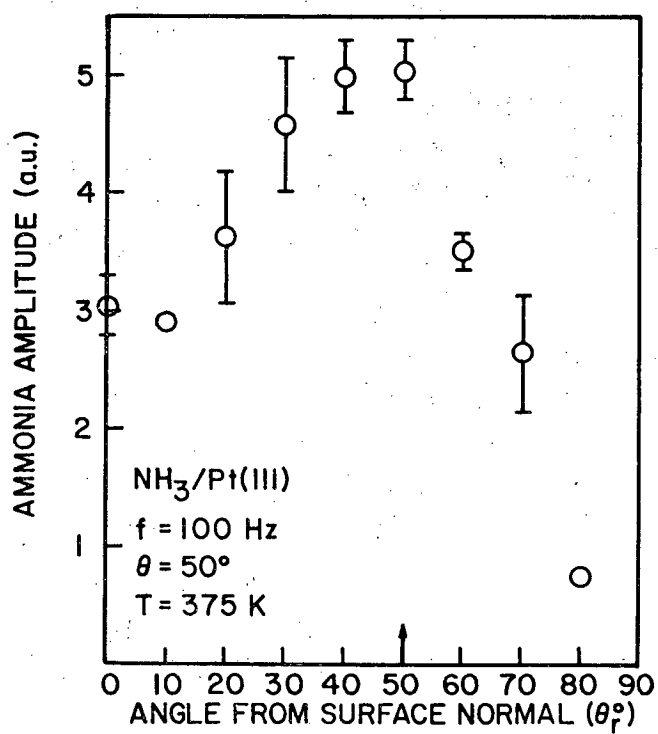
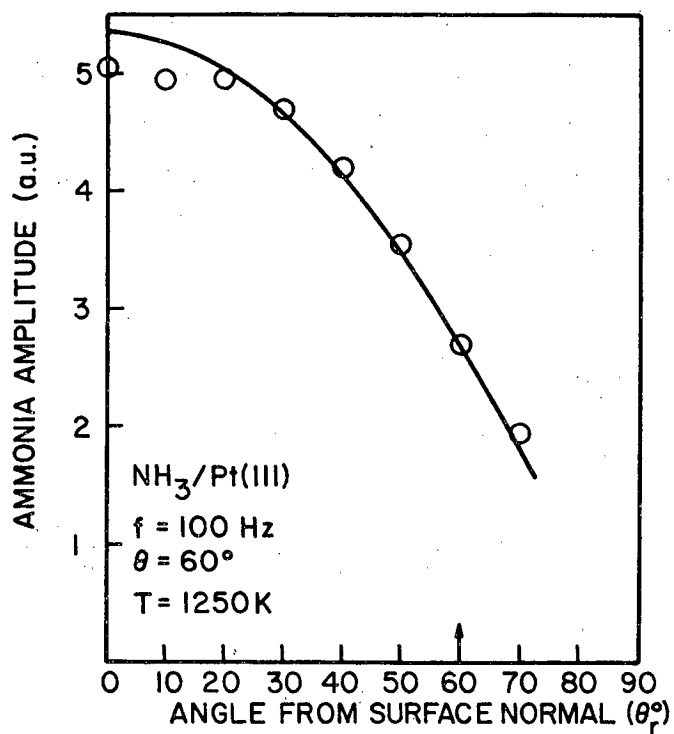
Figure 12



XBL 798-6756

Figure 13 (above)

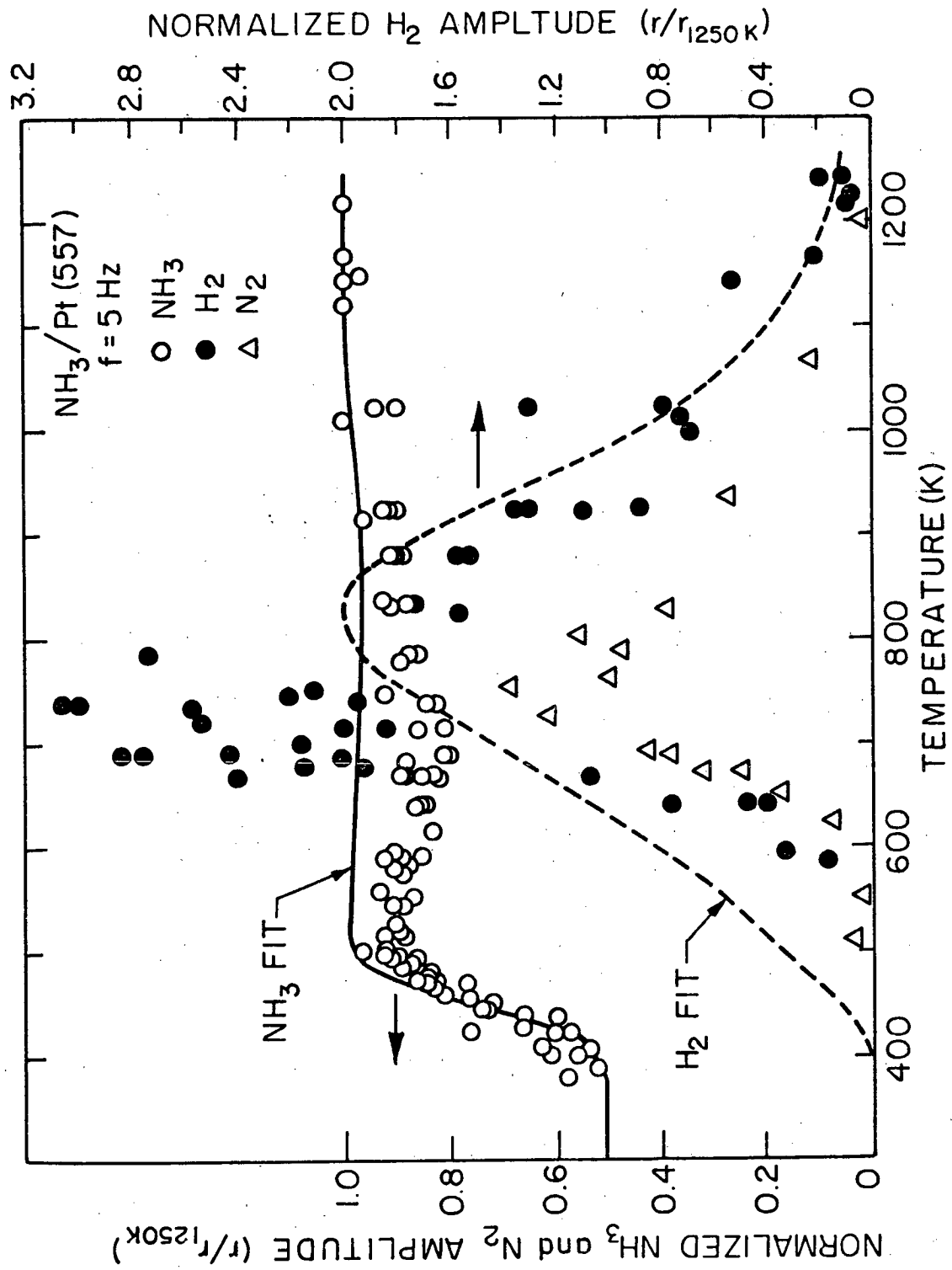
Figure 14 (below)



XBL 798-11048

Figure 15a (above)

Figure 15b (below)



XBL 798-6714

Figure 16a

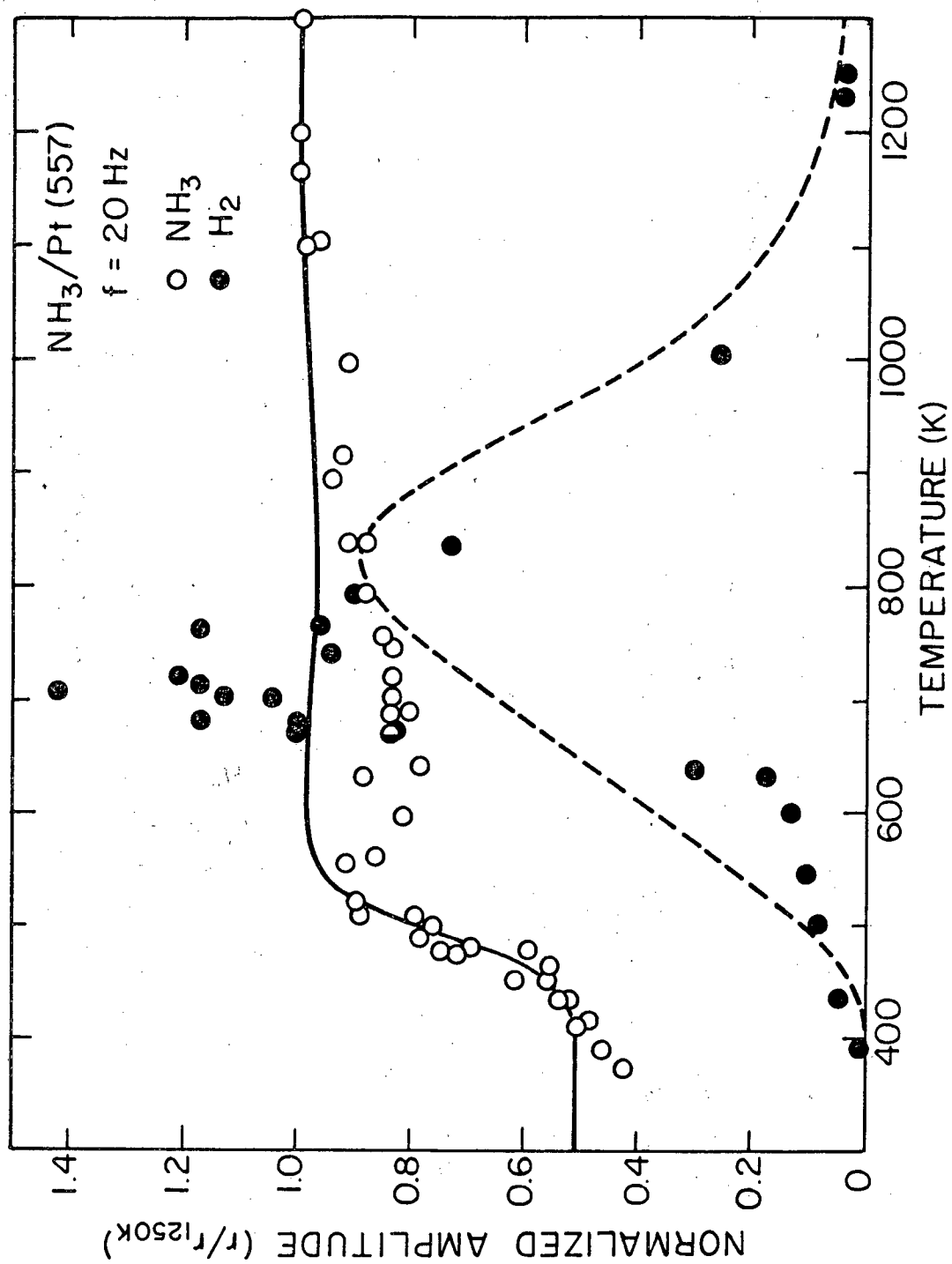
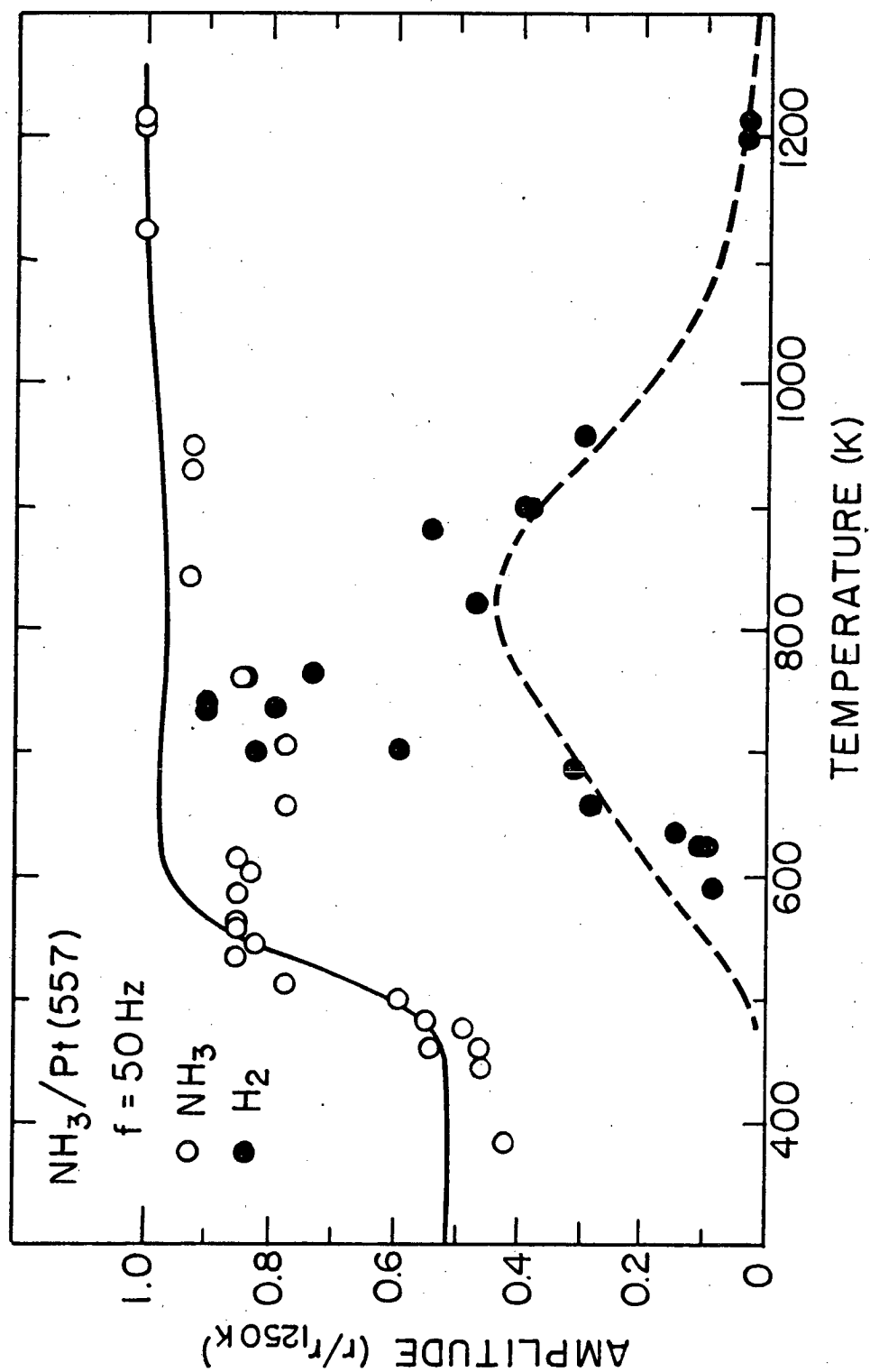


Figure 16b

XBL798-6713



XBL798-6755

Figure 16c

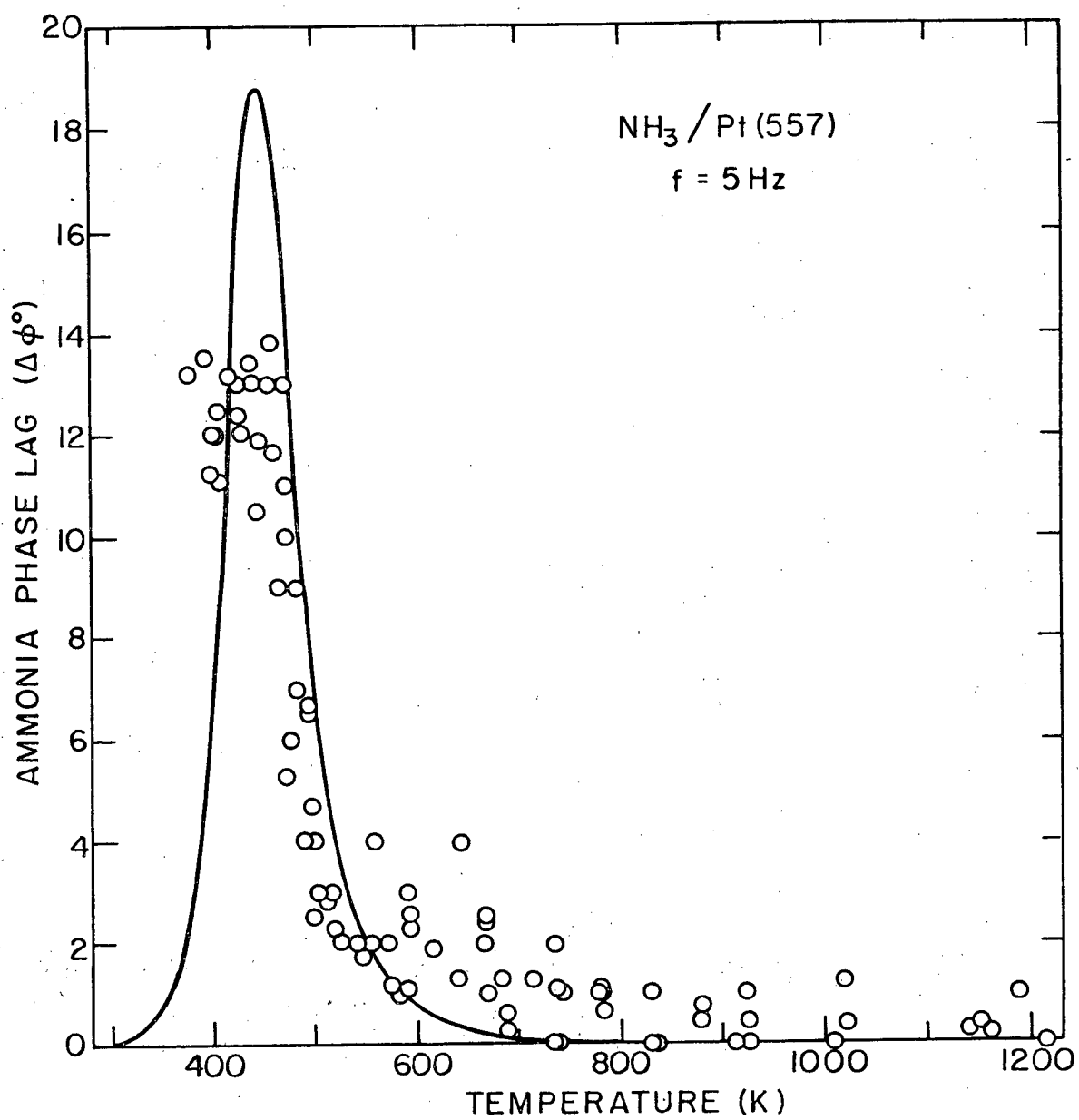


Figure 17a

XBL 798-6715

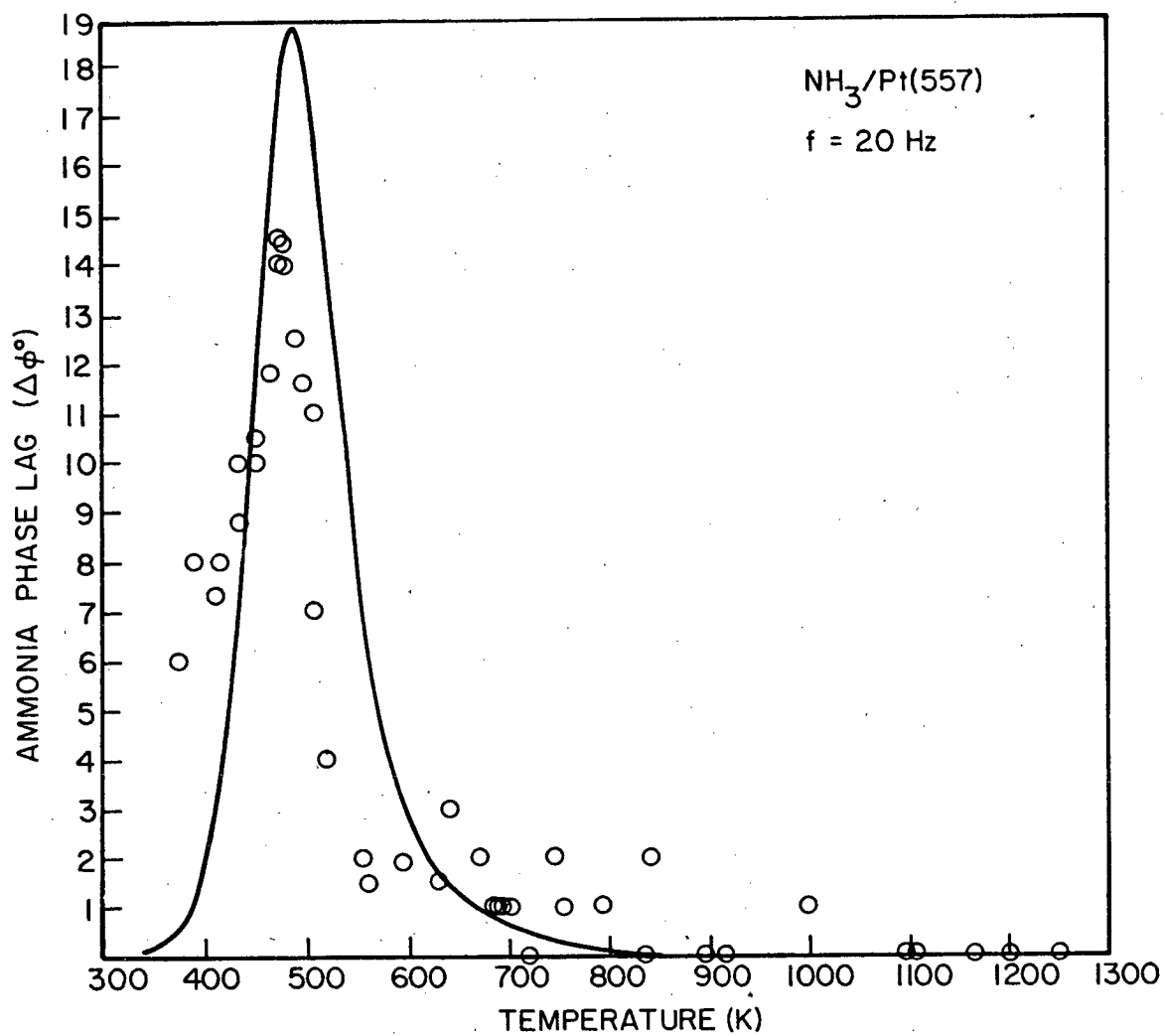


Figure 17b

XBL 798-11051

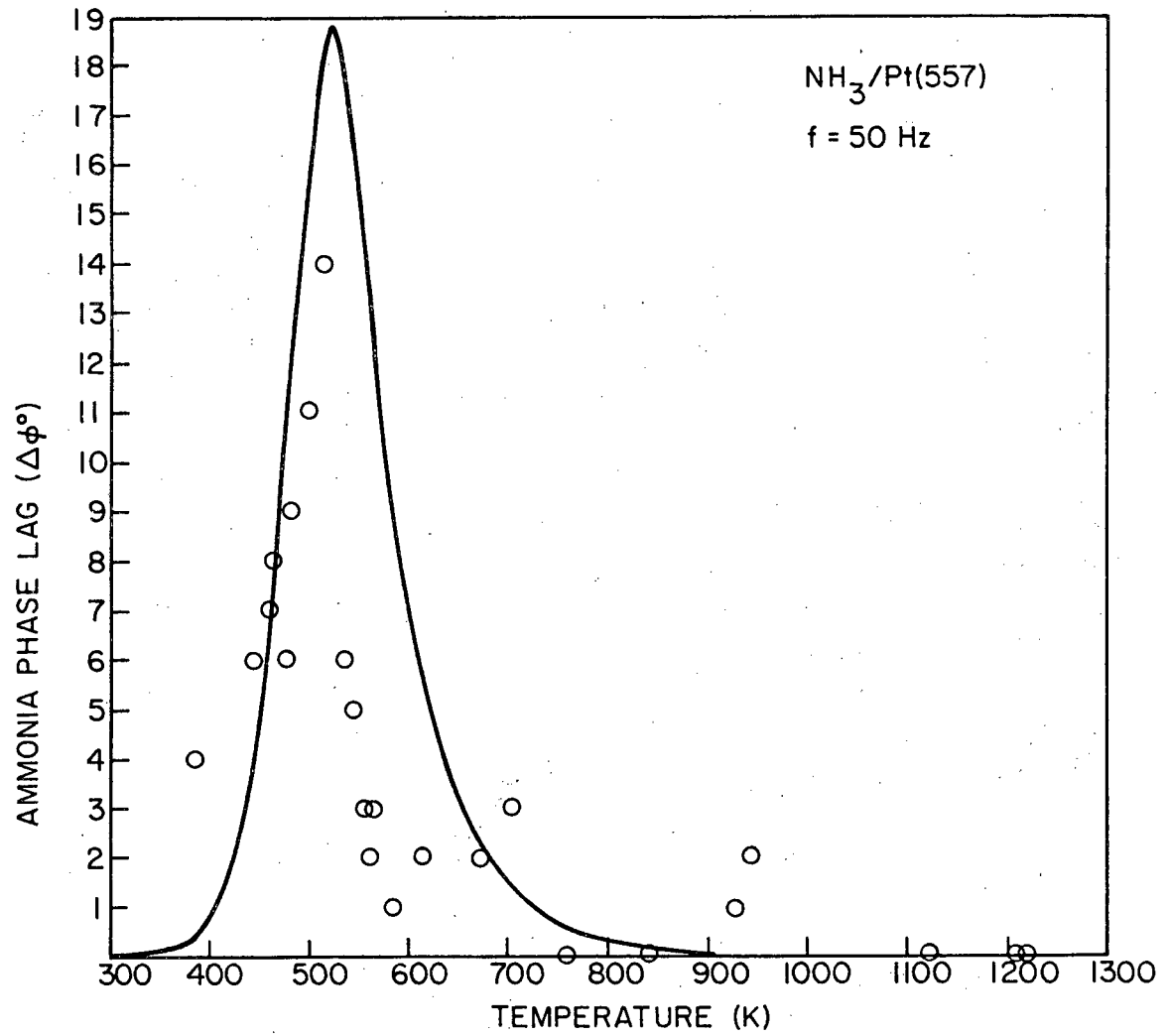
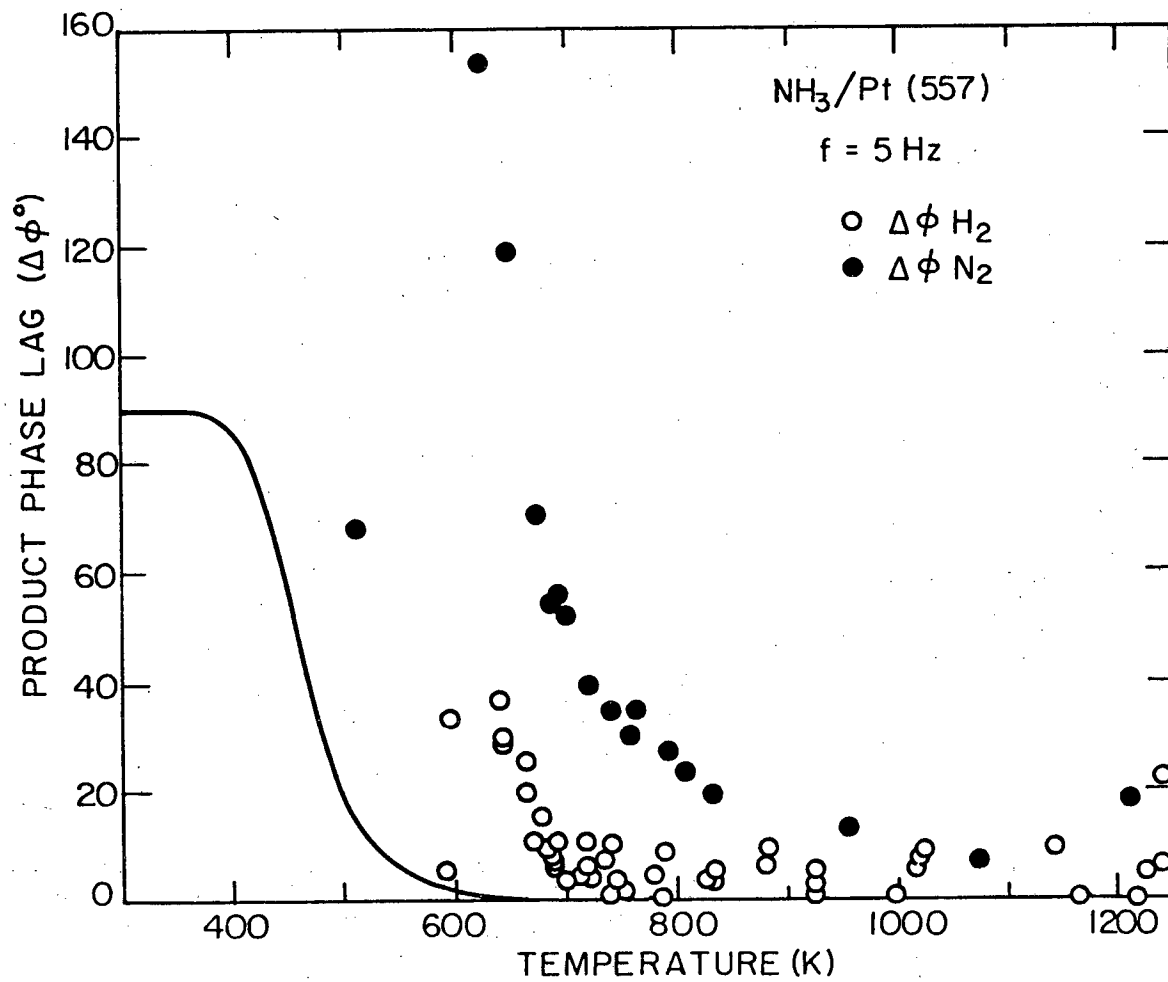


Figure 17c

XBL 798-11052



XBL 798-6716

Figure 18a

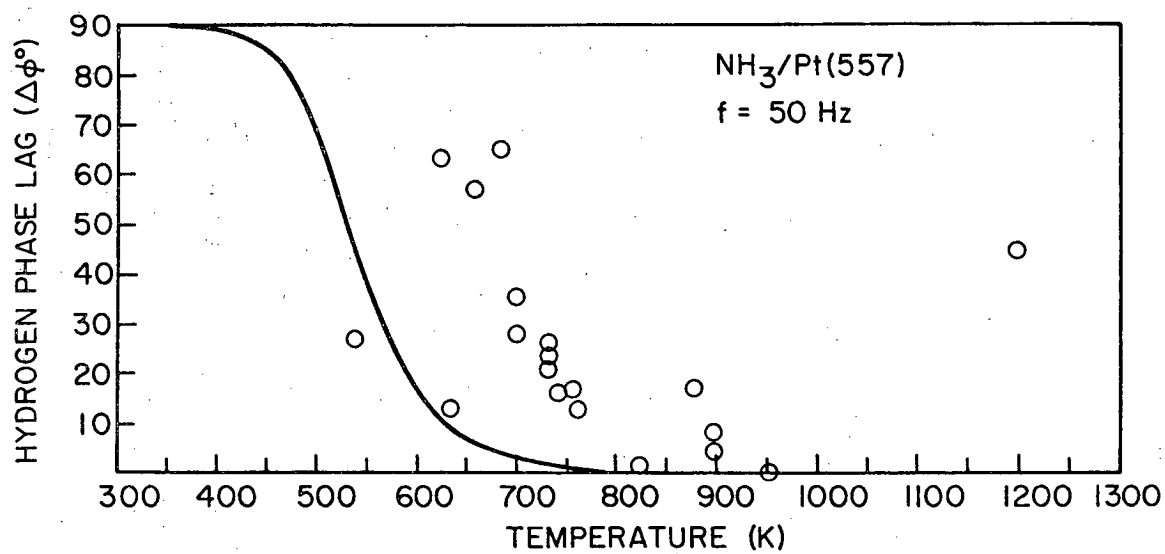
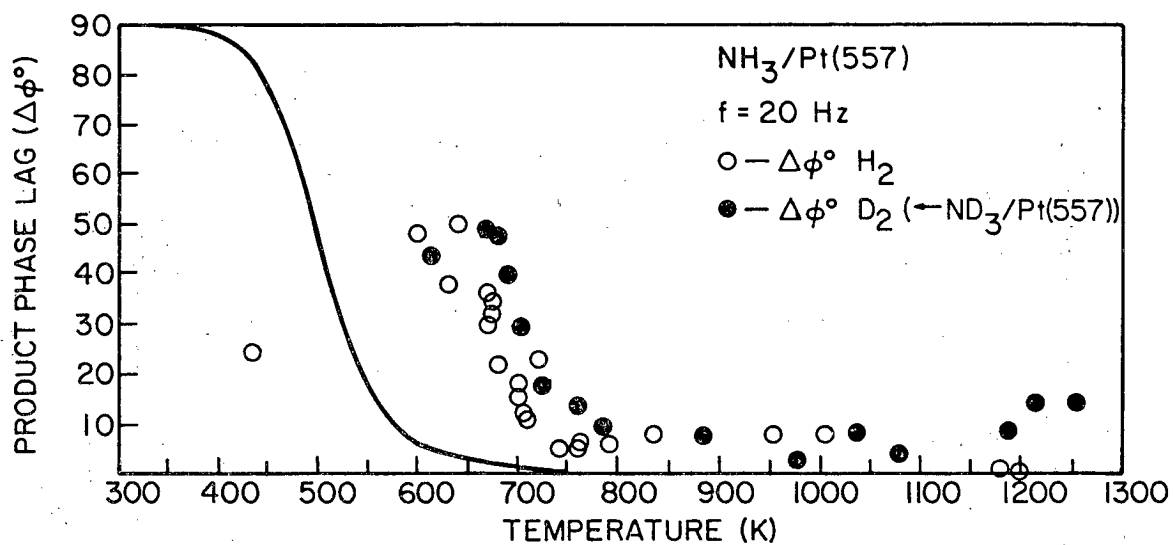


Figure 18b (above)

Figure 18c (below)

XBL 798-11050

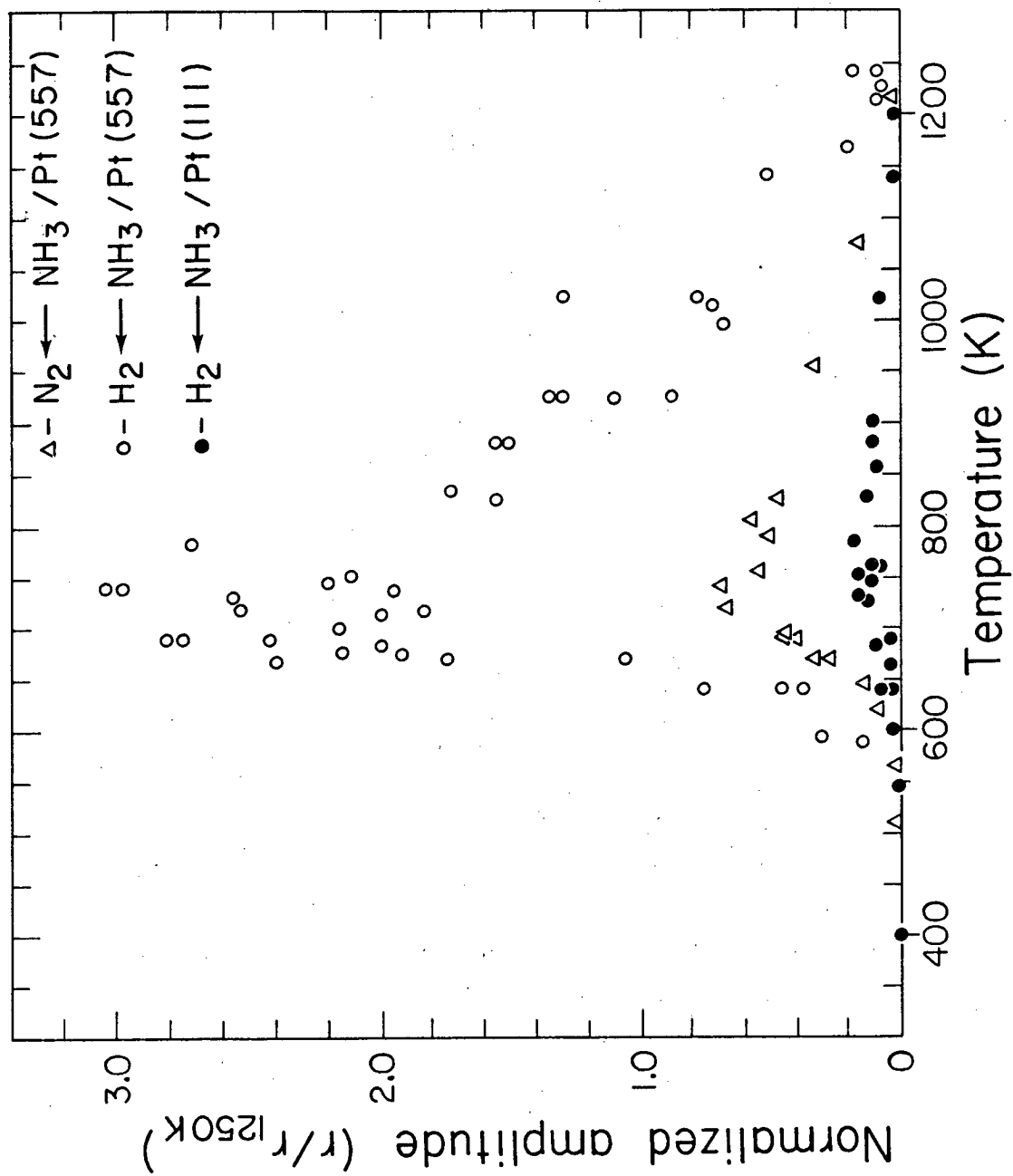
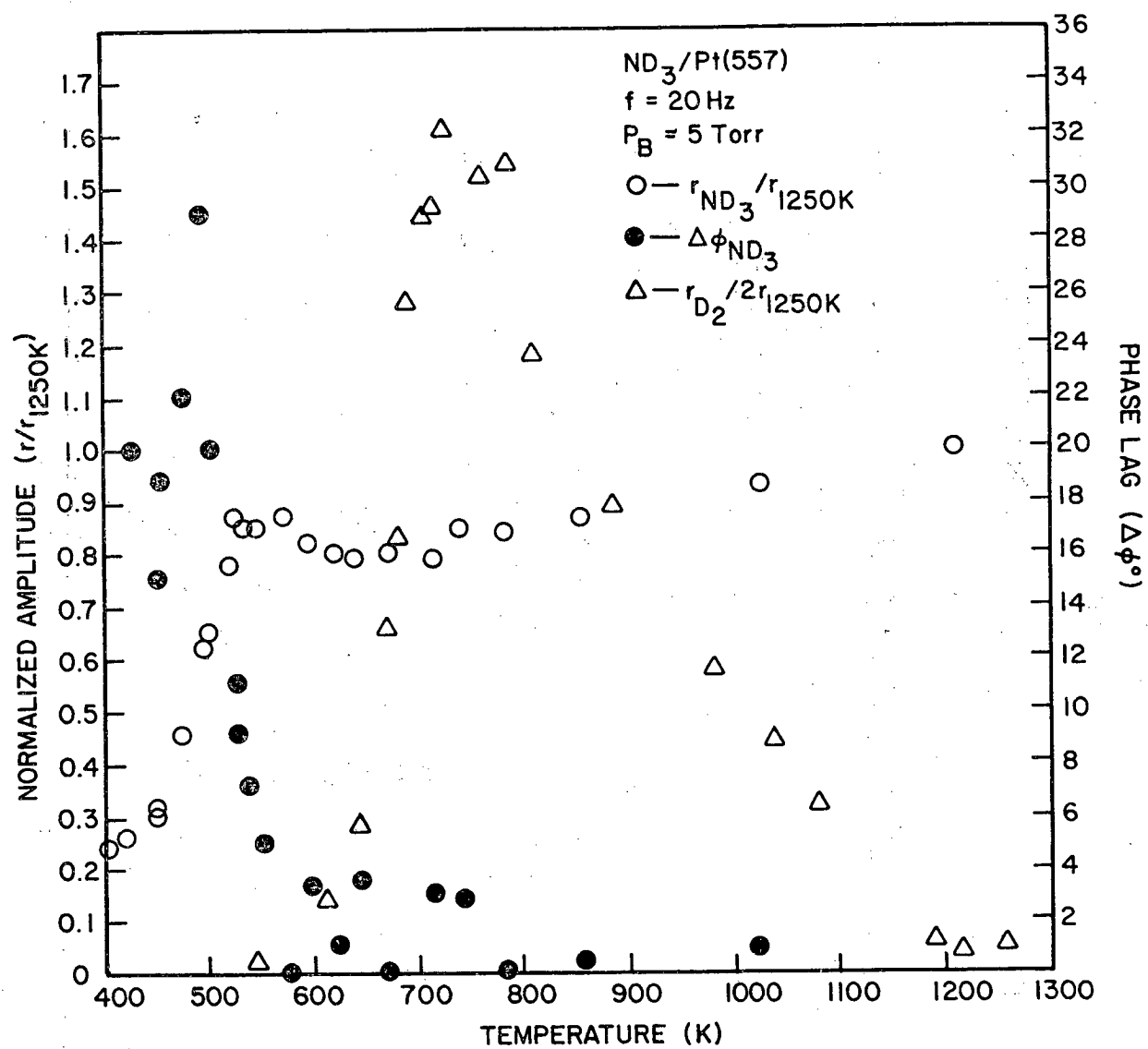
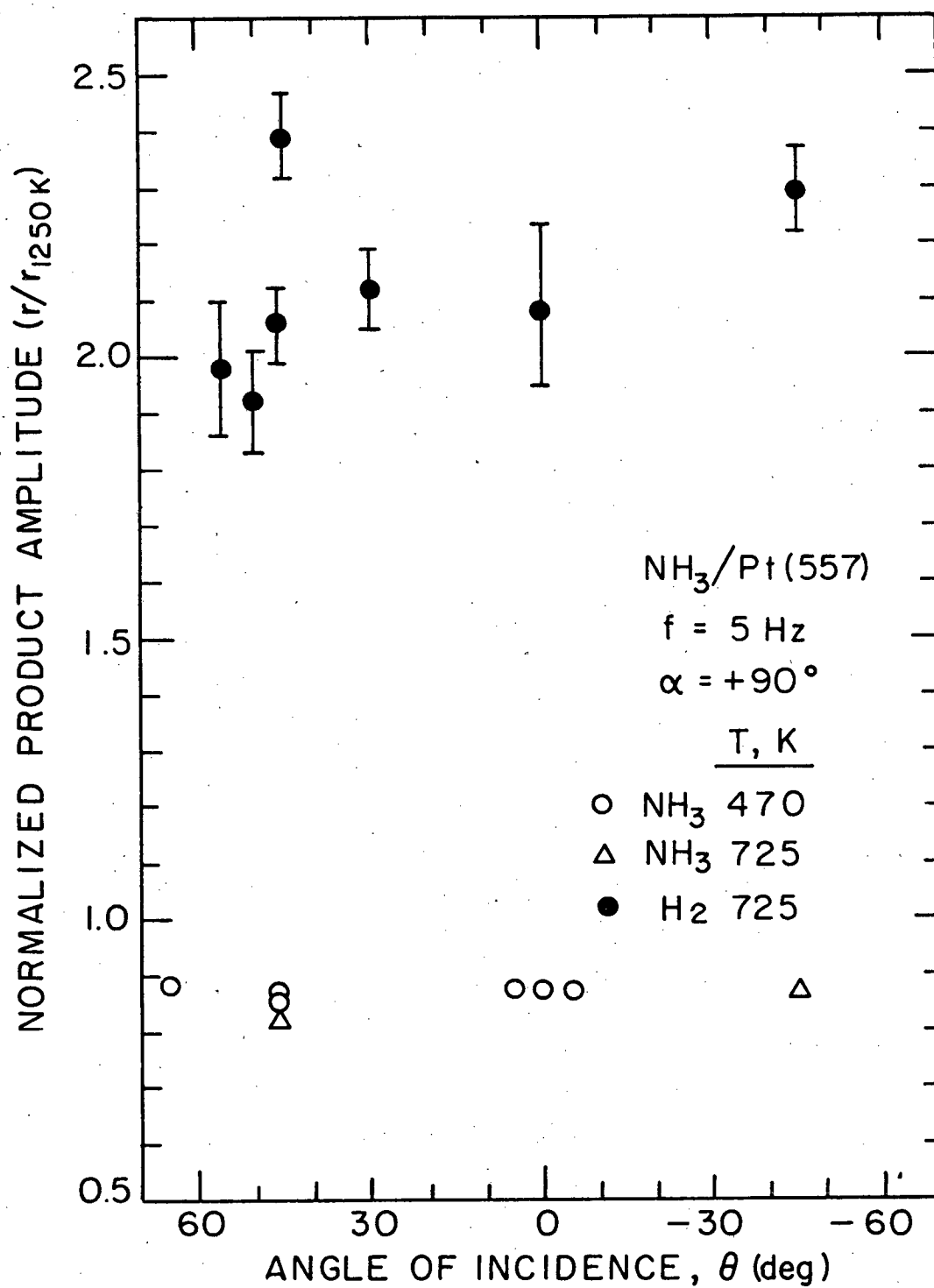


Figure 19 XBL 798-2534



XBL 798-11047

Figure 20



XBL798-6752

Figure 21

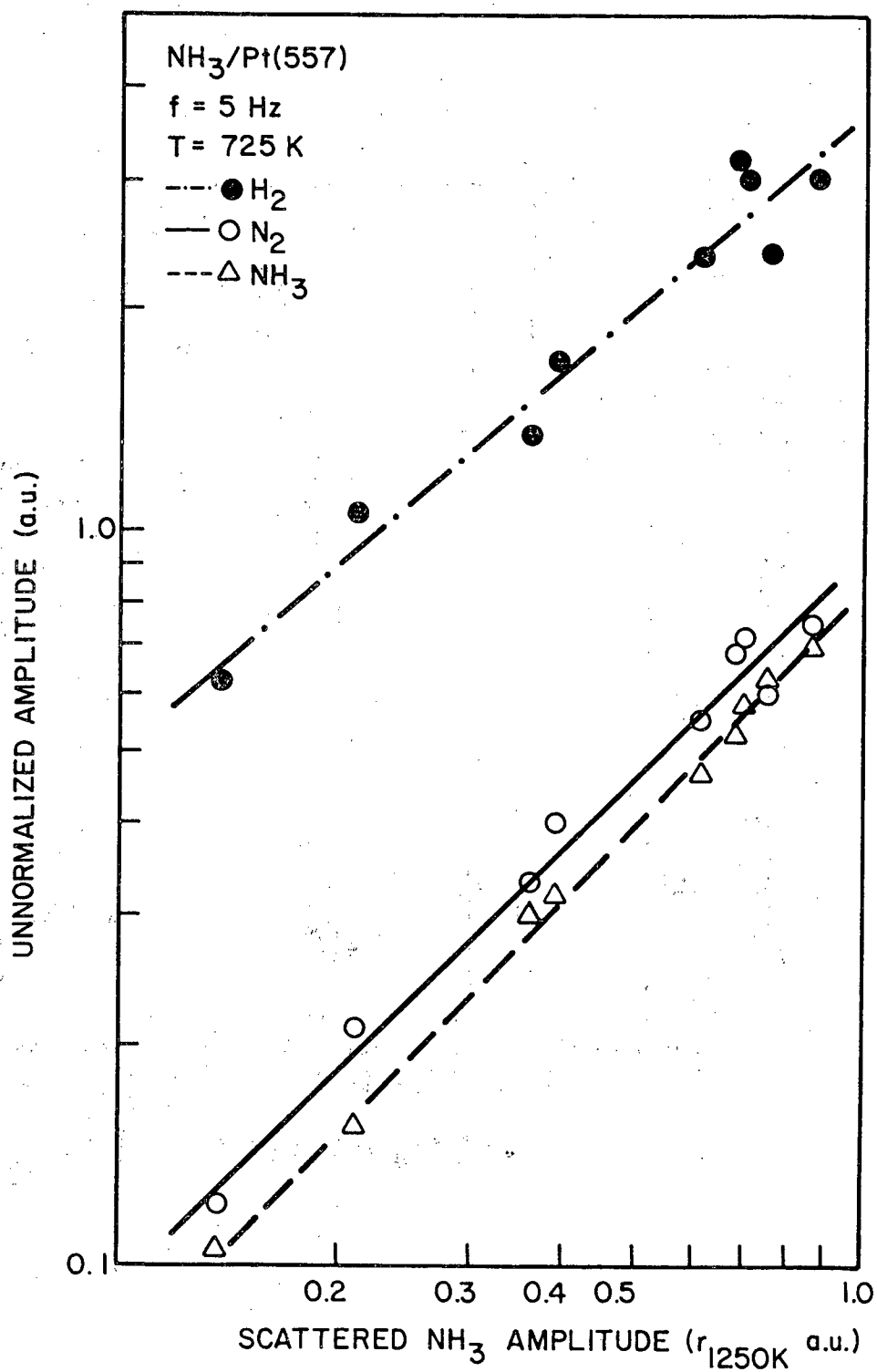


Figure 22a

XBL 798-11044

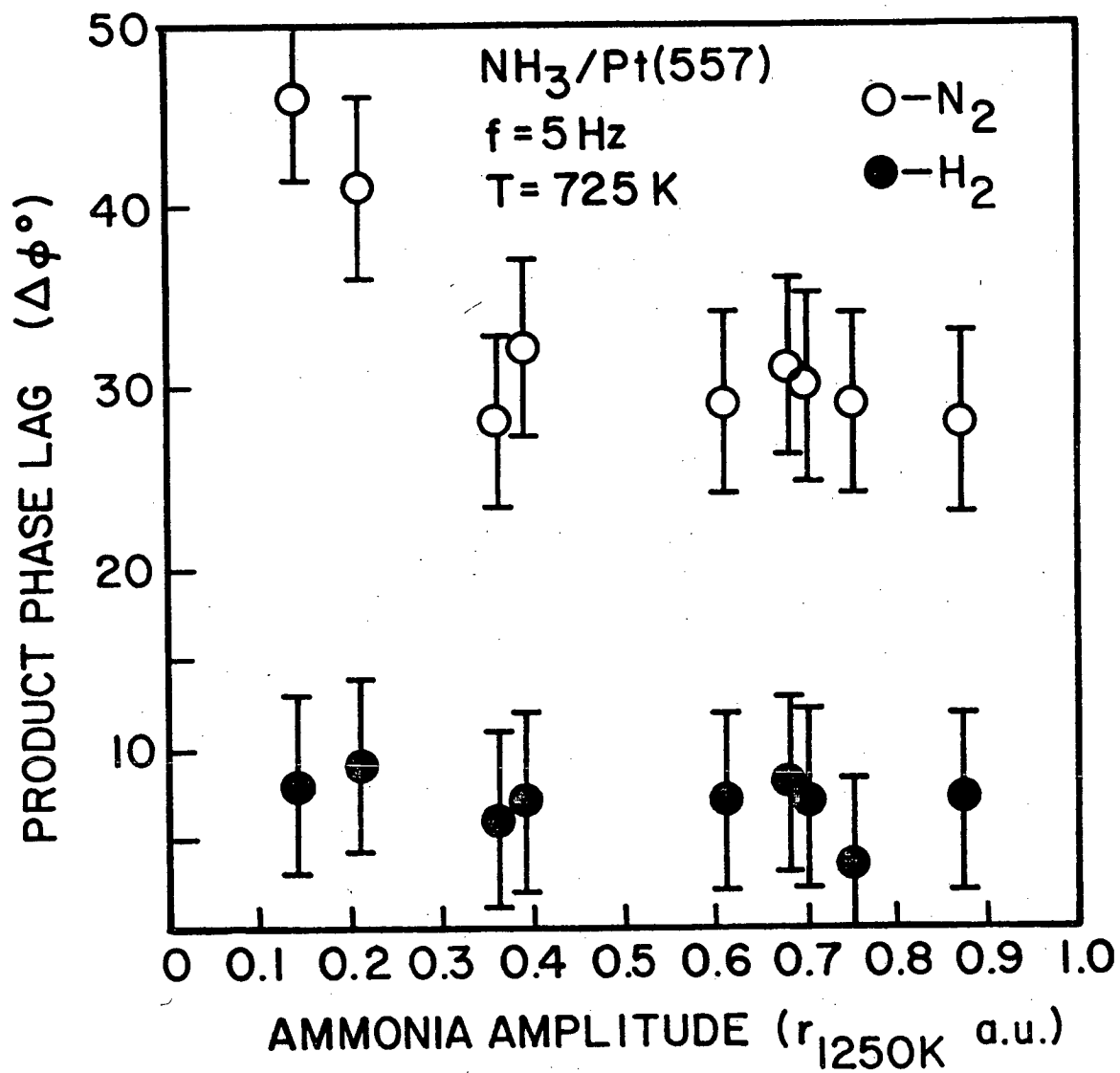


Figure 22b

XBL 798-11045

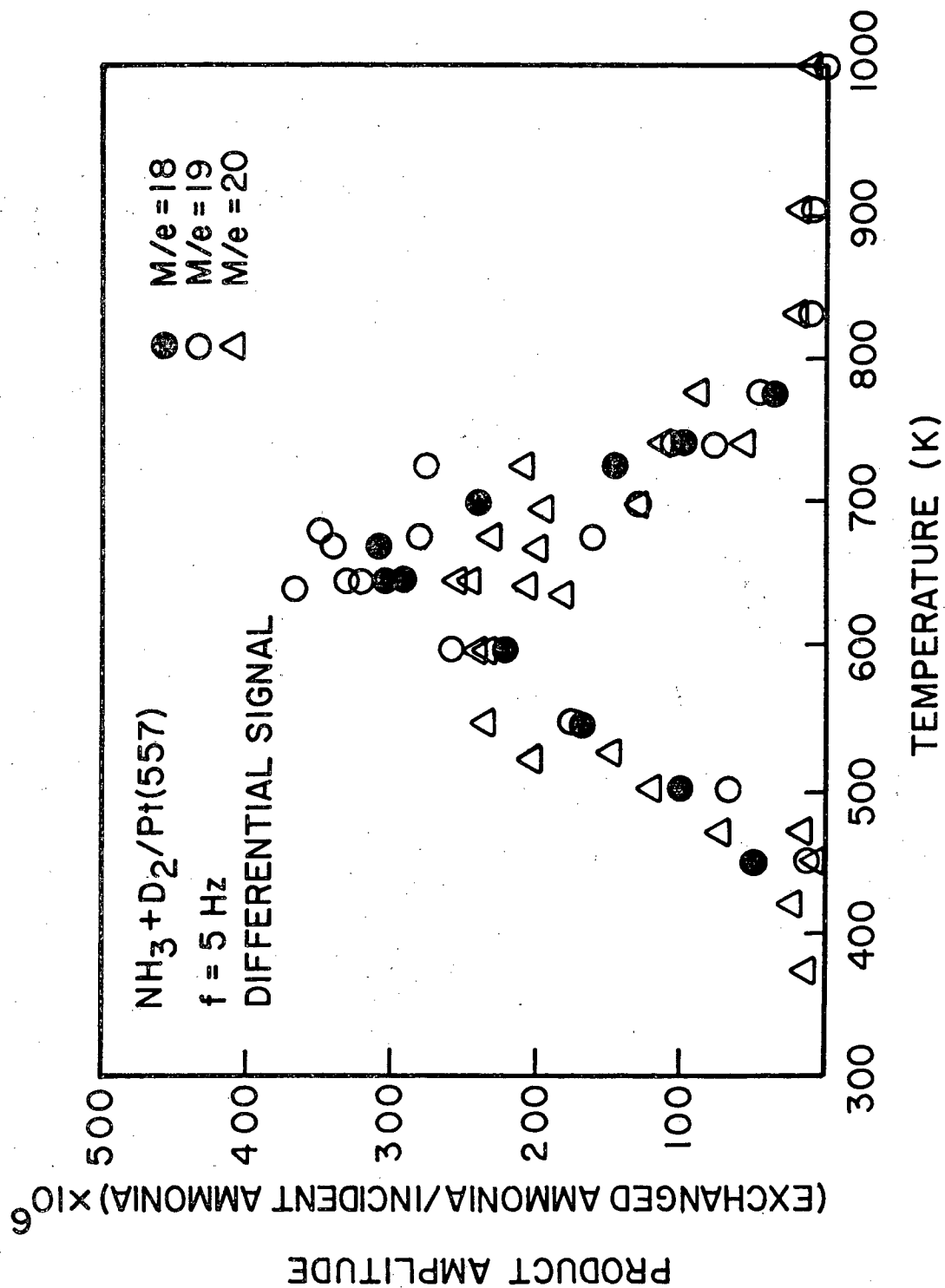


Figure 23

XBL 798-11046

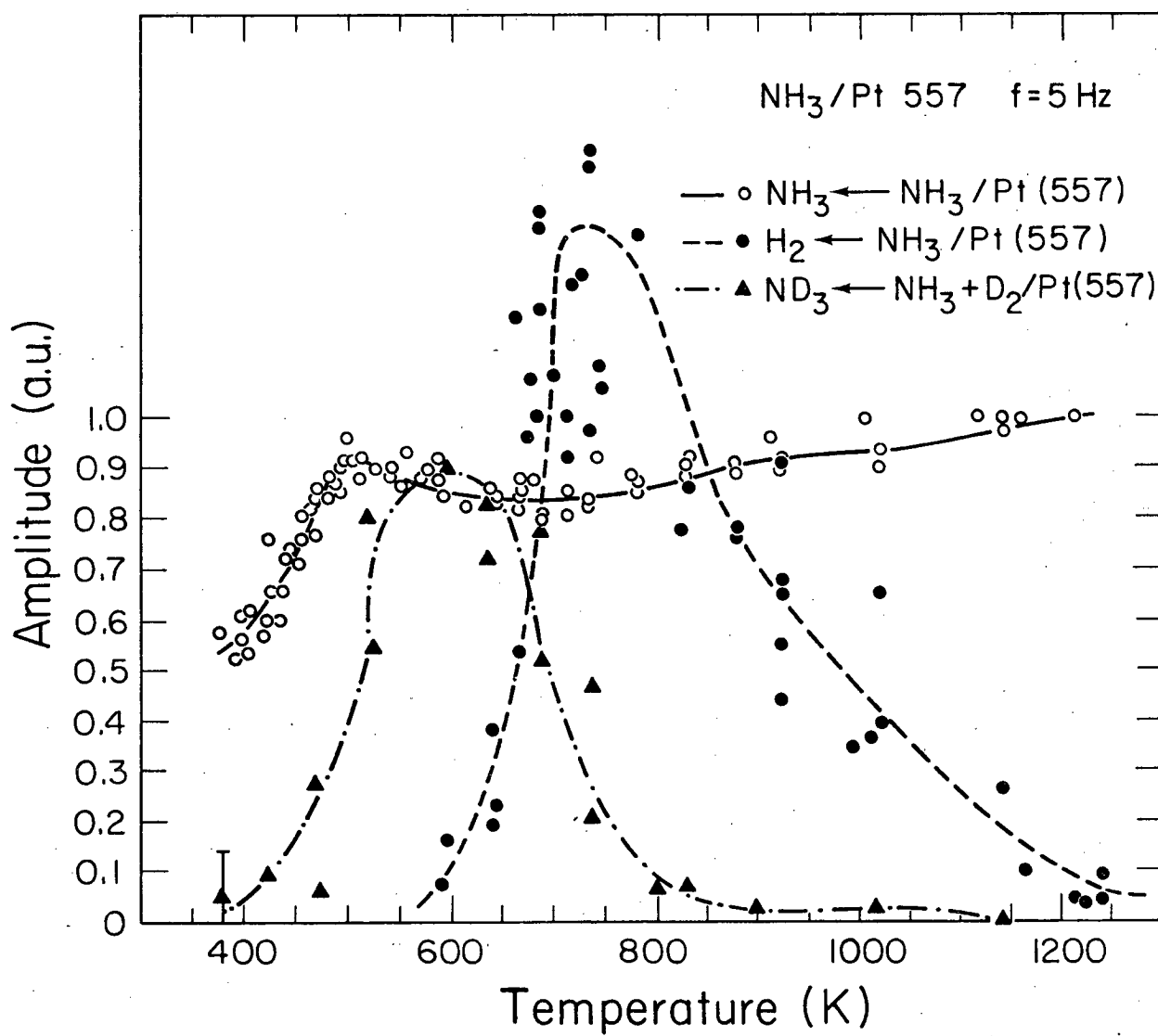


Figure 24

XBL 798-2530

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