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Reactive Scattering of N_2O Molecular Beams from Clean and Carbon Covered (100)Platinum Single Crystal Surfaces

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ABSTRACT

Thermal energy molecular beams of N_2O have been scattered from a platinum (100) surface maintained in the temperature range 900K to 1500K in an ultra high vacuum chamber. The angular distribution of the scattered beams was monitored with a quadrupole mass spectrometer, the target surface structure by low energy electron diffraction, and the surface composition by Auger spectroscopy. The effect of surface temperature and surface structure on the surface decomposition of N_2O has been studied. At 1200K, using a clean surface, the angular distribution of one of the reaction products, NO, follows the cosine law but deviations from this behavior seem to occur if the surface is covered by a layer of carbon. At still higher temperatures N_2O reacts with the carbon layer on the surface and removes it by the oxidation reaction $N_2O + C \longrightarrow CO + N_2$. The mechanisms of reactive scattering based on the experimental observations will be discussed.

INTRODUCTION

The scattering of atomic or molecular beams from surfaces gives information about the dynamics of the interaction between the incident particles and the surface atoms.[1] Until recently, most investigators in this field have restricted their attention to the scattering of beams of inert gases or hydrogenic molecules from a variety of surfaces.[2] From the angular distribution of the scattered gas atoms as a function of the nature of the surface (temperature, orientation, order) and of the incident beam (energy, direction), the dynamics of the gas-surface interaction have been probed. Several theories have been proposed using relatively simple scattering models to account for the experimental observations.[3,4,5,6]

The scattering of gases that react during collision with the solid surface have been studied to a much lesser extent. Such studies could provide information about the dynamics of surface chemical reactions. There are at least three types of reactive collisions that may occur. 1) The gas molecule may dissociate or undergo rearrangement during collision with the surface while the surface acts as a catalyst.[7] 2) The incident molecule may react with the surface yielding a surface atom among the reaction products.[8] 3) The gas molecule may react with a gas previously adsorbed on the surface.[9] The dissociation of nitrous oxide (N_2O) on the (100) crystal plane of platinum and on a carbon covered platinum surface has been studied. The reactive scattering of N_2O seems to be representative of the first two classes depending upon the state of the surface.

EXPERIMENTAL

The apparatus that allows one to carry out molecular beam scattering studies from clean single crystal surfaces in an ultra high vacuum environment is described in detail elsewhere.[10] A schematic diagram of the equipment is shown in Figure 1. In brief, the molecular beam of flux 10^{12} to 10^{13} molecules per square centimeter per second at the target is formed by a multi-channel array of glass capillaries and passes through two differentially pumped chambers before reaching the crystal surface. The platinum sample has the shape of a disc 8 mm in diameter. It had previously been oriented to within 1° of the (100) plane, mechanically polished, and finally chemically etched before being placed in the vacuum system. Its surface structure could be monitored <u>in situ</u> by low energy electron diffraction (LEED) and the chemical composition of the surface ascertained when desired by Auger electron spectroscopy (AES). The average speed of the beams used in this work was approximately 4×10^4 cm/sec but no attempt was made to measure the complete velocity distribution of either the incident or scattered N_2O beam. The species in the scattered beam and their angular distributions were obtained by means of a quadrupole mass spectrometer that could be rotated about the sample in the plane of incidence. In order to enhance the detection of the scattered particles, the incident beam was modulated at 150 hertz. Electron impact ionization of N_2O in the mass spectrometer yields predominantly the molecular ions N_2O^+

and NO^+ and a smaller amount of N_2^+. The observed cracking pattern, which was found to be very sensitive to the ionizer potential, is listed in Table I along with values reported in the API tables for a magnetic instrument.

Scattering experiments were carried out from both clean and carbon covered (100) platinum surfaces at temperatures between 900 K and 1500 K. Although the background pressure in the scattering chamber is roughly 5×10^{-10} torr, during the higher temperature experiments, the ambient pressure sometimes rose to as high as 10^{-8} torr due to outgassing of the system walls by radiant heating. Hydrogen, carbon monoxide, carbon dioxide, and water vapor are the dominant species in the background gas. Carbon was deposited on the platinum surface by dissociating acetylene that was added to the ambient gas by means of a controlled leak valve. To clean the surface, the crystal was heated at elevated temperatures in the presence of 10^{-6} torr of oxygen for half an hour.

N_2O is a linear molecule ($\overset{-}{N}{=}\overset{+}{N}{=}O$).[11] Spectroscopic studies indicate that the energy of the NN bond is 113.7 kcal/mole while the energy of the NO bond is 38.7 kcal/mole. Photochemical dissociation of gaseous N_2O yields primarily N_2 with the atomic oxygen subsequently undergoing further chemical reactions with other N_2O molecules to form NO and O_2.

$$N_2O \xrightarrow{(a)} N_2 + O \begin{cases} \xrightarrow[(b)]{+N_2O} NO + NO \\ \xrightarrow[(c)]{+N_2O} N_2 + O_2 \end{cases} \qquad (1)$$

Table I. N_2O Cracking Pattern

m/e	Quadrupole	API*
28	.223	.108
30	.436	.311
44	1.000	1.000

*Serial No. 96, Mass Spectral Data, American Petroleum Institute Research Project 44.

Surface dissociation of N_2O has been observed by Muschlitz and his co-workers on a polycrystalline tungsten ribbon between 1800 K and 2500 K[12,13]. They found both N_2 and NO in the scattered beam and reported that the ratio of the two species (N_2/NO) was approximately 12 to 1 at 2500 K.

Since we have studied the scattering of N_2O from both clean and carbon covered platinum surfaces, it is worth while considering the various possible reactions that may occur. These are listed below:

$$N_2O(g) \xrightarrow{Pt} N(ads) + NO(g) \quad (2)$$

$$N_2O(g) \xrightarrow{Pt} O(ads) + N_2(g) \quad (3)$$

$$C(s) + N_2O(g) \xrightarrow{Pt} NO(g) + CN(ads) \quad (4)$$

$$C(s) + N_2O(g) \xrightarrow{Pt} N_2(g) + CO(g) \quad (5)$$

$$C(s) + 2N_2O(g) \xrightarrow{Pt} 2N_2(g) + CO_2(g) \quad (6)$$

The free energy changes for reactions 3,5 and 6 are negative at the temperatures of this work, indicating that all are thermodynamically feasible. However, because the scattering experiments are carried out far from thermodynamic equilibrium, it is likely that kinetic factors (i.e. relative magnitude of reaction rates at a given temperature) will predominate. This is apparent from the fact that Muschlitz observes both NO and N_2 in the scattered beam in the case of tungsten. While free energy change for equation 4 can only be estimated, it appears also to be a likely reaction since the enthalpy change is negative due to the strength of the CN bond

(187 kcal in the gas phase). Also, Auger electron spectroscopy indicates the presence of nitrogen on the carbon covered surface, even though experiments have shown that N_2O does not adsorb in the temperature range of this study (900 - 1500 K). Low energy electron diffraction studies indicate that N_2O does not form an ordered surface structure at 300 K.

RESULTS

From equations 2 through 6 of the preceeding section, it is apparent that all the potential gaseous reaction products have atomic masses of 28, 30, or 44. These species can result from either the dissociation of N_2O on platinum, or from the surface reaction of N_2O with carbon [NO (m/e = 30), N_2 (m/e = 28), CO_2 (m/e = 44)] or from the electron impact ionization of unreacted N_2O in the mass spectrometer ionizer [N_2O (m/e = 44), N_2 (m/e = 38), NO (m/e = 30)]. Due to the presence of carbon monoxide in the ambient, the peak at m/e = 28 cannot be reliably monitored during the experiment because random noise from the high DC background saturates the detection electronics. Thus we have monitored the ion ratio NO^+/N_2O^+ throughout the experiment as a function of scattering angle and surface temperature, comparing the observed ratio in the scattered beam with that in the incident beam. We have assumed that the NO^+/N_2O^+ ratio from the ionization of N_2O is independent of the vibrational energy of the molecule. In view of the small number of vibrational modes, their relatively large energy spacing compared to the thermal energy, kT, and the fact that vibrational transitions are optically allowed (thus permitting energy release via

radiation), this assumption should be justified in the case of N_2O. If the NO^+/N_2O^+ ratio increases after surface scattering with respect to that of the incident beam, NO molecules have been formed by the dissociation of N_2O at the platinum surface. If the NO^+/N_2O ratio remains unchanged, presumably the reactive scattering produced N_2 and O as this process would not change the ratio. Of course, a ratio that remains unchanged may also indicate that reaction did not take place at a detectable rate on the surface. If the NO^+/N_2O^+ ratio decreases, it can only be due to a chemical reaction that produces CO_2 (m/e = 44) since within our mass resolution, the ion signals from N_2O^+ and CO_2^+ are indistinguishable. The smaller ratio arises because the CO_2^+ intensity increases the denominator of the NO^+/N_2O^+ ratio.

We have found indications that all of the reactions that can affect the NO^+/N_2O^+ ratio can take place in the temperature range of the study (900 - 1500°K) using clean platinum and carbon covered (100) surfaces. Figures 2 and 3 show the angular distributions of the scattered NO^+/N_2O^+ ratios at $T_{surface}$ = 1125°K from a clean and a carbon-covered surface. The intensities have been normalized to the strength of the incident beam, and the arrow indicates the angle of incidence. The solid circles show the ratio obtained from the fragmentation pattern while the open circles indicate the observed ratio; by subtraction one obtains the angular distribution of that portion of the NO that is the result of the dissociation at the platinum surface. It appears that the angular distribution of the product NO

molecule that formed by dissociation at the clean platinum surface is of the cosine type, indicating complete accomodation of the NO molecule on the surface prior to reemission. The angular distribution is quite different however for the NO product molecules that are scattered from carbon covered platinum surfaces at 1125°K. As is shown in Figure 3, the dissociation product does not peak at the surface normal and the angular distribution is not cosine. Such a peaked angular distribution reflects a lack of energy accommodation during the surface dissociation reaction of N_2O on the carbon-covered platinum (100) surface and suggests a direct reactive scattering mechanism.

The angular distribution and the NO^+/N_2O^+ ratio are senstive functions of the carbon surface concentration. Frequently, especially at higher temperatures, N_2O beam scattering from the platinum (100) surface yielded a NO^+/N_2O^+ ratio that was smaller than in the incident beam. Such negative deviations from the fragmentation ratio indicate the formation of CO_2 as a direct result of the chemical reaction between the incident N_2O and surface carbon. In fact, it has been found that during long periods of N_2O exposure at about 1300°K the surface carbon could be completely removed unless acetylene was added to the ambient background to replenish the carbon deposit on the platinum surface.

In addition, in a few instances using both clean and carbon-coated platinum surfaces, the NO^+/N_2O^+ ratio remained unchanged, indicating that the surface had somehow been passivated, or that the reaction products had changed to dominantly N_2 and O. Unfortunately, this latter possibility could not be investigated in either the DC or AC detection modes due to the relatively large concentration of CO in the background.

DISCUSSION

N_2O may undergo a variety of different chemical surface reactions upon scattering from platinum surfaces. It appears that most of the reactions that have been considered in equations 2 through 6 can and do take place in the temperature range of this study. A clean platinum surface seems to dissociate N_2O only poorly, at the surface temperatures employed in this work only a few percent of the incident molecules undergo bond breaking. This reaction appears to be endothermic and shows only a very small temperature dependence. The incident molecules that dissociate are fully accommodated on the surface before reemission as indicated by the cosine angular distribution of the scattered beam. On the carbon covered platinum (100) surface, the scattering process appears to be entirely different. Due to the interaction between N_2O and surface carbon, the surface reaction can be strongly exothermic. As a result, it appears that we have detected evidence for direct reactive scattering that has not been previously observed in surface reaction studies. The NO molecules are scattered without energy accommodation between the incident beam and the surface as indicated by the non-cosine angular distribution of the scattered beam in Figure 3. Direct scattering is commonly observed in studies of chemical reactions between crossed molecular beams that are exothermic and exoergic.[14] (For example, $K + CH_3I \longrightarrow KI + CH_3$.[15])

However, the evidence for direct scattering of N_2O on the carbon covered platinum surface is not quite conclusive since the NO^+/N_2O^+ ratio depends on both the carbon concentration at the surface and the surface temperature. Other surface reactions between N_2O and carbon can compete with the reaction mechanism yielding the direct interaction. In addition, the possibility that the scattered N_2O molecules may be vibrationally excited and thus give rise to larger NO^+/N_2O^+ ratios cannot be ruled out. Clearly more studies are needed to verify the results that indicate direct scattering of NO product molecules. It is hoped that more conclusive evidence will become available in the near future from continued work in this laboratory. This study however demonstrates that reactive scattering of molecular beams can be studied by present techniques using single crystal surfaces and can provide detailed information about the dynamics of surface chemical reactions.

ACKNOWLEDGEMENT

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* National Science Foundation Predoctoral Fellow.

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Figure Captions

Fig. 1. Schematic diagram of molecular beam apparatus.

Fig. 2. Scattered NO due to the dissociation of N_2O on a clean platinum (100) surface. The reaction product is indicated by the dotted line.

Fig. 3. Scattered NO due to the dissociation of N_2O on a carbon coated platinum (100) surface. The reaction product is indicated by the dotted line.

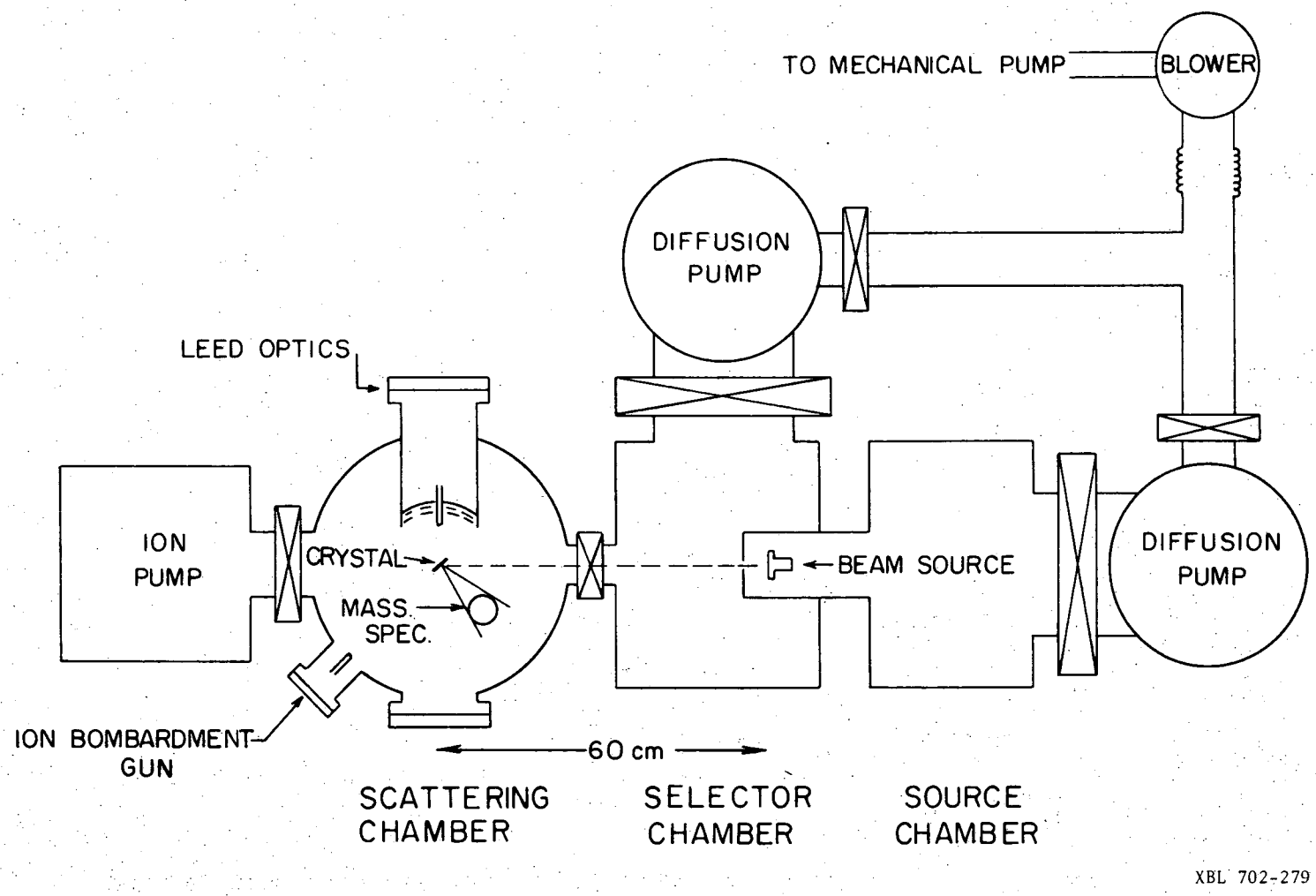
TO MECHANICAL PUMP
BLOWER
DIFFUSION PUMP
LEED OPTICS
ION PUMP
CRYSTAL
MASS. SPEC.
BEAM SOURCE
DIFFUSION PUMP
ION BOMBARDMENT GUN
60 cm
SCATTERING CHAMBER
SELECTOR CHAMBER
SOURCE CHAMBER
XBL 702-279

Fig. 1

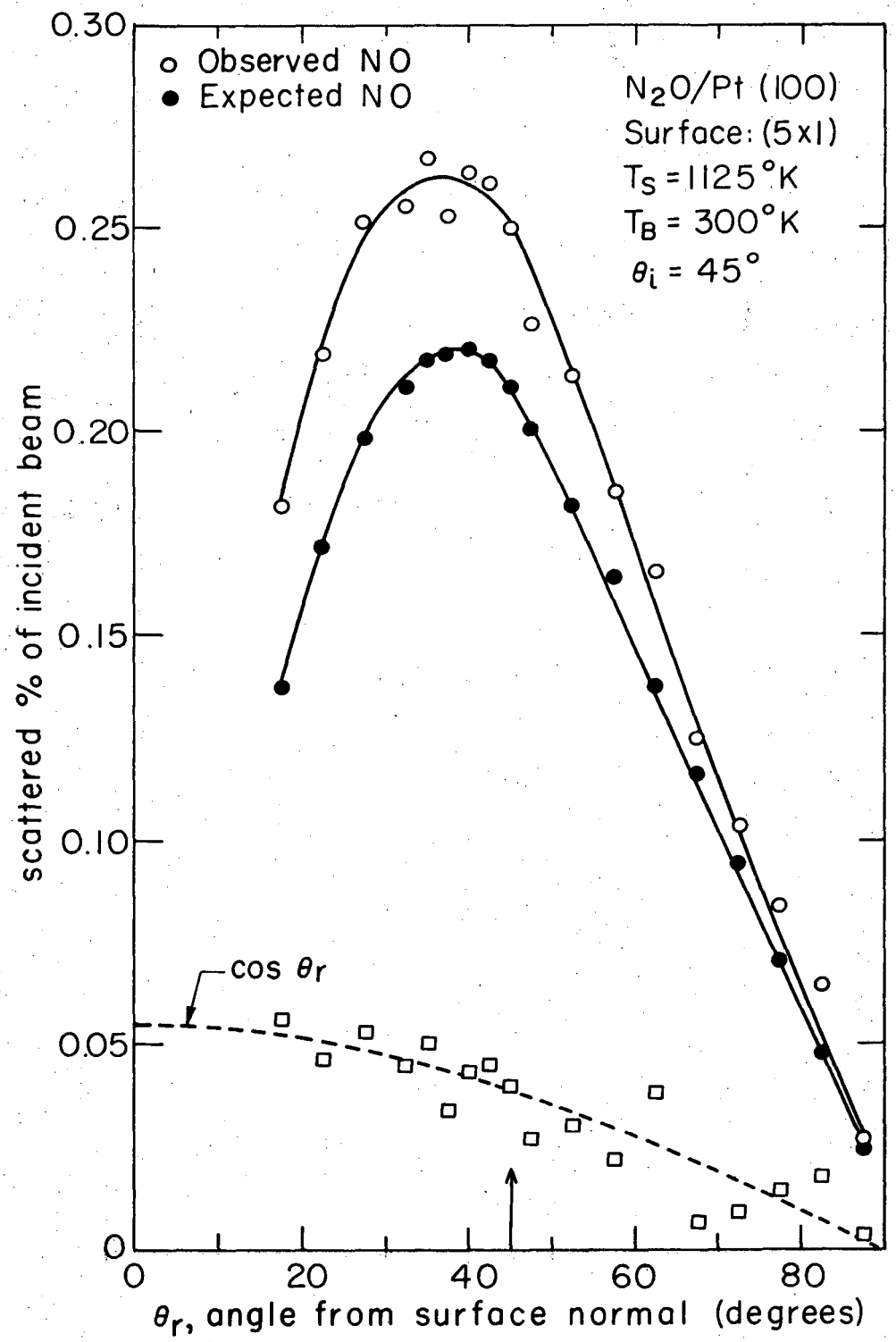

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Fig. 2

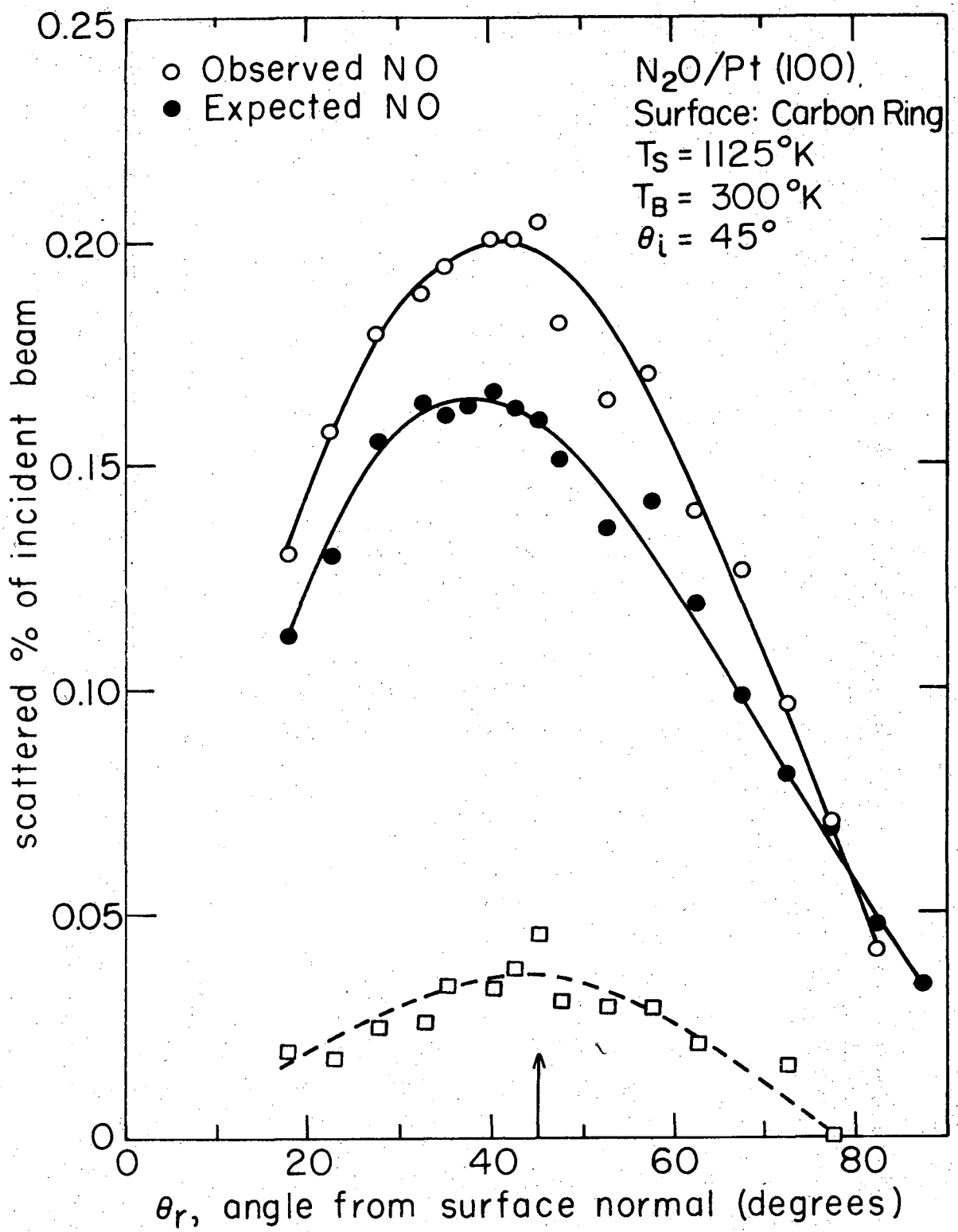

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Fig. 3

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