Introduction

In recent years the modulated molecular beam method has been extensively applied in investigations of the scattering of atoms and molecules from solid surfaces\(^1\), yet few attempts have been made in applying the method to studies of molecular dissociation on surfaces since the pioneering experiments of Smith and Fite\(^2\) on the dissociation of hydrogen on tungsten. Nitrous oxide is particularly suitable for this type of investigation since the enthalpy change for the reaction, at 298\(^0\)K,

\[
N_2O(g) \rightarrow N_2(g) + O(g) \quad (1)
\]

is only 40 kcal while the enthalpy change for the reaction,

\[
N_2O(g) \rightarrow NO(g) + N(g) \quad (2)
\]

is 103 kcal. The first reaction is therefore expected to be the predominant one, and this has been found to be the case for the gas phase thermal decomposition of nitrous oxide. Furthermore, the molecule is linear and the complete absence of spherical symmetry should provide an interesting contrast with hydrogen.

* Supported by a National Aeronautics and Space Administration Institutional Grant to the University of Florida.

\# Visiting Fellow, Joint Institute for Laboratory Astrophysics, the National Bureau of Standards and the University of Colorado, 1968.
The modulated molecular beam apparatus used in these experiments is shown schematically in Figure 1. A beam of N₂O molecules is formed by a multi-channel source consisting of a closely-packed array of glass capillaries 7 microns in diameter. The beam is collimated by two slits each 0.040 inch wide and chopped mechanically at 90 hertz. The tungsten surface is a polycrystalline ribbon 1, 0.150 inch wide, located 12.5 cm from the beam source. The ribbon was heated electrically by passing a D.C. current through it. X-ray analysis of several aged samples showed the surface to consist predominantly of the (112) planes of small crystals, and that these surfaces were parallel to each other within one degree. The detector is an EAI quadrupole mass spectrometer mounted so that it could be rotated about the surface. The entrance slit of the spectrometer is located 1.2 cm from the surface and has an acceptance angle of 4 degrees. The ionizer of this instrument was modified in order to increase its sensitivity as a molecular beam detector as shown in Figure 2. In this arrangement electrons from the filament are accelerated by a positive potential of 60 volts on the grid. The outer can is operated at a small negative potential so that electrons are reflected back and forth through the molecular beam several times before being collected on the grid. An electron current to the grid of 10 ma was used in these experiments.

Although the incident angle of the molecular beam could be changed, all measurements were made at an incident angle of 50° from the normal to the surface. The detector could be rotated within 10° from the normal to the surface, and the data were taken at angles ranging from 10° to 80° from the normal. It was found necessary to avoid angles approaching 90° since the spectrometer begins to pick up some of the modulated beam that misses the target.

The signal from the quadrupole electron multiplier was first amplified by
narrow band amplifier and the in-phase component measured by a PAR Model J8-4 lock-in amplifier. The chopper simultaneously interrupted a light beam which was detected by an NPN silicon light sensor thereby generating a reference signal.

The vacuum chamber was pumped by a 10-inch liquid nitrogen baffled oil diffusion pump. In the absence of a molecular beam the background pressure was $10^{-7}$ torr while in the presence of a beam background pressures rose as high as $10^{-6}$ torr. Since a pressure of the order of $10^{-9}$ torr is required to maintain a clean tungsten surface below 2500$^\circ$K, the surface under investigation is covered with chemisorbed oxygen. Nevertheless, with beams of argon or nitrogen incident on the surface, the angular distribution of the reflected particles is diffuse (cosine law) at low temperatures, but a distinct lobular pattern begins to appear at temperatures of about 1800$^\circ$K and as the temperature is increased further the lobe becomes sharper with its maximum in the neighborhood of the specular angle. These results are quite similar to those of Hinchen and Foley who investigated the effect (on the angular distribution of argon atoms reflected from a platinum surface) of chemisorbed oxygen. They interpreted their results in terms of a gradual clean-up of the surface as the temperature is increased. However, the tungsten surface in this investigation cannot be considered completely clean below 2500$^\circ$K.

Results and Discussion

Figures 3, 4, and 5 illustrate the transition from a diffuse to a lobular distribution of reflected N$_2$O molecules when a beam of N$_2$O is incident on the tungsten surface as the temperature is increased. The data in these figures are the directly observed mass spectrometer signals. In Figure 5, the data at all temperatures are shown on the same scale. In comparing these distributions with those for reflected argon or nitrogen from the same surface, several distinct differences are evident. Significant deviations from diffuse
reflection for N₂O are not observed at temperatures below 2100°K, indicating a stronger interaction with the surface. Furthermore, the lobular distribution observed at high temperatures for N₂O is a markedly flattened one rather than having a distinct maximum in a specific direction, as is the case for Ar or N₂.

Dissociation of N₂O was found to be insignificant below 1800°K and to increase rapidly between 1800 and 2500°K. The only dissociation product observed in the mass spectrometer was N₂. It is likely that the residence time of the oxygen atoms resulting from the dissociation is 10 milliseconds or longer in the temperature range of this investigation, which would prevent their observation by the technique employed. This conjecture is consistent with the observations of Steele⁵ on the desorption of oxygen atoms from a tungsten surface.

The angular distribution of the dissociated nitrogen molecules was found to obey the cosine law throughout the entire range of temperatures investigated. Smith and Fite² found this to be the case also for the dissociation of hydrogen on tungsten. On the other hand, the reflected N₂ molecules exhibited a lobular distribution with a distinct maximum in contrast to the flattened lobe observed in this investigation for N₂O. Since the N₂ distribution was found to be diffuse, a reasonable assumption to make is that the velocity distribution of these molecules is a Maxwellian distribution characteristic of the surface temperature. The N₂ mass spectrometer signals can then be put on the same basis by first correcting for the N₂⁺ ions formed by dissociative ionization of N₂O, then multiplying by the square root of the absolute temperature. The first correction could be avoided if the electron energy were kept below 17.0 ev, the appearance potential⁶ for N₂⁺ from N₂O, but above 15.6 ev, the ionization potential of N₂. However, the ionization efficiencies are much lower in this range of electron energies. It is assumed that the N₂⁺/N₂O⁺ ratio in the ionization of N₂O is independent of vibrational energy in the molecule, which
may increase as the temperature of the surface is increased. However, part
of this excitation will be lost by radiation before the molecule reaches the
ionizer, since the vibrational transitions are optically allowed for N₂O. When
these corrections are made, the results shown in Figure 6 are obtained, where
the relative N₂ flux density at an angle of 40° from the normal as a function
of the absolute temperature is shown. The N₂ intensity rises very rapidly
at temperatures above 1800°C, then levels off at temperatures above 2200°C.
Since the N₂O signal has practically disappeared at this point, the inference
is that dissociation on the surface is nearly complete above 2500°C.

References

1. R. E. Stickney, In "Advances in Atomic and Molecular Physics,"
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37, 1551 (1966).


Fig. 1. Modulated Molecular Beam Apparatus.

Fig. 2. Quadrupole Mass Filter Molecular Beam Detector.
**Fig. 3.** Angular Distribution of Reflected N\textsubscript{2}O Beam at 300°K.

**Fig. 4.** Angular Distribution of Reflected N\textsubscript{2}O Beam at 2500°K.
Fig. 5. Comparison of the Angular Distributions of Reflected N$_2$O at Various Temperatures. The data are normalized to the same incident beam intensity.

Fig. 6. Flux Density of the N$_2$ Dissociation Product Measured at 40° from the Normal to the Surface as a Function of Temperature.