N69-33598
NASA CR-103829

THE INTERACTION OF OXYGEN ATOMS WITH SOLID SURFACES AT eV ENERGIES

Second Annual Status Report
1 June 1968 to 31 May 1969
NASA Grant NGR-47-005-077

Submitted by:

G. D. Magnuson

J. W. Boring

R. R. Humphris

Research Laboratories for the Engineering Sciences

University of Virginia

Charlottesville

Report No. AEEP-4011-104-69U

June 1969

THE INTERACTION OF OXYGEN ATOMS WITH SOLID SURFACES AT eV ENERGIES

Second Annual Status Report
1 June 1968 to 31 May 1969
NASA Grant NGR-47-005-077

Submitted by:
G. D. Magnuson
J. W. Boring
R. R. Humphris

Submitted to:
National Aeronautics and Space Administration
Washington, D. C. 20546

Department of Aerospace Engineering and Engineering Physics
RESEARCH LABORATORIES FOR THE ENGINEERING SCIENCES
SCHOOL OF ENGINEERING AND APPLIED SCIENCE
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

Report No. AEEP-4011-104-69U
June 1969

Copy No. 9

I. INTRODUCTION

This report covers the second year of work performed under NASA Grant NGR-47-005-077 during the period June 1, 1968 through May 31, 1969.

In order to understand in detail the behavior of space vehicles in rarefied atmospheres it is necessary to have specific knowledge concerning the interaction of the atoms and molecules of the atmosphere with surfaces of the vehicle, particularly for particle energies corresponding to space vehicle orbital and escape velocities. The goal of the present research program is to investigate the mass spectrum resulting when oxygen atoms, moving with satellite velocities, strike a solid surface. In addition to adding to the small amount of information presently available concerning particle-surface interactions at energies corresponding to satellite velocities, the results will be of particular value in providing information that will aid in the interpretation of mass spectrometric studies of the neutral constituents of the earth's upper atmosphere. Although the principal concern of the research reported here is with monatomic oxygen the technique described in this report can be used for studies of other components of the atmosphere and interstellar space.

In the study of the interactions of neutral atomic oxygen with solid surfaces one must consider the possibility that the oxygen atoms spend a relatively long time on the surface and as a consequence the character of the particles leaving the surface does not depend to an appreciable extent on the energy of the incident atoms. In this event one could study the interaction of O atoms with surfaces using the more conventional thermal techniques. However, the few measurements that have been made on particle-surface interactions in the 1-10 eV range indicate that the molecules leaving the surface are far from fully accommodated to the temperature of the surface and hence have probably suffered only a few collisions with surface atoms before leaving the surface. There are, unfortunately, no such measurements for oxygen atoms, but one should probably be hesitant about applying results obtained from studies of the interaction of thermal oxygen atoms with surfaces to situations where the relative velocity between atom and surface is in the range of satellite velocities, particularly since the kinetic energy of these atoms is close to the dissociation energy for the O_2 molecule.

SECTION II
BACKGROUND

The principal objective of the research reported here is an investigation of the distribution of masses that result when oxygen atoms strike a solid surface. The interest is concentrated on oxygen atoms having a kinetic energy in the range of 4-10 eV, corresponding to velocities in the satellite range.

Several recent studies [1],[2] have been made of the recombination of atoms with surface atoms to form various species of molecules. These measurements have been conducted under conditions where the incident particles have thermal energies. If one is to use the results of such studies for application to practical situations where the atoms striking the surface have velocities in the satellite range, then it must be demonstrated that the results are essentially independent of the incident particle's energy in the range from thermal up to several eV.

Even though the development of the space program has generated great interest in particle-surface interactions in the eV energy range, very little experimental information is currently available. This is due to the rather awkward experimental techniques that must be used to perform measurements at these energies. However, within the past two years several measurements of the momentum transfer to surfaces by atoms, molecules, and ions in the energy range 1-200 eV give some indication of the character of the particle surface interaction at these energies. A study of the dependence of normal momentum transfer to surfaces by argon and helium atoms [3] with energies up to 4 eV indicate that at the higher energies investigated the momentum of the atoms leaving the surface is roughly 30 percent of the incident momentum. Work at the University of Virginia [4] indicates that for 10 eV N_2 molecules the momentum of the particles leaving the surface is about 15 percent of the incident momentum. Similar measurements using N_2^+ ions [5] in the energy range 5-100 eV show that the reflected momentum is 30-100 percent of that of the incident ions.

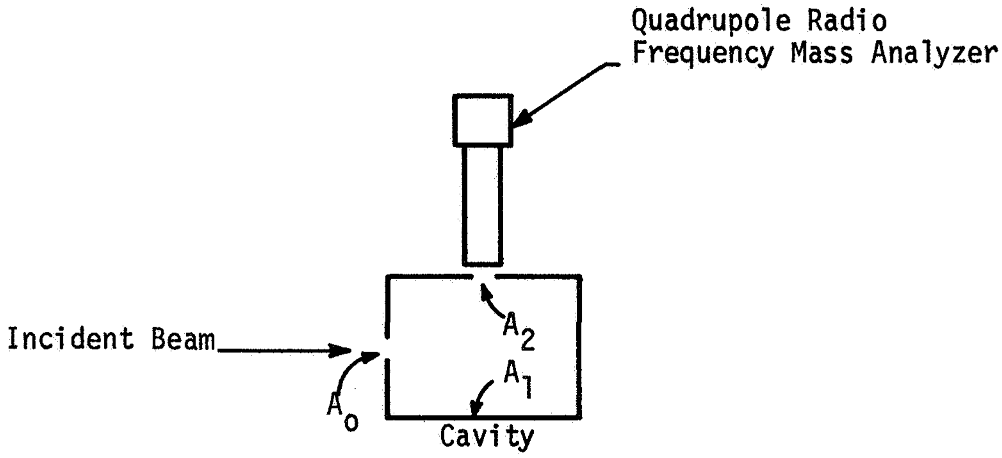
While these studies were carried out under conditions where the character of the surfaces was not well controlled, they all indicate that when atoms, molecules, or ions moving with energies of several eV strike a solid surface a large number of the particles leaving the surface have velocities comparable to the velocity of the incident particles. This suggests that at these energies many of the incident particles collide with only a few of the surface atoms and that they do not spend an appreciable amount of time on the surface. Although no similar studies have been carried out for monatomic oxygen, in light of the results for other particles one should not anticipate that O atoms striking a surface at satellite velocities will accommodate sufficiently to the temperature of the surface to cause processes such as adsorption and recombination to proceed at a rate that is independent of the energy of the O atoms. Current theories on the thermal accommodation coefficient [6] also indicate that at high energies (in the eV range) one expects the particles striking the surface to experience only a few collisions with surface atoms and that the energy of the reflected particles will be comparable to the incident energy.

SECTION III
EXPERIMENTAL APPARATUS

The apparatus that has been constructed for the performance of these experiments has been fully described in a previous status report.[7]

We have constructed a new accommodation cavity of a size to approximate the ante chamber of satellite and rocket-borne mass spectrometers. The cavity is a cube about 1.5 cm on a side with 1/4 in. diameter entrance and analysis apertures. The residual gas analyzer (RGA) is positioned immediately outside the analysis aperture. Figure 1 shows the arrangement of the cavity and the RGA. A_1, the total wall area is 17.4 cm^2 and A_0 and A_2 are equal, each of area 0.309 cm^2. On the average, an oxygen atom would make about 28 collisions before escaping the cavity.

The cavity was made of 0.020 in. OFHC copper, silver soldered together, cleaned with a mixture of HNO_3 and $HC\ell$, followed by a water rinse and a final rinse with acetone.



Wall Area = A_1 cm^2
Entrance Aperture = A_o cm^2
Analysis Aperture = A_2 cm^2

FIGURE 1. Arrangement of Accommodation Cavity and the Detector System

SECTION IV

PRESENT STATUS OF RESEARCH

A. Data Analysis

The data analysis given here is made using the following two assumptions. (1) The gas density in the cavity is small enough that gas phase collisions can be neglected. Since the background pressure is 10^{-9} to 10^{-8} Torr, corresponding to particle densities about 10^6 particles/cm^3, this assumption seems warranted. (2) Surface reactions are first order with respect to gaseous atoms. With these two assumptions we can write for the time rate of change of density of atomic oxygen n_1 in the cavity as:

$$\frac{dn_1}{dt} = \frac{Q}{V} - \frac{1}{4V} n_1\bar{c}_1A_1\gamma - \frac{1}{4V} n_1\bar{c}_1A_e, \qquad (1)$$

where Q is the number of atoms entering the cavity per second, V is the volume of the cavity, $\bar{c}_1$ is the average velocity of the oxygen atoms, A_1 is the total wall area of the cavity and $A_e = A_0 + A_2$, the total area of the entrance and analysis apertures. The recombination coefficient γ is here defined as the fraction of oxygen atoms striking the walls that recombine to form O_2 molecules. The second term on the right hand side of Equation (1) represents the rate of loss of O atoms to recombination and the last term on the right is the rate of loss of O atoms leaving the cavity through the apertures. If a portion of the oxygen atoms chemically combine with the cavity wall material to form non-volatile oxides these atoms are lost to further reaction but this does not affect the analysis presented here.

Equation (1) is easily solved to give:

$$n_1 = \frac{\tau Q}{V}(1 - e^{-t/\tau}), \qquad (2)$$

where

$$\tau = \frac{4V}{\bar{c}_1(\gamma A_1 + A_e)}. \qquad (3)$$

The steady state value of n_1 is therefore,

$$n_1 = \frac{4Q}{\bar{c}_1(\gamma A_1 + A_e)} . \qquad (4)$$

A similar equation can be written for the molecular number density n_2. It is,

$$\frac{dn_2}{dt} = \frac{1}{4V} n_1 \bar{c}_1 A_1 \frac{\gamma}{2} - \frac{1}{4V} n_2 \bar{c}_2 A_e, \qquad (5)$$

where $\bar{c}_2$ is the average velocity of the O_2 molecules. The first term on the right of Equation (5) is the rate of production of O_2 molecules and the negative term expresses the rate of loss of the molecules from the cavity. Equation (5) is also easily solved and gives,

$$n_2 = B\Gamma(1 - e^{-t/\Gamma}) + \frac{B}{(1/\Gamma - 1/\tau)} (e^{-t/\Gamma} - e^{-t/\tau}), \qquad (6)$$

where

$$B = \frac{1}{8} \bar{c}_1 A_1 \gamma \tau \frac{Q}{V^2} \qquad (7)$$

and

$$\Gamma = \frac{4V}{\bar{c}_2 A_e} . \qquad (8)$$

The steady state value of n_2 is therefore,

$$n_2 = \frac{2Q}{\bar{c}_2} \frac{A_1 \gamma}{A_e(\gamma A_1 + A_e)} \qquad (9)$$

If we take the ratio of the number densities we obtain,

$$\frac{n_2}{n_1} = \gamma \frac{A_1}{2A_e} \left(\frac{\bar{c}_1}{\bar{c}_2}\right), \tag{10}$$

from which we obtain an expression for γ,

$$\gamma = \frac{2A_e}{A_1} \left(\frac{\bar{c}_2}{\bar{c}_1}\right)\left(\frac{n_2}{n_1}\right). \tag{11}$$

Equation (11) is an expression for γ in terms of known constants, and the number densities of atomic and molecular oxygen in the cavity. Note further that this expression for γ is independent of the incident beam flux. Since the ionizing volume of the RGA is not located within the cavity the RGA signal does not give n_1 and n_2 directly but rather a signal directly proportional to these densities. We must therefore relate the RGA signal to the densities n_1 and n_2.

Let N_1 and N_2 designate the total number of oxygen atoms and molecules respectively, escaping from the analysis aperture per second. N_1 and N_2 are given by

$$N_1 = \frac{1}{4} n_1 \bar{c}_1 A_2 \;\&\; N_2 = \frac{1}{4} n_2 \bar{c}_2 A_2. \tag{12}$$

Therefore, the ratio n_2/n_1 is,

$$\frac{n_2}{n_1} = \frac{\bar{c}_1}{\bar{c}_2} \frac{N_2}{N_1}, \tag{13}$$

and thus our expression for γ becomes,

$$\gamma = \frac{2A_e}{A_1} \left(\frac{N_2}{N_1}\right). \tag{14}$$

We are still left with the task of relating the RGA signals S_1 and S_2 (the RGA ion current of masses 16 and 32 respectively) and N_1 and N_2. Now N_1 and N_2 are proportional to the flux of particles that enter the ionizing volume, i.e.

$$N_1 = K\bar{v}_1\rho_1 \text{ and } N_2 = K\bar{v}_2\rho_2, \tag{15}$$

where $\bar{v}_1$ and $\bar{v}_2$ are the respective average velocities in the effusing beam from the analysis aperture and ρ_1 and ρ_2 are the number densities of the effusing beam at the ionizing volume. The proportionality constant K is related to the area of the effusing beam at the ionizing volume of the RGA. However, using ratios eliminates the need to know K exactly, since all we must realize is that K is identical for both types of particles. Hence, $N_2/N_1 = \bar{v}_2\rho_2/\bar{v}_1\rho_1$ and Equation (14) for the recombination coefficient becomes,

$$\gamma = \frac{2A_e}{A_1}\left(\frac{\bar{v}_2}{\bar{v}_1}\right)\left(\frac{\rho_2}{\rho_1}\right). \tag{16}$$

The RGA signal S is given by S = kP where k is the sensitivity of the RGA to a particular species in Amps/Torr and P is the partial pressure of that gaseous species. We can convert this to a number density relation since $n = \alpha P$ where α is a known constant so,

$$S = \frac{k}{\alpha} n. \tag{17}$$

Assuming background currents of masses 16 and 32 of S_{1B} and S_{2B} respectively, we can write for the RGA signals,

$$S_1 = S_{1B} + \frac{k_{11}}{\alpha}\rho_1 + \frac{k_{12}}{\alpha}\rho_2, \tag{18}$$

and

$$S_2 = S_{2B} + \frac{k_{22}}{\alpha}\rho_2, \tag{19}$$

where,

k_{11} = RGA sensitivity for 0 in Amps/Torr,

k_{12} = RGA sensitivity for producing O^+ ions from O_2

in Amps/Torr,

and k_{22} = RGA sensitivity for O_2 in Amps/Torr.

The increase in signals due to the beam is thus,

$$\Delta S_1 = S_1 - S_{1B} = \frac{k_{11}}{\alpha} \rho_1 + \frac{k_{12}}{\alpha} \rho_2, \tag{20}$$

and,

$$\Delta S_2 = S_2 - S_{2B} = \frac{k_{22}}{\alpha} \rho_2 . \tag{21}$$

From these last two equations we see that,

$$\frac{\rho_2}{\rho_1} = (\frac{k_{11}}{k_{22}}) \frac{\Delta S_2}{(\Delta S_1 - \Delta S_2 \frac{k_{12}}{k_{22}})} . \tag{22}$$

Using this expression we obtain for γ,

$$\gamma = \frac{2A_e}{A_1} (\frac{\bar{v}_2}{\bar{v}_1})(\frac{k_{11}}{k_{22}}) \frac{\Delta S_2}{(\Delta S_1 - \Delta S_2 \frac{k_{12}}{k_{22}})} . \tag{23}$$

We know that $(\bar{v}_2/\bar{v}_1) = 1/\sqrt{2}$. The ratio k_{11}/k_{22} is given, for fixed RGA parameters, by Q_1/Q_2 where Q_1 is the total cross section for the reaction $O + e^- \rightarrow O^+ + 2e^-$ and Q_2 is the total cross section for the reaction $O_2 + e^- \rightarrow O_2^+ + 2e^-$, measured at the same electron energy. The ratio k_{12}/k_{22} is the measured cracking fraction for O_2 for the given electron energy of the

RGA. Therefore, our final expression for γ becomes,

$$\gamma = \sqrt{2}\ (\frac{A_e}{A_1})(\frac{Q_1}{Q_2})\ \frac{\Delta S_2}{(\Delta S_1 - \frac{k_{12}}{k_{22}}\ \Delta S_2)}\ . \tag{24}$$

From this equation we see that we can determine γ by measuring the increase in the mass 16 and 32 signals due to the incident oxygen beam independent of the absolute beam flux.

B. Use of Ion Beams to Measure Recombination Coefficients

We would like to suggest here that recombination coefficient measurements can be made using ion rather than neutral beams. We present below a brief argument supporting this thesis.

It is well known that neutralization of an ion at a metal surface can take place by either of two distinct processes: resonance neutralization or Auger neutralization. Resonance neutralization occurs when a metal electron tunnels through the potential barrier between the metal surface and the approaching ion. Since tunneling is a conservative process it can occur only if an energy level of the neutralized atom is available for the transiting electron. The excited atom thus formed in the resonance neutralization process can consequently lose its excitation by Auger de-excitation, the energy released perhaps resulting in the ejection of secondary electrons. For Auger neutralization the ion is neutralized directly to the ground state and the energy released in this process can also result in the ejection of secondary electrons. The broadening of the energy levels as the particle nears the metal surface reduces the likelihood of the above two stage process (resonance neutralization followed by Auger de-excitation) and it is thought that most neutralization of ions at surfaces occurs by the Auger neutralization process. The point that we wish to make however, is that it can be shown, that for low energy ions the probability of neutralization is very nearly unity.[8] Thus, the incident ion becomes a neutral atom within a few Angstroms of the surface and strikes the surface as a neutral particle. Further, if the energy is small, ionization is improbable and the oxygen remains neutral from that point onward. Although for O^+ ions it is quite possible that the atom will be in an excited state, an O^- ion will be neutralized to the ground state and hence use of O^- ions will definitely assure that the resulting neutral atom is in the ground state.

Use of ion beams to measure recombination coefficients at satellite velocities (4-10 eV) has three distinct advantages over the use of neutral beams. (1) Ion beams are at least one order of magnitude greater in intensity than a neutral beam formed by charge transfer or electron detachment. (2) If necessary the flux of particles can be determined directly by measuring the ion current to the cavity. (3) Neutral beams formed by charge transfer or collisional detachment have associated with them the flux of gas used to neutralize the beam. Although this problem is not serious since a neutralizing gas can be employed that differs significantly in mass from the species in question, it does introduce some unwanted gas into the cavity which may or may not interfere with the recombination process.

C. Results

Using ion beams we have made some recombination measurements of atomic oxygen on the copper walls of the accommodation cavity at high beam energies, 200 eV to 900 eV. These data were obtained by measuring the increase in the mass 16 and 32 signals when an ion beam was introduced into the cavity. Background currents were determined by electrostatically deflecting the ion beam away from the cavity.

With the present cavity the ratio $A_e/A_1 = 0.0355$. The cross sections for ionization were taken from Fite and Brackmann [9], who obtained $Q_1/Q_2 = 0.91$. The measured cracking fraction (k_{12}/k_{22}) was 0.06. Figure 2 shows the preliminary results we have obtained using beams of O^+ and O^- ions, with beam intensities of about 5×10^{-9} A. We have included in Figure 2 the thermal energy measurements of Greaves and Linnet [10],[11], Hartunian, et al. [12], Dickens and Sutcliffe [13], and a very recent measurement by Meyerson. [14] Since no treatment was given to the Cu cavity other than the cleaning procedure mentioned in Section III, it is impossible to determine the precise condition of the cavity walls. For this reason we believe it is premature to draw conclusions on the basis of these meagre data. But, we do

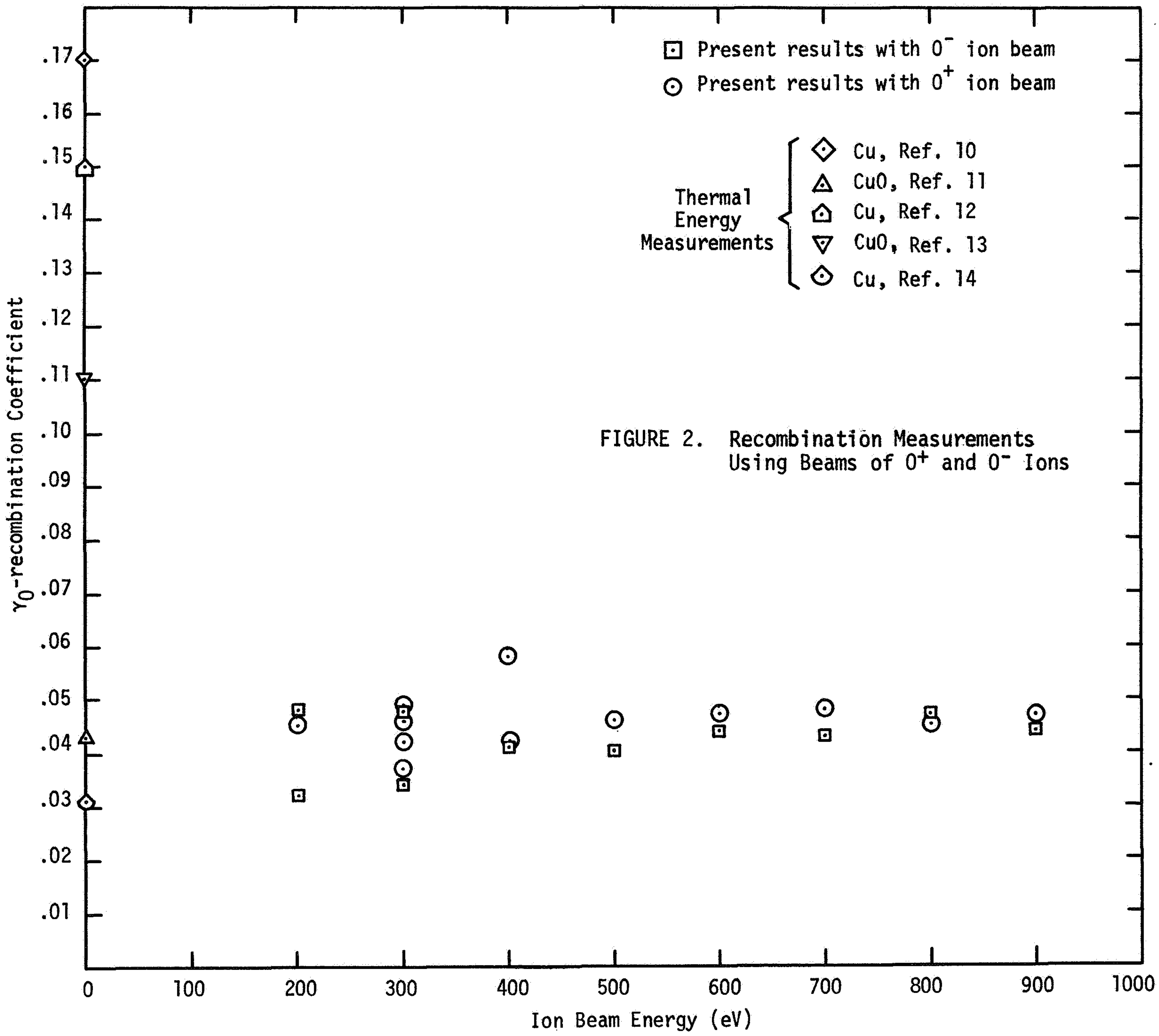


FIGURE 2. Recombination Measurements Using Beams of O^+ and O^- Ions

feel that these data are good initial evidence that γ_0 measurements can be made using ion rather than neutral beams.

D. Future Plans

Perhaps more important than the measurements themselves the results given in C. above have given us an indication of the RGA signals we can expect to measure. For example, with 5×10^{-9} A of O^- ions entering the cavity, the smallest rise in the mass 16 signal we measured was 1×10^{-10} A or about 2% of the incident beam. From this we estimate that we should have sufficient intensity to make recombination measurements for neutral atomic oxygen beams formed by electron detachment. However, it is now not a question of intensity, but of reducing the background current of mass 16 sufficiently so as to be able to detect the increases we expect with low intensity beams. Future efforts will be directed mainly to reducing the background current of mass 16 so that recombination measurements, using both ion and neutral beams, can be carried out at lower energies than reported here.

SECTION V

REFERENCES

1. Wood, B. J. and H. Wise, Jr., J. Phys. Chem. 65, 1976 (1961).

2. Wise, H. and B. J. Wood, Third International Symposium on Rarefied Gas Dynamics, Vol. I, p. 470, Academic Press (1963).

3. Abauf, N. and D. G. H. Marsden, Fifth International Symposium on Rarefied Gas Dynamics, Vol. I, p. 199, Academic Press (1967).

4. Boring, J. W. and R. R. Humphris, Sixth International Symposium on Rarefied Gas Dynamics, MIT, Cambridge, Massachusetts, July 1968.

5. Mair, W. N., B. W. Viney, and J. S. Colligon, Fifth International Symposium on Rarefied Gas Dynamics, Vol. I, p. 187, Academic Press (1967).

6. Goodman, F. O., J. Phys. Chem. Solids 23, 1269 (1962); J. Phys. Chem. Solids 24, 1451 (1963).

7. Magnuson, G. D., J. W. Boring and R. R. Humphris, "The Interaction of Oxygen Atoms with Solid Surfaces at eV Energies," RLES Report No. EP-4011-102-68U, June 1968.

8. Kaminsky, M., "Atomic and Ionic Impact Phenomena on Metal Surfaces," Chapter 12 (Academic Press, New York, 1965).

9. Fite, W. L. and R. T. Brackmann, Phys. Rev. 113, 815 (1959).

10. Greaves, J. C. and J. W. Linnett, Trans. Far. Soc. 54, 1323 (1958).

11. Greaves, J. C. and J. W. Linnett, Trans. Far. Soc. 55, 1346 (1959).

12. Hartunian, R. A., W. P. Thompson, and S. Safron, J. Chem. Phys. 44, 1765 (1966).

13. Dickens, P. G. and M. B. Sutcliffe, Trans. Far. Soc. 60, 1272 (1964).

14. Myerson, A. L., J. Chem. Phys. 50, 1228 (1969).

DISTRIBUTION LIST

Copy No.	
1-10	National Aeronautics and Space Administration Attn: Technical Reports Officer Scientific and Technical Information Office Code US Washington, D.C. 20546
11-12	G. D. Magnuson
13	J. W. Boring
14	R. R. Humphris
15-16	University Library, Attn: Dr. R. Frantz
17	A. R. Kuhlthau
18	R. A. Lowry
19	C. E. Carlston
20	M. S. Miller
21-25	RLES Files