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THE INTERACTION OF O^+ IONS WITH THE INTERIOR SURFACE OF A COPPER CHAMBER

FINAL REPORT

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Research Laboratories for the Engineering Sciences

University of Virginia

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ABSTRACT

Modulated beams of O^+, Ar^+, and Kr^+ in the 100-300 eV range are directed into a copper box simulating the antechamber of an orbiting mass spectrometer. An RF quadrupole mass spectrometer and phase sensitive detection extract the component of the internal mass spectrum correlated with the beam. Intense Ar and Kr signals are observed; however, no O or O_2 is detectable, indicating loss of the primary O^+ beam to surface interactions. All four primary ions stimulate sizeable signals at masses 26 and 28. The relevance of these experiments to the interpretation of mass spectra obtained by orbiting satellites is discussed.

SECTION I
INTRODUCTION

Density and composition measurements of the terrestrial atmosphere at satellite altitudes (i.e., several hundred kilometers) have been made <u>via</u> several rocket [1] and satellite [2] borne experiments during the last decade. Composition, in terms of relative mass abundances [3], has been measured by several mass spectrometer configurations. Absolute particle densities may be obtained by combining relative abundances with total drag measurements, as determined by orbital decay observations [4].

Of particular interest has been the abundance of atomic oxygen [5], believed to be a major constituent. Laboratory data [6] on the adsorption of thermal energy atomic oxygen on various surfaces indicate the need to consider the possibilities of adsorption and surface recombination in interpreting satellite data. To complement these data, we endeavor to simulate more realistically the primary particle energy during the satellite experiments.

We find that it is not at present feasible for us to simulate the lowest ambient pressures and primary energies encountered in the satellite environment. We can, however, complete a set of experiments (using positive ions in place of neutrals) at higher particle energies (≈200 eV) than the satellite apparatus encounters. Thus our work and Ref. 6 bracket the primary energy range of the satellite experiments (≈5 eV).

SECTION II
DISCUSSION

In the satellite rest frame, the residual atmosphere is seen as a low energy multi-mass neutral particle beam having the orbital velocity ($\approx 10^6$ cm/sec). The orbital velocity corresponds to an energy of about 10 eV for N_2, and scales linearly with mass number. Thus low energy laboratory atomic and molecular beams incident on a mass spectrometer of appropriate design may simulate the satellite apparatus with a variety of known single component atmospheres.

Two general configurations, "open" and "closed," are used in the satellite experiments [7].

In the open configuration, the entrance cone of the apparatus is oriented along the orbital velocity direction, and with proper design precautions the data must represent the true external mass spectrum. For high orbits, the sampled densities are low, and signal may be marginal. For example, an ambient pressure of 10^{-12} torr corresponds to 0.2×10^5 particles/cm^3, or (at 10^6 cm/sec) a flux of 0.2×10^{11} particles/cm^2-sec. At typical ionizer-transmission-detection efficiencies ($\sim$0.1%) [8], a total detectable current of 10^{-12} Amp may be anticipated.

In the closed configuration, the particle density available to the mass spectrometer is increased by allowing the incident particle flux to enter a low pumping speed aperture in a vessel referred to as an antechamber. Multiple collisions with the walls tend to thermalize the beam, and at equilibrium a pressure differential

$$\Delta P = \frac{RT}{S} J \qquad (1)$$

exists across the aperture [9]. Here R is the molar gas constant, T the absolute temperature of the walls, S the pumping speed of the aperture, and J the flux of neutral particles in moles/sec. [For easy comparison with laboratory beams, we shall henceforth discuss neutral particle currents in terms of the equivalent current of singly charged particles, where 1 Amp $\approx 6 \times 10^{18}$ particles/sec. Then J in Eq. (1) is replaced by I/F, where I is the equivalent current in Amps, and F is the Faraday constant, 96,500 coulomb/mole.]

As a rule of thumb, for an aperture of area A cm^2, we can take [9]

$$S \approx 10 \times A \text{ liters/sec.} \tag{2}$$

Thus, using the above external pressure of 10^{-12} torr and current of 0.2×10^{11} particles/cm^2-sec = 0.3×10^{-8} Amps/cm^2, and an aperture of 0.25 cm^2, we obtain, at 300°K,

$$\Delta P \approx 0.7 \times 10^{-10} \text{ torr.} \tag{3}$$

Thus, the advantage, in terms of particle density available to the mass spectrometer, of the closed over the open configuration is clear.

The interaction of the incoming species with the walls of the antechamber may produce, however, an internal mass spectrum quite different from the (desired) external spectrum. It is this possibility which we have investigated by directing a beam of mass and energy selected particles into a closed mass spectrometer, observing the resulting mass spectrum for various primary species and energies.

SECTION III
METHOD

The above numerical estimates indicate that were we able to produce the ambient pressure of the satellite environment, accurate simulation would be possible: 10^{-9} Amp into 0.25 cm^2 at about 10 eV is a feasible neutral beam current, in which case the estimated pressure of 0.7 x 10^{-10} torr in the box would be about two orders of magnitude above the detection limit of our mass spectrometer [8]. We could, with considerable modification of our present apparatus, deliver an appropriate low energy neutral beam current to the box; but impractically extensive modifications would be required to obtain a low energy background pressure for a faithful simulation. Our background pressure with the beam on is limited, by streaming source gas, to about 10^{-8} torr. Thus, at best we expect a signal of about 1% of that due to the total background.

As an alternative, employing the available apparatus with minimal modification, we have chosen to do a series of higher energy experiments to compare with the thermal energy results of Ref. 6. The background pressure at which we work makes signal extraction difficult, but with modulated beam and phase sensitive detection techniques an adequate signal is obtained. Our working pressure is low enough so that collisions with the walls dominate gas phase collisions by many orders of magnitude, and we have no reason to anticipate any new effects at lower background pressures.

At first sight the substitution of relatively high energy positive ion beams for lower energy neutral beams appears to be a serious compromise. However, there is considerable justification for arguing that neither the charge state nor the higher energy of our beam negates extension of our conclusions to the lower energy, neutral particle regime. First, we expect that for the majority of incoming particles, neutralization will occur <u>before</u> the first wall collision, some 10 Å from the wall [10]. Second, we expect rather rapid thermalization to occur <u>via</u> a large number of collisions with the walls, and surface-chemical effects to be strongest at the low energy, many collision end of the energy degradation process [11]. These arguments notwithstanding, we emphasize that our admonition of caution to the interpreters of satellite data is made with its own appropriate measure of caution.

SECTION IV
APPARATUS

The ion beam apparatus is quite conventional. Positive ions are produced by electron bombardment in a magnetically confined weak arc discharge in ~0.05 torr of an appropriate source gas. The source is of a design by Carlston and Magnuson [12]. The O^+ beam is produced with CO_2 or O_2 source gas; Ar^+ and Kr^+ beams are produced from the parent gas. Ions are extracted and accelerated to a transport energy of ~400 eV, mass analyzed by a 30° magnetic sector, and decelerated to the desired working energy. Two three-element-cylinder lenses in einzel configurations provide focusing at appropriate points before and after mass analysis. The beam is focused into the simulated ante-chamber ("box") by two thin-disk einzel lenses, one just after deceleration, the other a few cm in front of the box aperture. Deflection plates at several places along the beam path are arranged to provide angular deflection and transverse translation of the beam. The beam to the box is monitored by a standard Keithley electrometer in the fast mode (input = virtual ground). During operation of the mass spectrometer, electron current from the ionizer to the box is bucked-out to allow continuous monitoring of the ion beam.

A copper box, simulating a possible orbiting mass spectrometer antechamber, was used in these experiments. To aid the trapping and thermalization of primary particles, the box was constructed as shown in Figure 1. The entrance tube decreases the pumping speed of the input aperture without appreciably limiting the current into the box. For ease of construction, and to minimize the volume of the box (keeping its time constant small), we choose not to put the ionizer in the box, but to use a short length of tubing to connect an exit aperture in one side of the box to the inlet

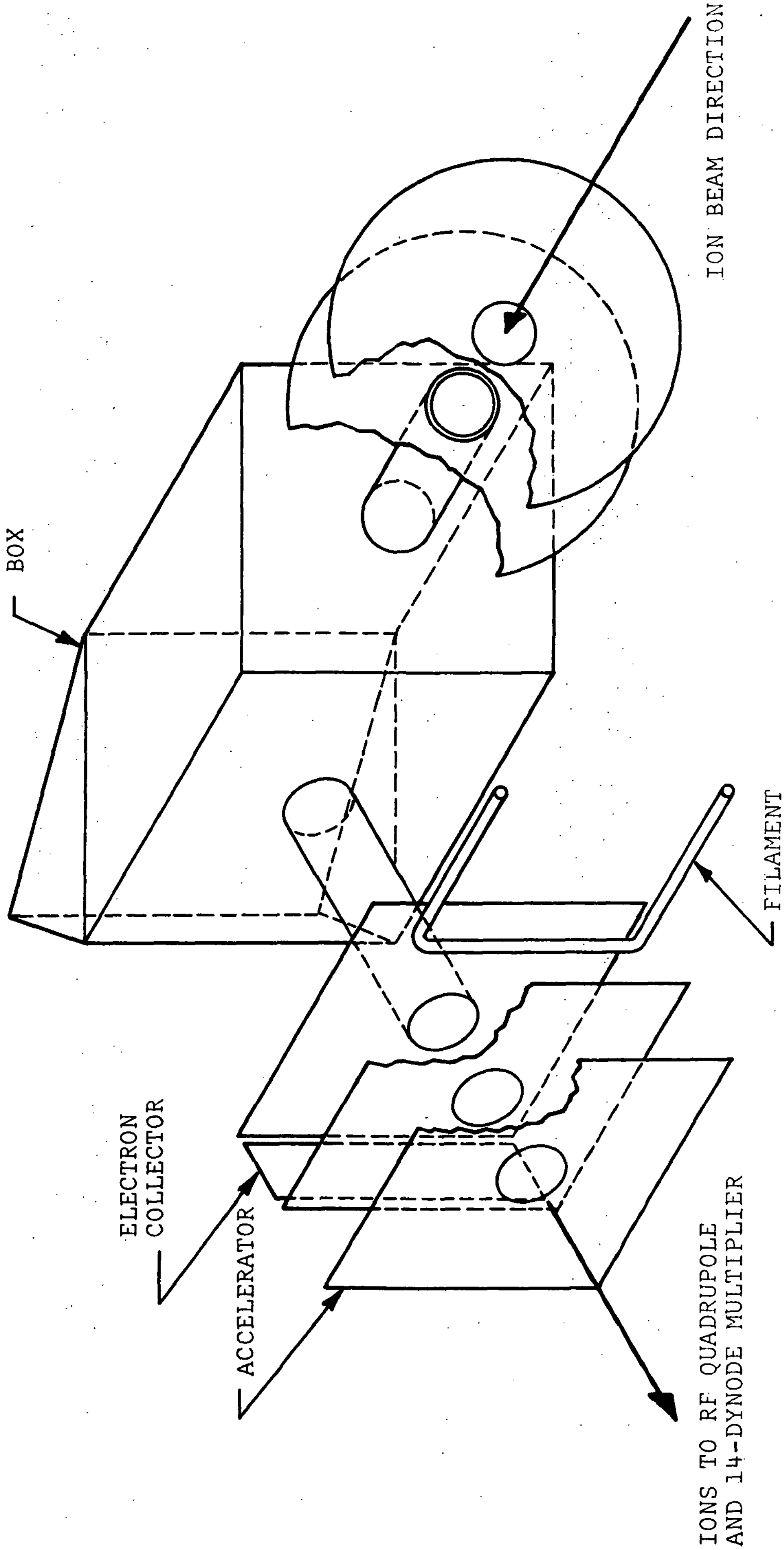

ION BEAM DIRECTION
BOX
FILAMENT
ELECTRON
COLLECTOR
ACCELERATOR
IONS TO RF QUADRUPOLE
AND 14-DYNODE MULTIPLIER

FIGURE 1

aperture of the ionizer. We estimate this costs roughly a factor of four in available DC signal; however, the increased available AC signal accompanying the decrease in box volume makes this a worthwhile tradeoff. The volume of the box is about 3 cm^3, and the parallel pumping speed of the two tubes about 4 liters/sec, yielding a time constant of (V/S)=0.75 msec.

We use a commercial RF quadrupole mass spectrometer [8]. The output is taken from a 14-dynode multiplier operated as a current amplifier. The multiplier current is integrated (low pass filtered) and amplified by a Keithley Fast Picoammeter, whose 0-3 volt output is analyzed for a component locked to the beam chopping signal. The mass range of interest is swept slowly (~30 sec/amu), and the output of the lock-in amplifier plotted against mass number on an x-y recorder.

The chopping frequency employed was usually 210 Hz. This choice is determined by the following considerations. If we chop much faster than 200 Hz, we lose signal for three reasons: 1) the high frequency rolloff of the picoammeter becomes unbearable; 2) the attentuation due to the "low pass filter" characteristic of the box becomes serious; and 3) as the duration of each cycle is decreased, the number of signal counts becomes statistically less significant compared to the shot noise in the background. If we chop much slower than about 75 Hz, we again experience problems: 1) the lock-in amplifier responds to the rise and fall in the background as a mass peak is scanned, yielding a systematic effect roughly describable as the derivative of the background spectrum; 2) charged insulators near the beam line do not maintain an equilibrium charge, and it becomes difficult to deliver a stable beam to the box; and 3) fluctuations become serious. To minimize the differentiation effect, we decrease the mass resolution until the tails of adjacent peaks begin to overlap.

SECTION V
DATA

Data have been taken with beams of O^+, Ar^+, and Kr^+, primarily at 300 eV; O^+ and Ar^+ data have been taken as low as 100 eV. In each case five traces were recorded:

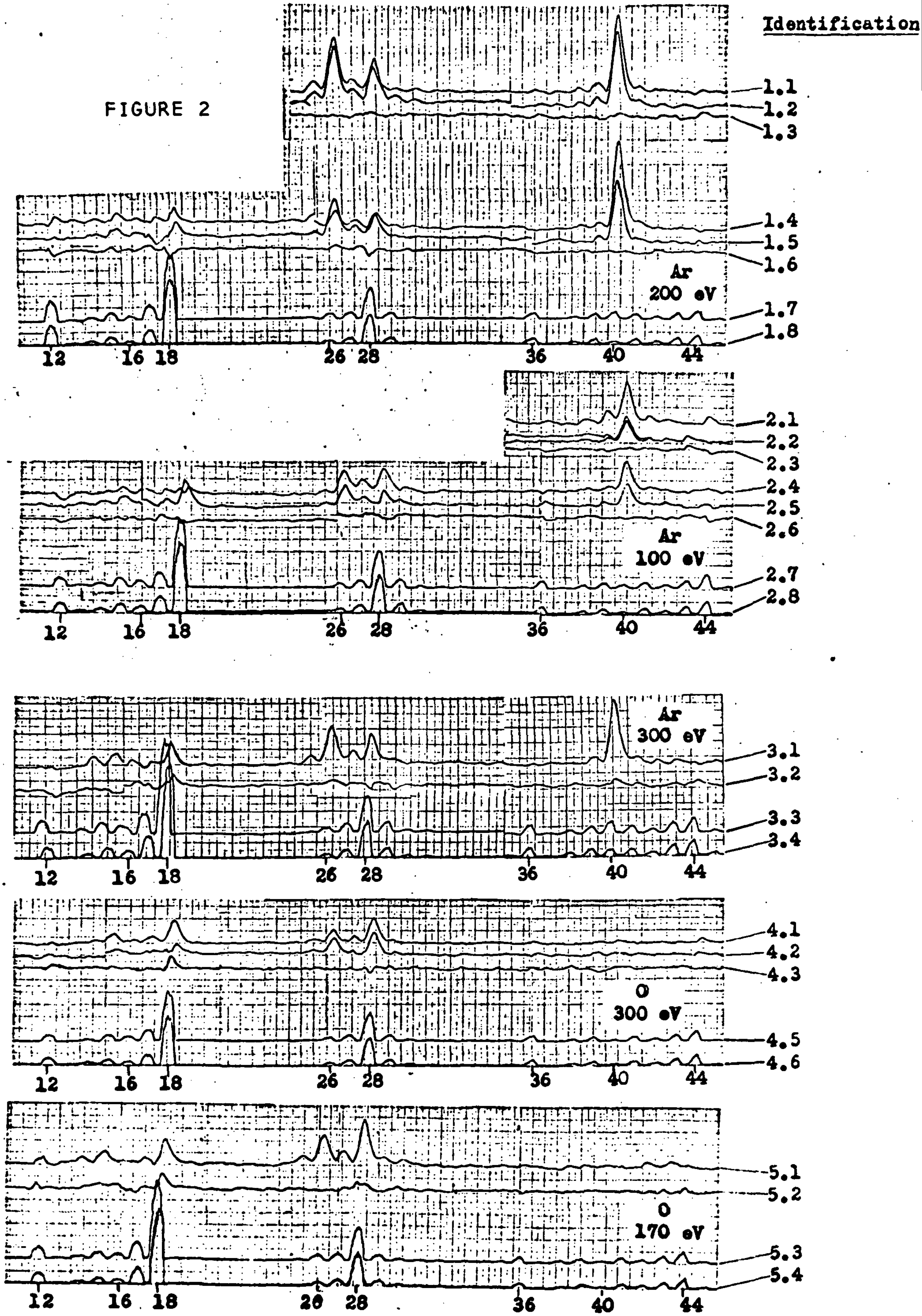
1) DC background spectrum (beam line valve to interaction chamber closed);
2) DC spectrum with beam into interaction region, but deflected from box;
3) AC spectrum with beam into interaction region, but deflected from box;
4) DC spectrum with beam into box; and
5) AC spectrum with beam into box.

Spectrum 5) is the ultimate data. Spectra 1) - 4) provide various checks, as discussed below. The data shown in Fig. 2 are reproductions of the x-y recorder traces; occasional discontinuities occur because each full spectrum required, for clarity, four sheets of paper, and these were later appropriately joined.

Spectrum 1) provides a measure of the background in the absence of source gas and beam perturbations. Comparison of Spectra 2) and 1) shows the effect of streaming source gas on the background. Spectrum 3) checks for unintentional modulation of the background, and other systematic effects. Spectrum 4), always indistinguishable from Spectrum 2), confirms that the signal we seek is effectively buried by the background.

We see a small systematic effect in Spectrum 3), roughly corresponding to the first derivatives of the largest background peaks. This effect seems to be attributable to a spurious response by our lock-in amplifier when it is

FIGURE 2



Identification
1.1
1.2
1.3
1.4
1.5
1.6
Ar
200 eV
1.7
1.8
12 16 18 26 28 36 40 44
2.1
2.2
2.3
2.4
2.5
2.6
Ar
100 eV
2.7
2.8
12 16 18 26 28 36 40 44
Ar
300 eV
3.1
3.2
3.3
3.4
12 16 18 26 28 36 40 44
4.1
4.2
4.3
O
300 eV
4.5
4.6
12 16 18 26 28 36 40 44
5.1
5.2
O
170 eV
5.3
5.4
12 16 18 26 28 36 40 44

presented with a large, rapidly slewing, "DC level." The size of the effect is clearly small compared to the ultimate signal, spectrum 5), and we neglect it.

The argon and oxygen data, and sensitivity calibration information, are given in Table 1. The krypton experiments, which were done primarily to confirm that the oxygen rather than the argon is "special," are essentially similar to the argon results, and are not shown.

TABLE 1

Trace	Species	Energy	Type*
1.1			5
1.2			5
1.3			3
1.4	Ar	200 eV	5
1.5			5
1.6			3
1.7			4
1.8			2
2.1			5
2.2			5
2.3			3
2.4			4
2.5	Ar	100 eV	5
2.6			3
2.7			4
2.8			2
3.1			5
3.2	Ar	300 eV	3
3.3			4
3.4			2
4.1			5
4.2			5
4.3	O	300 eV	5
4.5			4
4.6			2
5.1			5
5.2	O	170 eV	3
5.3			4
5.4			2

*"Type" refers to the data type discussed on page 9. Data sets 1.1-4.6 have a vertical scale of 1.7 x 10^{-14} torr (of Ar, measured by an ion gauge)/large division for the AC traces, and 2.8 x 10^{-10} torr/large division for the DC traces. Data sets 5.1-5.4 have a slightly larger, but uncalibrated gain. The AC gain takes into account the attentuation of the signal component at the modulation frequency by the picoammeter filter.

SECTION VI
RESULTS

The Ar^+ and Kr^+ results both demonstrate the operation of the apparatus with primary beams expected to experience minimal surface chemical effects. In these two cases the locked-in mass spectrum shows, at the primary beam mass, a clear peak, about ten times larger than the instrumental peaks seen at various masses large in the background spectrum. With the modulated beam entering the detector region, but deflected from the entrance aperture of the box, the instrumental effects remain, but the locked-in peaks disappear. Thus, we are confident that the apparatus is working according to design.

Genuine locked-in peaks are also observed at masses 26 and 28, corresponding to (perhaps) CN and N_2 and/or CO, and at significantly smaller amplitude, at several other masses, especially 15 (CH_3 ?, NH ?). That this is a surface effect is strongly indicated by the fact that while mass 28 (N_2) is a dominant peak in the background gas spectrum, mass 26 is not. In the locked-in spectrum, the mass 26 peak is, with the exception of the primary beam mass peak, the dominant one in the spectrum.

The O^+ beam stimulates the appearance of peaks at masses 26, 28, and perhaps 15. However it produces no significant O or O_2 signal. Thus we conclude that <u>via</u> surface interactions atomic oxygen disappears from the gas phase, reappearing, if at all, only after having lost all significant "memory" of its origin.

SECTION VII
CONCLUSIONS

The disappearance of primary oxygen is consistent with the thermal energy data, which indicates that only at pressures approaching 1 torr, and only after about 40 minutes of bombardment with O, does surface saturation occur, the atomic oxygen then being returned as O_2.

Thus, we reach the same conclusion reported at thermal energies: antechamber surfaces in orbiting mass spectrometers may contribute to anomalously low atomic (and perhaps molecular) oxygen concentration measurements until such time as equilibrium with the surfaces is established. Furthermore, with primary energies in the 100-300 eV range, molecular species, particularly masses 26 and 28, are profusely released, essentially independently of the primary species used. The extension of this second conclusion to primary energies in the 10 eV range seems risky, and must await appropriate experimental evidence.

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[2] Reber, C. A., and M. Nicolet, Planet. Space Sci. 13, p. 617 (1965).

[3] While results are frequently quoted in terms of absolute densities, the possibility of calibration uncertainties makes it preferable to think of the mass spectra as providing only relative densities.

[4] The average momentum transfer per collision for various species incident on appropriate satellite exterior materials has been measured in the laboratory by Boring and Humphris (AIAA Journal 8, p. 1658 (1970)), enabling determination of absolute densities from the drag measurements. Keating et al have proposed an experiment using two coplanar satellites to determine simultaneously density and composition.

[5] Brennan, D., D. O. Hayward, and R. Trapnell, Proc. Roy. Soc. A256, p. 81 (1960).

[6] Riley, J. A., and C. F. Giese, J. Chem. Phys. 53, p. 146 (1970). Also, see Wood, B. J., and B. R. Baker, "Research Related to Measurements of Atomic Species in the Earth's Upper Atmosphere," Final Report of Stanford Research Institute Project PGU-6682 (June 1970).

[7] Compare the configurations of Explorer XVII (open) and Explorer XXXII (closed).

[8] We use the Spectrascan 750 (TM of Granville-Phillips Co., Boulder, Colorado) Quadrupole Mass Spectrometer, with a nominal sensitivity of 100 Amp/torr for N_2. Under our operating conditions, with a reduced electron multiplier gain, we measure 1.8 amps/torr for Ar, with partial pressure measured by a Bayard-Alpert ionization gauge. For a 0.1 cm^2 working aperture, unity efficiency corresponds

to 2.5 x 10^3 amp/torr of N_2. Thus, we estimate an order of magnitude efficiency of 10^{-3}.

[9] A discussion providing the necessary formulae is given by K. R. Spangenberg, Vacuum Tubes (McGraw-Hill, New York, 1948), p. 775.

[10] Carter, G., and J. S. Colligan, Ion Bombardment of Solids (American Elsevier, New York, 1968), p. 97.

[11] Except for the stimulated appearance of several peaks (masses 26 and 28), the results of this experiment are essentially the same as those of Ref. 6 (in the low pressure regime), indicating that the low energy interactions are of primary importance.

[12] Carlston, C. E., and G. D. Magnuson, Rev. Sci. Instr. 33, p. 905 (1962).

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