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An atomic oxygen target for absolute differential cross section measurements

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Rice University, 1992
RICE UNIVERSITY

AN ATOMIC OXYGEN TARGET FOR ABSOLUTE DIFFERENTIAL CROSS SECTION MEASUREMENTS

by

Dean R. Sieglaff

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF ARTS

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Abstract

An Atomic Oxygen Target for Absolute Differential Cross Section Measurements

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Dean R. Sieglaff

An atomic oxygen target suitable for absolute differential cross sections has been developed. Molecular oxygen gas is partially dissociated in a microwave discharge and flowed through a collision cell to serve as a fast beam target. Determination of the atomic oxygen density is carried out using an electron impact time-of-flight mass spectrometer, which uses the exit aperture of the cell as a sample leak.
Acknowledgements

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Thank you Mom and Dad for maintaining a high level of enthusiasm through what must seem to be an endless career in higher education. Thank you Kristin for your patience and support through the creation of this thesis.

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Chapter I
Introduction.

A. Why an Atomic Oxygen Target?

Motivation for the generation of a laboratory source of ground state atomic oxygen suitable for use as a fast beam target has been extensively discussed by Hakes.\textsuperscript{1,2} Briefly, it is known that O is the most abundant constituent of the earth's atmosphere between roughly 200 and 600 km of altitude. Therefore O is an important atmospheric target for energetic H, He, and O ions and neutrals which precipitate from greater altitudes. Energy deposition and particle loss from the atmosphere depend upon not only total cross section magnitudes, but also the \textit{angular distribution} of scattered projectiles in various collisional reactions. Few measurements have been made of total cross sections for relevant projectiles in collision with O, and none of differential cross sections (DCS's) with respect to laboratory scattering angle, forcing atmospheric modelers to assume DCS forms and magnitudes. With the development of a suitable atomic oxygen target, these crucial DCS measurements can be made.

Atomic oxygen is formed in the earth's upper atmosphere via photolysis of O\textsubscript{2}:\textsuperscript{3}

\begin{align*}
O\textsubscript{2} + h\nu\textsubscript{H} & \rightarrow O(^3P) + O(^3P), \quad \text{(I.A.1)} \\
O\textsubscript{2} + h\nu\textsubscript{S-R} & \rightarrow O(^3P) + O(^1D). \quad \text{(I.A.2)}
\end{align*}

The subscript "H" refers to absorption in the \textit{Hertzberg continuum}, 210 < \lambda < 240 nm. It involves the A \ ^3\Sigma^+_u \rightarrow \ X \ ^3\Sigma^-_g (see section I.C) electronic transition. This transition is dipole-forbidden (rule 10, Appendix A.6, Hasted\textsuperscript{4}), therefore the absorption cross section is small (\sim 10^{-24} \text{ cm}^2). The subscript "S-R" refers to absorption in the \textit{Schumann-Runge continuum}, 100 < \lambda < 200 nm. It involves the B \ ^3\Sigma^-_u \rightarrow \ X \ ^3\Sigma^-_g transition, with a large
absorption cross section ($\sim 10^{-17}$ cm$^2$). The former process plays its largest role in the stratosphere, while the latter is important at around 100 km of altitude.

Ozone ($O_3$) is formed in the presence of $O$ via

$$O + O_2 + M \rightarrow O_3 + M,$$  \hspace{1cm} (I.A.3)

where $M$ is an unspecified third body, necessary from the standpoint of energy and momentum conservation (see sections II.A.1 and II.C, part 5). Ozone may be destroyed in reaction with $O$,

$$O + O_3 \rightarrow O_2 + O_2,$$  \hspace{1cm} (I.A.4)

or reconverted to $O$ in the photochemical reaction

$$O_3 + h\nu \rightarrow O + O_2,$$  \hspace{1cm} (I.A.5)

by absorption in the 200-300 nm range (cross section $\sim 10^{-17}$ cm$^2$). (The ozone layer in the stratosphere efficiently absorbs this harmful UV radiation, making life on earth possible.) Equations I.A.1-5 are the main components of oxygen chemistry in the upper atmosphere.$^3$

---


B. About Atomic Oxygen.

Oxygen has atomic number 8. Its electron configuration is 1s²2s²2p⁴. The four 2p valence electrons govern the chemical and spectroscopic properties of the atom. It is possible to determine the so-called terms (defined below) of ground state O by considering all the ways these valence electrons can configure themselves in the 2p subshell.

The multi-electron atom may be characterized by the quantum numbers L, M_L, S, and M_S, which enumerate the angular momentum and its projection along a space-fixed axis for both orbital and spin types, respectively. These are related to the quantum numbers l, m_l, s, m_s of the individual electronic spin orbitals through straightforward addition of angular momentum. For instance, for the case of two electrons:

\[
\begin{align*}
L &= l_1 + l_2 \\
S &= s_1 + s_2 \\
M_L &= m_{l1} + m_{l2} = L, L - 1, ..., -L \\
M_S &= m_{s1} + m_{s2} = S, S - 1, ..., -S
\end{align*}
\]

The spectroscopic term for the electronic configuration of an atom is a code which includes L, S, and sometimes also J, the total angular momentum quantum number (J = L + S). It is written \(2S + 1L_J\), with \(2S + 1\) referred to as the multiplicity. Also, L = 0, 1, 2, 3, 4, ... is represented by the letters S, P, D, F, G, ... in analogy to the single electron case.

In order to discuss the possible terms for O, it is useful to mention two things. First, the electron configuration for any completely occupied shell (filled in accordance with the Pauli exclusion principle) must belong to the \(1S\) term, since \(M_L\) and \(M_S\) must be 0. Second, in any shell which can contain \(n\) electrons, the possible terms of the configuration of \(x\) electrons is the same as that for \(n - x\). This follows from the first point in that considering the resultant \(L_1\) and \(S_1\) for the \(x\) electrons, its complimentary electrons apparently have resultants \(L_2\) and \(S_2\) such that \(L_1 + L_2 = 0\) and \(S_1 + S_2 = 0\) for every
possible configuration of the electrons in the shell. Therefore the \((n - x)\)-electron configuration shares the same \(L\) and \(S\) quantum numbers as the \(x\)-electron configuration in the shell.

Therefore it is sufficient to determine the terms of \(p^2\) in order to determine those for \(O\). In the case of two \(l = 1\) electrons, the possible values of \(L, S\) are \(L = 0, 1, 2\) and \(S = 0, 1\) (as seen from the above equations), which immediately exclude all but \(^1S, ^3S, ^1P, ^3P, ^1D,\) and \(^3D\) from consideration as possible terms. To decide among these, we note that the degeneracy of a spin orbital is \(2(2l + 1)\), which means that in the case of two \(p\) electrons, there are 36 possible ways to configure them, with only 15 allowed by Pauli exclusion (see chapter I, table 12 of Hertzberg\(^1\)). At the same time, the degeneracy of a term is \((2S + 1)(2L + 1)\), and if the degeneracies of the above terms are summed, the result is 36 as well (as it must be by the Ehrenfest adiabatic theorem\(^1\)). In this simple case it is seen that choosing the terms whose degeneracies sum exactly to 15, namely \(^3P, ^1D,\) and \(^1S,\) is tantamount to determining the valid terms of the ground state of \(O\). Rejection of \(^3D\) is clear from Pauli exclusion, since \(m_l = 1, m_\sigma = 1/2\) is required for both electrons. The same is true for \(^3S,\) in which \(m_l = 0, m_\sigma = 1/2\) is required for both. That \(^1P\) is excluded cannot be demonstrated in this way. However, the fact that of the 15 allowed states, at least one of them can be shown to belong to \(^3P, ^1D,\) or \(^1S\) is sufficient grounds to reject it as a valid term.

Figure I.B.1 shows the ground configuration of atomic oxygen.\(^2\) The lowest energy electron configurations belong to \(^3P,\) after Hund's rule.\(^1\) Decay of \(O(^1D)\) and \(O(^1S)\) to the \(O(^3P)\) state is forbidden by the approximate selection rule \(\Delta S = 0.\(^3\)

---

Figure I.B.1. Ground configuration, $1s^22s^22p^4$, of O, showing term and level splitting. The diagram gives transition probabilities $A$ ($s^1$) for the forbidden transitions, the dominant multipole term ($m$ or $q$) in the transitions, the wavelengths, and mean lifetime $\tau$ of the levels. The level splitting of the $3P$ term is exaggerated. The transition probability for $3P - 1D$ is the total; the ratio for $\lambda 6300/\lambda 6364$ is $3/1$.\(^2\)
C. About Molecular Oxygen.

Recombination effects (see section II.A.1) insure the existence of \( \text{O}_2 \) along with \( \text{O} \) in the atomic oxygen target apparatus to be described. This is not a problem, since its contribution to the DCS signal can be subtracted out using previously measured cross sections with a pure \( \text{O}_2 \) target as described by Hakes.\(^1\) In fact, target gas analysis using the electron-impact time-of-flight mass spectrometer depends upon the \( \text{O}_2^+ \) signal from a pure \( \text{O}_2 \) versus mixed \( \text{O}, \text{O}_2 \) target for absolute determination of \( \text{O} \) density in the target (see section III.B.3). These statements presuppose that the \( \text{O}_2 \) in the mixed target is entirely in its ground state electronic configuration, which is not by any means guaranteed (see section II.C). Intelligent consideration of these topics requires a certain degree of familiarity with the molecular oxygen system.

Figure I.C.1 shows potential energy curves for various states of \( \text{O}_2 \).\(^2\) These are obtained by fitting rotational, vibrational, and electronic spectroscopic data to a multi-parameter functional form.\(^3\) Molecular electronic states are also denoted by terms, similar to those for atomic states. The term symbol is written \( 2S + 1 \Lambda \alpha \Sigma \). The multiplicity \( 2S + 1 \) is the same as for atoms, and is not dependant upon the orientation of the molecule's figure axis. Orbital angular momentum about the figure axis is denoted by the quantum number \( \text{M}_L \), taking on values \( 0, \pm 1, \pm 2, \ldots \). The symbol \( \Lambda \) is defined as \( |\text{M}_L| \), with its values \( 0, 1, 2, \ldots \) encoded \( \Sigma, \Pi, \Lambda \), \ldots in analogy to the atomic case. It is seen that all but \( \Sigma \) states bear 2-fold degeneracy (a degeneracy which is removed in molecular rotation). Spin angular momentum projected onto the figure axis is denoted by \( \Sigma \) (not to be confused with the symbol for \( \Lambda = 0 \)), taking on values \( 0, \pm 1/2, \pm 1, \pm 3/2, \ldots \) similar to \( \text{M}_S \) for atoms. The value \( \Lambda + \Sigma \) is the total axial angular momentum, useful for specifying the energy levels of a spin-orbit multiplet (similar to \( J \) for atoms). These are consequently omitted in the potential energy diagram.
Figure I.C.1. Potential energy diagram for O₂.²
In addition, eigenvalues of two symmetry operations (operating on the electronic wave function $\psi_e$ of the molecular system) are included in the term designation where appropriate. One symmetry operator, known as $O(\sigma_v)$, performs a reflection of $\psi_e$ in a "vertical" plane containing the figure axis (that is to say, with the axis along $z$, $\sigma_v$ in the $xz$ plane results in the transformation $\psi_e(x, y, z) \leftrightarrow \psi_e(x, -y, z)$). For $\Sigma$ states, the eigenvalue $+1$ ($-1$) is denoted by superscript $+ (-)$. For others ($\Pi, \Delta, \ldots$), $\psi_e$ is not necessarily an eigenfunction of this operator, and therefore this designation does not pertain to them. The other symmetry operator, $O(\sigma_h)$, performs a reflection of $\psi_e$ in a plane perpendicular to the figure axis, and containing a center of symmetry (consequently pertaining only to homonuclear diatomics). An eigenvalue of $+1$ ($-1$) is denoted by a subscript $g$ ($u$), from gerade (ungerade) meaning "even" ("odd").

The ground state of most diatomics is a closed shell, entirely symmetric $^1\Sigma_g^+$ (for homonuclear diatomics) configuration, with $O_2$ being an exception. The ground state is traditionally labelled $X$ ($X^3\Sigma_g^-$ in this case), and all higher states of the same multiplicity go by $A, B, C, \ldots$ in order of either energy or discovery. Other excited states are labelled $a, b, c, \ldots$ Selection rules governing transitions between these states in the dipole approximation are listed in Appendix A.6 of Hasted.

Additional references include Weissbluth, and Bransden and Joachain.

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Chapter II
Flowing Gas Target.

A. Apparatus.

1. Requirements.

Target requirements for absolute differential cross section measurement are discussed by Hakes.\(^1\) These include a well collimated fast beam, achieved by using collimating apertures, and a localized target of known density, length, and composition, achieved through the design of a target cell. Target density determination and target composition are the primary concerns in this thesis.

In the case of an atomic oxygen target, it is necessary to continually refresh the target presented to the fast beam, due to atomic oxygen's tremendous propensity for recombination to the molecular state. This is achieved by flowing partially dissociated oxygen gas through the target cell. In a flowing system, distance along the flow conduit is directly related to the time elapsed for gas particles (on average) by the mean drift velocity of the gas. The goal is to have the total time elapsed, or residence time, for particles in transit from source to target cell be small relative to time scales over which recombination reactions occur.

There are two recombination mechanisms: surface, where O atoms that have temporarily alighted on a surface are approached by and recombine with other O atoms, and gas phase, in which two free O atoms meet and recombine. The 5 eV kinetic energy gain that would have to occur as the result of forming an O-O bond (by energy conservation) cannot be acquired solely by the resulting molecule (by momentum conservation). Furthermore, the energy cannot be radiated away by the homonuclear molecule because it possesses no electric dipole moment. Therefore a third body is required to carry off energy and momentum. In the former reaction the surface itself provides this, but in the latter
another atom or molecule must be in simultaneous collision with two O atoms. For this reason gas phase recombination is also referred to as three body recombination.

2. Flow System.

The flow system is shown schematically in Figure II.A.1. Oxygen gas (extra dry grade, Linde Specialty Gases) is admitted via a micro-metering valve (Whitey type SS-22RS4) to the discharge region. All lines are 1/4 inch stainless or stainless bellows, all seals are Teflon ferrule Swagelok or Ultra-Torr (UT) o-ring sealed unions. The discharge region consists of a 20 cm long section of 12 mm quartz, 1/4 inch glass-to-metal sealed at the inlet side, and straddled by a microwave resonant cavity. This is attached to 12 cm of 25 mm quartz tubing, which is coated with crystalline boric acid to inhibit recombination at the wall. The remaining 35 cm of flow conduit to the target cell is made up of Teflon tubing, approximately 7/8 inch I. D. Teflon, a fluorocarbon plastic, inhibits surface recombination, it is believed, because it is very inert. Atomic oxygen does not "stick" to or react with the surface, and therefore is unlikely to undergo surface recombination. The first section of tubing is sleeved in a thin-walled stainless tube, since Teflon is not a reliable sealing surface. The steel tube is sealed to the glass tube by a bored through 1 inch UT union. A Teflon aperture constricts the entrance of the Teflon tube to maintain the discharge region at a relatively high pressure (around 0.5 torr).

The steel sleeve is fed through an UT male connector, which is sealed to the vacuum wall of the collision chamber. Inside the chamber, the flow system is primarily constructed of bulk Teflon, including the target cell, with its pieces connected by o-ring sealed Teflon unions and elbows. Because of the localized target requirement, a pedestal is made to protrude into the cell body, so that the small 30 μm fast beam collimating aperture mounted upon it is brought to within 1 mm of the 300 μm exit aperture. The pedestal is wrapped in Teflon tape, and the exit aperture plate is covered with a Teflon
Figure II.A.1. Schematic of the flowing gas target apparatus.
guard. There remain small bare metal surfaces near the fast beam axis, but not enough
collisions occur with them to warrant concern.

Teflon conduit is replaced by approximately 1 1/2 inch I. D. copper and stainless
steel tubing once outside the vacuum wall. The flowing gas is pumped with a Welch
Model 1397 two-stage rotary vane mechanical pump (500 l min\(^{-1}\) free air displacement),
through a molecular sieve trap (Leybold Model FA). The trap utilizes Zeolite adsorbent to
trap pump oil and water which would otherwise backstream into the flow system. Periodic
purging of the trap is accomplished by baking at 300 C. A valve placed upstream from the
trap is closed and kept at high temperature (around 150 C) during bake-out to prevent
backstreaming oil and water from condensing in the flow system. The true speed of the
pump at operating pressure is approximately 5 l s\(^{-1}\). Flow system conductance is estimated
to be around 1 l s\(^{-1}\).

Pressure is monitored two places in the flow system. A thermocouple gauge gives
indication of the discharge region pressure. An MKS Baratron capacitance manometer is
used to measure pressure in the target cell for determining target density in absolute cross
section measurements. The maximum tolerable target density is dictated by the thin target
requirement for the fast beam, namely, projectiles must rarely undergo multiple scattering.
When operating the flow system, this requirement is met by adjusting the gas flow rate to
maintain no more than around 20 mtorr in the target cell. The Baratron meter does not give
an accurate total pressure when O is present, since the O recombines in the metal surfaces
of the steel inlet line to the transducer head. It can be shown from mass flow conservation
that the Baratron will underestimate the total pressure in the target cell. For this reason,
Baratron readings taken while O is present are not useful in determining the O density (see
section III.B.3 for O density determination details).
3. **RF Discharge Equipment.**

Flowing O$_2$ gas is dissociated in a microwave-frequency discharge. Large electric field amplitudes maintained in a resonant cavity give free electrons sufficient energy to dissociatively ionize O$_2$. Electrons released from ionizing reactions sustain an oxygen plasma in the cavity region. The plasma is usually ignited by arcing to the quartz vessel with a Tesla coil, although ignition from auto-ionization of gas molecules has been observed. Presently, a modified McCarroll type cavity (Optos Instruments), fed by approximately 2 m of RG-214 co-axial waveguide is used. The power source is a Raytheon PGM-30A microwave power generator, capable of delivering $>300$ W. A power meter placed inline along the waveguide reads transmitted/reflected power. The cavity is tuned for minimum reflected power by adjusting its resonant frequency (which can change with temperature) and by impedance matching, which is done by adjusting the length that the waveguide's central electrode extends into the cavity. At sufficient discharge region pressures ($>0.1$ torr) reflected power can be made negligibly small.

Grounded conductive apertures straddling the flowtube adjacent to the cavity serve to stop discharge fields from extending too far from the cavity. This technique was originally employed to protect the flowtube coating from damage due to excessive exposure to the oxygen plasma. The position of these barriers seems to have crucial effect upon the O yield, possibly since they greatly effect the cavity's resonance. Therefore these barriers are now considered to be tuning elements of the discharge system.

---

B. Flow Characteristics.

Consider a tube of radius \( r \), cross sectional area \( A \). In a time \( \Delta t \), the number of particles which pass area \( A \) is \( F\Delta t \), where \( F \) is the particle flow rate in the tube. Evidently it is also \( nAv\Delta t \), where \( n \) is the local particle number density and \( v \) the average drift speed along the tube. Equating these gives

\[
v = \frac{F}{nA},
\]

for the drift speed. If the tube has length \( L \), the total residence time is simply

\[
T = \frac{L}{v}.
\]

The number of wall and gas phase collisions made per particle, on average, can be determined. From statistical mechanics and particle kinetics, the flux of gas particles that strike a unit area is \( \phi = n\bar{c}/4 \), where \( \bar{c} \) is particle mean speed (450 m s\(^{-1} \) for room temperature \( O_2 \)). The total number of wall collisions per particle may then be written

\[
N_{\text{wall}} = \frac{\phi A_{\text{wall}}}{nA} T = \frac{\bar{c}}{2r} T,
\]

where \( A_{\text{wall}} \) is the total wall surface area. Of course, this is a per particle average. Principles of particle diffusion will take over in cases of sufficiently high density. The root-mean-square displacement of a gas particle along one direction is

\[
\text{RMS } z = \sqrt{z^2} = \sqrt{2Dt}, \quad D = \frac{1}{3} \bar{c} \lambda
\]
where \( D \) is the diffusivity, \( \lambda \) is the particle mean free path, and \( t \) is the time elapsed. From this the transit time \( T_r = r^2/2D \) for a particle diffusing the length of one flow tube radius can be estimated. Then a lower limit on the number of wall collisions may be taken to be roughly \( N_{\text{wall, min}} = T/2T_r \) if we imagine the worst-case scenario of a particle traveling along a tube diameter during its entire residence. Finally, while in the tube, a particle will cover a total distance of \( L_{\text{tot}} = \bar{c} T \) and undergo \( N_{\text{gas}} = L_{\text{tot}} / \lambda \) gas phase collisions, where \( \lambda \) is the particle mean free path.

In the flow system there are bound to be density gradients along the tube according to the transport rule \( Q = \Delta p \ C \), where \( C \) is the conductance of the tube (l sec\(^{-1}\)), \( \Delta p \) is the pressure drop from one end to the other, and \( Q \) is the so-called throughput. \( Q \) is numerically equal to the volumetric flow rate, but taken at the pressure in the tube. Actually it bears units of power (torr l sec\(^{-1}\), equal to 0.13 W), and is equal to the work expended per unit time transporting the gas. Through the ideal gas law, it is related to the flow rate by \( Q = F k T \) (\( T \) is temperature, \( k \) the Boltzmann constant). Therefore estimates for \( \Delta p \) can be made given information on tube conductance.

The Knudsen number, defined as the ratio of the mean free path to vessel dimensions, gives rough indication of the flow regime: a value of 1 or greater means molecular flow, 0.01 or less means fluid flow, and in between is referred to as transitional, or slip, flow. The Teflon tube portion of the flow system happens to operate in the slip flow regime, which is the least well understood. The main problem it could present in this apparatus is in providing the opportunity for significant backstreaming of \( O_2 \) particles from metal walled portions of the flow system to the target cell area.

Table II.B.1 shows general constants and the results of the above analysis applied to the coated quartz region of the flow tube, and the post-aperture Teflon portion of the flow conduit to the target cell. The value for \( F \) is based upon direct measurement of \( dp/dt \) using a Baratron while the flow was diverted to fill a known volume. Results are obtained from consideration of room temperature \( O_2 \) gas, which is to say that they are most
applicable to the discharge-off flow. However, they may be considered loosely applicable to O flow as well, in the Teflon region. It is not known how reliable they are in the discharge region with the presence of the oxygen plasma, but presumably they are in so far as the gas is reasonably cool throughout most of that region.

<table>
<thead>
<tr>
<th></th>
<th>Coated quartz region</th>
<th>Teflon tubing</th>
</tr>
</thead>
<tbody>
<tr>
<td>F (s⁻¹)</td>
<td>9.6 x 10¹⁷</td>
<td>same</td>
</tr>
<tr>
<td>Q (torr l s⁻¹)</td>
<td>0.031</td>
<td>same</td>
</tr>
<tr>
<td>C (l s⁻¹)</td>
<td>-</td>
<td>5²</td>
</tr>
<tr>
<td>p (mtorr)</td>
<td>500</td>
<td>= 20</td>
</tr>
<tr>
<td>n (cm⁻³)</td>
<td>1.6 x 10¹⁶</td>
<td>6.4 x 10¹⁴</td>
</tr>
<tr>
<td>τ (cm)</td>
<td>1.1</td>
<td>same</td>
</tr>
<tr>
<td>A (cm²)</td>
<td>3.8</td>
<td>same</td>
</tr>
<tr>
<td>L (cm)</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>λ (cm)</td>
<td>0.01³</td>
<td>0.25</td>
</tr>
<tr>
<td>v (cm s⁻¹)</td>
<td>16</td>
<td>390</td>
</tr>
<tr>
<td>T (s)</td>
<td>0.75</td>
<td>0.090</td>
</tr>
<tr>
<td>Nₚₗₜ (1 s⁻¹)</td>
<td>16 000</td>
<td>1 900</td>
</tr>
<tr>
<td>Tₚ (ms)</td>
<td>4.0</td>
<td>0.16</td>
</tr>
<tr>
<td>Nₚₗₜ, min (ms)</td>
<td>94</td>
<td>280</td>
</tr>
<tr>
<td>Lₜₜ (cm)</td>
<td>3.4 x 10⁴</td>
<td>4.1 x 10³</td>
</tr>
<tr>
<td>Nₗₜ (cm³)</td>
<td>3.4 x 10⁶</td>
<td>1.6 x 10⁴</td>
</tr>
<tr>
<td>Δp (mtorr)</td>
<td>-</td>
<td>= 6</td>
</tr>
<tr>
<td>Knudsen number</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>RMS z (cm)</td>
<td>15</td>
<td>26</td>
</tr>
</tbody>
</table>

Table II.B.1. Flow characteristics for flowing gas target system.

RMS displacement values shown in the table are calculated for the average residence time T from equation II.B.3. Comparison with the tube length shows that backstreaming occurs in the discharge region, but won't to a significant degree in the fast flowing portion of the system. Clearly, since the gas in the discharge region can sample
the entire region, there is an equilibrium of O and O₂ particles maintained in the region. This mixture is then leaked into the subsequent portion of the flow system.

C. Oxygen Discharge Products.

In addition to the desired ground state O, it is certain that excited neutral atoms and molecules are formed in the oxygen plasma, all of which are unwanted in the target. It is possible to draw conclusions as to the danger presented by the existence of excited species by appealing to chemical kinetics. Many investigators have studied oxygen discharges, and reaction rates have been measured for quenching of the known long-lived excited states of O and O₂.

In a reaction where a species is destroyed or created, one can write an expression for the rate change of the density of the species as shown:

<table>
<thead>
<tr>
<th>BIMOLECULAR</th>
<th>TERMOLECULAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B ---&gt; C + D + ...</td>
<td>A + B + C ---&gt; D + E + ...</td>
</tr>
<tr>
<td>( \frac{dn_A}{dt} = k n_A n_B )</td>
<td>( \frac{dn_A}{dt} = k n_A n_B n_C )</td>
</tr>
</tbody>
</table>
| \( \tau_A = \frac{1}{k n_B} \) | \( \tau_A = \frac{1}{k n_B n_C} \).

Here \( n_X \) represents the particle number density (cm\(^{-3}\)) of species \( X \), and \( k \) is the reaction rate, or reaction coefficient. Furthermore, as is indicated, the mean life of species \( A \), \( \tau_A \), can be written by noting that it is the reciprocal of the rate of loss of \( A \) (per particle), which is simply \( (dn_A/dt)/n_A \). The reaction rate has units of cm\(^3\) s\(^{-1}\), where \( n = 1 \) for bimolecular reactions and \( n = 2 \) for termolecular reactions.

In some cases, loss of species from wall collision has been studied, and is reported as a surface deexcitation, or surface recombination \( \gamma \), as the case may be. In this case, the probability of survival can be reported, as \( P(t) = \exp(-\gamma Rt) \), where \( R \) is the per particle wall
collision rate, and t is the time elapsed. Below, \( P(T) = \exp(-\gamma N_{\text{wall}}) \) is reported from table II.B.1 values.

Listed below are all known relevant contaminants created in an oxygen discharge, meaning species other than \( O(3\text{P}) \) and \( O_2(X 3\Sigma_g^+) \). Where quenching rates are available, mean lifetimes are calculated, and when formation rates are available, final densities (denoted \( n(T) \)) based upon residence times shown in table II.B.1 are calculated. These are calculated assuming a negligible change in the abundance of reactants, which, if inaccurate, will provide an upper limit. Rate constants are presented per molecule and adjusted to 300 K where necessary. Densities for \( O \) and \( O_2 \) are 0.1n and 0.9n respectively, n from table II.B.1. Subscript "Q" refers to the coated quartz region, and "T" refers to the Teflon flow conduit.

1) \( O(^1\text{D}) \). Its radiative lifetime is 147 s.¹

<table>
<thead>
<tr>
<th>quenching reaction</th>
<th>( k ) (cm³ s⁻¹)</th>
<th>( t_Q ) (s)</th>
<th>( t_T ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O(^1\text{D}) + O_2 \rightarrow O + O_2 )</td>
<td>( 3.7 \times 10^{-11} )²</td>
<td>( 1.9 \times 10^{-6} )</td>
<td>( 4.7 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Clearly this species does not survive to the target cell.

2) \( O(^1\text{S}) \). Its radiative lifetime is 0.74 s.¹

<table>
<thead>
<tr>
<th>quenching reactions</th>
<th>( k ) (cm³ s⁻¹)</th>
<th>( t_Q ) (s)</th>
<th>( t_T ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O(^1\text{S}) + O_2 \rightarrow O + O )</td>
<td>( 2.6 \times 10^{-13} )³</td>
<td>( 2.7 \times 10^{-4} )</td>
<td>( 6.6 \times 10^{-3} )</td>
</tr>
<tr>
<td>( O(^1\text{S}) + O \rightarrow O + O )</td>
<td>( 7.5 \times 10^{-12} )⁴</td>
<td>( 8.3 \times 10^{-5} )</td>
<td>( 2.1 \times 10^{-3} )</td>
</tr>
<tr>
<td>( O(^1\text{S}) + O_2(a) \rightarrow O + O_2(a) )</td>
<td>( 1.7 \times 10^{-10} )⁵</td>
<td>( 3.7 \times 10^{-5} )</td>
<td>( 9.2 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Here \( O_2(a) \) is the \( O_2(1\Delta_g) \) state (see I.C). Slanger and Black warn that quenching studies of \( O(^1\text{S}) \) done prior to their work are questionable, since the fast quenching due to \( O_2(a) \)
was unknown, and discharges are prone to produce it. However, our concern is only that it is quenched, regardless of how.

3) $\text{O}_2(a^1\Delta_g)$. Its radiative lifetime is 45 min.\textsuperscript{6}

<table>
<thead>
<tr>
<th>quenching reactions</th>
<th>$k$ (cm$^3$ s$^{-1}$)</th>
<th>$t_Q$ (s)</th>
<th>$t_T$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2(a) + O \rightarrow \text{O}_2 + O$</td>
<td>$1.3 \times 10^{-16}$, 7.8</td>
<td>5</td>
<td>120</td>
</tr>
<tr>
<td>$\text{O}_2(a) + O \rightarrow 2\text{O}_2$</td>
<td>$2.4 \times 10^{-18}$, 7.8</td>
<td>30</td>
<td>720</td>
</tr>
<tr>
<td>$\text{O}_2(a) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_3$</td>
<td>$4.5 \times 10^{-15}$, 8</td>
<td>1.4</td>
<td>35</td>
</tr>
<tr>
<td>$\text{O}_2(a) \rightarrow \text{O}_2$ (quartz wall)</td>
<td>$\gamma = 2 \times 10^{-5}$, 8</td>
<td>$P = 0.73$</td>
<td>$P = 0.96$</td>
</tr>
</tbody>
</table>

This species cannot be shown to efficiently decay. In the third reaction an $\text{O}_3$ density of 0.01n was used, but actually the amount of ozone that may be coming from the discharge is strictly unknown (see below). Nevertheless, it is the fastest reaction and would seem to be the only possibility for removal of $\text{O}_2(a)$.

There is information on formation of $\text{O}_2(a)$ from several sources:

a) Slanger and Black\textsuperscript{5,9} report that 20-30% of $\text{O}$ recombinations at surfaces (Pyrex) result in the formation of $\text{O}_2(a)$. They report other authors report yields of 5-20% of $\text{O}_2$.

b) Samson and Pareek\textsuperscript{10} report seeing ~1% of $\text{O}_2$, and note other authors report 3-10%. Their system is most like ours (0.2 torr, boric acid coated Pyrex).

c) Arnold and Ogryzlo\textsuperscript{11} report a yield of 6.5% with 1-5 torr $\text{O}_2$ discharge, independent of pressure. They measure a collisional deexcitation lifetime in their glass flow system of around 7 s, also independent of pressure.

d) Herron and Schiff\textsuperscript{12} report 10%, and believe it to come from the discharge, not from wall recombination of $\text{O}$. They also say other authors report 10-20%.

It is evident that $\text{O}_2(a)$ may exist in our flow system. In the past, a negative result in its effect upon differential cross section measurements involving the charge transfer of $\text{He}^+$ in collision with $\text{O}_2$ has been reported\textsuperscript{13}, however, that is a rather inconclusive experiment.
The definitive approach to assessing the level of O$_2$(a) contamination is to go to threshold ionization energies in the electron-impact mass spectrometer (see chapter III), but that would be difficult if not impossible in the present machine.

4) O$_2$(b $^1\Sigma_g^+$). Its radiative lifetime is 7 s.$^{11}$

<table>
<thead>
<tr>
<th>formation reaction</th>
<th>$k$ (cm$^3$ s$^{-1}$)</th>
<th>$\eta_{O}$(T) (cm$^3$)</th>
<th>$\eta_{T}$(T) (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$(a) + O$_2$(a) $\rightarrow$ O$_2$(b) + O$_2$</td>
<td>$2.2 \times 10^{-18}$ $^{11}$</td>
<td>$4.2 \times 10^{12}$</td>
<td>$8.1 \times 10^{8}$</td>
</tr>
<tr>
<td>quenching reaction</td>
<td>$\gamma$</td>
<td>$P_{O}$</td>
<td>$P_{T}$</td>
</tr>
<tr>
<td>O$_2$(b) $\rightarrow$ O$_2$ (quartz wall)</td>
<td>$2.2 \times 10^{-3}$ $^{11}$</td>
<td>.0</td>
<td>0</td>
</tr>
</tbody>
</table>

An O$_2$(a) density of 0.1n is assumed in the formation reaction. Wall deexcitation seems sufficiently efficient. Arnold and Ogryzlo$^{11}$ have done the most work on this, but they don't seem to indicate the initial density of O$_2$(b) from the discharge. Slanger and Black$^5$ consider the existence of O$_2$(b) and vibrationally excited O$_2$, and dismiss them as being rapidly quenched. They measured a system lifetime for O$_2$(b) at 20 ms, and their understanding is that the amount of O$_2$(b) from a discharge is always much less than O$_2$(a).

5) O$_3$ (ozone). Let it first be remarked that Siegel$^{14}$ has reported an O$_3$ + e$^-$ $\rightarrow$ O$_3^+$ + 2e$^-$ cross section for 40-100eV of around $1 \times 10^{-16}$ cm$^2$, comparable to that for Ar. Therefore, if there is appreciable O$_3$ in the flow, it should be detectable with the mass spectrometer (see chapter III). However, there are some rates available:
<table>
<thead>
<tr>
<th>formation reactions</th>
<th>k (cm$^6$ s$^{-1}$)</th>
<th>n$_0$(T) (cm$^{-3}$)</th>
<th>n$_T$(T) (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + O$_2$ + O$_2$ $\rightarrow$ O$_3$ + O$_2$</td>
<td>3.7 x 10$^{-34}$ 8</td>
<td>8.7 x 10$^{13}$</td>
<td>7.2 x 10$^8$</td>
</tr>
<tr>
<td>O + O$_2$ + O$_3$ $\rightarrow$ O$_3$ + O$_3$</td>
<td>4.5 x 10$^{-34}$ 8</td>
<td>smaller than above</td>
<td>smaller than above</td>
</tr>
<tr>
<td>destructive reaction</td>
<td>k (cm$^3$ s$^{-1}$)</td>
<td>$\tau_0$ (s)</td>
<td>$\tau_T$ (s)</td>
</tr>
<tr>
<td>O$_3$ + O $\rightarrow$ 2O$_2$</td>
<td>8.8 x 10$^{-15}$ 8</td>
<td>8.1 x 10$^{-3}$</td>
<td>1.8</td>
</tr>
</tbody>
</table>

It seems that ozone is not formed rapidly. Herron and Schiff\textsuperscript{12} report seeing no O$_3$ in their mass spectrometer with the discharge on. Furthermore, it is efficiently destroyed in reaction with O in the discharge region. This suggests that ozone, if formed in the discharge, will set an upper limit upon the O yield, since it acts to promote recombination.

6) O($^3$P). It is impossible to estimate the amount of O formed in the discharge, but there are rates available for 3-body and wall recombination.

<table>
<thead>
<tr>
<th>recombination reactions</th>
<th>k (cm$^6$ s$^{-1}$)</th>
<th>$t_0$ (s)</th>
<th>$t_T$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + O + O $\rightarrow$ O$_2$ + O</td>
<td>3.6 e -32 8</td>
<td>11</td>
<td>6.8 e 3</td>
</tr>
<tr>
<td>O + O + O$_2$ $\rightarrow$ O$_2$ + O$_2$</td>
<td>10 e -32 8</td>
<td>0.45</td>
<td>270</td>
</tr>
<tr>
<td>O $\rightarrow$ 1/2O$_2$ (quartz wall)</td>
<td>$\gamma = 5$ e -4 8</td>
<td>P = 0</td>
<td>P = 0.39</td>
</tr>
</tbody>
</table>

Three body recombination can become a threat in the discharge region. Also, severe, but not complete loss of O at a quartz wall is observed in our apparatus using an uncoated quartz tube, indicating that mean diffusion length scales are short enough to protect many particles from the wall.

2 G. A. Germany, G. J. Salmo, and R. J. Anderson, Production of O(1S) and O(3P) by Vacuum Ultraviolet Photodissociation of Molecular Oxygen, J. Appl. Phys. 54, 8 (1983).


4 W. Felder and R. A. Young, Quenching of O(1S) by O(3P), J. Chem. Phys. 56, 12, 6028 (1972).

5 T. G. Slanger and G. Black, Quenching of O(1S) by O₂(a 1Δg), Geophys. Res. Lett. 8, 5, 535 (1981).


D. Atomic Oxygen Yield and Target Contamination.

Recently, it has been realized that the most important factor pertaining to both maximizing O yield and minimizing contamination in the flowing gas target is the material which coats the quartz discharge region. It must inhibit surface recombination so that O can survive to reach the Teflon flow tube, yet be inert to assault by an oxygen discharge, so that it does not itself become a source of contamination.

A tremendous amount of time was spent testing various materials. Hakes\(^1\) found that a coating of syrupy phosphoric gave high yields, but more recently this coating has been shown to degrade too quickly and evolve too much water to be useful. Teflon itself was tried as a discharge region material, but it decomposes in an oxygen discharge. Decomposition products include a great deal of CO and CO\(_2\), some fluorine, and CF\(_X\). All metals in lengths needed to protect the Teflon material were found to remove O too efficiently, however, among them aluminum was the best (perhaps due to its oxide coating).

A series of trials involving passivation of ceramics were carried out, motivated by some work of Koontz.\(^2\) First, a Pyrex tube was rinsed in HF acid, then in de-ionized water and installed. It performed no better than bare Pyrex. The tube was soaked in HF acid for a long period of time, rinsed and installed, with the same result. Also, the water rinse stage was omitted, with negative results. Next, \textit{in situ} passivation was attempted via fluorine-containing gas discharge in quartz. Both CF\(_4\) and HF gas were used, with no improvement in yield over bare glass. The quartz discharge tube was replaced with alumina, and all techniques repeated to no avail. An unpassivated sapphire tube was also tried, but it worked as well as bare glass.

A series of attempts were made using fluorine-containing compounds deposited on the discharge tube walls. A tube of iron foil was reacted with HF acid and used as a sleeve inside the quartz flow tube. AlF\(_3\) powder was stuck to the inside wall of the quartz tube.
with epoxy resin. These were dismal failures in that yields were small and in the case of the latter, contamination was incredibly high. Adhering aluminum fluoride and iron fluoride powders to the inside wall of quartz tubing was tried, but they wouldn't stick well enough. Two semi-cylindrical pieces of Vycor glass were coated with MgF$_2$ (an optical coating) and slid into the quartz tube as a sleeve. They became discolored and etched in the oxygen discharge, and it is presumed that they overheated due to bad thermal contact with the tube walls. Before being destroyed, however, they did provide a moderately respectable yield. A similar material, BaF$_2$, or fluorite, which is available as vacuum wall window material, was considered but never tried.

Most recently, boric acid has been discovered to give the best results. It, like phosphoric acid, is a known passivation material.$^3$ While it doesn't offer as high of an O yield as phosphoric acid, it is stable over many hours, as demonstrated in figure II.D.1. Furthermore, it can be deposited dry, so that it sources less water, and its properties don't change as a result of losing water. A coating is made by either dipping the quartz tube into a boiling, saturated solution of boric acid, or pouring the solution into the tube and pouring it out again. Then the material is dried and further adhered to the tube by applying a propane torch flame to the outside of the tube. Most of the water comes out of the coating in this stage, and the coating recrystalizes to provide nearly 100% coverage of the inside wall. Finally, the tube, along with the rest of the flow system and vacuum chamber, is baked at 100-150 C for approximately 24 hr.

The topic of target contamination is intimately associated with atomic oxygen yield. If the yield is large, the threat is diminished, but if the yield is low, the problem is seriously aggravated. In the present system, contamination can comprise roughly 1% of the total flow rate, which translates into roughly 10% relative to O alone (based upon present yield capabilities). This is very dangerous, since the mentioned contaminants possess collisional cross sections which are 2 to 4 times greater than O for charge transfer with keV energy H$^+$, for example, as seen in table II.D.1.
Figure II.D.1. Atomic oxygen yield as a function of time, using a boric acid-coated quartz discharge tube. (Data from files taken 28, 29 Sep 1991.)
<table>
<thead>
<tr>
<th>X</th>
<th>( \text{H}^+ (1.5 \text{ keV}) + X ) charge transfer cross section (10^{-16} \text{ cm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>6.4</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>10.5</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>25.5</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>20.5</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>15.5</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table II.D.1. Cross section values for keV \( \text{H}^+ \) charge transfer.

Contamination comes from three sources. Vacuum seals leak \( \text{N}_2 \), \( \text{O}_2 \), and \( \text{H}_2\text{O} \) into the system. Seals presently used are generally thought to be good for even high vacuum, but it must be stressed that the amount of contamination required to comprise 1% of the O signal in the present flow system is a fairly small amount of gas (\( 1 \times 10^{15} \text{ s}^{-1} \) flux, or \( 3 \times 10^{-5} \text{ torr l s}^{-1} \)). Any flaw in one of more than a dozen seals along the flow system would contaminate the system. Therefore, it is desirable to minimize the number of seals and eliminate unreliable ones, such as those on glass or Teflon.

Walls outgas \( \text{N}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). This is exacerbated by the presence of a microwave discharge, which heats the quartz glass to several hundred C. Heated glass is known to evolve these gases, and in the case of the present apparatus it has been observed. If the discharge is operated for a long period, the quartz tube will degas most of these contaminants in a few hours. However, since the heating is non-uniform, there remains a trickle of gas from fringe areas which may still be significant. The only way to degas glass is to keep it uniformly at high temperature (400-600 C for quartz) in an inert gas environment or under vacuum for at least 30 minutes, but we are ill equipped to perform this operation in our lab. As far as other wall materials in the flow system are concerned, all tubing external to the vacuum chamber is heated with electrical tracing, and Teflon pieces inside may be heated slightly using an incandescent bulb to provide IR
illumination. Vacuum chamber walls are also heated with electrical tracing to drive down the base pressure of these contaminants in the chamber. Otherwise it is impossible to accurately probe for contamination in the flow system with the mass spectrometer (see section III.C.3).

Boric acid, fortunately, does not seem to decompose in the presence of the oxygen discharge, as long as temperatures are less than its boiling point. This is evidenced by a lack of BOX fragments in mass spectra of target cell gas. As mentioned above, Teflon does. By putting boric acid between the discharge and the Teflon in the flow tube, the process is greatly diminished. However, these products are still observed to some extent any time the O yield is favorable. That is to say, there seems to be a relationship between the amount of O and the amount of Teflon-originated contamination. It suggests that perhaps the plastic is attacked by ions or metastables, whose chances of survival while in transit to the Teflon would be proportional to that for O itself. It is difficult to isolate this problem from the other sporadic sources of contamination, though.

Motivated by this problem, investigations were carried out to find the best operating pressure in the discharge region. By increasing this pressure, it is more difficult for offending agents originating in the discharge to diffuse to the Teflon. However, too high of a pressure will incite 3-body recombination. It was found that 100-500 mtorr is preferable to running without an aperture constriction (which results in about 30 mtorr). Choosing the pressure is complicated by two things. First, in operating a "straight-through" flow system, the only way to change the pressure is to change the gas throughput. This changes the overall dilution of contaminant gases by the O2. Secondly, by changing the pressure, the load seen by the microwave power source changes. Consequently, the net discharge power may change.

The microwave power source and cavity are also of the utmost importance when discussing O yield and contamination. The power delivered to the gas must be sufficient to provide an acceptable degree of dissociation, but should be minimized to limit flow tube
wall heating, which contributes to contamination. The spatial distribution of the plasma is important as well. The cavity, in addition to supporting the plasma near its axis where the E field strengths are large, is observed to launch so-called surface waves,\textsuperscript{7} in which the plasma is maintained at rather large distances from the cavity in evanescent TM waves travelling along the surface of the quartz tube. It is desirable to control the extent of the plasma so that an inordinate amount of wall heating is prevented, but it also may be desirable to concentrate the power delivered to the gas as much as possible to create the largest net dissociation. This comes from reasoning that the O density, considered as a function of distance along the flow tube, $n_O(x)$, along with recombinative loss mechanisms embodied in first order differential equations, constitute a boundary value problem. Therefore, the higher the value of $n_O(0)$ that can be mustered, the higher $n_O(12 \text{ cm})$ will be achieved, irrespective of the fact that the total number of oxygen molecules dissociated is the same in any case. There is some observational evidence to support this notion, but controlling the discharge using conductive barriers is tricky in practice, since they affect cavity tuning, and the limit of confinement is governed largely by the TM surface wave wavelength.

\begin{enumerate}
\end{enumerate}
Chapter III

A. Apparatus.

1. Theory.

An electron-impact time-of-flight mass spectrometer is used to determine the O density in the target cell, which is necessary if absolute cross sections for O are to be reported. This instrument, schematically represented in figure III.A.1, consists of the same position sensitive detector (PSD) used for scattering data acquisition (although used differently), along with a movable electrode system which can be positioned adjacent to the exit aperture of the target cell along the beam line to sample the target gas which effuses from this aperture. Some of the particles traveling from the target cell which pass through the mass spectrometer's entrance aperture are ionized by a crossed electron beam and accelerated to the detector. The number of ions counted at the detector can be shown to be directly proportional to the target density in the cell, without dependence upon particle mass. Therefore, by separating out by mass and tallying the relative number of counts of each target cell species, the relative abundances of the species may be attained. Furthermore, by having an independent determination of the absolute density of at least one species, the mass spectrometer measurements may also be made absolute. Proof of the above claim concerning the relationship between detector counts and target gas density will be immediately presented, but detailed discussion of mass spectrum analysis will appear in section III.B.3.

Imagine the overlap of the quasi-collimated effusive beam from the target cell with the crossed electron beam. Our goal is to determine the number of particles in this overlap, then calculate the number of ions formed and detected. It can be shown from particle
Fig. III.A.1. Schematic of the mass spectrometer. Electrodos bear cylindrical symmetry for the most part.
kinetics and statistical mechanics that the flux density at \((r, \theta)\) of particles effusively flowing from an aperture is

\[
F(r, \theta) = \frac{n \bar{c} A \cos \theta}{4 \pi r^2}, \tag{IIIA.1}
\]

where

- \(n\) = particle density within the target cell,
- \(\bar{c}\) = mean speed of particles,
- \(A\) = area of target cell exit aperture,
- \(r, \theta\) = spherical coordinates, with \(z\) along symmetry axis and origin at the target cell exit aperture.

\(F(r, \theta)\) is the flux (\# per unit time) of particles which pass through unit area normal to \(r\).

Therefore, referring to the illustration,
any tiny volume element of the overlap will have

$$dN = \frac{F(r, \theta)}{c} \frac{da}{dt} = F(r, \theta) r^2 d\Omega \frac{dr}{c} \quad \text{(III.A.2)}$$

number of particles in it, making the total number in the entire overlap equal to

$$N = \int_V dN = n \frac{A}{4\pi} \int_V \cos \theta \ dr \ d\Omega, \quad \text{(III.A.3)}$$

where $V$ refers to integration over the overlap volume. The integral depends only on geometry and may be regarded as a constant. Also note that with the introduction of $\bar{c}$ in the denominator of III.A.2, the mass dependency vanishes. Finally, the number of counts seen at the detector may be written

$$\{X\} = N \sigma_X \frac{N_e}{A_e} \zeta_X \eta_X, \quad \text{(III.A.4)}$$

where

- $\{X\}$ = number of $X^+$ ions counted at the detector,
- $\sigma_X$ = cross section for $X \rightarrow X^+$ by electron impact,
- $N_e$ = the number of electrons which traversed the overlap,
- $A_e$ = the cross sectional area of the electron beam overlap,
- $\zeta_X$ = probability that $X^+$, created in the ionization region, arrives at the detector face; the collection efficiency,
- $\eta_X$ = probability that $X^+$ is detected if it hits the detector front face; the detection efficiency.

This can be seen by considering that $N \sigma_X$ is the total cross sectional area presented to the electron beam, the fraction $N_e/A_e$ is the electron beam density, so that their product is the total number of ions created. Finally, the efficiency factors take into account some real-
world limitations. These efficiencies are discussed further in III.B.3, as they appear in the expression from which the O density is calculated. Gathering constants yields:

\[ \{X\} = K_1 \ n_X \ \sigma_X \ N_e \ \zeta_X \ \eta_X, \tag{III.A.5} \]

where

\[ K_1 = \frac{A}{A_e} \frac{1}{4\pi} \int \cos\theta \ dr \ d\Omega. \]

and \( n_X \) refers to the density of species \( X \) in the target cell.

Not only must the particles coming from the target cell be taken into account, but also those making up the residual pressure in the vacuum chamber. Signal from this source can be expressed similarly:

\[ \{B\} = l \ n_B \ \sigma_B \ N_e \ \zeta_B \ \eta_B. \tag{III.A.6} \]

where \( B \) stands for "background" species, \( n_B \) is the ambient density, and \( l \) is the effective electron beam length. Even though \( n_B \) is small (the chamber is at high vacuum), the value of \( K_1 \) is small enough to make background signal quite significant.

Since we are not prepared to make a direct absolute measurement of the electron beam current, and thereby determine \( N_e \), a background gas, argon, is admitted to the chamber via a reservoir. The pressure in this reservoir is monitored using an ion gauge. The argon signal can be written as a slight variation of the above:

\[ \{Ar\} = K_2 \ p_{Ar} \ \sigma_{Ar} \ N_e \ \zeta_{Ar} \ \eta_{Ar}. \tag{III.A.7} \]
where $K_2$ is a constant which includes the ratio of pumping speeds of the bleed inlet aperture versus the chamber diffusion pump, ion gauge efficiency, and $I$ from above, and $p_{Ar}$ is the argon pressure seen by the ion gauge. $N_c$ can be explicitly solved for, in which case equations (III.A.5, 6) can be rewritten:

$$
\{X\} = \frac{K_1 n_X \{Ar\} \sigma_{X} \xi_{X} \eta_{X}}{K_2 p_{Ar} \sigma_{Ar} \xi_{Ar} \eta_{Ar}}, \quad (III.A.8)
$$

$$
\{B\} = \frac{1}{K_2} \frac{n_B \{Ar\} \sigma_{B} \xi_{B} \eta_{B}}{p_{Ar} \sigma_{Ar} \xi_{Ar} \eta_{Ar}}, \quad (III.A.9)
$$

The argon gas signal is an indispensable component of the mass spectrum analysis for this reason, and for another reason discussed in section III.B.2. While these expressions may seem complicated, it will be shown in section III.B.3 that rather straightforward results follow.

2. Electrode System.

One will always achieve some degree of mass spectrometry using electrostatic fields to accelerate ions, since the time-of-flight of an ion in any region of uniform electric field is dependent upon the square root of its mass/charge ratio. However, acceptable mass resolution is not guaranteed with any electrode geometry. For a mass spectrum to be useful in our case, for instance, there must be complete separation of mass 16 (atomic oxygen) from other species. There are two considerations in trying to maximize the overall resolution- initial energy and spatial distribution of ions formed in the ionization region.¹

Room temperature particles ionized by the electron beam possess a range of velocities as described by the Maxwell Velocity Distribution. This initial velocity spread will cause flight time spreading among same mass species. In order to minimize this effect, ions must be brought to a large energy quickly, so that any initial velocity becomes
negligible compared to its velocity leaving the ionization region. This necessitates a pulsed extraction strategy (described further in section III.B.1), since a large field cannot be present when the electron beam needs to cross. It is not obvious that by increasing the ionization region field that a resolution increase can be achieved, since it appears that the flight times will decrease and therefore mass peaks would fall closer together in the mass spectrum, resulting in decreased resolution. For the worst case scenario of two particles with equal but oppositely directed velocities along the electrode axis, the defocusing is simply the "turn-around" time for the lagging one,

$$\Delta T_{\text{turn-around}} = \frac{2v_0 m}{qE_1},$$  \hspace{1cm} (III.A.10)

where $v_0$ is the initial velocity, $m$ the mass, $q$ the charge, and $E_1$ the electric field strength in the ionization region. The total flight time (which is a function of initial position and velocity) can be written as a sum of the residence times in each of the four regions (three acceleration, one drift) of the mass spectrometer:

$$T(x_0, v_0) = T_1 + T_2 + T_3 + T_4.$$  \hspace{1cm} (III.A.11)

Here

$$T_i = \frac{v_i - v_{i - 1}}{a_i}, \quad \text{for } i = 1, 3 \quad \quad T_4 = \frac{x_4 - x_3}{v_3}$$

$$a_i = \frac{qE_i}{m}, \quad i = 1, 3$$

$$v_i = \sqrt{v_{i - 1}^2 + 2a_i(x_i - x_{i - 1})}, \quad i = 1, 3$$

with $x_i$ referring to the position of the $i$th mesh (see figure III.A.1, mesh 4 being the PSD front face), and $v_i$ being the particle velocity component along the electrode axis at $x_i$. The
$E_i$ are the electric field strengths in the three acceleration regions, and the $a_i$ are the corresponding accelerations felt by charged particles in these regions. This comes from the constant acceleration equations, assuming perfectly uniform fields. It is possible to see from equations III.A.10, 11 that while the mass spectrum peak broadening due to initial energy differences goes as one over $E_1$, the total flight time goes more weakly than one over its root. Therefore the larger the field in the ionization region, the sharper the mass peaks.

Focusing in time the arrival of ions formed at different locations in the ionization region depends upon the ability to impart higher energies to lagging ions so that they catch up to the leading ones by the time they get to the detector. It is highly dependent upon electrode geometry, and was a primary consideration during its design. A so-called two-field acceleration system was chosen, in which maximizing spatial resolution involves setting up a ratio of field strengths in the first two acceleration regions of the system to achieve the tightest grouping of flight times for a given mass. In our system, actually all but the mesh 2 electrode are constrained by other considerations, so focusing is achieved by adjusting its voltage. The ion trajectory simulation program SIMION$^3$ has been used most recently to predict the best electrode potentials for maximum resolution. Figure III.A.2 shows a simulated pulsed extraction. An ensemble of ions released from the same point, with thermal mean speed directed radially in selected directions is allowed to drift in the temporarily field-free region before being extracted. Bunching of the "tick marks" demonstrates the good over-all focusing capability of the spectrometer. The simulated flight times and peak widths are extremely faithful to apparatus values. In the present apparatus, a high degree of energy focusing has been achieved, leaving spatial resolution as the visible source of broadening. Peaks are $< 100$ ns in width, and their shapes may be deduced from figure III.B.4 (see section III.B.2).
Figure III.A.2. A SIMION simulation of mass 16 (amu) ion extraction. Lag time is 3 μs, and elapsed time-of-flight is indicated by 0.2 μs-spaced tick marks.

The electron beam source is a commercially available SW-21Z electron gun from Southwest Vacuum Devices. Its small size ideally suits it for application on the movable electrode system of the mass spectrometer. The ionization region is kept at 200 V at times other than ion extraction, therefore electrons attain that energy coming out of the gun. Electron current emanating from a heated (grounded) cathode is controlled by the video grid and extractor elements, and monitored using an electrometer at the Faraday cup, which is biased at 220 V using dry cells. The cathode is activated before each use by intense heating, causing a low-work-function metal to diffuse to the surface. Voltages required on the control elements vary slightly from gun to gun, but generally the video grid is kept at @ -5 V to stop the beam, and pulsed to @ +5 V turn the beam on. Meanwhile, the extractor is kept between 0 and 20 V, and is used as a fine adjustment. The beam is steered directly into the center of the cup, maximizing the overlap volume, by two small pairs of deflection plates. The beam is collimated with two apertures, and its width, estimated using the Faraday cup entrance aperture diameter, is roughly 1 mm.

4. Detector.

The particle detector used in the time-of-flight mass spectrometer is the same position sensitive detector (PSD) used for the acquisition of scattering data. However, in addition to the impact-position signal leads, the detector is equipped with a timing signal line. The timing signal originates at the back face of the second microchannel plate of the PSD, where the tiny pulse created by particle impact is capacitively coupled to the input of a LeCroy MVL-100 amplifier/discriminator, where it is converted to an ECL logic pulse. Characteristics of time-detection efficiency in and of itself as well as relative to position-detection has been investigated, and plays an important role in absolute density measurements using the mass spectrometer (see section III.B.3). While position information is not directly used in mass spectrometric analysis as described in section
III.B, it has demonstrated in the past the complete collection of thermal target cell species which is now taken for granted.\textsuperscript{2} Furthermore, it is invaluable as a mass spectrometer diagnostic, for many failure modes are immediately evident by a glance at the impact position pattern, which is always monitored.

5. **Beam Stop.**

To effect subtraction of background gas signal in the mass spectrum, it is necessary to somehow stop the effusive beam from the target cell. This is done with a flag which runs in a groove on the backplate. The flag is beryllium-copper ribbon connected to a soft iron rod surrounded by a pair of solenoids, one nearer the mass spectrometer (to close the flag), one farther away (to open it). The solenoids are activated by logic signals issued by the computer. The advantage of computer control is that the flag open and flag closed signals can be sampled frequently enough to make any long term changes in background gas pressure or electron gun instability inconsequential. An annoying side-effect of the presence of the flag is the slight time-of-flight shift it creates in the flag closed data, as seen in figure III.B.7 (see section III.B.2).

\begin{itemize}
\end{itemize}
B. Data Acquisition and Analysis.

1. Timing Sequence.

To build up a time-of-flight mass spectrum, many flight time measurements of target cell species must be accumulated. Each measurement consists of a timing sequence, in which ion formation, extraction and detection can occur. A free running pulse generator initiates this sequence of events. At time zero, it turns on the electron gun by pulsing its video grid element. Simultaneously, it triggers a delay generator, a logic gate circuit, and a high voltage (HV) pulser. The HV pulser, using its own internal delay generator, waits the lag time before extracting any ions from the ionization region by raising the voltage on the backplate. The logic gate circuit suppresses "pick-up" noise from both electron and ion extraction, which would be converted to phantom particle impacts by the sensitive MVL-100 amplifier/discriminator circuitry, while allowing signals due to real particle impacts to be passed. If such an event occurs, the impact signal is used to start a time-to-digital conversion. The signal from the delay generator, which is pre-programmed to wait an appropriate time from time zero, marks the end of the time to be digitized. The TDC then completes the conversion, and presents this reversed time-of-flight to the computer. These start signals are also tallied independently by a scaler, along with the strobe from the "black box" (Surface Science 239 Particle Imaging Detector electronics), and these tallies are also available to the computer. Figure III.B.1 schematically outlines the timing sequence, and figure III.B.2 shows timing of critical signals in the sequence.

The rate at which this sequence is repeated is limited by the lag time and actual particle flight times, and is roughly (10 μsec)-1, or 100 khz maximum. The average ion formation rate, which is controlled by adjusting the electron current, must be kept low so that the probability of more than one ion being created per repetition is low. Otherwise, the resulting spectrum of flight times will be skewed by the preferential detection of lighter species, which hit the detector first and tie up the TDC before heavier species can arrive.
Figure III.B.1. Time-of-flight spectrum data acquisition scheme. Labeled signals are featured in timing diagram figure III.B.2.
Figure III.B.2. Timing diagram for time-of-flight spectrum data acquisition.
This problem would result in an overestimation of the O density, which is determined by comparing O and O$_2$ signals. However, it is important to maintain the highest count rate as possible to minimize statistical uncertainty. A formation rate of, say, 1% of the repetition rate, or 1 khz, would ensure a negligible (0.01%) probability of double ion formation. This turns out to be conservative, however, since O makes up a relatively small component of the spectrum, making the problem less drastic. Since the probability of ion formation per repetition is small, Poisson statistical results are valid, and, along with knowledge of the relative abundances of O and O$_2$, can be used to estimate at what count rate the effect will become significant. It is far easier, though, to experimentally determine the maximum limit by measuring the ratio of O to O$_2$ signal as a function of count rate (as determined by the scaler). Figure III.B.3 shows the effect for discharge off signal (where O comes purely from dissociatively ionized O$_2$), which is sufficient to conclude that a count rate of 5-7 khz is acceptable.

The lag time prior to ion extraction serves to allow relatively fast O from dissociatively ionized O$_2$ to escape the ionization region, and hence detection. Since the fast O signal contributes only to the noise when trying to count thermal O from the target cell, a large lag time is preferable. However, the time must not be so long as to allow thermal O to escape the region before being extracted. By choosing the optimal time lag, the minimum uncertainty in the O density measurement can be achieved.

An estimate of the maximum acceptable time lag can be made by appealing to the Maxwellian velocity distribution, as illustrated in figure III.B.4. The time-of-flight curve in this figure was generated by SIMION, though it could have been calculated using equation III.A.11. Particles of different initial velocities along the electrode axis were allowed to drift for 3 $\mu$s before being extracted (as in figure III.A.2). The initial starting positions reflect these velocities, therefore it is appropriate to superimpose velocity distribution curves. The distribution of the z component of particle velocity pertains to background gas, while that for a collimated effusive beam, the so-called transmission
Figure III.B.3. Ratio of [O]/[O2] signal (taken with beam stop open, discharge off). The preferential detection of O due to the simultaneous formation of O+ is observed for count rates exceeding 7 kHz.
Figure III.B.4. The solid line shows flight time $T(x_0, v_0)$ (see equation III.A.11) as calculated by SIMION for a mass 16 ion, using the position of the vertical hashed line as the mean ion formation point (electron beam axis) and a 3 $\mu$s lag time. Superimposed are rough sketches of the velocity distributions for $v_x$ (symmetric about the e-beam axis) and for a collimated effusive beam.
distribution pertains to target cell-originated species. These are also shown in the figure, and indicate that particles are well contained in the ionization region. Choosing the correct lag time can also be verified by directly checking the residence time of a mass 16 species. A plot of ion signal as a function of lag time using methane gas is shown in figure III.B.5. Large lag times are detrimental to focusing, which complicated this measurement, but it tends to corroborate the above analysis. Therefore, in consideration of residence time as well as focusing, a lag time of 3 μs is presently used.

To measure ion flight times, it is sufficient to measure with respect to any fixed time reference. The so-called "reversed timing" strategy, where a particle's impact signal starts the time to digital conversion, is adopted due to the design of the Lecroy 2228A TDC. At the moment a start is received, the TDC begins charging a capacitor. When the delay generator's stop pulse arrives, the TDC stops charging. The capacitor is then slowly discharged while a clock upcounts. The whole conversion period can take up to 100 μsec for the 2228A, during which time it disregards other start signals. On the other hand, if the TDC receives a stop signal without a start, it will take no action. Therefore, it is advantageous to engage the TDC when and only when a start signal is received.

The large dead time during which the TDC performs a time conversion places a maximum limit on the number of start pulses which are processed and contribute to the spectrum. This dead time is dependent upon the length of time it is required to digitize, as well as the digital resolution it is called on to deliver. By using the minimum possible values for these, the dead time has been reduced to around 20 μsec. Adding in the time it takes for the computer to read and clear it, around 20 μsec as well, the total effective dead time is around 40 μsec. This means that over 70% of the counted start signals can be processed at a 7 khz count rate, or a roughly 5 khz processed rate.

Monitoring the start signal rate and the strobe from the position encoding electronics using the scaler allows the relative efficiencies for time-of-flight and impact-position detection to be compared. As a rule of thumb, the timing signal rate should be slightly
Figure III.B.5. Measurement of mass 16 species (CH₄) signal versus lag time. Loss of signal is clearly seen after 4 µs, indicating that CH₄ molecules are leaving the ionization region and are defocused from the mass peak.
higher than that for position detection, due to the lack of so-called "upper level discrimination" in the MVL-100 timing signal detection circuitry. By adjusting the threshold for timing detection in the MVL-100 circuitry, and setting the PSD operating bias correctly, this result can be achieved. Furthermore, comparing the number of starts that got processed to the total number that occurred gives an easy check of the computer activity level. Other users can cause the computer servicing dead time to be unacceptably high.

2. Algorithm and Data Structure.

The computer acquires time-of-flight data using a subroutine flow-charted in figure III.B.6. The algorithm is a cycle in which target cell and background data are alternately taken. The computer controls the beam stop, and thereby, with the help of an external timer, controls the cycle rate. The computer begins by moving the beam stop. Then it must wait momentarily for the magnetic field generated by the beam stop driving solenoids, which affects the electron beam, to die away. During this brief wait time (nominally 1 second) it collects target cell and the argon background gas pressure data. Next it enters a time-of-flight data acquisition loop (nominally 5 seconds) in which the computer constantly polls the TDC. When the TDC receives a start signal and completes a conversion, it strobes the computer. The computer reads the information in the form of a 9 bit binary number, with a value of 0 indicating the greatest time-of-flight, and 511 the least. After performing a coordinate reflection about the middle of the time window (so that heavy mass peaks appear leftmost), an array element indexed by the time-of-flight value is incremented. It is possible for a start pulse to arrive outside the TDC's time window if it is a result of random noise or if the window is misaligned, in which case the TDC indicates overflow. It is useful to monitor the number of overflows as a diagnostic of these problems. At the end of this half-cycle of time-of-flight data acquisition, it reads the scaler's tallies of start pulses and black box strobes, and processes pressure data. It then moves the flag and repeats the steps for the other half-cycle of acquisition.
Figure III.B.6. Time-of-flight data acquisition algorithm.
The result of an acquisition run is two time-of-flight mass spectra, one for beam stop "open" and one for "closed", and the average and standard deviation for target cell and background gas pressures obtained from many measurements taken over the course of the entire run. Figure III.B.7 shows typical spectra, including their difference, which gives gross indication of the pure target signal. However, the difference array is actually useless for two reasons. First, since the count rate is greater for beam stop open than for stop closed, that array suffers more from TDC/computer servicing dead time, meaning that even though equal time is spent acquiring both arrays, it experiences slightly less time polling the TDC. This is strictly equivalent to decreasing the value of $N_e$ (as discussed in section III.B.1) for the stop open array, and the effect is therefore evident in the number of argon counts in the spectrum. For this reason, direct subtraction of the arrays gives close but wrong values for target cell signal. Instead, all peaks used in O density analysis are rescaled using the argon peaks for reference, as will be explicitly shown in the next section. Also for this reason, the presence of argon in the background is indispensable. The difference array shown is actually a scaled subtraction, and is therefore a correct indication of target cell signal.

The second reason is evident from viewing the difference spectrum. There is an imperfect subtraction due to small time-of-flight shifts presumably caused by a change in the extraction electric field in the ionization region when the beam stop is present or absent. The shift is mass dependent and therefore rather difficult to correct for. The amount of shift can be shown to be less than one digital channel width (< 5 nsec) in all cases, determined by array shifting software. As a result of this problem, it can not easily be seen whether complete subtraction is occurring where it should. Since target cell-originated particles have a larger average velocity toward the detector, peaks with a significant target cell gas contribution (O and O$_2$, stop open array) are actually shifted toward faster flight times. This offsets the other shift problem so that those peaks seem to subtract fairly well.
Figure III.B.7. Plot of time-of-flight spectra. Abscissa is correct for beam stop "closed" array, others shifted for convenience.

Application of equation III.A.8, which relates the density of a species in the target cell to the number of counts seen by the detector of the mass spectrometer:

\[
\{ X \} = \frac{K_1}{K_2} \frac{n_X \{ Ar \} \sigma_X \zeta_X \eta_X}{p_{Ar} \sigma_{Ar} \zeta_{Ar} \eta_{Ar}},
\]  

(III.A.8)

along with equation III.A.9 for background gas signal:

\[
\{ B \} = \frac{1}{K_2} \frac{n_B \{ Ar \} \sigma_B \zeta_B \eta_B}{p_{Ar} \sigma_{Ar} \zeta_{Ar} \eta_{Ar}},
\]  

(III.A.9)

to the problem of determining O density in the target cell is as follows. From mass spectrometric data we can measure only two numbers pertaining to any given mass, namely \( \{ X \}_{\text{open}} \) and \( \{ X \}_{\text{closed}} \), referring to the number of counts, or peak sum, of species X in the beam flag "open" (FO) and "closed" (FC) arrays, respectively. Furthermore, in any experiment to determine the O density, there must be a spectrum for the discharge "on" (DON) case, where O is present in the target cell, as well as the discharge "off" (DOFF) case, where only \( O_2 \) flows, to serve as a reference. The species used in the analysis scheme to be described are Ar, \( O_2 \), and, of course, O, which means twelve peak sums corresponding to the four permutations of open/closed, on/off for each species are needed for the analysis.

**Step 1. Discharge Off \( O_2 \).** To determine the DOFF \( O_2 \) signal, or \( \{ O_2 \}_{\text{off}} \), write the measurable quantities in terms of their target cell (TC) and background (BG) components:
\[
\{O_2\}^{\text{off}}_{\text{open}} = \{O_2, \text{TC}\}^{\text{off}} + \{O_2, \text{BG}\}^{\text{off}}_{\text{open}}, \quad \text{(III.B.1)}
\]
\[
\{O_2\}^{\text{off}}_{\text{closed}} = \{O_2, \text{BG}\}^{\text{off}}_{\text{closed}}. \quad \text{(III.B.2)}
\]

Next, these components are expressed as dictated by equations III.A.8, 9:

\[
\{O_2, \text{TC}\}^{\text{off}} = \frac{K_1 \{O_2\}^{\text{off}} \{Ar\}^{\text{off}}_{\text{open}} \sigma_{O_2} \gamma_{O_2} \xi_{O_2} \eta_{O_2}}{K_2 \rho_{Ar}^{\text{off}} \sigma_{Ar} \gamma_{Ar} \xi_{Ar} \eta_{Ar}}, \quad \text{(III.B.3)}
\]

\[
\{O_2, \text{BG}\}^{\text{off}}_{\text{open/closed}} = \frac{1 \{O_2\}^{\text{off}}_{\text{BG}} \{Ar\}^{\text{off}}_{\text{open/closed}} \sigma_{O_2} \gamma_{O_2} \xi_{O_2} \eta_{O_2}}{K_2 \rho_{Ar}^{\text{off}} \sigma_{Ar} \gamma_{Ar} \xi_{Ar} \eta_{Ar}}, \quad \text{(III.B.4)}
\]

where the symbol \([X]\) replaces \(n_X\) (the number density of species \(X\)) for convenience.

Note that background \(O_2\) density is distinguished by a "BG" subscript, and that collection efficiencies are also distinguished since they are not necessarily the same. Going back to III.B.1,

\[
\{O_2, \text{TC}\}^{\text{off}} = \{O_2\}^{\text{off}}_{\text{open}} - \{O_2, \text{BG}\}^{\text{off}}_{\text{open}}. \quad \text{(III.B.5)}
\]

Renaming \(\{O_2, \text{TC}\}^{\text{off}}, \{O_2\}^{\text{off}}, \) equation III.B.4 allows

\[
\{O_2\}^{\text{off}} = \{O_2\}^{\text{off}}_{\text{open}} - \frac{\{Ar\}^{\text{off}}_{\text{open}}}{\{Ar\}^{\text{off}}_{\text{closed}}} \{O_2, \text{BG}\}^{\text{off}}_{\text{closed}}, \quad \text{(III.B.6)}
\]

which is just, by equation III.B.2:
{O_2}^{off} = \frac{\{O_2\}_\text{open}^{off}}{\{Ar\}_\text{closed}^{off}} - \frac{\{Ar\}_\text{open}^{off}}{\{Ar\}_\text{closed}^{off}} \{O_2\}_\text{closed}^{off}. \quad (\text{III.B.7})

In this way the desired number of counts is isolated in terms only of measurable peak sums.

**Step 2. Discharge On O_2.** This is completely similar to the above (one need only replace the word "off" with "on" everywhere), so we immediately write

\[ \{O_2\}_\text{on}^{on} = \frac{\{O_2\}_\text{open}^{on}}{\{Ar\}_\text{closed}^{on}} - \frac{\{Ar\}_\text{open}^{on}}{\{Ar\}_\text{closed}^{on}} \{O_2\}_\text{closed}^{on}. \quad (\text{III.B.8}) \]

Furthermore, dividing the analogous equation to III.B.3 by III.B.3 itself yields

\[ \{O_2\}_\text{on}^{on} = \frac{\{O_2\}_\text{open}^{on} p_{Ar}^{on}}{\{O_2\}_\text{off}^{off} p_{Ar}^{off}} \frac{\{Ar\}_\text{open}^{off}}{\{Ar\}_\text{closed}^{on}} \{O_2\}_\text{off}^{off}. \quad (\text{III.B.9}) \]

This is how the density of O_2 in the DON flow is calculated. The DOFF density is determined using a Baratron capacitance manometer which measures the pressure in the target cell during DOFF flow, when O_2 is the only gas present.

**3. Discharge Off O.** In this case, no thermal O comes from the target cell, but we need to find out how much O from dissociative ionization of O_2, so-called fragment O, comes from target cell originated O_2.

\[ \{O\}_\text{open}^{off} = \{O_{\text{frag. TC}}\}_\text{open}^{off} + \{O_{\text{frag. BG}}\}_\text{open}^{off}. \quad (\text{III.B.10}) \]

\[ \{O\}_\text{closed}^{off} = \{O_{\text{frag. BG}}\}_\text{closed}^{off}. \quad (\text{III.B.11}) \]
To isolate \( \{O_{\text{frag, TC}}\}^{\text{off}} \), to be renamed \( \{O\}^{\text{off}} \), we follow the same procedure as in part 1 for \( \text{O}_2 \) (since it is the parent species), except that the electron impact cross section would be that for dissociative ionization, and the collection and detection efficiencies would be that for high energy fragment \( \text{O} \) ions. The form of the result is nevertheless similar:

\[
\{O\}^{\text{off}} = \{O\}^{\text{off}}_{\text{open}} - \frac{\{\text{Ar}\}^{\text{off}}_{\text{open}}}{\{\text{Ar}\}^{\text{off}}_{\text{closed}}} \{O\}^{\text{off}}_{\text{closed}}.
\]  

(III.B.12)

4. **Discharge On** \( O \). Now thermal \( O \) is (hopefully) present as a component of the FO peak sum:

\[
\{O\}^{\text{on}}_{\text{open}} = \{O_{\text{therm, TC}}\} + \{O_{\text{frag, TC}}\}^{\text{on}} + \{O_{\text{frag, BC}}\}^{\text{on}}_{\text{open}},
\]  

(III.B.13)

\[
\{O\}^{\text{on}}_{\text{closed}} = \{O_{\text{frag, BC}}\}^{\text{on}}_{\text{closed}}.
\]  

(III.B.14)

To isolate it, rename \( \{O_{\text{therm, TC}}\} + \{O_{\text{frag, TC}}\}^{\text{on}} \) to \( \{O\}^{\text{on}} \), so that we can immediately write, as in part 3:

\[
\{O\}^{\text{on}} = \{O\}^{\text{on}}_{\text{open}} - \frac{\{\text{Ar}\}^{\text{on}}_{\text{open}}}{\{\text{Ar}\}^{\text{on}}_{\text{closed}}} \{O\}^{\text{on}}_{\text{closed}}.
\]  

(III.B.15)

Rename \( \{O_{\text{therm, TC}}\}, \{O\} \).

\[
\{O\} = \{O\}^{\text{on}} - \{O_{\text{frag, TC}}\}^{\text{on}},
\]  

(III.B.16)

where, appealing again to III.A.8,
\[ \{O_{\text{frag, TC}}\}_{\text{on/off}} = K_1 \frac{[O_2]_{\text{on/off}} \{Ar\}_{\text{open}} \sigma_{\text{frag}} O_2 \zeta_{\text{frag}} O_2 TC \eta_O}{K_2 \frac{p_{\text{Ar}}^{\text{on/off}}}{\sigma_{\text{Ar}}} \zeta_{\text{Ar}} \eta_{\text{Ar}}}. \] (III.B.17)

The above allows, remembering that \( \{O_{\text{frag, TC}}\}_{\text{off}} = \{O\}_{\text{off}} \),

\[ \{O\} = \{O\}_{\text{on}} - \frac{[O_2]_{\text{on}} \{Ar\}_{\text{open}} p_{\text{Ar}}^{\text{off}}}{[O_2]_{\text{off}} \{Ar\}_{\text{open}} p_{\text{Ar}}^{\text{on}} \{O\}_{\text{off}}}, \] (III.B.18)

which is more easily expressed using III.B.9 as

\[ \{O\} = \{O\}_{\text{on}} - \frac{\{O_2\}_{\text{on}}}{\{O_2\}_{\text{off}}} \{O\}_{\text{off}}. \] (III.B.19)

An expression for \([O]\), the \(O\) density, is close at hand. A final appeal to III.A.8 for \(O\) and \(O_2\) is necessary:

\[ \{O\} = \frac{K_1 [O] \{Ar\}_{\text{open}}^{\text{on}} \sigma_{O} \zeta_{O} TC \eta_O}{K_2 \frac{p_{\text{Ar}}^{\text{on}}}{\sigma_{\text{Ar}}} \zeta_{\text{Ar}} \eta_{\text{Ar}}}, \] (III.B.20)
\[
{[O_2]}_{on}^n = \frac{K_1 [O_2] [Ar]_{open}^n \sigma_{O_2} \zeta_{O_2 TC} \eta_{O_2}}{K_2 p_{Ar}^n \sigma_{Ar} \zeta_{Ar} \eta_{Ar}}.
\] (III.B.21)

These together yield

\[
{[O]} = \frac{\sigma_{O_2} \zeta_{O_2 TC} \eta_{O_2} {[O]}_{on}^n}{\sigma_{O} \zeta_{O TC} \eta_{O} {[O_2]}_{on}^n}.
\] (III.B.22)

It is seen that absolute determination of the O density requires electron impact cross section information, as well as knowledge of efficiencies. Thermal TC species have unit collection efficiency as determined by impact-position-detection information. Detection efficiency is believed to reach saturation for particles at least as massive as \(O_2\) when impact energies exceed a couple of kilovolts, so that ratio may be considered to be unity as well. Therefore, the outstanding scaling ratio is the electron impact cross section ratio.

Surprisingly, there are no reliable literature sources for determining this ratio. Fite and Brackmann made direct measurement of the \(\sigma_{O_2}/\sigma_{O}\) ratio, but reported absolute cross sections.\(^1\) While these were obtained by reliance upon additional cross section measurements (those for the total ionization of \(O_2\) from Tate and Smith\(^2\)), recovery of the ratio should eliminate any systematic error introduced. At 200 eV the results are \(\sigma_{O_2} = 1.9 \times 10^{-16}\) cm\(^2\), \(\sigma_{O} = 1.5 \times 10^{-16}\) cm\(^2\), and \(\sigma_{O_2}/\sigma_{O} = 1.3\).

Brook, Harrison and Smith made absolute measurement of \(\sigma_{O}\) using beam techniques.\(^3\) Uncertainties due to random error were reported to be ±5%, and in addition there were discrepancies of up to 6% (not consistent) between measurements made using a 2 keV versus 4 keV O beam which ideally should not have made a difference. Therefore,
their $\sigma_0 = 1.24 \times 10^{-16}$ cm$^2$ can be taken to approximately 10%. This measurement stands alone as an accepted *bona fide* absolute measurement, to the author's knowledge.

Rapp and Englehorn-Golden measured total ionization cross sections for O$_2$ using static gas target techniques.\footnote{4} However, results were admitted to bear an inordinate amount of uncertainty due to difficulties in pressure measurement. Also, Rapp, Englehorn-Golden and Briglia investigated dissociative ionization,\footnote{5} but their quantitative results were strictly approximate. If forced to extract $\sigma_{O_2}$ from the above work by attempting to subtract the dissociative ionization portion from the total, a value of $1.6 \times 10^{-16}$ cm$^2$ can be obtained, but it is doubtful that the accuracy is better that $\pm 20\%$. If Brook's value is used in conjunction, $\sigma_{O_2}/\sigma_0 = 1.3$.

While the above ratio determinations actually agree, there is sufficient uncertainty associated with them as to require additional corroboration. An alternate strategy for determining the scaling factor in this equation is described by Hakes.\footnote{6} It requires a known absolute cross section for the He + O system, which is attainable by coordinate transformation of fast O on He data.

There are two parameters which are used to conveniently quantify the O yield of the flowing gas source, since reporting the absolute O density is awkward. The first, known as the *O fraction*, is simply

$$f = \frac{[O]}{[O] + \langle O_2 \rangle^{on}},$$  \hspace{1cm} (III.B.23)

which is the fractional contribution of O to the discharge-on, or *mixed*, target to the target components as a whole (excluding trace contamination). The second is the *dissociation fraction*,

$$d = \frac{[\text{flux of dissociated O}_2\text{'s}]}{[\text{original flux of O}_2\text{'s}]},$$  \hspace{1cm} (III.B.24)
which may be written

\[ d = \frac{[O]}{2 [O_2]^{\text{off}}} \]  

(III.B.25)

if it is assumed that

\[ [O_2]^{\text{off}} = \frac{1}{2} [O] + [O_2]^{\text{on}}, \]

which would be the case if the O\textsubscript{2} flow rate and pumping speed remained the same between DOFF and DON cases (which is not necessary for the analysis leading to equation III.B.22 to be valid). This provides an easy way to relate the two, though:

\[ f = \frac{2d}{2d + (1 - d)} = \frac{2d}{1 + d}, \quad d = \frac{f}{2 - f} \]  

(III.B.26)

The O fraction is more easily calculated from the analysis results, but the dissociation fraction is generally used in the literature to describe yields of atomic sources.

Any species other than O and O\textsubscript{2} that appear in the target are also detectable with the mass spectrometer. Absolute determination of their abundances would be done analogously to equation III.B.22. Common impurities are H\textsubscript{2}O, N\textsubscript{2}, and CO\textsubscript{2} from vacuum walls and intensely heated glass, as well as CO and CO\textsubscript{2} from Teflon decomposition. Vigilance to minimize these is of the utmost importance, since their contribution to the scattering signal may easily be non-negligible (see section II.D). Table III.B.1 shows cross section values for single ionization by electron impact, which are important in determining abundances of these species in the target cell.
<table>
<thead>
<tr>
<th>X</th>
<th>e⁻ + X ---&gt; X⁺ + 2e⁻ cross section (10⁻¹⁶ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.24 ± 0.05 (4%) ³</td>
</tr>
<tr>
<td>O₂</td>
<td>1.6 ± 0.3 (20%) ⁴</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.1 ± 0.2 (15%) ⁷</td>
</tr>
<tr>
<td>CO</td>
<td>1.8 ± 0.2 (10%) ⁴</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.4 ± 0.2 (10%) ⁴</td>
</tr>
<tr>
<td>N₂</td>
<td>1.8 ± 0.2 (10%) ⁴</td>
</tr>
</tbody>
</table>

Table III.B.1. Cross section values for single ionization by 200 eV electron impact.

---


A. Results.

Figure IV.A.1 shows some recent results of target gas analysis. Relative abundance is reported, which includes the effect of electron impact cross section differences among species. The abundance of O is maintained at around 20%. This coating has seen roughly 12 hr of discharge time. The mass 28 (N₂/CO) contribution is small and steady, which may indicate that it is mostly from Teflon (CO). The most disturbing feature is the H₂O contamination. It is rather large and sporadic, and is assumed to come from the coating itself. This coating was under vacuum for a significant amount of time and the flow tube was baked with electrical tracing at @150 C for roughly 24 hr. Further efforts must be made to free the coating of absorbed water, if this is indeed possible.

Is this yield sufficient for the purpose of measuring the O DCS? It is possible to estimate the expected statistical uncertainty in a DCS measurement, given a fast beam flux and total time of acquisition, by estimating the number of primary beam particles deflected by O and O₂ (the primary components of the mixed target). For the case of discharge on (DON) and discharge off (DOFF), the number of fast beam primaries scattered into solid angle ΔΩ(θ) at angle θ may be written

\[
ΔN_{DON}(θ) = N₀ \left[ O \frac{dσ_o}{dΩ}(θ) + [O₂]^{on} \frac{dσ_{o₂}}{dΩ}(θ) \right] ΔΩ(θ)
\]

\[
ΔN_{DOFF}(θ) = N₀ [O₂]^{off} \frac{dσ_{o₂}}{dΩ}(θ) ΔΩ(θ),
\]

where \( N₀ \) is the total number of primary beam particles incident upon the target, \( l \) is the target length, \( dσ/dΩ \) is the differential cross section, with subscripts denoting O or O₂ as
Figure IV.A.1. Relative abundance of O, H$_2$O, and N$_2$/CO in the flowing gas target. H$_2$O is shifted slightly for convenience. (Data taken 1 Apr 1992.)
target species (projectile and reaction is as yet unspecified), and square brackets denote number density of species in the target cell (as in section III.B.3). Solving explicitly for \( \frac{d\sigma_O}{d\Omega} \) from equations IV.A.1, 2 gives

\[
\frac{d\sigma_O(\theta)}{d\Omega} = \frac{1}{N_0 [O]} \frac{\Delta N_{DON}(\theta)}{\Delta \Omega(\theta)} \left\{ \frac{[O_2]^{on}}{[O_2]^{off}} \Delta N_{DOFF}(\theta) \right\}.
\]

There are four sources of statistical uncertainty here: \([O]\) and \([O_2]^{on}\) from mass spectrum data, and the scattering signals \(\Delta N_{DON}\) and \(\Delta N_{DOFF}\). The uncertainty in the O cross section can be calculated from straightforward propagation of uncertainties if the uncertainties in these four quantities can be estimated. Different O fractions can be modeled in existing mass spectrum analysis computer code, which allows realistic estimation of \([O]\) and \([O_2]^{on}\) and their uncertainties. A 20 mtorr \(O_2\) pressure in the target cell is assumed, as well as the condition \([O_2]^{off} = [O_2]^{on} + [O]/2\) (a good enough assumption in this case). \(\Delta N_{DON}\) and \(\Delta N_{DOFF}\) are calculated using equations IV.A.1, 2, and their uncertainties are simply their square roots, from the principles of binomial statistics.

Let's consider a particular reaction: \(H^+(1.5 \text{ keV}) + O\), charge transfer. Using a nominal 1 khz primary beam, a 5 hr acquisition time, known apparatus geometry, and previously measured DCS's (Gao et al.\(^1\) for the \(O_2\) cross section, and Hakes\(^2\) for preliminary cross section curves for O), the uncertainties in the O cross section may be estimated. Results are shown in table IV.A.1 for two angular positions, \(\theta = 1^\circ, 0.1^\circ\), reflecting the angular range of that reaction.
<table>
<thead>
<tr>
<th>O fraction</th>
<th>$\theta = 0.1^\circ$</th>
<th>$\theta = 1.0^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>0.10</td>
<td>29</td>
<td>53</td>
</tr>
<tr>
<td>0.15</td>
<td>19</td>
<td>34</td>
</tr>
<tr>
<td>0.20</td>
<td>14</td>
<td>25</td>
</tr>
<tr>
<td>0.25</td>
<td>11</td>
<td>19</td>
</tr>
<tr>
<td>0.30</td>
<td>8.4</td>
<td>15</td>
</tr>
</tbody>
</table>

Table IV.A.1. Estimated percent error bars at specified angular positions for $H^+(1.5$ keV) + O $\rightarrow$ H + O$^+$ differential cross section measurement.


B. Difficulties and Improvements.

1. Atomic Oxygen Yield and Contamination.

The ability to improve the O yield of our source depends upon a good understanding of the recombination mechanisms working in the flow system. This requires sufficiently detailed knowledge of particle kinetics and particle transport within the system to be able to judge what mechanisms are playing the most important role. For example, within the discharge region of the flow system, particle densities are large enough so that gas phase recombination is important, while at the same time wall recombination is diminished due to small diffusivity. On the other hand, in the Teflon flow conduit, gas phase recombination is negligible, and wall recombination is the only mechanism acting. As a result, the use of Teflon is absolutely necessary there, while boric acid is adequate in the discharge region.

We are just beginning to understand the complexity of the flow system, and we must work to increase our understanding of how the performance of the O source depends upon issues such as discharge power (and discharge plasma), discharge region pressure, and residence time. It is necessary to perform systematic investigations of O yield with respect to these variables, so that we can be certain we are running under optimum conditions overall.

Contamination originating from leaks and outgassing can presumably be reduced to acceptable levels by use of reliable seals and outgassing techniques, so that the solution to this problem is straightforward, if not easy. Contrarily, we are presently at an impasse concerning contamination originating from Teflon decomposition and the possible existence of the \(^1\Delta_g\) state of O$_2$.

Teflon is a necessary component of the flow system, so eliminating it is impossible. Furthermore, the fact that it is not known by what mechanism the Teflon decomposes makes the problem especially difficult to address. The resulting contamination is,
however, typically overshadowed by outgassing, and sometimes leaks. The problem is similar to other contamination problems in that, if nothing else, contaminants may be diluted and diverted in a bypassing flow system (see below).

Direct detection of $O_2(^1\Delta_g)$ in the present system is impossible. This is rather dangerous situation given that its absence is by no means certain. Of the two methods known to the author which could be used to assess the problem—threshold ionization in the mass spectrometer, and optical spectroscopy (such as absorption or fluorescence)—both would be practically impossible to implement in the present apparatus. Sufficiently drastic design changes could conceivably accommodate the latter strategy. Still, the feasibility is suspect. It may be necessary to rely upon negative experiments such as those performed by Hakes$^1$ (see section II.C, part 3).

In light of some of the above comments, a few suggestions come to mind. The ability to independently control variables such as $O_2$ gas throughput, discharge pressure, discharge power, and target cell pressure would allow the most efficient systematic determination of their optimal values from the standpoint of both maximizing $O$ yield and minimizing contamination. This may be achieved using a bypassing flow system, in which the flow system is configured in a "T". One arm of the "T" flows through the target cell as in the present apparatus, but the other arm (the "bypass") is pumped on with another pump. Both arms have Teflon stopcocks to control flow independently. The bypass would have larger conductance, so that adjusting the target cell pressure would not upset discharge conditions. Not only would this be a convenient operating strategy, but it would definitely assuage the contamination problem to a certain degree, as some of the contaminants (which in the present system must go through the target cell) would be drawn off in the bypass.

Of course, discharge power must be adequate to sufficiently dissociate the flowing gas in all cases. Considering the discharge cavity, it would remain a very inconvenient component in the above scenario. The cavity resonance depends too sensitively upon cavity temperature, position with respect to the quartz tube, discharge pressure, and
operating power to allow easy investigation of the effect of discharge power and pressure. While there are other ways to deliver power to the gas, such as a surface wave generator, it is not clear that any other method would dissociate the gas as efficiently as the resonant cavity when it is adjusted properly.

The recombination $\gamma$ (see section II.C) for Teflon, while relatively low, may still be large enough to cause discernable loss of O atoms during their residence in the Teflon flow tube. Furthermore, there may be no benefit in having an intervening length of Teflon, considering the discussion in section II.C: metastable contaminants are either very efficiently quenched, so that an excessive residence time is not needed, or quenched so slowly that the residence time provided by the the present length is not nearly sufficient. Therefore, removal of this length is advisable.

Whatever the final design of the flow system is, it must be bakeable, lest outgassing contaminants from the walls contribute to contamination. In the present apparatus, electrical tracing is wrapped only around parts outside the vacuum wall, and even that is inconvenient in some places. Evacuation of the discharge region is hindered by the aperture, lengthening bake-out time required. The coated quartz vessel should be baked at a high temperature (> 400 C) for at least 30 min to adequately degas it. It may also be beneficial to be able to completely isolate the flow system and its coating once baked, so that having to break vacuum for some reason won't affect a carefully prepared flow system.

2. **Target Gas Analysis.**

   Much effort has gone into improving the mass spectrometer-based target gas analysis scheme. Its ability to measure the relative abundance of O in the target is satisfactory. (Determining absolute abundance, of course, is another matter. See section III.B.3.) Its ability to measure the relative abundances of trace contaminants is marginal, but it serves adequately. Present mass resolution is adequate. Of course, it is
straightforward, if not easy, to improve the time-of-flight spectrometer inasmuch as it is a widely used and understood type of apparatus. Such improvements would include lowering the base pressure of the vacuum chamber to increase signal to noise, lengthening the drift region to increase resolution, or using higher speed detection electronics to gather more ion signal. However, within the limitations of the present apparatus (not to mention budget), the system is run optimally.

It is useful to touch upon alternatives to target gas analysis with respect to O density determination, since it would be nice to have an independent indication of the source yield (especially one which doesn't involve the PSD). There are several well known methods for measuring atomic oxygen densities. Some are complicated, such as resonance fluorescence and absorption techniques, or electron paramagnetic spectroscopy. Some are relatively simple, such as chemiluminescent titration, the Wrede-Harteck gauge, or catalytic probes. Catalytic probes consist of exposing a silver surface (plated upon a glass or metal substrate) to an atmosphere containing O atoms. Silver catalyses the recombination of O atoms upon its surface, and the heat of recombination (5 eV per pair) elevates the probe temperature. This effect is used in various ways to make absolute determination of the O atom flux incident on the surface. In a variation of this effect, the deposition of silver oxide upon the silver-coated surface of a quartz microbalance is used to determine O atom flux.

Chemiluminescent titration has been attempted on a former version of the present system by Hakes, although the luminescent glow in the target cell was deemed too faint (for the human eye, anyway) to be reproducible. The technique used there was to introduce NO₂ into the mixed target flow at the target cell. NO is quickly formed via O + NO₂ \rightarrow NO + O₂, then may recombine with O in the slower reaction NO + O \rightarrow NO₂ + hv, emitting green light. The lowest flow rate of NO₂ which extinguishes the green glow downstream from the target cell is presumed to be just equal to the O flow rate, since in this
case all the O atoms are consumed at the target cell. The dissociation fraction $d$ (see section III.B.3) is then simply $\frac{[\text{NO}_2 \text{ flow rate}]}{2[\text{O}_2 \text{ flow rate}]}$.

Such methods may be used in the high-pressure arm of the bypassing flow system described above, where the O flux is sufficiently high. Their response could conceivably be calibrated with the mass spectrometer to make the measurement absolute. Then the O yield could be monitored simultaneously with fast beam use. The only drawback to such methods are that they are not sensitive to contamination.


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