[16]Note that $\varphi(\underline{G})$ is simply a product of the normal distributions associated with each of the (independent) points in the profile. $\varphi(\underline{G}) = \Pi_{j=0}^{m}[\sigma_j(2\pi)^{1/2}]^{-1} \times \exp[-(J(q_j) - J_j)^2/2\sigma_j^2]$.

[17]W. C. Hamilton, *Statistics in Physical Science* (Ronald, New York, 1964), pp. 149–150.

[18]If one preserves the term $-2p_h^{k+1} j(p_h)$ and uses Eq. (7) rather than Eq. (8) to estimate $\langle p^n \rangle$, the results obtained are $s_i^2 = 4\Sigma_{k=0}^{m} \{q_k^i \sigma_k [(i+1) w_k - \delta_{km}^q]\}^2$. That is, only the mth term in the sum is affected. Since, for example, for $1s$ orbitals $J(p_h) = J(p_0)/(1+s^2)^3$, the difference between Eqs. (7) and (8) is generally small, even for $i = 3$ or 4.

[19]Although this behavior may appear counter intuitive, the explanation lies in the fact that the higher expectation values weight heavily high momentum points for which (under the assumed condition of constant absolute variance) the relative variance is quite large.

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Electron Spectra from Collisions of O^- and O with Helium*

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Three new autodetaching states of O^- have been found and an electron configuration has been assigned one of two previously observed transitions. This gives a total of five known autodetaching states of O^-. Transitions from these states appear as peaks in the spectrum of electrons produced in collisions of O^- ions with a helium target. These peaks lie at 9.50, 10.11, 10.87, 12.12, and 13.71 ± 0.02 eV. The electron spectrum produced by collisions of neutral O with helium shows four autoionizing series of oxygen lying just above the first ionization potential.

INTRODUCTION

The autodetaching states of negative ions have been observed in both electron-scattering experiments[1,2] and in collisional excitation experiments.[3] These states usually take the form of doubly excited configurations which decay by a radiationless transition into a neutral atom and a free electron. The kinetic energy of the free electron is equal to the difference between the excitation energy of the excited ion and that of the remaining neutral atom. In collisional excitation experiments these autodetaching electrons appear as peaks in the energy spectrum of electrons freed by collisions of fast negative ions with target gases.

Collisions of O^- ions with He atoms populate five autodetaching states of O^-. Four are doubly excited states and the other is reached by a $2s \rightarrow 2p$ inner-shell excitation. The four doubly excited states of O^- have been identified theoretically by Matese, Rountree, and Henry (MRH),[4] and our assignment of the inner-shell excitation configuration has been verified by the recent calculations of Chase and Kelly (CK).[5] The good agreement between theory and experiment should remove the unspecified doubts raised by Smith[6] about the acceptableness of the experimental data.

In collisions of H^+ ions with O_2, Rudd and Smith[7] were able to produce several series of autoionizing atomic-oxygen states which lie just above the first ionization potential of oxygen. We have produced these same series by colliding neutral oxygen atoms with helium.

EXPERIMENTAL PROCEDURE

The O^--ion beam is formed in a duoplasmatron ion source[8] using either hydrogen or argon as the discharge gas. The oxygen which forms the negative ions comes, presumably, from the oxide-coated filament of the source. The mass 16 O^- beam is easily separated from the mass 17 OH^- beam by an analyzing magnet placed along the beam path.

The negative ions from the discharge are accelerated (500 eV to 5 keV), momentum-analyzed by deflecting the ions through 45° with a magnet, and focused into a differentially pumped chamber containing a target gas. The target-gas pressure is usually 1–2 m Torr. The beam is collected in a Faraday cup after traversing the collision region and monitored with a beam integrator and microammeter. The method used to record data is shown schematically in Fig. 1.

The electrons leaving the collision region are energy-analyzed using a simple parallel-plate analyzer[9] with a resolution of about 1%, and de-

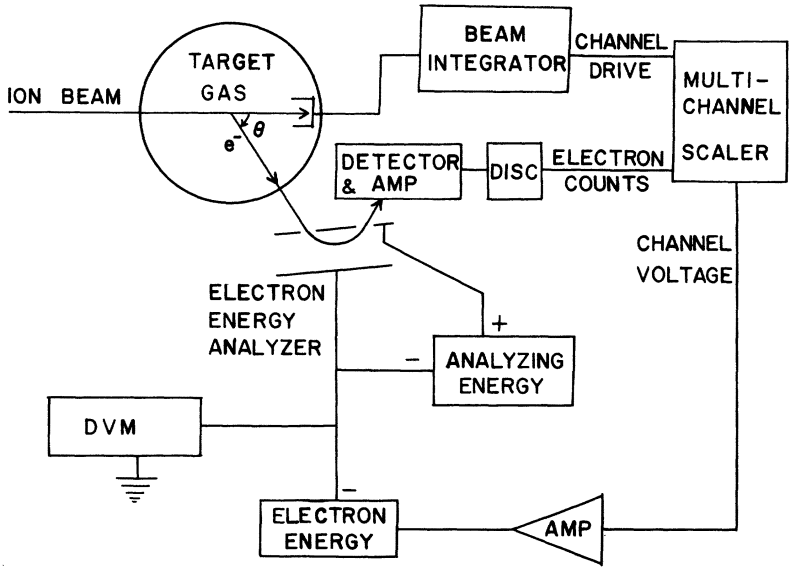

FIG. 1. Schematic diagram of the experimental apparatus used in obtaining the electron spectra for O^- on He collisions.

tected with a channel electron multiplier. The multiplier pulses are amplified, discriminated, and counted with a multichannel scaler. The staircase ramp voltage proportional to the channel address is amplified and added to the voltage on the back plate of the parallel-plate energy analyzer. In this way, each channel corresponds to a particular voltage on the analyzer, and hence to a given electron energy. The back-plate voltage is monitored with a differential voltmeter.

The angular position of the parallel-plate analyzer can be moved continuously between 10° and 75° from the beam direction and can be set to $\pm\frac{1}{2}°$. The analyzer acceptance angle is about $\pm\frac{1}{2}°$. The analyzing voltage between front and back analyzer plates was maintained at 10 V for the O^- spectra and at 5 V for the O spectra. The collision chamber and analyzer were coated with gold black to reduce the reflection of electrons. The earth's magnetic field and stray fields were reduced to below 0.01 G by a set of three perpendicular pairs of Helmholtz coils.

The multichannel scaler can be stepped from channel to channel by allowing it to sweep on its internal time base or by using an external signal. The external signal can be supplied by the beam integrator after a preset amount of charge has been collected in the Faraday cup.

To obtain fast neutral oxygen atoms a stripping cell is placed directly in front of the collision chamber and filled with the gas from the chamber. The negative ions that are not stripped are deflected electrostatically into a Faraday cup at the end of the cell. The multichannel scaler operates on its own internal sweep during the neutral-beam experiment.

ENERGY CALIBRATION

The electrons that are ejected by the moving beam particle are shifted in energy. The energy of the electron in the frame of the beam particle is given by[10]

$$E_e = E_{\rm obs} + (m/M)E_B - 2[(m/M)E_B E_{\rm obs}]^{1/2}\cos\theta, \quad (1)$$

where $E_{\rm obs}$ is the observed electron energy, E_B is the beam energy, m/M is the ratio of the electron mass to the beam particle mass, and θ is the angle of observation measured from the beam direction. The energy of the ion beam was calibrated using the retarding-potential method.

The zero of the electron energy scale was established in every case by measuring energies relative to a feature of known energy that could be observed in the same experimental run. Difficulties due to contact and space-charge potentials are thereby avoided. The electron energy scale for the O^- collisions was calibrated using the 10.11-eV O^{-*} transition. This transition has been calibrated previously[3] against the ^1D H^{-**} level and checked against the Ar^{-**} level below the first excited state of argon. The ^1D H^{-**} level has been measured by Ormonde *et al.*[11] as 10.13 ± 0.015 eV, and more recently by Sanche and Burrow[12] as 10.128 ± 0.010 eV. The 10.11-eV O^{-*} transition energy was checked again for this experiment and provides an absolute calibration point accurate to within ± 0.015 eV. Energies of the other features are absolutely determined to within ± 0.02 eV. The electron spectra were measured using different beam energies and different angles of observation and then using Eq. (1) to

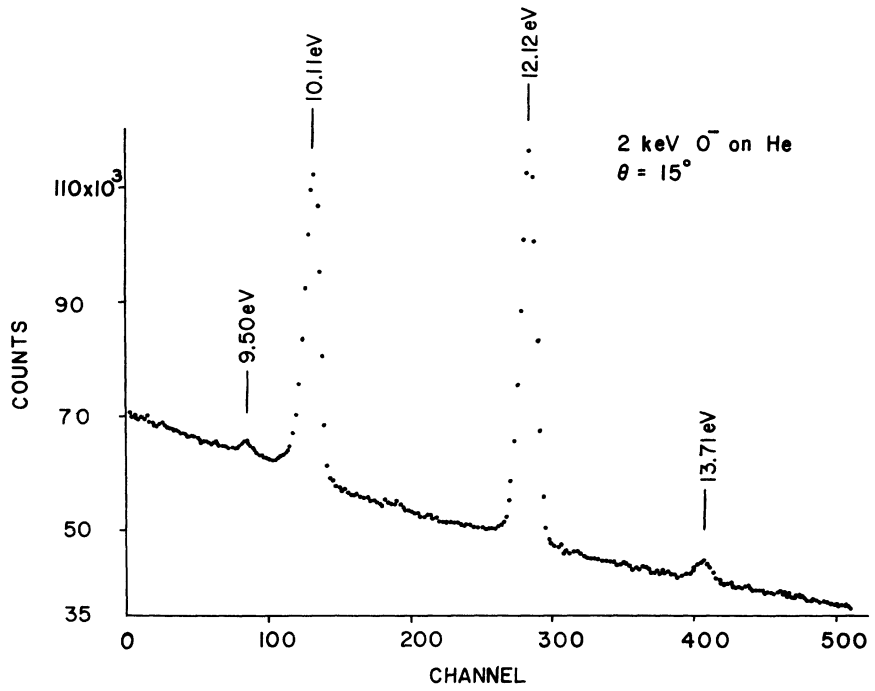

FIG. 2. Electron spectrum produced by collisions of 2-keV O^- ions with helium. The transition energies are given above the peaks.

find the unshifted transition energies for each set of conditions.

The electron energy scale for the neutral-oxygen collisions was calibrated using the $(^2D)\ 4s'\ ^3D$ level as measured in vacuum ultraviolet absorption by Huffman, Larrabee, and Tanaka.[13] An uncertainty of ± 0.04 eV was assigned to the measured electron energies in these observations.

O^- SPECTRUM

Figures 2 and 3 show electron spectra from collisions of O^- with helium. The two strong transitions at 10.11 and 12.12 eV were reported previously.[3] The weaker transitions at 9.50, 10.87, and 13.71 eV have been found because of a more efficient method of collecting data. The 10.87-eV peak was found after having been predicted theoretically by Matese, Rountree, and Henry.[4] In Fig. 3, in the region of the weak transition, the data have been smoothed by averaging adjacent data points.

The 10.11-eV transition is believed to be a transition from a $2s2p^6\ ^2S\ O^{-*}$ level to the neutral-oxygen ^1D level plus a free electron. The transition to the ^3P ground state is forbidden in an

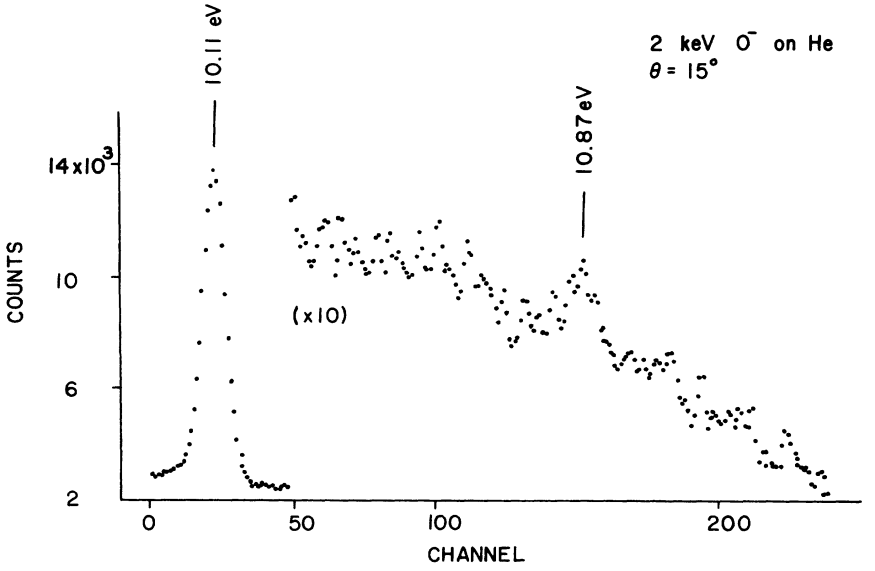

FIG. 3. Electron spectrum showing the peak corresponding to an O^- transition of 10.87 eV as predicted theoretically in Ref. 4. The data points beyond channel 50 have been smoothed by averaging adjacent points.

LS coupling scheme. Since the ^1D term is 1.97 eV above the ground state ^3P, the O^{-*} state lies 12.08 eV above the neutral-oxygen ground state, or 13.55 eV above the O^--ion ground state (the electron affinity of oxygen is 1.47 eV [14]). A recent calculation[5] of the photodetachment cross section of O^- gives the energy of the $2s \rightarrow 2p$ absorption of O^- as 14.09 eV. This places the theoretical value of the $2s2p^6\ ^2S$ level at 12.62 eV above the oxygen-atom ground state. Since the main interest of the calculation was to obtain a cross section rather than energy levels, the agreement between experiment and theory in the location of the state is believed to be satisfactory.[15] The transition energy from this level to the ^1S term of neutral oxygen would be 7.89 eV. A search was made for this transition but no peak was found. We estimate that the branching ratio of the decay to the ^1S versus the ^1D oxygen term is less than 1:100.

The doubly excited states are observed to decay to the neutral-oxygen ^3P ground term. If the O^{-**} state at 12.12 eV were to decay to the ^1D term, it would eject an electron at 10.15 eV, producing a subsidiary peak on the side of the 10.11-eV peak. There is no indication of this transition occurring; we estimate its strength as being less than 5% that of the 12.12-eV transition. The decay of this

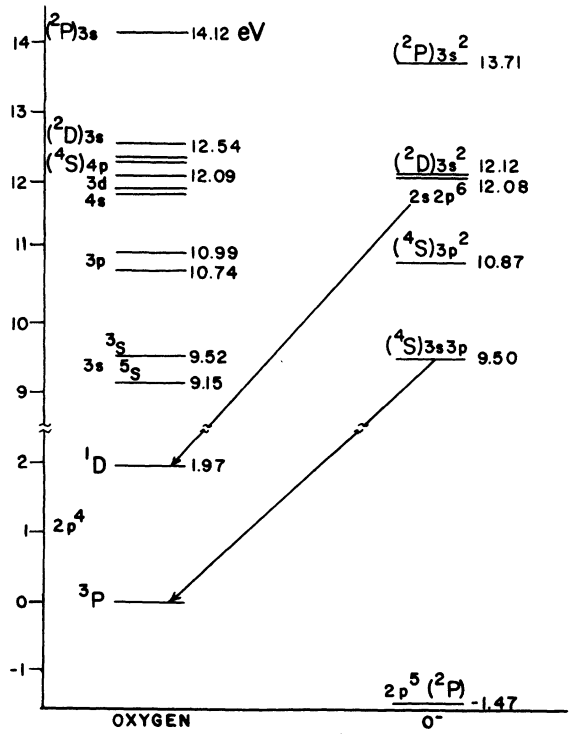

FIG. 4. Energy-level diagram of the O^- states. The zero energy point is the neutral O ^3P ground state.

TABLE I. Autodetaching states of O^-. The energies are measured with respect to the ^3P ground-state term of the neutral-oxygen atom.

Autodetaching O^- state	Theoretical (eV) (MRH) [a]	(CK) [b]	Experimental energy (eV ± 0.02)
$2p^3(^4S)3s3p\ ^2P$	9.50		9.50
$2s2p^6\ ^2S$		12.62	12.08 [c]
$2p^3(^4S)3p^2\ ^2P$	10.87		10.87
$2p^3(^2D)3s^2\ ^2D$	12.05		12.12
$2p^3(^2P)3s^2\ ^2P$	13.65		13.71

[a] Reference 4.
[b] Reference 5.
[c] This state decays to the ^1D oxygen term with a transition energy of 10.11 eV.

O^{-**} state to the ^1S neutral term is forbidden. Similar branchings from the states at 9.50, 10.87, and 13.71 eV are possible, but likewise unobserved. Because of the small intensity of these peaks, we choose not to assign upper limits for the unobserved transitions to other neutral terms.

The widths of all the observed features are indistinguishable from a purely instrumental width. The intervals between the levels of the neutral-oxygen ^3P term or between levels of the excited-ion terms are too small to add an observable component to the width of the peaks.

Since the negative-ion ground state is a ^2P term,

TABLE II. Autoionizing levels of oxygen. The energies are measured with respect to the ^3P ground-state term of the neutral-oxygen atom.

Oxygen level	Huffman *et al.* [a]	Rudd and Smith [b]	Present work
$(^2D)4s'\ ^3D$	15.179	15.15	15.18
$5s'$	15.992	15.95	15.93
$6s'$	16.349	···	16.40
$(^2D)3p'\ ^3P$		14.16	14.21
$4p'$		15.62	15.62
$5p'$		16.22	16.20
$6p'$		···	16.48
$(^2D)3d'\ ^3S$	15.416	15.41	15.41
$4d'$	16.085	16.10	16.09
$5d'$	16.395	16.41	16.44
$6d'$	16.562	16.58	16.58
$7d'$	16.664	···	16.68
$(^2P)3p''\ ^3P$		15.77	15.80
$4p''$		17.31	17.36

[a] Reference 13.
[b] Experimental values measured by Rudd and Smith, Ref. 7.

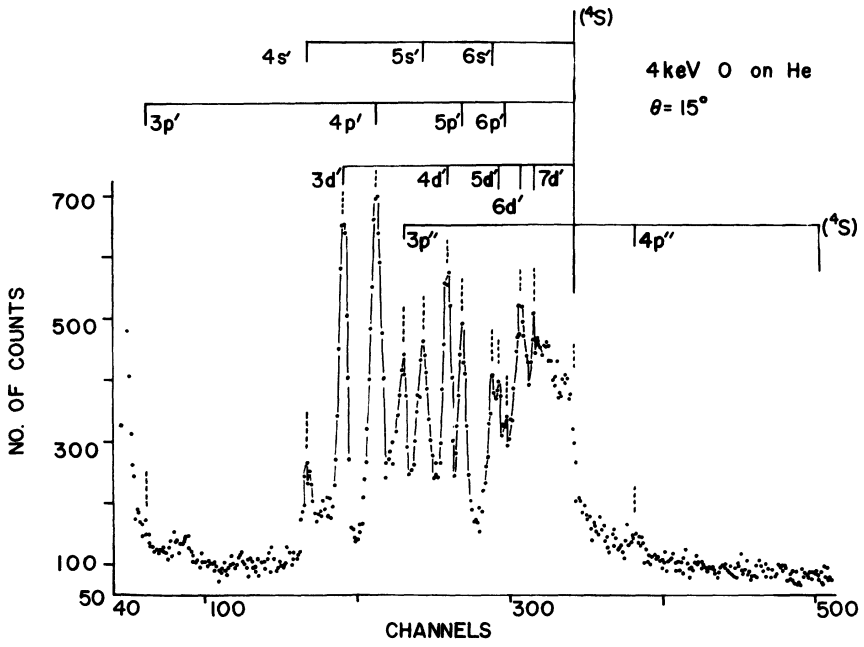

FIG. 5. Electron spectrum produced by collisions of 4-keV O atoms with helium. The autoionizing transitions are into the O^+ ^4S continuum.

the observed excited terms are expected to be doublets. In order to form a term of different multiplicity, a spin exchange with the helium target is necessary. This would require another 19.8-eV excitation energy, making the process much less likely at these low collision-energies (0.1–1.0 keV in the center-of-mass frame). An energy-level diagram showing the position of the O^- levels with respect to the oxygen levels is shown in Fig. 4. Table I lists the measured energy levels and the theoretical values.

O SPECTRUM

Figure 5 shows the electron spectrum from collisions of O atoms with helium. Four different autoionizing series of oxygen are found which decay to the O^+ ^4S ground state. The energy of the oxygen levels is found by adding the first-ionization potential of oxygen, 13.62 eV, to the measured transition energy. The transition energies range from about $\frac{1}{2}$ to 4 eV. The energy levels are listed in Table II. The unidentified peak corresponding to a transition energy of 1.68 eV seen by Rudd and Smith[7] does not appear in this work. This transition may be due to an autoionizing level of O_2. Also, the hump in the electron spectrum above 4 eV seen by Rudd and Smith[7] is absent, supporting their interpretation of this feature as being due to molecular states.

The peaks in the electron spectrum produced by O^- collisions do not appear in the O-atom collisions. It had been anticipated[3] that perhaps some of these peaks may be due to stripping of the O^- beam particle during the collision, along with excitation to an autoionizing oxygen level. These peaks are found to appear only when the beam particle is O^-, confirming their assignment as O^- autodetaching states.

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Photon-Particle Coincidence Measurement of Charge-Transfer Excitation of the N_2^+ First Negative 3914-Å Band by Protons*

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The cross section for charge-transfer excitation of the N_2^+ first negative 3914-Å band by protons (5–65 keV) has been measured using a photon-particle coincidence technique. The target N_2 is collisionally excited to the N_2^+ ($B^2\Sigma_u^+$) state and emits a 3914-Å photon in the (0,0) transition. This photon is detected in coincidence with the scattered particle, a proton or hydrogen atom, allowing separation of the two reactions which contribute to 3914-Å emission. The cross section for charge-transfer excitation indicates that charge transfer is the dominant contributor to 3914-Å excitation at energies below 10 keV, and that ionization with excitation becomes increasingly important with increasing energy. The by-product measurements, which include the cross section for charge transfer, the total cross section for 3914-Å emission, and the lifetime of the N_2^+ ($B^2\Sigma_u^+$) state, agree well with those of other workers.

I. INTRODUCTION

The excitation of the $B^2\Sigma_u^+$-$X^2\Sigma_g^+$ (0,0) emission of N_2^+ by protons of 5–65-keV energies has been studied by use of a coincidence technique. Specifically, photons emitted in the predominant (0,0) band at 3914 Å are detected in coincidence with the fast scattered proton or hydrogen atom. Because the experiment determines the final charge state of the exciting particle in an individual collision, two possible processes of ionization with excitation are separately measurable.

Protons incident on N_2 can participate in two reactions, both of which can produce the same band emission. A charge exchange can occur, leaving the N_2^+ ion in an excited state which subsequently emits a 3914-Å photon. Alternatively, the proton can excite and ionize the molecule without picking up the electron. In standard experiments the total fluxes of photons and of particles are measured, and there is no way to correlate the excitation of the N_2^+ ion with a charge-exchange collision. However, this present study of the time-interval spectrum between photons and scattered particles allows the competing reactions to be studied independently.

In addition to the measurement of the charge-exchange excitation cross section, it is possible to measure the total charge-exchange cross section, the total excitation cross section, and the lifetime of the $B^2\Sigma_u^+$ level of N_2^+. The charge-exchange and excitation cross sections have been studied by many workers; reviews of measurements and some new work have recently been presented by deHeer,[1,2] and by McNeal and Birely.[3]

Recent experiments by Jaecks, Crandall, and McKnight[4] have used an atom-photon coincidence technique to study differential cross sections for capture into excited states in $H^+ + He$ collisions. They detect photons from the neutralized H atom in coincidence with the atom itself. An ion-photon coincidence technique has been used by Barat and co-workers[5] to investigate the differential cross section for excitation of the 3^3P level in He by He^+ ions. Both of these experiments use relatively large ($\simeq 7°$) scattering angles, infer impact parameters through the quantity $\tau = E\theta$, and analyze their data in terms of level crossings.

In the experiment described here detection of the fast beam particle can be differential in angle or integrated over a forward-scattering cone which intercepts most of the scattered incident particles. The data presented here were taken using the large angular acceptance mode to define charge states of the primary reactants.

The application of coincidence techniques in analysis of the products of atomic collisions is a relatively recent development. The original work of Afrosimov, Gordeev, Panov, and Fedorenko[6] detected the principal reactants in $Ar^+ + Ar$ collisions, and very similar techniques were developed independently by Kessel and Everhart.[7] Bingham[8]