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KINETIC REACTION COEFFICIENTS IN ROCKET EXHAUST PLUMES

1 Mar 1974 - 30 Sept 1978

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ABSTRACT

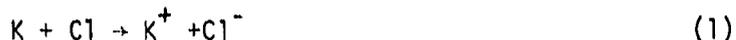
Model calculations for a solid fuel rocket plumes indicated a need for measurements of electron production and loss reactions involving potassium and atomic chlorine. During the grant period we have used a drift tube to study $H + Cl^- \xrightarrow[k_2]{k_1} HCl + e$, a crossed atomic beams apparatus to

measure the cross section for $K + Cl \rightarrow K^+ + Cl^-$, and a laser generated plasma to study the recombination of K^+ and e . We believe the available data indicate $k_1 = 1 \times 10^{-9}$ and $k_2 = 4.8 \times 10^{-10} e^{-7440/T} \text{ cm}^3/\text{sec}$ best describe the kinetics of HCl and electrons. As the plume cools, clustering of Cl^- with HCl becomes important; we measured a three body rate of approximately $1 \times 10^{-25} \text{ cm}^6/\text{sec}$ at $E/N = 12 \text{ Td}$. The cross section for collisional ionization of potassium and chlorine was found to have a threshold at $0.65 \pm .1 \text{ eV}$ and rise to a value of approximately $8 \times 10^{-18} \text{ cm}^2$ at 1 eV , the highest collision energy measured. A study of $K^+ + e$ recombination in the presence of a krypton buffer gas shows competition between dielectronic, three body, and molecular (KKr^+) dissociation recombination channels. As part of this study the photoionization cross section of excited potassium (4^2P) was measured; the maximum value of the cross section is $6 \times 10^{-17} \text{ cm}^2$ at threshold, $\lambda = 4550 \text{ \AA}$.

1. INTRODUCTION

Pergament and Jensen¹ recently have developed a model for estimating the densities of neutral and charged species for an afterburning plume of a solid fuel rocket as a function of distance along the plume. They have compared the predicted electron densities with experimental radar cross section measurements of electron density and find agreement at least within an order of magnitude. The predictions of the model are dependent on the accuracy with which the rate constants used are known. This report describes the work done under AFOSR 74-2672 toward rate constant measurements for those reactions that Pergament and Jensen pointed out as critical to the model and poorly known; dissociative attachment of electrons in HCl, collisional ionization of potassium and chlorine, and three body recombination of potassium.

The reactions are closely related in the rocket plume, but diverse experimental procedures are required to measure the rates of the reactions. Potassium is a contaminant of the perchlorate oxidizer in some solid fuels, but because of its low ionization potential, it can make an inordinately large contribution to ionization in the plume. The first two reactions above lead to production of a free electron



Three body recombination is a loss mechanism for free electrons



The experiments used were crossed beams of variable energy for (1), a drift tube for (2), and a laser-generated-plasma decay cell for (3).

2. DISSOCIATIVE ATTACHMENT IN HCl.

A drift tube apparatus was assembled to measure the dissociative attachment rate in HCl. A schematic diagram of the apparatus is shown in Fig. 1. Photoelectrons are ejected into the drift region by illuminating a 2 cm^2 sensitized area on the cathode with uv radiation. The photoelectron current in vacuum for a freshly prepared copper iodide coating, or for one sensitized by a glow discharge in hydrogen, approached 10^{-7} A . The emission current dropped upon admission of gas, however, and stabilized at $5 \times 10^{-10} \text{ A}$. A small fraction of the negative ions formed in the 2.6 cm drift space passes through an orifice (diam = 0.34mm) into the mass analysis region.

The negative ions are focussed and accelerated by an arrangement of electrostatic lenses. The lens potentials are set for maximum signal detection and are not changed during the course of a run. The ions selectively transmitted through the quadrupole are then accelerated to an energy of 1 keV as they hit the first dynode of a 20 stage Johnston's Laboratory Multiplier, whose pulse output is amplified and counted by an appropriate scaler.

The relative concentration of HCl to N_2 was $730 \text{ ppm} \pm 3\%$. The total gas pressure was measured by a Texas Instruments quartz spiral manometer, and was in the range from 0.2 - 5 Torr. The range of E/N was from 1 - 30 Td.

A typical scan of the $^{35}\text{Cl}^-$ and $^{35}\text{Cl}^- \cdot \text{H}^{35}\text{Cl}$ count rates as a function of applied electrode voltage is shown in Figure 2. One striking aspect of Fig. 2 is the presence of cluster ions at very low E/N. This effect is due to formation of Cl^- by dissociative attachment from CCl_4 , which is introduced into the system as a result of the process used to sensitize the photocathode. The large rate for dissociative attachment of CCl_4 at low energies (maximum at $\sim 0.02 \text{ eV}$) and rapid decline of the rate increasing electron energy¹¹ are consistent with the observed anomalous cluster formation at low E/N.

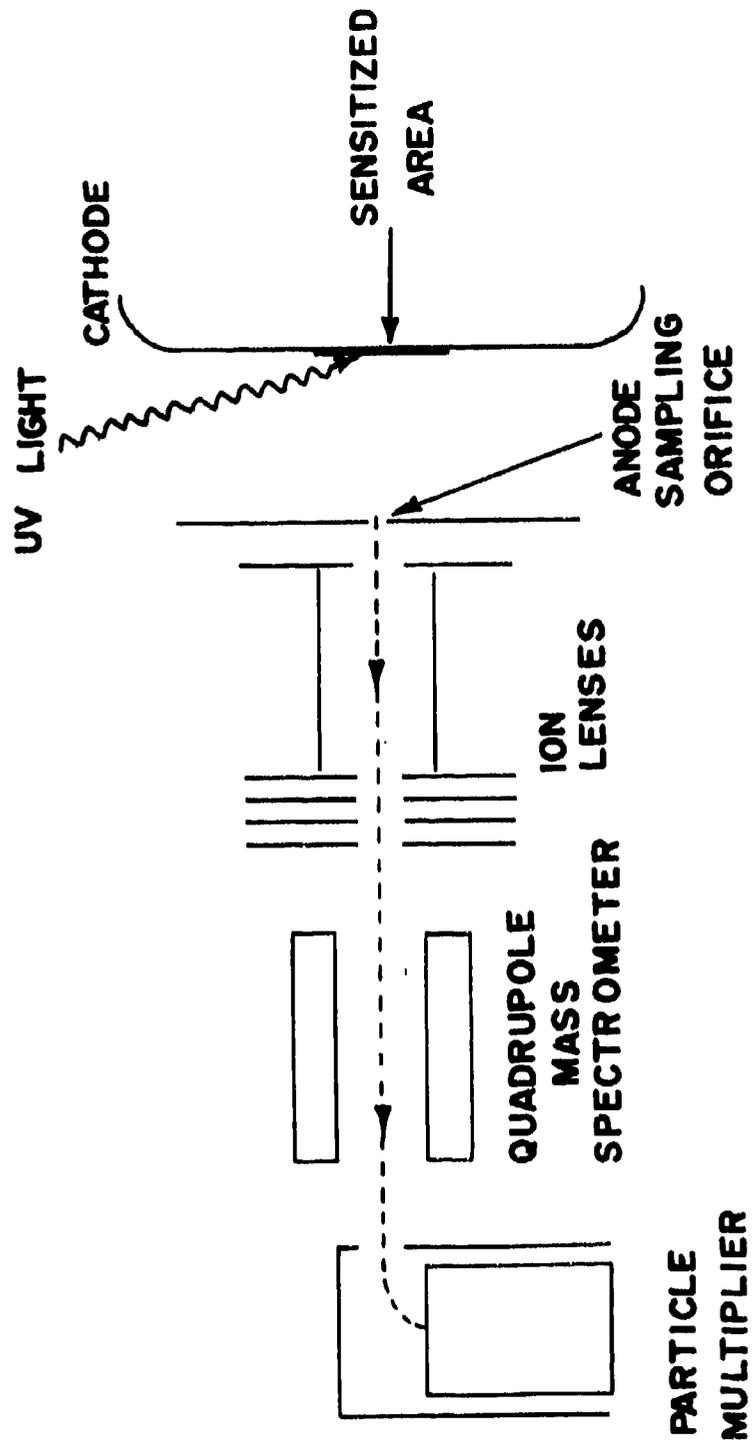


FIGURE 1. Drift tube mass spectrometer apparatus. The pressure in the drift region was typically 1 Torr and in the detection region about 10^{-6} Torr. The particle multiplier is offset from the axis to improve on the signal-to-noise ratio.

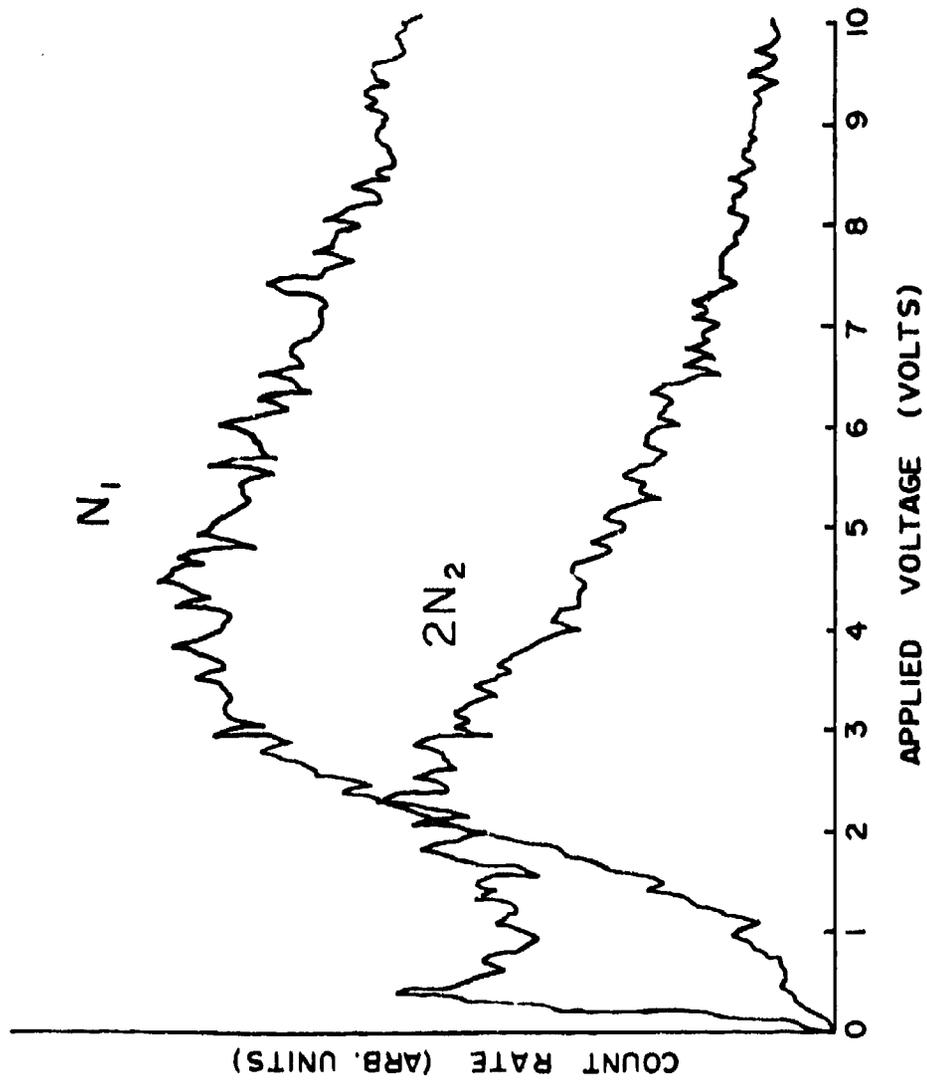


FIGURE 2. Probability for formation of Cl^- -HCl ions from Cl^- ions drifting

1 cm in a gas with partial HCl pressure p.

The appearance of large numbers of Cl^- ions at electron drift energies below the threshold for $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$ made measurement of the rate for this reaction impossible in the apparatus without modification. We were struck with the apparent very large rates for cluster formation and proceeded to measure the rate for formation of the first cluster

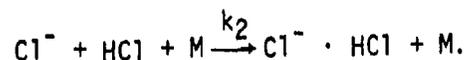


Figure 3 shows the results of taking the ratio of the cluster to primary ion count rates and evaluating n_2 , the attachment coefficient. It is assumed here that both the primary and cluster ions are detected with the same overall probability. (The value of n_2/p expresses the results per unit HCl concentration.) From this data a reaction rate for clustering can be calculated provided a drift velocity for Cl^- in N_2 is known. Since no data are available, the drift velocity was calculated from the polarization limit of Langevin mobility theory. Thus, at $E/N \sim 12 \text{ Td}$, we calculated $k_2 \sim 1 \times 10^{-25} \text{ cm}^6/\text{sec}$ to within a factor of two.

The details of this measurement have been published² and will not be reproduced here.

It should be pointed out that $10^{-25} \text{ cm}^6/\text{sec}$ is a very large rate constant and implies that at low temperature the clustered ion will dominate. As the temperature rises the collisional destruction of the cluster becomes more likely. Kebarle³ has measured the equilibrium rate constant for the process and finds $k_{\text{eq}} = 1$ at a pressure of 1 Torr and a temperature of about 600°K . The temperature dependence is fast; at 1200°K the ion ratio is 1000:1 in favor of the Cl^- . However, some consideration should be given to the possibility that cluster ions may be important in the late plume. Such clustered ions could form nucleation sites for droplet growth.

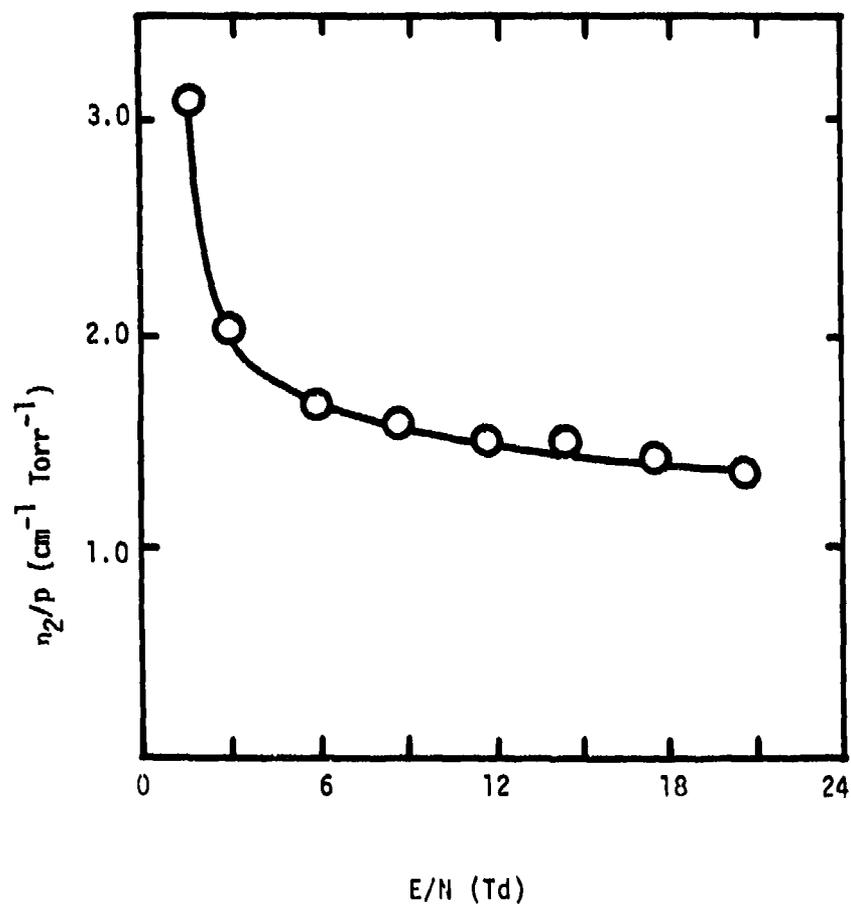
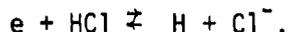


FIGURE 3. Probability for formation of $\text{Cl}^- \cdot \text{HCl}$ ions drifting 1 cm in a gas with partial HCl pressure p .

We believe the following review of the available measurements may provide sufficient information to improve the plume model with regard to



In the forward direction this reaction would be a source of Cl^- and a possible rapid energy loss mechanism for fast electrons. The reverse reaction is relatively fast at plume temperatures and is probably the dominant reaction for the production of free electrons from Cl^- ions in a solid fuel rocket plume with a perchlorate oxidizer.

For non-equilibrium calculations of particle densities in the plume, the individual forward and backward rates must be known. Christophorou⁴ has made measurements of the forward rate which gave anomalously high results at plume temperatures. We have found that this difficulty is likely due to an impurity in the gas. Mass analysis of the ions formed at low E/N shows that they are highly clustered, and we have measured the rate for the formation of the first cluster. Christophorou also measured the cross section for this dissociative attachment in a crossed beam experiment, so that the threshold energy for the process is known. A measurement of the reverse reaction has been made by Fehsenfeld⁵ at 300°K in a flowing afterglow. This low temperature measurement can be extrapolated to several thousand degrees with the results of a theoretical treatment of associative detachment by Herzenberg⁷. The sum of these measurements yields an estimate of the reaction rates which should improve the modeling of the plume electron density profile.

Christophorou's beam experiment gives a threshold for $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$ of 0.64 eV, so that the exponential term in the general rate form, $k = Ae^{-\Delta E/KT}$, becomes $-7440/T$. Figure 4 is a plot of Christophorou's swarm measurement of attachment in HCl in which his measurement of $\alpha\omega$ versus E/P has been transformed to k versus T. The rate in cm^3/sec is related to $\alpha\omega$ by $3.5 \times 10^{16} k = \alpha\omega$. The E/P scale is transformed by means of a table of measured electron mean energy as a function of E/P in nitrogen given by Christophorou⁶, where $T \approx \frac{\langle E \rangle}{k}$. A fit of

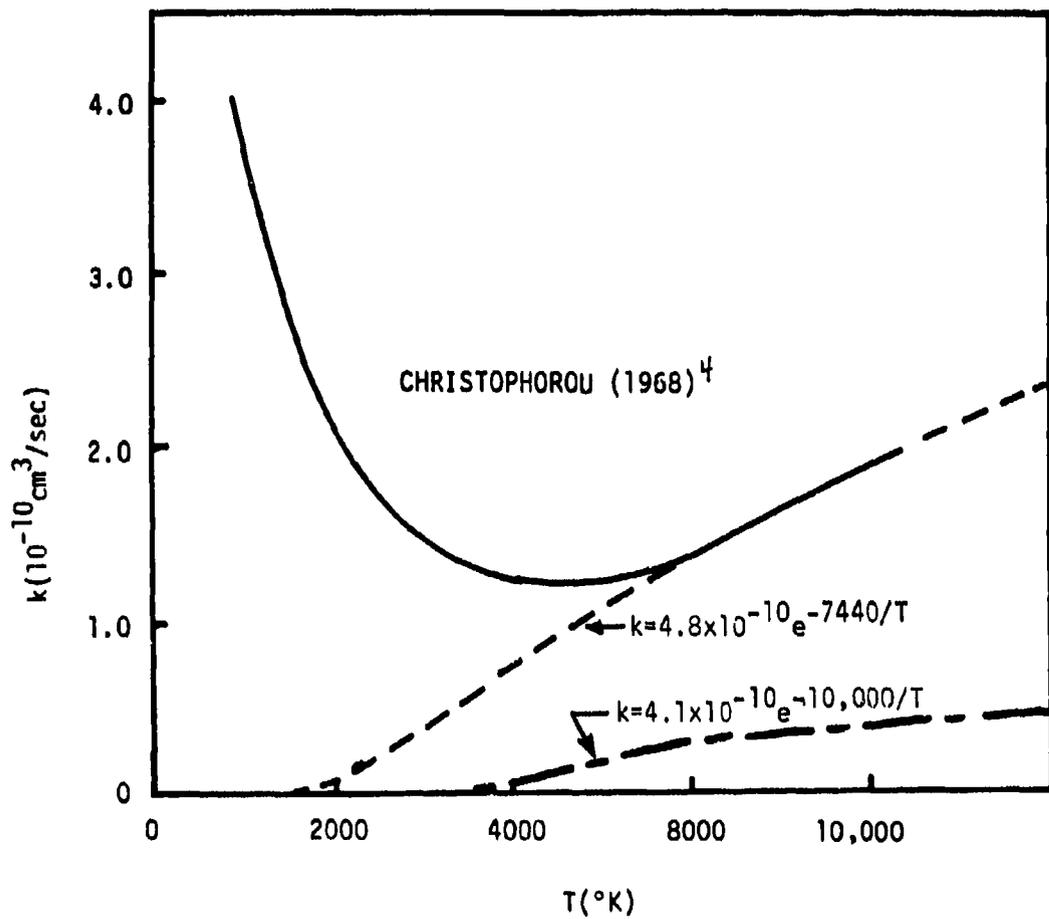


FIGURE 4. Dissociative Attachment in HCl. Solid curve is adapted from swarm measurement by Christophorou⁴. Dashed curve is a plot of $k = 4.8 \times 10^{-10} e^{-7440/T}$.

$k = Ae^{-7440/T}$ to the high temperature end of the curve in Fig. 4 should determine the preexponential constant A. Recent measurements of attachment rates in $\text{HC}\ell$ ^{27,28} indicate that the rapid rise at low temperatures seen in Fig. 4 is not due to attachment to $\text{HC}\ell$, but the cause is still unexplained. The dashed curve is a plot of $k = Ae^{-\Delta E/kT}$ for $A = 5 \times 10^{-10}$ and $\Delta E = 0.64$ eV. The dash-dotted curve is for $A = 1 \times 10^{-10}$ and $\Delta E = .86$ eV which Pergament and Jensen¹ used in their model calculations.

At plume temperatures of the order of 1600°K the exponential term will depress the rate two orders of magnitude so that $k_{\text{forward}} \approx 5 \times 10^{-12}$ cm³/sec. However, the rate of the reverse reaction is about 10^{-9} cm³/sec so that the equilibrium concentrations will strongly favor $e + \text{HCl}$ over $\text{H} + \text{Cl}^-$.

Herzenberg⁷ has shown that for temperatures below a few thousand degrees, the cross section for associative detachment is essentially equal to the Langevin spiraling cross section for collision partners that will form a molecule in which the dissociation energy is larger than the electron affinity of the ion. Essentially all of the collisions result in $A^- + B \rightarrow AB + e$, if $EA(A) + KE < D(AB)$. The Langevin cross section depends on the polarization potential and leads to an expression for the cross section of

$$\sigma = \frac{(2\pi^2 \alpha e^2)^{1/2}}{E^{1/2}}$$

Since the reaction rate is approximately given by:

$$\bar{k} = \bar{\sigma} \bar{v} = \sigma \sqrt{2E/\mu},$$

where α = polarizability, e = atomic charge, E = kinetic energy, and μ reduced mass, the rate is

$$\bar{k} \approx \frac{(4\pi^2 \alpha e^2)^{1/2}}{\mu}$$

and \bar{k} is independent of energy. This leads to a maximum value of the rate constant of $2 \times 10^{-9} \text{ cm}^3/\text{sec}$, assuming a value of α for H atoms of $7 \times 10^{-25} \text{ cm}^3$. Fehsenfeld's measurement of $1.0(\pm .2) \times 10^{-9} \text{ cm}^3/\text{sec}$ at 300°K is a factor of two smaller than this maximum value. Herzenberg's analysis leads to an energy of 0.3 eV (or 3600°K) below which the rate should be constant. For the plume model, then, a constant rate of $1 \times 10^{-9} \text{ cm}^3/\text{sec}$ should be appropriate.

3. THREE-BODY RECOMBINATION IN POTASSIUM

Electron-ion recombination and other collisional processes for systems of alkali vapor in the presence of high pressure (~ 1 atm) noble gas have been of interest in connection with alkali exciplex laser^(8,9) and rocket exhaust plume studies. Electron-ion recombination studies to date, reviewed in ref. 10 and 11, have been mainly concerned with hydrogen, noble gases or atmospheric gases constituents, except for the experiments on Cs^(12,13). Most experiments employed an electrical discharge at low pressure to produce the ionization.

A novel technique was developed to measure the loss rate of ions and electrons of the alkali metals due to 3-body recombination. The technique involves ionization of the potassium by a pulsed laser, two photon process and analysis of the recombination using the time dependence of a line in the recombination spectrum of the potassium. Such a laser initiated plasma has the advantage of high plasma density ($[e] \sim 10^{14} \text{ cm}^{-3}$), a well defined geometry for the plasma region and, importantly, a short (~ 4 nsec) impulse source so that fast decay rates can be measured and diffusion can be neglected.

In this experiment, 4 nsec, 120 μJ laser pulses from a dye laser pumped by a N_2 laser and tuned to the 404 nm ($4^2\text{S}_{1/2} - 5^2\text{P}_{3/2}$) line of K were focussed into a beam of waist ~ 1 mm wide inside an alkali-resistant glass (Corning #1720) cell containing distilled K with Kr of density $[\text{Kr}] = 2.4 \times 10^{19} \text{ cm}^{-3}$ in an oven. Ionization of K was produced by resonance excitation to the $5^2\text{P}_{3/2}$ state followed by photoionization: $\text{K}(5^2\text{P}_{3/2}) + h\nu \rightarrow \text{K}^+ + e$, as shown in Fig. 5. As discussed below, superelastic

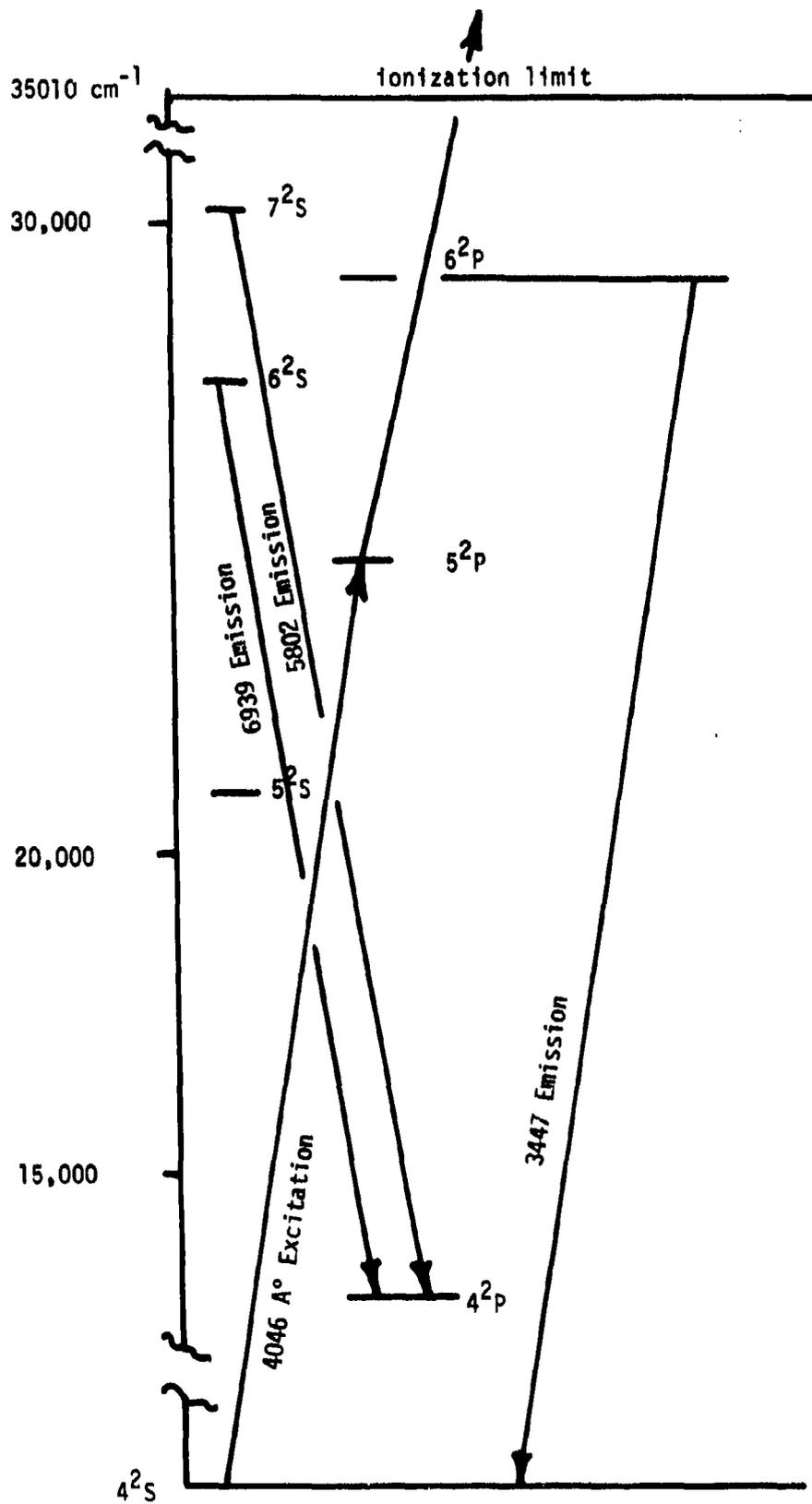


FIGURE 5. Partial energy level diagram for potassium.

atom-electron collisions and electron impact ionization may also contribute as in McIlrath et al⁽¹⁴⁾ and Tam et al⁽¹⁵⁾'s experiments, but the simple stepwise optical excitation and ionization scheme described above is adequate to account for most of the ionization. Fluorescence from the plasma region was detected by a S-20 photomultiplier through a scanning monochromator and the amplified signal was viewed with an oscilloscope or fed to a PAE 160 box-car integrator for averaging and temporal dispersion.

The spectral width of the dye laser pulse was measured to be $\sim 0.03 \text{ nm} \sim 2 \text{ cm}^{-1}$ at 404 nm, which matched fairly well the collision broadened absorption width of $\sim 1 \text{ cm}^{-1}$ per atmosphere of noble gas so that no hole burning in either the laser or the absorption profile occurred. The first resonance absorption step $4^2S_{1/2} \rightarrow 5^2P_{3/2}$, was definitely saturated, followed by rapid collisional mixing $5^2P_{3/2} \leftrightarrow 5^2P_{1/2}$. Photoionization from the 5^2P states was the limiting step. With $\sim 3 \times 10^{14}$ photons per pulse focussed into an area of $\sim 10^{-2} \text{ cm}^2$ and using a photoionizing cross-section of $\sim 10^{-17} \text{ cm}^2$ ⁽¹⁶⁾, the ionization fraction was estimated to be $\sim 1 - e^{-0.3} \sim 0.2$. We observed a linear response versus the laser power at low power and a gradual falloff from linearity at higher powers, roughly consistent with a $\sim 20\%$ saturation at the highest intensity of $\sim 2 \text{ Mw/cm}^2$.

Figure 6 shows the long decay tail of the line fluorescence transient at 580.2 nm ($7^2S_{1/2} - 4^2P_{3/2}$) at a cell temperature of 239°C. The initial fast component was broadened because of the time resolution of the boxcar averager. The long decay tail is of the order of 10 μsec , which is much longer than the excited states' lifetimes. We believe this slow decay is due to a slow energy loss process in electron-ion recombination.

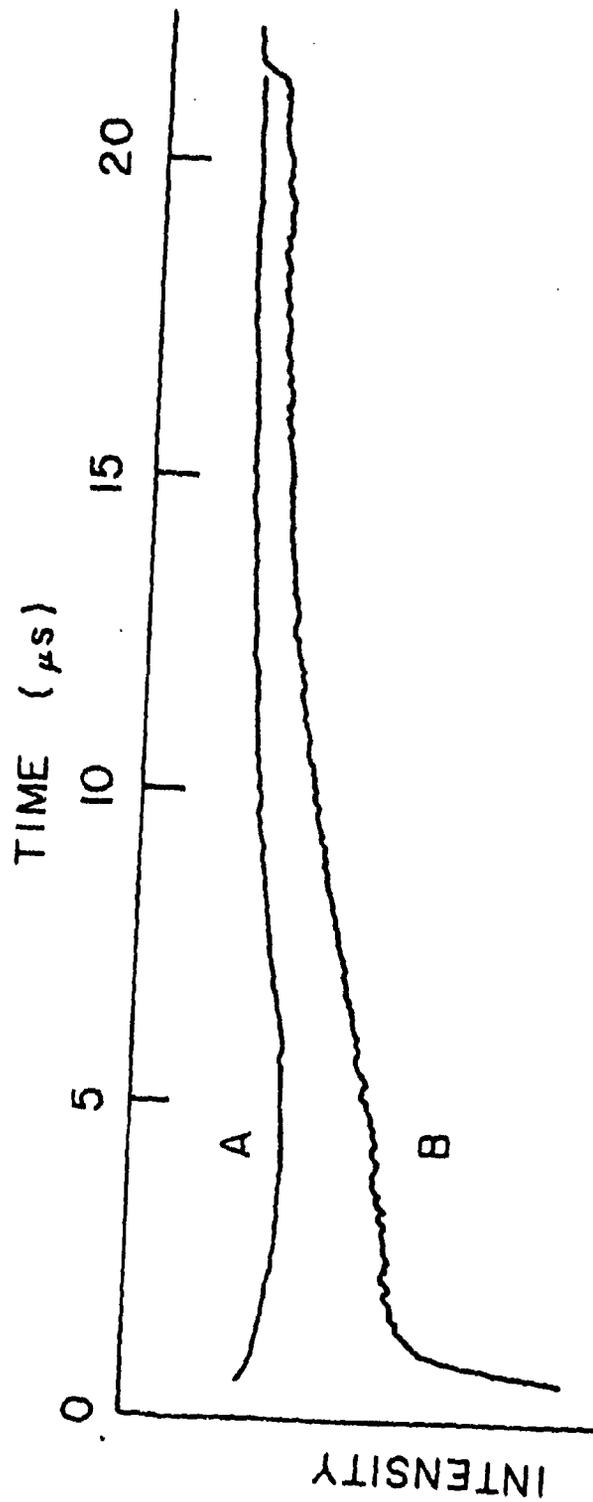


FIG. 6. FLUORESCENCE FROM $K^+ - e$ PLASMA.
Recorder trace of the long decay tail for the 580 nm fluorescence line averaged by a
boxcar integrator. Trace A is the instrument baseline with the laser beam blocked.
Trace B is signal with laser beam on, except for the last segment on far right.

The competing primary electron-ion recombination processes are (1) two electron stabilized recombination: $K^+ + 2e \rightarrow K^* + e$ with a temperature dependence of $\sim T_e^{-4.5}$,^(11,17) (2) third body neutral stabilized recombination: $K^+ + e + Kr \rightarrow K^* + Kr$ with a temperature dependence of $\sim T_e^{-2.5}$,⁽¹⁸⁾ and (3) molecular ion dissociative recombination involving three bodies: $KKr^+ + e + Kr \rightarrow K^* + 2Kr$.⁽¹⁹⁾ The two body dissociative recombination process: $KKr^+ + e \rightarrow K^* + Kr$ is considered to be insignificant due to lack of curve crossing in alkali-noble gas systems.⁽²⁰⁾ At electron temperatures of 1800-3500°K in this experiment, process (3) could be important compared to (1) and (2). Dissociative recombination with K_2^+ is negligible. Using an equilibrium constant K_{eq} of $\sim 10^{-20} \text{ cm}^3$, we have $[K_2^+]/[K^+] = K_{eq}[K] \sim 10^{-20} \times 6 \times 10^{14} \sim 6 \times 10^{-6}$. If we use room temperature ratio coefficients of $k_{DR} \sim 10^{-7}, \text{ cm}^3 \text{ sec}^{-1}$ ⁽²³⁾ for K_2^+ dissociative recombination and $k_1 \sim 10^{-21} \text{ cm}^6 \text{ sec}^{-1}$ ⁽²⁴⁾ for process (1), the rate ratio of the two processes is $k_{DR}[K_2^+][e]/k_1[K^+][e]^2 \sim 10^{-7} \times 6 \times 10^{-6}/10^{-21} \times 2 \times 10^{14} \sim 3 \times 10^{-6}$. At elevated electron temperatures, this ratio is larger, but is still $\ll 1$ for our experimental conditions.

This work has been published²⁶ and the interested reader is referred to the published article for further details.

It was originally intended that the laser production of the $K^+ - e$ plasma would be done as a one-step process using a Xenon ion laser. The development of this laser was completed partly under the support of this grant and a descriptive article has been published²¹. Therefore, the following description is abbreviated.

The laser has an active length of 120 cm. An additional 25 cm is provided by the internal electrodes to the Brewster windows. The electrodes are high-current indium cathodes that were constructed by melting indium metal around

Kovar electrode feedthroughs. The inside tube diameter is 4 mm. One mirror of 15 mm diameter and nominally of 100 percent reflectivity for the standard argon-ion laser lines has a radius of curvature of 3 m. The output mirror is composed of flat, broadband reflectors with either 20, 50, or 80 percent reflectivity.

In Table IV is listed the measured peak power output for the eight observed lines, when the system is optimized for maximum total power output. It should be mentioned that the pulse width and peak power for each line depend on both the discharge current density and the pressure of the xenon gas.

TABLE IV

<u>Wavelength</u> <u>(Å)</u>	<u>Peak Power</u> <u>(watts)</u>
5956	110
5395	480
5353	800
5280	680
5190	250
4954	800
4306	50

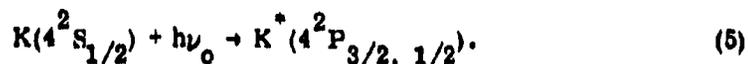
The large gain of the laser transitions suggest that relatively lossy elements may be inserted in the cavity. Intracavity frequency doubling of the stronger lines in the xenon laser should be easily accomplished with an ADP crystal. The doubled frequency of the transitions is greater than the frequency required to photoionize directly the potassium atoms in the ground state.

By using typical photoionization cross sections, it can be easily shown that a significant fraction of the potassium atoms in a beam can be photoionized. Use of the laser makes it possible to produce the ions in a field-free region with an intense brightness.

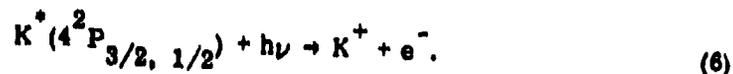
Improvements in available power levels permitted use of the N_2 laser pumped dye laser for the two photon scheme described above, and the doubling of the output of the Xenon laser was not attempted.

4. TWO-STEP PHOTOIONIZATION OF POTASSIUM ATOMS.

Because high densities of excited atoms and molecules may exist in the high temperature region of rocket exhaust plumes, there is an interest in describing reactions involving these excited states. One reaction of interest, which represents a source of free electrons in the plume, is the photoionization of excited potassium atoms. It was also of interest to us because of our desire to use such a method to produce the K^+, e^- plasma for the recombination experiment. In this experiment, a potassium resonance lamp was used to excite a neutral beam of ground state potassium in the reaction



The reaction of interest then involves the subsequent photoionization of K^* ;



The threshold for reaction (6) for the unresolved P state is about 4550\AA and is indicated by the vertical dashed line in Fig. 7. The dashed line has been drawn through the data points to show the approximate shape of the cross section down to 2500\AA . Further details are given in Phys. Rev. A, 17, 1543 (1978)²².

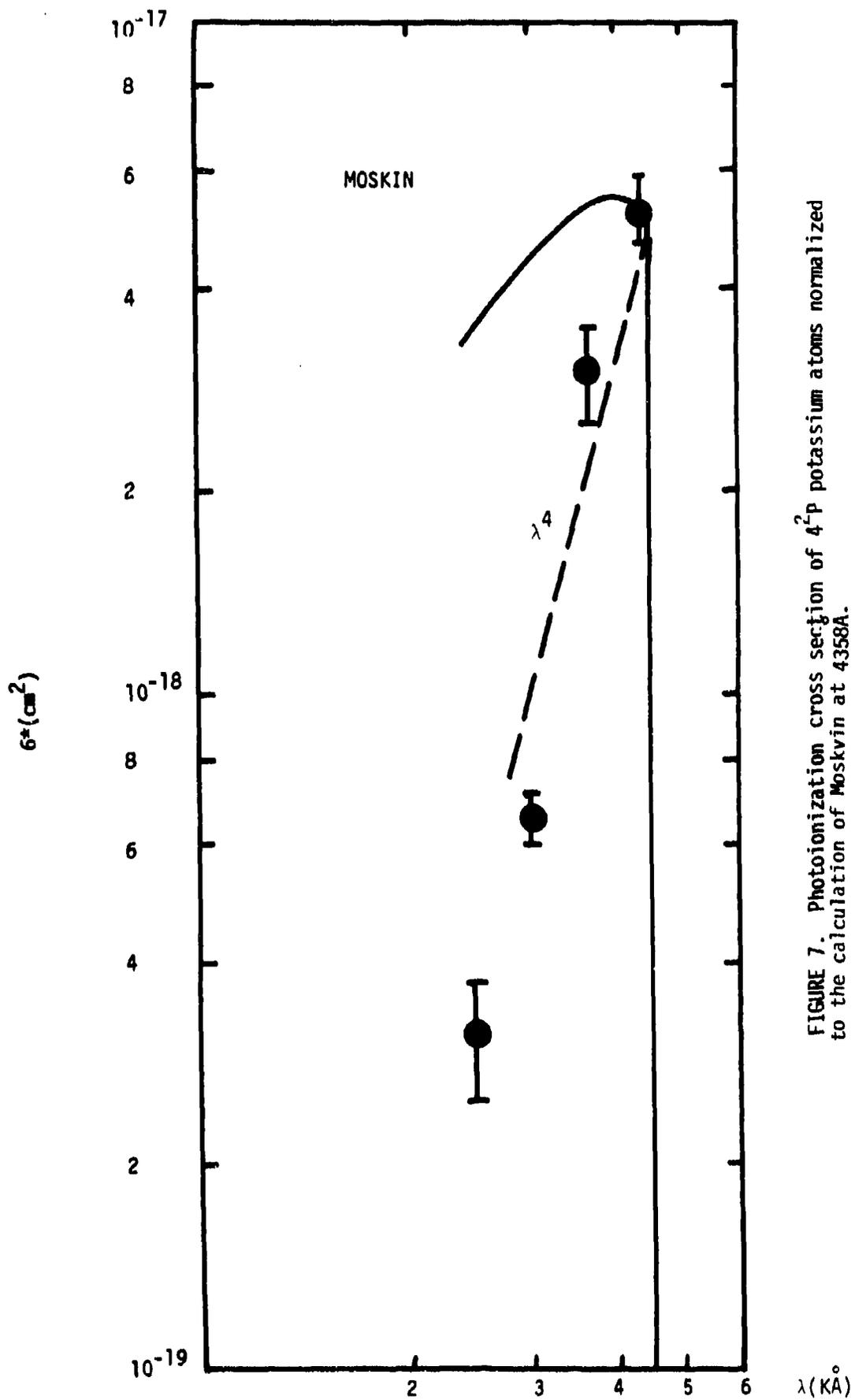


FIGURE 7. Photoionization cross section of 4^2P potassium atoms normalized to the calculation of Moskin at 4358A.

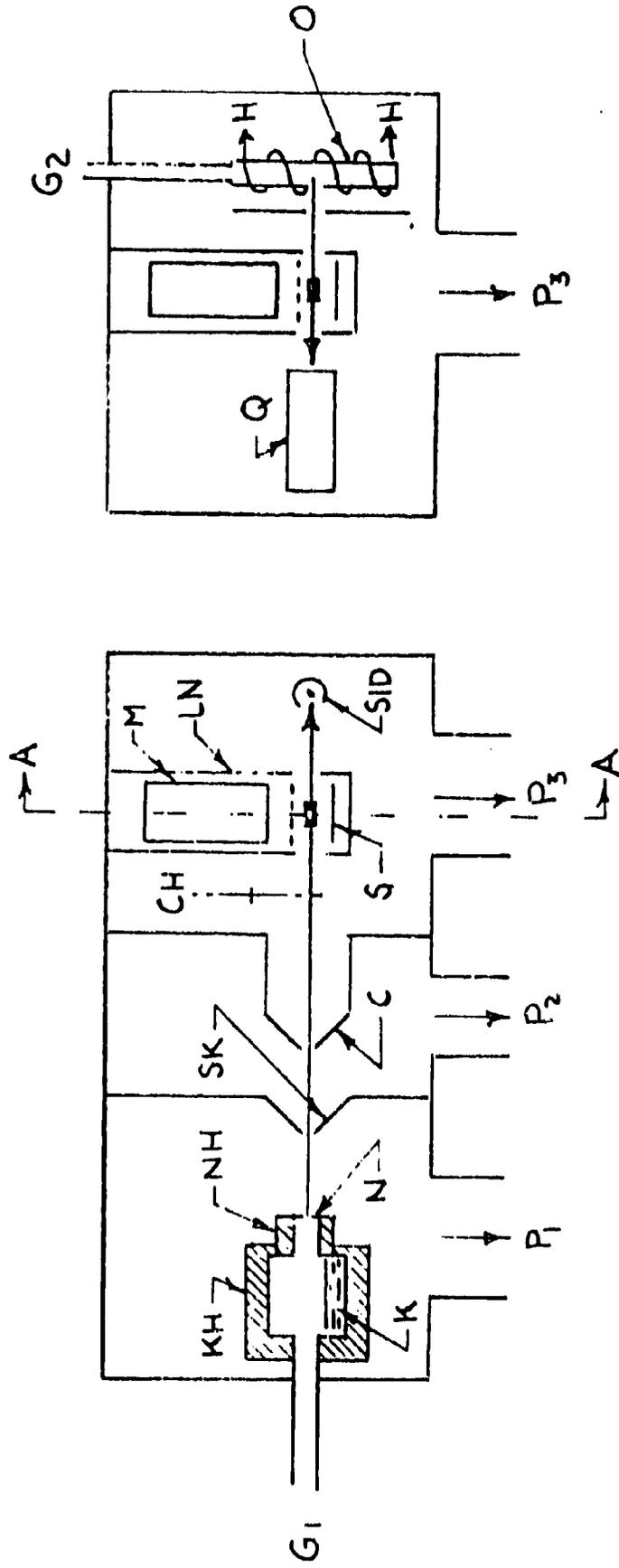
5. COLLISIONAL IONIZATION

The collisional ionization of potassium and chlorine, $K + Cl \rightarrow K^+ + Cl^-$, may be an important reaction in the production of free electrons in the plasma. Once Cl^- is formed, the rapid associative detachment reaction, $Cl^- + H \rightarrow HCl + e$, produces free electrons. Plume modeling attempts have underestimated the electron density in plumes containing a potassium impurity and it was suspected that the reaction rate used for collisional ionization with atomic chlorine was too small¹.

The need for an experimental determination of the cross section is evident from the disparate result of three recent theoretical estimates of it. Olsen²² has used quantum close coupling techniques to calculate the cross section from threshold to a few eV. The reaction rate derived from this calculation for temperatures characteristic of the plume is of the order of three times higher than would be predicted by radar attenuation measurements quoted by Pergament and Jenson. A Landau-Zener curve crossing calculation by Faist and Levine²³ gives a result about one order of magnitude lower than Olsen's. The same treatment gave cross sections in good agreement with experiment for Na-I collisional ionization. A third estimate by Arora²⁴ is based on a Born approximation and yields a cross section two orders of magnitude lower than Olsen when extrapolated to threshold energy.

We have made a measurement of the cross section for the reaction using crossed atomic beams in the apparatus shown in Fig. 8. As discussed in earlier reports, the potassium vapor in the oven is forced out of the heated nozzle by a supersonic stream of hydrogen. A beam of fast potassium atoms is formed which is varied in energy by changing the nozzle temperature and the H_2/K gas mixture ratio.

The potassium beam intersects an atomic chlorine beam formed by thermal dissociation in a resistance heated mullite oven. Potassium ions formed in



SIDE VIEW

SECTION A-A

Fig. 8. NOZZLE BEAM APPARATUS. Helium (G_1) flows into potassium oven (KH) which forms reservoir for potassium (K). The nozzle (N) is separately heated (NH). Skimmer (SK) and collimator (C) form beam which is chopped (C) and monitored by a surface ionization detector (SID). Ions formed at intersection of beams are extracted by sweep plates (S) and counted by cooled (LN) multiplier (M). Section AA shows Cl atom oven (O) with heater (H). Fraction of atoms is monitored by mass spectrometer (Q).

the intersection region are extracted by suitable grids and counted by an electron multiplier.

The beam densities were low enough so that single collision approximations for the cross section are applicable, therefore

$$\sigma = \frac{I(K^+)}{I(K) [Cl] l}$$

when $I(K^+)$ is the current of K^+ produced from the reaction, $I(K)$ is the current of neutral potassium atoms passing through the chlorine beam, $[Cl]$ is the density of chlorine atoms, and l is the interaction length. The chlorine density was estimated for effusive flow conditions from an orifice of known size and known stagnation pressure. The fraction of the Cl_2 gas dissociated as a function of oven temperature was based on measurements of the Cl/Cl_2 ratio in the beam using a mass spectrometer. There was a rather large uncertainty in this measurement and consequently the chlorine density could be in error by a factor of two in absolute magnitude. This would give the same factor of two uncertainty in the absolute magnitude of the final cross section, however, the relative values are much better than this.

The potassium beam was formed by vaporizing potassium in the nozzle oven, mixing it with hydrogen [$P(K)/P(H_2) < 1/100$] and letting it flow through the nozzle. In principle the K would reach nearly the free jet velocity of the H_2 , however, in our experiment the nozzle orifice was large enough (to reduce clogging) that the total pressure was low and significant slippage occurred. We estimated the velocity of the K beam from measurements of H_2 - Ar mixtures ($M_{Ar} = 40$; $M_K = 39$) using a time-of-flight technique which involved a high speed slotted wheel to form the gas pulse and a mass spectrometer detector. The possible errors in this measurement could lead to a ± 0.1 eV error in the energy scale of the cross section vs. energy.

The energy scale is center of mass energy for the collision:

$E = 1/2 \mu V_{rel}^2$, where μ is the reduced mass and $V_{rel}^2 = V_{Cl}^2 + V_K^2$ since the intersection is at normal incidence.

The current density of the K beam was measured with a surface ionization detector of known area and an assumed efficiency of ionization of 100%.

The signal ions were collected by an electron multiplier operated in the current mode. The area of the multiplier was large compared to the area of intersection of the K and Cl beams, so the cross-sections plotted assume 100% collection efficiency. The gain of the multiplier was subject to degradation by exposure to the chlorine vapor. The gain of the multiplier was measured periodically by comparing the multiplier in count mode and current mode in response to a weak ion current. Care was taken to eliminate background current by flagging off the beams. The threshold for production of ions in a K + Cl₂ collision is 1.9 eV and was not expected to contribute to the signal. No signal could be seen with the oven cold (all Cl₂ in target beam).

Figure 9 shows the measured cross section over the energy range near threshold. The velocity spread in the beam is about $\pm 10\%$ FWHM so that the energy spread of the beam is about $\pm 20\%$. The experiment therefore is not capable of resolving the structure in the threshold of the cross section due to the splitting of the 3/2 and 1/2 states. The solid curve is a plot of the expected cross section from Olsen in which the 3/2 and 1/2 states have been weighted 2:1 as would be expected for a statistical distribution of states.

This work is being prepared for publication.

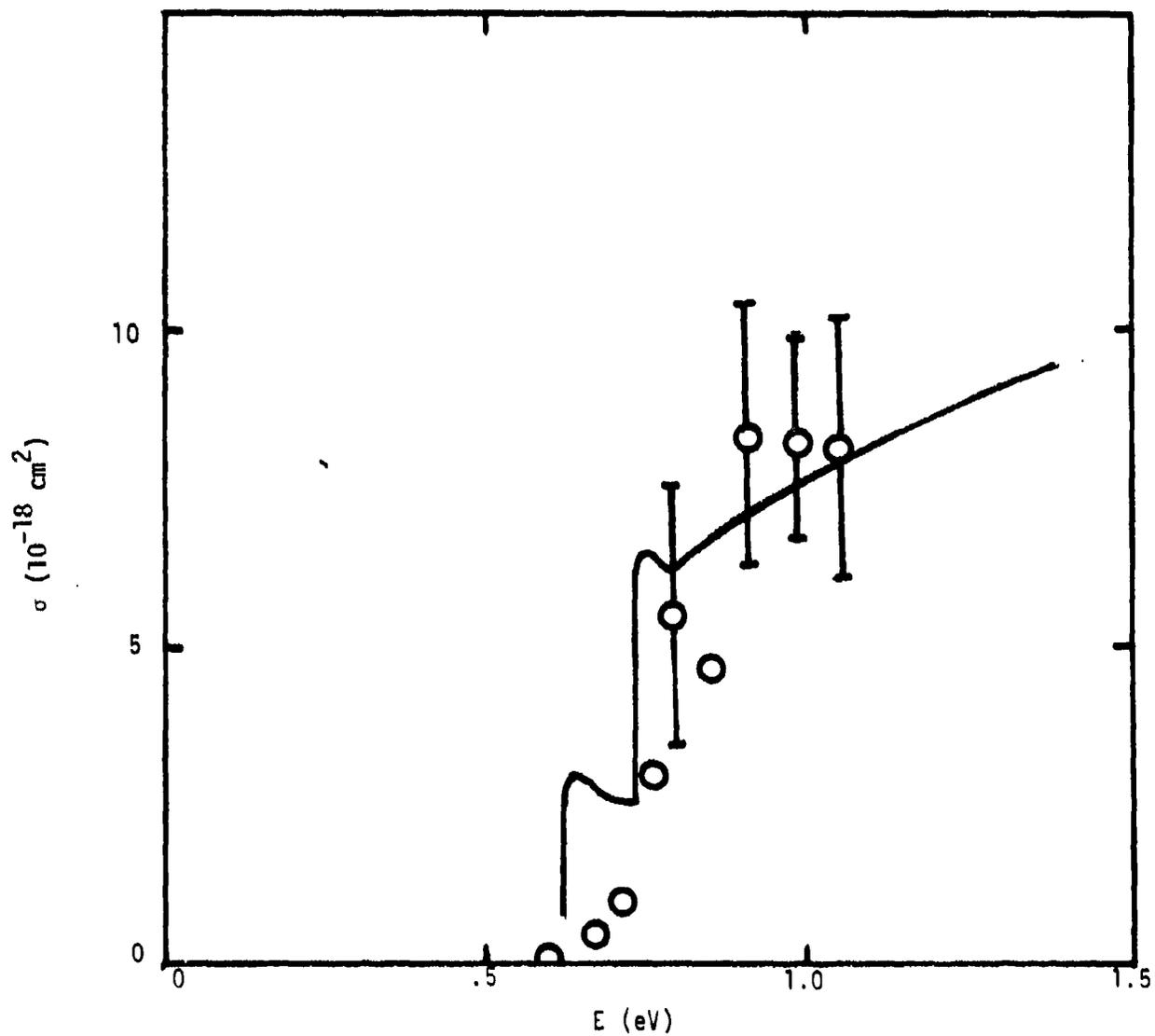


FIG. 9. Cross section for $K + Cl \rightarrow K^+ + Cl^-$ versus energy. The error bars represent scatter in the data only. The solid curve is adapted from Olsen²³.

REFERENCES

1. D. E. Jensen and H. S. Pergament, *Comb. and Flame* 17, 115 (1971).
2. R. J. Corbin, Kaare J. Nygaard, W. R. Snow, and Laird D. Schearer, *J. Chem. Phys.*, 68, 4373 (1978).
3. R. Yamdagni and P. Kebarle, *Can. J. Chem.* 52, 2449 (1974).
4. L. G. Christophorou, R. N. Compton, and H. W. Dickson, *J. Chem. Phys.* 48, 1949 (1968).
5. F. C. Fehsenfeld, C. H. Howard, E. E. Ferguson, *J. Chem. Phys.* 58, 5841 (1973).
6. A. A. Christodoulides and L. G. Christophorou, *J. Chem. Phys.*, 54, 4691 (1971).
7. A. Herzenberg, *Phys. Rev.* 160, 80 (1967).
8. A. V. Phelps, "Tunable Gas Lasers Utilizing Ground State Dissociation," JILA Report 110, Univ. of Colorado, Boulder, Colorado.
9. G. York and A. C. Gallagher, "High Power Gas Lasers Based on Alkali-Dimer A-X Band Radiation," JILA Report 114, Univ. of Colorado, Boulder, CO.
10. D. R. Bates and A. Dalgarno, in "Atomic and Molecular Processes", ed. D. R. Bates, Academic Press, New York, 1962.
11. L. M. Biberman, V. S. Vorobev and I. T. Yakubov, *Soviet Physics, Uspekhi*, 15, 373 (1973).
12. B. Sayer, J. C. Jeannet, J. Lozinoot and J. Berlaude, *Phys. Rev. A*, 8, 3012 (1973); G. Gonsset, B. Sayer and J. Berlaude, *Phys. Rev. A*, 16, 1070 (1977).
13. Yu. M. Aleskovskii, *Soviet Phys. JETP* 17, 570 (1963).
14. T. B. Lucatorto and T. J. McIlrath, *Phys. Rev. Lett.* 37, 428 (1976); T. J. McIlrath and T. B. Lucatorto, *Phys. Rev. Lett.* 38, 1390 (1977).
15. A. C. Tam and W. Happer, *Optics Communications*, 21, 403 (1977).
16. K. J. Nygaard, R. E. Hebner, Jr., J. D. Jones and R. J. Corbin, *Phys. Rev. A*, 12, 1440 (1975).
17. E. Hinnov and J. G. Hirschberg, *Phys. Rev.* 125, 795 (1962).
18. J. J. Thompson, *Philos. Mag.* 47, 337 (1924); L. P. Pitaevskii, *Soviet Phys. JETP*, 15, 919 (1962).

19. J. N. Bardsley, private communications.
20. M. Biondi, private communications.
21. L. D. Schearer, IEEE J. Quant. Elec., QE-11, 935 (1975).
22. K. J. Nygaard, R. J. Corbin, and J. D. Jones, Phys. Rev. A, 17 1543 (1978).
23. R. E. Olsen, submitted to Combustion and Flame (1977).
24. M. B. Faist and R. D. Levine, J. Chem. Phys. 64, 2953 (1976).
25. D. Arora, J. E. Turner, and P. G. Khubchandani, Phys. Rev. A, 14 2089 (1976).
26. L. Lam and L. D. Schearer, Chem. Phys. Lett. (to be published).
27. A. A. Christodoulides, R. Schumacher, and R. N. Schindler, J. Phys. Chem. 79, 1904 (1975).
28. F. J. Davis, R. N. Compton, and D. R. Nelson, J. Chem. Physics, 59, 2324 (1973).