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DEVELOPMENT OF A SUPERSONIC ATOMIC OXYGEN NOZZLE BEAM SOURCE FOR CROSSED BEAM SCATTERING EXPERIMENTS

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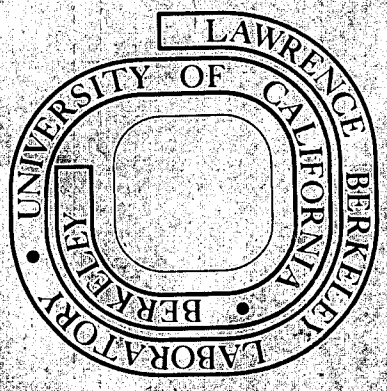

DISCLAIMER

DEVELOPMENT OF A SUPERSONIC ATOMIC OXYGEN NOZZLE BEAM SOURCE FOR CROSSED BEAM SCATTERING EXPERIMENTS

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ABSTRACT

A high pressure, supersonic, radio frequency discharge nozzle beam source has been developed for the production of intense beams of ground state oxygen atoms. An efficient impedance matching scheme has been devised for coupling the radio frequency power to the plasma as a function of both gas pressure and composition. Techniques for localizing the discharge directly behind the orifice of a water-cooled quartz nozzle have also been developed. The above combine to yield an atomic oxygen beam source which produces high molecular dissociation in oxygen seeded rare gas mixtures at total pressures up to 200 torr: 80-90% dissociation for oxygen/argon mixtures and 60-70% for oxygen/helium mixtures. Atomic oxygen intensities are found to be greater than 10^{17} atom sr^{-1} sec^{-1}. A brief discussion of the reaction dynamics of O + ICl → IO + Cl is also presented.

I. INTRODUCTION

The reactions of ground-state oxygen atoms are of considerable interest and importance due to their fundamental role in combustion processes and atmospheric chemistry. A high pressure, supersonic, radio frequency discharge nozzle beam source has been developed in order to determine the products and reaction dynamics of $O(^3P)$ reactions in crossed molecular beam experiments. Our motivation for constructing this beam source is that supersonic nozzle sources characteristically produce beams of greater intensity, and have lower translational velocity dispersion than effusive sources.[1] Also the translational energy of the atomic beam can be varied using the seeded beam technique.[2]

The production of a stable and efficiently coupled high pressure discharge for the generation of atomic species is much more difficult than the production of a low pressure (~1 torr) discharge. Impedance matching of the plasma to the radio frequency power as a function of both gas pressure and composition is required. Plasma localization directly behind the

orifice must also be achieved in order to limit atomic recombination before the expansion. Finally, sufficient cooling of the nozzle in order to prevent meltdown and to limit wall recombination - while not interfering with power coupling to the plasma - is mandatory. The beam source described in this paper meets all of the above criteria. A boron nitride skimmer is used and is found to be completely stable with respect to the atomic oxygen beam.

Miller and Patch[3] have previously reported an atomic oxygen radio frequency discharge beam source with ~35% dissociation at 60 torr for a 5% O_2/He mixture. Grice[4] has recently reported a microwave discharge source with dissociation characteristics similar to those of Miller and Patch. The impedance matching scheme, nozzle construction and, in particular, plasma localization techniques described in this paper permit a higher degree of molecular dissociation to be achieved at total pressures of 200 torr. A brief description of the reaction dynamics of $O + ICl \rightarrow IO + Cl$ is included in the latter part of this paper as evidence of this beam source's applicability to crossed beam reactive scattering studies.

II. SOURCE CONSTRUCTION AND OPERATION

A cross-sectional view of the source mounted in the differential pumping region of our universal scattering machine is shown in Fig. 1, with an enlarged view of the internal source components and nozzle tip appearing in Fig. 2. Low conductivity water is used as the nozzle coolant and is flowed through the concentric quartz water jacket at a rate of 10 cm^3/sec. Use of regular conductivity water as the coolant is precluded due to excessive radio frequency power loss to the water.

The orifice is blown on a spinning glassblowers lathe in an operation requiring two people. One person locally heats the tip of the quartz nozzle and actually blows the hole while the other simultaneously views the hole diameter with a 60X power measuring microscope. Hole size readjustment can be carried out with this procedure to within 0.005 mm of the desired diameter. When an orifice of the desired size is achieved its straightness is always checked by placing a small positive pressure of oxygen behind the nozzle, which produces a small oxygen jet at the orifice. This jet is then ignited with a small torch flame while the entire nozzle is rotated on the lathe. If any wobble or precession of the flame jet is detected the orifice is reblown. Nozzle diameters are typically 0.075 mm for oxygen/argon discharges and 0.200 mm for oxygen/helium discharges. Nozzle preparation is completed by briefly etching the inner quartz tube with a dilute solution

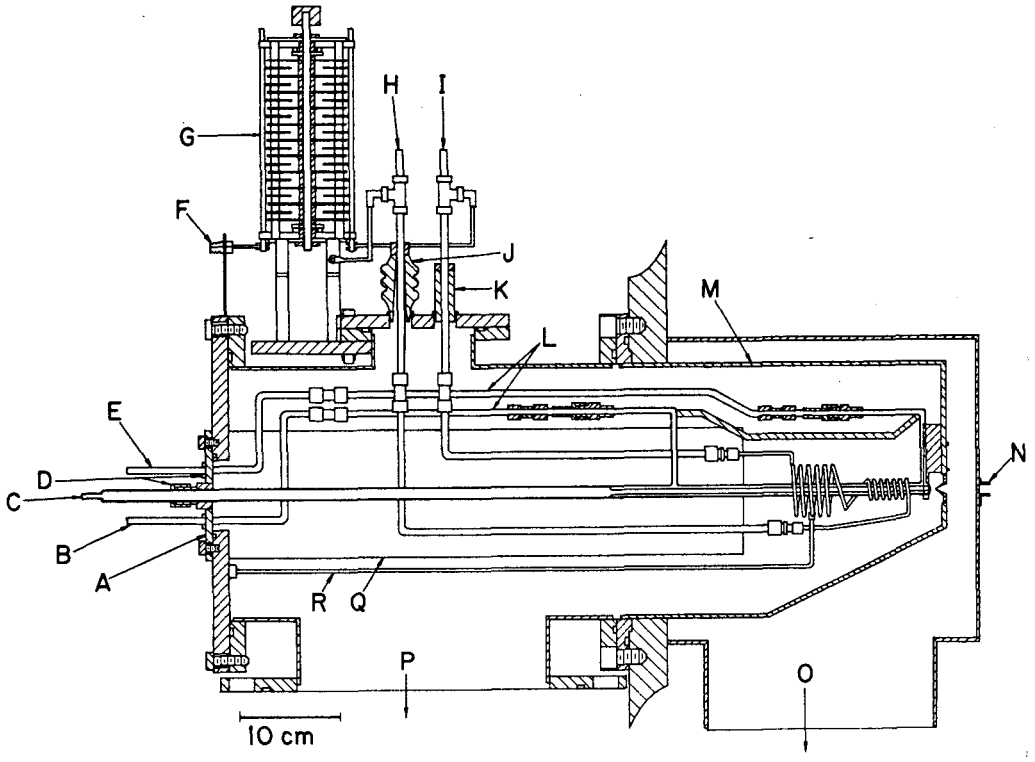

Fig. 1. Sectioned view of the plasma beam source mounted in a differentially pumped chamber. A-Lucite insulating flange. B-Nozzle coolant return. C-Quartz nozzle gas inlet. D-Cajon ultra-torr fittings. E-Nozzle coolant inlet. F-RF power input from RG-213/u coaxial cable. G-Variable air capacitor. H-Coupling coil coolant outlet. I-Coupling coil coolant inlet. J-Ceramic feedthrough for RF return and coil coolant. K-Ceramic feedthrough for RF input and coil coolant. L-Poly-Flo tubing sections. M-Stainless steel source chamber. N-Plates for 5000 V/cm ion deflecting field. O-1200 ℓ/sec diffusion pump, differential region. P-4200 ℓ/sec diffusion pump, source region. Q-Epoxy resin mechanical support. R-Electrical ground wire. Not shown: Wire mesh RF shielding which covers the air capacitor/RF feedthrough assembly.

of hydrofloric acid. This is believed to inhibit atomic recombination at the walls of the tube.

The radio frequency power (hereafter, RF) is generated by a Viking radio transmitter which can deliver a maximum output of approximately 150 watts over a continuously variable frequency range of several hundred kilohertz centered at a frequency of 14 megahertz. A linear amplifier can also be operated to produce RF levels in excess of 1000 watts. However,

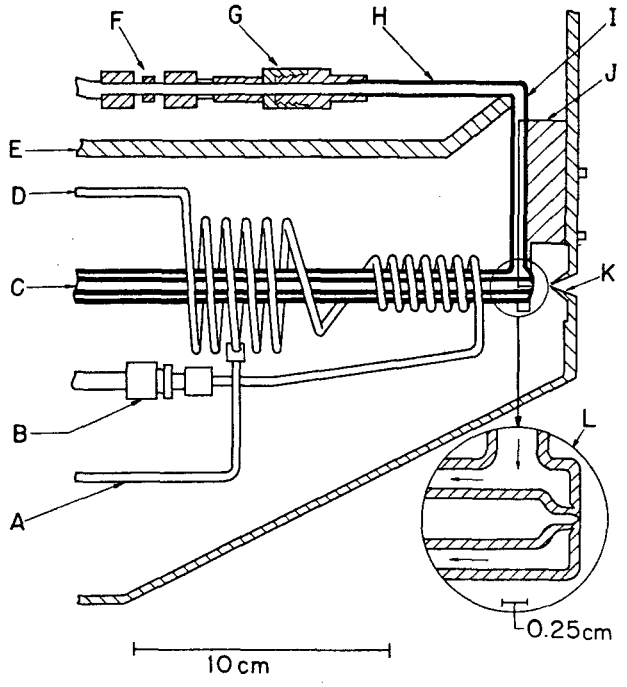

Fig. 2. Sectioned view of the internal source components. A - Variable ground tap. B - Swagelock reducer. C - Water-cooled quartz nozzle. D - Coupling coil. E - Quartz support rod for water inlet/outlet assembly. F - Swagelock union joining copper and Polyflow tubing. G - Cajon VCO fitting. H - Kovar-pyrex section. I - Graded seal, pyrex to vycor. J - Aluminum support block at electrical ground. K - Boron nitride skimmer, 0.88 mm. L - 4X enlargement of nozzle tip; arrows indicate low conductivity water flow direction.

power levels on the order of only 100-200 watts seem to be adequate for atomic oxygen generation. The plasma coupling tank coil and capacitor can be clearly seen in Fig. 1. The variable air capacitor (0-75 pf) is mounted outside of the vacuum to facilitate initial frequency matching of the tank circuit to the electronics. A grid-drip meter is used for this preliminary frequency tuning of the beam source.

We have developed a novel impedance matching scheme which enables the source to routinely operate at a standing wave ratio (SWR) of less than 1.05:1. Figure 3 presents a schematic outline of the impedance matching circuitry, which can best be viewed in two stages. First, a variable ground tap on the tank coil (Fig. 2, A) produces a large stepdown of the plasma impedance, as seen by the final RF amplifier, to approximately 50Ω. This allows the RF power to be delivered by coaxial cable (RG 213/u) to the beam source from a remote location. Then a PI-network,[5] series capacitor arrangement is used to critically

IMPEDANCE MATCHING

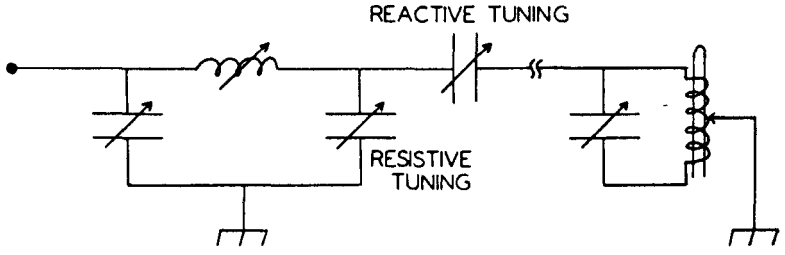

Fig. 3. Schematic outline of the impedance matching circuitry.

tune the impedance match. This circuit is capable of remotely tuning out any reactive or resistive impedances presented to the RF electronics by the plasma coupling tank circuit. Impedance variation occurs when the plasma is first started, and as the pressure is raised from 1 torr to the desired value-usually 200 torr. Tuning of the impedance matching circuitry is greatly facilitated by continuous use of an inline RF wattmeter and a standing wave ratio bridge. Power coupling to the plasma is extremely efficient (> 99%) and power levels must be limited in order to avoid meltdown of the quartz nozzle. The beam source is doubly interlocked to protect both the nozzle and the electronics. The nozzle coolant flow rate is monitored with a waterwheel flowswitch, which turns off the RF power if the coolant rate drops belows a preset point. The electronics are protected by a fast electronic switch which continuously monitors the SWR level.

Finally, we have been successful in localizing the plasma directly behind the orifice. This is of critical importance in order to achieve high molecular dissociation in a high pressure discharge. This localization is achieved by placing around the nozzle tip (outside of the water jacket, not along the front surface of the nozzle) a carefully shaped, electrically grounded block of aluminum (Fig. 2, J). We observe that the discharge changes from an inductively coupled plasma at low pressures to a capacitively coupled discharge at high pressures - with this coupling occuring between the front, small diameter coil turns and the grounded aluminum block. As this capacitive coupling becomes stronger the plasma localizes towards the front of the discharge tube. The tank coil has also been differentially wound (Fig. 2, D) in order to further localize the plasma and increase its energy density. The first seven coil turns nearest the orifice are of 1.37 cm I.D. while the six further coil turns are of 5.08 cm I.D. These larger turns decouple from the plasma as the pressure is increased, and

thus the energy density of the (localized) plasma is considerably increased. The coil is constructed of 0.32 cm O.D. copper tubing and was wound on a low-speed lathe. One other construction point should also be mentioned here - the entire tank circuit is floated with respect to electrical ground. This is required if this coupling scheme is to be effectively used.

The beam source is pumped by a 25.4 cm diffusion pump (4200 l/sec). This large pumping speed is required to maintain the source pressure below 7×10^{-5} torr while running any oxygen/argon mixtures. For higher background pressures the RF decouples from the nozzle and a glow discharge of the entire source region occurs. This glow discharge problem is what ultimately constrains the orifice size to 0.075 mm diameter for gas mixtures containing argon. A larger diffusion pump will soon be added to this beam source with hopes of increasing nozzle throughput - allowing higher Mach numbers and intensities to be obtained. Fluxes are presently 10^{17} - 10^{18} atoms sr^{-1} sec^{-1}.

III. BEAM CHARACTERIZATION

The beam characteristics for four oxygen/rare gas mixtures are listed in Table I. The time-of-flight apparatus used in these studies consisted of a 17.78 cm diameter aluminum disk having four equally spaced 1 mm slots around its circumference. The disk was rotated at either 300 or 350 Hz. The detector aperature was narrowed to 0.125 mm diameter, and the distance between the TOF disk and the electron bombardment ionizer was 18.4 cm. The ionizer/quadrupole mass spectrometer has previously been described in detail.[6] A 256-channel scaler interfaced to an on-line minicomputer was used to record signal intensity as a function of flight time. The scaler channel width was set at 2.2 μs for the helium mixtures and 4.2 μs for the argon mixtures. Corrections for instrumental broadening and ion flight times have been included in these reported values.

The molecular dissociation was calculated with the following two equations:

$$R = \frac{N_o}{N_{o_2}} = \frac{(\sigma_D/\sigma_{o_2})}{\eta} \left(\frac{\sigma_{o_2}}{\sigma_o}\right) \left(\frac{I_o - \eta I_{o_2}}{I_{o_2}}\right) \qquad (1)$$

$$\text{Percent Dissociation} \simeq \frac{R}{R+2} \qquad (2)$$

where I_o and I_{o_2} are the experimentally observed mass 16 and 32 number densities, η is the observed I_o/I_{o_2} count ratio with the discharge off, and the cross sections represent the following

processes:

$$\sigma_{O_2} : O_2 + e \rightarrow O_2^+ + 2e$$
$$\sigma_O : O + e \rightarrow O^+ + 2e$$
$$\sigma_D : O_2 + e \rightarrow O + O^+ + 2e$$

For bombardment by 250 eV electrons $\sigma_{O_2} = 1.52$ Å^2, $\sigma_O = 1.15$ Å^2, and $\sigma_D = 0.88$ Å^2.[7,8] An equivalent expression has been used by Miller[3] where the approximations leading to the use of Eq. 1 are also explained. The $(\sigma_D/\sigma_{O_2})/\eta$ term corrects for any differential detection of masses 16 and 32 by our detector - which is due, in part, to differential transmission of masses 16 and 32 through our quadrupole mass filter.

Table I
Beam Characterization

Gas Mixture	Pressure (torr)	RF Power (watts)	Mach Number	Dissociation (percent)	Oxygen Velocity (10^5 cm/sec)
5%O_2/Ar	100	140	1.3	86	1.43
	150	140	2.1	84	1.30
	200	140	3.0	80	1.20
10%O_2/Ar	100	140	1.1	77	1.43
	150	140	2.2	74	1.30
	200	140	3.0	71	1.28
5%O_2/He	100	140	4.9	58	2.39
	150	140	6.1	70	2.47
10%O_2/He	100	140	4.5	58	2.20
	150	140	5.8	70	2.25

Table I indicates a novel property of our oxygen beam source: even at total pressures of 200 torr the dissociation percentage remains very high. The intense discharge located at the nozzle tip undoubtedly contributes to this. The questions of actual nozzle temperature, the dependence of dissociation on RF power, and further analysis of beam characteristics will appear elsewhere in the literature. However, an analysis of nozzle temperature for 10%O_2/He and 10%O_2/Ar discharged by 140 watts at 150 and 200 torr, respectively, is now presented. Assuming the overall energy balance:[9,10]

$$(\Sigma X_i C_{P_i}) T_n = \Sigma X_i C_{P_i} T_i + \frac{1}{2}\Sigma X_i M_i V_i^2 \qquad (3)$$

(where X_i is the mole fraction, C_{P_i} the heat capacity, V_i the terminal velocity, M_i the mass, and T_i the terminal temperature of each component of the beam), we can calculate T_N, the nozzle temperature using the data presented in Table II.

Table II

Gas Mixture	Component	Velocity (10^5 cm/sec)	Temperature (K)
10% O_2/Ar (200 torr)	O	1.28	207
	O_2	1.23	250
	Ar	1.17	200
10% O_2/He (150 torr)	O	2.25	176
	O_2	2.13	256
	He	2.53	244

The O_2/Ar discharge is found to produce T_N = 1400 K, and the O_2/He discharge yields T_N = 1100 K.

IV. REACTIVE SCATTERING: O + ICl → IO + Cl

We would like to conclude this paper by presenting the experimental data, and its convolution into the center-of-mass reference frame, for the reaction O + ICl → IO + Cl. The oxygen atoms for this study were produced by discharging a 5% O_2/Ar mixture, and were found to have a peak translational velocity of 1.29 x 10^5 cm/sec. The atomic oxygen Mach number was 3.8 for these studies. The ICl was seeded in argon to a velocity of 4.95 x 10^4 cm/sec and a Mach number of 7.0. Figures 4,5, and 6 present the laboratory angular distribution, velocity distributions, and center-of-mass contour map, respectively, for this experiment. The high degree of forward-backward symmetry apparent in the contour map about the center-of-mass indicates that this reaction proceeds *via* a long-lived complex whose lifetime exceeds one rotational period of the OICl complex. Analysis of the IO product translational energy distribution reveals that the decomposition follows RRKM-AM[11] statistical predictions when an IO bond strength of 53 kcal/mole is assumed. This is in excellent agreement with Grice's[12] proposed bond strength for the IO radical obtained in a similar manner.

V. CONCLUSION

An atomic oxygen supersonic beam source has been constructed and its operating characteristics described for four rare gas mixtures. Plasma localization at the nozzle tip in

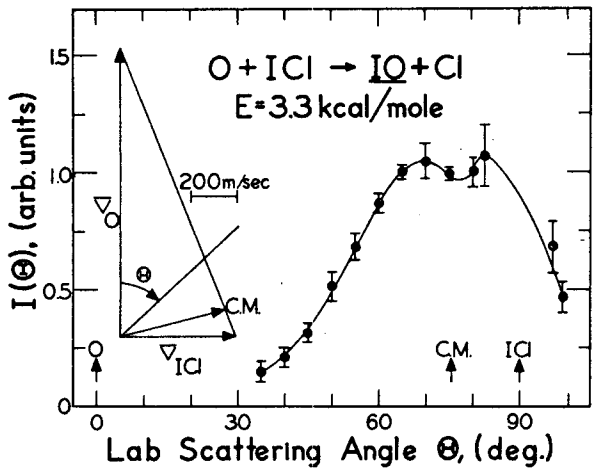

Fig. 4. Angular distribution of reactively scattered IO product.

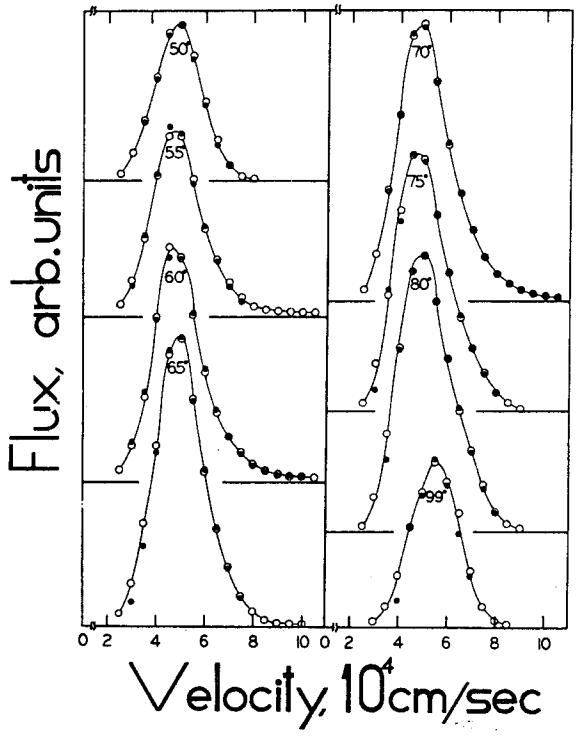

Fig. 5. Flux distributions for reactively scattered IO at eight laboratory angles. • Experimental distributions obtained from cross-correlation TOF; o Calculated best fit distributions.

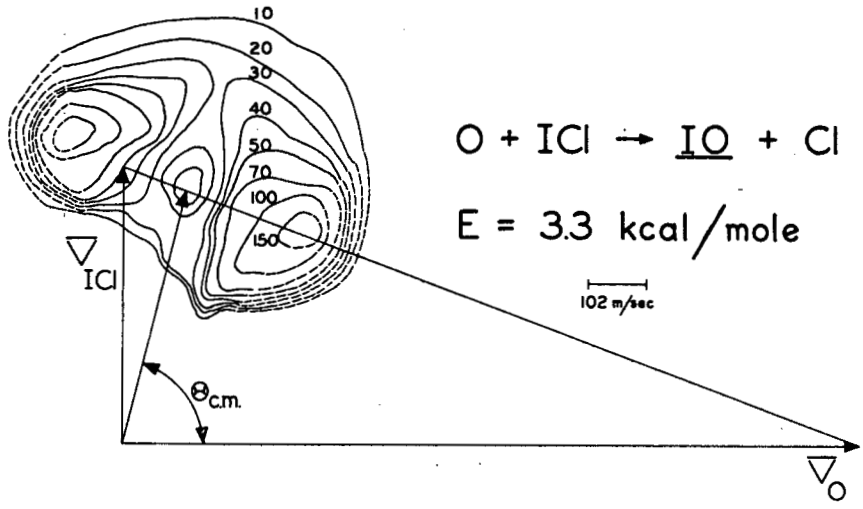

Fig. 6. Contour map of the IO product flux in the center-of-mass coordinate system produced in the reaction O + ICl.

conjunction with a novel impedance matching circuit has been shown to produce very efficient molecular dissociation at pressures as high as 200 torr. Reactive scattering results for the reaction O + ICl were also briefly described to demonstrate that reactive scattering experiments can be successfully carried out with this beam source. It is hoped that the addition of higher pumping speed will allow beams of still higher intensity and Mach number to be produced by allowing larger nozzle orifices or pressures to be used.

VI. ACKNOWLEDGEMENT

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