# Design and operation of a stable intense high-temperature arc-discharge source of hydrogen atoms and metastable trihydrogen molecules

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We report a design for a stable intense beam source of hyperthermal hydrogen atoms. The basis for the design is an arc heater used first by Knuth for the generation of high-translational energy He–Ar beams. In the case of hydrogen atom generation this source is very unstable due to the corresponding higher temperatures which are generated by the plasma discharge. We have substantially eliminated these difficulties by the insertion of discharge-localizing insulators and the use of a tungsten nozzle mounted in the center of a 1-kG electromagnet. This source generates exceptionally high hydrogen atom beam intensities of $\sim 10^{22}$ atoms $s^{-1}$ $sr^{-1}$ with translational energy distribution functions which extend to 18 eV and whose peak occurs at energies as high as 13 eV. In addition metastable $H_3$ molecules having an intensity between $10^{20}$ and $10^{21}$ molecules $s^{-1}$ $sr^{-1}$ are formed.

## INTRODUCTION

The use of molecular beams to elucidate the dynamics of molecular collisions has been widely demonstrated. However, due to the high barrier heights of most reactions only a relatively small number of systems have been studied[1,2] by this technique. It would therefore be attractive to be able to produce neutral atomic beams with translational energies in the 1–20 eV energy range, a regime which would permit the dissociation of all chemical bonds. Many different sources for the generation of such hyperthermal beams have been devised[3–7] but all suffer from various drawbacks, such as low intensities, instabilities, metastable state atomic species, and poor duty factors.

The most promising approach for the generation of fast atoms lies in the plasma jet technique[8,9] where the nozzle is one of the electrodes between which an arc is struck. The resulting effective stagnation temperature can be 10 000 K or higher. Despite the obvious advantages of these arc discharges, their operation is not straightforward. A major difficulty is that corrosion of the anode and cathode surfaces creates dimensional instabilities in the electrodes making the discharge itself unstable. With this problem in mind Knuth and co-workers[10–12] developed an arc heater for argon which (a) had lower electrode erosion rates, (b) a more stable arc, (c) higher thermal efficiency, and (d) greater ease of construction and maintenance.

In the generation of hyperthermal hydrogen atoms, early work was unsuccessful in sustaining a continous $H_2$ plasma beam source with a dc discharge.[13] It was not until Stwalley and co-workers[14,15] adapted the Knuth source to operate with $H_2$ that hydrogen atoms with hyperthermal energies were generated. However, this source still suffered from instabilities due to the high temperature of the plasma.

We report in this paper an improved design for this discharge source which is capable of producing routinely much greater beam intensities than have been previously observed, having in addition enhanced stability and reliability.

## I. SOURCE DESIGN

Following the design of Knuth and co-workers[10–12] an arc-heated source was constructed. The concept of the source is a simple one in that gas is introduced into the area between a fixed anode and a movable cathode tip. Placing the source in a vacuum chamber causes the gas to flow through the nozzle into the chamber due to the large pressure differential. An arc is initiated with a high-voltage pulse applied between the anode and cathode. The plasma flame created extends, due to the expansion of gas through the nozzle, beyond the anode itself, thus carrying away much of the heat generated. As described later, this arc produces very high temperatures which demand efficient cooling of the components of the source to avoid their destruction.

In the original use of this design we achieved little success in creating and sustaining a reliable hydrogen plasma. These difficulties were surmounted by a total redesign which in turn generated new insights as to what parameters were important in creating a stable discharge. What follows is a description of the evolution of the system.

The cathode portion of the source is shown in Fig. 1. It consists of a water-cooled hollow tube (A) with a cylindrical cathode rod (B) attached to the front of the tube by two set screws (C) placed perpendicularly to each other. This rod is made of 2% thoriated tungsten and is capable of withstanding temperatures in excess of 3000 K. Many different shapes for the tip of the rod have been tried, with the best one having the end rounded. While running the source this rod tends to erode in such a way that tungsten sputters off it and will sometimes clog the nozzle. After an extended run its tip is shaped to a sharp point by this process. The hollow tube (A) is fitted inside a support structure (D) in such a way that it can be moved 3/4-in. back or forth with respect to this structure. A bellows (E) is welded between the tube and the support structure to provide a vacuum tight assembly. Once set, the position of the tube may be held in place with the help of three Teflon screws connecting the outside casing (F) with

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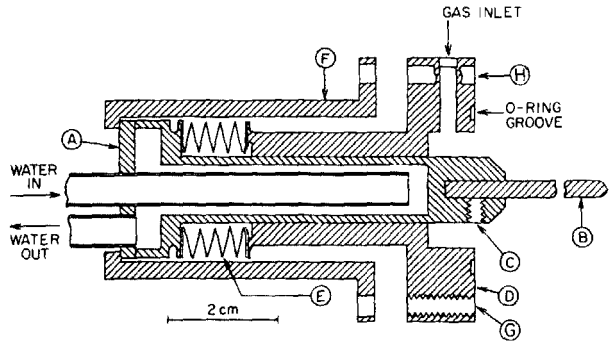


FIG. 1. Scale drawing of cathode assembly: A, hollow tube; B, thoriated tungsten cathode rod; C, set screw hole; D, support structure; E, bellows; F, outside casing; G and H, Teflon screw holes. Originally the assembly (other than the cathode) was made out of brass but is now made out of stainless steel.

the support structure (D). The hole for one of these screws is shown in Fig. 1 (G).

Two gas inlets are drilled at sharp angles through the cathode support structure (D) (i.e., nearly tangential to its inner surface) on opposite sides of the chamber located between the cathode and the anode. This has the effect of causing the gas to swirl around inside the source creating a more stable flow through the nozzle and thereby stabilizing the arc. It has been observed that when one of these inlets is clogged the arc will not operate, probably due to gradients in the gas density which make the discharge medium less uniform and therefore unstable. The entire cathode section (except the cathode itself) was originally made of brass but is now made of stainless steel and the gas inlets are welded to it so as not to become loose at the high temperatures generated.

The anode assembly, as shown by an expanded view in Fig. 2, consists of a large cylindrical brass piece [D(1) and D(2)] which has six water-cooling channels bored into it. The front of the device (at the right side of Fig. 2) holds the nozzle anode assembly through which the gas passes and to which the arc is struck. It appears that a large part of the

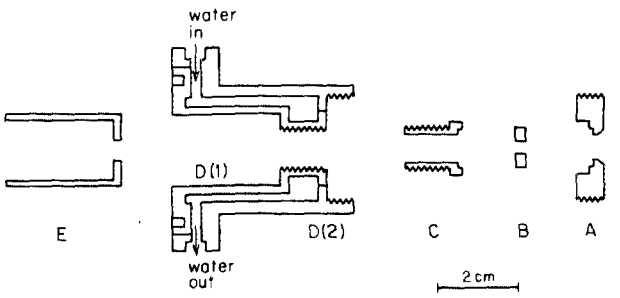


FIG. 2. Expanded view of anode assembly: A, threaded copper front holder; B, thoriated tungsten nozzle anode; C, threaded copper back holder; D (1) and (2), brass anode housing; E, macor cylinder.

problem we had in the past with creating a stable discharge was due to the difficulty of keeping the arc confined to the small region between the tip of the cathode and the nozzle. What apparently occurred is that once the arc was struck between the cathode tip and the anode nozzle, it would migrate to the back of the anode housing creating an internal arc which would severly damage the source. To circumvent this problem it was decided that the anode section of the source should be shielded from the cathode everywhere except near the tip of the cathode rod. This was accomplished by inserting a Macor cylinder (E) between the anode and cathode regions. With this insulator in place the arc remains limited to the small region between the cathode tip and the anode. After prolonged use the only damage to the Macor cylinder is a slight charring at its exit hole. A problem that this geometry does not eliminate is that the arc will sometimes strike along the inside area of the nozzle back holder [Fig. 2 (C)] causing severe erosion of its surface.

Since much heat is generated at or near the exit aperture of the nozzle, this part has been designed for easy replacement. In principle, a material which is highly conductive electrically and thermally would make an excellent nozzle. We initially followed the example of Stwalley and coworkers[15] by using a replaceable copper nozzle which simply screwed into the front of the brass anode. Using this design we quickly encountered the same problem they had, namely that during a typical run the nozzle opening would enlarge from an initial 2 mm diameter to as much as 6 mm after about 1/2-h operation. We tried, as they did, to use molybdenum as the material for the nozzle but it melted too easily. After many attempts with these materials we eventually came to the conclusion that the nozzle would have to be made out of a material having a substantially higher melting point, such as tungsten. However, due to the grave difficulties in machining that metal a simpler nozzle design was essential. Also because of the poorer thermal conductivity of tungsten, efficient cooling was critical in order to avoid having the nozzle aperture enlarge as much as with the other materials used. The optimal design involved cutting a 1/8-in.-thick disk of 2% thoriated tungsten from a 0.375-in. welder's rod. A 1.2-mm hole is drilled into this disk with a carbide drill. This disk is shown as part (B) in Fig. 2. It is held in place by two copper pieces [parts (A) and (C)] which are threaded into the brass anode housing (D). These copper pieces provide excellent thermal contact between the tungsten nozzle and that water-cooled housing. This design has been much more successful in that we are able to run repeatedly (5 to 8 times, several hours each time) using the same nozzle, before nozzle replacement is necessary.

When assembled, the anode and cathode are joined by six Teflon screws. One of the corresponding screw holes is indicated by H in Fig. 1. The assembled source is shown in Fig. 3. The anode and cathode are electrically insulated from one another by a Teflon spacer and a Viton O-ring which also provides a vacuum seal between these two components. Great care must be taken in acertaining that a seal has been established since otherwise less gas will pass through the nozzle and the plasma will become hot enough to damage the anode. Likewise, when tightening the six Teflon screws it

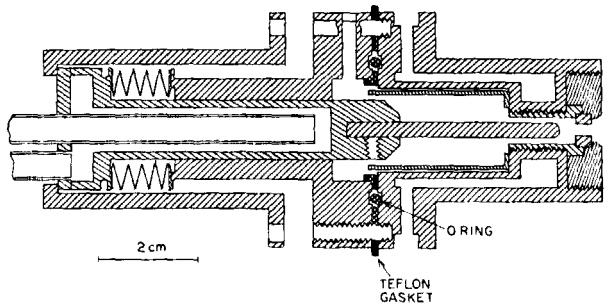


FIG. 3. Cross-sectional view of assembled anode and cathode structures.

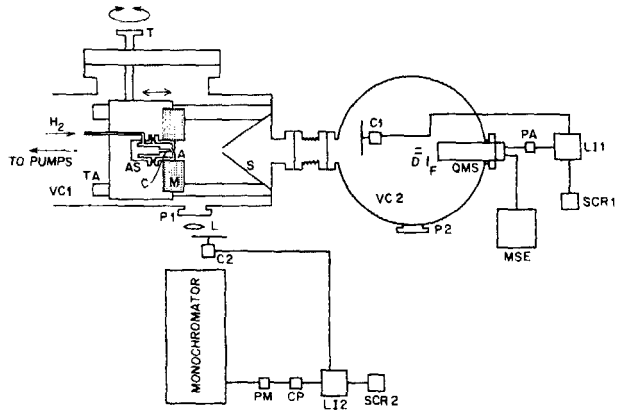


FIG. 4. A schematic top view of the apparatus: VC1 and VC2, vacuum chambers; AS, anode assembly; A, anode; C, cathode; M, electromagnet; S, water-cooled copper skimmer; TA, translation assembly; T, translator; P1 and P2, viewports; L, optical lens; C1 and C2, choppers; PM, photomultiplier; CP, current preamplifier; LI1 and LI2, lock-in amplifiers; SCR1 and SCR2, strip-chart recorders, D, electric deflector plates; F, mechanical flag; QMS, quadrupole mass spectrometer; PA, preamplifier; MSE, mass spectrometer electronics.

is necessary that the cathode rod remain centered with respect to the anode body. If the rod should be off axis, damage will occur to the copper pieces which retain the tungsten nozzle, because the arc will strike localized regions of those pieces preferentially and the nozzle hole itself will enlarge in an asymmetric fashion, i.e., it will open up in the region to which the rod is pointing, causing the plume to be off axis, with a concomitant decrease in the detected beam intensity.

Once the system is assembled, the space between the cathode tip and the anode nozzle forms a small chamber into which the gas is introduced via the inlet lines. To ensure that the cathode is insulated from the rest of the chamber (thus preventing any shorts) all water lines to it are made of 1/4-in. polyethylene tubing. The metal gas inlet line is insulated from the anode by a piece of glass tubing.

When the system is assembled the cathode tip to anode nozzle distance can be adjusted by compressing the cathode bellows [Fig. 1, (E)] with the help of three Teflon screws. One of the corresponding screwholes is indicated by G in Fig. 1. Trial and error have shown the optimum gap between the tip of the cathode and the surface of the anode disk to be 0.5 mm; if it is smaller than that value the nozzle hole will immediately short out to the cathode rod and if it is much larger the arc will be extinguished during the changeover from argon to hydrogen. This distance appears to be fundamental to the stable operation of the system. For example, Toennies and co-workers[16] have recently developed a source similar to the one described here and had great difficulty maintaining a stable discharge until they also began to use the operational parameters just described.

Power for our arc source is provided by a Westinghouse type WS variable current arc welder supply. This unit can generate a maximum current of 180 A and an open circuit voltage of 90 V dc. A Westinghouse 0–150 V dc meter is used to monitor the output voltage, while a 0–250 A dc ammeter is used to monitor the current. The arc itself is started by using a 200-A lamp starter (Hanovia model 29912) which generates a high-voltage pulse.

Figure 4 shows a schematic top view of the entire machine, with the arc source (AS) installed. The source is placed in a vacuum chamber (VC1) pumped by a 20-in. Westinghouse oil diffusion pump. That chamber is connected by a flexible bellows to a test stand consisting of a bell jar (VC2) pumped by a system comprising a 6-in. mercury diffusion pump, a Freon-cooled chevron baffle, and a liquid-nitrogen trap. Differential pumping between these two chambers is provided by a skimmer (S) with an orifice diameter of about 1 mm having a knife-sharp edge. Chamber VC2 contains a beam flag (F), a beam chopper (C1) which modulates and allows ac detection of the beam, a pair of electric deflector plates which eliminate ions from the beam (D), and an EAI 300 quadrupole mass spectrometer with an electron bombardment ion source (QMS).

The arc source is mounted so as to have its nozzle in the center of a 6-in. diameter by 1.4-in.-thick electromagnet (M). This device has no ferromagnetic core and is formed by wrapping approximately 450 turns of 14 gauge armored polythermaleze insulated antenna wire (Belden, 8009-500) around an aluminum support structure. The magnet is typically operated at 20 V and 20 A which provides a 1-kG axial field. Because of the heat generated by this electromagnet it is water cooled by two layers of 3/16-in. copper tubing which are imbedded in the wire windings and by a brass cooling channel which acts as the inner sleeve of the magnet. The assembled arc source is surrounded by this cooling channel during operation of the discharge. We have found that the 1-kG field is of critical importance in stabilizing the plasma. This stabilization occurs by providing a force perpendicular to the direction of motion of the ions. For ions moving along the magnet's axis the magnitude of this force is zero. For ions moving off axis, this force tends to make them spiral around the axial direction, thereby confining them to the center of the free jet expansion. In Stwalley's and co-workers[15] and Knuth's and co-workers[10–12] original design the nozzle was placed at the exit edge of the magnet. In this configuration Stwalley[17] observed that his discharge characteristics were independent of magnetic field and that he could operate his arc source with that field entirely turned off. In our apparatus, in which the nozzle is located in the center of the magnet, the magnetic field greatly influences the plasma: by decreas-

ing that field from 1000 G to about 700 or 600 G one can visually observe that the luminous plasma displays a larger divergence. This effect is reversible: increasing the applied magnetic field the beam becomes once more narrower and better defined. In contrast to Stwalley's[17] observation, we have found it impossible to operate the discharge without a magnetic field of at least 500 G.

As shown in Fig. 4, the magnet (M) is mounted on a movable rail track so that once the arc is operating the arc source and the magnet may be jointly moved closer to the downstream skimmer (S) via a mechanical vacuum feedthrough (T) mounted on a 10-in. flange which permits the whole translation assembly (TA) to be moved back and forth.

## II. OPERATION OF SOURCE

Any attempt to start the discharge in pure $H_2$ results in the destruction of the source and anything in its vicinity due to the unstable nature of this hot arc. It was found by Stwalley and co-workers[15] that a safe, reliable way to generate a hydrogen atom beam with this technique is to first start the plasma with argon and then gradually switch over to molecular hydrogen. This technique is so delicate that they filmed the changeover in order to document the operation.[18] A second-by-second table of the values of flow rates, voltage, and source pressure with some pertinent description is available.[19] Our current technique is very similar to theirs.

After evacuating VC1 and VC2 (Fig. 4), a flow of argon is established. The flow is regulated by a valve attached to a Dwyer gas flowmeter until a constant flow, equivalent to seven standard cubic feet per hour, is achieved. The stagnation pressure was measured by a 0 to 1-atm Wallace and Tiernan gauge on that line and was about 340 Torr. At this time the pressure in VC1 is about 50 mTorr, and that in VC2 about $4\times10^{-4}$ Torr.

The argon arc is now initiated by turning on the Hanovia lamp starter which provides the voltage pulse between the anode and the cathode. The welder power supply indicates a voltage of 15 V and a current of 100 A. For 5 to 10 s after the start of the discharge, streams of sparks will sometimes be emitted from the nozzle. Eventually the discharge will stabilize and a steady intense light blue plume will be observed.

Once the discharge appears stable, hydrogen gas is slowly mixed into the argon flow. The gas is introduced into the system via a Granville–Phillips variable leak valve (series 203). No visible change appears in the plasma until approximately a 24-Torr partial pressure of hydrogen has been introduced. At this time there is a dramatic change in the appearance of the plume: it becomes much reduced in size and turns less intense and its color becomes a beautiful crimson red. The hydrogen flow is continuously increased until the hydrogen pressure reaches 150 Torr. The intensity of the plasma emission (as detected by the naked eye) continues to decrease as the hydrogen flow increases. This procedure takes approximately 10 min.

Once this hydrogen pressure has been reached the argon flow is slowly turned off, which results in a decrease of the arc current and an increase in its voltage. It is however, vital that during this changeover the current be kept at a constant value of 100 A or the discharge will be extinguished. This is achieved by manually increasing the power supplied. During the decrease in the argon flow the emission becomes progressively more intense and the cooling water flowing through the anode and cathode progressively hotter. It is at this point that the greatest chance of losing the discharge occurs, if the proper procedure is not carefully followed. The argon should be slowly turned off over a period of 10 min. If the current is kept at a constant value of 100 A, the voltage will rise from the initial 15 to 45 V at the end of this operation.

Once the argon flow has been totally turned off and the electric current and hydrogen gas flow have stabilized, a brilliant diffuse crimsom red plume is observed at about 150-Torr stagnation pressure. According to Stwalley and coworkers,[15] who call the discharge at this time the "standard" discharge, reducing the $H_2$ pressure but keeping the input power constant will produce a more intense beam of hydrogen atoms. Indeed, by slowly lowering the $H_2$ pressure to 70 Torr the discharge is observed to go into this "pencil" mode having the appearance of a sharp very intense beam of white light surrounded by a diffuse dull red plume. After the beam is placed in this mode further lowering of the stagnation pressure to 55 Torr produces a much higher flux of hydrogen atoms as measured by the mass spectrometer (Fig. 4). Under these conditions the pressure in VC2 (Fig. 4) is about $2\times10^{-5}$ Torr while in VC1 it can be anywhere from 0.1 to 1 Torr, depending on how much use the nozzle has previously had, and on how much its diameter may have changed during the current run. After about 25 min, the voltage to the source will appear to drop to a value of about 30 V, and stay at that value for the rest of the run. Under these conditions the beam becomes quite stable and may be operated for a long time, 5 h being the longest we have kept it on before deciding to turn it off.

The nozzle is at first operated far away ($\sim$17 cm) from the skimmer. Once the pencil mode is stabilized the source may be brought closer to the skimmer using the translation assembly [(TA) in Fig. 4]. After being placed within 8 cm of the latter there is a dramatic increase in the observed hydrogen atom beam intensity. This intensity steadily increases as the source is brought closer to the skimmer. Two centimeters is the closest the source has ever been brought to the skimmer without the latter deforming due to heating. Normally it is operated 3 to 4 cm away. However, if the beam is returned to the "standard" mode it is possible to bring the source even closer without fear of damaging the skimmer. This is undoubtly due to the plasma temperature being much lower when there is more gas flowing through the discharge, at constant power input.

The procedure which has been outlined above provides a reliable routine which results in a stable high-temperature (pencil) arc source. The cw arc discharge in the H-atom source can be run continuously for many hours with a $H_2$ stagnation pressure of 50–100 Torr such that the pressure in chamber VC1 is of the order of $10^{-1}$ Torr and in VC2 of the order of $10^{-5}$ Torr. The source can be used for five to eight times (as stated previously) before it becomes necessary to replace its tungsten nozzle.

## III. RESULTS

With this source we are able to generate a beam of H atoms with 95% of the $H_2$ present in the beam dissociated as estimated by the relative height of the $m/e = 1$ and $m/e = 2$ peaks measured by using the mass spectrometer in VC2 (Fig. 4). With the help of absolute mass spectral peak intensity measurements we are able to estimate the H atom beam flux per unit solid angle as $1.3 \times 10^{22}$ atoms $s^{-1}$ $sr^{-1}$.[20] Stwalley and co-workers[15] determined a lower bound of $4 \times 10^{17}$ and an upper bound of $1 \times 10^{20}$ atoms $s^{-1}$ $sr^{-1}$ for their beam source. The reason for our significantly greater intensity, which is consistent with all our operating conditions, appears unclear at present. However, the nature of these discharges can apparently change appreciably from what would otherwise be considered simple modifications in the arc source. We feel one reason for our larger intensities lies in the higher degree of collimation of the beam which we are able to achieve due to the focusing of the plasma by the applied magnetic field.

We have also observed that under appropriate conditions this source can produce a beam of metastable $H_3$ molecules having an intensity of the order of $10^{20}$ to $10^{21}$ molecules $s^{-1}$ $sr^{-1}$.[20] This intensity is sufficiently high to permit interesting spectroscopic and dynamics experiments to be performed with this molecule.

We have also been able to make a crude energy analysis of the H atom beam by application of a repulsive potential to the first lens of the quadrupole mass spectrometer such that only ions having translational energies greater than needed to overcome that repulsive potential are able to pass through the mass analysis system and be detected. By scanning this repulsive potential and measuring the corresponding decrease in intensity, one can measure an approximate integral of the energy distribution function. Numerical differentiation of this curve furnishes a crude estimate of the energy distribution function.

Performing this measurement while operating the H atom source in the "pencil" mode at a stagnation pressure of 55 Torr we measure an H atom energy distribution function with a maximum intensity at 13 eV and a FWHM of 5 eV. By contrast, Stwalley's and co-workers'[15] distribution (measured by deflection of the H atom beam by an inhomogeneous magnetic field) has a maximum at 5 eV and a FWHM of 5 eV. This difference in hydrogen atom translational energy indicates that our discharge is considerably hotter than theirs. This higher temperature may also in part account for our higher intensities.

If the stagnation pressure is increased to 70 Torr (for which the beam is still in the pencil mode) the intensity maximum in the translational energy distribution is observed to shift down to 8 eV and the FWHM is reduced to 3 eV. Increasing the stagnation pressure (in the pencil mode) not only decreases the translational energy of the hydrogen atoms but also decreases the intensity of the beam as well. It appears from these results that increasing the stagnation pressure, at constant arc power, decreases the effective temperature of the plasma. As a result, the stagnation pressure may be used as a crude means of shifting the overall translational energy of the beam. The intensity maximum in the energy distribution function of $H_3$ at 70 Torr stagnation pressure also occurs at 8 eV but the FWHM is now 7 eV.

It should be noted that the high intensity and broad energy distribution function of the H atoms produced coupled with an appropriate velocity selector,[21] could provide a beam of monoenergtic hydrogen atoms whose translational energies would be continuously tunable from 0.1 to 5 eV. Such a source should be of great utility for a whole family of reactive scattering experiments.

[a] Work performed in partial fulfillment of the requirements for the Ph.D. in Chemistry at the California Institute of Technology. Present address: Department of Chemistry, UCLA, Los Angeles, CA 90024.

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