Note: A modular and robust continuous supersonic expansion discharge source

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A direct current discharge has been coupled with a continuous supersonic expansion to provide a source of rotationally cold molecular ions for gas phase spectroscopy. Constructed primarily of machinable ceramic and stainless steel, this source design is modular, customizable, and robust. Its performance has been assessed by recording transitions within the ν_2 fundamental band of H_3^+ using cavity ringdown spectroscopy to determine the rotational temperature of ions produced in the free-jet expansion. Temperature and column density were recorded as a function of discharge current as the source was operated over a period of 200 h. Observed temperatures ranged between 50–110 K, and the ion column densities between 8×10^{10} and 2×10^{12} cm^{-2}. © *2010 American Institute of Physics.* [doi:10.1063/1.3478019]

High-resolution spectroscopy of gas-phase molecular ions provides information of both fundamental and astrochemical importance. The observed transition frequencies in a high-resolution spectrum serve as useful benchmarks for improving *ab initio* theory.[1] In the low-temperature and low-density conditions of the interstellar medium, molecular ions are key intermediates that drive molecular evolution because of fast ion-neutral reaction rates.[2] High-resolution spectroscopy is a critical tool for observing the presence and abundances of various species in space, leading to an understanding of the chemistry that occurs around us in the universe.

For these reasons, high-resolution gas-phase spectrosopy of molecular ions in the laboratory has been a highly active field during the past three decades. A persistent challenge, however, is the production of these transient species in enough abundance to be observable. While a number of ionization techniques have been developed, an electrical discharge has been most widely used for spectroscopic purposes owing to the higher ion densities produced. Two particularly effective and widely used ionization techniques have been the positive column glow discharge[3] in conjunction with velocity modulation spectroscopy[4] and the negative glow of a hollow cathode.[5,6] However, even when the walls of these ion sources are cryogenically cooled, the ions produced exhibit translational and rotational temperatures upwards of 150 K. For larger ions, the spectral congestion and intensity dilution at these high temperatures poses a challenge for understanding the spectra of more complex ions.

Supersonic expansions have been coupled with electrical discharges to produce ions and radicals at low temperatures. As the plasma expands into vacuum, the transient species produced in the discharge are adiabatically cooled, resulting in rotational temperatures as low as 2–3 K for molecules that cool efficiently.[7] The earliest of these were the "corona-excited" supersonic expansion discharge sources,[8] consisting

of a drawn glass or quartz capillary containing a long needle electrode. As gas passes through a small orifice at the end of the capillary, it is discharged between the needle electrode and a second electrode located outside of the source and further downstream. This source design, however, suffers from limited discharge stability and nozzle clogging.[9] Pulsed supersonic expansion discharge sources have been preferred in recent years owing to less-demanding pumping requirements, and have proved to be reliable sources of a variety of cold radicals and ions.[10,11] However, such pulsed sources have intrinsic properties undesirable for achieving the highest spectral sensitivity, namely, limited duty cycle and shot-to-shot intensity fluctuations. To overcome these limitations, we have constructed a continuous supersonic expansion discharge source based on the design of the pulsed sources referenced above.

The continuous supersonic expansion discharge nozzle designed in our laboratory is illustrated in Fig. 1. Gas enters the system through a 1/4 in. stainless steel tube welded to a 1–1/3 in. Conflat flange. A pinhole is drilled into a second Conflat flange, which acts as the grounded anode of the discharge. The stainless steel cathode is separated from the anode by a Macor spacer and is enclosed in a Macor cap. The assembly is sealed by means of three high-temperature silicone o-rings, and is held together by six screws which provide compression from the cap to the anode. The modularity of the various components allows for easy replacement of individual components in the case of failure, and also gives a very flexible design. The parameters of the source used in this particular experiment are listed in Table I.

The supersonic expansion was formed in a chamber evacuated by a roots blower (Leybold WS-2001, pumping speed 2460m^3/h) backed by a rotary vane pump (Leybold SV-630, pumping speed 840 m^3/h). Hydrogen gas at pressures ranging from 2–3 bar was passed through the source, which resulted in a chamber pressure of 300–400 mTorr. A discharge was struck by applying negative high voltage to the cathode through a 10 kΩ ballast resistor and grounding
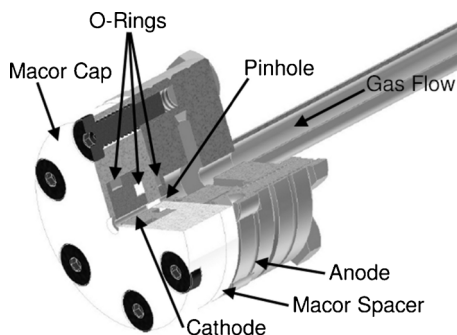
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FIG. 1. Cutaway view of the supersonic expansion discharge source. Dimensions are listed in Table I.

FIG. 2. Sample H_3^+ spectra acquired at different pressures and currents. The top trace has been offset for clarity.

the anode. The discharge current was varied between 10 mA (-500 V) and 130 mA (-1300 V). The reported voltages were the voltages at the power supply, and do not take into account the voltage drop across the ballast resistor.

To assess the performance of the source, the R(1,0), R(1,1)^u, and R(2,2)^l transitions within the ν_2 fundamental band of H_3^+ at $\sim$3.67 μm were probed to determine the rotational temperature of this ion in the free-jet zone of silence. This molecular ion, whose high-resolution spectrum was first recorded by Oka in 1980,[12] has been well-studied in the laboratory[13] as well as in dense[14] and diffuse[15,16] interstellar clouds, planetary atmospheres,[17–19] and the galactic center.[20] It was chosen for this study because the R(1,0) and R(1,1)^u transitions are separated by only 0.32 cm^{-1}, allowing for spectra to be rapidly acquired under a variety of conditions. The R(2,2)^l line was measured on occasion to verify the temperature inferred from the relative intensities of the R(1,0) and R(1,1)^u lines.

A difference frequency generation laser was employed to perform continuous-wave cavity ringdown spectroscopy in a setup similar to that described in Ref. 21. Briefly, a 532 nm Nd:YVO$_4$ laser (Coherent Verdi V-10) was split into two beams. One beam (7.5 W) was used to pump a tunable cw ring dye laser (Coherent 899-29) using rhodamine 640 dye to produce 622 nm single-frequency radiation. The other 532 nm beam (2.5 W) was sent through an acousto-optical modulator (AOM), and the first-order beam was combined with the 622 nm beam on a dichroic beamsplitter and focused into a MgO-doped periodically poled LiNbO$_3$ crystal. The 500 μW of tunable 3.67 μm light was coupled into a high-finesse cavity defined by two high-reflectivity mirrors (R $\sim$99.98%, Los Gatos Research), which surrounded the expansion jet. A piezoelectric transducer attached to one of the mirrors dithered the length of the cavity, causing it to move in and out of resonance with the laser. The light leak-

ing out of the cavity was collected by a cryogenically cooled InSb detector. When the detector output reached a predetermined threshold, the AOM was turned off, and the decay trace was recorded on a computer for analysis.

The operation of the source over its lifetime can be roughly divided into two regimes: the "low current" regime ($I<50$ mA) and the "high current" regime ($I\geq50$ mA). Sample spectra of the R(1,0) and R(1,1)^u lines are shown in Fig. 2. For the first 150 h, the source was operated entirely in the low current regime. At a current of 25 mA and backing pressure of 2 bar H_2, the rotational temperature of the H_3^+ ions was 80 K. As the current was raised from 10 to 50 mA, the ion density noticeably increased. The rotational temperature also appeared to increase in the range of 50–100 K; however, the signal-to-noise ratio was quite low at the lowest currents. Operation in the high current regime was sustained for around 50 h. The ion density increased with increasing current, but the rotational temperature was constant throughout this regime, varying between 80–110 K. After 50 h of runtime at high current, the o-rings in direct contact with the cathode failed.

The performance of the source is summarized in Fig. 3. In the low current regime, the source was able to produce spectroscopically detectable quantities of ions for an extended period of time (>150 h). No indication of source failure was observed when operating at low current. Operation at high current offered a greater ion density without a significant increase in temperature; however, operation could not be sustained for the same duration of time. At present, it

TABLE I. Dimensions of source components.

Component	Material	ID (mm)[a]	Thickness (mm)
Anode	Stainless steel	0.5	2.5
Spacer	Macor	1.0	2.5
Cathode	Stainless steel	1.0/2.5	6.4
Cap	Macor	2.5/4.1	1.0

[a]The cathode and cap inner diameters are flared like the bell of a trumpet. The listed dimensions are the beginning and ending inner diameters.
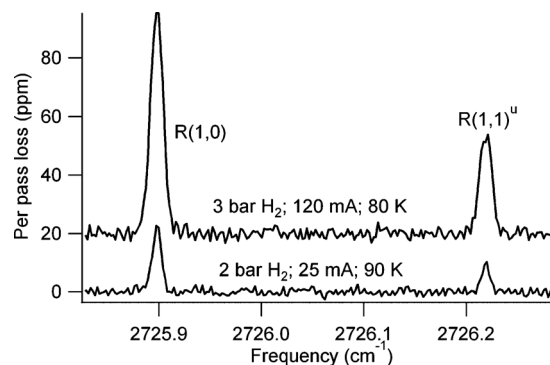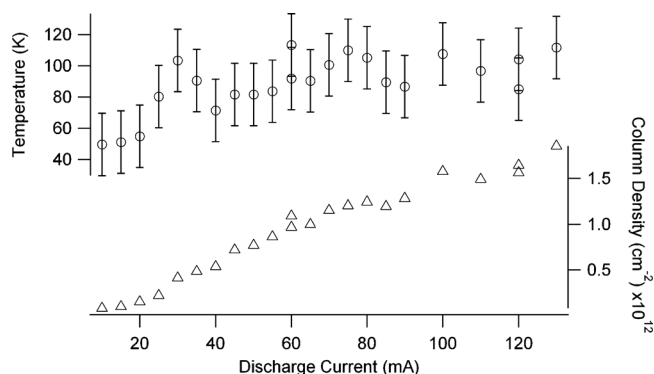

FIG. 3. Temperature and column density of H_3^+ as a function of discharge current at a 3 bar backing pressure. The error bars are representative of typical scatter in the temperature measurements.

is unclear whether damage to the o-rings was induced slowly over the entire operation period or if the source temperature at high current increased beyond the thermal tolerance of the o-rings. To prevent this failure mode, it might be possible to braze the cap and spacer to the cathode, thereby sacrificing design modularity in exchange for a longer lifetime.

The most critical aspect of the performance of this supersonic expansion source is the rotational cooling it offers. H_3^+ was cooled to temperatures ranging from 50–110 K. These results are in agreement with the temperatures observed in a pulsed supersonic expansion source by Tom *et al.* (60–100 K),[22] and in a continuous slit-jet corona source by Xu *et al.* (77 K).[23] Due to its large rotational constant ($B=43.56$ cm^{-1}),[13] H_3^+ does not cool as efficiently in an expansion as larger molecules. Future measurements with this ion source will be performed on the ν_1 fundamental band of HN_2^+ ($B=1.554$ cm^{-1}),[24] which cools much more efficiently in a supersonic expansion environment.[10,23]

The ion density produced is another important facet of the source performance. The observed H_3^+ column density (probed 1 cm downstream of the source exit) ranged between 8×10^{10} and 2×10^{12} cm^{-2} as a function of the discharge current. By visually observing emission from the discharge plume through a glass viewport, the plasma diameter appeared to be approximately 1 cm. Although the density across the plasma is not expected to be homogeneous, using that diameter the observed column densities indicate that the H_3^+ ion density 1 cm downstream is on the order of 10^{10}–10^{12} cm^{-3}, which is similar to the observed ion densities produced in pulsed slit jet discharge sources.[10,25] With a comparable number density and higher operating duty cycle, this source should provide greater spectroscopic sensitivity in an equal integration time in comparison with pulsed sources. Compared with other continuous sources, this source avoids the stability issues associated with the source of Xu *et al.*,[23] and has a longer lifetime than continuous electron impact sources.[26]

In summary, we have constructed a continuous supersonic expansion discharge source and performed initial performance characterization by measuring the temperature and density of H_3^+ ions produced as a function of discharge current. These ions are generated with temperatures in the range of 50–110 K, and the source is capable of sustaining this operation for at minimum 50 h. Ion densities produced are comparable to the densities afforded by pulsed sources, but with a high duty cycle which further enables sensitive spectroscopy. Improvements to the design will be tested by observing the ν_1 fundamental band of HN_2^+.

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