Supersonic Discharge Radical Source: Nozzle Geometry Influence on the OH Radical Generation

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Abstract. In our experiment we produce molecular radicals by stable precursor dissociation in an electric discharge followed by a supersonic expansion into vacuum. Although it is well known that the discharge properties depend quite significantly on the geometry of the discharge region, we are not aware of any systematic research of the relation between production of molecular radicals and the discharge geometry for this type of radical source. We have, however, discovered that easily implemented modifications in the geometry can dramatically change the radical concentrations and properties. In this contribution we study three different geometries of the radical source. Changes in the molecular radical concentrations and other important features, such as their temperature, are presented for those three geometries along with theoretical calculations describing the discharge behavior.

Introduction

Molecular radicals are some of the most chemically reactive species in the gas phase. They play a key role in the chemistry of Earth and planetary atmospheres as well as the interstellar medium. Developing techniques for their studies both in the field and in laboratory is therefore of high importance (SOLOMON et al. 1986).

Due to their high reactivity radicals are usually rather short-lived transient species and this greatly complicates their detection and characterization. In most cases they have to be produced and detected in situ, and obtaining high concentrations is generally difficult. In laboratory they are mainly produced by photolysis or in plasmas and spectroscopic techniques are often used to detect and characterize generated species. Because of the high temperatures associated with those production methods, hot, highly excited transient species are typically created. Not only they could have different properties than the atmospheric ones, but they are also hard to measure spectroscopicaly as the spectra are complicated at high temperatures. For this reasons there is a need to cool them down. Supersonic molecular beams have proven ideal for producing species at low temperatures.

In our work we use a custom designed radical source that combines high pressure glow discharge plasma for radical production coupled to slit-geometry supersonic expansion for cooling the produced transient species (Masat and Votava 2008). Although similar sources have been used for several years now (Anderson et al. 1996), no thorough study has been made to characterize various geometry effects on radical production.

We have observed that the radical source operates in two distinct stable discharge regimes at low (P_0<150 Torr) and high (P_0>150 Torr) stagnation pressures respectively. The low pressure mode is characterized by lower current density, lower plasma luminosity, yet, surprisingly, higher radical yield. The high pressure mode on the other hand exhibits high current density, the plasma is noticeably more luminous and observed radical concentrations are significantly lower.

It has been proposed, that those modes are associated with a different discharge geometry at low and high pressure regimes: At low pressure the discharge is localized in the interelectrode volume, where the flow speed is low, while at high pressure the discharge is predominantly localized in the exit slit, where the flow velocity reaches local speed of sound. This discharge localization is due to hollow cathode effect (C. Popovici et al. 1967). In this contribution we present detailed characterization of this behavior and show how details of the discharge geometry influence both the electrical characteristics and the radical yield. We also present calculations that support our interpretation of the observed discharge regimes.

Experiment

Although spectroscopic experiments and radical plasma sources are commonly used, our experiment combines them in not so common way and we therefore describe the setup in more detail. The experiment layout is schematically shown in Fig. 1. Description of apparatus can be divided into two main parts, radical preparation (creation and cooling) and spectroscopic detection.

A pulsed supersonic jet source with slit nozzle configuration derived from the original design of Anderson, Lovejoy and Nesbitt (Anderson et al. 1996) is used to produce the supersonic expansion of radicals generated in high pressure glow discharge (Fig. 2A). *He* carrier gas saturated with water vapor by bubbling through distilled water is brought to the nozzle enter valve at defined stagnation pressure, which was changed between 40 to 450 Torr. The valve produces short ($\Delta t \sim 1$ ms), high intensity gas pulses at repetition rates of up to 10 Hz. The gas flows through opening in the metal body of the source, which usually serves as the anode, into discharge chamber. The chamber is formed between the nozzle body and the exit jaws by the Teflon insulator. Current measurements were performed with 1mm thick insulator forming $40\times1\times1\text{mm}^3$ slit discharge chamber.

The supersonic molecular beam is formed at an exit slit orifice of dimensions 40 mm × 0.1 mm, defined by a pair of precision machined stainless steel jaws. The width of the slit is determined by a thin spacer inserted between the jaws during assembly. The impact of different jaw shapes and electrical connection on radical creation and properties is studied in this work.

High resolution diode laser spectrometer is used to record overtone rovibrational spectra of molecular species in the supersonic beam. The laser beam is double-passed through the expanding gas along the slit direction, typically 3 mm bellow the nozzle. The long slit configuration of radical source permits high sensitivity direct absorption measurements with sub-Doppler spectral resolution. The laser absorption is measured with dual beam autobalanced photodetector. The time-dependent absorption signal is recorded during each valve opening period and processed with computer that also controls the laser wavenumber, scanning over selected spectral range.

Three geometries of the radical source were used for testing the source. The cross section views of the discharge chamber perpendicular to the slit are schematically depicted in Fig. 2. In the original geometry (Fig. 2A) discharge is ignited between exit jaws, serving as cathode, and the body of a nozzle. Dimension of this discharge chamber are $40\times1\times1$ mm^3 for all geometries. Exit jaws are 0.1mm apart and 1mm thick. The gas flows approximately 0.5mm between parallel sides of the jaws, which form exit channel of dimension $40\times0.5\times0.1\text{mm}^3$. In transversal geometry (Fig. 2B) just electrical connections are modified, so that discharge is ignited in the exit slit. With one jaw as an anode and the other serving as cathode the discharge is mainly localized between jaws but with some extent into discharge chamber. Sharp jaw geometry (Fig. 2C) has the exit jaws modified to minimize the length of the exit channel. Both jaws are again at the same negative potential and so they serve as cathode while the nozzle body is serving again as anode. Discharge is ignited in the discharge chamber. Because of the jaw geometry the length of exit channel is negligible.

In the next section we will examine the measured discharge behavior under such various conditions as well as at theoretical calculations explaining those behaviors.

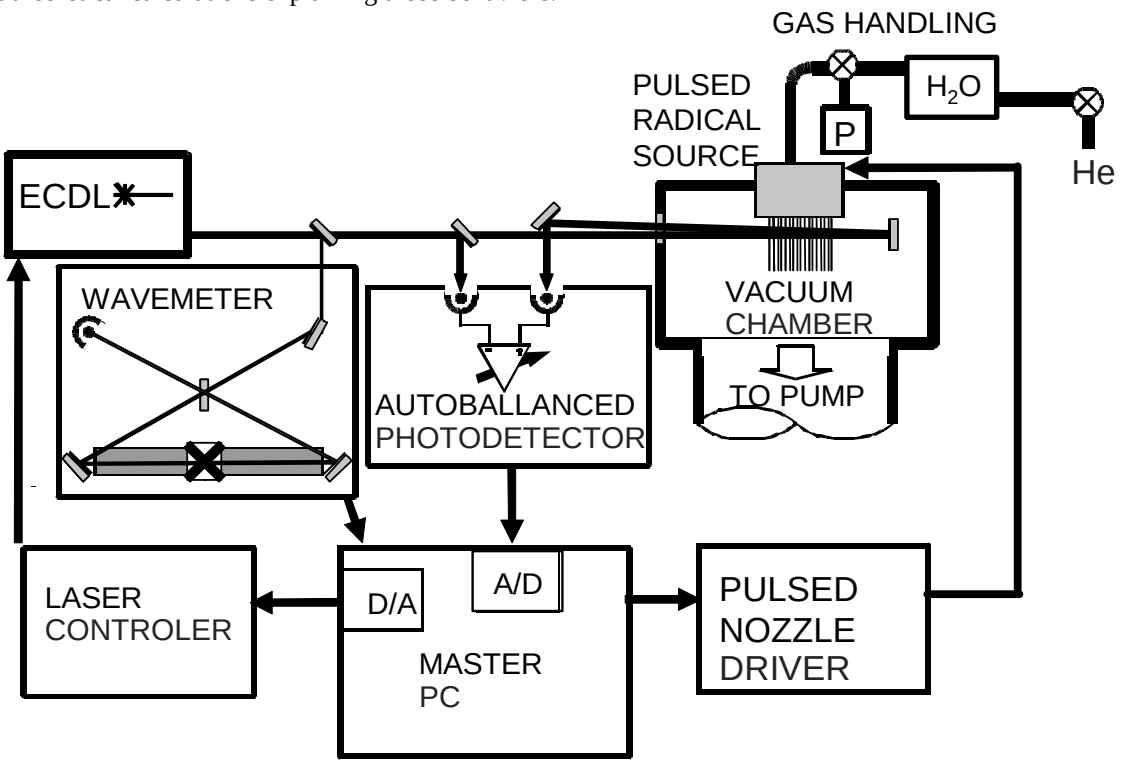

Figure 1. Experimental setup diagram. Integral parts are radical source and detection system. The source consists of discharge producing radicals and supersonic nozzle to cool them. Detection system is absorption spectrometer in near IR with interferometer to measure wavelength and a differential detector. Extended cavity diode laser (ECDL) is used as a light source.

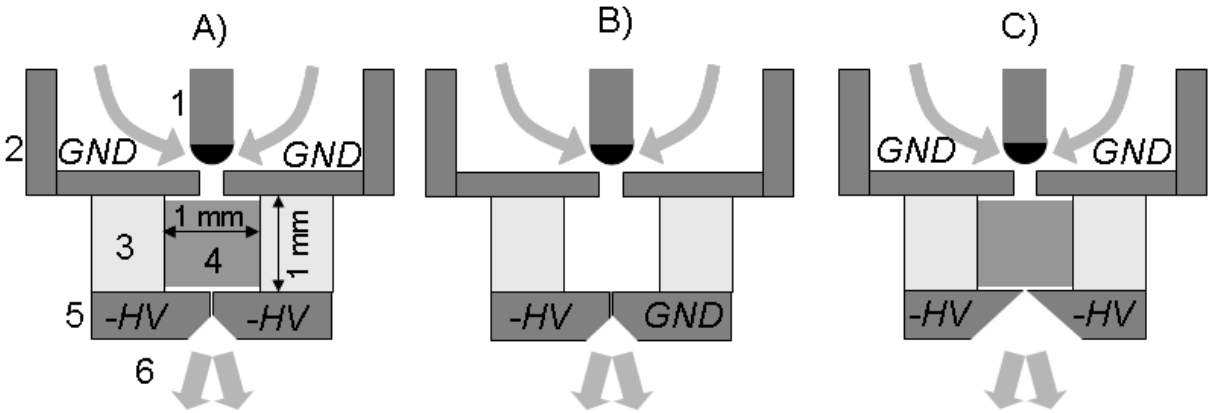

Figure 2. Discharge geometry modifications: A) Original geometry; B) Transversal discharge geometry; C) Sharp jaw geometry. Parts of the discharge source are as follows: 1) pulsed valve; 2) nozzle body, in geometries A) and C) serving as anode; 3) Teflon insulator; 4) discharge chamber; 5) exit jaws 6) gas expanding into vacuum chamber. In original geometry there is 0.5 mm long exit channel, and both jaws are connected as cathode. In Transversal geometry we used the same jaws, but one serving as anode and other as cathode. In sharp jaws geometry the jaws are modified, so that the exit channel length is negligible. Connection is the same as in original geometry.

Results and discussion

A) Discharge electrical characteristics

Hollow cathode regime of a glow discharge is observed when two cathode surfaces are placed opposite to each other. Electrons accelerated in the cathode sheath near one of the surfaces thus follow oscillating path between the opposing cathode surfaces, repeatedly passing through the plasma. This significantly increases ionization probability and therefore the hollow cathode discharges exhibit higher current density compared to the ordinary glow discharges. To establish this oscillatory motion of electrons the cathode sheath thickness must be small compared to the distance between opposing cathode surfaces.

In the context of discussed radical source the two opposing cathode surfaces are formed by the walls of the exit slit, that are both at cathode potential and are spaced by the slit widths of 0.1mm. Transition from the ordinary glow discharge in the volume between cathode and anode and the hollow cathode discharge inside the exit slit is determined by the cathode sheath thickness relative to the exit slit widths.

At low pressures, where ion mean-free-path is large compared to Debye lengths, the cathode sheath thickness is pressure independent (Sheridan and Goree 1991). As the pressure rises and more collisions between ions and neutral particles occur, cathode sheath becomes influenced by ion-neutral collisions and so its thickness becomes pressure dependent. Under such conditions the discharge voltage is proportional to the J/p^2 ratio (so called J/p^2 scaling) as demonstrated by Ito and Cappelli (Ito and Cappelli 2006), where J is the current normalized to electrode dimension ($J=I/S$) and p is a pressure.

If the stagnation pressure is low, and so the ion mean-free-path is long, the cathode layer is so thick that the exit slit in cathode could be neglected and the cathode could be considered as flat. As the stagnation pressure rises, the cathode layer gets thinner until the layer is so thin that it can easily cover cathodes inside the exit orifice.

To determine the value of critical pressure for this ordinary-to-hollow discharge transition we use the high pressure glow discharge theory, relating the measured discharge voltage and current to the cathode sheath thickness. For this purpose the Volt-Ampere (VA) characteristic of the discharge were determined at various stagnation pressures P_0. Those VA measurements are presented in Fig. 3. Good agreement with the expected J/p^2 scaling over wide range of stagnation pressures is observed.

To yield a quantitative estimate of the cathode sheath thickness the collisional Child-Langmuir law will be used. This relationship derived from the collisional sheath model, links the saturated current density J, the discharge voltage U and gas pressure p to the cathode sheath thickness L.

$$J = \left(\frac{2}{3}\right)\left(\frac{5}{3}\right)^{\frac{3}{2}} \varepsilon_0 \sqrt{\frac{2q}{\pi . m_i}} \left(\frac{\sigma . p}{kT}\right)^2 \frac{U^{\frac{3}{2}}}{(L/\lambda)^{\frac{5}{2}}} \tag{1}$$

Thickness of the cathode layer L can be expressed from this as

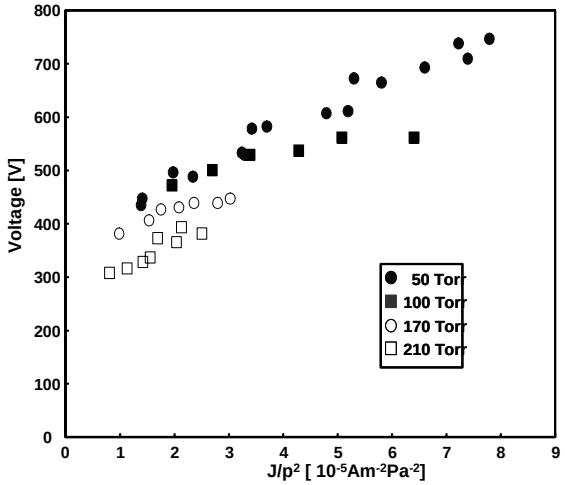

Figure 3. Glow discharge at various conditions. J/p^2 scaling is followed for all stagnation pressures.

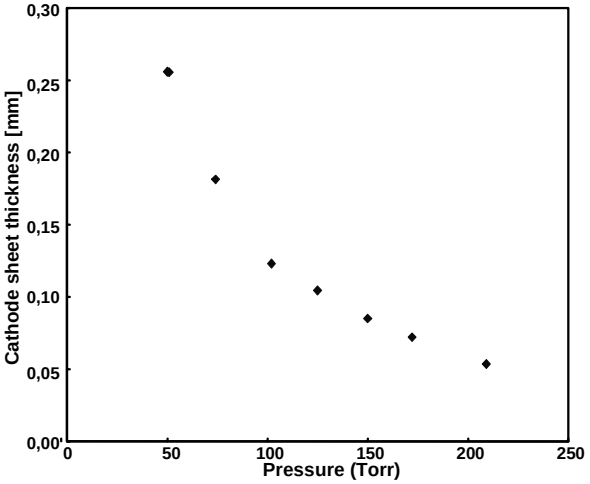

Figure 4. Pressure dependence of cathode sheath thickness. Around 150 Torr the dimension of the sheath became comparable to our 0.1 mm width exit slit.

$$L = \lambda\left\{\left(\frac{2}{3}\right)\left(\frac{5}{3}\right)^{\frac{3}{2}}\varepsilon_0\sqrt{\frac{2q}{\pi.m_i}}\left(\frac{\sigma.p}{kT}\right)^2\frac{U^{\frac{3}{2}}}{j}\right\}^{\frac{2}{5}} \tag{2}$$

with calculated results shown in Fig. 4. From these calculations we can see that around 150–210 Torr dimension of cathode sheath thickness and our exit slit become comparable thus confirming our explanation of discharge change.

Two new discharge geometries were used to further experimentally confirm the interpretation with additional goal in suppressing hollow cathode effect, so that our source could operate at higher stagnation pressures: 1) In transversal discharge geometry we put either exit jaw on different voltage, with nozzle body on floating potential so that we try to ignite glow discharge across the exit slit. Hollow cathode effect should not be formed, because there are no opposing cathode surfaces in this configuration. The discharge is not restricted only into the exit slit as with hollow cathode discharge, but it can also reach into the discharge chamber at some extent. 2) The shape of exit jaws was changed, so that the exit slit is formed by sharp edges. Although both jaws are at the same negative potential with this nozzle geometry oscillatory motion of electrons is eliminated and so hollow cathode effect should be prevented. The discharge should stay localized in the discharge chamber such as with the original geometry at low pressures.

Measured voltage–current characteristic confirmed that transversal geometry maintain stable glow discharge from 150 Torr up to the pressures of 450 Torr. Sharp jaw geometry characteristic could not be measured at pressures over 170 Torr, because of high instability in discharge. Either geometry which restricts the hollow cathode discharge does not exhibit the transition into high current discharge, which further confirms our interpretation.

B) Radical concentration and temperature measurements

Depending on geometry there are three distinct regimes of discharge that affect the OH radical production. In the classical configuration at stagnation pressures up to 150 Torr and also with the sharp jaw configuration we have standard glow discharge through the whole discharge chamber. With the classical geometry at pressures over 150 Torr hollow cathode discharge is formed and the discharge is localized just in the exit channel between the jaws. In the transversal discharge geometry we obtain glow discharge between the jaws with some extend into the discharge chamber.

Radical temperature measurement is based on Boltzmann analysis assuming a thermal equilibrium between measured quantum states and also based on line broadening caused by Doppler shift. The translational temperatures calculated from Doppler broadening are presented in Fig. 5. We can see that the temperature of OH radicals drops with rising stagnation pressure. Transversal discharge is capable of stable glow discharge mode even at high stagnant pressures thus allowing us to measure lowest temperature of radicals among all three discharge geometries.

The OH radical concentration was measured in vibrational overtones with near IR spectroscopy. Overall concentration calculation is based on measurement of concentration in particular quantum state and the knowledge of rotational temperature.

Pressure dependence of OH radical concentration is shown in Fig. 6.

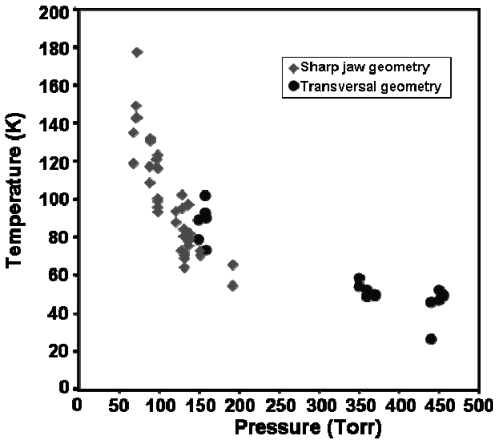

Figure 5. Pressure dependence of radical temperature. Transversal geometry achieves lower temperatures than sharp jaw geometry due to higher operational pressures.

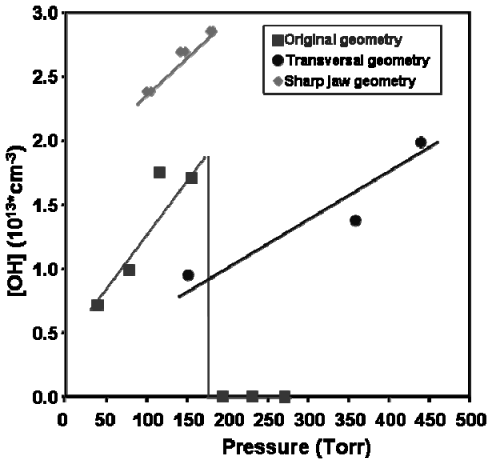

Figure 6. Pressure dependence of OH radical concentration. Transversal geometry suppress hollow cathode mode, but produces less radical thanks to its partial localization in exit slit. Hollow cathode discharge in original geometry at higher pressure is fully localized into exit slit, thus not providing measurable OH concentration.

With the original geometry concentration of OH radical rises with rising stagnation pressure up to 150 Torr. After the transition into hollow cathode regime the concentration of OH drops under detection limit for any measured stagnation pressure. With the transversal geometry steady increase in concentration with pressure is observed up to the maximum stagnation pressure value of 450 Torr. However overall concentrations at given pressure are lower compared to the original geometry. Maximum concentrations of both geometries are comparable, although they are measured at different stagnation pressures and temperatures. Finally OH concentrations observed with the sharp jaw geometry are also proportional to the stagnation pressure, but operational maximum pressure is at 170 Torr. Overall concentrations are higher than in previous geometries.

Difference in OH radical generation could be explained with various discharge localization. Speed of gas flow is approximately ten times higher in the exit slit than in discharge chamber with the chamber two times longer path from enter to exit area. Most of the radicals are created in the discharge chamber and thus the strictly localized hollow cathode discharge does not produce any detectable amount, while the transversal discharge with some extent into discharge chamber produces measurable amount of radicals. For original geometry in the glow discharge regime and sharp jaw geometry the discharge is entirely in the discharge chamber and so they produce highest OH concentrations.

Conclusion

We have presented experimental and theoretical confirmation of hollow cathode effect in the discharge nozzle radical source at high stagnation pressures. Also we demonstrated that geometry modification of the exit jaws can effectively suppress the hollow cathode effect.

From the analysis of these three different discharge geometries we conclude that the OH radical is predominantly produced in the discharge chamber volume and not just in the thin cathode sheath region. For given stagnation pressure and discharge current the sharp jaw geometry produces higher OH radical concentrations but the discharge becomes unstable for pressures above 170 Torr. The transversal discharge geometry, on the other hand, results in stable glow discharge up to 450 Torr of stagnation pressure which increases the supersonic cooling efficiency producing the OH radical at temperatures down to 40 K.

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