

Planar Plasma Expansions as a Tool for High Resolution Molecular Spectroscopy

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Abstract

Supersonic planar plasma expansions offer a new way to study high resolution rovibronic spectra of molecular transients. Particularly their implementation in highly sensitive spectroscopic detection schemes, such as cavity ring down and plasma-frequency double modulation set-ups, has made possible a detailed study of fully resolved spectra of unstable species. This article presents the state-of-the-art in planar plasma spectroscopy and discusses in detail the operation of a recently constructed pulsed slit nozzle discharge system.

1. Introduction

Molecular transients—radicals, ions and cluster ions—belong to the chemically most reactive species and are considered important intermediates in plasma reactions and in processes that are relevant to atmospheric and interstellar chemistry. This high reactivity, however, also complicates systematic spectroscopic gas phase studies, as it is hard to generate large abundances under laboratory controlled conditions. In the past this problem has been partly overcome by using electrical discharges in long and cryogenically cooled cells [1–4]. Although these plasma tubes were shown to be effective sources for the production of transient species, the spectroscopy through a cell generally suffered from high rovibrational temperatures and Doppler limited resolution. Under these conditions spectra of even simple systems can become rather complicated and single lines may hide spectral information. In addition, the relatively high temperatures decrease the quantum state population density which affects the maximal achievable sensitivity.

Plasma jet expansions were shown to overcome these problems [5]. Particularly *planar*, i.e. two dimensional plasma expansions through a long and narrow slit offer a Doppler free environment and combine high molecular densities and large absorption path lengths with an effective adiabatic cooling [6,7]. Furthermore, the density in the expansion decreases linearly with the distance downstream, whereas in pinhole expansions this is quadratically. As a consequence, the number of collisions in a slit jet expansion is larger than in any other geometry and the combination with a plasma therefore offers a highly reactive environment. However, for a long time it has been a severe problem to generate a stable plasma over the total length of the slit.

2. Plasma sources

During the last decade a number of planar plasma sources has been designed, using discharge [6–10], ablation [11], photolysis [12] and electron impact ionization [13] techniques. Applications ranged from small transients [14] and cluster ions [15] to long pure and highly unsaturated carbon chain radicals [16] and polycyclic aromatic hydrocarbon (PAH) cations [17]. In this article a very successful design—a pulsed high pressure multi-layer discharge slit nozzle geometry—is discussed in detail. The performance is demonstrated on the example of rotationally resolved spectra of the iso-electronic C_6H and HC_6H^+ linear carbon chain radicals. The reactive nature of these species necessitated the use of very sensitive spectroscopic detection techniques, such as cavity ring down spectroscopy [18]. In addition, it was also possible to explicitly use the short lifetime of molecular transients, combining production and other sensitive modulation schemes [19,20].

2.1. Pulsed planar plasma source

In Fig. 1 a 3-D view of the pulsed high pressure multi-layer discharge slit nozzle is shown. The orifice of the nozzle comprises two jaws that form an adjustable slit ($100\text{--}300\ \mu\text{m} \times 3\ \text{cm}$) and three slotted plates consisting of a grounded metal plate in between two ceramic insulators. The jaws and plates are floating and connected to the nozzle body by electrically isolated screws. A pulsed valve is mounted on top of the body and controls a 1 ms long gas flow into the body through a short circular channel. A reservoir in front of the valve (not shown in the figure) operates as a gas buffer zone and guarantees a stable gas flow. A negative high voltage pulse of $300\ \mu\text{s}$ (typically between -500 and $-1000\ \text{V}$ and about $100\ \text{mA}$) coinciding in time with the gas pulse is applied to both jaws and strikes through the orifice to the grounded plate, i.e., the discharge is confined to a small volume upstream of the supersonic expansion and as a consequence a very efficient adiabatic cooling becomes possible as no excess energy is put into the expansion. Strongly diluted gasses (i.e. 0.5% C_2H_2/Ar) are used with backing pressures that vary from 2 to 10 bar. The operation is demonstrated in the lower trace of Fig. 2. Here a discharge pulse is offered that is considerably longer than the gas pulse. Only when gas is actually flowing it will be possible to strike a plasma and this results in a change of the current/voltage characteristics as shown.

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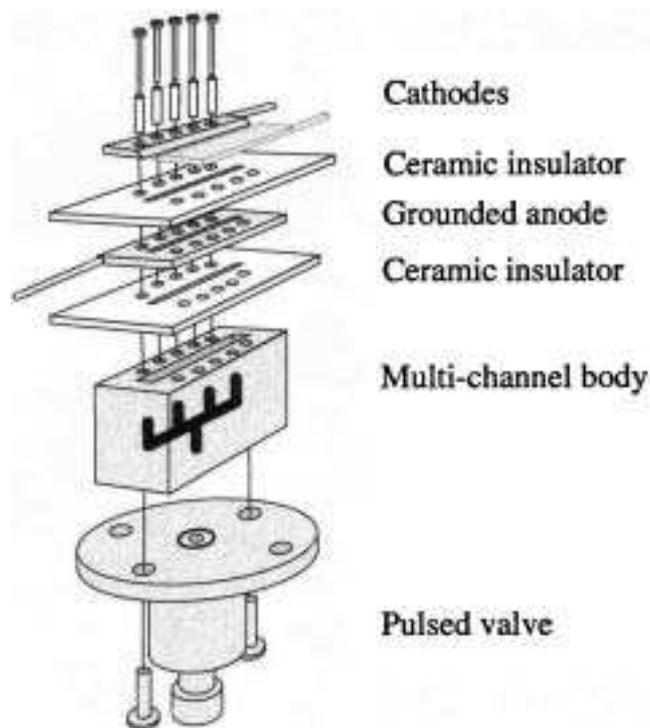


Fig. 1. A 3-D art view of the pulsed slit nozzle discharge system that is suitable to generate an intense supersonic planar plasma. Details on the construction are listed in the text. (Reprinted from Chem. Phys. 228, Birza *et al.*, Cw cavity ring down spectroscopy in a pulsed planar plasma expansion, pp. 119–224, Copyright (2002), with permission of Elsevier).

2.2. Mass specific information

The major disadvantage for spectroscopic use of a source as described above is that a large number of species is formed simultaneously in the expansion: the plasma is a “chemical goulash” in which a rich variety of radical species is formed. As a consequence a unique attribution of a spectrum to a specific carrier can be hard, particularly when a rotational structure is not resolved. However, low resolution spectra available from mass selective matrix experiments [21] are helpful in guiding gas phase searches and when such information is lacking mass spectrometry becomes very useful. For continuous plasma expansions online monitoring by a quadrupole mass spectrometer was shown to be very effective [13]. For a pulsed plasma expansion a time-of-flight analysis is more appropriate. In recent work [22] it was shown that a large variety of molecular transients—both cations, anions and cluster ions—is produced in the pulsed plasma source shown in Fig. 1. This allows plasma control as well as optimization for a particular species in the expansion.

3. Performance and results

The source described here has been successfully implemented in a cavity ring down (CRD) [10] and in a frequency-plasma double modulation detection scheme [20]. The principle, experimental details and performance of these methods are discussed below.

3.1. Cavity ring down spectroscopy

In the cavity ring down experiment tunable laser light of a pulsed dye laser (0.035 cm^{-1} bandwidth) is focused into an optical cavity that consists of two highly reflective plano

concave mirrors with a reflectivity $R > 0.99995$, capable of confining a light pulse tens of μs [18]. The rate of light leaking out of the cavity is detected by a photodiode. This signal has an envelope which simply reflects a first order exponential decay (upper trace Fig. 2). The so called ring down time τ , is determined by $\tau = d/[c(1 - R + \sigma nl)]$, where d is the optical length of the cavity, c the speed of light, R the averaged reflectivity of the mirrors and σnl the absorbance for a sample present in the cavity with absorption coefficient σ , density n and effective absorption path length l . I.e. the ring down time reflects the rate of absorption rather than its magnitude and as such it is immune to pulse-to-pulse fluctuations. When the laser light is tuned into resonance with a molecular absorption, light is absorbed and the ring down time decreases, and consequently an absorption signal is simply measured by recording τ as function of the frequency. The two main advantages of this detection technique are that very long absorption path lengths (up to several tens of km) are obtained and that the method is intrinsically insensitive to power fluctuations. The slit nozzle source is mounted in between the cavity mirrors with its orifice parallel to the optical axis. The laser beam crosses the expansion between 2 and 10 mm downstream. A sensitive delay generator is used to trigger gas, discharge and laser pulse in such a way that the ring down event coincides with the plasma pulse, as shown in the upper trace of Fig. 2. By combining a pulsed production and a pulsed detection technique no problems arise because of a low duty cycle.

The performance of this technique is demonstrated in Fig. 3, where the origin band of the $A^2\Pi - X^2\Pi$ electronic transition of the unsaturated linear carbon chain radical C_6H is shown. The P, Q and R-branch of both spin-orbit components ($A^2\Pi_{3/2} - X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} - X^2\Pi_{1/2}$) are

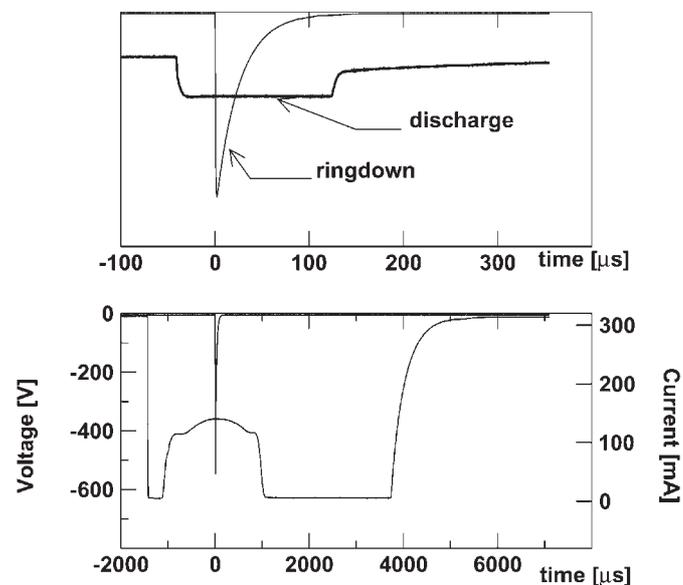


Fig. 2. The length of the discharge pulse is set to the same order as the cavity ring down exponential decay curve, typically $300\ \mu\text{s}$, as shown in the upper trace. The gas pulse through the slit lasts much longer. This is visualized by extending the length of the discharge pulse to several ms and by monitoring the voltage at one of the jaws (lower trace). The voltage characteristics provide direct information on the actual discharge voltage and discharge current (see vertical axis). (Reprinted from Rev. Sci. Instrum. 70, Motylewski and Linnartz, Cavity ring down spectroscopy of radicals in a supersonic slit nozzle discharge, pp. 1307–1312, Copyright (1999) with permission of AIP).

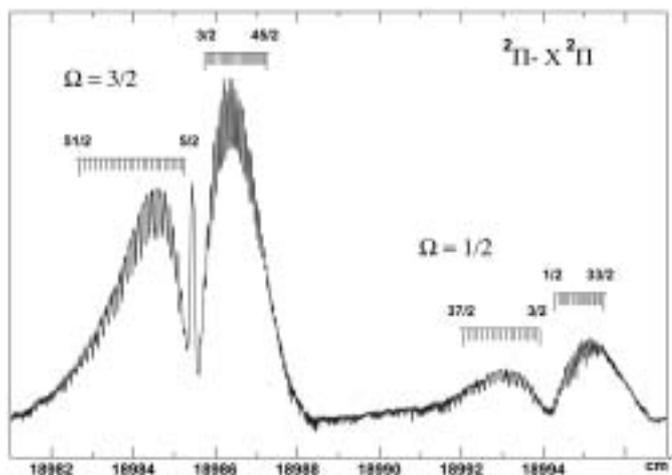


Fig. 3. The two rotationally resolved spin-orbit components of the origin band of the $A^2\Pi - X^2\Pi$ electronic transition of C_6H measured by cavity ring down spectroscopy through a supersonic planar plasma. The intensity profile corresponds to a rotational temperature of about 15 K. (Reprinted from *J. Mol. Spectrosc.* 197, H. Linnartz *et al.*, Electronic ground and excited state spectroscopy of C_6H and C_6D , pp 1–11, Copyright (1999) with permission of Elsevier).

visible, with clear rotational progressions in P- and part of the R-branch. Because of the cooling in the expansion and a spin-orbit splitting of -15 cm^{-1} in the electronic ground state an intensity difference between both components is observed. This intensity difference corresponds to a rotational temperature of $T_{\text{rot}} = 15(5)\text{ K}$. A detailed rotational analysis has been given in Ref. [23] and shows that the moment of inertia of this molecular chain corresponds to a rotational constant of approximately 0.045 cm^{-1} , that the molecule is linear and that it slightly stretches upon electronic excitation. Estimates yield a C_6H density of 10^{10} mol/cm^3 .

3.2. Plasma-frequency double modulation spectroscopy

Cavity ring down spectroscopy utilizes longer absorption path lengths to increase signal-to-noise ratios. The same goal is achieved by decreasing the noise level in an effective modulation and phase-sensitive detection scheme. This becomes possible by implementing the discharge source in a combined frequency and discharge (i.e. production) modulation setup. For this the output of a single-mode ring dye laser with a resolution of the order of a few MHz is phase modulated at a radio frequency of 192 MHz by an electro-optic modulator (EOM). First order sidebands are generated, typically with 25% of the intensity of the carrier frequency. The modulated laser beam is guided through the plasma onto a fast photo-diode via a small multi-pass system ($L_{\text{tot}} = 0.5\text{ m}$). Production modulation is obtained by using a rectified AC (15 kHz) voltage for the discharge pulse. The high frequency portion of the signal is demodulated in a double balanced mixer referenced to the radio frequency that drives the EOM. This signal is fed to a lock-in amplifier that demodulates the signal at the discharge modulation frequency. It is because of the intrinsic difference in timescales between frequency and production modulation that the two frequencies can be treated independently. In this way all major noise sources can be filtered out, yielding sensitivity as good as in the CRD experiment. The resulting instrumental lineshape is approximately first derivative. The

low duty cycle in this setup is compensated by synchronizing a box car integrator with the repetition rate of the nozzle. An additional advantage of this set-up is that the right choice of the production modulation frequency allows a discrimination between very short lived and rather stable species, i.e. by choosing a modulation cycle that is considerably shorter than the averaged lifetime of the more stable species.

An example of a spectrum recorded in this way is given in Fig. 4. The rotationally resolved spectrum of the $A^2\Pi_g - X^2\Pi_u$ electronic transition of the tri-acetylene cation HC_6H^+ is shown, a carbon chain radical that is iso-electronic with C_6H . Only the P-, Q- and R-branches of the lower spin-orbit component ($A^2\Pi_{g,3/2} - X^2\Pi_{u,3/2}$) are observed, because of a spin-orbit splitting in the electronic ground state that is approximately two times as large as in the case of C_6H . The upper component is hardly populated for a rotational temperature of about 15 K. The improvement in spectral resolution is clearly visible, but still limited to $\sim 0.01\text{ cm}^{-1}$, presumably because of residual Doppler broadening in the expansion. More information is available from Ref. [24].

Both techniques allow an accurate determination of molecular parameters, using standard spectroscopic fitting routines. An overview for species studied in this way is available from Refs. [16,25]. The pulsed plasma source as described above has also been used in a cw-CRD detection scheme, in which the sensitivity of a cavity ring down and the resolution of a continuous detection technique are combined [26]. Not only rovibronic but also pure rotational spectra have been recorded in the MW and submillimeter region through planar plasma [27]. Comparable sources have been used for high resolution spectroscopy of cluster ions (see e.g. Ref. [28]). Although the plasma processes in the expansion are not studied in detail yet, it has become clear that plasma expansions can be used to record rotationally cold spectra of electronically and

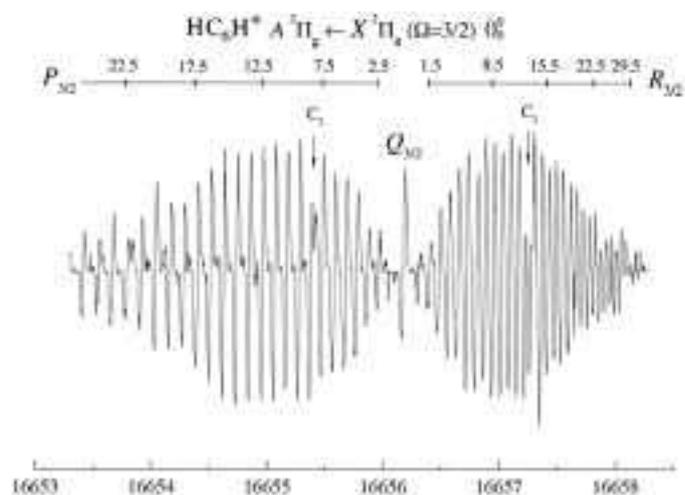


Fig. 4. Rotationally resolved lower spin-orbit component of the origin band of the $A^2\Pi_g - X^2\Pi_u$ electronic transition of the linear centrosymmetric HC_6H^+ triacetylene cation measured by frequency plasma double modulation spectroscopy through supersonic planar plasma. The rotational assignment is indicated in the figure. The higher resolution of the cw laser system is clearly reflected in the figure and limited to about 0.01 cm^{-1} by residual Doppler broadening in the expansion. (Reprinted from *Chem. Phys. Lett.* 313, D. Pfluger *et al.*, Rotationally resolved electronic absorption spectra of triacetylene cation in a supersonic jet, pp 171–178, Copyright (1999) with permission of Elsevier).

vibrationally highly excited species [22,29,30]. Another application is the use of plasma for destruction modulation; recently it was shown that also weakly bound van der Waals complexes can be studied at high resolution in expanding plasma without loss of rotational cooling [31].

4. Conclusions

Planar plasma expansions offer a very effective tool for high resolution spectroscopy of molecular transients. The number of different species formed in the expansion is remarkably large and offers much potential for high resolution studies of molecular transients. Abundances are high and direct absorption spectroscopic techniques are applicable, which makes this source a general tool for high resolution spectroscopy.

Acknowledgements

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