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Mass spectrometric and laser spectroscopic characterization of a supersonic planar plasma expansion

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Abstract

A mass spectrometric and laser spectroscopic experiment has been performed to characterize reactive species that are formed in a supersonic planar plasma expansion generated by discharging a high-pressure gas pulse in a multi-layer slit nozzle geometry. Discharges through mixtures of nitrogen, water and acetylene in He have been studied. The *mass spectrometric* study uses a state-of-the-art time-of-flight setup. Besides (cluster) cations, with sizes as large as $(H_2O)_{56}H^+$, a variety of pure carbon chain anions has been observed. The *spectroscopic* study uses cavity ring down spectroscopy and shows that a planar plasma is also suited to obtain rotationally resolved spectra of vibrationally excited metastable electronic states. The latter is demonstrated by the example of rotationally resolved transitions of the $(v', v'') = (3, 0)$ and $(4, 1)$ bands in the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ electronic transition of molecular nitrogen.

Keywords: Planar plasma expansion; Molecular ions; Cavity ring down spectroscopy; Time-of-flight mass spectrometry

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1. Introduction

Plasma jet expansions have been used as a powerful technique for high resolution spectroscopy of molecular transients [1–5]. In recent years rotationally resolved spectra have been recorded for a number of radical and ionic species, combining plasma expansion techniques and sensitive spectroscopic detection techniques, such as LIF [1], REMPI-TOF [2], REMPI-PES [3], photo-detachment [4] and vibrational predissociation [5] spectroscopy. In the case of *direct absorption* experiments *planar* plasma expansions, i.e., expansions through a long and narrow slit, have turned out to be particularly useful. Such an expansion provides a Doppler free environment and combines high molecular densities and relatively long absorption path lengths with effective adiabatic cooling. During the last decade a number of planar plasma sources has been designed, using discharge [6,7], ablation [8], photolysis [9] and electron ionization [10] techniques, with spectroscopic applications ranging from cluster ions [11] to long and highly unsaturated carbon chain radicals [12]. The major disadvantage of such a plasma for spectroscopic use is that a large variety of species is formed simultaneously in the expansion. As a consequence a unique attribution of a spectrum to a particular carrier is usually not possible without mass specific information. In the case of cw expansions the incorporation of a quadrupole mass spectrometer sampling the expansion downstream was shown to be effective [10], but for pulsed and particularly highly energetic plasma expansions cw mass spectrometric detection is much harder to realise.

In this work a mass spectrometric study of a pulsed supersonic planar plasma expansion is described, using a state-of-the-art time-of-flight mass spectrometer. The plasma is generated by discharging a high-pressure gas pulse through a multi-layer slit nozzle geometry that has been used successfully in a number of previous spectroscopic experiments [13]. The present study is an extension of this work and provides additional information on plasma composition and its dependence on discharge conditions in order to show the potential of this source for future experiments.

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Additional plasma information is obtained in a spectroscopic way. Most of the previous spectroscopic studies focused on molecular transients (both charged and neutral species) in their electronic and vibrational ground state. The present work goes one step further and shows that a planar plasma expansion also serves to probe the formation of metastable electronic states in the downstream plasma, some of which are vibrationally excited as well. In most cases information on such transitions is only available from combination differences following emission studies. The technique described here uses cavity ring down spectroscopy and its performance to study highly excited species in direct absorption as well is demonstrated on rotationally resolved spectra of the weak $(v', v'') = (3, 0)$ and (4, 1) bands of the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ electronic absorption spectrum of molecular nitrogen.

2. Experiment

The plasma source has been described in detail before [7]. A three-dimensional picture is shown in Fig. 1. The orifice of the nozzle comprises two jaws that form an adjustable slit (3 cm × 100 μm–300 μm) and three slotted plates consisting of a grounded metal plate between two ceramic insulators. Jaws and plates are mounted to the floating slit nozzle body by electrically isolated screws. A pulsed valve (General Valve, 2 mm orifice) is mounted on top of the body and controls the 0.5–1 ms long gas flow (backing pressure between 2 and 10 bar) into the system through a short circular channel. A reservoir in front of the valve operates as a gas buffer zone and guarantees a stable gas flow. A negative high voltage pulse (typically −400 to −700 V and 100 mA during a 300–500 μs interval coinciding 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. This results in a very efficient adiabatic cooling as no excess energy is put into the expansion. This allows spectroscopy at low rotational temperatures. The source has been implemented in two different systems, a time-of-flight mass spectrometer at FORTH (Crete) and a cavity ring down setup at the LCVU (Amsterdam).

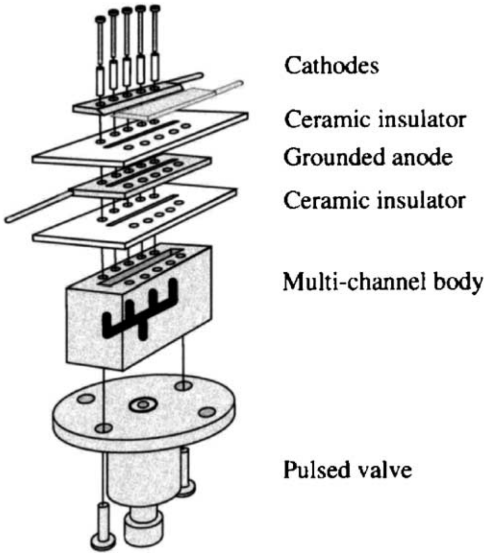

Fig. 1. A 3D view of the high pressure slit nozzle discharge. Details are listed in the text and available from Ref. [7]. Reprinted from Chem. Phys. 228, Birza et al., cw cavity ring down spectroscopy in a pulsed planar plasma expansion, pp. 119–124, Copyright (2002), with permission of Elsevier.

3. Time-of-flight system

The plasma constituents, both positively and negatively charged species, have been detected using the molecular beam apparatus ARIADNE [14], a time-of-flight (TOF) spectrometer that has been used in a number of experiments concerning cluster formation [15,16]. The machine consists of three differentially pumped chambers: a source, an acceleration and a reflectron/detection chamber. The plasma jet is mounted in the source chamber that is kept at a pressure of 2×10^{-4} mbar during a 10 Hz pulse rate. Part of the planar plasma expansion enters the second chamber through a 4 mm diameter skimmer, where the ions are accelerated. The ions are subsequently mass sensitively detected after passing via a 6 mm collimator in the third chamber, which houses the detection assembly for the TOF analysis of the produced ions. The ions are measured with a microchannel plate (MCP) detector. The output is directly connected to a computer controlled digital storage oscilloscope, where the TOF mass spectra are stored shot-by-shot. The spectra are obtained by averaging typically 500 single shot spectra. The pulsed nozzle and the triggering of the TOF are synchronised through coupled delay generators. The delays are optimised for maximum time-of-flight signal.

4. Cavity ring down spectrometer

The laser spectroscopic experiment consists of a recently constructed cavity ring down setup sampling the planar plasma generated in the slit nozzle discharge. The latter is mounted in a vacuum chamber that is pumped by a small roots blower pump system with a total pumping capacity of 1000 m^3/h that keeps the pressure below 0.1 mbar during jet operation. On opposite sides of the vacuum chamber two highly reflective mirrors are mounted in precision holders defining a 42 cm long cavity. Helium curtains are used to shield the mirrors from pollution. Tunable light (0.06 cm^{-1} bandwidth) from a Nd:YAG pumped dye laser (SIRAH) is focused into the cavity with an optical axis that is aligned parallel to and slightly below (2–8 mm) the orifice. Light escaping from the cavity is detected by a photomultiplier and the resulting exponential decay is monitored by a 350 MHz oscilloscope. A Labview programme is used for data acquisition for on-line analysis of the ring down events. Typical ring down times amount to 25–30 μs, equivalent to an effective absorption path length through the 3 cm long expansion of several hundred meters. The entire experiment runs at 10 Hz. A delay generator is used to trigger the Nd:YAG laser as well as the gas and discharge pulses independently in order to obtain an optimum overlap between ring down event and plasma pulse. A spectrum is obtained by averaging 20 ring down events and recording the averaged ring down time as function of the laser frequency. A wavemeter (ATOS) is used for absolute frequency calibration (accuracy ∼0.003 cm^{-1}).

5. Results

5.1. Mass spectrometric results

In Figs. 2–5 mass spectra are shown that were obtained with discharges through nitrogen, water and acetylene in He. The mass spectrum of the nitrogen plasma in Fig. 2 shows that cluster ions, such as $[N_2–N_2]^+$, are formed. Such species are of particular interest for the study of charge induced intermolecular interactions [5,17,18], but an effective production has prohibited systematic spectroscopic studies of many cluster ions up to now. Signal strengths indicate cation densities of the order of 10^{10} ions/cm^3 for a distance of the nozzle orifice to the skimmer of 17 mm, i.e., well above the detection limit of sensitive spectroscopic direct absorption techniques, such as cavity ring down spectroscopy. The binding energy of $[N_2–N_2]^+$ is about 1 eV [18] and consequently cluster ions with comparable binding strengths are expected to be formed in the plasma as well. This is demonstrated in Fig. 3 where a clear progression of species of the form $(H_2O)_nH^+$ is observed through a water plasma up to very large values for n (=56). Just very recently a low resolution spectrum for the protonated water dimer ($n = 2$) was reported [19], but spectroscopic data for the larger clusters are still completely lacking. The present setup shows that the planar plasma source described here is capable of producing such cluster ions.

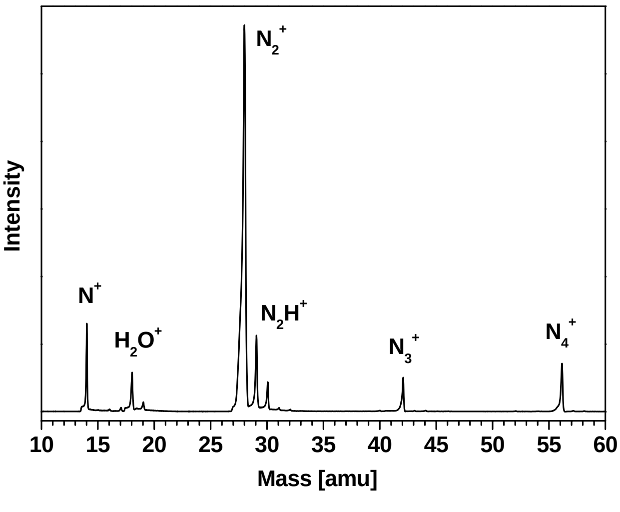

Fig. 2. A TOF mass spectrum of a discharge through pure N_2.

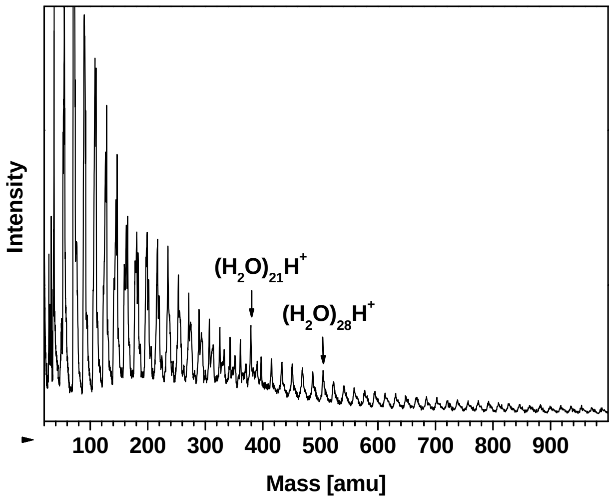

Fig. 3. A TOF mass spectrum of a discharge through H_2O in He. Large protonated cluster ions of the form $(H_2O)_nH^+$ with n as high as 56 are observed. For $n = 21$ and $n = 28$ stronger peaks are found that correspond to magic cluster sizes [33,34].

The source described here has been used in the past to study electronic transitions of a number of long carbon chain radicals (for an overview, see [20]), specifically following low resolution matrix data. The present study shows the large range of different species that are actually formed in the expansion with C_2H_2 as a precursor (Fig. 4). Besides the poly-acetylene progression HC_nH^+, with n as high as 8, a number of other carbon chain cations—for example, species of the series $C_{2n}H_4{}^+$ are found. Such radicals are

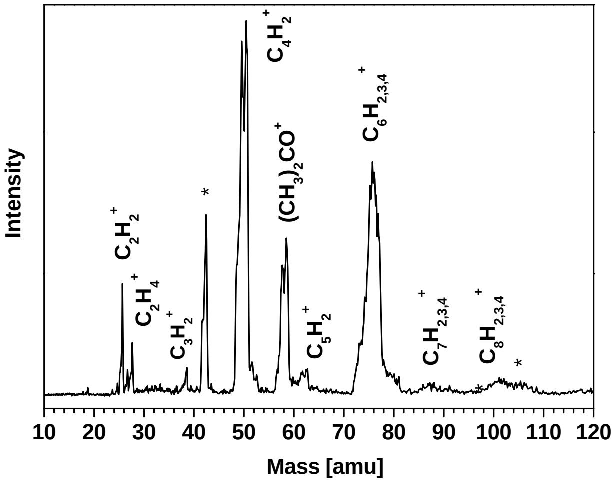

Fig. 4. A TOF mass spectrum of cations formed in a discharge of 8% C_2H_2 in He. Traces of acetone derivatives (indicated by ∗) are observed as this is routinely used in pressurised acetylene bottles. Typical ion densities amount to 10^{10} ions/cm^3.

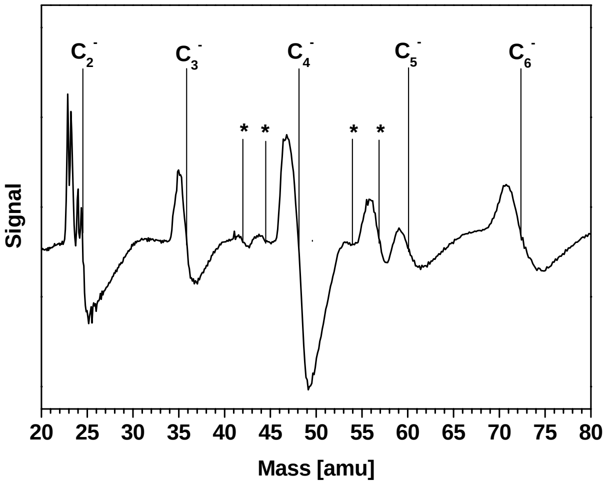

Fig. 5. A TOF mass spectrum of anions formed in a discharge through C_2H_2 in He. The line shape of the peaks is different now and due to differentiation caused by the decoupling capacitor between anode and oscilloscope. Therefore, the signal is proportional to the derivative of the intensity. The (∗) indicate acetone fragments. At this stage it is not possible to determine absolute anion densities.

currently under research in spectroscopic studies; $C_6H_4^+$, for example, was just recently shown to have a non-linear non-cyclic ground state structure [12].

Surprising is the effective production of anions in the plasma. To observe these negatively charged species the time-of-flight setup had to be modified; the polarity of the acceleration field and the detection system had to be reversed and the MCP cathode and anode had to be put at ground potential and +1500 V, respectively. A decoupling capacitor was used to connect the latter to a digital storage oscilloscope. In Fig. 5 the mass spectrum of a discharge through acetylene is shown, resulting in an effective production of species of the form C_n^-. Up to now only C_2^- has been observed in direct absorption in a planar plasma expansion [7], but clearly also much larger species are produced. It appears very promising to use such a source for high resolution studies of pure carbon chain anions, particularly as the oscillator strength increases with increasing chain length. So far gas phase studies of carbon chain anions have been limited to rather low resolution multi-photon detachment approaches [4,21]. Rotationally resolved spectra, as previously obtained for carbon chain cations and carbon chain radicals using cavity ring down spectroscopy (see e.g., Refs. [12,13,22]) are within range and of particular astrophysical interest in view of the role carbon chain anions are expected to play in interstellar chemistry [23].

6. Laser spectroscopic results

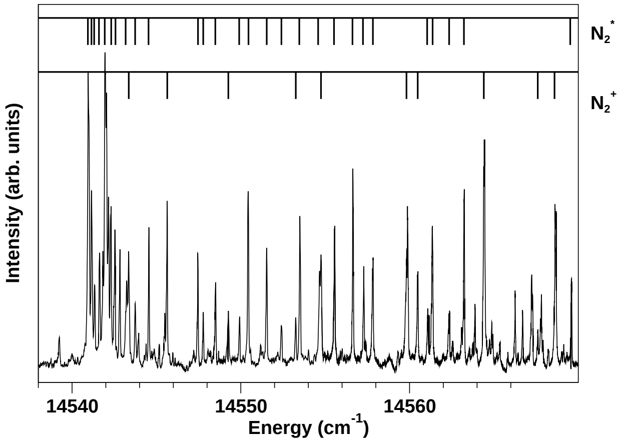

Fig. 6. A spectrum recorded by CRD in a pure N_2 plasma is shown. Transitions due to the $(v', v'') = (3, 0)$ band of the $A^2\Pi_u - X^2\Sigma_g^+$ electronic transition of N_2^+ and transitions belonging to the (3, 0) band of the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ electronic transition of electronically excited molecular nitrogen are indicated. A quantummechanical labeling is available from Refs. [25–27].

The mass spectrometric study gives information on charged species that are formed in the plasma. It does not produce information on neutrals or on which states are populated in the plasma. This information is obtained from a laser spectroscopic study. In Fig. 6 a cavity ring down spectrum around 688 nm is shown that has been recorded in a discharge of pure N_2. Some of the observed transitions belong to the well known $(v', v'') = (3, 0)$ band of the $A^2\Pi_u - X^2\Sigma_g^+$ electronic transition of N_2^+, a molecular ion that has been used in numerous studies to test the sensitivity of new spectroscopic equipment (see e.g., Ref. [24]). Apart from transitions belonging to the (3, 0) band of the N_2^+ cation a number of other transitions is observed. These belong to the $(v', v'') = (3, 0)$ vibrational band of the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ electronic transition starting from electronically excited $(A^3\Sigma_u^+)$ N_2. Transitions starting from electronically *and* vibrationally excited N_2 are observed as well. This is shown in detail in Fig. 7 where an assignment (taken from Refs. [25–27]) for the observed rotational transitions in the (4, 1) band is given.

In the past, a few direct absorption studies were reported in which mainly cell discharges are used to get access to elec-

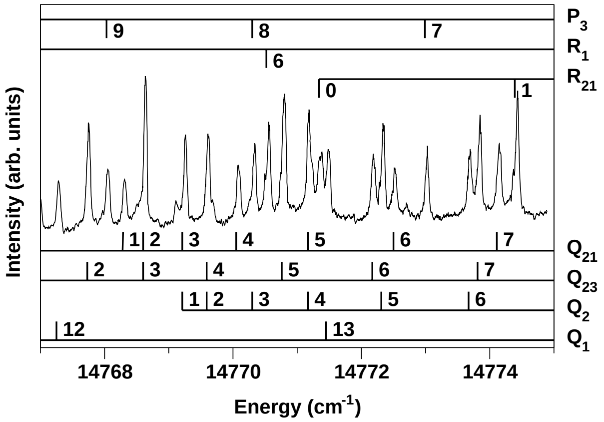

Fig. 7. An assigned CRD spectrum recorded in a pure N_2 plasma expansion of the $(v', v'') = (4, 1)$ band of the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ electronic transition starting from rovibronically excited molecular nitrogen.

tronically [28] and vibrationally [29] excited states of N_2; the present study demonstrates that a planar plasma expansion is suited for these purposes as well. In recent studies on jet cooled NO [30,31] and CF [32] it was shown that plasma expansions can be used to study vibrationally excited species ($T_{vib} \sim 7000\,K$) at much lower final rotational temperatures ($T_{rot} \sim 10–30\,K$). This can be understood when ground state vibrational levels are populated from higher electronic states that are excited during the discharge pulse. The subsequent relaxation is more effective for rotationally than for vibrationally excited levels. The present result shows that a similar principle applies for electronically excited states in molecular nitrogen as well—presumably because of the long lifetime of $A^3\Sigma_u^+$ (1.9 s for $v'' = 0$). In addition, vibrationally excited levels in the electronically excited state become directly accessible. For a vibrational temperature of the order of 4000 K rotational temperatures between 10 K (strongly diluted expansion) and 150 K (pure expansion) are found[1].

7. Conclusion

It has been shown that a supersonic planar plasma expansion can be used to generate small and large cluster ions as well as a variety of positively and negatively charged carbon chain radicals. This offers much potential for future spectroscopic studies, particularly of molecular transients of atmospheric and interstellar interest that are typically formed in highly reactive environments. It is found that plasma conditions are critical and that on-line monitoring is very useful to determine the optimal conditions. In addition, an extension of spectroscopic applications to vibrationally and electronically excited species at (relatively) low rotational temperatures has been demonstrated using cavity ring down spectroscopy.

Acknowledgements

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[1] Following rotational intensity simulations with PGOPHER (C. Western, University of Bristol) much lower rotational temperatures of the order of 10 to 25 K are achieved in diluted mixtures of 2 to 5% N_2. This is also the case for transitions starting from vibrationally excited states.

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