



# Multiplex integrated cavity output spectroscopy of cold PAH cations

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## Abstract

Multiplex Integrated Cavity Output Spectroscopy (MICOS) is a new cavity-enhanced absorption method that allows the use of broadband dye nanosecond pulsed laser sources and offers a sensitivity equivalent to CRDS. MICOS has been coupled to a pulsed discharge slit nozzle to measure the spectra of the cold naphthalene ( $C_{10}H_8^+$ ), acenaphthene ( $C_{12}H_{10}^+$ ) and pyrene ( $C_{16}H_{10}^+$ ) cations in the gas phase. A femtosecond relaxation timescale is measured for the  $D_5 \leftarrow D_0$  (0–0) transition of  $C_{16}H_{10}^+$ . Spectra recorded at high plasma energies also show evidence of fragmentation. The CH radical is observed and carbon nanoparticles are generated in the plasma.

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## 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are an important component of interstellar dust and are found in meteorites and interplanetary dust particles. PAHs are thought to carry the infrared emission bands (UIBs) that are detected in a wide variety of galactic and extragalactic environments [1]. PAHs are also thought to carry some of the diffuse interstellar bands (DIBs) seen in absorption in the near ultraviolet to near infrared spectra of stars that are obscured by diffuse interstellar clouds [2,3]. Interstellar PAHs can be neutral or ionized depending on the environmental conditions (density and radiation field). In the diffuse interstellar medium, however, PAHs are expected to be primarily present as free, cold, molecular ions [4]. The identification of the carriers of the DIBs has important implications for our understanding of the evolution of the interstellar medium and this issue has motivated an extensive laboratory effort over the past decade (for a recent review see [5]). New insights in the electronic [6–9] and vibrational [10, 11] spectroscopy and the intramolecular dynamics of free PAH ions have

recently been gained through the application of state-of-the-art laser-based techniques specifically developed to address this challenging problem.

Here, we describe a new technique, Multiplex Integrated Cavity Output Spectroscopy (MICOS) that we have developed to measure the absorption spectrum of free, cold, large carbon-bearing molecular ions and discuss the new results that have been obtained with this method. In our previous studies [7], we followed an approach based on Cavity Ring Down Spectroscopy (CRDS). CRDS is a *time-domain* method which monitors the time dependence of photons escaping the cavity after their injection in the cavity mode(s). The high sensitivity of cavity-based methods rests upon the long residence time of the photons trapped inside the high finesse cavity. Recently, *intensity-domain* methods exploiting high finesse cavities have been introduced: Cavity Enhanced Absorption Spectroscopy (CEAS) and Integrated Cavity Output Spectroscopy (ICOS) [12,13].

A number of groups [14,15] have also taken advantage of the use of a broadband source for injection of photons in a high finesse cavity. We have adopted yet another approach, and developed a MICOS spectrometer that uses a broadband nanosecond pulsed dye laser that is robust (a crucial requirement when coupled to a pulsed discharge nozzle that is a recognized source of

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noise and instability), simple to setup and to operate, and of moderate cost. Our technique combines the ICOS detection scheme with the use of a spectrally broad light source. In this design, the output of the cavity is sent through a wavelength dispersing element (such as a grating) to a linear CCD detector array. The operating principle of this method was first demonstrated with Ringdown Spectral Photography by measuring the weak oxygen b–X (1–0) band [16]. In our implementation, the broadband dye laser output coupler is absent and the light is thus generated after only two passes in the active medium. This optical configuration results in a *modeless* laser emission. Although the broadband amplified spontaneous emission spectrum is structured, it was found that these structures are stable over time and can be removed by dividing two consecutive spectra.

In this Letter, we report direct absorption measurements in the gas phase of the electronic bands of the cold naphthalene ( $C_{10}H_8^+$ ), acenaphthene ( $C_{12}H_{10}^+$ ) and pyrene ( $C_{16}H_{10}^+$ ) cations and describe the method developed for this specific purpose. The MICOS spectrometer is described in Section 2. The results are discussed in the following section where they are compared with CRDS measurements. The conclusions are discussed in Section 4.

## 2. Experimental

The experimental apparatus combines a pulsed discharge slit nozzle (PDN) for the production of free, cold

aromatic ions with a MICOS spectrometer for the detection and the measurement of the spectra of these ions. The PDN component of the experimental system has been modified from the original design of Saykally et al. [17] and is described in detail in [7]. Fig. 1 shows a schematic of the experimental setup. Briefly, in our typical running conditions (1 atm backing pressure of Argon, <1% PAH dilution) the PDN source produces very intense, 500  $\mu$ s-long, ionized gas pulses every 100 ms. The plasma expansion generated by the PDN is probed by the spectrometer about 2 mm downstream the electrodes. The photon source is a broadband homemade dye laser. The pump beam generated by the second/third harmonic of a nanosecond pulsed Nd:YAG laser (Spectra Physics GCR-130 with 6350 injection seeder, 210 mJ at 532 nm and 100 mJ at 355 nm) is focused into the dye cell with a cylindrical lens. The dye laser consists of one 40-mm long side-pumped dye cuvette and one back mirror (Lambda Physik). The output coupler is removed from the dye laser cavity because it induces strong ( $\sim$ 15% amplitude) periodic modulations of the spectrum of the laser. As a consequence, light is generated after only two passes in the active medium by amplified spontaneous emission precluding the emergence of a dye laser modes comb. The output characteristics of this modeless laser are intermediate between a truly coherent laser oscillator and a completely incoherent thermal source. Dye solutions of a mixture of DCM ( $\sim$ 450 mg/l dissolved in DMSO) and of Coumarin 440 ( $\sim$ 300 mg/l in methanol) were prepared for the 640–680 nm and the 425–465 nm spectral regions, respec-

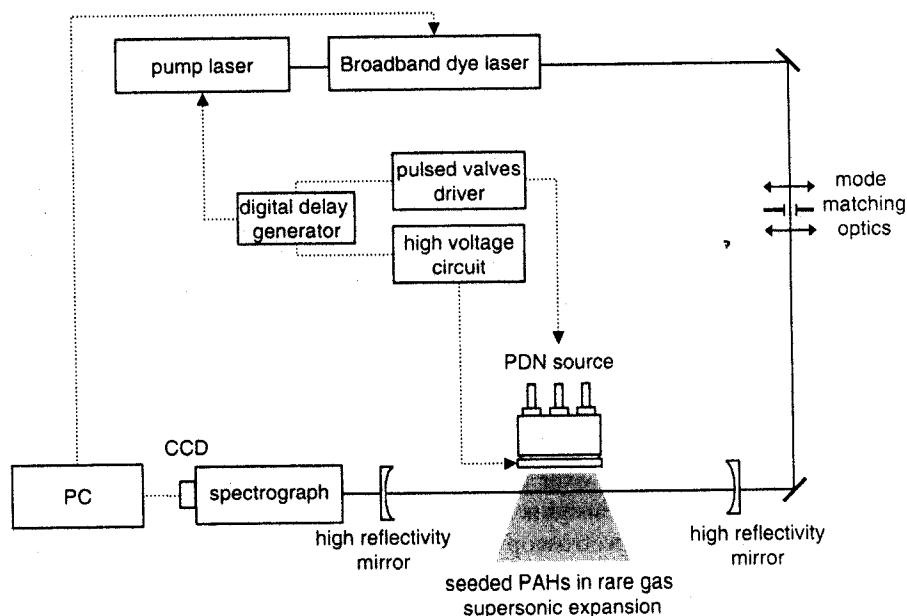


Fig. 1. MICOS-PDN experimental setup. The MICOS spectrometer relies on a broadband dye laser combined to a high finesse cavity,  $\mathcal{F} \leq 20000$ , and a medium resolution spectrograph. The optical configuration of the dye laser consists in one back mirror and a side-pumped dye cuvette, resulting in a modeless broadband emission.

tively. For pump energy above  $\sim 100$  mJ, the conversion efficiency is about 5%. The divergence of the output beam is  $\sim 4.2$  mrad. The energy coupled into the cavity is typically  $\sim 1$   $\mu$ J (spread over 20 nm at half maximum) equivalent to a number of photons in the  $4\text{--}7 \times 10^{12}$  range depending on the wavelength window. The beam is collimated to maximize the throughput of the cavity. The cavity output mode pattern is imaged using a progressive scan high resolution camera (PULNIX TM-1300) and a 8-bit frame grabber (PIXCI SV5) looking through the rear mirror of the cavity. The photons leaking out the cavity are collected by a 68 mm spectrograph (Ocean Optics USB2000) in a Czerny–Turner configuration. The spectrograph is equipped with a 50  $\mu$ m entrance slit, a 1200 grooves/mm holographic grating and a 2048 pixels linear CCD array with a 12-bit A/D vertical resolution (Sony ILX511) that allows to cover the whole 400–700 nm range with a typical 0.75 nm resolution. The acquisition is triggered by a digital delay generator (SRS DG535) and the collection time set to its minimum value of 50  $\mu$ s. The data is transferred through a Universal Serial Bus to the PC for treatment by commercial software (Ocean Optics, OOIBase32). The signal collected on the CCD array, and displayed in Fig. 2, usually shows some asymmetry as the spectral profile corresponds to the convolution of the dye gain curve with the transmission curve of the high reflectivity mirrors – and marginally with the response curve of the spectrograph. The treatment of the signal is performed in three steps. First a reference jet spectrum (R) is recorded that consists of 1000 averaged single beam spectra with the gas jet pulse expanding and the plasma off. A sample spectrum (S) is then recorded over the same duration with the plasma turned on. The absorbance spectrum (A) is finally retrieved by dividing the sample spectrum (S) by the reference spectrum (R). Note that a dark spectrum (D) is subtracted from both the reference and sample spectra.

In addition to shot to shot cavity-input power fluctuations ( $\sim 10\%$ ) exemplified on Fig. 2a, each single beam spectrum shows noise at the three CCD counts level ( $\leq 0.3\%$  of the peak envelope) that can be reduced by averaging (Fig. 2b). Possible sources of noise are inhomogeneities of the dye gain and seeding photon noise. The latter phenomenon arises from the statistical nature of the spontaneous emission of photons from excited levels. Noise cancellation is obtained after averaging 1000 spectra leading to an absorbance noise level below 0.1%. This value translates into 0.1 ppm/pass for typical 100 ppm/pass high reflectivity mirrors or  $5.75 \times 10^{-8}$  cm/ $\sqrt{\text{Hz}}$  for a  $l = 55$  cm long cavity. To account for multiplexing, the detection limit is divided by the square root of the number of spectral elements that are sampled simultaneously. A spectral element (active detector), defined by the extent of the coverage of the image of the slit on the grating, is about 6.5 pixels

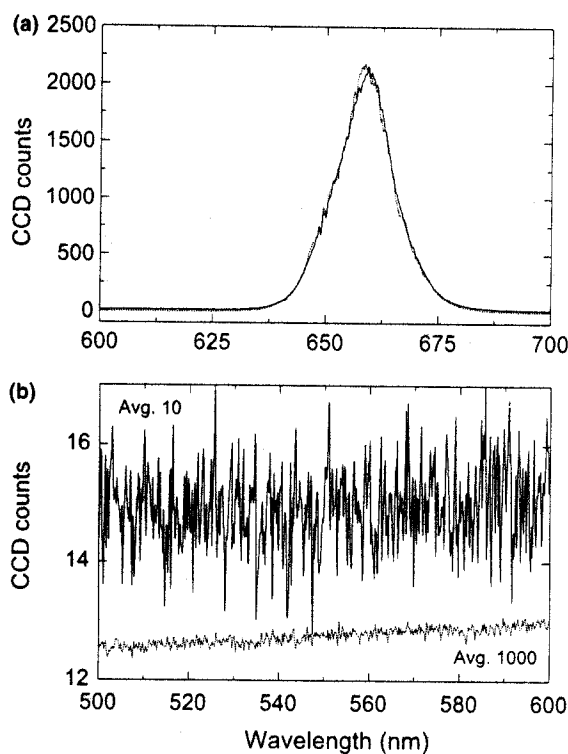


Fig. 2. Cavity output spectra of the broadband dye (DCM diluted in DMSO) pulse with the plasma turned off. Displays result from the averaging of 10 (full line) and 1000 (dotted line) single beam spectra. (a) The spectral profile corresponds to the convolution of the dye gain curve with the transmission curve of the high reflectivity mirrors and with the response curve of the spectrograph. The output is affected by shot-to-shot power fluctuations ( $\sim 10\%$ ). (b) Close up of the off-peak region of the cavity output spectrum. Top and bottom traces, slightly shifted for convenience, show standard deviation of 1.05 and 0.108, respectively. Note: a high quality dark spectrum has been subtracted from all spectra shown here.

under the current design. This leads to an estimated detection limit of  $3.2 \times 10^{-9}$  cm/ $\sqrt{\text{Hz}}$ , a value that is about one order of magnitude higher than the CRDS detection limit measured under similar conditions. MICOS is, however, much less affected by the long term fluctuations of the PDN source as all spectral data points are recorded simultaneously. Moreover, our experimental studies show that it is extremely difficult to achieve detection limits better than 0.1 ppm/pass with either of those two techniques when coupled to a PDN plasma source. The spectra are calibrated using Xe and Ne emission lines (Oriel calibration lamps 6033 for Xe and 6032 for Ne) placed before the entrance cavity mirror to ensure the same light path. In contrast to CRDS, MICOS is not an absolute measurement method. The absorption scale can be either inferred from the mirror reflectivity curve (when available) or calibrated using previously recorded CRDS spectra of the empty cavity. For example, if the losses of the empty cavity are of the order of 100 ppm/pass, a 1% absorbance spectral feature will correspond to a  $\sim 1$  ppm/pass absorption in a first approximation. To be valid, this calibration

procedure requires that measurements be performed under very similar conditions with the two techniques.

### 3. Results and discussion

The electronic absorption spectra of gas-phase naphthalene ( $C_{10}H_8^+$ ), acenaphthene ( $C_{12}H_{10}^+$ ) and pyrene ( $C_{16}H_{10}^+$ ) cations were measured with the MICOS technique. The  $D_2 \leftarrow D_0$  (0–0) and (1–0) vibronic bands of the naphthalene cation and the  $D_2 \leftarrow D_0$  (0–0) vibronic band of the acenaphthene cation are reported in Sections 3.1 and 3.2, respectively. These first two PAH cations were chosen because detailed CRDS data are available for comparison with the MICOS data [7]. The gas-phase spectrum of the  $D_5 \leftarrow D_0$  (0–0) band of the pyrene cation is reported for the first time and is discussed in Section 3.3. Evidence for fragmentation and soot formation is also seen at higher discharge energies through the observation of the (A–X) (0–0) CH radical absorption band and the detection of carbon nanoparticles in the PDN source. These results will be discussed separately [18].

#### 3.1. The naphthalene cation ( $C_{10}H_8^+$ )

Naphthalene was initially selected in this work because it is a prototype for linear PAHs. The first two absorption bands of the vibrational progression of the  ${}^2B_{3g}(D_2) \leftarrow X^2A_u(D_0)$  electronic band system of the naphthalene cation ( $Np^+$ ) were measured at 670.7 and 648.9 nm, respectively. The widths of the two bands before deconvolution, which include the contribution of the complexes formed with argon atoms, are 1.5 nm in both cases. The MICOS spectrum of  $Np^+$ , displayed in Fig. 3a, is well reproduced by the convolution of the synthetic spectra of  $Np^+$ ,  $Np^+-Ar$  and  $Np^+-Ar_2$  (in the 20:6:1 ratio derived from the CRDS spectra) with the apparatus function ( $\delta v_{app} \sim 0.75$  nm FWHM Gaussian lineshape). When accounting for extra losses, one can derive the absolute absorption intensity at each wavelength. By following this procedure, the maximum absorption values are found to be 33 and 14 ppm/pass for the (0–0) and (1–0) vibronic bands, respectively. These values are in good agreement with the absolute intensities derived from CRDS experiments performed under very similar conditions, the only exception being that the temperature of the  $Np$  sample was slightly higher in the MICOS experiments (80 °C instead of 66 °C). This should have no or little effect, however, since all previous experiments show that there is an optimum sublimation temperature for  $Np$  around 70 °C beyond which point the number density of  $Np^+$  tends to stabilize. The small, 7 ppm/pass, discrepancy found for the strongest band (40 ppm/pass in CRDS [7]) between the two sets of experiments can be easily accounted for

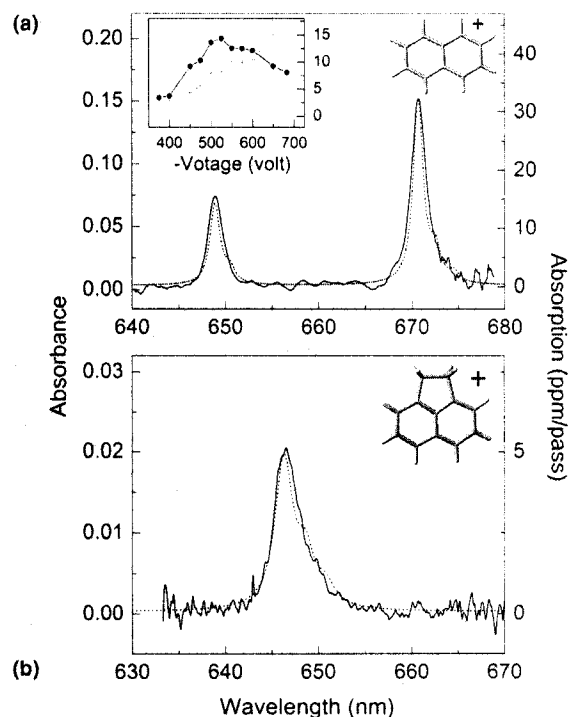


Fig. 3. Experimental and simulated MICOS spectra. (a) Spectrum of the (0–0) and (0–1) vibrational bands of the  ${}^2B_{3g}(D_2) \leftarrow X^2A_u(D_0)$  electronic band system of the naphthalene cation ( $C_{10}H_8^+$ ). Dotted line: synthetic spectrum corresponding to the spectrum of  $Np^+$ ,  $Np^+-Ar$  and  $Np^+-Ar_2$  (in the 20:6:1 ratio derived from the CRDS spectra) convolved with the apparatus function of the spectrograph. Insert: Variation of the global extinction (dotted line) and of the absorption of the  $D_2 \leftarrow D_0$  (1–0) band at 648.87 nm of the naphthalene cation (solid line) with the applied discharge voltage. (b) Spectrum of the (0–0) vibrational band of the  $B_2(D_2) \leftarrow XA_2(D_0)$  electronic band system of the acenaphthene cation ( $C_{12}H_{10}^+$ ). Dotted line: synthetic spectrum corresponding to the spectrum of  $Ac^+$ ,  $Ac^+-Ar$  and  $Ac^+-Ar_2$  (in the 7.5:3:1 ratio derived from the CRDS spectra) convolved with the apparatus function of the spectrograph.

by the slight variability of the PDN source conditions from one experiment to another. The derived value for the relative intensity ratio of the two bands is 2.35 in MICOS measurements, in very good agreement with the value of 2.38 measured in previous experiments [6,9].

Taking advantage of the multiplex aspect of the MICOS spectrometer, we were also able to investigate the variation of the absorption intensity of  $Np^+$  with the pressure of its neutral precursor (i.e., the dilution factor of  $Np$  in the carrier gas Ar) and with the discharge voltage applied to the PDN source. For instance, Insert of Fig. 3 shows that the  $Np^+$  absorption signal (full line) reaches a maximum for a discharge voltage of about –550 V. The decrease observed for the signal from this point on is interpreted as due to the apparition of other formation/destruction channels for  $Np^+$ . An increase of the global losses with the discharge voltage is also simultaneously observed and is attributed to the combination of two factors: an increase in the extinction