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Mid-infrared continuous wave cavity ring-down spectroscopy of a pulsed hydrocarbon plasma

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ABSTRACT

We describe an ultra-sensitive method to record high-resolution mid-IR spectra of hydrocarbon-chain species and other astrophysically relevant molecular transients in a pulsed planar plasma expansion. The method uses an all fiber-laser-based optical parametric oscillator (OPO) light source, in combination with continuous wave cavity ring-down spectroscopy (cw-CRDS) as a direct absorption detection tool. A hardware based multi-trigger concept is introduced to apply cw-CRDS to pulsed plasma. The performance and potential of the method are illustrated and discussed, based on extended and fully rotationally resolved sample spectra of HC_4H and HC_6H, generated in the discharge of an expanding C_2H_2/He/Ar gas mixture.

1. Introduction

Carbon chains and their derivatives, $X_mC_nY_l^{(+/-)}$, with X and Y typically H, N, O, or S, have attracted much interest because of their relevance to the chemistry of the interstellar medium (ISM). The spectroscopic characterization of these reactive species, both in the laboratory and in the ISM, from the microwave to the UV, has been the topic of many studies over the last few decades. Fourier transform laboratory microwave studies [1] have made possible the discovery of tens of highly unsaturated carbon-chain species [2], including linear $HC_{11}N$ [3], and ions such as $HCCCNH^+$ [4], C_6H^- [5], and C_8H^- [6]. For linear centro-symmetric chains, like the bare carbon species C_n [7–11] and polyacetylenes ($HC_{2n}H$) [12,13] – radio-silent due to the lack of a permanent dipole moment – mid- or far-infrared (IR) spectroscopy offers a powerful alternative approach for detection and characterization. Since carbon-chain species are considered to be potential carriers of the diffuse interstellar bands (DIBs), i.e., optical absorption features observed in star light crossing translucent interstellar clouds [14,15], electronic spectra of carbon-chain species have also been studied extensively in the laboratory (see Refs. [11,16,17] for a review).

The present letter focuses on the laboratory detection of hydrocarbon-chain species in the mid-IR, a spectroscopic range well known as a molecular fingerprint region. Fourier transform IR spectroscopy has been widely used to investigate the ro-vibrational spectra of gas-phase molecules with high resolution and broad coverage [18,19]. The ongoing improvements and upgrades of narrow-band mid-IR light sources, such as tunable diode lasers (TDLs), quantum cascade lasers (QCLs), continuous wave optical parametric oscillators (cw-OPOs) and difference frequency generation (DFG) devices, allow laser based IR spectroscopic techniques to achieve high detection sensitivity and molecule selectivity [20]. Recently, ultra-sensitive cavity enhanced mid-IR spectroscopic techniques, such as continuous-wave cavity ring-down spectroscopy (cw-CRDS) [21–24] and noise-immune cavity-enhanced optical heterodyne velocity modulation spectroscopy (NICE-OHVMS) [25,26] have been introduced and applied to the study of astrophysically relevant molecular ions.

To date, laboratory high-resolution IR spectra of gas-phase bare carbon (C_n) chains [9–11,27] and the linear C_3Si_2 species [28,29] have been studied with IR-laser absorption spectroscopy and laser ablation of carbon rods. For other carbon-chain derivatives, particularly highly unsaturated hydrocarbon-chain species ($C_nH_m^{(+/-)}$, typically with $n > 2$ and $m \leqslant n$), accurate gas-phase IR data are only available for di- and tri-acetylene (HC_4H and HC_6H) [30,31]. High-pressure pulsed planar plasma expansions, generated by specially designed multi-layer slit discharge nozzles [32,33], have proven to be successful in producing large abundances of highly reactive molecular transients, and have been employed in a series of electronic spectroscopic studies of hydrocarbon-chain radicals [16,17,34,35]. The work presented here describes a flexible OPO-based cw-CRDS spectrometer capable of recording high-resolution mid-IR spectra of molecular transients in a pulsed plasma, specifically hydrocarbon-chain species. A new boxcar gated integrator based trigger and timing scheme is introduced to apply cw-CRDS as a continuous technique to a pulsed plasma expansion. The performance of this method is illustrated with a substantial spectral extension of the available transitions in the C–H stretch region of the polyacetylenes HC_4H and HC_6H.

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2. Experimental details

A schematic of the experimental setup is shown in Figure 1, consisting of a slit-jet discharge nozzle, a cw-CRDS detection scheme, and a trigger and data acquisition (DAQ) system.

2.1. Slit-jet discharge nozzle

The pulsed planar plasma is generated by discharging an acetylene/rare gas mixture in a multi-layer slit discharge nozzle and is used to produce carbon-chain species. Details of this pulsed plasma source have been described previously [32,33]; recent applications are described in Refs. [34–36]. A 1:1 helium–argon gas mixture is seeded with 0.5% C_2H_2 and is expanded through the 300 μm × 3 cm slit throat of the discharge nozzle into a vacuum chamber that is evacuated by a roots blower pump station with a total pumping capacity of 4800 m^3/h. A high voltage pulse (~1.2 ms, and $V/I \sim -1200$ V/50 mA) is applied to the two electrodes of the discharge nozzle, and timed to coincide with the gas pulse (~1.5 ms) controlled by a pulsed valve (General Valve, Series 9, 2 mm orifice) mounted on top of the nozzle body. With the backing pressure of the precursor gas mixture at ~15 bar, the local pressure at the slit throat is ~5–6 bar when the pulsed valve is on, which is suitable for producing long carbon chains and other complex transient species in the plasma. The typical stagnation pressure in the chamber during jet operation is ~0.02 mbar.

2.2. OPO-based cw-CRDS

The narrowband mid-IR light source used is the idler output of a commercial single-frequency single-mode cw-OPO system (Aculight, Argos 2400-SF, Module B). The cw-OPO uses a periodically-poled lithium niobate (PPLN) crystal and is pumped with a total power of 10 W at 1.06 μm by a distributed feedback (DFB) fiber laser (NKT Photonics, Koheras Basik Y-10) amplified in a fiber amplifier (IPG Photonics, YAR-10K-1064-LP-SF). The idler wave of the OPO has an effective bandwidth of ~1 MHz over 80 ms, and a total output power of ~1.2 W. The idler wavelength covers roughly the 3100–4200 cm^{-1} (3.2–2.4 μm) region and is continuously tunable over ~100 GHz by tuning the wavelength of the seed laser (DFB fiber laser). A precisely controlled voltage (0–200 V) is applied to the piezo-electric transducer (PZT) of the seed laser to guarantee fine, 'mode-hop-free' tuning of the OPO-idler wavelength. Coarse tuning is achieved by adjusting both the intracavity etalon angle and the position of the PPLN crystal in the cw-OPO system.

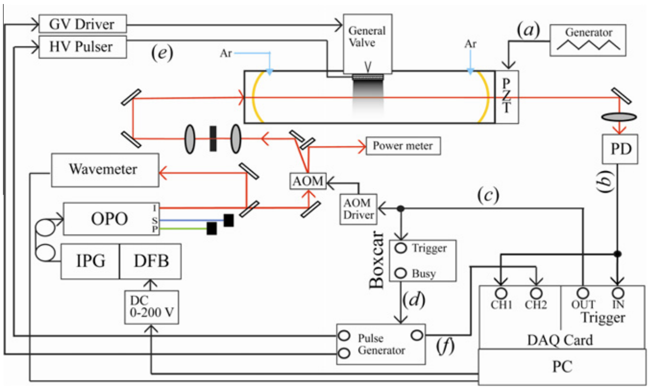

Figure 1. Schematic overview of the experimental setup. DFB: distributed feedback fiber laser (seeder); IPG: fiber amplifier; OPO: optical parametric oscillator with pump (P), signal (S) idler (I) beams; AOM: acousto-optic modulator; PZT: piezoelectric transducer; PD: photovoltaic detector. The time sequence of (a)–(f) is illustrated in Figure 2 and details are listed in the text.

The mode structure of the OPO idler output is mainly TEM_{00}, facilitating the use of cw-CRDS. The beam is directed through a germanium acousto-optic modulator (AOM). The first-order deflection, ~10% of the idler wave under an angle of 15°, is spatially filtered by a two-lens telescope system configured with a 150 μm pinhole, and then coupled into the 56 cm long ring-down cavity. The cavity comprises two high reflectivity (R > 99.97% at 3 μm) plano-concave (1 m curvature) mirrors incorporated in high precision alignment tools that are mounted on opposite sites of an ISO-160 cross piece that also holds the plasma source. The optical axis of the ring-down cavity is parallel to, and ~5 mm downstream from the slit throat of the discharge nozzle. Ring-down events are generated using a standard passive mode-locking scheme, as described in Refs. [21,37]. The cavity length is modulated at 20 Hz by applying a periodic triangle-wave voltage (trace a of Figure 2) to a PZT mounted on one of the mirror holders, ensuring that the cavity length is in resonance with the IR wavelength at least twice and at most four times in one period (trace b of Figure 2). This corresponds to a mirror translation of a little more than 1.5 μm. The cavity-transmitted light is detected by an IR-photovoltaic detector (Vigo System S.A., PVI-3TE-5, 50 MHz) and used as input to the signal and trigger channels of a fast DAQ card (Gage, Razor 1422, sampling rate 200 MS/s per channel). At the moment that the intensity of the cavity-transmitted light reaches a preset threshold value, the DAQ card is triggered and a synchronized TTL pulse from the trigger-out channel is generated (trace c of Figure 2). This TTL pulse is used to switch off the AOM, initiating a ring-down event that is quantified by its ring-down time (τ) using a fast exponential fitting algorithm [38]. Typical ring-down times in the present experiment amount to $\tau \sim 5$ μs.

2.3. Trigger and DAQ system

To apply cw-CRDS measurements to a pulsed plasma expansion, it is necessary to guarantee that the plasma pulse and the ring-down event coincide in time. To achieve this, several passive-mode-locking based detection methods have been successfully introduced in the past by a number of groups [22,33,39–41]. In general, these methods employ a programming-based multi-trigger and ring-down prediction scheme in the DAQ system. The latest variant of such DAQ software and software interfacing with pulse generators has been described in detail in the Supplementary material of Ref. [22].

In this work, we introduce a different concept, facilitating a hardware-based timing and trigger scheme. The detection principle is similar to that described in Refs. [22,39,41], but the implementation of a boxcar gated integrator (SRS, SR250) comes with a number of specific advantages. The trigger-out of the DAQ card (trace c of Figure 2) is not only used to control the AOM, but also to trigger the boxcar integrator, as shown in Figure 1. By setting a suitable delay time in the boxcar, a TTL pulse with a duration longer than one full PZT-ramp period (i.e., >50 ms) is generated at the 'busy' output channel. This long pulse is then used as a busy-time window within which one plasma pulse is generated and absorptions are measured using cw-CRDS. In practice, the detection scheme is operated as follows:

(1) A cavity resonance generates a TTL pulse from the trigger-out terminal of the DAQ card at time t_{00}. This pulse triggers the boxcar, which has a delay time set to 75 ms. In this way, a busy-time window, beginning at t_{00} and with a 75 ms duration, is generated by the boxcar (trace d in Figure 2).
(2) The rising edge of the busy-time window triggers the multi-channel pulse generator (SRS, DG535) which provides an appropriately time-delayed pair of pulses to trigger the pulsed valve and the high voltage pulser for plasma genera-