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Cavity enhanced plasma self-absorption spectroscopy

Anton Walsh, Dongfeng Zhao (赵东锋),^{a)} and Harold Linnartz

Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, University of Leiden,
P.O. Box 9513, NL 2300 RA Leiden, The Netherlands

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We introduce *cavity enhanced plasma self-absorption spectroscopy* (CEpSAS), a sensitive spectroscopic diagnostic tool that is used here for plasma analysis, but can also be used for any light emitting sample. It works *without* an additional external light source. In CEpSAS, plasma is located in an optically stable cavity consisting of two high reflectivity mirrors, and here it acts both as light source and absorbing medium. We present proof of principle results to illustrate the performance of this technique that literally combines “sense and simplicity.” Quantitative absorption experiments are described on a supersonically expanding hydrocarbon plasma. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4748125>]

Non-equilibrium plasma by low-pressure gas discharges has attracted increasing interest not only in fundamental research but also in industrial applications, such as thin film deposition, semiconductor processing, surface activation or cleaning, and waste treatment. To understand the physical and chemical processes at play in plasma, *in situ* diagnostic techniques are required. Optical diagnostics based on molecular spectroscopy, such as absorption spectroscopy (passive) and emission spectroscopy (active), are well-suited as they are non-intrusive, molecule-specific, and allow for a good time and spatial resolution. Passive absorption spectroscopy with an external light source provides a tool for direct measurements of population densities in ground or long-lived excited states, and can be used to determine plasma temperature. With the development of tunable narrow-band lasers, laser-based absorption techniques such as infrared laser absorption spectroscopy (IRLAS),¹ laser induced fluorescence (LIF),² frequency and frequency-plasma double modulation spectroscopy,^{3,4} or cavity enhanced absorption techniques⁵ have been used to search for species that are formed in very low abundances, such as molecular transients. Given the excess energy in plasma, spectral and temporal analysis of plasma induced emission, optical emission spectroscopy (OES), or OES based actinometry^{6–10} have become popular plasma diagnostic techniques that in addition provide information on electronically excited states. In this Letter, a spectroscopic technique is introduced that is conceptually different from all these previous analytical methods as no external light source is needed. This makes the concept simple and generally applicable. The principle is based on plasma self-absorption spectroscopy.

Plasma self-absorption is a process, in which a photon emitted by an excited atom or molecule may be absorbed by another species in the same plasma source, contributing to the spectrum either as a result of radiative decay or collisional de-excitation of the absorbing species.^{11,12} In recent years, experimental and theoretical studies^{11–13} have evaluated the importance and influence of self-absorption on accurate OES diagnostics. In fact, it was shown that spectral line shapes and

line intensities measured by OES are affected by self-absorption.¹² Here we demonstrate that this process is also suited as a starting point for passive spectroscopy. Cavity enhanced plasma self-absorption spectroscopy (CEpSAS) is introduced as a sensitive spectroscopic tool. Cavity enhanced absorption spectroscopic techniques, based on an artificial augmentation of the absorption pathlength (up to 10^4 – 10^5 times) by placing the absorbing medium inside an optical cavity, provide powerful means to detect trace species up to sub-ppbv (part per 10^9 by volume) levels.^{14,15} Well known methods include intracavity laser absorption spectroscopy (ICLAS), cavity ringdown spectroscopy (CRDS), cavity enhanced absorption spectroscopy (CEAS), and incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS). In IBBCEAS,^{16,17} the absorption is determined from the time-integrated intensity of a broadband light source, which is transmitted by the cavity and subsequently dispersed by a monochromator. CEpSAS uses a similar principle, however, without the need for an external light source, by using the plasma emission in the optical cavity as an intracavity light source for the direct absorption measurement.

In CEpSAS, the plasma source is placed at the center of an optical cavity, which consists of two plano-concave high-reflective mirrors mounted on high-precision alignment tools. The optical axis of the cavity crosses the selected plasma gas-phase area, as indicated in Fig. 1. To achieve a sufficient augmentation of the pathlength, light must be resonant inside the cavity, i.e., light rays are refocused within the cavity after successive reflections from the mirrors, so that optical energy is contained within the cavity. To efficiently gather the plasma-emitted light to the cavity resonance, the plasma source has to be imaged by both concave cavity mirrors; the distance from the edge of the plasma area to both concave mirrors needs to be greater than their focus length. Under paraxial approximation, the focus length of a slightly concave mirror is half the radius of curvature (ROC). Thus, we have

$$(L/2 \pm l/2) > r/2, \quad (1)$$

where L is the length of the optical cavity, l is the length of the plasma along the optical axis, and r is the ROC of the concave mirror. For an optically stable cavity,

^{a)}Electronic mail: zhao@strw.leidenuniv.nl.

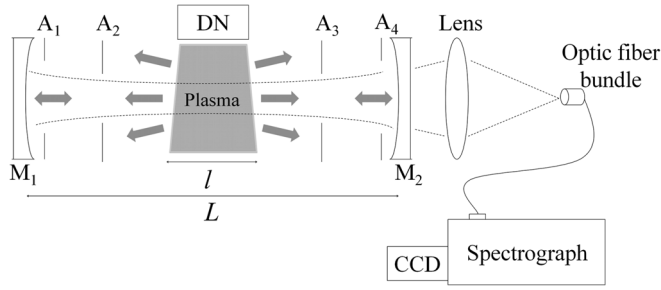


FIG. 1. Experiment set-up schematic. DN is the discharge nozzle, M_1 and M_2 are HR mirrors (positioned on high precision alignment tools) separated by distance L . The plasma pathlength is given by l . Four apertures are placed along the optical cavity axis, with diameters of 15 mm (A_1 and A_4) and 10 mm (A_2 and A_3). Light exiting the cavity is focused onto a circular to rectangular optic fiber bundle connected to a 13 μm slit of a spectrograph which contains a charge coupled device (CCD) detector.

$$0 < L < r \text{ or } r < L < 2r \quad (2)$$

is required. Combining Eqs. (1) and (2), the cavity optics need to satisfy

$$r + l < L < 2r. \quad (3)$$

Under the configurations of Eq. (3), most of the plasma-emitted light incident to the cavity mirrors will be resonantly coupled into the high-finesse cavity. Meanwhile, some of the non-resonant light inside the cavity may also be incident to the cavity mirrors. This amount can be effectively reduced by placing several small apertures along the cavity axis. The cavity resonant light will be reflected and finally leaks out of the cavity only through one of the two cavity mirrors, while the non-resonant cavity light will be reflected back to walls of the experimental chamber and scattered. Considering the reflectivity (R) of the cavity mirrors is always very high, typically $>99.99\%$, the amount of leaking light relative to the non-cavity resonant part can be approximately neglected.

Absorption of the cavity resonant plasma-emitted light by the plasma itself will be enhanced by a factor of $1/(1-R)$, similar as in the case of IBBCEAS.¹⁶ In conventional IBBCEAS, white light from a Xe arc lamp, LED or supercontinuum laser is coupled into an optical cavity containing the sample. The absorbance, A , of the sample is determined using

$$A = \left(\frac{I_0}{I} - 1 \right) (1 - R), \quad (4)$$

where I is the light leaking out of the cavity containing the sample, and I_0 is the light leaking out of an empty cavity. R is the averaged reflectivity of the two mirrors. I_0 can be approximated by

$$I_0 = \frac{I_{\text{in}}(1-R)}{2}, \quad (5)$$

where I_{in} is the light incident on the front mirror of the cavity and therefore I_{res} , the cavity resonant light is given by $I_{\text{in}}(1-R)$.

In CEpSAS, the situation is different; I_{res} is generated inside the cavity and therefore the absorbance of the sample in the cavity can be calculated using

$$A = \left(\frac{I_{\text{res}}}{2I} - 1 \right) (1 - R). \quad (6)$$

To calculate A , we need to measure I_{res} . To do this, we replace the mirrors of the optical cavity with quartz windows and measure the optical emission spectrum (I_{oes}). We then assume that I_{res} , for light leaking out of one cavity mirror, is linearly proportional to the sum of I_{oes} (light directly from the plasma incident on the mirror) and RI_{oes} (light reflected from the opposite mirror)

$$I_{\text{res}} = \chi I_{\text{oes}}(1 + R) \approx 2\chi I_{\text{oes}}, \quad (7)$$

where χ is a wavelength independent constant and $0 < \chi < 1$. For $\chi = 1$, all emission from the plasma incident on both mirrors of the cavity is resonant in the cavity. As χ decreases, the quantity of emission which is trapped inside the cavity decreases and more light becomes scattered to the walls of the chamber after reflection from the mirrors. Therefore,

$$A = \left(\frac{\chi I_{\text{oes}}}{I} - 1 \right) (1 - R). \quad (8)$$

In addition, over a short wavelength range of about 20 nm, the reflectivity of the mirrors can be approximated to be a constant. Using this assumption and the above expression, spectroscopic fingerprints of the absorbing species in the plasma can be identified quantitatively.

In this work, a supersonically expanding planar hydrocarbon plasma is used. A 0.4 mm \times 3 cm multi-layer slit nozzle geometry connected to a general valve (Series 9) is used to generate a 1 ms long gas pulse of a $\sim 0.5\%$ C_2H_2 in $\sim 50\%/50\%$ He/Ar gas mixture. The expanding gas is discharged by a negative high voltage pulse. This planar plasma source has been previously used to produce transient carbon-chain species and details are available in Refs. 5 and 18. Typical running conditions in the present experiment are: plasma pulse of $\sim 300\text{--}500 \mu\text{s}$, $V/I \sim -700 \text{ V}/80 \text{ mA}$, ~ 10 bars backing pressure for the jet expansion, and 20 Hz operation rate. The discharge nozzle is mounted in a vacuum chamber with its slit parallel to and ~ 7 mm away from the optical axis of the high-finesse cavity formed by two highly reflective mirrors ($r = 0.5 \text{ m}$, $R > 99.995\%$ at 532 nm¹⁹). The cavity length (L) is configured at 0.58 m to satisfy the requirement of CEpSAS derived in Eq. (3). A modest flow of N_2 gas is admitted into the arms of the main chamber near the mirrors, providing gas curtains that prohibit contaminations on the mirrors. The main chamber is pumped by a roots blower system with a total capacity of 1000 m^3/h .

The light leaking out of the cavity from one cavity mirror is focused onto a circular to rectangular optic fiber (180 \times 50 μm), which couples the light into a spectrograph (Shamrock 750 equipped with a 13 μm entrance slit, a 750 mm focal length, and a 1800 grooves/mm grating). From the spectrograph, light is dispersed onto a charge coupled device (Andor Newton CCD containing 2048 \times 512 square pixels of 13.5 μm width). A spectrum covering a 20 nm range can be measured at one time, with a typical spectral resolution of 0.03 nm. The absolute wavelength is calibrated using

plasma emission lines originating from argon. Several transmissions of the plasma through the cavity are accumulated for each measurement. A typical CCD exposure time lasts 90 s and a total of 10 transmissions are accumulated to give one measurement of $I_{\text{o es}}$ or I . It should be noted that this method works equally well for a pulsed plasma source with a low duty cycle as for a continuous plasma, as only signal is recorded at the moment that the plasma emits light. That is, in our case, no time gating or complex trigger schemes are needed.

Fig. 2(a) shows the measured $I_{\text{o es}}$ spectrum of the hydrocarbon plasma at ~ 525 nm by replacing the cavity mirrors (M_1 and M_2 in Fig. 1) with quartz windows. Dense and narrow spectral lines due to emission features of excited atoms or small species (such as Ar^* , C_2 , CH) can be clearly seen. Continuous emission is also present, although weak, and is likely due to free-free and bound-free transitions of transient species formed in the hydrocarbon plasma.²⁰

By replacing the windows by high reflectivity (HR) mirrors, a CEPsAS measurement is realized and the recorded spectrum I of light leaking out one cavity mirror, at ~ 525 nm, is shown in Fig. 2(b). It is found that strong narrow emission features in $I_{\text{o es}}$, such as CH features (Fig. 2(a)), are reproduced in I (Fig. 2(b)), but much weaker. This can be attributed to broad absorption and scattering by large hydrocarbons and particles created in the plasma. It is indeed found that the line intensities measured by OES are affected by self-absorption. The high finesse cavity enhances this effect. A measurement of the light leaking out of the cavity, I , yields not only emission but also absorption features. A clear absorption is visible at ~ 526.1 nm. By comparing the wavelength and spectral profiles to previous CRDS work

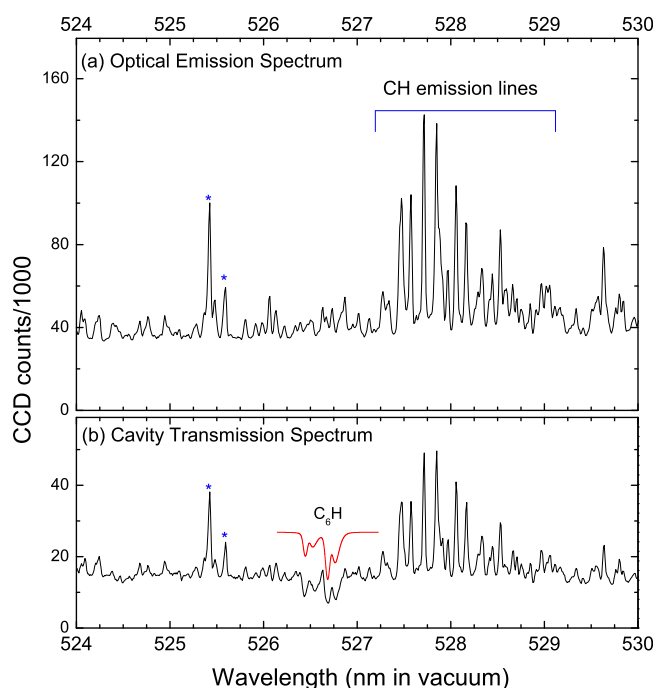


FIG. 2. Experimental spectrum of an expanding hydrocarbon plasma positioned in a high reflectivity cavity. (a) Optical emission spectrum, $I_{\text{o es}}$. (b) cavity transmission spectrum, I . The inset shows the C_6H simulated spectrum. Argon emission lines are marked with blue asterisks. Units of spectra are in absolute counts.

with the same plasma source and similar discharge conditions,^{18,21} the absorption spectrum can be assigned to the two spin-orbit components of the $\text{B}^2\Pi\text{-X}^2\Pi$ electronic origin band transitions of the open shell carbon chain radical C_6H . Using the calculated oscillator strength,²² the C_6H expansion densities are estimated to be $\sim 10^{10} - 10^{11}$ molecules/ cm^3 . The experimental spectrum shown in Fig. 2(b) is a proof that weak plasma self-absorption is efficiently enhanced by the high-finesse cavity.

To extract an absolute absorbance spectrum of the plasma, knowledge of the cavity mirror reflectivity is required and of the constant χ , see Eq. (8). Reflectivity curves for cavity mirrors in the present experiment are measured using CRDS in advance, and details can be found in the supplementary material.¹⁹ We assume that all light measured in the $I_{\text{o es}}$ spectrum is trapped inside the cavity and we choose $\chi = 1$. The resulting absorbance spectrum is shown in Fig. 3(a). Rotationally unresolved absorption features of the P and R branches of the $\text{B}^2\Pi_{3/2}\text{-X}^2\Pi_{3/2}$ and $\text{B}^2\Pi_{3/2}\text{-X}^2\Pi_{3/2}$ transitions can be identified clearly. The P and R branches of the $11_1^1 \mu^2\Sigma - \mu^2\Sigma$ transition of C_6H around 524.4 nm as well as an electronic transition of C_5H_3 at ~ 529.6 nm,^{18,23} not apparent in the $I_{\text{o es}}$ spectrum, also become visible in the extracted absorption spectrum.

The maximum absorbance of the C_6H R-branch peak of the $\text{B}^2\Pi_{3/2}\text{-X}^2\Pi_{3/2}$ component band transition in the hydrocarbon plasma is estimated to be 150 ± 20 ppm per pass, from previous CRDS measurements, in agreement with the absorbance measured here. This confirms the assumption that the bulk of light incident on either mirror is resonant, i. e., that χ can be set to 1.

The estimated sensitivity of the measurement is better than 10 ppm. The sensitivity can be further improved by using even higher reflectivity mirrors to increase the effective pathlength of the light resonant in the cavity. In contrast to other cavity based optical detection techniques (e.g., CRDS and IBBCEAS), the use of higher reflectivity mirrors is not complicated in CEPsAS, as the light source is intracavity and there is no difficulty coupling light into the cavity. Consequently, the ultimate sensitivity is dependent on the intensity of the OES of the plasma. Plasma with an intense broad emission will decrease the signal to noise ratio (S/N), increasing the detection sensitivity. The S/N can also be improved by using longer exposure times.²⁴ A measurement of light leaking out of both mirrors simultaneously can also improve S/N.

Simulations of the C_6H and C_5H_3 spectra, using the PGO-PHER software,²⁵ are shown in Figs. 3(b)–3(d). Rotational temperatures are estimated to be 32 ± 2 K. This value is only an average temperature, as light resonant in the cavity covers a ca. 10 mm downstream cut through the expanding plasma—a value determined by the diameter of the iris on either side of the plasma—and this large cross-section does not allow to determine one specific temperature. This also applies to the decreasing downstream plasma density. Improvements in spatial resolution, however, can be realized by placing a further set of limiting apertures ($A1$ – $A4$ in Fig. 1, with diameters of 10 and 15 mm) inside the cavity.

Measurements discussed in the present work have an effective exposure time of ca. 7 s, taking the plasma duration

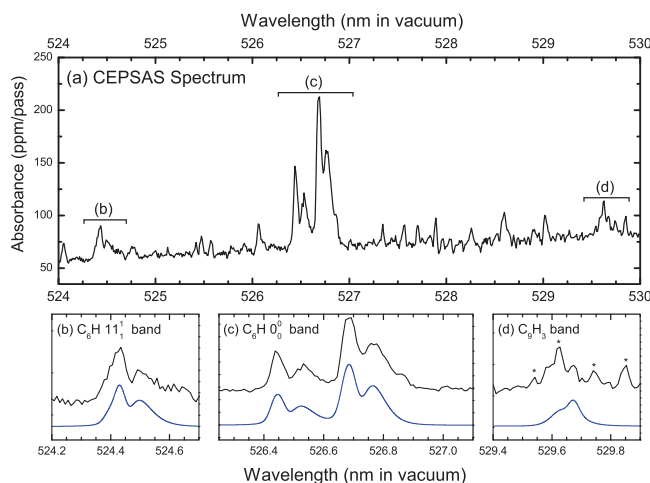


FIG. 3. (a) Extracted CEpSAS spectrum of an expanding hydrocarbon plasma between 524 and 530 nm. The insets show zoomed in views of electronic transitions of C_6H ((b), (c)) and C_9H_3 (d), together with simulated spectra. The asterisks in panel (d) mark absorption from other species in the plasma (see more details in the supplementary material).

as ca. 400 μs . Effective exposure times as low as 2 s were also used to observe C_6H . Consequently, CEpSAS is also suited to provide time-resolved information, on a scale of a few seconds. A higher time resolution may be realized by using a time-resolved Fourier-transform spectrometer as detector. This will realize a time resolution at the order of 1 μs .²⁶

It is expected that cavity enhanced self-absorption spectroscopy will be useful beyond the field of plasma research. Cavity enhanced self-absorption can be applied, for example, to combustion and flame studies. Similar with a plasma source, combustion samples or flames emit light with a complicated spectral structure. By placing for example a combustion flame into a high-finesse cavity, the chemical and physical processes in the flame can be monitored, such as absolute concentration and spatial distributions of species in the flame. The latter can be realized by moving the burner with respect to the optical cavity axis. CESAS therefore is expected to be a general tool for monitoring key chemical and dynamical light emitting processes; in a single measurement, it is possible to record both emission and absorption signals.

To conclude, the experimental results presented here demonstrate that plasma self-absorption can be effectively enhanced with a factor of $(1 - R)^{-1}$ by a high-finesse optical cavity. Spectroscopic information of plasma absorption can be extracted from the CEpSAS spectrum, and further used for *in situ* plasma diagnostics and accurate investigation of plasma self-absorption effects. CEpSAS has a comparable detection sensitivity of trace species to other cavity enhanced spectroscopic techniques, but while other techniques can be more selective because of a higher resolution, CEpSAS is far less complicated, not needing an external high-quality light

source. CEpSAS also gives access to time-resolved details in ongoing plasma, making it a generally applicable analytical tool for laboratory and industrial use that will find its way also outside the field of plasma applications.

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