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Note: Cavity enhanced self-absorption spectroscopy: A new diagnostic tool for light emitting matter

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We introduce the concept of *Cavity Enhanced Self-Absorption Spectroscopy* (CESAS), a new sensitive diagnostic tool for analyzing light-emitting samples. The technique works *without* an additional light source and its implementation is straight forward. In CESAS, a sample (plasma, flame, or combustion source) is located in an optically stable cavity consisting of two high reflectivity mirrors, and here it acts both as light source and absorbing medium. A modest portion of the emitted light is trapped inside the cavity, making 10^4–10^5 cavity round trips while crossing the sample and an artificial augmentation of the path length of the absorbing medium occurs as the light transverses the cavity. Light leaking out of the cavity simultaneously provides emission and absorption features. The performance is illustrated by CESAS results on supersonically expanding pulsed hydrocarbon plasma. We expect CESAS to become a generally applicable analytical tool for real time and *in situ* diagnostics. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4792840]

In the past two decennia, the use of cavity enhanced spectroscopic (CES) absorption techniques has developed rapidly, yielding detection sensitivies up to the sub-ppbv (part per 10^9 by volume) level.[1] Present CES applications are used in many different disciplines and range from breath gas analysis[2] and environmental monitoring[3] to plasma diagnostics.[4] In this contribution, we introduce a conceptually new CES detection scheme based on cavity enhanced self-absorption spectroscopy (CESAS), for measuring weak broadband absorptions in light-emitting matter (e.g., plasma, flames, and combustion sources). The experimental approach is simple, allows a simultaneous measurement of both absorption and emission patterns, and has the unique feature that it does *not* require an external powerful light source. The potential of CESAS is demonstrated on the example of an *in situ* detection of low concentration transients in expanding plasma in real time.[5]

In regular CES-based methods, an absorption sample is placed inside an optical cavity formed by two high reflectivity (HR) mirrors, commonly with $R > 99.99\%$, that are mounted on high precision alignment tools. Light from an external light source, such as a dye laser, super continuum laser, or Xe-arc lamp, is incident on the front mirror of the cavity. Light crossing this mirror (typically, only a small fraction $(1-R)$ of the initial intensity) enters the cavity where it becomes trapped, reflecting between the HR mirrors and undergoing up to 10^4–10^5 transverses through an absorbent before leaking out via one of them. There it is detected, e.g., as a cavity ring-down signal, with a photodiode or photomultiplier tube and a spectrum is recorded by monitoring the wavelength dependent cavity response. Following Beer-Lamberts law, the artificial augmentation of the path length, by $1/(1-R)$, increases the relative intensity change of the absorption and hence the detection sensitivity of the

measurement. Moreover, measurements are largely insensitive to eventual power fluctuations decreasing noise levels. Different CES-based methods exist, such as regular cavity ring-down spectroscopy (CRDS),[1] cavity enhanced absorption spectroscopy (CEAS),[6,7] intra-cavity laser absorption spectroscopy (ICLAS),[1] Fourier transform cavity-enhanced absorption spectroscopy (FT-CEAS),[8] or cavity-enhanced frequency-comb spectroscopy.[2,9] The conceptual difference with the new method introduced here is that in CESAS, the absorbing sample acts also as an intracavity light source facilitating self-absorption. Self-absorption is a process, in which a photon emitted by an excited atom or molecule is absorbed by another species in the same sample.[10–12] As a consequence, no external light source is needed.

Figure 1 shows a schematic for CESAS to work; the optical cavity comprising two plano-concave mirrors has to obey the condition
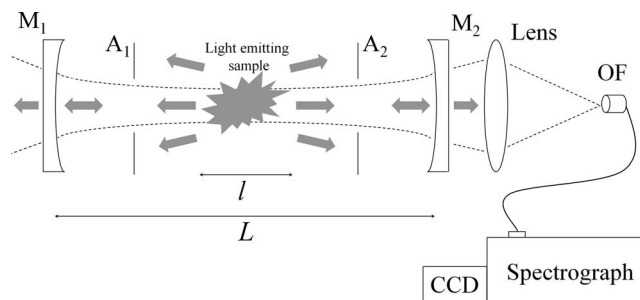
$$r + l < L < 2r, \tag{1}$$

FIG. 1. Schematic of a typical CESAS measurement. M_1 and M_2 are high reflectivity (HR) mirrors, separated by distance L. The light-emitting sample length is given by l. A_1 and A_2 are apertures, which tailor light through the cavity. Light exiting the cavity is focused onto an optical fiber, OF, connected to the slit of a spectrograph, which contains a charge coupled device (CCD) detector. Light exiting the cavity can also be focused directly into a spectrograph, but this can lead to reduced spectral resolution.

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where L is the length of the optical cavity, l is the length of the light-emitting absorbent along the optical axis, and r the radius of curvature of the cavity mirrors. A modest amount of light emitted from the sample is then trapped inside the cavity. The spectral energy distribution of the light-emitting sample determines for which wavelengths self-absorption is possible. As light transverses across the cavity, the self-absorption effect is enhanced. Light leaking out through either cavity mirror can be subsequently dispersed by a spectrograph onto a CCD—this combination determines the achievable spectral resolution—recording the wavelength dependent intensity pattern (I_ν). The absorbance spectrum (A_ν) of the sample is then calculated using

$$A_v = \left(\frac{\chi I_{oes}}{I_\nu} - 1 \right) (1 - R). \quad (2)$$

Here, χ is a wavelength independent constant, which is set to unity, assuming that all light emitted in the cavity and incident on both mirrors is also trapped in the cavity, and I_{oes} is the optical emission spectrum (OES). I_{oes} is measured by replacing the mirrors of the cavity with windows and measuring emission at the exit window. More details on the derivation of this formula are available from Ref. 5. The method works both for pulsed and continuous light sources as signal is only recorded when light is actually emitted, concurrent with the absorbing species. This makes the use of complicated trigger or time-gating systems to compensate, e.g., for low duty-cycles, redundant.

The performance of CESAS is demonstrated by monitoring supersonically expanding hydrocarbon plasma by discharging a 0.5% C_2H_2/He/Ar mixture that results in a reactive light-emitting hydrocarbon environment. Details of the sample application are described in Ref. 5. The plasma set-up employs a planar plasma discharge nozzle ($l = 0.03$ m) connected to a pulsed valve system to generate transient species at low final rotational temperatures and is described in detail in Ref. 13. The nozzle runs typically at 20 Hz with plasma pulses of the order of 500 μs. The plasma source is mounted in an optical cavity ($L = 0.58$ m) consisting of HR mirrors ($R_{532nm} > 99.995\%$ and $r = 0.5$ m). The use of CESAS is demonstrated on the example of the linear carbon chain radical C_6H.[13,14] The I_{oes}, I_ν, and the extracted CESAS absorbance spectrum are shown in panels (a), (b), and (c) of Fig. 2, respectively, between 526 and 528 nm, where the electronic origin band of C_6H has been identified before. It should be noted that all features shown in Figs. 2(a) and 2(b) represent fully reproducible signals; the noise level is not discernible here. I_{oes} compromises of a quasi-continuum emission, from free-free and bound-free transient species in the plasma, and strong narrow emission features of CH. The optical emission spectrum of the plasma was measured and the quasi-continuum component in the measured 350–850 nm range was found to be approximately constant. In Fig. 2(b), absorption signals become visible and the two highlighted bands correspond to the P, Q, R branch resolved $^2\Pi_{1/2}$-$^2\Pi_{1/2}$ and $^2\Pi_{3/2}$-$^2\Pi_{3/2}$ spin-orbit components of the B-X electronic origin band transition of C_6H. In Fig. 2(c), the expanded view is shown for the derived CESAS results. The resolution of the monochromator/CCD combination (~0.03 nm at 625 nm) is
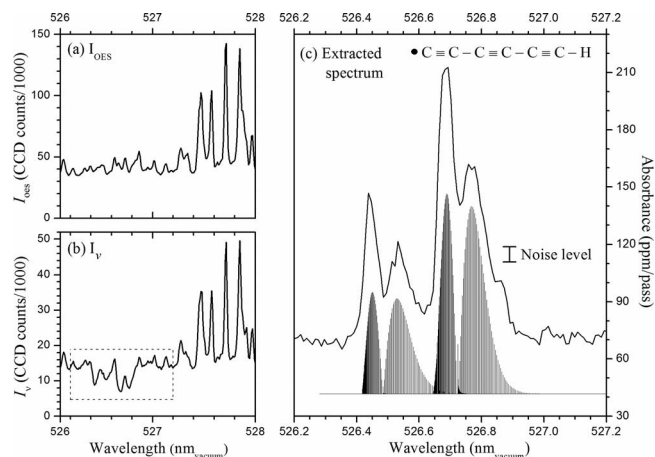

FIG. 2. Spectra of the transient C_6H species recorded through expanding hydrocarbon plasma using a supersonic planar plasma source. (a) Optical emission spectrum, I_{oes}, revealing continuous emission and discrete emission features, due to CH emission in the 527.2–528 nm range. (b) Cavity transmission spectrum, I_ν, showing both emission features as well as absorption features. The highlighted area contains the electronic origin band transition of C_6H and an expanded view is shown in the extracted CESAS absorption spectrum in panel (c). The noise level is indicated. A stick spectrum, simulated for previously reported molecular parameters[14] is incorporated for comparison.

not sufficient to resolve the spectrum rotationally, as indicated by the stick diagram based on previously derived molecular parameters.[14] The absolute absorbance of C_6H measured using CESAS matches previous CRD measurements recorded with an identical plasma set-up.[14] The C_6H transient is typically formed with densities of the order of 10^{11} particles/cm^3 and the spectrum in Fig. 2 demonstrates that self-absorption features indeed can be effectively enhanced by a high-finesse optical cavity. The estimated sensitivity, taking into account the oscillator strengths of the recorded transition, is better than 10 ppm, and comparable to other CES-based techniques. The sensitivity can be further enhanced by using longer exposure times, consequently improving the signal to noise (S/N) ratio, or using higher reflectivity mirrors, increasing the effective absorption path length. This does not cause any additional experimental problems, in contrast to regular CES-based optical techniques (e.g., CRDS or CEAS) where coupling light into the cavity becomes more and more difficult with increasing mirror reflectivity. In CESAS, the light source is situated inside the cavity and consequently the use of higher mirror reflectivity is intrinsically unproblematic. The achievable sensitivity of CESAS mainly depends on the intensity of the OES, i.e., a more intense broad emission will further improve S/N, along with detection sensitivity; i.e., the brighter the light source inside the cavity is, the easier its self-absorption spectrum can be recorded.

CESAS is a passive diagnostic tool for the study of light-emitting matter, such as plasma, combustion sources, and flames, and unique as a spectroscopic direct absorption technique as it does not need an external light source. It is the first broadband cavity enhanced absorption technique to use a light source placed *inside* the cavity. Other CES-related techniques may be more molecule selective, because of a higher spectral resolution, e.g., by providing rotationally resolved data, but CESAS is far less complicated, and still provides

comparable S/N achievable in measuring times of the order of a few seconds. The spectrum shown in Fig. 2(c) takes 15 min to record and taking into account the low duty cycle, corresponds to an effective measuring time of ~9 s. This short recording time in combination with a large spectral coverage also allows using CESAS as a real time diagnostic tool with a time response of a few seconds, depending on the level of averaging needed. In the practice of online diagnostics, many set-ups which currently employ OES can be easily adapted to a sensitive cavity enhanced system, but without the need for a high quality external light source. In fact, a measurement of I_ν provides both absorption and optical emission information simultaneously, enabling the detection of species in both ground and excited states, and providing a very versatile spectroscopic tool. We expect that CESAS will have applications far beyond plasma studies as demonstrated here, e.g., in combustion research, and will be ideally suited as a generally applicable, sensitive analytical tool of light-emitting matter, as long as the spectral energy distribution of the emitted light covers the wavelengths needed for self-absorption to occur.

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