

Cavity Ring-Down Absorption Spectrography based on filament-generated supercontinuum light

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Abstract: We performed simultaneous, multispectral CRDS measurements that for the first time use the Supercontinuum light source. We called this approach Supercontinuum Cavity Ring-Down Spectrography (SC CRDSpectrography) and successfully applied it to measuring the absorption spectrum of NO₂ gas at a concentration of 2 ppm. The extrapolated sensitivity of our setup was much greater, about 5 ppb. The ppb sensitivity level is comparable to this obtainable with single wavelength dye-lasers based CRDS systems. It is, therefore, feasible to construct extremely broadband and sensitive CRDS devices basing on the SC CRDSpectrography scheme.

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OCIS codes: (300.0300) Spectroscopy; (300.1030) Absorption; (320.7090) Ultrafast lasers; (260.5950) Self-focusing; (120.4640) Optical instruments.

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1. Introduction

Cavity Ring-Down Absorption Spectroscopy (CRDS) is a versatile spectroscopic tool, which permits the detection of trace absorbers in gaseous, liquid, as well as solid phase [1]. Already in one of the pioneering works on CRDS the first broadband studies have been reported [2]. Namely, the wavelength of a tunable narrowband laser was scanned across the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ transition of molecular oxygen and the corresponding cavity decay times were used to reconstruct the spectrum. Due to the repetitive wavelength selection this method was rather time-consuming. Several attempts have been made to overcome this drawback [3-6]. All of them rely on the same working principle. Basically, the broadband light of a dye-laser is coupled in to the cavity, followed by independent decay of its spectral components. These are next separated, typically by a spectrometer or a monochromator, and registered by a time resolving detector. Depending on the specific implementation, signals at different wavelengths are registered simultaneously [4-6] or sequentially [3]. The limited line widths of dye-lasers, which generally do not exceed 20-30 nm, constitute a major constraint of the described methods. Although the alternative Cavity Enhanced Absorption Spectroscopy (CEAS) was demonstrated with spectrally broad thermal light [7], this type of radiation is not a good choice for CRDS. Its spectral power density is much lower as compared to dye-lasers making the detection of the intensity leak extremely demanding. Two newly developed techniques, the Optical Frequency Comb CRDS (OFC CRDS) [8] and the very recent Supercontinuum CEAS (SC CEAS) [9], overcome deficiencies of the incoherent sources. The former uses a stabilized optical comb and the latter a Photonic Crystal Fiber-generated Supercontinuum (SC).

In this letter we report on broadband CRDS measurements that for the first time use the white light SC generated by filaments [10]. The possibility of such approach has already been reported in our previous communication [11], but to the best of our knowledge no evidence of real absorption spectra measurements has been disclosed since then. The method is free from the mode matching issues typical for OFC CRDS and, as opposed to SC CEAS, is not biased by the unknown reflection coefficient of cavity mirrors. Since the setup we used was similar to that of CRDSpectrography [6] we intend to call our approach Supercontinuum CRDSpectrography (SC CRDSpectrography).

2. Experimental setup and results

The beam of a femtosecond Ti:Sa amplifier operating at 800 nm was focused inside a quartz block giving rise to a bundle of approximately 200 filaments. Their strong SC emission spanned from UV to near NIR (350-1100 nm), but due to much narrower spectral range of the spectrometer only the UV-blue part of the spectrum could be effectively used during measurements (see Fig. 1). Two spherical mirrors constituted the cavity. Owing to their non-confocal alignment the effect of mode beating was effectively smoothed out [12]. The BG18 filters placed, respectively, before and after the cavity blocked the light at the fundamental laser wavelength. A bi-convex lens focused the light transmitted through the back-cavity mirror on a large aperture (1.5 mm) round-to-rectangle optical fiber bundle, which was attached to an imaging spectrometer. An iCCD camera was used as a detector. As opposed to the authors of [6] who sampled the light decays in short 50 ns intervals, the camera gate was significantly longer than the transients durations (see the caption of Fig. 1). Consequently, the time integrals of the CRDS signals rather than the signals themselves were measured. This had one main advantage, namely, substantial reduction of the photon number

fluctuations. The integral smoothing is in particular well suited for exponential signals [13]. It does not affect decay constants, because the exponential function and its integral have the same exponents.

An example of raw SC CRDS spectrography transients is shown in Fig. 1(a). Before measurements the cavity was purged with synthetic air (8:2 mixture of N₂ and O₂) at atmospheric pressure. Then it was hermetically closed. Since in the considered spectral range the Rayleigh scattering amounting to $\sim 10^{-7}$ cm⁻¹ and the absorption of molecular oxygen and nitrogen are negligible, the energy decrease was primarily caused by non-zero transmission of the cavity mirrors. To determine decay constants, a single exponential function was fitted to each measured transient. This was justified because: (i) for each delay step the registered integrated signal corresponded to an average of 5000 subsequent laser shots, additionally reducing the effect of multimode excitation [14], (ii) the residuum of the fit was normally distributed around the fitted values confirming the *Lambert-Beer*-like decay. The derived data set was used to calculate the reflectance of the cavity mirrors. The result is presented in Fig. 1(b). Although the qualitative agreement between the measured and theoretically predicted reflection coefficient, $R(\lambda)$, is fairly good, the absolute values of this parameter are consistently greater than those specified by the mirrors' manufacturer. Nonetheless, the

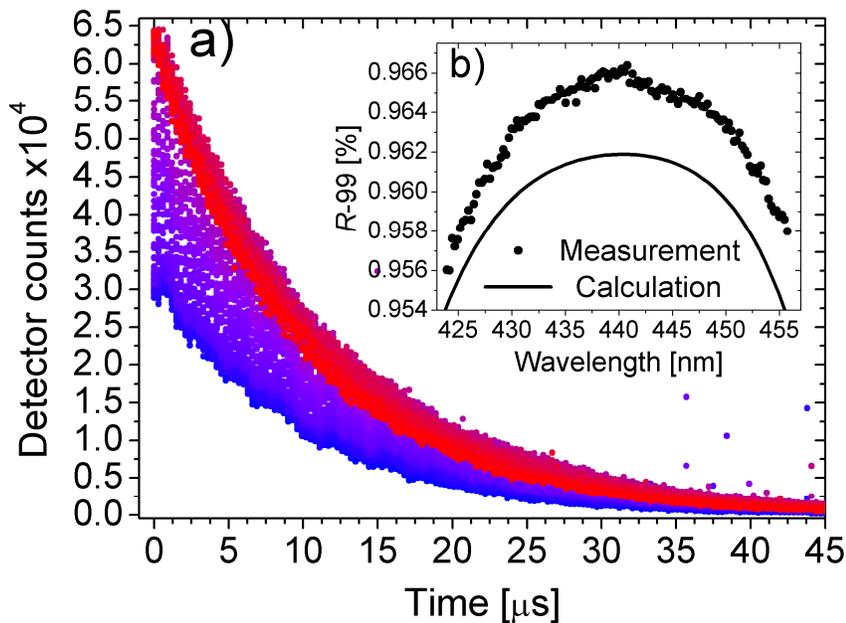


Fig. 1. a) Integrated SC CRDS spectrography transients of 128 wavelength channels; wavelengths from 423.92 nm (blue circles) to 454.25 nm (red circles). During the acquisition the camera gate was set to 300 μ s. The gate delay was shifted in steps of 0.3 μ s. b) The measured decay times, τ_0 , ranging from (9.595 ± 0.053) μ s to (12.090 ± 0.063) μ s were used to calculate the wavelength dependent reflection coefficient of the cavity mirrors, R .

discrepancy of only 0.0035% absolute is small and most likely results from difference between assumed and actual thicknesses of the mirror coatings. We note that the theoretical curve from Fig. 1(b) corresponds to the typical reflectance under normal incidence of light and was supplied together with the mirror set.

The cavity was next filled with a mixture of synthetic air and a small, but unknown amount of NO₂ gas (purity $\geq 99\%$). The decay of light in the presence of this absorber is shown in Fig. 2(a). Apparently, the transmission of the cavity is dominated by the

transmission of the mirrors; one can easily recognize the $1-R(\lambda)$ contour when looking at the $t=0$ plane. The modulation of the spectrum is caused by the absorption of NO_2 (see Fig. 2(b)) and the asymmetry by the non-uniform spectral power density of the SC, which was greater towards the laser wavelength.

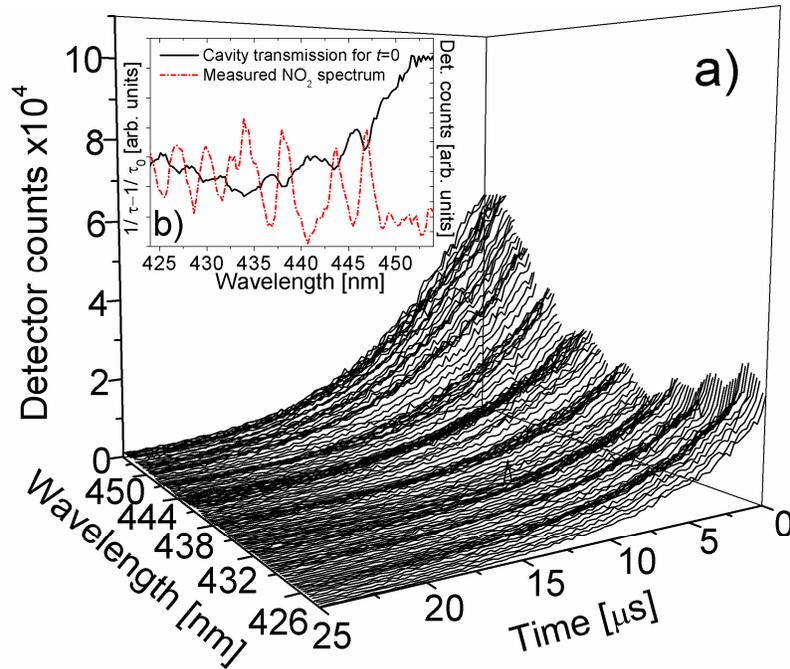


Fig. 2. a) Integrated SC CRDSpectrography transients as measured by the presence NO_2 absorber. The decay constants are approximately tenfold smaller than those of Fig. 1(a). b) Measured absorption spectrum of NO_2 superimposed on the transmission curve of the cavity. Symbols τ and τ_0 denote decay times, respectively, for the absorber-filled and empty cavity.

Figure 3 shows the SC CRDSpectrography-measured and the reference absorption spectrum of NO_2 . The reference data was taken at 294K and 0.06 Torr (about 80 ppm) partial pressure [15]. These conditions differed from those of experiments reported here. Note, that especially the concentration of NO_2 in our case was only about 2 ppm, as shown below. Several authors reported a considerable pressure dependence of the relative line strengths of the NO_2 absorption lines in the considered spectral range (see e.g. [16]). This is an important fact, which cannot be ignored when comparing the curves, and explains the observed differences. Keeping in mind this restriction, as well as the fact that the spectra in Fig. 3 were recorded with different wavelength resolutions of 0.25 nm for the upper and 0.01 nm for the lower curve, respectively, we can state a good correspondence between them.

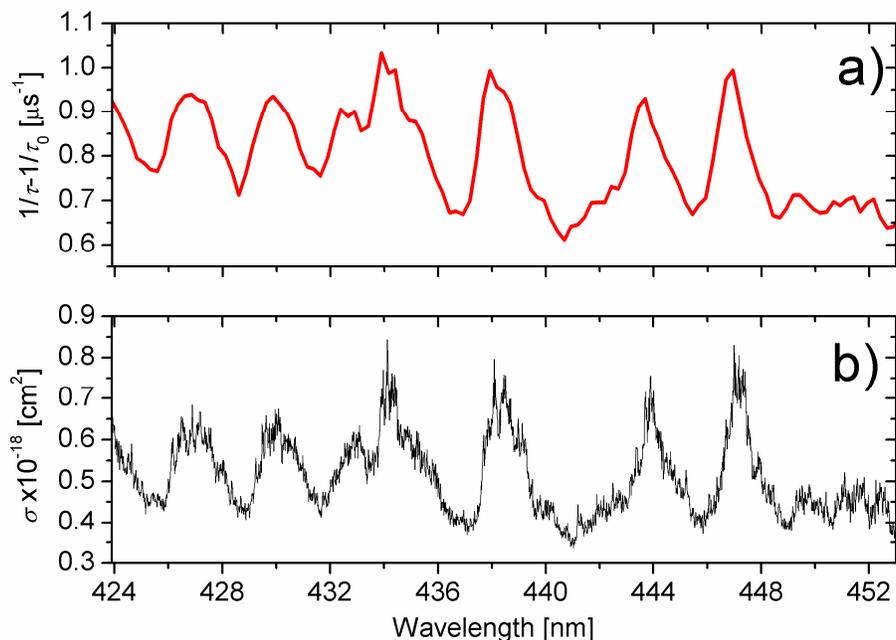


Fig. 3. a) Measured and b) reference [15] absorption spectrum of NO_2 . Symbols, $1/\tau$ and $1/\tau_0$ denote inverse decay times respectively, for the absorber-filled and empty cavity, σ denotes the absorption cross-section.

The concentration of NO_2 in our sample was estimated using the measured decay constants and the molecular absorption cross-sections of the reference spectrum [15], which was convolved with a $\text{FWHM}=0.25$ nm Gaussian function to match the measurement resolution. The average concentration derived from all 128 wavelength channels is $1.97 \text{ ppm} \pm 6\%$, where the specified error corresponds to the standard deviation of the distribution of concentrations as obtained from individual channels. This distribution is bell-shaped around the mean, but it has to be noted that it contains the aforementioned deviation of the relative line strengths. For the comparison the quality of the fit of individual channels is about $\pm 3\%$ on a 3σ level of confidence, typical for multi-mode systems [14]. This together with the high quality of the measured spectrum of the empty cavity puts forward the interpretation of the shape deviation between the considered spectra as due to the specific measurement conditions, mainly background pressure, rather than as a measurement artifact.

The detected absorption is about five times lower as compared to the firstly reported CRDSpectrography study on NO_2 [6]. Still this result is rather modest if taking into account monochromatic CRDS. The ppm level cannot be, however, considered as the detection limit of our apparatus. This can be extrapolated to 5 ppb if a 3σ deviation from the empty cavity spectrum is taken as the criterion. A complete characterization of the capabilities of our setup would require a more detailed error analysis (e.g. using the Allan deviation method [17]), as well as measurements with calibrated NO_2 samples. These are, however, beyond the scope of this short communication and will be the topic of further work.

4. Conclusions and outlook

In summary we have shown that the SC light generated by white light filaments enables broadband CRDS in the gas phase, using the CRDSpectrography scheme. This approach has several advantages over currently existing broadband CRDS techniques. First of all it allows one to trace the decay of several wavelengths at the same time and, as such, is much more

efficient than the wavelength-scan based methods. The measurement setup is relatively uncomplicated. It consists of one light source, a cavity with a simple design (contrary to OFC CRDS), and a single detection unit common for all wavelengths. The SC generated by filaments features a broad spectrum with high spectral power density. Currently the limitations of single-cavity SC CRDSpectrography are set by the bandwidth of the cavity mirrors, ranging from typically 20-30 nm in the UV to 100-150 nm in the NIR. Use of SC as the light source opens the perspective for compact ultrabroadband CRDS spectrographs.

Acknowledgment

The authors would like to express their gratitude to Dr. Axel Wiegand (Andor Technology), Mr. Olaf Koschützke (L.O.T. Deutschland) and Dr. Thorsten Pieper (L.O.T. Deutschland) for their support and help in preparing the experiments.