

Cavity Ring Down Spectroscopy with a Free-Electron Laser

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A Cavity Ring Down (CRD) absorption experiment is performed with a Free-Electron Laser (FEL) operating in the 10–11 μm region. A short infrared pulse of approximately 20 ns, sliced from the much longer FEL pulse, is used to measure CRD spectra of ethylene in two different ways. First, ‘ordinary’ CRD spectra with a resolution determined by the bandwidth of the FEL ($\approx 5\text{ cm}^{-1}$) are recorded. Second, Fourier Transform (FT) CRD spectra with a resolution that is in principle determined by the FT-spectrometer are obtained by analyzing the light exiting the ring down cavity with a FT-spectrometer while the FEL is operated in broadband mode.

Since 1988 when O’Keefe and Deacon reported the first results of the Cavity Ring Down (CRD) absorption technique on the atmospheric bands of molecular oxygen in the visible region of the spectrum [1], the spectral region in which CRD absorption spectroscopy has been applied has been extended to either side. In 1994 Meijer *et al.* demonstrated CRD detection of the hydroxyl radical (OH) in a flame in the near-UV region of the spectrum [2]. Measurements on the Herzberg absorption system of molecular oxygen [3], measurements of the absorbance of methyl radicals (CH_3) in a hot-filament reactor [4], and detection of trace amounts of (atomic) mercury and ammonia [5] have demonstrated the applicability of CRD spectroscopy down to 200 nm. Using a state-of-the-art narrowband tunable infrared (IR) laser system, Rakestraw and co-workers demonstrated the first CRD experiment in the IR spectral region out to 3500 nm [6]. As long as mirrors with a sufficiently high reflectivity, detectors with a sufficiently fast time-response and tunable (pulsed) light sources are available there is no intrinsic limitation to the spectral region to which CRD can be applied. CRD in the IR is of particular interest since this is the energy range of molecular vibrations and it yields a true molecular fingerprint. Over the last years Free-Electron Lasers (FELs) have become available to users [7–10]. Their wide and rapid continuous tunability make them ideally suited for IR studies.

In this Letter we report on the exploration of the use of a FEL for CRD experiments. The 10–11 μm spectral range is selected as mirrors of sufficient quality and fast, sensitive detectors are available for a reasonable price. Ethylene, with its strong ν_7 IR absorption around 10.53 μm is selected as test molecule. Both ‘ordinary’ CRD experiments, with a spectral resolution limited by the bandwidth of the FEL, and Fourier Transform (FT)-CRD experiments with a superior spectral resolution, limited in principle only by the FT-spectrometer [11],

are reported on.

The experiments have been performed at the FEL user facility FELIX (‘Free-Electron Laser for Infrared eXperiments’) in Nieuwegein, The Netherlands [10,12]. FELIX produces IR radiation that is continuously tunable over the 5–110 μm (90–2000 cm^{-1}) range with a minimum achievable bandwidth (FWHM) of 0.05 μm at 10 μm (5 cm^{-1} at 1000 cm^{-1}). In the present experiment FELIX runs at a 5 Hz repetition rate. The light output consists of so called macropulses of about 3 μs duration containing 20 mJ of energy. Each macropulse consists of a train of micropulses which are between 0.25 to 3 ps long (FWHM at 10 μm) and are separated by 1 ns.

The experimental details for the CRD setup do not differ substantially from the setup we have been using before [5,11], and a scheme of the experimental setup is given in Figure 1. The ring down cavity is formed by two identical plano-concave mirrors with a diameter of 25.4 mm and a radius of curvature of -1.0 m placed a distance $d = 45.5\text{ cm}$ apart. The reflection coatings are optimized for $\lambda = 10.50\text{ }\mu\text{m}$, and have a specified reflection coefficient $R \approx 0.995$. The ring down times thus expected for the empty cavity are on the order of 300 ns. To be able to use the FELIX pulse for CRD experiments it is important to have the trailing flank of the IR pulse decaying faster than the typical photon-lifetime in the cavity. To achieve this, the ‘semiconductor switching’ technique is applied. This technique is based on the dependence of the reflection and transmission properties of a material on the density profile of free carriers within it [13]. In our case, the second-harmonic radiation of a short-pulse Nd:YAG laser (532 nm, 100 ps, 30 mJ) is used to produce a high density of free carriers in a Si-slab, thereby temporarily changing its IR reflection and transmission characteristics.

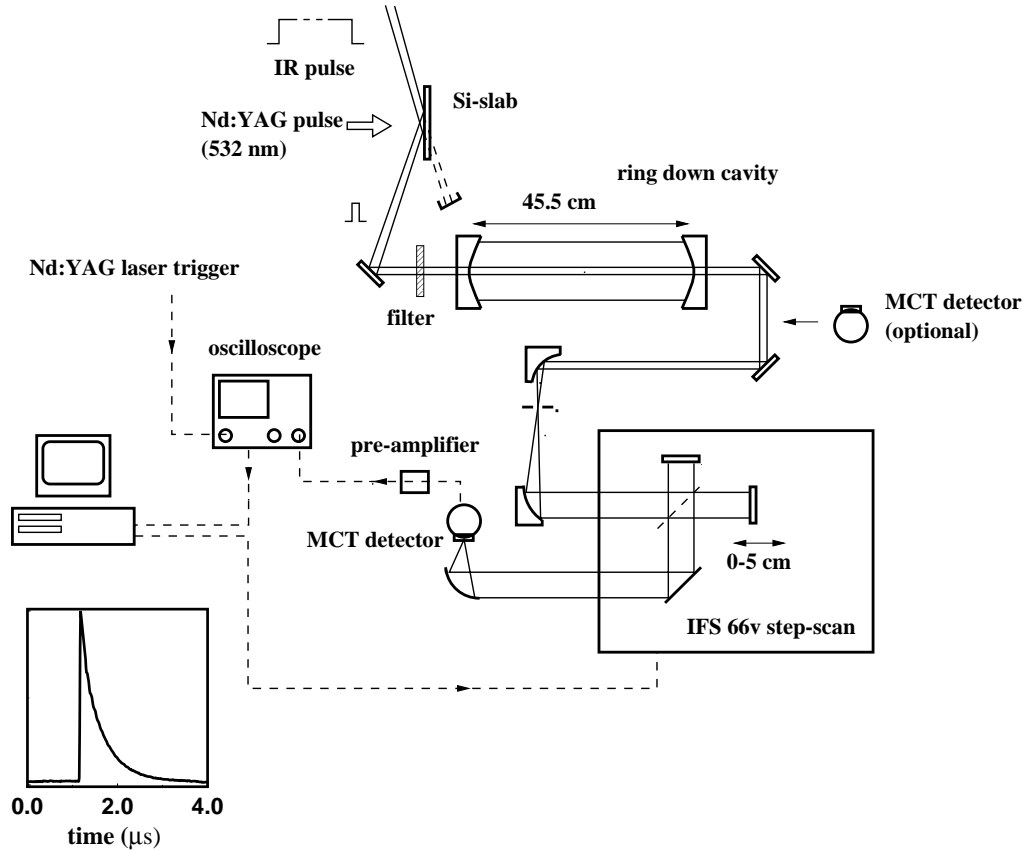


FIG. 1. Schematic view of the experimental setup. A short 20 ns duration IR pulse is sliced out of the FELIX macropulse and coupled into the ring down cavity. The light exiting the cavity is either measured directly or after passage through the FT-spectrometer. In the inset a typical ring down transient of the empty cavity is shown.

In the experimental setup, the linearly polarized radiation of the FEL is incident on the semi-conductor Si-slab under Brewster angle (74° @ 1000 cm^{-1}), and passes through the Si-slab in the absence of the Nd:YAG laser pulse. During and shortly after the Nd:YAG laser pulse the Si-slab becomes conducting, and a FEL pulse of approximately 20 ns duration ($10 - 20 \mu\text{J}$ pulse energy) is efficiently reflected from the Si-slab. This shortened IR pulse is used for the CRD experiments. The IR pulse is coupled into the cavity through one of the mirrors with a weakly focusing mirror ($f = 1 \text{ m}$). A long pass filter ($7.2 \mu\text{m}$ cut-off wavelength) is used to prevent the higher harmonics that might be present in the FELIX-beam from entering the cavity. The time dependence of the light intensity inside the cavity is monitored by detection of the light that leaks out of the cavity through the other mirror. This light is either detected directly or after passage through a FT-spectrometer (Bruker IFS 66v, with step-scan option) using a liquid-nitrogen cooled HgCdTe (MCT) detector (HCT-21-C, Braseby, UK), with a response time of about 40 ns. The signal of the detector is amplified and digitized with a fast (100 Ms/s) and high resolution (10 bit) digital oscilloscope (LeCroy 9430). After averaging of the ring down transients over a pre-defined number of shots (20–50) on the 16 bit on-board

memory of the oscilloscope the data are transferred to a PC for extraction of the frequency dependent ring down times [5,11]. In the inset of Figure 1 a typical ring down transient measured with the MCT-detector directly behind the (empty) ring down cavity is shown.

In Figure 2a the CRD spectrum of 1 atmosphere of 625 ppb C_2H_4 in argon as measured with the MCT-detector directly behind the ring down cavity is shown. FELIX is stepped in $0.01 \mu\text{m}$ steps over the $9.9 - 11.1 \mu\text{m}$ region with a bandwidth of approximately $0.05 \mu\text{m}$. At every wavelength position 40 transients are averaged. The frequency dependent ring down time $\tau(\nu)$ is extracted from the data points in a time-interval of typically three $1/e$ decay times, i.e. out to about $1 \mu\text{s}$. Some 100 data points prior to the onset of the ring down transient are used to accurately determine the baseline. The averaged baseline is subtracted from the transient and the natural logarithm of the data is fit to a straight line using a least-squares weighted fitting algorithm [5]. In Figure 2a the thus determined value of $1/c\tau(\nu)$ (where c is the speed of light), which is identical to an offset given by $(1 - R)/d$ plus the frequency dependent absorption coefficient κ_ν , is plotted as a function of wavelength. The curved background in this Figure is caused by the

frequency-dependent mirror-reflectivity R , which has a maximum value of $R = 0.995$ at $10.4 \mu\text{m}$. For comparison, the FTIR spectrum of 1 atmosphere of 100 ppm C_2H_4 in argon, measured in a 22 cm long cell, is shown in Figure 2b. Whereas the resolution in the FTIR spectrum is determined by the congestion of the molecular spectrum to be around 0.9 cm^{-1} for the central Q-branch and 0.4 cm^{-1} for the other Q-branches of the ν_7 out-of-plane bending mode, the resolution in the CRD spectrum is limited by the linewidth of FELIX to $\approx 5 \text{ cm}^{-1}$.

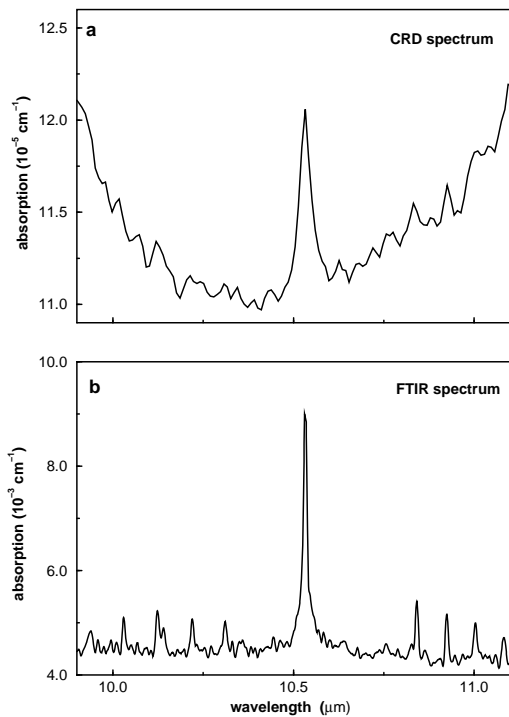


FIG. 2. (a) The CRD spectrum of 1 atmosphere of 625 ppb C_2H_4 in Ar, measured via ‘ordinary’ CRD using FELIX with a bandwidth of 5 cm^{-1} , and (b) the FTIR spectrum of 100 ppm C_2H_4 in Ar in a 22 cm long cell.

Due to the large mismatch in bandwidth between the light source and the absorber, it is difficult to extract reliable absorption coefficients from these CRD spectra as line-center saturation effects are hard to be completely avoided without losing the signal altogether [5,14].

We have recently demonstrated that the sensitivity of the CRD absorption detection method can be combined with the multiplex advantage of FT-spectroscopy. In such a FT-CRD setup accurate absorption information can be extracted even when a broadband excitation pulse is being used, as the spectral resolution that is obtained is in principle only limited by the resolution of the FT-spectrometer [11]. In applying the FT-CRD detection method in combination with FELIX, it is important to note that there is phase-coherence between the single micropulses within the sliced 20 ns IR pulse [10]. In the present FT-CRD experiment FELIX is operated with a

bandwidth of approximately 10 cm^{-1} , and is centered around the main Q-branch of ethylene at $10.53 \mu\text{m}$. The time dependence of the light intensity exiting the cavity and passing through the FT-spectrometer, $I(\Delta, t)$, is measured as a function of the path-length difference Δ between the arms of the interferometer. At every mirror position 20 transients, each recorded over $3 \mu\text{s}$, are averaged and transferred to the PC. A complete measurement cycle consists of the recording of transients $I(\Delta, t)$ at typically 400 mirror positions. At the end of the measurement, the data are rearranged such that arrays recorded at identical time points but at different mirror positions are formed. Thus full interferograms, measured at a specific time point are obtained. These interferograms are Fourier transformed to obtain the spectral intensity distribution at this point in time. This process is repeated for every time point at which the transients are recorded [15]. The data points belonging to the same frequency in the different spectra, are fitted to an exponentially decaying function of time. The resulting decay time is calculated as a function of frequency [11].

In Figure 3a $1/c\tau(\nu)$ is plotted as a function of frequency. The width of the central Q-branch is 0.9 cm^{-1} , about an order of magnitude smaller than the width of the spectral profile of FELIX, represented by the dashed curve in Figure 3a. The same part of the spectrum of ethylene measured with the FTIR spectrometer on a sample with a 75 times larger line-integrated absorption, is shown for comparison in Figure 3b. The noise in the FT-CRD spectra is mainly due to fluctuations in the spectral intensity distribution of the light source during the experiment [11]. The linewidth of the transitions is determined by the Doppler and pressure broadening of the ethylene/argon mixture in the ring down cell in combination with the spectral congestion.

In conclusion, we have successfully demonstrated the use of a FEL for CRD absorption spectroscopy. Problems associated with the rather large bandwidth of FELs can be circumvented if spectral analysis of the light that leaks out of the ring down cavity is performed, as in the FT-CRD experiment demonstrated here. Full advantage of the unique features of CRD with FELIX is only taken if experiments are performed throughout the complete $5\text{--}110 \mu\text{m}$ tuning range, using absorption detection of transient species produced in a repetitive pulsed manner or if sensitive kinetics measurements are being performed [16].

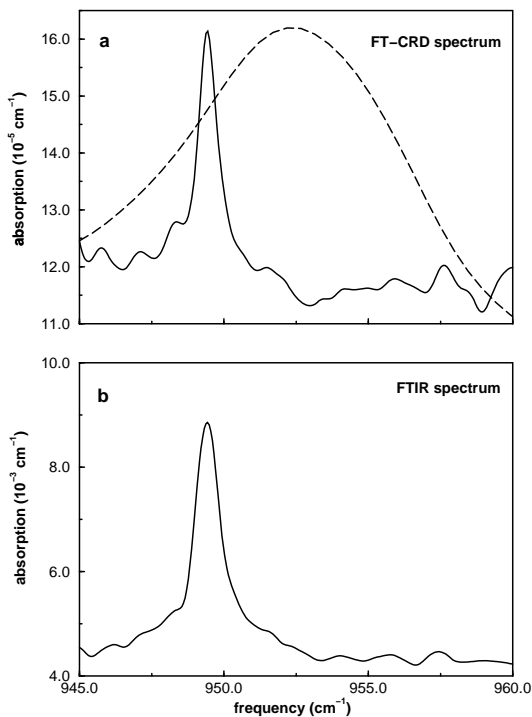


FIG. 3. (a) The FT-CRD spectrum of 1 atmosphere of 625 ppb C_2H_4 in Ar together with the spectral intensity profile of the FELIX pulse (dashed), compared to (b) the FTIR spectrum of 100 ppm C_2H_4 in Ar in a 22 cm long cell.

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