Cavity ring down spectroscopy on solid C_{60}

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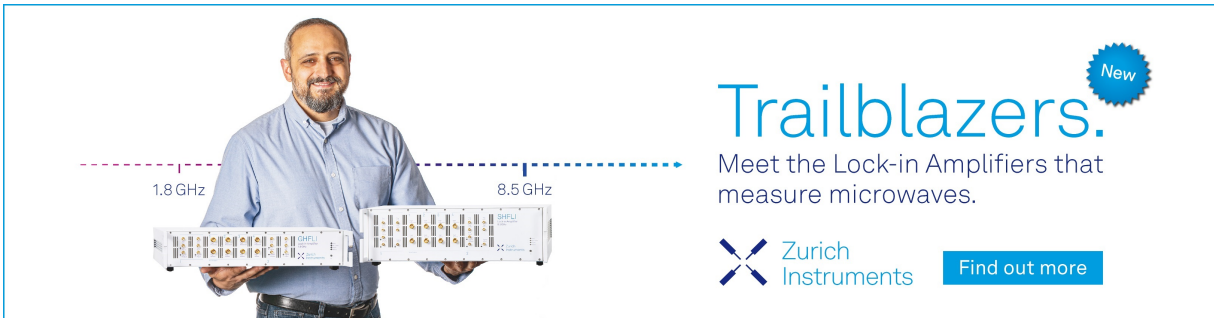Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources
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NOTES

Cavity ring down spectroscopy on solid C_{60}

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Following the success of cavity ring down (CRD) spectroscopy for quantitative optical absorption studies on gas-phase species,[1] various experimental schemes are currently being explored to make this technique applicable to the study of thin solid films as well. A straightforward way to proceed is to put a thin solid film on an optically transparent substrate inside the optical cavity such that the various (embedded) cavities are all optically stable; reflection losses from the substrate will not be noticed as overall losses from the cavity in this case and one can selectively measure the absorption or optical rotation in the solid. We used this approach to measure the polarization rotation at a fixed wavelength in a 2 mm thick optically flat BK7 window using the polarization dependent CRD scheme.[2] To be able to record an absorption spectrum of the solid, the wavelength range covered by the reflecting elements used for the optical cavity has to be sufficiently large to encompass the, often wide, spectral region over which the absorption in the solid occurs. Pipino *et al.*[3] have theoretically outlined that by using a total-internal reflection minicavity, absorption spectra of either thin solid films or species in solution on the outside of the internal-reflection surface are measurable via evanescent wave absorption throughout a 300 nm interval in the visible part of the spectrum. Shortening of the ring down time due to evanescent wave absorption of I_2 present on the surface of a Pellin–Broca prism placed inside a standard ring down cavity has recently been demonstrated.[4] In this Note we experimentally demonstrate the possibility to sensitively record the absorption spectrum of a thin solid film via CRD spectroscopy by the measurement of the absorption spectrum of a 20–30 nm thick C_{60} film deposited on a 3 mm thick ZnSe substrate in the 8.5 μm region.

A scheme of the experimental setup is shown in Fig. 1. Tunable pulsed radiation from the free-electron laser for infrared experiments (FELIX) in Nieuwegein, The Netherlands, is used for this study.[5] FELIX produces IR radiation that is continuously tunable over the 5–250 μm range with a minimum achievable bandwidth (FWHM) of 0.3% of the central frequency. The light output consists of macropulses

of about 5 μs duration containing up to 50 mJ of energy. Each macropulse consists of a train of micropulses with a duration of 0.3–5 ps, separated by 1 ns. In the present experiment FELIX runs at a 5 Hz repetition rate, and the full macropulse is used to excite the optical cavity in the 8–9 μm region. If required, a higher peak intensity in the optical cavity can be obtained when pulse-stacking, or synchronous pumping, is performed, as recently demonstrated using the Stanford FEL.[6] The temporal shape of the FELIX pulse is well-approximated by a flat-topped profile with an exponentially decaying tail with a time-constant of 360 ± 20 ns (ring down time of the 6 m long FELIX cavity, implying a Q-factor of less than 20 for the laser cavity). A long pass filter (7.2 μm cutoff wavelength) is used to prevent the higher harmonics that might be present in the FELIX-beam from entering the ring down cavity.

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 $d=36$ cm apart. With a specified reflectivity R of the mirror coatings of 0.9998 at 8.5 μm (Laser Power Optics), a ring down time of the empty
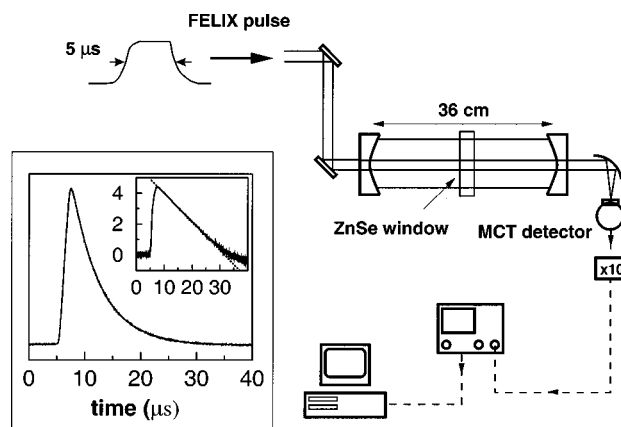

FIG. 1. Scheme of the experimental setup. In the inset the ring down transient of the empty cavity at 8.5 μm is shown, together with a linear fit to the natural logarithm of the decaying tail.
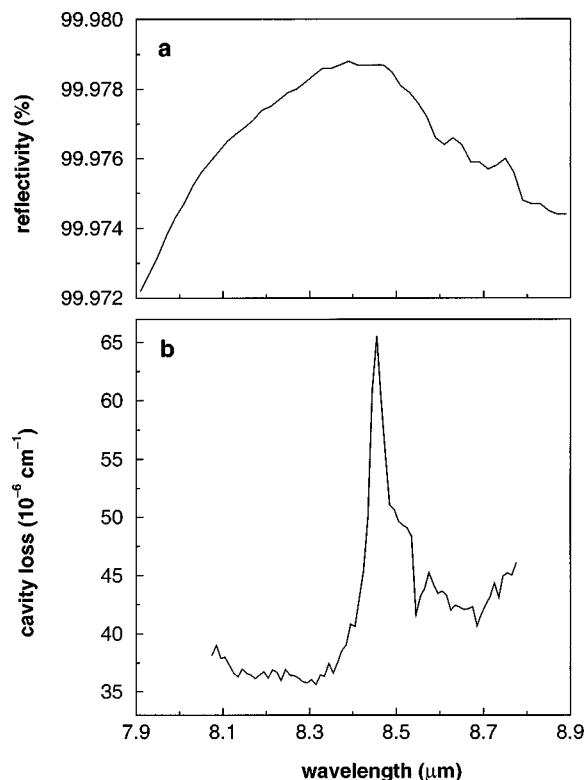
FIG. 2. (a) Mirror reflectivity as a function of wavelength as measured via CRD in the empty cavity. (b) CRD absorption spectrum of a 20–30 nm thick C_{60} film on a 3 mm thick ZnSe window.

cavity of 6 μs is expected. The light exiting the cavity is detected by a liquid-nitrogen cooled fast HgCdTe (MCT) detector (response time about 40 ns). The signal of the detector is amplified and digitized with a fast (100 Ms/s) 10 bit digital oscilloscope (LeCroy 9430). After averaging 25 shots on the 16 bit on-board memory of the oscilloscope, the data are transferred to a PC, which also controls the scanning of FELIX. The measured transients are deconvoluted with the temporal profile of the FELIX pulse to correct for the finite decay time of the laser cavity. The transients thus obtained are fitted to an exponentially decaying curve from which the ring down time is extracted using standard procedures. In the inset of Fig. 1 the ring down transient as measured behind the empty cavity at 8.5 μm is shown, together with a linear fit to the natural logarithm of the decaying tail. A ring down time of 5.6 μs is deduced from the fit, and true exponential decay is observed over three characteristic decay times.

The reflectivity curve of the mirrors in the spectral region of interest as measured using CRD in the empty evacuated cavity is shown in the upper part of Fig. 2. If a 3 mm thick optically flat ZnSe window is inserted in the cavity in such a way that the cavities that are formed are again optically stable, transients with a ring down time larger than 2.2 μs are found over the 8.1–8.8 μm region. This implies that the additional losses due to the presence of the ZnSe window are below 340 ppm per pass. The upper limit for the absorption losses for this particular sample of ZnSe in this wavelength region is therefore concluded to be below 1.1 $\times 10^{-3}$ cm^{-1}, which can be accurately measured using this experimental setup. With a thin film of C_{60} deposited on the ZnSe window the CRD spectrum shown in the lower part of Fig. 2 is recorded. The baseline of the spectrum is determined by the effective cavity losses, $(1-R_{\text{eff}})/d$, mainly due to the mirrors, the substrate and scattering losses from the thin film. Absorption of the thin film introduces an extra loss determined by $\kappa l/d$, in which κ is the absorption coefficient and l the thickness of the thin film. The absorption line centered at 8.46 μm is one of the four F_{1u} IR fundamental absorptions of C_{60}.[7] With an absorption coefficient (base e) of 0.24 μm^{-1} and taking the mismatch between the linewidth of the C_{60} absorption line in the thin film (2 cm^{-1}) and the width of the spectral profile of FELIX (8 cm^{-1}) into account, a sample thickness of approximately 20 nm is found, in good agreement with the 20–30 nm sample thickness found in independent FTIR measurements.

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