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Frequency-agile, rapid scanning spectroscopy

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Challenging applications in trace gas measurements require low uncertainty and high acquisition rates[1–4]. Many cavity-enhanced spectroscopies exhibit significant sensitivity and potential[5,6], but their scanning rates are limited by reliance on either mechanical or thermal frequency tuning[7]. Here, we present frequency-agile, rapid scanning spectroscopy (FARS) in which a high-bandwidth electro-optic modulator steps a selected laser sideband to successive optical cavity modes. This approach involves no mechanical motion and allows for a scanning rate of 8 kHz per cavity mode, a rate that is limited only by the cavity response time itself. Unlike rapidly frequency-swept techniques[8–11], FARS does not reduce the measurement duty cycle, degrade the spectrum's frequency axis or require an unusual cavity configuration. FARS allows for a sensitivity of $\sim 2 \times 10^{-12}$ cm^{-1} Hz$^{-1/2}$ and a tuning range exceeding 70 GHz. This technique shows promise for fast and sensitive trace gas measurements and studies of chemical kinetics.

A multitude of applications have emerged that require rapid sensing of trace gas species, encompassing areas as varied as greenhouse gas monitoring[1,4,12], breath analysis[2,13], explosive detection[3] and chemical process monitoring. Because of their sensitivity, continuous-wave (c.w.) cavity-enhanced spectroscopies have significant potential for addressing these challenging applications[6,14,15]. However, the low mechanical or thermal tuning rates of c.w. lasers have generally limited the use of these techniques to static or slowly varying analytes. Attempts to alleviate this limitation have relied on sweeping the laser frequency[8–11], which can compromise the fidelity of the spectrum and the instrument sensitivity[16] and reduce the measurement duty cycle. We present a new approach for cavity ring-down spectroscopy[17] in which the laser frequency is rapidly stepped to successive resonances through the use of high-bandwidth electro-optics. This technique, which we refer to as frequency-agile, rapid scanning (FARS) cavity ring-down spectroscopy, allows for ultrasensitive measurements in which the acquisition rate is limited only by the cavity response. Unlike earlier techniques[8–11,18,19], FARS allows for spectra to be recorded without any dead time due to scanning of the laser frequency, offers a metrology-level frequency axis and utilizes a conventional Fabry–Pérot resonator rather than more unusual and cumbersome cavity configurations.

This frequency stepping of the probe laser is enabled by the use of a microwave driver and a high-bandwidth electro-optic modulator (EOM) to generate a series of sidebands on the probe laser (Fig. 1). We then use the cavity as a spectral filter such that only a single, selected sideband is resonant. Thus, we are able to transfer the superior switching bandwidth and precision of microwave sources into the optical domain. Ring-downs are then initiated by simply switching off the microwave frequency, thus removing the need for an acousto-optic modulator.

To scan a molecular transition, we step the EOM modulation frequency in increments of the cavity's free spectral range (203.073 MHz). Importantly, because of the frequency agility of the microwave driver and the EOM, the step-scanned frequencies can be in any order. In our current configuration, our scanning range is over 70 GHz. This bandwidth is more than sufficient for simultaneously recording spectra of several atmospheric species (Fig. 2). Recent technology developments of low-insertion-loss (<3 dB) fibre-coupled waveguide EOMs have reduced the V_π condition to only a few hundred milliwatts of microwave power in a region where kilowatts of power are available. Continuing advancements in electro-optical device bandwidths, frequency multiplier/amplifier sources and the use of higher-order sidebands should allow for extension of scanning ranges to a few hundreds of gigahertz.

Here, we present two realizations of the FARS technique. The first offers high acquisition rates through the use of an ultranarrow-linewidth fibre laser as well as an absolute frequency axis. This configuration is intended to demonstrate the potential of FARS for metrology-level measurements. The second realization utilizes a low-cost distributed feedback (DFB) diode. These commonly used diode lasers are available over a wide wavelength range from the visible to the mid-infrared and are found in many commercially available spectroscopic sensors. This instrument was built to demonstrate that FARS can be readily incorporated into existing cavity-enhanced spectrometers. First, we will discuss the fibre laser-based instrument.

Owing to the narrow linewidth of the fibre laser (<100 Hz) and optical cavity (~10 kHz), stabilization of both the cavity length and the carrier frequency is required. This stabilization is performed in a two-step process. To simultaneously achieve an absolute frequency axis, the carrier frequency is offset-locked to an octave-spanning, self-referenced optical frequency comb. The spectral accuracy is limited only by the linewidth of the heterodyne beat signal between the probe laser and the optical frequency comb while the resolution is given by the cavity linewidth. If an absolute axis is not needed, the carrier frequency could instead be locked to an external etalon.

Stabilization of the cavity length is performed through the use of a co-resonant I_2-stabilized HeNe laser (12 kHz stability)[5]. Once these two locking schemes are realized, a single selected sideband can be made resonant with the optical cavity and can be stepped between successive cavity modes. Further technical details can be found in Supplementary Section S1. We note that because the frequency of the microwave source is digitally selected for each cavity resonance frequency, the effects of dispersion can be compensated, and are therefore inconsequential. Similarly, this technique could be used to quantify mirror dispersion, an important parameter in photonic design[20].

An example spectrum of CO_2 and HDO transitions in a room air sample is presented in Fig. 2. When these spectra were fitted with

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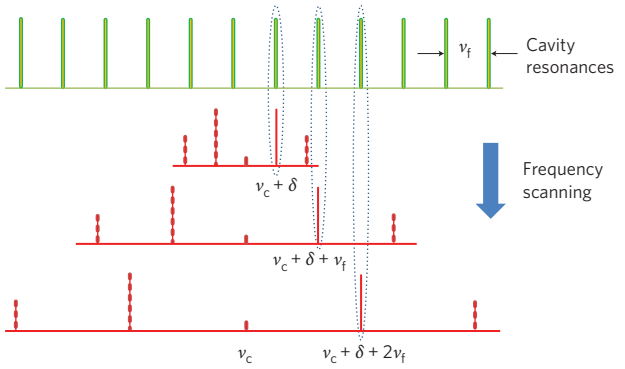

Figure 1 | Depiction of the principles of FARS. An electro-optic modulator is used to place a series of sidebands on our laser. The initial laser frequency (the carrier frequency ν_c) is locked to a self-referenced optical frequency comb such that it has a detuning of δ from the nearest cavity resonance. The frequency of this modulation is then set such that only a single, low-order sideband is resonant with the optical cavity. We can then record a spectrum by stepping the modulation frequency in increments of the mode spacing of the optical resonator (that is, the free spectral range ν_f). Although not indicated in the figure, both the negative and positive sidebands can be used to acquire the spectrum. To increase the step size and/or tuning range, higher-order side bands can be selected similarly.

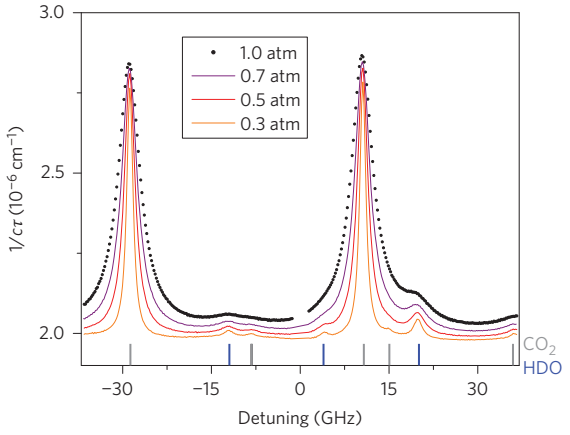

Figure 2 | Typical spectra measured with our rapid scanning approach using the narrow-linewidth fibre laser. The shown CO_2 and HDO transitions were measured using a sample of room air at the indicated pressures. These four 73 GHz wide spectra contain 348 spectral points. The shown spectra are each the average of 10 spectra and display signal-to-noise ratios of ~1,000:1. For clarity, the three lower pressures are interpolated. The measurement gap at low frequency is due to a limitation of our microwave source. Each spectrum was acquired in 2 s with broad tuning enabled by the use of higher-order sidebands. The carrier frequency was subtracted from the abscissa (ν_{ref} = 190,656.4055 GHz).

speed-dependent Nelkin–Ghatak line profiles[21], the relative standard uncertainties on the fitted area and pressure broadening parameter for the CO_2 transition at a detuning of 10.5 GHz were only 0.07% and 0.08%, respectively. These measurements are more than an order of magnitude more precise than those found in the HITRAN 2008 database[22], and the resulting residuals were structureless. Pressure shifting can clearly be observed with the uncertainty of the measured pressure shifting parameter being only 1%.

Our maximum scanning rate of 8 kHz per cavity mode is presently limited by the ring-down time itself. In addition, for applications such as measurements of isotopic ratios, which do not require a fast response, our high acquisition rate will allow for significant averaging and, therefore, even higher sensitivity and precision. Given our noise-equivalent absorption (NEA) coefficient of 2×10^{-11} cm^{-1} Hz$^{-1/2}$ we project detection limits of ~0.6 ppm for CO_2, ~4 ppb for CH_4 and ~1 ppb for C_2H_2 for a spectrum acquired in 3 ms within this wavelength region (for typical near-infrared transitions at a pressure of 13 kPa).

Owing to the widespread use of low-cost DFB lasers in many laboratories as well as in commercial sensors, it was important to show that FARS can be applied with these broader-linewidth lasers. For this demonstration we used a DFB laser centred at 1,599 nm with an output power of ~7 mW and linewidth of ~2 MHz (see Supplementary Section S2 for further information). Because of the wider linewidth, thermal stabilization of the diode with a commercial diode driver was sufficient to ensure that the laser remained on resonance with the optical cavity. This approach obviates the need for any complicated locking electronics or an optical frequency comb.

Even with this broad-linewidth laser, only moderate mode-matching of the laser to the cavity is required. We kept transmission in higher-order transverse modes below 10% of the TEM_{00} modes. The transverse mode spacing was 84.4 MHz. Importantly, because the EOM is stepped in increments of the cavity's free-spectral range, the frequency detuning between a non-selected EOM sideband and the nearest transverse mode remains constant during the scan. As a result, if only the selected sideband is resonant with the optical cavity at the initial EOM frequency, it will always be the only resonant sideband at each EOM frequency step.

This instrument exhibited a similar standard deviation of ring-down time constants as the fibre laser instrument, thus indicating that there was no significant excitation of unintended cavity modes. However, the use of a DFB laser leads to chaotic pumping of the optical cavity (due to phase fluctuations in the laser), which limits the rate of ring-down signals and, thus, the overall acquisition rate. We have achieved a scanning rate of 100 Hz with a NEA of 6×10^{-10} cm^{-1} Hz$^{-1/2}$.

We note that the use of an external-cavity diode laser (ECDL) offers an ideal combination of high optical pump rates and a wide wavelength tuning range (~60 nm). Preliminary experiments with an ECDL Pound–Drever–Hall-locked[23] to the optical cavity have achieved an acquisition rate of ~8 kHz and an NEA of 2×10^{-12} cm^{-1} Hz$^{-1/2}$. This is the best NEA achieved with a tunable diode laser (the only two lower NEA values reported in the literature[14,15] both used c.w. Nd:YAG lasers, which offer tuning ranges of only ~0.2 nm). We attribute this high sensitivity to the high pump rate of the locked laser source, as well as the high extinction ratio of the EOM[24]. Furthermore, we note that the use of a higher-finesse cavity would allow for corresponding increases in sensitivity.

The unique properties of FARS make it well suited for many existing challenges in trace gas sensing. We see clear applications in the real-time measurements of greenhouse gas fluxes, as well as in the monitoring of dynamic processes such as combustion. Furthermore, it should allow for a new class of measurements of chemical kinetics in which the entire spectral line shape can be readily interrogated at high rates, thus providing concomitant measures of the local state.

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Author contributions

D.F.P., K.O.D. and S.E.M. conceived the idea of rapid single-frequency broadband electro-optic modulator-based tuning and demonstrated its utility in absorption spectroscopy. D.A.L. and J.T.H. adapted the idea for application to high-finesse ring-down systems and designed the present implementation. G.-W.T., D.A.L. and J.T.H. performed the experiments. D.A.L. and G.-W.T. performed the data analysis. D.A.L. wrote the manuscript. D.A.L. and G.-W.T. prepared the Supplementary Information. All authors provided technical insight and assisted in the editing of the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.A.L.

Competing financial interests

A patent application has been submitted by NIST for the measurement principle described in this work. The patent title is "Fast switching arbitrary frequency light source for broadband spectroscopic applications."