

Saturated-absorption spectroscopy with low-power difference-frequency radiation

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We report high-resolution saturated-absorption spectra recorded by use of a few microwatts of radiation generated in a single pass by difference-frequency mixing. These results were obtained without the use of buildup cavities for the nonlinear mixing or for the saturation spectroscopy. We show high-quality saturated-absorption signals for the fundamental rovibrational band of CO₂ near 4.3 μm. Convenient sources and frequency-conversion devices open new possibilities for sub-Doppler spectroscopy in the infrared. © 2000 Optical Society of America

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The availability of efficient domain-engineered nonlinear optical materials for conversion of laser frequencies, combined with simple, tunable diode lasers, represents a revolution for spectroscopy and other scientific applications.

Difference-frequency generation (DFG) spectrometers have proved to be powerful tools for spectroscopy of many molecules in the IR. Detection sensitivities as high as a few parts in 10⁹ (Ref. 1) result from the high oscillator strength that is typical of fundamental rovibrational bands in the IR. Above threshold, optical parametric oscillators are also becoming useful for acquiring Doppler-limited absorption,² as well as photoacoustic, spectra.³ The large molecular dipole moment μ for these fundamental IR transitions also makes them suitable candidates for observing narrow saturated-absorption dips. The required saturation intensity I_S is proportional to $1/|\mu|^2$. Considering that pump lasers used for frequency conversion generally emit in the visible or the near IR, for which many frequency standards already exist, narrow line shapes can help to bridge the gap to the mid IR. Hence a grid of accurate frequency standards spanning a very wide spectral range (up to 4.5 μm) could be created, with implications for metrology, molecular spectroscopy, and fundamental physics.

We report saturation spectroscopy with a DFG spectrometer that generates radiation tunable near 4.3 μm. To observe the saturated-absorption spectra we recently built a tunable DFG source based on periodically poled lithium niobate (PPLN) that generates radiation with a linewidth of ~100 kHz and amplitude noise close to the quantum limit.⁴ IR output power up to 12 μW was generated, which corresponds

to an efficiency of 0.021% W⁻¹, already including reflection losses on crystal surfaces. Theoretical calculation with $d_{\text{eff}} = 14$ pm/V and the relation in Ref. 5 give an efficiency of 0.074% W⁻¹ (we neglect the crystal absorption at 4.3 μm), even if the highest efficiency experimentally reported near 4.3-μm wavelength is 0.010% W⁻¹.⁵ We use the 4.3-μm radiation to detect the rovibrational lines of CO₂ that belong to the fundamental band (0, 0°, 0-0, 0°, 1). The absorption line strength is $\sim 3 \times 10^{-18}$ cm for the strongest lines. The saturation intensity is given by

$$I_S = \frac{\epsilon_0 c \hbar^2}{2} \frac{\Gamma_{\parallel} \Gamma_{\perp}}{\mu^2}, \quad (1)$$

where Γ_{\parallel} and Γ_{\perp} are the relaxation rates for populations and coherences, respectively. They both depend on the transit time of molecules through the IR beam, and the latter also depends linearly on gas pressure. At low pressures, where the transit time broadening is dominant, $\Gamma_{\parallel} = \Gamma_{\perp} = \Gamma$. In this condition a saturation intensity $I_S \approx 1$ mW/mm² can be expected for a linewidth of $\Gamma/2\pi = 1$ MHz (HWHM) and a transition dipole moment $\mu = 7.69 \times 10^{-31}$ C m, as calculated from Eq. (1). Therefore $I \approx I_S$ can be achieved with only ~4 μW of DFG power if the beam is focused to a waist of 35 μm.

Our simple experimental setup is shown in Fig. 1. The 17.5-mm-long PPLN crystal is pumped by a Nd:YAG laser that delivers as much as 800 mW of cw single-mode radiation at 1064 nm and by a commercially available diode laser (maximum output power, 150 mW; wavelength, ~850 nm) that is injection

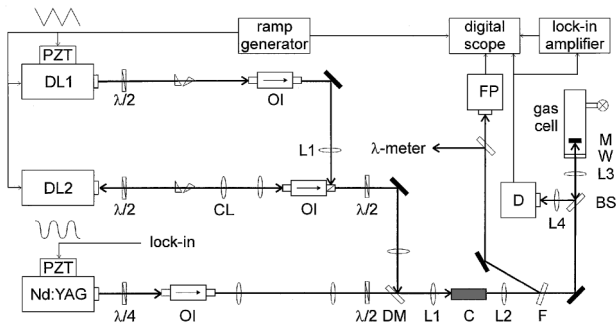


Fig. 1. Experimental setup: radiation is generated in PPLN crystal C by a mixture of light from the diode laser systems (DL1, master laser; DL2, slave laser) and the Nd:YAG laser. The IR beam is focused into the gas cell (0.5 mm length) filled with pure CO₂ at pressures of 6–10 Pa and retroreflected by mirror M. The other optical components are $\lambda/2$, $\lambda/4$, half-wave and quarter-wave plates, respectively; OI's, optical isolators; CL, cylindrical lens; L1–L4, lenses; DM, dichroic mirror; F, Ge filter; BS, beam splitter; W, CaF₂ window; D, InSb detector; FP, Fabry–Perot optical spectrum analyzers; PZT's, piezoelectric translators.

locked by a low-power diode laser (at the same wavelength) mounted in an extended-cavity configuration. The diode laser system has a stepwise tuning range of ~ 10 nm (with an ~ 75 -GHz step size) and a fast linewidth of ~ 100 kHz. The dichroic mirror combines two *s*-polarized laser beams, which are focused into the PPLN crystal by lens L1 ($f = 100$ mm), to a waist of ~ 30 μm . For optimal quasi-phase matching, the crystal is mounted in a thermally insulated copper oven that is controlled at a temperature of 287 °C. This high temperature is required only because the crystal (poling period, 22 μm) was designed, at the National Institute of Standards and Technology, for generation of 3.4- μm radiation at room temperature. Lens L2 ($f = 100$ mm) follows the oven and collimates the IR beam, while the input beams are blocked by the antireflection-coated Ge filter. The IR beam is then focused by lens L3 ($f = 50$ mm) to a waist of 35 μm onto the reflecting mirror that is inside the CO₂ cell. The mirror retroreflects the beam, and part of the beam is directed by a beam splitter to a liquid-nitrogen-cooled InSb detector. This design provides for simple saturated-absorption measurements, with the incoming beam serving as the pump and the reflected beam as the probe. A drawback of this scheme is the fringe formation that results from the back-and-forth propagation of the radiation. Some additional fringes were in fact observed, but they did not significantly degrade the signal-to-noise ratio for scans of a few megahertz because they had a much wider period. The interaction region, 0.5 mm long, was delimited by the CaF₂ window and by the mirror. This short interaction length corresponds to the Rayleigh length for the 35- μm spot size on the mirror. It was unnecessary to use the remaining part of the cell (21-cm total length and 65-cm³ internal volume) for this saturated-absorption experiment, but it did serve as a gas ballast to maintain a stable CO₂ pressure during the measurements.

We tuned the IR radiation to resonate with the *R*(14) CO₂ line at 4.237 μm , which is one of the strongest lines in the band, with a line strength of 3.5×10^{-18} cm.⁶ This means that, under normal atmospheric conditions (partial pressure of 33 Pa CO₂), a beam resonant with the *R*(14) peak undergoes in air a 1/*e* absorption within a path length as short as 5.8 cm. To reduce atmospheric CO₂ absorption of the 4.3- μm beam, we enclosed the whole setup following the PPLN crystal in a wooden box and flushed it with pure N₂. In this way the reduction of IR power within the 2.5-cm path length from the PPLN crystal to the box was limited to $\sim 35\%$. Figure 2(a) shows a first-derivative recording of the *R*(14) absorption profile. A strong saturated-absorption line shape is visible in the center of the line. The Lamb dip feature is shown in Fig. 2(b), which has an expanded frequency axis. To record this line shape we scanned the frequency of the master diode laser by feeding a voltage ramp to the piezoelectric translator (5-s scan time) while the Nd:YAG frequency was sinusoidally modulated at rate of 2 kHz with an amplitude of ~ 4 MHz (peak to peak). Inasmuch as we did not observe the Lamb dip in direct absorption, we used the size of the derivative signal to estimate that the contrast in direct absorption would be $\sim 2\%$. This estimate was made by numerical integration of the derivative Doppler profiles recorded with different

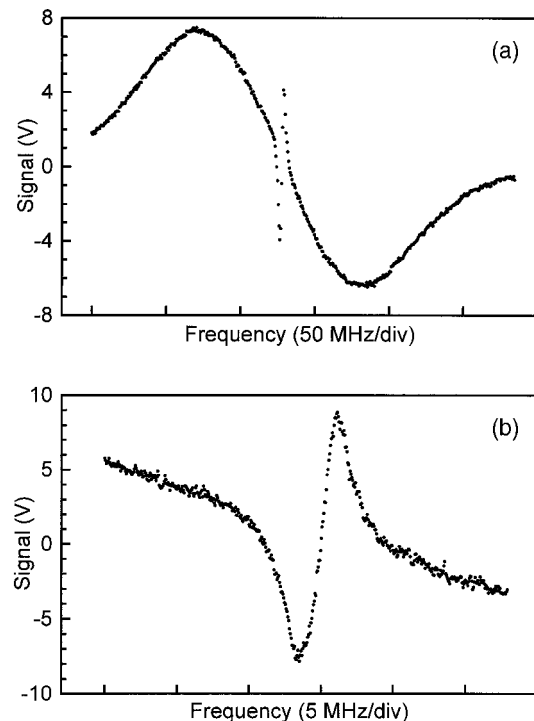


Fig. 2. Saturated-absorption dip of the CO₂ *R*(14) line recorded as a first-derivative FM spectrum for the following experimental conditions: (a) pressure $P = 8.0$ Pa, frequency span $\Delta\nu_{\text{span}} = 285$ MHz, lock-in time constant $\tau_{\text{lock-in}} = 10$ ms, scan time $T_{\text{scan}} = 20$ s, modulation frequency $\nu_m = 2$ kHz; modulation amplitude $A_m = 1.8$ MHz; (b) $P = 6.7$ Pa, $\Delta\nu_{\text{span}} = 28.5$ MHz, $\tau_{\text{lock-in}} = 3$ ms, $T_{\text{scan}} = 5$ s, $\nu_m = 2$ kHz, $A_m = 1.8$ MHz.

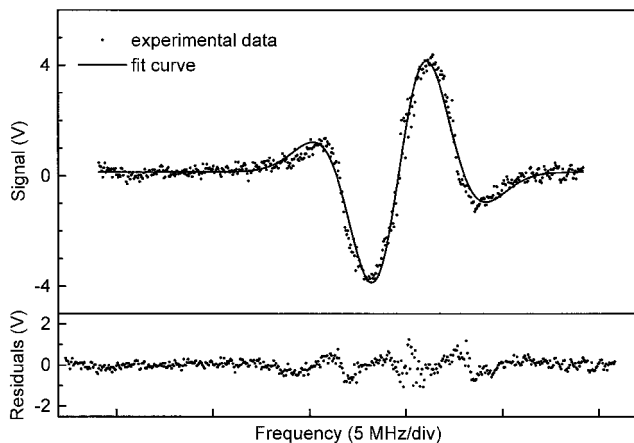


Fig. 3. Saturated-absorption dip of the CO_2 $R(14)$ line recorded as a third-derivative FM spectrum under the following experimental conditions: $P = 10.7$ Pa, $\Delta\nu_{\text{span}} = 28.5$ MHz, $\tau_{\text{lock-in}} = 3$ ms, $T_{\text{scan}} = 5$ s, $\nu_m = 2$ kHz, $A_m = 4$ MHz. The superimposed Gaussian fit gives $\Delta\nu = 2.56(2)$ MHz, and the plot of residuals is shown below the fit.

modulation widths. From the saturated-absorption contrast value it can be inferred that power broadening can contribute $\sim 2\%$ to the linewidth, which is comparable with the experimental uncertainty of the linewidth measurements. A residual sloping background that is evident in Fig. 2(b) is due to the broader Doppler profile, which has a linewidth of ~ 66 MHz (HWHM).

For precise frequency measurements, third-derivative detection could be used to achieve a flatter baseline. Indeed, a flatter baseline is obtained for the third-derivative recording of the $R(14)$ line shown in Fig. 3. All saturated-absorption recordings were taken with CO_2 pressures in the 6–10-Pa range, which was found to maximize the signal-to-noise ratio. The experimental data of Fig. 3 were fitted with a Gaussian profile (solid curve), and the residuals from the fit are also shown in the figure. The good quality of the fit is consistent with the main contribution to the measured linewidth of $2.56(2)$ MHz (HWHM) that results from the transit time of CO_2 molecules through the IR beam. The transit width of a saturated-absorption signal, for a beam waist w , a molecule with molar mass M , and temperature T , is⁷⁻⁸

$$\Delta\nu_{\text{TT}} \approx \frac{1}{8} \sqrt{\frac{2RT}{M}} \frac{1}{w}, \quad (2)$$

which yields an expected linewidth $\Delta\nu_{\text{TT}} \approx 1.2$ MHz (HWHM). The additional width measured experimentally is due to modulation broadening and third-derivative detection. The pressure-broadening contribution to the linewidth is expected to be only ~ 320 kHz if the value of 30.5 kHz/Pa (Ref. 6) is used. The natural linewidth is much smaller, contributing only ~ 110 Hz. This suggests that reduction of transit-time broadening for these lines could make them good candidates for frequency references in the IR. We can narrow the line by expanding the beam waist, down to the pressure-broadened width, without

significant loss in the signal-to-noise ratio. In fact, from relation (2) it follows that I_S , like beam intensity I , decreases quadratically with w , so the ratio I/I_S is independent of w .

We have demonstrated that, even without buildup cavities, saturated-absorption signals of high quality in the IR can be obtained with DFG spectrometers with powers as little as $10 \mu\text{W}$. This demonstration opens new possibilities for very high-resolution spectroscopy with a broadly tunable and convenient IR source. The saturated-absorption signals could in turn be used to stabilize the frequency of the IR beam, as has been done with other sources in this spectral region.⁹ We might expect the stability and accuracy to be similar to those achieved with other stabilized IR sources because they all tend to be limited by technical noise and systematic frequency shifts in the spectroscopy. Taking advantage of the wide spectral coverage of present-day DFG spectrometers, the rich and strong rovibrational spectra possessed by many simple molecules in this wavelength region can be studied in detail.

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