Rapid passage effects in nitrous oxide induced by a chirped external cavity quantum cascade laser

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A widely tunable pulsed external cavity quantum cascade laser operating around 8 μm has been used to make rotationally resolved measurements of rapid passage effects in the absorption spectrum of N_2O. Rapid passage signals as a function of laser power and N_2O pressure are presented. Comparisons are drawn with measurements performed on the same transition with a standard distributed feedback quantum cascade laser. The initial observations on rapid passage effects induced with an external cavity quantum cascade laser show that such high power, widely tunable radiation sources may find applications in both nonlinear optics and optical sensing experiments. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3079420]

Pulsed distributed feedback (DFB) quantum cascade lasers (QCLs) are becoming increasingly popular sources for high resolution molecular spectroscopy in the midinfrared region (4–10 μm) given their increasingly high output powers and near room temperature operation.[1] These sources are limited however by their tuning range, which is typically of the order of 5–10 cm^{-1}. Such a range is suitable for many specific applications involving small molecules with well-defined rovibrational spectra but is a clear limitation both for studying complex spectra in the gas phase and in the condensed phase. There has therefore been great interest in the development of external cavity QCLs (EC-QCLs) with wide tunability.[2–9] In this letter, we detail the performance of a commercially available EC-QCL system from Daylight Solutions operating around 8 μm and show its potential for use in high resolution spectroscopy and sensing applications.

Our light source was a pulsed EC-QCL supplied by Daylight Solutions[10] tunable in the range of 1195–1280 cm^{-1} without need of cryogenic or water cooling. The QCL was operated in the intrapulse mode in which resistive Joule heating of the laser during a current pulse causes a rapid frequency down chirp.[11,12] This allows a complete spectrum to be obtained on a nanosecond timescale, which enables the study of fast chemical processes.[13] As a result of the chirping, rapid passage (RP) structures will be observed in the absorption spectra of low-pressure gases as the intense rapidly swept radiation passes through a molecular resonance on a timescale that is much shorter than the relaxation time.[14,15]

The laser was operated at a temperature of 19.5 °C with a repetition rate of 90 kHz and pulse durations of up to 500 ns. The average output powers were in excess of 7.5 mW over the range of 1210–1276 cm^{-1} at the minimum injection current of 1300 mA and an average peak power of 12 mW at 1800 mA injection current was measured using a continuous wave power meter (Gentec XLP12–1S-H2). The radiation was passed through a 70 cm long glass cell with CaF$_2$ windows onto a thermoelectrically cooled mercury cadmium telluride detector (VIGO PVI-2TE-10.6) with a fast preamp-

lifier (Neoplas control) connected to a 2 gigasample/s 350 MHz bandwidth digital oscilloscope (LeCroy Wavesurfer 434). Frequency calibration was achieved by passing the radiation through a 75 mm germanium étalon whose free spectral range is 500 MHz.

Figure 1(a) shows a typical example of a 500 ns long laser pulse observed for an empty cell at a laser frequency around 1252.56 cm^{-1} at maximum output power. The spectral output from the laser is complex with multiple modes
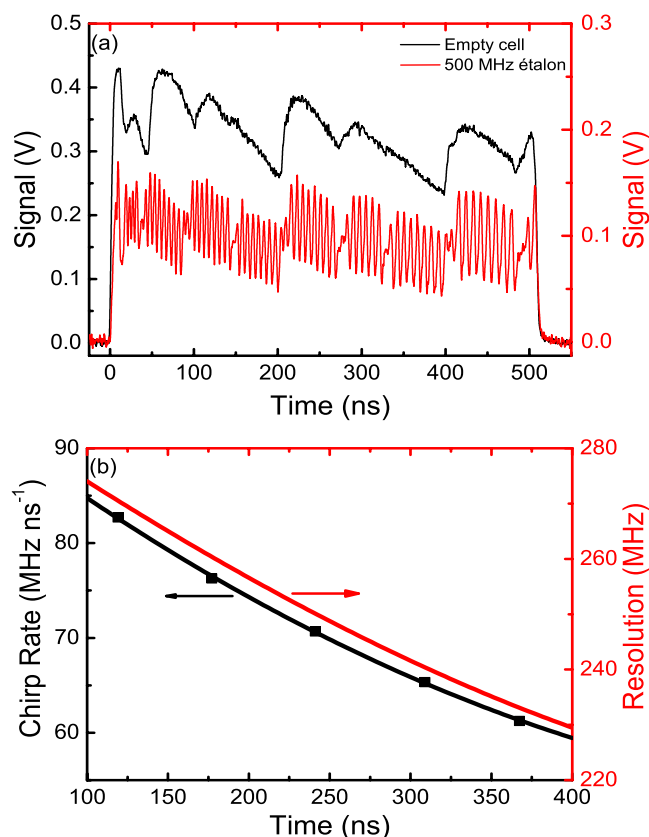

FIG. 1. (Color online) (a) An example of a 500 ns laser pulse at a laser frequency around 1252.56 cm^{-1} and the signal detected through a 500 MHz germanium étalon. (b) Measurements along with graphical representation of the variation in the chirp rate and system resolution across the pulse duration.

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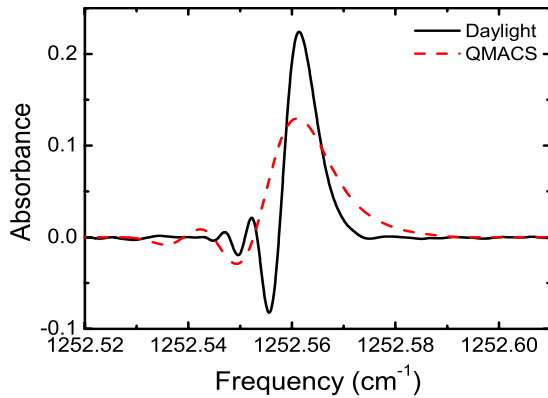[b]Author to whom correspondence should be addressed. Electronic mail: grant.ritchie@chem.ox.ac.uk.

FIG. 2. (Color online) Spectra of 20 mTorr of N_2O as measured with both laser systems for the $P36(e)$ rovibrational transition in the ν_1 band.

FIG. 3. (Color online) Spectra for varying pressures of N_2O gas measured using (a) the Daylight EC-QCL and (b) the Q-MACS QCL.

observable within a single pulse. Plotted on the same figure is the corresponding germanium étalon trace from which the chirp rate within a single mode, each of which is present for ~70 ns can be determined. We measured that the chirp rate of the laser α decreased from 85 to 60 MHz ns^{-1}, leading to a change in resolution from 275 to 230 MHz over the duration of the pulse [Fig. 1(b)], where $\Delta\nu_{resolution} = \sqrt{0.886\alpha}$.[12] The tuning range between mode hops is ~3 GHz, which is of the order of the free spectral range of the laser's external cavity. Changing the average laser output power between 8 and 12 mW resulted in a change in the chirp rate between 50 and 76 MHz for the third mode [152–204 ns in Fig. 1(a)] but did not appreciably change the accessible frequency range within a single mode.

The results obtained using this laser system are compared with measurements under the same conditions with a standard pulsed DFB QCL (Alpes laser) driven by a Q-MACS operating system (Neoplas Control). Details of the laser system have been published previously[16] and are summarized here. The laser radiation between 1253 and 1252.1 cm^{-1} was created by applying a current pulse with a duration of 190 ns to the laser at a chip temperature of 0 °C. The chirp rate of the laser was measured to decrease from 225 to 160 MHz ns^{-1}, while the resolution of the system changed from 445 to 375 MHz over the duration of the pulse. For both systems, the beam radius was determined using a "knife-edge" type method[17] and found to be 1.8 mm (Daylight) and 5 mm (Q-MACS) giving laser intensities of 12.5 and 0.25 mW/mm^2, respectively. The difference in chirp rate and power of the two systems is a result of different QCL chip design.

Despite the multiple mode hops during a single current pulse, the variation in pulse structure between pulses is still sufficiently small to allow RP structures to be observed in averaged transmission spectra through a sample of N_2O. However, we note that the absolute absorption is not always representative of the amount of gas as it is determined by the variation in the pulse structure. We probed the $P36(e)$ rovibrational transition in the ν_1 symmetric stretch mode of N_2O at 1252.561 cm^{-1} with an integrated cross-section at 300 K of 3.98×10^{-20} cm^{-1}/(cm^{-2} molecule).[18] In Fig. 2, an example of the absorption spectrum for a 20 mTorr sample of N_2O is shown for both laser systems, where the measured signals have been converted into absorbance $A = -\ln(I/I_0)$, where I and I_0 correspond to the spectral and background (with no N_2O present) signals, respectively, the data corre-
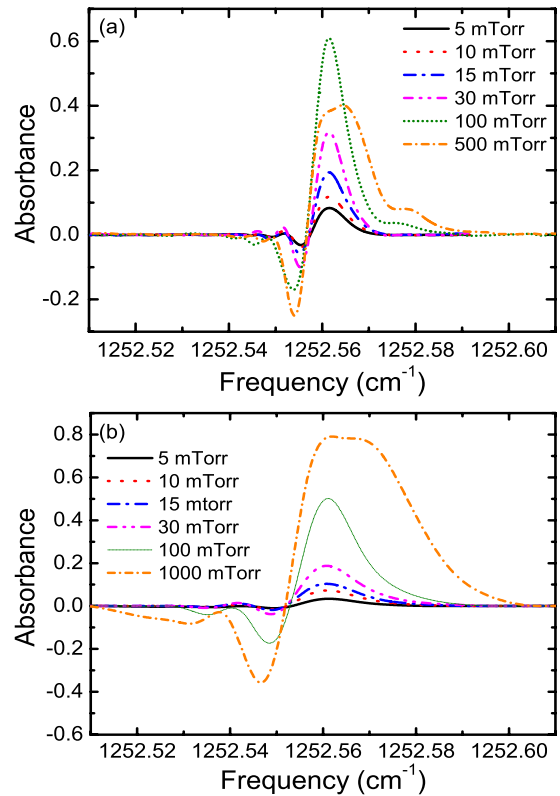
spond to 1000 averages. The spectral lines are asymmetric with a well-defined emission spike at the lower frequency side of the absorption, characteristic of RP. The differences between the full width at half maximum (FWHM) widths and oscillatory structures of the spectra are due to the differences in chirp rates 220 versus 75 MHz ns^{-1} and thus resolution.

The measured FWHM widths of the dominant absorptive part of the RP signals are 195 MHz (Daylight) and 350 MHz (Q-MACS), respectively. For measurements conducted using the intrapulse method, the resolution is not determined by the effective linewidth of the laser induced by the current pulse, as for the interpulse mode but by the chirp rate of the laser and the temporal resolution of the detection system. The measured linewidths are consistent with our expectations based on the convolution of the resolution of the laser systems and the Doppler width for this transition, which is 70 MHz.

The RP may be either linear or adiabatic depending on the value of the parameter β defined as α/Ω^2, where Ω is the Rabi frequency, itself defined as $\mu\mathcal{E}/h$, where μ is the transition dipole moment and $\mathcal{E}$ is the electric field strength of the laser radiation and h is the Planck constant. The limiting values of $\beta = 0$ and $\beta = \infty$ correspond to the adiabatic and linear regime, respectively. For the data shown in Fig. 2, the corresponding values of β are ≈ 50 (Daylight) and ≈ 1000 (Q-MACS) and both measurements are in the linear passage regime.[19]

Furthermore, we note that the peak absorbances measured in such RP experiments do not conform to our expectations from the Beer–Lambert law, which reflects the rapid excitation in the system compared to its relaxation time. For example, the peak absorbance shown in Fig. 2 is ~0.23,
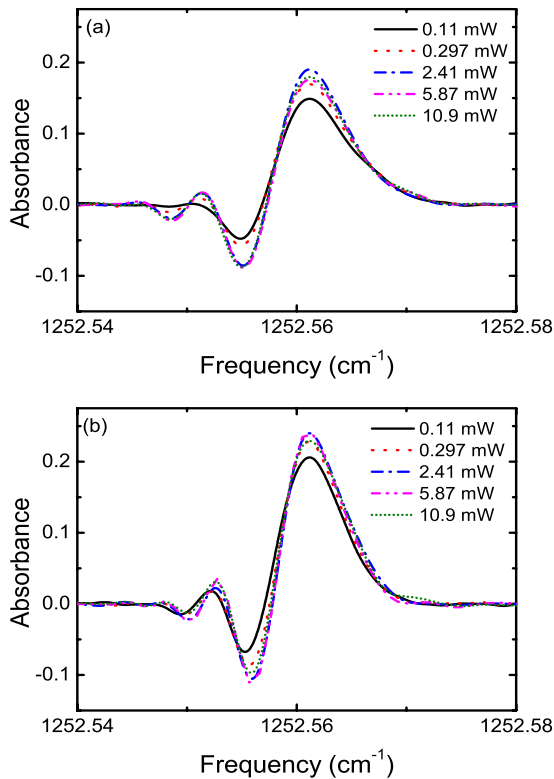
FIG. 4. (Color online) Spectra for varying powers in the Daylight EC-QCL (a) at a chirp rate of 75 MHz ns^{-1} and (b) at a chirp rate of 58 MHz ns^{-1}. The power levels correspond to the averaged power.

whereas a value of 0.76 is expected from the Beer–Lambert law. In Fig. 3, we present the variation in the RP signals as a function of N$_2$O pressure between 5 and 500 mTorr for the Daylight laser and up to 1000 mTorr for the Q-MACS system. In Fig. 3(a), a secondary absorption peak appears for pressures above 100 mTorr which is not observed in Fig. 3(b) reflecting the difference in resolution between the two laser systems. We observe an approximately linear increase in the magnitude of the signal with pressure up to about 50 mTorr with a gradient that is only 54% of that expected from the integrated absorption cross section. Thus, the deviation between the measured and experimental number densities is 46%. For comparison, the corresponding deviation is ~16% for the Q-MACS system, reflecting the nonequilibrium nature of the laser matter interaction and the larger driving provided by the Daylight system. These observations reflect the increased driving in the system leading to complex and rapidly varying temporal behavior of the refractive index and the presence of optical pumping effects in which the sample is (partially) aligned. By buffering of the low-pressure gas with 30 Torr of Ar, no RP structures are observed as the rate of collisional dephasing becomes competitive with the laser chirp rate. At even higher buffer gas pressures, a symmetric spectral line shape is recovered as expected.[16]

In Fig. 4(a), we show the data from an experiment in which the chirp rate was maintained at 72 MHz ns^{-1} by run-ning the laser at 12 mW averaged peak power but attenuating the power before the cell using a polarizer. It is clear that RP structure is observed over two decades of power, and it is only at the lowest powers that the smaller of the two secondary minima is lost. Interestingly similar measurements conducted at a slightly different chirp rate of 58 MHz ns^{-1} plotted in Fig. 4(b) show that the RP structure can be very sensitive to changes in the chirp rate with both secondary minima being observable at the lowest power.

In conclusion, initial observations on RP effects induced with an EC-QCL have been presented, and it is clear that such high power widely tunable radiation sources will find application in both nonlinear optics and optical sensing experiments.

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