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Chirped quantum cascade laser induced rapid passage signatures in an optically thick gas

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Abstract We report observations of rapid passage signals induced in samples of N_2O and CH_4 present in a multipass cell with an optical path length of 5 m. The effect of laser power and chirp rate upon the signals has been studied by utilising two different chirped quantum cascade lasers operating around 8 μm. The rapid passage signals exhibit an increasing delay in the switch from absorption to emission as a function of increased gas pressure (up to 8 Torr of gas). By comparing a selection of transitions in N_2O and CH_4, we show that, unlike ammonia, this 'pressure shift' is independent of the transition dipole moment, spectroscopic branch probed and laser chirp rate. As the transition dipole moment is much larger in nitrous oxide than methane, we believe that this indicates that N_2O–N_2O collisions are more efficient at removing coherence from the polarised sample than CH_4–CH_4 collisions. We have also observed this pressure shift in a short path length of 40 cm, although with a much reduced value, indicating that propagation effects are important in this optically thick minimally damped system.

1 Introduction

Rapid passage (RP) effects were first observed in the study of magnetic resonance, whereby the use of a rapidly swept rf field led to complex line shapes in the resultant spectra [1–6]. In later years, analogous behaviour has also been observed in optical spectra; initially, in Stark spectroscopy studies [7], and more recently the same effect has been found to be endemic in the applications of highly powered, intrapulse operated, quantum cascade lasers (QCLs) to low pressure molecular systems [8–15]. The intrapulse operation of these devices leads to rapid Joule heating of the laser chip during a single current pulse of tens up to hundreds of nanoseconds giving rise to a fast frequency down chirp of the laser output over a large wavenumber range (ca. 1–2 cm^{-1}). In these cases, the frequency of the swept radiation passes through the Doppler width of a spectroscopic transition on a timescale that is fast compared to that for relaxation, and an asymmetric line shape is observed with emissive and absorptive 'wiggles' following the expected absorption profile. This behaviour is a result of interference between the driving field and the polarised sample which itself has been prepared in a velocity selected phased array manner by the chirped laser radiation. Such behaviour has previously been termed by Rothenberg a *self-induced heterodyne* [16].

In NMR, a theoretical model describing the ideal case of a closed two level system interacting with a swept field was formulated in the so-called Bloch equations [4]. This model has since been further adapted for a two level system in a swept optical field, forming the coupled Maxwell-or Optical-Bloch equations [17]. While this model predicts the possibility for creating a complete population inversion adiabatically, in practice the chirp rate of pulsed QCLs is too fast to effectively couple the transition moment to the driving field, and the pulse power is too low, and consequently adiabatic following cannot occur. Instead, the detected signal is the result of beating between an induced polarisation of the system, and the driving field; this is known

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as rapid passage. Observation of such coherent effects is limited to low pressure media, as the major relaxation mechanism in most cases is collisional dephasing; it has been shown that increasing the collision rate by introducing a buffer gas (e.g. Ar, N_2) results in the recovery of a symmetric Voigt line shape [8–10].

The structure of a RP signal is very clearly dependent upon a number of experimental properties such as laser intensity, chirp rate, the pressure of the sample that is absorbing the chirped radiation and the presence of any buffer gas. In addition, there is evidence that propagation effects are important in such minimally damped systems and very recently, Duxbury et al. have reported experiments upon acetylene at 7.84 μm within a Herriot cell (with path length ∼60 m), demonstrating a drastically altered line shape, whose time (within a pulse) at which it switches from absorption to emission increased as the pressure of acetylene is increased [18]. In this paper, we report a complementary study of the delay in the switch from absorption to emission in RP signals in response to rapidly swept 8 μm radiation from both a distributed feedback (DFB), and an external cavity (EC), QCL. We observed that the evolution of this delay with pressure is the same for both lasers, irrespective of the variation in laser intensity and chirp rate, and that it does not show a dependence upon the magnitude of the transition dipole moment. The delay is observed for an optical path length of 5 m as well as for a short path length of 40 cm, although with a much reduced value for the shift indicating that propagation effects over extended path lengths contribute to the occurrence of these delays.

2 Experimental

Two different pulsed QCLs emitting around 8 μm are compared in this work: a standard DFB-QCL (Alpes laser) driven by a Q-MACS operating system (Neoplas Control), and an EC-QCL supplied by Daylight Solutions tunable in the range 1195–1280 cm^{-1}, without need of cryogenic or water cooling. Details of both laser systems have been published previously [10, 11] and are only summarized here. In the case of the Q-MACS system, laser radiation between 1254 and 1253.1 cm^{-1} was created by applying a 190 ns current pulse to the laser, at a heat sink temperature of −12.5°C and at a repetition rate of 20 kHz with a peak output power of 20 mW measured using a cw power meter (Gentec XLP12-1S-H2). The Daylight EC-QCL system 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 measured peak output powers were in excess of 70 mW with a maximum of 130 mW over the range 1210–1276 cm^{-1}.

The radiation was passed from the QCL through a multipass White cell (Specac Tornado T20) with a 5 m optical path length fitted with CaF_2 windows by the use of gold coated mirrors and focused by a silver coated off-axis parabolic mirror (156 mm focal length) onto a thermoelectrically cooled mercury cadmium telluride detector (VIGO PVI-2TE-10.6) with a fast pre-amplifier (Neoplas control) connected to a 2 Gs/s, 350 MHz bandwidth digital oscilloscope (LeCroy Wavesurfer 434). A holographic wire grid polarising filter was placed in front of the detector to attenuate the power onto it. Selection between the laser sources was achieved by the use of a flip mirror. The detector signal was used to trigger the data acquisition on the oscilloscope as the internal trigger of the systems caused an additional jitter on the recorded detector signal. Spectra were acquired as the average of 1000 shots to mitigate the effect of random laser fluctuations and noise. Frequency calibration was achieved by passing the radiation through a 75 mm germanium etalon with a free spectral range of 500 MHz (0.0167 cm^{-1}). For both systems, the beam radius was determined using a "knife-edge" type method [19] 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 cell and gas lines were evacuated through the use of a rotary vacuum pump and a range of Baratrons capacitance gauges with full-scale readings of 1, 10, and 100 Torr (with resolution of $10^{-3}\times$ full scale) were used to monitor the pressure.

3 Results and discussion

Figure 1 shows typical RP signals produced by each laser when driving a low pressure sample of 60 mTorr of N_2O on the P36(e) rovibrational transition of the ν_1 symmetric stretching mode at 1252.561 cm^{-1} [20], observed after 1000 averages. Plotted on the same figure are the corresponding germanium etalon traces from which the chirp rate for each laser can be determined. Over the pulse, the chirp rate of the Daylight laser decreased from 87 to 60 MHz ns^{-1}, while for the Q-MACS laser the chirp rate changed from 225 to 160 MHz ns^{-1}. The resolution of the system in this regime is determined largely by the chirp rates and changed from 275 to 230 MHz and 445 to 375 MHz, respectively, over the duration of the pulse [13]. The structure visible on the pulse from the Daylight laser (Fig. 1(a)) is due to the external cavity, and has been characterised previously [11]. We note that there are two types of mode hop within a given scan of the EC-QCL; one which leads to a relatively large change of output intensity and occurs roughly every 6 GHz and one which occurs every 3 GHz but leads to a much smaller variation in the output intensity. Both mode hops are clearly seen on the etalon trace presented in Fig. 1(a) and prevented an absolute wavenumber scale to be assigned to the spectrum. No such mode hopping is observed with the DFB-QCL system. For both lasers, the observed spectral lines are clearly

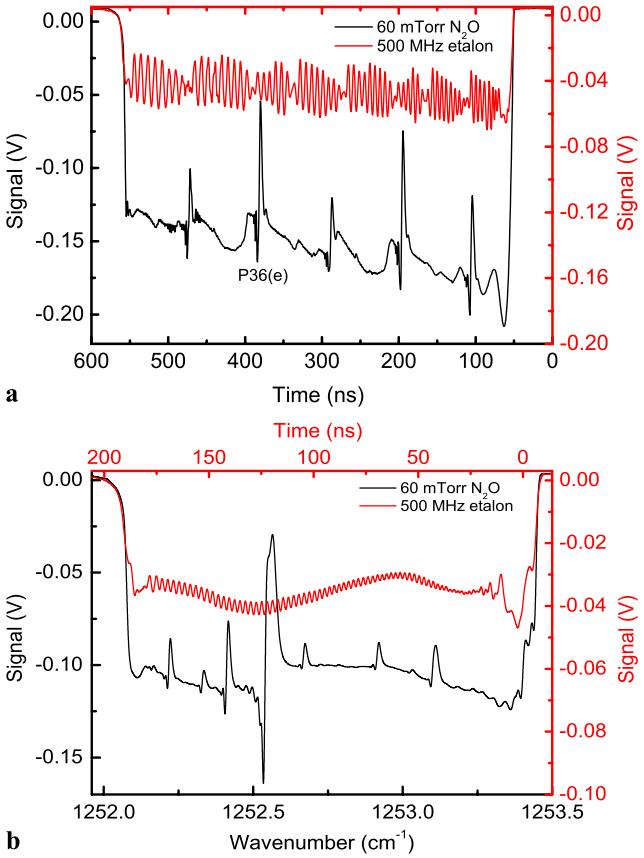

Fig. 1 Typical RP signals observed for a 60 mTorr sample of N_2O interrogated by (**a**) the Daylight and (**b**) the Q-MACS laser. Each trace is accompanied by that of the signal detected through a 500 MHz free spectral range Ge etalon used to determine the chirp rate and a corresponding wavenumber scale. (**a**) has no wavenumber scale as the spectra shows multiple modes

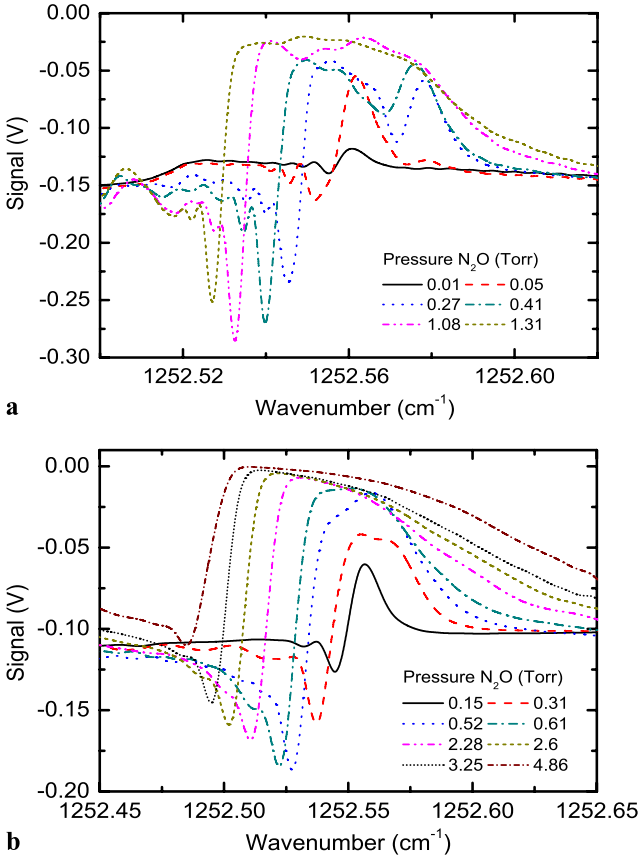

Fig. 2 Rapid passage signals as a function of N_2O pressure for the P36(e) transition measured with (**a**) the Daylight and (**b**) the Q-MACS laser. The spectrum measured using the Daylight laser contains extra structure almost certainly due to other weaker spectral lines which are present and are only resolvable when using the more slowly chirping Daylight laser

asymmetric with a well defined emission feature at the lower wavenumber side of the absorption (left side), characteristic of RP with a laser source that is frequency down-chirped. The difference in the full width at half maximum (FWHM) widths of the dominant absorptive peaks, and the oscillatory structure within the spectra are an effect of the variation in resolution.

In Fig. 2(a) and 2(b), we present the effect of increasing the pressure of N_2O upon the RP signals for the P36(e) transition using both the Daylight and Q-MACS lasers, respectively. It is clear that under these conditions, whereby the medium is optically thick but minimally collisionally damped, the emission features in the RP signatures consistently shift to lower wavenumber with added pressure: an effect that is at least three orders of magnitude larger than would be expected from traditional pressure induced shifts. Also of note is that, although the optical thickness (defined as σcl where σ is the peak absorption cross-section, c is the concentration and l is the optical path length) at 1 Torr is ca. 1000, a non-zero transmission through the cell is still observed. This is because even at these relative high pressures the hard sphere collision frequency is still only 11.2 MHz; the time between collisions is thus still at least one order of magnitude longer than the time it takes to chirp through the Doppler width of the transition, and so coherent effects are still expected to be observable. The data shown in Fig. 2(a), which were obtained using the Daylight laser, show more structure at higher wavenumber than that in Fig. 2(b). This additional structure is almost certainly due to other weaker spectral lines which are present and are only resolvable when using the more slowly chirping Daylight laser; however, we cannot rule out the possibility that the additional structure in Fig. 2(a) is due to the presence of a second mode within the sweep range of the EC system [11].

In order to verify that this pressure induced shift is a real effect, and not an experimental artefact induced by external factors such as laser drift or instability, we emphasise that etalon traces were taken alongside the molecular spectral data in order to show that the lasers were well behaved. Unfortunately, our setup did not permit simultaneous spectra and etalon traces to be recorded, as the power output of the Q-MACS laser was too low for etalon contrast to be

achieved from the split beam, but we were able to separately monitor the etalon traces over time. In Fig. 3(a), we show spectra recorded with the Q-MACS laser at 15 mTorr, and 380 mTorr of N_2O at 10 minute intervals, along with etalon traces taken immediately after the first measurement, and directly before the second. While there is a clear shift in the emission features of the rapid passage signatures, the two etalon traces are completely in-phase, indicating that the signals are not influenced by external factors such as intensity or frequency instability.

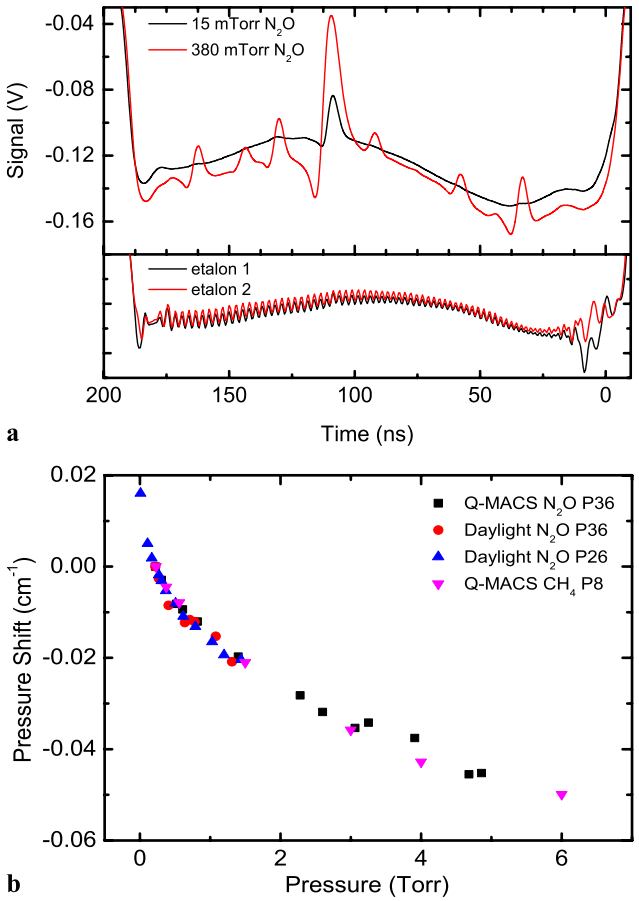

Fig. 3 (**a**) Spectra of the P36(e) transition for 15 mTorr and 380 mTorr of N_2O measured with the Q-MACS laser and taken with a 10 minute interval, alongside etalon traces taken following the first measurement (etalon 1) and immediately preceding the second (etalon 2). The spectrum at higher pressure exhibits a clear delay in RP signal. (**b**) Pressure shifts for a selection of transitions measured with both the Q-MACS and the Daylight laser

Having determined the validity of our measurements we now compare the transitions P26(e) and P36(e) of the ν_1 symmetric stretch mode of N_2O and the P8 transition of the ν_4 bending mode of CH_4 probed with these lasers. We note that the P26(e) transition was only accessible with the Daylight laser. The spectroscopic data pertinent to the probed transitions is given in Table 1. Figure 3(b) contains a plot of the shifts in the emission maxima relative to the position at 20 mTorr, as a function of gas pressure for these transitions measured with the Q-MACS and the Daylight laser. The shift for the P26(e) is positive in the beginning as the data were taken at pressures smaller than 20 mTorr. It is clear that for a given transition, the magnitude of the shift is independent of the laser used, and hence the power, and chirp rate, and that it does not vary significantly between the N_2O transitions and the CH_4 transition despite a difference in transition dipole moment of a factor of 6. We also note that each of tetrahedral splitting components of the P8 and P9 CH_4 transitions show the same behaviour (data not shown in graph). It therefore seems that the medium will couple to the laser equally efficiently for these transitions, leading to an equivalent change in the refractive index of the gas at a given pressure and a similar pressure shift is observed.

Other studies within our group using selected rovibrational transitions within the ν_2 band of NH_3 around 10 μm have shown that the measured shift is directly related to the magnitude of the transition dipole moment [21] and therefore the similarity in the shifts observed with N_2O and CH_4 is at first sight unexpected. However, we note that the rapid passage structure is determined not only by the magnitude of the polarisation that is induced within the sample but also on its dephasing rate due to collisions. In order to model the rapid passage signals, both population $(1/T_1)$ and polarisation decay rates $(1/T_2)$ are required, and in gas phase studies it is common to make the approximation that these two rates are very similar. The measurements presented here clearly show that the dephasing rates must be very different for both species, with the polarisation of the N_2O being more readily removed by self collisions than is the case for CH_4 and is in keeping with the longer range dipole-dipole interaction that operates between N_2O molecules compared

Table 1 The spectroscopic data for the N_2O and CH_4 transitions investigated in this work [20]

Molecule	Line position cm^{-1}	Integrated line strength $cm^2\,cm^{-1}$ molecules^{-1}	Einstein A factor s^{-1}	Transition dipole moment D	Rotational assignment
N_2O	1252.5608	3.98×10^{-20}	5.60	7.62×10^{-2}	P36(e)
N_2O	1261.9874	10.4×10^{-20}	5.77	6.48×10^{-2}	P26(e)
CH_4	1253.3491	2.08×10^{-20}	2.04	1.22×10^{-2}	P8

with the non-polar CH_4. The RP delay measurements reported here indicate that this form of coherent spectroscopy can provide intriguing insights into the roles of elastic and inelastic collisions and any velocity dependent effects. Further studies on a range of molecules and rovibrational transitions are currently being conducted in order to elucidate how the RP signatures are affected by the presence of different atomic and molecular colliders.

Furthermore, while one may initially expect changes in laser intensity and chirp rate to have an effect upon the pressure shift, previous work upon the P36(e) line of N_2O has shown that altering the power and chirp rate of the Daylight laser produced negligible changes to the non-linear effects observed in RP spectra [11]; a result rationalised by the fact that all of the measurements lie well within the linear RP regime as described by Ernst [4].

The behaviour that has been observed both in this work and previously by Duxbury et al. [18] and by Brickman et al. [22, 23], the latter of which involved the travelling wave amplification of short pulses from a CO_2 laser in a cell containing hot CO_2, is a direct result of the constructive and destructive interference between the incident laser field and the field generated by the response of the system. Complete destructive interference results if the incident field is changed slowly enough to allow the sample polarisation to reorient following that of the laser field. However, if the incident field is changed too rapidly for the sample to follow, interference may not be completely destructive, and a beating between the fields can be observed in the form of RP signals. In particular, we note a subtle difference between the earlier work by Brickman et al. [22, 23] and the current QCL studies. Namely, that the former study involved a shift in the phase of the laser radiation (imposed using a CdTe phase shifter), while the current studies have no such enforced phase shift. A phase shift may, however, occur due to the propagation of radiation through the sample gas over a long path length and indeed a phase difference is required to allow constructive interference to generate the gain observed in the form of RP signals.

Duxbury et al. have qualitatively simulated the RP delay observed in experiments in a similar manner to Brickman et al. by solving the coupled Maxwell–Bloch equations numerically for a closed two level system, incorporating a step-wise propagation of radiation through the sample [18]. However, while this model produces a RP signal like that observed, and an increased pressure shift with increasing pressure, the value of the modelled shift and that measured do not match; a factor of 5 deviation is reported for the shift observed for 3 Torr of C_2H_2 in a Herriott cell with a 60 m path length. From these simulations, it is thought that this shift only occurs over a long path length [18].

In order to probe whether the path length is indeed crucial in the observation of RP delay as currently assumed, studies were carried out in a 40 cm cell where propagation effects should play a minimal role in the interaction of radiation with the sample. The shifts previously measured over a 5 m path length for the CH_4 P8, and N_2O P36(e) transitions are plotted in Fig. 4, and alongside these are the shifts measured for the same transitions in the 40 cm cell. It is apparent that the RP delay still occurs for short path lengths, with a marked decrease of shift in the shorter cell, and that the measured shift for both molecules is once more the same. Clearly, a more elaborate model of the interaction and propagation of the chirped light field with the optically thick sample and the depolarisation caused by molecular collisions is required.

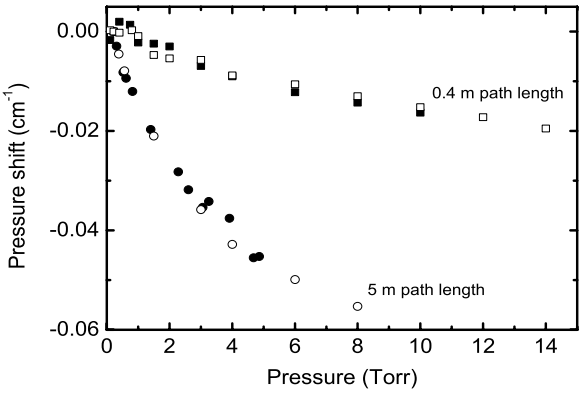

Fig. 4 Pressure shifts for the N_2O P36(e) (*closed symbols*) and CH_4 P8 (*open symbols*) transitions as measured with the Q-MACS laser for an absorption path length of 0.4 m and 5 m

4 Conclusions

A delay in the rapid passage signal, induced by a chirped radiation from a quantum cascade laser, has been observed as a function of optical density in a multipass cell. Within the operating regime of our lasers it has been found that the pressure dependence of this delay is invariant to changes in transition dipole moment, spectroscopic branch probed and chirp rate, most likely reflecting the greater degree of dephasing induced by N_2O self collisions compared to that for CH_4. This delay effect has also been observed for the first time over a short path length (40 cm) although with a much reduced value for the shift and indicates that the requirement of a long interaction path length between the light and the absorbing gas is less stringent for the manifestation of this shift than assumed until now.

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