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An Axial Molecular-Beam Mid-Infrared Diode Laser Spectrometer

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ABSTRACT

A novel molecular beam spectrometer for the purpose of trace gas sensing is described. Sensitivity is greatly enhanced and absorption interference by atmospheric H_2O and CO_2 is greatly reduced by using a molecular expansion. The expansion results in rotational cooling and population enhancement of low-lying energy levels. The instrument employs a tunable mid-infrared lead salt diode, which operates in single mode from 2348.5 to 2351.1 cm^{-1}, and a 36 m Herriott multipass cell. The sample gas is injected axially through a coupling hole in one of the spherical mirrors. The result is an increase of the residence time of the molecular beam in the sampling region. Pulsed operation of the nozzle allows background subtracted spectra to be acquired. The spectrometer can either be operated in fast scan mode, in which the laser frequency is rapidly scanned over the absorption feature of interest, or in frequency modulation mode with 2f-detection. A special adaptation of frequency modulation to the axial sampling system is described. Sample data of CO_2 are presented.
Keywords: Axial molecular beam, 2f-demodulation, rotational cooling, lead salt diode laser, mid-infrared

1. INTRODUCTION

Tunable diode laser absorption spectroscopy is a well-developed technique for the analysis of atmospheric trace gases.[1] Gases are typically extracted and analyzed in a White[2] or Herriott[3] multipass cell at reduced pressure. The advantages of these cells are increased optical absorption path lengths and reduction of the normally pressure-broadened line widths. The gain in the peak center absorption through the line shape factor more than offsets the decrease in the molecule density, compared with open path measurements at atmospheric pressure. Optimal results are obtained in the Voigt regime, between 10 and 100 torr. At pressures below 10 torr, the line widths become Doppler limited.[1] For the purpose of trace gas sensing, line width reduction below the Doppler limit is desirable to increase peak center absorption and to eliminate interference from overlapping absorption peaks.

Molecular spectroscopists routinely achieve sub-Doppler resolution using pulsed free jet expansions and molecular beams[4], for example to study weakly bound complexes in the gas phase. Free jet expansions also provide the benefit of sample gas cooling, i.e. the transfer of population from excited rotational and vibrational energy levels into lower energy states.[5] In this manner translational temperatures on the order of a few mK can be achieved. The cooling is less efficient for rotational and still less efficient for vibrational levels because the collisional cross sections for rotational and vibrational energy transfer are smaller.[5] Spectroscopists have recently[6-7] suggested the use of infrared diode laser molecular beam spectrometers for atmospheric applications.

Current mid-infrared molecular beam instruments employ gas injection perpendicular to the optical axis *via* slit[8] or pinhole nozzles.[4] It is known that circular nozzles produce "colder" beams, but slit nozzles provide a much longer absorption path than pinhole nozzles. Recently, Walker *et al.*[9] placed a pinhole nozzle axially to the main optical axis in a millimeter wave experiment. Axial injection of the gas sample led to the observation of two closely spaced Doppler peaks for each transition, and a sensitivity gain by at least a factor of two was realized.

In this paper, we describe a mid-infrared tunable diode laser absorption spectrometer that employs a molecular expansion parallel to the optical axis of the multipass cell. We present sample spectra near the ν_3 asymmetric stretch R(0) transition of CO_2 at 2349.917 cm^{-1}, and show the effects of the population redistribution of thermally populated

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CO_2 states into the J=0 level. One of the obstacles that had to be overcome in setting up this spectrometer, in particular for the purpose of trace gas sensing, was the development of a detection scheme that utilizes both Doppler components. A new 2f-demodulation scheme was developed to utilize both these components for concentration measurements. The concept of trace gas sensing with a molecular beam spectrometer is demonstrated.

2. EXPERIMENTAL

2.1 Setup

A mid-infrared lead salt laser diode (Laser Components F-2462-GMP) capable of lasing in single mode (verified by a clean etalon pattern) from 2348.5 to 2351.1 cm^{-1} was used as the excitation source in the experiments. The diode is housed in a liquid nitrogen cooled dewar (Laser Photonics L5736) and is current and temperature stabilized by the matching control unit (Laser Photonics L5830). An external voltage can be applied to the controller to achieve modulation of the laser current and laser frequency. The laser beam is collected by an off-axis parabola and split by a 92/8 pellicle beam splitter (Oriel 37400). The weaker portion travels through a 10 cm reference cell (Reflex Analytical Corp., model 5000), containing a few millitorr of carbon dioxide for absolute frequency calibration, and is focussed with a 100 mm focal length planoconvex CaF_2 lens (Janos A1404-110) onto an InSb photovoltaic detector (Infrared Associates G-170-15). The detector output is preamplified by a custom-built fast preamplifier. The main portion of the laser beam is mildly focussed by a 500 mm planoconvex CaF_2 lens into a in-house constructed Herriott multipass cell. The cell consists of two 50.8 mm diameter, 508 mm focal-length, gold-coated, spherical mirrors (Edmund Industrial Optics L32-822). The spherical mirrors were set up ~90 cm apart. The multipass cell is housed in a vacuum system that is pumped by a diffusion pump (Edwards cryo-cooled Diffstak CR160-700M). The laser beam enters and leaves the cell through a 5 mm diameter, off-axis coupling hole in one of the mirrors. The optical alignment of the multipass cell was periodically checked with a Helium-Neon laser co-aligned with the output of the lead salt diode. The mirror separation and the input coupling angle were then adjusted so that 20 spots were visible on the non-coupling mirror surface in a typical spherical Herriott pattern and that the laser beam cleanly re-emerged from the Herriott cell. A total absorption path length of 36 m was obtained. Higher path lengths, which had been implemented, led to a significant decrease in transmitted laser power.

A pulsed nozzle (General Valve, Series 9) is used to generate the pulsed molecular expansion. The pin hole (0.8 mm diameter) nozzle head was machined down to an outer diameter of 17 mm and mounted into a 20 mm hole in the center of the second mirror of the Herriott cell. A custom-built driver (CFC Consulting) controls the pulse nozzle. In a typical pulse, the nozzle delivered approximately 1 mmol of gas per pulse, estimated from the pressure increase in the isolated vacuum system. The pulse repetition rate was 5 Hz, limited by the throughput of the diffusion pump.

After leaving the Herriott cell, the laser beam passes again through the 500 mm focal length lens and is then focussed by a 50 mm focal length lens onto a second InSb detector (Laser Analytics L5911), whose output is also preamplified. Depending on the method of operation (see below) the two signals were either demodulated with a pair of lock-in amplifiers (Stanford Research Systems 830 for the main signal, Ithaco Dynatrac 391A for the reference signal) or acquired directly by a 12-bit dual channel transient recorder (Gage Compuscope 1250) that can be operated at sampling rates of up to 25 MHz. A diagram showing the major components of the instrument is shown in Figure 1.

2.2 Operation

The instrument was operated in two different modes: fast scan technique[10] and frequency modulation with 2f-detection. In the fast scan method the laser is scanned rapidly (on the order of 1 cm^{-1} ms^{-1}) and repetitively over the frequency region of interest. This is done by applying periodic voltage ramps to the laser controller separated by short (~200 μs) settling periods. The delay is necessary for the diode to return to its original frequency and to ensure high reproducibility of the frequency scan. We found that frequency drifts due to ohmic heating are minimized by starting this modulation scheme a few minutes before actual data are recorded. The modulation pattern is generated with an external function generator (Stanford Research Systems DS345). The operation of the spectrometer in fast scan mode is software controlled. The TTL signals for start of data acquisition and opening of the pulsed nozzle are generated with an I/O board (Iotech Daqboard 2000). An adjustable delay between the nozzle trigger pulse and the start of the fast scan, usually on the order of 0.4 ms, is implemented. Background spectra are acquired half way between the molecular pulses.

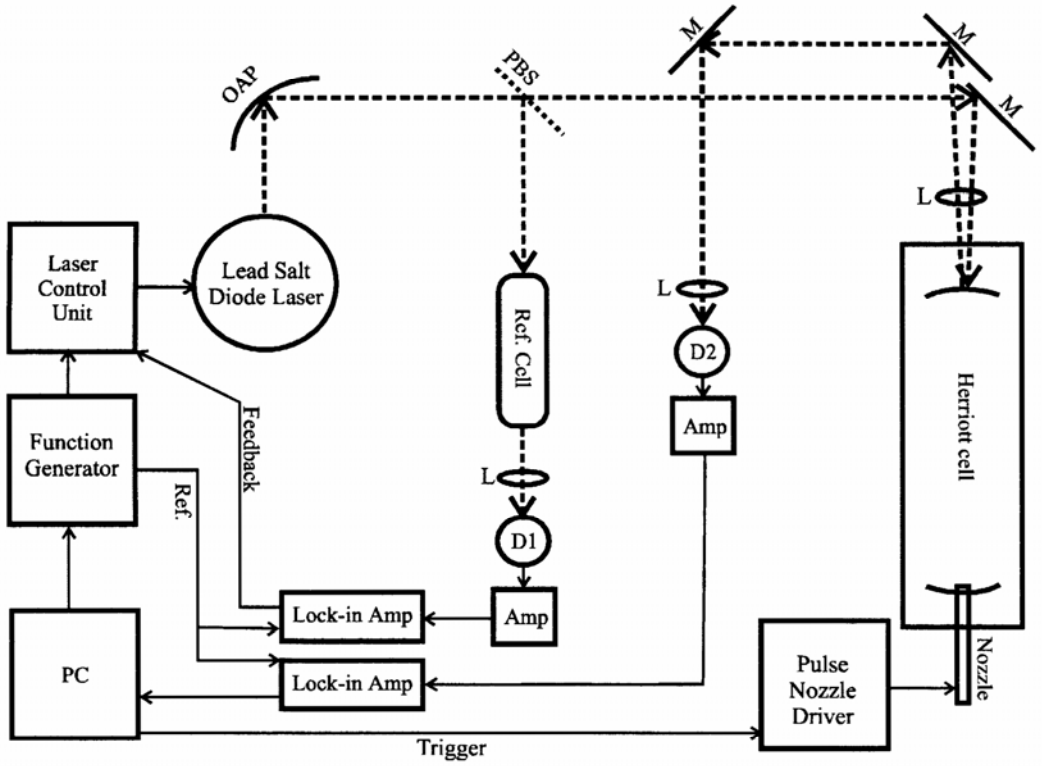

Figure 1

Schematic diagram of the spectrometer components.
M = gold coated mirror; D = InSb detector; L = lens; Amp = Preamplifier;
PBS = pellicle beam splitter; OAP = off-axis parabolic mirror

Without software lock, averaging of successive scans is limited by laser frequency drifts. If a software frequency lock is used, several hours of spectra accumulation can routinely be achieved without frequency drift or peak broadening. In a typical fast scan experiment, 100 spectra are averaged to yield a final spectrum.

The fast scan method was employed mainly to characterize the spectrometer performance in terms of line width, frequency determination, and Doppler splitting. For the purpose of trace gas sensing it is only necessary to monitor a single molecular transition rather than to scan a wider frequency region. The appearance of Doppler doubled lines in the axial molecular expansion allowed us to employ a newly developed modulation scheme while simultaneously maintaining a frequency lock of the laser. For the frequency lock, the laser was tuned to the center of the CO_2 R(0) transition and frequency modulated at 51 kHz. The reference signal was demodulated in 1f mode at a time constant of 125 μs. The zero-crossing of the reference lock-in amplifier output was used to keep the laser locked to the precise center frequency. In order to detect a signal from the main sample cell, the modulation amplitude was adjusted to reach both Doppler components. The signal was then 2f-demodulated with a time constant of 300 μs, and the output was acquired by the transient recorder card at a sampling rate of 10 MHz.

3. RESULTS AND DISCUSSION

3.1 Population redistribution in a molecular beam

The energy levels of an ensemble of gaseous molecules at thermal equilibrium are populated according to the Boltzmann distribution.[11] In a spectroscopic experiment, one particular ro-vibrational state is probed, and the vast majority of the molecules in other thermally populated states are not utilized for detection. For example, if one were to measure CO_2 using the R(0) transition at 2349.917 cm^{-1} at room temperature, less than 0.4% of the actually present CO_2 molecules are detected. On the other hand, if the molecules have a population distribution corresponding to a rotational temperature of 1 K, as it does occur in a molecular expansion, more than 85% of all CO_2 molecules are predicted to be in the rotational ground state. Because of symmetry reasons, half of the states of CO_2 have spin statistical weight of zero so that the R(1) and R(3) lines are absent from the spectrum. Other molecules, which do not have such symmetry restrictions, would have more thermally accessible states, and thus more to gain in a molecular expansion experiment than CO_2.

Shown in Figure 2 is the background subtracted fast scan spectrum of an expansion of 1% CO_2 in Helium carrier gas at a backing pressure of 8 atm. Superimposed is the spectrum of the reference cell containing CO_2 at a pressure of a few torr. The reference spectrum shows the for lead salt diodes typical sloped baseline, which is removed in the expansion spectrum by background subtraction. The reference spectrum shows a number of CO_2 lines originating from thermally populated rotational and vibrational states. In the expansion spectrum, the R(0) transition of CO_2 is the only remaining monomer line apparent in the spectrum. The peak appears twice because of the aforementioned Doppler splitting. The small peak at 2350.226 cm^{-1} is due to the $^{R}R_0(1)$ transition of the $HeCO_2$ van der Waals complex.[12] Because of the spotty coverage of our lead salt diode we could not observe the R(2) and R(4) lines of the CO_2 monomer. However, in the molecular expansion their ground states will be much less populated than the ground state of the R(0) transition. Using the intensities of ro-vibrational transitions in fast scan spectra of weakly bound complexes we determined a molecular beam temperature of 1-2 K.

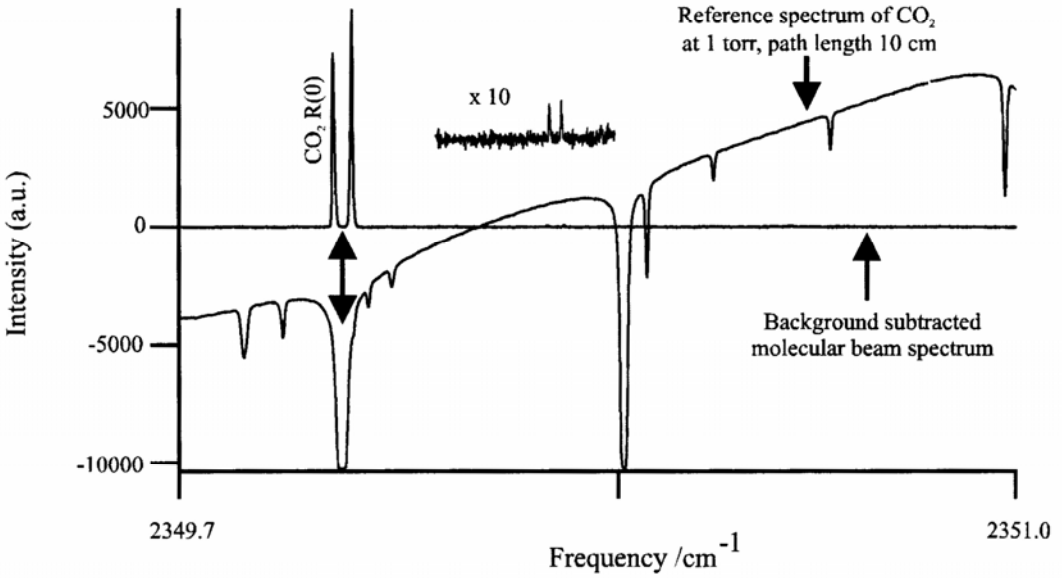

Figure 2

Spectrum of CO_2 in an expansion of 1% CO_2 in 8 atm Helium carrier gas.
Superimposed is the spectrum of CO_2 in the reference cell at a pressure of 1 torr.

3.2 Time evolution of molecular beam

The time evolution of the molecular beam was followed and characterized using both fast scan and lock-in amplification methods. The results are shown in Figure 3. The fast scan modulation pattern is shown in the top trace; the modulation amplitude was reduced to 6 mA (≈0.18 cm^{-1}) and the scan repetition rate increased for this experiment. The laser frequency was modulated near the R(0) transition of CO_2 at 2349.917 cm^{-1}. The position in the modulation pattern where this frequency is traversed is marked by the solid arrows. 100 scans were accumulated and co-added, and the background subtracted spectrum (bottom trace) was boxcar-averaged (51 points) before presentation. In the fast scan spectrum one can see the Doppler doublet arising from the coaxial expansion. The increase of the absorption at the center frequency from frame to frame is consistent with CO_2 molecules drifting back into the laser beam after colliding with the chamber walls. In the last frame only a single Doppler-broadened peak at the center frequency is visible. The difference in the peak heights of the two Doppler components is a result of the increase of laser power with frequency (see Figure 2). For the purpose of trace gas sensing, the fast scan method significantly undersamples the molecular beam, which can be observed for up to 4 ms.

The time evolution of the molecular beam was also monitored by frequency modulation spectroscopy (middle trace). In this experiment, the laser was detuned from the center frequency, slightly beyond one of the Doppler components, and modulated at 50 kHz. The resulting 1f-demodulated signal thus samples only one line of the Doppler pair. However, because of continuous sampling over the absorption line a duty cycle much higher than for the fast scan method is achieved. Note that only one molecular pulse was used to generate the 1f-demodulated signal (middle trace) compared to 100 molecular pulses for the fast-scan signal (bottom trace). The subsequently developed 2f-demodulation technique achieves even higher signal strength.

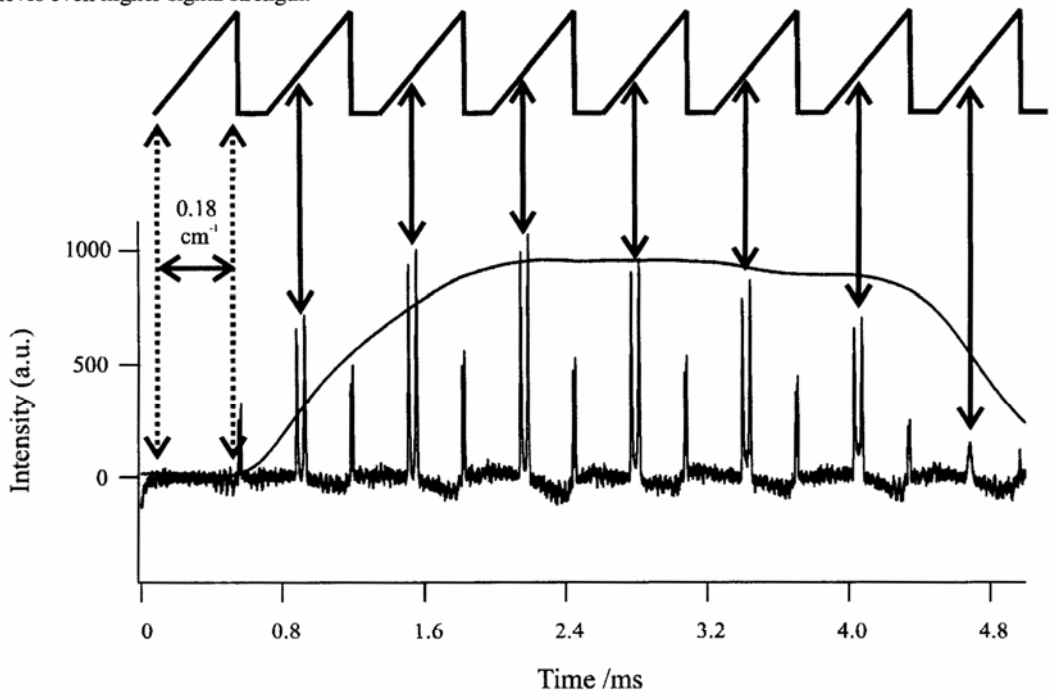

Figure 3

Time evolution of a pulse of ambient air characterized by fast scan and lock-in amplification methods. Shown in the top trace is the modulation pattern employed in the fast scan method. The bottom trace shows the series of fast scan spectra, averaged over 100 molecular pulses. The middle trace shows the 1f-demodulated signal of a single Doppler component of a single molecular pulse.

3.3 Line shape analysis (fast scan method)

We investigated the appearance of the CO_2 R(0) monomer transition in an air sample using the fast scan technique as described above. The parameters of a Gaussian function (Equation 1) were fitted to the observed line shapes.

$$I(x) = \frac{A}{\sigma\sqrt{2\pi}} \exp\left(\frac{-\left(x - \mu \pm B/2\right)^2}{2\sigma^2} \right) \quad (1)$$

I(x) is the intensity at frequency x, σ is the half-width at half maximum (HWHM), μ is the transition frequency of the sample molecules at rest, and B is the separation of the Doppler components. A spectrum obtained from the fitted parameters is superimposed on the experimental data in Figure 4. Equation 1 appears to fit the original data quite well. However, the peaks in the actual spectrum are slightly asymmetric and are somewhat broadened towards the band center. This can be explained by a subset of CO_2 molecules travelling at a slower average speed than the majority as a result of a less than perfect molecular expansion. This effect is much more pronounced at higher nozzle backing pressures. The difference in peak heights in Figure 4 is a result of recording the spectrum near the end of the lifetime of a relatively short molecular pulse.

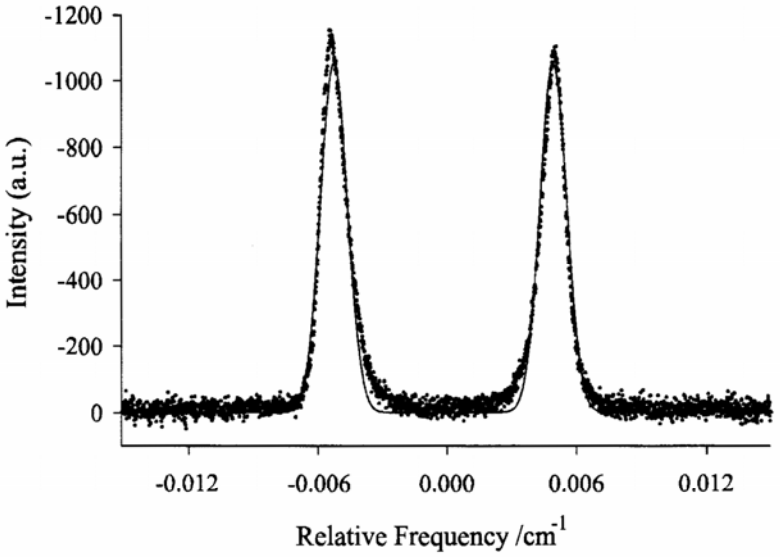

Figure 4

A high resolution spectrum obtained with the fast scan method of the R(0) line of CO_2 at 2349.917 cm^{-1} showing the Doppler splitting. The fitted spectrum is superimposed as a solid line. The laser scan rate was 0.32 cm^{-1} per ms and the molecular pulse repetition rate 2 Hz. 100 scans were accumulated. The sample was ambient air at 1 atm.

For determination of the peak frequencies, polynomial functions up to 6th order were fitted to the simultaneously recorded reference spectrum of CO_2. Line frequencies were then determined through interpolation. Even though the frequency output scaled nearly linearly with the applied laser current ($R^2 > 0.99$), the relative high polynomial order was essential to correct for residual non-linearity in the laser frequency scan. In this way, we were able to determine the center frequency μ to a precision (1 σ) of $\pm$ 0.0004 cm^{-1}.

The Doppler splitting arises because the pulsed molecular expansion travels with a certain velocity along the optical axis. The shifted frequency ν is related to the velocity v of the molecules by the Doppler equation:

$$\nu = \mu\left(1 \pm \frac{v}{c}\right) \tag{2}$$

Both red- and blue-shifted transitions were observed in the spectra because the laser beam travels in both forward and backward direction in the multipass cell. A typical Doppler splitting for a line in an air sample is ~0.011 cm^{-1} at a center frequency of ~2350 cm^{-1}, corresponding to a molecular beam velocity of ~700 m s^{-1}. The observed Doppler splitting is affected by sample composition and by the time evolution of the molecular expansion.

Fitting the line width parameter σ of Equation 1 to the observed lines shapes, typical half-widths of 6.6 10^{-4} cm^{-1}, corresponding to a full-width at half maximum (FWHM) of 40 MHz, are obtained. This is comparable to line widths obtained with slit nozzles in perpendicular expansions.[8] Possible contributions to the observed line widths are residual laser line width, transit time broadening, and a molecular velocity distribution Δv in the molecular expansion.

3.4 2f-demodulation scheme

Shown in Figure 5 is a typical output signal from the lock-in amplifier in a 2f-demodulation experiment. Both the height and the integrated area under the curve can be used to construct calibration curves. We observed large fluctuations in the signal amplitude between pulses. In work on our molecular beam Fourier transform microwave spectrometer, a comparable pulse variability of up to 20% was observed using similar nozzles.[13] In addition, oscillations of the laser frequency output, evident in the reference lock-in amplifier signal, strongly affected the results. Frequency jitter of this kind is typical of unstabilized lead salt diodes. [14] We are presently constructing a feedback circuit for laser stabilization to correct this problem.

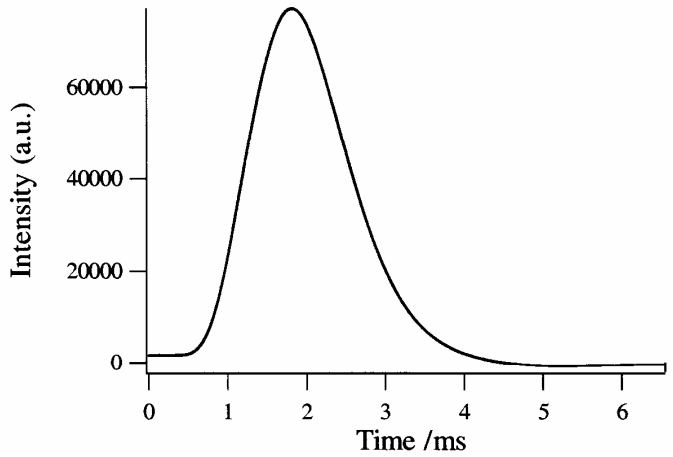

Figure 5

Typical response of the spectrometer operated in frequency modulation - 2f-demodulation mode. The sample was ambient air (approx. 360 ppm CO_2).

One of the advantages of axial over perpendicular sample injection lies in the longer time available to observe a molecular expansion. It is also evident that the effective optical absorption path length in the axial injection scheme is cut in half because of the splitting of each transition into a Doppler pair. Any modulation scheme for the axial spectrometer version should therefore sample both Doppler components simultaneously. Figure 6 demonstrates that a 51 kHz frequency-modulated signal, 2f-demodulated, samples the absorption of both Doppler peaks if the modulation amplitude equals the Doppler splitting. In this case, the two side lobes of the individual Doppler components add up to form a strong signal at the center frequency, as shown in Frame 3 in Figure 6. Detecting the signal at the center frequency is practical, because the laser can easily be frequency-locked to a stationary reference absorption line. If the laser is allowed to drift off the precise center frequency, strong fluctuations in the detector response occur.

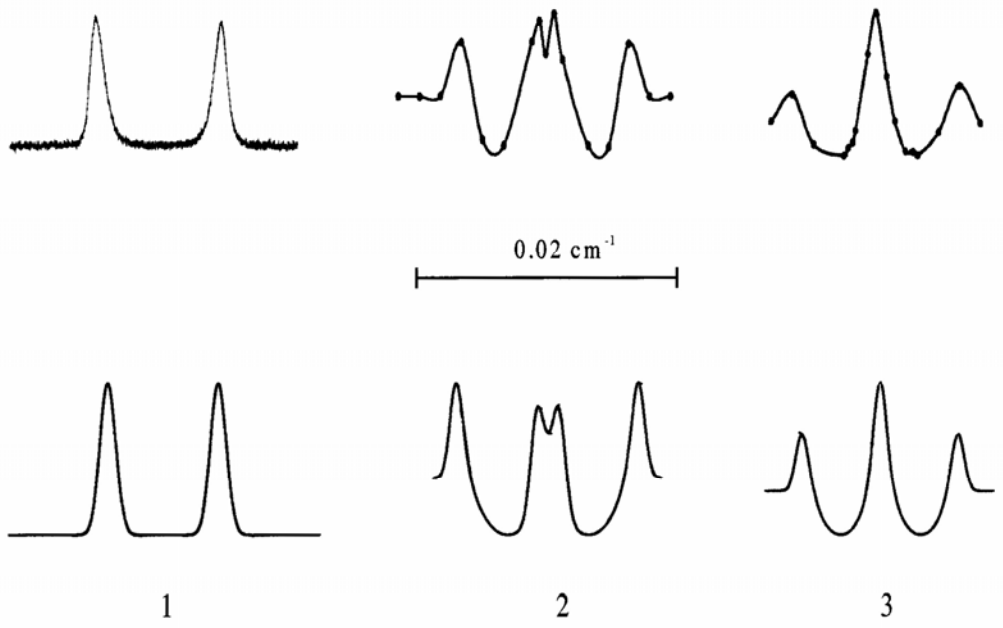

Figure 6

Actual (top) and simulated (bottom) spectra. The modulation spectra were assembled from a series of individual experiments. In the numerical simulation, a phase angle of $\pi/4$ between modulation and demodulation signal was used. 1) Two Gaussian absorption peaks identical to those shown in Figure 4. 2) 2f-demodulated signal. The modulation amplitude is slightly smaller than the Doppler splitting. 3) 2f-demodulated signal. The modulation depth equals the Doppler splitting.

3.5 Sensor Application

We constructed a preliminary calibration curve for CO_2 in order to estimate the detection limit of the spectrometer. Gas samples were prepared by mixing increasingly larger fractions of ambient air with purified nitrogen. Outgassing from the inner stainless steel reservoir walls and insufficient mixing of the sample gases affected our results. For example, a sample of purified N_2 gas (Praxair) left in the sealed gas reservoir at above atmospheric pressure, which initially had given no measurable signal, acquired substantial amounts of CO_2 over time. The CO_2 background signal was even higher when Argon was used as the carrier gas. In addition, laser frequency jitter and fluctuations in the total amounts of gas delivered in each molecular pulse affected the reproducibility of the individual pulse signals. Because of these presently uncontrolled noise sources, the minimum quantifiable amount of CO_2 is currently 1 ppm.

We expect to improve the sensitivity of the spectrometer into the ppb range by developing appropriate sample preparation techniques and by implementing an external diode laser stabilization scheme. The detector sensitivity will be further enhanced by increasing the modulation frequency beyond 1 MHz. We are also planning to purchase new lasers for the analysis of other trace gas molecules and anticipate that rotational cooling will be more beneficial for small molecules with more thermally populated states than CO_2.

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