



Diode Laser Spectroscopy of Ammonia and Ethylene Overtones

A. Lucchesini, S. Gozzini

IPCF-CNR, Area della Ricerca di Pisa

Via G. Moruzzi, 1 (Loc. San Cataldo)

I-56124 Pisa - Italy

Phone: +39 0503152-532, Fax: 0503152-230

E-mail: lucchesini@ipcf.cnr.it

Web: mail.ifam.pi.cnr.it/lucch/alex.html

Abstract

Some overtone absorption lines of ammonia and ethylene have been examined by using a diode laser (DL) spectrometer in the region around 12650 and 11800 cm^{-1} respectively. The spectrometer sources are commercially available double heterostructure InGaAlAs and AlGaAs DLs operating in "free-running" mode. The high resolving power ($\sim 10^7$) of the spectrometer permitted the detection and the study of the absorption features of such molecules with a precision of less than 0.01 cm^{-1} . In order to maximize the signal to noise ratio (S/N) and to extract the necessary informations either on the line width and on the line position for the detected molecular resonances, the wavelength modulation spectroscopy (WMS) along with the 2nd harmonic detection techniques have been applied. For this purpose the fit procedure took into account the instrumental effects and the amplitude modulation (AM) always associated to the frequency modulation (FM) of these type of sources. This technique permitted also the measurement of the collisional broadening and shifting coefficients by different buffer gases at room temperature.

Introduction

The availability of tunable laser sources, like commercial diode lasers (DLs), increased the interest on the spectroscopy of overtone and combination of ro-vibrational bands in the visible and in the NIR. Commercially available DLs are suitable radiation sources for high resolution spectroscopy and in particular for the study of the optical resonances of many molecules like CH_4 ¹, C_2H_2 ², CO_2 , H_2O ³, HCl ⁴, HCN , HF , NH_3 ⁵, NO_2 ⁶, O_2 ⁷, etc.. They can be easily modulated through their injection current, allowing the use of frequency modulation (FM) techniques. When the amplitude of the FM is chosen much lower than the resonance line-width, the FM spectroscopy is usually called wavelength modulation (WM) spectroscopy. Here we apply this technique to water vapor in order to determine the line-shape parameters.

Experimental set-up

The DL source is driven by a stabilized low-noise current supply. Its temperature is monitored within 0.001 K by a high-stability controller. The wavelength scan is obtained by adding a low frequency sawtooth signal to the driving current. The collimated DL radiation is split in three different beams, which go through a confocal Fabry-Perot interferometer, for marking the frequency, and through two different glass cells containing the sample gas: one at a constant pressure as reference, and the other at progressively increased pressure. The transmitted radiation is collected by silicon photodiodes and the resulting signals are simultaneously acquired by a desk-top computer. For the harmonic detection a sinusoidal modulation current is mixed to the diode laser injection current: the signals transmitted through the two cells are sent to a lock-in amplifier to extract the desired harmonic component.

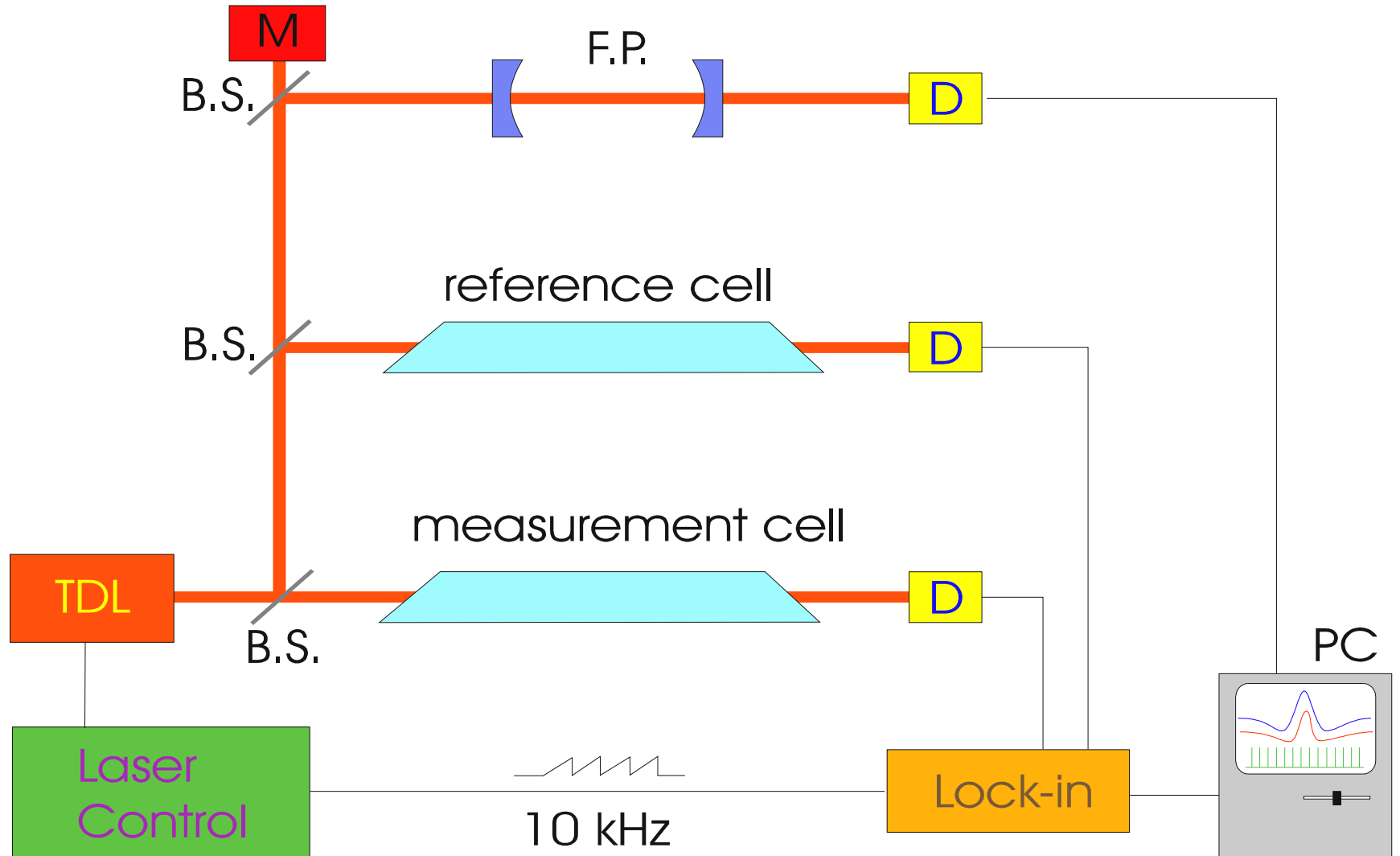


Fig. 1. Sketch of the experimental apparatus for the WM spectroscopy. D: photodiode; B.S.: beam splitter; F.P.: Fabry-Perot interferometer; TDL: tunable diode laser; M: monochromator; PC: desk-top computer.

Frequency modulation technique

When FM is used, the emission frequency $\bar{\nu}$ of the DL is sinusoidally modulated via the injection current,

$$\nu = \bar{\nu} + m \cos 2\pi\nu_m t;$$

and the n -th harmonic component of the transmitted signal is detected by a lock-in amplifier at a reference frequency $n\nu_m$, multiple of the modulation frequency. When the amplitude m of the modulation is small compared to the width of the absorption line, the n -th harmonic component is proportional to the n -th derivative of the transmitted signal. In particular we detected the second harmonic component ($2f$ detection).

The presence of a residual amplitude modulation (RAM) when modulating the DL emission frequency, even if it is relatively small, gives a sloping background in the direct absorption (DA) signal and an asymmetry in the $2f$ signal. As shown in Fig. 2, the center of the line does not match the maximum of the $2f$ signal. The displacement is proportional to the slope of the emission profile as well as to the width of the line. This issue is of

capital importance for what concerns the pressure induced shift since the apparent displacement of the center is proportional to the pressure.

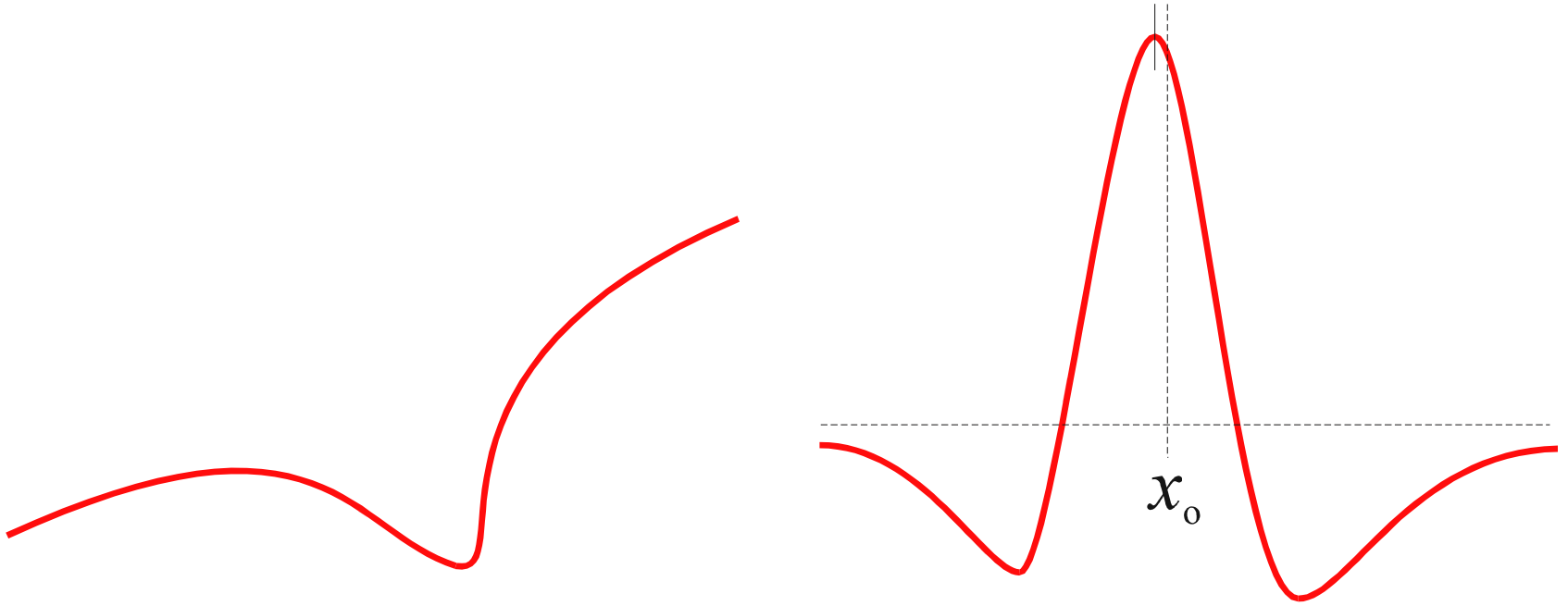


Fig. 2. DA (left) and 2nd harmonic WM signal (right) as detected by the DL spectrometer.

Generally the intensity of the radiation transmitted through a sample can be written as the product of the incoming intensity $I_0(\nu)$ and the transmittance $T(\nu)$, where ν is the distance from the central frequency of the line:

$$I(\nu) = I_0(\nu)T(\nu).$$

Let us assume a laser emission profile varying linearly with the frequency:

$$I_0(\nu) = \bar{I}_0(1 + s\nu),$$

where \bar{I}_0 is the intensity at $\nu = 0$ and s is the fractional variation per frequency unit. Hence the second derivative of the transmitted power is:

$$I''(\nu) = \bar{I}_0(1 + s\nu)T'' + 2s\bar{I}_0T'. \quad (1)$$

The apparent displacement of the center depends on the the slope s of the profile and on the width Γ of the line. By increasing the pressure, the width becomes larger and an apparent shift of the center occurs. This is proportional to the pressure in a way very similar to the *real* pressure induced shift. Let us write the transmittance in the weak absorption approximation:

$$T(\nu) = 1 - \Im x \frac{\Gamma_L}{\pi} \frac{1}{\nu^2 + \Gamma_L^2} \quad (2)$$

where a Lorentzian shape of the absorption line has been adopted, s is the line strength and x is the optical density. To get the shift of the maximum of the $2f$ signal we expand the second derivative of Eq. (2) around $\nu = 0$:

$$\nu_{\max} = \frac{1}{4}\Gamma_L \left(\xi - \frac{5}{16}\xi^3 + \dots \right) \quad (3)$$

where $\xi = s\Gamma_L$.

Putting $\xi = 0.1$, $\nu_{\max}/\Gamma = 1/4\xi = 0.025$, so the displacement can be of the same order of magnitude of the pressure induced shift. Thus, if the maximum of the second derivative signal is used to determine the center of the line, it occurs an error that is proportional to the width, giving an incorrect contribution to the measurement of the pressure-shift coefficient. A refined knowledge of the line-shape parameters is obtained by fitting the second derivative signal.

Experimental results

Ammonia

In this case a InGaAlAs SHARP Mod. LT025MD DL that emits 40 mW cw coherent radiation at 785 nm at RT was adopted as the source.

An example of spectrum obtained by using the DL spectrometer is shown in Fig. 3, where the second derivative of a small portion of the ammonia overtone band at around 792 nm is displayed with the best fit.

The excellent resolving power of the system with a “free running” diode ($\sim 10^7$) can be appreciated, where five absorption resonances are observed and two of them never observed before.

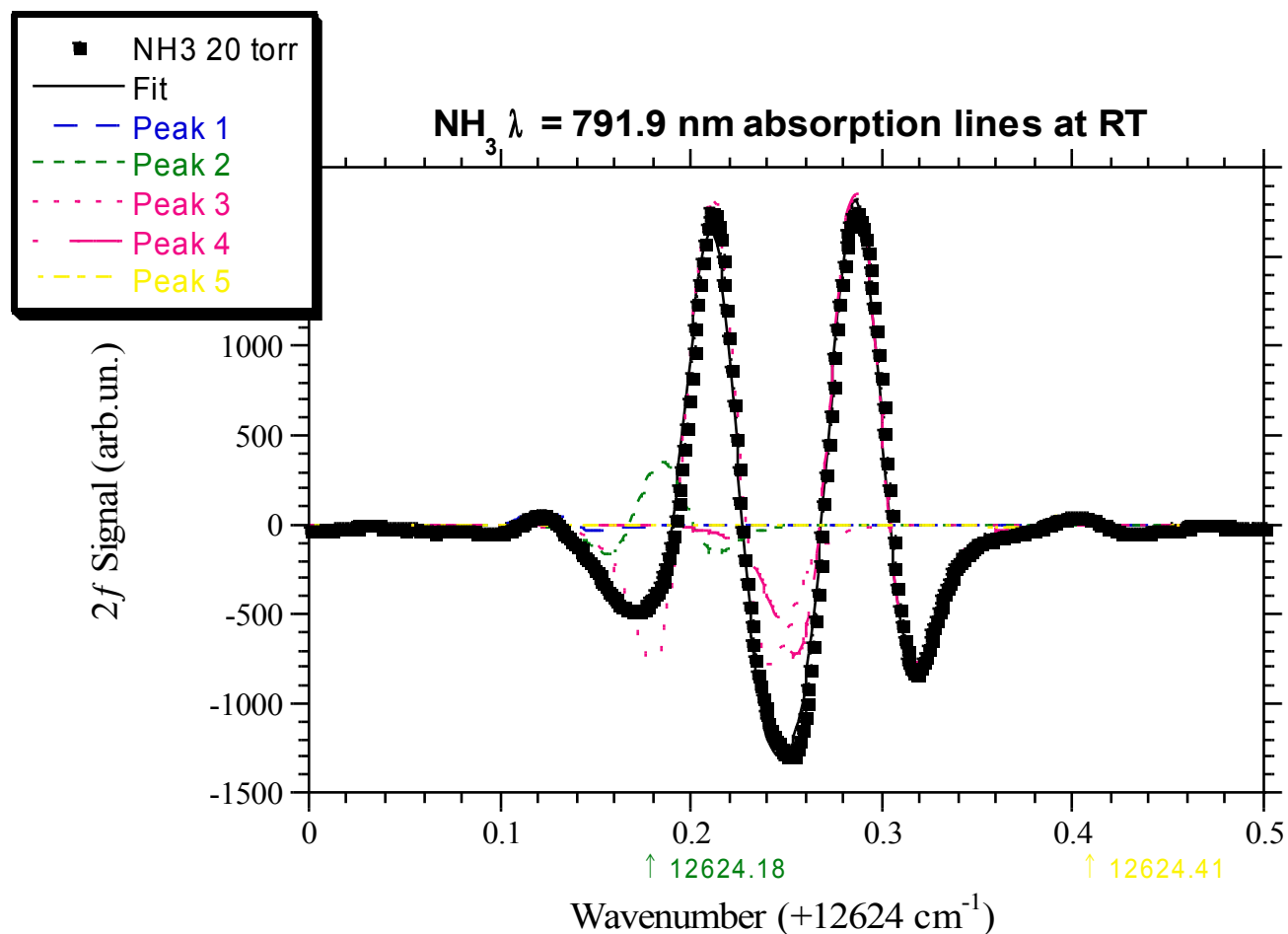


Fig. 3. Ammonia absorptions around 12624 cm^{-1} obtained by WMS and 2nd harmonic detection at $p = 20 \text{ Torr}$ and RT, with 10 Hz bandwidth.

An example of the fit results related to the self-broadened $12682.719 \text{ cm}^{-1}$ ammonia absorption line is shown in Fig. 4.

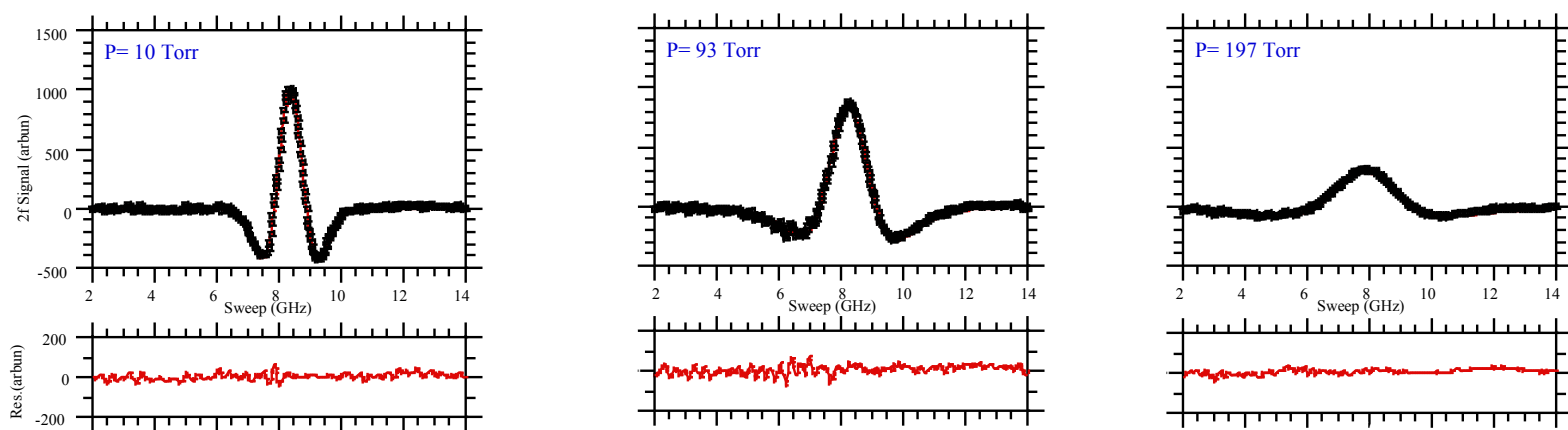


Fig. 4. 2nd derivative signals (empty squares) of the $12682.719 \text{ cm}^{-1}$ line obtained at three different ammonia pressures with the best fits (solid lines) and relative residuals (same units). The measurements are at RT, with 10 Hz bandwidth.

Stephen L. Coy and Kevin K. Lehmann⁸ gave us their measurement results on this same overtone bands and on them we could list the measured line broadening and shifting coefficients related to three different buffer gases. They are listed in the Tables I and II. All the errors are computed for three standard deviations.

In Fig. 5 the helium pressure-broadening of one ammonia overtone line is shown for example.

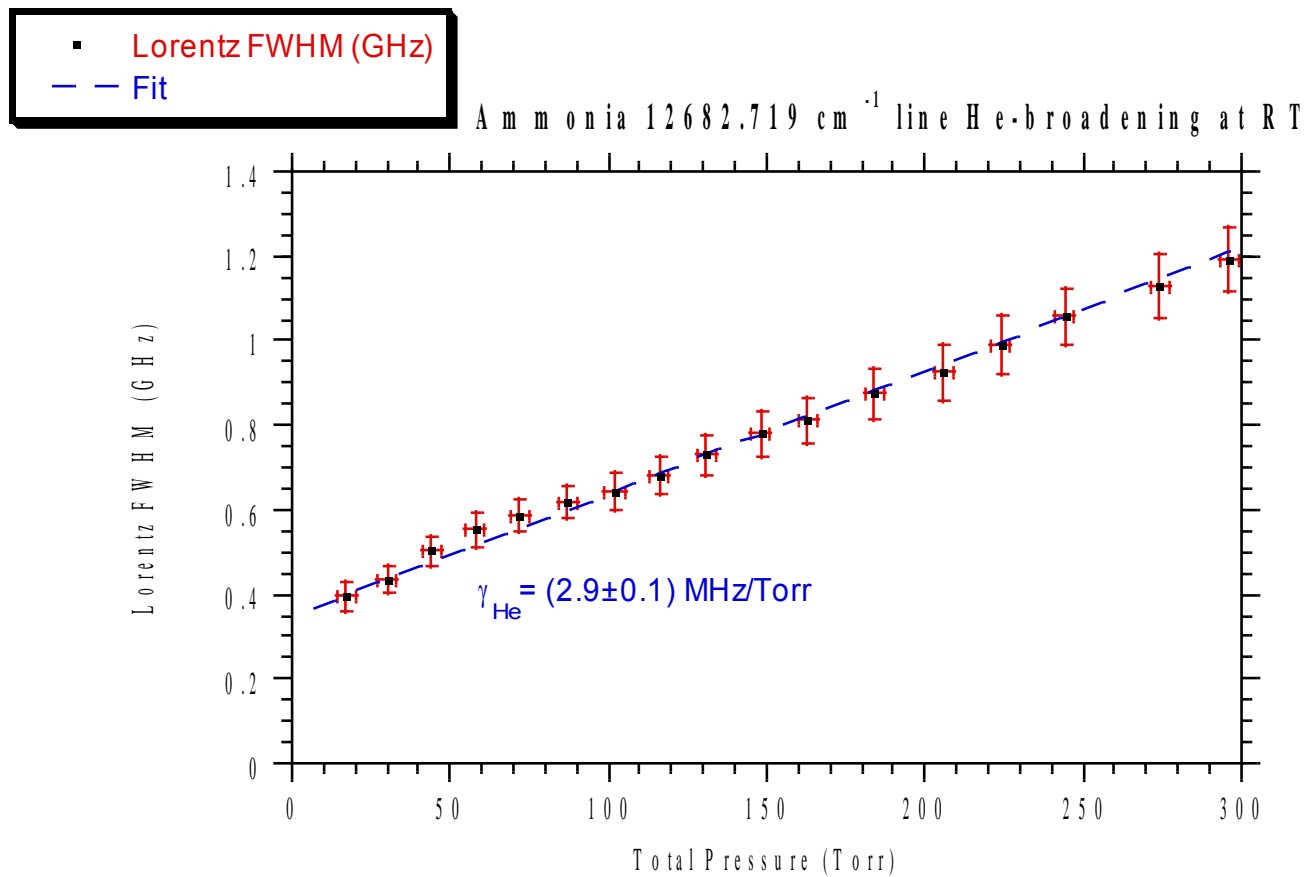


Fig. 5. Ammonia 12682.719 cm⁻¹ line He-broadening at RT

While in Fig. 6 the self-shifting measurement result is shown for another overtone absorption line.

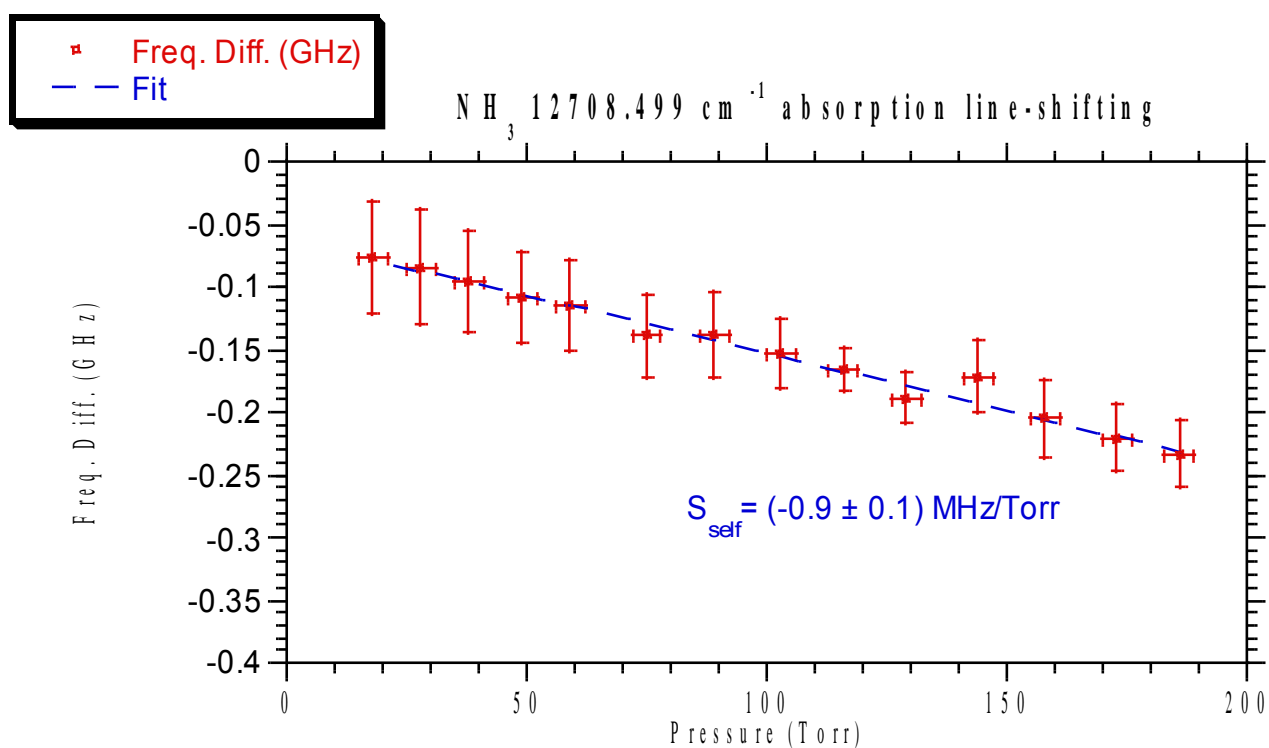


Fig. 6. Ammonia 12708.499 cm⁻¹ line self-shift at RT.

Table I. Ammonia collisional-broadening FWHM coefficients at RT.

Wavenumber	γ_{lf}	γ_{lr}	γ_2	γ_e
cm ⁻¹	MHz\Torr	MHz\Torr	MHz\Torr	MHz\Torr
12619.644 ^a	28.7 \pm 0.4	7.6 \pm 0.2	8.8 \pm 0.2	3.6 \pm 0.5
12627.605	22.8 \pm 0.4	7.4 \pm 0.1	8.5 \pm 0.1	3.6 \pm 0.2
12632.919	45 \pm 1	8.1 \pm 0.2	8.9 \pm 0.6	3.3 \pm 0.5
12666.263	25.2 \pm 0.6	7.6 \pm 0.1	7.9 \pm 0.3	2.9 \pm 0.2
12682.719	24.0 \pm 0.1	6.8 \pm 0.3	8.6 \pm 0.2	2.9 \pm 0.1
12686.888	39 \pm 1	8.2 \pm 0.9	9.6 \pm 0.6	3.8 \pm 0.3
12699.080	39.9 \pm 0.4	6.3 \pm 0.3	8.1 \pm 0.6	3.6 \pm 0.8
12708.499	22.8 \pm 0.1	8.3 \pm 0.7	8.1 \pm 0.2	3.2 \pm 0.2
12737.423 ^a	46.2 \pm 0.1	8.4 \pm 0.3	7.7 \pm 0.3	3.3 \pm 0.3
12739.054	45.4 \pm 0.7	7.8 \pm 0.1	9.0 \pm 0.1	4 \pm

Table II. Ammonia collisional-shifting coefficients at RT.

Wavenumber	S_{self}	S_{air}	S_{H_2}	S_{He}
cm ⁻¹	MHz\Torr	MHz\Torr	MHz\Torr	MHz\Torr
12619.644 ^a	-4.0 \pm 0.2	-1.0 \pm 0.2	-0.9 \pm 0.4	-0.4 \pm 0.1
12627.605	0.7 \pm 0.2	-0.5 \pm 0.2	-0.6 \pm 0.1	0.4 \pm 0.1
12632.919	2.0 \pm 0.1	-0.3 \pm 0.2	-0.5 \pm 0.2	0.0 \pm 0.1
12666.263	-2.9 \pm 0.1	-0.1 \pm 0.1	-0.4 \pm 0.1	0.1 \pm 0.1
12682.719	-0.7 \pm 0.2	-0.3 \pm 0.2	-0.3 \pm 0.2	0.4 \pm 0.1
12686.888	0.0 \pm 0.5	-0.4 \pm 0.3	0.5 \pm 0.2	0.8 \pm 0.1
12699.080	0.6 \pm 0.8	-0.3 \pm 0.2	-0.3 \pm 0.2	0.0 \pm 0.1
12708.499	-0.9 \pm 0.1	-0.2 \pm 0.2	-0.4 \pm 0.3	0.2 \pm 0.1
12737.423 ^a	2.8 \pm 0.1	-0.4 \pm 0.1	-0.4 \pm 0.1	0.1 \pm 0.1
12739.054	0.6 \pm 0.6	-0.4 \pm 0.1	-0.4 \pm 0.1	0.2 \pm 0.1

^aFor a tentative quantum attribution of these lines see the text.

Because of the complexity of the absorption spectrum for the symmetric top molecule NH₃ in this range, only partial attribution of the bands can be done. An attempt has been made by Chao⁹ and among them we could observe presumably one head of series ($\nu = 12619.644$ cm⁻¹) and one line (ν

= $12737.423 \text{ cm}^{-1}$) of the R branch with $J = 5$. By considering the frequency interval between the lines Chao claims that they belong to one of the four parallel bands expected in this region. By taking into consideration these two lines and excluding the self-broadening, the collisional broadening coefficients decrease in absolute value as J increases as it usually happens in the fundamentals¹⁰.

Ethylene

The ethylene observed absorption lines belong to the third overtone 4ν and are located at about 847 nm. The AlGaAs Roithner RLT85100G double heterostructure laser diode and a Herriot type multipass cell by SIT S.r.l. (total optical path length = 30 m) were adopted for the purpose (see Fig. 7).

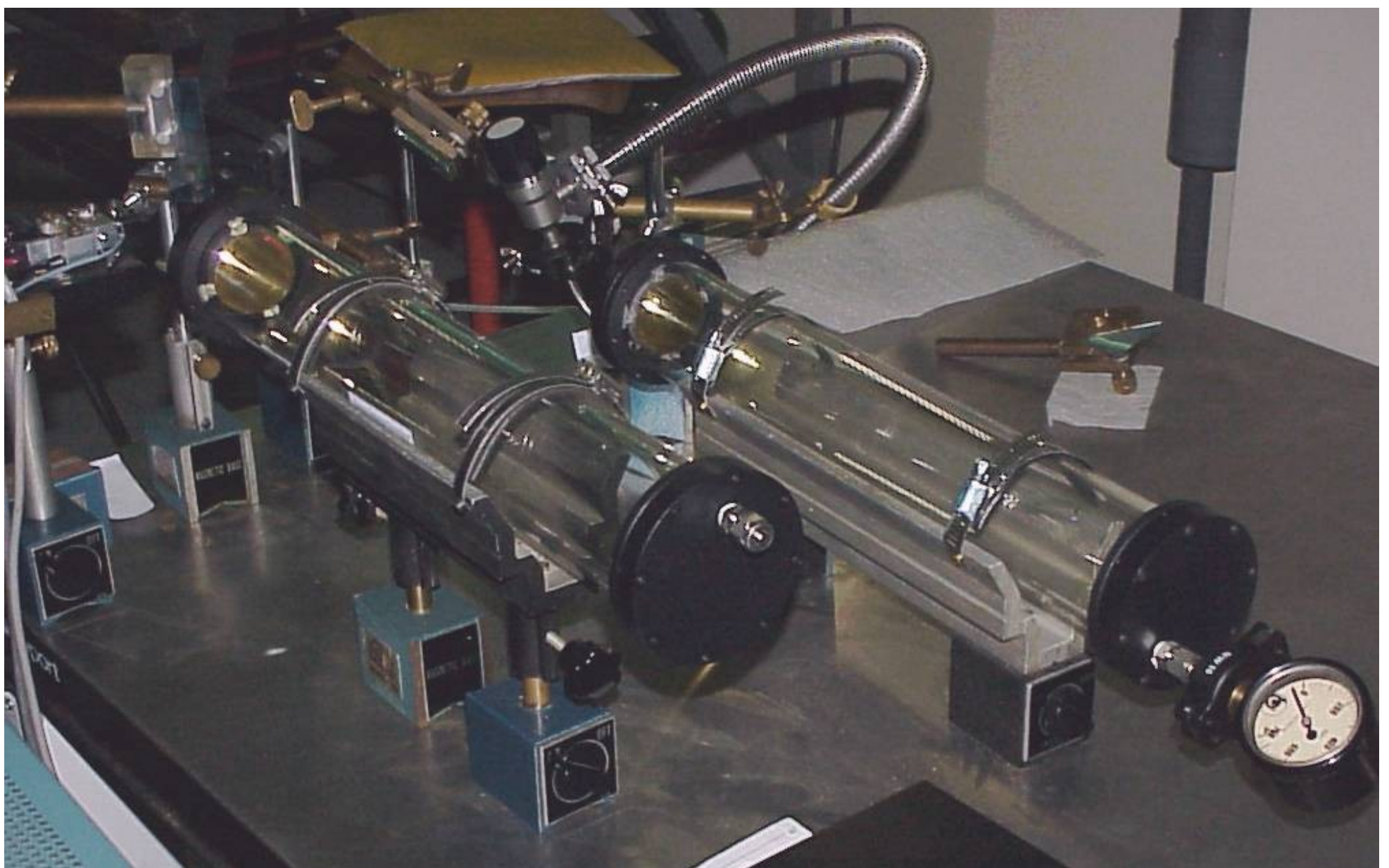


Fig. 7. Two Herriot type multipass cells (*S.I.T. model MPC-300*) used for the ethylene overtone diode laser spectroscopy.

24 lines has been observed and their position measured within 0.01 cm^{-1} by the aid of a I_2 reference cell and a very precise I_2 absorption atlas¹¹. The

results are shown in Table III with the peak absorption values for the most intense lines. The complexity of the structure of this spectrum does not permit a correct classification of the ro-vibrational resonances.

Table III. Observed ethylene absorption lines.

Wavenumber (cm⁻¹)	Wavelength (Å @ 21°C)	α_x (cm²/mol.)
11839.25	8444.21	
11836.64	8446.07	$8.1 \cdot 10^{-25}$
11831.23	8449.93	
11829.86	8450.91	$3.7 \cdot 10^{-25}$
11826.13	8453.58	
11821.77	8456.69	
11818.45	8459.07	$5.0 \cdot 10^{-26}$
11817.59	8459.68	
11813.92	8462.31	$8.7 \cdot 10^{-25}$
11810.54	8464.74	$4.3 \cdot 10^{-25}$
11803.90	8469.50	$6.3 \cdot 10^{-25}$
11800.01	8472.29	
11796.06	8475.13	
11791.73	8478.24	
11788.19	8480.78	
11784.37	8483.53	
11764.97	8497.52	
11751.57	8507.21	$2.0 \cdot 10^{-25}$
11751.48	8507.28	$7.8 \cdot 10^{-26}$
11746.54	8510.85	
11743.31	8513.20	
11732.26	8521.22	
11728.89	8523.66	
11728.55	8523.91	

Despite to the very low absorption intensities of these overtone resonances, pressure broadening measurements have been attempted on two of the more intense lines. The self-broadening on the 11810.54 cm⁻¹ line gives:

$$\gamma_{\text{lf}} = (7.4 \pm 0.4) \text{ MHz/Torr};$$

while the pressure broadening coefficients for the 11813.92 cm^{-1} line are:

$$\gamma_{\text{lf}} = (9.3 \pm 0.2) \text{ MHz/Torr},$$

$$\gamma_{\text{r}} = (5.8 \pm 0.1) \text{ MHz/Torr},$$

$$\gamma_{\text{N}_2} = (9.8 \pm 0.2) \text{ MHz/Torr},$$

$$\gamma_{\text{e}} = (5.0 \pm 0.1) \text{ MHz/Torr}.$$

Conclusions

Overtone absorption spectroscopy has been performed by using a spectrometer based on InGaAlAs and AlGaAs tunable diode lasers. For this purpose the simplest configuration, “free-running”, along with the wavelength modulation spectroscopy and the second harmonic detection techniques have been adopted. Collisional broadening and shifting coefficients for different perturber gases have been measured at RT for some ammonia combination overtone absorption lines located around 12600-12700 cm^{-1} and also self-broadening measurements have been attempted for two of the 24 ethylene observed absorption lines. For this purpose, special care has been put when analyzing the absorption features got by this kind of technique. The sensitivity of the diode laser spectroscope is of the order of some tens of ppm per meter of optical path length when applied to the most intense ammonia absorptions, with typical time constants of some hundreds of milliseconds. While it was limited to some parts per thousand per meter for ethylene, ought to the weakness of its 3rd overtone absorptions.

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