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Diode laser spectroscopy of methyl fluoride overtones at 850 nm

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ABSTRACT

One hundred fifty-six $^{12}CH_3F$ overtone absorption lines, comprised between 11 545 and 11 836 cm^{-1}, have been observed by using a tunable diode laser (TDL) spectrometer. Their intensities range around 10^{-26} cm/molecule and have been measured by utilizing commercial AlGaAs/GaAs laser diodes through the wavelength modulation (WM) and the 2nd harmonic (2*f*) detection techniques. Self-broadening coefficients and line strengths have been measured at room temperature for seven of the strongest transitions, while air-broadening coefficients have been obtained for two lines. In addition, self- and air-collisional shifts have been measured for the 11 564.25 cm^{-1} transition.

1. Introduction

CH_3F (methyl fluoride) is a symmetric top molecule very much investigated by conventional spectroscopic techniques as well as by the more sophisticated Fourier transform infrared (FTIR) spectrometers. It has a large permanent dipole moment, which explains the large self-collisional absorption line-broadening as it happens for ammonia [1,2]. Since some of CO_2 laser lines coincide with some resonances of the fundamental ν_3 vibrational absorption band of CH_3F, this has been at first studied by using the CO_2 laser as the source, by means of the Stark shift spectroscopy [3]. Later on, the use of the semiconductor tunable laser sources [4] widened the range of the spectroscopic investigation.

CH_3F overtones and combination of vibrational fundamentals in the near infrared (NIR) in the gas phase have been observed by Thompson [5] early in 1939. Later on the fifth overtone spectra of the C–H stretching vibrations of methyl fluoride (fluoro-methane) have been located at 15 972 cm^{-1} by using the intracavity dye laser photoacoustic spectroscopy [6]. More recently a systematic study of the overtone spectra of methyl halides, CH_3F included, has been carried on the 4 and 5 quanta of C–H stretching excitation by a FTIR spectrometer [7].

We focalized our attention to the ro-vibrational overtones and combinations located in the wavelength range between 845 and 865 nm, covered by our diode laser spectrometer. In particular this spectral interval covers the tail of the 4 quanta of C–H stretching excitation ($4\nu_{C-H}$) and probably the superposition of the two combinations $3\nu_{C-H}+2\nu_2$ and $3\nu_{C-H}+2\nu_5$ in analogy with what happens to CH_3Cl [8]. In this ro-vibrational high energy range it is very difficult to assign the absorption lines to the right quanta of vibration and rotation, ought to the many overlapping bands whose upper states are often coupled by various interactions, such as the Fermi and the Coriolis resonances [9]. Moreover the weakness of these absorption lines forced the use of long path cells and noise reduction techniques. From this viewpoint the availability of the laser diodes (LDs) facilitates the use of the wavelength modulation spectroscopy (WMS) technique to increase the signal-to-noise (S/N) ratio.

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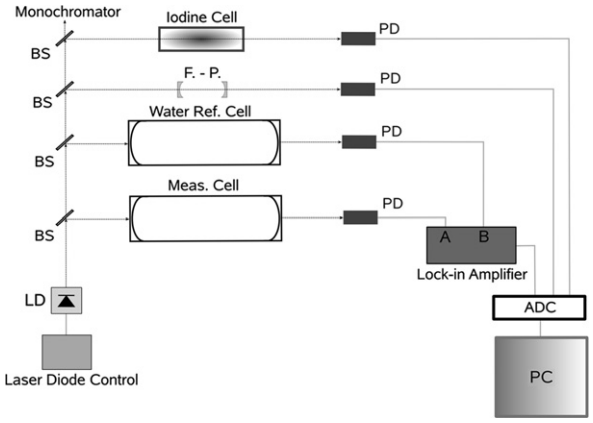

Fig. 1. Outline of the experimental apparatus. ADC: analog-to-digital converter; BS: beam splitter; F.–P.: Fabry–Perot interferometer; LD: laser diode; M: mirror; PC: desk-top computer; PD: photodiode.

By the aid of the LD and the WMS we observed almost 160 CH_3F absorption lines and we measured also the self-broadening coefficients for seven of the more intense of them; in addition, for the most intense line at 11 564.25 cm^{-1} the self- and air-shift coefficients have been obtained.

2. Experimental details

The experimental setup for the WMS with the 2nd harmonic detection technique follows what was used in a previous work [10].

In particular, referring to Fig. 1, the employed source at first was a Roithner Mod. RLT85100G AlGaAs/GaAs hetero-structure LD, which nominally emits 120 mW cw at 845–855 nm. Its emission has a longitudinal and transverse single mode. It was adopted in the part of the CH_3F absorption spectrum between 11 795 and 11 836 cm^{-1}. Thereafter the Thorlabs LP850P030 index-guided multiple quantum well LD has been utilized. It emits 30 mW cw monomodal radiation in a range of 840–860 nm and it was used here to cover the spectrum from 11 545 to 11 780 cm^{-1}. They were in turn mounted in a "free-running" configuration, that is without any electronic or optical feedback. In this condition the LDs measured emission line-widths were within 50 MHz for both of them. By varying the LDs temperatures and injection currents, as explained in the followings, we covered a total of 300 cm^{-1} (more than 20 nm), even if the LDs mode hops obscured part of this range. They were hosted in a small vacuum chamber, with a Brewster angle glass exit window. The vacuum was necessary to avoid any water condensation when working at low temperature and to better stabilize the LD temperature by eliminating the convection. It is well known that LD temperature control is critical as its typical emission wavelength regime is about 0.1 nm/K. In this experimental configuration the temperature could be changed from 277 K to 323 K by using a Peltier junction mounted in direct contact to the LD housing. The fine linewidth control was guaranteed by a fine and accurate current regulation within ± 10 μA as the LD emission characteristic slope is about 0.01 nm/mA.

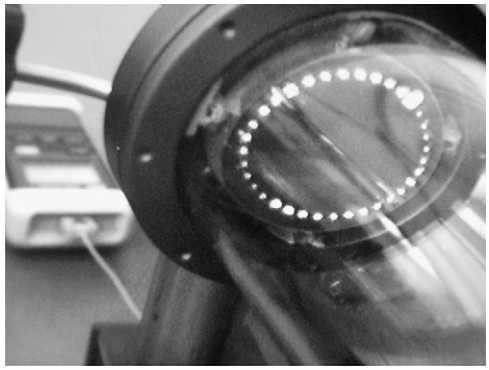

Fig. 2. A particular of the laser diode beam reflections on one of the two mirrors of the multipass Herriott type cell.

Another critical issue for the right utilization of the LDs in spectroscopy is related to their big solid angle emission divergence ($20^\circ \times 30^\circ$), therefore the right choice of a good collimating lens can improve their performance. In this case we put an antireflection coated lens of small focal length close to the LD emission edge, in order to collect as much as possible emission radiation and to obtain a good quality TEM00 laser beam for some meters path length.

The other important components of the spectrometer were the two 30 m path-length multipass cells, Herriott type (S.I.T. S.r.l., Mod. MPC-300 [11]), one containing the sample gas and the other containing water at vapor pressure ≃20 Torr: this second cell was used both for checking the eventual presence of water in the measurement cell, and contemporary as the reference for the precise wavenumber measurements through the utilization of the absorption lines database HITRAN [12]. Fig. 2, obtained by an infrared camera, exhibits the particular of the reflection spots on one mirror in the measurement cell.

In the region where there was a lack of tabulation of the water vapor absorption lines, an iodine reference glass cell was also used for the same purpose by referring to a specific atlas [13]. Unfortunately in some cases the iodine lines were too weak to be detected by the system, and therefore some CH_3F absorption lines could not be measured and they are not reported here. A confocal 5 cm Fabry–Perot (F.–P.) interferometer (f.s.r. = 1.5 GHz, 0.05 cm^{-1}) was utilized to check the amount and the linearity of the LD emission frequency variation obtained by sweeping the LD injection current. A 0.35 m focal length Czerny–Turner monochromator MacPherson EU-700 was used for the rough wavelength check (± 0.01 nm). The methyl fluoride pure gas was supplied by Matheson Tri Inc., with purity ≥99% : $N_2 \leq$ 150 ppm, $O_2 \leq$50 ppm, $H_2O \leq$20 ppm, $N_2 \leq$10 ppm. A capacitive pressure gauge (Varian, Model 6543-25-045) was connected directly to the measurement cell in order to make precise measurements (± 0.5 Torr).

In this experiment the transmittance $\tau(\nu)$ has been measured following the expression of Lambert–Beer:

$$\tau(\nu) = e^{-\sigma(\nu)z}, \quad (1)$$

where $z = \rho l$ is the product of the absorbing species density ρ (in molecule/cm^3) and the optical path l (in cm) of the radiation through the sample, in practice

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the column amount (in molecule/cm^2), and $\sigma(\nu)$ is the absorption cross section (in cm^2/molecule).

All the experiments object of this work developed in small optical depth regime, that is $\sigma(\nu)z \ll 1$, therefore the following approximation of Eq. (1) has been adopted:

$$\tau(\nu) \simeq 1-\sigma(\nu)z. \tag{2}$$

2.1. Wavelength modulation

The WMS technique applied here has been described in detail in a previous work [2]. Summarizing, the emission frequency of the source $\bar{\nu}$ is sinusoidally modulated at the frequency $\nu_m = \omega_m/2\pi$ (in this case ~5 kHz) through the injection current, and results in

$$\nu = \bar{\nu} + a\cos\omega_m t. \tag{3}$$

$$f_2(x,m) = \frac{2}{m^2} - \frac{2^{1/2}}{m^2} \times \frac{1/2[(M^2+4x^2)^{1/2}+1-x^2][(M^2+4x^2)^{1/2}+M]^{1/2} + |x|[(M^2+4x^2)^{1/2}-M]^{1/2}}{(M^2+4x^2)^{1/2}}, \tag{6}$$

The transmitted intensity depends on both the line shape and the modulation parameter; here the utilization of the phase detection technique, obtained by a lock-in amplifier tuned to double the modulation frequency (~10 kHz) permits to get the 2nd harmonic signal. The 2f detection has the advantage of a flat baseline of the signal and the final sensitivity is limited neither by the detector noise nor by the source noise, but by the étalon effect fringe patterns coming principally from the multipass cell mirrors.

For a low modulation amplitude a, that is $a/\Gamma \ll 1$, where Γ is the line width, the signal revealed by the lock-in amplifier gives a measurement comparable to the second derivative of the absorption feature.

Here all the experiments were carried on at pressures ranging between 20 and 300 Torr. In these conditions the absorption line shape as a function of the photon energy (frequency) can be well described by the Voigt function, a convolution of the Gaussian (Doppler width: *inhomogeneous* broadening) and Lorentzian (collisional width: *homogeneous* broadening) functions:

$$f(\nu) = \int_{-\infty}^{+\infty} \frac{\exp[-(t-\nu_\circ)^2/\Gamma_G^2 \ln 2]}{(t-\nu)^2+\Gamma_L^2}\, dt, \tag{4}$$

where $\nu_\circ$ is the gas resonance frequency, Γ_G and Γ_L are the Gaussian and the Lorentzian half widths at half the maximum (HWHM), respectively.

Eventual velocity changing collision effects, like the Dicke narrowing that occurs when the molecular mean free path is comparable to the wavelength of the sampling radiation [14], were not observed in our measurement conditions, at least within our sensitivity, and were not taken into account here.

A nonlinear least-squares fit procedure explained elsewhere [15] has been used in order to extract the line parameters and the relative errors. In particular, for the line broadening measurements the general expression of the collisional full width at half the maximum (FWHM) as a function of the pressure has been used:

$$w_c(p) = 2\Gamma_L(p) = \gamma_i p_i + \gamma_{self} p_\circ, \tag{5}$$

where p is the total pressure, $p_\circ$ is the partial pressure of the sample gas, p_i is partial pressure of the buffer gas i, γ_i is the FWHM broadening coefficient related to the buffer gas, and γ_{self} is the sample gas self-broadening coefficient.

The eventual systematic instrumental distortion was checked from the self-broadening linear fit, whether the intercept to $p=0$ always gave the $\Gamma_L = 0$ within the laser diode emission line-width, that is 50 MHz.

In case of high modulation amplitude, the second derivative of the Voigt function cannot describe the right line-shape behavior any more and a different approach is necessary. As explained in Ref. [2], in particular in the Appendix, the spectroscopic parameters can be still obtained with a good reliability by using the following fit function of the 2f signal:

where $x = \nu/\Gamma$ and $M = 1-x^2+m^2$.

By adopting these procedures 156 CH_3F absorption lines have been detected and their wavenumbers measured within 0.01 cm^{-1} (maximum error: 3σ) in both the reference cases: water vapor and iodine. The absorption cross sections were on the order of 10^{-25} cm^2/molecule, which corresponds to the line strength $S \approx 10^{-26}$ cm/molecule.

An example of a spectrum obtained near the limit of sensitivity of the spectrometer is shown in Fig. 3, which displays the CH_3F at 11 836.30 cm^{-1} and the H_2O at 11 836.46 cm^{-1} absorption lines at room temperature. The lines are broadened by modulation, the modulation index being $m = a/\Gamma = 1.6$. The methyl fluoride partial pressure was 32 Torr, while the water vapor pressure in its measurement cell was 19 Torr. The lock-in amplifier band-width was 10 Hz. The small étalon effect was

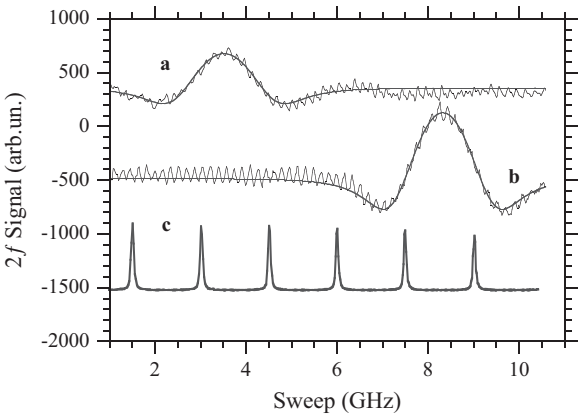

Fig. 3. Second harmonic absorption signal of CH_3F (a) and H_2O (b) around 844.6 nm obtained by WMS with 10 Hz bandwidth, along with the best peak fit. $p_{CH_3F} = 32$ Torr, $p_{H_2O} = 19$ Torr, $T = 293$ K. The transmission of the F.–P. interferometer (f.s.r. = 1.5 GHz) is shown (c) as frequency marker.

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Table 1
Wavenumbers (ν') and wavelengths (λ) of the measured CH_3F absorption lines, with maximum error within the second decimal unit.

ν' (cm^{-1})	λ (Å)	σ_{max} ($10^{-25}cm^2$/molecule)	ν' (cm^{-1})	λ (Å)	σ_{max} ($10^{-25}cm^2$/molecule)
11 545.28	8659.22		11 637.36	8590.70	
11 545.39	8659.14		11 637.57	8590.55	
11 545.55	8659.02	2.5 ± 0.5	11 637.66	8590.48	0.8 ± 0.2
11 545.80	8658.83		11 637.76	8590.41	
11 546.00	8658.68		11 638.47	8589.88	
11 546.17	8658.55		11 638.61	8589.78	1.4 ± 0.3
11 546.37[a]	8658.40	5.8 ± 0.2	11 646.32	8584.09	0.4 ± 0.2
11 554.85	8652.05	4.0 ± 0.2	11 647.37	8583.32	1.2 ± 0.2
11 555.08	8651.87	3.2 ± 0.2	11 652.94	8579.22	
11 564.73	8644.66	2.6 ± 0.2	11 653.03	8579.15	
11 564.25	8645.01	6.2 ± 0.4	11 653.15	8579.06	
11 571.88[b]	8639.31	2.6 ± 0.2	11 653.28	8578.97	
11 581.24[b]	8632.33	1.7 ± 0.3	11 653.39	8578.89	
11 583.56	8630.60	3.2 ± 0.2	11 653.50	8578.80	0.4 ± 0.1
11 583.81	8630.42	1.7 ± 0.2	11 653.63	8578.71	
11 587.25	8627.85	1.8 ± 0.2	11 653.68	8578.67	
11 587.38	8627.76	1.2 ± 0.2	11 653.80	8578.58	
11 587.52	8627.65	0.9 ± 0.2	11 653.88	8578.52	
11 587.63	8627.57	2.5 ± 0.2	11 654.03	8578.41	0.2 ± 0.1
11 588.27	8627.09		11 654.54	8578.04	
11 588.34	8627.04	0.3 ± 0.1	11 654.64	8577.96	0.3 ± 0.1
11 558.45	8262.96		11 655.02[a]	8577.69	0.7 ± 0.2
11 588.93	8626.60	2.7 ± 0.2	11 655.57	8577.28	0.7 ± 0.1
11 597.28	8620.39		11 663.71	8571.29	0.5 ± 0.1
11 597.41	8620.29	1.3 ± 0.2	11 664.42	8570.77	0.8 ± 0.2
11 597.51	8620.22		11 664.64	8570.61	
11 597.61	8620.15		11 666.52	8569.23	
11 610.69	8610.44	1.4 ± 0.2	11 666.58	8569.12	0.6 ± 0.2
11 635.25	8592.26		11 674.23[b]	8563.57	1.2 ± 0.3
11 635.40	8592.15	0.9 ± 0.2	11 677.00	8561.54	4.9 ± 0.2
11 635.88	8591.79		11 683.92	8556.47	0.3 ± 0.1
11 636.00	8591.71		11 692.81	8549.96	0.3 ± 0.1
11 636.17	8591.58	0.5 ± 0.2	11 694.26	8548.90	
11 636.30	8591.49		11 694.34	8548.84	
11 636.56	8591.29		11 694.60	8548.65	0.6 ± 0.1
11 636.83	8591.09		11 694.79	8548.52	
11 637.04	8590.94		11 694.89	8548.44	0.4 ± 0.1
11 637.16	8590.85	0.3 ± 0.1	11 711.17	8536.56	0.3 ± 0.1
11 637.26	8590.78		11 711.82	8536.09	
11 713.09	8535.16		11 762.58	8499.25	
11 713.22	8535.07		11 767.83	8495.46	0.2 ± 0.1
11 713.36	8534.96		11 767.86	8495.44	0.3 ± 0.1
11 713.74	8534.69		11 768.92	8494.67	
11 713.98	8534.51		11 769.02	9494.60	
11 714.82	8533.90	0.5 ± 0.1	11 769.16	8494.50	
11 714.93	8533.82		11 769.28	8494.41	
11 722.03	8528.65		11 769.38	8494.34	
11 722.19	8528.53		11 769.52	8494.24	0.2 ± 0.2
11 722.31	8528.45	0.7 ± 0.1	11 770.07	8493.84	0.6 ± 0.1
11 722.41	8528.37		11 770.26	8493.70	
11 731.56	8521.72	0.6 ± 0.2	11 770.46	8493.56	0.5 ± 0.2
11 732.96	8520.71	0.3 ± 0.1	11 770.69	8493.39	
11 733.07	8520.63		11 770.82	8493.30	
11 733.20	8520.53		11 770.91	8493.23	
11 740.72	8515.07		11 771.10	8493.10	
11 740.86	8514.97	1.5 ± 0.2	11 771.59	8492.74	0.6 ± 0.2
11 741.07	8514.82		11 772.05	8492.41	
11 741.33	8514.63		11 772.15	8492.34	
11 741.49	8514.52	0.3 ± 0.1	11 772.27	8492.25	0.4 ± 0.2
11 748.30	8509.58	0.8 ± 0.2	11 772.58	8492.03	0.8 ± 0.2
11 748.93	8509.12	0.5 ± 0.2	11 773.10	8491.65	
11 749.04	8509.04		11 773.22	8491.57	
11 749.24	8508.90		11 773.54	8491.34	
11 749.37	8508.80		11 773.76	8491.18	0.5 ± 0.2
11 749.65	8508.60	0.4 ± 0.1	11 777.84	8488.24	
11 758.32	8502.33	0.5 ± 0.1	11 777.92	8488.18	0.2 ± 0.1
11 759.64	8501.37	0.2 ± 0.1	11 778.01	8488.12	
11 759.73	8501.31		11 779.89	8486.76	1.5 ± 0.2
11 759.82	8501.24		11 795.51[b]	8475.52	

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Table 1 (*continued*)

ν' (cm^{-1})	λ (Å)	σ_{max} (10^{-25}cm^2/molecule)	ν' (cm^{-1})	λ (Å)	σ_{max} (10^{-25}cm^2/molecule)
11 759.89	8501.19		11 797.29[b]	8474.24	
11 761.36	8500.13		11 800.37[b]	8472.03	1.0 ± 0.1
11 761.47	8500.05		11 806.33	8467.75	1.7 ± 0.5
11 761.56	8499.99		11 829.55	8451.13	1.6 ± 0.5
11 761.76	8499.84	0.7 ± 0.1	11 830.19	8450.67	0.1 ± 0.1
11 762.12	8499.58	0.2 ± 0.1	11 834.78	8447.40	0.1 ± 0.1
11 762.24	8499.49		11 834.85	8447.35	
11 762.34	8499.42		11 835.92	8446.58	
11 762.47	8499.33		11 836.30	8446.31	0.4 ± 0.1

[a] The wavenumbers marked are probably related to double lines.
[b] The wavenumbers marked are measured with respect to iodine.

Table 2
Methyl fluoride absorption line strengths.

ν' (cm^{-1})	S (10^{-26}cm/molecule)
11 554.85	2.4 ± 0.2
11 564.25	2.9 ± 0.2
11 583.56	1.3 ± 0.1
11 588.93	1.0 ± 0.1
11 677.00	1.9 ± 0.1
11 779.89	0.7 ± 0.1
11 800.37	0.4 ± 0.1

originated by the reflections inside the multipass cell: the distance between the fringes is $\Delta\nu \simeq 0.175$ GHz, and the distance between confocal mirrors inside the multipass cell was $l = 42.8$ cm [$\Delta\nu = c/(4l)$]. The F.–P. interferometer transmission is also shown as frequency marker. The étalon effect could be reduced by improving the LD beam collimation with the utilization of specific aspheric lenses, which will be one of the future improvements of this spectroscope.

3. Experimental results

In Table 1 the detected absorption lines are listed. The very congested band observed could suggest a ⊥ type band [16]. The maximum absorption cross section (σ_{max}) is reported only where it could be measured by the direct absorption (DA) technique, as the WMS with high modulation amplitude can bring to big systematic errors in the absolute value of the absorbance. These measurements were performed at room temperature, at a pressure around 30 Torr and 30 m pathlength. The wavelengths are calculated in air at $T = 294$ K following the work of Edlén [17]. As previously said, ought to the mode hops suffered by the LDs, this list cannot pretend to be exhaustive; anyhow in our knowledge this is the first time these lines have been accurately measured.

By assuming a Voigt line shape, we could integrate the absorption coefficient in energy to obtain the line strength with an acceptable error for seven of the more intense observed lines. The results are shown in Table 2.

With the modulation amplitude kept low, we measured the self-broadening coefficients of the FWHM for the seven lines at room temperature, and for two of them also the air-broadening ones. In this case the CH_3F partial pressure was 20 Torr. Finally for the most intense line at 11 564.25 cm^{-1} the shift coefficients could be obtained too. The results are reported in Table 3.

During the least square fitting procedure the Doppler component of the Voigt function was a constant parameter kept to the value calculated at the measurement conditions.

Table 3
CH_3F pressure FWHM broadening (γ) and shift coefficients (δ).

ν' (cm^{-1})	γ_{self}	γ_{air} (MHz/Torr)	δ_{self} (MHz/Torr)	δ_{air} (MHz/Torr)
11 554.85	34 ± 1			
11 564.25	22.7 ± 0.5	12 ± 1	-1.3 ± 0.2	1.0 ± 0.8
11 583.56	11 ± 2			
11 588.93	18 ± 1			
11 677.00	9 ± 1	6 ± 1		
11 779.89	18 ± 3			
11 800.37	12.2 ± 0.1			

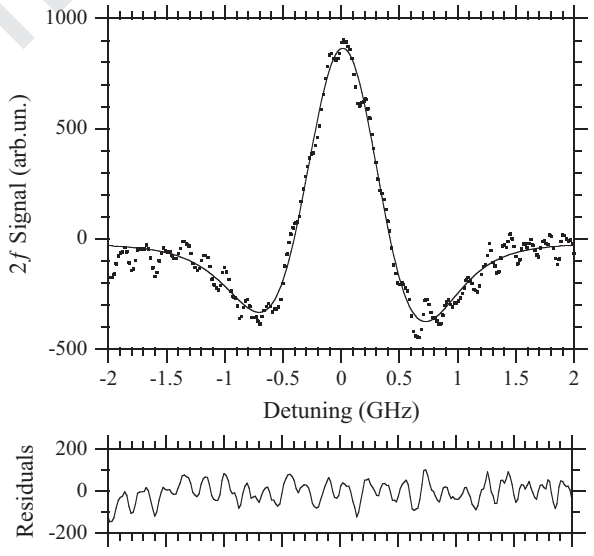

Fig. 4. Second derivative signal of the methyl fluoride absorption line at 11 564.25 cm^{-1} along with its best fit and related residuals.

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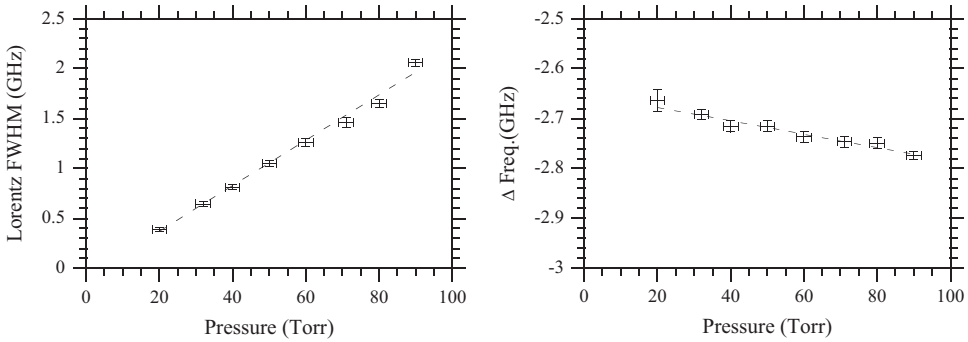

Fig. 5. Self-broadening (left) and self-shift (right) measurements for the 11 564.25 cm^{-1} methyl fluoride absorption line as a function of its pressure at room temperature.

In Fig. 4 there is an example of the 2*f* measurement of the 11 564.25 cm^{-1} line at $p_{CH_3F} = 32$ Torr, $T = 294$ K, and 10 Hz band width, with low modulation amplitude. The fit function is the 2nd derivative of the Voigt function. The étalon effect is observable in the residuals.

A graphical example of one of the collisional broadening and shift measurements is shown in Fig. 5. On the left the Lorentz FWHM component of the 11 564.25 cm^{-1} line shape is plotted as a function of the CH_3F pressure, while on the right the frequency difference (Δ Freq.) between the CH_3F line and a reference line at a fixed known position is shown as a function of the methyl fluoride pressure. All the measurements were performed at room temperature. It is remarkable that, even if the shift effect was an order of magnitude lower than the broadening, it was still observable with acceptable errors. In particular, all the errors are always the maximum errors (3σ), and for the pressure they were all within 1 Torr, while for the Lorentzian FWHM they came for the fit procedure and were principally affected by the above mentioned étalon effect.

In our knowledge no other pressure broadening and shift measurements can be found in the literature at these wavenumbers, therefore only a comparison with what obtained in different spectral regions can be done. As explained previously, this experimental work did not provide the quantum number classification of the single line, therefore here only an average comparison with what published by others can be tried.

Since the first self-broadening measurements performed in 1949 [18], results have been obtained in the microwave and in the infrared regions, ranging roughly between 10 and 40 MHz/Torr.

In the infrared region, self-broadening coefficients in the fundamental vibronic quantum ν_6 band have been measured by Leperè et al. [19] at 8.5 μm, on average their values result higher than ours; in particular they used a different fit function, the Rautian profile, that takes into account the velocity-changing collision effects. In their case the line shifting was negligible.

This happens also when we compare our self-broadening results with the ones reported in the work of Lerota et al. [20] on the ν_2 and ν_5 bands between 6.5 and 7 μm at room temperature.

A comparison can also be done with the results of the work on the fundamental ν_2 at 6.8 μm [21] and two of our measurements, at 11 554.85 and 11 564.25 cm^{-1}, are consistent with these results.

Still the self-broadening coefficient measured at 3.5 μm by using a difference-frequency laser by the $LiNbO_3$ nonlinear crystal and the Stark modulation technique [22] is similar to our result at 11 583.56 cm^{-1}.

On the ν_4 band at 3.3 μm also the self-broadening data of Cartlidge and Butcher [23], obtained by a tunable laser source consisting of two parametric mixed lasers through a lithium niobate crystal, are aligned to our values.

Ikram et al. [24] by a CO_2 Stark-tunable laser on the $\nu_3 : {}^{Q}Q(1,1)$ transition at 9.5 μm obtained $\gamma_{self}^{HWHM} = (18.7 \pm 1.1)$ MHz/Torr, which is comparable to our result at 11 554.85 cm^{-1}.

The self-broadening coefficients, and the self-shift in its absolute value, are also similar to the ones of Rohart et al. [25] in the millimeter wave range.

Finally, for what the air-broadening concerns, our results are aligned to what Guerin et al. [26] got in the ν_2 and ν_5 bands around 6.8 μm.

4. Conclusion

By using a tunable diode laser spectrometer 156 methyl fluoride overtone absorption lines have been detected by the aid of the wavelength modulation and the 2nd harmonic detection techniques. The line-shape parameters were obtained by fitting the observed signals with the standard Voigt profile through a nonlinear least squares fitting program. For the more intense of them the absorption cross sections have been measured giving line strengths of the order of 10^{-26}–10^{-27} cm/molecule. These absorption bands can only be detected by high sensitive techniques and very long path-lengths, in fact their extinction coefficients correspond to some tens of kilometers. For some of these lines the pressure broadening coefficients have been measured and for the most intense, pressure shift coefficients have been obtained too. Some comparisons with previous works, even if at different wavelengths, are consistent with our results.

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