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Note

Diode laser spectroscopy of ethylene overtones at 830 nm

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ABSTRACT

A tunable diode laser spectrometer has been employed to examine the 3rd overtone absorption lines of C_2H_4 at around $12\,000\text{ cm}^{-1}$ (830 nm). The spectrometer sources are heterostructure AlGaAs tunable diode lasers operating "free-running". By the aid of the wavelength modulation spectroscopy with the second harmonic detection technique and a Herriott type multipass cell 63 very weak absorption lines have been observed for the first time, with cross sections as low as $2 \times 10^{-26}\text{ cm}^2/\text{mol}$, equivalent to $\cong 0.05\text{ km}^{-1}/\text{amagat}$. The self-broadening coefficient has been measured for one of the most intense lines.

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1. Introduction

Ethylene is a plane symmetrical molecule with 12 normal vibrations (N nuclei means $3N-6$ vibrational degrees of freedom) [1], called "fundamentals". Therefore, its spectra and particularly the combination overtone bands are quite complicated. The ro-vibrational absorption bands span from the infrared, through the near infrared (NIR), up to the visible part of the e.m. spectrum.

In one of our previous spectroscopic works [2] we found their presence at $11\,800\text{ cm}^{-1}$ by using a diode laser spectroscope, so we took the advantage of this experience to do again an absorption spectroscopy applied to C_2H_4 in the range between $11\,900$ and $12\,100\text{ cm}^{-1}$, where very weak ro-vibrational lines, presumably with $\Delta v = 4$ (third vibrational overtone), are present. They can still be revealed by using the wavelength modulation spectroscopy (WMS) technique [3]. WMS is a well-known noise reduction technique that efficiently supports the use of the laser diodes (LD) as sources. In particular, by modulating its injection current, the emission is modulated as well. This

simplifies the utilization of the phase detection technique that increases considerably the signal-to-noise (S/N) ratio.

Ethylene is an interesting molecule for astrophysics as it is present in the atmosphere of the outer planets of the solar system as well as of satellites like Titan [4], where its overtones can be observed as the optical density is orders of magnitude higher than the one obtainable in the laboratory.

2. Experimental details

The experimental setup for the WMS and the 2nd harmonic technique has been described in a previous paper [5], but here the multipass measurement cell has been used in a different configuration as shown in Fig. 1, where a schematic of the experiment is presented.

The employed source was a HITACHI Mod. HL8325G, a triple quantum well structure (TQW) Fabry-Perot type LD, which nominally emits 40 mW at 830–835 nm at room temperature (RT). Its emission has a longitudinal and transverse single mode. It was mounted without any optical external feed-back, that is in "free-running" configuration. It was 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

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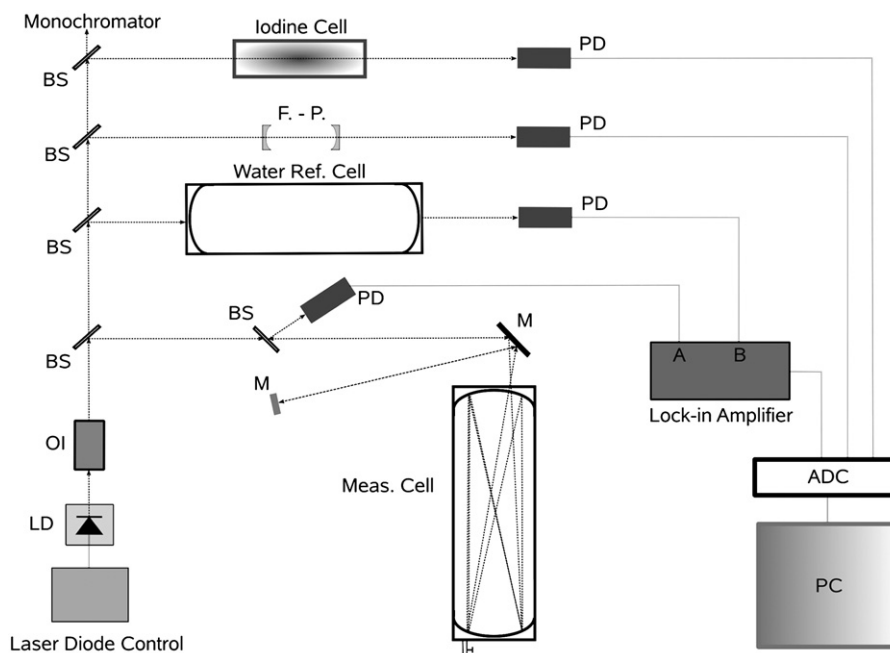


Fig. 1. Outline of the experimental setup. ADC: analog-to-digital converter; BS: beam splitter; F.-P.: Fabry-Perot interferometer; LD: laser diode; M: mirror; OI: optical insulator; PC: desk-top computer; PD: photodiode.

temperature by eliminating the convection effects. The LD temperature control is critical as its typical emission wavelength regime is about 0.1 nm/K. In this configuration the temperature can be spanned by ± 20 K around RT by using a Peltier junction. For an adequate fine linewidth control the current must be tuned within ± 10 μ A as its emission characteristic slope is about 0.01 nm/mA. A multipass Herriott type cell (S.I.T. S.r.l., Mod. MPC-300 [6]), was used in order to increase the absorption path-length necessary for detecting the very weak ethylene absorptions, final goal of this work. The nominal path-length of the cell (30 m) was doubled by retro-reflecting the output beam. A beamsplitter at the cell input coupled the double-passed beam to the photo-diode (PD) detector. An optical insulator at the LD case exit window was necessary in order to avoid any “feedback” effect on the LD itself, that could be a severe source of noise. In spite of the many reflections by the measuring cell windows, a detectable signal of some μ W was still available on the PD with acceptable interference effects as it will be shown later; this was facilitated also by the laser beam coherence length that does not extend more than 10 m. Doubling the pathlength conducted to almost doubling the S/N ratio and consequently the sensitivity of the apparatus. Another closed multipass cell containing water vapor at ~ 20 Torr was used for checking the eventual presence of water in the measurement cell, whose absorption lines could interfere with the measurements at this wavelengths. An iodine reference glass cell was used for the precise wavenumber measurements through the utilization of the relative absorption line atlas [7]. In some cases where the iodine lines were too weak to be detected, the water vapor lines from the “water cell” have been used as a reference as well, with a comparison

to the HITRAN database [8]. A confocal 5 cm Fabry-Perot (F.-P.) interferometer (f.s.r. = 1.5 GHz) was utilized to check the amount and the linearity of the LD emission frequency sweep obtained by sweeping the LD injection current. A 0.35 m focal length Czerny-Turner monochromator was used for the rough wavelength measurement (± 0.01 nm).

The ethylene pure gas was supplied by Praxair Inc.: grade 3.5 (purity $\geq 99.95\%$, $H_2O \leq 5$ ppmv, $O_2 \leq 10$ ppmv, $CO_2 \leq 10$ ppmv, $N_2 \leq 40$ ppmv, C_2H_2 and $C_2H_6 \leq 100$ ppmv). 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).

The WMS technique applied in this experiment has been described in our previous work [9]. In particular a sinusoidal modulation of the injection current results in the sinusoidal modulation of the LD emission intensity and frequency.

The emission frequency of the source $\bar{\nu}$ sinusoidally modulated at the frequency $\nu_m = \omega_m/2\pi$ results in

$$\nu = \bar{\nu} + a \cos \omega_m t. \quad (1)$$

The transmitted intensity depends on both the line shape and the modulation parameters, and this allows the utilization of the phase detection technique; in this case the utilization of a lock-in amplifier tuned to double the modulation frequency permitted to get the 2nd harmonic signal.

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

The absorption line shape as a function of the photon energy (frequency) at the pressures within 30–200 Torr, which the experiments were carried on, can be well described by the Voigt function.

This function should be used for the line fit, but in case of high modulation amplitude, the second derivative description fails and a different approach is necessary. As explained in Ref. [9], in particular in the Appendix, spectroscopic parameters can be still obtained with a good reliability by using the right convolution function [9, Eq. (13)].

By this way 63 absorption lines have been detected and their wavenumbers measured within 0.01 cm^{-1} (maximum error: 3σ) in both the reference cases: the iodine and water vapor. The absorption cross sections were on the order of $10^{-26} \text{ cm}^2/\text{mol}$, which corresponds to the line strength $S \approx 10^{-25} \text{ cm}^2/\text{mol}$, the lowest detectable line strength this LD spectroscope can reach so far. To understand how weak these lines are, it is useful to give the corresponding extinction coefficient at Standard Temperature (0°C) and Pressure (1 atm), that is $k_{\text{STP}} \approx 20 \text{ km}$.

3. Experimental results

In Table 1 the list of the observed absorption lines is showed. The maximum absorption cross section is listed only where it could be measured by the direct absorption

Table 1

Wavenumbers (ν') and wavelengths (λ) of the measured C_2H_4 absorption lines, with maximum error within the second decimal unit. The wavenumbers marked with ^a are measured with respect to water vapor.

ν' (cm^{-1})	λ (nm)	σ_{max} ($10^{-25} \text{ cm}^2/\text{mol}$)	ν' (cm^{-1})	λ (nm)	σ_{max} ($10^{-25} \text{ cm}^2/\text{mol}$)
11941.15	8372.15	1.3 ± 0.4	11973.54	8349.50	
11943.19	8370.72		11974.14	8349.08	0.5 ± 0.1
11953.05	8363.81		11974.46	8348.86	0.4 ± 0.1
11953.13	8363.76	1.0 ± 0.1	11975.05	8348.45	0.3 ± 0.1
11953.20	8363.71		11976.68	8347.31	
11953.25	8363.67		11976.91	8247.15	0.6 ± 0.2
11954.07 ^a	8363.10	0.7 ± 0.2	11979.33	8345.47	0.5 ± 0.2
11954.46	8362.83		11979.46	8345.38	0.7 ± 0.2
11954.60	8362.73		11979.93 ^a	8345.05	
11954.78	8362.60		11979.98 ^a	8345.01	
11954.84	8362.56		11980.04 ^a	8344.97	
11954.89	8362.53		11980.10 ^a	8344.93	0.3 ± 0.2
11954.99	8362.46	0.7 ± 0.2	11986.32	8340.60	
11955.08	8362.39		11987.05	8340.09	
11955.33	8362.22		11987.13	8340.04	0.3 ± 0.1
11955.41	8362.16		11988.02	8339.42	0.7 ± 0.3
11959.26 ^a	8359.47	0.2 ± 0.1	11988.14	8339.33	
11960.46	8358.63	0.6 ± 0.2	11988.92	8338.79	
11960.56	8358.56	0.7 ± 0.2	11988.97	8338.75	0.3 ± 0.2
11960.63	8358.51	0.8 ± 0.2	11989.95	8338.07	0.4 ± 0.2
11961.33	8358.02		11992.28	8336.45	0.3 ± 0.2
11962.29	8357.35	0.3 ± 0.1	11999.22	8331.63	0.3 ± 0.2
11962.40	8357.28		12000.94	8330.44	0.2 ± 0.1
11962.50	8357.21		12003.08	8328.95	0.3 ± 0.1
11962.95	8356.89	2.0 ± 0.5	12013.86	8321.45	0.3 ± 0.1
11969.35	8352.42	1.4 ± 0.2	12013.95	8321.42	
11969.62	8352.24	1.5 ± 0.2	12029.68	8310.54	
11971.58	8350.87	0.6 ± 0.3	12092.50 ^a	8267.36	
11971.74	8350.76		12092.57 ^a	8267.31	
11972.99	8349.88	0.4 ± 0.2	12088.88 ^a	8269.84	
11973.39	8349.61	0.3 ± 0.1	12113.50 ^a	8253.03	
11973.47	8349.55				

(DA) technique, as the WMS with high modulation amplitude can bring to big systematic errors in the absolute value of the absorption. These measurements were performed at RT, at pressure around 50 Torr and 60 m pathlength. The wavelengths are calculated in air at $T = 294 \text{ K}$ following the work of Edlén [10]. In our knowledge this is the first time these lines have been observed and their position measured.

Only for the most intense observed line (11962.95 cm^{-1}) we could integrate the absorption coefficient in energy in order to obtain the line strength with an acceptable error:

$$S = (0.9 \pm 0.2) \times 10^{-26} \text{ cm}^2/\text{mol}$$

This band seems to be centered at about 11970 cm^{-1} , where the vibrational 3rd overtone should be located [11].

An example of what was obtained when reaching the limit of the sensitivity of our spectrometer is shown in Fig. 2, where ethylene absorption lines at 11979.93, 11979.98, 11980.04 and 11980.10 cm^{-1} are shown as obtained by WMS and the 2nd harmonic detection technique, along with their best fit. The lines are broadened by modulation, in fact here the modulation amplitude normalized to the line-width was $m = a/\Gamma = 0.9$. Here the power of the laser beam incident to the measurement PD was only $\approx 1 \mu\text{W}$, while the LD laser beam power at the

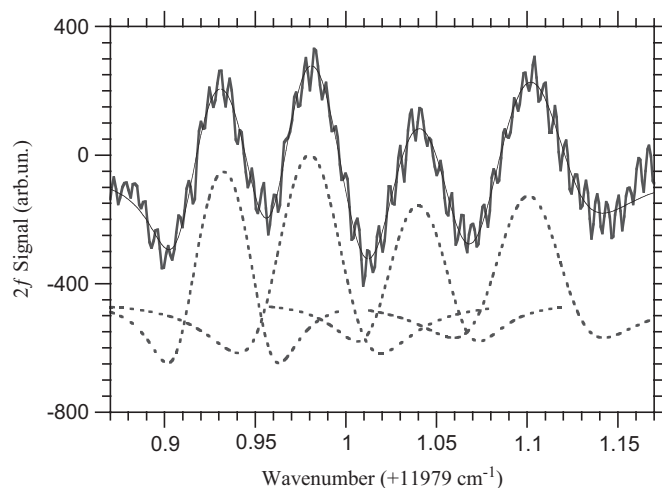


Fig. 2. 2nd derivative signal of ethylene around 834.5 nm obtained by WMS with 10 Hz bandwidth, $p_{\text{C}_2\text{H}_4} = 59$ Torr, $T = 294$ K, and $m = 0.9$. The peak fit results are shifted for clearness.

Table 2
Lorentzian FWHM (Γ_L) vs pressure (p) for the 11962.95 cm^{-1} line.

p (Torr)	Γ_L (GHz)
30	0.4 ± 0.3
51	0.4 ± 0.2
70	0.5 ± 0.2
90	1.1 ± 0.3
110	0.8 ± 0.2
130	1.6 ± 0.2
150	1.4 ± 0.2
170	1.7 ± 0.2
183	1.8 ± 0.1

exit of the vacuum case was around 10 mW; the absorption lines are still observable. The evident etalon effect was originated by the reflections inside the measurement cell. This probably could be reduced by a better collimation of the laser beam.

Still for the 11962.95 cm^{-1} line, reducing the modulation amplitude to avoid the instrumental distortion, we tried a self-broadening measurement of the full width at half the maximum (FWHM). In Table 2 the Lorentzian (collisional) FWHMs for different values of the ethylene pressure are listed. It can be noted that the measurement error decreases as the pressure increases, due to the increment of the ethylene concentration: the consequent increment of the absorption signal betters the S/N ratio. The maximum error in pressure is 1 Torr.

The corresponding self-broadening coefficient is

$$\gamma_{\text{self}} = (10 \pm 1) \text{ MHz/Torr}$$

This result is consistent with what obtained in our previous work [2], even if at different wavelength. A comparison can be done also with the result of the work on the fundamental ν_{10} at 10.8 μm [12]: it shows a similar value for the self-broadening coefficient.

4. Conclusion

By using a tunable diode laser spectrometer with high resolving power ($\lambda/\Delta\lambda \approx 10^7$), the aid of the wavelength modulation spectroscopy technique with the second harmonic detection, and a 60 m total path-length multipass measurement cell, 63 ethylene overtone absorption lines have been detected. For the most intense of them the absorption cross section has been measured giving a line strength of the order of 10^{-26} cm^2/mol . These absorption bands can be detected only by high sensitive techniques with very long path-lengths, in fact their extinction coefficients correspond to some tens of kilometers. The pressure broadening coefficient of one of the most intense line have been measured.

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