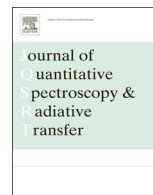




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## Notes

# Diode laser spectroscopy of methyl chloride overtones at 850–860 nm



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## ABSTRACT

By using a tunable diode laser (TDL) spectrometer 156  $\text{CH}_3\text{Cl}$  overtone absorption lines have been detected in the range between 11,590 and 11,760  $\text{cm}^{-1}$  (8500–8625 Å). Their strengths range around  $10^{-26}$ – $10^{-27}$   $\text{cm}^2/\text{molecule}$  and have been measured by utilizing commercial AlGaAs/GaAs laser diodes through the wavelength modulation spectroscopy (WMS) and the 2nd harmonic (2f) detection techniques. For one line the self-broadening coefficient has been obtained.

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## 1. Introduction

Methyl chloride or chloromethane ( $\text{CH}_3\text{Cl}$ ) is a symmetric top molecule ( $\text{C}_{3v}$  symmetry group) and the most abundant natural halocarbon in Earth's atmosphere with the two chlorine isotopes 35 (75.78%) and 37 (24.22%). Methyl chloride is present in the troposphere at a concentration of approximately 1.2  $\mu\text{g}/\text{m}^3$  (0.6 ppb); a certain amount of it reaches the stratosphere and there the photodissociation generates chlorine radicals, which contribute to ozone depletion [1]. This is one of the reasons why it has been object of many spectroscopic works especially in the infrared, where the fundamental vibrations are. It has been very much investigated by conventional spectroscopic techniques as well as by the more sophisticated Fourier transform infrared (FTIR) spectrometers [2].

In the gas phase in 1935 Mecke and Vierling [3] identified  $\text{CH}_3\text{Cl}$  overtones at 11,265  $\text{cm}^{-1}$  and later also

Thompson [4] with a glass Littrow spectrograph observed these overtones at 8880 Å in photographic plates.

Laser absorption spectroscopy has been used by Shang-I Chou et al. [5] for the detection of high-resolution absorption spectra of the first overtone  $2\nu_4$  band of  $\text{CH}_3\text{Cl}$  near 1.65  $\mu\text{m}$  by using a DFB InGaAsP diode laser.

The third overtone C–H stretching ( $\nu_{\text{CH}} = 4$ ) absorptions in the infrared spectrum of methyl chloride has been identified by Duncan and Law [6].

A systematic study of the overtone spectra of methyl halides has been carried on the 4 and 5 quanta of C–H stretching excitation by Law by using a FTIR spectrometer [7].

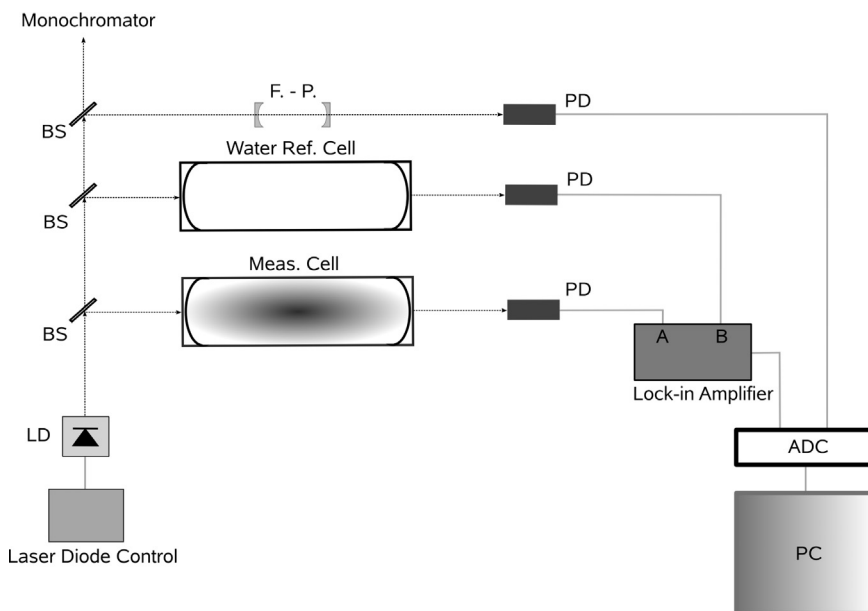
In the present work the diode laser absorption spectroscopy technique is utilized in order to observe the rovibrational resonances around 850 nm, presumably overtones ( $\nu_{\text{CH}} = 4$  polyad) and combinations not yet measured.

The employment of the laser diodes (LDs) enables the use of the wavelength modulation spectroscopy (WMS) technique, which, along with multipass sample cells, is a necessary requirement to increase the signal-to-noise (S/N) ratio and to observe such very weak absorptions lines.

Here we could not distinguish the chlorine 35, 37 isotopes belonging of these bands due to superposition of

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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.

absorption lines at these wavelengths. This is principally caused by the many overlapping bands whose upper states are often coupled by various interactions, such as the Fermi and the Coriolis resonances [7]. For the same reason it was impossible to identify the right quanta of vibration and rotation.

In these conditions more than 150  $\text{CH}_3\text{Cl}$  absorption lines have been detected and for one of them, at  $11,734.00\text{ cm}^{-1}$ , the self-broadening coefficient has been measured at room temperature.

## 2. Experimental details

The experimental setup for the WMS with the 2nd harmonic detection technique, sketched in Fig. 1, follows partially what used in a previous work [8].

In this case the employed sources have been AlGaAs/GaAs heterostructure LD Roithner RLT85100G and a Thorlabs LP850P030 index-guided multiple quantum well LD. As both of them in sequence were mounted in a “free-running” configuration, their spectral superposition permitted the wavenumbers coverage from  $11,590$  to  $11,760\text{ cm}^{-1}$  with some blank ranges where their mode hops coincided. Their emission has single longitudinal and transverse modes. They were hosted in a small vacuum chamber having a Brewster angle glass exit window. The vacuum was useful when working at low temperature in order to avoid any water vapor condensation and moreover it contributed to maintain the LDs temperature stable. In fact the LDs temperature control is critical as their typical emission wavelength varies as about  $0.1\text{ nm/K}$ . In this case the temperature stability and control was guaranteed by a high-stability bipolar temperature controller ( $\Delta T = 0.01\text{ K}$  within 1 h) driving a Peltier junction thermally connected to the LD.

A fine and accurate current control is mandatory ( $\pm 10\text{ }\mu\text{A}$ ) too, because the LD emission characteristic slope is about  $0.01\text{ nm/mA}$ . Therefore a stabilized low-noise ( $1 < \mu\text{A rms}$  with  $10\text{ MHz}$  bandwidth) Melles Griot 06DLD201 current supply has been adopted for the purpose.

Two  $30\text{ m}$  path-length Herriott type multipass cells were used as sample and reference cells. In particular the latter contained water at room temperature vapor pressure ( $\approx 20\text{ Torr}$ ) and was used as the reference for the precise wavenumber measurements. The HITRAN water vapor absorption lines database [9] has been employed for this purpose.

To check the LDs modes and the linearity of their emission frequency a confocal  $5\text{ cm}$  Fabry–Perot (F.-P.) interferometer (f.s.r. =  $1.5\text{ GHz}$ ) was utilized, while a  $0.35\text{ m}$  focal length Czerny–Turner monochromator was used for the rough wavelength check ( $\pm 0.01\text{ nm}$ ).

The methyl chloride was supplied by Matheson Tri Inc.: CP Grade, minimum purity  $99.9\%$  ( $\text{H}_2\text{O} \leq 50\text{ ppm}$ ).

The pressure inside the sample cell was measured directly by a Varian 6543-25-045 capacitive pressure gauge ( $\pm 0.5\text{ Torr}$ ). Here all the experiments were carried on at pressures ranging between  $20$  and  $100\text{ Torr}$ .

Pre-amplified silicon photodiodes (Centronic OSD5-5T,  $2.52\text{ mm}$  diameter) have been used as detectors; they did not need to be necessary fast, as the measurements lasted some seconds; the band-width of the lock-in amplifier was set to  $10\text{ Hz}$ .

The transmittance  $\tau(\nu)$  has been measured following the classical Lambert–Beer expression

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

where  $z = \rho l$  is the product of the absorbing species density  $\rho$  ( $\text{molecule/cm}^3$ ) and the optical path  $l$  ( $\text{cm}$ ) of the radiation through the sample, that is the column amount

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