



Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Laser-induced grating spectroscopy of highly excited overtone and combination vibrational states of methane

D.N. Kozlov^a, D.A. Sadovskii^b, P.P. Radi^{c,*}^aA.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russia^bDépartement de physique, Université du Littoral Côte d'Opale, F-59140 Dunkerque, France^cDepartment of General Energy, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

ARTICLE INFO

Article history:

Available online xxx

Keywords:

CH₄
Methane
Vibrational polyads
Overtone spectroscopy
Laser-induced gratings
Collisional deactivation processes
Four-wave mixing

ABSTRACT

Laser-induced grating spectroscopy is applied to investigate weak overtone and combination absorption bands of methane. The rotationally-resolved spectra of transitions to the polyads P_n , $n = 8-10$, 12 recorded at pressures ranging from 0.2 to 4 bar and temperatures 298 K and 124–130 K cover a broad interval between 891 and 618 nm (11220–16180 cm⁻¹) and contain a significant amount of prominent narrow lines which correspond to stationary rovibrational states. The absorption cross sections of the weakest detected methane transitions are estimated to be as small as $\approx 10^{-26}$ cm² molecule⁻¹. The technique is suitable to provide data for the development and verification of new models describing the complex energy structure of highly vibrationally excited molecules.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Weak visible and near-infrared (NIR) absorption bands of the small and highly-symmetric methane molecule are important for understanding of the atmospheric properties of the Jovian planets and their major satellites, as well as of some extrasolar objects (see, e.g., [1]). However, observed spectra of CH₄ are highly congested and complex. This is caused by Fermi coupling between closely spaced vibrational levels and strong Coriolis-type rotation–vibration interactions. The absorption measurements in the laboratory are necessary to provide data for the development and verification of adequate theoretical description and modeling of the CH₄ complex energy structure and identification of bands observed by astronomers. These data are, perhaps, our only source of information on the structure of highly excited (about half way to the dissociation energy) vibrational states of methane. The spectroscopic data may also provide the information of fundamental interest concerning the mechanisms and rates of internal energy relaxation in case of strong interactions of quasi-degenerate rovibrational levels [2].

During recent 20 years a variety of methods has been developed and applied to record complicated spectra of extremely weak

absorption transitions to high-lying overtone and combination vibrational states of methane. Highly sensitive intracavity laser absorption [3], intracavity photoacoustic [4,5] and tone-burst modulation [6] spectroscopy have been used to study CH₄ bands around 11300 cm⁻¹. Furthermore, the intracavity laser absorption technique has been employed to measure spectra and absorption coefficients between 10635 and 13300 cm⁻¹ [1]. More recently, the spectral region near 11900 cm⁻¹ has been investigated by using wavelength modulated diode laser spectroscopy [7]. Earlier intracavity photoacoustic [8–10] and laser absorption [11,12] spectroscopies have been applied to record weak CH₄ absorption lines in the range 16110–16170 cm⁻¹. Intracavity photoacoustic spectra have been also recorded near 13750 cm⁻¹ [10] and 14670 cm⁻¹ [13]. The spectral resolution in these studies was typically about 0.08–0.10 cm⁻¹ which is above the Doppler limit.

Recently [14], we have applied a non-linear technique – laser-induced gratings (LIGs) spectroscopy – for investigation of methane overtone–combination absorption bands. The LIGs technique had previously demonstrated excellent sensitivity and potential for recording high-resolution spectra of weak molecular transitions (see, e.g., [15–18]). In [14] three features of the methane NIR spectrum have been recorded with the resolution of about 0.06 cm⁻¹ in the spectral ranges near 889, 861 and 840 nm (between 11220 and 11930 cm⁻¹). These features have been assigned previously [19] to the combination bands $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_3$, and $\nu_1 + 3\nu_3$, respectively, which correspond to the pentacontakaipentad (P_5) [20].

* Corresponding author. Fax: +41 563102199.

E-mail address: peter.radi@psi.ch (P.P. Radi).URL: <http://rag.web.psi.ch/radi> (P.P. Radi).

In the present work, we provide more detailed spectroscopic information on the investigations of [14] and additionally describe newly recorded higher frequency (NIR and visible) CH₄ absorption spectra. These spectra can be assigned formally to combination bands $3\nu_1 + \nu_3 + (\nu_2 \text{ or } \nu_4)$ (780 nm), $4\nu_1 + \nu_3$ (727 nm), and $5\nu_1 + \nu_3$ (619 nm) [19], corresponding to the polyads P_9 , P_{10} , and P_{12} , respectively. The aim of the work was to record, using the LIGs technique, low-pressure spectra of all the bands in the broad spectral ranges, to obtain the resolved structure of the bands, and to make certain that narrow rovibrational components are present in the spectra even at the high levels of vibrational excitation. The possibilities of the technique to provide pressure-dependent parameters, like line frequencies and shapes, useful for characterization of highly-excited vibrational states of methane molecules, were investigated. It is worth to be noted that until recently the LIGs technique was employed mainly for gas diagnostics, while the advantages of the method in spectroscopy of weak molecular transitions have not been widely taken.

2. Experimental

Generally, spatially-periodic variations of the complex refractive index of the medium are referred to as laser-induced gratings (LIGs). Detailed description of LIGs in various media can be found in the book of Eichler et al. [21] and references therein. Recent investigations employing LIGs in the studies of gases are outlined in the reviews [22–24].

Resonant excitation of molecules by a short-pulse radiation of two pump laser beams at wavelength λ_{pr} , which are crossed at the angle $2\theta_p$ and interfere, produces a spatially-periodical variation of the population of the energy levels involved. The spatial modulation period equals to the interference fringe spacing $\Lambda = \lambda_p / 2\sin\theta_p$. Rapid collisional relaxation of the excited states results in local temperature and density variations which lead to formation of the corresponding modulations of the refractive index named thermal LIGs. Pulsed adiabatic compression of the gas by the spatially inhomogeneous pump electromagnetic field strength generates non-resonant electrostrictive LIGs. In the experiments LIGs are usually registered by detecting the part of probe laser radiation which crosses the pump beams interaction region and is diffracted by the modulations of the refractive index. For efficient diffraction, the probe beam, at wavelength λ_{pr} , should be directed to the planes of the fringes at the Bragg angle, θ_{pr} , defined as $\sin\theta_{pr} = \lambda_{pr} / 2\Lambda$. If a continuous wave (cw) probe radiation is employed, the temporal evolution of a short-pulse excited LIG diffraction efficiency can be recorded. A pulse of the diffracted light registered by a photodetector generates the LIG signal, $S(t)$.

Spectroscopy of the absorption transitions is accomplished by means of tuning the pump laser frequency through the range of interest and measuring the peak value of $S(t)$ or its integral within a definite time interval as a function of frequency. Theoretical considerations show [14,21] that the strength of the resonant LIG signal is proportional to the square of the product of the absorption coefficient and the amount of energy released in one collision.

The LIG spectrometer employed in this work is shown schematically in Fig. 1 and has been described in detail previously [14,25]. Briefly, a narrowband tunable pulsed dye laser providing up to 25 mJ/pulse is employed as a pump source with 10 ns pulses and a spectral bandwidth of $\approx 0.06 \text{ cm}^{-1}$. This laser is pumped by the frequency-doubled radiation of a 20-Hz repetition rate Nd:YAG laser. To obtain tunable radiation in appropriate wavelength ranges dye solutions in methanol of Pyridine (725–729 nm, P_{10}), DCM (618–621 nm, P_{12} , and 620–645 nm), and Sulforhodamine B (586–609 nm) are used. Coherent radiation in the near-IR regions of 835–895 nm (P_8) and 775–815 nm (P_9), with pulse energy of

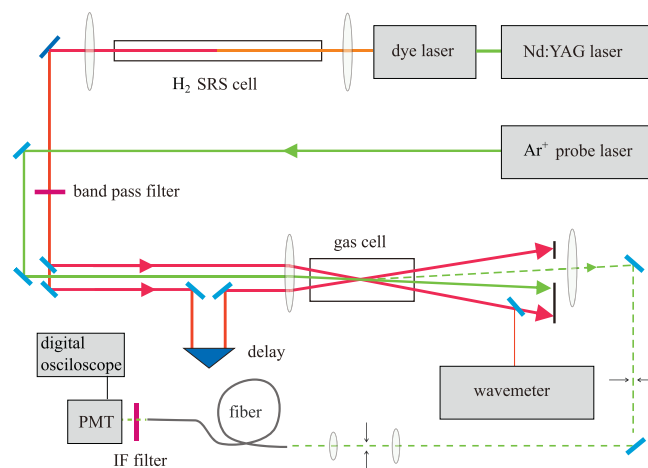


Fig. 1. Experimental setup.

about 2 mJ, is obtained by Raman-shifting the frequency of the dye laser in a 1.5-m-long cell containing H₂ at 5 bar. The pump radiation is split into a pair of roughly equally intense and parallel polarized LIG excitation beams. The beams pass through a focusing lens ($f = 900 \text{ mm}$) and intersect at the crossing angle of $2\theta_p \approx 1.20\text{--}1.44^\circ$ (depending on the wavelength range) to provide a fringe spacing $\Lambda \approx 30\text{--}35 \mu\text{m}$. A Fizeau-interferometers wavemeter with a specified accuracy of 10^6 is used to measure the absolute excitation wavelength in each pulse.

The LIGs are probed by utilizing the beam of an Ar⁺-laser delivering up to 0.5 W at 514.5 nm or 488.0 nm. The cw probe beam is propagating parallel to the pump beams and focused by the same lens into the interaction region at a Bragg angle of $\theta_{pr} \approx 0.42\text{--}0.47^\circ$. In this way, a 3-D forward phase-matching geometry is arranged. The diffracted part of the probe light is spatially filtered and coupled into a multimode fused silica fiber delivering it to a fast photomultiplier. Additional stray-light reduction is achieved by installing a band-pass interference filter centered at the probe laser wavelength in front of the photomultiplier. Temporally resolved acquisition of single-shot or accumulated LIG signals is performed by using a digital oscilloscope (1 GHz analog bandwidth, up to 4 Gsamples/s sampling rate). The signals are recorded during 2–10 μs , depending on pressure. The spectra are obtained by accumulating the LIG signals integrated within an optimized time interval after the excitation pulse while tuning the frequency of the dye laser. The spectral resolution achieves about 0.06 cm^{-1} .

The gas cell employed in the experiments can be evacuated to $< 10^{-4}$ bar and allows to work with gas pressures up to 5 bar. The gas pressure in the sample volume is measured by a capacitance pressure transducer. A copper cold-delivering finger cooled by liquid nitrogen is mounted to enter into the cell. The sample volume, with the dimensions of about 0.3 mm in diameter and 20 mm in length, is adjusted to be located at the axis of a narrow (5 mm in diameter and 30 mm in length) channel in a copper cylinder mounted at the end of the finger inside the cell. The cylinder wall temperature is measured by a thermocouple. High purity methane of quality 2.5 (Messer–Griesheim) is used for the measurements. Careful preparation of the sample and baking-out of the cell is performed to avoid contamination of the spectra by absorption lines of water and other trace species. The measurements in the gas cell were performed at CH₄ pressures of 0.2–4 bar and temperatures of 298 K and 124–130 K. Local gas temperature in the sample volume was calculated from the speed of sound derived from the LIG signal oscillation period at a calibrated fringe spacing Λ .

A characteristic LIG signal observed at resonant excitation is presented in Fig. 2a. It was recorded at 187 mbar of CH₄ and

Download English Version:

<https://daneshyari.com/en/article/5414735>

Download Persian Version:

<https://daneshyari.com/article/5414735>

[Daneshyari.com](https://daneshyari.com)