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High precision line profile measurements on ^{13}C acetylene using a near infrared frequency comb spectrometer

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ABSTRACT

Line profiles of a rovibrational transition of ^{13}C acetylene have been measured for various pressures in the near infrared region. In order to accomplish high precision in frequency, we have employed a diode-laser, the frequency of which is locked to an optical comb. By tuning the comb frequency we have achieved a continuous frequency tuning over 2 GHz for the measurement of Doppler broadened line profiles spread over 2 GHz. In addition we have stabilized the incident power of the laser on the sample cell by adjusting the gain of a fiber amplifier via a feed-back loop. Observed profile data have been analyzed by the generalized Voigt function to determine the Gaussian width precisely: at the present we realized a precision of 10^{-3}. The zero pressure line center position was determined with a precision of 10^{-9}.

1. Introduction

A spectral line profile obtained experimentally provides information not only for the line center position but also for the intensity and the width of the line. The intensity and the width carry the thermodynamical information of the molecules in the sample cell: temperature and pressure.

Among them the Gaussian width of the line profile reflects the temperature T through the Doppler shift of the resonance frequency. Assuming the Maxwell–Boltzmann distribution for the translational energy of the molecule, the half width at $(1/e)$ maximum (HWM/e) of the Gaussian contribution of the line profile Γ_G is expressed as

$$\Gamma_G = \nu_0\sqrt{\frac{2kT}{Mc^2}}, \qquad (1)$$

where ν_0 is the line center position, k the Boltzmann constant, M the molecular mass, and c the speed of light.

From the metrological point of view, it is very interesting to study the Gaussian width in a spectral line profile, since the analysis may open the possibility to measure gas temperature T very accurately from observable quantities, Γ_G and ν_0. The method is categorized as primary thermometry and therefore is also useful to determine the Boltzmann constant k [1]. Bordé has been proposing the spectroscopic methods to obtain fundamental constants [2,3] and recently he and coworkers determined the Boltzmann constant k with the relative uncertainty of 2×10^{-4} using the spectroscopic method on a rovibrational line in the ν_2 band of $^{14}NH_3$ [4].

In the present study we have measured a ^{13}C acetylene line, $P(16)$ of the $\nu_1+\nu_3$ band in the near infrared (NIR) region (~1.5 μm), for which the line center position is well known with a very high accuracy: 194 369 569 383.6(1.3) kHz [5]. Because of the collisional narrowing effect, the Gaussian width depends on the gas pressure, and Eq. (1) is valid only for the zero pressure limit. Thus, in the present study, we have extracted the Gaussian width as well as the Lorentzian width from the observed profiles, in dependence on the gas pressures, by using the Voigt function. To our knowledge, the collisional effects on line profiles have been studied in high pressures, where the Lorentzian width dominates over the Gaussian. On the contrary we present here the effects in the low pressure limit, which may supply interesting information relevant to molecular physics. The Γ_G of the line at zero pressure has been obtained as 271.29(32) MHz, which should be compared to 271.12(14) MHz calculated for 294.65(30) K with the most accurate value of the Boltzmann constant k [6], *i.e.*, $1.380\,650\,5(24)\times10^{23}$ JK^{-1}; the accuracy of the calculated Γ_G is limited here by the experimental uncertainty of the cell temperature in the present study.

2. Experimental procedure

The comb-stabilized diode-laser system used in the present study is illustrated by block diagrams in Figs. 1 and 2. To maximize the precision of measurement, we stabilized the frequency and the

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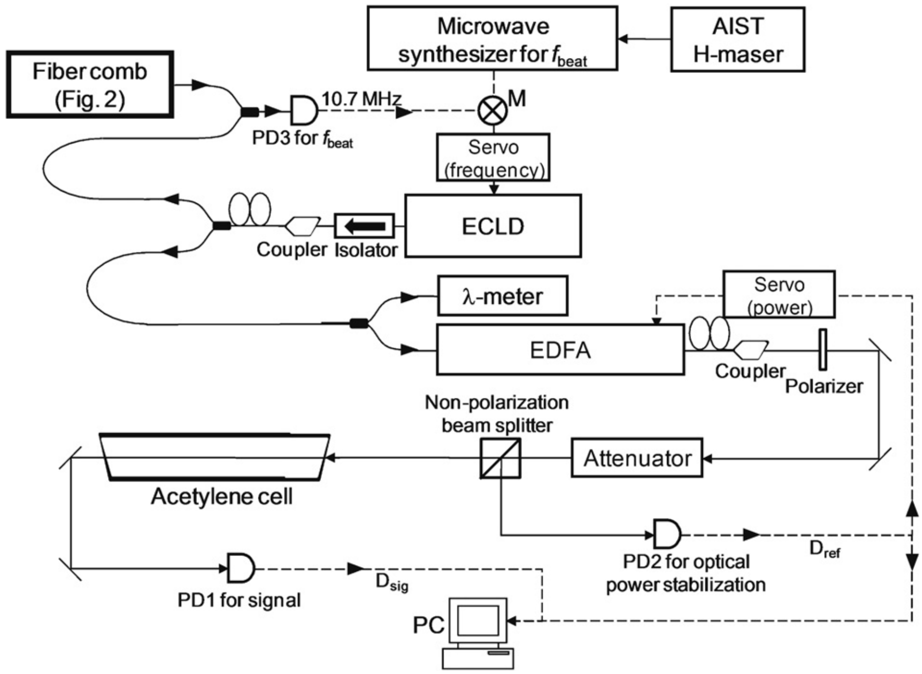

Fig. 1. The diagram of the spectrometer used in the present study is illustrated. The output voltage D_{sig} of the photodetector PD_1 for the signal and D_{ref} of PD_2 for amplitude stabilization were measured by digital voltmeters and recorded by a PC. The beat frequency f_{beat} produced by the PD_3 by mixing the radiation of the ECLD and the comb signal, is used to lock the frequency of the ECLD. The generator of optical frequency comb, indicated by the box of "Fiber comb", is a fiber-based frequency comb system developed at NMIJ (AIST), which is illustrate in Fig. 2.

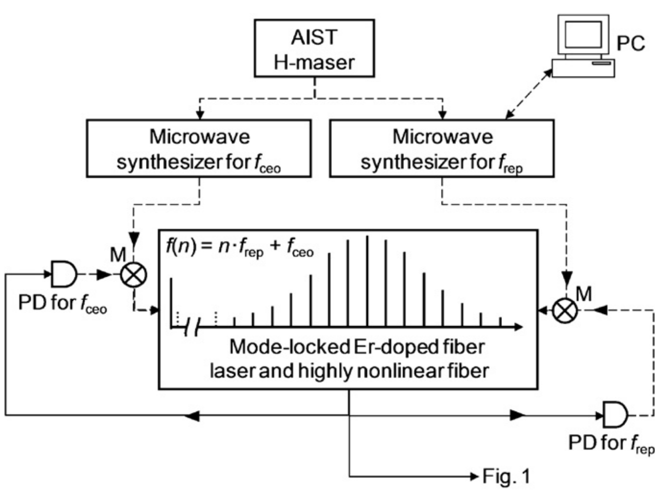

Fig. 2. The block diagram of the fiber comb system is illustrated; for detail see text and Ref. [7].

optical power of an external-cavity laser-diode (ECLD) as shown in Fig. 1. The frequency is phase-locked to a fiber-based optical frequency comb signal, which is developed at NMIJ (AIST); see for details Ref. [7]. The power is stabilized by controlling the gain of an erbium-doped fiber amplifier (EDFA).

As presented by Onae et al. [8], a frequency scan of ECLD for 2 GHz, required to measure Doppler broadened line profiles in the present study, was realized by tuning the repetition frequency (f_{rep}) of the comb system as shown in Fig. 2. The optical frequency of the ECLD, locked to the nth mode of the mode-locked fiber comb, is expressed as:

$$f(n) = nf_{rep} \pm f_{ceo} \pm f_{beat}, \quad (2)$$

where, f_{ceo} and f_{beat} are the carrier envelope offset frequency of the fiber comb and the frequency of the beat note between the ECLD and the comb, respectively. Both frequencies are phase-locked at 10.7 MHz generated by synthesizers referenced to a hydrogen maser. The signs for the f_{ceo} and the f_{beat} in Eq. (2) are determined by checking the increase or decrease of f_{beat} when f_{rep} or f_{ceo} is increased under the condition of locking f_{ceo} or f_{rep}, respectively.

The f_{rep} and the mode number n are approximately 54 MHz and 3.6 million, respectively, for the present cases. The f_{rep} can be tuned by a drum-type PZT, around which a part of the fiber ring-cavity of the mode-locked fiber oscillator is wound, and further by the temperature of the cavity container. The phase-locking of f_{rep} is achieved basically by controlling the PZT; the slow component of the error signal is fed back to the Peltier device which regulates the temperature of the cavity; the temperature is set slightly lower than room temperature. This technique enables us to tune the f_{rep} widely. In the present experiment, we could easily tune the frequency of a comb mode more than 2 GHz in the 193 THz region. The phase-locking of f_{ceo} is achieved by controlling the injection current for the fiber laser oscillator.

The frequency of the ECLD depends on the injection current and on the cavity length. Thus, the ECLD frequency is phase-locked to a comb signal by controlling the injection current. In addition the slow component of the error signal is fed back to the PZT to change the cavity length. In this manner, the wide frequency tuning of the ECLD was realized over 2 GHz. We would like to emphasize that such a wide range scan with frequency locking can be achieved only by the comb-locked diode-laser system presented here.

While scanning the repetition frequency (f_{rep}) stepwise, we record two voltage signals from the detectors, PD_1 and PD_2 by digital voltmeters: D_{sig} for signal, and D_{ref} for amplitude stabilization. Since slight drifts in the voltage signal of D_{ref} were observed, we deduced the transmittance spectra by D_{sig}/D_{ref}. First we plot the transmittance against the f_{rep} frequencies and fit the observed spectra with the Gaussian profile to determine the line center. Since the line center frequency is known very accurately, we can extract the mode number of the comb, n, by Eq. (2). In all cases, calculated values are very close to integer, showing the procedure to