

Measurement of the Hydrogen Cyanide Absorption Lines' Centers with the Potential for Mise en Pratique

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Abstract—We built a linear absorption spectroscopy setup to measure hydrogen cyanide ($\text{H}^{13}\text{C}^{14}\text{N}$) $2\nu_3$ rotational-vibrational band. The laser's frequency was locked to the minimum of the absorption line by using the 1f technique. We used a commercially available lock-in amplifier combined with a custom-made PID controller allowing for the short-term frequency stability of about 10^{-10} . The laser frequency was determined by measuring the beatnote between the laser and the optical frequency comb. The laser was locked to each absorption line for about 8 hours and the final time record allowed us to determine the absorption line central frequency with the uncertainty of about 40 kHz. This shows significant improvement compared to the data already available for HCN. Our work can potentially lead to the acceptance of HCN for Mise en Pratique (MeP), which means that laser locked to one of the HCN lines can become the official source of the one-meter unit.

Keywords—hydrogen cyanide, linear absorption spectroscopy, optical frequency comb, frequency reference, frequency stabilized lasers, SI meter

I. INTRODUCTION

The main goal of the LaVA project (Large Volume Metrology Applications), which the presented work is part of, is to improve the metrology capability of FSI (frequency scanning interferometry) instrumentation developed at NPL (National Physical Laboratory). One of the prerequisites for this method is the gas cell and the knowledge of its absorption lines' frequencies. Currently, the absorption media used in $1.55\ \mu\text{m}$ absorption band is acetylene (C_2H_2), which is recognized in the MeP for the SI meter. The main benefit of hydrogen cyanide (HCN) over C_2H_2 is its broader absorption spectrum. $^{12}\text{C}_2\text{H}_2$ has an absorption spectrum of about 25 nm broad, $^{13}\text{C}_2\text{H}_2$ about 30 nm and $\text{H}^{13}\text{C}^{14}\text{N}$ about 40 nm broad that again can improve the FSI measurement accuracy. The available data for HCN [1] does not provide comparable accuracy to C_2H_2 [2], [3] mainly due to the use of not so precise measurement methods. Concretely, authors in [1] measured the lines' positions by scanning laser frequency over the profile of HCN absorption line and fitting it by Voigt profile.

We firstly reported on our progress in [4]. Here we show that with the linear absorption spectroscopy method combined with the measurement of beat-note frequency between laser and optical frequency comb the HCN's absorption lines' centers can

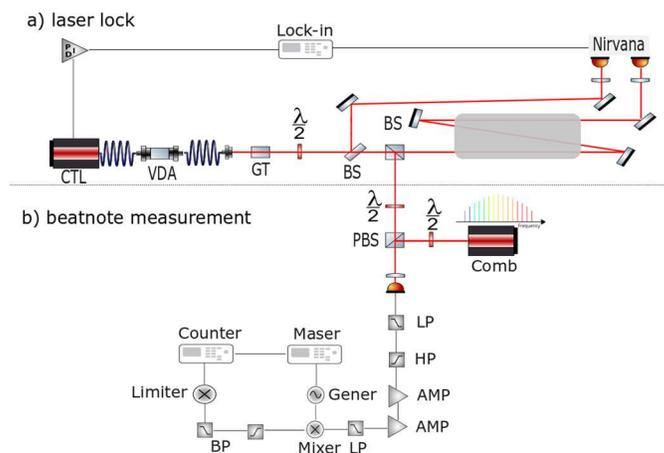


Fig. 1 Experimental setup – continuously tunable laser (CTL), voltage-driven attenuator (VDA), Glan-Taylor crystal (GT), beam splitter (BS), half-wave plate ($\lambda/2$), polarizing beam splitter (PBS), low-pass filter (LP), high-pass filter (HP), and band-pass filter (BP).

be determined more accurately by a factor of 100 in comparison with the previous results [1].

II. METHODS

The laser source we used in our experiment is a continuously tunable laser (CTL), allowing the wavelength of the laser to be tuned from 1510 nm to 1630 nm, which is more than sufficient for the measurement of HCN $2\nu_3$ rotational-vibrational band that spreads from 1525 nm to 1565 nm.

The linear absorption spectroscopy setup shown in Fig. 1., consists of two distinct parts. In the first part, the laser beam goes through a voltage-driven attenuator and Glan-Taylor crystal, which ensures that laser beam power and polarization are stable during the whole measurement. The beam is then split into three parts. Two of them are used in the lock of laser frequency and the last one in the beat-note measurement, which will be described later in this paragraph. The two beams used for the laser lock hit the Nirvana balanced optical receiver. One of them goes through a commercially available 0.4 m long HCN gas cell filled to 0.4 Torr ($\sim 53\ \text{Pa}$). Windows of the cell are wedged, AR coated and fitted to the tubes at a small tilt to minimize the interference effects. The gas cell was put in a

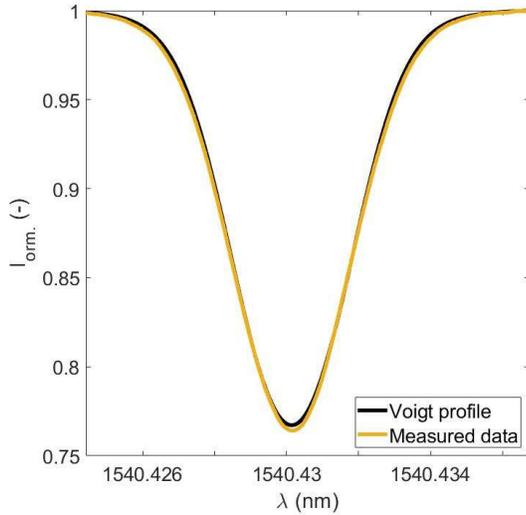


Fig. 2. Profile of the R2 absorption line.

temperature-controlling device, ensuring there are no temperature-induced changes of pressure in the cell during the measurement. We used a three-pass arrangement in order to improve the signal to noise ratio.

The signal from the Nirvana photodetector goes to the lock-in amplifier, which, combined with the PID controller, locks the laser frequency and closes the feedback loop. The lock-in amplifier referenced to active hydrogen maser produced the modulation frequency of 10 kHz and the modulation depth of about 6 MHz.

In the beat-note part of the experimental setup, the laser beam is combined with the optical frequency comb beam, and then hits the photodetector. The signal from the photodetector goes through a set of filters and amplifiers and then it is combined with the signal from the generator, which allows subtracting the modulation from beat-note. After the next filtering, the signal goes through a limiter that changes the shape of the beat-note, so it is more recognizable by a counter. The counter is referenced to 10 MHz coming from an H-maser.

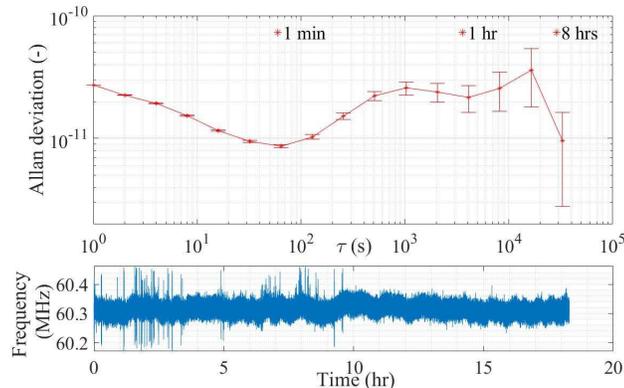


Fig. 3 Allan deviation (upper figure) calculated from the time record of laser frequency locked to R6 absorption line (lower figure).

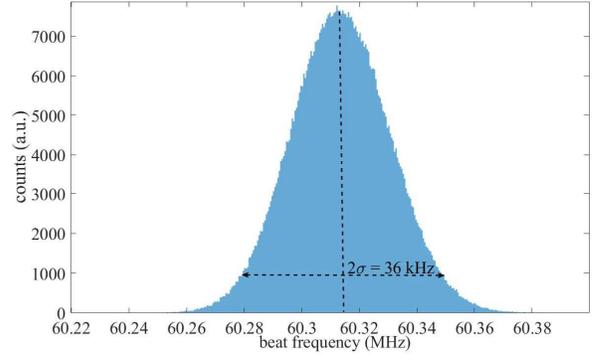


Fig.4. Histogram of frequency occurrences calculated from the laser frequency time record shown in Fig.3.

III. RESULTS

We measured the frequency of the absorption lines' centers in the $2\nu_3$ rotational-vibrational band of $\text{H}^{13}\text{C}^{14}\text{N}$ (see line profile in Fig. 2.). All the lines were about 400 MHz broad, and the line intensity was varying from 50 % for the strongest lines down to 30 %. The main broadening mechanism is the Doppler broadening which can be eliminated by using saturated absorption spectroscopy. On the other hand, this method makes the experimental setup much more complex.

The position of every single line was measured by locking the laser frequency to its minimum and keeping it locked typically for 8 hours. The example can be seen in Fig. 3, where the length of a time record is about 18 hours. The Allan deviations show the short term stability of the laser locked to absorption line minimum in 10^{-10} order. Calculation of histogram then shows the unwanted trend in time record if there is any, and ideally, it should correspond to the Normal distribution. In our case, the histogram corresponds to the Normal distribution very well (Fig. 4), and the 2σ calculations

Table 1. Lines' centers of R branch HCN absorption line with the corresponding uncertainties.

R branch	frequency (MHz)	uncertainty (MHz)
2	194,615,893.43	0.06
3	194,697,533.81	0.06
4	194,777,994.36	0.04
5	194,857,273.35	0.04
6	194,935,369.49	0.04
7	195,012,280.18	0.04
8	195,088,004.33	0.04
9	195,162,540.03	0.05
10	195,235,885.62	0.05
11	195,308,039.52	0.05
12	195,379,000.21	0.05
13	195,448,766.29	0.04
14	195,517,335.80	0.05

Table 2. Lines' centers of P branch HCN absorption line with the corresponding uncertainties.

P branch	frequency (MHz)	uncertainty (MHz)
3	194,101,383.63	0.06
4	194,011,539.87	0.05
5	193,920,532.34	0.04
6	193,828,363.34	0.05
7	193,735,034.34	0.04
8	193,640,548.56	0.04
9	193,544,907.37	0.04
10	193,448,113.37	0.05
11	193,350,168.82	0.04
12	193,251,076.07	0.04
13	193,150,837.24	0.05
14	193,049,454.45	0.06
15	192,946,931.25	0.07

gives the uncertainty of about 40 kHz for the strongest lines.

You can see the summarizing tables with positions of absorption lines' centers in Table 1 for R branch of $2\nu_3$ rotational-vibrational band and in Table 2 for P branch. In our measurement, the most important sources of uncertainty for the positions of lines are the 2σ uncertainty of time record and the repeatability, which is more or less equal to it. Other sources of uncertainty are much less significant.

IV. CONCLUSION

The results described in the last section show great potential for HCN to become an alternative absorption medium to C_2H_2 in 1.5 μm absorption band (so-called C-band). All measured lines' positions, if calculated to zero pressure using pressure

shift coefficients from [1], land well in the uncertainty interval of the previous results in [1] and [5].

Much work on this topic is still to be done, namely, e.g., evaluating the pressure shift coefficients of all HCN absorption lines to improve uncertainty from [1]. The results will then be compared with the same measurements done by other groups, and this set of results will hopefully lead to the application and the acceptance of HCN for MeP.

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REFERENCE

- [1] Swann, C., and Sarah G.. 2005. Line Centers, Pressure Shift, And Pressure Broadening Of 1530-1560 nm Hydrogen Cyanide Wavelength Calibration Lines. *Journal Of The Optical Society Of America B* 22 (8). J. Clerk Maxwell, A Treatise on Electricity and Magnetism, 3rd ed., vol. 2. Oxford: Clarendon, 1892, pp.68–73.
- [2] Nakagawa, K., M. de Labachellerie, Y. Awaji, and M. Kourogi. 1996. "Accurate optical frequency atlas of the 15- μm bands of acetylene." *Journal of the Optical Society of America B* 13 (12). <https://doi.org/10.1364/JOSAB.13.002708>.
- [3] Edwards, C. S., H. S. Margolis, G. P. Barwood, S. N. Lea, P. Gill, and W. R. C. Rowley. 2005. "High-accuracy frequency atlas of $^{13}\text{C}_2\text{H}_2$ in the 1.5 μm region." *Applied Physics B* 80 (8): 977-983. <https://doi.org/10.1007/s00340-005-1851-0>.
- [4] Hosek, M, S. Reřucha, L. Pravdova, M. Cizek, J. Hrabina, O. Cip, and P. Zemanek. 2018. "Investigating the use of the hydrogen cyanide (HCN) as an absorption media for laser spectroscopy." 21st Czech-Polish-Slovak Optical Conference on Wave and Quantum Aspects of Contemporary Optics, October: 8-. <https://doi.org/10.1117/12.2517761>.
- [5] Gilbert, S. L. , W. C. Swann, and C. M. Wang, Hydrogen cyanide $\text{H}^{13}\text{C}^{14}\text{N}$ absorption reference for 1530{1560 nm wavelength calibration|SRM 2519, Natl. Inst. Stand. Technol. (US) Spec. Publ. 260-137 (National Institute of Standards and Technology, 1998).