

# Saturation Spectroscopy of $\text{H}^{13}\text{C}^{14}\text{N}$ Absorption Lines

Hosek M. \*, Hrabina J., Rerucha S., Cizek M., Pravdova L., Cip O.  
Institute of Scientific Instrument of the CAS, Brno, Czech Republic  
\*mhosek@isibrno.cz

**Summary**—We present a saturated spectroscopy measurement of  $\text{H}^{13}\text{C}^{14}\text{N}$  hydrogen cyanide  $2\nu_3$  band absorption lines. The system employed a continuously-tunable laser referenced to stabilised optical frequency comb, which allowed us to scan the  $\text{H}^{13}\text{C}^{14}\text{N}$  spectrum with sub-kHz precision. The sub-Doppler spectroscopy scheme and the third-harmonics synchronous detection allowed us to determine the position of absorption lines with a fortyfold improvement in precision against the most up-to-date published results [1] and expanded the list of lines measured by this technique published in [2].

**Keywords** — saturated absorption spectroscopy; hydrogen cyanide, laser spectroscopy; third-harmonic detection

## I. INTRODUCTION

Laser spectroscopy in absorption reference cells represents a classic method for developing optical frequency standards. In the visible spectral range, He-Ne lasers at 633 nm and frequency-doubled Nd:YAG lasers at 532 nm stabilised to absorption lines of molecular iodine vapours represent a suitable and well-described option [3].

In the near-infrared spectral range, the acetylene isotopes  $^{13}\text{C}_2\text{H}_2$  and  $^{12}\text{C}_2\text{H}_2$  are the main optical frequency reference gases, especially for the telecommunication C-band (1530 – 1565 nm). The fractional uncertainty of the line centre determination achieved by using the Doppler-free spectroscopic method for  $^{13}\text{C}_2\text{H}_2$  measurement was below  $10^{-11}$  in [4]. Combined with the measurements performed by other scientific groups, it led to the admission of the P(16) absorption line in the  $(\nu_1+\nu_3)$  band to the “Recommended values of standard frequencies for applications including the practical

realisation of the metre and secondary representations of the second” in 2007.

Hydrogen cyanide ( $\text{H}^{13}\text{C}^{14}\text{N}$ ) represents an alternative to the acetylene isotopes with the advantage of having a wider absorption spectrum covering the whole telecom C-band (Fig.1). The most comprehensive study of  $\text{H}^{13}\text{C}^{14}\text{N}$  so far shows the optical frequencies of  $2\nu_3$  band absorption lines with the uncertainty of about 1 MHz [1]. That work used the linear spectroscopy method to scan the Doppler-broadened absorption lines. The wavemeter was calibrated at 1560 nm, where the published results correspond well with our measurement. However, the farther the other measured lines lay from this calibration point, the higher the possible error entered the measurement (possible wavemeter error influence). The data from the measured 25 lines were then used to calculate the molecular constants, which helped calculate the positions of the rest (not measured) lines.

The first experiments with saturated absorption in HCN have been done in [6], [7] and [8]. In [6], the authors measured the P27 line in  $\text{H}^{12}\text{C}^{14}\text{N}$ . “Many narrow lines” were observed using  $\text{H}^{13}\text{C}^{14}\text{N}$  in [8]. Authors in [8] reported measurement of R7 absorption line using 6.35 m long hollow-core optical fibre filled with  $\text{H}^{13}\text{C}^{14}\text{N}$ . Even though the earlier attempts, the complete atlas of  $2\nu_3$  band absorption lines measured by saturated spectroscopy is still missing. This work represents the extension of previously published results [2] by covering the whole  $\text{H}^{13}\text{C}^{14}\text{N}$  absorption spectrum.

Our results could lead to adding  $\text{H}^{13}\text{C}^{14}\text{N}$  as an alternative reference gas to the “Recommended values of standard frequencies for applications including the practical realisation of the metre and secondary representations of the second” and as a reference for dimensional measurements and metrological applications. One example is a significant improvement in distance measurement using frequency scanning interferometry (FSI), where determining the absorption lines’ centres is a key parameter influencing achievable measurement accuracy. The measurements in [9] discuss calibration issues using  $\text{H}^{13}\text{C}^{14}\text{N}$  in the FSI technique in detail. Another potential application is represented by calibrations in optical telecommunication, where covering the whole C-band spectrum by a single reference is advantageous.

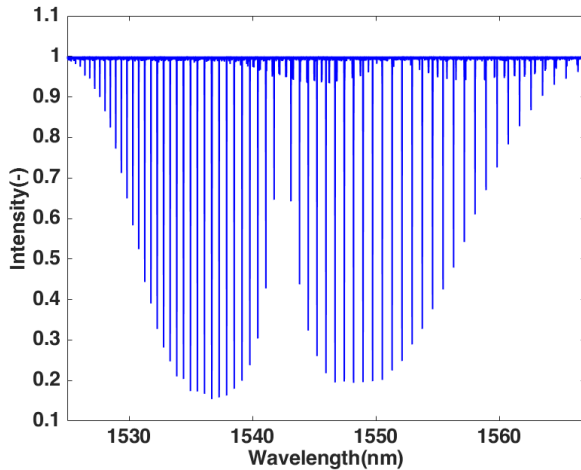


Fig.1. The absorption spectrum of  $\text{H}^{13}\text{C}^{14}\text{N}$ . The rolling ball filter [5] was used to remove the signal background.

## II. EXPERIMENTAL SETUP

The experimental setup is described in detail in [10]. The experiment (Fig. 2) used a continuously-tunable extended cavity diode laser (CTL), offering a wide tuning range from 1510 nm to 1630 nm (CTL 1550, TOPTICA Photonics AG). The laser frequency was locked through a tunable frequency offset (digitally controlled) to a selected tooth of stabilised optical frequency comb (a hydrogen maser and GPS receiver reference the comb itself). Thanks to this arrangement, the actual frequency of CTL was known with an accuracy of  $10^{-13}$  and controllable down to the  $10^{-15}$  level. Digital control of the laser and offset-lock loop parameters allowed us to scan the  $\text{H}^{13}\text{C}^{14}\text{N}$  spectrum.

As the low-pressure cells filled with  $\text{H}^{13}\text{C}^{14}\text{N}$  are not commercially available, we built a refillable absorption cell connected to a vacuum and filling setup (Fig. 3). This allowed us to evacuate the cell with a turbomolecular pump and fill the cell with precisely known pressures (1.6 Pa in this experiment) before each performed measurement. The cell body was made of stainless steel and was equipped with fused silica optical windows connected together by vacuum-compatible glue. The active length of the cell was 0.4 m.

During the measurement, we faced the problem of adsorption/desorption of  $\text{H}^{13}\text{C}^{14}\text{N}$  on the wall of the absorption cell. We managed to significantly reduce this effect by activating the inside surface of the cell with ozone, filling the cell with the 1% solution of chlorotrimethylsilane in methanol, and leaving the solution inside the cell for 90 minutes at room temperature. After that, the solution was discarded, and the cell was washed with pure methanol. Finally, we dried the cell with filtered air and heated it to  $50^\circ\text{C}$  with a hot air gun.

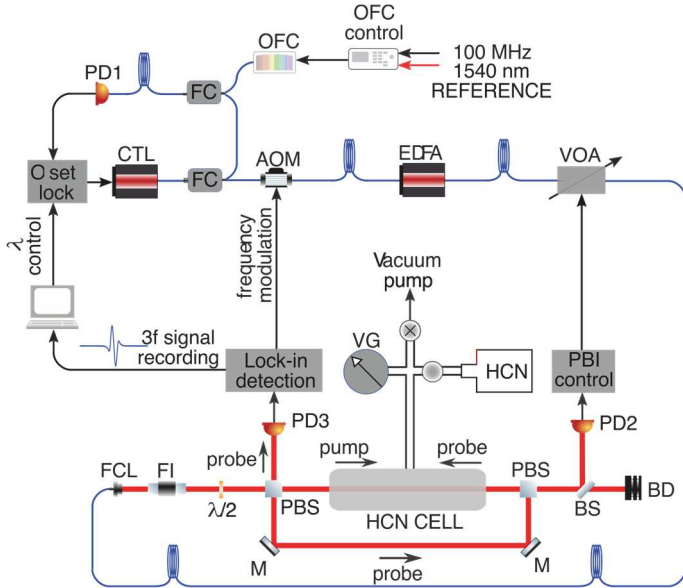


Fig. 2. Experimental arrangement: optical frequency comb (OFC), continuously-tunable laser (CTL), Faraday isolator (FI), acousto-optical modulator (AOM), Er:doped fibre amplifier (EDFA), voltage-controlled optical attenuator (VOA), photodetectors (PD), polarising beam splitters (PBS), mirrors (M), beam sampler (BS), beam dump (BD), vacuum gauge (VG), fibre couplers (FC), fibre collimator (FCL), probe beam intensity (PBI). Adapted from [2].

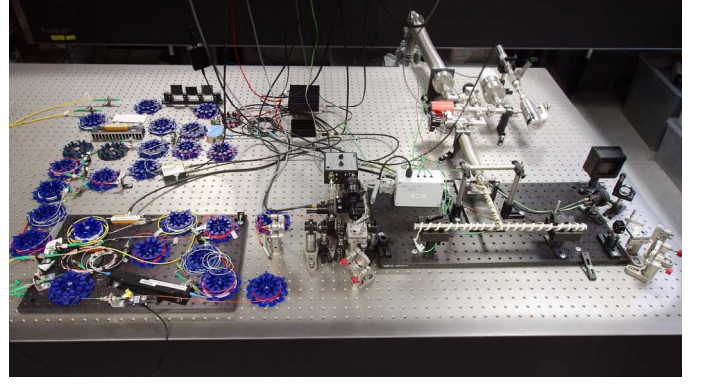


Fig. 3. Experimental setup for saturated absorption measurement. The vacuum part serves for evacuating and filling/refilling the absorption cell with low pressure ( $\sim 1.6$  Pa) of  $\text{H}^{13}\text{C}^{14}\text{N}$ .

The saturated spectroscopy setup employed a traditional pump-probe scheme with frequency modulation of the laser beam by an acousto-optical modulator (1.5 MHz frequency modulation width, 5 kHz modulation frequency). The high-power pump beam (about 120 mW) went through the absorption cell, causing saturation of the  $\text{H}^{13}\text{C}^{14}\text{N}$  molecules. The counter-propagating probe beam (about 10 mW) then probed the saturated line profile and was detected by a balanced photo-detector.

The CTL frequency was tuned over the saturated absorption line profile (Fig. 4) in the range of  $\pm 12.5$  MHz around its centre, with a step of 1 kHz in the close part to the centre and a step of 5 kHz everywhere else. The recorded data were fitted, and the exact centre of the absorption line was obtained with an uncertainty  $\leq 40$  kHz.

The synchronous detection and demodulation at the third derivative technique using a digital lock-in amplifier allowed

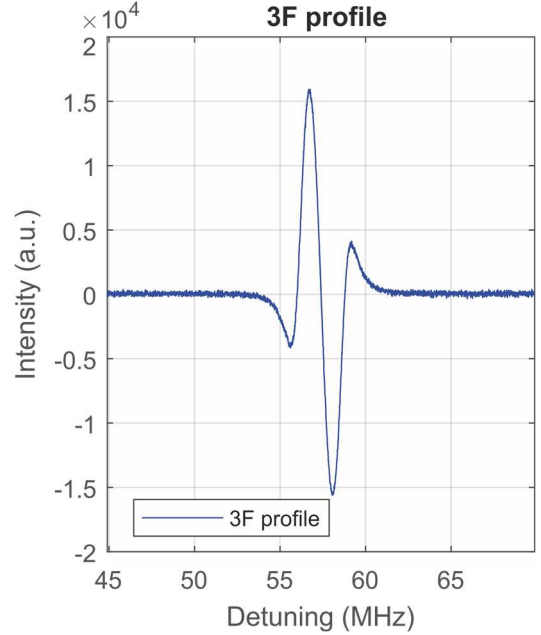


Fig. 5. Third-harmonic profile of the R7 line of the  $2v_3$  band obtained using a 40 cm long cell filled to a pressure of 1.6 Pa. Adapted from [2].

obtaining of a saturated absorption profile while the laser frequency was tuned by variable offset lock.

### III. RESULTS

We used the experimental setup described in the previous section to measure the Doppler-free line profiles of fifty-six  $\text{H}^{13}\text{C}^{14}\text{N}$   $2\nu_3$  band absorption lines. The frequency of CTL was offset locked to the certain tooth of optical frequency comb (OFC) using optical mixing. The OFC's repetition rate was referenced to the hydrogen maser, and its absolute frequency was maintained by continuous tracking to the GPS receiver.

During the analysis, we observed the frequency shifts between our measured results and previously published frequencies, which are shown in Fig. 5. We believe these shifts may be due to a calibration point of the wavemeter used in the previous work [1]. In that work, the wavemeter was calibrated specifically for a selected wavelength (1560 nm), and the farther we moved away from this calibration wavelength, the larger the difference between results.

### IV. CONCLUSION

We present the measurement of  $\text{H}^{13}\text{C}^{14}\text{N}$  in the 1520-1565 nm region with a precision of about fortyfold better than previously published data [1]. Using the experimental apparatus, we scanned the profiles of  $\text{H}^{13}\text{C}^{14}\text{N}$  absorption lines with the step of 5 kHz (1 kHz close to the lines' centres), and we measured the frequencies of  $2\nu_3$  absorption band lines with the fractional uncertainty in the order of  $10^{-10}$ . The results show the high potential of hydrogen cyanide to serve as an absorption medium for telecom frequency standards and for use in frequency scanning interferometry methods, where a wider absorption spectrum brings better measurement resolution. In the follow-up work, we aim to measure the lines' pressure shift coefficients, allowing us to calculate the absorption lines' positions for zero gas pressure. Finalisation of these experiments will allow  $\text{H}^{13}\text{C}^{14}\text{N}$  to be added to the list of "Recommended values of standard frequencies for applications

including the practical realisation of the metre and secondary representations of the second" in 2007.

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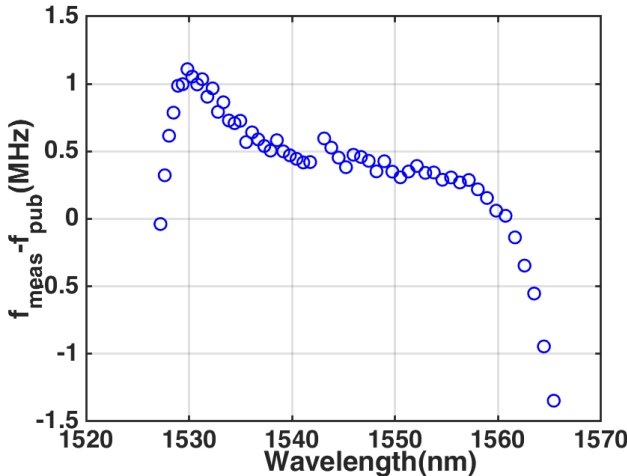


Fig.5. Frequency differences between measured and previously published data [1].