

Saturated Spectroscopy of HCN

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Abstract—This work brings the preliminary results of saturated absorption spectroscopy of Hydrogen Cyanide gas ($\text{H}^{13}\text{C}^{14}\text{N}$), a promising optical frequency reference medium for telecommunication C-band wavelengths. We optimized the experimental system based on parameters for detection of the selected hyperfine transition in low pressure $\text{H}^{13}\text{C}^{14}\text{N}$ absorption cell and observed and investigated the unwanted effect of degradation of the saturated spectroscopy signal due to $\text{H}^{13}\text{C}^{14}\text{N}$ molecules permanent dipole moment.

Keywords—saturated spectroscopy, laser standard, HCN

I. INTRODUCTION

The optical fiber networks represent a critical infrastructure for many of scientific and metrological applications. One of the most important are the wavelength calibrations or dissemination of precise time and frequencies, covering tasks like ions clocks comparisons, precise timing, security, or fundamental constants research). In the most frequently used telecomm C-band, the optical frequency standards based on spectroscopy in $\text{H}^{13}\text{C}^{14}\text{N}$ gas can offer an interesting alternative to widely used acetylene standards [1-3]. Besides the acetylene, $\text{H}^{13}\text{C}^{14}\text{N}$ is readily available and offers wider frequency span of its absorption spectra - which could lead to the laser standards with a wider range of optical frequencies [4]. This advantage strongly corresponds to the actual research of European metrology laboratories focused on large volume metrology applications. Here we demonstrate HCN saturated spectroscopy experimental arrangement and investigate the unwanted effects of HCN reactions with inner surface of the absorption cell.

II. METHODS/RESULTS

To investigate the spectral properties of the $\text{H}^{13}\text{C}^{14}\text{N}$ molecule, we have arranged an experimental setup based on saturated absorption spectroscopy with counter-propagating laser beams (Fig. 1).

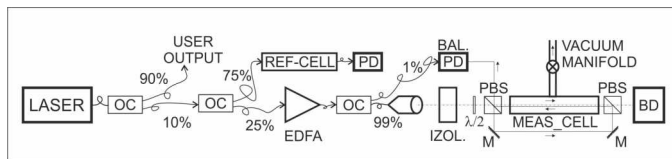


Fig. 1. Experimental setup for saturated spectroscopy of $\text{H}^{13}\text{C}^{14}\text{N}$ gas. OC-fiber splitter, PD-photodetectors, M-mirrors, PBS-polarizing beam splitters.

The laser beam from Erbium-doped single-frequency low-noise laser was amplified by Erbium-doped fiber amplifier and was divided into two parts. The first part was fed into a fibered reference mid-pressure $\text{H}^{13}\text{C}^{14}\text{N}$ cell (~ 50 Pa), which served as a tool for coarse tuning of the laser to the correct optical frequency (near desired absorption line). It was based on the linear absorption spectroscopy. The second part of the beam powered the saturated spectroscopy setup with the measuring bulk low-pressure $\text{H}^{13}\text{C}^{14}\text{N}$ cell. This 40 cm long refillable cell was permanently connected to the vacuum manifold, which allowed repeated filling of the cell with different gas pressures (photo at Fig. 2). Before each filling of the cell, the inner volume was evacuated down to 10^{-5} Pa level. During our first experiments, we changed the pressure inside the cell between 1 – 5 Pa and detected signal of R(2) absorption line @ 1540.4315 nm wavelength (example at Fig. 3). The laser frequency was modulated by PZT with 1 kHz modulation frequency and ~ 6 MHz modulation width, the probe signal of the saturated spectroscopy was captured with balanced photodetector and synchronously demodulated at the third harmonics. Corresponding pump (~ 130 mW) and probe (3.5 mW) beams had diameters of ~ 2 mm.

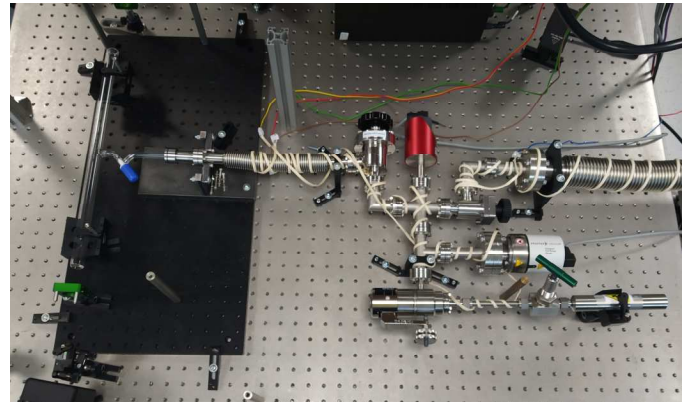


Fig. 2. Photo of refillable absorption cell and vacuum manifold part of the experimental setup.

Considering the system parameters, we found the optimum cell pressure at ~ 2.5 Pa, where the 3rd harmonics error signal reached the signal-to-noise level of ~ 100 . Further optimization was limited by a strong and fast degradation of the saturated signal in time, an unwanted effect probably caused by settling of the gas molecules on the cell's walls due to HCN's

permanent dipole moment or by effect of HCN's polymerization. In the initial experiment, the SNR dropped to its half level at about 45 minutes.

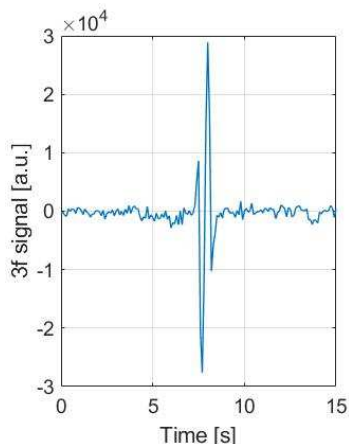


Fig. 3. Example of saturated spectroscopy signal scan over R(2) absorption line of $\text{H}^{13}\text{C}^{14}\text{N}$ (third harmonics error signal). During our experiments, we were able to optimize the system parameters and reach a signal-to-noise ratio of ~ 100 level.

To suppress and study this effect in detail, we have decided to apply two different approaches: 1/ Deactivation of the cell inner surface by various chemicals and 2/ „Presaturation” of the inner surface with high-pressure of HCN gas before the filling of the cell to its nominal pressure value.

The silanization of the inner surface was applied in two steps, A/ an activation of the inner surface with ozonized air, and B/ a deactivation/covering of the inner surface with selected silane compound. After the passivation and adequate drying of the cell, the cell was evacuated, filled with 2.5 Pa of HCN and the error signal of the transition was periodically scanned to monitor its SNR in time. By investigation of effects of different silane compounds, we were able to decelerate the SNR degradation effect from initial 50% level in 45 minutes, to 12% in 90 hours. The searching for optimal deactivation compound (correct chemical with minimal interaction with HCN) is still in progress. The sample record of the 3f signal scan in time is showed at Fig. 4 (in this case, the SNR decreased to its half at about 6.5 hours).

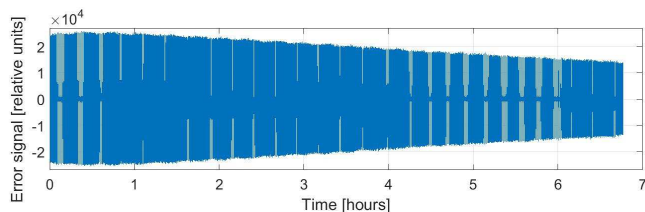


Fig. 4. The sample record of the 3f signal SNR degradation.

The second approach applied to decelerate the 3f signal SNR degradation was presaturation of inner surface with HCN gas of higher pressure. We filled the cell with ~ 10 Pa of HCN and left it on for several days. At the end, the pressure inside the cell was reduced to its nominal level (~ 2.5 Pa) and the error signal was monitored again. The scan showed that this „presaturation” had no effect, and the SNR degradation continues at the same speed as in case of non-presaturated cell.

The investigation of the observed effect is going to continue by testing of another silane compounds or usage of the cell from different materials.

III. CONCLUSIONS

We developed the experimental setup for saturated spectroscopy of HCN gas based on a low-pressure absorption cell. The observed effect of spectroscopy signal SNR degradation was significantly reduced by passivation of the cell inner surface, where we achieved decreasing of the effect speed from initial 50% SNR level drop in 45 minutes to 12% in 90 hours. The investigation of the effect is still ongoing, one potential solution of the problem can be seen in usage of small amount of acid inside the cell, which should bind residual H_2O and stop the HCN reactions. This should lead into the low-pressure HCN cell with adequate long-term stability.

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