Abstract - With the optical frequency synthesis based on femtosecond laser technology the use of iodine-stabilized Nd:YAG laser as an optical frequency reference appeared as a one step toward optical clock making possible the transfer of stable optical frequency into radiofrequency domain. Results of measurement of purity of a set of iodine cells for laser stabilization made at our institute are presented. The purity was tested by improved method based on measurement of induced fluorescence and evaluation by the Stern-Volmer formula. This method was improved by innovation of the fluorescence detection system by introducing compensation for the pumping laser spectral and power instabilities. Further the absolute frequencies of selected iodine hyperfine transitions were measured in direct laser frequency comparison performed with a set of iodine-stabilized Nd:YAG laser etalons with the reproducibility well below the kHz level. The results indicating the iodine cell purity are presented with relation to the absolute frequency shifts. This highlights the influence of iodine cell quality onto the stability and absolute frequency of lasers etalons and also shows the way towards improvements of the iodine cell manufacturing technology.

Keywords – Stabilized laser, Spectroscopy, Iodine.

I. INTRODUCTION

I Frequency doubled Nd:YAG iodine stabilized lasers evolved in the past few years into a reliable and relatively simple etalons of optical frequency with relative stability approaching the $10^{-14}$ limit. They exploit narrow linewidth and low noise of the laser source and good signal-to-noise ratio that can be achieved at the 532 nm in detection of hyperfine iodine components. Relative stability is limited by laser noise and quality of the stabilization setup but the absolute value of the optical frequency is given by center frequency of hyperfine component of the iodine transitions. Only near-ideal purity of the iodine in the absorption cell can result in optical frequencies corresponding to theoretical values. With the optical frequency synthesis based on femtosecond laser technology the use of stabilized Nd:YAG laser as an optical frequency reference appeared as a one step toward optical clock making possible the transfer of stable optical frequency into radiofrequency domain.

We concentrated on the development of iodine cell manufacturing and filling technology verified by measurement of iodine purity through induced fluorescence and by direct laser frequency comparison. We present results of measurement of purity of a set of iodine cells made at our institute, the purity was tested by improved method based on measurement of induced fluorescence and evaluation by the Stern-Volmer formula introduced into the metrology practice with relation to He-Ne iodine stabilized lasers. This method was improved by innovation of the fluorescence detection system by introducing compensation for the pumping laser spectral and power instabilities.

Further frequency-doubled Nd:YAG lasers equipped and stabilized with these cells operating at ISI (Institute of Scientific instruments) and CMI (Czech Metrology Institute) were compared to evaluate their frequency shifts. The absolute frequencies of selected iodine hyperfine transitions were measured in direct laser frequency comparison performed with a set of iodine stabilized Nd:YAG laser etalons with the reproducibility well below the kHz level. This extends the iodine cell tests done with He-Ne lasers to a new precision level and contributes to the design of laser optical frequency references in the visible spectral range. The results indicating the iodine cell purity are presented with relation to the absolute frequency shifts. This not only highlights the influence of iodine cell quality onto the stability and absolute frequency of lasers etalons but also shows the way towards improvements of the iodine cell manufacturing technology. The results aspirate to reduce the standard uncertainty presented in the CIPM recommendation below the kHz level.

II. MEASUREMENT OF INDUCED FLUORESCENCE

Our experimental arrangement is based on measurement of the level of fluorescence in the irradiated iodine cell with an Argon-ion laser for excitation of iodine. The most suitable seems the 502 nm wavelength coinciding with absorption lines in iodine characterized by a high sensitivity to collisional quenching that is caused by a long lifetime of the excited level. The strongest absorption line within the spectral width of the laser is the R(26) 62-0 of the $^{127}\text{I}_2$ which contributes predominantly to the fluorescence measured, [1,2,3].

The typical measured Stern-Volmer diagrams are in Fig. 1(a) and Fig.1(b). The measured Stern-Volmer coefficients ($K_1=0.85\pm0.03$ Pa for cell ISI-R and $K_2=0.88\pm0.034$ Pa for cell ISI-N) shows the very good purity of iodine in both cells, both results are close to the resolution limit of the method, [11].
III. IODINE CELL TECHNOLOGY

The cells manufactured at our institute are made of fused silica glass. This material allows perfect vacuum processing at a high temperature and thus additional releasing of gasses from the walls of the cell is eliminated. Joints between the cell tube and optical windows are a critical problem. We used either welding or soldering at a high temperature over 1000°C with a special solder. This technology was preferred for the cells with Brewster angle windows.

Iodine cells designed to operate in an extracavity arrangement for stabilization of frequency doubled Nd:YAG lasers are made with plane windows equipped with antireflection coatings on both sides of each window. The coatings are a traditional multilayer structure of TiO$_2$ and SiO$_2$, while the top covering layer is SiO$_2$, the same material as the cell tube itself. This was intended to avoid any possible contamination of the cell.

IV. MEASUREMENT OF FREQUENCY SHIFTS

We assembled a beat-frequency arrangement with two frequency doubled 532 nm Nd:YAG lasers stabilized by the saturated absorption spectroscopy technique to detect frequency shifts caused by iodine cell impurities, [4,5,6]. The systems used were the iodine luminescent optical frequency standard ILP I2 /532-3L from Time Base, Düsseldorf, Germany with a prestabilization to a passive Fabry-Perot cavity through a frequency-modulation spectroscopy Pound-Drever technique [7] and single Nd:YAG laser Prometheus from Innolight, Germany with the in-line configuration of the saturated absorption spectroscopy and third-harmonic detection chain and stabilization system of our design. The optical setup was designed to allow simple exchange of the iodine cells for frequency shift measurements. The absolute frequency shift of the system ILP was calibrated by frequency comparison with pulsed mode-locked Ti:Sa optical frequency comb generator locked to the radiofrequency standard in the CMI in Prague (Czech Metrology Institute).

To achieve good resolution of the beat signal to be measured by a counter (HP 53132A) we have chosen a hyperfine component $a_{10}$ of the R(56) 32-0 transition in molecular iodine $^{127}$I$_2$, [8,9,10]. Improvement of signal-to-noise ratio of the beat signal and suppression of the phase jitter was performed by a synchronous modulation of both laser systems which reduced interference of the modulation signals. Precise equalization of both amplitude and phase was adjusted by monitoring of the beat signal with a radiofrequency spectrum analyzer and by reducing the signal linewidth down to the level of a beat signal of free running unmodulated lasers. Synchronization of the modulation signals was derived directly from a single quartz oscillator and following set of dividers generating the modulation signals with adjustable attenuator and phase shifter (Fig. 2).
Fig. 2. Simplified schematic of the arrangement for synchronization of amplitudes and phase of modulation signals of a pair of frequency doubled Nd:YAG iodine stabilized lasers and beat signal detection. CU1, CU2 - Control unit; OSC - Xtal oscillator; FG - Fmod generator; SU1, SU2 - Stabilization unit; FD - Frequency divider; PAR - phase and amplitude regulator; LS1, LS2 - Laser system; AOM – acousto-optic modulator, PD - polarization divider; DET - photodetector; SA - spectral analyzer; CNT - counter; PC - computer.

Result of the stability recording confirms the stabilities that can be achieved with frequency doubled Nd:YAG stabilized laser standards of optical frequencies and approaches the $10^{-14}$ level for integration time 100 s. The recording of Allan variances in Fig. 3(a) and Fig. 3(b) shows that frequency noise of both systems is dominated by random noise fluctuations and the mean value of the detected frequency shift is not influenced by drifts. Together with careful elimination of DC offsets in the key components of the detection chain and servo loop we can consider the relative frequency shift of the pair of lasers given predominantly by the difference between absolute frequency shifts of hyperfine components of the iodine spectrum of the cells. Our comparison was performed with two cells tested to their purity by the evaluation of the Stern-Volmer coefficient through induced fluorescence measurement. Measured frequency shifts of both cells and comparison with its Stern-Volmer coefficients are in Table 1. The values of absolute frequency shift are corrected here with respect to the shift of the reference ILP laser.

### Table 1. Comparison of Stern-Volmer coefficients and measured frequency shifts.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Stern-Volmer coeff.</th>
<th>Absolute freq. shift</th>
<th>Rel. stability (100 sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISI-N</td>
<td>K=0.88±0.034 Pa</td>
<td>Δ=0.8 kHz</td>
<td>5.6e-14</td>
</tr>
<tr>
<td>ISI-R</td>
<td>K=0.85±0.03 Pa</td>
<td>Δ=0.9 kHz</td>
<td>6.3e-14</td>
</tr>
</tbody>
</table>

**IV. CONCLUSIONS**

We measured Stern-Volmer coefficients of two iodine cells made at our institute and compared results with absolute frequency shifts of a testing Nd:YAG laser stabilized with these...
cells by beat-signal comparison measurement with relation to a calibrated laser etalon. The results at resolution limit of the Stern-Volmer method [11] show very good purity of iodine in both cells (measured coefficients 0.88±0.034 Pa for cell ISI-N and 0.85±0.03 Pa for cell ISI-R). Measured absolute frequency shifts (Δ=0.8 kHz for ISI-N cell and Δ=0.9 kHz for ISI-R cell) correspond well with the excellent purity of our cells measured through the Stern-Volmer method.

In [9], taking into account the frequency dependence on the cell quality and other effects, CCL preferred for absorbing media of 127I2 molecules, component a10, R(56) 32-0 transition to adopt a standard uncertainty of 5 kHz, corresponding to a relative standard uncertainty of 8.9e-12.

Apparently, our results show, that with very good purity of iodine in absorption cells, it is possible to achieve the absolute frequency shift of iodine-stabilized Nd:YAG lasers below kHz level and relative stability near 5e-14 level for integration time 100 s. The standard uncertainty presented in the CIPM recommendation might be even reduced below the 1 kHz level as we have proven by our experiment with stabilization of the Nd:YAG laser with two different high-purity iodine cells that perform sub-kHz frequency shifts.

We plan to use both experimental setups for further verification and improvement of the preparation and filling process and evaluating of our cells. The agreement of both results and good reproducibility of recordings of the Stern-Volmer diagram together with the relative stability expressed through the Allan variances show not only the quality of the cells but also the good potential of the Stern-Volmer method for the cell verification even on the sub-kHz level of frequency shifts achievable by Nd:YAG laser etalons.

V. ACKNOWLEDGEMENTS

Authors wish to express thanks for support to the grant projects from Grant Agency of the Academy of Sciences of the Czech Republic, project no. A20065050, Ministry of Education, Youth and Sports of the Czech Republic, projects No.:
LC06007, 2C06012, Academy of Science of the Czech Republic, projects No.: AV0Z20650511 and KAN311610701,
Ministry of Industry and Commerce, projects No: 2A-1TP1/127, FT-TA3/133 as well as to the Petr Balling and Peter Křen from the Czech Metrology Institute who helped with calibration of the reference laser etalon.

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