OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 5, May 2007 p. 202 - 206

# Purity of iodine cells and optical frequency shift of iodine-stabilized He-Ne lasers

J. HRABINA[a,b], F. PETRŮ[a], P. JEDLIČKA[a], O. ČÍP[a], J. LAZAR[a]
[a]*Institute of Scientific Instruments, Academy of Science of the Czech Republic, Královopolská 147, 61264 Brno, Czech Republic*
[b]*Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2, 61669 Brno, Czech Republic*

In this paper we present an investigation of a set of short iodine cells designed to operate in the intracavity arrangement in iodine-stabilized Helium-Neon laser etalons. The cells were made over a longer period of time, their absolute optical frequencies were measured in international comparisons and their frequency shifts are compared here to independent measurement of iodine purity performed by measurement of induced fluorescence and evaluation by the Stern-Volmer formula. The manufacturing technology of the cells and the filling process is mentioned briefly and the arrangement for measurement of the induced fluorescence is described. The main goal of this effort is to recognize the limits of the absolute precision of the optical frequency of iodine transitions and look for further improvements in the iodine cell manufacturing technology that may lead to even smaller frequency shifts.

(Received October 24, 2006; accepted after revision April 5, 2007)

*Keywords*: Absorption cells, Frequency stability, Impurities estimation, Spectroscopy

## 1. Introduction

With the molecular iodine being still the cornerstone of laser frequency metrology not only the linewidth and signal-to-noise ratio is a subject of a significant investigation but also the search of the precision of the absolute values of central frequencies of the transitions is gaining importance. Frequency drifts can be reduced by control of pressure, temperature, laser power density and other quantities but an intrinsic offset associated with each absorption iodine cell is given by the iodine purity, and the cell once filled and sealed cannot be changed. This is a problem of absorption cell manufacturing technology which has great consequences.

In our group the absorption cell technology was developed over the past years and we put a great effort into achievement of the best purity of the cell before filling as well as of the iodine itself. Our iodine cells were made for many prestigious metrological laboratories in the world and are in use in various laser stabilized systems of the highest precision at different optical frequencies and in a large variety of detection and stabilization schemes: INM Paris, France, Bureau International des Poids et Mesures, France, Metrology Research Institute, Finland, Danish Institute of Fundamental Metrology, MPI fuer Quantenoptik, Germany, Physikalisch Technische Bundesanstalt, Germany.

The properties of an iodine-filled absorption cell are determined on one hand from the direct definition of the impurity volume, and on the other hand also from the possibility of verification of its function and limiting parameters in the final employment in a stabilized laser system. The volume of contaminating gases may be estimated directly from the technology process (the level of vacuum in the cell before filling or the quality of degasing). It is useful to have a chance to verify the filling process by an independent method at least for a feedback when improving the cell preparation. This independent data could help also when searching for the present offset of an iodine-stabilized laser system. There are several methods of the impurities estimation, such as the Hanle effect [1]. In case of very small levels of impurities it can be verified also by means of evaluation of Stern-Volmer formula [2,3] on the experimental basis. The technique based on the Stern-Volmer formula requires excitation of a selected transition in the molecular iodine and investigation of the level of induced fluorescence. We have chosen this technique also because it has been used by the Bureau International des Poids et Mesures (BIPM), to have a chance to compare our results. The fluorescence intensity here is limited by several relaxation processes such as ionization, predissociation and collisional quenching. The quenching – nonradiative transitions – can be caused by collisions with either iodine molecules or by collisions with molecules or atoms of impurities (foreign-gas quenching). The latter process is the one that reflects the purity by reduction of the lifetime of a state and can be evaluated by monitoring the level of spontaneous emission from the irradiated cell.

To measure the absolute level of fluorescence is not always an easy task. Problems include the drop of laser beam intensity along its propagation through the absorbing media, and the presence of stray light. It is thus useful to apply the normalized Stern-Volmer formula [4], where the

coefficient representing the pressure ratio of foreign gas and iodine depends only on the dependence of relative intensity and iodine vapor pressure. This gives the chance to compare measurements on iodine cells of various lengths and cross-sections.

## 2. Measurement of the level of induced fluorescence

The setup for measurement of fluorescence level is based on excitation of the molecular iodine at one of the strongest transitions which is close to 502 nm. This coincides with absorption lines in iodine characterized by a high sensitivity to collisional quenching that is caused by a long lifetime of the excited level [4]. The strongest absorption line within the spectral width of the laser is the R(26) 62-0 of the $^{127}I_2$ which contributes mostly to the measured fluorescence. An Argon-ion laser was used for this excitation, able to deliver up to 35 mW of the output power at this wavelength. The experimental arrangement is derived from [4]. Significant improvement had to be added due to the laser behavior influencing reproducibility of the measurement. The emission spectrum of the laser according to the output intensity varies from a near single-frequency operation up to chaotic multimode regime. Practical linewidth at the maximum output power exceeds 6 GHz. The instability of the multimode regime causes severe variations in the measured level of induced fluorescence because only small part of the emission spectrum coincides with the spectral profile of the R(26) 62-0 line. Moreover, operation of the laser close to its maximum output power resulted in more uniform distribution of power spectral density over the emission profile. To avoid saturation of the absorbing medium the output power was reduced by gray filters. The schematic of the assembly is given in Fig. 1.

We introduced an approach compensating both power fluctuation and varying power spectral distribution of the laser. The intensity detected by a photomultiplier at the cell under investigation consists of a useful signal arising from the induced fluorescence and partially also from stray light that cannot be suppressed completely especially in case of small cells. Both values are influenced by the laser power and spectral fluctuations. The stray light is proportional to the overall laser power while the fluorescence signal varies with total laser power and changes in the power spectral density as well.

To compensate both effects we introduced not only monitoring of the laser power with a photodetector but also a reference iodine cell with photomultiplier detection assembly identical to the measured cell. The reference cell is held at a constant cold finger temperature a little below the laboratory environment temperature during the whole measuring process and gives the information about the variations of laser power coinciding with the R(26) 62-0 line. To separate the value of the stray light level from the total signal we used cooling of the iodine cell cold finger with liquid nitrogen. This reduces the pressure of the iodine vapor down to the negligible level where no fluorescence could be detected. At this moment the photomultiplier detects only the stray light.

The whole assembly with the cell under investigation and with the photodetectors was enclosed in a black metal box to reduce the presence of any extra light. The laser beam was chopped by a mechanical rotating chopper running at 500 Hz. Both photomultipliers output signals are phase-sensitively demodulated to further suppress the presence of any external or stray light. Synchronization of the lock-in detector was derived from the auxiliary photodetector. The beam chopper being quartz-oscillator controlled and held in a phase-lock loop has shown too large phase jitter. Data acquisition and processing was performed by an analog/digital module with a controller and digital signal processor communicating with a control computer via a CAN bus. To eliminate the laser intensity noise we applied analog low-pass filtering with a cut-off frequency 0.1 Hz and a further digital filtering (averaging) over a period of 1 minute. The whole experiment was controlled by a PC computer able to adjust also the temperature controller. This allowed us to let the whole measurement run without personal presence. We performed around ten data acquisitions within an iodine temperature range from -10 $^{o}$C up to 20 $^{o}$C. Each time the temperature was changed at least a 5 minute delay was necessary for the settling of the iodine pressure.

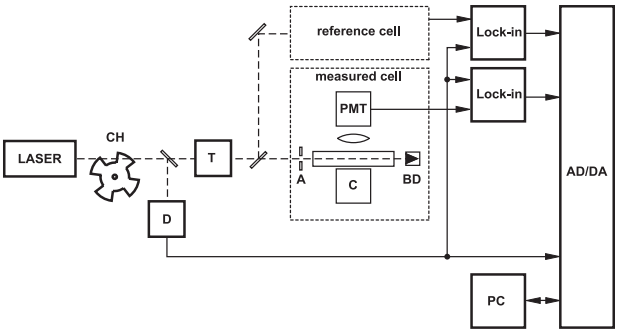


*Fig. 1. Experimental arrangement of the iodine excitation and fluorescence measuring apparatus. CH – chopper; PD – photodetector; T – telescope; A – aperture; PMT – photomultiplier; BD – beam dump; C – Peltier cooler with a radiator.*

## 3. Technology of iodine cell processing

The cells built at our institute are made of fused silica glass. This material allows perfect vacuum processing at a high temperature and thus additional releasing of gases 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 $^{o}$C with a special solder. This technology was preferred for the cells with Brewster angle windows.

Iodine cells with plane windows are 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 last layer is the $SiO_2$, the same material as

the cell tube itself. This was intended to avoid any possible contamination of the cell.

The iodine cell filling process starts with distillation of the iodine from a commercial form into vacuum ampoules. The first distillation is done while the tubing is vacuum pumped simultaneously. This first degree of distillation is a crucial one, when the iodine is purified from impurities adsorbed from its surface. The next distillation steps of the multistage process are performed only at vacuum between sealed ampoules with iodine and the impurities are removed by several types of molecular sieves. Finally the iodine is distilled into the evacuated and degased cell via a break-seal and the cell is sealed.

The iodine cells of our design we started to test on impurities are designed for operation in our compact iodine-stabilized He-Ne lasers with internal-cell design. They are short (75 mm long) to keep the laser with a short resonator and thus in a single-mode operation. In the configuration of the laser the cell has a bridge-like cold finger to get over the rear-mirror assembly together with the photodetector. These cells are equipped with Brewster-angle windows and are fixed into metal flanges attached to dust-free covers. The sketch of the cell configuration is given in Fig. 2 and photo in Fig. 3.

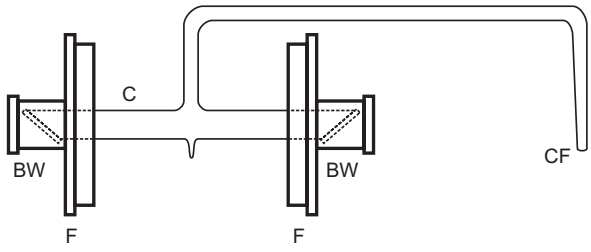


*Fig. 2. Iodine cell for intracavity operation in a He-Ne-iodine stabilized laser. C – cell body; F – steel flange; BW – Brewster angle window; CF – cold finger.*

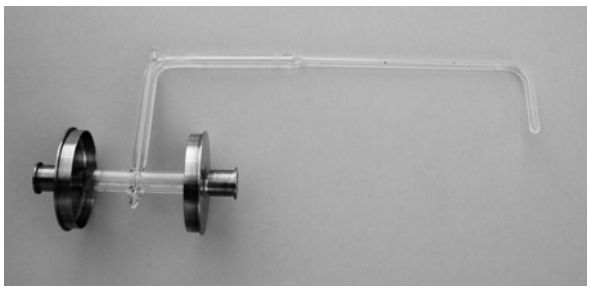

*Fig. 3. Photo of one of the iodine cells designed for iodine-stabilized He-Ne lasers and measured within this experiment.*

## 4. Results

We investigated a set of iodine cells of the type according to Figs. 2, 3 designed to operate in He-Ne stabilized lasers of our design [9] with an invar resonator body. These cells, respectively lasers were tested during international comparisons with full traceability to the BIPM standards [5,7,10,11,12]. The recordings of Stern-Volmer diagrams of the four selected cells are given in Fig. 4. Each of these cells was measured several times with both ascending and descending iodine temperature (pressure). No tendency to any hysteresis caused by measurement during heating or cooling was observed. The diagram shows good linearity and reproducibility of the slope for lower iodine pressures and tendency of smaller slope for higher pressures. This can be caused by linear absorption according to Beer's law while the observed region was not close enough to the entrance window. Similar effects were found by [4] and are stronger for high-purity iodine cells. The values of the Stern-Volmer diagram were calculated from the linear part of the diagrams representing approximately two thirds of the whole measured curves. The measurement of the cell no. 11 (ISI/11) was influenced partially by degradation of its output window which resulted in higher level of stray light and consequently in worse signal-to-noise ratio. Still recording of its Stern-Volmer diagram even at the limit of resolution showed very low level of the $K_0$ coefficient approximated at the 0.8 Pa level.

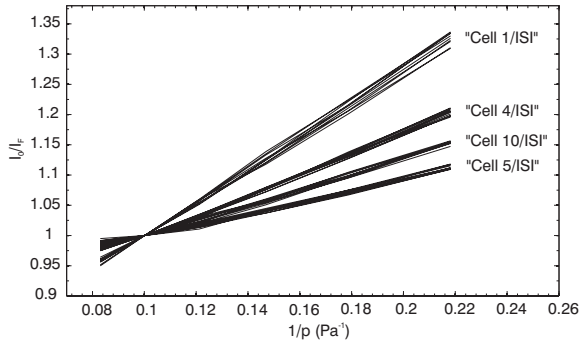


*Fig. 4. The Stern-Volmer diagrams of the set of iodine cells.*

The reproducibility of discrete measurements is shown in Fig. 5. Odd points in the line represent measurements with descending temperature (pressure) of iodine while even those with rising temperature. The solid lines represent here mean values of the Stern-Volmer coefficients $K_0$ and the dashed lines their standard deviations.

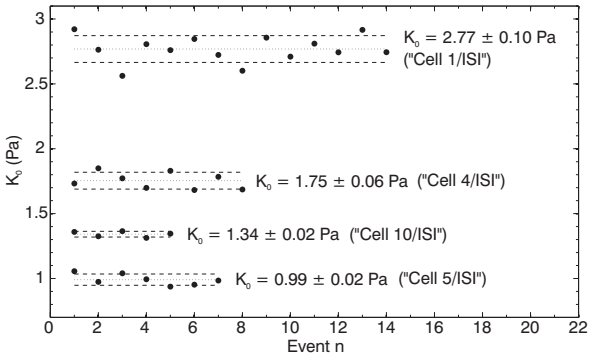


*Fig. 5. Recording of a set of discrete measurements of the $K_0$ coefficient representing the level of reproducibility. The solid lines represent mean values while the dashed ones their standard deviations.*

Values of the Stern-Volmer coefficient $K_0$ of the three cells with corresponding frequency shifts are shown in Table 1. The frequency shifts were measured during an international comparison of iodine stabilized He-Ne lasers held in Physikalish-Technische Bundesanstalt (PTB) Braunschweig, Germany [5], in Slovak Institute of Metrology (SMU) Bratislava, Slovakia [11] and in the Institute of Scientific Instruments in Brno, Czech Republic [7] where the stabilized lasers with these cells were compared to lasers with traceability to the BIPM standards. The set of measurements presented in Table 1 represents measurements in various conditions and in the period over several years. The frequency shifts on the kHz level are the resolution and reproducibility limit of the iodine-stabilized He-Ne lasers operating at the 633 nm. At least the relation between iodine cells 1/ISI and 11/ISI with comparison to the BIPM standards (BIPM 10 and BIPM 3, 4) reflect the direct influence of iodine purity to the frequency offset. High purity cell 11/ISI represents even positive shift compared to BIPM 3 and BIPM 4 (shift towards higher optical frequency) while the less pure 1/ISI cell is shifted towards lower frequencies.

*Table 1. Values of the Stern-Volmer coefficient $K_0$ with corresponding frequency shifts measured in comparison with various stabilized lasers. Negative frequency shifts represent shift towards higher frequencies.*

| Cell no. | Direct comparison | Freq. shift (kHz) | Measured $K_0$ (Pa) |
|---|---|---|---|
| 1/ISI | with PTB 3 | -4 | 2.77 ± 0.10 |
| | with BIPM 10 | -5.8 | |
| 4/ISI | | | 1.75 ± 0.06 |
| 5/ISI | | | 0.99 ± 0.04 |
| 10/ISI | with CSMU B2 | -7 | 1.34 ± 0.02 |
| 11/ISI | with BIPM 3 | +10.4 | ~0.8 |
| | with BIPM 4 | +8.5 | |

## 5. Conclusions

The main aim of this work was to assemble and to put into operation a laboratory setup which would allow us to monitor the iodine purity in our cells with another independent method. Mainly due to comparability of our results we decided for the Stern-Volmer formula method which was introduced by BIPM. Final absolute value of laser frequency stabilized by means of subdoppler spectroscopy of iodine vapour is of course influenced by various other factors and effects, physical as well as technical but the quality (purity) of the cell is the most crucial one. Once the cell is sealed there is no way to change it and this technique of monitoring of the level of impurities in iodine cells seems to be the only chance how to distinguish the factors influencing the frequency precision. The other parameters with direct relation to the absolute laser frequency shift are technical and can be measured and eliminated relatively easily, such as electronic offsets in the detection chain, iodine cell cold finger temperature, modulation amplitude, non-harmonic distortion of the modulation signal, etc.

Our effort is oriented toward the improvement of the iodine cell technology where the purity measurement is one of the ways to get the feedback from the independent source. Moreover, nowadays the frequency doubled Nd:YAG lasers stabilized to saturation spectroscopy in iodine reach the 10-14 limit of relative stability due to much better signal-to-noise ratio achievable at the 532 nm wavelength. From the metrological point of view not only relative stability matters but also the absolute frequency shift is a question. With the present-day iodine cell technology we need to be able to resolve the iodine impurity caused shifts well below the kHz limit. In our experiments the Stern-Volmer coefficient $K_0$ can be evaluated with a reproducibility on the few % level. Thanks to measurements made on older cells we show that with the relation between K0 and frequency shift of about 9 kHz/Pa (when the frequency shift between BIPM 10 and BIPM 4 is -3.1 kHz [10]) we achieved good agreement with [4]. The reproducibiliy of the impurity measurement gives us the chance to evaluate the future shift of new cells with the needed precision. Iodine cells made to operate in the Nd:YAG stabilized lasers have not yet been measured this way yet. We prepare now a comparison of the fluorescence based purity measurement data of these cells with absolute frequency shift measurements performed with a pair of Nd:YAG stabilized lasers where we expect to be able to resolve sub-kHz shifts and to further improve the cell technology to eliminate them.

**Acknowledgements**

The authors wish to express thanks for support to the Grant agency of the Academy of Sciences of the Czech Republic. This work was done within the grant project no. A200650504. It was supported also by Ministry of Education, Youth and Sports of the Czech Republic, project No.: LC06007 and by the Academy of Science of the Czech Republic, project No.: AV0 Z20650511.

## References

[1] W. R. C. Rowley, B. R. Marx, Verification of iodine cells for stabilized lasers using the Hanle effect, Metrol. **17,** 65-66 (1981).
[2] O. Stern, M. Volmer, Phys. Z. **20**, 183-188 (1991).
[3] F. Spieweck, Influence of small impurities in absorption cells of $I_2$ stabilized lasers upon their frequency, IEEE Trans. on Instrum. and Meas. **IM-34**, 246-248 (1985).
[4] S. Fredin-Picard, A study of Contamination in $^{127}I_2$ Cells Using Laser-Induced Fluorescence, Metrol. **26**, 235-244 (1989).
[5] F. Petrů, B. Popela, Z. Veselá, H. Darnedde, J. Helmcke, Intercomparison of $I_2$-Stabilized He-Ne Lasers (λ=633 nm) of the Institute of Scientific Instruments, CSSR, and the Physikalish-Technische Bundesanstalt, FRG, Metrol. **27**, 19-23 (1990).

[6] L. S. Ma, J. L. Hall, Optical heterodyne spectroscopy enhanced by an external optical cavity: toward improved working standards, IEEE Jour. of Quant. Electron. **26**, 339-347 (1990).

[7] F. Petrů, J. Lazar, O. Číp, G. Popescu, J.-M. Chartier, Frequency comparison of He-Ne/iodine lasers at 633 nm between the NILPRP and the ISI, and traceability through the BIPM, Metrol. **34**, 515-518 (1997).

[8] J. Lazar, O. Číp, Electronics for He-Ne-$I_2$ stabilized laser with digital control, Rev. of Sci. Instr. **68**, 3660-3665, (1997).

[9] F. Petrů, B. Popela, Z. Veselá, Design and performance of compact iodine stabilized He-Ne lasers at $\lambda$ = 633 nn with a short optical resonator, Meas. Sci. Technol. **4**, 506-512, (1993).

[10] J.- M. Chartier, L. Robertsson, M. Sommer, J. Tschirnich, V. Navratil, R. Gata, B. Pucek, J. Blabla, J. Smydke, M. Ziegler, V. Zeleny, F. Petru, Z. Vesela, K. Tomanyiczka, E. Banreti, Yu. G. Zakharenko, L. F. Vitushkin, International comparison of Iodine-stabilized Helium-neon lasers at $\lambda$ = 633 nm involving seven laboratories, Metrol. **28**, 19-25 (1991).

[11] V. Navrátil, A. Fodrekova, R. Gata, J. Blabla, P. Balling, M. Ziegler, V. Zeleny, F. Petru, J. Lazar, Z. Vesela, J. Gliwa-Gliwinski, J. Walczuk, E. Banreti, K. Tomanyiczka, A. Chartier, J.-M. Chartieret al., International comparison of He-Ne lasers stabilized with $^{127}I_2$ at $\lambda$ = 633 nm (July 1993 to September 1995), Metrol. **35**, 799-806 (1998).

[12] T. J. Quinn, Results of recent international comparisons of national measurement standards carried out by the BIPM, 1996, Metrol. **33**, 271-287 (1996).

*Corresponding author: shane@isibrno.cz