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Comb-assisted mercury spectroscopy in the deep-ultraviolet: towards the development of a new primary thermometer / Gravina, S; Clivati, C; Chishti, N A; Castrillo, A; Fasci, E; Bertiglia, F; Lopardo, G; Sorgi, A; Coluccelli, N; Galzerano, G; Cancio Pastor, P; Levi, F; Gianfrani, L. - In: JOURNAL OF PHYSICS. CONFERENCE SERIES. - ISSN 1742-6588. - 2439:1(2023). [10.1088/1742-6596/2439/1/012015]

Availability:

This version is available at: 11696/78760 since: 2024-02-09T11:12:20Z

Publisher:

IOP

Published

DOI:10.1088/1742-6596/2439/1/012015

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To cite this article: S Gravina *et al* 2023 *J. Phys.: Conf. Ser.* **2439** 012015

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Comb-assisted mercury spectroscopy in the deep-ultraviolet: towards the development of a new primary thermometer

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Abstract. We report on the development of a new primary thermometer based upon high-precision spectroscopy of mercury vapors in the deep-ultraviolet region for the practical realization of the new kelvin. The line profile of the $(6s^2)^1S_0 \rightarrow (6s6p)^3P_1$ intercombination transition of the ^{200}Hg bosonic isotope is observed with a high spectral fidelity using a coherent radiation source at 253.7 nm. This latter consists of a near-IR external cavity diode laser followed by a double-stage second-harmonic generation apparatus. Metrology grade UV spectroscopy is demonstrated by locking the diode laser to a self-referenced optical frequency comb synthesizer.

1. Introduction

Since 20 May 2019, the fundamental units of the International System (SI) are defined in terms of fundamental Physics constants, whose values have been fixed. Such a revolution was made necessary in order to assure the future stability of the SI [1, 2]. The implementation of the new definitions paves the way to the development of new methods and techniques, including those of quantum nature. The unit kelvin is linked to the Boltzmann constant, k_B , whose value has been set to 1.380649×10^{-23} J/K [3]. As it is well known, Doppler Broadening Thermometry (DBT) is a laser-based method that directly probes the thermal motion of the particles of a gaseous sample at the thermodynamic equilibrium [4]. In its best implementation, performed in a gas of acetylene, thermodynamic temperature determinations have been demonstrated with a global relative uncertainty of about 10 ppm [5].

Here, we report on the status of a new DBT experiment that is based upon the precise observation of the shape of the mercury intercombination transition $(6s^2)^1S_0 \rightarrow (6s6p)^3P_1$ at 253.7 nm, by using a comb-assisted laser spectrometer.

Past literature shows a few examples of DBT implementation in which an atomic sample has been used as thermometric substance. More particularly, low-pressure alkali-metal vapors, such



as rubidium and cesium, have been successfully tested [6, 7]. These atomic systems offer the advantage of the simple structure of their absorption spectra, especially when compared with those of polyatomic molecules. Furthermore, collisional perturbations of the absorption profile can be neglected, the vapour pressure being extremely small.

Mercury has a variety of favorable features for the aims of DBT. It is ideally suited for temperature measurements between 230 and 300 K, the vapor pressure ranging from 10^{-4} to 0.3 Pa, namely, orders of magnitude larger than that of Rb, K, or Sr in the same temperature interval. On the other hand, the pressure is small enough to completely neglect collisional perturbations to the line profile and, at the same time, sufficiently large to produce a measurable absorption signal in a compact gas cell, with a length of a few millimeters. Furthermore, mercury includes six stable isotopes, four of which having zero nuclear spin. In this respect, it is possible to exploit the possibility of probing a line with no hyperfine structure, thus leading to a further simplification of the spectral analysis of Doppler-limited profiles.

2. Method

DBT is based on the precise observation of the shape of a given atomic or molecular line in a gas at the thermodynamic equilibrium, in a laser-based absorption spectroscopy experiment, under the linear regime of radiation-matter interaction. The absorption process is described by the Beer-Lambert law, which relates the attenuation of a laser beam travelling into a gaseous medium to the properties of the gas, as it follows:

$$I(\nu) = I_0 e^{-NSLg(\nu-\nu_0)}, \quad (1)$$

where $I(\nu)$ is the intensity of the transmitted beam at frequency ν , ν_0 is the line center frequency, I_0 is the incident intensity, N is the gas density, S is the line strength, L is the absorption path-length and $g(\nu - \nu_0)$ is the line shape function, normalized to 1 by convention.

When the intensity of the probe laser is orders of magnitude smaller than the saturation intensity of the selected transition, the absorption profile is well described by a Voigt convolution, provided that the gas pressure is so small that collisional narrowing effects are totally negligible. This is the case of mercury vapors under the operation conditions of the present experiment. The thermodynamic temperature can be measured by retrieving the Doppler width and the absolute center frequency from a non-linear least squares fit of the experimental line profile and using the following equation:

$$T = \left(\frac{\Delta\nu_D}{\nu_0} \right)^2 \frac{Mc^2}{2\ln 2k_B}, \quad (2)$$

where $\Delta\nu_D$ is the Doppler half-width at half maximum (HWHM), c is the speed of light in vacuum and M is the absorbers' mass.

3. The UV spectrometer

The deep-UV spectrometer is schematically shown in figure 1. It is based on a coherent, continuous wave, tunable, UV source, whose detailed description is reported in [8]. Such a source essentially consists in a double stage of second-harmonic generation (SHG) of the single mode radiation from an external cavity diode laser (namely, the pump laser), this latter being mounted in the common Littrow configuration and emitting at 1014.8 nm.

The first-stage duplication (from 1014.8 nm to 507.4 nm) is performed in a fiber-coupled periodically-poled lithium niobate (PPLN) crystal in a waveguide. The produced green radiation seeds a high-power multi-mode diode laser at the same wavelength, namely the slave laser, for amplifying the optical power up to five times by injection locking. The second-stage duplication (from 507.4 nm to 253.7 nm) occurs through a 12 mm long β -barium borate (BBO) crystal,

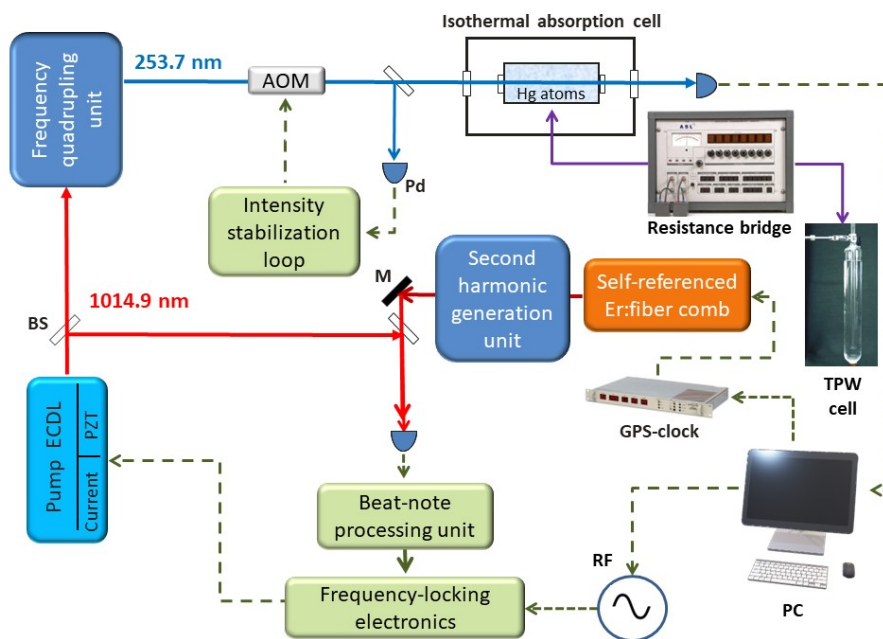


Figure 1. Sketch of the UV absorption spectrometer. AOM, acousto-optic modulator; BS, beam splitter; Pd, photodiode; M, mirror; RF, radio frequency synthesizer; PC, personal computer.

placed inside a bow-tie resonant cavity. The cavity is locked to the incoming beam through the Hänsch-Couillaud technique [9].

An intensity control feedback loop based on an acousto-optic modulator is implemented to stabilize the power of the probe laser beam. A portion of the first-order diffracted beam is sent to a 2-cm long quartz cell, in which low-pressure mercury vapors are in equilibrium with the liquid phase. The spectroscopic cell is placed inside a thermostatic chamber so that the gas temperature is actively controlled and stabilized within 0.05 mK at the triple point of water over a time span of several hours [10]. After the interaction with mercury vapors, the transmitted UV beam is focused on a preamplified SiC photodetector, whose responsivity is linear within the uncertainty of 0.004% (1σ) [11].

For the aims of DBT, the transmitted signal should be acquired while scanning the UV frequency around the intercombination transition of mercury so as to cover a frequency interval at least 3 times wider than the Doppler width of the line, namely, 3 GHz or larger. In the free-running mode of operation, by tuning the near-IR pump laser, it is possible to satisfy this requirement. Figure 2 shows an example spectrum that is obtained by means of a continuous, mode-hop free, frequency scan of the UV radiation over the ^{198}Hg , ^{200}Hg and ^{202}Hg line profiles, in coincidence with the intercombination transition. The weakest peak is perturbed by an hyperfine structure component of the fermionic isotope ^{201}Hg . The scan width is as wide as 16 GHz, which is a quite remarkable result for a sophisticated frequency chain like the one of this work. Frequency calibration of the spectrum is achieved by using the absolute center frequencies of the three Hg isotopes that are reported in [12]. Nonetheless, a calibration based on three points cannot be sufficiently accurate for a metrology grade experiment.

For this reason, a novel comb-locked configuration was implemented, using a self-referenced optical frequency comb synthesizer (OFCS, FC1500-250-WG, MENLO Systems) in conjunction to a second-harmonic generation unit [13]. More particularly, the highest wavelength portion

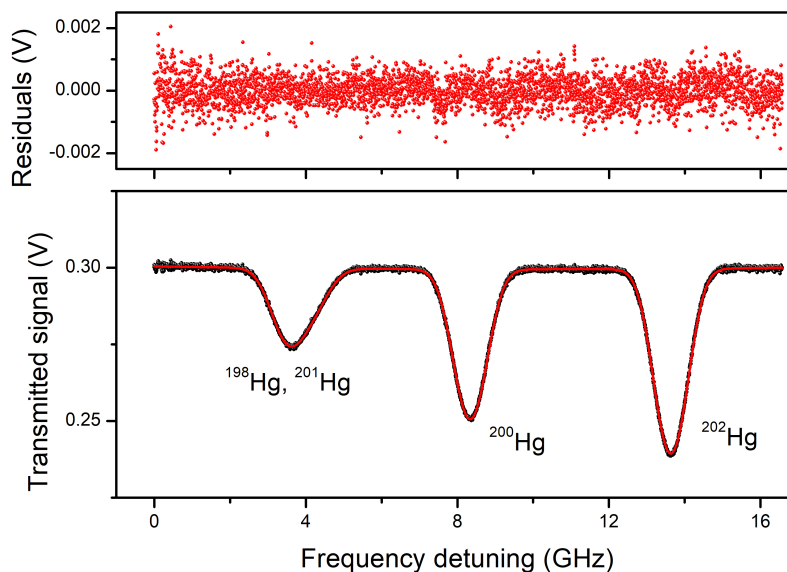


Figure 2. Absorption spectrum for mercury isotopes at 253.7 nm. The upper panel shows the absolute residuals, as a result of a nonlinear least-squares fit to Voigt convolutions.

of the comb was frequency-doubled so as to make it possible the comparison with the pump laser and the consequent observation of a beat note with a sufficiently high signal-to-noise ratio. After proper processing, the beat note was used to tightly lock the pump laser to the comb. It is worth mentioning that the comb repetition rate (f_{rep}) and the carrier-envelope offset frequency were stabilized against a GPS-disciplined rubidium clock. Highly accurate and reproducible frequency scans of the pump laser frequency were obtained by finely tuning the repetition rate. A scan of f_{rep} of 750 Hz yielded a frequency tuning in the near-IR of about 900 MHz, which translated into a 3.6-GHz wide scan in the UV domain. This is about a factor of 4 narrower than that achievable in the free-running mode. The current limitation is due to the locking electronics acting on the pump laser which do not support larger scans in the comb-locked configuration.

4. Results

Figure 3 displays a set of 20 repeated acquisitions of absorption spectra, as recorded at the temperature of the triple point of water across the intercombination transition of the ^{200}Hg isotope. Each Doppler-limited profile is recovered with 751 points that are obtained from a step-by-step tuning of f_{rep} with a resolution of 1 Hz. The total acquisition time for the entire set amounts to 1 hour. The signal-to-noise ratio (SNR) results to be about 250. The data set allowed us to determine the line center frequency with a precision of 2×10^{-10} , while the gas temperature could be retrieved with a relative statistical uncertainty of 1.1‰. It is clear that the noise level should be significantly reduced in order to approach an uncertainty smaller than 10 ppm. In this regard, a further optimization of the UV laser source will be necessary to lower the intensity noise. Furthermore, spectral averaging over several hours can be a viable solution that can be implemented by exploiting the frequency stability of the spectrometer. In figure 4 we report the outcome of spectral averaging over 20 consecutive scans. The signal to noise ratio is close to 1000. The Doppler width that is retrieved from the Voigt fit gives a thermodynamic temperature of 273.34 ± 0.11 K, the uncertainty being the internal error corresponding to 1σ .

This in good agreement with the set-point (273.16 K).

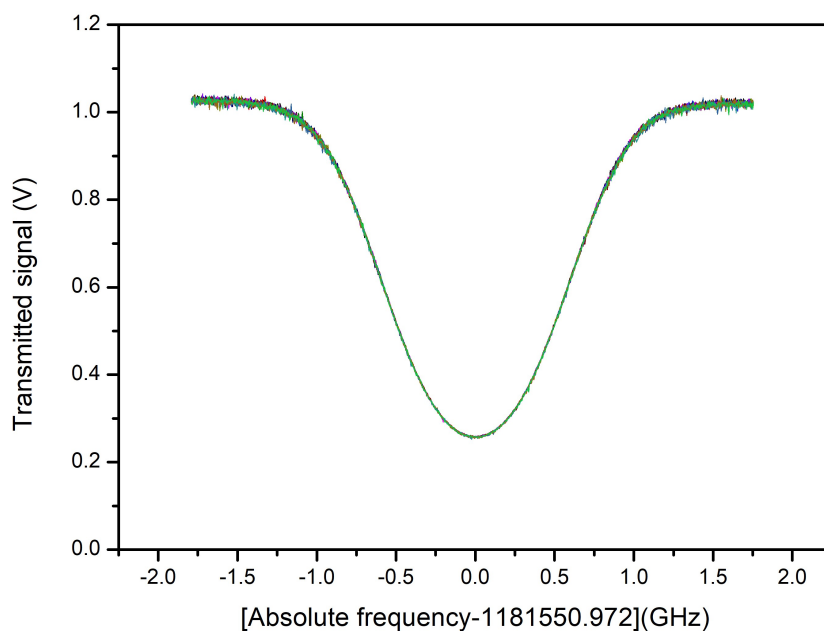


Figure 3. Plot of 20 repeated acquisitions of the ^{200}Hg absorption spectrum at 253.7 nm. The x-axis represents the absolute frequency as measured by means of the OFCS.

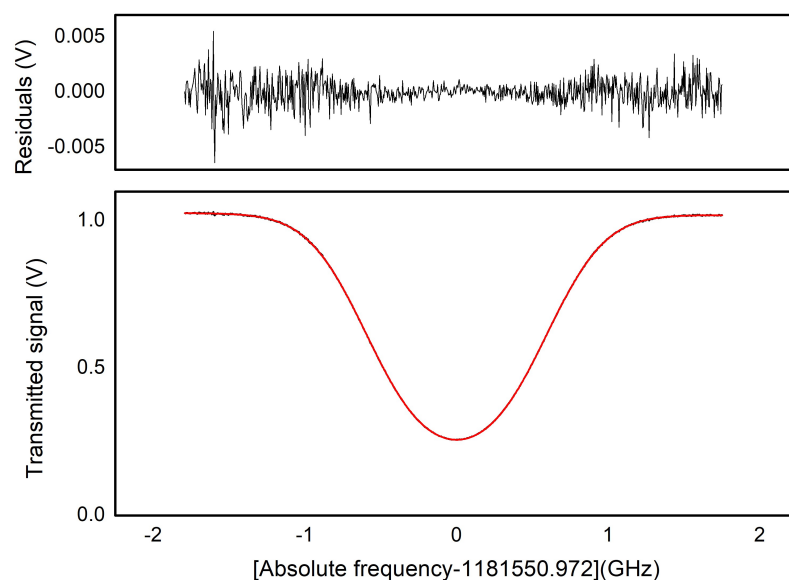


Figure 4. Example of spectral averaging over 20 consecutive scans. The upper panel shows the absolute residuals resulting from a nonlinear least-squares fit to a Voigt profile.

5. Conclusion

We have reported on the recent progress regarding the development of a new primary thermometer based upon Doppler-broadened precision spectroscopy of mercury atoms at 253.7 nm. The apparatus is based on a frequency chain that links the UV domain to the near-IR region. We have demonstrated highly-accurate and reproducible frequency scans around the Hg line by direct referencing of the near-IR pump laser to an optical frequency comb synthesizer and tuning the comb repetition rate. The results of the first test experiment are very encouraging and stimulate further work to be done to pursue the goal of a low-uncertainty realization of the new kelvin.

Acknowledgments

This research was supported by the Italian Ministry for University and Research (Program type PRIN 2015) and by Università degli Studi della Campania “Luigi Vanvitelli” within the V:ALERE program (Call published in 2019, Project V:ANS).

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