Frequency reference in the 732-nm region for precision laser spectroscopy of muonium

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Abstract. A search is performed for a frequency reference in the 732-nm region, which is required to calibrate a laser spectrometer in experiments on precision measurements of the $1S - 2S$ transition frequency in muonium. The adequate reference is found in the absorption spectrum of molecular iodine vapours heated to $600°C$. The reference frequency is less than 1 GHz away from the required spectrometer frequency tuned to the resonance in muonium.

1. Introduction

Precision measurements of the transition frequencies in one-electron atoms such as hydrogen and deuterium, as well as in exotic atoms of the type of muonium, positronium, etc., for which the transition frequencies can be exactly calculated, open up the possibilities for precision measurements of one of the fundamental physical constants — the Rydberg constant, and also for measurements of isotopic and relativistic shifts and verification of fundamentals of quantum electrodynamics [1, 2].

Experiments on precision laser spectroscopy of the hydrogen atom have been started as early as 1975 [3], and at present the accuracy of measurement of the transition frequency exceeds that of theoretical calculations [4]. Interest in muonium is explained first of all by the fact that its energy levels can be theoretically calculated more exactly than in hydrogen. Insufficient information on the size and structure of a nucleus in the hydrogen atom presents the main obstacle to the improvement of the accuracy of calculations of the energy levels in hydrogen. A nucleus in muonium represents a lepton particle, which has no inner structure upon detection with an accuracy of 10^{-18} m; therefore, the restriction on the possibility of calculating energy levels with a higher accuracy is removed.

The first laser spectroscopy measurements of muonium [5] have been performed using a 488-nm pulsed dye laser. The second harmonic of this laser was used to observe two-photon resonance at the $1S - 2S$ transition. The systematic error of the frequency measurement in this experiment

was 46 MHz. The error was mainly caused by the dynamic Stark shift and the chirp generated by a pulsed amplifier. To reduce the influence of these factors, a new spectrometer based on a cw Ti:sapphire laser and a pulsed alexandrite amplifier was used in the next experiments. This spectrometer can operate with pulses that are longer by a factor of $5 - 6$ than pulses used earlier; therefore, the effects resulting in systematic errors should be weaker by $5 - 6$ times.

The third harmonic of the 732-nm Ti : sapphire laser provided the emission at 244 nm required for observing the two-photon resonance at the $1S - 2S$ transition of muonium. To precisely tune the laser frequency to the two-photon absorption line of muonium and to measure exactly the $1S - 2S$ transition frequency, one should have the frequency standard in the emission region of the Ti : sapphire laser. Because experiments with muonium are performed on an accelerator, they are restricted in time and require highly reliable measurement systems. For this reason, to simplify the frequency measurement, it is desirable that the standard frequency would differ from the measured frequency no more than by 1 GHz. This rather strict requirement substantially decreases the probability of finding a proper frequency reference.

The aim of this work is to find absorbing media and absorption lines that could be used as references for the development of a frequency standard, to study the reference chosen, to observe the saturated absorption resonance on the line chosen, and to stabilise the frequency by the resonance.

2. Search for the frequency reference

The frequency reference that is intended for the use in precision spectroscopy of muonium should satisfy the following requirements. The reference frequency should be equal to $1/6$ of the $1S - 2S$ transition frequency, i.e., 409254.7 ± 1 GHz, which corresponds to the wavelength 732.5325 ± 0.0018 nm. The instability and the error of reproducibility of the reference frequency should be no worse than 10^{-11}. In the spectral range under study, the most intense absorption lines belong to rovibronic transitions of some molecules.

Kremser et al. [6] have demonstrated the possibility of using absorption lines of molecular iodine heated to $500°C$ as frequency references in the 800-nm region. Because the absorption lines of I_2 in this spectral range correspond to transitions from highly excited vibrational levels of the ground electronic state, it is necessary to heat the I_2 vapour to achieve the acceptable population of these levels that provides the noticeable absorption.

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We chose for studies first of all diatomic molecules. They have spectra consisting of many well-resolved lines, whereas polyatomic molecules exhibit continuous broad absorption bands due to the overlap of their spectral lines. The systematic data on spectroscopic constants of diatomic molecules, from which the positions of absorption bands can be approximately determined, are presented, for example, in [7]. Based on these data, we chose for our studies diatomic molecules I_2, Br_2, Bi_2, Sb_2, IBr, ICl and polyatomic molecule CF_3NO, which has the absorption band in the spectral region of interest to us.

A detailed analysis of spectroscopic parameters of these molecules showed that for most of the molecules, except I_2, the accuracy of the spectroscopic constants taken from the literature is inadequate for calculations of the transition frequency with the accuracy required for the frequency reference (lower by one-two orders of magnitude). For this reason, we performed a spectroscopic study of these molecules using a laser spectrometer.

2.1. Linear absorption laser spectrometer

To identify the spectral lines reliably, it is necessary to record the spectrum containing a sufficient number of lines. For most of the molecules under study, this condition can be satisfied if the spectrometer provides a continuous scan within several tens of gigahertz. The spectrometer resolution should provide the recording of individual Doppler-broadened lines. Finally, the spectrometer should provide the measurement of the individual line frequency with an accuracy of no worse than 0.01 cm^{-1}. We made such a spectrometer based on a single-frequency tunable Ti : sapphire laser. Fig. 1 shows the schematic of the spectrometer. We used a home-made Ti : sapphire laser with a conventional ring cavity. A three-plate Lyot filter was used for tuning to the required frequency. Single-frequency lasing was achieved with the help of an intracavity etalon with an air gap. The laser frequency was tuned within ~ 40 GHz by varying the voltage on the etalon piezoelectric ceramics. The single-frequency output power at 732 nm was 0.5 W. The laser linewidth in the free-running mode did not exceed 1 MHz.
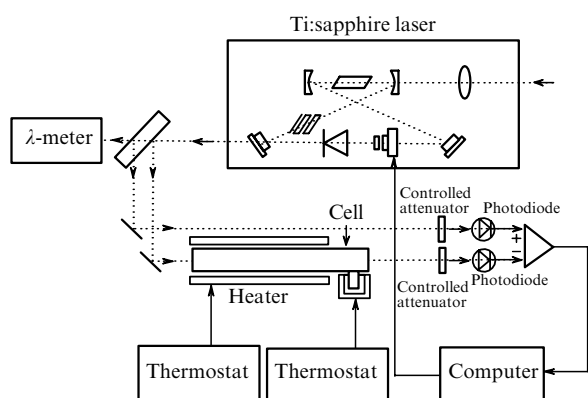

Figure 1. Schematic of a linear absorption laser spectrometer.

Absorption measurements were performed by splitting the Ti : sapphire laser beam into two beams of equal intensities. One of the beams passed through an absorbing cell and another bypassed it. The intensities of both beams at photodetectors were equalised in the absence of absorption

in the cell with the help of controlled attenuators. The output signals from photodetectors were amplified by a differential amplifier. The difference signal appearing in the presence of absorption in the cell is proportional to absorption.

The absorption spectrum was recorded by tuning the laser frequency by varying the control voltage on a piezoelectric element of the intracavity etalon. The laser frequency was computer-controlled by forming the control voltage according to the specified program. Both the spectral region and rate of the frequency scan could be varied in a broad range. It was also possible to supply an alternate voltage with a frequency of 50 Hz and to observe the spectrum on the oscilloscope. Upon the etalon tuning, the laser frequency changed not continuously but in steps because of the hops between modes. The step was equal to the mode interval of the laser cavity and was about 300 MHz. The stepwise tuning did not prevent obtaining the total spectrum because typical linewidths were a few times larger than the step width.

The wavelength was measured with a λ-metre based on a three-base Fiseau interferometer and a photodiode array for the interferogram detection. The λ-metre was preliminary calibrated using a 0.63-μm He–Ne laser stabilised to the Lamb dip whose wavelength was determined with an accuracy of 10^{-7}. The accuracy of the λ-metre was checked by measuring the wavelengths of the known lines of neon using an optogalvanic cell, as well as by measuring the known lines of molecular iodine. The wave numbers of the lines of I_2 measured with an accuracy of 2.5×10^{-7} are presented in the atlas [8]. The results of our measurements coincided with these data within ± 150 MHz. Based on this comparison, we estimated the error of our measurements as ± 200 MHz. Because of a nonlinear dependence of the wavelength on the voltage across the piezoelectric ceramics, it was impossible to measure exactly the wavelength of the individual absorption line from the spectrogram. For this reason, we measured the wavelength of each line in a separate experiment by tuning the laser frequency to the maximum of this line.

Most of the substances under study are very chemically active. To fill cells with these substances, we made a glass vacuum system with Teflon valves. All the substances, except IBr, were studied ready for use. IBr was prepared directly inside the vacuum system and was contained in a separate reservoir connected with the vacuum system. It was used, if necessary, to fill the absorbing cell.

Cells were made of quartz tubes of diameter 15 – 25 mm and length from 30 to 60 cm. At the ends of the tubes, quartz windows were welded. Before filling with the substance under study, cells were carefully degassed by heating at 900 °C for several hours and were evacuated to a pressure of about 10^{-5} Torr. After the cell sealing off, the vapour pressure in it was controlled by varying the temperature of its walls and of a special side arm whose temperature was lower than that of the cell walls. The temperature of the cooled side arm was regulated and maintained constant using a special Peltier thermostat made by us. The temperature of the side arm was kept constant with an accuracy of 0.1 °C.

2.2. Study of the linear absorption spectra

At the first stage of our study, we determined the presence of the absorption lines near the specified frequency. The spectra were observed on the oscilloscope screen. The substances that exhibited the absorption lines located close to the specified frequency were studied in more detail. We recorded their spectra and accurately measured frequencies of the maxima

of absorption lines. As a result, we chose molecules IBr and I_2 as candidates for the role of the frequency reference. Note that we considered the IBr molecule as more promising because it exhibited a sufficiently strong absorption at room temperature of the cell walls.

In the first experiments, the absorption spectrum of IBr was measured in a sealed cell. However, we found that Br_2 was formed in the cell with time, probably, due to photodissociation of IBr. For this reason, the cell was later connected to a vacuum unit and was evacuated before each measurement and then was filled again from a reservoir by vacuum distillation of the IBr vapour to the cooled side arm.

Fig. 2 shows the absorption spectrum of IBr measured in a 60-cm cell at room temperature of the cell walls and side arm. The arrow indicates the frequency equal to 1/6 of the $1S - 2S$ transition frequency in muonium. One can see that there is a weak absorption line near the required frequency, whose maximum is 300 ± 200 MHz away from the muonium line frequency. Using the data from Ref. [9], we assigned this line to the $R(64)23 - 2$ transition in the $A^3\Pi_1 \to X^1\Sigma^+$ electronic system of the $^{127}I^{79}Br$ molecule. Unfortunately, we could not measure the IBr vapour pressure in the cell because we failed to find the reliable data on the IBr saturated vapour pressure.
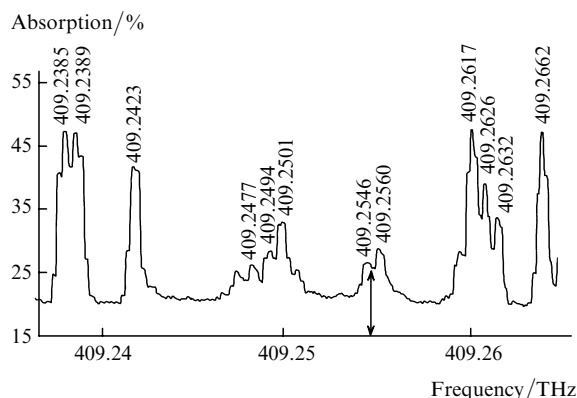

Figure 2. Linear absorption spectrum of IBr in a 60-cm cell at the temperature of the cell walls and the side arm equal to $21\,^\circ$C. The arrow indicates the required frequency of the spectrometer tuning to the two-photon resonance in muonium.
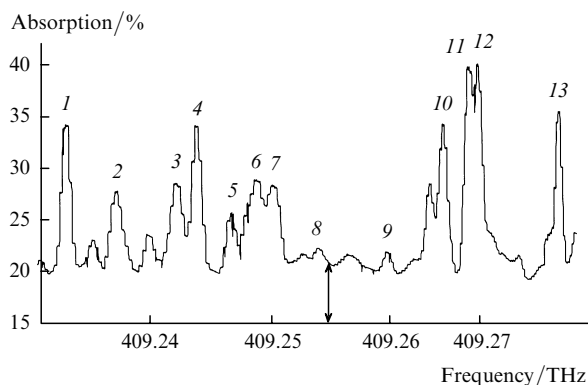

Figure 3. Linear absorption spectrum of I_2 in a 60-cm cell at the temperature of the cell walls and the side arm equal to $41\,^\circ$C (see Table 1). The arrow indicates the required frequency of the spectrometer tuning to the two-photon resonance in muonium.

The cell with I_2 was analogous to that with bromide. The vapour pressure in the cell was determined by the temperature of the cooled side arm. Fig. 3 shows the linear absorption spectrum of I_2 recorded at the temperature of the cell walls equal to $600\,^\circ$C and the temperature of the side arm equal to $41\,^\circ$C. This temperature of the side arm corresponds to the iodine vapour pressure $p = 1.1$ Torr, which is calculated from the expression [10]

$$\lg p = 9.7522 - 2863.54(273 + t - 19)^{-1},$$

where pressure is measured in Torr and the temperature t in Celsius degrees.

Table 1 presents the measured frequencies of the line maxima and, for comparison, the frequencies of these lines taken from the atlas [8]. One can see that our measurements are in good agreement with the data from the atlas. Fig. 3 shows that the nearest strong lines of I_2 are almost 10 GHz away from the required frequency and there is only very weak adjacent line at a distance of 1.1 ± 0.2 GHz. Using the data from Ref. [11], we assigned this line to the $R(26)5 - 13$ transition in the $B^3\Pi_{ou}^+ \to X^1\Sigma_g^+$ electronic system. One can see from Fig. 3 that absorption in this line is a sum of two components: a nonselective part (background) α_{ns} and a selective part α_s. We find from Fig. 3 for the $R(26)5 - 13$ line that $\alpha_{ns} = 0.37$ m^{-1} Torr^{-1} and $\alpha_s = 0.04$ m^{-1} Torr^{-1}. The parameters of this absorption line are very close to those of the $R(127)11 - 5$ line that is used to stabilise the 633-nm He – Ne laser. Indeed, according to Ref. [12], for this line, $\alpha_{ns} = 0.5$ m^{-1} Torr^{-1} and $\alpha_s = 0.038$ m^{-1} Torr^{-1}.

Table 1. Absorption lines of I_2.

The line number in Fig. 3	Measured in this paper frequency/THz	Measured in [8] frequency/THz
1	409234.0	409234.07 ± 0.15
2	409237.5	–
3	409242.6	–
4	409244.0	409244.14 ± 0.063
5	409246.8	–
6	409248.6	–
7	409250.3	–
8	409253.5	–
9	409259.6	–
10	409265.4	409265.27 ± 0.145
11	409267.8	409267.91 ± 0.081
12	409269.0	409269.14 ± 0.090
13	409277.6	409277.87 ± 0.078

3. Study of the hyperfine structure of the absorption line

The linewidth of the observed spectral lines of I_2 and IBr is of the order of $1 - 1.5$ GHz. These lines are superpositions of the overlapped Doppler profiles of the components of the hyperfine structure, which is caused by the interaction of the nuclear electric quadrupole moment and spin with the molecular rotation. The number of the components depends on the total moment and is equal to 15 or 21 for I_2, if the rotational quantum number is even or odd, respectively [13, 14]. The hyperfine structure of IBr is more complex; it contains 24 strong components and many weak components [15].

As a frequency reference, the saturated absorption resonances of the individual hyperfine structure components can be used. We constructed an ultrahigh resolution spectrometer for obtaining and studying such resonances. The schematic of this spectrometer is shown in Fig. 4. The spectrometer is based on the Ti: sapphire laser. Because the linewidths of saturated absorption resonances can be of the order of 1 MHz, the laser linewidth should be substantially smaller than this value. The laser line was narrowed by stabilising its frequency by the resonance of an external interferometer. The error signal was obtained by scanning the central frequency of the interferometer resonance with a frequency of 90 kHz with the help of a piezoelectric element on which one of the interferometer mirrors was mounted.
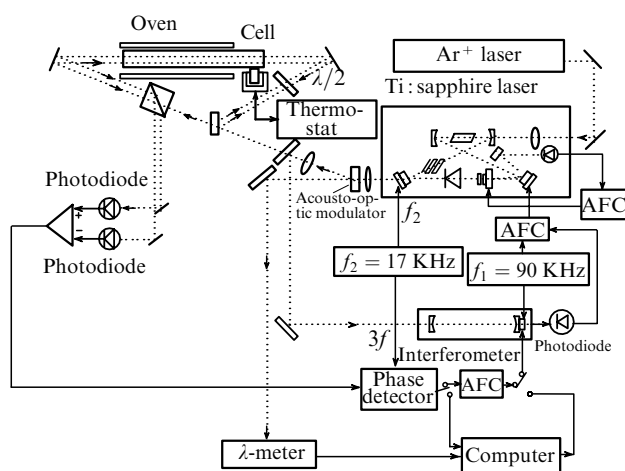

Figure 4. Schematic of a saturated absorption laser spectrometer.

To study the line structure inside the Doppler profile, the laser should be continuously tuned at least within the linewidth, i.e., within ± 1.5 GHz. This was accomplished by automatically tuning the intracavity etalon frequency to the laser frequency. As a result, when the laser frequency was tuned, the intracavity etalon frequency was synchronously tuned due to the displacement of one of the cavity mirrors with the help of the piezoelectric element. The error signal for the system of automatic etalon tuning was generated by scanning the etalon frequency at a frequency of 4.5 kHz. The laser was continuously tuned within 1.2 GHz, this range being determined by the piezoelectric element used. Because the laser frequency was locked to the external interferometer frequency, the frequency tuning was performed by varying the control voltage across the piezoelectric element of the external interferometer.

The optical resonances were obtained by the method of saturated absorption, which is based on the interaction of the strong and weak counter-propagating waves with the absorbing medium. A powerful saturating beam and two weak probe counter-propagating beams formed after reflection from a plane-parallel quartz plate passed through an absorbing cell. The polarisation of the probe beams was rotated by an angle of $90°$ with the help of a $\lambda/2$ plate. For this reason, the probe beams emerging from the cell were reflected from the Polaroid face. One of the beams was made exactly coincident with the saturating beam and experienced absorption saturation produced by this beam at the centre of the Doppler line. The second beam passed

near the first one and experienced only unsaturated absorption. The difference between the signals detected by photodetectors was proportional only to the saturated part of the absorption.

The detection scheme used by us reduced fluctuations of the laser output approximately by $10 - 20$ times. The saturating beam power in the cell was $50 - 100$ mW and that of the probe beams was about 1 mW. Strong and weak beams were focused to the centre of the absorbing cell. The diameter of the beam waist was about 0.5 mm. The saturated absorption signal was obtained by modulating the laser frequency by supplying the alternate voltage at a frequency of 17 kHz to the piezoelectric element of one of the laser mirrors. The useful signal was detected at the third harmonic of the modulation frequency. This excluded the influence of spurious modulation of the laser power, which appears upon frequency modulation. An acousto-optic modulator operating at a frequency of 160 MHz was used to decouple the laser from the interferometer and the optical scheme.

The saturated absorption spectrum was recorded by tuning the laser frequency by varying the control voltage supplied from a computer to a piezoelectric element of the external interferometer. The measured output signal from a synchronous detector was proportional to the third derivative of the Lamb dip at the centre of the Doppler absorption line. The signal was detected with the computer and was displayed on the monitor. To calibrate the frequency scale more accurately, the transmission signal of the Fabry – Perot interferometer was recorded simultaneously with the absorption signal.

Using this spectrometer, we obtained and recorded the saturated absorption spectra of the hyperfine structure of IBr and I_2. Fig. 5 shows the saturated absorption spectrum of the IBr molecule for the line whose frequency is most close to the required reference frequency. The spectrum was recorded at room temperature of the walls of a cell containing IBr and the side arm cooled to $-14°C$. The preliminary studies showed that the signal-to-noise ratio increased with decreasing temperature of the side arm and, hence, with decreasing the vapour pressure in the cell. Fig. 5 distinctly demonstrates individual resonances. The repeatability of the spectrum upon repeated recording confirms that this is not noise. The characteristic feature of the spectrum is the presence of many incompletely resolved resonances and the low signal-to-noise ratio.

Another picture was observed for I_2. Fig. 6 displays the spectrum of the $R(26)5 - 13$ line. We obtained good signal-
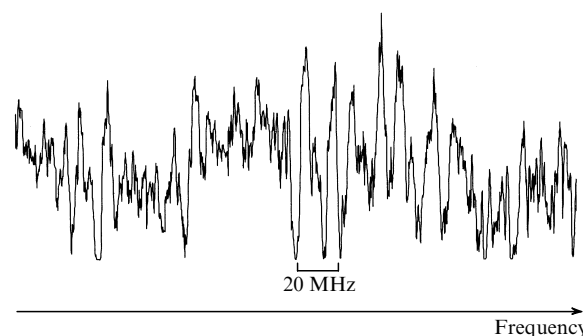

Figure 5. Saturated absorption spectrum of the hyperfine structure components of the $R(64)23-2$ line of the IBr molecule at the temperature of the cell walls and of the side arm equal to $21°$ and $-13°C$, respectively.

to-noise ratio even for such a weak line. The spectrum was recorded at the cell temperature of 600°C and the side arm temperature of 35°C. The amplitude of the frequency deviation was 15 MHz. Comparison of the spectra of hyperfine structure lines of the two molecules shows that the I_2 molecule has definite advantages over IBr. The signal-to-noise ratio in the spectrum of I_2 is substantially greater and the spectrum exhibits separate well resolved resonances. For this reason, we have chosen I_2 as an absorbing medium for the frequency reference. As the frequency reference, an extreme single resonance in the high-frequency part of the spectrum can be used. It is located approximately 400 MHz away from the line centre and its frequency is equal to 409253.9 ± 0.2 GHz.

Thus, the frequency of the found reference differs from the required frequency less than by 1 GHz and, hence, satisfies the imposed requirement. The resonance width is about 10 MHz and is mainly determined by collision broadening.
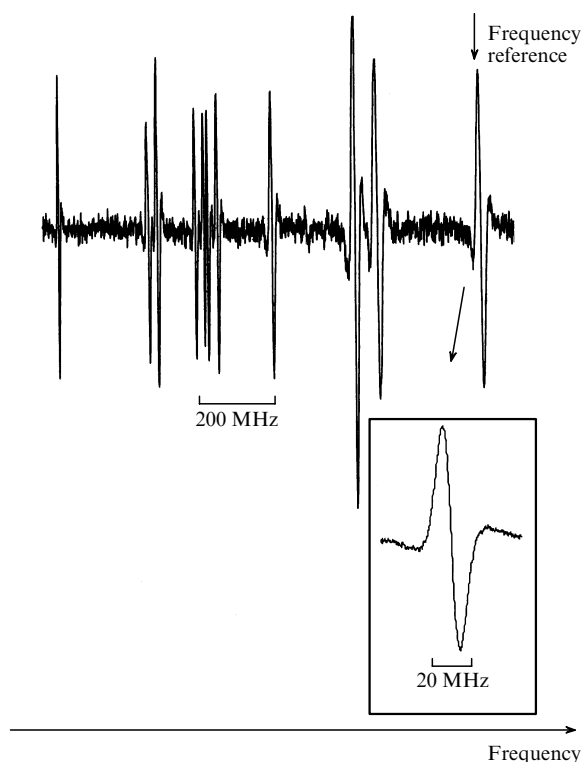

Figure 6. Saturated absorption spectrum of the hyperfine structure components of the $R(26)5-13$ line of the I_2 molecule at the temperature of the cell walls and of the side arm equal to 600 and 35°C, respectively. The insert shows the shape of the resonance chosen as a frequency reference on a larger scale.

The Ti:sapphire laser frequency was locked to the reference using the system of automatic frequency tuning. Our estimates showed that for the signal-to-noise ratio obtained, the frequency instability can be no worse than 10^{-10}. To elucidate the influence of various physical and technological factors on the reproducibility of the laser frequency, special investigations are required.

However, many characteristics can be quite reliably predicted in advance because molecular iodine is extensively used and well studied as an absorbing medium for laser stabilisation. The dependence of the frequency shift on the

iodine vapour pressure has been studied at the wavelengths of 514 [16], 532 [17], 612 [18], 633 [19], 640 [20], and 790 nm [6]. The typical values lie in the range from 0.17 to 1 MHz Torr^{-1} for the iodine vapour pressure between 0.015 and 0.53 Torr at the temperature of the cell walls from +20 to +500 C. For the saturated vapour pressure at 41°C, we have $dp/dt = 84.2$ mTorr K^{-1} and, hence, $dv/dt = 14.5 - 84$ kHz K^{-1}.

Therefore, if the temperature of the cooled side arm is stabilised with an accuracy of no worse than ±0.5, the error of the frequency reproducibility caused by the pressure-induced frequency shift can be no worse than ±40 kHz or in the relative units 10^{-10}. The frequency shift caused by variations in the cell walls temperature does not exceed 0.2 kHz K^{-1} [19]. If we take into account that the instability and the error of the reproducibility of the frequency of the 633-nm He $-$ Ne/I_2 laser achieved at present are equal to 10^{-12} and 10^{-11}, respectively, and that the parameters of the frequency reference found in this work and the reference used to stabilise a He $-$ Ne laser are close, we can expect that the reference found here will possess the same instability.

4. Conclusions

We have found the frequency reference in the 732-nm region, whose frequency differs less than by 1 GHz from the frequency of tuning of a laser spectrometer to the two-photon resonance in muonium. The suitable absorption line has been found in the absorption spectrum of the molecular iodine vapour heated to 600°C. As a frequency reference, we have chosen an extreme high-frequency component of the hyperfine structure of the $R(26)5 - 13$ line of the $B \to X$ electronic transition in the $^{127}I_2$ molecule. The spectroscopic parameters of this line are similar to those of the $R(127)11 - 5$ line, which is used to stabilise the frequency of the 633-nm He $-$ Ne laser. This suggests that the instability and the error in the reproducibility of the frequency of the laser stabilised with the help of the frequency reference found in this study can be of the same order of magnitude as for the 633-nm He $-$ Ne laser, i. e., about 10^{-11}.

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