Absolute frequency measurement for the emission transitions of molecular iodine in the 982 – 985 nm range

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Abstract. **We report high-precision frequency measurements of the separate hyperfine structure (HFS) components of the emission B–X system transitions of $^{127}I_2$ molecules in the 982 – 985 nm range. To resolve the HFS of the emission lines, advantage was taken of the method of three-level laser spectroscopy. The function of exciting radiation was fulfilled by the second harmonic of a cw Nd : YAG laser, and the probe radiation in the 968 – 998 nm range was generated by an external-cavity diode laser. The output Nd : YAG laser frequency was locked to an HFS component of the absorption transition and the probing laser radiation to the emission transition component. When both frequencies were locked to HFS components with a common upper level, the output diode laser frequency was precisely equal to the emission transition frequency. The output frequency of the thus stabilised diode laser was measured with the help of a femtosecond optical frequency synthesiser based on a Ti : sapphire laser. We present the results of the absolute frequency measurements of 20 HFS components belonging to six vibrational–rotational transitions of the B–X system of iodine [R56(32–48)a1, P58(32–48)a1, P85(33–48)a1, R87(33–48a1, R88(33–48)a10] and all 15 components of the R86(33–48) line. The relative measurement uncertainty is equal to 7×10^{-10} and is determined by the frequency instability of the diode laser radiation.**

1. Introduction

It is well known that the hyperfine structure (HFS) components free from Doppler broadening are excellent reference lines for stabilising the output frequencies of lasers in the 500 – 650 nm range. On heating iodine vapour to a temperature of 600 – 700 °C, the range may be extended to 900 nm [1, 2]. In the 500 – 900 nm range it is possible to obtain $\sim10^6$ frequency references which are not broader than 1 MHz and provide a relative frequency instability down to 10^{-14} and a reproducibility of at least 10^{-12}.

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In 1983 the first absolute frequency measurements were made of two iodine transitions with wavelengths of 576 nm [$^{127}I_2$ 17 – 1 P(62)] and 633 nm [$^{127}I_2$ 11 – 5 R(127)g] [3, 4]. The measurement precision was equal to $\sim10^{-10}$. Subsequently the high-precision measurements of iodine transition frequencies were carried out systematically. Measurements were made of the absolute frequencies of individual HFS components as well as of the frequency intervals between them. The results of these measurements were reported in a large number of papers. A comprehensive bibliography on this subject (prior to 2007) was given in Refs [5 – 7].

The objective of the research performed was to improve the precision of determining the spectroscopic parameters for the B–X band of molecular iodine. The improved parameters in turn make it possible to calculate with a high precision the frequencies of any transitions of this band. As a result, the iodine absorption spectrum may fulfil the function of a frequency scale, with which it is possible to calibrate laser frequencies to at least $\sim10^{-9}$. The high-precision experimental data are also of considerable interest in studying various subtle physical processes concerning intramolecular interactions in the iodine molecule as well as in other diatomic molecules.

In Refs [5, 6] the first attempt was made to systematize the data of all measurements performed by that time and to calculate on their basis the improved spectroscopic parameters of iodine molecules for at least a limited spectral domain. Two different models were employed to determine the spectroscopic parameters. One of the models permitted obtaining the parameters that furnished a high precision in determining transition frequencies, though in a limited domain for which there was a sufficient amount of high-precision experimental data. Specifically, for the 775 – 815 nm range, in which a large number of transition frequencies were measured to much better than 80 kHz, the resultant parameters enabled calculating the transition frequencies accurate to 200 kHz. In the second model, use was made of the whole body of available experimental data. Relying on these data, improved potential curves were constructed for X and B states, and spectroscopic parameters were determined, which enabled calculating the energies of vibrational–rotational levels of these states. This model permitted determining transition frequencies in a substantially broader range, though with a lower precision. The parameters derived were shown to assure a frequency determination accuracy of about ±3 MHz for the 526 – 667 nm range. The data of measurements carried out more recently provided the basis for the further elaboration of the models in use and for the derivation of more precise spectroscopic parameters [8 – 10].

As follows from the foregoing, to make possible the use of entire iodine absorption spectrum as a frequency reference

scale requires executing high-precision measurements for the remaining parts of the spectrum. We believe that similar high-precision measurements should also be performed for iodine emission transitions in the B−X band. The point is that the measurement of only the absorption transitions it is possible to obtain the exact energy values of the vibrational–rotational levels for primarily the B state, because only the transitions originating from the lowest thermally populated vibrational levels of the X state participate in the formation of the absorption spectrum. An analysis of the entire body of high-precision measurements performed in Ref. [6] showed that the transitions under investigation are due to the participation of the vibrational B-state levels with quantum numbers $v' > 43$ and the vibrational X-state levels with $0 \leqslant v'' \leqslant 7$ and $12 \leqslant v'' \leqslant 17$. One can see that the high-precision experimental data required for constructing an improved potential curve for the X state are considerably fewer than those for the B state. This potential curve was constructed primarily from the data obtained in the series of works mentioned in Ref. [11]. In these works the luminescence spectrum of molecular iodine excited by laser radiation was studied with a Fourier spectrometer. Recorded were Doppler luminescence lines with an unresolved hyperfine structure. The luminescence line frequencies were measured accurate to 5×10^{-8}. As far as we know, high-precision frequency measurements for the individual HFS components of emission transitions have not been carried out to date.

In our work [7] we showed the feasibility of the high-precision frequency measurement of the individual hyperfine structure components of iodine emission transitions. To obtain the HFS emission components free from Doppler broadening, advantage was taken of the method [12] involving the resonance interaction of two laser fields with two neighbouring transitions with a common upper level. In this case, the radiation of one laser tuned to an iodine absorption line transfers the molecules from the ground X state to the electron-excited B state. When use is made of single-frequency radiation, excited to the upper level are the molecules lying in a very narrow velocity projection interval to give rise to a narrow, of the order of the homogeneous linewidth, amplification peak. Transitions are possible from the excited level to any of the 108 vibrational levels of the X state. The probing laser radiation tuned to the frequency of one of such transitions and spatially superposed with the exciting laser radiation interacts with the molecules excited by the laser. As a result, as the probe laser is tuned in frequency it records a narrow gain peak. In Ref. [7] we demonstrated the possibility of using this peak as a frequency reference. When the exciting field frequency is tuned to precisely the centre of the Doppler profile of an individual HFS component of the absorption line, the peak in the neighbouring transition will also correspond to the centre of the Doppler profile of the corresponding HFS component of the emission transition; therefore, by measuring the frequency of the laser stabilised to this component we measure the frequency of this transition.

In the present work we outline the results of absolute frequency measurements of the HFS components of $^{127}I_2$ molecular emission lines corresponding to the (32−48) and (33−48) bands of the B−X system. To lock the laser radiation frequency to the HFS components, use was made of the previously elaborated facility described in Ref. [7]. The radiation frequency was measured with the aid of a femtosecond optical frequency synthesiser.

2. Experimental facility

The experimental facility comprises a laser spectrometer, which provides the frequency locking of diode laser radiation to the emission transition of the B−X molecular system of I_2, and a measuring complex, which affords the absolute frequency measurement of the diode laser. The spectrometer is described at length in Ref. [7]. The spectrometer (Fig. 1) is a combination of two laser spectrometers: a saturated absorption spectrometer and a three-level laser spectrometer, in which optical resonances at a neighbouring transition can be obtained at any point of the Doppler profile. Their position depends on the pump radiation frequency offset from the central frequency of the profile. For the resonances at the emission transition to be at the centre of the Doppler profile of one of HFS components, the pumping must therefore be effected at precisely the centre of the Doppler profile of the neighbouring HFS absorption component.

The function of locking the pump radiation frequency to the centre of the Doppler profile is fulfilled by the saturated absorption spectrometer designed according to the traditional scheme. Two counterpropagating laser beams – the saturating beam and the probing one – are transmitted through an iodine cell. To obtain an error signal, use is made of the phase modulation of the saturating beam.

In our configuration the three-level laser spectrometer is combined with the saturated absorption spectrometer. The second probing beam at the frequency of the probe laser is introduced into the iodine cell, which is employed in the saturated absorption spectrometer, in the opposite direction to the saturating beam. The frequencies of both probing beams turn out to be modulated as a result of interaction with the molecules excited by the modulated pumping beam. The error signals obtained on detection of each of the probing beams is used to stabilise the frequencies of the radiation of both lasers the pump laser and probe one.

The function of the exciting radiation in the spectrometer is fulfilled by the second harmonic of a cw diode-pumped Nd : YAG laser with intracavity frequency conversion [13]. The laser is tuneable over the 1064.0–1065.3 nm wavelength range, in this case the second harmonic is tuneable over the 18775–18797 cm^{-1} range. The frequency tuning of the laser radiation over this broad range is effected by changing the temperature of a KTP crystal, which fulfils the function of frequency doubling and that of the phase element in a Lyot filter. The temperature of the crystal and of the entire cavity is controlled by a Peltier element and is stabilised to within 5 mK. The fine frequency tuning is effected with a piezoelectric element, which one of the cavity mirrors is attached to. The range of continuous (without jumping) frequency tuning measures ~5 GHz. The laser cavity is structurally highly rigid, which underlies the high short-term frequency stability of lasing (~10 kHz).

The probe radiation in the 968–998 nm range is generated by an external-cavity diode laser. The laser is described at length in Ref. [7]. Here, we discuss only those its features which to a large degree determine the procedure of measurements and their precision. In our work use was made of single-mode laser diodes made by the Polyus Research and Production Association (Moscow). The typical values of the threshold current and the maximum output power were equal to 40 mA and 50 mW, respectively. Since the output face was made only partly transparent (with a reflectivity of ~20%), the effect of intrinsic diode resonator was quite significant,
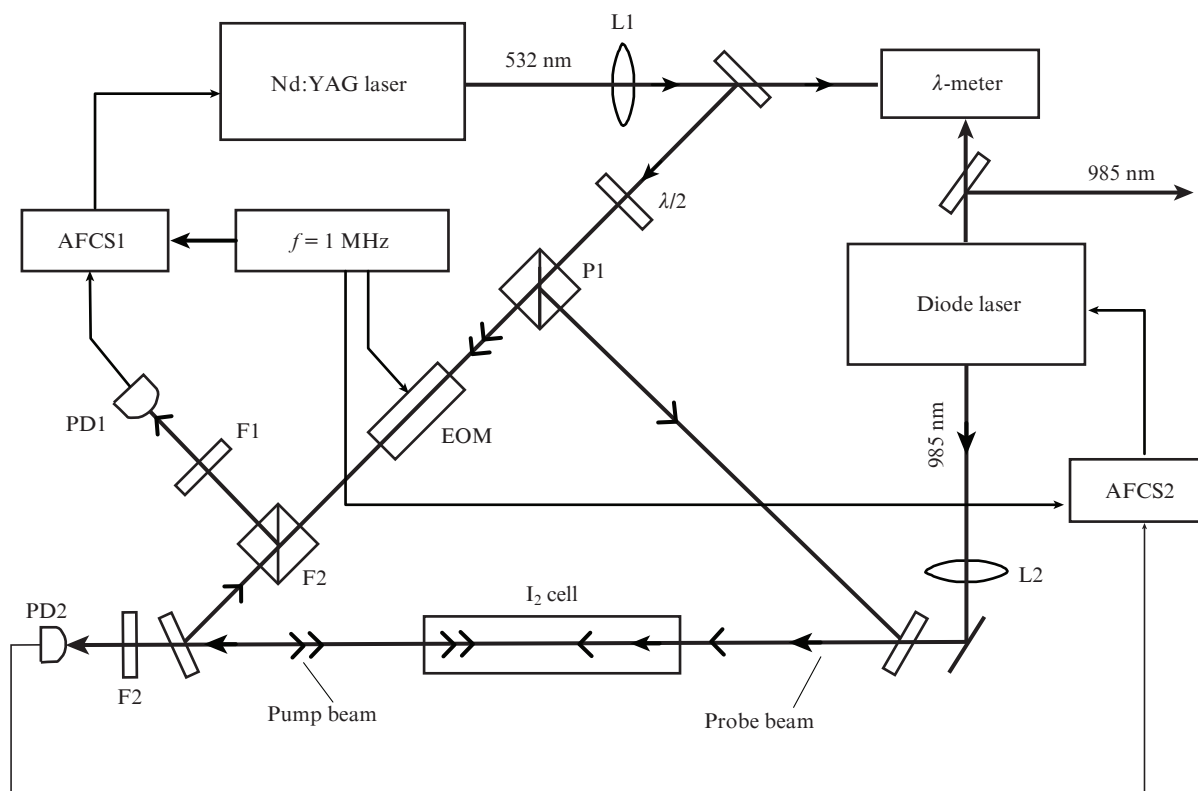
Figure 1. Schematic representation of the laser spectrometer: (AFCS1, AFCS2) automatic frequency control systems; (EOM) electro-optical modulator; (PD1, PD2) photodetectors; (F1, F2) optical filters; (P1, P2) polarisers; (L1, L2) lenses.

which substantially complicated tuning the laser to a given frequency. Four adjustment parameters were employed for the tuning. With the help of a diffraction grating the laser frequency was tunable throughout the amplification line of the laser diode. This tuning takes place stepwise, with an increment of about 60 GHz. This frequency interval corresponds to the mode spacing of the intrinsic cavity of the laser diode. The bounds of frequency jumping may be shifted to one or other side by changing the laser diode temperature over a $1-3\,^{\circ}$C range. Exact laser tuning to a given frequency was realised by changing the voltage applied to a piezoelectric element, which the diffraction grating was attached to. In this case, the range of continuous tuning without frequency jumps amounts to about 2.5 GHz. The bounds of these jumps may be slightly shifted (by up to 2 mA) by changing the excitation current.

All cavity elements were mounted on a brass block, whose temperature was controlled with a Peltier element and stabilised to within 5 mK. Accordingly stabilised were the laser diode temperature and the length of the external cavity enclosed in a hermetic casing made of plexiglass. The temperature regime was stabilised within about half an hour on turning the laser on. To protect the laser from acoustic and vibrational perturbations, its body was mounted on a marble block resting on a massive cast-iron plate, which served as the base for the entire experimental facility. The marble block was separated from the cast-iron plate with a sound-absorbing spacing.

The output beam of diode laser radiation with a power of ~5 mW was split in two: one was directed to the iodine cell and the other to the measuring complex. The power of the beam in the cell was equal to ~0.8 mW and it had an approximately round 0.8-mm diameter cross section at the beam

waist. The pump beam and the probe beam at a wavelength of 0.532 nm, which passed through the cell, were $5-8$ mW and $0.8-1$ mW in power, respectively; the cross sectional areas of these beams were equal to ~0.9 mm^2 in the cell. The outputs of the Nd:YAG laser and the diode laser were tuned to required wavelengths using a λ-meter (Angstrem), which ensured measurements accurate to 10^{-7}.

The iodine vapour glass cell of our fabrication was 30 cm in length, the cell's wall temperature was not stabilised and was equal to room temperature. The vapour pressure in the cell was controlled by varying the temperature of its cooled appendix. A Peltier element was employed for its cooling. The temperature of the appendix was stabilised to within 10 mK using an electronic control system. In the measurement of radiation frequency it was maintained equal to $8\,^{\circ}$C, which corresponds to an in-cell iodine vapour pressure of ~9 Pa.

The phase modulation of the pump radiation was effected with an electro-optical modulator (EOM). The modulation frequency was equal to 1 MHz for a modulation index of 0.5. The diode laser radiation frequency could be scanned by applying voltage to the piezoelectric element with a frequency of 50 Hz. When the diode laser radiation frequency was scanned within the Doppler width of the luminescence line in the absence of pump radiation frequency modulation, the signal from the photodetector PD2 was recorded by an oscilloscope in the form of a series of gain peaks corresponding to individual HFS components of the emission transition. In the phase modulation of the pump radiation and oscillographic recording of the signal from the AFCS2 phase detector, instead of peaks we observed dispersion-profiled resonances, which were used as an error signal for stabilising the diode laser radiation frequency. In the frequency measurement of

the HFS components of emission transitions, the Nd:YAG laser frequency was tuned to the frequency of the selected HFS component of the absorption transition and locked to it. The diode laser radiation frequency was tuned to the same component of the emission transition and stabilised.

The system of automatic control of diode laser frequency has two control loops – fast and slow ones. The fast loop provides protection against high-frequency perturbations of the frequency, which is tuned in this case by controlling the diode laser excitation current. The slow loop provides protection against low-frequency perturbations as well as against slow frequency variations that may arise from ambient temperature and pressure changes. In this ring the radiation frequency is controlled with the piezoelectric element that controls the external cavity length.

The frequency-measuring complex intended for absolute frequency measurements [14] is diagrammed in Fig. 2. It was made on the basis of a modernised GigaJet 20C femtosecond Ti:sapphire laser with a pulse repetition rate of ~495 MHz. For a pump we employed a commercially available Verdi-8 laser. To generate a supercontinuum, the laser radiation is transmitted through a microstructured optical fibre (Femtowhite800), with the result that the spectrum broadens

by more than an octave (0.5–1.1 μm). The frequency of an arbitrary supercontinuum component f_n may be written as $f_n = f_0 + nf_m$, where f_m is the pulse repetition frequency, or the intermode frequency; n is an integer; and f_0 is an offset frequency common of all supercontinuum components. From this relationship it follows that stabilising the supercontinuum requires stabilising two parameters – the offset frequency and the intermode frequency. Measuring these frequencies with a high precision defines the values of the remaining supercontinuum frequencies. As a result, we obtain a reference frequency scale: to measure an arbitrary laser output frequency which falls into the spectral range of the synthesiser it will suffice to measure the beat frequency between the frequency under measurement and the nearest reference frequency.

In our synthesiser the supercontinuum was stabilised by phase-locking one of supercontinuum frequency components to the Nd:YAG/I_2 frequency standard and phase-locking the offset frequency f_0 to the frequency synthesised from a radio frequency standard. As a result of this locking, the intermode frequency is stabilised, and its exact value may be calculated from the known value of the Nd:YAG/I_2 standard frequency and the measured value of f_0. To determine the mode number
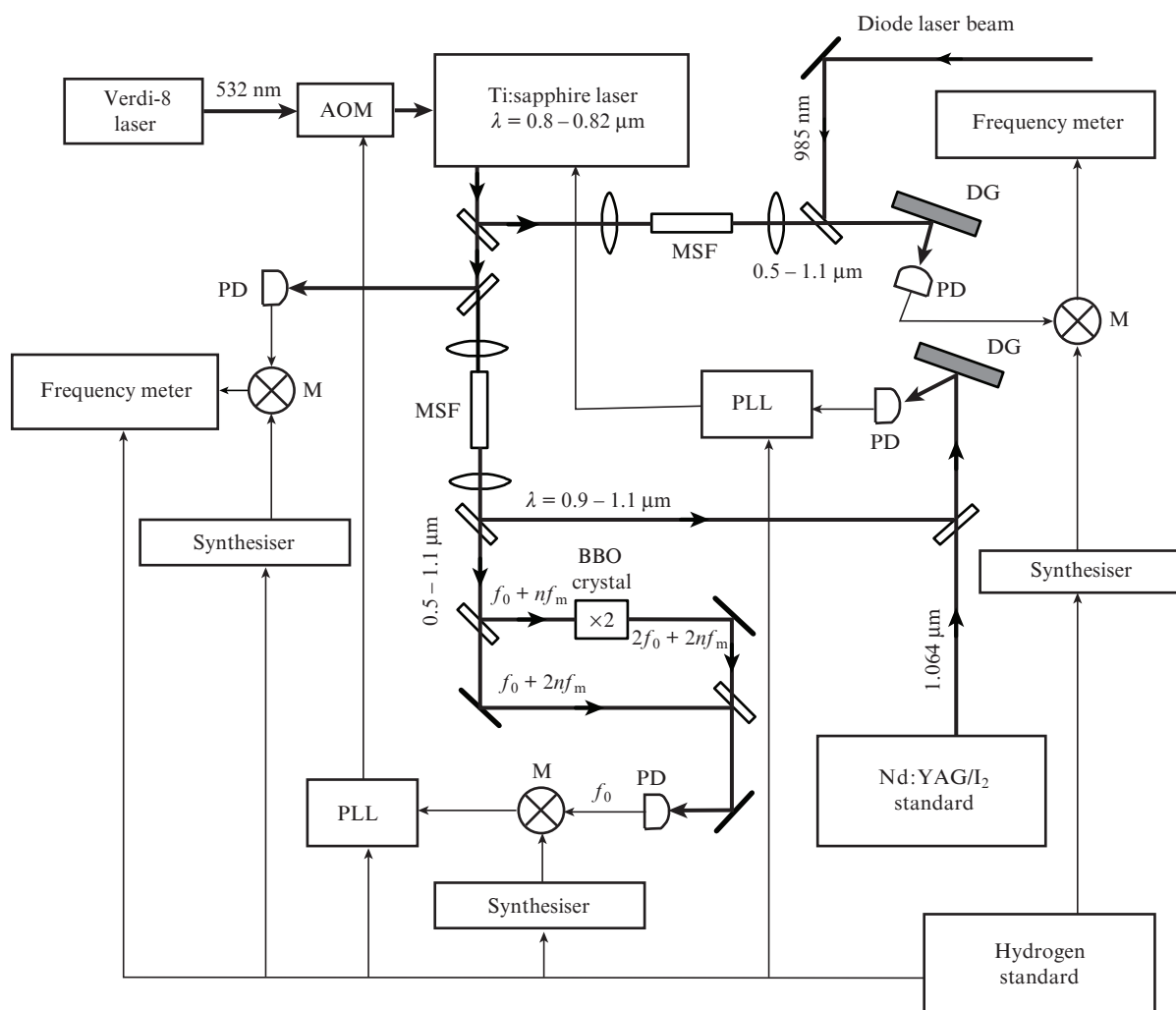

Figure 2. Schematic representation of optical frequency synthesiser: (AOM) acousto-optical modulator; (MSF) microstructured fibre; (PLL) phase-locked loop; (PD) photodetector; (M) mixer; (DG) diffraction grating.

n, which should be known in the calculation, it will suffice to measure the intermode frequency to better than 10^{-8}. The value of the intermode frequency determined in this way in turn permits calculating the frequency of any supercontinuum component.

A beat signal between a supercontinuum frequency component and the $Nd:YAG/I_2$ standard frequency is obtained in the mixing of the $Nd:YAG$ laser radiation with the long-wavelength part of the radiation transmitted through the microstructured fibre. The beat signal from the photodetector is delivered to a phase-locked loop (PLL), which produces an error signal employed to tune the Ti:sapphire laser cavity. Its frequency is controlled by varying the cavity length with the use of two piezoelectric elements which the cavity mirrors are attached to. One of the piezoelectric elements performs adjustments in a band up to 5 kHz and the other in a band up to 30 kHz. The $Nd:YAG/I_2$ standard frequency is shifted by 100 MHz relative to the frequency of the iodine transition to which it is stabilised, and therefore the phase locking of the frequency component to the standard is realised with precisely the same shift in magnitude and sign. As a result, the component has a frequency precisely equal to half the iodine transition frequency, because the frequency of the standard is locked to the iodine transition using the second harmonic.

To extract the offset frequency, use is made of a so-called $f:2f$ interferometer. The radiation emanating from the microstructured fibre is divided with a dichroic mirror into the short- and long-wavelength parts. The frequency of the long-wavelength part is doubled with a nonlinear crystal after which the radiation with the doubled frequency is mixed with the short-wavelength part of the radiation and is detected. In the case of this mixing, the detector is illuminated by the radiation whose spectrum is comprised of two combs of frequencies spaced at f_m, these combs being shifted relative to each other by the f_0 frequency. As a result, the beat signal obtained in the detection contains a large set of frequencies. The frequencies $f_0, f_m, f_m - f_0, f_m + f_0$, and $2f_m - f_0$ fall into the band of our detector (~1 GHz). The lowest frequency is normally separated out by filters. This may be either the f_0 frequency or the $f_m - f_0$ frequency, depending on which of the two is lower. Then the frequency of the filtered signal is mixed with a heterodyne frequency, which is synthesised from the standard frequency. The resultant intermediate frequency signal is fed to the phase-locked loop which phase-locks f_0 to the intermediate frequency. The offset frequency is controlled by changing the Ti:sapphire laser pump power with the aid of an acousto-optical modulator, which receives the error signal from the PLL.

The synthesiser provides for a high-precision measurement of the intermode frequency using a hydrogen standard. For this purpose a small fraction of the Ti:sapphire laser power is split off and fed to a photodetector, which records the intermode beat signal at a frequency of ~495 MHz. This frequency is then mixed with the 500 MHz frequency synthesised from the hydrogen standard frequency, and the resultant ~5 MHz difference frequency is measured with a frequency meter. Since the frequency meter is also synchronised to the hydrogen standard, the measurement accuracy is determined by the accuracy of the standard. The measured frequency value is represented by a twelve-digit number. Usually we employed both methods of determining the intermode frequency: by way of direct measurement with the use of the hydrogen standard and by way of calculation from the known values of the $Nd:YAG/I_2$ standard frequency and the offset

frequency, as described above. By comparing two frequency values obtained by the different methods it was possible to check the measurement accuracy. Normally their difference did not exceed ±500 Hz.

To obtain the beat signal between the frequency under measurement and a supercontinuum frequency component, we planned to divert a part of the radiation emanating from the microstructured fibre and mix it with the diode laser radiation. However, it turned out that there was a dip of the supercontinuum intensity in the 980–985 nm range: the intensity of frequency components was too low to produce a beat signal sufficiently intense to be measured. In an attempt to modify the spectrum by varying the Ti:sapphire laser power we found that the dip may be shifted, but the intensity of components in the domain of lasing of the $Nd:YAG$ laser lowered in this case. That is why we had to employ another microstructured fibre and divert a part of the output power of the Ti:sapphire laser to feed the fibre.

The diode laser radiation was directed to the frequency measuring complex with the help of mirrors. The distance of the diode laser output from the point of mixing of its radiation with the radiation of the Ti:sapphire laser was equal to about 10 m; the parameters of the radiation beams of these lasers were matched. The superimposed beams were directed to a focusing diffraction grating, which extracted a narrow portion of the spectrum about the frequency being measured and focused the beam onto the sensitive area of a fast-response photodetector. The beat signal was then mixed with the heterodyne frequency, which was synthesised from the hydrogen standard frequency and was selected in such a way that the difference frequency was close to 10 MHz. The resultant signal was filtered, amplified, and applied to the frequency meter. The signal-to-noise ratio was normally at a level of 30 dB. The measurement data averaged over 1 s were fed to a computer to be stored and processed. The period of one measurement ranged from 10 to 40 minutes. The time variation of the frequency was graphically displayed on the monitor screen as were the results of data processing – the average frequency, the average frequency deviation, and the rms deviation.

The transition frequency equal to the diode laser output frequency f_d was determined from the relation $f_d = nf_m \pm f_0 \pm f_{bd}$, where f_{bd} is the beat frequency between the diode laser output frequency and the supercontinuum component. To find f_d requires measuring the intermode frequency f_m, determine the number n of the supercontinuum component closest to the diode laser output frequency, and measure the offset frequency f_0 and the beat frequency f_{bd}. On phase-locking the offset frequency to the supercontinuum frequency component, measurements were made of the intermode frequency and the offset frequency. In the measurement of the latter it is necessary to determine which frequency the recorded beats correspond to: f_0 or $f_m - f_0$. This is important, because in the calculation of the frequency f_n under measurement in the former case the f_0 frequency is taken with the plus sign and in the latter case with the minus sign. We determined the sign in the following way. Provided that one of supercontinuum components was locked to the $Nd:YAG/I_2$ standard frequency, the intermode frequency was measured for two different ofset frequencies. When the intermode frequency lowered with increasing offset frequency, the beat sign had to be positive, and when the intermode frequency rose the sign had to be negative. The component's number was determined based

on the measured values of the intermode frequency, the off-set frequency, and the approximate value of the diode laser output frequency measured with a λ-meter. To determine the sign of f_{bd}, the diode laser output frequency was tuned over a narrow range, and in doing this we recorded the character of beat frequency variation. When the beat frequency increased with increase in output laser frequency, the beat sign was positive, but when it lowered, the sign was negative.

The precision of our measurement system is determined by the precision of the frequency standards in use – the hydrogen standard and the Nd:YAG/I_2 one. Prior to commencement of our measurements, the hydrogen standard was certified in the Novosibirsk Metrology Centre. At the present time, a GPS-based calibration has been set up. The frequency reproducibility of the standard in our use is equal to 10^{-13}. The reproducibility of the Nd:YAG/I_2 standard frequency was checked by comparing it with the frequency of the second similar standard. Furthermore, the absolute Nd:YAG/I_2 standard frequency was measured employing our synthesiser by way of determining the offset frequency and the intermode frequency with the use of the hydrogen standard. The resultant values were compared with the data available from the literature; the frequency reproducibility of the Nd:YAG/I_2 standard turned out to be better than 1 kHz.

3. Experimental results

Figure 3 shows one of the records of the time variation of the frequency being measured. The rms deviation over a period of ~100 s was equal to ~2 kHz. For longer time intervals we observed substantially greater deviations, which took place cyclically, with a period of 15–30 min. Over the period of measurement the maximum frequency deviation from the average value amounted to 30 kHz. Proceeding from these records made in the measurement of the frequency, we obtained the frequency stability characteristics of the diode laser radiation stabilised to the hyperfine structure component of emission iodine transition (Fig. 4). The frequency stability is equal to $(1-3)\times10^{-11}$ for an averaging period of 1–100 s. The measures of stability deteriorate with lengthening the averaging period. This signifies that there is a slow though significant frequency drift. So far we have not examined the reason for this behaviour of the laser. It is not unlikely that the parameters of the slow automatic frequency control loop have not been optimised.

Frequency measurements have been made of 20 I_2 molecular transitions: R56(32−48)a1, P58(32−48)a1, P85(33−48)

Figure 4. Diode laser frequency stability. The Allan function σ was calculated proceeding from the data shown in Fig. 3.

a1, R87(33−48)a1, R88(33−48)a10, and all 15 components of the R86(33−48) line. Since the tuning of laser radiation frequency from one line to another involves variations of the temperature, additional time was required for the steady-state temperature regime to set in. That is why during one day it was possible to measure several times the frequency of only one vibrational–rotational transition. Several days later the measurements were repeated. When frequency measurements were made of individual hyperfine structure components within one line, it was possible to tune the output laser frequencies without changing the temperature, and we were therefore able to measure several frequencies during one day. The measurement data are collected in Table 1. The rms frequency deviation calculated from the data of several measurements made during one day ranged from 11 to 22 kHz for different lines. The scatter of the measurement data obtained in different days amounted to 40 kHz. The frequencies of individual components of the R86(33−48) line were measured twice (at an interval of several days). For the resultant value we accepted the average of two measurements, and so the accuracy of frequency measurements for these transitions is lower. Since the accuracy of our measurement system is esti-
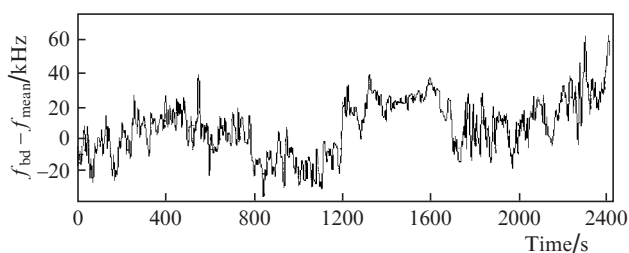

Figure 3. Record of the beat frequency between the output frequency of the diode laser, which was stabilised to the component a1 of the emission iodine transition R86(33−48), and the radiation frequency of the femtosecond optical frequency synthesiser.
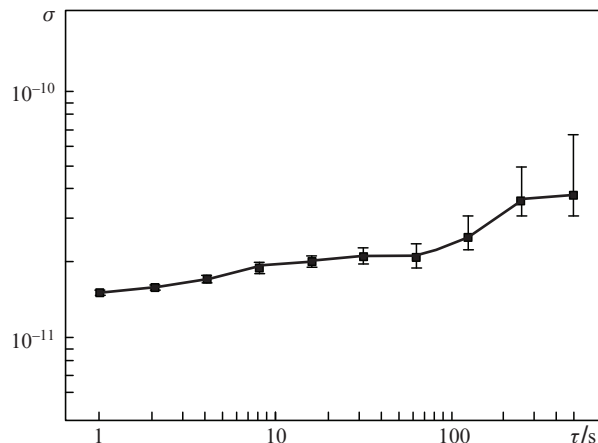
Table 1. Measurement data for iodine transition frequencies.

Line	Component	Transition frequency/kHz
P58 (32−48)	a1	304 360 509 340(14)
R56(32−48)	a1	304 569 862 427(19)
R87 (33−48)	a1	305 158 831 718(13)
P85 (33−48)	a1	305 473 035 236(11)
P88 (33−48)	a10	305 112 914 648(15)
R86 (33−48)	a1	305 430 191 096(22)
R86 (33−48)	a2	305 430 419 457(65)
R86 (33−48)	a3	305 430 450 726 (5)
R86 (33−48)	a4	305 430 460 143 (48)
R86 (33−48)	a5	305 430 490 794 (10)
R86 (33−48)	a6	305 430 556 161 (63)
R86 (33−48)	a7	305 430 570 683 (3)
R86 (33−48)	a8	305 430 604 295 (53)
R86 (33−48)	a9	305 430 618 684 (36)
R86 (33−48)	a10	305 430 719 880 (30)
R86 (33−48)	a11	305 430 832 083 (28)
R86 (33−48)	a12	305 430 839 995 (27)
R86 (33−48)	a13	305 430 864 083 (33)
R86 (33−48)	a14	305 430 872 845 (36)
R86 (32−48)	a15	305 430 984 743 (31)

mated at 1 kHz, the observed scatter of the measurement data is attributable primarily to the instability of the diode laser output frequency.

As regards systematic measurement errors, the greatest contribution is made, in our opinion, by the neglected offset frequency determined by the iodine vapour pressure in the cell. We did not investigate this shift. However, data obtained by other authors are available from the literature, primarily for absorption transitions. According to Ref. [15], for iodine absorption lines this shift is equal to -5 kHz Pa^{-1} in the IR range. Our measurements were made for a $8\,°C$ temperature of the cooled appendix of the iodine cell. This temperature corresponds to an iodine vapour pressure of 9 Pa. If it is assumed that the line frequency shift takes place primarily due to the upper level shift, the emission transition should exhibit the same shift as that for the absorption transition. In our case, this amounts to -45 kHz. There is a number of largely disregarded factors, which may be responsible for shifting the frequencies of both lasers and may thereby affect the precision of measurements. Among them are the mutual influence of the radiation fields of both lasers on the offset frequency of each of them, the effect of uncontrollable contaminating gases in the cell, parasitic amplitude modulation, backscattered laser radiation, etc. In order to investigate the influence of the factors mentioned above, the second similar laser system is presently under construction, which will enable us to validly determine the precision of our measurements. At the same time, we believe that it is expedient to publish the resultant data as preliminary ones, since we anticipate that the measurement uncertainty is within 200 kHz.

4. Conclusions

High-precision frequency measurements of individual HFS components of the $^{127}I_2$ emission lines corresponding to the B–X system were made for the first time. With the help of an optical frequency femtosecond synthesiser we measured the frequencies of 20 HFS components of six emission lines corresponding to the bands (32–48) and (33–48). The measurement precision was equal to $\sim7\times10^{-10}$, which is two orders of magnitude higher than the precision of the presently available experimental data for these transitions [11]. Systematic measurements relying on the proposed technique permit obtaining new and more exact experimental data; these data may underlie determination of more exact energy values of any vibrational levels of the X-state and, in the long run, of more exact spectroscopic parameters for calculating the frequencies of emission transitions. This will permit making the emission spectrum, along with the absorption one, suitable for the calibration of laser radiation frequencies and thereby extend the frequency scale to nearly 1.4 µm.

In this work we demonstrated the feasibility of using the HFS components of iodine emission transitions as frequency references for stabilising laser radiation frequencies. The output frequency of a diode laser operating in the 968–998 nm range was locked to the HFS components of emission lines in the 982–985 nm range. A frequency stability of $(1-3)\times10^{-11}$ was achieved for an averaging period of 1–100 s. The employment of frequency references corresponding to the emission spectrum of the B–X system of iodine, which occupies the range from 0.5 to 1.34 µm, significantly enhances the potentialities for stabilising laser radiation frequencies. This is particularly important for the 0.9–1.34 µm

range, where references suitable for frequency stabilisation are scarce. At the same time, there is a number of efficient tunable lasers radiating in this range, which are employed for the purposes of spectroscopy, communication, and metrology; consequently, there is a need for stabilising their frequencies.

In our opinion, the frequency references of emission spectra may be validly employed also in those spectral regions where use is presently made of absorption references, in particular in the 700–900 nm range. To attain appreciable absorption in this range requires a higher iodine vapour pressure, i.e. a cell heated to a temperature of 500–600 °C. Because of an enhanced gas release by cell walls at a high temperature there arises the possibility of uncontrollable reference frequency shifts under the action of contaminant gases, while the higher pressure is responsible for line broadening and an additional frequency shift. As a result, the accuracy of frequency locking to the transition centre becomes lower and hence the reproducibility of laser radiation frequency deteriorates. Specifically, in the visible range, when use is made of a lower cell pressure and there is no need to heat the cell walls, the best results in frequency reproducibility are at a level of 2.7×10^{-12} [16]. The best value in the 700–900 nm range is lower by more than an order of magnitude and amounts to 6.7×10^{-11} [17].

In individual cases, emission references may prove to be useful in the visible range as well. For instance, when a reference with the requisite frequency is missing from the absorption spectrum, there is a possibility to find such a reference in the emission spectrum.

The reader's attention is drawn to an important circumstance, which permits obtaining narrow emission lines in the 0.55–1.35 µm spectral range. It is well known that the homogeneous linewidth of iodine transitions at low pressures is defined primarily by the decay rate of the upper electron-excited level caused by the radiative decay and predissociation of the molecules [18]. In this case, the predissociation width may exceed the radiative one by more than an order of magnitude. Most amenable to the predissociation broadening are the lines of transitions involving the vibrational levels of the B-state, which are located in the lower and middle parts of the potential curve. As a result, the natural width of absorption lines in the long-wavelength and middle parts of the absorption spectrum is significantly greater than in the short-wavelength part. The narrowest lines lie in the 500–523 nm range and have widths of 30–150 kHz [19, 20]. If iodine molecules are excited by the radiation lying in this range, molecules with velocities lying in a very narrow value range will be excited to the upper level. Accordingly, all HFS components of the emission transitions originating from this level and terminating in any of the vibrational–rotational levels of the ground state will have a small breadth. Consequently, narrow frequency references may be obtained in almost every portion of the emission spectrum in the 0.55–1.34 µm range. Today the most promising radiation source for the excitation of iodine molecules in the range of interest is a diode-pumped solid-state with frequency doubling based on Yb^{3+} ion doped crystals [21, 22]. This laser can lase in the 1000–1049 nm range, and the wavelengths of the second harmonic radiation will range from 500 to 520 nm.

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