Application of the methane saturated dispersion resonance near $2.36\ \mu\text{m}$ over the temperature range of 77–300 K for optical frequency standards

Mikhail K. Tarabrin^{a,b}, Vladimir A. Lazarev^{a,*}, Valeriy E. Karasik^a,
Alexey N. Kireev^b, Yuri V. Korostelin^b, Alexander S. Shelkovnikov^b,
Dmitry A. Tuyrikov^b, Vladimir I. Kozlovsky^{b,d}, Yuri P. Podmarkov^{b,c},
Mikhail P. Frolov^{b,c}, Mikhail A. Gubin^{b,d}

^a*Bauman Moscow State Technical University, Moscow, Russia, 105005*

^b*P. N. Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, Russia, 119991*

^c*Moscow Institute of Physics and Technology, Moscow, Russia, 117303*

^d*National Research Nuclear University MEPhI, Moscow, Russia, 115409*

Abstract

New spectroscopic knowledge of the $\nu_1 + \nu_4$ R(2) E line of methane over the temperature range 77–300 K is reported. Theoretical calculations of the absorption coefficient and the amplitudes of saturated dispersion resonances at $4234\ \text{cm}^{-1}$ were derived. The theoretical dependence on the temperature of the amplitudes of the saturated dispersion resonances was obtained. A novel setup based on a $\text{Cr}^{2+} : \text{ZnSe}$ laser was used for Doppler-free spectroscopy of methane. The amplitudes of the saturated dispersion resonances of the $\nu_1 + \nu_4$ R(2) E line of methane were measured experimentally at different temperatures. A comparison with theoretical dependence supports the reliability of the experiment. The obtained results are of immediate interest in applications demanding laser frequency stabilization.

Keywords: spectroscopy, methane, saturated dispersion, local oscillators, frequency stability, optical frequency standard

*Corresponding author

Email address: vladimir.al.lazarev@gmail.com (Vladimir A. Lazarev)

1. Introduction

The accurate frequencies of the methane molecular transitions have been widely used in laser stabilization. The frequency of an external-cavity diode laser has been stabilized through $1.637\text{ }\mu\text{m}$ by using the methane absorption line as a reference [1, 2]. The laser-saturated absorption lines of methane at $3.39\text{ }\mu\text{m}$ have been shown to have remarkable characteristics for the frequency stabilization of a He-Ne laser [3, 4, 5]. The frequency of the $3.39\text{-}\mu\text{m}$ He-Ne laser stabilized by methane lines was measured using several methods [6, 7]; as a result, an optical frequency standard was designed [8, 9, 10, 11, 12] and several approaches for optical frequency combs stabilization were proposed [13, 14, 15, 16]. To date, much research has considered the methane P(7) line of the ν_3 band parameters at $3.39\text{ }\mu\text{m}$ [17, 18]; however there are a number of lines in the mid-IR region that are free from magnetic hyperfine structures that have better prospects for use in laser frequency stabilization. The development of cw tunable solid-state lasers based on crystals of A_2B_6 compounds doped with divalent ions of transition metals [19, 20, 21] solved the problem of choosing appropriate lines [22, 23, 24]. The lack of detailed information regarding the line positions, the line intensities and their temperature dependencies, and the linewidths has often hindered the further development of lasers with high frequency stability. A solid-state cw $\text{Cr}^{2+}:\text{ZnSe}$ laser has been used for Doppler-free spectroscopy of methane vibrational-rotational $\nu_1 + \nu_4$ band lines [25, 26]. Saturated-dispersion resonances of the R(2) line component near $2.36\text{ }\mu\text{m}$ were observed [27]. A compilation of methane line data for the frequency range of 4136 to 4666 cm^{-1} [28] has been obtained, but more information must be obtained regarding the methane line characteristics and their dependencies on external factors, such as the temperature, pressure, and saturation parameter.

To facilitate such studies, in this paper, we report on the Doppler-free spectroscopy of the $\nu_1 + \nu_4$ R(2) E line of methane over the temperature range of 77 to 300 K . The theoretical temperature dependence of the saturated dispersion resonances amplitudes was derived. This dependence was compared with the

experimental data and perfectly supports the reliability of the experiment.

2. Theory

2.1 The dependence on the temperature of the absorption coefficient of methane

35 To obtain the theoretical dependence on the temperature of the amplitudes of the saturation dispersion resonances, first, the absorption coefficient relation versus temperature must be obtained [29].

Let us consider the temperature dependence of the methane absorption coefficient. The absorption coefficient k_D at the top of an isolated Doppler-broadened line is linked with the absolute intensity of the line S_{line} by the relation (3) in ref. [30]. The absorption coefficient $\alpha = k_D/p$ reduced to a gas pressure p is:

$$\alpha = \left(\frac{\ln 2}{\pi}\right)^{1/2} \cdot \frac{S_{line}}{\gamma_D}, \quad (1)$$

where $\gamma_D = (2 \cdot \ln(2) \cdot kT/Mc^2)^{1/2} \sigma$ – the Doppler width of the line; σ – the wavenumber; k – the Boltzmann constant; T – the temperature; and M – the mass of the molecule (for methane $M = 2.662 \cdot 10^{-23}$ g = $k \cdot [1.733 \cdot 10^{14}$ K]/ c^2).
40

Then we will derive a simplified analytical expression for obtaining the functional temperature dependence of the absorption coefficient and its further comparison with the experimental data.

At first, the absolute intensity of the vibrational-rotational transition separate line $J \rightarrow J'$ in the $\nu_1 + \nu_4$ band is (with a bias less than 1% for $T < 300$ K) [31, 32]:

$$S_{JJ'} = \frac{8\pi^3}{3hc} \frac{N}{Z(T)} \exp\left[\frac{-B_0 J(J+1)hc}{kT}\right] \cdot \sigma_{JJ'} g_J \langle \mu_{JJ'} \rangle^2, \quad (2)$$

where $N = n/p$ – the density of molecules n reduced to a gas pressure p with a temperature T ; $B_0 = 5.241 \text{ cm}^{-1} = hc \cdot [7.541 \text{ K}]/k$ – the rotational constant of the ground state; $Z(T) = Z_v(T) \cdot Z_r(T)$ – the total statistical sum, which is equal to multiplication of vibrational (Z_v) and rotational (Z_r) statistical sums; $\sigma_{JJ'}$ – the wavenumber of the $J \rightarrow J'$ transition; J and J' – the rotational

quantum numbers of the total angular momentum of the lower level and upper level; g_J – the nuclear-spin statistical sum, which is corresponded to 5, 2 or 3 for A-, E- or F-symmetry transitions; and $\langle \mu_{JJ'} \rangle$ – the dipole matrix element of the vibrational-rotational transition. The density of molecules N in $\text{cm}^{-3} \cdot \text{Torr}^{-1}$ can be represented by a simple relation:

$$N = \frac{n}{p} = n_0 \frac{T_0}{T} \frac{1}{p_0}, \quad (3)$$

where $n_0 = 2.687 \cdot 10^{19} \text{ cm}^{-3}$ – the Loschmidt constant (density of molecules under normal conditions: $T_0 = 273.15 \text{ K}$, $p_0 = 760 \text{ Torr}$).

For temperatures $T \leq 300 \text{ K}$ rotational statistical sum Z_r is a good approximation for the total statistical sum $Z(T)$ because $Z_v < 1.0065$. In turn, for temperatures $40 \text{ K} \leq T \leq 300 \text{ K}$ rotational statistical sum can be expressed with an error of less than 1% as [33]:

$$Z_r(T) = \frac{4\pi^{1/2}}{3} \left(\frac{B_0 hc}{kT} \right)^{-3/2} \exp \left(\frac{B_0 hc}{4kT} \right). \quad (4)$$

To calculate the dipole moment, the equation for Einstein coefficient for spontaneous emission was used:

$$A_{ij} = \frac{64\pi^4}{3h} \cdot \nu_{ij}^3 \cdot \frac{g''}{g'} \cdot \Re_{ij}, \quad (5)$$

where $\Re_{ij}$ is the weighted transition-moment squared ($\Re_{ij} = \langle \mu_{ij} \rangle^2$); ν_{ij} is the wavenumber of the spectral line transition.

For the $J \rightarrow J'$ transition $\nu_{JJ'} = 4234.4168 \text{ cm}^{-1}$, the lower and upper state statistical weights are equal to $g'' = 10$ and $g' = 14$, respectively, and the Einstein coefficient for spontaneous emission is $A_{JJ'} = 1.318 \text{ s}^{-1}$, $\Re_{JJ'} = 7.749 \cdot 10^{-48} \text{ J} \cdot \text{cm}^3 = 7.749 \cdot 10^{-5} \text{ D}^2$.

Collecting the results of Eq. (2) - Eq. (5) into Eq. (1), the absorption coefficient (in $\text{cm}^{-3}/\text{Torr}$) of the transition $J \rightarrow J'$ can be expressed as

$$\alpha_{JJ'} \approx \frac{\sqrt{2}\pi^2}{hc} \frac{N_0 T_0 M^{1/2} B_0^{3/2} T^{-3}}{760} \cdot \exp \left[\frac{-B_0 (J + 1/2)^2}{T} \right] \sigma_{JJ'} g_J \Re_{JJ'}, \quad (6)$$

where B_0 and M are in units of kelvins.

The final expression for the absorption coefficient follows from Eq. (6):

$$\alpha_{JJ'} \approx \frac{[1.4334959 \cdot 10^5 \text{ K}^3 \cdot \text{cm}^{-1} \cdot \text{Torr}^{-1}]}{T^3} \cdot \exp\left[\frac{[-47.13125 \text{ K}]}{T}\right]. \quad (7)$$

The last equation, which expresses the dependence of the absorption coefficient on temperature, is shown in Fig. 1.

Figure 1: The calculated dependence of the absorption coefficient on temperature and data from SPECTRA based on the information from the HITRAN database [34, 35]

55 As illustrated in Fig. 1 the absorption coefficient at 77 K is $128.915 \text{ cm}^{-1} \text{ atm}^{-1}$ and the value at 300 K is $3.4141 \text{ cm}^{-1} \text{ atm}^{-1}$. This means that the absorption coefficient will increase by approximately 40 times when cooling methane from room temperature to 77 K.

2.2 The theory of saturated dispersion resonances of methane

An expression for the amplitude of a saturated dispersion resonance of methane (peak-to-peak value) A could be derived from the coefficient of a non-linear frequency pulling S (a frequency stabilization coefficient), which has been set for the first time by Vladilen S. Letokhov [36]:

$$S = \frac{\omega - \omega^{res}}{\omega_0 - \omega},$$

60 where ω – the oscillation frequency (hereinafter ω is a frequency in units of Hz);
 ω^{res} – the resonator tuning frequency (the bare resonator frequency); ω_0 – the
center of an absorption line.

Using the theory of a gas laser in a strong field, the following expression for
the frequency stabilization coefficient was obtained [37]:

$$S = \frac{\omega - \omega^{res}}{\omega_0 - \omega} = \frac{l}{2\pi L} \frac{\alpha \cdot p \cdot c}{2\gamma_0} \cdot F(x, I), \quad (8)$$

where

$$F(x, I) = \frac{\sqrt{1+I+x^2} - \sqrt{1+x^2}}{\sqrt{1+I+x^2} \sqrt{(\sqrt{1+I+x^2} + \sqrt{1+x^2})^2 - 4x^2}} \quad (9)$$

is the function, which defines a profile of a frequency stabilization coefficient;
 p – the gas pressure; c – the speed of light; l – the gas cell length; L – the cavity
65 length; γ_0 – the unsaturated homogeneous halfwidth of a resonance in units
of Hz; $x = (\omega - \omega_0)/\gamma_0$ – the detuning of the oscillation frequency reduced to
 γ_0 ; and I – the field intensity inside the cavity, which is measured in units of
saturation power (saturation parameter).

For saturated dispersion resonance registration, the two mode technique[18]
is used in the experiment. Laser operates in two longitudinal modes regime with
frequencies ω_1 and ω_2 , where intermode frequency $\omega_{12} = \omega_1 - \omega_2$ is much more
than the saturated homogeneous halfwidth of a resonance γ :

$$\omega_{12} = |\omega_1 - \omega_2| \gg \gamma.$$

Saturated dispersion resonance is registered in the intermode beat frequency
70 ω_{12} , when one mode ω_1 coincides with the methane line. The other mode ω_2
is used as a heterodyne. High sensitivity of this technique is determined by
subtraction of the correlated technical frequency fluctuations of the modes. A
typical profile of a saturated dispersion resonance $\Delta\omega_{12} = \omega_{12} - \omega_{12}^{res}$ is depicted
in Fig. 2, where $\omega_{12}^{res} = \omega_1^{res} - \omega_2^{res}$ is an intermode frequency of a bare resonator.

An expression for the profile of the saturated dispersion resonance follows
from Eq. (8):

$$\Delta\omega_{12} = \omega_1 - \omega_1^{res} = -\frac{\alpha \cdot p \cdot cl}{4\pi L} \cdot x \cdot F(x, I), \quad (10)$$

Figure 2: A typical profile of a saturated dispersion resonance

Field broadening gives saturation resonance halfwidth as:

$$\gamma = \gamma_0 \sqrt{1 + I}.$$

And the resonance amplitude follows from Eq. (10) and Eq. (9) by substituting a reduced detuning x_0 :

$$x_0 = \pm \sqrt{1 + I}. \quad (11)$$

Using Eq. (9) and Eq. (11), the dependence $F_0(I) = F(x_0, I)$ can be represented as follows:

$$F_0(I) = \frac{\sqrt{1 + I} - \sqrt{1 + I/2}}{\sqrt{1 + I} \sqrt{4\sqrt{1 + I} \sqrt{1 + I/2} - I}}. \quad (12)$$

⁷⁵ $F_0(I)$ is shown in Fig. 3. The function has a maximum of 0.067 at the saturation parameter $I = 3$. From Eq. (10) using Eq. (11), the resonance amplitude is in proportion to the product of $x_0 \cdot F_0(I)$, which is also depicted in Fig. 3.

Next, Eq. (12) is substituted in Eq. (10) to obtain the resonance amplitude:

$$A = \Delta\omega_{12}(x_0 = -\sqrt{1 + I}) - \Delta\omega_{12}(x_0 = \sqrt{1 + I}) = \frac{\alpha_{JJ'} p c l}{2\sqrt{2}\pi L} \cdot F_0(I). \quad (13)$$

Figure 3: $F_0(I)$ and $x_0 \cdot F_0(I)$ versus the saturation parameter I

Figure 4: The dependence on the temperature of the resonance amplitude

80 The last expression describes the dependence on the temperature of the resonance amplitude, which is proportional to the absorption coefficient; the dependence is shown in Fig. 4. The theoretical curve shape of the dependence on temperature is determined by Eq. (7), and the scale is defined by the gas pressure, gas cell length, cavity length and saturation parameter.

85 3. Experimental setup and results

The experimental setup (shown in Fig. 5) used in this research is similar to one that has been described in detail in [27]. Therefore, only a brief description of the setup is given here. The laser active element (AE) was composed of a $\text{Cr}^{2+} : \text{ZnSe}$ crystal [38, 39]. The AE oriented at the Brewster angle was placed

Figure 5: Experimental setup for the observation of the saturation dispersion resonances

in the middle of a four-mirror cavity that was assembled with astigmatism compensation [40]. The plane mirror M_1 and intermediate spherical mirrors M_2 and M_3 had reflectances close to 100% in the spectral range of 2.35 to 2.65 μm . The transmittance of the output mirror M_4 was 2%. The total cavity length was 1.2 m. Spectrally-selective elements were applied for tuning of the lasing spectrum, performing its narrowing for the stable two-mode operation of the $\text{Cr}^{2+}:\text{ZnSe}$ laser. Optical pumping of the $\text{Cr}^{2+}:\text{ZnSe}$ laser was performed by unpolarized radiation of a cw commercial thulium-doped fiber laser with a wavelength of 1.94 μm and a maximum output power of 2.8 W. The pump beam propagation direction made a small angle ($\sim 3.5^\circ$) with the optical axis of the $\text{Cr}^{2+}:\text{ZnSe}$ laser cavity. In this way, we excluded the influence of the pump radiation reflected from the elements of the $\text{Cr}^{2+}:\text{ZnSe}$ laser cavity on the operation of the thulium-doped fiber laser. The $\text{Cr}^{2+}:\text{ZnSe}$ laser radiation was partially directed to a detector PD 1 to observe the beat signal of two adjacent axial modes, which was observed on the spectrum analyzer. After that, this signal was amplified and was subtracted from the frequency of synthesizer on the double balanced mixer (DBM). Next, the signal contained a dispersion profile was demodulated by a frequency-to-voltage convertor and was visualized by the

oscilloscope.

Figure 6: Saturated dispersion resonances at different temperatures

A cryo-cooler based on a closed cycle compressor is used instead of liquid
 110 nitrogen, which was used previously [27, 41]. This cooler could operate in the
 temperature range of 77 to 300 K . The methane cell was cooled to 77 K and was
 then heated to the room temperature. Saturation dispersion resonances were
 obtained by means of scanning the length of the cavity and fine adjustment
 of the spectral-selective elements transmission. Thus, resonances appeared due
 115 to the nonlinear frequency pulling of one of the laser longitudinal modes. The
 saturated dispersion resonances, which we observed at different temperatures,
 are shown in Fig. 6 [42]. In this figure, calibration of the frequency axis was
 made using the external confocal scanning Fabry-Perot interferometer. Part of
 the output radiation was passed through the interferometer, detected by the
 120 photodiode PD 2 and registered by the oscilloscope.

The dependence on the temperature of the resonance amplitude was ob-
 tained by using the results of the previous data. A comparison between the
 corresponding results and the theoretical expectations via both Eq. (13) and
 Eq. (7) with values of $p = 2.2 \mu\text{bar}$, $L = 1200 \text{ mm}$ and $I = 0.85$ is shown in
 125 Fig. 7. In our experiments, the gas cell length is 400 mm and with it for reasons

of design the length of a cooled part of a gas cell $l = 250$ mm.

Figure 7: Results of the measurement of the dependence on the temperature of the resonance amplitude

The figures show good agreement between both the calculated and the measured results; the maximum relative difference of the two sets of values is 20% near 130 K. The results explain that the temperature from the cryo-cooler is fully transferred to methane. We suppose that the temperature of the cooling system is the same as the gas temperature and that theoretical dependence perfectly supports the reliability of the experiment.

To estimate the frequency instability of the future optical frequency standard, Allan variance is usually used [43]. The minimum achievable Allan deviation $\sigma(\tau)$ of the passive standards in the case of white noise is given by:

$$\sigma(\tau) = \frac{\delta\omega_{12}}{S_0\omega_1\sqrt{2\tau}},$$

where $\delta\omega_{12}$ – the intermode beat frequency spectral density noise; τ – the average time; and $S_0 = A/\gamma$ – the frequency stabilization coefficient.

In our experiments, the lower limit of $\delta\omega_{12}$ is equal to $0.03 \text{ Hz}/\sqrt{\text{Hz}}$ and is determined by natural frequency fluctuations (Schawlow-Townes noise [44]). Other parameters were experimentally obtained: $\gamma \approx 200 \text{ kHz}$, $A \approx 12 \text{ kHz}$, $S_0 \approx 0.06$, and $\omega_1 = 125 \text{ THz}$.

Collecting these results, the maximum achievable relative frequency instability $\sigma(\tau)$ can be expressed as

$$\sigma(\tau) = \frac{2.5 \cdot 10^{-15}}{\sqrt{\tau}}.$$

Future development will pay particular attention to increasing the amplitude
 140 by means of tuning the pressure and laser power values and to increasing the
 beam diameter by means of using a beam expander and a new detection system.

4. Conclusion

In summary, we observed, for what is believed to be the first time,
 the saturated dispersion resonances of the $\nu_1 + \nu_4$ R(2) E line of methane over
 145 the temperature range of 77 to 300 K. We developed a novel setup based on a
 $\text{Cr}^{2+} : \text{ZnSe}$ laser, which was used for the Doppler-free spectroscopy of methane.
 The saturated dispersion resonance amplitudes of the $\nu_1 + \nu_4$ R(2) E line of
 methane were measured experimentally at different temperatures over the range
 of 77 to 300 K. The theoretical temperature dependence of the methane reso-
 150 nance amplitude at 4234 cm^{-1} was derived and compared with the experimental
 data. Theoretical predictions correctly describe the temperature dependence of
 the methane resonance amplitude and support the reliability of the experiment.
 These results provide essential information for the design and development of
 frequency-stabilized lasers; the results are also of interest for optical frequency
 155 standards.

5. Acknowledgment

The authors would like to thank Linda R. Brown (NASA Jet Propulsion Lab-
 oratory), Laurence S. Rothman (Harvard-Smithsonian Center for Astrophysics),
 Andrei V. Nikitin (V.E. Zuev Institute of Atmospheric Optics) for the valuable
 160 discussions and help with HITRAN data.

The reported study on frequency measurements of $\text{Cr}^{2+} : \text{ZnSe}$ laser was
 carried out by Stanislav O Leonov and was funded by RFBR, according to the
 research project No. 16-38-60147 mol_a.dk.

6. References

- [1] W. Ma, L. Dong, W. Yin, C. Li, S. Jia, Frequency stabilization of diode laser to $1.637\ \mu\text{m}$ based on the methane absorption line, Chin. Opt. Lett. 2 (8) (2004) 486–488.
URL <http://col.osa.org/abstract.cfm?URI=col-2-8-486>
- [2] C. Ishibashi, M. Kourogi, K. Imai, B. Widiyatmoko, A. Onae, H. Sasada, Absolute frequency measurement of the saturated absorption lines of methane in the $1.66\ \mu\text{m}$ region, Optics Communications 161 (46) (1999) 223 – 226. doi:[http://dx.doi.org/10.1016/S0030-4018\(99\)00045-0](http://dx.doi.org/10.1016/S0030-4018(99)00045-0).
URL <http://www.sciencedirect.com/science/article/pii/S0030401899000450>
- [3] R. L. Barger, J. Hall, Wavelength of the $3.39\text{-}\mu\text{m}$ laser-saturated absorption line of methane, Applied Physics Letters 22 (4) (1973) 196–199. doi:10.1063/1.1654608.
- [4] J. L. Hall, C. J. Borde, Shift and broadening of saturated absorption resonances due to curvature of the laser wave fronts, Applied Physics Letters 29 (12) (1976) 788–790. doi:<http://dx.doi.org/10.1063/1.88949>.
URL <http://scitation.aip.org/content/aip/journal/apl/29/12/10.1063/1.88949>
- [5] Brillet, A., Cerez, P., Laser frequency stabilization by saturated absorption, J. Phys. Colloques 42 (1981) C8–73–C8–82. doi:10.1051/jphyscol:1981809.
URL <http://dx.doi.org/10.1051/jphyscol:1981809>
- [6] K. M. Evenson, G. W. Day, J. S. Wells, L. O. Mullen, Extension of absolute frequency measurements to the cw He-Ne laser at 88 thz ($3.39\ \mu$), Applied Physics Letters 20 (3) (1972) 133–134. doi:<http://dx.doi.org/10.1063/1.1654077>.
URL <http://scitation.aip.org/content/aip/journal/apl/20/3/10.1063/1.1654077>

- [7] K. Evenson, J. Wells, F. Petersen, B. Danielson, G. Day, Accurate frequencies of molecular transitions used in laser stabilization: the 3.39- μm transition in CH₄ and the 9.33- and 10.18- μm transitions in CO₂, Applied Physics Letters 22 (4) (1973) 192–195. doi:<http://dx.doi.org/10.1063/1.1654607>.
URL <http://scitation.aip.org/content/aip/journal/apl/22/4/10.1063/1.1654607>
- [8] C. Borde, The physics of optical frequency standards using saturation methods, in: A. De Marchi (Ed.), Frequency Standards and Metrology, Springer Berlin Heidelberg, 1989, pp. 196–205. doi:10.1007/978-3-642-74501-0_36.
URL http://dx.doi.org/10.1007/978-3-642-74501-0_36
- [9] M. Gubin, D. Tyurikov, A. Shelkovnikov, E. Kovalchuk, G. Kramer, B. Lipphardt, Transportable He-Ne/CH₄ optical frequency standard and absolute measurements of its frequency, Quantum Electronics, IEEE Journal of 31 (12) (1995) 2177–2182. doi:10.1109/3.477744.
- [10] A. Benedick, D. Tyurikov, M. Gubin, R. Shewmon, I. Chuang, F. X. Kärtner, Compact, Ti:sapphire-based, methane-stabilized optical molecular frequency comb and clock, Opt. Lett. 34 (14) (2009) 2168–2170. doi:10.1364/OL.34.002168.
URL <http://ol.osa.org/abstract.cfm?URI=ol-34-14-2168>
- [11] M. Gubin, A. Kireev, A. Konyashchenko, P. Kryukov, A. Shelkovnikov, A. Tausenev, D. Tyurikov, Femtosecond fiber laser based methane optical clock, Applied Physics B 95 (4) (2009) 661–666. doi:10.1007/s00340-009-3525-9.
URL <http://dx.doi.org/10.1007/s00340-009-3525-9>
- [12] M. A. Gubin, A. N. Kireev, A. V. Konyashchenko, P. G. Kryukov, A. V. Tausenev, D. A. Tyurikov, A. S. Shelkovnikov, Realisation of a compact

methane optical clock, *Quantum Electronics* 38 (7) (2008) 613.

URL <http://stacks.iop.org/1063-7818/38/i=7/a=L01>

- [13] T. Udem, R. Holzwarth, T. W. Hansch, Optical frequency metrology, *Nature* 416 (6877) (2002) 233–237.

- 225 [14] L.-S. Ma, Z. Bi, A. Bartels, L. Robertsson, M. Zucco, R. S. Windeler, G. Wilpers, C. Oates, L. Hollberg, S. A. Diddams, Optical frequency synthesis and comparison with uncertainty at the 10⁻¹⁹ level, *Science* 303 (5665) (2004) 1843–1845. [arXiv:http://www.sciencemag.org/content/303/5665/1843.full.pdf](http://arxiv.org/abs/http://www.sciencemag.org/content/303/5665/1843.full.pdf), doi:10.1126/science.1095092.

230 URL <http://www.sciencemag.org/content/303/5665/1843.abstract>

- [15] V. Lazarev, S. Sazonkin, A. Pniou, K. Tsapenko, Y. Gladysheva, A. Krylov, N. Arutunan, A. Pozharov, E. Obraztsova, Hybrid mode-locked ultrashort-pulse erbium-doped fiber laser, *Journal of Beijing Institute of Technology (English Edition)* 22 (SUPPL.1) (2013) 119–122.

235 URL <http://www.scopus.com/inward/record.url>

- [16] A. A. Krylov, S. G. Sazonkin, V. A. Lazarev, D. A. Dvoretzkiy, S. O. Leonov, A. B. Pnev, V. E. Karasik, V. V. Grebenyukov, A. S. Pozharov, E. D. Obraztsova, E. M. Dianov, Ultra-short pulse generation in the hybridly mode-locked erbium-doped all-fiber ring laser with a distributed polarizer, *Laser Physics Letters* 12 (6) (2015) 065001.

240 URL <http://stacks.iop.org/1612-202X/12/i=6/a=065001>

- [17] R. L. Barger, J. L. Hall, Pressure shift and broadening of methane line at 3.39 μm studied by laser-saturated molecular absorption, *Phys. Rev. Lett.* 22 (1969) 4–8. doi:10.1103/PhysRevLett.22.4.

245 URL <http://link.aps.org/doi/10.1103/PhysRevLett.22.4>

- [18] M. A. Gubin, E. D. Protsenko, Laser frequency standards based on saturated-dispersion lines of methane, *Quantum Electronics* 27 (12) (1997) 1048.

URL <http://stacks.iop.org/1063-7818/27/i=12/a=R05>

- [19] L. D. DeLoach, R. Page, G. Wilke, S. Payne, W. Krupke, Transition metal-doped zinc chalcogenides: spectroscopy and laser demonstration of a new class of gain media, *Quantum Electronics, IEEE Journal of* 32 (6) (1996) 885–895. doi:10.1109/3.502365.
- [20] T. Konak, M. Tekavec, V. V. Fedorov, S. B. Mirov, Electrical, spectroscopic, and laser characterization of γ -irradiated transition metal-doped II-VI semiconductors, *Opt. Mater. Express* 3 (6) (2013) 777–786. doi:10.1364/OME.3.000777.
URL <http://www.opticsinfobase.org/ome/abstract.cfm?URI=ome-3-6-777>
- [21] M. K. Tarabrin, A. Kovtun, V. Lazarev, V. Karasik, A. Kireev, V. Kozlovsky, Y. Korostelin, Y. Podmar'kov, M. Frolov, M. Gubin, Tunable cw solid-state mid-ir cr²⁺:cdse single crystal laser with diode laser array pumping, in: *Advanced Solid State Lasers*, Optical Society of America, 2015, p. AM5A.34. doi:10.1364/ASSL.2015.AM5A.34.
URL <http://www.osapublishing.org/abstract.cfm?URI=ASSL-2015-AM5A.34>
- [22] I. T. Sorokina, E. Sorokin, A. D. Lieto, M. Tonelli, R. H. Page, K. I. Schaffers, Efficient broadly tunable continuous-wave Cr²⁺:ZnSe laser, *J. Opt. Soc. Am. B* 18 (7) (2001) 926–930. doi:10.1364/JOSAB.18.000926.
URL <http://josab.osa.org/abstract.cfm?URI=josab-18-7-926>
- [23] M. Raybaut, A. Godard, R. Haïdar, M. Lefebvre, P. Kupecek, P. Lemasson, E. Rosencher, Generation of mid-infrared radiation by self-difference frequency mixing in chromium-doped zinc selenide, *Opt. Lett.* 31 (2) (2006) 220–222. doi:10.1364/OL.31.000220.
URL <http://ol.osa.org/abstract.cfm?URI=ol-31-2-220>
- [24] V. I. Kozlovskii, Y. V. Korostelin, A. I. Landman, Y. P. Podmar'kov, M. P. Frolov, Efficient lasing of a Cr²⁺:ZnSe crystal grown from a vapour phase,

Quantum Electronics 33 (5) (2003) 408.

URL <http://stacks.iop.org/1063-7818/33/i=5/a=A05>

- 280 [25] M. A. Gubin, A. N. Kireev, V. I. Kozlovskii, Y. V. Korostelin, A. B. Pnev, Y. P. Podmar'kov, D. A. Tyurikov, M. P. Frolov, D. A. Shelestov, A. S. Shelkovnikov, Tunable two-mode $\text{Cr}^{2+} : \text{ZnSe}$ laser with a frequency-noise spectral density of $0.03 \text{ Hz/Hz}^{-1/2}$, Quantum Electronics 42 (6) (2012) 509.
URL <http://stacks.iop.org/1063-7818/42/i=6/a=A08>

- 285 [26] M. Gubin, M. Frolov, A. Kireev, Y. Korostelin, V. Kozlovskiy, Y. Podmar'kov, A. Shelkovnikov, D. Tyurikov, V. Lazarev, A. Pnev, Cr:ZnSe laser with $0.03 \text{ hz/hz}^{1/2}$ frequency noise for compact methane based ofs, in: European Frequency and Time Forum (EFTF), 2012, 2012, pp. 459–461. doi:10.1109/EFTF.2012.6502425.

- 290 [27] M. A. Gubin, A. N. Kireev, V. I. Kozlovskii, Y. V. Korostelin, V. A. Lazarev, A. B. Pnev, Y. P. Podmar'kov, D. A. Tyurikov, M. P. Frolov, A. S. Shelkovnikov, Observation of saturated dispersion resonances of methane in a two-mode $\text{Cr}^{2+} : \text{ZnSe}$ laser, Quantum Electronics 42 (7) (2012) 565.
URL <http://stacks.iop.org/1063-7818/42/i=7/a=L01>

- 295 [28] L. R. Brown, L. S. Rothman, Methane line parameters for the $2.3\text{-}\mu\text{m}$ region, Appl. Opt. 21 (13) (1982) 2425–2427. doi:10.1364/AO.21.002425.
URL <http://ao.osa.org/abstract.cfm?URI=ao-21-13-2425>

- [29] M. A. Gubin, A. N. Kireev, E. V. Koval'chuk, D. A. Tyurikov, A. S. Shelkovnikov, Prospects for increasing the precision of optical frequency
300 standards based on transitions in the methane molecule, Quantum Electronics 26 (10) (1996) 928.
URL <http://stacks.iop.org/1063-7818/26/i=10/a=A23>

- [30] S. Gherissi, A. Henry, M. Loete, A. Valentin, Transition moment and line strengths of the 3 band of 12ch_4 , Journal of
305 Molecular Spectroscopy 86 (2) (1981) 344 – 356. doi:http:

[//dx.doi.org/10.1016/0022-2852\(81\)90286-1](http://dx.doi.org/10.1016/0022-2852(81)90286-1).

URL <http://www.sciencedirect.com/science/article/pii/S0022285281902861>

- [31] K. Fox, Theory of absolute intensities for vibration-rotation transitions in methane, Phys. Rev. A 8 (1973) 658–662. doi:10.1103/PhysRevA.8.658.
310 URL <http://link.aps.org/doi/10.1103/PhysRevA.8.658>
- [32] K. Fox, W. B. Person, Transition moments in infraredactive fundamentals of sphericaltop molecules, The Journal of Chemical Physics 64 (12) (1976) 5218–5221. doi:<http://dx.doi.org/10.1063/1.432196>.
315 URL <http://scitation.aip.org/content/aip/journal/jcp/64/12/10.1063/1.432196>
- [33] R. S. McDowell, Rotational partition functions for spherical-top molecules, Journal of Quantitative Spectroscopy and Radiative Transfer 38 (5) (1987) 337 – 346. doi:[http://dx.doi.org/10.1016/0022-4073\(87\)90028-8](http://dx.doi.org/10.1016/0022-4073(87)90028-8).
320 URL <http://www.sciencedirect.com/science/article/pii/S0022407387900288>
- [34] L. R. Brown, D. C. Benner, J. P. Champion, V. M. Devi, L. Fejard, R. R. Gamache, T. Gabard, J. C. Hilico, B. Lavorel, M. Loete, G. C. Mellau, A. Nikitin, A. S. Pine, A. Predoi-Cross, C. P. Rinsland, O. Robert, R. L. Sams, M. A. H. Smith, S. A. Tashkun, V. G. Tyuterev, Methane line
325 parameters in HITRAN, J. Quant. Spectrosc. Radiat. Transfer 82 (2003) 219–238. doi:10.1016/S0022-4073(03)00155-9.
- [35] L. Daumont, A. V. Nikitin, X. Thomas, L. Régalia, P. Von der Heyden, V. G. Tyuterev, M. Rey, V. Boudon, C. Wenger, M. Loëte, L. R. Brown, New assignments in the 2 μm transparency window of the $^{12}\text{CH}_4$ Octad
330 band system, J. Quant. Spectrosc. Radiat. Transfer 116 (2013) 101–109. doi:10.1016/j.jqsrt.2012.08.025.
- [36] V. S. Letokhov, Self-stabilization of laser optic-oscillation frequency by non-linear absorption in gas, Soviet Journal of Experimental and Theoretical

- 335 Physics Letters 6 (1967) 101.
 URL http://www.jetpletters.ac.ru/ps/1662/article_25341.shtml
- [37] N. B. Koshelyaevskii, V. M. Tatarenkov, A. N. Titov, Frequency pulling in lasers with nonlinear absorption, Soviet Journal of Quantum Electronics 4 (3) (1974) 286.
 340 URL <http://stacks.iop.org/0049-1748/4/i=3/a=A03>
- [38] Y. Korostelin, V. Kozlovsky, A. Nasibov, P. Shapkin, Vapour growth of II-VI solid solution single crystals, Journal of Crystal Growth 159 (14) (1996) 181 – 185, proceedings of the seventh international conference on II-VI compounds and devices.
 345 doi:[http://dx.doi.org/10.1016/0022-0248\(95\)00833-0](http://dx.doi.org/10.1016/0022-0248(95)00833-0).
 URL <http://www.sciencedirect.com/science/article/pii/S0022024895008330>
- [39] V. A. Akimov, M. P. Frolov, Y. V. Korostelin, V. I. Kozlovsky, A. I. Landman, Y. P. Podmar'kov, A. A. Voronov, Vapour growth of II-VI single
 350 crystals doped by transition metals for mid-infrared lasers, physica status solidi (c) 3 (4) (2006) 1213–1216. doi:10.1002/pssc.200564723.
 URL <http://dx.doi.org/10.1002/pssc.200564723>
- [40] H. Kogelnik, E. Ippen, A. Dienes, C. Shank, Astigmatically compensated cavities for CW dye lasers, Quantum Electronics, IEEE Journal of 8 (3)
 355 (1972) 373–379. doi:10.1109/JQE.1972.1076964.
- [41] M. Tarabrin, M. Frolov, M. Gubin, A. Kireev, Y. Korostelin, V. Kozlovsky, V. Lazarev, A. Pnirov, Y. Podmar'kov, D. Shelestov, A. Shelkovnikov, D. Tyurikov, Testing of Cr:ZnSe laser with intracavity methane cell in 77–300 K temperature range, in: Laser Optics, 2014 International Conference, 2014, pp. 1–1. doi:10.1109/L0.2014.6886221.
 360
- [42] V. A. Lazarev, M. K. Tarabrin, V. E. Karasik, A. N. Kireev, A. S. Shelkovnikov, Y. P. Podmarkov, Y. V. Korostelin, M. P. Frolov, V. I.

- 365 Kozlovsky, M. A. Gubin, Study of methane saturated dispersion resonances
amplitude near $2.36\text{ }\mu\text{m}$ over the temperature range 77-300 K, in: CLEO:
2015, Optical Society of America, 2015, p. JTh2A.72.
URL [http://www.osapublishing.org/abstract.cfm?URI=CLEO_
SI-2015-JTh2A.72](http://www.osapublishing.org/abstract.cfm?URI=CLEO_SI-2015-JTh2A.72)
- [43] F. Riehle, Laser Frequency Standards, Wiley-VCH Verlag GmbH & Co.
KGaA, 2005, pp. 255–313. doi:10.1002/3527605991.ch9.
370 URL <http://dx.doi.org/10.1002/3527605991.ch9>
- [44] A. L. Schawlow, C. H. Townes, Infrared and optical masers, Phys. Rev. 112
(1958) 1940–1949. doi:10.1103/PhysRev.112.1940.
URL <http://link.aps.org/doi/10.1103/PhysRev.112.1940>