ABSTRACTS OF PAPERS

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PART I

INVITED LECTURES

COLLISION NARROWING AND SPEED DEPENDENT EFFECT ON BROADENING IN V-R LINE PROFILES PERTURBED BY DIFFERENT BUFFER GASES UP TO ONE ATMOSPHERE.— DIFFICULTIES IN THESE ANALYSIS COMING FROM THE QUALITY OF THE TDL EMISSION.

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A Voigt function gives a rough description for spectral lines when both the Doppler-Fizeau and the collision broadening effects shape their profiles. As well a Lorentz function gives a coarse line profile description when collision broadening overcomes the Doppler effect. Nevertheless recent advances in precision spectroscopy using, among other spectrometers, tightly controlled Tunable Diode Laser allow to observe more easily departures from these simple models.

Then the profile associated to the collision broadening may take account of the absorber speed dependent effect and will be given by a weighted sum of Lorentz functions, each function associated with a class of speed of the observed molecules. (We will disregard in the present paper other effects acting on line profile broadening at pressures exceeding one atmosphere).

We will take a special interest in the line profile modifications occurring at lower pressures, when the confinement effect of molecules is observable, that is to say, when the mean free path is shortened and tends to be comparable with the wavelength of the absorbed radiation. This ‘caging‘ effect on the molecules progressively narrows their absorption line profile which, instead of being described by a Gauss function, is finally described by a Lorentz function when the gas pressure increases. These changes are connected to physical properties of the molecules and to their mass, as compared to the mass of the buffer gas molecules.

For the analysis of all the effects considered here, the real line shape, as obtained with a perfectly monochromatic emission source, has to be drawn out from the recorded spectra, taking into account the spectral distribution of the intensity emitted within the mode of the used TDL; this is done by convolution process.

CO and HCl will be considered with different buffer gases.

GROWTH AND CHARACTERIZATION OF IV-VI SEMICONDUCTOR LASER STRUCTURES ON SILICON SUBSTRATES AND PROGRESS TOWARDS FABRICATION OF HIGH OPERATING TEMPERATURE MID-IR LASERS

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This talk will review recent results from research conducted at the University of Oklahoma on the development of new IV-VI semiconductor (lead salt) epitaxial growth and laser fabrication procedures that can ultimately lead to dramatic increases in mid-IR laser operating temperatures. Work has focused on growth of IV-VI semiconductor laser structures on silicon substrates using buffer layers that contain BaF_2. Such growth allows removal of IV-VI semiconductor laser structures from the silicon growth substrate by dissolving the BaF_2 layer with water. This allows epitaxially-grown laser structures to be sandwiched between two heat sinks with a minimum of thermally resistive IV-VI semiconductor material. Theoretical modeling predicts that IV-VI lasers fabricated this way will have maximum cw operating temperatures at least 60 degrees higher than those of presently available IV-VI lasers fabricated on PbSe or PbTe substrates [1].

Silicon has a number of advantages (e.g. low cost, large size, good on-axis orientation, and high crystalline quality) over materials such as PbSe or PbTe as a substrate for IV-VI semiconductor epitaxial growth. On the other hand, silicon and IV-VI semiconductors such as PbSe have a thermal expansion coefficient mismatch of 750% and a lattice parameter mismatch of 13%. Although these large mismatches would normally cause severe problems in obtaining good epitaxy, recent experiments show that it is possible to obtain high crystalline quality IV-VI semiconductor layer structures on (111)-oriented silicon substrates using molecular beam epitaxy (MBE) [2] or on (100)-oriented silicon using a combination of MBE and liquid phase epitaxy (LPE) [3]. It is believed that the relative softness of the fluoride buffer layers (CaF_2 and BaF_2) and the IV-VI materials allows plastic deformation via complete dislocation glide through the thin layers.

Experimental data for IV-VI semiconductor layer structures grown on silicon substrates will be presented and will include crystalline quality information as determined by high resolution x-ray diffraction (HRXRD) measurements, absorption edge information as determined by Fourier transform infrared (FTIR) transmission measurements, and electronic properties as determined by Hall effect measurements. Results show that these materials can be used to fabricate lasers that will cover the 3 μm (3333 cm^{-1}) to 16 μm (625 cm^{-1}) spectral range. Results from recent experiments on removing MBE and LPE-grown IV-VI layer structures from the silicon growth substrate and efforts to fabricate lasers will also be presented.

[1] K. R. Lewelling and P. J. McCann, "Finite Element Modeling Predicts Possibility of Thermoelectrically-Cooled Lead-Salt Diode Lasers", *IEEE Photonics Technology Letters* **9**, 297 (1997).

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[3] B. N. Strecker, P. J. McCann, X. M. Fang, R. J. Hauenstein, M. O'Steen, and M. B. Johnson, "LPE Growth of Crack-Free PbSe Layers on (100)-Oriented Silicon Using MBE-Grown PbSe/BaF_2/CaF_2 Buffer Layers", *Journal of Electronic Materials* **26**, 444 (1997).

This work was supported by the National Science Foundation through grant number DMR-9416871.

LEAD SALT DIODE LASER AND DIFFERENCE FREQUENCY SPECTROMETER IN THE MID-IR-REGION - BASIC RESEARCH AND APPLICATION

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In the mid infrared spectral region between 3 and 30 µm the majority of atmospheric relevant gases have pronounced rotational-vibrational absorption lines. Prerequisite for the use of these transitions for trace gas detection is the precise knowledge of line parameters like position, intensity, broadening, and shift. This requires the application of high resolution spectroscopic techniques. Beside the Fourier-Transform spectroscopy, laser techniques like the tunable diode laser spectroscopy with lead salt lasers and the difference frequency spectroscopy become more and more important.

In this paper, spectroscopic measurements with self-built high resolution spectrometers applying diode lasers as light sources will be presented. For basis research a lead salt diode laser spectrometer was applied for the determination of line parameters of the molecules SO_2, H_2S, and NO_2 belonging to the symmetry group C_{2v}. With a resolution better $5 \cdot 10^{-4}$ cm^{-1} and a signal-to-noise-ratio better than 1000 a detailed study of the line intensities in the ν_2, ν_3, and $\nu_1+\nu_3$ bands of SO_2, the vibrational, rotational, and perturber dependence of the collisional line broadening and line shift in the ν_1, ν_2, ν_3, and $\nu_1+\nu_3$ bands of SO_2, the ν_3 band of NO_2, and the ν_1, ν_2, ν_3 and $2\nu_2$ bands of H_2S were carried out. In the collisional experiments up to 12 perturbs were included to study the dipole-dipole-interaction (self-broadening experiments), the dipole-quadrupole-interaction (collisions with N_2, O_2, H_2, and D_2) and the dipole-induced dipole-interaction (collisions with He, Ne, Ar, Kr, and Xe).

As an alternative technique without the necessity of cryogenic cooling, as in the case of lead salt diode lasers, diode laser-diode laser-difference frequency systems applying $AgGaS_2$ and $AgGaSe_2$ with Peltier cooled VIS and NIR excitation diode lasers were established. The resolution of about 10^{-3} cm^{-1} at a signal-to-noise-ratio better 100 was determined by spectroscopic measurements in the fundamental band of CO and the ν_3 band of SO_2. The line parameters obtained show an excellent agreement to well-known data measured with lead salt diode laser systems. Using the home made modular $AgGaS_2$ system it was possible to detect CO with a detection limit of 50 ppb·m at a time resolution of 1 second.

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THE DIODE LASER: A VERSATILE SPECTROSCOPIC TOOL

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The wide use of tunable diode lasers (TDL) in the infrared and near infrared spectral region for spectroscopic and analytical investigations has revealed the broad range of problems which can be tackled not only successfully but often can be approached uniquely only by TDL techniques. The important characteristics of TDLs are that they provide a fairly monochromatic beam, which guarantees high spectral resolution and high sensitivity, with detection of absorbances as low as 10^{-6} to 10^{-7}. Amongst these unique applications, two have been investigated and perfected in the Cologne laboratories:

1) the combined absorption-wavelength modulation technique and
2) the use of tunable diode lasers as local oscillators for IR-heterodyne detection.

1) The double modulation technique, used in supersonic jet experiments, is based on a simultaneous modulation of the jet and a 10 kHz wavelength modulation of the TDL. This technique enables measurement of very weak transitions of different van der Waals complexes, e.g. Ar-CH_4 and many others.

2) The spectral purity of TDL, if frequency stabilized, is sufficient to use this source as a local oscillator for heterodyne detection techniques throughout the entire IR region covered by TDLs. Due to low output power of available single mode diode lasers, a newly developed infrared diplexer is used to efficiently superimpose the signal and the local oscillator signals. Additionally, the diplexer serves as optical filter that establishes controlled optical feedback between the laser diode and the detector. This diplexer arrangement allows stable laser operation with line widths in the order of 1 MHz. The heterodyne signal from the HgCdTe detector is HEMT amplified and is analyzed by means of a 2000 channel acousto-optical spectrometer (AOS) with a spectral resolution of about 1 MHz and a total bandwith of 1.4 GHz. This system is currently used in the 10 μm region for astrophysical studies.

Examples of recent spectroscopic work will be presented together with some novel technical advances incorporated into the appropriate spectrometers.

DIODE LASER ABSORPTION SPECTROSCOPY OF FREE RADICALS AND IONS

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Diode laser absorption spectroscopy at Doppler Limited resolution has produced many impressive results over the past two decades, particularly on the structures of free radicals and molecular ions. These transient molecules can be produced in discharges or by photolysis or thermolysis. This talk will describe some of the latest results from the diode laser spectrometers in Cambridge. A variety of new phosphorus containing molecules have been made using the oxidation of phosphorus in a low pressure cell to generate them. A multi pass diode laser spectrometer has been used to detect P_2O, PNO and, most recently Cl PO. These studies are allied to ***ab initio*** calculations of these previously unobserved gas phase species. Recently, we have extended earlier studies on transition metal carbonyl-rare gas clusters to iron pentacarbonyl and produced new spectra of this carbonyl Van der Waals bonded to argon and neon. A second jet spectrometer has been developed to produce radicals by pulsed thermolysis. We have detected the methyl radical in this way and the $\square_2$ mode J = K Q-branch shows a rotational temperature of about 30 K. Combined with diode laser spectroscopy this pulsed thermolysis supersonic jet technique promises to be an important spectroscopic area. The design and performance of the heated jet, operating near 1000 K, will be described. Discharges continue to be important sources of both free radicals and ions. By using alternating current discharges (10 kHz - 50 kHz) short lived species can be detected by ***population modulation*** (radicals and ions) or ***velocity modulation*** (cations). The use of these techniques to measure diode laser spectra will be described, illustrated with recent results on HeH^+, HeD^+ and B Br.

The following abstracts of invited lectures are not available:

1. ***A. A. Popov, Yu.Yakovlev*** InAsSb lasers for 3 μm wavelength: the performance and applications.

2. ***R. Cingolani.*** Many-body processes and lasing in nanostructures. A brief overview of the physics and technology quantum wire / quantum dot lasers from the many-body-theory to the fabrication of real devices.

3. *A. W. Mantz*. 30 years of tunable diode laser spectroscopy. What have we accomplished, and what is the future?

4. *A. I. Nadezhdinskii. Tunable diode laser spectroscopy at General Physics Institute.*

PART II

POSTER PRESENTATIONS

PRESSURE-INDUCED SHIFT AND BROADENING IN THE ν_2 BAND OF H_2S COLLISIONS WITH NOBLE AND MOLECULAR GASES

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Investigations concerning line shift and line broadening of absorption lines in the ν_2 fundamental band of H_2S due to collisions with noble (He, Ne, Ar, Kr, Xe) and molecular (H_2, D_2, N_2, O_2, CO_2) gases were carried out using a three channel diode laser spectrometer with a resolution better than $5 \cdot 10^{-4}$ cm^{-1} and two multipass Herriott cells. In this paper data for 11 lines from the P-branch ($3 \leq J'' \leq 8$; $2 \leq K_C'' \leq 8$), for 19 lines from the R-branch ($2 \leq J'' \leq 11$; $0 \leq K_C'' \leq 11$), and for 4 lines from the Q-branch ($8 \leq J'' \leq 10$; $7 \leq K_C'' \leq 9$) will be presented. The experiments were carried out for a pressure of the buffer gases in the region from 0 Torr up to 250 Torr in steps of 20 - 25 Torr. The experimental profiles of absorption lines were approximated by a Voigt contour. Using non-linear least-squares methods the collisional line width and the pressure-induced line shift were obtained. From the linear dependence of these parameters on the partial pressure of the perturber broadening and shift coefficients were determined. The dependencies of broadening and shift coefficients on the rotational quantum numbers J'' and K_C'', on the polarizability of noble gases, and on the quadrupole moment of molecular gases are discussed. The broadening data will be compared to previous measurements [1, 2, 3, 4]

The project is supported by the “Volkswagen Stiftung”. B.Sumpf acknowledges a grant from the “Deutsche Forschungsgemeinschaft”. A.Kissel thanks for a “NaFöG” grant.

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MEASUREMENTS OF HALF-WIDTH AND SHIFT OF H_2S ABSORPSION LINE INDUCED BY H_2O AND ARGON IN THE THREE-COMPONENT MIXTURE

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Lorentzian halfwidth (HWHM) and shift of H_2S absorption line 1294.5083 cm^{-1} induced by the pressure of H_2O and Ar in three-component mixture H_2S–H_2O–Ar were measured using a diode laser spectrometer with a spectral resolution of about $5*10^{-4}$ cm^{-1}.

The mixture of H_2S–Ar–H_2O was prepared with a fixed partial pressure of H_2S and Ar. The H_2O pressure varied from 0 till 12 Torr when total pressure varying from 4.1 tills 18 Torr.

The data obtained (see for example Table) are applied to verify the additivity of the collisional partners to the broadening and shift of the individual spectral line.

Table. HWHM and Line Shift of 1294.5083 cm^{-1} H_2S absorption line

Pressure P_{total}[Torr]	Perturber	Lorentzian Halfwidth (HWHM) $\gamma[10^{-3}cm^{-1}]$	Line Shift $\delta[10^{-3}cm^{-1}]$
1.8	H_2S	0.4531 ± 0.01	-0.0079 ± 0.04
4.1	H_2S+Ar	0.6239 ± 0.01	-0.0037 ± 0.03
6.1	(H_2S/Ar)+H_2O	1.2561 ± 0.01	0.0220 ± 0.03
8.0	(H_2S/Ar)+H_2O	2.0386 ± 0.02	0.0427 ± 0.03
10.3	(H_2S/Ar)+H_2O	2.7414 ± 0.02	0.1376 ± 0.03
12.1	(H_2S/Ar)+H_2O	3.3285 ± 0.02	0.1534 ± 0.03
14.1	(H_2S/Ar)+H_2O	4.1372 ± 0.03	0.1359 ± 0.03
16.1	(H_2S/Ar)+H_2O	4.6442 ± 0.03	0.2575 ± 0.03

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INVESTIGATION OF LINE PROFILES IN THE ν_2 BAND OF H_2S. PRELIMINARY RESULTS.

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Experiments with a three channel lead salt diode laser spectrometer like described in Ref.1. concerning collisional effects for lines from the ν_2 band of H_2S were carried out in the laser spectroscopy group at the Optisches Institut of the Universitaet Berlin. To analyze the measured line profiles three types of contours, i.e. Voigt, Rautian-Sobel'man, and Galatry, were taken into account. As result of this study line broadening, line shift, and line narrowing coefficients could be determined for a number of lines.

This work presents preliminary results of this analysis. Collisional narrowing effect was clearly observed for some of the high-*J* H_2S lines, that could be explained by the smaller for these lines collision broadening that mask the Dicke effect.

The mist significant narrowing coefficients (0.047 ± 0.010) cm^{-1}/atm was found for the line (12,1,12) ← (11,0,11) perturbed by Ne.

It was shown for the lines under study that the broadening and shift coefficient's deviation due to Dick narrowing not taken into account lies in the range of the uncertainties of this coefficients determination.

The deviation from linear dependence of narrowing parameter on pressure is found out for example for pressures higher 30-40 Torr for the line (6,4,2) ← (5,3,3) perturbed by Kr, or for pressures larger than 150-180 Torr for the line (12,1,12) ← (11,0,11) perturbed by Ne. It's caused perhaps by the absorber speed dependent broadening effect[2].

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DIFFERENTIAL HELMHOLTZ RESONATOR AS AN PHOTOACOUSTIC TRACE GAS DETECTOR WITH NEAR-INFRARED DIODE LASERS

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The optimum design of a spectrophone for the air pollution monitoring requires the consideration of the following rather practical aspects:

1) high sensitivity of spectrophone and high signal-to-noise (S/N) ratio;
2) feasibility of flow measurements for continuous air pollution monitoring and particularly for solving the adsorption and desorption problem;
3) feasibility of measurements in noisy environments, e.g., close to traffic;
4) feasibility of measurements under reduced pressure to increase the spectral selectivity and to decrease the interference of gases in multi-component mixtures;

A cell designs that fulfills well these requirements use, as a rule, acoustic resonance phenomena in the cell chamber and they often are of sophisticated design of acoustically resonant cell. The feasibility of application of well-known Helmholtz resonator (HR) for air pollution monitoring will be discussed here.

The HR is simple in design and consists of two cell volumes connected together by thin capillary. Compared to other resonators, the Helmholtz arrangement has the advantages of using cells of small volumes with low resonance frequency and the possibility to enhance the S/N ratio using differential schemes. The differential Helmholtz resonator (DHR) allows one to double the signal amplitude and to minimize a art of the noise (ambient noise). The double differential Helmholtz resonator (DDHR) additionally eliminates the most important part of the noise, the background signal.

The research discussed here, includes experimental study of the HR and DHR responsivenesses, as applied to the detection of trace gases and the predictions of these responsivenesses as a function of frequency, cell pressure, and cell design. We present also simple Helmholtz resonator configuration for the flow measurements and simple arrangement to enhance the main photoacoustic signal of the whole system by a factor of about 2 (in addition to factor 2*Q in the Busse and Herboeck DHR configuration). The idea is to use the half of the laser energy that is lost on the chopper and to light both cells of HR and DHR opposite in phase using mirror chopper. We use the acoustic analog to electric circuits to calculate the response of such PA system.

The experimental measurements of the HR and DHR responsivenesses as functions of frequency, pressure and cell design were obtained using the CO_2 and 1.66 μm diode lasers, C_2H_4 and CH_4 as an absorbing gases respectively. The measurements of the signal to noise ratio for amplitude and wavelength (first and second derivative) modulations were carried out.

The experimental explorations of the pressure dependence of the HR and DHR responses and influence of additional volumes on these responses when conducting flow measurements.

ANALYSIS OF INFRARED DIODE LASER SPECTRA OF KH

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High-resolution vibration-rotational spectra of diatomic molecules with infrared diode lasers provide many spectral lines for many vibrational states of various isotopomers. Simultaneous analyses of those spectral lines of all isotopomers by a least-squares fit to a single set of molecular parameters requires consideration of adiabatic and nonadiabatic corrections to the Born-Oppenheimer approximation (1).

Although the Δ_ω and Δ_B formalism of Thompson et al. (2) works well for such analysis of heavier molecules, the model failed in reproducing the spectra of light diatomic molecules. Recently, we modified the Δ_ω and Δ_B scheme of the potential model by an algebraic WKB treatment of the Schroedinger equation given by Watson's effective Hamiltonian (3,4). A compact expression was given for the contributions from the adiabatic and nonadiabatic correction terms in the Hamiltonian to Dunham's Y_{ij} coefficients. The modified Δ_ω and Δ_B scheme of the potential model worked well for LiH (3,4) and was applied, in this study, to the analysis of vibration-rotational spectra of KH.

Spectra of LH and LD were observed using a diode laser spectrometer, Spectra Physics (Laser Analytics) SP5000, equipped with a discharge cell of a White cell type. KH and KD were generated in K + H_2 glow and D_2 glow, respectively.

The spectral data set consisted of 20 line measures in this study and also 107 lines from the literature (5, 6). In total, 127 spectral lines for four isotopomers, ^{39}KH, ^{41}KH, ^{39}KD, and ^{41}KD, were simultaneously fitted to a single set of only 11 molecular parameters, U_ω, U_B, a_1, a_2, a_3, a_4, a_5, Δ_ω^H, Δ_B^H, $r_0{}'^H$ and Δ_{a1}^H, well within experimental errors. The results have been improved slightly over those published very recently (7). Values of $\omega_e(^{39}\text{KH})$ and $r_e(^{39}\text{KH})$ within the Born-Oppenheimer approximation are 986.6431(22) cm^{-1} and 224.01621(97) pm, respectively, assuming that Δ_ω^k, Δ_B^k are equal to zero.

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TUNABLE LASER DIODE WITH THE EMISSION WAVELENGTH 1.65 μm FOR SPECTROSCOPY

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The results of making and investigation of tunable injection laser diodes with the emission wavelength 1.65 μm for the high-resolution spectroscopy are presented.

The epitaxial structures were made by the method of the liquid phase epitaxy InGaAsP/InP on p-InP substrate. The structures were made up into mesa-stripe laser diodes with the mesa width 3…5 μm and the cavity width 200 μm. The laser diode was placed on the thermocooler for the tuning of the temperature and of the emission wavelength. The slope of the wavelength-temperature characteristic is about 4.5…5 A/ C.

The threshold current was 25…30 mA. The output power was 5 mW when the injection current was 80…100 mA. The width of the tuning was 300…400 A.

By this time we made the single-frequency semiconductor lasers with Bragg gratings in the optical fiber with the emission wavelengths 0.98; 1.06; 1.31; 1.53 μm. The width of the spectrum was less than 1 MHz.

A MID–INFRARED TUNABLE DIODE LASER HETERODYNE RECEIVER

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Heterodyne spectrometry is a potentially powerful technique for astronomical or geophysical investigations. A heterodyne receiver works by mixing the radiation under study with the laser radiation from a local oscillator on a fast photodetector. In the infrared CO_2 lasers allow to reach the detection limits, but such systems with fixed local oscillator have limited spectral range (1 GHz) near coincidences between the laser lines and the absorption gas signature. We present here some results about the use of a continuously tunable laser as the local oscillator.

We designed a tuneable diode laser heterodyne receiver. The apparatus uses Pb–salt diodes as the local oscillator and operates between 1050 and 1150 cm^{-1}. The effects of the characteristics of the diode on the performances of the heterodyne receiver have been studied. Signal to Noise Ratio of the TDL heterodyne receiver is compared to SNR using a CO_2 laser as the local oscillator. The power, the spectral width and the Intensity Noise of the diode are important parameters.

Ground–based heterodyne atmospheric spectra of the ν_1 band of ozone have been recorded using the sun as a source.

The resolution (30 MHz $\approx 10^{-3}$ cm^{-1}) is lower than the ozone Doppler width. The spectral range is enhanced to 0.33 cm^{-1} ($\approx$ 10 GHz) and it permits to record entirely several lines. High quality spectra have been recorded within 10 minutes. These characteristics allow retrieving the total ozone amount and the ozone distribution between 15 and 40 km.

DIODE LASER SPECTROSCOPY OF AR-CH_4 AND KR-CH_4 IN THE 7μ REGION

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The absorption spectra of the Ar-CH_4 and Kr-CH_4 van der Waals complexes were observed in the 7μ region. The complexes were produced in a pulsed slit jet and detected by a tuneable diode laser spectrometer. The allowed transitions from the three $^{R}P_0$, $^{R}Q_0$ and $^{Q}R_0$ branches, corresponding to the $j = 1 \leftarrow 0$ transition of the CH_4 part inside the complexes, were measured for both Ar-CH_4 and Kr-CH_4 close to the R(0) line of the ν_4 fundamental band of methane. Additionally, several weaker nearly forbidden low J transitions from $^{Q}P_0$ and $^{R}R_0$ were found, enabling an unambiguous determination of the rotational and centrifugal distortion constants for the $j = 0 \leftarrow 1$ level of the ground vibrational state of the complexes. The separation between the rare gas atom and the methane molecule in the ground vibrational state was determined to be 3.999 Å and 4.094 Å for Ar-CH_4 and Kr-CH_4, respectively. We have further recorded and assigned the allowed transitions from the $^{P}Q_1$, $^{Q}P_0$ and $^{P}R_1$ branches, corresponding to the $j = 0 \leftarrow 1$ transition in the region close to the P(1) line of methane. The spectroscopic analysis of the recorded transitions will be presented.

REMOTE DETECTION OF METHANE CH_4 USING A 3.3 μm TUNABLE LEAD SALT DIODE LASER

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Lasers tend to become more and more widely used for environmental monitoring purposes. They constitute a practical and powerful tool to monitor in real time the presence of gaseous pollutants in the atmosphere. Our present experiments deal with the detection of methane CH_4 using an infrared diode laser and a differential absorption type of detection.

The CH_4 molecule has four normal vibration modes with respective frequencies of 2914 cm^{-1}, 1533 cm^{-1}, 3019 cm^{-1} and 1306 cm^{-1}, among which only ν_3 and ν_4 are infrared active. We considered the case of three absorption bands related to $\nu_2+2\nu_3$, $2\nu_3$ and ν_3, lying in the near infrared around the wavelengths 1.3 μm, 1.7 μm and 3.3 μm. In each of these bands, the Q branch lies in the central part of the spectrum and generally provides the strongest absorption. Estimating the maximal absorption cross sections σ_{max} from high resolution spectra found in the literature [1-2], we found respective values of 1.3 10^{-25} m^2, 5.4 10^{-25} m^2 and 4.5 10^{-23} m^2, reached for the wavelengths 1.331 μm, 1.666 μm and 3.31 μm. Absorption in the ν_3 band is thus two orders of magnitude stronger than it is in the two other bands. In view of the fact that atmospheric transmission is high around 3.3 μm, we chose to work in that wavelength range notwithstanding the unusualness and the still high price of adapted tunable laser sources.

The acquired laser system is based on a liquid Nitrogen cooled lead salt diode, which emission frequency is tunable over a 100 cm^{-1} bandwidth around 3020 cm^{-1} (3.31 μm), by adjusting the pumping current intensity and/or the operating temperature. The typical cw emission power is 0.2 mW. CH_4 detection experiments are being run in a sample cell containing pure methane at controlled pressures, before extending them to the open atmosphere.

The differential absorption measurement technique consists in producing a periodic modulation of the laser emission frequency between two values ν_r and ν_{nr}, through a current modulation. In the present case, we adopt ν_r = 3020 cm^{-1} and ν_{nr} = 3030 cm^{-1}. Synchronous detection of the laser beam intensity after propagation through the cell, achieved with a lock-in amplifier, yields the methane number density in the sample, provided that intensity variations are only due to the presence of CH_4. Nevertheless, the diode pumping current modulation always induces a laser intensity modulation -about 10% in our case. We discuss the possibility of separating this undesirable effect from CH_4 contribution by appropriate adjustment of the lock-in detection phase. The detection threshold expected from such a set-up, expressed as the product between the lowest detectable CH_4 number density N and the sample length L, is determined by the smallest measurable intensity modulation $D = (\Delta I/I)_{th}$. $(NL)_{th}$ is given by $\Delta\sigma(NL)_{th} = D$, where $\Delta\sigma = \sigma(\nu_\rho)-\sigma(\nu_{\nu\rho})$ is the differential absorption cross section. Since $\Delta\sigma$ = 4.5 10^{-23} m^2, and assuming a value of 10^{-3} for D, $(NL)_{th}$ would be 2.2 10^{15} molecules/cm^2. Expressed in terms of methane pressure at a temperature of 25 °c, that level corresponds to 0.7 mTorr.m, and to 0.9 ppm.m if CH_4 is mixed with air at a pressure of 1 atm.

Finally, the sensitivity of the system is expected to be improved by typically two orders of magnitude if the laser diode emission frequency is rather modulated symmetrically around ν_r with a frequency f, the lock-in amplifier being used in a 2f synchronous detection scheme [3].

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TEMPERATURE AND CURRENT TUNING OF INGAASSB/INASSBP DIODE LASERS IN THE 3-3.6 μM SPECTRAL RANGE

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The report presents characterization of double heterostructure (DH) diode lasers composed of In(Ga)As(Sb) active layers and InAsSbP cladding layers with respect to diode laser spectroscopy in the 3÷3.6 μm spectral range.

The N-$InAs_{1-x-y}Sb_xP_y$/n-$In_{1-v}Ga_vAs_{1-w}Sb_w$/P-$InAs_{1-x-y}Sb_xP_y$(Zn) DHs were grown by LPE method on an InAs (111) substrate. To obtain different wavelengths the composition of 1÷3 μm thick active and 3-5 μm thick cladding layers was varied in the $0.05<x,w,v<0.1$, $0.1<y<0.16$ range. Structures with $InAs_{1-w}Sb_w$ or InAs active layer were also fabricated and studied. Lasers with 200-500 μm resonator length and mesa stripe width of 10 or 20 μm were fabricated by photolithography and wet chemical etching and had thresholds in the 16÷100 mA (77 K) range. Lasers emit single mode at currents up to $I=2I_{th}$ and have maximum output power up to 3 mW (77 K, $I=20I_{th}$). Differential quantum efficiency as high as 14% ($I=I_{th}$) have been obtained. The longitudinal mode emission is characterized by $FWHM_{\perp}$=30÷35 deg and $FWHM_{||}$=10÷15 deg.

On temperature increase the band gap of enriched with InAs allows decreases and one can expect the 'red' decrease of the laser emission photon energy. This is the case for the lasers with Type I heterojunction which have 0.5÷2 cm^{-1}/K temperature tuning rate. On the contrary lasers of Type II heterojunction exhibit 'blue' (-3 cm^{-1}/K) or weak drift of an emission line with temperature increase in the 77÷160 K range. The differences in temperature behavior are accompanied by differences in light polarization: TE is a characteristic mode for Type I lasers, while Type II lasers in most cases emit TM polarized light. The above laser features we explain by strong interface recombination arises from the existence of the states in the wells at Type II heterojunction. In contrast to this bulk recombination is dominating in Type I lasers.

It is also possible to distinguish Type 1 from Type II heterojunction by measuring a I-V characteristic. The latter one for Type II junction exhibits S-type feature at currents below threshold which is usually an indication of tunnel current flow.

Type II lasers appeared to be superior to Type 1 lasers in terms of higher current tuning rate (60 cm^{-1}/A). Type II laser with emission at λ=3.319 μm (77 K) was used for methane transmission measurements through the use of current tuning within ~1 cm^{-1}. The obtained fine structure of the CH_4 absorption spectrum with several peaks indicates good stability of laser mode structure. Direct measurements of a linewidth by self mixing time resolved technique gave FWHM=10 ÷15 MHz for the I_{th}÷3 I_{th} current range. Thus, fairy small linewidth together with high output and high tuning rate shows the applicability of InGaAsSb/InAsSbP Type II lasers for molecular spectroscopy in the mid-IR region.

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DESIGN AND CHARACTERISTICS OF WIDELY TUNABLE QUANTUM-WELL LASER DIODES

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Laser diodes with a wide range tuned spectrum are successfully applied in spectroscopy and environment monitoring instead of solid-state laser systems and other more complicated and expensive sources. The use of diffraction gratings as dispersive elements in external selective cavities gives opportunity to enhance the output laser power and spectral brightness. Sources based on laser diodes distinguish by compactness, reliability, absence of complex optics, long operating time, and high stability of the output signal.

In the work, tuning characteristics of semiconductor injection lasers in an external cavity are analyzed. The active region of lasers investigated is an asymmetric multiple quantum-well heterostructure with quantum wells of various widths. In such a heterostructure laser it is possible to obtain practically a flat modal gain spectrum in a wide spectral range. It occurs since the differ quantum wells give certain contributions to the total gain in different intervals of the spectrum. To make even the gain contributions of the quantum wells, conditions of non-uniform excitation in a structure are fulfillment, so that the excitation level of the narrow quantum wells much exceeded as compared the excitation of the wide quantum wells. The non-uniform excitation conditions are provided for the potential profile in the doped barrier layers and are changed with their mole compositions and thicknesses.

As an example of wavelength selective external cavities, the modified Littman and Metcalf configuration is considered. In this case, the front facet of a semiconductor laser crystal on the diffraction grating side is coated with anti-reflection coating and the other facet of the crystal is coated with a highly reflective coating. In this configuration, the diffraction grating is used at grazing incidence conditions and the feedback proceeds through a tuning mirror at the first-order collateral reflection maximum. The output of radiation comes true in a narrow spectral pass band that results in a single-mode laser oscillation in the whole tuning range.

At the analysis of the tuning characteristics, the dependence of the feedback factor of the external cavity on the lasing wavelength is considered. When calculating the waveguide spectra of the quantum-well laser heterostructures, effects of optical confinement, line spectral broadening, polarization dependence of the optical transitions probabilities, and narrowing of the semiconductor band gap versus the level of excitation of the laser structure are taken into account as well. The calculations have been performed in the GaAs-AlGaAs system. The continuous tuning at output powers up to 20 mW occurs in the wavelength interval of 805 to 855 nm. Use of the other ternary or quaternary semiconductor compounds gives possibilities to transfer the tuning range to a necessary spectral region.

IR MOLECULAR SPECTRAL LINE PRESSURE BROADENING DEPENDENCE ON RELATIVE VELOCITY OF COLLIDING PARTICLES.

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The IR linewidth of CO_2 molecules has been measured by means of tunable diode laser spectroscopy technique in wide field of a gas temperature and rotational quantum numbers. It has been found that there are no existing semiclassical models of pressure broadened linewidths to describe satisfactorily our and other published experimental results.

A new cutoff-free semiclassical model of pressure broadening of rotation-vibration spectra in gases was provided. It corresponds to all experimental results quite well. The model takes into account:

1. trajectory bend of moving particles by intermolecular forces, and
2. increasing of optical cross section for molecules with low relative energy of translation motion due to orbiting collisions.

It takes not so much computing time to calculate the impact broadened linewidths by our method (only slightly more time than calculations by Anderson-Tsao-Curnutte theory). It enables us to compute the shape of IR spectral lines with correct averaging over a distribution of relative velocities. The important role of particles collisions with low relative energy of translation motion $E\mu$ ($E\mu/\varepsilon < 0.8$, where ε is constant of Lennard-Jones itermolecular potential) even under room temperature has been shown. This role is increased essentially at lower temperature.

It has been found that ordinary applied calculation scheme of average linewidths over a Maxwell-Boltzmann distribution of relative velocities leads to essential systematic errors.

The above features make our results attractive for its usage for determinations of exact linewidths in molecular infrared spectra.

GaInSbAs/GaSb MULTIPLE QUANTUM WELL LASERS FOR TUNABLE DIODE LASER SPECTROSCOPY BETWEEN 2 AND 2.65 µm

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Tunable Diode Laser Absorption Spectroscopy (TDLAS) is one of the most sensitive, selective and fast response technique for gas analysis. Traditionally lead-salt diode lasers emitting in the 3-25 µm spectral range are used in TDLAS. However, these lasers can not work at room temperature (RT) and should be cooled down to 80-100 K, which limits their application to laboratory measurements. Because of material restrictions, their emission can not be extended to wavelengths shorter than 3 µm. Semiconductor laser based on III-V compounds seems to be very attractive for TDLAS because of higher optical power and their ability to lase continuously near RT at wavelengths shorter than 3 µm. Despite the fact that absorption lines are in general weaker in the 2-3 µm range, the availability of multipass cells, high sensitivity detectors and the possibility of RT operation for lasers and detectors open a way for the development of high sensitivity portable systems for gas analysis.

In this work we present GaInSbAs/GaSb Multiple Quantum Well (MQW) diode lasers operating near RT between 2.0 and 2.65 µm. These lasers can be used for TDLAS of CH_4, CO, CO_2, H_2CO, and N_2O.

The laser structures have been grown by molecular beam epitaxy on GaSb substrates. The active zone of the devices contained 4-6 GaInSbAs quantum wells embedded between GaSb barriers. The quantum wells were compressively strained. The QW thickness was typically 60-80 Å, the In mole fraction varied between 0.26 and 0.5 and the As mole fraction was in the range 0 - 0.22. Fabry-Perot resonator lasers were fabricated from the grown wafers with the mesa stripe width of 80 or 8 µm.

The threshold current density J_{th} at room temperature (RT) measured on the wide lasers varied between 280 A/cm^2 for devices emitting near 2.0 µm and 1.5 kA/cm_2 for lasers operating at 2.65 µm. The pulsed output power reached 200 mW. Narrow lasers designed to operate in the vicinity of 2.35 µm exhibited threshold currents as low as 30-100 mA at RT and could be used in continuous wave (cw) regime. The laser emission linewidth was estimated to be smaller than 20 MHz. Tunability of the lasers by temperature and current has been studied.

With these lasers absorption spectra of CH_4 and CO have been studied near 2.35 µm as a function of concentration and pressure. Basic parameters of some absorption lines have been found. Using a low frequency wavelength modulation technique methane and carbon monoxide could be detected at concentrations in the sub-ppm range. The obtained results show a potential ability of the studied lasers for use in portable low-cost trace pollutants sensors.

OPTICO-MAGNETIC EFFECTS IN DIODE SPECTROSCOPY OF Rb VAPOURS

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We present the results of experimental researches on optical pumping, orientation and alignment of Rb atoms in weak magnetic field. The experiments were carried out with a Rb vapor cell at room temperature without buffer gases. The semiconductor lasers we have used were single mode heterostructure AlGaAs and InGaAsP emitting near D_1 and D_2 absorption lines of Rb (795 and 780nm correspondingly). Several schemes of experimental setup were used to detect both linear and saturated absorption in Rb vapors.

The first group of experiments[1] was carried out on the base of two external cavity lasers emitting at D_1 line of Rb. Laser beams were circularly polarized. Frequency of one of them was set on certain hyperfine resonance of D_1 line. Emission of another laser was used as a probe field to measure absorption in differential scheme and its frequency was scanned across the spectrum of absorption. In that setup the effects of optical pumping and orientation by detecting the changes in the absorption coefficient were observed.

Other group of experiments was carried out to observe free Larmour oscillations of induced magnetic momentum in weak transverse magnetic field. In this case we have used one free running pulsed laser (strong emission) and one external cavity laser (probe emission). Circularly polarized radiation of both lasers was fixed on two different hyperfine resonances of D_1 absorption line . Absorption of the probe field was registered after short pulsed action of the strong field which induced macroscopic magnetic momentum in the atomic ensemble. In the presence of weak transverse magnetic field the specific oscillations of probe absorption at Zeeman splitting frequency were observed. These oscillations were arisen due to precession of macroscopic magnetic momentum around the direction of magnetic field. The similar oscillations were observed at pulsed changing of the direction of magnetic field.

The last group of experiments was carried out with use of one external cavity laser working at D_2 absorption line of Rb. In this case the conventional setup for saturated spectroscopy was applied. The saturated absorption spectrum of D_2 line of Rb in magnetic field was investigated. Saturating and probe laser beams were linearly polarized. When the direction of magnetic field was perpendicular to polarizations of probe and strong beams there were observed anomalous 'negative' crossover resonances (absorption peaks instead the peaks of transmission), similar to those predicted by the theory of Nakayama[3]. Detailed study of the structure of transitions (in particular for ^{87}Rb, characterized by more simple structure of levels) has shown, that this phenomenon is connected with the alignment effect. When orientation of magnetic field was along the polarizations of laser beams the crossover resonances had right sign (transmission).

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AIR BROADENING AND SHIFT OF ACETYLENE IN 1.5 μm REGION

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Preliminary results on pressure induced broadening and shift of acetylene lines by air in 1.5 μm spectral region (ν1+ν3 band) were obtained using $A_{III}B_V$ DFB diode laser.

High quality of the laser and data acquisition system allowed us to record spectral line shape with an accuracy better than 1%.

Dike narrowing of a Gaussian component of a line shape was observed.

CURRENT AND TEMPERATURE DEPENDENCE OF EMISSION CHARACTERISTIC OF SEMICONDUCTOR LASERS MEASURED BY FOURIER TRANSFORM SPECTROSCOPY

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We present a new quick technique of laser emission characteristics investigation by high resolution Fourier Transfer Spectrometer (Bruker-113v) in spectral interval 0.8 to 25 mkm with resolution up to 0.03 cm^{-1}. Current (10 mA to 2 A) and temperature (5 to 50°C) dependence of emission spectra of different diode lasers types measured by Fourier Transfer spectroscopy are described.

PORTABLE METHANE ANALYZER BASED ON TUNED NEAR IR DIODE LASER FOR MEASUREMENTS IN OPEN ATMOSPHERE.

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Near infrared (IR) diode laser based instruments for measuring gas concentration have essential advantage over mid IR instruments for they do not require cooling equipment. The main disadvantage of the near IR spectral range is that for most molecules of interest only overtones and combination bands are located in this range, which have much less absorption in comparison with fundamental bands in mid IR. The multipass cell with optical path length up to 100 m, low noise electronic unit, original signal processing and the gas concentration calculation procedure, used in the portable methane analyzer, allow to overcome this disadvantage and achieve very high sensitivity in the near IR range.

The gas analyzer was intended for continuous automatic gas concentration measurements with stocking of the results in computer memory. The measurements could be done in the open atmosphere as well as for gas mixture samples in closed cell. Described variant of the device is made for methane concentration measurements and can be easily reconstructed for other gas by changing the diode laser.

The diode laser with composition GaInPAs manufactured on the base of getherostructure technology and operating at room temperature was used. The laser radiated at wavelength approximately 1.65 mkm, where rather strong lines of methane absorption band 2v3 could be observed. The line R6 of this band was chosen for methane concentration measurement. The laser radiation power was 3 mW, threshold current 50 mA.

The Chernin four objective mirrors multipass cell [1] with base length 0.5 m and diameter 0.15 m tuned to 156 passes was an analytical optical part of the analyzer. Measurements of the gas concentration were performed with the help of reference channel including the closed cell with pure methane. The laser was capable to radiate in two opposite directions through the analytic (multipass) cell and reference cell. Photodetectors' signals at the outputs of both channels were used for the normalization and gas concentration calculation in analytic channel.

Pulse technique was applied for absorption line detection. In this method the diode laser is driven by current pulses of sawtooth form, thus allowing registering small portion of the spectra, including the absorption line of interest. Then computer program compare the filtered photodetector signals in both channels and the gas concentration was calculated with the help of correlation function.

Sensitivity limit of methane detection was found to be 50 ppb. The relative accuracy of the methane concentration measurements was 2% unless this value does not exceed 50 ppb. Long term sensitivity was estimated as 100 ppb. The main systematic error is due to optical interference. Minimum duration of one measurement was 1 sec. The gas analyzer is fully automatized and can function continuously without operator, checked duration of the device continuous operating was 1 week.

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MEASUREMENT OF ETHANOL CONCENTRATION WITH NEAR IR DIODE LASERS.

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An attempt was made for distant detection of alcohol vapour in the open atmosphere with the help of diode laser (DL) spectroscopy technique. We tried to use the same method that was successfully applied for detection of simple molecules such as CO, CO2, CH4 and others. In this method a DL was driven by current pulses of sawtooth form, and small portion of the gas absorption spectrum was compared with reference spectrum. The gas concentration was calculated as correlation function between reference and detected portions of spectra.

Contrary to the situation with simple molecules, spectrum of C2H5OH consists of rather wide bands, which could not be resolved into separate lines at atmosphere pressure. The task was to find the region in ethanol absorption spectrum with large variations of intensity within the DL current tuning and try to use this portion of spectrum for DL detection technique. The task was complicated by the desire to find that portion in near IR range where commercially available diode lasers do not require cooling.

The ethanol absorption spectrum in the range 1000 - 10000 cm-1 was recorded by FTIR spectrometer Bruker IFS 113-v. The near IR absorption band was from 7050 cm-1 to 7250 cm-1 was chosen for more detailed inspection. The only unique feature of ethanol absorption spectrum in this range was Q-branch near 7180 cm-1. The main difficulties of ethanol detection with our DL technique were rather wide range of the Q-branch (more than 6 cm-1, which is large compared to typical DL current tuning range) and the presence of rather strong water absorption lines in the range, overlapping with ethanol Q-branch.

Developed for ethanol measurements DL spectrometer included two cells, which can be filled by ethanol-air gas mixtures at various concentrations and pressures. One of the cells was just a tube cell 2m length, the second cell was tuneable White multipass cell with optical path length from 0.8 m up to 30 m. Selection of DL modes was done with the help of monochromator. Distributed feed back DL with composition GaInAlAs radiating near 7185 cm-1 was chosen for our experiments. This DL allowed radiation wavenumber scans from 7177 to 7183 cm-1 at each current pulse, so the central part of the ethanol Q-branch could be registered. The ethanol concentration was assumed to be proportional to the logarithm of ratio of the absorption intensities at the centre of Q-branch and at the distance 4 cm-1 away from the centre; coefficient of proportionality was found with the help of ethanol-air mixture with known concentration. Water absorption lines in processed spectrum portions were excluded by special procedure. Computer program allowed recording ethanol concentration at real time mode.

Detection limit of our spectrometer for ethanol in open atmosphere with 3 m optical path was found to be 50 ppm in open atmosphere. Relative accuracy of the measurements was 2% or 50 ppm, whichever is larger. Minimum time for one measurement was 1 sec.

NEW PROMISING MULTIPASS SYSTEMS FOR FTIR AND TDL SPECTROSCOPY

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New mirror systems long path length were developed for high-resolution spectroscopy. As compared to the classical White system, the new ones involve new design features as well as improved optical and performance characteristics.

V-shaped mirror system has the highest f Number=f/3.7 among other multipass systems due to nontraditional choice of base length equal to 1.5 f between opposite mirrors. V-shaped six-pass system consists of two mirror-symmetrical three-pass systems of forward and reverse passages, which is unfolded into a Z-shaped Czerny scheme. This optical system served as a basis for the cells designed for FTIR and TDL spectroscopy. The total absorption length was 1.2 m (0.5 l) in the cell for FTIR and 3m (6.6 l) in the device for TDL spectroscopy. V-shaped system has practically no aberrations. The creative process of system improvement was researched off and on for more than 20 years in total. At present this Chernin cell for FTIR spectrometers is being prepared for serial production at the Bruker plant.

The number of passes may reach 1000 in a new promising variation of four-objective matrix system. In this variation entrance and exit openings are located on opposite sides of auxiliary field mirror. This location simplifies light beam coupling and design arrangement of a light source and a detector. Matrix of images consists of odd number of rows, and images of lowest row corresponding of even numbers are absolutely vibrostable. New original procedure of mirror systems adjustment is presented. New effective principle of matrix cell and FTIR spectrometer coupling is developed. Multipass matrix cell with the length pass up to 200 m (0.5 m base) was used in diode laser gasanalyzer AGL-34 for background amount (~1 ppm) measurement of methane in atmosphere.

The matrix two-objective multipass system was created through radical modification of Horn-Pimentel system. Improving of optical scheme and placing of objectives on common rotating plate eliminated substantial drawbacks of the latter.

APPLICATION OF DIODE LASERS FOR MEASUREMENT OF WATER VAPOR DIFFUSION THROUGH LAMINATED FABRICS AND MEMBRANES

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A spectroscopic system based on vapor phase absorption of infrared radiation produced by a diode laser is shown to be useful for measuring water vapor diffusion rates through barrier materials. Measurements of water diffusion through four polymer membranes and membrane laminates show an excellent correlation with an existing water vapor transport apparatus, which uses hygroscopic polymer film capacitance sensors. The diode laser spectrometer eliminates sorption hysteresis artifacts present in the capacitance sensors.

Protective clothing systems for industrial, military, and agricultural applications require materials with barrier properties against toxic chemicals in vapor, liquid, and aerosol form. For many situations, these materials must also have high permeability to water vapor to allow evaporative cooling for the humans wearing them, otherwise the protective clothing system imposes an intolerable thermal burden upon the user. Convenient and accurate laboratory vapor permeation test methods are required to develop and test new materials for protective clothing.

The aim of the work presented here was to evaluate the usefulness of a diode laser spectrometer (DLS) in an existing water vapor permeation apparatus the Dynamic Moisture Permeation Cell (DMPC). The results of this evaluation will be used to refine the prototype DLS and suggest modifications to the design and associated software and instrumentation. The eventual objective is to add the ability to determine the concentrations of multiple gases of various compositions, including water vapor, to create a vapor permeation apparatus capable of measuring multicomponent steady-state and transient mass transport across various protective membranes and membrane laminates.

The diode laser spectrometer has potential advantages over the existing water vapor concentration measurement transducers in the DMPC, which are based on electrical capacitance measurements of a thin hygroscope to attack from organic vapor components in a multicomponent gas diffusion test. They are not designed for measurements at very low concentration levels, and may sometimes give misleading results due to factors such as sorption hysteresis in the hygroscopic polymer film portion of the transducers. Because the DLS system is a non-contact optical method, it also has the potential to give better response times to vapor concentration changes than the polymer film transducers, since the polymer takes some time to absorb the vapor and come to a new equilibrium state before the local vapor concentration can be measured.

Using DLS, the resolution of +/- 0.0025 in relative humidity (+/- 0.25% r.h.) was achieved. This is already an improvement over the maximum resolution of the hygroscopic polymer film sensors (usually about +/- 0.005), but is more variation than we expected of the DLS. Minor design improvements should be able to improve the sensitivity and error range of the DLS system significantly.

SPATIAL MAPPING OF COLLISIONALLY COOLED GAS MOLECULES IN A COLD CELL

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We used a collisional cooling cell which was designed to mount directly on the second stage of a CTI-Cryogenics model 22C CRYODYNE CRYOCOOLER. The cell was maintained at approximately 14 K for all measurements reported. The absorption pathlength in the cell was 3.4 cm, and the window clear aperture was 1.27 cm. The injector was designed to be adjustable, so we could probe the cold gas cloud from the exit plane of the injector to approximately 11 millimeters downstream from the injector. We also could probe the cloud in a direction orthogonal to the previous direction. Our beam is imaged to a spot diameter of approximately 1 millimeter in the center of the cell.

Gas temperatures as low as 24 K were measured approximately 11 millimeters from the nozzle, and temperatures of approximately 40 K were measured close to the plane of the nozzle. Carbon Monoxide was used as the analyte gas for all measurements. Absorbance values for the R(1) line varied between 0.27 and 0.52 units (-ln T) and for the R(4) line the lowest absorbance values used were 0.02 units. Rotational temperatures were in agreement with Doppler determined temperatures.

A REANALYSIS OF THE STRENGTHS FOR SEVERAL LINES IN THE ν2 AND ν5 BANDS OF METHYL FLUORIDE

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Several years ago, J. Mol. Spectrosc. 164, 79-83 (1994) and J. Mol. Spectrosc. 166, 130-136(1994) we published line strength and gas broadening coefficients for several unblended lines in the ν2 and ν5 bands of methyl fluoride. In the analysis of these lines we employed the method of equivalent widths, assuming the lines were Gaussian. This assumption was based upon modeling calculations we performed to estimate the errors we should expect using this assumption.

More recently Lepere, et al, J. Mol. Spectrosc. 180,218-226 (1996), J. Mol. Spectrosc. 182, 184-188 (1997) and Lance, et al, J. Mol. Spectrosc. 180, 100-109 (1996) also reported on line intensity measurements of methyl fluoride. They reported discrepancies between their and our measurements; we have begun a reanalysis of several lines which were measures by both groups in order to better understand the source of these discrepancies.

This paper is report of the progress we have made in this reanalysis.

PERFORMANCE CHARACTERISTICS OF A 0.5 METER ABSORPTION PATH COLLISIONAL COOLING CELL.

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We designed a collisional cooling cell with a 0.5 meter absorption pathlength. The cell is mounted on two CTI cryogenics refrigerators. We will report on preliminary performance tests we‘ve performed on this cell.

LOW TEMPERATURE MEASUREMENTS OF ABSORPTION LINE INTENSITIES IN THE CARBON MONOXIDE FUNDAMENTAL BAND AT TEMPERATURES BETWEEN ROOM TEMPERATURE AND 30 K

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We measured absorption line strengths for one R branch line of carbon monoxide in a 3 cm absorption path length cell a different temperatures between room temperature and 12 Kelvins. We were able to measure pure CO absorptions to temperatures as low as approximately 30 Kelvin. Below this temperature the gas froze out on the cell walls, and we had to use helium butter gas to collisionally cool the carbon monoxide. We will report on the results of these measurements.

DIODE LASERS OF PbSnSe/PbEuSe GROWN BY MBE

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Lead salt tunable diode lasers (TDL) for 4 to 12 μm spectral range have been made by growing $Pb_{1-x}Eu_xSe$ double heterostructures and more complicated $Pb_{1-y}Sn_ySe/Pb_{1-x}Eu_xSe$ separate confinement (DHSC) laser structures on (100) PbSe with $p=1*10^{19}$ cm^{-3}. Stripe contact laser diodes have been fabricated by deposition of BaF_2/MgF_2 insulating admixture on the top n-type contacting epilayer.

At the first stage along with PbSe, Eu, SnSe and Se effusion sources Bi_2Se_3 and Ag sources were applied for n- and p-type doping respectively. Diode lasers grown operate in CW regime up to 120 K. Total power output at 80K attained 400 μW.

Laser heterostructures were studied through depth profiling by means of secondary ion mass spectroscopy (SIMS). Distribution of Sn, Eu and Bi shows abrupt profiles on the 0.1 μm scale, while Ag diffuses into active area and even in the n-type confinement layer. Further unlike Bi behavior, in the carrier concentration range below $p < 8x10^{17}$ cm^{-3} Ag was found to have two diffusion components with at least three orders of magnitude difference in corresponding diffusion coefficients. A lower limit for the coefficient of the fast diffusion component was evaluated to be $D_f > 1*10^{12}$ cm^2/sec.

To reduce free carrier looses the active area of the lead salt TDLs usually is not doped and is believed to results in p-type in the low 10^{17} cm^{-3}. However its concentration increases under operation. Moreover, from our SIMS studies we concluded that using Ag for p-type doping leads to uncontrollable doping of the active layer. This can be a major limiting factor for the high power output and increasing operation temperatures of DH lasers, and would be detrimental for quantum well lasers.

For telluride rich systems, doping with Tl for growing p-type films is the common procedure. According to the data obtained by Preier(1) Tl is not incorporated as an acceptor under MBE conditions in selenides and sulfides. However, we introduced in our MBE Tl_2Te instead of Ag for p-type doping. P-type $Pb_{1-x}Eu_xSe<Tl>$ thin films with hole concentration in the $1*10^{17}$ to $2*10^{19}$ cm^{-3} range were reproducibly grown on (111) BaF_2 substrates. Carrier mobility at 80K decreases from 15000 to 2000 $cm^2/V*sec$ as composition x increases from zero to upper laser relevant value of 5%.

Diode lasers made from heterostructures grown with Tl_2Te p-doping demonstrate improved characteristics. Maximum CW operating temperature of 150 K was achieved and total power output at LN_2 temperature was raised up to 1.5 mW. Single mode output as high as 800
μW was observed. Mode tuning range and mode spacing was 1 to 6 cm^{-1} and 1 to 3 cm^{-1} respectively. Current tuning rate of 50 to 1000 cm^{-1}/sec was obtained under pulsed operation. Fabricated TDLs were successfully used in a variety of spectroscopic and applied analytical studies. Recent results are presented.

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TDL BASED ANALYZER OF THE $^{13}C/^{12}C$ RATIO IN EXHALED CO_2 AND IT'S CLINICAL APPLICATIONS

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Application of tunable diode lasers to the measurements of carbon isotope ratio in carbon dioxide could give very simple and effective solution of the analytical problem when applied to breath test medical diagnostics using ^{13}C-labeled substances. It is based on high quality of the spectroscopic analysis that could be obtained in routine spectral measurements with tunable diode lasers.

The analytical problem of the CO_2 isotope species detection with high accuracy in breath has some specifics that are the following: CO_2 content in breath may vary significantly from breath to breath depending on human metabolism rate and cardio-respiration specifics. CO_2 concentration in exhaled air is usually ranged from 2 to 4 %. The natural $^{13}C/^{12}C$ abundance is 0.011237 and determines the necessary dynamic range in the concentration studies. Sensitivity and accuracy for the detection of $^{13}CO_2$ content variations need to be as high as possible to minimize chemical load of tested organism with used ^{13}C-labeled substances because its amount could define the breath test cost and organism exposure to chemicals. Natural metabolic variations of the $^{13}C/^{12}C$ ratio in exhaled air reach 0.3% (or 3 $^{0}/_{00}$) and desirable accuracy and sensitivity of its determination is believed to be better than 0.5 $^{0}/_{00}$. Exhaled air contains a lot of water vapor that could reach 3 to 4 % at human body temperature. For more convenient and comfort clinical diagnostics it is desirable also to minimize the volume of breath sample used.

Technical characteristics of the TDL spectroscopy meet very well the demands of the problem of the exact $^{13}C/^{12}C$ ratio measurements in the exhaled carbon dioxide. High spectral resolution of better than 10^{-4} cm^{-1}, continuos tuning of 3 to 6 cm^{-1} in one lasing mode, high amplitude stability, single mode power of the order of 300 to 500 μW, and an ability for easy selection of the spectral range the most suitable for the isotope ratio detection are available with use of A4B6 MBE TDLs and secure high quality, low noise and selective detection of $^{12}CO_2$ and $^{13}CO_2$ absorption spectra and exact measurements of their content ratio in small volume breath sample.

TDL based analyzer with very simple optical schematics aimed to the detection of the $^{13}C/^{12}C$ ratio in exhaled CO_2 is described. 4.2 micron lead-salt tunable diode laser fabricated by MBE technology and operating at ~100K was applied in the system. It was used in pulse generation mode providing fast and accurate detection of the exhaled air mixture transmission spectra. Used 50 ml analytical cell was of 100 mm length. Cooled InSb photodiode was used for TDL radiation detection. Special electronics to control laser temperature and current pulses as well as for fast 12-Bit acquisition of the detected transmission spectra was applied. Achieved accuracy of the $^{13}C/^{12}C$ ratio measurements is estimated as 0.5 $^{0}/_{00}$ and is defined by feedback interference on the system optical elements.

Data on practical application of the system to clinical diagnostics including detection of the *Helicobacter Pylori* bacteria using ^{13}C Urea Breath Test are presented.

DETECTION OF ENDOGENOUS NO AND CO IN BREATH USING TDL: APPLICATIONS FOR HUMAN PHYSIOLOGY AND CLINICAL DIAGNOSTICS

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At present, notions of very important role of endogenous NO and CO in human physiology and biochemistry are developing intensively. These molecules act as mediators taking part in signal transfer in the course of various selfregulation processes in organism.

NO was found to play an important role in blood pressure control, in maintaining blood vessel tonus, in providing blood micro-circulation in tissues, in performing a set of immunity reactions by effector cells and in information transfer between neurons. A level of constituitive and inducible NO synthesis reflects a state of many important systems in organism and could be used as an indicator of health or disease as well as a measure of applied therapy efficiency.

The last studies of CO activity in organism indicate a specific role not only in metabolism regulation of haem-containing protein structures, but also in transmission of nerve pulses, maintaining of micro vessel muscle tonus, inducing of chemoreceptor activity, control of some hypothalamus hormone secretion etc.. Besides, CO elimination with breath is sensitive to blood pH variations and to extent of blood saturation with oxygen and thus could characterize gas transportation properties of blood, its acid-base balance and biochemistry.

In connection with the key role of these molecules in the numerous biochemical processes in organism, research and development of a technique for the noninvasive diagnostics of endogenous CO and NO generation, transport and removal via breath became topical. Such technique could provide a possibility for deeper research of processes going on in human and animal organisms, for development of new therapeutic and pharmacology approaches to disease treatment and for prompt diagnostics in course of any therapy.

Application of high resolution spectral analysis based on the use of TDL is one of the most adequate to the problem. Due to the combination of excellent TDL analytical characteristics, such as sensitivity, speed of response, and selectivity, that could be realized when applied to the molecule detection in multi-component gas mixtures, it is possible to analyze chemical composition of the exhaled air carefully and in real time. In solving the problem this approach has the following advantages as compared with conventionally used analytic techniques:

- possibility to simultaneously measure in the exhalation the microconcentrations of several gaseous substances which are significant from the clinical diagnostics viewpoint;
- high concentration sensitivity, i.e. at the level of 0.1-1 $\mu g/m^3$;
- possibility for fast recording and analysis of data with the time constant of 0.01 sec, which allows to diagnose the physiological processes dynamics;
- high selectivity detection of the substances under research in the presence of the dominating components of the exhaled air (N_2, O_2, CO_2, H_2O), and traces of hundreds of other volatile substances;
- on-line detection of the gas substances under study in the exhalation without a preliminary concentration and/or accumulation of the studied air samples.

TDL based systems for high sensitive detection of endogenous NO and CO in breath and the last data on their application to human physiology and clinical diagnostics are presented.

STUDY OF THE ν_7 BAND OF THE ETHYLENE MOLECULE WITH TUNABLE DIODE LASERS

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The absorption spectrum of the C_2H_4 molecule was studied in 930 to 1030 cm^{-1} spectral region by means of tunable diode laser spectroscopy.

PbSnSe tunable diode lasers manufactured from single crystal lead-salt semiconductor alloys by means of Molecular Beam Epitaxy were used in this studies. These lasers operates at 80 to 120 K temperature region that gives an ability to cover 50 to 100 cm^{-1} spectral region using one diode. Continuos tuning range in one single mode was from 2 to 6 cm^{-1}. Mode spacing was 1 to 3 cm^{-1}. Longitudinal mode linewidth was estimated to be 10^{-4} cm^{-1}. Single mode output power of the lasers reached 0.5 mW. Threshold current was 100 to 250 mA at 80 K. For the high resolution spectroscopy studies, these lasers were used in pulse generation mode. Typical duration and amplitude of the used current pulses were usually varied from 2 to 10 ms and from 0.3 to 2.5 A, respectively.

For the C_2H_4 transmission spectra recording, 1.0 m gas cell was used. The pressure of the studied gas (of 99.95% purity) was limited to 4 Torr to avoid line pressure broadening. Near room temperature of the studied gas was measured with 0.2K accuracy.

More than 200 transitions of the Q and P branches of the “allowed” ν_7 and “forbidden” ν_4 bands were observed. 60 transitions of the ν_7-band of ethylene were measured with an absolute accuracy of better than 0.0003 cm^{-1} and were identified. NH_3 and CO_2 absorption lines were used for absolute frequency calibration of the ethylene absorption lines.

Intensities of more than 20 ethylene absorption lines from the studied ν_7 band were accurately measured. This data were used for precise determination of the constant of the ethylene transition moment $\delta m_c/\delta q_7$.

For accurate spectra treatment and absorption line assignment, special programs for spectra calculation and analysis were developed. The programs are based on the Watson Hamiltonian using up to sixtic distortion coefficients and the interaction Hamiltonian taking into account the Corriolis interaction between ν_{10}, ν_7, ν_4 and ν_{12} transitions centered in the 10 micron spectral region studied. The last one includes up to third-order Corriolis resonance interaction terms.

ν_7 ethylene spectra calculated with use of the programs was compared with the GEISA and the HITRAN spectral data.

The experimental and calculated data on the ethylene absorption in the 10 micron spectral region were used for selection of the ethylene absorption lines the best for the detection of these molecules in different analytical problems including atmosphere pollution monitoring and biomedical diagnostics. Developed and tested program support for spectra modeling and calculation could be applied for other molecules having strong interaction of vibrational states.

A MULTICOMPONENT TDL ANALYZER FOR OPEN-PATH MONITORING OF GASEOUS ATMOSPHERIC POLLUTANTS

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Most of analytical problems need in multicomponent gas detection. Some of them requiring extra high sensitivity, selectivity and fast response can be solved using TDLs. In this case all analytical advantages are related with high spectral resolution of TDLs and possibility of simple electronic driving of their spectral parameters.

Presented TDL gas analyzer was developed for the detection of three gaseous pollutants with sub-ppb concentration sensitivity in open atmosphere at a stationary site. General schematics of the TDL single-gas open-path system reported earlier was used. Three TDLs of different spectral region, each for specific molecule, as well as three IR detectors are located on the heat sink of 1-litter LN_2 cryostat. Operation temperature of each laser can be separately controlled. The cryostat position is electronically controlled providing transverse alignment of any selected pair of laser and detector on main optical axis of the system to detect the molecule of interest. TDL radiation sent to open atmosphere is collimated by two-lens objective. Radiation returned by the mirror corner is collected to the detector using the Cassegren telescope. Up to 600 meter to-and-fro distance is available with used optics.

Current pulses are used to pump TDLs and to tune their frequency due to laser crystal heating. The current pulse parameters and working temperatures are specially selected and controlled by PC for every laser to obtain detection of the desirable analytical line. For the MBE lead-salt TDL used for CO, NO, CH_4, C_2H_4 and NH_3 detection, typical pulse amplitude is 0.4 to 1.5 A, pulse repetition rate is about 100 Hz and pulse duration is up to 10 ms. Laser operation temperatures are from 80 to 130K. Stability of the analytical line position inside the pulse is defined by fluctuations of the laser temperature in the cryostat, thus the last one is controlled with 10^{-3}K accuracy.

Studied gas transmission spectra formed by laser frequency sweeping during the pulse are detected using fast acquisition system driven by IBM PC. Measured amplitude of the resonance absorption is used to calculate gas concentration together with database line and optical path parameters. Sensitivity of the analyzer is defined by a limit in detecting optical density variations with used acquisition system. Used 50 ns, 8 bit ADC and accumulation of the signal with fast amplitude sweeping provide $2*10^3$ S/N ratio.

Special soft- and hardware was developed to support this multicomponent analyzer. For every laser channel algorithmic and programming support of the method ensure visualization of spectral and service information, clamp-on of the data management and record system, set-up automatic calibration and spectral data processing, control of the laser parameters and automatic adjustment of the laser to the analytical absorption line. Special possibilities for alternate channel multiplexing were provided.

At the first stage of the project the system was adjusted for the detection of CO, NH_3 and CH_4 in open atmosphere. The system was tested in the field experiments on the detection of air pollution in Siberia nearby Nefteugansk oil production fields in summer 1996.

DIODE LASER STARK SPECTROSCOPY ON PERSISTENT HOLES

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Persistent spectral hole burning (HB) [1,2] makes possible to perform spectral investigations of molecules in matrices with spectral resolution up to the dozens of GHz and now is broadly used for science and applications. In particular, this technique is very promising to investigate the influence of an external electric field effect (Stark effect) on complex molecules in solids [3]. It is important to note that in all papers devoted to the Stark effect on the holes (except of [4]) to field strengths of up to 5×10^4 V/cm no quadratic but only linear Stark effect have been obtained (even for centrosymmetric molecules because an internal electric field in matrix has broken centrosymmetry to such an extent as to make the quadratic Stark effect negligible).

The main instrument in hole burning spectroscopy is usually an expensive and complicated tunable single frequency dye laser. But it seems very promising to use for this purpose much more simple and cheap diode lasers. In this paper the Stark effect on the hole-burning spectra of Zn- and Mg-phthalocyanine (Zn-, Mg-PhC) in polyvinylbutyral (PVB) films at 4,2 K have been measured using a tunable diode laser technique in visible region. Simultaneously with linear Stark effect a quadratic effect was also recorded (some first results for one system - Zn-PhC were presented in [5]). For an analysis of the experimental data we also performed numerical calculations of the hole profile under external field for different models.

The high resolution HB-setup is based on a single-mode diode laser with the operation system and included helium cryostat, Stark cell, photon counting system and PC. The operation system was controlling temperature of the laser with accuracy 2×10^{-3} ^{o}C in the range from -20^o till 40^o C. Power source permitted to adjust a current in the laser with accuracy 10^{-4} at very low noise.

For both systems under investigation we obtained nonlinear Stark effect which was used to obtain Stark parameters of the molecules and also value of the internal electric field in polymer system. From the comparison of the experimental data with the model calculation results we obtained:

for Zn-PhC in PVB: $\Delta\mu_{ind}$=0.105 D, $\Delta\alpha$=62 A^3, $E_i=7\times10^5$ V/cm;

for Mg-PhC in PVB: $\Delta\mu_{ind}$=0.095 D, $\Delta\alpha$=50 A^3, $E_i=6{,}5\times10^5$ V/cm.

These first results show very clear that diode lasers can be successfully used in Stark spectroscopy on the persistent holes.

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FAST TUNING OF 3.3μm InAsSb/InAsSbP DIODE LASERS DUE TO NONLINEAR OPTICAL EFFECTS

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The key elements of superhigh resolution laser spectrometers are wavelength tuning diode semiconductor lasers. Earlier lasing frequency was usually tuned by heating[1]. In this paper we discuss for the first time a new conception of fast tuning of the wavelength in diode lasers by using nonlinear optical effects and its utilization for 3.3μm diode lasers. Laser structures based on InAsSb/InAsSbP double heterostructures with different refraction index were grown by liquid phase epitaxy. Emission spectra, far-field patterns, wavelength tuning direction and its value were studied in depending on current change from threshold value I_{th} up to 3 I_{th} in the temperature interval 77-100K. Emission properties of lasers driven by rectangular and sawtooth current pulse have been compared. Controlled by current wavelength shift in single-mode lasing was obtained both towards the shorter wavelength (up to 4.56cm^{-1}) and towards the longer wavelength (up to 0.9cm^{-1}) in the spectral range of 3.33-3.34 μm. It was determined, that with current increase a spatial distribution of the emission changed, and then nonequilibrium carriers concentration decreased in the center of the laser stripe (in the region of the maximum emission intensity) and rose on the edges. Thus, self-focusing effect occurred. It resulted in variation of refractive index within the active region with emission intensity and led to lasing wavelength shift. Conditions of the high speed tuning of lasing spectrum both in shortwavelength and long one were determined. The quantum-mechanical model of the fast tuning effect was proposed. It was shown that, quantum-mechanical nature of using this nonlinear optical phenomenon provides high-speed operation of tuning (approximately 10^{-12}c) for mid-infrared tunable diode lasers understudy.

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SUPPRESSION OF INTERFERENCE FRINGES AT ULTRA LOW ABSORPTION MEASUREMENTS

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When employing diode lasers for sensitive absorption measurements the application of double-beam logarithmic detection technique in combination with wavelength modulation allows to achieve in actual conditions the minimum detected absorptions determined by shot noise of laser radiation [1]. This technique suppresses as common-mode (in-phase) noise components, such as residual amplitude modulation (RAM) and noise of the laser, and also differential interferences caused by low frequency fluctuations of transmission, absorption and detection, which spectra lie outside the measurement passband. Unique unremovable interferences are fluctuations of residual Fabry-Perot fringes. They do not correlate in different arms of optical setup, thus determine the limiting characteristics of a method. This problem is not purely technical, because even in carefully constructed optical setup it is very difficult to reduce a level of Fabry-Perot fringes below 10^{-5}.

Used techniques of suppression of residual Fabry-Perot interference fringes are connected with vibrations and consequent signal averaging [2]. At measurement of ultra low absorptions these methods are suitable a little, because at absorption level of ~ 10^{-6} and lower the sources of interference fringes are not localized and such fringes can arise in various parts of optical setup. In our optical scheme we use an angular modulation of a diode laser beam. Thus simultaneously for each local source of interference fringes the effective optical path varies, resulting in oscillating character of interference pictures. At an optimal choice of amplitude and frequency of angular modulation the value of the interference contribution in transmission can be reduced on 20-40 dB without noticeable deterioration of the noise characteristics of the measurement system. It is important, that the strong flicker noises, inevitably arising at mechanical modulation, are effectively rejected by the logarithmic amplifier, while in a usual linear mode these low frequency noises of transmission are transferred into the registration passband and result in deterioration of the detection limit.

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LOGARITHMIC DETECTION OF ABSORPTION SIGNALS

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At the previous conference we presented the first results about using of a logarithmic scheme for detection of absorption signals [1]. It was pointed that the main reason, which extremely degrade the characteristics of an usual transmission technique in actual devices, is the multiplicative character of the contributions of the various factors in the beam intensity at passing it from a source (diode laser) to the photodetector. These factors are nonselective absorption, reflection, dispersion, conversion coefficient of the detector, *etc*. Because of multiplicative character of a transmission signal the low frequency fluctuations of parameters are transferred into the passband of registration and limit the sensitivity. A radical method eliminating these features, is the application of wavelength modulation of diode laser radiation and logarithmic registration of a photodetector output signal. In this scheme the multiplicative components of a signal are transformed into the additives and noise components outside the detection passband can be effectively suppressed.

New results along with the theoretical considerations will be presented in our report. We investigated different schemes of logarithmic amplifier and chose a few with the best noise characteristics. The schemes were used for real analytical measurements with near-IR diode lasers: detection of Rb in conventional graphite tube analyzers and detection of chlorinated molecules by gas chromatography applying diode laser - plasma detection. It was shown that the double-beam arrangement with logarithmic subtraction of sample and reference detector currents allows to suppress variations of the laser radiation power outside the registration passband and achieve a detection limit as low as 3×10^{-8} absorbance units (AU) for a 1-sec time constant. The detection limit achieved is determined by shot noise of radiation [2,3] and can be improved with increasing time of averaging. If the developed technique is used the background signal and its variations become negligible. The technique allows to measure an absorption in actual devices if there are vibrations, smoke, turbulent gas streams, temperature drift of parameters, non-uniformity of a photodetector sensitivity, *etc*. As it is realized now, the analytical calibration curve remains linear from 3×10^{-8} up to 2.3 AU [4].

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TDLAS-DIAGNOSTICS OF HYDROCARBON CONTAINING MICROWAVE PLASMAS

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Low pressure, non-equilibrium, molecular microwave plasmas have become of growing interest due to their advantageous properties in the field of plasma processing as well as for their importance in basic research. The monitoring of plasma reaction products such as transient species and stable molecules, in particular the measurement of ground state concentrations, is the key to an improved understanding of the plasma chemistry. This contribution presents our recent results of spectroscopic diagnostics of hydrocarbon containing microwave plasmas (f= 2.45 GHz). The methyl radical and a group of stable molecules, CH_4, CH_3OH, H_2CO, C_2H_2, C_2H_4, C_2H_6, H_2O, CO and O_2, were detected for the first time in $H_2/Ar/O_2$ microwave plasmas, at methane and methanol admixtures of only a few percent using IR-TDLAS. Chemical modeling of the plasma has been carried out to predict the concentrations of the ten gaseous species detected so far [1].

The experiments were performed in a planar microwave plasma reactor [2] (P= 1.5 kW, p= 1.5 mbar, total flow rate: 555 sccm). The feed gas was a mixture of *x* sccm H_2+ 60 sccm Ar + *y* sccm O_2 + *z* sccm (CH_4 or CH_3OH). For the methane or methanol mixtures different flow rates *z*: 5 - 40 sccm were chosen corresponding to between 0.9 and 7.2 % of the total flow rate. When oxygen was added the content of hydrogen was reduced proportionally.

The degree of dissociation of the added hydrocarbon gas is required for studying the conversion of the source gas mixture into radicals and stable molecules and for understanding the mass balance of the plasma process. The dissociation degree of methane and methanol in principle increases while adding oxygen, but reaches a much higher level for methanol. Since electron impact can be expected to be the major process contributing to hydrocarbon dissociation, presumably the higher rate of electron impact dissociation of methanol is due to the weaker C-O bond in methanol than the C-H bond in methane. The methyl radical is a major product in both cases. In the presence of oxygen the methyl radical concentration appears to decay exponentially. This behavior was found to be independent of the type of hydrocarbon used and was also observed for methane, and for all other hydrocarbons produced in the plasma [3]. More than 50 reactions were considered in the chemical modeling leading to a relatively successful match of experimental and calculated concentrations.

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NEW TECHNOLOGY FOR RISING THE SENSETIVITY OF THE CONCENTRATION DETERMINATION.

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It is known that TDLS promotes the very high degree of selectivity and sensitivity of gaseous components detection. For evaluation of the mean density of a specific molecular constituent the differential absorption method is employed.

Before it was shown that probing by a frequency-modulated single sideband signal and measuring the resulting radio-frequency beat signal phase associates absorption and dispersion and permits to provide species detection limit well below 1 party per billion if multiple-pass cell was used [1].

At the same time, the theoretical researches are showing that the amplitude modulation of the sounding ray and dispersion nonlinearity of the refractive index near absorption line can ensure an appearance of a new measurable parameter such as the received carrier frequency deviation (RCFD) which is more sensitive to the component concentration than absorption and more workable than the beat phase [2].

Comparising of the sensitivities for the same measurement conditions may be written as

$$dN_{mod}/\, dN_{absorp} \approx (\Delta\omega)^2\, d(\delta\omega)/\, \Omega^3\, (dI/I)$$

where $\Delta\omega$ is halfwidth of the measured line, $d(\delta\omega)$ is measurement accuracy of the RCFD (let it as 1), dI/I is the relative registrator sensitivity and Ω is the modulating frequency. The estimations of real conditions show increasing of the sensitivity more than million times.

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HIGH-POWER TUNABLE LASER DIODES FOR SELECTIVE EXCITATION OF RARE-EARTH IONS IN CRYSTALS

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We present a study on narrowing and tuning the lasing spectrum of InGaAsP MQW hetero-lasers with a power of ~ 1 W. The study was aimed at increasing the pump efficiency of a miniature laser based on GGG crystals doped with 15 at.% Yb^{3+}.

Fig. 1a shows a schematic of a laser, whose selective resonator includes a diffraction grating with 1200 grooves/mm. The grating operates in the first order with an efficiency of 10%. The laser was pumped with 90% of the zeroth order light. Fig. 1b gives the absorption spectrum of a laser medium, a 1-mm thick GGG-Yb plate. The emission spectrum of an LD without a feedback is shown in Fig. 1d. It can be seen that pumping of Yb^{3+} ions in the narrow band centred at 0.9705 μm is most efficient. The emission spectrum of an LD with external cavity (EC) tuned to the 0.9705 μm is depicted in Fig. 1c. By varying the grating angle, it was possible to tune a narrow lasing spectrum in the range from 0.920 to 0.9750 μm, wheras by narrowing the spectrum, we increased pumping efficiency in less intense lines centred at 0.9315 and 0.944 μm. The width of the laser chip in this experiment was 100 μm.

By using a tunable powerful laser, we improved the pump selectivity of GGG-Yb crystals in the 0.9705 μm band, lasing being achieved in a compact scheme with an active medium, 1 mm in thickness. A scheme with a semi-spherical cavity (the curvature raduis of the output mirror of 5 cm and its tramsmittance of 2.5%) yielded stimulated emission at 1.038 μm. This emission corresponds to transitions between levels $^2F_{5/2}$ and $^2F_{7/2}$ with eneregies of 10304 and 670 cm^{-1}, respectively. The transitions occurred in accordance with a four-level scheme.

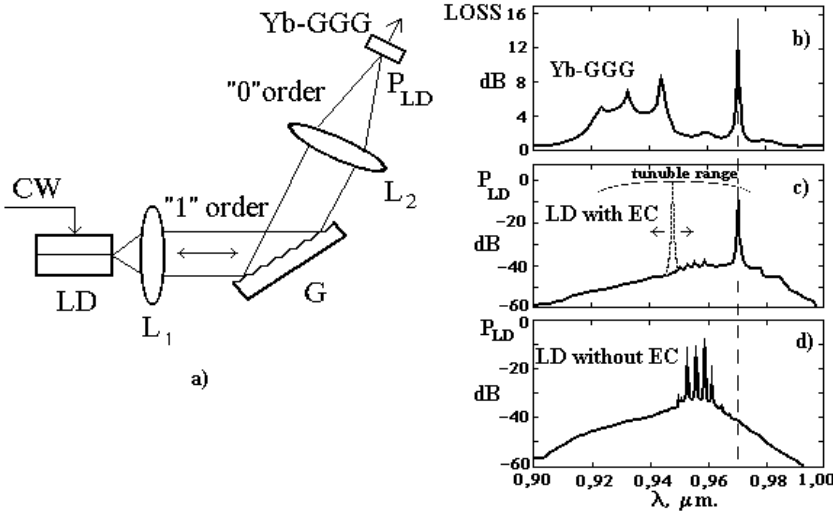

Fig.1. a- scheme of the tunable LD with EC,
b- absorption spectrum of Yb^{3+} ions in GGG crystal,
c- tunability characteristics of LD+EC for YB-GGG pumping,
d- free running spectrum of 1-W LD without EC.

TUNABILITY OF TWO-FREQUENCY DFB LASER DIODES

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Two-frequency tunable laser diodes are finding increasing use in high-precision interferometric measurements, as master lasers in fiber-optic soliton generators with a frequency in the range 10 - 100 GHz , and in self-calibrated fiber-optic sensors. In this report, we investigate tunability of the spectra (fig.1b,c) of a single one-section two-frequency DFB-LD with a homogeneous diffraction grating (without a $\lambda/4$ shift) using confocal interferometer (fig.1a).

DFB-LDs with a homogeneous grating can provide either two-frequency or single-frequency lasing depending on the pump current. We investigated tunability of the lasing spectrum depending on the size of the Bragg slit, its position with respect to the optical gain contour of the active medium, and on the strength of the grating-cavity coupling. It was found that with a large Bragg slit, steady single-frequency lasing can be achieved on the DFB mode of the grating, whereas the other frequency corresponds to the longitudinal mode of the Fabri-Perot resonator and can be smoothly tuned by current and temperature. This fact opens up possibilities for the creation of lasers with a smoothly tunable frequency difference. In the interferometric systems for absolute physical measurements, the light intensities at different frequencies may differ by a value as high as one order of magnitude, because this difference can be compensated for by amplification following demultiplication. The dependencies of the width of two lines, generated independently of one another, on the pump current have been obtained. We discuss practical applications of the two-frequency lasing of a single laser in systems based on phase-sensitive measuring techniques and in analogue systems with increased stability of the intensities of the probe optical signals.

In summary: Two-frequency mode of DFB-LDs lasing with wavelength difference λ_1-λ_2 in the range of 2 - 25 nm and linewidths of $\Delta\nu$=30-100 MHz was obtained.

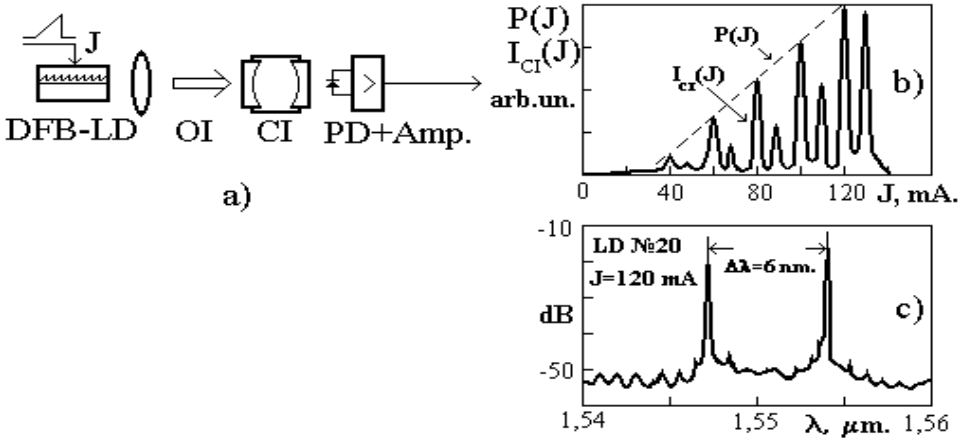

Fig.1. Experimental setup (a), two-frequency tuning characteristics (b) and typical two-wavelength spectrum of DFB-LD ©.
OI - optical isolator, CI - confocal interferometer, FSR=1,5 GHz, finesse - 100.

FIBER-OPTIC INTERFEROMETER - A NEW TOOL FOR NARROW-LINEWIDTH ANALYSIS OF HIGHLY COHERENT TUNABLE LASER

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Nowadays, the use of semiconductor lasers has expanded considerably (coherent communication, fiber-optic sensors, and high-precision physical measurements), and the requirements on their performance are becoming more and more rigid. First and foremost, these requirements relate to coherence and tunability. We present simple fiber-optic devices and techniques for wide-range analysis of coherence and tunability of narrow-linewidth lasers. The fiber-optic interferometric techniques are based on the fact that modern single-mode fibers can maintain and transmit the main coherent characteristics of laser radiation - frequency spectrum and polarization - over distances from 1 m to ~ 10 km.

Fig. 1a shows an experimental arrangement for measuring the power-current characteristics P(J) of laser diodes (LD) with an external cavity and a Mach-Zender fiber interferometer with an arm length difference ΔL in the range from ~ 1 m to 1 km. The output signal of the interferometer I_{MZ} (J) contains information on a change of the lasing frequency ν_L and on linewidth $\Delta\nu_L$. One period of the beat signal corresponds to a frequency change $\delta\nu=c/n\Delta L$ = 10 MHz for ΔL=20m and n=1,5. The Lorentzian linewidth $\Delta\nu_L$ is determined by formula $\Delta\nu_L= -2\ln\gamma/\tau$, where $\tau=n\Delta L/c$, $\gamma=V(1+X)/2\sqrt{X}$ is the coherence degree, V is the visibility of the interference pattern, and $X=I_1/I_2$ is the ratio of the intensities of the interfering beams (i.e. the interferometer parameter). The relations given above allow us to calculate the linewidth $\Delta\nu_L$ at any point of the power-current characteristic P(J) (fig.1b) and at any point of the tuning characteristic $\nu_L(J)$ to a high accuracy set by ΔL only.

The above technique was applied to studying 1.3 μm MQW laser diodes with a high-Q-factor external cavity. Continuous tuning was achieved in single-frequency regime, the current being varied within a range ΔJ~50 mA and the tuning rate being $\Delta\nu/\Delta J$ = 2 MHz/mA. The latter value of $\Delta\nu/\Delta J$ is indicative of a strong selective coupling with the external cavity. One can see that the self-stability of single-frequency lasing is suitable for high-precision interferometric measurements.

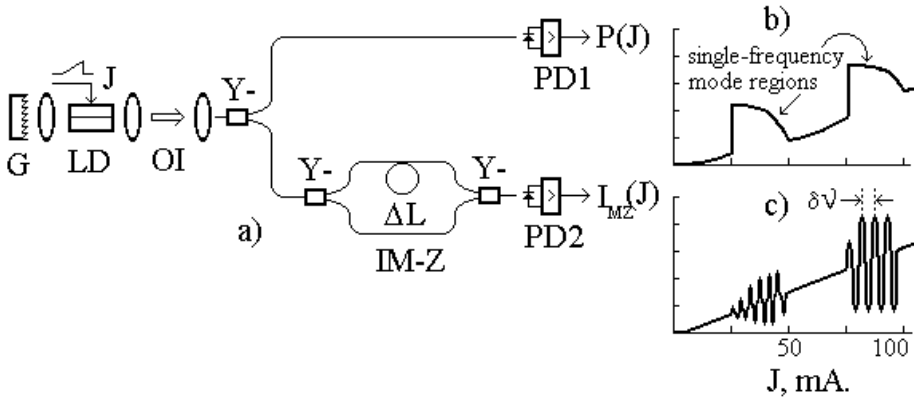

Fig.1. The setup a) and signals of a fiber-optic Mach-Zender Interferometer c), which allow one to determine the tunability characteristics: V(J), $\gamma(\vartheta)$, $\nu_\Lambda(\vartheta)$, $\delta\nu(\vartheta)$, $\Delta\nu_\Lambda(\vartheta)$.