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HighRus-2015

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Symposium Schedule

Time	**Tuesday, June 30**	**Wednesday, July 1**	**Thursday, July 2**	**Friday, July 3**	**Saturday, July 4**
9:00 – 10:30	Registration	**Invited Lectures E**	**Invited Lectures J**	**Invited Lectures L**	**Invited Lectures Q**
10:30 – 11:00	Opening	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00 – 12:30	**Invited Lectures A**	**Invited Lectures F**	**School Lectures K**	**Oral Session M**	**Oral Session R**
12:30 – 14:30	Lunch Break	Lunch Break	Lunch Break	Lunch Break	Lunch Break
14:30 – 16:00	**Oral Session B**	**Oral Session G**	Excursion	**Oral Session N**	**School Lectures S**
16:00 – 16:15	Coffee Break	Coffee Break		Coffee Break	Coffee Break
16:15 – 18:00	**Poster Session C**	**Poster Session H**		**Poster Session O**	**Round Table T**
17:30 – 19:00	**School Lectures D**	**School Tutorials I**		**Round Table P**	Closing
19:00 – 22:00	Cocktail party		Banquet		

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Session Program

June 30, 2015, Tuesday

Invited Lectures A, 11^{00}–12^{30}

Chair: Yurii N. Ponomarev

A1 Microwave Coherence Spectroscopy: How to use real high resolution – and why
Jens-Uwe Grabow

A2 Laser spectroscopy of some MH molecules with astrophysical "overtones"
Amanda Ross

Oral Session B, 14^{30}–16^{00}

Chair: Vladimir G. Tyuterev

B1 A new triplet transition of the V_2 molecule
A.S.C. Cheung, Yue Qian, Y.W. Ng

B2 Accurate non-adiabatic corrections to ro-vibrational levels of small molecules through effective nuclear masses
J.R. Mohallem, L. Diniz, L. Adamowicz, A. Alijah

B3 A database of NO_2 spectral line parameters at $T = 1000$ K
O.K. Voitsekhovskaya, O.V. Egorov, D.E. Kashirskii

B4 Numerical construction of symmetry-adapted ro-vibrational basis sets for variational nuclear motion calculations
S.N. Yurchenko

B5 Nitrous Oxide Spectroscopic Databank (NOSD)
S.A. Tashkun, V.I. Perevalov, N.N. Lavrentieva

B6 High-resolution spectra of polarized thermal radiation in atmosphere: simulation for satellite remote sensing
B.A. Fomin, V.A. Falaleeva

Poster Session C, 16^{15}–18^{00}

C1 Millimeter-wave measurements and ab initio calculations of the NH_3–CO complex
L.A. Surin, A.V. Potapov, S. Schlemmer, A.A. Dolgov, I.V. Tarabukin, V.A. Panfilov, Yu.N. Kalugina, A. Faure, A. van der Avoird

C2 High resolution analysis of $S^{18}O_2$ spectrum: The ν_1 and ν_3 interacting bands
Yu.V. Krivchikova, V.A. Zamotaeva, S.A. Zhdanovich

C3 The disagreements between calculation results of water vapor spectral characteristics at high temperatures
O.K. Voitsekhovskaya, O.V. Egorov, D.E. Kashirskii

C4 On the "expanded local mode" approach applied to ethylene
A.S. Belova, A.L. Fomchenko, Yu.S. Aslapovskaya

C5 High resolution analysis of the v6 band of the $CH_2=CD_2$ molecule
K.B. Berezkin, N.V. Kashirina

C6 The absorption spectrum of ^{17}O enriched water vapor by CRDS between 5850 and 6670 cm^{-1}
S.N. Mikhailenko, A. Campargue, D. Mondelain, S. Kassi, E.V. Karlovets

C7 High resolution absorption spectra of $^{12}C^{18}O_2$ and $^{16}O^{12}C^{18}O$ in the 11 260–11 430 cm^{-1} wavenumber range
L.N. Sinitsa, A.A. Lugovskoi, V.I. Serdyukov, S.A. Tashkun, V.I. Perevalov

C8 High sensitivity cavity ring down spectroscopy of CO_2 overtone bands near 830 nm
Y. Tan, X.-Q. Zhao, J. Wang, A.-W. Liu, S.-M. Hu, O.M. Lyulin, S.A. Tashkun, V.I. Perevalov

C9 *Ab initio* calculation of ro-vibrational spectra for GeH_4 molecule
A.A. Rodina, A.V. Nikitin, M. Rey, Vl.G. Tyuterev

C10 First principles calculation of rovibrational spectra for SiH_4 molecule
Y.S. Chizhmakova, A.V. Nikitin, M. Rey, Vl.G. Tyuterev

C11 Combined effect of small- and large-angle scattering collisions on a spectral line shape
V.P. Kochanov

C12 Accuracy and precision of line center frequency measurements of $^{16}O^{12}C^{32}S$ rotational lines of in MM and Sub-MM wave range
G.Yu. Golubiatnikov, S.P. Belov, A.V. Lapinov

C13 Numerical model of Zeeman splitting of ro-vibrational lines in the NO fundamental band
Yu.G. Borkov, O.N. Sulakshina, Yu.M. Klimachev

C14 Wave functions and lifetimes of ozone metastable states above the dissociation threshold: Impact on the dynamics
V. Kokoouline, D. Lapierre, A. Alijah, Vl.G. Tyuterev, R.V. Kochanov, J. Blandon

C15 Estimations for line parameters of SO_2
B.A. Voronin

C16 Retrievals of the CH_4 and CO_2 atmospheric amount from the high resolution absorption spectra of solar radiation with the use of different spectroscopic databanks
T.Yu. Chesnokova, A.V. Chentsov, N.V. Rokotyan, V.I. Zakharov

C17 Evidence of stable Van Der Waals CO_2 clusters relevant to CO_2-rich atmospheres
T.N. Sinyakova, R.E. Asfin, D.V. Oparin, N.N. Filippov, J.V. Buldyreva

C18 Temperature dependence of self-, N_2-broadened line widths of methyl cyanide vibrational lines
A.S. Dudaryonok, N.N. Lavrentieva, J.V. Buldyreva

C19 Study of the H_2O–H_2O line broadening in 15 500–16 000 cm^{-1} region
L.N. Sinitsa, V.I. Serdyukov, A.P. Shcherbakov, N.N. Lavrentieva, A.S. Dudaryonok

C20 Contribution of different components of bimolecular absorption to the water vapour continuum in rotational and fundamental rovibrational spectral bands
T.A. Odintsova, E.A. Serov, M.A. Koshelev, M.Yu. Tretyakov

C21 Addition of the H_2, He and CO_2 broadening and shifting parameters and their temperature dependences. Part 1: SO_2, NH_3, HF, HCl, OCS, and C_2H_2
J.S. Wilzewski, I.E. Gordon, L.S. Rothman, R.V. Kochanov, C. Hill

C22 Broadening parameters for H_2O lines perturbed by argon in infrared region
T.M. Petrova, A.M. Solodov, A.A. Solodov, V.M. Deichuli, V.I. Starikov

C23 DRIADA—compact high-resolution spectrometer for atmospheric monitoring of greenhouse gases in near IR
A.Yu. Trokhimovskiy, O.I. Korablev, I.A. Dzyuban, A. Patrakeev, A.A. Fedorova, S. Mantsevich, A. Shapkin, Yu.V. Smirnov, M.A. Poluarshinov

C24 Integrated cavity output spectroscopy using reflected radiation
P.V. Korolenko, I.V. Nikolaev, V.N. Ochkin, S.N. Tskhai, A.A. Zaytsev

C25 A cavity ring down spectrometer for high sensitivity absorption in the 2.35 μm atmospheric window
S.S. Vasilchenko, D. Mondelain, S. Kassi, P. Cermak, A. Campargue

C26 New features of FT spectrometer using LED sources
L.N. Sinitsa, V.I. Serdyukov

C27 Fine structure of *Q*-branch $\nu_1+\nu_3$ band of UF_6 absorption spectra: Tunable QCL and FTIR spectroscopy studies
Sh.Sh. Nabiev, V.M. Semenov, P.L. Men'shikov, L.I. Men'shikov, G.Yu. Grigor'iev, D.B. Stavrovskii, Ya.Ya. Ponurovskii

School Lectures D, 17^{00}–18^{30}

Chair: Valery I. Perevalov

D1 The diatomic spectroscopy of excited states beyond adiabatic approximation
Elena A. Pazyuk

D2 High resolution spectra of molecules with variational methods
Sergei N. Yurchenko

July 1, 2015, Wednesday

Invited Lectures E, 9^{00}–10^{30}

Chair: Alain Barbe

E1 Rotational action spectroscopy in cryogenic ion traps
Sandra Brünken, L. Kluge, A. Stoffels, P. Jusko, O. Asvany, S. Schlemmer

E2 Molecular line lists for exoplanets and other atmospheres
Jonathan Tennyson

Invited Lectures F, 11^{00}–12^{30}

Chair: Alain Campargue

F1 Coherent effects in the terahertz region and their spectroscopic applications
Evgeni N. Chesnokov, P.V. Koshlyakov, V.V. Kubarev

F2 Using synchrotron radiation for high resolution molecular spectroscopy in the terahertz
Olivier Pirali

Oral Session G, 14^{30}–16^{00}

Chair: Leonid A. Surin

G1 A hot spot in the high resolution spectroscopy of methanol
S.P.Belov, G.Yu.Golubiatnikov, A.V. Lapinov, V.V. Ilyushin, E.A. Alekseev, A.A. Mescheryakov, J.T. Hougen, Li-Hong Xu

G2 Self broadening and foreign broadening of methane lines in the tetradecade between 5880 cm^{-1} and 5900 cm^{-1}
A. Rausch, O. Werhahn, V. Ebert

G3 D_2O dimers in silicon airgel nanopores
A.A. Lugovskoi, V.I. Serdyukov, L.N. Sinitsa

G4 Predissociation of high-lying Rydberg states of molecular iodine via ion-pair states
A.S. Bogomolov, A.V. Baklanov, B. Grüner, M. Mudrich, S.A. Kochubei

G5 Speed dependence, velocity change and line mixing in self-colliding CO_2 under high pressures in the 30013 ← 00001 band: Measurements and test of models
V.A. Kapitanov, K.Yu. Osipov, A.E. Protasevich, Ya.Ya. Ponurovskii

G6 Self-broadening and collision mixing of the spectral lines in the fundamental bands of NH_3
M.R. Cherkasov

Poster Session H, 16^{15}–18^{00}

H1 Analysis of six new bands of $^{18}O_3$ recorded by CRDS technique in the 7400–7920 cm^{-1} spectral range
E.N. Starikova, A. Barbe, Vl.G. Tyuterev, D. Mondelain, S. Kassi, A. Campargue

H2 High sensitivity cw-cavity ring down spectroscopy of N_2O near 1.22 μm
E.V. Karlovets, A. Campargue, S. Kassi, S.A. Tashkun, V.I. Perevalov

H3 A high resolution analysis of weak absorption bands of $C_2H_2D_2$-*trans*: the $\nu_8+\nu_{10}$ (Au) band
A.G. Litvinovskaya, N.I. Raspopova, F. Zhgan

H4 Nitrogen dioxide high temperature line list in the 466–3374 $см^{-1}$ region
A.A. Lukashevskaya, V.I. Perevalov, A. Perrin

H5 Fourier transform absorption spectrum of $D_2{}^{16}O$ in 14 800–15 200 cm^{-1} spectral region
I.A. Vasilenko, O.V. Naumenko, V.I. Serdyukov, L.N. Sinitsa

H6 Intensities and self-broadening coefficients of the strongest water vapour lines in 2.7 and 6.25 μm absorption bands
I.V. Ptashnik, R.A. McPheat, K.M. Smith, K.P. Shine

H7 High pressure Cavity Ring Down spectroscopy: Application to the absorption continuum of CO_2 near 1.7 μm
S. Kassi, D. Mondelain, H. Tran, A. Campargue

H8 Calculation of rotation-vaibarion energy levels of the ammonia molecule based on an *ab initio* potential energy surface
O.L. Polyansky, R.I. Ovsyannikov, A.A. Kyuberis, N.F. Zobov, L. Lodi, J. Tennyson, A.A.Yachmenev, S.N. Yurchenko

H9 The line lists of the $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{18}O$ ozone isotopologues of the S&MPO database
A. Barbe, S.N. Mikhailenko

H10 Small molecules in external magnetic fields
H.M. Cobaxin, A. Alijah, J.C. López Vieyra, A.V. Turbiner

H11 Present status and perspectives of line-by-line analyses of the PH_3 absorption spectrum in the Octad range between 2800 and 3600 cm^{-1}
Y.A. Ivanova, A.V. Nikitin, S.A. Tashkun, M. Rey, Vl.G. Tyuterev, L.R. Brown

H12 First principles calculation of energy levels and spectra for AB_4, ABC_3 type molecules
A.V. Nikitin, B.M. Krishna, M. Rey, Vl.G. Tyuterev

H13 Radiative properties of the low-lying states of Rb_2 and Cs_2 based on *ab initio* calculations
E.A. Pazyuk, E. Revina, A.V. Stolyarov

H14 Speed-dependent spectral line profile including line narrowing and mixing
V.P. Kochanov

H15 Calculating the "hot" line intensities ($Ka \leq 25, J \leq 30$) of water vapor (000)–(000) band
O.V. Egorov, O.K. Voitsekhovskaya, D.E. Kashirskii

H16 Global modeling of high-resolution spectra of acetylene (C_2H_2)
O.M. Lyulin, V.I. Perevalov

H17 $^{12}C^{16}O$ line profile parameters for Mars and Venus atmospheres
N.N. Lavrentieva, B.A. Voronin, A.A. Fedorova

H18 Broadening, shifting and speed dependence coefficients of diagnostic water lines
I.N. Vilkov, M.A. Koshelev, G.V. Fedoseev, M.Yu. Tretyakov

H19 Hitran.org : new website, new structure, new interface for the HIRAN spectroscopic database
C. Hill, I.E. Gordon, R.V. Kochanov, J.S. Wilzewski, P. Wcisło, L.S. Rothman

H20 Water vapour self-continuum absorption within 0.94 and 1.13 μm bands at high temperatures
I.V. Ptashnik, A.A. Simonova, R.A. McPheat, K.M. Smith, K.P. Shine

H21 The line shape problem of high-precision spectra of self-colliding CO_2 molecules in the pressure range between 0.002 and 1 atm: Measurements and test of models
V.A. Kapitanov, K.Yu. Osipov, A.E. Protasevich, Yu.N. Ponomarev, Ya.Ya. Ponurovskii

H22 Measurements of absorber density based on examination of spectral line shape
Yu.A. Adamenkov, Yu.V. Kolobyanin

H23 He-broadening and -shift parameters of the water vapor spectral lines in the wide spectral range
T.M. Petrova, A.M. Solodov, A.A. Solodov, V.I. Starikov

H24 Diode-laser spectrometer concept for Martian atmosphere studies
I.I. Vinogradov, Yu.V. Lebedev, A.V. Rodin, A.Yu. Klimchuk, V.M. Semenov, O.V. Benderov, A.A. Pereslavtseva, M.V. Spiridonov, V.V. Barke

H25 Reference wavenumbers and assessment of trust in spectral database
O.V. Naumenko, A.I. Privezentsev, N.A. Lavrentiev, A.Z. Fazliev

H26 A W@DIS-based data quality analysis of the energy levels and wavenumbers of isotopologues of the water molecule
A.Z. Fazliev, O.V. Naumenko, A.I. Privezentsev, A.Yu. Akhlyostin, N.A. Lavrentiev, A.V. Kozodoev, S.S. Voronina, A.V. Apanovich, A.G. Császár, J. Tennyson

H27 Measurements of carbon dioxide isotopic ratio in ambient air using an optical cavity and tunable diode laser in 1.605 μm area
I.V.Nikolaev, V.N. Ochkin, S.N. Tskhai, A.A. Zaytsev

H28 Feature of IR spectra of ICAO taggants in the vapor state
Sh.Sh. Nabiev, L.A. Palkina, D.B. Stavrovskii, E.N. Golubeva, V.L. Zbarskii, N.V. Yudin, V.M. Semenov

School Tutorials I, 17^{00}–18^{45}

Chair: Igor V. Ptashnik

I1 Retrieving spectroscopic data from Virtual Atomic and Molecular Data Center (VAMDC)
Mikhail V. Doronin

I2 W@DIS information system. Spectral data analysis
Alexander Z. Fazliev

I3 SPECTRA—An interactive tool for molecular spectroscopy
Semen N. Mikhailenko

July 2, 2015, Thursday

Invited Lectures J, 9^{00}–10^{30}

Chair: Iouli E. Gordon

J1 Infrared quantitative spectroscopy and atmospheric satellite measurements
Jean-Marie Flaud

J2 Cold molecules and high-resolution spectroscopy: Experiments on two-, three- and four-electron molecules
P. Jansen, S. Scheidegger, L. Semeria, Frédéric Merkt

School Lectures K, 11^{00}–12^{30}

Chair: Yury I. Baranov

K1 Remote sensing of the atmosphere using satellite and ground-based high resolution spectrometers in IR
Vyacheslav I. Zakharov

K2 Importance of the proper data presentation in submitted manuscripts and a look beyond the impact factor of the journal: Primer of JQSRT
Iouli E. Gordon, L.S. Rothman

July 3, 2015, Friday

Invited Lectures L, 9^{00}–10^{30}

Chair: Nikolai N. Filippov

L1 Challenges and applications of synchrotron based and laser based - line shape studies
Adriana Predoi-Cross

L2 Calculation of rovibrational line broadening and shifting of symmetric and asymmetric top molecules
Nina N. Lavrentieva

Oral Session M, 11^{00}–12^{30}

Chair: Jonathan Tennyson

M1 Rotational spectrum of the NH_3–H_2 van der Waals complex
L.A. Surin, I.V. Tarabukin, V.A. Panfilov, S. Schlemmer, A. Breier, T. Giesen, M.C. McCarthy

M2 Influence of nanoconfinement on the line parameters for 2–0 absorption band of CO
A.A. Solodov, Yu.N. Ponomarev, T.M. Petrova, A.M. Solodov

M3 Water vapor continuum in the range of rotational spectrum of H_2O molecule: New experimental data and their comparative analysis
M.Yu. Tretyakov, T.A. Odintsova, P. Roy, O. Pirali

M4 H_2CO molecule vibrational energy spectrum. Re-summation of divergent perturbation series for highly excited states
A.N. Duchko, A.D. Bykov

M5 Combining *ab initio*, variational and contact transformation methods for accurate spectra predictions: from three- to six-atomic molecules
Vl.G. Tyuterev, M. Rey, T. Delahaye, A.V. Nikitin, S.A. Tashkun, R.V. Kochanov, E.N. Starikova

M6 Spectral sensitivity of Fourier transform spectrometer based on relative intensity measurements and *ab initio* calculations
A. Kruzins, I. Klincare, O. Nikolayeva, M. Tamanis, R. Ferber, E.A. Pazyuk, A.V. Stolyarov

Oral Session N, 14^{30}–16^{00}

Chair: Andrei V. Stolyarov

N1 Analyses of $^{16}O^{16}O^{18}O$ asymmetric ozone isotopic species in the whole 800–6500 cm^{-1} infrared spectral region
A. Barbe, M.-R. De Backer, X. Thomas, Vl.G. Tyuterev, E.N. Starikova, A. Campargue, D. Mondelain, S. Kassi

N2 Sub-THz molecular spectroscopy with radioacoustic detection and high-power radiation source
M.A. Koshelev, A.I. Tsvetkov, M.V. Morozkin, M.Yu. Glyavin, M.Yu. Tretyakov

N3 Tunable diode laser absorption spectroscopy for the measurement of accurate and traceable line strengths of different analytes
A. Pogány, A. Klein, O. Werhahn, V. Ebert

N4 FTIR spectrometer with 30-m base length absorption cell for spectra investigation in wide spectral region: improvement of optical setup
A.M. Solodov, T.M. Petrova, Yu.N. Ponomarev, A.A. Solodov

N5 UV-Photoexcitation of oxygen encounter complexes X–O_2 as a new channel of singlet oxygen $O_2(^1\Delta_g)$
A.P. Pyryaeva, A.V. Baklanov, S.A. Kochubei, V.G. Goldort

N6 Introduction to HITRAN Application Programming Interface (HAPI)
R.V. Kochanov, C. Hill, P. Wcisło, J.S. Wilzewski, I.E. Gordon, L.S. Rothman

Poster Session O, 16^{15}–18^{00}

O1 Rotational study of the CH_4–CO van der Waals complex in the millimeter-wave range
I.V. Tarabukin, V.A. Panfilov, L.A. Surin

O2 CRDS spectrum of the $3\nu_1 + 3\nu_2 + \nu_3$ band of NO_2 near 7587 cm^{-1}
A.A. Lukashevskaya, O.V. Naumenko, V.I. Perevalov, D. Mondelain, S. Kassi, A. Campargue

O3 High-resolution study of the $\nu_{10} + \nu_{12} - \nu_{10}$ "hot" band of the $^{13}C_2H_4$
G.A. Onopenko, N.V. Kashirina, A.G. Litvinovskaya

O4 High resolution analysis of the ν_{12} band and re-analysis of the ground vibrational state of *cis*-d_2-ethylene
Yu.V. Chertavskikh, A.S. Belova, I.A. Konov

O5 Assignment and modeling of $^{13}CH_4$ from 5853 to 6200 cm^{-1}: Preliminary results
E.N. Starikova, A.V. Nikitin, S.A. Tashkun, M. Rey, Vl.G. Tyuterev

O6 Line parameters of $HD^{16}O$ from LED-based Fourier transform spectroscopy between 11 200 cm^{-1} and 12 400 cm^{-1}
L.N. Sinitsa, V.I. Serdyukov, E.R. Polovtseva, B.A.Voronin, A.P. Shcherbakov, A.D. Bykov

O7 Approximation of Voigt contour for atmosphere transmission spectra calculation
A.Ya. Sukhanov

O8 Vibrational states of the triplet electronic state of H_3^+: the role of non-adiabatic Jahn-Teller coupling
A. Alijah, V. Kokoouline

O9 Methane high-T partition function from contact transformations and variational calculations
B.M. Krishna, A.V. Nikitin, M. Rey, S.A. Tashkun, Vl.G. Tyuterev

O10 Absorption spectra of combustion products of aircraft and rocket engines
O.K. Voitsekhovskaya, D.E. Kashirskii, O.V. Egorov, O.V. Shefer

O11 CRDS absorption spectrum of ^{17}O enriched water vapor between 12277 and 12894 cm^{-1}
A.-W. Liu, S.-M. Hu, X.-Q. Zhao, J. Wang, S.N. Mikhailenko

O12 Reanalysis of line centers of HCl isotopologues in the ground electronic state
T.I. Velichko, S.N. Mikhailenko

O13 FTIR spectra of Ne I in 1300–7000 cm^{-1} range: Rydberg *h*-states
S. Civiš, P. Kubelik, A. Pastorek, E.M. Zanozina, L. Juha, V.T. Chernov, A.A. Voronina

O14 Fourier transform spectrum of water vapor in the 3–5 μm transparency window
T.M. Petrova, A.M. Solodov, A.A. Solodov, O.V. Naumenko

O15 Modeling of CRDS $^{12}CH_4$ spectra at 80 K in the 6539–6800 cm^{-1} region
A.V. Nikitin, M. Rey, S.A. Tashkun, Vl.G. Tyuterev, S. Kassi, A. Campargue

O16 Molecular complexes $(H_2S)_n$, $n = (1–6)$
D.A. Sunchugashev, Yu.N. Kalugina, V.N. Cherepanov

O17 Conformational analysis of the *N*-methylformamide molecule in the ground S_0 and lowest excited S_1 and T_1 electronic states
N.V. Tukachev, V.A. Bataev, I.A. Godunov

O18 Retrieving the ratios of soft to hard velocity-changing collision's frequencies from H_2O line profiles near 0.8 μm
V.P. Kochanov, L.N. Sinitsa

O19 NO absorption dynamics in gas mixtures excited by pulsed electric discharge
S.P. Derevyashkin, A.A. Ionin, Yu.M. Klimachev, I.O. Kinyaevskiy, A.A. Kotkov, A.Yu. Kozlov, A.K. Kurnosov

O20 Simulation of the atmospheric radiative transfer in the water vapor near-infrared absorption bands
T.Yu. Chesnokova, A.V. Chentsov, B.A. Voronin

O21 CO_2 absorption lines measuring in the Earth's atmosphere using NIR heterodyne spectrometer
A.A. Pereslavtseva, A.Yu. Klimchuk

O22 Dependence of $H_2O–N_2$ broadening coefficients on the vibrational quantum indices
L.N. Sinitsa, V.I. Serdyukov, N.N. Lavrentieva, A.S. Dudaryonok

O23 Broadening parameters of water vapor lines induced by hydrogen and helium pressure
A.S. Dudaryonok, N.N. Lavrentieva, J. Tennyson, E. Barton, S.N. Yurchenko

O24 The dependence of the optical parameters XeCl-excilamp of the dynamic pressure jump
M.V. Didenko

O25 *Ab initio* calculation of the photodissociation processes in the NaO molecule
A. Berezhnoy, A.A. Buchachenko, V.V. Meshkov, A.V. Stolyarov

O26 Application of a near-IR tunable diode laser absorption spectroscopy (TDLAS) for temperature and concentration measurements of methane at various pressures
Sh.Sh. Nabiev, V.M. Semenov, G.Yu. Grigor'iev, D.B. Stavrovskii, Ya.Ya. Ponurovskii

O27 Electronic spectra of molecular quasicrystals with Frank-Kasper structure
A.K. Drozdova, A.V. Nyavro, V.N. Cherepanov, L.I. Kveglis

O28 Electronic structure and spectra of 3-nitroformazan
P.V. Petunin, P.S. Postnikov, M.E. Trusova, A.K. Drozdova, R.R. Valiev, V.N. Cherepanov

Round Table P. Quality of spectral data, $17^{30}–19^{00}$

Chair: Leonid N. Sinitsa

P1 On the accuracy of atomic and molecular data needed for stellar spectroscopy
Tatiana A. Ryabchikova

P2 How to compile line lists from diverse experimental and theoretical sources while letting through a minimum of errors
Iouli E. Gordon, L.S. Rothman

P3 Expert spectral data quality
Alexander Z. Fazliev

July 4, 2015, Saturday

Invited Lectures Q, 9^{00}–10^{30}

Chair: Frédéric Merkt

Q1 High-resolution spectroscopy to study the atmospheres of terrestrial planets
Anna A. Fedorova

Q2 Molecular spectroscopy as a probe for quantum water potentials
Claude Leforestier

Oral Session R, 11^{00}–12^{30}

Chair: Mikhail Yu. Tretyakov

R1 Application of methane saturated dispersion resonances near 2.36 μm over the temperature range 77–300 K for optical frequency standards
V.A. Lazarev, M.K. Tarabrin, V.E. Karasik, A.N. Kireev, Yu.V. Korostelin, Yu.P. Podmarkov, M.P. Frolov, A.S. Shelkovnikov, V.I. Kozlovsky, M.A. Gubin

R2 Spectral line-shape model tests with precision spectroscopy of hydrogen molecule
Y. Tan, A.-W. Liu, J. Wang, C.-F. Cheng, S.-M. Hu

R3 Band wing shape calculation using spectral characteristics of collision-induced rotational perturbations: application to CO and CO_2 infrared spectra
D.V. Oparin, I.M. Grigoriev, N.N. Filippov

R4 The water self- and foreign- continua in the 2.3 and 1.6 μm atmospheric windows
D. Mondelain, S.S. Vasilchenko, S. Kassi, D. Romanini, I. Ventrillard, A. Campargue

R5 Retrieval of the water vapour continuum absorption from the high-resolution Fourier spectra in 2.7 and 6.25 μm bands
I.V. Ptashnik, T.E. Klimeshina, T.M. Petrova, A.A. Solodov, A.M. Solodov

R6 Spectral composition of the water vapour self-continuum absorption in 2.7 and 6.25 μm bands
I.V. Ptashnik, T.E. Klimeshina

School Lectures S, 14^{30}–16^{15}

Chair: Sergei N. Yurchenko

S1 Collision-induced absorption of IR-radiation by the major atmospheric species
Yury I. Baranov

S2 Water vapour continuum absorption: History, hypotheses, experiment
Igor V. Ptashnik

Round Table T. Water vapour continuum absorption, 16^{30}–18^{00}

Chair: Igor V. Ptashnik

Invited Lectures A

Tuesday, June 30, 11^{00}–12^{30}

Chair: Yurii N. Ponomarev

A1

Microwave coherence spectroscopy: How to use real high resolution – and why

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Motivated by the ongoing search for the parity violating effects originated by an electron electric dipole moment (e-EDM) or a nuclear anapole moment, the rotational spectra of heavy atom diatomic radicals like, e.g., $^2\Pi_{1/2}$ PbF are studied at the unrivalled resolution offered by supersonic-jet Fourier transform microwave spectroscopy. Obtaining accurate information on such relativistically behaving systems will be the key to provide a delicate test to the proposed theories in extension to the Standard Model of Physics.

Employment of an MW method to hunt down these tiny effects, easily obscured by the line width inherent to other techniques, in rotational transitions is a promising approach to observe the tiny energy difference of terms that are degenerate without parity violation. Already before an experiment sensitive to parity violation, the exceptional resolution of the microwave time-domain technique can be exploited to provide accurate tests on the quantum chemical predictions that are part of the calculation of the anticipated e-EDM or anapole moment sensitivity of a given species since nuclear quadrupole and magnetic hyperfine effects in the rotational spectra are closely related.

In our current experiment, transitions can be observed with 0.2 kHz accuracy for unblended lines over a range of 2–26.5 GHz. The observation of field dependent spectra (in magnetic fields up to 4 Gauss) allows for the determination of the two body fixed g-factors, $G_\perp$ and $G_{||}$ which can then be compared with recent theoretical values.

While $^2\Pi_{1/2}$ and $^3\Delta_1$ electronic states ease the requirements for precise B-field control in nuclear-spin independent (NSI) e-EDM sensitive experiments because of small molecular g-factors, diatomic molecules in $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states can exhibit nuclear-spin dependent (NSD) parity non-conservation (PNC) effects that are enhanced by a factor of 10^5 due to the mixing of close rotational states of opposite parity. The nuclear anapole of heavy nuclei, which couples the un-paired electron's spin to toroidal currents inside the nucleus, provides the dominant contribution to the nuclear-spin-dependent (NSD) parity-violating effect in atoms and molecules.

YbF provides the current e-EDM upper limit. Although it is more sensitive to magnetic fields than $^2\Pi_{1/2}$ PbF, the nuclear quadrupole hyperfine structure of $^2\Sigma_{1/2}$ ^{173}YbF constitutes a direct probe on the electric field gradient and thus can help characterize the critical electric field at the heavy atom nucleus. We will report on 14 GHz transitions and global multi-isotopolog fit including the vibratioinal ground and first excited state for the main and 3 of the less abundant even isotopologues of YbF as well as the dual nuclear spin ^{207}PbF analogue ^{171}YbF, important steps towards observing ^{173}YbF.

A2

Laser spectroscopy of some MH molecules with astrophysical 'overtones'

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Zeeman-broadened lines in the near IR electronic spectrum of FeH have been proposed as a magnetic probe of cool stellar atmospheres [1]. Interpretation of the noticeably broadened but unresolved profiles of individual lines measured at telescopes [2] assumes there are reference values for the zero-field transition frequencies, and for their Zeeman response. It has also been noted that the molecular Landé factors for these open-shell, high multiplicity species are hard to predict because of extensive interstate mixing [3]. This situation led us to investigate the electronic structure and spectra of two such species in the laboratory: NiH, as a prototype with strong transitions in the visible spectrum, and FeH (the primary focus of our work. Laser excitation and (Fourier Transform) resolved fluorescence techniques have been used to investigate the Zeeman effect in excited electronic states in NiH, providing a wealth of data and a satisfactory model for the lower lying electronic states. For FeH, only resonant fluorescence has been detected so far in the bands of astrophysical interest, close to 1 micron [4].

To illustrate the connection between information derived in the laboratory and telescope observations, we consider polarimetric spectra from sunspots, recorded at the solar telescope THEMIS in Tenerife [5]. This instrument is equipped to record full Stokes spectra resolved with an Echelle spectrometer. Stokes V spectra, showing the difference in absorption by right- and left- circularly polarised light, are most sensitive to the Zeeman effect, and FeH lines can be recognized in sunspot spectra. Atomic lines dominate, so comparison can be made with atomic data.

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Oral Session B

Tuesday, June 30, 14^{30}–16^{00}

Chair: Vladimir G. Tyuterev

B1

A new $C^3\Sigma_u^- - X^3\Sigma_g^-$ transition of the V_2 molecule

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The high resolution electronic transition spectrum of the vanadium dimer (V_2) molecule in the visible region between 480 and 528 nm has been observed using laser ablation free jet expansion and laser-induced fluorescence (LIF) spectroscopy. Six vibrational bands have been recorded and analyzed, they belong to two groups of sub-band transitions: $1_u - 1_g$ and $0_u^+ - 0_g^+$, which is very well correspond to a $^3\Sigma_u^- - {}^3\Sigma_g^-$ transition. Since the ground state is $X^3\Sigma_g^-$, these bands were assigned to a new $C^3\Sigma_u^- - X^3\Sigma_g^-$ transition.

Rotational analysis has been performed to these bands and the measured line positions were fit by a least squares routine, which yielded molecular constants for the v = 0 level of the excited $C^3\Sigma_u^-$ state. The measured vibrational separation, $\Delta G_{1/2}$, and bond length, r_o, of the $C^3\Sigma_u^-$ state are respectively 393.04 cm^{-1} and 2.029 Å in this work. A molecular orbital energy level diagram has been used to aid the assignment of the newly identified $C^3\Sigma_u^- - X^3\Sigma_g^-$ transition, which is likely to arise from the promotion of an electron from the $d\delta_g$ to the $d\delta_u$ molecular orbitals. Detailed analysis of the electronic structure of the V_2 dimer and a comparison of similar metal dimer molecules will be presented.

The work described here was supported by a grant from the Committee on Research and Conference Grants of the University of Hong Kong.

B2

Accurate non-adiabatic corrections to ro-vibrational levels of small molecules through effective nuclear masses

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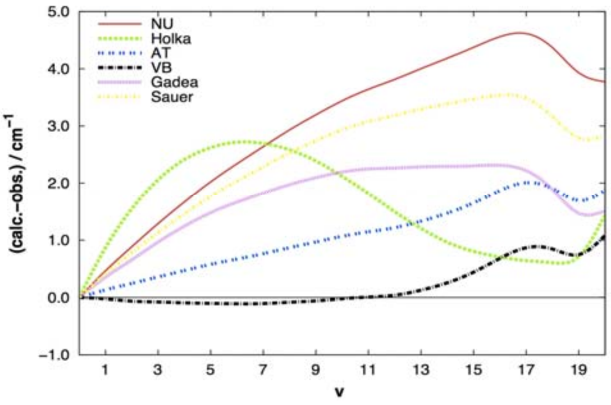
Non-adiabatic corrections to ro-vibrational levels of small molecules are necessary to account for the experimental accuracy of few cm^{-1}. However, general ab initio calculations of these corrections are at present out of reach.

In a recent work[1], we introduce the separation of motions of the nuclei plus a fraction of electrons that they pull in their movement (the core) and the fraction of immobile electrons (the valence). These fractions depend on the nuclear distances **R**. In consequence, a nuclear equation is obtained in which the nuclear reduced mass is replaced with the R-dependent core reduced mass $\mu(\mathbf{R})$. Except for the effects of avoided-crossings (or intersections), this approach accounts very well for the non-adiabatic effects. The ro-vibrational levels are usually calculated with very accurate PECs (PESs) augmented with DBOC (diagonal Born-Oppenheimer corrections) and relativistic corrections. The non-adiabatic corrections to the ro-vibrational levels are obtained as the difference between the energies of these states calculated with $\mu(\mathbf{R})$ and those calculated with the reduced mass of the bare nuclei.

$\mu(\mathbf{R})$ is obtained from the molecular electronic structure of the molecule. Two recipes have been developed in our group so far. For H_2^+, H_2 and their isotopologues[2] and H_3^+ [3], the diagonal Mulliken populations are taken as the core electron fractions attached to the nuclei. Results are quite good and the first mass surface was developed for H_3^+. For LiH, Mulliken populations do not describe the electronic density appropriately for our purposes. A combination of valence bond ionic and covalent components gives the best results so far[4] (see figure). The VBCI orbitals show to be quasi-orthogonal, allowing an interpretation of the bonding in LiH as resulting from a quantum superposition of one-electron ionic and covalent states.



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B3

A database of NO_2 spectral line parameters at $T = 1000$ K

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Databases of spectral line parameters (SLP) of high-temperature gases are necessary to create for interpretation experimental spectra of hot gas plumes, produced, for example, by fuel combustion or volcanic eruption. The well-known high-temperature database HITEMP [1] includes SLP of only several gases, which are not enough, particularly, to simulate the spectral signature of air-jet engines. At present work, the database of SLP of high-temperature nitrogen dioxide (NO_2) was generated in conformity with HITRAN2012 [2] type format. The line position parameters of the effective spin-rotation Hamiltonian for 21 vibrational states were used from literature. The set of the dipole moment function parameters of NO_2, determined in this work up to the second order inclusive, was applied for calculation the intensities of vibrational-rotational lines with $\sum\Delta\upsilon \le 2$. The intensity cutoff was equaled to 10^{-35} $\mathrm{cm^{-1}/(molecule\cdot cm^{-2})}$ for temperature of 1000 K. Finally, the NO_2 spectral characteristics, simulated by line-by-line method on the basis of this work SLP and HITRAN2012, are compared.

The reported study was funded by RFBR according to the research project nos. 15-01-03176 and 13-07-98027, and by the nonprofit "Dynasty" Foundation.

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B4

Numerical construction of symmetry-adapted ro-vibrational basis sets for variational nuclear motion calculations

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In a variational solution of nuclear motion problems a matrix representation of the rotation-vibration Hamiltonian is diagonalized. A general, numerical approach to the construction of symmetrized ro-vibrational basis functions for polyatomic molecules according to their irreducible representations in the Molecular Symmetry (MS) group [1] is presented. Symmetry-adapted basis sets help reducing size of the variational problem by factorizing the Hamiltonian matrix into independent symmetry blocks and are important for intensity calculations through their nuclear spin statistical weights and symmetry selection rules.

The approach is based on diagonalization of reduced Hamiltonian matrices. The numerical form of the approach allows one to generate irreducible representations of the basis functions on the fly for any rotational or vibrational excitations required for standard variational calculations. It has been implemented as a part of the program TROVE [2] and successfully applied for a number of systems covering the MS groups from C_s(M) to T_d(M). The efficiency of the approach and importance of the molecular symmetries for variational nuclear motion calculations will be illustrated by a number of examples for different molecules and symmetries.

This work is supported by the ERC under Advanced Investigator Project 267219.

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B5

Nitrous Oxide Spectroscopic Databank (NOSD)

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We present two versions of the Nitrous Oxide Spectroscopic Databank (NOSD): version for atmospheric applications (reference temperature 296 K) and version for high temperature applications (reference temperature 1000 K). The databank contains the following line parameters: line position, line intensity, Einstein coefficient, energy of lower state, self-broadening coefficient, air- and CO_2- broadening coefficients and their temperature exponents. The atmospheric version is generated using intensity cut off 10^{-30} cm/molecule at 296 K and that for high temperature applications is done using intensity cut off 10^{-25} cm/molecule at 1000 K. The latter covers 477–7232 cm^{-1} spectral range and contains about 11 799 000 spectral lines.

The databank is based on the global modeling of the line positions and intensities performed within the framework of the method of effective operators [1, 2]. The parameters of the effective Hamiltonian and effective dipole moment operator have been fitted to the observed values of the line positions and intensities collected from the literature. The broadening coefficients as well as temperature exponents are calculated using the semi-empirical approach [3]. This approach is a modification of the impact theory performed by introduction of the empirical correction factor. The utilization of only two empirical parameters provides a good reproduction of experimentally observed N_2O line widths.

As an example we present the comparison of the simulated low resolution N_2O spectrum to the observed one [4] recorded at 873 K in the spectral region 2000–2300 cm^{-1}. The respective plots show very good agreement between simulated and observed spectra.

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B6

High-Resolution spectra of polarized thermal radiation in atmosphere: Simulation for satellite remote sensing

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It’s well known that cirrus clouds and stratospheric aerosols play major role in regulating the thermal regime of the stratosphere and the formation of the ozone layer. Carried out by satellites equipment, polarization measurements of the outgoing solar radiation are successfully used for their investigation. However, the use of solar radiation restricts measurements to the daytime. So a natural interest arises in application of such measurements for thermal radiation, especially because thermal radiation is polarized due to only particle scattering, not molecules (as for solar radiation). This fact gives an extra reason to consider satellite polarization measurements of thermal radiation as highly informative in the investigation of atmosphere scattering layers. However in a case of thermal radiation the polarization effects are noticeable only in the limb geometry, where there is a known problem of radiation absorption on long paths in the atmosphere. So the high-resolution molecular absorption spectra need to be considered together with the polarization effects in any radiative transfer model for planning and analyzing such measurements.

We present a vector Monte Carlo (MC) technique for line-by-line model that calculates spectra of the polarized thermal radiation emitted by multiple scattering layered atmospheres. Also we discuss the numerical experiments on remote sensing of the cirrus clouds and stratospheric aerosol with use of the realistic vector optical model of scattering media. In general, these experiments confirmed the possibility of the cirrus clouds and stratospheric aerosol investigation by techniques of satellite infrared high resolution polarimetry.

This work is supported by RFBR (grant nos. 15–01–00783 and 14–01–00197).

Poster Session C

Tuesday, June 30, 16^{15}–18^{00}

C1

Millimeter-wave measurements and *ab initio* calculations of the NH_3–CO complex

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The rotational spectrum of the van der Waals complex NH_3 – CO has been measured with the intracavity OROTRON jet spectrometer in the frequency range of 112–139 GHz. Newly observed and assigned transitions belong to the K = 0–0, K = 1–1, K = 1–0 and K = 2–1 sub-bands correlating with the rotationless $(j_k)_{NH3} = 0_0$ ground state of free *ortho*-NH_3 and the K = 0–1 and K = 2–1 sub-bands correlating with the $(j_k)_{NH3} = 1_1$ ground state of free *para*-NH_3. The (approximate) quantum number K is the projection of the total angular momentum J on the intermolecular axis. Some of these transitions are continuations to higher J values of transition series observed previously [1], the other transitions constitute newly detected sub-bands. The new data were analyzed together with the known millimeter-wave and microwave transitions in order to determine the molecular parameters of the *ortho*-NH_3–CO and *para*-NH_3–CO complexes.

Accompanying *ab initio* calculations of the intermolecular potential energy surface (PES) of NH_3–CO have been carried out at the explicitly correlated coupled cluster level of theory with single, double and perturbative triple excitations [CCSD(T)-F12a] and an augmented correlation-consistent triple zeta (aVTZ) basis set. The global minimum of the five-dimensional PES corresponds to an approximately T-shaped structure with the N atom closest to the CO subunit and binding energy $D_e = 359.21$ cm^{-1}. The bound rovibrational levels of the NH_3–CO complex were calculated for total angular momentum J = 0 to 6 on this intermolecular potential surface and compared with the experimental results. The calculated dissociation energies D_0 are 210.43 and 218.66 cm^{-1} for *ortho*-NH_3–CO and *para*-NH_3–CO, respectively.

The authors acknowledge the Russian Foundation for Basic Research (grant no. 15-03-09333) for financial support.

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C2

High resolution analysis of $S^{18}O_2$ spectrum: The ν_1 and ν_3 interacting bands

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High accurate ro-vibrational spectrum of $S^{18}O_2$ was recorded with Bruker IFS 120 HR Fourier transform interferometer in the region of 1030–1350cm^{-1} where the bands ν_1 and ν_3 are located. More than 1300 and 1450 transitions were assigned in the experimental spectrum with the maximum values of quantum numbers J_{max}/K_{max} equal to 58/16 and 65/19 to the bands ν_1 and ν_3, respectively.

The further weighted fit of experimentally assigned transitions was made with the Hamiltonian model, which takes into account Coriolis resonance interaction between the vibrational states (100) and (001). To make the ro-vibrational analysis physically more suitable, the initial values of the main spectroscopic parameters have been estimated from the values of the corresponding parameters of the $S^{16}O_2$ species on the basis of the results of the Isotopic Substitution theory.

Finally, the set of 17 spectroscopic parameters obtained from the fit reproduces values of 1100 initial "experimental" ro-vibrational energy levels (more than 2750 transitions assigned in the experimental spectrum) with the *rms* error d_{rms} = 0.00018 cm^{-1}. Also, the ground state parameters of the $S^{18}O_2$ molecule were improved as compared with the set obtained in [1].

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C3

The disagreements between calculation results of water vapor spectral characteristics at high temperatures

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A global analysis of spectroscopic database HITEMP [1] for calculation of the high-temperature emission and absorption spectra of water vapor and carbon dioxide in the temperature range of 500–1770 K was carried out in Ref. [2]. According to Ref. [2], good agreements between the experimental and calculated by line by line method transmission spectra are observed, but there are spectral intervals in which the differences exceed the experimental error. This was the reason for a more careful study of the H_2O spectral lines parameters (SLP) in the wide temperature range.

In Ref. [2] the water vapor lines, not observed in the experimental spectra, but presented in the spectra calculated using the database HITEMP are reported. The values of water vapor SLP from the database HITEMP (bold) and SLP, calculated by us according to the methodology described in Refs. [3, 4] are shown in table. The line intensities, obtained by us, are much smaller and correspond to the experimental data. To calculate the line intensities, the eigenvectors of the effective rotational Hamiltonian in the I^r representation were applied. If the intramolecular effects are taken into account, the values of the presented line intensities change in the range of 10 % and agree well with the recent data of Ref. [5].

Table. Significant differences in the values of H_2O SLP at T = 1000 K

Wavenumber, cm^{-1}	Intensity, $\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$	Halfwidth, cm^{-1}	Low state energy, cm^{-1}	n	$v_1' v_2' v_3'$ $v_1'' v_2'' v_3''$ $J' K_a' K_c'$ $J'' K_a'' K_c''$
903.5328	0.004428	0.01394	5204.7486	0.75	0 1 0 0 1 0 18 5 14 17 2 15
	0.204803	**0.01793**	**5204.7485**	**0.11**	
914.6067	0.008271	0.0099	3940.5449	0.75	0 0 0 0 0 0 19 5 15 18 2 16
	0.076948	**0.02275**	**3940.5449**	**0.10**	
933.5128	0.001088	0.01828	5015.7043	0.75	0 1 0 0 1 0 16 8 9 15 5 10
	0.078656	**0.04233**	**5015.7041**	**0.14**	

Spectral intervals and experimental conditions for which the differences with the theoretical calculation exceed the experimental error - 5% and reach 20% were selected. Using several databases of SLP [1, 3, 6] and the software [7] the transmittances were calculated. The analysis of the causes of differences in the values of the SLP and transmittances was carried out.

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C4

On the "expanded local mode" approach applied to ethylene

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Earlier derived [1–5] for the XY_2 (C_{2v}), XY_3 (C_{3v}), and XY_4 (T_d) molecules "expanded local mode model" is applied to the ethylene, X_2H_4, molecule. On the basis of specially obtained values of the ambiguity parameters, $sin\gamma_i$, simple values of all transformation coefficients, $l_{N\alpha\lambda}$, are obtained for the C_2H_4 molecule. It gives us possibility, on the one hand,

– to derive simple relations between different spectroscopic parameters (harmonic frequencies, anharmonic parameters and rotational-vibrational coefficients) of the C_2H_4 molecule, and, on the other hand,

– on the basis of the general isotopic substitution theory [6] to obtain very simple values of transformation $l'_{N\alpha\lambda}$ coefficients for the different isotopic species of the ethylene molecule.

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C5

High resolution analysis of the ν_6 band of the CH_2=CD_2 molecule

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The object of the present study is the CH_2=CD_2 molecule, which is asymmetric top of the C_{2v} symmetry group. There are 12 vibration modes of four different types of symmetry (A_1, A_2, B_1, B_2) available in the molecule. Here we continue our study of this molecule [1].

The transmission spectrum of CH_2=CD_2 in the 1130–1310 cm^{-1} region was recorded with Bruker IFS-120 HR Fourier transform infrared spectrometer in the Braunschweig infrared laboratory at room temperature with a pressure of 1.5 mbar and an optical pathlength of 4 m at the resolution 0.0021 cm^{-1}. In that region the ν_6 band of B_1 symmetry is located.

For the description of the upper-state ro-vibrational levels, there was used the effective Hamiltonian model which takes into account strong resonance interactions between the ($v_6 = 1$) and ($v_3 + 1$) (A_1), ($v_7 = 1$) and ($v_8 = 1$) (B_2) states. In the result of our analysis, more than 1100 transitions were assigned with the values $J_{max} = 42$ and $K_{a\ max} = 18$. It is more than was reported before [2].

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C6

The absorption spectrum of ^{17}O enriched water vapor by CRDS between 5850 and 6670 cm^{-1}

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The room temperature absorption spectrum of ^{17}O enriched water vapor has been recorded by high sensitivity CW-CRDS between 5850 and 6670 cm^{-1}. More than 10 300 lines with intensity ranging from 1.4×10^{-30} to 3.6×10^{-24} cm/molecule were retrieved from the recorded spectrum. 8511 water lines were assigned to 9631 transitions of six water isotopologues ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$). In addition, 1255 lines of OCS, CH_4, HCN, and different isotopologues of carbon dioxide were identified, leaving about 580 weak lines unassigned.

The assignments of all water transitions were performed using known experimental energy levels and calculated line lists based on variational calculations by Schwenke and Partridge [1, 2]. In particular, all the transitions of the $H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$, and $HD^{18}O$ isotopologues were already known: 2398 $H_2{}^{16}O$ and 1171 $H_2{}^{18}O$ transitions were assigned using energy levels of Refs. [3, 4]; the results of Refs. [5, 6] were used to assign 1507 $HD^{16}O$ transitions. 500 line positions of the $\nu_1+\nu_3$, $2\nu_2+\nu_3$ and $\nu_1+2\nu_2$ bands of $HD^{18}O$ are in good agreement with those calculated from energy levels of Ref. [7].

More than half (1310) of the 2519 assigned $H_2{}^{17}O$ transitions correspond to new or corrected upper energy levels compared to those reported in Ref. [4]. About 1000 new $H_2{}^{17}O$ transitions are associated with upper states of the second triad {(030), (011), (110)} and the first hexad {(040), (021), (120), (002), (101), (200)}.

712 of 1536 $HD^{17}O$ transitions are assigned for the first time. Most of the newly assigned transitions belong to the $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ bands. The assigned transitions with high values of the *J* and *Ka* rotational numbers allow us to determine term values of several new levels of the $HD^{17}O$ ground state.

Comparisons of extended sets of the $H_2{}^{17}O$ and $HD^{17}O$ energy levels with those reported in Refs. [4, 5, 8] will be presented.

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C7

High resolution absorption spectra of $^{12}C^{18}O_2$ and $^{16}O^{12}C^{18}O$ in the 11260–11430 cm^{-1} wavenumber range

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The absorption spectrum of $^{12}C^{18}O_2$ was recorded using the Bruker IFS 125M Fourier-transform spectrometer in the 11260–11430 cm^{-1} frequency range at temperature 297 K with resolution of 0.05 cm^{-1}. The optical pass length was 2400 cm. The $C^{18}O_2$ pressure was 75.65 mbar.

Using a 2.5 W Edixeon EDEI-1LS3-R emitter in the range of 11 100–12 500 cm^{-1} as a light source for the spectrometer with a 60-cm multipass cell during a 24-hour measurement time, we have achieved a signal-to-noise ratio of 4.5×10^4 which corresponds to the minimal detectable absorption coefficient of 1.2×10^{-8} cm^{-1}[1].

Such enhanced sensitivity spectrometer has been used to measure the transition frequencies of vibrational bands 00051–00001 and 01151–01101 of $^{12}C^{18}O_2$ and 00051–00001 and 01151–01101 of $^{16}O^{12}C^{18}O$ in the range of 11 260–11 430 cm^{-1}.

The assignment of the spectrum was done on the basis of the predictions with the effective Hamiltonian published in Ref. [2].

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C8

High sensitivity cavity ring down spectroscopy of CO_2 overtone bands near 830 nm

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Three bands 4003i – 00001 ($i = 2, 3, 4$) of the Fermi pentad of $^{12}C^{16}O_2$ near 830 nm have been recorded with a continuous wave cavity ring down spectrometer. High sensitivity of the 5×10^{-11} cm^{-1} level allowed us obtaining the line positions and intensities of these very weak bands. The measured line intensities of these three bands together with those published for the 10051–00001 and 10052–00001 bands were used to fit the effective dipole moment parameters of $^{12}C^{16}O_2$ for the $\triangle P = 17$ series of transitions, where $P = 2V_1+V_2+3V_3$ is a polyad number (V_i ($i = 1, 2, 3$) are vibrational quantum numbers). A comparison of the measured line positions and intensities of the 4003i – 00001 ($i = 2, 3, 4$) bands to those from AMES and GEISA line lists is given.

C9

Ab initio calculation of ro-vibrational spectra for GeH_4 molecule

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New potential energy surface (PES) and dipole moment surfaces (DMS) of molecule GeH_4 are constructed using extended *ab initio* CCSD(T) calculations at 19882 nuclear configurations. The PES [1] and DMS[2] analytical representation are determined through an expansion in symmetry adapted products of internal nonlinear coordinates involving 282 and 692 parameters up to the 8th order and 6th order. The PES and DMS precision are discussed. Lower rovibrational levels are calculated [3].

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C10

First principles calculation of rovibrational spectra for SiH_4 molecule

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New potential energy surface (PES) and dipole moment surfaces (DMS) of molecule SiH_4 are constructed using extended *ab initio* CCSD(T) calculations at 19882 nuclear configurations. The PES [1] and DMS [2] analytical representation are determined through an expansion in symmetry adapted products of internal nonlinear coordinates involving 282 and 692 parameters up to the 8th order and 6th order. The problem of spectra calculations [3] is discussed.

This work is supported by French-Russian LIA "SAMIA". Y.S. Chizmakova thanks the Tomsk State University for support.

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C11

Combined effect of small- and large-angle scattering collisions on a spectral line shape

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Algebraic approximations for line profiles calculated on the basis of quantum-mechanical collision integral kernels for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole intermolecular interaction potentials were obtained. In derivation of the profiles velocity-changing collisions of molecules with scattering on small and large angles also with the speed-dependence of collision relaxation constants have been taken into account following the detailed scheme of calculations presented in Ref. [1]. It was shown on the basis of numerical calculations that the relative contribution of small-angle collisions into the frequency of elastic velocity-changing collisions is more pronounced for the long-range dipole-dipole and dipole-quadrupole potentials. A sensitive criterion for analysis of a line narrowing was proposed and tested.

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C12

Accuracy and precision of line center frequency measurements of $^{16}O^{12}C^{32}S$ rotational lines of in MM and Sub-MM wave range

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It is known, that precision of spectral line center frequency obtained by fitting of the microwave experimental line shape data to the model line profile can be in order of 1 Hz. But the real value of the uncertainty of the mm and sub-mm microwave frequency measurements, including Lamb-dip measurements, is usually larger than 1 kHz. On the other hand, the most accurate secondary frequency standards used in radio astronomy are based on the precise Lamb-dip data for the rotational transitions of some molecules, including CO [1] and OCS [2] molecules. For some astrophysical projects, including a project for the search of possible time and space variations of the fundamental physical constant [3], it would be superb to increase accuracy of the Lamb-dip measurements to a few Hz.

In this talk we present and discuss the results of our experimental study of a possibility of improvement of the accuracy of the frequency measurements with our BWO Lamb-dip spectrometer [4].

New accurate center frequencies of the rotational transitions of $^{16}O^{12}C^{32}S$ molecule in mm and sub-mm wave region (up to 522-GHz) based on many years Lamb-dip measurements and improved rotational constants of $^{16}O^{12}C^{32}S$ are obtained. The different sources of systematic errors in center line frequency measurements with Lamb-dip technique will also be discussed.

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C13

Numerical model of Zeeman splitting of ro-vibrational lines in the NO fundamental band

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As is well known, the ro-vibrational spectral lines of paramagnetic molecule are split into Zeeman components in a magnetic field. Such Zeeman splitting is used by laser magnetic resonance (LMR) spectroscopy to detect paramagnetic molecules like NO. In a variable magnetic field some transitions between Zeeman components are shifted into a resonance with external laser radiation producing some peaks of laser absorption in dependence on the magnetic field strength, i.e. producing the LMR spectrum.

To analyze observed LMR spectrograms, a numerical model of Zeeman splitting of ro-vibrational lines in the nitric oxide molecules was developed. This model is based on the numerical diagonalization the matrix of the effective molecular Hamiltonian, which includes Zeeman operator corresponding to interaction an external magnetic field with a molecule [1].

The observed LMR spectrograms appeared to be in adequate agreement with the numerical data [2].

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C14

Wave functions and lifetimes of ozone metastable states above the dissociation threshold: Impact on the dynamics

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The new potential energy surface (PES) of ozone recently developed [1, 2] is used to determine energies of vibrational bound and predissociated resonances of O_3. For the vibrational state calculations, the hyperspherical coordinates and the methods of slow-variable discretization with a complex absorbing potential are used [3]. The bound vibrational states obtained in this study perfectly agree with the previous calculations [1] and reproduce the experimental energies up to the region 8000 cm^{-1} above the minimum of the potential. The method takes into account the coupling between the three potential wells of the ozone molecule. The correct representation of the coupling between the three wells is important for the correct treatment of excited vibrational levels and resonances. The method can treat symmetric and asymmetric isotopologues. For symmetric isotopologues, states of all possible irreducible representations are calculated.

The widths of the resonances in the region 0–3000 cm^{-1} above the dissociation have been determined. Most of the obtained resonances have widths between 0.1 cm^{-1} and 10 cm^{-1}. The widths depend on the nature of the short-range part of resonance wave functions: The resonances differ from each other by a degree of excitation of different vibrational modes and also by the relative angular momentum of the dissociating O-O_2 system, which can also be viewed as motion between the three potential wells. Wave functions of the predissociated resonances obtained for asymmetric molecules provides information about the exchange reaction ${}^{x}O + {}^{y}O{}^{z}O \rightarrow {}^{y}O + {}^{x}O{}^{z}O$ or ${}^{x}O + {}^{y}O{}^{y}O \rightarrow {}^{y}O + {}^{x}O{}^{y}O$. A possible impact on the dynamics will be discussed.

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C15

Estimations for line parameters of SO_2

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Sulfur dioxide (also sulphur dioxide) is the chemical compound with the formula $^{32}S^{16}O_2$. At standard atmosphere, it is a toxic gas with a pungent, irritating, and rotten smell. It is released naturally by volcanic activity [1]. Also this SO_2 have interest to study Venus.

The HITRAN2012 database contains spectroscopic line parameters for two isotopologs of SO_2 molecules: $^{32}S^{16}O_2$ (72 460 lines) and $^{34}S^{16}O_2$ (22 661 lines) [2]. Also as a result of the new calculations which are carried out recently by Huang, Schwenke, Lee [3], spectroscopic parameters for more than 4 000 000 lines of SO_2 were obtained. In HITRAN2012, there is so-called "*Ka*-dependence" of the self-broadening coefficients $\gamma(SO_2 - SO_2)$ on the quntum number *Ka*:

$$\gamma(SO_2 - SO_2) = 0.471 - 0.0143 \times Ka''. \quad (1)$$

We propose to use another dependence of self-broadening parameters on *Ka* that leads to more correct extrapolation:

$$\gamma(SO_2 - SO_2) = k_1 \times \text{arccot}\,(k_2 \times Ka'' + k_3) + k_4, \quad (2)$$

where $k_1 = 1/11.8$, $k_2 = 0.269$, $k_3 = -3.5$, $k_4 = 0.29$.

For evaluation of spectroscopic line parameters of SO_2 experimental data from [4–10] were used. Air-broadening coefficients for SO_2 molecule in HITRAN were estimated as 0.10 and 0.10250 cm^{-1}/atm. During analysis of the published experimental data we defined weak *J*-dependence for air-broadening coefficients that will be present at poster.

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C16

Retrievals of the CH_4 and CO_2 atmospheric amount from the high resolution absorption spectra of solar radiation with the use of different spectroscopic databanks

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An influence of discrepancy in the spectroscopic databanks in the near-infrared region on results of atmospheric radiative transfer simulation and retrievals of atmospheric total amount of greenhouse gases is investigated. The HITRAN [1] and GEISA [2] spectroscopic databases, new versions of the GOSAT CH_4 spectral line list [3], and the CDSD CO_2 line parameters databank [4] are used in the atmospheric simulation. It is shown that the difference in the high resolution atmospheric absorption spectra, calculated with the CH_4 spectral line parameters from HITRAN2008, HITRAN2012, GEISA2011, and GOSAT2014 can reach 0.03 and more.

A comparison of the simulated spectra with the atmospheric solar spectra measured by a Fourier transform spectrometer in Kourovka observatory (Russia, 57.038 N, 59.545 E, elevation 300 m, forest area with background atmospheric condition) is made. The spectral resolution is 0.02 cm^{-1}. The atmospheric total amounts of CH_4 and CO_2 are retrieved from the measured spectra. The values of the CH_4 atmospheric total content, retrieved with the use of two versions of the spectroscopic database HITRAN2008 and HITRAN2012 differ up to 2% [5]. The maximum difference is revealed in summer conditions. The CH_4 atmospheric total content data, obtained with use of the CH_4 line list GOSAT2014 and the GEISA2011 database, are close to the data, retrieved with the HITRAN2008. As compared with $CH_{4,}$ a smaller discrepancy is observed between data, retrieved with different spectroscopic databanks of CO_2 absorption line parameters. The difference does not exceed 0.7%.

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C17

Evidence of stable Van Der Waals CO_2 clusters relevant to CO_2-rich atmospheres

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Knowledge of line shape parameters of carbon dioxide clusters is required for radiative transfer modeling of the atmospheres of Mars and Venus due to its high abundance. Current experimental studies of weakly bound van der Waals CO_2 complexes are mainly performed at low pressure for example in supersonic jets [1], and contributions of dimers varying as the squared gas density cannot be disentangled experimentally.

In this work we present experimental and theoretical results on CO_2 dimers at very high pressure approaching the liquid phase. We obtain that the shape of CO_2 dimer bands is influenced by the line-mixing effects [2], what demonstrate an unexpected stability of the dimers despite the collisions with bath molecules and negates the common belief that CO_2 dimers are shot-lived complexes. The simple strong collision model [3] is used to describe the band shape in a qualitatively correct manner. Our results allow a better modeling of CO_2-rich atmospheres and provide also a new spectroscopic tool for studying of the stability of molecular clusters.

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C18

Theoretical study of self-, N_2-broadened linewidths of methyl cyanide vibrational lines

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The first extensive theoretical list on self- and nitrogen-broadening coefficients of methyl cyanide (CH_3CN) *P*-, *R*-branch lines for wide ranges of rotational quantum numbers requested by spectroscopic databases is reported. Due to the big dipole moment value (3.913 D) and a strong electrostatic interaction occurring between two colliding molecules, very favourable conditions appear for the use of the semi-empirical method [1]. The calculations are performed at the room temperature (T=296 K) for ~1400 lines, rotational quantum numbers vary in the range of $0 \le J \le 70$, $0 \le K \le 20$. At the first time using the semi-empirical method, uncertainties of theoretical linewidths have been deduced. In addition the temperature exponents for every value of broadening in the case of the Earth and Titan atmosphere temperature ranges are provided. There is a good agreement obtained data with the experimental ones at different temperatures.

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C19

Study of the H_2O–H_2O line broadening in 15 500–16 000 cm^{-1} region

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Line broadening coefficients of the H_2O–H_2O system were investigated in the region 15 500–16 000 cm^{-1} using a high resolution Fourier-transform spectrometer IFS-125M. The White type multipass absorption cell with a basic length of 60 cm was used. The absorption path of 34.8 m and resolution of 0.05 cm^{-1} were chosen to record the spectrum. Light-emitting diode (LED) was used as a source of radiation [1]. Signal-to-noise ratio amounted to about 10^4, which allowed to measure parameters of lines with intensity about $2*10^{-27}$ cm/molecule. Least-square-fitting algorithm WXSPE was used to retrieve of the spectroscopic parameters from measured spectral data set [2]. The experimental uncertainties for broadening coefficients vary from 2 to 5%. Line-broadening coefficients derived from the fitting were compared with theoretical data.

Calculations of self-broadening are performed using a semi-empirical approach [3]. This method is based on impact theory modified by introducing additional parameters to extend the use of empirical data. These model parameters are determined by fitting the broadening coefficients on experimental data. The method is further developed by using anharmonic wavefunctions in the estimates of line profiles [4]. The main feature of the present calculation is the use of a complete set of high accuracy vibration-rotation dipole transition moments calculated for all possible transitions using wavefunctions determined from variational nuclear motion calculations and an *ab initio* dipole moment surface. This approach explicitly takes into account all scattering channels induced by collisions. Calculated data are in a good agreement with the measured ones.

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C20

Contribution of different components of bimolecular absorption to the water vapour continuum in rotational and fundamental rovibrational spectral bands

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In spite of essential progress in theoretical and experimental studies of the water vapour continuum and its physical origin the problem of quantitative contribution of different mechanisms to the continuum is still unsolved. This work is aimed at finding a uniform approach to the determination of contribution of different components of bimolecular absorption to the observed continuum. Pure rotational and fundamental rovibrational spectra of water vapour at room temperature are analyzed. For analysis we used several semi-empirical models taking into account the contribution of bound and metastable water dimers as well as the contribution of the water monomer far wings. Water dimer absorption was calculated using the most accurate to date theoretical [1] and experimental [2, 3] data on the dimerization constant. Experimental spectra of water vapour continuum in the IR range were taken from the work [4] and the continuum spectrum in the range of pure rotational band of water monomer was taken from the very recent study reported in this conference [5]. The results of the spectra analysis as well as qualitative and quantitative estimations of the continuum constituents will be presented and compared with previously published data.

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C21

Addition of the H_2, He and CO_2 broadening and shifting parameters and their temperature dependencies. Part 1: SO_2, NH_3, HF, HCl, OCS and C_2H_2

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The goal of this work is to increase the potential of the HITRAN database [1] towards the exploration and modeling of the atmospheres dominated by noble gases (gas giants) or carbon dioxide (planets like Venus and Mars). Line-broadening coefficients, line shifts and temperature dependence exponents of molecules of planetary interest perturbed by H_2, He and CO_2 are being assembled from both experimental and theoretical studies obtained from available peer-reviewed sources, or their extrapolations. The first step in this direction was made by us in Li et al [2] where we made complete datasets of H_2- and CO_2-broadened lines of CO. In this work we have extended this study to six more molecules: SO_2, NH_3, HF, HCl, OCS and C_2H_2. Semi-empirical approaches used in this work will be described for each system. Every line for these molecules now has the relevant parameters, which will be accessible through the new HITRAN online interface: www.hitran.org.

The present work helps to identify the need for further investigations of broadening, shifting and the temperature dependence of spectral lines in planetary environments. A “wishlist” for additional studies in this area will be presented at the meeting.

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C22

Broadening parameters for H_2O lines perturbed by argon in infrared region

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The water vapor line broadening (γ) and shift (δ) coefficients for H_2O spectral lines of 10 vibrational bands ν_1, ν_3, $2\nu_2$, $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, $2\nu_2 + \nu_3$, $2\nu_1$, $\nu_1 + \nu_3$, $2\nu_3$, and $\nu_1 + 2\nu_2$ induced by argon pressure were measured with Bruker IFS 125 FTIR spectrometer (IAO, Tomsk). The spectra measurements were performed at room temperature, at the spectral resolution of 0.01 cm^{-1} and in wide pressure range of Ar. The calculations of the coefficients γ and δ were performed in the framework of semiclassical method. The effective vibration-rotation interaction potential for H_2O–Ar system [1] was taken to analysis the vibrational and rotational dependence of the line broadening and shift coefficients. The vibrational dependence of the interaction potential is confirmed by the vibrational dependence of two parameters from the isotropic part of the potential. The calculated values of the broadening and shift coefficients were compared with the experimental data.

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C23

DRIADA—compact high-resolution spectrometer for atmospheric monitoring of greenhouse gases in near IR

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The problems related to the climate change call for global monitoring of greenhouse gases, specifically carbon dioxide and methane. Ground based measurements do not provide required spatial and temporal coverage needed to identify CO_2 and CH_4 sources and sinks. One of the methods to obtain complete data on these gases is to perform space-borne high-resolution spectroscopy measurements in near-IR spectral range. The main parameter of the instrument in this case is its high resolving power, allowing detectionof isolated unsaturated lines. From 2009 the GOSAT experiment (Japan) provides a monitoring of the greenhouse gases based on the measurements of infrared solar radiation reflected from the surface and scattered in the atmosphere using the near IR gaseous bands (Kuze et al. 2009)**.** The OCO-2 (Orbiting Carbon Observatory) was launched in 2014 and use high-resolution measurements of 1.61 μm and 2.04 μm bands of CO_2 to determine a column abundance of the gas (Crisp et al. 2004).

Experiment DRIADA at the International Space Station (ISS) is planned for three years starting from 2018 and will consist of two high-resolution channels working in the range of 0.7–1.7 μm and a camera. The instrument will be installed on the exterior of the ISS on a steerable platform allowing both nadir and sun glint observations. The ISS orbit inclination restricts the observed latitudes to $\pm 52^0$. The column abundance of CO_2 will be retrieved from 1.61 μm absorption band (spectrometer's range of 1.595–1.620 for 48 diffraction order), and the band at 1.64 μm will be used for CH_4 (spectrometer's range of 1.629–1.654 μm for 47 diffraction order). The second channel will work in parallel, providing a reference using O_2 absorption in 0.76 μm A-band to account for changes in the atmospheric pressure, clouds and aerosols. Camera will be used for cloud thickness evaluation. The planned resolving power in mail channel is 20 000 and in oxygen channel is 23 000. The DRIADA development relies on the precursor experiment, RUSALKA, operated by the ISS cosmonauts from August 2009 to July 2012 (Korablev et al., 2010).

In 2012 the DRIADA experiment has successfully passed the preliminary design review. By the end of 2015 DRIADA will have finalized product drawings & descriptions.

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C24

Integrated cavity output spectroscopy using reflected radiation

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New method of weak absorption measurements is based on the classical ICOS scheme with continuous radiation. In this method we use three-channel scheme of detecting absorption spectra in which we record radiation transmitted through the cavity and reflected from it. The usage of all the three channels allows suppressing noises related to mismatching of laser frequency with cavity eigenmodes. The record time in proposed method is reduced. Using linear regression scheme we can calculate absorption spectrum.

Features of detected signal allow gradually extending dynamic range of measurements in comparison with standard ICOS-scheme.

We also report the advantage of the scheme with non-symmetric cavity; in this scheme it is possible to increase level of recording signal twice.

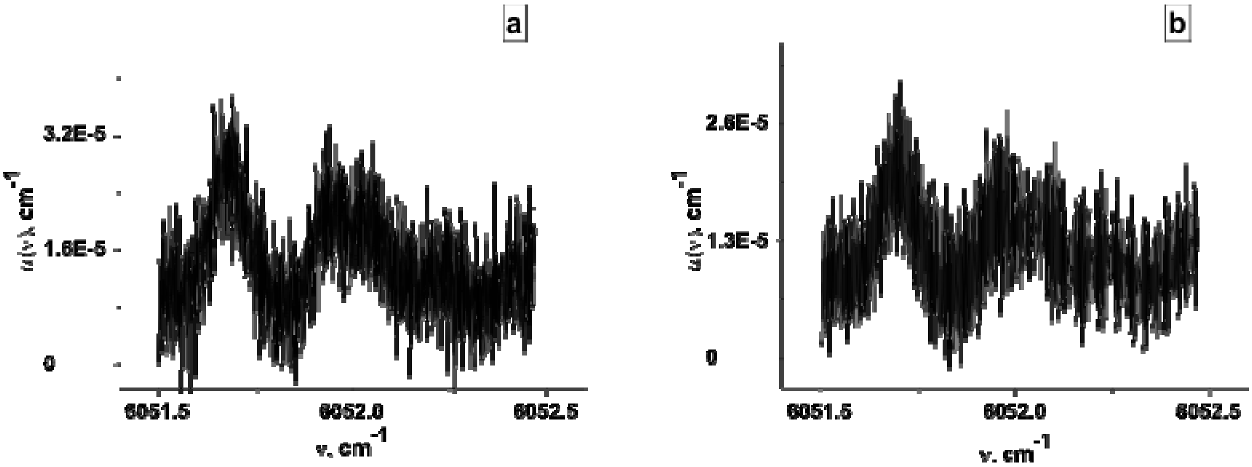

Fig. 1. Absorption spectra of natural gas recorded (a) using R-ICOS scheme for one laser scanning time (5 μs) and (b) conventional ICOS scheme with integration during 1000 laser scanning times (50 s).

We applied the proposed method for measuring methane concentration in gases with various concentrations. We used different cavity mirrors with reflectivity up to 99%. We measured background concentration of methane ($\alpha \sim 1.6\cdot10^{-6}$ cm^{-1}) for 320 μs. The sensitivity of these measurements was $2\cdot10^{-8}$ cm^{-1} using an integration time of 20 sec.

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C25

A cavity ring down spectrometer for high sensitivity absorption in the 2.35 µm atmospheric window

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Near infrared atmospheric transparency windows are low absorption spectral regions widely used for probing the atmosphere of the Earth and other planets. The accurate characterization of the atmospheric absorbers in such windows is a prerequisite to increase the performance of airborne and ground-based spectrometers.

Within the framework of the *Improved Atmospheric Spectroscopy Databases program* (as part of the ESA SEOM), a new high sensitivity cavity ring down spectrometer has been developed for high sensitivity spectroscopy in the 2.35 µm region transparency window.

The CRDS spectrometer has a 1.4-meter-long high-finesse cavity and uses a Distributed Feed Back (DFB) laser diode as light source. The laser diode is frequency tuned between 4248.8 and 4257.3 cm^{-1} with a typical spectral step of 2×10^{-3} cm^{-1} by changing its temperature from 18°C to 40°C. An almost constant noise level of ~6×10^{-10} cm^{-1} on the absorption coefficient is achieved by increasing the number of averaged ring down events for a single spectral point with the absorption coefficient. The accessible spectral range will be extended in the future by purchasing new laser sources as we have done for our other CRD spectrometers in the 1.20 to 1.72 µm spectral region [1].

From spectra recorded in a wide variety of experimental conditions, new spectral information could be derived about water vapor lines, self- and foreign- water continua and air pressure-induced broadening and shift of methane and water lines. For instance, the analysis of our pure water vapor spectra was found to show significant differences with HITRAN2012 [2] for the intensity of a few lines and some new water lines were measured.

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C26

New features of FT spectrometer using LED sources

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It was shown that the use of high luminance LED emitters as a light source for Fourier transform spectrometers permits to enhance their threshold sensitivity in the visible and near-IR ranges by orders of magnitude [1]. Using a 2.5W Edixeon EDEI-1LS3 emitter as a light source for the spectrometer with a 60-cm multipass cell during a 24-h measurement time, we have achieved a signal-to-noise ratio of 4.5×10^4 which corresponds to the minimal detectable absorption coefficient of 1.2×10^{-8} cm^{-1}. Combining LED sources with a greater luminance and large-base multipass cells with silver or interference coated mirrors with the reflection coefficient $R > 0.97$ makes it possible to achieve in the visible range the sensitivity to absorption as low as 10^{-9}–10^{-10} cm^{-1}.

Such enhanced sensitivity spectrometer has been used to measure the transition frequencies of $H_2{}^{16}O$, $HD^{16}O$, $D_2{}^{16}O$, $H_2{}^{18}O$, $C^{18}O_2$, I_2 molecules in the range 9000–22 500 cm^{-1}. The comparisons of recorded spectra with those obtained by the long-path observations will be done.

The results of H_2O–N_2 and H_2O–H_2O broadening investigation recorded by a high resolution Fourier-transform spectrometer IFS-125M with LED sources in the region 15 500–16 000 cm^{-1} are shown. Least-square-fitting algorithm Wxspe was used to retrieve of the spectroscopic parameters from measured spectral data set [2]. Line-broadening and line-shifting coefficients derived from the fitting were compared to calculated data.

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C27

Fine structure of *Q*-branch $\nu_1 + \nu_3$ band of UF_6 absorption spectra: Tunable QCL and FTIR spectroscopy studies

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The absorption spectra of *Q*-branch $\nu_1 + \nu_3$ vibrational band of uranium hexafluoride (UF_6) have been recorded in 1290–1292.5 cm^{-1} spectral region with QCL-based tunable laser spectrometer and in 1260–1320 cm^{-1} spectral region with Bruker Vertex 80v FTIR spectrometer. Spectra of UF_6 with natural isotopic abundance (0.7 % of U^{235}), enriched sample (90% of U^{235}) and its mixtures (2%, 5% and 20% of U^{235}) have been studied at various pressures (10–70 Torr) and T = 23 °C at optical path length L = 30 cm. In addition, spectra of natural isotopic abundant UF_6 have been acquired at T = –30 ÷ +20 °C in liquid nitrogen (LN) cooled cell with L = 230 cm.

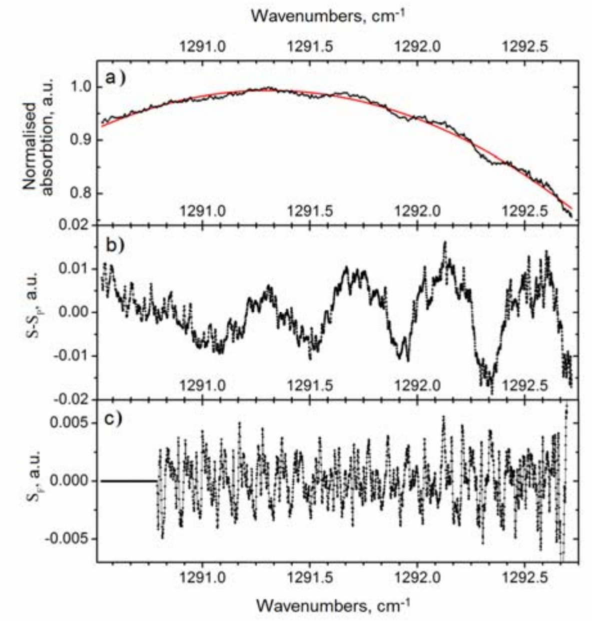

Fig. 1. (a) spectra of $U^{238}F_6$ (S) and its 2nd order polynomic fit (S_p); (b) residual $S - S_p$; (c) result of high pass filtering of $U^{238}F_6$ spectra (S_F). T = 23 °C.

All spectra which have been achieved with QCL demonstrates noticeable fine structure (Fig. 1a, b, c). This structure consists of broad features (HWHH ~0.2 cm^{-1}, Fig. 1b) and sharp peaks (HWHH ~ 0.02 cm^{-1}, Fig. 1c). All this features are the same for both isotopomers and demonstrates pressure broadening and isotopic shift of 0.59 cm^{-1} (same value as for $\nu_1 + \nu_3$ vibrational band). Broad features were also recorded with FTIR spectrometer with spectral resolution of 0.075 cm^{-1}. A theoretical estimation has been made in order to identify this fine structure. Periodical broad structure (Fig. 1b) has been interpreted for the first time as a reflection of hot band transitions in a *Q*-branch. Previously unknown anharmonicity parameters X_{21}, X_{31}, X_{32} and combinations of $X_{i1} + X_{i3}$ (i = 4, 5, 6) have been estimated. Sharp peaks (Fig. 1b) and broad features (Fig. 1c), as well as original spectra (Fig. 1a), were used to determine isotopic ratio of specified mixture. Results are in the agreement with estimated values. Accuracy analysis requires calibration of these data with mass spectrometry measurements.

School Lectures D

Tuesday, June 30, 17^{00}–18^{30}

Chair: Valery I. Perevalov

D1

The diatomic spectroscopy of excited states beyond adiabatic approximation

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The challenges of experimental and theoretical molecular spectroscopy are: (a) unambiguous assign the observed transitions; (b) fit the directly sampled energy levels to a quantum mechanical model constructed on the physically meaning molecular parameters (c) make predictions about other spectra within the experimental accuracy and (d) capture the intramolecular dynamics and wave functions behavior that are encoded in intensity distribution of the spectrum.

Despite their small size diatomic molecules at high excitation do not demonstrate the simple energy structure and transition intensity patterns following by a conventional adiabatic (Born-Oppenheimer) approximation. Sometimes the transgressions lead to catastrophic changes of the spectrum making the assignment to be unfeasible procedure.

Nowadays the advanced deperturbation models (based on couple-channel approach) and highly efficient computation schemes are used to realize more complex quantum mechanical calculation including numerous intramolecular interactions. The success of these procedures depends on both experimental data field and results of state-of-art *ab initio* calculation involved. The molecular parameters used to fit the experimental line positions and intensities contain insights into molecular structure which concerns non-adiabatic wave function behavior. This information can be more useful than the phenomenological parameters themselves, especially when simplifying assumptions are made and tested.

The recent success in the direct deperturbation treatment of the excited alkali diatomic states will be shown as example how to use the often huge body of highly accurate spectroscopic data for obtaining reliable predictions of non-adiabatic structure in a wide excitation energy range and internuclear distance.

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D2

High resolution spectra of molecules with variational methods

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In order to solve the Schrödinger equation for the motion of nuclei of a polyatomic molecule, the Hamiltonian has to be transformed into a body-fixed coordinate system and expressed in terms of translational, vibrational and rotational modes. The transformation can be done in a number of different ways (numerical or analytical) and results in a complex, non-linear Hamiltonian operator. The corresponding ro-vibrational Schrödinger equation can be solved by perturbation theory, variational calculations, or propagation of awavefunction in imaginary time as well as by a combination of these methods. In this lecture I will present the variational approach to solve the ro-vibrational Schrödinger equation for a polyatomic molecule towards generating high resolution spectra.

In contrast to the effective Hamiltonians the full-dimensional variational methods have the potentialto address a wider range of frequencies, energy levels, or vibrational states, therefore they are often referred to as ‘global’ methods. These methods are expected to better describe states with high excitations. Howevera very detailed and accurate knowledge of molecular properties (potential energy and dipole momentsurfaces) is needed for their applications to high-resolution spectroscopy. There have been a number of implementationsof global methodologies. The rotation-vibration Schrödinger equation for a molecule is solvedmost efficiently by variational methods, either in a Fixed-Basis Representation (FBR), where the Hamiltonianmatrix is constructed in terms of a suitable rotation-vibrational basis set and diagonalized numerically or in therelated Discrete-Variable Representation (DVR), where the Hamiltonian matrix is diagonalized in a coordinaterepresentation.

Within the Born-Oppenheimer approximation, the calculation of high-resolution rotation-vibration spectra for astable polyatomic molecule consists of the following steps: (a) accurate ab initio calculations to create potentialenergy surface (PES) and dipole moment surfaces (DMSs); (b) nuclear motion calculations to provide energy levels and wave functions; (c) calculation of transition dipole moments using the wave functions and dipole moment surfaces.

Ab initio DMS computed at high levels of theory (such as the coupled cluster CCSD(T) method with a large basis) provides very reasonable description of the intensities. An ab initioPES, however, cannot deliver ro-vibrational energies with sufficiently high accuracy. It is therefore commonto empirically refine ab initio PES by least-squares fitting to experimental energies or frequencies to give a‘spectroscopic’ potential; such potentials can provide theoretical line positions with near-experimental accuracy.

I will discuss these topics and present a number of illustrations based on our recent work on the spectroscopy of hot molecules within the ExoMol project. The goal of the project is to provide a comprehensive description of the absorption of all molecules likely to be important for the atmospheres of exoplanets and cool stars.

ExoMol is supported by ERC Advanced Investigator Project 267219.

Invited Lectures E

Wednesday, July 1, 9^{00}–10^{30}

Chair: Alain Barbe

E1

Rotational action spectroscopy in cryogenic ion traps

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Action spectroscopy is a versatile technique for spectroscopy of molecular ions, in particular of elusive and reactive species. One example is the method of Laser Induced Reactions (LIR), which has been developed in the Cologne group in the past years [1]. For LIR measurements only a few thousand mass-selected ions are stored and cooled in a 22-pole ion trap, and their light-induced excitation is probed by the outcome of an endothermic ion-molecule reaction. Highly accurate (sub-MHz) ro-vibrational transition frequencies are obtained by using a narrow-bandwidth cw light source calibrated with a frequency comb as excitation source in combination with the cold temperature of the ions [2]. In certain cases even purely rotational transitions have been measured with high-resolution either directly [3] or via a two-photon double-resonance scheme [4].

This talk will focus on a novel and general action spectroscopic scheme based on LIR, which utilizes a change of the rate of ternary He-attachment to the stored, cold ions depending on their internal excitation [5, 6, 7]. We will present recent examples of the application of this method for high-resolution IR spectroscopy (CH_5^+, CD_2H^+ and H_3^+), where the ro-vibrational excitation efficiently inhibits the formation of He-ion complexes (LIICG - Laser Induced Inhibition of Complex Growth). Furthermore, we were able to observe a difference in the ternary He attachment rate depending on the rotational excitation of the ion, enabling pure rotational action spectroscopy for a wide class of molecular ions. Recent examples include CD_2H^+, CF^+, and NH_3D^+.

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E2

Molecular line lists for exoplanets and other atmospheres

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Fundamental molecular data play a key role for spectral characterization of astrophysical objects cool enough to form molecules in their atmospheres (cool stars, extrosolar planets and planetary discs) as well as in a broad range terrestrial applications. However, at elevated temperatures, the laboratory data for a number of key species is absent, inaccurate or incomplete. The ExoMol project aim to providing comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future [1]. This is a huge undertaking which will mean providing in excess of a hundred of billions of spectral lines for a large variety of molecular species [2].

The physics of molecular absorptions is complex and varies between different classes of absorbers, which are therefore divided into following topics (a) diatomic, (b) triatomics, (c) tetratomics, (d) methane and (e) larger molecules. The methodology is based on direct solution of the nuclear motion Schrodinger equation using variational methods. Calculations start from high accuracy *ab initio* studies to compute potential energy and dipole moment surfaces. Experimental data is then used to produce spectroscopically-determined potential energy surfaces but *ab initio* dipole moment surfaces are found to be best.

Line lists for a number of key species are currently available from ExoMol (www.exomol.com): NH_3 [3], CaH, MgH, BeH [4], SiO [5], HCN/HNC [6], KCl, NaCl [7], CH_4 [8], PN [9], PH_3 [10], H_2CO [11], AlO [12], NaH [13] ScH [14] and HNO_3 [15]. The line lists currently being constructed include those for SO_2, SO_3, AlH, C_2, C_3, PO, PS, PH, SH, SiH, CrH, TiH, H_2S, C_2H_4, CH_3Cl and C_2H_2. I will present examples of molecular spectra computed using the ExoMol line lists.

I thank the members of the ExoMol group: A.F. Al-Refaie, A.A.A. Azzam, R.J. Barber, K.L. Chubb, P. Coles, R. Diamantopoulou, M.N. Gorman, C. Hill, L. Lodi, L. McKemmish, A.T. Patrascu, A. Pavlyuchko, O.L. Polyansky, C. Sousa-Silva, D.S. Underwood, A. Yachmenev, S.N. Yurchenko, E. Zak. This work by the ERC under Advanced Investigator Project 267219.

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Invited Lectures F

Wednesday, July 1, 11^{00}–12^{30}

Chair: Alain Campargue

F1

Coherent effects in the terahertz region and their spectroscopic applications

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Novosibirsk Free Electron Laser emits a continuous sequence of short (100–150 psec) pulses of coherent radiation tunable the region of 120–250 microns. Significant pulse energy (5–20 mJ) allows a variety of experiments in linear and non-linear regime.

We observed the optical free induction decay (FID) signals on rotational lines of different gases. Signals were detected in real time using ultra-fast Schottky diode detectors. The FID signals feed exhibit various oscillation, corresponding to splitting of the absorption lines in rotation spectra [1]. The spectral resolution in these experiments was determined by the duration of the FID. The longest signal we have observed in the HBr was 180 ns that corresponds to the spectral resolution about 10 MHz [2]. Free induction decay signals could be detected in a single shot. This observation allowed obtaining a spectrum in one laser pulse, which facilitates studies of very fast processes.

The transformation of the short optical pulse in the case of narrow absorption line with high optical density was studied. We have observed the formation of the so-called 0-π pulse, which propagates without loss of energy.

In experiments with gaseous nitrogen dioxide NO_2 we observed the coherent transients within a free induction decay [3]. The laser excited different sub-bands of rotation spectra of NO_2 containing about 50–70 lines. The free induction signal continued more than 30 ns and consisted of many echo-like bursts duration about 0.2 ns. Unlike the similar effect observed previously for linear and symmetric top molecules, the sequence of echo bursts is not periodic. The values for delay of individual echo are stable, and the set of these delays can be considered as a “molecular fingerprint” in the time domain.

Effect of rotation of the polarization plane of Free Induction Decay in magnetic field is observed. Experiments were performed using short pulse of terahertz Free Electron Laser in the region of pure rotation transitions of NO molecule. Rotation of polarization was observed in real time. Angle of rotation depends on time after the laser pulse and exceeds 180^0 in field < 1kG. Observed effect could be used in time-domain spectroscopy for the selection of the Free Induction Decay of paramagnetic species.

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F2

Using synchrotron radiation for high resolution molecular spectroscopy in the terahertz

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The AILES beamline of SOLEIL synchrotron extracts photons in the mid- and far-IR regions allowing high resolution spectroscopic studies in the 3–1500 cm^{-1} (0.1–45 THz) with relatively high performances [1]. Since 2006 high resolution spectra of many gas-phase species are recorded using an IFS125 Bruker interferometer which resolution is 30 MHz. This set-up associated to several sample environments (such as long absorption cells, high pressure supersonic jet, discharge cells) allowed us to obtain the far-IR spectra of stable species, molecular complexes, radicals and ions.

Very recently, in collaboration with the teams of LPCA (Dunkerque) and IEMN (Lille) laboratories, we developed a heterodyne receiver (working at 200GHz, 400 GHz and 600 GHz) allowing a large improvement of the spectral resolution [2]. This new spectrometer revealed new properties of the synchrotron radiation and may open new activities concerning molecular spectroscopy in the THz range on the AILES beamline.

In this talk I will present a survey of studies using both the FT interferometer and the heterodyne receiver.

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Oral Session G

Wednesday, July 1, 9^{00}–10^{30}

Chair: Leonid A. Surin

G1

A hot spot in the high resolution spectroscopy of methanol

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Beginning in 2012 a large number of 30 to 70 kHz doublet splittings in the Lamb-dip spectra of certain E-species transitions in methanol were observed in Nizhny Novgorod. These doublets were not predicted and have not been observed earlier. A first inclination was to ascribe these doublets to nuclear magnetic hyperfine structure due to the nuclear spins of the 4 protons. But the problem was that only certain transitions showed the doubling, but other transitions involving the same upper or lower energy levels did not. Such behaviour is not in line with the hfs selection rules ΔF = 0 and ± 1. Moreover, the doubling was not observed in *A*-state transitions of methanol ($v_t = 0$) where hfs has to be even larger. The second explanation of these and some other experimental data was based on idea of splitting of each *E*-state torsion-rotation energy levels into 2 components with the opposite parity [1]. This empirical model was able to explain the observed regularities of the splitting vs no-splitting patterns in the E-state methanol spectra and to predict the new branches of the doublets, but did not look correct one because there is no inversion motion in the methanol molecule. Next turn in explanation is based on group theory and consideration of three torsionally-mediated proton-spin-overall-rotation hyperfine interaction operators, which connect the two components of a doubly degenerate *E* torsion-rotation level in methanol [2]. This theoretical explanation of the observed doubling as a special case of spin-rotation interaction in *E*-methanol is internally consistent and let us to get a quantitative explanation for the large 40–70 kHz doublet splittings and their *J*-dependence. From the other hand we still do not fully understand some features of the observed spectra and can't rule out other possible explanation at this time.

Experimental and theoretical results of study of *E*-methanol doublets will be presented and discussed.

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G2

Self broadening and foreign broadening of methane lines in the tetradecade between 5880 cm^{-1} and 5900 cm^{-1}

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The complete and accurate determination of the methane spectrum is required for remote sensing of various methane-containing planetary atmospheres in the universe, for earth observations as well as the investigation of industrial emission sources like power plants, emissions due to transportation or biological sources. In the HITRAN2012 [1] methane compilation positions and intensities up to 4800 cm^{-1} are mainly based on model calculations. For larger wavenumbers position and intensity values given in the database are taken from line-by-line measurements [2, 3]. Broadening coefficients of the tetradecade around 6000 cm^{-1} given in HITRAN2012 are either taken from the GOSAT2009 database [4] or they are rough estimates inserted as a function of lower-state J or even default constants. The accuracy of these broadening coefficients is estimated to be approximately 20%. The temperature dependencies of air broadening in HITRAN2012 are either based on line-by-line data with deviation between different measurements of up to 50% or are estimated.

In this contribution we report on recently measured self-broadening coefficients, air broadening coefficients and nitrogen broadening coefficients, self broadening temperature dependencies and air broadening temperature dependencies for six methane lines between 5880 cm^{-1} and 5900 cm^{-1} having intensities stronger than 10^{-22} cm/molecule. Measurements were taken at pressures in between 20 mbar and 1200 mbar at gas temperatures between 219K and 310K.

The measurements were performed using a Bruker IFS125 high resolution Fourier-Transform-Infrared spectrometer on methane of a purity of better than 0.999995 mol/mol. The synthetic air used for the foreign broadening investigations had a purity of $0.9999998 \pm 8.5\times10^{-5}$ mol/mol. The 20 cm path length gas cell used for the measurements was temperature stabilized and pressure and temperature of the gas were recorded online during the whole measurement.

These measurements were realized within the framework of the EUMETRISPEC project and the authors acknowledge financial support within the EMRP. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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G3

D_2O dimers in silicon airgel nanopores

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The absorption spectra of D_2O in silica airgel were recorded at high and middle spectral resolution. Silica airgel samples made at the Institute of Catalysis Boreskov SB RAS (Novosibirsk) had length 25 mm, density 0.035 g/cm^3, pore size 50 nm. Fourier spectrometer IFS-125M with a quartz beam splitter used for registration of the absorption spectrum in the range of 4000–6000 cm^{-1} with a spectral resolution of 0.03 cm^{-1}. For the analysis of the broadband, the absorption spectra were calculated from the interferograms with a resolution of 10 cm^{-1}. Experimental setup was described in [1].

Absorption of the D_2O dimers was found in the SiO_2 airgel nanopores when the dynamics of adsorption-desorption process was studied. It was shown that the difference between the absorption spectrum of heavy water in the airgel from the bulk D_2O take place due to the presence of additional absorbent structures: dimers and near-wall water.

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G4

Predissociation of high-lying Rydberg states of molecular iodine via ion-pair states

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The photodissociation of the two-photon excited molecular iodine in the energy range 73500–74 500 cm^{-1} covering the bands of high-lying *gerade* Rydberg states $[^2\Pi_{1/2}]_c$ 6d;0_g^+ and $[^2\Pi_{1/2}]_c$ 6d;2_g has been studied with velocity map imaging technique. The ion signal was dominated by the atomic fragment ion I^+. Up to 5 dissociation channels yielding I^+ ions with different kinetic energy were observed when the I_2 molecule was excited within discrete peaks of Rydberg states and their satellites in this region. One of these channels gives rise to images of I^+ and I^- ions with equal kinetic energy indicating predissociation of I_2 via ion-pair states. The contribution of this channel was up to about 50% of the total I^+ signal. The four other channels correspond to predissociation via lower lying Rydberg states giving rise to excited iodine atoms providing I^+ ions by subsequent one-photon ionization by the same laser pulse. The ratio of these channels varied from peak to peak in the spectrum but their total ionic signal was always much higher than the signal of (2+1) REMPI of I_2, which was previously considered to be the origin of ionic signal in this spectral range. The first-tier $E0_g^+$ and $D'2_g$ ion-pair states are concluded to be responsible for predissociation of Rydberg states $[^2\Pi_{1/2}]_c$ 6d;0_g^+ and $[^2\Pi_{1/2}]_c$ 6d;2_g, respectively. Further predissociation of these ion-pair states via lower lying Rydberg states gives rise to excited I ($5s^25p^46s^1$) atoms responsible for major part of ion signal. The isotropic angular distribution of the photofragment recoil directions observed for all channels indicates that the studied Rydberg states are long-lived compared with the rotational period of the I_2 molecule [1].

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G5

Speed dependence, velocity change and line mixing in self-colliding CO_2 under high pressures in the 30013 ← 00001 band: Measurements and test of models

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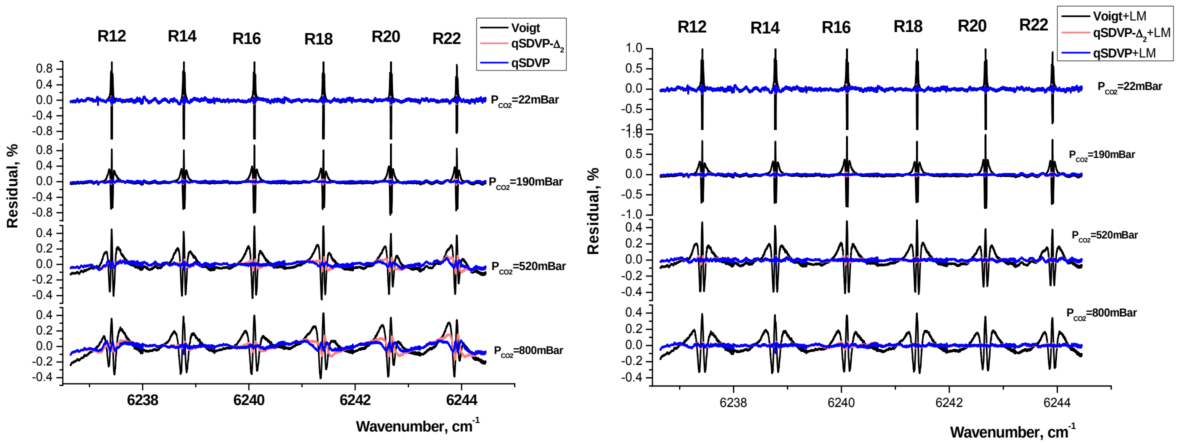
High-precision measurements of the 30013 ← 00001 *R* branch of pure CO_2 were performed using 2-channel diode laser spectrometer [1] with resolution of $1 \cdot 10^{-4}$ $cm^{-1}$and signal-to-noise (S/N) ratio up to 7000. Lines from *R*(12) to *R*(22), that may be treated as isolated unlike other lines of this branch, were measured in pressure range from 0.005 to 1 atmosphere at a temperature of 296 K. Spectra were analyzed using spectrum-by-spectrum and multispectrum fittings with a variety of up-to-day models including speed dependence, velocity change and line mixing effects. Including in line shape profiles velocity change or Dicke narrowing parameters does not lead to the improvement in obtained residuals and, moreover, results in nonlinear pressure dependences of other collisional line shape parameters i.e., speed dependent narrowing, shifting and line mixing parameters. It was showed that the quadratic Speed Dependent Voigt Profile with Line Mixing (qSDVP+LM) [2, 3] was able to model the measured spectra to the experimental noise (measured-calculated residual does not exceed 0.02%) Fig.1.All retrieved collisional parameters from spectrum-by-spectrum fitting are linear with pressure. The self-colliding line shape collisional coefficients were determined and presented using spectrum-by-spectrum and multispectrum fittings.



(a) (b)

Fig. 1. Measured-calculated residuals, using Voigt, qSDVP without speed-dependent shifting parameter Δ_2 and qSDVP: (a) without and (b) with Line-Mixing parameter.

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G6

Self-broadening and collision mixing of the spectral lines in the fundamental bands of NH_3

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In the line space formalism, the absorption coefficient in the impact approximation is described as

$$\alpha(\omega) \sim \frac{1}{3} \mathrm{Im} \sum_q (-1) q Tr \left\{ d_q [\, \hat{\omega} - \hat{L}_0^S - \hat{\Lambda}\,]^{-1} \, [d_{-q}, \rho^S]_+ \right\}$$

where d_q is the q-component of the dipole moment of the absorbing molecule (system), $\hat{L}_0^S$ and ρ^S are its unperturbed Liouville operator and the density matrix, $\hat{\Lambda}$ is the relaxation operator in the impact approximation. Its diagonal elements determine the broadening and the shift coefficients of spectral lines i.e., $\gamma_{\hat{m}} = -\mathrm{Im}\,\hat{\Lambda}_{\hat{m}\hat{m}}$, $\delta_{\hat{m}} = \mathrm{Re}\,\hat{\Lambda}_{\hat{m}\hat{m}}$, whereas the off-diagonal ones, $\xi_{\hat{m}\hat{n}} = \hat{\Lambda}_{\hat{m}\hat{n}} \quad (\hat{m} \neq \hat{n})$, are the cross-relaxation parameters which are responsible for the mixing of the spectral lines by collisions, due to the spectrum shape may differ from the simple sum of contours of the individual lines. For dealing with the problem of the collision line mixing the Rosenkranz theory [1] is the most widely used. But this theory is based on the first order perturbation theory and the calculation of the line mixing parameters is generally released by the artificial methods with some adjustable parameters. The general theory of relaxation parameters of the spectrum shape in the impact approximation free of these limitations is described in paper [2]. We applied this theory for calculation of the sets of the self-broadened relaxation parameters of spectral lines of the NH_3 fundamental bands. In spite of the dominant role of the dipole-dipole interaction, the dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole and the first order induction and dispersion interactions were taken into account. The calculations were carried out in approximations of an average velocity and a straight line trajectory, which applicability were discussed and it was shown that in the case of self-broadening these approximations caused the errors less than the uncertainties of the typical experiments. It has been shown that in all bands only the doublet components may be mixed by collisions and this effect plays important role in broadening doublets of the ν_1, ν_3 and ν_4 bands and may be ignored in the case of the ν_2 band. In all bands the calculations were carried out for lines up to $J = 12$ in all sub-branches. The theoretical results have been compared with the available experimental data and in many cases wary well agreement is obtained. The causes of discrepancies in the other cases are discussed.

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Poster Session H

Wednesday, July 1, 16^{15}–18^{00}

H1

Analysis of six new bands of $^{18}O_3$ recorded by CRDS technique in the 7400–7920 cm^{-1} spectral range

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This work is a continuation of our systematic study of the $^{18}O_3$ isotopologue of ozone by the analysis of the high resolution infrared spectra ,which has been early performed up to 7400 cm^{-1} [1]. The CRDS (Cavity Ring Down Spectroscopy) spectra [2] of ozone was recorded in the 7400–7920 cm^{-1} spectral range approaching the dissociation limit D_0 at about 8560 cm^{-1} [3, 4]. The absorption spectrum under consideration also includes the weak $^3A_2(000)$ – X(110) hot vibronic band at 7877.53 cm^{-1} affected by predissociation broadening [5].

Here we present the results of the analysis of 6 new bands of $^{18}O_3$: 1017 rovibrational transitions were assigned, corresponding to 639 determined energy levels. For observed line positions modelling, we used the effective Hamiltonian taking into account the resonance couplings with the “dark” states. The initial parameters (band centres and rotational constants) for “observed” and “dark” single state model have been predicted from the potential energy surface of ozone [6, 7].

The root mean square deviations between observed and calculated values for the line positions of the six bands are better than of 0.01 cm^{-1}. The obtained sets of effective parameters and the experimentally determined energy levels were used to generate a list of 1461 transitions. The specific points of line-lists calculations will be discussed.

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H2

High sensitivity cw-cavity ring down spectroscopy of N_2O near 1.22 µm

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The absorption spectrum of nitrous oxide (N_2O) in natural isotopic abundance has been recorded with very a highly sensitive CW-Cavity Ring Down Spectrometer. The room temperature recordings were performed with a pressure of 10 Torr in the 7915–8334 cm^{-1} spectral range (1.26–1.19 µm). The achieved sensitivity (noise equivalent absorption, $\alpha_{min} \sim 3\times10^{-11}$ cm^{-1}) allowed for the detection of lines with intensity smaller than 5×10^{-29} cm/molecule.

More than 3000 transitions belonging to 59 bands of four isotopologues ($^{14}N_2{}^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{14}N_2{}^{18}O$) have been rovibrationally assigned on the basis of the predictions with the effective Hamiltonian models [1–3]. For comparison, only 12 bands were previously measured by Fourier transform spectroscopy in the studied region. All identified bands belong to the $\Delta P = 14$ series of transitions, where $P = 2V_1+V_2+4V_3$ is the polyad number (V_i are vibrational quantum numbers). The line positions and intensities have been measured for all assigned lines.

The spectroscopic parameters have been determined for all newly detected bands from a fit of the measured line positions. The global modeling of the line positions was performed to refine the corresponding set of the effective Hamiltonian parameters of the $^{14}N_2{}^{18}O$ isotopologue. A number of interpolyad resonance interactions were identified.

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H3

A high resolution analysis of weak absorption bands of $C_2H_2D_2$-*trans*: The $\nu_8 + \nu_{10}$ (Au) band

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$C_2H_2D_2$-*trans* is a near prolate asymmetric top. This molecule has twelve vibrations and belongs to the C_{2h} point group, whose selection rules predict two A_u and four B_u infrared active fundamentals. The A_u modes give rise to type-*c* bands which have the selection rule $\Delta K_a = \pm 1$ in the symmetric top limit. The B_u modes give hybrid bands of type-*a* and -*b*. The parallel type-a component has the selection rule $\Delta K_a = 0$ while the perpendicular type-b component has $\Delta K_a = \pm1$ in the symmetric top limit.

In the present study we consider the $\nu_8+\nu_{10}$ band. It has A_u level of symmetry, which brings about *C*-type component and corresponds following selection rules: $\Delta J = 0, \pm 1$; $\Delta K_a = \pm 1$; $\Delta K_c = \pm 1$. The experimental spectrum of $C_2H_2D_2$-*trans* in the 1200–2000 cm^{-1} region was recorded with the Fourier-transform spectrometer IFS-120 HR at Technische Universität Braunschweig (Germany) at room temperature with a pressure of 0.62 mbar, an absorption path length of 16m and an optical resolution of 0.0025 cm^{-1}.

In this region seven bands are located and the analysis of these bands is complicated by numerous strong resonances. In this way, the interactions between other states have been taken into account. For interpretation model of effective Hamiltonian was used. As initial approximation parameters for $\nu_4+\nu_8$ (B_u) and $\nu_7+\nu_8$ (B_u) bands were taken by references [1–2]. Other parameters for the $\nu_6+\nu_{10}$ (B_u), $\nu_6+\nu_7$ (A_u), $\nu_3+\nu_{10}$ (B_u) and $\nu_4+\nu_6$ (A_u) bands were fixed to ground state values. It is necessary note that the $\nu_8+\nu_{10}$ band was analyzed in our study for the first time. As a result of analysis, 416 transitions with $J_{max} = 25$ and $K_{a\,max} = 14$ were assigned to the $\nu_8+\nu_{10}$ (A_u) band.

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H4

Nitrogen dioxide high temperature line list in the 466–3374 см$^{-1}$ region

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We present the nitrogen dioxide high temperature line list which is allocated on the web site of V.E. Zuev Institute of Atmospheric Optics SB RAS on the address: ftp://ftp.iao.ru/pub/NDDB/. The line list contains the following line parameters: line position, line intensity, energy of lower state and self-broadening coefficient. It is generated using intensity cut off 10^{-25} cm/molecule at 1000 K. This line list covers 466–3374 cm^{-1} spectral range and contains more than one million lines.

The line list is based on the global modeling of the line positions and intensities performed within the framework of the method of effective operators [1, 2]. The parameters of the effective Hamiltonian and effective dipole moment operator have been fitted to the observed values of the line positions and intensities collected from the literature. The used polyad model of effective Hamiltonian takes explicitly into account both the spin-rotation interactions and numerous vibration-rotation resonances interactions arising due to the approximate relations between harmonic frequencies: $\omega_1 \approx \omega_3 \approx 2\omega_2$.

Using this high temperature line list the simulations of low resolution NO_2 spectra have been performed for several spectral regions for two temperatures 296 K and 720 K. The comparison of the spectra at these two temperatures shows the considerable changing of the spectra with the temperature growth.

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H5

Fourier transform absorption spectrum of $D_2{}^{16}O$ in 14 800–15 200 cm^{-1} spectral region

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The FTIR absorption spectra of $D_2{}^{16}O$ were recorded for the first time in the spectral range 14 800–15 200 cm^{-1} with spectral resolution of 0.05 cm^{-1}. As a source of radiation the bright light emitting diode 3GR-R was applied. White type optical system and the cell of 60 cm length were used. All measurements were performed at a room temperature (297°K ± 1°K). Experimental setup makes it possible to reach signal to noise ratio about 10^4 and to record weak $D_2{}^{16}O$ lines with intensity about 10^{-27} cm/molecule [1].

The rovibrational assignment of the $D_2{}^{16}O$ spectra was based on the results of variational calculations [2]. Transitions of the $5\nu_1+\nu_3$, $6\nu_1$, and $4\nu_1+2\nu_2+\nu_3$ bands centered at 15 050.88, 15 049.50 and 14 979.16 cm^{-1}, respectively, are identified. Deviations up to 0.5 cm^{-1} between observed and calculated line positions are encountered.

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H6

Intensities and self-broadening coefficients of the strongest water vapour lines in 2.7 and 6.25 μm absorption bands

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Intensities and self-broadening coefficients of about 460 of the strongest water vapour lines (intensity $S \geq 2\times10^{-23}$ cm/molec) are retrieved within the 2.7 and 6.25 μm water vapour absorption bands (spectral intervals 1400–1840 and 3440–3970 cm^{-1} respectively) from high-resolution Fourier transform spectroscopy measurements at room temperature with a 5-mm-path-length absorption cell.

The retrieved spectral line parameters are compared with those in the HITRAN database v. 2008 and 2012 [1]. Both the retrieved intensities and half-widths are on average in reasonable agreement with those in HITRAN-2012. Maximum systematic differences do not exceed 4% for intensities (1600 cm^{-1} band) and 7% for self-broadening coefficients (3600 cm^{-1} band), and lie within the average total uncertainty of the retrieval. For many lines, however, strong deviations from the HITRAN-2012 data were detected that markedly exceed the error of retrieval for these lines.

In addition, our earlier reported water vapour line parameters for 5300 cm^{-1} (1.9 μm) band [2, 3] are also compared with HITRAN-2012. Again, although the systematic deviation lies within 4–5%, however, for many line parameters, especially for the self-broadening coefficients, deviations markedly exceed 10%.

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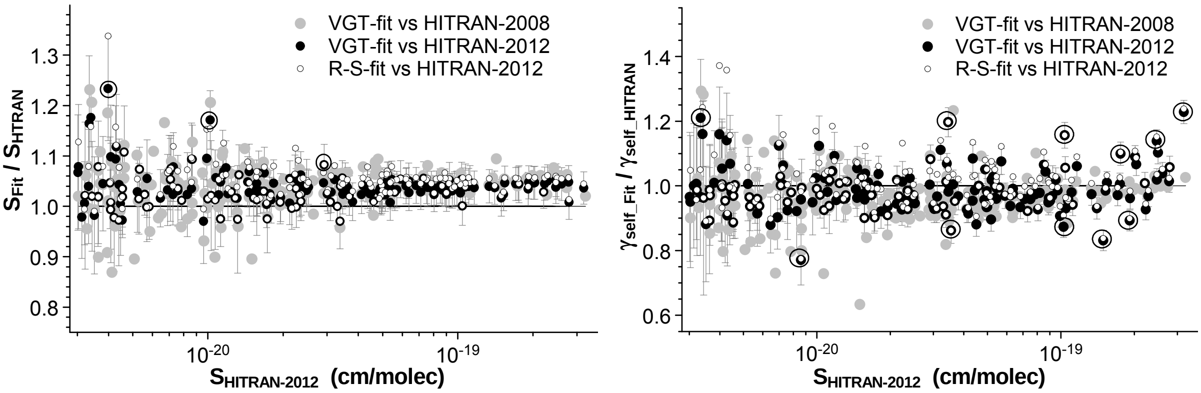

Figure 1. Example of water vapour line intensities and self-broadening coefficients, derived by fitting to the experimental spectra in 6.25 μm band, compared to HITRAN v. 2008 and 2012 [1]. The 'VGT' and 'R-S' denote fitting using Voigt and Rautian-Sobelman's line profiles respectively

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H7

High pressure Cavity Ring Down spectroscopy: Application to the absorption continuum of CO_2 near 1.7 µm

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A Cavity Ring Down Spectrometer has been developed for high sensitivity absorption spectroscopy at pressure up to 10 bars in the near infrared. In order to strictly avoid perturbations of the optical alignment by pressure forces, the pre-aligned CRDS cavity is inserted inside the high pressure cell. We present here the first application of this newly developed CW-CRDS spectrometer to the study of the room temperature spectrum of CO_2 at high pressure. The spectra were recorded between 5850 and 5950 cm^{-1} for a series of pressure values up to 6400 Torr. The studied spectral interval corresponds to the high energy range of the 1.75 µm transparency window of CO_2 of particular interest for Venus.

The stability of the spectra baseline was checked by injecting Ar and N_2 up to 10 atm. The CO_2 absorption coefficient at a given pressure value was obtained as the increase of CRDS loss rate from its value at zero pressure. The CO_2 absorption spectrum includes the contribution of the self broadened local rovibrational lines and of a broad and weak continuum. The CO_2 continuum was obtained after subtraction of the local lines obtained from a simulation based on the CO_2 HITRAN line list and a (truncated) Voigt profile. The pressure dependence of the absorption continuum was checked to be quadratic with a binary absorption coefficient on the order of 8×10^{-9} cm^{-1}/atm^2 in the studied spectral interval. The derived continuum shows an unexpected spectral feature located in the region of a band $^{16}O^{12}C^{18}O$ (present in natural abundance) which dominates the spectrum in the region. This spectral feature was quantitatively accounted for on the basis of requantized classical *ab initio* calculations performed in the frame of the Energy Corrected Sudden (ECS) approximation.

H8

Calculation of rotation-vaibarion energy levels of the ammonia molecule based on an *ab initio* potential energy surface

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This work is a step towards the global *ab initio* potential energy surface (PES) of ammonia NH_3 with the accuracy approaching 0.1 cm^{-1}. This accuracy has not been achieved here, but we demonstrate here clearly, that this is possible and show the way towards this level of accuracy. This extremely high accuracy has been achieved for water molecule for the levels up to 15 000 cm^{-1} [1] and about 1 cm^{-1} for the dissociation energy [2].

The most accurate NH_3 *ab initio* potential energy surface (PES) has been constructed here. The underlying Born-Oppenheimer electronic structure calculations were performed in a few steps. MOLPRO *ab initio* package is used to calculate multireference CI points in quadruple and 5z basis set with complete basis set (CBS) extrapolation. We do not perform 5z-6z CBS scheme, as in water molecule, because this is too hard to calculate for ammonia molecule. 50 000 points of the born-Oppenheimer (BO) surface are calculated that way. The residual error in the electron correlation treatment also must be corrected. This can be achieved by performing calculations with active spaces larger than the full-valence one. Some experimentation may be required when choosing the enlarged reference space. Relativistic and adiabatic surfaces are also calculated using MOLPRO and CFOUR packages respectively. The *ab initio* points have been fitted to the analytical PES, BODC and relativistic surfaces.

Nuclear motion problem was solved utilizing final PES, which includes all mentioned above corrections, using TROVE package [3]. Two parameters – equilibrium bond length and equilibrium angle were adjusted in analytical PES representation to perform better coincidence with experiment. The rovibrational energy levels have been calculate using two versions of the TROVE program - one used linearised coordinates and the other - curvilinear coordinates. Better convergence for the high energy levels was achieved using curvilinear version. In particular the accuracy of about 1 cm^{-1} has been achieved for the levels up to 9 000 cm^{-1} and reasonable accuracy about 5 cm^{-1} up to 18 000 cm^{-1} compering to experiment [4, 5].

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H9

The line lists of the $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{18}O$ ozone isotopologues of the S&MPO database

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The line positions and line intensities of two ozone isotopic species, $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{18}O$, have been calculated using previously published spectroscopic parameters of mentioned above species [1–3]. The generated line lists of more than 80 vibrational bands between one and 4822 cm^{-1} have been included in the database of the S&MPO information system [4].

Comparison of current $^{16}O^{18}O^{16}O$ line list to those of the HITRAN database [5] as well as the precision of presented data is discussed. Several examples of a comparison of synthetic spectra with FTS recorded spectra are given for both $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{18}O$.

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H10

Small molecules in external magnetic fields

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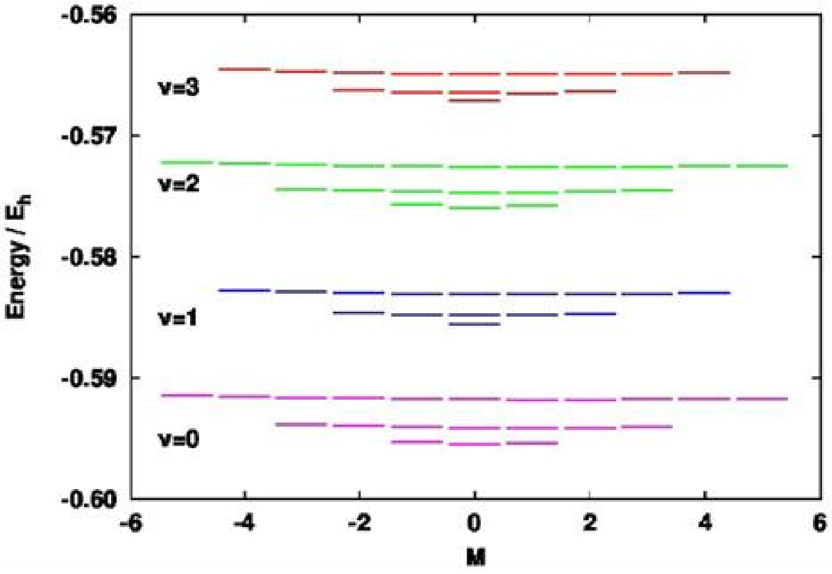
This work is focused on the study of properties of the molecular ions H_3^+ and H_2^+ in the electronic ground states when placed in a uniform weak magnetic field. Two methods were considered for the calculation of the electronic energy: perturbation theory and a fully variational approach by means of trial functions which contain magnetic terms. Results were obtained within the Born-Oppenheimer approximation. For the H_3^+ molecular system, potential energy surfaces (PES) were calculated using standard *ab initio* methods. The magnetic interaction terms were then evaluated by first order perturbation theory for fields of up to 2350 T (0.01 B_0 in atomic units). These terms were fitted to a functional form and the deformations of the field-free PES investigated[1]. For the H_2^+ molecule, potential energy curves were obtained variationally using tailored trial functions that mimic the behavior of such a system in the presence of a magnetic field, $0 \leq B \leq 2.35\times10^5$ T (1.0 B_0), for different orientations. For the first time, rotational energy levels were computed considering the full nuclear Hamiltonian containing magnetic terms and using the hindered rotation approximation[2]. The rotational structure of the four lowest vibrational states is shown in the figure below for B = 0.2 … B_0.



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H11

Present status and perspectives of line-by-line analyses of the PH_3 absorption spectrum in the Octad range between 2800 and 3600 cm^{-1}

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A new study of PH_3 line positions and intensities was performed for the lower portion of the Octad region [1] between 2800 and 3600 cm^{-1} using high resolution Fourier transform spectra. Line positions and intensities were retrieved by least square curve-fitting procedures and analyzed using the ab initio based effective Hamiltonian [2] and the effective Dipole moment expressed in terms of irreducible tensor operators adapted to spherical top molecules. A new measured linelist produced positions and intensities for more 7200 features. Assignments were made for 60% of these; 4500 experimental line positions and 1300 selected line intensities were fitted with RMS standard deviations of 0.006 cm^{-1} and 15%, respectively. The sum of calculated intensities between 2700 and 3650 $cm^{-1}$is in a good agreement with HITRAN2012 [3] and is5–13% lower than sum of calculated intensities from different ab initio dipole moment surfaces.

Acknowledgments

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H12

First principles calculation of energy levels and spectra for AB_4, ABC_3 type molecules

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Molecules of type of AB_4, ABC_3 are interesting both for experimental and theoretical spectroscopy and for intramolecular dynamics. The spectra of ABC_3 molecules could be calculated on a similar manner as AB_4 molecules (like methane [1, 2]) but specific for these molecules problems are appeared. A big number of PES and DMS parameters requiring much larger number of *ab initio* points for a robust PES and DMS fit. The big number of parameters could also lead to non-physical behavior of PES far from equilibrium geometry in the 9D space. A full account of the symmetry properties [3] involve smaller dimensions of basis sets and is benefic for handling strict degeneracies and selection rules, particularly in case of transitions among highly excited vibration-rotation states and high temperatures spectra. Full symmetry variational calculations of vibration-rotation energy levels of symmetric five-atomic molecules CH_3Li, CH_3F [4, 5], CH_3Cl [6], CH_3Br, CH_4 from a PES are discussed.

Acknowledgments

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H13

Radiative properties of the low-lying states of Rb_2 and Cs_2 based on *ab initio* calculations

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The electric dipole transition moments (EDTM) of rubidium and cesium dimers have been calculated between all electronic states converging to the lowest three dissociation limits. The adiabatic energies and relevant quasi-relativistic matrix elements were evaluated for a wide range of internuclear distance in the basis of the spin-averaged wave functions corresponding to pure Hund's coupling case (**a**) by using of both shape and energy consistent small (9-electrons) effective core pseudopotentials (ECP) [1]. The dynamic correlation has been accounted for a large scale multi-reference configuration interaction method which was applied for only two valence electrons keeping the rest frozen, i.e. in a full valence (2-electrons) CI scheme. The angular-independent core-polarization potential (CPP) was employed together with the above small core ECPs to take into account for the residual core-valence effect. All calculations were performed by means of the MOLPRO v.2010.1 program package [2].

The asymptotic behavior of the transition moments at large internuclear distances is analyzed in the framework of long-range and single channel quantum-defect theories. The assessment of accuracy of the present results is discussed by a comparison with preceding *ab initio* calculations [3] and their atomic counterparts. The semi-empirically scaled EDTM functions were finally applied to predict lifetimes and emission branching ratios for the low-lying states of rubidium and cesium dimmers due to little-known approximate sum rules [4]. These radiative properties could be useful, for example, for the decay rate estimates of the states involved in multi-state optical cycles to produce ultra cold ground state molecules by photoassociation and stimulated Raman processes.

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H14

Speed-dependent spectral line profile including line narrowing and mixing

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A model line profile was developed that includes all essential physical mechanisms of its forming: the Doppler and the collision line broadening; the Dicke's line narrowing reduced by the presence of soft collisions (i.e. small-angle scattering); the wind effect leading to the speed-dependence of collision relaxation constants, and the line mixing. The model is based on the quantum-mechanical collision integral kernel calculated for intermolecular interaction potentials $\propto r^{-n}$ with $n = 3 \ldots 6$ where r is the distance between colliding molecules [1, 2]. The collision integral was represented as a sum of the common hard collision model term and the integral term having the asymmetrical kernel caused by classical scattering on small angles ~ 0.1 … 0.3 rad that leads to reducing to certain extent the Dicke's line narrowing. Processing recorded line profiles of a high quality with the obtained line profile allows retrieving qualitatively new information on the relation between frequencies of soft and hard velocity-changing collisions. The line mixing was accounted following the scheme presented in Ref. [3].

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H15

Calculating the "hot" line intensities (K_a ~ 25, J ~ 30) of water vapor (000)-(000) band

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The "hot" line intensities, produced by the transitions between high-excited energy levels, are needed to calculate in the case of high-temperature databases. The application of the traditional scheme for prediction the eigenvalues and eigenvectors of levels with high quantum numbers is restricted by the divergence of the effective rotational Hamiltonian. At present work, the line intensities of (000)-(000) band of water vapor (H_2O) are considered. The eigenvectors of the effective rotational Hamiltonian, approximated by Pade-Borel method [1], were applied. The parameters of the effective rotational Hamiltonian of (000) state from Ref. [2] were used. The intramolecular effects for line intensities were taken into account by traditional scheme and Pade approximation [3]. The data of Ref. [4] were used as a source of experimental intensities. Moreover, the line intensities of $K_a \geq 14$ transitions were predicted by symmetric rotor approximation. Finally, the obtained results are compared with HITEMP2010 database [5] and database of Ref. [6] up to high quantum numbers $K_a \sim 25, J \sim 30$).

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H16

Global modeling of high-resolution spectra of acetylene (C_2H_2)

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The global modeling of both line positions and intensities of acetylene molecule in the 50–9900 cm^{-1} region has been performed using the effective operators approach. The parameters of the polyad model of effective Hamiltonian suggested in our paper [1] have been fitted to the line positions collected from the literature. This polyad model of effective Hamiltonian written up to the six-order of perturbation theory takes into account the centrifugal distortion, rotational and vibrational ℓ-doubling terms and both anharmonic and Coriolis resonance interaction operators arising due to the approximate relations between harmonic frequencies: $\omega_1 \approx \omega_3 \approx 3\omega_2 \approx 5\omega_4 \approx 5\omega_5$. The dimensionless weighted standard deviation of the fit is 3.1. The fitted set of 238 effective Hamiltonian parameters allowed reproducing 28837 measured line positions of 494 bands with an RMS value of 0.0044 cm^{-1}.

The eigenfunctions of the effective Hamiltonian corresponding to the fitted set of parameters were used to fit the observed line intensities collected from the literature for 15 series of transitions: ΔP = 0–13, 15, where $P = 5V_1+5V_3 +3V_2 V_4+V_5$ is the polyad number (V_i are principal vibrational quantum numbers). The respective approach is presented in details in our papers [2, 3]. Using eigenfunctions of a polyad model of global effective Hamiltonian one can describe simultaneously the line intensities of cold and hot bands belonging to the same series of transitions. Our fitted sets of the effective dipole moment parameters reproduce the observed line intensities within their experimental uncertainties.

The obtained sets of the effective Hamiltonian and effective dipole moment parameters will be used in the future for the generation of the high temperature spectroscopic data base for acetylene molecule.

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H17

$^{12}C^{16}O$ line profile parameters for Mars and Venus atmospheres

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The atmospheres of Mars and Venus are composed of CO_2 predominately. CO is directly produced by the photolysis of CO_2. The processes of production and recycling of CO on Mars have been studied in detail in photochemical models [1]. As a non-condensable species, the abundance of carbon monoxide and its variation with season and location as well as vertical distribution provide important keys about atmospheric transport dynamics [2]. Therefore, CO will be one of the minor atmospheric species measured by high resolution MIR echelle spectrometer as a part of ACS (Atmospheric Climate Suite) and NOMAD experiment onboard Exomars 2016 orbiter [3,4]. For accurate measurement of the CO abundance with high spectral resolution precise information about line spectroscopic parameters, especially, CO–CO_2 line broadening is needed.

Calculations of vibration-rotation line broadening coefficients and their temperature exponents for CO due to pressure effects of CO_2 and self broadening coefficients at the room temperature were performed using semiempirical method [5]. This method is based on the impact theory which is modified to widen the use of empirical data by introducing additional parameters. The model parameters are determined by fitting the broadening and shifting coefficients to experimental data. Calculations were made for wide ranges of rotational quantum numbers $0 < J < 100$. Obtained data were compared with available experimental values. Semiempirical results agree well with the measurements and provide identical values for high J. The computed line profile parameters can be therefore considered as reliable and worthy of use in the spectroscopic databases. Moreover, because of the insignificant vibrational dependence of CO–CO_2 broadening coefficients, the calculated values can be safely used for different vibrational bands.

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H18

Broadening, shifting and speed dependence coefficients of diagnostic water lines

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Role of the water vapour in the Earth's atmosphere is well known. Spectral lines of water molecule are widely used for different atmospheric applications, such as remote sensing, meteorology, etc. Water lines located near 183 and 380 GHz are important diagnostic lines whose parameters were accurately measured in present study.

A BWO-based spectrometer with radio-acoustic detection of absorption was employed. Experimental spectra of water molecule perturbed by H_2O, O_2, N_2, Ar, CO_2, CO, He, Ne, Kr, Xe, H_2, and D_2 were recorded with high signal-to-noise ratio (up to 10000) at room temperature in a wide pressure range from 0.1 to 4 Torr. Data analysis was performed using Voigt and Quadratic Speed Dependent Voigt profiles. Pressure broadening, shifting and speed dependence parameters were retrieved from a fit of the theoretical profiles to the experimental spectra. Obtained results might be useful for developing line shape models and spectroscopic databases as well as for improving accuracy of methods of remote sensing data analysis.

The study was partially supported by RFBR and by government of Nizhny Novgorod region.

H19

Hitran.org: New website, new structure, new interface for the HIRAN spectroscopic database

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We present HITRANonline, an online interface to the HITRAN spectroscopic database [1] which is now hosted at www.hitran.org.

As the amount and complexity of spectroscopic data on molecules used in atmospheric modelling has increased, the existing 160-character, text-based format has become inadequate for its description. As examples: (1) The line shapes that take into account speed-dependence and Dicke narrowing are needed, for instance, the Hartmann-Tran profile (HTP) [2]. However, HTP requires up to six parameters for full description (each with uncertainties and references) as opposed to two parameters available with the Voigt profile. (2) Modelling of the planetary atmospheres requires knowledge of line broadening by H_2, He and CO_2. (3) More than the current maximum of 10 isotopologues of some molecules (for example, CO_2) can be important for accurate radiative transfer modelling. The new relational database structure overcomes all of these limitations as well as allowing for better data provenance through "time stamping" of transitions and a direct link between items of data and their literature sources.

To take full advantage of this new database structure, the online interface HITRANonline, available at www.hitran.org, provides a user-friendly way to make queries of HITRAN data with the option of returning it in a customizable format with user-defined fields and precision. Binary formats such as HDF-5 are also supported. In addition to the data, each query also produces its own bibliography (in HTML and BibTeX formats), "README" documentation and interactive graph for easy visualization.

The capabilities of the new interface will be demonstrated at the poster.

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H20

Water vapour self-continuum absorption within 0.94 and 1.13 μm bands at high temperatures

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The water vapour self-continuum absorption was retrieved from experimental high-resolution spectra within 8800 and 10600 cm^{-1} absorption bands. Experimental data were obtained in the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory (UK) using a Fourier transform spectrometer and a heated multipass absorption cell, as a part of the NERC-EPSRC funded CAVIAR consortium (Continuum Absorption at Visible and Infrared wavelengths and its Atmospheric Relevance) [1]. The water vapour continuum was derived for pure water vapour as the difference between the total optical depth (experimental spectrum) and calculated local water vapour lines contribution using UCL (University College London) compilation [2]. The comparison shows that the retrieved in-band continuum has well-pronounced spectral features (peaks) that are not described by the MT_CKD continuum model [3] (Fig. 1). Similar features were earlier reported within the strongest near-infrared absorption bands and have been attributed to water dimer absorption [4]. The presence of similar peaks within the bands investigated here is reported for the first time.

The experimental part of the work was performed by the NERC-EPSRC funded consortium CAVIAR (UK) [1]; processing and analysis of the experimental data were carried out under support of the Fundamental Research Program II.10.3.8 (Russia).

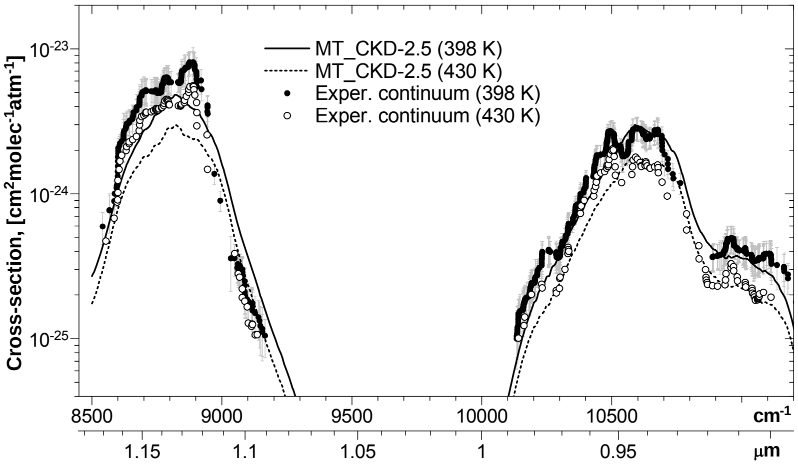

Figure 1. Comparison of the experimental pure water vapour continuum, retrieved in this work at two temperatures, with the MT_CKD continuum model [3]. Continuum is derived from absorption spectra in pure water vapour at pressure 1000 mbar and path length 17.7 m.

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H21

The line shape problem of high-precision spectra of self-colliding CO_2 molecules in the pressure range between 0.002 and 1 atm: Measurements and test of models

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A dual-channel diode laser absorption spectrometer [1] was used to perform ahighly accurate study of the shape of self-colliding CO_2 absorption line, belonging to the 6231.713421 cm^{-1}, R4, 30013–00001combination band, at a temperature of 296 K.

Standard models, including Voigt, Hard-collisional (Rautian), Soft-collisional (Galatry), and quadratic Speed-dependent Voigt (Boone), were applied, tested, and compared in the pressure range between 0.005 and 1 atm, in order to prove the spectral line parameters linear pressure dependences, i.e. the binary collision approximation.

It was shown an essentialeffect of small closely spaced lines on shifting, narrowing and broadening spectral coefficients. The usage of Rautian and Galatrylineshape models leads to a significant deviation from linear pressure dependence of the velocity changes due to collision coefficients$\nu_{VChard}\nu_{VCsoft}$while coming to the high pressures range. Most appropriate for the common description of whole experimental spectra in entire range of pressures (up to 1 atm.) is the quadratic Speed-Dependent (Boone) profile (Fig. 1).

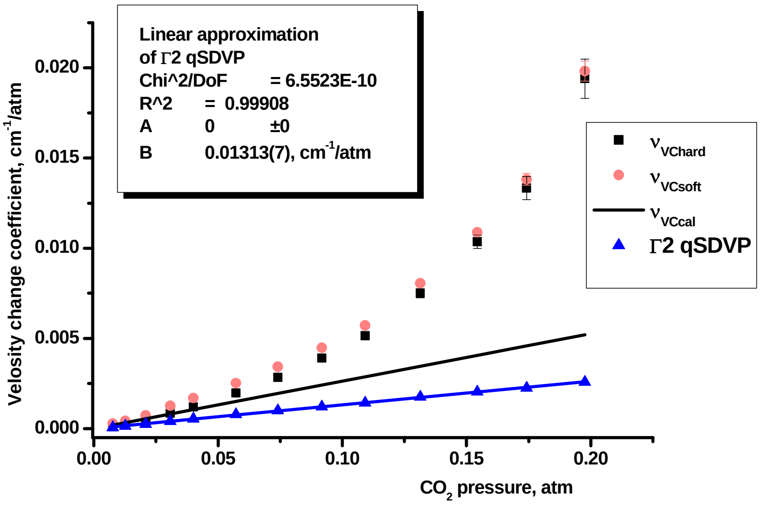

Fig.1 Self-colliding CO_2 pressure dependents of line profile velocity change and speed dependent parameters.

This work was supported by the program of theRussian Academy of Sciences (RAS), project II.10.3.7.

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H22

Measurements of absorber density based on examination of spectral line shape

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A method for the real-time technique of absorber density measurements is discussed. This method is based on research of Voight function shape without estimation of Lorenzian and Gaussian width in convolution. Voight function numerical integration in dependence of relations of function widths on half-height and 10% of maximum height was investigated. Experiments were held on chemical Singlet Oxygen Generator (SOG) setup. Obtained results improved performance of SOG-measurement techniques.

H23

He-broadening and -shift parameters of the water vapor spectral lines in the wide spectral range

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In the present work we continue the study of He-broadening effect on water vapor transitions. The water vapor line broadening and shift coefficients in the $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, $\nu_1 + \nu_3$, $2\nu_3$, $2\nu_1$, $2\nu_2 + \nu_3$, and $\nu_1 + 2\nu_2$ vibrational bands induced by helium pressure were measured using a Bruker IFS 125HR spectrometer. The vibrational bands $2\nu_3$ and $\nu_1 + 2\nu_2$ were investigated for the first time. The interaction potential used in the calculations of broadening and shift coefficients was chosen as the sum of pair potentials, which were modeled by the Lennard-Jones (6–12) potentials. The vibrational and rotational contributions to this potential were obtained by use of the intermolecular potential parameters and intramolecular parameters of H_2O molecule. The calculated values of the broadening and shift coefficients were compared with the experimental data. It was shown that the rotational contributions as well as the contributions connected with the accidental resonances in an effective interaction potential are important in the calculation of pressure shifts coefficients.

The authors acknowledge support from the Russian Foundation for Basic Research (RFBR, grant no. 15-02-06808).

H24

Diode-laser spectrometer concept for Martian atmosphere studies

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Diode-laser spectrometer concept for Martian atmosphere studies was developed by collaboration of participants from IKI RAS, MIPT, GPI RAS, University of Reims (France). An experiment, named as M-DLS, has been proposed for the stationery Landing Platform scientific payload of the ExoMars-2018 mission.

The M-DLS instrument is targeted for long-term studies of:

– chemical and isotopic composition of atmosphere near the Martian surface, and its diurnal and seasonal variations,

– integral chemical and isotopic composition of Martian atmosphere at low scales of altitude at the Landing Platform location area, and its variations in respect to local time at the light time of a day,

– thermal and dynamic structure of the Martian atmosphere at low scales of altitude at the Landing Platform location, and its variations in local time at the day-light time.

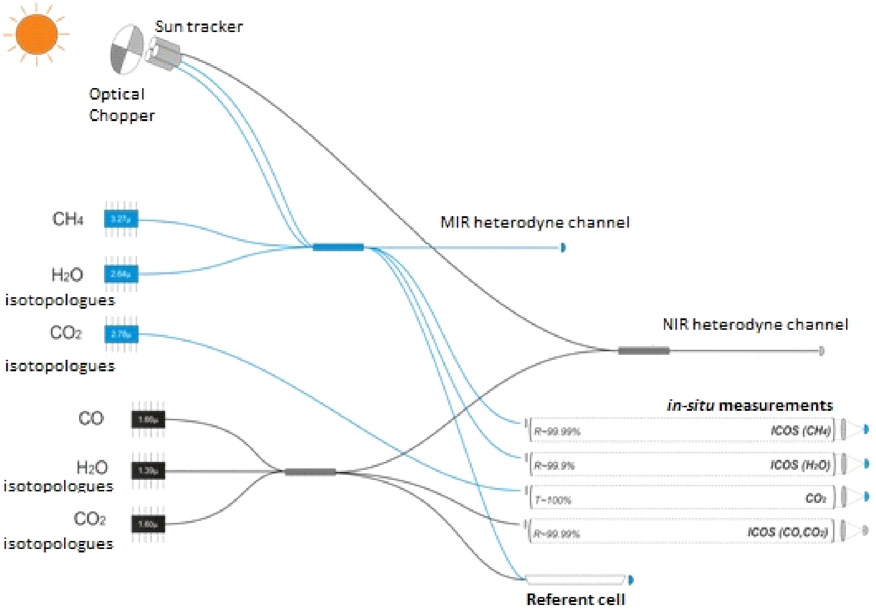
The M-DLS studies are based on of regular periodic measurements of molecular absorption spectra in the Infrared range along several optical path trajectories, including:

– a suite of several ICOS optical cells of up to ~1 km effective optical path, which are directly linked to the ambient atmosphere,

– passive heterodyne open atmosphere measurements by direct Solar observations with sun-tracker.

The M-DLS measurements will take place in series of narrow-band intervals of 2 cm^{-1} wide, with spectral resolution of ~3 MHz (~0.0001 cm^{-1}), providing for detailed recording of absorption line contours. By measurements of diurnal and seasonal variations of H_2O, CO_2 and CO main molecules and their isotope ratios D/H, $^{18}O/^{17}O/^{16}O$, $^{13}C/^{12}C$, we expect to get data for specifying of physical and chemical interactions between surface and atmosphere of Mars. The data related to seasonal variations of H_2O and CO_2 molecular concentration vertical profiles, as well as other atmospheric parameters, will be obtained by detailed recording of molecular absorption line form factors during one Martian year. Continuous measurements near the surface and in the atmospheric column at the fixed point of landing will provide for contribution into the campaign of methane search in the Martian atmosphere.

Basic optical layout of the proposed M-DLS instrument is shown in the figure. Butterfly packaged single mode (SM) optical fiber pigtailed DFB-laser modules are schematically shown for the near-IR region around 1.5 microns (in grey) and for the medium-IR region around 3 microns (in blue). A bundle of SM optical fibers and directional couplers



efficiently distributes monochromatic laser output across analytical and reference optical channels, providing for versatility of the M-DLS instrument parts use. Direct Solar observation through the total Martian atmosphere depth, and radically enhanced effective optical path for the ambient atmosphere, sampled inside the ICOS cells, provide for an outstanding optical accumulation of the absorption signal, and high resulting sensitivity of the M-DLS instrument for all the considered molecular targets and isotopic ratios.

The M-DLS experiment basics, M-DLS instrument realization issues, forthcoming M-DLS team activity planning, and other moments of the mission are discussed in the report.

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H25

Reference wavenumbers and assessment of trust in spectral databases

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Building expert spectral databases relies solely on published and accessible spectral characteristics consistent with the entire historical series of measurements. However, our assessments have shown that databases, like HITRAN and GEISA, contain transitions for which spectral characteristics have not been published or are inconsistent with the pertinent published data. In recent years, “reference” or “empirical”, as they are called, lists of lines based on consistent experimental energy levels and calculated intensities have found ever increasing use in different applications, among which is formation of canonical databases. The aim of this presentation is to demonstrate a procedure for assessing trust in expert databases, using a water molecule as an example, and determine the role of reference wavenumbers in this procedure.

A characteristic feature of the recent HITRAN and GEISA realizations is the fact that, say, for $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, and $HD^{16}O$ isotopologues, the number of reference transitions has increased dramatically. As to an $H_2{}^{17}O$ molecule, the number of reference transitions accounts for 95 % of the total number of lines. However, the quality of the lists of reference lines made by different researchers on the basis of different sets of energy levels and calculated intensities may vary widely. On the other hand, proper formation of the lists and their combination with the most accurate experimental data used in recent versions of HITRAN and GEISA is far from being a simple task in the case of ambiguous ro-vibrational labeling and high dimensionality of the datasets being compared.

In this work, lists of reference lines are made on the basis of a set of experimental energy levels IUPAC (see, for example, [1]) extended and refined with invoking new published experimental ro-vibrational transitions for four main water vapor isotopologues — $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$ — and high-accuracy variational intensities (see, for example, [2]). The resultant reference lists of lines along with checks on the validity of and assessments of trust in the spectral data provided by the W@DIS information system are used to control the accuracy, consistency, and completeness of the information available in the spectroscopic HITRAN and GEISA databases. In particular, a comparison of the set of data for $H_2{}^{16}O$ available in HITRAN-2012 with the reference list of lines has revealed considerable inconsistency: the centers of 2700 lines deviate from the empirical evidence within $0.03 \div 2.0$ cm^{-1}. Technical details of assessing trust in the spectroscopic databases according to a publishing criterion are furnished elsewhere [3].

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H26

A W@DIS-based data quality analysis of the energy levels and wavenumbers of isotopologues of the water molecule

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A critical evaluation of the ro-vibrational spectra of nine major water isotopologues was performed in [1–4]. One of the subjects of these IUPAC-sponsored activities [5] was the evaluation and validation of all the published measured spectra of these isotopologues. Following the MARVEL (Measured Active Rotational-Vibrational Energy Levels) algorithm [6] and employing high-level first-principles data, in [1–4] the measured transitions and energy levels were made fully consistent. A small part of the measured transitions had to be rejected, while some of the published spectra had to be recalibrated. The results obtained and lists of the validated and rejected transition and energy values were imported into the W@DIS [7] and ReSpecTh [8] information systems.

The development of the W@DIS system was motivated partly by the publication of tens of articles about spectral parameters of water, including the energy levels and molecular transitions, every year. These publications contain new data about parameters of relevance to the water molecule or list more accurately measured energy levels, transitions, etc. In a few cases the newly published data were found to be inconsistent with the data published in [1–4].

W@DIS contains several applications which provide facilities for spectral data export and import, comparison of spectral data related to certain spectroscopic tasks, and representation of data and data properties. Most of the data properties are indicative of data quality, i.e., validity of data and trust in the expert data available. In this work the user interfaces are described and computer-generated reports on spectral data quality for all isotopologues of the water molecule are presented.

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8. Information system ReSpecTh, http://ReSpecTh.hu

H27

Measurements of carbon dioxide isotopic ratio in ambient air using an optical cavity and tunable diode laser in 1.605 μm area

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We present method of measuring carbon isotope ratio based on recording CO_2 absorption spectra in optical cavity filled with ambient air. Concentrations of isotopologues were determined using absorption coefficients measured in the analytical channel. We applied the linear regression scheme to spectrum recorded in this channel in which the optical cavity was located. For linear regression we used synthesized data and absorption cross sections data from spectroscopic databases. The CO_2 concentration is several orders of magnitude smaller than in mixtures previously studied with laser techniques. Precision of measurements is 0.3‰.

The work was supported by the Russian Scientific Foundation (project no. 14-12-00784).

H28

Feature of IR spectra of ICAO taggants in the vapor state

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Nowadays, a number of laser-optical methods featuring high sensitivity of the analysis of trace amounts of substances in the atmosphere have come into practice of local and remote detection of explosive vapors and microparticles [1]. However, the evolution of laser-optical methods of detection of explosive vapors is still at the initial stage [1]. A successful solution of the tasks of detection and identification of explosive vapors in actual practice is restricted by a number of problems the major of which is relatively low concentration of explosives in the air at room temperature.

In order to increase the efficiency of detection of concealed plantings of explosives with low saturated vapor pressure, on March'1 of 1991 in Montreal under the convention of the International Civil Aviation Organization (ICAO) [2] it was suggested to make highly volatile additions (ICAO taggants), at the level of 0.1–0.5 % mass, components of explosives, plastic explosives included. The four compounds suggested for use for chemical marking of explosives were: ethylene glycol dinitrate (EGDN), para-nitrotoluene (4-NT), ortho-nitrotoluene (2-NT), and 2,3-dimethyl-2,3-dinitrobutane (DMDNB). These compounds have the following saturated vapor pressure values (at T=298 K): 7.6×10^{-2} Torr (EGDN), 4.89×10^{-2} Torr (4-NT), 14.4×10^{-2} Torr (2-NT), and 2.07×10^{-3} Torr (DMDNB).

In this work studied experimentally IR absorption spectra of ICAO taggants in the vapor state at room temperature and those of 2,4-DNT vapors at T=330 K over a wide frequency range (from 500 to 4000 cm^{-1}). The observed vibrational bands have been pre-assigned. IR spectra of ICAO taggants and 2,4-DNT are shown to be free of bands of gaseous decomposition products, in contrast to high explosives hexogen (RDX) and pentaerythritol tetranitrate (PETN) [3]. Absorption cross-section rates have been estimated for the most intensive bands in the experimental IR spectra of 4-NT, 2-NT and 2,4-DNT.

On the grounds of the analysis of modern laser technologies, a conclusion has been made that their use in conjunction with the spectroscopy data obtained will provide the means of reliable local and stand-off detection and identification of ICAO taggants and a range of explosives with a sufficient selectivity level in both the condensed and vapor states in the open atmosphere.

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School Tutorials I

Wednesday, July 1, 9^{00}–10^{30}

Chair: Igor V. Ptashnik

I1

Retrieving spectroscopic data from Virtual Atomic and Molecular Data Center (VAMDC)

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On behalf of VAMDC collaboration

A uniform way to access heterogeneous molecular and atomic databases was developed in the frame of VAMDC collaboration since 2009. Actual system enables access to 28 databases including HITRAN, CDMS, VALD and few other spectroscopy databases, but also to databases on electron scattering, photodissociation, ion scattering, chemical reactions.

VAMDC is designed as a network of interacting web-services and clients, based on a set of open standards and protocols. The current version of standards was released in 2012, and since then many databases have joined the team and various clients and libraries were implemented.

Initial development collaboration was funded by the European Union FP7 framework; long-term sustainability is provided by a decentralized nature. Parts of the infrastructure are maintained by partner institutions, mirroring of critical elements enables fault-tolerance and continuous operation.

The session will begin with a short introduction followed by a demonstration of several use-cases during a hands-on tutorial. Attendees are advised to bring their laptops to be able to query VAMDC for the data of their interest.

References

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I2

W@DIS information system. Spectral data analysis

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A spectral data analysis performed by means of the W@DIS information system is described. The W@DIS function and resources as well as data import, export, and presentation facilities and procedures used to compare and analyze spectral data are outlined. The terms “validity” of and “trust” in expert data are defined in the framework of the approach presented in this work. The objects picked up for the analysis are publications containing spectral data and molecular states and transitions. The W@DIS applications are demonstrated using a complete set of data about the isotopologues of the water molecule.

I3

SPECTRA—an interactive tool for molecular spectroscopy

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The general structure and main functionality of the “Spectroscopy of Atmospheric Gases”, SPECTRA system [1] will be presented. The SPECTRA (http://spectra.iao.ru) is an Internet accessible system. The system is intended to access the spectroscopic data and to solve some spectroscopic problems.

Some examples of the problems which can be solved using the SPECTRA system will be demonstrated: (*i*) search, extracting and visualization of different spectroscopic information; (*ii*) gas mixture preparation; (*iii*) simulation of different spectral functions at high and low resolution; (*iv*) saving the results in the system and/or download those to a user’s computer.

References

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Invited Lectures J

Thursday, July 2, 9^{00}–10^{30}

Chair: Iouli E. Gordon

J1 *Winner lecture of the Benedict Spectroscopy Award 2015*

Infrared quantitative spectroscopy and atmospheric satellite measurements

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Optical measurements of atmospheric minor constituents are carried out using spectrometers working in the UV, visible, infrared and microwave spectral ranges. In all cases the quality of the analysis and of the interpretation of the atmospheric spectra requires the best possible knowledge of the molecular parameters of the species of interest. To illustrate this point we will concentrate on laboratory studies of various molecules including nitric acid, formaldehyde, phosgene and propane.

The high resolution spectra of nitric acid are difficult to model because of the numerous ro-vibrational resonances affecting its energy levels as well as its large amplitude motion. We will show that a careful modeling of the spectra of this molecule has allowed the first detection of $H^{15}NO_3$ in the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) spectra

The retrievals of formaldehyde are performed either in the infrared or in the UV spectral regions. If many UV and IR absorption coefficients have been published in the literature, to our knowledge no study has ever verified the consistency between the cross-sections in both spectral ranges. We will present the results of such a comparison as well as the first detection of this molecule using MIPAS spectra.

Phosgene is absorbing in the same spectral region as CFC11 and in order to retrieve properly this latter species it was necessary to provide precise line lists and intensities for the phosgene molecule.

Propane gas was first detected in the atmosphere of Titan by the Voyager 1 IRIS spectrometer, during the 1980 encounter. The Composite Infrared Spectrometer (CIRS) instrument carried on-board the Cassini spacecraft possesses a much improved spectral and spatial resolution and sensitivity over IRIS showing then clearly for the first time a multitude of propane bands. Thanks to a new line atlas for three bands of propane at shorter wavelengths (6–8 micron) it proves possible to model these weaker bands and to check the measurements usually made by CIRS using the “usual” 13 micron band alone. We will report on the progress in the modelling of the 6–8 and 13 micron bands, and give an update on the propane abundance at low latitudes.

Finally we will show that in some cases (NO^+ species) atmospheric spectra are useful to improve the spectroscopy of the species.

J2

Cold molecules and high-resolution spectroscopy: Experiments on two-, three- and four-electron molecules

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The ability to manipulate the translational motion of atoms and molecules using radiation and inhomogeneous electric and magnetic fields offers new opportunities for precision atomic and molecular spectroscopy and collisional studies. The talk will present the results of recent experiments on cold samples of few-electron molecules generated by supersonic-beam-deceleration techniques. The use of these techniques to produce cold samples will be illustrated by experiments on molecular hydrogen and helium.

The interest of precision measurements on few-electron molecules results from the fact that the properties of these molecules can be calculated extremely precisely using *ab initio* quantum-chemical methods which include the evaluation of relativistic and quantum-electrodynamics contributions. The comparison of experimental and theoretical results in these systems thus enables rigorous tests of the theory, potentially only limited by the uncertainties in fundamental constants [1, 2, 3]. The talk will focus on recent unpublished precision spectroscopic measurements of the Rydberg spectrum of He_2 using a cold, slow beam of metastable He_2 produced by multistage Zeeman deceleration [4]. Rydberg-series extrapolation using multichannel quantum defect theory and parameters determined in Ref. [5] enabled the determination of the energy level structure of He_2^+ with unprecedented precision. The comparison with the latest *ab initio* calculations [6] provides information on the magnitude of relativistic and QED contributions to rovibrational energies in He_2^+. The advantage of using multistage Zeeman deceleration does not only result from the longer transit times of the decelerated molecules through the radiation field. The spin-rotational state selectivity of the Zeeman deceleration process can also be exploited to reduce the spectral congestion, minimize residual Doppler shifts, resolve the Rydberg series beyond $n = 200$, and assign their fine structures.

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School Lectures K

Thursday, July 2, 11^{00}–12^{30}

Chair: Yury I. Baranov

K1

Remote sensing of the atmosphere using satellite and ground-based high resolution spectrometers in IR

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Global warming and present climate change is result of rapid accumulation of greenhouse gases in the atmosphere. Monitoring of the greenhouse gases CO_2, CH_4, H_2O etc in the atmosphere in local and global scales is one of the most important applications of molecular spectroscopy. Interferometric Monitor for Greenhouse gases (IMG) on board of polar orbit Japanese ADvanced Earth Observing Satellite (ADEOS) launched in 1994 opened new Era for remote sensing of the atmosphere in thermal infrared using high resolution FTS from Space. Same time, first half of 1990-th, commercial ground-based Bruker IFS (FTIR) spectrometers begin spread over the world for purpose of recording direct solar spectra with high resolution in the near infrared. From these spectra, accurate and precise column-averaged abundance of carbon greenhouse gases CO_2, CH_4, CO and water vapor isotopologues $H_2{}^{18}O$ and HDO are retrieved. The ground-based FTIR are combining into international network TCCON (Total Carbon Column Observing Network) in order to provide validation resource for satellite data regarding carbon greenhouse gases in the atmosphere.

In this lecture, we focus on methods and results of solution of inverse problem of infrared radiative transfer in the atmosphere for retrieval of concentration of key greenhouse gases and a tracer of water cycle from high resolutions atmospheric spectra in thermal and near infrared. The HDO to H_2O ratio in the atmosphere is informative tracer of water cycle. The HDO/H_2O data are using for validation of modern atmospheric general circulation models taking into account isotopic fractionation in the processes of evaporation and condensation.

In the lecture, results of retrieval of methane concentration, water vapor, and water vapor isotopologues ratio (HDO/H_2O) in the atmosphere from spectra of outgoing to Space thermal radiation in the range of 600 cm^{-1}–2000 cm^{-1} measured with high resolution from satellite borne spectrometers IMG, AIRS (Atmospheric InfraRed Sounder) and IASI (Infrared Atmospheric Sounding Interferometer) are presented. Mapping of the target atmospheric constituents in local and global scales using the retrieved data is discussed.

Literature and original results of retrieval of water vapor, methane, carbon dioxide and water vapor isotopologues concentration in the atmosphere from spectra of solar radiation in near infrared in the range of 4000 cm^{-1}–9000 cm^{-1} transmitted though the atmosphere and measured with high resolution ground-based FTIR are considered. A problem of validation of the satellite data using the ground-based FTIR observation of the atmosphere is discussed. Some results of comparison of satellite data with ground-based FTIR data are presented. Impact of errors in spectroscopic parameters from HITRAN database on precision of results of retrieval of the target atmospheric constituents is discussed.

K2

Importance of the proper data presentation in submitted manuscripts and a look beyond the impact factor of the journal: Primer of JQSRT

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In this talk important correlations between proper presentation of the data and metrics of an article and authors (such as citations and h-index) will be demonstrated.

Spectroscopy is an established and indispensable tool in science and industry with myriads of applications including terrestrial atmospheric remote sensing, disease detection in a patient's breath, characterizing planetary, stellar, and exoplanet atmospheres, and surveillance. The potential user of spectral data, which is not available in HITRAN [1], searches the spectroscopy publications and often encounters the following problems: 1) The data described in the paper is not available. There can be many reasons for this: nothing is provided in the paper itself or supplementary material; the authors are not responding to any requests; the web links provided in the paper have long been broken; etc. 2) The data is presented in a reduced form, for instance only through the fitted spectroscopic constants. While this is a long-standing practice among spectroscopists, there are numerous serious problems with this practice, such as users getting different energy and intensity values because of different representations of the solution to the Hamiltonian, or even just despairing of trying to generate usable line lists from the published constants.

We state that the best way is to present the data either within the paper or in the properly described and well organized supplementary materials.

Additionally a brief history of the Journal of Quantitative Spectroscopy and Radiative Transfer (JQSRT) and some of its interesting metrics beyond the impact factor will be shown.

Reference

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Invited Lectures L

Friday, July 3, 9^{00}–10^{30}

Chair: Nikolai N. Filippov

L1

Challenges and applications of synchrotron based and laser based line shape studies

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One of the challenges of spectroscopic remote sensing is the extrapolation of data from the laboratory to atmospheric applications. Besides considerations related to the number of parameters involved, the situations which we meet in the laboratory are considerably different from those in the atmosphere, since in the former case most extrinsic quantities (e.g. concentration, pressure, temperature) are constant over the experimental volume, whereas in the latter case they are almost always spatially variable.

This talk will give an overview of laser-based or synchrotron-based high-resolution spectroscopic studies performed by our research group will be presented. Several line shape models with associated components accounting for line mixing effects were used to analyze the spectra. Contributions to the observed line shapes from the shape of the potential were also explored. The high quality of the spectra enabled us to observe variations of the line parameters with transition quantum numbers and with temperature. Selected sets of self- and foreign-broadening coefficients were compared with modelled results obtained the Energy Corrected Sudden and Exponential Power Gap scaling models.

Another area of research in our group is focused on metrological applications, more precisely on accurate measurements of fundamental constants. The results of our recent retrievals of the fundamental Boltzmann constant based on a laser-based study of acetylene spectra will be also presented.

L2

Calculation of rovibrational line broadening and shifting of symmetric and asymmetric top molecules

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Line broadening and shifting of H_2O, O_3, CH_3Cl and CH_3CN molecules assume an important place in the physical chemistry of the terrestrial and planetary atmospheres. They are needed to model the radiation balance of the Earth's atmosphere and to aid analysis of atmospheric spectra in general. Due to low molecular symmetry and a great number of vibrational modes, their spectra recorded in the infrared and microwave regions appear as manifolds of close-spaced lines hardly accessible for accurate and exhaustive measurements. Measured data of the line shape parameters should therefore be completed by reliable theoretical predictions in order to allow the precise temperature and concentration extraction via usual multifit procedures.

More complicated versions of the cut-off-free method describe the line broadening processes rather well, but due to the complexity of the calculations, do not allow visualizing and analyzing processes occurring in colliding molecules, in particular, the effect of compensation for contributions of different scattering channels in the pressure-induced shift. An efficient semi-empirical method has been developed [1] to calculate broadening and shifting coefficients of spectral lines and their temperature exponents. It includes correction factors whose parameters can be determined by fitting the calculated broadening or shifting coefficients to experimental data. The semi-empirical method distinguished by the relative simplicity of calculations is effective in description of line broadening processes for molecules characterized by so-called strong interactions, when the distance of closest approach is less than the interruption parameter in the cut-procedure.

This method has been modified by the use of anharmonic wavefunctions resulting from extensive variational nuclear motion calculations [2,3]. This extends the range of applicability of the method, in principle, up to dissociation. The present calculations use a complete set of high accuracy vibration-rotation dipole transition moments calculated for all possible transitions and an *ab initio* dipole moment surface. This approach takes into account all the scattering channels induced by collisions. Such massive calculations are not possible with the wavefunctions obtained in the frame of Effective Hamiltonian approach.

Last time a new method to the calculation of rotation-vibrational line half-width of asymmetric top molecules is proposed (the averaged energy difference method) [4]. The influence of the buffer gas on the internal state of the absorbing molecule is emphasized in this method. The averaged energy differences method was used for the calculation of H_2O and HDO lines broadening. Semi-empirical method was successfully used for calculations of broadening and shifting coefficients and their temperature exponents for H_2O-N_2(O_2,H_2O,CO_2), O_3-N_2(O_2), CO_2-N_2(O_2, N_2O), CH_3Cl-CH_3Cl(CO_2) and CH_3CN-CH_3CN(N_2) colliding systems. Some of these data are present in this report with the ccomparison of the calculated line shape parameters to the experimental values in different absorption bands. The results of present calculations have been partly included in a freely-available carbon dioxide spectroscopic data bank, (ftp://ftp.iao.ru/pub/CDSD-1000) in the “W@DIS” Information System (http://wadis.saga.iao.ru/) and in the databank GEISA (http://ara.lmd.polytechnique.fr).

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Oral Session M

Friday, July 3, 11^{00}–12^{30}

Chair: Jonathan Tennyson

M1

Rotational spectrum of the NH_3–H_2 van der Waals complex

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The rotational spectrum of the NH_3–H_2 van der Waals complex in a supersonic jet has been measured for the first time. This study is intended to reveal the intermolecular interaction between ammonia and dihydrogen and to test the recent *ab initio* potential energy surface (PES) calculations [1, 2]. Detailed knowledge of the NH_3–H_2 interaction parameters is important for a number of applications in astrophysics.

Three different experimental techniques, namely, molecular beam Fourier transform microwave spectrometer, millimeter-wave OROTRON intracavity jet spectrometer and supersonic jet spectrometer with multipass cell, were used to detect pure rotational transitions in the wide frequency range from 39 to 230 GHz. The hyperfine splitting due to the ^{14}N nuclear spin of ammonia was observed for the J = 1–0 transitions. The obtained data were analyzed in order to determine the molecular parameters and structure of the $o$$NH_3$–$o$$H_2$ and $p$$NH_3$–$o$$H_2$ complexes. The experimental results were compared with the bound states calculations [3] using earlier reported *ab initio* interactionpotential [2].

L.S., I.T., and V.P. acknowledge the Russian Foundation for Basic Research (grant no. 15-03-09333) for financial support.

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M2

Influence of nanoconfinement on the line parameters for 2–0 absorption band of CO

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Absorption spectra of carbon oxide, confined in nanoporous silica aerogel, have been measured within 4100–4400 cm^{-1} region at room temperature and at several pressures using Bruker IFS-125 HR Fourier spectrometer. The half-width of CO spectral lines vary from 0.173 to 0.204 cm^{-1}, and line positions are shifted by –0.005 cm^{-1} relative to the lines of free gas. Dependence of the HWHM values on rotational quantum numbers is studied and compared with the data available in literature [1]. It is found that variations in the half-width values for the confined CO at small quantum numbers are larger than at moderate ones. The influence of confinement tightness on rotational dependence and mechanism of formation of spectral line half-widths is discussed.

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M3

Water vapor continuum in the range of rotational spectrum of H_2O molecule: New experimental data and their comparative analysis

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Water vapor continuum plays an important role in the Earth radiation balance affecting weather and global climate changes. In spite of long considerable experimental and theoretical efforts through all over the world the continuum is still poorly studied and understood. We present new experimental measurements of the water vapor continuum absorption in the range covering the essential part of the pure rotational spectrum of H_2O molecule from 15 up to 200 cm^{-1}. The continuum absorption was derived from the broad band water vapor spectra recorded at room temperature at Soleil synchrotron. Spectra were recorded using the IFS 125 interferometer together with the 150-m mutipass gas cell using several water vapor pressures. In order to optimize the S/N of the spectra we employed both incoherent synchrotron radiation and coherent synchrotron radiation. The new data considerably extend and unify diverging results of previous measurements of the continuum performed in several spots within the range from about 3 up to 84 cm^{-1}. The new evidence of significant contribution of the water dimer to the continuum formation is revealed in the range of 15–35 cm^{-1}. The continuum spectrum in this range show the characteristic knee very similar to that predicted by the most rigorous to date *ab initio* calculation of the water dimer absorption. The continuum retrieved in the 40–200 cm^{-1} range revealed that the widely used in atmospheric applications MT-CKD empirical formulation of the continuum gives qualitatively correct frequency dependence but overestimate the continuum amplitude by about 40%. Analysis of the possible cause of the observed continuum reveals that the significant part of the observed continuum in the range of the maximum intensity of water monomer rotational spectrum can not be explained within the current understanding of the continuum origin.

The work is partly supported by RFBR.

M4

H_2CO molecule vibrational energy spectrum. Re-summation of divergent perturbation series for highly excited states

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Calculation of H_2CO molecule vibrational energy levels is held by the means of High-Order Rayleigh-Schrödinger perturbation theory [1]. To perform calculations we use the model of coupled anharmonic oscillators. Anharmonic part of potential energy is considered as perturbation.

To overcome the divergence of perturbation series several re-summation techniques are used. High-order Hermite-Pade approximants [2,3] (up to 10-th order) are used for all states with the energy of up to 5000 cm^{-1} above ZPE. In the case of highly excited resonant states when the series divergence is extremely quick we use repartition of the Hamiltonian by shifting the vibrational frequencies and compensating modification of the perturbation operator.

Accuracy of calculations is comparable to the accuracy of variational approach both for isolated and resonating states. To confirm the applicability of this approach the vibrational energy is considered as a function of a complex perturbation parameter. Lay-out and classification of its singularities allow us to model the asymptotic behavior of the perturbation series and prove the robustness of the algorithm.

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M5

Combining *ab initio*, variational and contact transformation methods for accurate spectra predictions: from three- to six-atomic molecules

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Several independent and complementary methods are currently in progress in Reims and Tomsk groups for accurate spectra prediction at high energy range using new *ab initio* potential energy (PES) and dipole moment surfaces (DMS) constructed for ozone, phosphine, methane and ethylene molecules [1–3]. Global variational calculations permit accessing highly excited molecular states and transitions. In case of ozone this was mandatory for analyses [4, 5] of six ^{18}O-enriched isotopic species near the dissociation threshold [1, 6]. The corresponding issues of the impact of the symmetry breaking isotopic substitutions on wavefunctions and assignment will be discussed. Comparison with observations have brought new insight [6] on the existence of the barrier along the minimum energy path with implications on the dynamics. First-principles variational results [2, 7–9] for of PH_3, $^{12}CH_4$, $^{13}CH_4$, CH_3D, CH_2D_2 are now in a good overall agreement with experimental data in a large infrared range: 0.1–0.5 cm^{-1} for line positions and ~ 3–5 % for integrated band intensities in average. Recently *ab initio* predictions have been extended to six-atomics (C_2H_4 [3]) and to high-temperatures up to T = 2000 K (methane [9]) for astrophysical applications. A new combined spectroscopic model [10] for vibrational polyads will be discussed. This involves all resonance terms precisely derived from the molecular PES via high-order contact transformation method with a subsequent "fine tuning" of few parameters. The aim is generating line lists for molecular spectra that contain line positions determined within experimental accuracy and predicted *ab initio* intensities in a consistent way.

This work is supported by French IDRIS/CINES/ROMEO computing centers, by Tomsk State University Academic D.I. Mendeleev Fund Program and by French-Russian LIA "SAMIA".

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M6

Spectral sensitivity of Fourier transform spectrometer based on relative intensity measurements and *ab initio* calculations

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A state-of-art first principle calculation of the electronic structure of an alkali diatomics provides nowadays the transition dipole moment functions in a wide range of the internuclear distances with systematic errors which do not often exceed few percent [1]. This uncertainty of calculations is comparable or even better than accuracy of relative intensity measurements of laser-induced fluorescence (LIF) spectra recorded by Fourier transform (FT) spectrometer [2]. Furthermore, comprehensive deperturbation treatment of the excited states of alkali dimers performed in the framework of the rigorous coupled-channel approach allows one to represent energies and radiative properties of both local and regular perturbed rovibronic levels with experimental accuracy [3].

Aim of the present work was to calibrate the spectral sensitivity of FT spectrometer matching the relative intensity distribution measured in the long LIF progressions with their theoretical counterparts. In particular, the spectral sensitivity of the Bruker IFS-125HR FT spectrometer operated with InGaAs diode detector and CaF beamsplitter was determined in the near infrared region $\nu = 8250–11700$ cm^{-1} by a direct comparison of the calculated $A^1\Sigma^+ \sim b^3\Pi \rightarrow X^1\Sigma^+$ rovibronic transition probabilities of KCs and K_2 molecules with experimental relative intensity distribution in the relevant A~b → X laser induced fluorescence spectra [4]. The resulting sensitivity calibration function $S(\nu)$ rapidly increases as ν increases according to the exponential fall of the InGaAs diode sensitivity at $\nu > 10000$ cm^{-1}. We are planning to extend the calibration $S(\nu)$ function for low at $\nu < 8000$ cm^{-1} region by means of the measured and calculated $(4)^1\Sigma^+ \rightarrow A^1\Sigma^+ \sim b^3\Pi$ LIF spectra starting from the higher excited “shelf-like” state of the RbCs and KCs molecules.

Moscow team thanks for the support by the RFBR grant No. 13–03–00446a. Riga team acknowledges Latvian Science Council Grant No. 119/2012.

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Oral Session N

Friday, July 3, 14^{30}–16^{00}

Chair: Andrei V. Stolyarov

N1

Analyses of $^{16}O^{16}O^{18}O$ asymmetric ozone isotopic species in the whole 800–6500 cm^{-1} infrared spectral region

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Continuing the ongoing effort for analyses of various ozone isotopic species [1, 2 and references herein], high resolution infrared spectra of $^{16}O^{16}O^{18}O$ were recorded in two ranges. The first one covers 800–5800 cm^{-1} using the GSMA FTS [3] and the second one covers 5800–6850 cm^{-1} using the CRDS set-up of LIPhy Grenoble [4]. Several spectra of ozone generated from various $^{18}O/^{16}O$ oxygen mixtures allow discriminating among the six forms of ^{18}O-enriched ozone isotopic species. A total of 33 bands of $^{16}O^{16}O^{18}O$ have been fully analysed: 24 bands involving 12441 transitions, in the FTS domain, and 9 bands (3771 transitions) in the CRDS spectral region.

The analyses for C_S species are more complicated than those of C_{2V}, as fewer constraints are imposed on dipole selection rules and on resonance coupling terms. A total of 17 dark states have been included in the analyses permitting to reproduce the observed line positions with nearly experimental accuracy. Achieving a good agreement between observed and calculated line intensities is a challenge, due to experimental and theoretical difficulties, that will be discussed.

We present examples of results for a part of the bands: Hamiltonian and dipole transition moment parameters, statistics of fits, examples of agreement between observed and synthetic spectra, and the whole set of comparisons of band centres and rotational constants with recent theoretical predictions [5,6], these predictions being mandatory for efficient analyses in the high energy domain.

An important improvement of FTS ozone data for atmospheric applications in 5 and 10 microns ranges will be discussed as well. The whole set of results allows a significant improvement in the knowledge of the potential energy surface of ozone particularly in the transition range towards the dissociation [6].

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N2

Sub-THz molecular spectroscopy with radioacoustic detection and high-power radiation source

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Spectrometer with radio-acoustic detection of absorption (RAD spectrometer) [1] is well known to be a powerful tool for studying molecular spectra in THz region. Line shape parameters (central frequency, pressure shifting narrowing and broadening coefficients and their temperature exponents) can be measured using RAD spectrometer with high accuracy supplying important information for different applications including remote sensing, astrophysics, metrology, etc.

The output signal of the spectrometer is in direct proportion with a radiation power passing through a gas cell. In all previous studies, a series of Backward Wave Oscillators (BWOs) radiating from microwaves up to THz range were employed as a radiation source. A typical power of the BWOs is usually less than 100 mW decreasing down to 1 mW (or less) in the THz region.

In this report we present results of using the sub-THz medium power (up to 1 kW / continuous waves) gyrotron setup [2] as a radiation source for the RAD spectrometer. It is demonstrated that using the gyrotron radiation with power level of about 10W allows significant (by a few orders of magnitude) improvement of the spectrometer sensitivity comparing with the use of BWO.

The study was partially supported by RAS, RFBR, and government of Nizhny Novgorod region.

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N3

Tunable diode laser absorption spectroscopy for the measurement of accurate and traceable line strengths of different analytes

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Direct tunable diode laser absorption spectroscopy (dTDLAS) has been combined with metrological principles on the determination of uncertainties to measure line strengths of carbon-dioxide[1] (CO_2) and water vapor[2] (H_2O) absorption lines in the near-infrared range. Altogether, eleven application-specifically selected absorption lines have been studied in the wavenumber range of 3680 to 7300 cm^{-1}, with line strengths in the range of $5 \cdot 10^{-23}$ to $2 \cdot 10^{-20}$ cm/molecule. The obtained uncertainties (k =2, corresponding to 95 % confidence level) are in the range of 1.0–2.5 %. Four different light sources have been used for the experiments: three distributed feedback (DFB) diode lasers radiating around of 3685 cm^{-1}, 3920 cm^{-1} and 7300 cm^{-1}, and a vertical-cavity surface-emitting laser (VCSEL) in the wavenumber range of 7180 to 7190 cm^{-1}. Despite the different analytes, wavenumber ranges and line strengths, a uniform measurement and data evaluation method has been applied for all lines. A simple experimental setup based on a single-pass gas cell has been used, which can easily be applied in a wide wavelength range. Application of the presented method for further analytes with similar uncertainties is possible, provided that a suitable light source and gas cell with appropriate length are available.

We have compared the measured line strength values to line strengths listed in the HITRAN and GEISA databases, as well as further publications on measured and computed line strengths. Good agreement has been found between our measured line strengths and literature values; however, our values usually show a factor of 2–10 lower uncertainty. We have also validated our line strengths in spectroscopic amount fraction measurements[3].

In our presentation we put special emphasis on metrological traceability and a concise, well documented uncertainty assessment. We evaluate the contributions of the individual experimental parameters to the uncertainty of the derived line strengths, and discuss possibilities to further decrease the uncertainty. We compare the results obtained for the different analytes, wavenumber ranges and line strengths to estimate the general capabilities of the presented method.

The work has been conducted within the EMRP projects[4] MACPoll, METEOMET and EUMETRISPEC. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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N4

FTIR spectrometer with 30-m base length absorption cell for spectra investigation in wide spectral region: improvement of optical setup

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A detailed description of the Fourier transform spectrometer IFS-125 HR and 30-meter base length multipass cell with a White optical system for investigation of the absorption spectra in a wide spectral range (from 500 to 40 000 cm^{-1}) with a high sensitivity is presented. The improved design of 30 m base length cell and the optical scheme are described, the comparison to the known analogous complexes is considered. This cell can be used to achieve absorption path lengths as long as 1065.5 m. This new setup allows us to perform spectroscopic analysis of very small absorption lines. For example for CO_2 molecule in spectral region 9250–9500 cm^{-1} the achieved sensitivity (noise equivalent absorption) at the level of $k_\nu = 7.2\times10^{-10}$ cm^{-1} allowed detection of numerous new transitions with the intensity values down to 10^{-29} cm/molecule [1].

The results of the study of selective and nonselsective absorption spectra, as well as spectra of gases confined in nanopores are presented. The advantages of the spectral complex are illustrated by some experimental results [1–7].

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N5

UV-photoexcitation of oxygen encounter complexes X–O_2 as a new channel of singlet oxygen O_2 ($^1\Delta_g$)

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The spectroscopy of oxygen has important applications in atmospheric and planetary science as well as the photoprocesses in oxygen play major role in photobiochemistry, oxidative organic photochemistry and other fields. The photoabsorption of “isolated” oxygen molecules is very weak within the whole UV-IR spectral region where all electronic transitions of ground state O_2 molecule are spin and/or orbital symmetry forbidden. But the interaction of O_2 molecules with molecular environment provides the strong enhancement of UV-absorption by oxygen. This drastic effect is governed by encounter complexes X – O_2 and takes place both in the gas phase when molecules collide and in condensed phase when oxygen is dissolved in some solvent or placed in cryogenic matrixes. This collision-induced enhancement dramatically changes the oxygen photochemistry resulting in new photochemical processes such as formation of highly reactive singlet oxygen species O_2 ($^1\Delta_g$) which play major role in many photooxidation processes such as photosynthesis, oxidative stress etc.

In recent investigations we have established a new mechanism of the UV-photoexcitation of pure oxygen and oxygen-isoprene C_5H_8–O_2 mixture resulting in O_2 ($^1\Delta_g$) formation [1, 2]. In the present work the main attention is paid to the qualitative and quantitative description of the mechanism of this new photochemical process proceeding via UV-photoexcitation of O_2–O_2, N_2–O_2 and C_5H_8–O_2 encounter complexes in the gas phase. In the experiments gas mixtures with oxygen elevated pressure have been excited by laser UV-radiation. Singlet oxygen O_2 ($^1\Delta_g$) was detected by its IR-luminescence centered at 1.27 μm. The quantum yield of O_2 ($^1\Delta_g$) molecules photogenerated via X–O_2 complexes excitation was found to possess rather high maximum values close to two for O_2–O_2 (262.6 nm) and 1.7 for O_2–C_5H_8 (278 nm).

We assume two processes to be responsible for singlet oxygen formation. One results from collision-induced absorption of O_2 giving rise to Herzberg III state O ($A'\,^3\Delta_u$) molecules with their further annihilation in collisions with the ground state O_2 molecules giving rise to singlet oxygen. Another process consisting in cooperative X–O_2 encounter complex excitation with further simultaneous change of the both partner spins is one of peculiar interest. We suppose that this process may result in O_2 ($^1\Delta_g$) formation in widespread wavelength region including visible spectral region depending on oxygen collisional partner X. We also assume singlet oxygen generation to follow the excitation of any encounter complexes X–O_2 in any media (gas or condensed) containing oxygen.

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N6

Introduction to HITRAN Application Programming Interface (HAPI)

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A HITRAN Application Programing Interface (HAPI) providing tools for working with the HITRAN [1] data has been developed. Currently HAPI is a Python library giving a functional interface for the main data searching capabilities of the HITRANonline [2] web service. HAPI also incorporates functions related to calculation of absorption coefficients using different line profiles (including the recent Hartmann-Tran profile [3]).

The results of comparisons of HAPI calculated absorption coefficients with PNNL [4, 5] data are presented for several molecules [6]. We give a demonstration that using HAPI with the data from HITRAN-2012 gives good agreement with independent laboratory experiments.

The library has the following features: **1)** Downloading and parsing the line-by-line data from HITRANonline **2)** Filtering and processing the data in SQL-like fashion **3)** Access to conventional Python structures (lists, tuples, and dictionaries) representing spectroscopic data **4)** High-resolution spectra calculation accounting for pressure, temperature and optical path length **5)** Python implementation of the Partially Correlated Quadratic Speed Dependent Hard Collision line profile (also known as the Hartmann-Tran profile) which can be reduced to a number of conventional line profiles such as Voigt, Rautian and their speed dependent counterparts. **6)** Python implementation of total internal partition sums (TIPS-2011 [7]) **7)** Instrumental functions to simulate experimental spectra **8)** Possibility to extend HAPI's functionality by custom line profiles, partition sums, instrumental functions etc. **9)** Possibility to use a large set of third-party Python libraries for data processing and imaging.

HAPI uses Numpy library providing fast array operations and is designed to deal with data in multiple formats such as ASCII, CSV, HDF5 and XSAMS (more formats will follow).

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Poster Session O

Friday, July 3, 16^{15}–18^{00}

O1

Rotational study of the CH_4–CO van der Waals complex in the millimeter-wave range

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Previously, the pure rotational spectrum of the van der Waals complex, CH_4–CO, was measured [1] using the intracavity OROTRON jet spectrometer in the frequency range of 116–146 GHz. The observed and assigned transitions belong to the *R*-branch with *J* numbers from 9 to 16 of the K = 1–0 sub-band. The (approximate) quantum number *K* is the projection of the total angular momentum *J* on the intermolecular axis. This series is a continuation to higher *J*-values of transitions correlating with the rotationless $j_M = 0$ state (*A* symmetry state) of free methane observed at lower frequencies [2].

In the present work, two new sub-bands of CH_4–CO were detected. The observed and assigned transitions belong to the *P*-branch of the K = 2–1 sub-band and *R*-branch of the K = 2–1 sub-band, correlating with $j_M = 0$ and $j_M = 2$, respectively. New data sets were analyzed together with known microwave transitions in order to determine the molecular parameters of the CH_4 – CO complex. The observed millimeter-wave spectrum shows numerous additional transitions which belong to other states of CH_4–CO, composed of methane in the *F* ($j_M = 1$) and *E* ($j_M = 2$) symmetry states. Their assignments are in progress.

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O2

CRDS spectrum of the $3\nu_1 + 3\nu_2 + \nu_3$ band of NO_2 near 7587 cm^{-1}

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The absorption spectrum of nitrous oxide has been recorded in the 7530–7630 cm^{-1} region by high sensitivity Cavity Ring Down Spectroscopy (CRDS). In this work, we report the first detection and analysis of the very weak $3\nu_1 + 3\nu_2 + \nu_3$ band at 7562 cm^{-1}. The spectrum assignment and modeling were performed within the framework of the effective Hamiltonian approach. About 150 spin-rotational energy levels are derived for $J \leq 31$ and $Ka \leq 3$. We found out that the rotational-vibrational energy levels of the (331) vibrational state at 7587.078 cm^{-1} are perturbed by Coriolis-type resonance interactions with the (350), (062) and (312) dark vibrational states at 7562.5, 7544.6, and 7627.1 cm^{-1}, respectively [1]. The mixing coefficients of the determined eigenfunctions reach 12% in the cases of (331) – (350) and (331) – (062) interactions. The weak anharmonic resonance interaction of the (331) vibrational state with the (043) vibrational state at 7609.6 [1] is also taken into account.

The set of the experimental energy levels and rotational, centrifugal distortion, spin-rotational and resonance coupling constants will be presented for the (331) vibrational state as well as the list of the assigned transitions for the corresponding (331) – (000) band.

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O3

High-resolution study of the $\nu_{10} + \nu_{12} - \nu_{10}$ “hot” band of the $^{13}C_2H_4$

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Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and the global climate and has been detected as a trace component of the atmospheres of the outer giant planets and the satellite of Titan. Therefore, for many years, the ethylene molecule and its isotopomers have been subjects of extensive both experimental (see, for example, [1]) and theoretical (see, Ref. [2]) studies.

In this investigation we present results of analysis of rotational structure of the excited vibrational state ($v_{10} = v_{12} = 1$, B_{1g}) of the $^{13}C_2H_4$ molecule. The researched band is forbidden by symmetry and cannot be appeared in absorption spectra. There is only one method of high absorption spectroscopy to study the rotational structure of that state. It is analysis of “hot” bands, such as ν_{10}+ν_{12}-ν_{10}. This “hot” band (and corresponding upper vibrational state ($v_{10} = v_{12} = 1$, B_{1g})) is analyzed for the first time.

In the present research the experimental spectrum in the region of 1300–1500 cm^{-1} was recorded with Bruker IFS-120HR Fourier transform interferometer in the Technische Universität Braunschweig (Germany). The lower state spectroscopic parameters of the $^{13}C_2H_4$ molecule were taken from [3].

The $\nu_{10} + \nu_{12} - \nu_{10}$ band is located in the region of the considerably stronger band, ν_{12}. Therefore, in the beginning of our study, we made assignments of transitions of the stronger band and deleted them from the spectrum. After that, assignments of transitions which belonging to “hot” band were made. As the result of analysis we assigned more then 200 transitions with $J_{max} \leq 20$, $K_{a\ max} \leq 9$ for the $\nu_{10} + \nu_{12} - \nu_{10}$ band. Strong local resonance interactions of the vibrational state $v_{10} + v_{12} - v_{10}$ with the five other states were taken into account, and a set of spectroscopic parameters was obtained.

The obtained from the fit set of varied parameters reproduced the initial experimental data with an accuracy which is close to experimental uncertainties.

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O4

High resolution analysis of the ν_{12} band and re-analysis of the ground vibrational state of *cis*-d_2-ethylene

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In the present study we consider ro-vibrational structure of the *a*-type ν_{12} (B_2) band of the $C_2H_2D_2$-*cis* molecule. $C_2H_2D_2$-*cis* is an asymmetric top molecule with twelve different vibrational modes. Because of its symmetry (C_{2v}), all vibrational states of the $C_2H_2D_2$-*cis* molecule are divided into 4 groups of the states of different symmetry.

The FTIR spectrum was recorded with a Brucker 120HR spectrometer at room temperature with a pressure of 0.37 mbar, an absorption path length of 16 m and a spectral resolution of 0.0025 cm^{-1}.

The ro-vibrational analysis revealed deterioration of the combinational differences observed with increasing quantum numbers J and Ka. On that reason rotational and centrifugal distortion parameters of the ground vibrational state were improved on the basis of assigned transitions.

For this band transitions were assigned with high values of quantum numbers $J_{max} = 45$ and $Ka_{max} = 20$. The assigned transitions have been used in the fit of parameters of the effective Hamiltonian. A set of fitted parameters reproduce the initial experimental date with accuracy close to experimental uncertainties.

O5

Assignment and modeling of $^{13}CH_4$ from 5853 to 6200 cm^{-1}: Preliminary results

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This work is devoted to the rovibrational assignment and analysis of $^{13}CH_4$ in the 5853–6200 cm^{-1} spectral range corresponding to upper part of the tetradecad. The analysis was based on the line-list previously obtained in Grenoble by Differential Absorption Spectroscopy (DAS) at T = 296 and 80 K [1]. Non-empirical effective Hamiltonian for the methane polyads was formed using high-order Contact Transformations (CT) [2] from an *ab initio* PES [3]. The initial assignment was made for the cold spectrum using the effective dipole moment and variational calculations [4] using *ab initio* dipole moment surface [5].

At this moment more than 2000 line positions were assigned in the cold bands of the tetradecad. These new data were added to the global fit of Hamiltonian and dipole moment parameters of the systems, included ground state, dyad, pentad, octad and tetradecad. The details of data fitting will be discussed.

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O6

Line parameters of $HD^{16}O$ from LED-based Fourier transform spectroscopy between 11 200 and 12 400 cm^{-1}

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The high resolution absorption spectrum of deuterated water has been recorded in 11 200–12 400 cm^{-1} spectral region by IFS-125M Fourier transform spectrometer at spectral resolution of 0.05 cm^{-1}. As a source of radiation the bright light emitting diode EDEI-1LS3-R [1] was applied. White type optical system and the cell of 60 cm of length were used and all measurements were performed at room temperature (297°K ± 1°K). Experimental setup makes it possible to reach signal to noise ratio about 10^4 and to record weak $HD^{16}O$ lines.

Three spectra were measured: (i) the spectrum of pure water $H_2{}^{16}O$ with natural abundance of water isotopic species; (ii) spectrum of deuterated water with maximal concentration of deuterium and spectrum of mixture $H_2{}^{16}O + HD^{16}O + D_2{}^{16}O$ with maximum concentration of $HD^{16}O$. Comparison of all three spectra allows one to easy refer each absorption lines to given isotopic variant.

Spectral line parameters (line positions, intensities and half-widths) were determined using Wxspe software [2] which allows one to find line peaks and to fit contour parameters to measured data by least square method. The observed line centers were calibrated using the published line positions of Ref. [3] and line assignment was carried out using the line list [4]. As a result more than 1500 lines of $HD^{16}O$ molecule with intensities of 2×10^{-26}–1.6×10^{-23} cm/molecule were observed and corresponding line list was created.

The spectra under study include mainly transitions to vibration-rotation states belonging to $\nu_2 + 3\nu_3$, $3\nu_1 + 3\nu_2$, $\nu_1 + \nu_2 + 2\nu_3$, $3\nu_2 + 2\nu_3$ and $3\nu_1 + \nu_3$ bands. Recorded spectra also contain a number of transitions to “dark” vibration states resonating with upper states of these “bright” bands. The observed lines have been attributed in total to 14 vibration-rotation bands. New experimental data on absorption $HD^{16}O$ were obtained between 11600 and 11640 cm^{-1}. The spectral line parameters of $HD^{16}O$ determined in our study were compared with the previous measured and calculated data.

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O7

Approximation of Voigt contour for atmosphere transmission spectra calculation

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Voigt profile contour used for calculations of the absorption lines and takes into account the effect of Doppler broadening and collision effects [1]:

$$\chi(\nu) = \frac{x_0 y}{\pi} \int\limits_{-\infty}^{\infty} \frac{\exp\left(-t^2\right)}{y^2 + (x-t)^2} dt \,, \tag{1}$$

where $x_0 = \frac{S}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}$, $y = \frac{\gamma_L}{\gamma_D}\sqrt{\ln 2}$, $x = \frac{\nu - \nu_0}{\gamma_D}\sqrt{\ln 2}$, γ_D, γ_L – Doppler and Laurence half width, $\gamma_D = \frac{\gamma_0}{c}(\ln 2)^{1/2}\sqrt{\frac{2kT}{m}}$, T – temperature, m – molecular mass, k – Boltzmann constant, ν_0 – absorption line frequency.

Different algorithmic approaches are used to calculate the integral in (1), some of them described in Refs. [2–5]. Quick approximation for different intervals of x and y based on orthogonal polynomials Hermite, functions given in analytical form and linear interpolation is offered:

$$f(x,y) = \sum_{i=1}^{10} \frac{A_i}{y^2 + (x - Ax_i)^2}, \text{ for } |y| \geq 0.7 \text{ or } |x| > 3.55,$$

where $A_i.Ax_i$ – pre-calculated weight Hermite quadrature. The error in this case less than 0.25%;

$$f(x,y) = \frac{\exp\left(\frac{-x^2}{1+2y}\right)}{y(0.319 + 0.34y) + 10^{-10}}, \text{ for } |y| \leq 0.01 \text{ and } |x| < 1.6,$$

error less than 0.5% for $y = 0.01$ and less than 0.25% for $|y| < 0.005$.

It is suggested to use a linear approximation of integral in expression (1) on a uniform x and y grid for the case $|y| < 0.7 \cap |y| > 0.01 \cap |x| > 1.6 \cap |x| < 3.55$, the accuracy will depend on the amount of memory allocated for the approximation coefficients. Computation speed does not depend on grid spacing, as the respective numbers of coefficients are linear based on it. The calculation itself also is based on a simple linear transformation. For negative x in this case, the integral function is symmetric.

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O8

Vibrational states of the triplet electronic state of H_3^+: The role of non-adiabatic Jahn-Teller coupling

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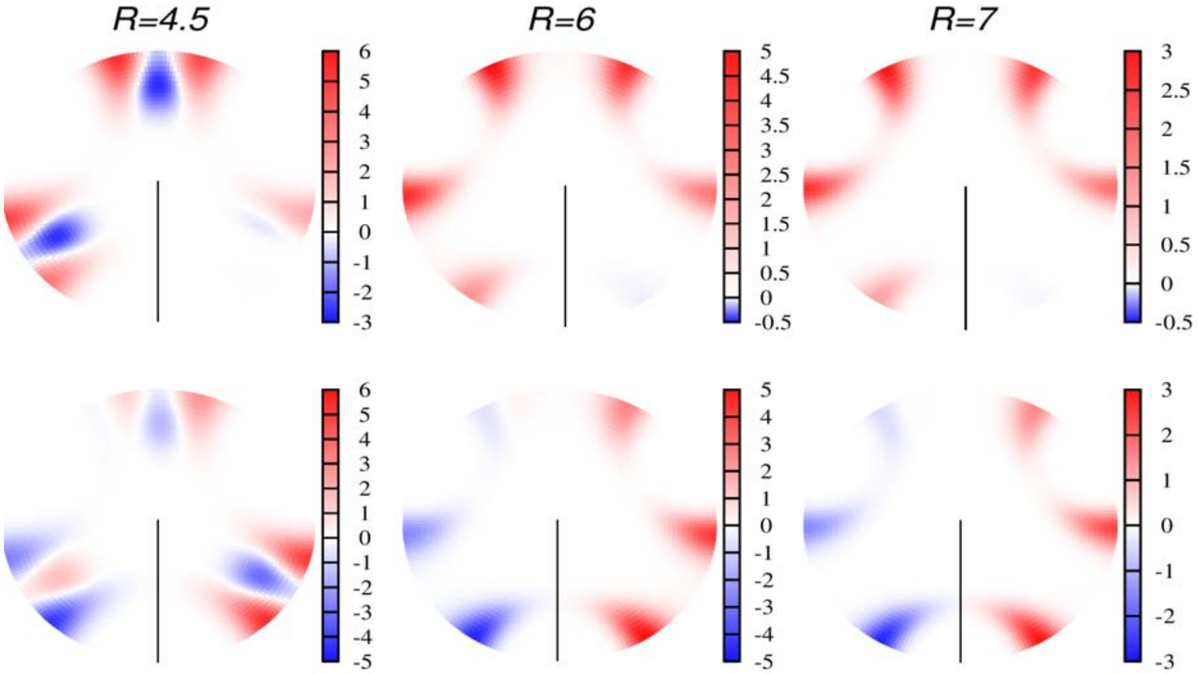
Vibrational energies and wave functions of the triplet state of the H_3^+ ion have been determined. In the calculations, the ground and first excited triplet electronic states are included as well as the most important part of the non-Born-Oppenheimer coupling between them. The diabatization procedure proposed by Longuet-Higgins is then applied to transform the two adiabatic ab initio potential energy surfaces of the triplet-H_3^+ state into a 2×2 diabatic matrix. The diabatization takes into account the effect of the geometrical phase due to the conical intersection between the two adiabatic potential surfaces. The results are compared to the calculation involving only the lowest adiabatic potential energy surface of the triplet-H_3^+ ion and neglecting the geometrical phase. The energy difference between results with and without the non-adiabatic coupling and the geometrical phase is about a wave number for the lowest vibrational levels. The figure shows contour plots of the two adiabatic components of the lowest vibrational state for three values of the hyperradius, *R*. Due to the conical intersection a geometrical phase of π is built up in the circular coordinate, clearly seen as discontinuity in the 6 o'clock position.



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O9

Methane high-T partition function from contact transformations and variational calculations

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Precise knowledge of methane absorption is oftencrucial in the study of planetary systems because its spectral features are used to determine the physical properties of these atmospheres. The Total Internal Partition Sum [1–3] of methane enables one to calculate a wide range of spectroscopic and thermodynamic characteristics. In our approach, we obtain the partition function from 10–3000K by modelling rovibrational energy levels, by consistently combining, for lower polyads individual levels obtained from exact rovibrational calculations and for higher polyads energy levels from statistical estimations based on extrapolations with appropriate physical approximations. In both cases high order contact transformation Hamiltonian was applied [4] to obtain effective Hamiltonian from potential energy surface [5, 6]. To estimate contributions from higher polyads, we fit the average contributions of the polyads to the partition function obtained from exact calculations at a particular temperature at each polyad with a second order polynomial. The values from the polynomial fit are used to make an estimation formula for higher polyad contributions with the power function to good accuracy. The value of Total internal partition sum is compared with previous reports [3].

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O10

Absorption spectra of combustion products of aircraft and rocket engines

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A determination of a quantitative composition of jet exhausts by optical methods is based on radiation or absorption spectral dependences of fuel combustion products, mainly consisting of different gases and aerosol particles. To divide molecular and aerosol absorptions, a theoretical estimation of aerosol absorption, depending on parameters of aerosol particles in different ways, must be applied. The modelling of the gas and aerosol absorption spectra as combustion products of aircraft and rocket engines allow determining the suitable wavelength for remote sounding the gas content of the flame.

In the present work, the absorption spectra of the common exhaust gases (H_2O, CO, CO_2, NO, NO_2, and SO_2) were modelled by line by line method at temperatures of 400 K, 700 K, and 1000 K. The spectral line parameters of the hot gases were taken both from the developed by us databases (in the case of NO_2 and SO_2 gases) and HITEMP2010 database [1]. The atmospheric transmittance (summer, middle latitude) was taken into account. The impact of the different factors, such as gas content, microphysical and optical properties of the aerosols (soot and Al_2O_3), geometric and thermodynamic features of the medium, on the transmission of the laser radiation through the exhaust plumes was analyzed. The spectral ranges of the exhaust gases, suitable for gas concentration measuring, were supposed, taking into account the aerosol absorption.

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O11

CRDS absorption spectrum of ^{17}O enriched water vapor between 12277 and 12894 cm^{-1}

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The absorption spectrum of a water vapor mixture enriched by oxygen-17 has been recorded in the 12277–12894 cm^{-1} spectral region at room temperature with pressure of 10 torr using cw-CRDS technique. More than 3000 lines with the intensities above 1×10^{-28} cm/molecule were found in recorded spectrum.

Observed lines were assigned to three most abundant water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$ and $H_2{}^{17}O$). Assignments of the line transitions have been done using literature data on experimental energy levels [1, 2] and calculated variational line lists [3] based on the results of Partridge and Schwenke [4, 5]. About 700 lines have been assigned to the transitions of previously unknown energy levels of 12 vibrational states of $H_2{}^{16}O$ and of 17 vibrational states of $H_2{}^{17}O$. Firstly assigned $H_2{}^{17}O$ transitions associated with the (013), (023), (032), (051), (061), (070), (080), (090), (112), (131), (150), (160), (211), (230), (301), (310), and (320) upper vibrational states. The maximum values of the rotational numbers *J* and *Ka* are 16 and 9 respectively.

Extended sets of $H_2{}^{17}O$ and $H_2{}^{16}O$ energy levels are compared to those of Refs. [1, 2]. Comparison of experimental line positions with calculated data [3] is discussed.

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O12

Reanalysis of line centers of HCl isotopologues in the ground electronic state

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More than 2150 HCl line positions of rotational and rotational-vibrational transitions up to $V_{max} = 7$ reported in the literature have been analyzed in order to check their consistency and to identify the most reliable experimental data.

Isotopically invariant U_{mj}, Δ^{H}_{mj} and Δ^{Cl}_{mj} Dunham parameters were determined from the simultaneous fitting of the line positions of all isotopologues. Significant corrections to a number of measurements were found in the fitting process. The obtained values of Dunham parameters allowed to calculate a complete list of the line positions up to $V_{max} = 8$.

A comparison of the calculated line centers with those of other authors is discussed.

O13

FTIR spectra of Ne I in 1300–7000 cm^{-1} range: Rydberg *h*-states

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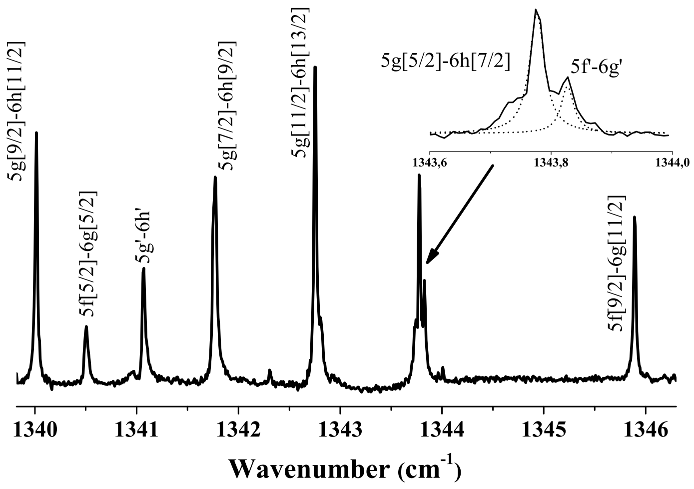
Although neon spectra have been studied from the very beginning of the spectrometric technique development [1], the experimental Ne I spectrum below 1800 cm^{-1} (wavelengths longer than 5.6 µm) have not been reported yet. We present an extensive laboratory study of Ne I energy transitions in the IR spectral region from 1300–7000 cm^{-1}. A big portion of the transitions measured were not observed experimentally before. From the recorded spectra we extract the energies of 6*h* and, 7*h* levels of Ne not reported previously.

The excited energy states of Ne I were produced in a pulsed discharge plasma. A 20 cm long discharge tube with water-cooled stainless steel electrodes was filled with pure neon and during the measurement slow flow of the gas was maintained. The neon pressure was set to 2.1 torr. The voltage drop across the discharge was 0.9 kV, with a pulse width of 22 µs and a peak-to-peak current of 50 mA. The IR spectra of Ne I were recorded using the time-resolved Fourier transform spectrometric method developed in J. Heyrovský UFCH [2, 3]. The classification of unknown lines was performed using relative values of the transition intensities calculated in the quantum defect approximation. An example of the recorded spectra is given in Figure.



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O14

Fourier transform spectrum of water vapor in the 3–5 µm transparency window

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A spectrum of natural water vapor is recorded in the 3–5 µm transparency window using Bruker IFS 125HR high-resolution Fourier transform spectrometer (IAO, Tomsk). The records of the H_2O absorption spectra were made at temperature of 12.5 C with the optical path length of 1065.5 m. The minimal detectable absorption coefficient k_ν is 1×10^{-9} cm^{-1}. The water vapor pressure was 8.2 mbar. About 160 weak water absorption lines between 2390 and 2570 cm^{-1} are assigned, more than 100 of them are newly observed. Measured line intensities are compared both with available experimental data and calculated intensities included in the HITRAN2012 and GEISA2014 databases. Disagreements between the experimental and calculated [1, 2] intensities are discussed.

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O15

Modeling of CRDS $^{12}CH_4$ spectra at 80 K in the 6539–6800 cm^{-1} region

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This work reports the assignment of rovibrational transitions of the lower part of Icosad of $^{12}CH_4$ in the 6439–6800 cm^{-1} region.Based on an *ab initio* potential energy surface [1], a full Hamiltonian [2] for $^{12}CH_4$ was reduced using high-order Contact Transformations [3] to *ab initio* based effective Hamiltonian. The effective dipole moment was applied for spectra calculation. The analysis used line list previously obtained in Grenoble by Cavity Ring Down Spectroscopy [4] at $T = 79$ K. Combinational differences routine of MIRS [5] program was applied for assignment. About 2443new experimental line positions and 1000 line intensities were fitted with RMS standard deviations of 0.007 cm^{-1} and 11.1%, respectively. Vibrational energy levels of lower part of Icosad were found.

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O16

Molecular complexes $(H_2S)_n$, $n = (1–6)$

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Studies of the molecular structure for the complexes $(H_2S)_n$, $n = 1–6$ were carried out at the MP2 level of theory and at the DFT level using the density functionals B3LYP, CAM-B3LYP, B97D3, and PBE0 with the aug-cc-pvtz basis. As a result, the stable configurations of considered complexes were found. As an example, Fig. 1 shows the two stable configurations of H_2S trimer. The harmonic frequencies of all studied complexes and anharmonic frequencies for the dimer and trimer are reported. The harmonic frequencies for the most stable configurations calculated with the B3LYP functional are given in Fig. 2. Analysis of the figure shows that the largest frequency shifts (~ 2550–2690 cm^{-1}) for considered complexes are related to the symmetric vibration ν_1 of H_2S. It is also noticeable that with the increasing of the size of a complex the frequencies related to the ν_1 and ν_3 bands of H_2S are shifted to the lower ones. At the same time, the bands related to the bending vibration ν_2 of H_2S are shifted in both directions.

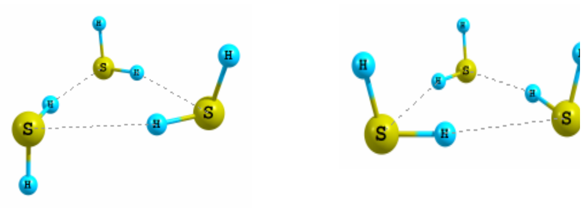

Fig.1. Stable configurations of $(H_2S)_3$. (on the left – like in [1], on the right – new found).

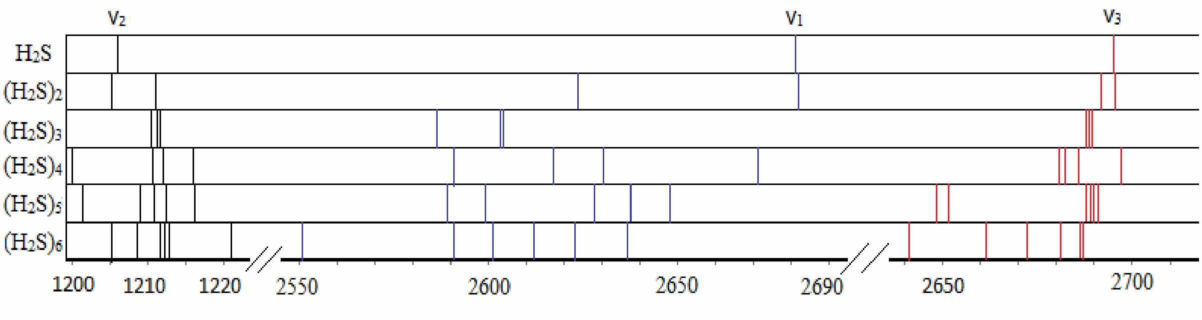

Fig. 2. Harmonic frequencies of the molecular complexes $(H_2S)_n$, $n = (1–6)$.

We also report the multipole electric moments and polarizabilities of studied complexes. The simulated Raman and IR spectra of considered complexes are presented. The analysis of the polarization properties of Raman scattering was carried out.

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O17

Conformational analysis of the *N*-methylformamide molecule in the ground S_0 and lowest excited S_1 and T_1 electronic states

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Structure and conformational dynamics of the *N*-methylformamide molecule ($HCONCH_3$) in the ground (S_0) and lowest excited singlet S_1 and triplet T_1 electronic stateswere studied by means of different *ab initio* methods.

Conformational properties of molecules are known to be somehow determined by the so-called large amplitude motions (LAM): torsion, inversion and in some particular cases out-of-plane vibrations. In particular it was discovered that in the simple stamides RCONR'R" internal rotation around central CN bond is coupled with pyramide-like deformations of CNR'R" fragment. For the *N*-methylformamide molecule in the ground S_0 three LAM such as internal rotation around $C_{carb}N$ and $C_{met}N$ bonds as well as out-of-plane NH vibration were described in detail.Basedonpotential energy surface (PES) sections by LAM coordinates calculated by MP2/aug-cc-pVTZ, vibrational levels energies and corresponding wave functions were calculated variationally. Anharmonic frequencies such obtained showed essential discrepancy depended on the dimension of solved vibrational problem.

Table 1. Vibrational frequencies (cm^{-1}) of the *N*-methylformamide molecule (S_0)

	Harm.	1D	2D**(1,2)**	2D**(1,3)**
Trans-N-methylformamide				
NHwag **(1)**	219	258	220	282
τ(C_{carb}N)**(2)**	482	—	460	—
τ(C_{met}N)**(3)**	46	55	—	60
Cis-N-methylformamide				
NHwag **(1)**	198	285	134	357
τ(C_{carb}N)**(2)**	596	—	538	—
τ(C_{met}N)**(3)**	91	101	—	103

PESofthe *N*-methylformamide molecule in $S_1(^1(n,\pi^*))$ and $T_1(^3(n,\pi^*))$ electronic states were computed by means of CASSCF and CASPT2 methods. Electronic excitation was shown to cause strong pyramide-like deformation of both HNCC and HCON fragments as well as shift of mutual orientation owing to rotation around $C_{carb}N$ bond (Fig. 1). Our calculation for $^{1,3}(n,\pi^*)$ states of *N*-methylformamide predicted six different minima to exist (Fig. 2). Geometry parameters of these conformers were determined and 1D and 2D PES sections by coordinates describing internal rotations and pyramide-like deformations of the given molecule were calculated.

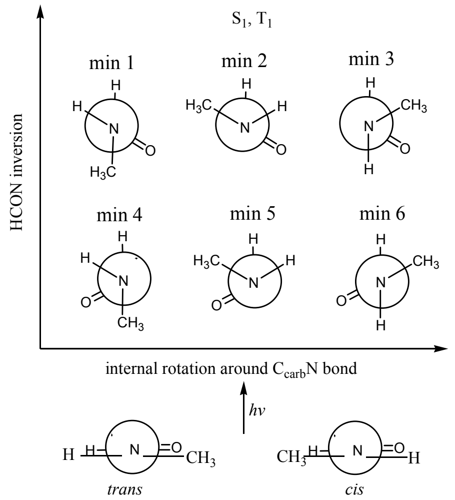

Fig. 1. Newman projections of conformers corresponding to PES minima.

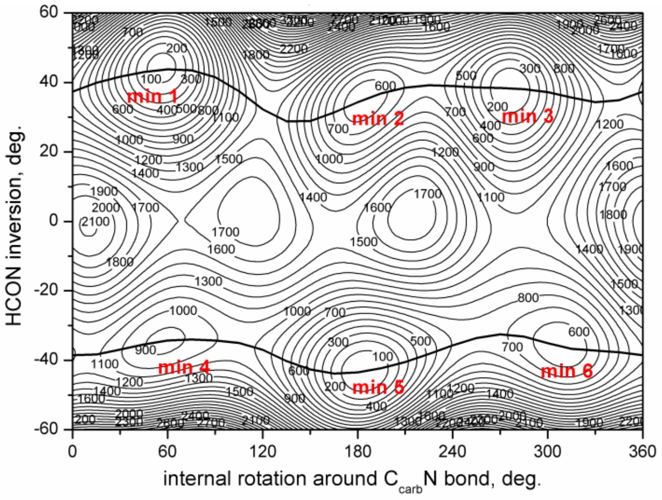

Fig. 2. 2D PES section (CASPT2/cc-pVTZ) by internal rotation around C_{carb}N bond and HCON inversion coordinates. Energy is given in cm^{-1}. Solid lines correspond to minimal energy paths.

PES shape analysis reveals that the couplings of considered large amplitude motions of the *N*-methylformamide molecule in the ground and excited electronic states have different nature, namely in S_0 state internal rotation around central CN bond results in strong pyramide-like deformation of HNCC whereas in excited S_1 and T_1 electronic statesmentioned rotation has very limited influence on non-planar HCON and HNCC fragments.

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O18

Retrieving the ratios of soft to hard velocity-changing collision's frequencies from H_2O line profiles near 0.8 μm

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It was shown in Refs. [1–3] that soft velocity-changing collisions with scattering on small angles ~0.1…0.3 rad flatten a line profile due to reducing the Dicke's line narrowing caused by hard collisions with large-angle scattering. In the limit of negligible hard collisions the line profile tends to the Voigt one. The theory [1–3] contains the parameters additional to the parameters inherent in the conventional hard collision model profiles, i.e. the frequency and mean angle of scattering for soft collisions. Thus, there is an opportunity to retrieve the ratio (R) of soft to hard collision's frequencies from processing experimental line profiles with the theory simultaneously taking into account both soft and hard collisions. As a result of such processing it was ascertained that in the case of dipole-dipole interaction between water vapor molecules soft collisions dominate hard ones ($R > 0.95$) and for dipole-quadrupole interaction of H_2O and N_2 molecules this ratio is lesser ($0.8 > R > 0.5$) that agrees with the theoretical estimations [3] made with the aid of calculated collision integral kernel.

Water vapor line self-broadening and broadening by nitrogen pressure was studied in 12411–12421 cm^{-1} spectral range using optoacoustic spectrometer with Ti-Sapphire laser having 50 kHz linewidth of generation [4].

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O19

NO absorption dynamics in gas mixtures excited by pulsed electric discharge

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Nitric oxide molecules were excited in gas mixtures NO:He = 1:5, NO:Ar = 1:5 and $NO:N_2$ = 1:10 by pulsed e-beam sustained electric discharge (EBSD) with pulse duration of ~100 μs. To study vibrational excitation of NO molecules in the ground electronic state, as a probe we applied a cw CO laser operating on more than 200 spectral lines. We chose several CO laser lines which coincided with ro-vibrational transitions of NO molecule within detuning frequency range <0.1 cm^{-1}.

At initial gas temperature of T = 293 K for all the gas mixtures an absorption for the lowest NO transition $\Pi_{1/2}$ 2–1 $R(8.5)$ appeared almost immediately with the start of the EBSD (t=0). We observed well-defined maximum of absorption at t = 100 μs for NO transition $\Pi_{1/2}$ 2–1 $R(8.5)$ with time duration of ~180 μs (FWHM) and then slowly falling tail up to 3 ms. The maximum absorption coefficient for NO transition $\Pi_{1/2}$ 2–1 $R(8.5)$ was 5 times higher for nitrogen-reach gas mixture at specific input energy of Q_{in}=250 J/(l*atm) than for argon-reach mixture at Q_{in}=50 *J*/(*l**atm). NO absorption for gas mixtures $NO:N_2$ = 1:10 and for higher vibrational transitions of NO from 3–2 to 13–12 band peaked almost simultaneously at t = 160–200 μs. After this moment NO absorption for these transitions decreased slowly for a few milliseconds.

A numerical model of vibrational kinetics in an ensemble of NO molecules and buffer gases was developed by comparing the experimental and calculated data on absorption dynamics of vibrationally excited NO molecules. The theoretical model includes a self-consistent numerical solution of equations of vibrational kinetics in mixtures of NO:He, NO:Ar and $NO:N_2$ and Boltzmann equation for the distribution function of electron energy of pulsed EBSD. The numerical model of vibrational kinetics of NO molecules was developed for conditions of our experiment. The model was applied to calculate rate constants for vibrational-vibrational (V-V) exchange between NO molecules and V-V' exchange between N_2 and NO molecules. The calculated time behavior of the absorption coefficients on NO transitions is in good agreement with the measured absorption.

Another time behavior was observed when probing the NO absorption in mixtures NO:Ar = 1:6 and $NO:N_2$ = 1:10 cooled down to T = 122±2 K. Dynamics of absorption slowed down with decreasing of gas temperature. Absorption for NO transition $\Pi_{1/2}$ 2–1 $R(8.5)$ and higher transitions was observed for about 3 s at the level 0.1 of maximum. This fact suggests that under these conditions the mixture accumulates a sufficiently large amount of vibrational energy and the energy relaxes very slowly to heat due to VV' exchange between N_2 and NO molecules and VT-relaxation of the NO molecules.

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O20

Simulation of the atmospheric radiative transfer in the water vapor near-infrared absorption bands

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The atmospheric absorption spectra of solar radiation are calculated with a high spectral resolution using different spectroscopic H_2O line parameters data. The HITRAN2008 [1], HITRAN2012 [2] and GEISA2011 [3] databases, the UCL08 H_2O line parameter databank [4], and SP (Schwenke-Partridge) H_2O line list [5] are used in the calculation. The SP line parameters of $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HT^{16}O$ and others isotopologues were obtained with use of the method [6, 7].

The spectral intervals with the most differences between the calculated atmospheric spectra are revealed. Also, the simulated spectra are compared with the atmospheric solar spectra measured by a Fourier transform spectrometer with high spectral resolution [8]. The simulation results obtained with using the UCL08 line list are close to the spectra calculated with the HITRAN2008. The spectral regions are found where the spectra simulated with use of the HITRAN2008 and GEISA2011 databases are better agreed with the atmospheric measurements than the spectra calculated with the HITRAN2012.

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O21

CO_2 absorption lines measuring in the Earth's atmosphere using NIR heterodyne spectrometer

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The CO_2 absorption lines in the Earth's atmosphere were measured using heterodyne spectrometer in near infrared range with solar occultation technique. During research the parameters of CO_2 absorption line with $\nu = 6231.713$ cm^{-1} (line intensity, self-broadening and shift coefficients) were determined using classic diode laser spectroscopy [1]. For the absorption CO_2 line to be analyzed the diode laser with fiber output with $\nu = 1.605$ μm was used. Recoding spectra realized on the optical length $L = 2$ m, gas pressure varied from 1.8 mbar to 1004 mbar, temperature T = 23 °C. Experimental spectra were fitted using Rautian-Sobel'man model.

For the CO_2 absorption line contour to be measured with high resolution (≈12 MHz) in the Earth's atmosphere there was constructed the heterodyne spectrometer oh NIR [2]. Diode laser with ($\nu = 1.605$ μm) was used as a local oscillator. For the signal to be detected the quadric detector which registers the signal dispersion was chosen. Frequency scale linearization realized using Fabry-Perot etalon with $D* = 0.04933(2)$ cm^{-1}. As a result the Doppler center CO_2 line shift was registered with accuracy ~ 10^{-4} см$^{-1}$. This shift caused by stratospheric wind. The stratospheric wind velocity was estimated with the help of the dependence of absorption line center shift from azimuth Sun angle.

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O22

Dependence of H_2O–N_2 broadening coefficients on the vibrational quantum indices

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Halfwidths of spectral lines in the case of H_2O – N_2 colliding system only slightly depend on vibrational quantum indices. The largest difference in the broadening coefficients of different bands is as small as several percent. Usually the halfwidths obtained for only one band is extrapolated to other vibrational bands. Indeed, in the case of low-lying states the vibrational amplitudes are usually small in comparison to the equilibrium distances between the atoms. However, for transitions to highly excited states, the intra-molecular motion cannot be treated as small amplitude vibrations, and as a consequence, corrections due to the intra-molecular interactions are large.

To study the vibrational dependence of the line widths we have analyzed the results of H_2O–N_2 broadening investigation recorded by a high resolution Fourier-transform spectrometer IFS-125M in the region 15500–16000 cm^{-1}. The absorption path of 34.8 m and resolution of 0.05 $см^{-1}$ were chosen to record the spectrum. White type multipass absorption cell with a basic length of 60 cm were used. Light-emitting diode (LED) was applied as a source of radiation. Signal-to-noise ratio amounted to about 10^4, which allowed to measure parameters of lines with intensity about $2*10^{-27}$ cm/molecule [1]. Least-square-fitting algorithm Wxspe was used to retrieve of the spectroscopic parameters from measured spectral data set [2]. Line-broadening and line-shifting coefficients derived from the fitting were compared to calculated data.

Experimental results were compared with theoretical calculations based on the semi-empiric technique with the accurate wave functions, resulting from extensive variational nuclear motion calculations [3]. The comparison of our calculations with experimental values argues that the semi-empirical method is quite acceptable for estimating the widths of water ro-vibrational absorption lines.

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O23

Broadening parameters of water vapor lines induced by hydrogen and helium pressure

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The majority of atmospheres (cool stars, planets, extra solar planets) are composed of molecular hydrogen and helium. The lines of water vapor are pressure broadened by collisions with hydrogen and helium remains very poorly determined, particularly at elevated temperatures. Similar issues arise with radiative transport models in combustion.

Theoretical hydrogen- and helium-broadening coefficients of water vapor lines (rotational quantum number *J* up to 50) were obtained for temperature range 300–2000 K. Two approaches for calculation of line-widths for H_2O – He system were used: (*i*) the averaged energy difference method [1] and (*ii*) the empirical expression for *J*-dependence. A vibrational dependence was not taken into account in the present work.

The averaged energy difference method allows to calculate line-widths of asymmetric top with an approximately the same precision as in modern calculated and experimental methods but without using a complicated calculation scheme. The approach is based on matching so called the coupled state energy difference with line broadening value. The dependence of broadening on the averaged energy difference of coupled states is smooth (Fig. 1 shows for H_2O – H_2 system [2–4]). Similar situation is for the temperature exponents, they can be also obtained by the same method. Temperature exponents for H_2O – H_2 line broadening [5] calculated by Robert-Bonamy formalism as function of the averaged energy difference are visualized in Fig. 2.

As it is clearly seen from the Fig.1, one can estimate corresponding line-widths with a simple fitting formula. Restored line broadening coefficients from obtained fitting formula agree well with the experimental values.

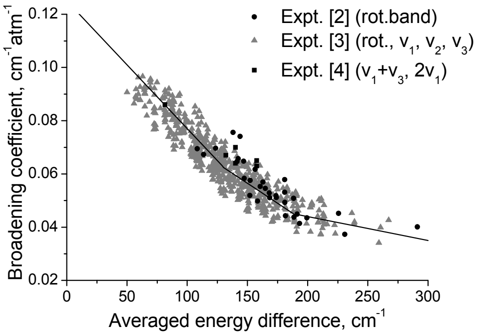

Fig. 1. Line-widths for H_2O–H_2 system [2–4] vs. the averaged energy difference, and their approximation.

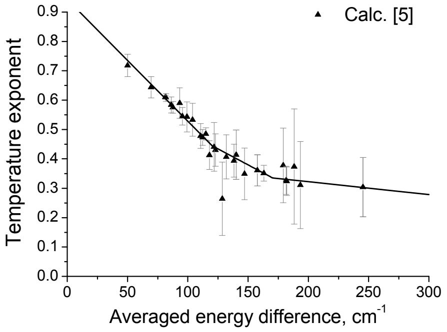

Fig. 2. Temperature exponents of line-widths for H_2O–H_2 system [5] vs. the averaged energy difference, and their approximation.

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O24

The dependence of the optical parameters XeCl-excilamp of the dynamic pressure jump

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Over the past few years, sources of spontaneous ultraviolet (UV) and vacuum ultraviolet (VUV) radiation of bound-free transitions of excimer or exciplex molecules have become intensive develop. Today the most widespread excilamps are dielectric barrier discharge driven (DBD) excilamps [1].

Today is the actual search for alternative methods of investigating the characteristics of excimer lamps in a long-term operation.

In the work [2] it was proposed for determining thermodynamic parameters to use the results of measurement of the pressure jump in the ditch DBD excilamp, when it is turned on. This method was used to determine the conditions for obtaining the maximum optical parameters DBD excilamps and capacitive discharge in different modes and different working molecules [3].

The objective of the work is test conclusions of works [2–3] at different durations of the supply voltage pulse (600 ns < τ <1.4 mks). The test was conducted on the DBD XeCl-excilamp. Record the value of the dynamic pressure jump and irradiance lamps when turned on. It is known that the thermal power W, dissipated in coaxial DBD excilamp proportional $\Delta p/p$, where Δp is the dynamic pressure jump, p is the the pressure starting to turn on the lamp. That is to characterize value W can $\Delta p/p$. Figure 1 shows the thermal power (rel. units.) and the radiation power XeCl-excilamp depending on the pressure of the mixture. It is seen, that the maxima of W and radiation power are in the pressure of 45–60 Torr. That is, without using the optical measuring instrument can select the pressure at which the maximum radiation power. Similar dependences were valid for the other values τ.

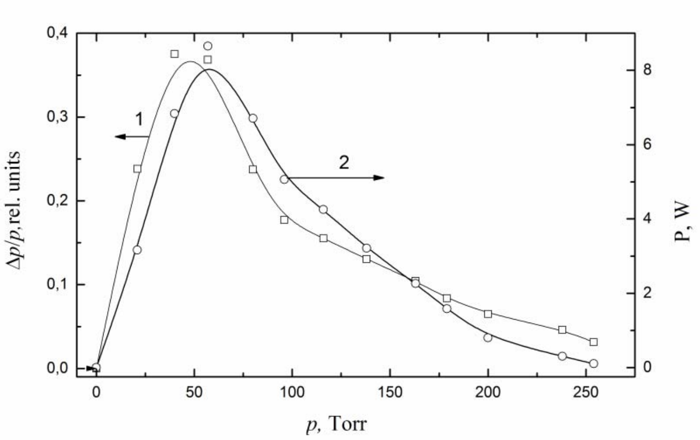

Figure 1 .Dependence of the thermal power (1) and the radiation power (2) from the pressure of the mixture Xe:Cl_2 = 200:1, τ = 600 ns.

In the work, we confirmed experimentally previously identified [2, 3] connection between the thermodynamic and optical values, shown that the established correlation is valid for modes with different values of voltage pulse from the power supply excilamp.

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O25

Ab initio calculation of the photodissociation processes in the NaO molecule

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The rates of molecular dissociation induced by light are important parameters of various atmospheric and astrophysical models. In particular, solar photons are believed to be the main source of destruction of molecules formed by the meteoroid impact on the planets and moons with rarified exospheres. For sodium, as the most important spectroscopic tracer, some correlations were found between the meteor showers and appearance of the high kinetic energy atoms [1]. Thermodynamic models point out that NaO is one of the main products of the cooled impact-produced cloud [2]. Its photolysis cross sections at selected wavelength were measured in the laboratory and solar photolysis rate is estimated [3]. Thus, NaO molecule becomes an attractive model for the first-principle studies.

Potential energy curves, transition dipole moments, spin-orbit (SO) and angular coupling matrix elements for the states correlating to three lowest dissociation limits were calculated *ab initio* using the multi-reference configuration interaction method. It was found that several pathways may contribute to the photolysis at the wavelengths up to 200 nm, where intense solar radiation produces the products with high kinetic energies. The photodissociation rates from the thermally populated rovibronic levels of the ground $X^2\Pi$ and the closely-lying (T_e < 2000 cm^{-1}) excited $A^2\Sigma^+$ states were estimated for the spectral region in the framework of both quasi-static and quantum adiabatic approaches. First, the spin-allowed transitions to the repulsive $B^2\Sigma^-$ и $(3)^2\Pi$ states, converging to the first and second dissociation limits, were considered. Then the indirect photodissociation via the intermediate “shelf-like” bound $2^2\Pi$ state, which is coupled with the $B^2\Sigma^-$ by SO interaction, was accounted for. The non-adiabatic effects in the rovibronic energies and wave functions of the $X^2\Pi$ and $A^2\Sigma^+$ were estimated as well. Preliminary results indicate the non-Boltzmann population of the initial rovibronic $X^2\Pi$ and $A^2\Sigma^+$ states.

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O26

Application of a near-IR tunable diode laser absorption spectroscopy (TDLAS) for temperature and concentration measurements of methane at various pressures

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During last years transportation of liquid natural gas (LNG) is growing to very large scale. Besides of all profits storage and transport of LNG may involve a relatively large environmental risk. Practically all LNG equipment operates at very low temperature −162 °C. At this temperature storage tank on a ship or on land could be burst and the contents spill out onto the ground or water surface. To make models of LNG vapor plume and hazards it is necessary to know parameters of plume such as density and temperature of methane. In laboratory and field experiments it is difficult to measure these parameters by usual sensors. Most popular optical sensors can't be used because of fast saturation of absorption bands of methane. We have tried to measure density and temperature of cold methane by tunable diode laser spectroscopy of hot bands which are transparent enough even at high density of methane.

The Absorption spectra of a hot band multiplet of pure methane (CH_4) and its mixture with nitrogen (CH_4+N_2, 5% of CH_4) have been recorded in the 6062.2–6063.9 cm^{-1} spectral range using tunable diode laser spectrometer. The lasing linewidth (HWHH) was at least 10^{-4} cm^{-1}. A liquid nitrogen cooled analytical cell with an optical path L=235 cm has been used in order to study the temperature dependence of absorption spectra. CH_4 and CH_4+N_2 spectra have been recorded in the temperature range ΔT= −127–+23 °C. Additionally, CH_4 spectra have been studied at T = +23 °C in the pressure range ΔP + 0.35–25 kPa. Spectra of CH_4+N_2 are presented in Fig. 1 as an example.

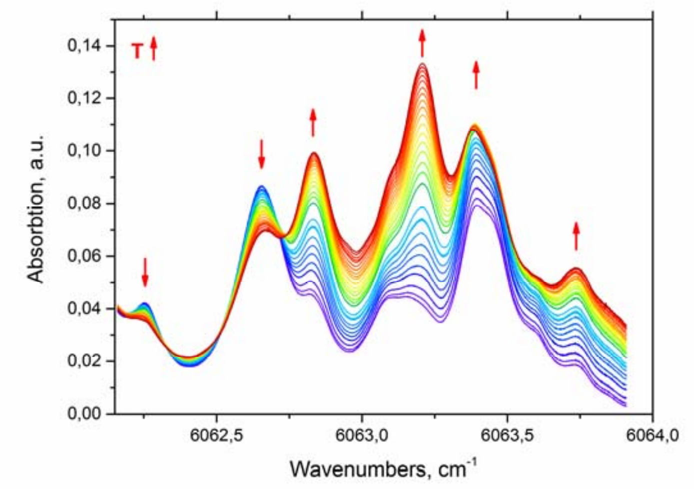

Fig. 1. Absorption spectra of CH_4+N_2 mixture (5% of CH_4) in temperature range ΔT= −127–+23 °C. Evolution of spectral bands with temperature growth is shown with arrows.

Recorded spectra demonstrate a good agreement with calculations, which was based on HITRAN-2012 database with CH_4 partition function from V.E. Zuev Institute of Atmospheric Optics database (http://spectra.iao.ru/). Special software has been developed in order to fit an experimental spectrum with a model one. The software is based on LabVIEW engine, Levenberg-Marquardt algorithm and data from spectral databases (HITRAN, http://spectra.iao.ru/). Possibility of temperature and CH_4-concentration measurements in is CH_4+N_2 mixture is demonstrated.

O27

Electronic spectra of molecular quasicrystals with Frank-Kasper structure

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The considered quasicrystal structures are an alloy of iron-manganese-carbon (86% Fe; 13% Mn; 1% C). Under the influence of dynamic loading or as a result of cryomechanical processing the crystal lattice of Hadfield's steel is destroyed and some fragments are appeared which have the icosahedral structure (the symmetry axis of order 5 is appeared which is forbidden for ideal crystals). So, these fragments have the molecular quasicrystal structure. They are also called as the Frank-Kasper (FK) structures [1].

In this work the electron states both for clusters of the ideal twelve vertex polyhedron structure (FK12) and the clusters with the atoms Fe, Mn and C have been considered. The calculations carried out by the method of scattered waves [2, 3] show that in contrast to an ideal crystal the molecular clusters have magnetic properties.

The spectra of single-electron states for each of the spin subsystems were calculated. The curves of the state density have been found.

The measurements of the absorption spectra of thin films of the alloy $Fe_{86}Mn_{13}C$ after cryomechanical processing were carried out the use ShimadzuUV-3600 spectrometer.

The good agreement between the calculated and experimental spectra confirms the appearance of the molecular quasicrystals with the Frank-Kasper structures.

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O28

Electronic structure and spectra of 3-nitroformazan

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Formazan dyes are considerable interest as organic reactants and widely known for several decades. In addition to its value as synthetic intermediates in the preparation tiocarbazons, tetrazolium salts and verdazyl radicals [1], they are also promising dyes to form the brightly colored compounds due to their ability to form stable complexes with various metals [2].

Some characteristics of the electronic absorption spectra of formazan molecules with nine different substituents have been calculated using the RI-CC2 and TDDFT quantum chemical methods (see table and figure). Also, the electronic absorption spectra have been measured. The experimental electronic energies and oscillator strengths are agreed well with the theoretical results obtained by the both methods. The discrepancies are not exceeded of 800 cm^{-1}. Therefore, the use of these methods for the modeling of the electronic properties and spectra of considered molecules is adequate.

Fig. 3-nitroformazan structure.

Table. Wave numbers of the $S_0 \rightarrow S_1$ transitions and Hammett and Brown constants for 3-nitroformazan

Substituent	Hammett constant σ_{para}	Wavenumber, cm^{-1} TDDFT/B3LYP/6–31G(d,p)	Brown constant σ^{+}_{para}	Wavenumber, cm^{-1} TDDFT/B3LYP/6–31G(d,p)
–O–C_2H_3	-0.28	19406.00	-0.78	19406.00
–C_4H_9	-0.16	18818.00	-0.33	18818.00
–C_2H_3	-0.14	18817.00	-0.31	18817.00
–H	0.00	18650.00	0	18650.00
–Ph	0.05	18564.00	-0.179	18564.00
–Br	0.26	18583.00	0.15	18583.00
–COO–C_2H_3	0.44	17988.00	0.48	17988.00
–CN	0.70	17900.00	0.66	17900.00
–NO_2	0.81	17600.00	0.79	17600.00

The calculations show that the electronic donor groups –C_2H_3, –C_4H_9, –O–C_2H_3, and –H increase the electronic density at LUMO orbitals increasing the wavenumbers of the transition $S_0 \rightarrow S_1$. In turn, the electron-accepter substituents –CN, –COO–C_2H_3, C_2H_3, –NO_2 attract the electronic density of LUMO orbitals to itself decreasing the calculated wavenumbers for the transition $S_0 \rightarrow S_1$.

The found high correlation between Hammett and Brown constants and the wavenumber changes shows that the proposed model may be used to calculate the spectra of 3-nitroformazan.

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Round Table P. Quality of spectral data

Friday, July 3, 17^{30}–19^{00}

Chair: Leonid N. Sinitsa

P1

On the accuracy of atomic and molecular data needed for stellar spectroscopy

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Spectroscopy is the most powerful tool in astrophysics. Significant part of information about stellar temperature, gravity, chemical composition, dynamical structure of galaxies is extracted from the analysis of stellar spectra. Modern methods of determination of stellar atmosphere parameters and chemical abundances are based on the fitting the synthetic spectrum to the observed one. The rapid development of the technique of astronomical observations, in particular, unprecedented accuracy in spectroscopic observations requires the adequate response from the laboratory and the theoretical spectroscopy. The quality of the fitting depends on the accuracy of input atomic parameters: wavelengths (transition energy levels), transition probabilities, damping parameters, etc. For example, modern stellar spectroscopy provides the position accuracy better than 10^{-6} (0.005 Å, at λ=5000 Å). Laboratory measurements by means of Fourier Transform Spectroscopy provide the requested accuracy [1], but they are available for a limited number of spectral lines of each chemical species. We show that in most cases the use of Ritz wavelengths is preferable.

Accurate determination of stellar atmospheric parameters (temperature, gravity, metallicity) is often based on excitation and ionization equilibrium for an element that have statistically significant number of lines for, at least, two ionization stages. It means that astronomers require the 5–10 % accuracy of the absolute transition probabilities for most important species: CNO, Fe-peak elements, diatomic molecules. These data should be available for spectral lines in large range from ultraviolet to infrared. Unfortunately, the lack of such data for commonly used reference element in astrophysics – Fe, makes problems in study of the oldest stellar populations in our Galaxy [2].

Stellar spectroscopy may serve as a powerful tool for testing the quality of the laboratory data as well as theoretical calculations. Analysis of spectra of the objects with known atmospheric parameters, Sun, Procyon, Vega, Arcturus, etc. allows to evaluate the real accuracy of the laboratory measurements and to find misidentifications of spectral lines in laboratory analysis. It also allows us to extend and improve energy levels classifications for many atomic species [3, 4].

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P2

How to compile line lists from diverse experimental and theoretical sources while letting through a minimum of errors

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The HITRAN spectroscopic database [1] consists of data from experimental, theoretical and semi-empirical sources. Each of these sources has distinct advantages and disadvantages. One has to make best use of knowledge of these pros and cons. After the combined list is created it has to undergo a vigorous validation process, which includes cross-comparison of data, comparison with raw experimental or field data, or even simple plotting of the parameters to identify possible outliers. Indeed, apart from general concerns about the data, there are very often human errors which have to be weeded out if possible. At the round table discussion we will share some of the methods we use for data validation as well as offer some suggestions for data providers.

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P3

Expert spectral data quality

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The problem of published spectral data quality is examined. Two groups of criteria are used in the analysis under consideration. One group includes formal criteria that characterize individual properties of data sources and physical quantities describing molecular states and transitions. Among the properties of interest are selection rules and restrictions imposed on the quantum numbers of states derived from mathematical models of molecules. Binary relations between data sources (or, say, physical quantities) are the relative properties characterizing the data consistency. Verification of the formal criteria is a check on the expert data validity.

The other group incorporates criteria describing actions taken by researchers in the formation of data arrays, specifically of expert datasets. We have formulated a publishing criterion [1, 2] that makes it possible to assess trust in expert data. By way of illustration, trust in the published data for several molecules is assessed.

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Invited Lectures Q

Saturday, July 4, 9^{00}–10^{30}

Chair: Frédéric Merkt

Q1

High resolution spectroscopy to study the atmospheres of terrestrial planets

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Among the most intensely developing areas in planetary science are the studies of planetary atmospheres and climate systems. High resolution spectroscopy is one of the most efficient methods in this research area, benefiting from relatively narrow ro-vibrational spectral lines of atmospheric gases in the IR range. Despite the atmospheric structure and main composition of our nearest neighbors - Mars and Venus - are well known now, their atmospheres are actively studied from ground-based telescopes and spacecrafts to investigate the dynamical phenomena and to search and measure the distribution of minor species.

For Mars and Venus the high-resolution spectroscopy is mostly used in ground-based observations with different spectrometers. The observations of echelle spectrograths TEXES and CSHELL at the NASA IRTF telescope, the CRISES spectrograth at the Very Large Telescope and others give new information about isotopic ratios, provide the monitoring of water vapor, hydrogen peroxide, search of volatile organic species on Mars, SO_2, SO, HDO, HCl, HF on Venus [1, 2, 3]. The heterodyne spectroscopy in mid-IR range allows measuring of ozone on Mars, thermospheric/mesospheric temperatures and winds on Mars and Venus [4].

In spite of extensive space explorations of planets the high-resolution spectrometers on board interplanetary spacecrafts are still rare. The SOIR echelle spectrometer with the acousto-optical filtration of light as a part of SPICAV/SOIR experiment was the first high-resolution spectrometer on Venus' orbit. Working in solar occultation it provided unique information about vertical distribution of many gases in the mesosphere at altitudes of 70–110 km including H_2O, HDO, CO, HF, HCl, SO_2 and obtained vertical profiles of atmospheric density and temperature [5–8].

The Exomars 2016 Trace Gas Orbiter (TGO) will be the first spacecraft to Mars having on board several high-resolution spectrometers from visible to long-wavelength infrared. The payload includes the NOMAD instruments with two AOTF echelle spectrometers in the mid-infrared range [9] and the Atmospheric Chemistry Suite (ACS) with three spectrometers: the AOTF echelle spectrometer NIR (0.73–1.6 μm), the echelle spectrometer MIR (2.3–4.3 μm) and the Fourier spectrometer TIRVIM in the range of 2–17 μm [10]. The Exomars 2016 has to resolve the question of methane variations in the Martian atmosphere, search of minor gases including organic molecules, measuring of isotopic ratios. Working in different observation modes from nadir to solar occultations spectrometers will measure the 3D spatial distribution and temporal variations of different atmospheric constituents and atmospheric structure.

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Q2

Molecular spectroscopy as a probe for quantum water potentials

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Keywords: Water potential; Molecular spectroscopy

All of existing liquid water potentials are intrinsically *classical* as they were obtained by fitting a simple functional form to some experimental properties of the bulk, using Molecular Dynamics simulations. True *quantum* potentials, *i.e.* independent of any experimental input, and capable of describing both water aggregates in the gas phase and liquid water, are presently under development. This approach consists in a many-body expansion performed at the *ab initio* level

$$V(M_1, M_2 \ldots M_N) = \sum_{a} V^{(1)}(M_a) + \sum_{a<b} V^{(2)}(M_a, M_b) + \sum_{a<b<c} V^{(3)}(M_a, M_b, M_c) + V_{pol}$$

truncated at third order, but augmented from the overall polarization term $V_{pol}(M_1 \ldots M_N)$. While the 1-body term $V^{(1)}$, essential to describe the monomers' flexibility, has been known at *spectroscopic* accuracy for two decades [1], high quality 2- and 3-body terms are still under development [2, 3, 4] based on high quality calculations performed at the CCSD(T) and MP2 levels respectively. One approach to test these terms is to compare, for the lower clusters $(H_2O)_n$ (n = 2, 3, …), the predicted observable values to their experimental counterparts obtained from high resolution molecular spectroscopy, such as THz spectra and infrared shifts. We will show that the specificity of these clusters, which undergo Large Amplitude Motions between the multiple equivalent minima of their potential energy surfaces (8 for the dimer, 48 for the trimer …), has to be explicitly considered to achieve a meaningful comparison.

This work has been supported by a grant ANR-12-BS08-0010-01 from the Agence Nationale de la Recherche.

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Oral Session R

Saturday, July 4, 11^{00}–12^{30}

Chair: Mikhail Yu. Tretyakov

R1

Application of methane saturated dispersion resonances near 2.36 µm over the temperature range 77–300 K for optical frequency standards

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Spectroscopic knowledge of the methane spectrum is required for numerous applications. The laser-saturated absorption lines of methane at 3.39 µm have been shown to have prospective characteristics for frequency stabilization of He–Ne laser [1] and as a result optical frequency standard was designed [2]. There are a number of methane lines in mid-IR region, which are more prospective for laser frequency stabilization, for example, line at wavelength 2.36 µm. Cr^{2+}:ZnSe laser allow us to obtain such a wavelength and to record narrow sub-Doppler resonances [3, 4]. For further development of optical frequency standards, it is necessary to carry out preliminary study of saturated dispersion resonances for the proper choice of laser parameters. Such study allows estimate laser noise level and parameters of saturated dispersion resonances – amplitude and width. We report on the Doppler-free measurement of the $E(2)$ line of $\nu_1 + \nu_4$ methane band saturated dispersion resonances with two-mode Cr^{2+}:ZnSe laser.

The theoretical temperature dependence of saturated dispersion resonances amplitudes was calculated [5]. The saturated dispersion resonances measurements were made with the two-mode laser with intracavity methane absorption cell. Cryo cooler based on closed cycle compressor was used for methane cooling in 77–300 K temperature range. Saturated dispersion resonances observed at different temperatures are shown in Fig. 1. Temperature dependence of saturated dispersion resonances amplitude is shown in Fig. 2.

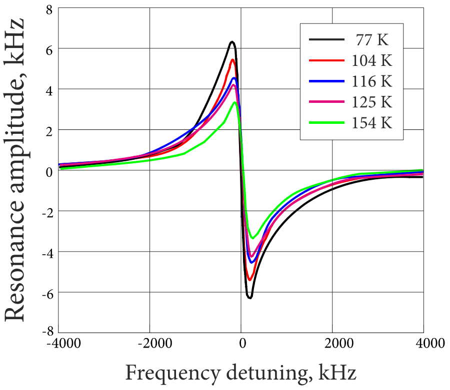

Fig. 1. Saturated dispersion resonances at different temperatures.

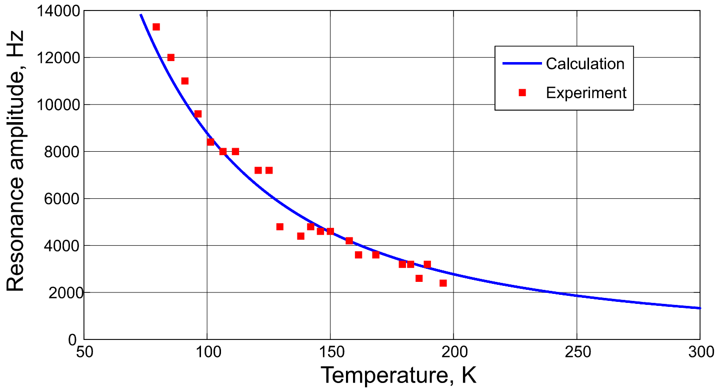

Fig. 2. Temperature dependence of saturated dispersion resonances amplitude.

Comparison with theoretical expectations showed that the temperature decrease leads to the increase of both resonance amplitude and amplitude-to-width ratio. These results are very important for frequency-stabilized lasers based on two-mode method of saturated dispersion spectroscopy.

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R2

Spectral line-shape model tests with precision spectroscopy of hydrogen molecule

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Precision spectroscopy of the quadruple transition $S_3(1)$ line of H_2 were measured by a cavity ring-down spectrometer with ultra-high sensitivity as well as high precision at room temperature up to 1.7 amagat. Foreign gas effects with helium, argon and nitrogen at various dilution ratios in H_2 were also investigated. We simulated the Voigt profiles to the experimental spectra as well as line profiles, taking into account collisional narrowing (Galatry [1] and Rautian [2] profiles). A speed-dependent line-shape model combining with the hard collisions (SDHC [3, 4] profile) was also used to simulate the spectra of the $S_3(1)$ line. The results demonstrate that the effect of velocity changes due to collisions played more important role than the effect of the speed-dependence of the relaxation rates to the $S_3(1)$ spectrum in the Dicke regime. And the experimental Ar-broadened H_2 spectra could not be well reproduced with the SDHC profile. More experiments in a wide density and temperature range need to be performed to test the SDHC profile.

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R3

Band wing shape calculation using spectral characteristics of collision-induced rotational perturbations: Application to CO and CO_2 infrared spectra

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The region of band wings has attracted a great interest since the intensities observed in the wings were dramatically lower than those predicted by the line-by-line sum of the Lorentz line shapes. As shown in Refs. [1, 2], the band wing shape can be described by the expression dependent on Fourier transform of the vector **G** correlation function. **G** is defined as the vector product of the vibrational transition dipole moment and the molecular torque arising in a binary collision. In the present work, we consider spectral characteristics of rotational perturbation for CO – Rg and CO_2 – Rg collisions (Rg = He, Ar, Xe) using vector **G** correlation function and three-dimensional classical trajectories without several conventionally used simplifications. The results obtained were applied to the band wing calculation. The calculated profiles depend on the potential energy surface and correspond with the experimental data. The relative contribution of collision-induced absorption and the role of dimer absorption are discussed.

This work was supported by Saint-Petersburg State University under grant 11.38.265.2014.

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R4

The water self- and foreign-continua in the 2.3 and 1.6 μm atmospheric windows

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In spite of its importance in radiative budget and in climate change, very few measurements of the water vapor continuum are available in the near infrared atmospheric windows especially for temperature conditions relevant for our atmosphere. This is in particular the case for the 2.3 and 1.6 μm windows where the very few available measurements show a large disagreement. This lack of experimental data is directly linked to the difficulty to measure weak broadband absorption signals.

We have recently used the Cavity Ring Down spectroscopy technique (CRDS) to measure the water vapor self-continuum cross-sections in the 1.6 μm transparency window [1, 2]. The derived self-continuum cross sections, $C_s(T = 296\text{ K})$, ranging between 3×10^{-25} and 3×10^{-24} cm^2 molec^{-1} atm^{-1} were found much smaller than derived by Fourier Transform Spectroscopy [3, 4] and in a reasonable agreement with the last version of the MT_CKD 2.5 model [5], except for the temperature dependence in the center of the window which was found significantly smaller than predicted.

We report here new measurements of the water self-and foreign- continua in the 2.3 μm window, near 4250 and 4300 cm^{-1}, by CRDS and OF-CEAS, respectively. (The Optical Feedback Cavity Enhanced Absorption Spectroscopy technique [6] is a high sensitive absorption technique using a high finesse cavity like CRDS). Self-continuum cross-sections were retrieved from the quadratic dependence of the spectrum base line level measured for different water vapor pressures between 0 and 15 Torr, after subtraction of the local water monomer lines contribution calculated using HITRAN2012 line parameters. The C_S values were determined with an accuracy estimated to 5%. Their values are found 20% higher than predicted by the MT_CKD V2.5 model but 2–3 times smaller than reported by FTS [3, 4].

The foreign-continuum was evaluated by injecting various amounts of synthetic air in the CRDS cell while keeping the initial water vapor partial pressure constant. The foreign-continuum cross-section, C_F, is larger by a factor of 4.5 compared to the MT_CKD values [5] and smaller by a factor of 2.5 compared to previous FTS values [7].

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R5

Retrieval of the water vapour continuum absorption from the high-resolution Fourier spectra in 2.7 and 6.25 μm bands

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The water vapour continuum absorption is an important component of the radiative balance of the Earth atmosphere. Different hypothesis on the nature of the continuum have been debated for a long time [1]. Recent experimental [2–4] and theoretical [5] study presented strong evidence for dominating water dimers contribution to the water vapour self-continuum within near-infrared absorption bands [2–4]. To investigate particular features of this contribution (for example, contribution from metastable dimers [6]), the low-temperature (-9 to 15 °C) laboratory measurements of high-resolution pure water vapour absorption spectrum were carried out in the near-infrared spectral region using Fourier transform spectrometer Bruker IFS 125 HR and multipass absorption cell.

The approach [2, 4] was used to derive the water vapour continuum absorption spectrum within 1600 cm^{-1} (6.25 μm) and 3600 cm^{-1} (2.7 μm) bands from the experimental spectra. Continuum absorption is derived only in microwindows between water vapour spectral lines where inaccuracy in parameters of these lines has relatively small effect on the retrieved continuum. Local contribution of the water monomer lines is simulated and subtracted using "line-by-line" code and UCL [7] linelist. Microwindows with the smallest error of the continuum retrieval were selected using a few criteria on the basis of specially developed code. Obtained spectral features (peaks) of the continuum in-band absorption have strong negative temperature dependence (Fig. 1) and a square dependence on water vapour pressure.

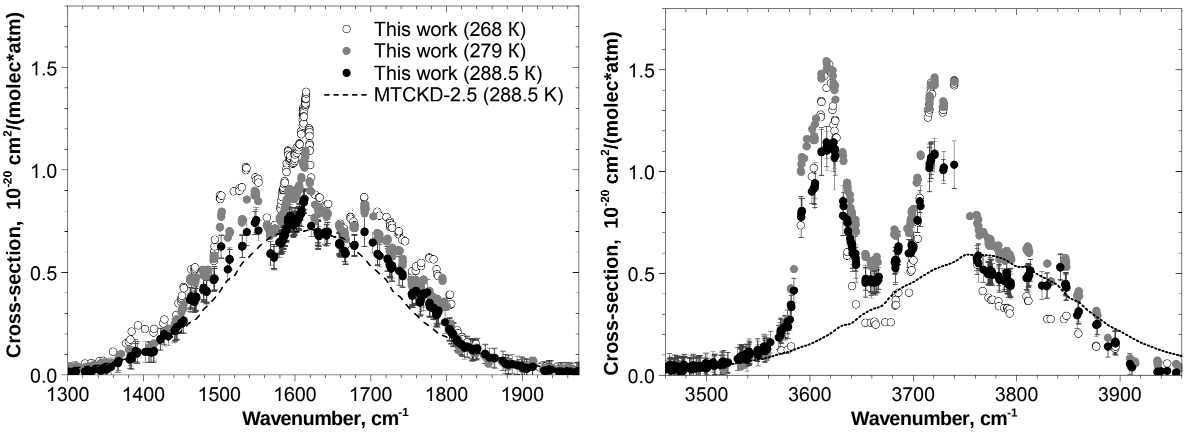

Fig. 1. Example of the pure water vapour continuum absorption within 1600 and 3600 cм$^{-1}$ absorption bands, retrieved from high-resolution Fourier-transform spectra at several temperatures. Uncertainty in the retrieved continuum is shown for 288.5 K. The MT_CKD-2.5 continuum model [8] is shown for comparison.

This work was supported by the Program of Basic scientific investigations II.10.3.8 (no. 01201354620) and by Russian Foundation for Basic Research (grant no. 13-05-00382).

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R6

Spectral composition of the water vapour self-continuum absorption in 2.7 and 6.25 μm bands

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The water vapour continuum absorption, its role in the radiative balance of the Earth's atmosphere and possible contribution of water dimers, has being discussed for decades [1]. Recent experiments [2–4] and theoretical study [5, 6] have presented strong evidence of dominating water dimers contribution to the water vapour self-continuum within near-infrared absorption bands. It was revealed also that not all spectral features of the continual absorption within these bands could be attributed to the bound (stable) water dimers. As a result, it has been suggested [4] that some spectral peaks of the water continuum within bands can be caused by contribution of quasibound (metastable).

To verify this hypothesis in-band spectra of the self-continuum absorption are required in a broad temperature region. The high-temperature data (from 296 to 350 K) were taken from experiment [7], while the lower temperature data were provided by recent FTS laboratory measurements in 1600 cm^{-1} (6.25 μm) and 3600 cm^{-1} (2.7μm) bands at temperatures from 265 to 288 K [8] .

Simulated spectra of stable and metastable water dimers were fitted to the experimental continuum data [7, 8] with the dimerization constant for the stable dimers and ratio of partition functions of the stable and metastable dimers used as fitting parameters [4]. This fitting allowed obtaining relative contribution of stable water dimers in the equilibrium water vapor in temperature region from 264 to 350 K. The results are in reasonable agreement with statistical calculations and confirm the idea of a complementary contribution of stable and metastable dimers to the spectral structure of the water vapour continuum absorption within bands [4].

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School Lectures S

Satursday, July 4, 14^{30}–15^{45}

Chair: Sergei N. Yurchenko

S1

Collision-induced absorption of IR-radiation by the major atmospheric species

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Collision-Induced Absorption (CIA) by homo-nuclear (N_2, O_2, H_2) or symmetric (CO_2, CH_4, etc.) molecules play an important role in radiative transfer processes in some planetary atmospheres including atmosphere of the Earth. This absorption was a subject of extensive theoretical and experimental study during past many decades since 1949, when Crowford et al. [1] had observed for the first time the fundamental CIA bands of nitrogen and oxygen. Despite this long investigation some experimental facts regarding CIA band intensities and shapes are still not understood and explained. The first one is a clear wave modulation of the N_2 and O_2 fundamental band shapes. The other fact is related to the $\nu_2+\nu_3$ CO_2 CIA band profile. This profile has a hump at 3017 cm^{-1} although the band center should be located at 3004 cm^{-1}. The profile does not exhibit clear (CO_2…CO_2) stable dimer spectral features in contrast to the (ν_1, $2\nu_2$) carbon dioxide CIA Fermi-doublet. The third unexplained fact is an existence of central weak component in-between of two much stronger major components of the (ν_1, $2\nu_2$) carbon dioxide Fermi-doublet. This component located at 1335 cm^{-1} is clearly seen in spectra at low temperatures [2]. Note also that this component is extremely enhanced in CO_2-Xe mixtures [3] and this enhancement does not have theoretical explanation.

Very important statement should be noted here. Any allowed ro-vibrational band in molecular spectra contains weak collision induced “sub-band” as its natural part not attributed to lines of allowed transition. This statement discredits conception of “far line wings” in molecular spectra. Absorption far away from line centers (far wing of a band) represents rather that CIA “sub-band” profile. This statement establishes close relation between allowed and CIA spectra.

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S2

Water vapour continuum absorption: History, hypotheses, experiments

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In addition to the absorption of electromagnetic radiation by individual spectral lines, water vapour possesses a slowly-varying component of absorption, known as the *continuum*, which pervades both the bands and the windows from the visible through the infrared to the microwave. The absorption due to the water vapour spectral lines within the bands is normally so strong that the continuum in these regions is of secondary importance to the radiation budget (although it turned to be very important for understanding the *origin* of the continuum). In the windows, by contrast, it is often the dominant cause of absorption and is of much greater importance both for the radiation balance of the Earth's atmosphere and for remote sensing techniques.

The nature of the water vapour continuum absorption and possible contribution from different factors, like far wings of strong water monomer lines, water dimers (WD) and so called "collision-induced" absorption, has been debated for more than 50 years [1]. There are large difficulties in identifying WD absorption in equilibrium atmospheric or even in laboratory conditions at near-room temperatures. This, together with the absence of sufficiently reliable calculations for both the water monomer (WM) far-wing line shapes and WD spectrum at room temperatures, has so far made it difficult to unambiguously resolve this debate for the whole spectral region from microwave to visible.

However, advances in both spectroscopic experiments and theoretical quantum chemistry over the past decade have given a second wind to this old discussion. On the one hand, detailed comparison 22, 3] of the recent and some older measurements with *ab initio* calculations [4, 5] for WD bands' intensities and positions reveals strong evidence for a dominant contribution of WD to the self-continuum absorption *within* near-infrared water vapour bands. On the other hand, new experimental data on the continuum absorption in the middle-infrared atmospheric window [6] were declared to be in a reasonable agreement with WM far-wing theory [7]. Recent *ab initio* calculations [8] presented evidence of a possible WD contribution to the self-continuum, ranging from 20 to 40% in the middle- and far-infrared to totally dominating in mm-wave spectral region. The later was recently experimentally confirmed in [9]. The MTCKD continuum model [10], which is currently the most widely-used model in atmospheric applications, suggests that the main contribution to the in-band water vapour continuum comes from *collision-induced* WM transitions, while out-of-band continuum is dominated by the far-wing contribution of strong WM lines. Finally, extensive development of the statistical approach to the partitioning of the pair states in phase space for polyatomic molecules [11, 12] seem to give increasing evidence [13] about what components of bimolecular water-water absorption are most responsible for the water continuum at ambient temperature and pressure.

This talk will present a retrospective review and critical analysis of some most interesting theoretical and experimental works devoted to the water continuum.

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Saturday, July 4, 16^{00}–17^{45}

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