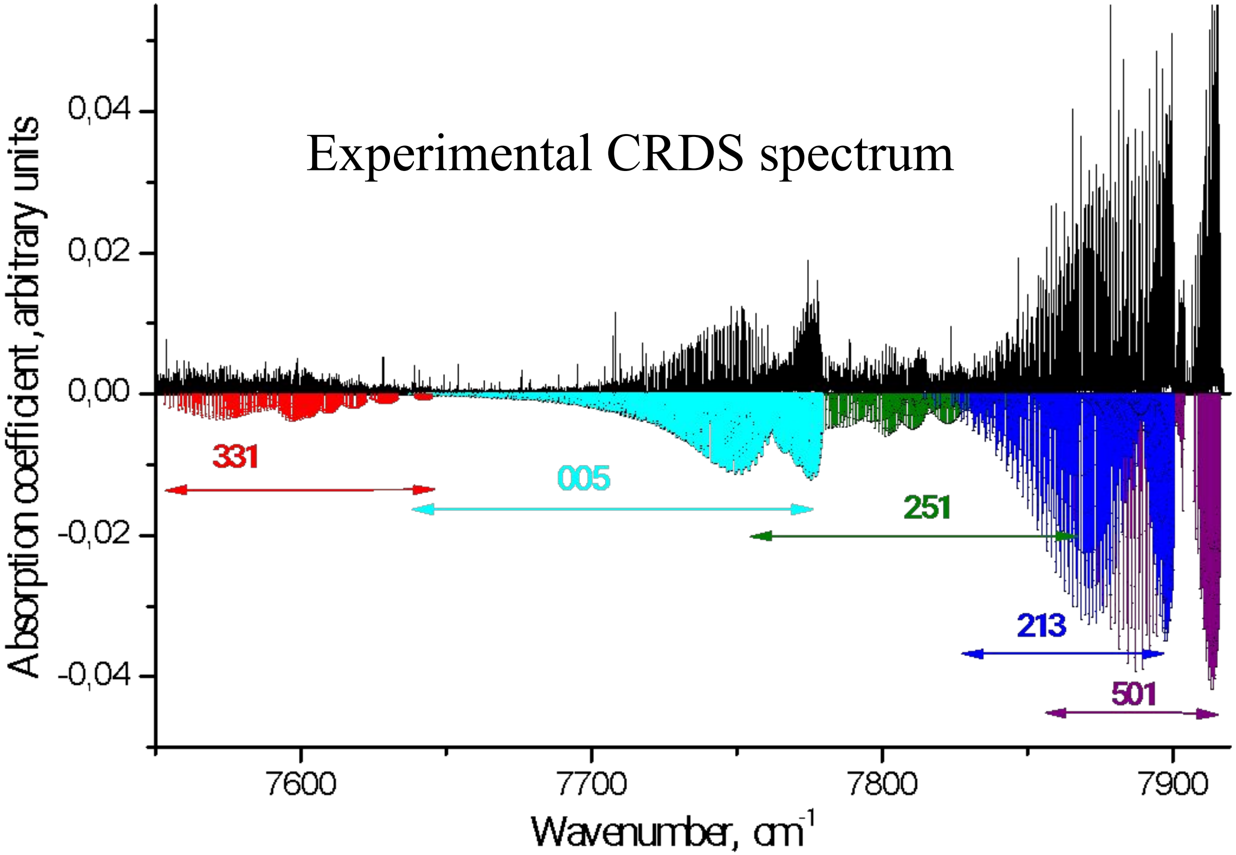
Отчет за 2015 год
Планы на 2016 год

Н.с. ЛТС Лукашевская А.А.

1. 15.05.2015г.: защита кандидатской диссертации «Анализ и моделирование колебательно-вращательных спектров высокого разрешения молекулы двуокиси азота»
(научный руководитель: Перевалов В.И.)

2. Анализ полосы $3\nu_1+3\nu_2+\nu_3$ (совместно с О.В. Науменко, D. Mondelain, S. Kassi, A. Campargue) [1]



1. A.A. Lukashevskaya, O.V. Naumenko,D. Mondelain, S. Kassi, A. Campargue. High sensitivity cavity ring down spectroscopy of the $3\nu_1+3\nu_2+\nu_3$ band of NO_2 near 7587 cm^{-1} // J. Quant. Spectrosc. Radiat. Transfer. – 2015 (in press)

Центры линий

Модель H^{eff}

(331) ↔ (312), (350), (062)*

Схема матрицы H^{eff}

	(350)	(331)	(312)	(062)
(350)	*VR+SR*		$C^{(2)}$	
(331)	$C^{(2)}$	*VR+SR*	$C^{(2)}$	C
(312)		$C^{(2)}$	*VR+SR*	
(062)		C		*VR+SR*

состояние	[Jost], cm^{-1}
331	7587.04
312	7627.14
350	7562.47
062	7544.62

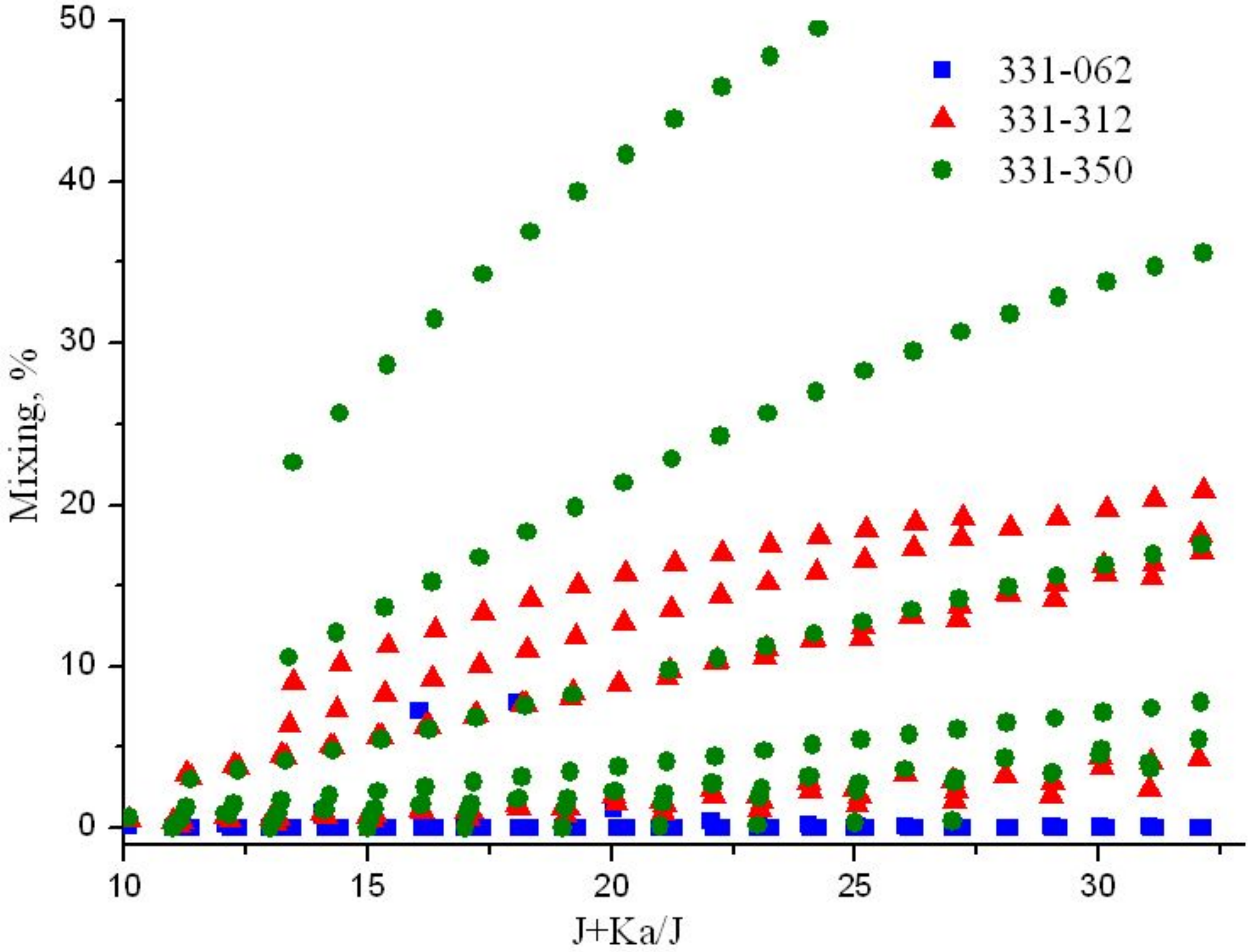
***(331), (312), (350)** принадлежат полиаде P=11, **(062)** принадлежит полиаде P=10

Начальный набор параметров H^{eff} был определен на основе [2]
Центры из [3]

2. Lukashevskaya A.A, Lyulin O.M., Perrin A, Perevalov V.I. Global modelling of NO_2 line positions. Atmospheric and Oceanic Optics 2015;28:216–31.

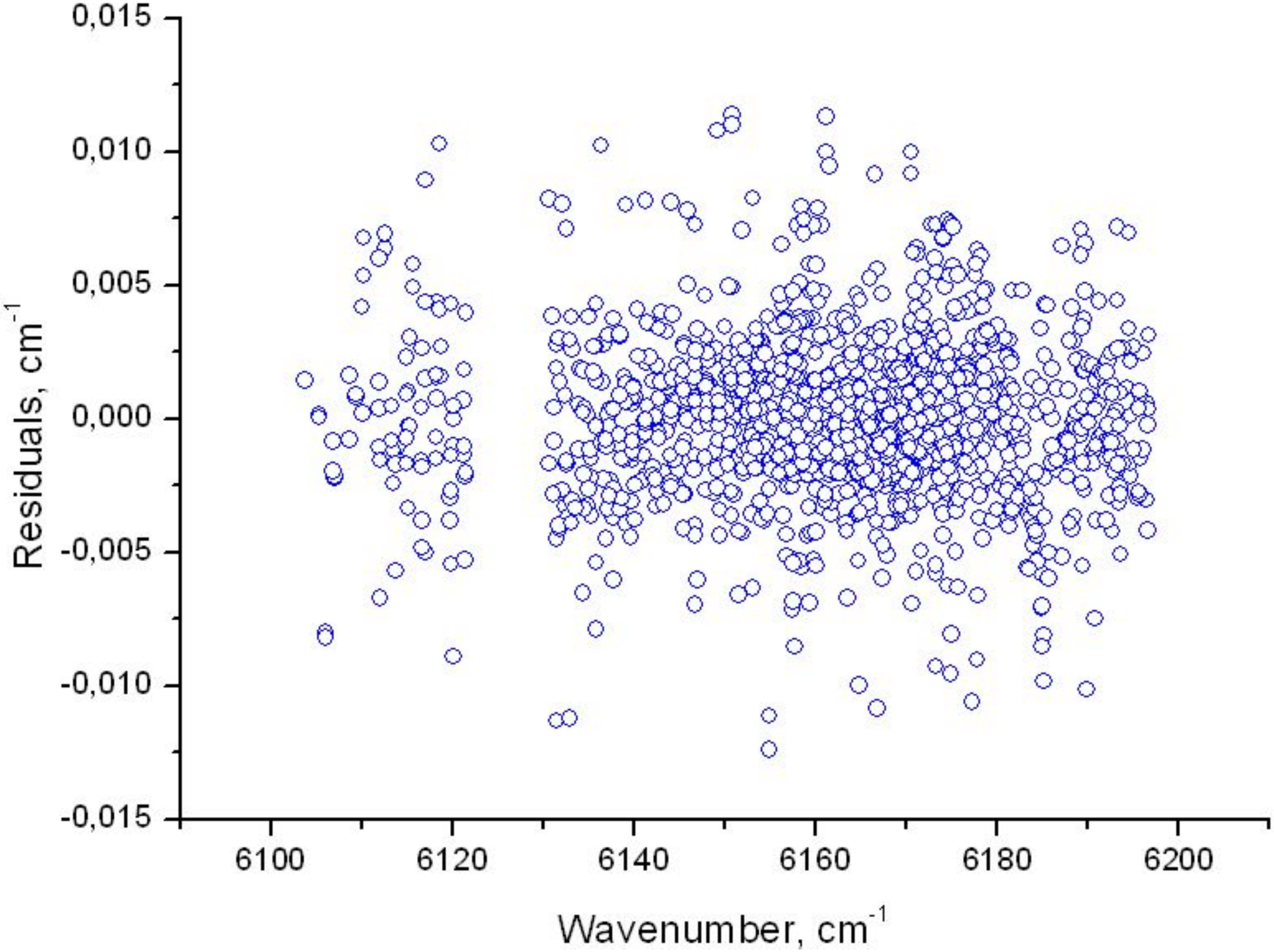
3. Delon A., Jost R. Laser induced dispersed fluorescence spectra of jet cooled NO_2: The complete set of vibrational levels up to 10000 cm^{-1} and the onset of the X^2A_1–A^2B_2 vibronic interaction // J. Chem. Phys. – 1991. – V.95, № 8. – P. 5686–5700.

Коэффициенты смешивания волновых функций колебательно-вращательных уровней энергии NO_2

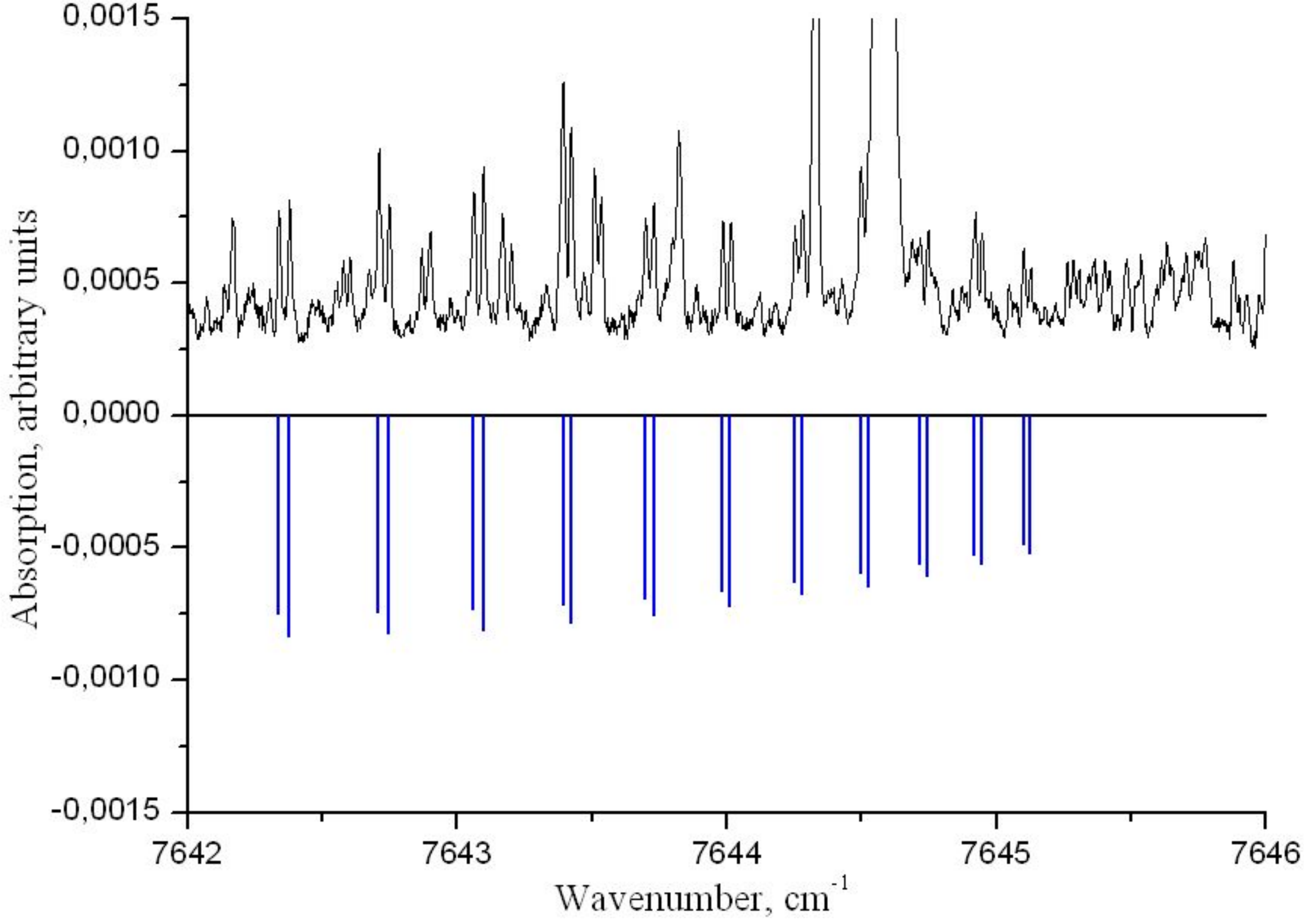


Результат подгонки МНК параметров H^{eff} состояний {(331),(350),(312),(062)}

кол-во КВ переходов	518
кол-во СВ уровней энергии	316
Макс N	32
Макс K_a	6
СКО:	0.006 см $^{-1}$

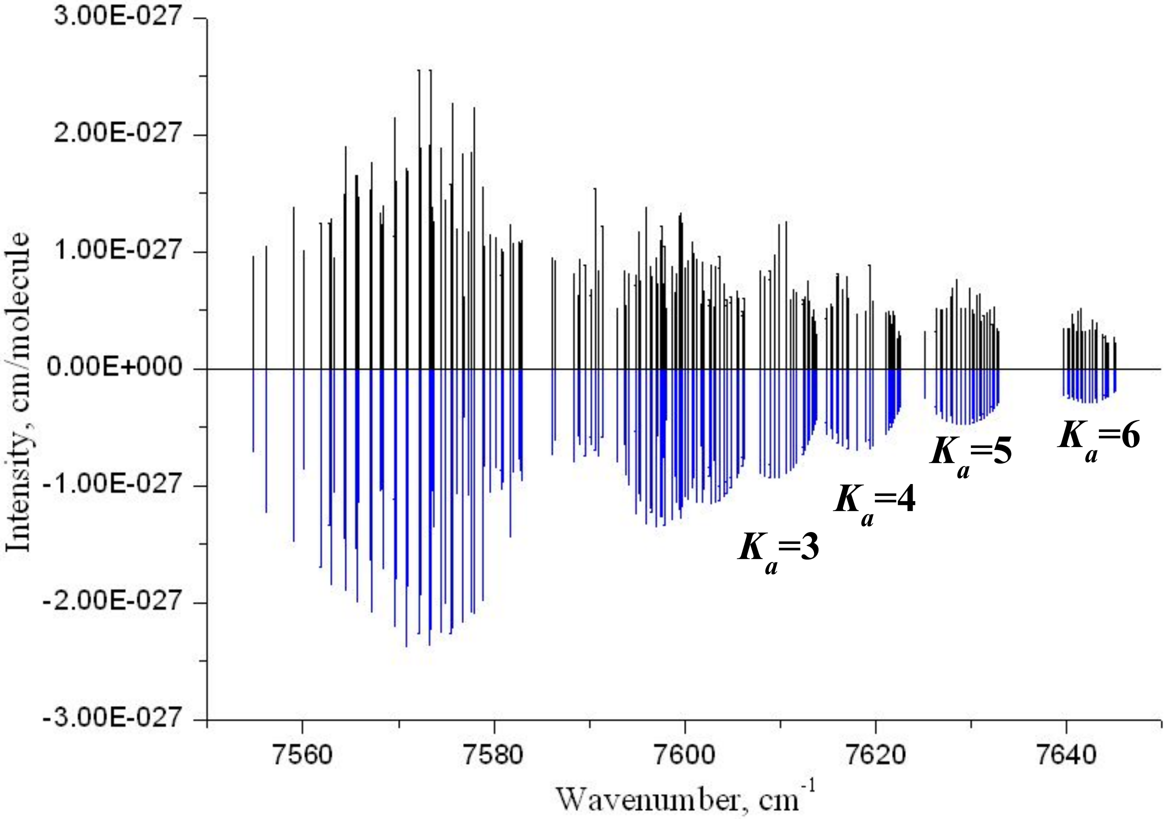

0,015
0,010
0,005
0,000
-0,005
-0,010
-0,015
Residuals, cm^{-1}
6100
6120
6140
6160
6180
6200
Wavenumber, cm^{-1}

Особенности $3\nu_1+3\nu_2+\nu_3$ спектра

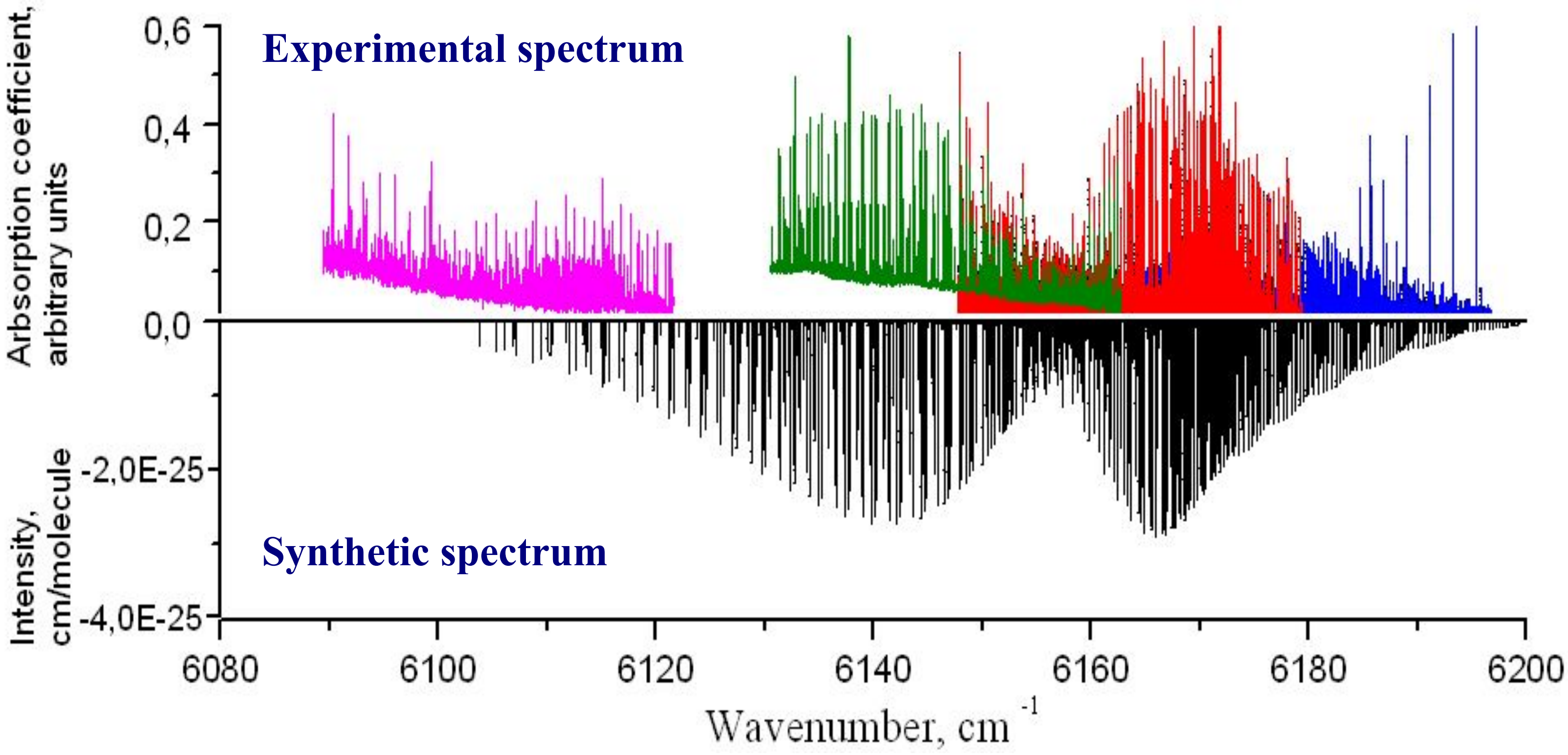


Интенсивности линий

параметр	значение (10^{-4} Дебай)
$^{331}\mu_1$	0.1714(10)
СКО:	9%



3. Анализ полосы $3\nu_1+\nu_2+\nu_3$ (совместно с О.В. Науменко, D. Mondelain, S. Kassi, A. Campargue) (in process)



Центры линий

Модель H^{eff}

(330),(311), (042),(023)*

Схема матрицы H^{eff}

	(330)	(311)	(042)	(023)
(330)	***VR+SR***	C^2		
(311)	C^2	***VR+SR***	C	C
(042)		C	***VR+SR***	
(023)		C		***VR+SR***

состояние	[Jost], cm^{-1}
330	6112.11
311	6156.25
042	6101.80
023	6183.61

(330), (311),** принадлежат полиаде ***P=9
(042), (023) принадлежит полиаде ***P***=8

Начальный набор параметров H^{eff} был определен на основе [2]

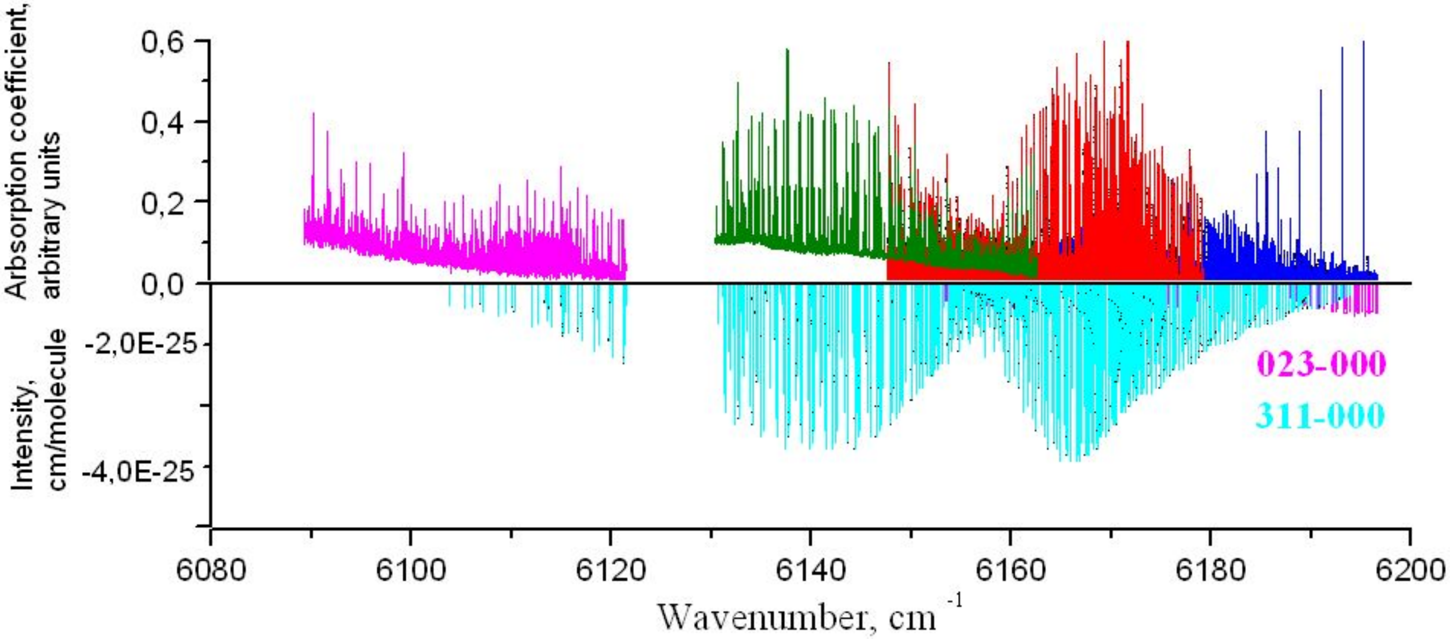
Центры из [3]

2. Lukashevskaya A.A, Lyulin O.M., Perrin A, Perevalov V.I. Global modelling of NO_2 line positions. Atmospheric and Oceanic Optics 2015;28:216–31.

3. Delon A., Jost R. Laser induced dispersed fluorescence spectra of jet cooled NO_2: The complete set of vibrational levels up to 10000 cm^{-1} and the onset of the X^2A_1–A^2B_2 vibronic interaction // J. Chem. Phys. – 1991. – V.95, № 8. – P. 5686–5700.

Результат подгонки МНК параметров H^{eff} состояний (330),(311), (061), (042),(023)

	(311)	(023)
Кол-во КВ переходов	1190	161
Макс N	40	30
Макс K_a	8	2
СКО	0.0031 см$^{-1}$	



Интенсивности линий

параметр	значение
$^{311}\mu_1$	$0.315(19)\cdot 10^{-3}$D
d_k	$0.191\cdot 10^{-5}(14)$
СКО: 8.14%	

Планы 2016:

1. Глобальное моделирование спектров высокого разрешения NO_2 в рамках неполиадной модели H^{eff}

   1.1. Определение начальных колебательных параметров, используя данные [3]

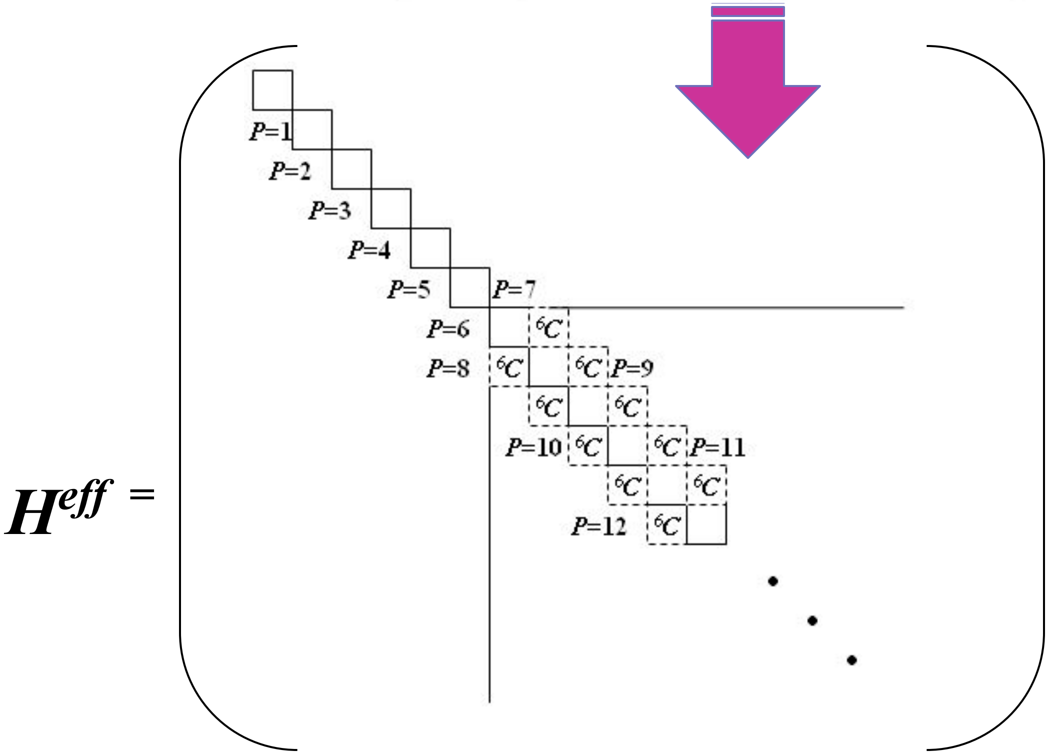
   1.2. Проведение взвешенной подгонки параметров H^{eff}

   1.3. Учет межполиадных резонансных взаимодействий

3. Delon A., Jost R. Laser induced dispersed fluorescence spectra of jet cooled NO_2: The complete set of vibrational levels up to 10000 cm^{-1} and the onset of the X^2A_1–A^2B_2 vibronic interaction // J. Chem. Phys. – 1991. – V.95, № 8. – P. 5686–5700.

1.3 Учет резонансного взаимодействия Кориолиса 6 порядка:

$$\langle V_1\ V_2\ V_3\ N\ K|H^{6c}|V_1-3\ V_2+3\ V_3+1\ N\ K\pm 1\rangle$$
$$=\pm\sqrt{(V_1-2)(V_1-1)V_1(V_2+3)(V_2+2)(V_2+1)(V_3+1)[N(N+1)]-(K\pm 1)K}$$
$$\times\left(C_e^6+C_1^6(V_1-3/2)+C_2^6(V_2+3/2)+C_3^6(V_3+1/2)\right)$$



2. Завершить анализ 311–000

3. Интерпретация и моделирование линий полосы типа *B* 004 – 000

JQSRT, 2016

NDSD-1000: high-resolution, high-temperature nitrogen dioxide spectroscopic databank

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Abstract

We present a high-resolution, high-temperature version of the Nitrogen Dioxide Spectroscopic Databank called NDSD-1000. The databank contains the line parameters (positions, intensities, air- and self-broadened half-widths, coefficients of temperature dependence of air-broadened half-widths) of the principal isotopologue of NO_2. A reference temperature for line intensity is 296 K and an intensity cutoff is 10^{-25} cm^{-1}/molecule cm^{-2} at 1000 K. A reference temperatures for broadening parameters are 296K and 1000 K. The databank has 1046811 entries, covers five spectral regions in the 466-4775 cm^{-1} spectral range and designed for the temperature range up to 1000 K. The format of NDSD-1000 is similar to HITRAN-2012. The databank is based on the global modeling of the line positions and intensities performed within the framework of the method of effective operators. 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. This approach is a modification of the impact theory performed by introduction of the empirical correction factor. The databank is useful for studying high-temperature radiative properties of NO_2. NDSD-1000 is freely accessible via the Internet site of V.E. Zuev Istitute of Atmospheric Optics SB RAS ftp://ftp.iao.ru/pub/NDSD/

Number of Pages: 19
Number of Figures: 5
Number of Tables: 5

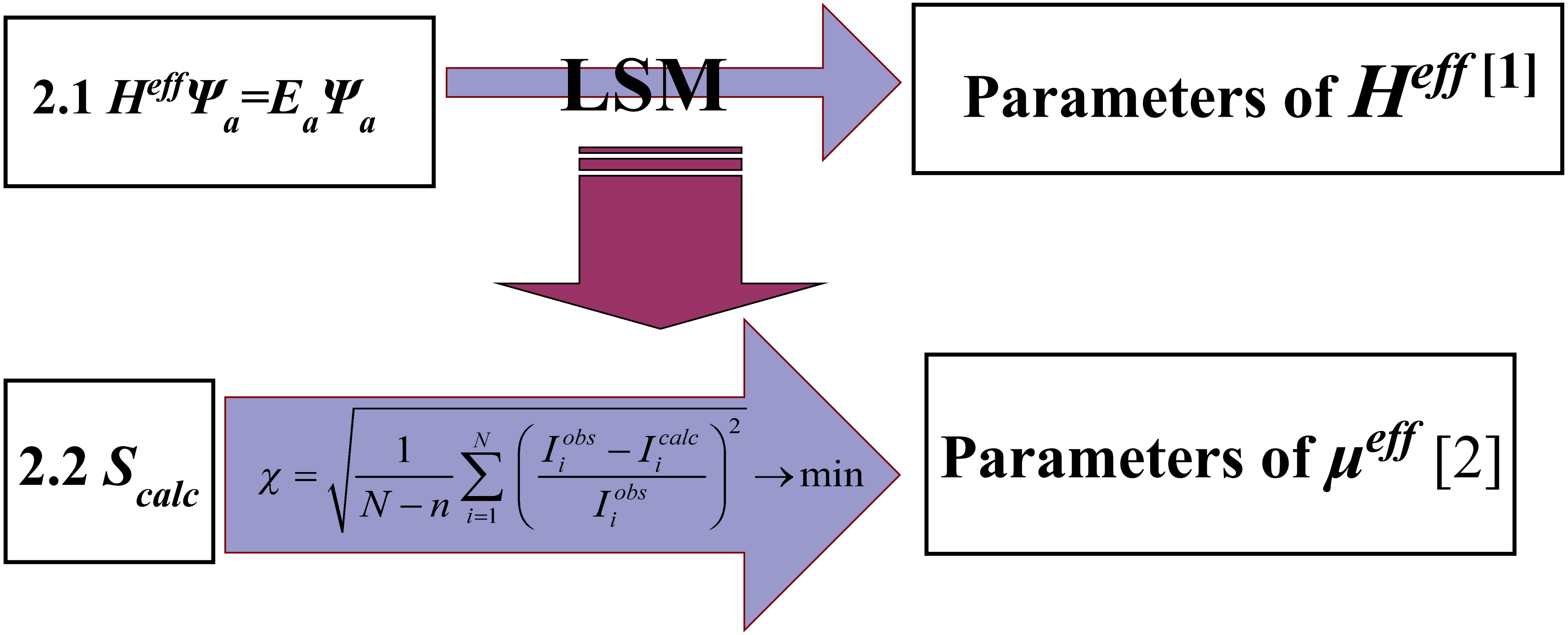
1. Introduction

Applicationshe of IR high temperature spectra of nitrogen dioxide ($^{14}N^{16}O_2$):

- investigation of exoplanets atmosphere
- detonation theory
- description of emission and absorption processes in a violation of local thermodynamic equilibrium in the upper stratosphere

2. Theoretical background

Effective Hamiltonian approach



2.1 $H^{eff}\Psi_a = E_a\Psi_a$

LSM

Parameters of H^{eff} **[1]**

2.2 S_{calc}

$$\chi = \sqrt{\frac{1}{N-n}\sum_{i=1}^{N}\left(\frac{I_i^{obs}-I_i^{calc}}{I_i^{obs}}\right)^2} \to \min$$

Parameters of μ^{eff} [2]

1. Lukashevskaya AA, Lyulin O.M., Perrin A, Perevalov V.I. Global modelling of NO_2 line positions. Atmospheric and Oceanic Optics 2015;28:216–31.

2. Perevalov VI, Lukashevskaya AA. Parameterization of the effective dipole moment matrix elements in the case of the asymmetric top molecules. Application to NO_2 molecule. Atmospheric and Oceanic Optics 2015;28:17–23.

2.3. Line intensity fits

Series	Number of lines	Number of adjusted parameters	RMS, %
ΔP=1	122	3	3.6
ΔP=2	1048	11	11.5
ΔP=3	107	6	8.6
ΔP=4	1033	5	6.2
ΔP=6	5225	2	7.3

2.4. Line profile parameters

1. Calculation of the air- and self- broadened linewidths as well as the coefficients of temperature dependence of the linewidths: **semi-empirical approach [3]**

2.Calculation of coefficients of the temperature dependence of air-and self- broadened linewidths, *n*:

$$\boxed{\gamma = \gamma_{ref}(T_{ref} / T)^{\mathrm{n}}}$$

γ - half-widths at temperature T

γ_{ref} - half-widths at temperature T_{ref}

3. Bykov AD, Lavrentieva NN, Sinitsa LN. Calculation of CO_2 spectral line broadening and shifting coefficients for high-temperature databases. Atmos Oceanic Opt 2000; 13: 1015–9.

3. Creation of the databank

T_{ref} = 1000 K
$S_{cut} = 10^{-25}$ cm^{-1}/(molecule cm^{-2})
N_{max} = 100
$K_{a\ max}$ = 20

Characteristic of BD:

File name	Number of entries	ν_{min}, cm^{-1}	ν_{max}, cm^{-1}	S_{min}, (cm/molecule)	S_{max}, (cm/molecule)	E_{low} (max), cm^{-1}
dp1.txt	243550	466.611	1115.65	1.1E-37	1.2E-21	8223.201
dp2.txt	469996	983.05	2070.94	2.3E-47	1.31E-19	10153.823
dp3.txt	78160	1895.421	2431.202	1.184E-34	4.197E-23	6765.5812
dp4.txt	236031	2400.299	3374.667	9.355E-37	6.838E-21	8162.3014
dp6.txt	19071	3966.403	4775.320	8.989E-32	5.387E-23	4798.268

Number of transitions : 1 046 808

Fragment of NDSD

ν	S	E_{low}	γ^a_{air}	n^a_{air}	γ^b_{air}	n^b_{air}	γ^a_{self}	n^a_{self}	γ^b_{self}	n^b_{self}	$v'_1v'_2v'_3$ – $v''_1v''_2v''_3$	$N'K'_aK'_c J'S'$	$N''K''_aK''_c J''S''$
696.897	3.05E-22	129.327	0.07833	0.762	0.03116	0.741	0.10806	0.856	0.04299	0.833	010–000	3 3 1 3.5 +	4 4 0 4.5 +
697.523	6.11E-24	128.701	0.07833	0.762	0.03116	0.741	0.10806	0.856	0.04299	0.833	010–000	3 3 1 3.5 +	4 4 0 3.5 –
769.842	7.09E-23	20.073	0.08518	0.728	0.03487	0.738	0.11207	0.818	0.04588	0.829	010–000	4 2 2 4.5 +	5 1 5 5.5 +
769.860	2.16E-24	20.056	0.08518	0.728	0.03487	0.738	0.11207	0.818	0.04588	0.829	010–000	4 2 2 4.5 +	5 1 5 4.5 –
1052.766	2.39E-31	5040.836	0.07109	0.657	0.03311	0.636	0.07190	0.739	0.03349	0.714	050–040	32 15 17 32.5+	31 14 18 31.5+
1052.783	2.65E-31	5015.108	0.07150	0.656	0.03334	0.637	0.07254	0.737	0.03382	0.715	050–040	31 15 17 31.5+	30 14 16 30.5+
1616.199	9.83E-21	200.901	0.08105	0.731	0.03223	0.761	0.10473	0.821	0.04165	0.855	001–000	6 5 2 6.5 +	5 5 1 5.5 +
1616.373	7.55E-21	200.109	0.08105	0.731	0.03223	0.761	0.10473	0.821	0.04165	0.855	001–000	6 5 2 5.5 –	5 5 1 4.5 –
1607.886	2.43E-22	287.728	0.07398	0.693	0.02977	0.773	0.10258	0.779	0.04128	0.869	001–000	6 6 1 5.5 –	6 6 0 6.5 +
1608.801	3.97E-20	287.728	0.07398	0.693	0.02977	0.773	0.10258	0.779	0.04128	0.869	001–000	6 6 1 6.5 +	6 6 0 6.5 +
1508.892	7.41E-32	5094.391	0.06493	0.680	0.02978	0.625	0.08609	0.764	0.03948	0.702	150–050	13 13 1 13.5 +	13 12 2 13.5 +
1508.536	5.77E-32	5092.059	0.06493	0.680	0.02978	0.625	0.08609	0.764	0.03948	0.702	150–050	13 13 1 12.5 –	13 12 2 12.5 –

Note:

Transition between states with different spin component, hot transition;

ν – line position, cm^{-1}; S – line intensity, cm/molecule at 296 K;

^{a} – at 296 K; ^{b} – at 1000 K;

γ_{air} - air-broadening coefficient, cm^{-1}atm^{-1}; γ_{self} - self-broadening coefficient, cm^{-1}atm^{-1};

E_{low} – calculated lower state energy, cm^{-1};

n_{air} – temperature exponent of γ_{air} ; n_{self} – temperature exponent of γ_{self} ;

$v'_1v'_2v'_3$ and $v''_1v''_2v''_3$ –vibrational quantum numbers of upper and lower states, respectively;

$N'K'aK'c$ and $N''K''aK''$c–rotational labels of upper and lower states, respectively;

J' and J'' – angular momentum quantum numbers of upper and lower vibrational states, respectively;

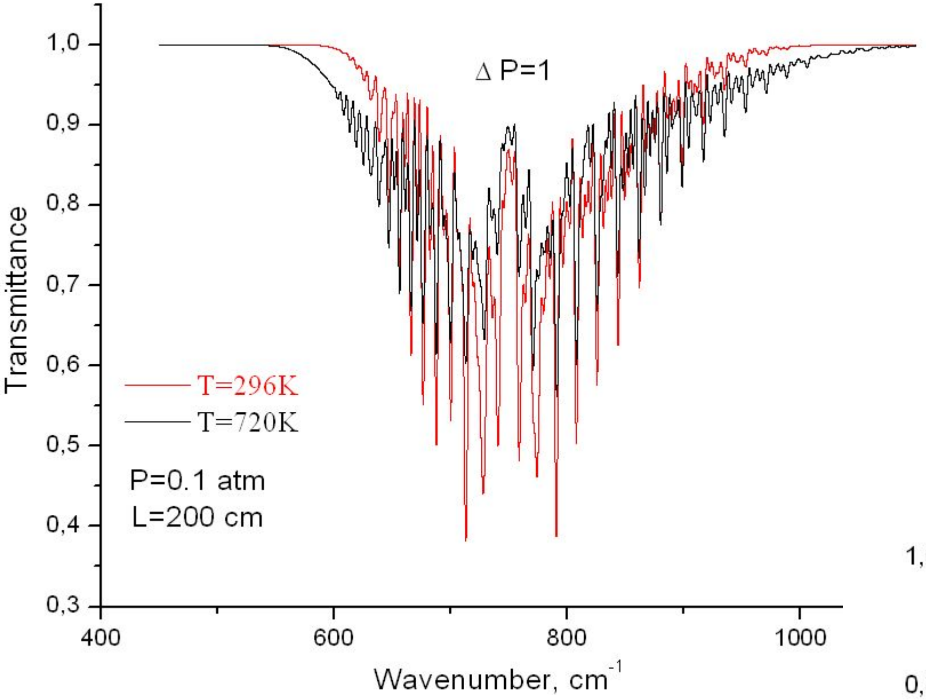
S' and S'' – electron spin components of upper and lower states, respectively.

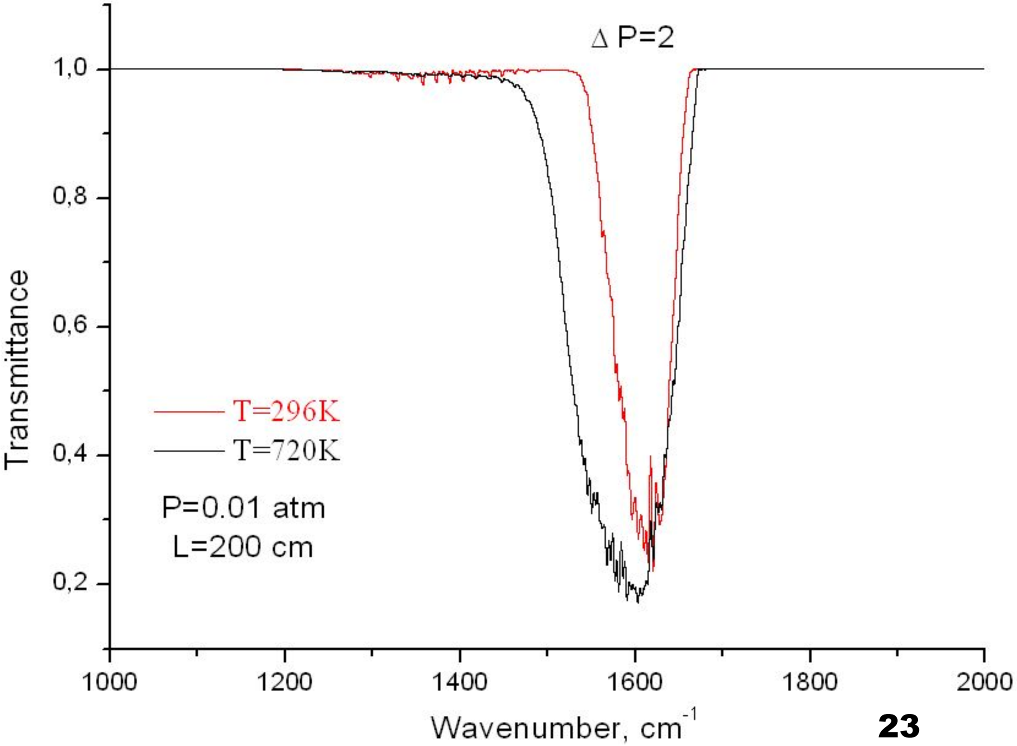
γ_{air} , γ_{self} , n_{air} , n_{self} – were calculated using the semi-empirical approach [3,4] by N.N. Lavrentieva and A.S. Dudaryonok.

3. A.D. Bykov, N.N. Lavrentieva, L.N. Sinitsa. Semi-empiric approach to the calculation of H_2O and CO_2 line broadening and shifting // Mol. Phys. 2004. V.102. P. 1653-1658.

4. A.S. Dudaryonok, N.N. Lavrentieva, Q. Ma. The average energy difference method for calculation of line broadening of asymmetric tops // Atmospheric and oceanic optics 2015. V.28. P. 403-409.

4. Simulation of high-temperature NO_2 spectra (resolution: 4 cm^{-1})





Спасибо за внимание!