High-temperature spectral dependences of $^{14}N^{16}O_2$ in the range of pure rotational and vibrational-rotational transitions

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ABSTRACT

The modelled absorption coefficients of $^{14}N^{16}O_2$ are performed in the range of pure rotational and vibrational-rotational transitions at $T = 300$ K and $T = 1000$ K temperatures. The calculations were carried out on the basis of the developed by authors high-temperature database of NO_2 spectral line parameters and database HITRAN2012. The dipole moment function parameters of NO_2 up to the second order inclusive were also determined.

Nitrogen dioxide, spin-rotation interaction, dipole moment, high-temperature spectrum

1. INTRODUCTION

Among asymmetric rotor molecules, there is a specific type with uncompensated electron spin (for example, NO_2, ClO_2, and NH_2). The dioxides of the nitrogen and chlorine effect on the Earth's ozone layer formation and on a quality of city air. On the other hand, the determination of the concentration and temperature of the exhausts is needed for a distant sounding of the jet engine operation. As the NO_2 spectrum is the part of the spectral signature of the aircraft exhaust emission [1], the calculation of the NO_2 spectral line parameters at high temperatures is the prospective task.

The spin-rotational interaction lead to appearance of doublet lines in NO_2 spectra, corresponding to positive and negative projections of the electron spin. The value of energy splitting decreases with increasing of the total rotational momentum (N). Moreover, the hyperfine structure is observed due to interaction between the magnetic fields of the nuclear and moving electron. At present, many theoretical and experimental works deal with NO_2 spectra at room temperature have been included in the database HITRAN2012 [2]. In this work, the spectral line parameters of NO_2 at temperature of 1000 K were calculated and the high temperature database in HITRAN's format for spectral interval of 0-4000 cm^1 was created. The generated high-temperature database includes the following line parameters: line position (cm^{-1}), line intensity (cm^{-1}/(molecule·cm^{-2})), Einstein A-coefficient (s^{-1}), air-broadening coefficient (cm^{-1}·atm^{-1}), self- broadening coefficient (cm^{-1}·atm^1), lower state energy (cm^{-1}), temperature coefficient, identification, and statistical weights of upper and lower states. The spectral dependencies of NO_2 at $T = 300$ K and $T = 1000$ K in infrared and microwave ranges were modelled on the basis of the developed database and HITRAN2012.

2. CALCULATION OF SPECTRAL LINE PARAMETERS

The conducted calculations were based on the empirical parameters of the effective spin-rotational Hamiltonian and resonance operators of the 21 vibrational states (Table 1). As the sources of the parameters, the more recent experimental works were used, where the full diagonalization method were applied. To validate the calculated energies the comparison with HITRAN's line positions was carried out. Since the hyperfine structure is not examined here, the spin-rotational line positions of the ground, (010)-(010), and v_2 bands were obtained from the line positions and low state energies, included in HITRAN. Generally, the good agreement between the two results is observed (average deviation ~ 0.01 cm^{-1}). The maximum deviations (~0.5 cm^1) occur for line positions with high K_a values, exceeding the corresponding maximum quantum numbers of the measuring line positions (Table 1). Thus, for such line positions there are only theoretical results, which differ when different sets of the parameters are used.

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Table 1. The sources of the spin-rotational parameters of NO_2 used in this work.

$\upsilon_1\upsilon_2\upsilon_3$	J^{max}	K_a^{max}	Ref.	Range (cm^{-1})*	$\upsilon_1\upsilon_2\upsilon_3$	J^{max}	K_a^{max}	Ref.	Range (cm^{-1})*
000	54	14	[3]	8-200	040	60	5		
010	53	11	[4]	570-960	021	60	6	[10]	3000-3400
100	56	15			002	60	8		
020	62	6	[5]	1200-1850	210	**	**	[11]	2500-3800
001	81	15			130	**	**		
110	61	10	[6]	1900-2300	111	55	12		
030	**	**	[7]	2270-2400	220	**	**	[12]	4130-4200 4690-4780
011	63	9			201	55	11		
200	57	10	[8]	2520-2795	022	**	**		
120	**	**	[9]	2630-3510	003	57	10		
101	55	10							

*the boundaries of spectral range correspond to experimental conditions of the referenced work;
**no experimental data were observed. The set of parameters was extrapolated from the constants of other states (see details in the referenced work).

Table 2. The integrated intensities (S_υ) and vibrational transition moments ($^\alpha\tilde{\mu}^{VV'}$) of NO_2 (T = 296 K).

Band	S_υ, cm^{-1}/(molecule·cm^{-2})	$^\alpha\tilde{\mu}^{VV'}\times 10^2$, Debye
ν_1	$0.705\cdot10^{-19}$ [13]	-0.6735 ± 0.0041 [13]; -0.6652 ± 0.0098 [14]
ν_2	$0.542\cdot10^{-18}$ [15]	-4.272 ± 0.26 [15]
ν_3	$0.5688\cdot10^{-16}$ [13]	29.561 ± 0.021 [13]; -29.57 ± 0.60 [16]
$2\nu_1$	-	-
$2\nu_2$*	$0.652\cdot10^{-19}$ [13]	0.0 [13]
$2\nu_3$	$0.38\cdot10^{-20}$ [10]	0.1145 ± 0.0026 [10]
$\nu_1+\nu_2$	$0.164\ 10^{-19}$ [6]	0.4035(25) [6]
$\nu_1+\nu_3$	$0.29\cdot10^{-17}$ [9]	4.9689 ± 0.0028 [9]
$\nu_2+\nu_3$	$0.853\ 10^{-20}$ [7]	0.3219 ± 0.0015 [7]

*band intensity was obtained from intensities of $K_a = 0 - 2$ and $K_a = 5 \leftarrow 6$ series in Ref [13].

Table 3. The parameters of the NO_2 dipole moment function.

Parameter	Value$\times 10^2$, Debye		
	Other works	This work	
		Set I	Set II
$^x\mu_1$	-0.940 ± 0.014 [14]	-0.9525	-0.9408
$^x\mu_2$	-6.04 ± 0.37 [15]	-6.0415	-6.0415
$^z\mu_3$	-41.82 ± 0.85 [16]	41.8055	-41.8183
$^x\mu_{11}$	-	-	-
$^x\mu_{12}$	-	0.8732	0.8739
$^x\mu_{22}$	-	-	-
$^z\mu_{13}$	-	18.6463	1.2266
$^z\mu_{23}$	-	0.7790	0.5085
$^x\mu_{33}$	-	0.0426	0.0440

The line positions and intensities were calculated, taking into account spin-rotational and resonance interactions. Besides of the doublet lines, the spectral lines, produced by intercombination transitions were considered. The dipole moment function parameters up to the second order inclusive were determined to obtain the probability of the vibrational–rotational transitions. The inverse problem was solved on the basis of the vibrational transition moments, taken from the literature (Table 2). As there are two variants of the sing for ν_3 band vibrational transition moment ($^z\tilde{\mu}^{000,001}$ in Table 2),

the two sets of the parameters are determined (Set I and Set II in Table 3). In this work, the calculations were carried out with the Set I parameters for which the vibrational transition moments from the latest work were applied.

Finally, the spectral line parameters of NO_2 were calculated at $T = 1000$ K with the cutoff of 10^{-35} cm^{-1}/(molecule·cm^{-2}). The high-temperature database was formed in the HITRAN's format. The developed database includes the vibrational-rotational transitions of the 100 bands, from which the 11 bands are presented in the HITRAN2012 database. The absorption coefficients, modelled by line-by-line method, using the "TRAVA" software [17], demonstrate a considerable increasing of the absorption in the wings at $T = 1000$ K, if the created in this work database is applied (Fig. 1).

Since there are no experimental data for NO_2 spectra at high-temperatures, the comparisons with measuring results at room conditions are carried out. In Ref. [18] the measured absorption spectra of some engine exhausts, including NO_2, are shown. On the Fig.2 the absorption coefficient, measured at pressure of 0.93758 atm (95 kPa) and $T = 295$ K, is compared with the theoretical dependences. A good agreement between this work results and the absorption coefficient, calculated using the HITRAN2012 database is observed.
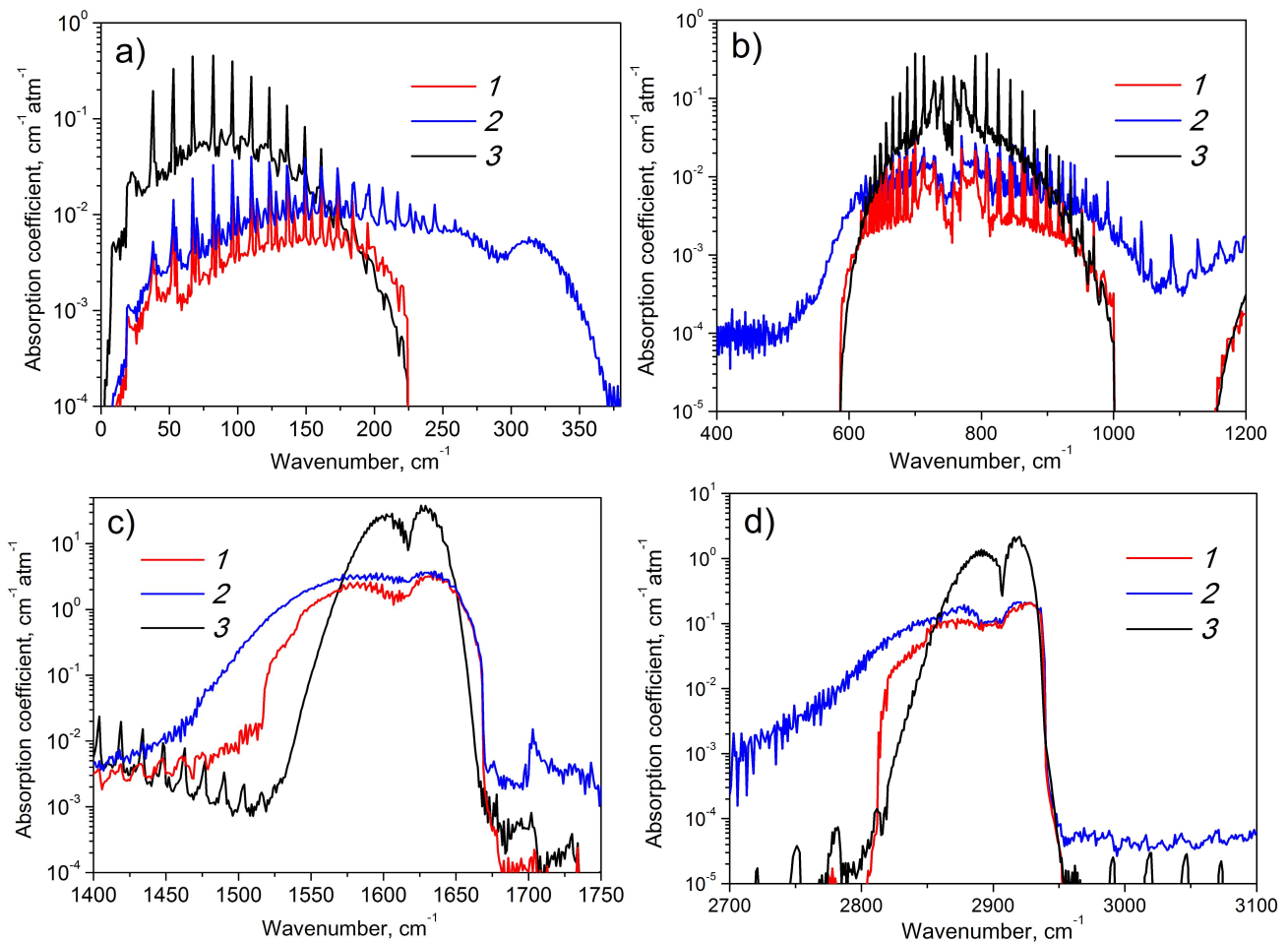

Figure 1. The absorption coefficient of NO_2 ($\Delta\nu$ = 1 cm^{-1}, *resolution* = 1 cm^{-1}), calculated at $T = 1000$ K in the range of (a) - pure rotational transitions, (b) – ν_2, (c) - ν_3, and (d) - $\nu_1 + \nu_3$ bands: *1* – HITRAN2012; *2* – this work; *3* – HITRAN2012 at $T = 300$ K (all curves in a logarithmic scale).
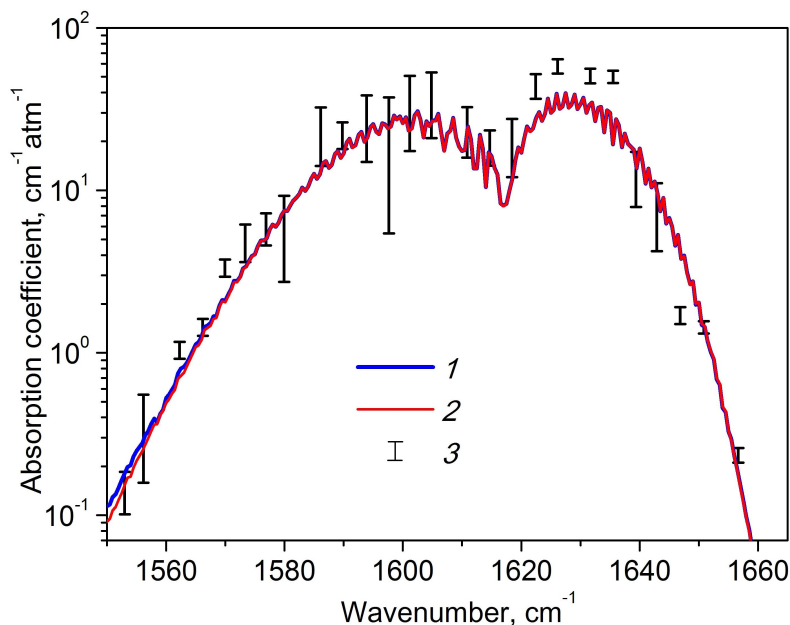
Figure 2. The absorption coefficient of NO$_2$, modelled in the range of 1550-1660 cm^{-1} at T = 295 K: *1* – this work *2* – HITRAN2012, and *3* - the measured result from Ref. [18].

In Ref. [19] the NO$_2$ absorption coefficients were measured by means of $^{12}C^{16}O$ and $^{13}C^{16}O$ lasers at room temperature (T = 300 K). The examples of the calculated absorption coefficients in comparison with experimental values in Table 4 are shown. This work results agree well with HITRAN data. Due to poor accuracy of the theoretical laser line, presented in Ref. [19], the discrepancies between experimental and theoretical values only in some cases fall into experimental uncertainty, estimated of 10 %. Therefore, a small changing the line position value (column *b* in Table 4) results in the absorption coefficient, satisfying experimental uncertainty. However, for some lasing lines, for example, 1637.142 cm^{-1} ($P_{19-18}(12)$) and 1655.761 cm^{-1} ($P_{17-16}(13)$), the measured values are not founded on the theoretical curves.

Table 4. The examples of the NO$_2$ calculated absorption coefficients in comparison with experimental values from Ref. [19]

Lasing line (cm^{-1})			Absorption coefficient, cm^{-1}·atm^{-1}		
$^{12}C^{16}O$	*a*	*b*	[19]	This work	HITRAN2012
$P_{20-19}(12)$	1612.486	1612.335	13	16.973^a 13.066^b	17.246^a 13.202^b
$P_{19-18}(18)$	1614.912		15	14.855^a	14.913^a
$P_{19-18}(17)$	1618.700	1618.960	18	12.861^a 18.014^b	12.655^a 17.539^b
$P_{19-18}(12)$	1637.142	-	10	11.303^a	11.376^a
$P_{18-17}(17)$	1643.265	1643.030	11	3.419^a 10.971^b	3.494^a 11.108^b
$P_{18-17}(16)$	1647.054		1.5	1.405^a	1.532^a
$P_{18-17}(15)$	1650.811	1650.782	1.5	1.184^a 1.506^b	1.236^a 1.526^b
$^{13}C^{16}O$					
$P_{18-17}(18)$	1614.052		10	10.138^a	10.263^a
$P_{17-16}(19)$	1633.910	1633.944	26	20.823^a 26.046^b	20.937^a 26.050^b
$P_{17-16}(18)$	1637.625	-	51	37.881^a	37.763^a
$P_{17-16}(17)$	1641.313	1641.352	27	19.584^a 24.458^b	19.608^a 24.260^b
$P_{17-16}(15)$	1648.601		4	4.019^a	3.823^a
$P_{17-16}(14)$	1652.192	1652.012	1	1.524^a 1.002^b	1.522^a 1.031^b
$P_{17-16}(13)$	1655.761	-	1.5	0.174^a	0.172^a

a – the lasing lines, taken from Ref. [19];

b – the lasing lines, obtained in this work, from the analysis of the theoretical spectral dependences of NO$_2$ absorption coefficient.

3. CONCLUSION

The line positions and intensities of $^{14}N^{16}O_2$ were calculated at $T = 1000$ K with the cutoff of 10^{-35} cm^{-1}/(molecule·cm^{-2}) on the basis of the empirical parameters of the effective spin-rotational Hamiltonian and resonance operators, taken from the literature. The dipole moment function parameters up to the second order inclusive were determined to obtain the probability of the vibrational–rotational transitions. The modelled NO_2 absorption coefficients, performed in the range of pure rotational and vibrational-rotational transitions, demonstrate a considerable increasing the wing absorption at $T = 1000$ K, if the created in this work database is applied.

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