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SPECTROSCOPY OF AMBIENT MEDIUM

Global Modeling of NO₂ Line Positions

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Abstract—The global modeling of NO_2 line positions has been performed within the effective operators method. One hundred and ninety five parameters of the polyade model of the effective Hamiltonian have been fitted to 28016 line positions collected from the literature for the 0.006–7916 cm⁻¹ wavenumber range. The global root mean square residual of the fit is 0.017 cm⁻¹. The effective Hamiltonian used explicitly takes into account both the spin-rotation interactions within each vibrational state and numerous vibrational-rotational resonances. Indeed, resonances due to the first and second order C-type Coriolis interactions and Fermi and Darling–Dennison resonances had to be considered because of the approximate relations $\omega_1 \approx \omega_3 \approx 2\omega_2$ between three harmonic frequencies of NO₂.

Keywords: nitrogen dioxide, ¹⁴NO₂, line positions, global modeling, effective Hamiltonian, electron spinrotation interactions, Coriolis type resonances, anharmonic resonances

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INTRODUCTION

Nitrogen dioxide $({}^{14}N{}^{16}O_2)$ is a gas polluting the troposphere, which is generated during fossil fuel combustion and contributes to the generation of photochemical smog. Nitrogen dioxide is involved in photochemical reactions in the stratosphere, which regulate natural ozone concentrations. Sufficiently accurate measurements of NO₂ concentrations in the atmosphere are executed presently by remote sensing methods with the use of spectra of the molecule in ranges 6.2 and 3.4 μ m, which correspond to the v_3 and $v_1 + v_3$ bands [1, 2].

Since accurate parameters of NO₂ spectral lines are required for the analysis of atmospheric spectra, numerous detailed investigations of NO₂ spectra were performed, from micrometer to infrared (1.2 µm) wavelength ranges (see [3-18] and references therein). Theoretical models used for the analysis of such spectra take into account peculiarities of this molecule. $^{14}N^{16}O_2$, being an asymmetrical top, gives a spectrum with the doublet structure in the infrared range due to the spin-rotation interaction [3, 7]. At the same time, depending on the spectral range, resonance vibrational-rotational interactions should be taken into account in order to calculate accurately centers and intensities of NO₂ spectral lines.

The results of the performed investigations were spectral line lists, including centers and intensities. These lists for regions 6.2 and 3.4 µm entered into the databases HITRAN [19] and GEISA [20]. Since these lists were composed for normal atmospheric temperatures ($T \sim 296$ K), they do not include transitions from highly excited vibrational and rotational states. This can be a problem in the description of infrared characteristics of NO₂ in vehicle exhausts [21], because the contribution of hot bands in these characteristics can be significant. Actually, the predicted ratio of intensities of hot bands to cold ones under conditions of the local thermodynamic equilibrium has the form Hot/Cold (T) \approx $Z_{\text{vib}}(T) - 1$, where $Z_{\text{vib}}(T)$ is the vibrational partition function; Hot/Cold (296 K) = 3%; Hot/Cold (500 K) = 17%; and Hot/Cold (650 K) = 34%.

Nitrogen dioxide is one of indicators of life on planets; therefore, the description of NO₂ infrared characteristics at high temperatures is necessary for investigation of hot atmospheres of exoplanets [22].

HITRAN and GEISHA databases include an insufficient quantity of NO₂ spectral line parameters for studying radiation and absorption processes under conditions of non-LTE (local thermodynamic equilibrium) in the upper stratosphere [1]. In these conditions, a large fraction of molecules are in highly excited states, because the number of collisions is insufficient for "thermalizing" the gas to the local thermodynamic temperature.

Therefore, there is a need to create high-temperature line lists of NO₂. To do this, the information on highly excited states of the molecule is required. Twenty years ago, using the method of laser-induced dispersed fluorescence spectroscopy in a supersonic jet, a full set of 191 low-lying vibrational states (up to 10161 cm⁻¹), belonging to the electron ground state $\tilde{X}^2 A_1$, was determined by A. Delon and R. Jost [23]. However, this investigation dealt only with vibrational energy levels. Consideration of the 0–8000 cm⁻¹ energy range has shown that the spin-rotational structure was studied only for a few vibrational states. Corresponding states and bands are shown in Table 1. These bands are often "perturbed" by "dark" bands. The information on the character of corresponding resonance interactions is also given in Table 1.

Our work is aimed at a global modeling of NO₂ line positions. This gives a possibility of calculating energy levels of this molecule in the 0-8000 cm⁻¹ wavenumber range, including the vibrational states which were not observed in infrared spectra. To do this, we used the method of effective operators, which was successfully applied to the global modeling of high-resolution spectra of linear molecules [26].

As far as we know, the global modeling of line positions of assymetric top molecules within the effective operator approach was conducted only in [27, 28] for two H₂S isotopologues. However, in these works, vibrational energies of each vibrational state were considered as independent parameters, which were fitted to experimental line centers together with other parameters. Therefore, the sets of parameters [27, 28] cannot be used for calculation of vibrational-rotational energy levels of the vibrational states not involved in the fitting. As for the NO_2 molecule, the global modeling of its energy levels was conducted in [29] by the MORBID method. For fitting parameters of their Hamiltonian, the authors of [29] used the set of vibrational energy levels up to 9500 cm⁻¹, found by the method of laser-induced fluorescence [23], together with a limited set of low-lying rotational energy levels ($N \le 5$) of vibrational states (0, 0, 0), (0, 1, (0), (1, 0, 0), (0, 2, 0), and (0, 0, 1). In [29], the spinrotation interaction was not considered. The application of the fitting to them resulted in sufficiently accurate potential energy surface along with parameters characterizing the equilibrium geometrical configuration of the molecule. However, the energy levels accuracy was insufficient for high-temperature applications described in the introduction. Thus, the standard deviation is 0.2984 cm⁻¹ for rotational energy levels and 2.20 cm^{-1} for vibrational energy levels.

1. EFFECTIVE HAMILTONIAN

We have performed the global modeling of NO₂ line positions in the spectral region 0.006–7916 cm⁻¹, using the polyade model of the effective Hamiltonian. Nitrogen dioxide is a nonlinear triatomic molecule of C_{2V} symmetry with three vibrational modes. Vibrational states are characterized by a set of three vibrational quantum numbers (v_1 , v_2 , v_3), relating to the symmetric stretch vibration $\omega_1 \approx 1316 \text{ cm}^{-1}$, symmetric bending vibration $\omega_2 \approx 750 \text{ cm}^{-1}$, and asymmetric stretch vibration $\omega_3 \approx 1633 \text{ cm}^{-1}$, respectively. Due to the approximate relation between harmonic frequencies $\omega_3 \approx \omega_1 \approx 2\omega_2$, vibrational energy levels are grouped into clusters (polyades), which can be numbered by $P = 2v_1 + v_2 + 2v_3$. Thus, it is possible to perform contact transformations, which reduce the initial vibrational-rotational Hamiltonian with accounting for the spin-rotation interaction to a block-diagonal form in the basis of eigenfunctions of harmonic oscillators. Each block is associated with a certain polyade *P*.

In the case of the NO₂ molecule, N is the operator of the rotational angular momentum, N and K are quantum numbers of the rotational angular momentum and its projection on the molecular-fixed axis z, respectively. Because the radical NO₂ has one unpaired electron with spin S ($S = \pm 1/2$), then the total angular momentum operator J is the sum of the rotational angular momentum and the unpaired electron spin $(J = N \pm 1/2, \text{ where})$ J is the quantum number of the total angular momentum). Due to interaction between the unpaired electron spin and the rotational angular momentum (spin-rotation interaction) each rotation energy level is split into two sublevels. The effective Hamiltonian used takes into account the spin-rotation interaction for each vibrational-rotational state, as well as a few intrapolyade resonance vibrational-rotational interactions. First and second order Coriolis resonances, which couple, correspondingly, the vibrational states $(v_1, v_2, v_3) \leftrightarrow (v_1 \pm 1, v_2, v_3)$ $v_2, v_3 \neq 1$) and $(v_1, v_2, v_3) \leftrightarrow (v_1, v_2 \neq 2, v_3 \pm 1)$, are among them. Perturbations caused by second order C-type Coriolis resonances were distinctly observed throughout all studies of NO₂ infrared bands [6, 8, 10– 18, 24, 30]. At the same time, the perturbation, caused by a first order Coriolis resonance was observed only for two pairs of vibrational states: $(1, 0, 0) \leftrightarrow (0, 0, 1)$ [6] and $(2, 1, 0) \leftrightarrow (1, 1, 1)$ [18].

The theoretical model of the Hamiltonian, proposed in this work, takes into account also Fermi and Darling-Dennison resonances. It is supposed that these resonances couple the vibrational states $(v_1, v_2, v_3) \leftrightarrow (v_1 \pm 1, v_2 \mp 2, v_3)$ and $(v_1, v_2, v_3) \leftrightarrow (v_1 \mp 2, v_2, v_3 \pm 2)$, respectively. These resonances have not been observed up to now in the explicit form; however, inclusion of them into the effective Hamiltonian increases the quality of the global fitting. Note that W.J. Lafferty and R.L. Sams [30] also took into account the Darling-Dennison resonance for fitting the vibrational parameters. Finally, the hyperfine splitting observable in microwave and far infrared spectral regions [3, 4] is ignored in this work.

Thus, the effective Hamiltonian used in the global fitting can be written as the sum of several operators

$$H^{\rm eff} = H_{VR} + H_{SR} + H_C + H_A, \tag{1}$$

LUKASHEVSKAYA et al.

Sourco	"Bright" state		Perononce type		D	"Dark" state		
Source	<i>v</i> ₁ , <i>v</i> ₂ , <i>v</i> ₃	energy, cm ⁻¹	Kesonance type		Г	<i>v</i> ₁ , <i>v</i> ₂ , <i>v</i> ₃	energy, cm ⁻¹	
[3, 5]	(0, 0, 0)*	0			0			
[4, 7]	(0, 1, 0)*	749.649			1			
	(1, 0, 0)*	1319.794	$C^{(1)}$	$(1, 0, 0) \leftrightarrow (0, 0, 1)$	2			
[6, 7]	(0, 2, 0)*	1498.34	<i>C</i> ⁽²⁾	$(0, 2, 0) \leftrightarrow (0, 0, 1)$	2			
	(0, 0, 1)*	1616.852			2			
[9]	(1, 1, 0)*	2063.118			3			
[8]	(0, 1, 1)*	2355.151	<i>C</i> ⁽²⁾	$(0, 3, 0) \leftrightarrow (0, 1, 1)$	3	(0, 3, 0)	2246.04	
[24]	(2, 0, 0)*	2627.337			4			
[11]	(1, 0, 1)*	2906.074	<i>C</i> ⁽²⁾	$(1, 2, 0) \leftrightarrow (1, 0, 1)$	4			
[10]	(0, 2, 1)*	3092.476	<i>C</i> ⁽²⁾	$(0, 4, 0) \leftrightarrow (0, 2, 1)$	4			
[10]	(0, 0, 2)*	3201.448	<i>C</i> ⁽²⁾	$(0, 2, 1) \leftrightarrow (0, 0, 2)$	4			
	(0, 4, 0)*	2992.78			4			
[18]	(1, 1, 1)*	3637.843	$C^{(1)}$	$(2, 1, 0) \leftrightarrow (1, 1, 1)$	5	(2, 1, 0)	3364.57	
			<i>C</i> ⁽²⁾	$(1,3,0) \leftrightarrow (1,1,1)$	5	(1, 3, 0)	3547.1	
[12]	(2, 0, 1)*	4179.938	<i>C</i> ⁽²⁾	$(2, 2, 0) \leftrightarrow (2, 0, 1)$	6	(2, 2, 0)	4100.58	
[12]	(0, 0, 3)*	4754.209	$C^{(2)}$	$(0, 2, 2) \leftrightarrow (0, 0, 3)$	6	(0, 2, 2)	4656.34	
[25]	(3, 0, 1)*	5437.54			8			
[12]	(1, 0, 3)*	5984.705	<i>C</i> ⁽²⁾	$(1, 2, 2) \leftrightarrow (1, 0, 3)$	8	(1, 2, 2)*	5898.94	
[13]			С—Х	$(0, 8, 0) \leftrightarrow (1, 0, 3)$	8	(0, 8, 0)	5965.61	
			Anh	$(0, 8, 0) \leftrightarrow (1, 2, 2)$	8			
[14]	(4, 0, 1)	6676.86	<i>C</i> ⁽²⁾	$(4, 2, 0) \leftrightarrow (4, 0, 1)$	10	(4, 2, 0)	6653.54	
[14]			С—Х	$(0, 9, 0) \leftrightarrow (4, 0, 1)$	$9 \leftrightarrow 10$	(0, 9, 0)	6705.23	
			Anh	$(4, 2, 0) \leftrightarrow (0, 9, 0)$	$9 \leftrightarrow 10$			
[17]	(2, 0, 3)*	7192.29	<i>C</i> ⁽²⁾	$(2, 2, 2) \leftrightarrow (2, 0, 3)$	10	(2, 2, 2)	7125.60	
[1/]			C–X	$(2, 0, 3) \leftrightarrow (5, 1, 0)$	$10 \leftrightarrow 11$	(5, 1, 0)	7193.35	
[15]	(0, 0, 5)*	7766.28	$C^{(2)}$	$(0, 2, 4) \leftrightarrow (0, 0, 5)$	10			
	(2, 5, 1)*	7791.18	<i>C</i> ⁽²⁾	$(2,7,0) \leftrightarrow (2,5,1)$	11	(2, 7, 0)	7757.29	
[16]	(2, 1, 3)*	7888.16	$C^{(2)}$	$(2, 3, 2) \leftrightarrow (2, 1, 3)$	11	(2, 3, 2)*	7834.97	
	(5, 0, 1)	7903.54	$C^{(2)}$	$(2, 3, 2) \leftrightarrow (2, 5, 1)$	11			
			<i>C</i> ⁽²⁾	$(5,2,0) \leftrightarrow (5,0,1)$	12	(5, 2, 0)	7909.46	
			C–X	$(2, 3, 2) \leftrightarrow (5, 0, 1)$	$11 \leftrightarrow 12$			
			$C - \overline{X}$	$(2, 5, 1) \leftrightarrow (\overline{5, 2, 0})$	$11 \leftrightarrow 12$			
			C - X	$(2,7,0) \leftrightarrow (5,0,1)$	$11 \leftrightarrow 12$			
			Anh	$(2, 5, 1) \leftrightarrow (5, 0, 1)$	$11 \leftrightarrow 12$			
			Anh	$(2, 5, 1) \leftrightarrow (2, 1, 3)$	11			
			Anh	$(2, 1, 3) \leftrightarrow (\overline{5, 0, 1})$	$11 \leftrightarrow \overline{12}$			

Table 1. List of NO₂ vibrational states in the region 0-8000 cm⁻¹ and vibrational-rotational resonance interactions

 $C^{(1)}$ is the first order C-type Coriolis resonance; $C^{(2)}$ is the second order C-type Coriolis resonance; C-X are the Coriolis resonances of higher orders; *Anh* are anharmonic resonances of high orders; *P* is a polyad number, $(P = 2v_1 + v_2 + 2v_3)$. For "dark" states, involved in the corresponding resonance [23], only vibrational energies are known (interpolyade resonance interactions are shown for polyades $P \ge 9$); asterisks mark vibrational states, vibrational-rotational energy levels of which are involved into the global fitting.

where H_{VR} and H_{SR} are the v-diagonal vibrational-rotational and electron spin-rotation interaction operators, respectively; H_C and H_A are the off diagonal in v operators of Coriolis resonance interactions and anharmonic interactions (Fermi or Darling–Dennison).

Matrix elements of the effective Hamiltonian written in the basis composed from products of eigenfunctions of harmonic oscillators $|v_1, v_2, v_3\rangle$ and of coupled eigenfunctions $(|NK\rangle \times |S\sigma\rangle)_M^J$ of the rigid symmetric top $|NK\rangle$ and spin $|S\sigma\rangle$ operators are determined in [31]. Here, σ and $M = K + \sigma$ are the quantum numbers of projections of the spin and total angular momentum on the molecular-fixed axis z. Since matrix elements are independent of the guantum number M, below we use simplified designations $|N K J\rangle$ (with $J = N \pm 1/2$) instead of $(|NK\rangle \times |S\sigma\rangle)_{M}^{J}$. In the designations $|N K J\rangle$ accepted for basis functions, all nonzero matrix elements of the effective Hamiltonian obey the selection rules $\Delta J = 0$ and $\Delta N = 0$. An exception is the H_{SR} operator, for which nonzero matrix elements with $\Delta N = \pm 1$ exist.

1.1. v-Diagonal Operators

As usually, the operators H_{VR} and H_{SR} , diagonal in v, are written for the NO₂ molecule in the I^r representation, and A-type reduction is used for both vibrational-rotational [32] and spin-rotation [33] Hamiltonians. Consequently, nonzero matrix elements for them exist only in the case where $\Delta K = 0, \pm 2$.

Vibrational-Rotational Matrix Elements $(\Delta K = 0, \pm 2 \text{ and } \Delta J = \Delta N = 0)$:

$$\langle v_{1} v_{2} v_{3} N K J | H_{VR} | v_{1} v_{2} v_{3} N K J \rangle$$

$$= E_{v} + \left[A^{v} - \frac{1}{2} (B^{v} + C^{v}) \right] K^{2} + \frac{1}{2} (B^{v} + C^{v}) N(N+1)$$

$$- \Delta_{K}^{v} K^{4} - \Delta_{NK}^{v} N(N+1) K^{2} - \Delta_{N}^{v} [N(N+1)]^{2}$$

$$+ H_{K}^{v} K^{6} + H_{KN}^{v} N(N+1) K^{4}$$

$$+ H_{NK}^{v} [N(N+1)]^{2} K^{2} + H_{N}^{v} [N(N+1)]^{3}$$

$$+ L_{K}^{v} K^{8} + L_{KKN}^{v} N(N+1) K^{6}$$

$$+ L_{NK}^{v} [N(N+1)]^{2} K^{4} + P_{K}^{v} P^{10} + Q_{K}^{v} P^{12},$$

$$(2)$$

$$\langle v_1 v_2 v_3 N K J | H_{VR} | v_1 v_2 v_3 N K \pm 2J \rangle$$

= $\sqrt{[N(N+1) - K(K\pm 1)][N(N+1) - (K\pm 1)(K\pm 2)]}$
× $\left\{ \frac{1}{4} (B^{\vee} - C^{\vee}) - \delta^{\vee}_N N(N+1) - \delta^{\vee}_K (K^2 + (K\pm 2)^2) + h^{\vee}_N [N(N+1)]^2 + h^{\vee}_{KN} N(N+1) (K^2 + (K\pm 2)^2) + h^{\vee}_K (K^4 + (K\pm 2)^4) \right\}.$ ⁽³⁾

Here E_v is the vibrational energy; A^v , B^v , and C^v are the rotational constants; Δ^v , δ^v , H^v , h^v , L^v , P^v , and Q^v are the centrifugal distortion constants.

Operator of Spin-Rotation Interaction

$$(\Delta K = 0, \pm 2, \Delta J = 0 \text{ and } \Delta N = 0, \pm 1)$$
:

+

$$\langle v_1 v_2 v_3 N K J | H_{SR} | v_1 v_2 v_3 N K J \rangle$$

$$= F(N,J) \left[\left(\frac{\varepsilon_{bb}^v + \varepsilon_{cc}^v}{2} \right) N(N+1) + \left(\varepsilon_{aa}^v - \frac{\varepsilon_{bb}^v + \varepsilon_{cc}^v}{2} \right) K^2 + {}^v \Delta_N^S \left[N(N+1) \right]^2 \right]^{(4)}$$

$$+ {}^v \Delta_{KN}^S N(N+1) K^2 + {}^v \Delta_K^S K^4 + {}^v H_K^S K^6 + {}^v L_K^S K^8 \right],$$

$$\langle v_1 v_2 v_3 N K J | H_{SR} | v_1 v_2 v_3 N K \pm 2J \rangle$$

= $F(N, J) \left(\frac{\varepsilon_{bb}^v - \varepsilon_{cc}^v}{4} \right)$ (5)

×
$$\sqrt{[N(N+1) - K(K\pm 1)][N(N+1) - (K\pm 1)(K\pm 2)]}$$
,

$$\left\langle v_{1} v_{2} v_{3} N K J \left| H_{SR} \right| v_{1} v_{2} v_{3} N \pm 1 K J \right\rangle$$

$$= -\frac{K}{2} \sqrt{\frac{\left(J + \frac{1}{2}\right)^{2} - K^{2}}{\left(J + \frac{1}{2}\right)^{2}}}$$

$$\left(\varepsilon_{aa}^{v} - \frac{\varepsilon_{bb}^{v} + \varepsilon_{cc}^{v}}{2} \right) + {}^{v} \Delta_{K}^{S} K^{2} + {}^{v} \Delta_{NK}^{S} \left(J + \frac{1}{2}\right)^{2} \right\},$$

$$(6)$$

$$\left\langle \nabla_{1} \nabla_{2} \nabla_{3} N K \left(J = N + \frac{1}{2} \right) \middle| H_{SR} \middle| \nabla_{1} \nabla_{2} \nabla_{3} N + 1 K \pm 2 \left(J = N + \frac{1}{2} \right) \right\rangle$$

$$= \pm \left(\frac{\varepsilon_{bb}^{\vee} - \varepsilon_{cc}^{\vee}}{8} \right) \sqrt{\frac{(N \pm K + 1)(N \pm K + 2)(N \pm K + 3)(N \mp K)}{(N + 1)^{2}}},$$

$$(7)$$

$$\left\langle v_{1} v_{2} v_{3} N K \left(J = N - \frac{1}{2} \right) \middle| H_{SR} \middle| v_{1} v_{2} v_{3} N + 1 K \pm 2 \left(J = N - \frac{1}{2} \right) \right\rangle$$

$$= \mp \left(\frac{\varepsilon_{bb}^{v} - \varepsilon_{cc}^{v}}{8} \right) \sqrt{\frac{(N \mp K - 2)(N \mp K - 1)(N \mp K)(N \pm K + 1)}{N^{2}}}.$$

$$(8)$$

In the above-written expressions, $F(N, J) = -\frac{1}{2N}$ for

$$J = N - \frac{1}{2}$$
 and $F(N, J) = \frac{1}{2(N+1)}$ for $J = N + \frac{1}{2}$; ε_{aa}^{\vee} ,

 $\varepsilon_{bb}^{v}, \varepsilon_{cc}^{v}, {}^{v}\Delta_{N}^{s}, {}^{v}\Delta_{KN}^{s}, {}^{v}\Delta_{NK}^{s}$ and ${}^{v}\Delta_{K}^{s}$ are the constants of the spin-rotation interaction. Within our global approach, the vibrational energy, rotational, centrifugal distortion, and spin-rotation constants, as well as constants of the Coriolis interaction are functions of vibrational quantum numbers. We use power series expansions for them. Thus, for example:

$$E_{v} = \sum_{i} \omega_{i} v_{i} + \sum_{i \ge j} x_{ij} v_{i} v_{j}$$

+
$$\sum_{i \ge j \ge k} y_{ijk} v_{i} v_{j} v_{k} + \sum_{i \ge j \ge k \ge l} z_{ijkl} v_{i} v_{j} v_{k} v_{l};$$
(9)

$$A^{\nabla} = A_0 - \sum_{i} \alpha_i^A \nabla_i + \sum_{i \ge j} \gamma_{ij}^A \nabla_i \nabla_j$$

+
$$\sum_{i \ge j \ge k} \chi_{ijk}^A \nabla_i \nabla_j \nabla_k + \sum_{i \ge j \ge k \ge l} \phi_{ijkl}^A \nabla_i \nabla_j \nabla_k \nabla_l;$$
(10)

$$\Delta_{K}^{v} = \Delta_{K} + \sum_{i} \beta_{i}^{\Delta_{K}} v_{i} + \sum_{i \ge j} \eta_{ij}^{\Delta_{K}} v_{i} v_{j} + \sum_{i \ge j \ge k} \tau_{ijk}^{\Delta_{K}} v_{i} v_{j} v_{k};$$

$$(11)$$

$$H_K^{\nabla} = H_K + \sum_i \delta_i^{H_K} \nabla_i; \qquad (12)$$

$$L_K^{\rm v} = L_K + \sum_i \kappa_i^{L_K} v_i; \tag{13}$$

$$\varepsilon_{aa}^{\vee} = \varepsilon_{aa} + \sum_{i} \zeta_{i}^{aa} v_{i} + \sum_{i \ge j} \xi_{ij}^{aa} v_{i} v_{j} + \sum_{i \ge j \ge k} \vartheta_{ijk}^{aa} v_{i} v_{j} v_{k}; (14)$$
$${}^{\vee} \Delta_{K}^{S} = \Delta_{K}^{S} + \sum_{i} \theta_{i}^{\Delta_{K}^{S}} v_{i}.$$
(15)

1.2. Operators Off Diagonal in v

For these operators we took into account only contributions that involve the N rotational angular momentum. This means that interactions considered between different vibrational states are independent of spin operator. Thus, $\Delta N = 0$ for all matrix elements off diagonal in v.

Operators of Resonance Coriolis Interactions

Due to the symmetry, matrix elements of these operators differ from zero only for odd ΔK . In this work, we take into account only matrix elements with $\Delta K = \pm 1$ and $\Delta K = \pm 3$.

First-order Coriolis resonances

$$\langle v_1 \, v_2 \, v_3 \, N \, K \, J \, \big| \, H_C^{(1)} \, \big| \, v_1 + 1 \, v_2 \, v_3 - 1 N \, K \pm 1 \, J \rangle$$

$$= \pm \sqrt{(v_1 + 1)v_3 \left[N \left(N + 1 \right) - K \left(K \pm 1 \right) \right]}$$

$$\times \left\{ C_0^{(1)} + C_1^{(1)} \left(v_1 + \frac{1}{2} \right) + C_2^{(1)} v_2$$

$$+ C_3^{(1)} \left(v_3 - \frac{1}{2} \right) + C_{11}^{(1)} \left(v_1 + \frac{1}{2} \right)^2$$

$$+ C_{12}^{(1)} \left(v_1 + \frac{1}{2} \right) v_2 + C_{13}^{(1)} \left(v_1 + \frac{1}{2} \right) \left(v_3 - \frac{1}{2} \right)$$

$$+ C_{22}^{(1)} v_2^2 + C_{23}^{(1)} v_2 \left(v_3 - \frac{1}{2} \right)$$

$$+ C_{33}^{(1)} \left(v_3 - \frac{1}{2} \right)^2 + C_N^{(1)} N (N + 1) + C_K^{(1)} \left(K + \left(K \pm 1 \right) \right) \right\},$$

$$(16)$$

$$\langle v_1 \, v_2 \, v_3 \, N \, K \, J \, \big| \, H_C^{(1)} \, \big| \, v_1 + 1 \, v_2 \, v_3 - 1N \, K \pm 3 \, J \rangle$$

= $\pm C_{\Delta}^{(1)} \left\{ (v_1 + 1) v_3 \big[N(N+1) - K(K \pm 1) \big]$
 $\times \big[N(N+1) - (K \pm 1)(K \pm 2) \big]$
 $\times \big[N(N+1) - (K \pm 2)(K \pm 3) \big] \right\}^{1/2} .$ (17)

Table 2.	Example of the block $P = 4$ of the effective Hamiltonian matrix for interacting vibrational states	(2, 0)	0, 0),	(1, 2,	, 0),
(0, 4, 0),	$(1, 0, 1), (0, 2, 1), and (0, 0, 2) of NO_2$ molecule				

P = 4	(2, 0, 0)	(1, 2, 0)	(0, 4, 0)	(1, 0, 1)	(0, 2, 1)	(0, 0, 2)
(2, 0, 0)	VR + SR	F		$C^{(1)}$		DD
(1, 2, 0)	F	VR + SR	F	$C^{(2)}$	$C^{(1)}$	
(0, 4, 0)		F	VR + SR		$C^{(2)}$	
(1, 0, 1)	$C^{(1)}$	$C^{(2)}$		VR + SR	F	$C^{(1)}$
(0, 2, 1)		$C^{(1)}$	$C^{(2)}$	F	VR + SR	$C^{(2)}$
(0, 0, 2)	DD			$C^{(1)}$	$C^{(2)}$	VR + SR

VR and *SR* are the vibrational-rotational and spin-rotation operators, respectively, for blocks diagonal in v. $C^{(1)}$, $C^{(2)}$, *F*, and *DD* are the first and second order Coriolis interaction operators and Fermi and Darling–Dennison interaction operators, respectively, in blocks non-diagonal in v.

Example of vibrational-rotational VR - and spin-rotation SR-blocks diagonal in v				Example of Coriolis interaction C or anharmonic interaction Anh (Fermi or Darling–Dennison) in blocks non-diagonal in v			
		(v_1, v_2, v_3)				(v ₁ , v	(v_2, v_3)
		$N = J - \frac{1}{2}$	$N = J + \frac{1}{2}$			$N = J - \frac{1}{2}$	$N = J + \frac{1}{2}$
()	$N = J - \frac{1}{2}$	VR + SR	SR		$N = J - \frac{1}{2}$	C and Anh	
(v_1, v_2, v_3)	$N = J + \frac{1}{2}$	SR	VR + SR	(v'_1, v'_2, v'_3)	$N = J + \frac{1}{2}$		C and Anh

Second-order Coriolis resonances

$$\langle v_{1} v_{2} v_{3} N K J | H_{C}^{(2)} | v_{1} v_{2} + 2 v_{3} - 1N K \pm 1 J \rangle$$

$$= \pm \sqrt{(v_{2} + 1)(v_{2} + 2)v_{3}[N(N + 1) - K(K \pm 1)]}$$

$$\times \left\{ C_{0}^{(2)} + C_{1}^{(2)}v_{1} + C_{2}^{(2)}(v_{2} + 1) + C_{3}^{(2)} \left(v_{3} - \frac{1}{2} \right)$$

$$+ C_{11}^{(2)}v_{1}^{2} + C_{12}^{(2)}v_{1}(v_{2} + 1) + C_{13}^{(2)}v_{1} \left(v_{3} - \frac{1}{2} \right)$$

$$+ C_{22}^{(2)}(v_{2} + 1)^{2} + C_{23}^{(2)}(v_{2} + 1) \left(v_{3} - \frac{1}{2} \right)$$

$$+ C_{33}^{(2)} \left(v_{3} - \frac{1}{2} \right)^{2} + C_{N}^{(2)}N(N + 1) + C_{K}^{(2)} \left(K + (K \pm 1) \right) \right\},$$

$$\langle v_{1} v_{2} v_{3} N K J | H_{C}^{(2)} | v_{1} v_{2} + 2 v_{3} - 1N K \pm 3 J \rangle$$

$$= \pm C_{\Delta}^{(2)} \left\{ (v_{2} + 1)(v_{2} + 2)v_{3} [N(N + 1) - K(K \pm 1)] \right\}$$

$$\times [N(N + 1) - (K \pm 1)(K \pm 2)]$$

$$\times [N(N + 1) - (K \pm 2)(K \pm 3)] \right\}^{1/2}.$$

$$(19)$$

Here $C_0^{(1)}$, $C_0^{(2)}$, $C_{\Delta}^{(1)}$, $C_{\Delta}^{(2)}$, $C_i^{(1)}$, $C_i^{(2)}$, $C_{ij}^{(1)}$, $C_{ij}^{(2)}$, $C_N^{(1)}$, $C_N^{(2)}$, $C_K^{(1)}$, and $C_K^{(2)}$ (*i*, *j* = 1,2,3) are the constants of the Coriolis interaction and parameters accounting their vibrational and rotational dependencies.

Operators of Anharmonic Resonance Interactions

Due to the symmetry, matrix elements of these operators differ from zero only for $\Delta J = \Delta N = 0$ and

even ΔK . We took into account only matrix elements with $\Delta K = 0$ for Fermi (F) and Darling–Dennison (DD) operators:

$$\begin{cases} \langle v_1 \, v_2 \, v_3 \, N \, K \, J \, \big| \, H_A \, \big| \, v_1 + 1 \, v_2 - 2 \, v_3 \, N \, K \, J \rangle \\ = \sqrt{(v_1 + 1)v_2(v_2 - 1)} \left\{ F_e + F_N N(N+1) + F_K K^2 \right\}, \end{cases}$$
(20)
$$\langle v_1 \, v_2 \, v_3 \, N \, K \, J \, \big| \, H_A \, \big| \, v_1 + 2 \, v_2 \, v_3 - 2N \, K \, J \rangle \\ = \sqrt{(v_1 + 1)(v_1 + 2)(v_3 - 1)v_3} \\ \times \left\{ D_e + D_N N(N+1) + D_K K^2 \right\}, \end{cases}$$
(21)

where F_e and D_e are the Fermi and Darling–Dennison constants; F_N , F_K , D_N , and D_K are the parameters that describe their rotation dependence. We could not find the pure vibrational constants F_e and D_e due to a strong correlation with diagonal vibrational parameters; they were fixed as zero. Parameters that describe their rotational dependence were well determined and decreased the dimensionless standard deviation of the fitting.

Figure 1 shows schematically the effective Hamiltonian matrix of a block-diagonal form. Because we take into account different perturbations (first and second order C-type Coriolis resonances, Fermi and Darling–Dennison resonances), each block, numbered by the integer P, involves vibrational states, quantum numbers of which satisfy the relation

$$P = 2v_1 + v_2 + 2v_3. \tag{22}$$

As an example, Table 2 shows in detail the submatrix that corresponds to the poliade P = 4, which con-



Fig. 1. The view of NO_2 matrix of the effective Hamiltonian. The structure of the block marked is shown in Table 2.

sists of six interacting vibrational states: (2, 0, 0), (1, 2, 0), (0, 4, 0), (1, 0, 1), (0, 2, 1), and (0, 0, 2). In this work, for fitting parameters of the effective Hamiltonian, we use transitions between vibrational states that belong to polyades from P = 0 up to P = 12.

2. LEAST-SQUARES FITTING

Parameters of the effective Hamiltonian were fitted to experimental line positions taken from [3-13, 15-18, 24, 25] by the least-squares method. We performed nonweighted fitting, aimed at minimization of the standard deviation

$$\chi = \sqrt{\frac{\sum_{i} (v_i^{\text{obs}} - v_i^{\text{calc}})^2}{N - n}},$$
(23)

where v_i^{obs} and v_i^{calc} are the experimental and calculated line positions; N is the number of involved line

centers; n is the number of parameters to be fitted. Input data are presented in Table 3.

Microwave transitions in the vibrational states (0, (0, 0) and (0, 1, 0) [3–5] were excluded from the fitting, because we ignored the hyperfine structure. It follows from Table 1 that bands $4v_1 + v_3$ [14], $5v_1 + v_3$ v_3 [16], $2v_1 + 3v_3$ [17], and $v_1 + 3v_3$ [13] are perturbed by interpolyade resonance interactions, neglected by our effective Hamiltonian. Moreover, starting from the poliade $P = 10 \ (E_v \ge 6000 \ \text{cm}^{-1})$, interpolyade resonance interactions become regular. These extra resonances lead to strong perturbations, for example, of such vibrational states as (2, 5, 1), (2, 1, 3), and (5, 0, 1) [16]. Since our effective Hamiltonian ignores interpolyade resonance interactions, lines of the bands $4v_1 + v_3$ and $5v_1 + v_3$ [vibrational states (4, 0, 1) and (5, 0, 1)] did not participate in the fitting. However, in order to retrieve as many vibration parameters as possible, bands $v_1 + 3v_3$,

Source	Type of spectrometer	Accuracy, 10^{-3} cm ⁻¹	$v_{min} - v_{max}$, cm ⁻¹	N _{fit}	RMS, 10^{-3} cm ⁻¹
Perrin et al. [3]	FTS	0.15	8-200	_	—
Perrin et al. [7]	FTS	0.4	720-920	205	24.91
Perrin et al. [4]	FTS	0.7	735-798	125	24.25
Perrin et al. [6]	FTS	0.2	1274-1689	7494	8.85
Perrin et al. [9]	FTS	0.8	1955-2256	2340	10.94
Perrin et al. [8]	FTS	0.2	2069-2392	1429	10.13
Cabana et al. [24]	Grating	5	2520-2775	870	25.33
Mandin et al. [11]	FTS	0.25	2876-2935	1228	11.17
Perrin et al. [10]	FTS	0.1	3043-3302	2143	15.47
Gueye et al. [18]	FTS	3	3594-3666	1608	26.40
Stephen et al. [12]	FTS	0.1	4112-4776	3347	7.21
Blank et al. [25]	Grating	3	5394-5454	401	37.79
Miljanic et al. [13]	FTS	0.4	5915-6001	1147	27.05
Raghunandan et al. [17]	FT-IBBCEAS	20	7128-7205	543	36.85
Mondelain et al. [15]	CRDS	1-2	7661-7780	929	23.71
Lukashevskaya et al. [16]	CDRS	1-2	7756-7915	1766	33.37

Table 3. Characteristics of input experimental data and statistics for the NO_2 global line positions fit

FTS is Fourier transform spectroscopy; Grating is grating spectroscopy; FT-IBBCEAS is high-resolution Fourier-transform cavityenhanced absorption spectroscopy in the near-infrared using an incoherent broad-band light source; CRDS is cavity ring-down spectroscopy; $v_{min} - v_{max}$ are the minimal and maximal wavenumbers in the given source; N_{fit} is the number of lines included in the fitting; RMS is the standard deviation of the global fitting for the given source. Microwave data from [3] are not included in the fitting, because the effective Hamiltonian model used does not consider the hyperfine structure of NO₂ lines.

 $2v_1 + v_2 + 3v_3$, $2v_1 + 3v_3$, and $2v_1 + 5v_2 + v_3$ were included into the fitting. Table 1 shows the vibrational states included in the fitting.

Thus, 195 parameters of the effective Hamiltonian were determined from the least-square fitting to 28016 line positions (14657 energy levels) of 25 vibrational bands. The standard deviation of the fit was 0.017 cm^{-1} . Table 3 shows the standard deviations for each experimental source used. The fitting results for each band are shown in Table 4, and the set of the effective Hamiltonian parameters, in Table 5. Residual between experimental and calculated line positions is shown in Fig. 2 as a function of the wavenumber, and in Fig. 3, as a function of the rotational quantum number *N*.



Fig. 2. Residual between experimental and calculated NO₂ line positions as a function of the wavenumber.



Fig. 3. Residual between experimental and calculated NO_2 line positions as a function of the rotation quantum number N.

Band	N _{fit}	N _{max}	K _{a max}	$RMS, 10^{-3} cm^{-1}$
(0, 0, 0) - (0, 0, 0)	2441	55	14	1.7
v_2	121	62	5	24.3
$v_2 - v_2$	4	25	7	50.0
ν_1	2476	56	15	7.3
$2v_2$	397	62	6	26.0
$2v_2 - v_2$	205	30	6	25.3
v_3	4621	81	15	6.3
$v_1 + v_2$	2340	61	10	10.9
$v_2 + v_3$	1429	60	8	10.1
$2v_1$	870	57	8	25.3
$2v_3$	1097	51	8	4.4
$v_1 + v_3$	1228	55	10	11.2
$2v_2 + v_3$	970	50	6	22.4
$4v_2$	76	27	5	9.1
$\nu_1+\nu_2+\nu_3$	1608	55	12	26.4
$3v_3$	1595	57	10	7.0
$2v_1 + v_3$	1752	55	11	7.4
$v_1 + 3v_3$	1087	47	8	27.2
$\nu_1 + 2\nu_2 + 2\nu_3$	60	34	5	23.4
$3v_1 + v_3$	401	35	5	37.8
5v ₃	929	47	9	23.7
$2\nu_1+\nu_2+3\nu_3$	1124	47	7	37.8
$2v_1 + 3v_2 + 2v_3$	14	24	4	43.7
$2\nu_1+5\nu_2+\nu_3$	628	30	6	23.2
$2v_1 + 3v_3$	543	42	7	36.9

Table 4. Band by band statistics describing the results of the global line positions fit

 N_{fit} is the number of lines of the given band, involved in the fitting; N_{max} is the maximal rotational quantum number N for a given band; $K_{a max}$ is the maximal rotational quantum number K_a for a given band.

When fitting, we used constants from [5] as initial values of parameters for the ground vibrational state. They were adapted to our computer program by fitting to the line positions of the transitions inside the ground vibrational state. Our fitted set of parameters is very close to the initial set [5]. During the further fitting, parameters for the ground vibrational state were fixed to the values obtained, while the parameters that describe their vibrational dependence and resonance interactions varied. The main problem was to fit the vibrational parameters. Our experience in modeling the CO₂ and N₂O line positions [34, 35] shows that it is necessary to use parameters of anharmonicity of the fourth order z_{ijkl} for gaining the line position calculation accuracy at a level of 0.001 cm⁻¹. In the case of NO₂, the existing experimental data are insufficient to find all these parameters. Therefore, firstly one set of vibrational parameters was varied, and then a part of them was fixed to the values obtained, and the additional vibrational parameters were varied.

Table 6 shows the comparison between our values of vibrational parameters found from the fitting and those from works [23, Table III] and [30]. It is seen that our values of ω_i (i = 1, 2, 3) and x_{ij} (i, j = 1, 2, 3) well agree with the values from [23, 30]. However, parameters y_{ijk} (i, j, k = 1, 2, 3) strongly differ for all three sources. One of the causes is the fact that our parameters are effective. We fitted more parameters as compared to the number of involved vibrational states. At the same time, parameter values strongly depend on the wavenumber range, where input vibrational energy levels are chosen (see, for example, two sets of parameters [37, Table VII]).

Table 7 shows our fitted values of the vibrationalrotational parameters α_i^A , γ_{ij}^A , and $\beta_i^{\Delta_K}$, as well as values from [30, 36, 37]. It is seen that our values agree better with the values from [30, 36].

There are several causes of the difference. First, it is connected with different input data sets to which the parameters have been fitted. For example, very exact wavenumbers from the infrared wavelength region published recently [12–18] were unknown at the time of publishing works [30, 36]. Second, vibrational-rotational parameters were found in [37] on the basis of the study of spectra of laser-induced fluorescence, which gave the information on vibrational states of the electronic ground state X^2A_1 up to 13900 cm⁻¹. At such energies, perturbations from the electron state A^2B_2 cannot be ignored. Moreover, laser-induced fluorescence spectra were recorded at a low resolution of \sim 0.5 cm⁻¹, and only lines with low rotational quantum number (N = 0, 1, 2, and 3) were observed, while the spin-rotation structure was not resolved in these spectra.

CONCLUSIONS

The polyade model of effective Hamiltonian globally describes NO_2 high-resolution spectra is suggested. A set of parameters of this Hamiltonian is found, which reproduces positions of spectral lines, involved into the fitting in the region 0.006–7916 cm⁻¹ at a standard deviation of 0.017 cm⁻¹. However, prediction capabilities of the set of parameters found are expected to be somewhat worse, because we failed to determine (due to the absence of experimental data)

Parameter	Value, cm ⁻¹	Order***	Parameter	Value, cm ⁻¹	Order***
		Vibrational	parameters		
ω_1	1325.67256(50)**		<i>y</i> ₁₃₃	3.9064(74)	_
ω_2	750.10483(20)		<i>Y</i> ₂₂₂	0.893(14)	10^{-2}
ω	1633.06607(30)		<i>Y</i> ₂₂₃	-0.1856(78)	10^{-1}
<i>x</i> ₁₁	-5.9129(53)		<i>Y</i> ₂₃₃	-0.7930(16)	_
<i>x</i> ₁₂	-6.0084(24)		<i>Y</i> ₃₃₃	0.441(13)	10^{-1}
<i>x</i> ₁₃	-31.8422(95)		z_{1111}	-0.3416(75)	10^{-1}
<i>x</i> ₂₂	-0.5041(14)		z ₁₁₁₂	-0.4536*	10^{-2}
<i>x</i> ₂₃	-10.4843(21)		z ₁₁₁₃	-0.430(44)*	10^{-1}
<i>x</i> ₃₃	-16.2741(32)		z ₁₁₂₃	-0.1429*	—
<i>Y</i> ₁₁₁	-0.02806*		<i>z</i> ₁₁₃₃	-0.9566(36)	10^{-1}
<i>Y</i> ₁₁₂	0.0521(35)		z ₁₂₂₂	0.2306(29)	10^{-1}
<i>Y</i> ₁₁₃	-1.664(13)		Z ₁₂₂₃	0.6313*	10^{-1}
<i>Y</i> ₁₂₂	-0.3201(27)		Z ₁₃₃₃	-0.8569(19)	_
<i>Y</i> ₁₂₃	-0.1998(17)		Z ₃₃₃₃	0.331(15)	10 ⁻²
	Diagona	al rotational and vibr	ational-rotational	parameters	
A_0	8.002335*	—	χ ^A ₁₂₃	0.3206(87)	10^{-2}
α_1^A	-0.8745(23)	10^{-1}	χ ^A ₁₃₃	-0.7796(41)	10^{-1}
α_2^A	-0.36309(18)	_	χ^A_{222}	-0.4964(57)	10^{-3}
α_3^A	0.23112(15)	_	χ^A_{223}	-0.899(19)	10^{-3}
γ_{11}^A	0.606(32)	10^{-2}	X ^A 333	0.386(59)	10^{-3}
γ_{12}^A	0.2929(21)	10^{-1}	χ ^A ₁₁₃	0.816(25)	10^{-2}
γ^{A}_{13}	0.3866(28)	10^{-1}	ϕ^A_{1333}	0.2021(10)	10^{-1}
γ^{A}_{22}	0.16500(73)	10^{-1}	ϕ^A_{1113}	-0.3085(87)	10^{-2}
γ^{A}_{23}	-0.4039(13)	10^{-1}	φ ^A ₃₃₃₃	0.418(65)	10^{-4}
γ^{A}_{33}	0.305(15)	10^{-2}	φ ^{<i>A</i>} ₁₁₃₃	0.431*	10^{-5}
χ^A_{111}	-0.213(11)	10^{-2}	ϕ^A_{1223}	0.5613*	10^{-4}
χ^A_{112}	-0.2147(25)	10^{-1}	ϕ^A_{1222}	-0.567(12)	10^{-3}
χ^A_{122}	0.998(12)	10^{-2}	ϕ^A_{1112}	0.4504(37)	10^{-2}
X233	0.1571(52)	10^{-1}	_	_	_
$(B_0+C_0)/2$	0.422076*	-	$\chi_{111}^{(B+C)/2}$	-0.1115(63)	10^{-4}
$\alpha_1^{(B+C)/2}$	0.23102(21)	10^{-2}	$\chi^{(B+C)/2}_{233}$	0.4054(80)	10^{-4}
$\alpha_2^{(B+C)/2}$	0.440(12)	10^{-3}	$\chi_{123}^{(B+C)/2}$	0.189(11)	10^{-4}
$\alpha_3^{(B+C)/2}$	0.28538(11)	10^{-2}	$\chi_{112}^{(B+C)/2}$	-0.739(67)	10^{-5}
$\gamma_{11}^{(B+C)/2}$	0.497(23)	10^{-4}	$\chi_{133}^{(B+C)/2}$	0.64(30)	10^{-6}

Table 5. (Contd.)

Parameter	Value, cm ⁻¹	Order***	Parameter	Value, cm ⁻¹	Order***
$\gamma_{12}^{(B+C)/2}$	-0.133*	10^{-7}	$\chi_{222}^{(B+C)/2}$	0.1039(53)	10 ⁻⁵
$\gamma_{13}^{(B+C)/2}$	-0.1084(19)	10^{-3}	$\chi_{113}^{(B+C)/2}$	0.1402(52)	10^{-4}
$\gamma_{23}^{(B+C)/2}$	-0.583(16)	10^{-4}	$\chi_{223}^{(B+C)/2}$	0.988*	10^{-6}
$\gamma_{22}^{(B+C)/2}$	-0.179*	10^{-5}	$\chi^{(B+C)/2}_{333}$	0.2268(88)	10^{-5}
$\gamma_{33}^{(B+C)/2}$	-0.2552(82)	10^{-4}	-	_	_
$(B_0 - C_0)/4$	0.58164*	10^{-2}	$\gamma_{12}^{(B-C)/4}$	-0.1307(78)	10^{-4}
$\alpha_1^{(B-C)/4}$	-0.91(13)	10^{-5}	$\gamma_{13}^{(B-C)/4}$	0.254(12)	10^{-4}
$\alpha_2^{(B-C)/4}$	-0.1745(13)	10^{-3}	$\gamma_{22}^{(B-C)/4}$	0.1712(41)	10^{-4}
$\alpha_3^{(B-C)/4}$	-0.6569(66)	10 ⁻⁴	$\gamma_{23}^{(B-C)/4}$	0.9383*	10^{-7}
$\gamma_{11}^{(B-C)/4}$	-0.2212(59)	—	$\gamma_{33}^{(B-C)/4}$	0.631(45)	10^{-5}
Δ_K	0.268621*	10^{-2}	$\eta_{23}^{\Delta_K}$	-0.1721(21)	10^{-3}
$\beta_1^{\Delta_K}$	0.1255(21)	10^{-3}	$\eta_{33}^{\Delta_K}$	0.1249(12)	10^{-4}
$\beta_2^{\Delta_K}$	0.9584(33)	10^{-3}	$ au_{111}^{\Delta_K}$	-0.2334(39)	10^{-4}
$\beta_3^{\Delta_K}$	-0.17019(95)	10^{-3}	$ au_{113}^{\Delta_K}$	-0.964(74)	10^{-5}
$\eta_{11}^{\Delta_K}$	0.663(17)	10^{-4}	$ au_{123}^{\Delta_K}$	0.1365(18)	10^{-3}
$\eta_{12}^{\Delta_K}$	-0.879(36)	10^{-4}	$ au_{133}^{\Delta_K}$	0.1327(30)	10^{-4}
$\eta_{13}^{\Delta_K}$	-0.509(11)	10^{-4}	$ au_{112}^{\Delta_K}$	0.5915(82)	10^{-4}
$\eta_{22}^{\Delta_K}$	0.228(11)	10^{-4}	$ au_{122}^{\Delta_K}$	0.4123(61)	10^{-4}
Δ_{KN}	-0.19673*	10^{-4}	$\eta_{12}^{\Delta_{KN}}$	-0.752(33)	10^{-6}
$eta_1^{\Delta_{KN}}$	-0.291*	10 ⁻⁸	$\eta_{13}^{\Delta_{KN}}$	-0.1524(19)	10^{-5}
$eta_2^{\Delta_{KN}}$	0.341(42)	10 ⁻⁶	$\eta_{23}^{\Delta_{KN}}$	-0.2481(39)	10^{-5}
$eta_3^{\Delta_{K\!N}}$	0.272*	10 ⁻⁹	$\eta_{33}^{\Delta_{KN}}$	0.686(72)	10^{-7}
$\eta_{11}^{\Delta_{\mathit{KN}}}$	0.234*	10^{-7}	-	_	_
Δ_N	0.30186*	10 ⁻⁶	$eta_2^{\Delta_N}$	0.789*	10^{-10}
$eta_1^{\Delta_N}$	0.225(29)	10 ⁻⁸	$eta_3^{\Delta_N}$	0.761(14)	10^{-8}
δ_K	0.20000*	10^{-5}	$\eta_{12}^{\delta_K}$	0.36(24)	10^{-6}
$\beta_1^{\delta_K}$	0.981(18)	10^{-5}	$\eta_{13}^{\delta_K}$	0.144*	10 ⁻⁶
$\beta_2^{\delta_K}$	-0.392(29)	10^{-5}	$\eta_{22}^{\delta_K}$	0.1988(97)	10^{-5}
$\beta_3^{\delta_K}$	-0.699(66)	10 ⁻⁶	$\eta_{23}^{\delta_K}$	0.231(21)	10^{-5}
$\eta_{11}^{\delta_K}$	-0.448(10)	10^{-5}	-	—	_
δ_N	0.321387*	10^{-7}	$\beta_2^{\delta_N}$	-0.593(40)	10^{-8}
$\beta_1^{\delta_N}$	0.175(31)	10 ⁻⁸	$\beta_3^{\delta_N}$	0.196(11)	10^{-8}
H_K	0.29803*	10^{-5}	$\delta_3^{H_K}$	-0.2217(67)	10^{-6}

Table 5.	(Contd.)
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Parameter	Value, cm ⁻¹	Order***	Parameter	Value, cm ⁻¹	Order***
$\delta_1^{H_K}$	0.3516(94)	10 ⁻⁶	$\delta_{33}^{H_K}$	0.2548*	10 ⁻⁷
$\delta_2^{H_K}$	0.3419(44)	10^{-5}	_	_	_
$\tilde{H_{KN}}$	-0.26169*	10^{-7}	H_{NK}	0.15155*	10^{-10}
H_N	0.112398*	10^{-11}	-	—	_
h_K	0.146485*	10^{-7}	$\delta_2^{h_K}$	-0.496(29)	10^{-7}
$\delta_1^{h_K}$	0.1415*	10 ⁻⁹	$\delta_3^{H_K}$	-0.1032(39)	10^{-7}
h_{KN}	-0.18185*	10^{-10}	h_N	0.24629*	10^{-12}
L_K	-0.453462*	10 ⁻⁸	$\kappa_2^{L_K}$	-0.806(18)	10^{-8}
$\kappa_1^{L_K}$	-0.441(24)	10 ⁻⁹	$\kappa_3^{L_K}$	0.131(17)	10^{-9}
L_{KKN}	0.301464*	10^{-10}	L_{KN}	0.138*	10^{-12}
P_K	0.59773*	10^{-11}	Q_K	-0.391667*	10^{-14}
		Parameters of spin	-rotation resonanc	e	
Eaa	0.180455*	_	ξ_{33}^{aa}	-0.1633*	10^{-4}
ζ_1^{aa}	0.1421(92)	10^{-1}	$artheta_{111}^{aa}$	0.54(17)	10^{-3}
ζ_2^{aa}	0.2345(83)	10^{-1}	ϑ^{aa}_{112}	-0.323(15)	10^{-2}
ζ_3^{aa}	-0.766(15)	10^{-2}	ϑ^{aa}_{113}	0.757(35)	10^{-2}
ξ_{11}^{aa}	-0.126(10)	10^{-1}	ϑ^{aa}_{122}	0.191(14)	10^{-2}
ξ_{13}^{aa}	-0.391(61)	10^{-2}	ϑ^{aa}_{222}	0.147*	10^{-3}
ξ_{22}^{aa}	-0.113(30)	10^{-2}	ϑ^{aa}_{223}	0.895*	10^{-3}
ξ_{23}^{aa}	-0.619(43)	10^{-2}	ϑ_{133}^{aa}	-0.165(18)	10^{-2}
$(\varepsilon_{bb} + \varepsilon_{cc})/2$	-0.13805*	10 ⁻²	$\zeta_2^{(\varepsilon_{bb}+\varepsilon_{cc})/2}$	-0.87(11)	10^{-4}
$\zeta_{1}^{(\varepsilon_{bb}+\varepsilon_{cc})/2}$	-0.379(95)	10 ⁻⁴	$\zeta_3^{(\varepsilon_{bb}+\varepsilon_{cc})/2}$	0.152(58)	10^{-4}
$(\varepsilon_{bb} - \varepsilon_{cc})/4$	0.853*	10 ⁻³	_	_	_
Δ^S_K	-0.175978*	10^{-3}	$\theta_3^{\Delta_K^S}$	0.80(16)	10^{-5}
$\theta_2^{\Delta_K^S}$	-0.652(82)	10^{-4}	_	_	_
Δ_{KN}^{S}	-0.904581*	10^{-5}	H_K^S	0.309577*	10^{-6}
L_K^S	-0.397732*	10 ⁻⁹	_	—	_
Parameters of	of the matrix element $\langle \tau$	$v_1 v_2 v_3 NK H_C v_1 +$	$+1v_2v_3 - 1NK \pm 1$) of the Coriolis resonar	ice interaction
$C_{e}^{(1)}$	0.167315*		$C_{3}^{(1)}$	0.1382(29)	10^{-1}
$C_{1}^{(1)}$	-0.572(14)	10^{-2}	$C_K^{(1)}$	0.3155*	10 ⁻³
$C_{2}^{(1)}$	-0.362(45)	10^{-2}	_	-	_
Parameter o	f the matrix element $\langle v$	$v_1 v_2 v_3 NK H_C v_1 +$	$-1v_2v_3 - 1NK \pm 3$	s angle of the Coriolis resonan	ce interaction
$C^{(1)}_{\Lambda}$	-0.20625*	10 ⁻⁶			
- 4	1		11	<u> </u>	L

Parameter	Value, cm ⁻¹	Order***	Parameter	Value, cm ⁻¹	Order***			
Paramete	Parameters of the matrix element $\langle v_1 v_2 v_3 NK H_C v_1 v_2 + 2 v_3 - 1 NK \pm 1 \rangle$ of the Coriolis resonance interaction							
$C_{e}^{(2)}$	0.15297*	10 ⁻¹	$C_{133}^{(2)}$	-0.2349(71)	10^{-3}			
$C_{1}^{(2)}$	0.286*	10^{-4}	$C_{111}^{(2)}$	-0.103(10)	10^{-3}			
$C_{3}^{(2)}$	-0.554(22)	10^{-3}	$C^{(2)}_{333}$	0.625(16)	10^{-4}			
$C_{12}^{(2)}$	0.1959(96)	10 ⁻³	$C_{N}^{(2)}$	-0.2154*	10^{-6}			
$C_{13}^{(2)}$	0.1059*	10^{-4}	$C_{K}^{(2)}$	-0.6652*	10^{-4}			
$C_{22}^{(2)}$	-0.1525(22)	10 ⁻³	-	—	_			
Paramete	er of the matrix element \langle_V	$v_1 v_2 v_3 NK H_C v_1 v$	$v_2 + 2v_3 - 1NK \pm 3$	angle of the Coriolis resonan	ce interaction			
$C^{(2)}_{\Delta}$	0.424*	10 ⁻⁷	-	-	—			
Parameter of the matrix element $\langle v_1 v_2 v_3 NK H_C v_1 + 2 v_2 v_3 - 2NK \rangle$ of the Darling–Dennison resonance interaction								
D_K	0.30951*	10 ⁻¹	-	—	—			
Parameter of matrix element $\langle v_1 v_2 v_3 NK H_C v_1 + 1 v_2 - 2 v_3 NK \rangle$ of the Fermi resonance interaction								
F_N	0.1484*	10 ⁻³	-	_				

Table 5. (Contd.)

* The value is fixed at the final stage of the fitting.

** The numbers in parentheses correspond to one standard deviation in units of the last quoted digit.

*** Order of magnitude of the parameter.

Parameter, cm ⁻¹	This work	Lafferty et al. [30]	Delon and Jost [23]**
ω_1	1325.67256(50)***	1325.325(55)	1325.456
ω_2	750.10483(20)	750.141(22)	749.954
ω_3	1633.06607(30)	1633.860(51)	1633.108
x_{11}	-5.9129(53)	-5.471(32)	-5.864
<i>x</i> ₁₂	-6.0084(24)	-6.433(23)	-5.787
x_{13}	-31.8422(95)	-29.549(52)	-28.661
<i>x</i> ₂₂	-0.5041(14)	-0.469(15)	-0.335
x_{23}	-10.4843(21)	-11.399(20)	-11.205
x_{33}	-16.2741(32)	-17.062(51)	-16.295
<i>y</i> ₁₁₁	-0.02806*	-	0.0405
<i>Y</i> ₁₁₂	0.0521(35)	-	-0.08345
<i>Y</i> ₁₁₃	-1.664(13)	-	-1.97265
<i>Y</i> ₁₂₂	-0.3201(27)	-	-0.1263
<i>Y</i> ₁₃₃	3.9064(74)	-1.146(31)	0.35835
<i>Y</i> ₂₂₂	0.00893(14)	-	-0.02341
<i>Y</i> ₂₃₃	-0.7930(16)	-	-0.09965
<i>Y</i> ₃₃₃	0.0441(13)	0.068(11)	0.1585

Table 6. Comparison of vibrational parameters found in this work and in [23, 30]

* Parameter is fixed at the final stage of the fitting.

** Recalculated values. In [23], the expansion for vibrational energy in powers of $(v_i + 1/2)$ (i = 1, 2, 3) was used instead of v_i , while the expansion in powers of v_1 is used in this work and in [30].

*** The confidence interval (1 SD in units of the last quoted digit).

Parameter, cm ⁻¹	This work	Lafferty et al. [30]	Morino et al. [36]***	Kirmse et al. [37]**
A_0	8.002335	8.0023657(65)	8.00235	8.002
$lpha_1^{\mathcal{A}}$	-0.08745(23)*	-0.0835(22)	-0.09118	-0.09123
α_2^A	-0.36309(18)	-0.3577(18)	-0.35542	-0.3294
α_3^A	0.23112(15)	0.2313(15)	0.23249	0.22238
γ^{A}_{11}	0.00606(32)	0.0038(11)	-0.00006	_
γ_{12}^A	0.02929(21)	0.0309(15)	0.02533	-0.02559
γ^{A}_{13}	0.03866(28)	-0.0140(13)	-0.01182	0.02756
γ^{A}_{22}	0.016500(73)	0.01433(71)	0.01631	0.04099
γ^{A}_{23}	-0.04039(13)	-0.0203(16)	-0.02014	0.01806
γ^{A}_{33}	0.00305(15)	0.00374(75)	0.00433	_
$(B_0 + C_0)/2$	0.422077	0.42207665(160)	0.422074	0.42194
$\alpha_1^{(B+C)/2}$	0.0023102(21)	0.00245(12)	0.00247	0.00252
$lpha_2^{(B+C)/2}$	0.000440(12)	0.000482(11)	0.000460	0.00011
$\alpha_3^{(B+C)/2}$	0.0028538(11)	0.002707(12)	0.00264	0.00264
$eta_1^{\Delta_K}$	0.0001255(21)	0.000209	_	—
$eta_2^{\Delta_K}$	0.0009584(33)	0.000866	_	_
$\beta_3^{\Delta_K}$	-0.00017019(95)	-0.000234	_	—

Table 7. Comparison of vibrational-rotational parameters found in this work and in [23, 30]

* The confidence interval (1 SD in units of the last quoted digit).

** We have corrected the wrong signs for the parameters $\alpha_i^{(B+C)/2}$ (*i* = 1, 2, 3) in the work [37, Table II].

*** Recalculated values. In [36], the expansion in powers of $(v_i + 1/2)$ (i = 1, 2, 3) was used, while the expansion in powers of v_i is used in this work and in [30, 37].

several important vibrational parameters z_{ijkl} . Moreover, the polyade model of the effective Hamiltonian used does not take into account the interpolyad resonance Coriolis and anharmonic interactions [13, 14, 16, 17] (see Table 1). However, the accuracy provided by predictions with the found set of the effective Hamiltonian parameters satisfies many applications: for example, to study hot spectra and violations of the local thermodynamic equilibrium, a resolution of approximately 0.20 cm⁻¹ is required, which allows the use of the predicted line positions with the found set of parameters of the effective Hamiltonian.

In the future we plan to find parameters of the NO_2 effective dipole moment through fitting them to experimental values of line intensities and, finally, generate a list of NO_2 line positions and intensities for high-temperature applications.

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