GLOBAL TREATMENT OF THE MICROWAVE, INFRARED AND VISIBLE SPECTRA OF THE CO_2 AND N_2O LINEAR MOLECULES IN THE FRAMEWORK OF THE EFFECTIVE OPERATOR METHOD

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The method of the effective operators is applied to the global treatment of the vibrational–rotational spectra of the linear CO_2 *and* N_2O *triatomic molecules. The problems in calculations of the line centers and the line intensities are considered. For these purposes the models of the reduced effective Hamiltonians and the corresponding effective dipole moment operators are proposed. The parameters of these operators are found by the least–square fittings of the experimental line centers and line intensities. Good extrapolation properties of the proposed models are demonstrated.*

1. INTRODUCTION

In recent years there is observed growing interest in the problem of the global description of the vibrational–rotational spectra of the triatomic molecules, caused by the transitions between the levels of the ground electronic state, (see, for example, Refs. 1–20). The interest in this problem is stimulated by the circumstances, that the models, describing globally the vibrational–rotational molecular spectra in the ground electronic state, can be used to obtain new spectroscopic information on the transitions between the high–excited vibrational–rotational states, using the experimental spectroscopic information on the transitions between the low–excited vibrational–rotational states. Such an opportunity is widely used in the problem of high–temperature spectra of molecules.

At present two approaches are discussed in the literature to the global description of the vibrational–rotational spectra of molecules. The first approach is based on the determination of the potential field and the dipole moment function of a molecule from experimental spectra. The second approach is based on the method of effective operators. In the framework of the latter approach one constructs an effective Hamiltonian and the corresponding effective dipole moment operator and reconstructs the parameters of these effective operators from the experimental spectra.

Several methods are developed in the framework of the former approach. First, we draw attention to the so-called variation methods: the DVR method (the method of exact representation of the kinetic energy operator, Refs. 1–4), the MORBID method (the representation of the coordinates as Morse functions, Refs. 5–7), the DND method (the direct numerical diagonalization, Refs. 10, 21–23). Among these methods the DVR method is potentially the most accurate method, since it does not use any approximations for the kinetic energy operator. But it is very cumbersome for calculations. The MORBID method, within which the approximations for the kinetic energy operator are used, is more useful for calculations. Therefore, in papers[8, 9] a combination of these two methods was used for calculations of the vibrational–rotational energy levels of H_2O and H_2S molecules. Finally, the DND method assumes in the direct numerical diagonalization of the matrix of the vibrational–rotational Hamiltonian in the basis of the harmonic oscillators and rigid symmetric top eigenfunctions. This method uses the power series expansions over normal coordinates of the potential function and the inverse inertia tensor, which appears in the expressions for the kinetic energy, and dipole moment function. This method was successfully used by Wattson and Rothman[10] for the global treatment of line centers as well line intensities of CO_2 molecule.

In the method, which was used by Chedin[11] and Chedin–Teffo[12] for the global treatment of energy levels of CO_2 molecule and Teffo–Chedin[13] for the global treatment of energy levels of N_2O molecule, the vibrational–rotational Hamiltonian of the molecule was preliminarily subjected to the contact transformations. Transformed Hamiltonian has the block–diagonal form, that allows one to easily find the eigenvalues, by performing the diagonalization of each block separately. To simplify the calculations

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Chedin[11] has developed special computer codes for constructing an intermediate effective Hamiltonian. These computer codes enable one to establish analytical relations between the parameters of the effective Hamiltonian and the molecular constants, which characterize the geometry and the force field of the molecule.

All the above–mentioned methods require significant computer resources both in operative memory, operative rate. The approach, based on the determination of the molecular potential function, is intended for simultaneous description of all isotopic modifications of a molecule. On the one hand, it is its advantage as compared to the effective operator method, since in this case it is possible to calculate the spectra of one isotopic modification of the molecule using the experimental information about other isotopic modifications. On the other hand, such an approach limits the calculation accuracy of the line centers by the value $\lambda = \sqrt{2\,\bar{B}/\bar{\omega}}$, because of the neglect of the adiabatic corrections and nonadiabatic effect. Here $\bar{B}$ and $\bar{\omega}$ are the average values of the rotational constants and the harmonic frequencies of the molecule.

In the second approach, which is used in this paper, one proceeds directly from the effective Hamiltonian, which globally describes all vibrational–rotational energy levels of the ground electronic state and takes into account all resonance interactions in an explicit form. Such an effective Hamiltonian as a power series over the elementary vibrational and rotational operators can be constructed *a priori* by the methods of the group theory without very complicated analytical calculations within any method of the perturbation theory. The effective Hamiltonian parameters and parameters of the corresponding effective dipole moment operator are not already the expansion coefficients of the potential function and dipole moment function. The experimental data are directly fitted to these parameters. The form of the operator expansion for the effective Hamiltonian and for the effective dipole moment operator depends on the zero–order approximation used. In this paper the operator of the harmonic oscillators energy is used as the zero–order approximation. It results in a power series for the effective Hamiltonian and the effective dipole moment operator. The requirement to the effective Hamiltonian to be block–diagonal relative to polyads of the interacting vibrational states, as we have already mentioned, considerably simplifies the calculations. This circumstance enabled us to implement the discussed approach for the CO_2 and N_2O molecules on a personal computer with the Pentium processor. As known, the adiabatic and nonadiabatic corrections have the same functional dependence on the vibrational and rotational operators, as that of the principal contributions to the vibrational–rotational Hamiltonian. Hence, the corrections can be taken into account by the effective Hamiltonian parameters. Therefore, the fitting of the effective Hamiltonian parameters gives much better agreement between the experimental and calculated values, than the fitting of the experimental data on various isotopic modifications to the parameters of a molecular force field.

2. LINE CENTERS

The CO_2 molecule

The following approximate relations between the frequencies of normal vibrations of a CO_2 molecule are valid:

$$\omega_1 \approx 2\omega_2,\ \omega_3 \approx 3\omega_2 \tag{1}$$

Owing to these relations the vibrational energy levels make up polyads, which can be numbered using the parameter

$$P = 2v_1 + v_2 + 3v_3, \tag{2}$$

where v_1, v_2, and v_3 are the vibrational quantum numbers.

The effective Hamiltonian taken in the form involving the fourth order terms in Amat–Nielsen ordering scheme, which describes globally all the vibrational–rotational energy levels in the ground electronic state and takes into account, in an explicit form, the resonance interactions has been proposed by Chedin[11] and used by Chedin[11] and Chedin and Teffo[12] as an intermediate operator for fitting the experimental values of the spectroscopic constants G_v, B_v, and D_v to the anharmonic force field of the molecule. In our paper, Ref. 14, we added to this Hamiltonian all terms, allowed by the symmetry, up to the fourth order. This Hamiltonian has been reduced with the help of the unitary transformations.

The effective Hamiltonian can be presented by its matrix elements in the basis of eigenfunctions of harmonic oscillators and a rigid symmetric top:

$$|v_1\, v_2\, \ell_2\, v_3\, J> = |v_1\, v_2\, \ell_2\, v_3>|JK = \ell_2>. \tag{3}$$

In the expression (3) the Hougen[24] condition $K = \ell_2$ is used.

The diagonal matrix elements are

$$< v_1\, v_2\, \ell_2\, v_3\, J\ |\mathbf{H}^{\mathrm{ef}}|\, v_1\, v_2\, \ell_2\, v_3\, J > = \sum_i \omega_i \left(v_i + \frac{g_i}{2}\right) + \sum_{ij} x_{ij} \left(v_i + \frac{g_i}{2}\right)\left(v_j + \frac{g_j}{2}\right) +$$

$$+ x_{\ell\ell}\, \ell_2^2 + \sum_{ijk} y_{ijk} \left(v_i + \frac{g_i}{2}\right)\left(v_j + \frac{g_j}{2}\right)\left(v_k + \frac{g_k}{2}\right) + \sum_i y_{i\ell\ell} \left(v_i + \frac{g_i}{2}\right) \ell_2^2 +$$

$$+ \left\{B_e - \sum_i \alpha_i \left(v_i + \frac{g_i}{2}\right) + \sum_{ij} \gamma_{ij} \left(v_i + \frac{g_i}{2}\right)\left(v_j + \frac{g_j}{2}\right) + \gamma_{\ell\ell}\, \ell_2^2\right\} [J\,(J+1) - \ell_2^2] -$$

$$- \left\{D_e + \sum_i \beta_i \left(v_i + \frac{g_i}{2}\right)\right\} [J\,(J+1) - \ell_2^2]^2 + H_e\, [J\,(J+1) - \ell_2^2]^3 . \tag{4}$$

The matrix element of the ℓ–type doubling is

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathrm{H}^{\mathrm{ef}}|\, v_1\, v_2\, \ell_2 \pm 2\, v_3\, J > = \sqrt{(v_2 \pm \ell_2 + 2)\,(v_2 \mp \ell_2)}\, \times$$

$$\times \sqrt{[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)]\,[J\,(J+1) - (\ell_2 \pm 1)\,(\ell_2 \pm 2)]}\, \left\{L_e + \sum_i L_i \left(v_i + \frac{g_i}{2}\right) + L_J\, J\,(J+1) + L_K (\ell_2 \pm 1)^2\right\} . \tag{5}$$

The matrix elements of the Fermi–interaction operators are

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1 - 1 v_2 + 2\, \ell_2\, v_3\, J > =$$

$$= \sqrt{v_1\,(v_2 + \ell_2 + 2)\,(v_2 - \ell_2 + 2)}\, \left\{F_e + \sum_i F_i \left(v_i + \frac{\Delta v_i + g_i}{2}\right) + F_J\, [J\,(J+1) - \ell_2^2]\right\}, \tag{6}$$

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1 - 2\, v_2 + 4\, \ell_2\, v_3\, J >= F^{\mathrm{IV}} \sqrt{v_1\,(v_1 - 1)\,(v_2 + \ell_2 + 2)\,(v_2 + \ell_2 + 4)\,(v_2 - \ell_2 + 2)\,(v_2 - \ell_2 + 4)}. \tag{7}$$

The Fermi + ℓ–type interaction matrix element is

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1 - 1\, v_2 + 2\, \ell_2 \pm 2\, v_3\, J > =$$

$$= \sqrt{v_1\,(v_2 \pm \ell_2 + 2)}\, \sqrt{(v_2 \pm \ell_2 + 4)\,[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)]\,[J\,(J+1) - (\ell_2 \pm 1)\,(\ell_2 \pm 2)]}\, \{F^L \pm F^L_\ell\,(\ell_2 \pm 1)\}. \tag{8}$$

The matrix elements of the resonance Coriolis interaction operators are

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1 - 1\, v_2 - 1\, \ell_2 \pm 1\, v_3 + 1\, J > = \sqrt{v_1\,(v_2 \mp \ell_2)\,(v_3 + 1)\,[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)]}\, \times$$

$$\times \left\{C_e \pm C_\ell \left(\ell_2 \pm \frac{1}{2}\right) + \sum_i C_i \left(v_i + \frac{\Delta v_i + g_i}{2}\right) + C_J\, J\,(J+1) + C_K \left[\ell_2\,(\ell_2 \pm 1) + \frac{1}{2}\right]\right\} ; \tag{9}$$

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1\, v_2 - 3\, \ell_2 \pm 1\, v_3 + 1\, J > =$$

$$= - \sqrt{(v_3 + 1)\,(v_2^2 - \ell_2^2)}\, \sqrt{(v_2 \mp \ell_2 - 2)\,[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)]}\, \left\{C_{e1} \pm C_{\ell 1} \left(\ell_2 \pm \frac{1}{2}\right)\right\} ; \tag{10}$$

$$< v_1\, v_2\, \ell_2\, v_3\, J\, |\mathbf{H}^{\mathrm{ef}}|\, v_1 + 2\, v_2 - 1\, \ell_2 \pm 1\, v_3 - 1\, J > =$$

$$= - \sqrt{v_3\,(v_1 + 1)}\, \sqrt{(v_1 + 2)(v_2 \mp \ell_2)\,[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)]}\, \left\{C_{e2} \pm C_{\ell 2} \left(\ell_2 \pm \frac{1}{2}\right)\right\} . \tag{11}$$

The choice of the phases of rotational wave functions is made so that the matrix elements of the operator J_x in the molecule–fixed frame are real and positive, and the choice of phases of vibrational wave functions is made so, that eigenfunctions of the double degenerate oscillator under reflection in the *yz* plane of a molecule–fixed frame are transformed as follows:

$$\sigma_{yz} |v_2\, \ell_2 > = |v_2 - \ell_2 >. \tag{12}$$

Here z is the symmetry axis of the molecule, while the degenerate normal coordinates q_{2a} and q_{2b} are oriented along x– and y–axes, respectively. The choice of the wave function phases is considered in our paper, Ref. 25 in a more detail.

In our paper, Ref. 14, it is shown that the effective Hamiltonian, presented by the matrix elements, Eq. (4)–(11), is ambiguous. This ambiguity is connected with the existence of the unitary transformations

$$\tilde{H}^{ef} = e^{iS} H^{ef} e^{-iS}, \qquad (13)$$

which do not change the form of the Hamiltonian and its eigenvalues, but contribute essentially to its parameters. The ambiguity revealed leads to the correlations between the effective Hamiltonian parameters, that makes their determination by the fitting of the experimental data by the least–square method rather difficult. In this paper[14] the ambiguity of the effective Hamiltonian is removed by reducing this Hamiltonian, with the help of the unitary transformations, Eq. (13). The reduced effective Hamiltonian is not ambiguous. One of the reduced forms of the effective Hamiltonian can be obtained, if one assumes that

$$x_{\ell\ell},\ y_{1\ell\ell},\ y_{2\ell\ell},\ y_{3\ell\ell},\ \gamma_{\ell\ell},\ F^{L}_{\ell},\ C_{\ell},\ C_{\ell 1},\ C_{\ell 2} = 0 \qquad (14)$$

and imposes the following limitations, Ref. 14, on L_K and C_K parameters:

$$L_K = -L_J\ ,\ C_K = -C_J. \qquad (15)$$

TABLE I. Weighted standard deviations for the spectroscopic parameters of CO_2*–molecule.*

Number of a Hamiltonian parameters	Weighted standard deviations		
	G_v	B_v	D_v
52	0.690	0.483	1.077

In Ref. 14 the parameters of the above derived reduced effective Hamiltonian have been found by means of the least–square fitting of the experimental spectroscopic constants of a $^{12}C^{16}O_2$ molecule, determining the vibrational–rotational energy levels by the expression

$$E_{VJ} = G_v + B_v J\ (J + 1) - D_v\ [J\ (J + 1)]^2. \qquad (16)$$

Seventy three vibrational constants G_v, 119 rotational constants B_v, and 111 centrifugal distortion constants D_v from Ref. 26 have been used in the fitting. The results of the fitting are given in Table I.

The most impressive results[27] were achieved in the direct fitting of the experimental wave numbers of the vibrational–rotational transitions to the parameters of the effective Hamiltonian. The file of the experimental data was kindly given us by Rothman. This file contains more than 15000 lines, taken from Refs. 28 – 48. It should be noted that we used the experimental information about transitions between the vibrational–rotational energy levels, with the wave numbers up to 24000 cm^{-1}. The calculations were performed with the help of GIP computer codes, Ref. 49, specially adapted for the CO_2 molecule. The effective Hamiltonian was extended up to the sixth order to achieve a higher fitting quality. But, in the fitting we have neglected some fifth and sixth order parameters. It has been established during the fittings that the best improvement is reached by the sixth order diagonal parameters z_{ijlk}, which are determined by the expression

$$\sum_{ijlk} z_{ijlk} \left(v_i + \frac{g_i}{2}\right)\left(v_j + \frac{g_j}{2}\right)\left(v_l + \frac{g_l}{2}\right)\left(v_k + \frac{g_k}{2}\right), \qquad (17)$$

and the fifth order parameters, describing the quadratic dependence of the Fermi interaction constant on the vibrational quantum numbers and the quadratic dependence of this constant on the quantum number of angular momentum J, i.e.,:

$$F_{11}v_1^2 + F_{12}v_1(v_2 + 2) + F_{13}v_1\left(v_3 + \frac{1}{2}\right) + F_{22}(v_2 + 2)^2 +$$
$$+ F_{23}(v_2 + 2)\left(v_3 + \frac{1}{2}\right) + F_{33}\left(v_3 + \frac{1}{2}\right)^2 +$$
$$+ F_{JJ}[J\ (J+1) - \ell_2^2]^2. \qquad (18)$$

The results of fitting are given in Table II.

TABLE II. The results of fitting of the wave number of CO_2 *molecule*

Number of Hamiltinian parameters	Number of lines	Number of bands	rms deviation, cm^{-1}
130	15038	166	0.00105

In order to demonstrate the extrapolation abilities of the obtained parameters of the effective Hamiltonian we have performed calculations and compared with the experiment from Ref. 50, of the line centers of the band 20033 ← 00001, lying in the region of 9400 cm^{-1}, i.e., on the border between the visible and IR regions. It should be noted, that the experimental data used for fitting of the effective Hamiltonian parameters, belong to the microwave, far and middle IR regions. Predicted and experimental values of the line centers of the band 20033 ← 00001 are given in Table III. The authors of Ref. 50 give the experimental accuracy for the line centers to be about 0.05 cm^{-1}.

TABLE III. Experimental and predicted values of the wave numbers, cm^{-1}*, for the band* 20033 ← 00001 *of the* CO_2 *molecule.*

Line	Experiment, Ref. 50	Calculation	Experiment minus calculation
*P*2	9387.39	9387.41	–0.02
*R*2	9391.18	9391.24	–0.06
*P*4	9385.76	9385.77	–0.01
*R*4	9392.68	9392.66	0.02
*P*6	9384.08	9384.07	0.01
*R*6	9393.99	9394.01	–0.02
*P*8	9382.29	9382.31	–0.02
*R*8	9395.28	9395.31	–0.03
*P*10	9380.47	9380.48	–0.01
*R*10	9396.49	9396.54	–0.05
*P*12	9378.60	9378.59	0.01
*R*12	9397.67	9397.71	–0.04
*P*14	9376.61	9376.64	–0.03
*R*14	9398.79	9398.81	–0.02
*P*16	9374.62	9374.62	0.00
*R*16	9399.80	9399.85	–0.05
*P*18	9372.52	9372.54	–0.02
*R*18	9400.83	9400.83	0.00
*P*20	9370.40	9370.40	0.00
*R*20	9401.69	9401.74	–0.05
*P*22	9368.18	9368.19	–0.01
*R*22	9402.56	9402.59	–0.03
*P*24	9365.93	9365.92	0.01
*R*24	9403.36	9403.37	–0.01
*P*26	9363.61	9363.59	0.02
*R*26	9404.07	9404.09	–0.02
*P*28	9361.14	9361.19	–0.05
*R*28	9404.75	9404.75	0.00
*P*30	9358.73	9358.73	0.00
*R*30	9405.31	9405.34	–0.03
*P*32	9356.22	9356.21	0.01
*R*32	9405.85	9405.87	–0.02
*P*34	9353.65	9353.62	0.03
*R*34	9406.29	9406.33	–0.04
*P*36	9351.04	9350.96	0.08
*R*36	9406.69	9406.72	–0.03
*P*38	9348.31	9348.24	0.07
*R*38	9407.04	9407.05	–0.01
*P*40	9345.51	9345.46	0.05
*R*40	9407.33	9407.31	0.02
*P*42	9342.61	9342.61	0.00
*P*44	9339.74	9339.69	0.05
*P*46	9336.68	9336.71	–0.03

As follows from Table III, all predicted values of the line centers coincide within the experimental errors with the experimental values.

The comparison of the prediction abilities of our effective Hamiltonian model and DND–method[10] is given in Table IV. The comparison was performed with the experimental values of line centers of the band 05511 → 05501, recorded recently by Bailly and others.[51] As follows from this table, the accuracy of our predictions is one order better than the accuracy of the predictions by the DND–method.

TABLE IV. Comparison of predictive abilities of our approach and DND method (HITRAN 92). The centers of lines, cm^{-1}*, for the band* 05511 → 05501 *of the* $^{12}C^{16}O_2$ *molecule.*

Line	Our calculation	Calculation minus experiment	DND	DND minus experiment
*P*10	2278.6423	0.001	2278.66505	0.024
*P*20	2269.9238	0.002	2269.94472	0.023
*P*30	2260.6293	0.002	2260.64744	0.020
*P*40	2250.7640	0.003	2250.77907	0.018
*P*50	2240.3341	0.003	2240.34650	0.016
*P*59	2230.4704	0.004		
*R*10	2295.0569	0.001	2295.07937	0.023
*R*20	2301.9642	0.001	2301.98457	0.022
*R*30	2308.2814	0.001	2308.29894	0.019
*R*40	2314.0071	0.002	2314.02156	0.017
*R*50	2319.1404	0.002	2319.15247	0.014
*R*60	2323.6820	0.004		
*R*69	2327.2650	0.006		

In Table V is given the comparison of our predicted values with the experimental values of Bailly and coauthors, Ref. 35, for the line centers of the "hot" bands 000(10)1 → 00091, 000(11)1 → 000(10)1, and 000(12)1 → 000(11)1 of $^{12}C^{16}O_2$ molecule. As it follows from this table the prediction is quite satisfactory, if takes into account the fact that these bands are formed by the transitions between the vibrational–rotational energy levels lying higher then 20000 cm^{-1}. It is necessary to emphasize that the vibrational states 00081 and 00091 were the most high–excited states involved into the fitting of the effective Hamiltonian parameters. The last column of the Table V also shows the energy values of the low states.

TABLE V. The comparison of the predicted and experimental line centers of "hot" bands 000(10)1 → 00091, 000(11)1 → 000(10)1 *and* 000(12)1 → 000(11)1 *of the* $^{12}C^{16}O_2$ *molecule.*

Transition		Calculation, cm^{-1}	Calculation minus experiment, cm^{-1}, Ref. 35	$E_{low.}$, cm^{-1}
1		2	3	4
000(10)1 → 00091	*P*7	2120.9279	0.0026	22798.9541
000(10)1 → 00091	*P*9	2119.3862	0.0026	22811.2826
000(10)1 → 00091	*P*11	2117.8201	0.0025	22826.5116
000(10)1 → 00091	*P*13	2116.2302	0.0029	22844.6407
000(10)1 → 00091	*P*15	2114.6159	0.0030	22865.6697
000(10)1 → 00091	*P*19	2111.3147	0.0032	22916.4256
000(10)1 → 00091	*P*21	2109.6271	0.0026	22946.1517
000(10)1 → 00091	*P*23	2107.9161	0.0027	22978.7758
000(10)1 → 00091	*P*27	2104.4220	0.0029	23052.7160
000(10)1 → 00091	*P*31	2100.8313	0.0027	23138.2410
000(10)1 → 00091	*P*33	2098.9999	0.0025	23185.3460
000(10)1 → 00091	*P*35	2097.1444	0.0022	23235.3450
000(10)1 → 00091	*P*39	2093.3618	0.0018	23344.0210
000(10)1 → 00091	*P*41	2091.4351	0.0020	23402.6963
000(10)1 → 00091	*P*45	2087.5101	0.0024	23528.7162
000(10)1 → 00091	*P*55	2077.2801	0.0019	23894.2840
000(10)1 → 00091	*R*3	2128.9727	0.0028	22782.9990
000(10)1 → 00091	*R*5	2130.3560	0.0028	22789.5261
000(10)1 → 00091	*R*9	2133.0488	0.0023	22811.2826
000(10)1 → 00091	*R*11	2134.3592	0.0028	22826.5116
000(10)1 → 00091	*R*13	2135.6444	0.0025	22844.6407
000(10)1 → 00091	*R*17	2138.1415	0.0026	22889.5981
000(10)1 → 00091	*R*19	2139.3529	0.0024	22916.4256
000(10)1 → 00091	*R*21	2140.5399	0.0023	22946.1517
000(10)1 → 00091	*R*23	2141.7025	0.0026	22978.7758
000(10)1 → 00091	*R*25	2142.8400	0.0024	23014.2975
000(10)1 → 00091	*R*33	2147.1437	0.0027	23185.3460
000(10)1 → 00091	*R*37	2149.1462	0.0021	23288.2369
000(10)1 → 00091	*R*39	2150.1105	0.0022	23344.0210
000(10)1 → 00091	*R*41	2151.0496	0.0019	23402.6963
000(10)1 → 00091	*R*53	2156.1628	0.0025	23815.4019
000(10)1 → 00091	*R*55	2156.9267	0.0018	23894.2840
000(10)1 → 00091	*R*59	2158.3803	0.0014	24060.6917
000(11)1 → 000(10)1	*P*6	2097.2923	0.0112	24919.8794
000(11)1 → 000(10)1	*P*8	2095.7743	0.0105	24930.6662
000(11)1 → 000(10)1	*P*10	2094.2333	0.0110	24944.3292
000(11)1 → 000(10)1	*P*14	2091.0770	0.0104	24980.2826
000(11)1 → 000(10)1	*P*18	2087.8252	0.0108	25027.7370
000(11)1 → 000(10)1	*P*20	2086.1629	0.0109	25055.7762
000(11)1 → 000(10)1	*P*22	2084.4759	0.0103	25086.6893
000(11)1 → 000(10)1	*P*30	2077.4901	0.0106	25239.0696
000(11)1 → 000(10)1	*P*32	2075.6831	0.0100	25284.3434
000(11)1 → 000(10)1	*P*34	2073.8529	0.0102	25332.4871
000(11)1 → 000(10)1	*P*36	2071.9983	0.0099	25383.4999
000(11)1 → 000(10)1	*P*44	2064.3429	0.0104	25616.2239
000(11)1 → 000(10)1	*P*46	2062.3693	0.0104	25681.5679
000(11)1 → 000(10)1	*P*50	2058.3517	0.0109	25820.8439
000(11)1 → 000(10)1	*P*56	2052.1471	0.0113	26051.2089
000(11)1 → 000(10)1	*R*2	2103.8188	0.0107	24906.9348
000(11)1 → 000(10)1	*R*4	2105.2020	0.0105	24911.9689

TABLE V (continued)

1	2	3	4	5
000(11)1 ← 000(10)1	*R*8	2107.8960	0.0107	24930.6662
000(11)1 → 000(10)1	*R*10	2109.2061	0.0106	24944.3292
000(11)1 → 000(10)1	*R*12	2110.4919	0.0107	24960.8681
000(11)1 → 000(10)1	*R*14	2111.7532	0.0108	24980.2826
000(11)1 → 000(10)1	*R*18	2114.2015	0.0103	25027.7370
000(11)1 → 000(10)1	*R*20	2115.3893	0.0106	25055.7762
000(11)1 → 000(10)1	*R*24	2117.6902	0.0102	25120.4758
000(11)1 → 000(10)1	*R*26	2118.8036	0.0100	25157.1351
000(11)1 → 000(10)1	*R*30	2120.9570	0.0102	25239.0696
000(11)1 → 000(10)1	*R*32	2121.9967	0.0103	25284.3434
000(11)1 → 000(10)1	*R*36	2124.0017	0.0105	25383.4999
000(11)1 → 000(10)1	*R*40	2125.9076	0.0108	25494.1294
000(12)1 → 000(11)1	*P*3	2075.2073	0.0255	27010.7429
000(12)1 → 000(11)1	*P*7	2072.2467	0.0264	27026.4300
000(12)1 → 000(11)1	*P*9	2070.7291	0.0259	27038.5515
000(12)1 → 000(11)1	*P*11	2069.1868	0.0249	27053.5247
000(12)1 → 000(11)1	*P*15	2066.0328	0.0258	27092.0250
000(12)1 → 000(11)1	*P*19	2062.7811	0.0255	27141.9282
000(12)1 → 000(11)1	*P*25	2057.7235	0.0254	27238.1557
000(12)1 → 000(11)1	*P*31	2052.4507	0.0260	27360.0165
000(12)1 → 000(11)1	*R*9	2084.1606	0.0254	27038.5515
000(12)1 → 000(11)1	*R*11	2085.4462	0.0251	27053.5247
000(12)1 → 000(11)1	*R*13	2086.7079	0.0252	27071.3493
000(12)1 → 000(11)1	*R*19	2090.3470	0.0266	27141.9282
000(12)1 → 000(11)1	*R*25	2093.7631	0.0259	27238.1557
000(12)1 → 000(11)1	*R*29	2095.9179	0.0259	27316.5492
000(12)1 → 000(11)1	*R*31	2096.9583	0.0259	27360.0165
000(12)1 → 000(11)1	*R*33	2097.9742	0.0262	27406.3298

The N_2O molecule

The effective Hamiltonian for the global treatment of the vibrational–rotational states, belonging to the ground electronic state of this molecule, was proposed by Pliva,[52] who found out its ambiguity. He has removed this ambiguity in the first orders, by imposing restrictions on the effective Hamiltonian parameters, following the explicit expressions for these parameters in terms of molecular constants. Later this Hamiltonian was used as an intermediate operator by Teffo and Chedin[13] for fitting the N_2O molecule force field, based on the experimental values of the spectroscopic constants G_v, B_v and D_v. In our paper, Ref. 15, we gave all the symmetry allowed effective Hamiltonian terms up to the fourth order inclusive. These terms that are the result of the approximate relation between harmonic frequencies

$$\omega_3 \approx 2\omega_1 \approx 4\omega_2. \tag{19}$$

The reduction of the obtained effective Hamiltonian by means of the unitary transformations was performed there.

The effective Hamiltonian discussed can be presented by its matrix elements in the basis of the products of harmonic oscillator eigenfunctions and the rigid symmetric top eigenfunctions. The diagonal matrix element has the same form, Eq. (4), as in the case of the effective Hamiltonian for the CO_2 molecule. The matrix elements of the interaction operators are given below.

The matrix elements of the Fermi interaction operators are

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\mathrm{ef}}\,|\,v_1 - 1\; v_2 + 2\ell_2\; v_3\, J> = \sqrt{v_1\,(v_2 + \ell_2 + 2)\,(v_2 - \ell_2 + 2)}\, \times$$

$$\times \left\{F_e^{(2)} + F_1^{(2)}\, v_1 + F_2^{(2)}\,(v_2 + 2) + F_3^{(2)}\left(v_3 + \frac{1}{2}\right) + F_J^{(2)}\,[J\,(J + 1) - \ell_2^2]\right\}, \tag{20}$$

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\mathrm{ef}}\,|\,v_1 - 2\; v_2\; \ell_2\; v_3 + 1J> = \sqrt{(v_1 - 1)\,v_1\,(v_3 + 1)}\, \times$$

$$\times \left\{F_e^{(3)} + F_1^{(3)}\left(v_1 - \frac{1}{2}\right) + F_2^{(3)}(v_2 + 1) + F_3^{(3)}\,(v_3 + 1) + F_J^{(3)}\,[J\,(J + 1) - \ell_2^2]\right\}. \tag{21}$$

The matrix element of the Fermi + ℓ – type interaction is

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\mathrm{ef}}\,|\,v_1 - 1\; v_2 + 2\; \ell_2 \pm 2\; v_3\, J> = \sqrt{v_1\,(v_2 \pm \ell_2 + 2)}\, \times$$

$$\times \sqrt{(v_2 \pm \ell_2 + 4)\,[J\,(J+1) - \ell_2(\ell_2 \pm 1)]\,[J\,(J+1) - (\ell_2 \pm 1)\,(\ell_2 \pm 2)]}\;\; \{F_L^{(8)} \pm F_L^{(8)}\,(\ell_2 \pm 1)\}. \tag{22}$$

The matrix element of the second order anharmonic interaction is

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1 - 1\; v_2 - 2\; \ell_2\; v_3 + 1\; J> =$$

$$= \sqrt{v_1\,(v_2 - \ell_2)\,(v_2 + \ell_2))}\;\; \sqrt{(v_3 + 1)}\; \{F_e^{(4)} + F_1^{(4)}\, v_1 + F_2^{(4)}\, v_2 + F_3^{(4)}\,(v_3 + 1) + F_J^{(4)}\,[J\,(J+1) - \ell_2^2]\}. \tag{23}$$

The matrix element of the anharmonic + ℓ – type interaction operator is

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1 - 1\; v_2 - 2\; \ell_2 \pm 2\; v_3 + 1\; J> =$$

$$= F_L^{(14)}\,\sqrt{v_1\,(v_2 \mp \ell_2)}\;\; \sqrt{(v_2 \mp \ell_2 - 2)\,(v_3 + 1)\,[J\,(J+1) - \ell_2\,(\ell_2 \pm 1)}\;\; \sqrt{[J\,(J+1) - (\ell_2 \pm 1)\,(\ell_2 \pm 2)]}. \tag{24}$$

The matrix element of the third order anharmonic interaction operator is

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1\; v_2 - 4\; \ell_2\; v_3 + 1\; J> = F_e^{(10)}\sqrt{(v_2 - \ell_2)\,(v_2 + \ell_2)\,(v_2 - \ell_2 - 2)\,(v_2 + \ell_2 - 2)\,(v_3 + 1)}. \tag{25}$$

The matrix elements of the fourth order anharmonic interaction operators are

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1 - 2\; v_2 + 4\; \ell_2\; v_3\, J> = F_e^{(11)}\,\sqrt{(v_1 - 1)\, v_1\,(v_2 - \ell_2 + 2)}$$
$$\sqrt{(v_2 + \ell_2 + 2)\,(v_2 - \ell_2 + 4)\,(v_2 + \ell_2 + 4)}, \tag{26}$$

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1 - 4\; v_2\; \ell_2\; v_3 + 2\; J> = F_e^{(12)}\,\sqrt{(v_1 - 3)\,(v_1 - 2)\,(v_1 - 1)\, v_1\,(v_3 + 1)\,(v_3 + 2)}\,, \tag{27}$$

$$<v_1\, v_2\, \ell_2\, v_3\, J\,|\,\mathrm{H}^{\,\mathrm{ef}}\,|\,v_1 - 3\; v_2 + 2\; \ell_2\; v_3 + 1\; J> = F_e^{(13)}\sqrt{(v_1 - 2)\,(v_1 - 1)\, v_1\,(v_2 - \ell_2 + 2)\,(v_2 + \ell_2 + 2)\,(v_3 + 1)}. \tag{28}$$

The choice of the molecule–fixed frame, the phase of the two–dimensional harmonic vibration and of the phases of the wave functions is made as in the previous case with the CO_2 molecule.

Figure 1 shows the form of the effective Hamiltonian matrix. This matrix is a block–diagonal one. The blocks correspond to the concrete polyads, which can be numbered with the index

$$P = 2v_1 + v_2 + 4v_3\,. \tag{29}$$

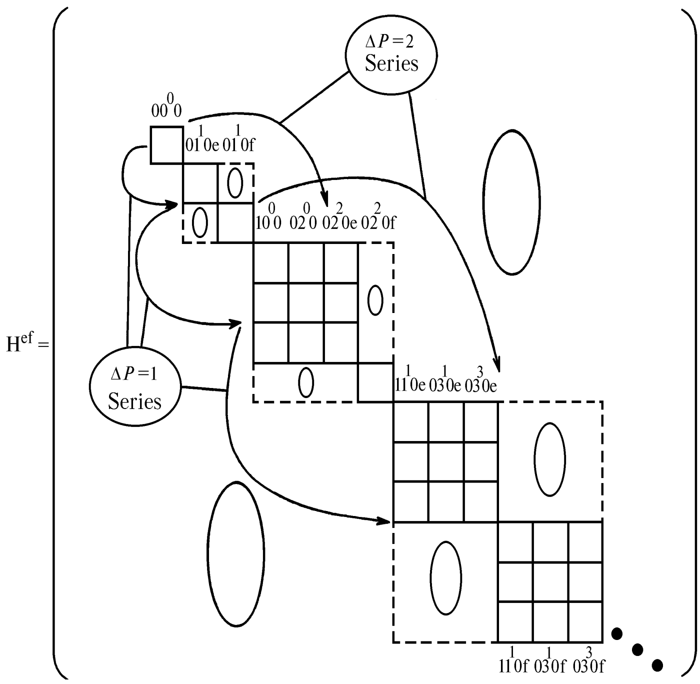

FIG. 1. The matrix of the effective rotational–vibrational Hamiltonian of the N_2O *molecule and the series of bands.*

In our paper[15] some variants of the reduced effective Hamiltonian were proposed. It was shown, that partially reduced effective Hamiltonian with fifty three parameters gives the best result. This operator is obtained from the effective Hamiltonian, given by the expressions (4) and (20)–(28), by elimination, using the unitary transformations, the following parameters:
$x_{\ell\ell}$, $y_{3\ell\ell}$, $\gamma_{\ell\ell}$, $F_e^{(3)}$, $F_e^{(10)}$, $F_e^{(11)}$, $F_e^{(12)}$, $F_1^{(4)}$, $F_2^{(4)}$, $F_J^{(4)}$, $F_{L\ell}^{(8)}$. Besides the limitation $L_K = - L_J$ is imposed besides on L_K and L_J parameters. The subsequent fitting of the experimental data has shown, that the parameters H_e and $F_L^{(14)}$ can be neglected in the considered approximation.

TABLE VI. The weighted standard deviations and rms deviations of the spectroscopic constants of $^{14}N_2{}^{16}O^*$ *molecule.*

Number of the adjusted parameters	Weighted standard deviations and rms deviations (in parentheses)*		
	G_v	B_v	D_v
53	5.10 (0.012)	6.64 (1.21)	14.00 (3.71)

*rms, cm^{-1}, for parameters G_v, 10^{-5} cm^{-1} for parameters B_v and 10^{-9} cm^{-1} for parameters D_v.

TABLE VII. Predicted and experimental[55] values of the spectroscopy parameters G_v and B_v of the $^{14}N_2{}^{16}O$ *molecule.*

State*	$G_v^{(obs)}$	$G_v^{(obs)}$ minus $G_v^{(calc)}$	$B_v^{(obs)}$	$B_v^{(obs)}$ minus $B_v^{(calc)}$
00^04	8714.117	−0.061	0.40518	0.00000
12^03	8877.028	0.337	0.40800	−0.00001
20^03	8976.497	−0.008	0.40512	−0.00023
40^02 a	9219.035	0.323	0.40747	−0.00042
40^02 b	9294.966	−0.206	0.40618	−0.00066
60^01	9606.305	−0.632	0.40724	−0.00081
10^04	9888.579	0.210	0.40333	−0.00008
30^03 a	10079.560	0.624	0.40616	−0.00013
30^03 b	10163.614	−0.016	0.40369	−0.0004
50^02	10429.117	0.366	0.40545	−0.00056
00^05	10815.274	0.769	0.40424	−0.00052
04^04	10820.143	−0.282	0.40473	0.00061
02^05	11844.970	1.130	0.40378	−0.00004
10^05	11964.252	0.573	0.40009	0.00018
00^06	12891.153	0.038	0.39838	−0.00044
10^06	14009.686	1.709	0.39657	0.00005
00^07	14934.267	0.116	0.39478	0.00013

*In the cases, when the indices (v_1, v_2, ℓ_2, v_3) do not allow to identify a level, the designations "a" and "b" for these levels are used.

The fitting of the effective Hamiltonian parameters was carried out[15] for the experimental data, obtained by Toth,[53] with addition of spectroscopic constants for high–excited vibrational states, published by Amiot and Guelachvili.[54] This set of experimental data contains 114 vibrational constants G_v, 112 rotational constants B_v, and 100 centrifugal distortion constants D_v. The weighted standard deviations and rms of fitting for the spectroscopic constants are given in Table VI.

A good extrapolation properties of our reduced effective Hamiltonian were later confirmed in the experimental paper,[55] where the absorption spectrum of the N_2O molecule in the range 8700–15000 cm^{-1} was investigated using the Fourier and intracavity laser spectroscopy methods. The comparison of the predicted values of the spectroscopic constants G_v and B_v with the experimental values is given in Table VII. It should be noted, that fitting of the effective Hamiltonian parameters involved the vibrational states, lying below 8000 cm^{-1}.

3. THE LINE INTENSITY

The intensity of the incident radiation absorption at the frequency ν, that induces the molecular transition from the state a to the state b, is given by well known formula

$$S_{b\leftarrow a}(T) = \frac{8\pi^3}{3hc}\, n\, \frac{273.15}{T}\, C\, \nu_{b\leftarrow a}\, \frac{\exp(-hc\,E_a/kT)}{Q(T)} \times$$

$$\times\,[1 - \exp(-hc\,\nu_{b\leftarrow a}/kT)]\; W_{b\leftarrow a}\,, \qquad (30)$$

where $S_{b\leftarrow a}(T)$ is the absorption line intensity, cm^{-2}/atm, at temperature T, K; n is the Loschmidt number; C is the isotopic abundance; $\nu_{b\leftarrow a}$ is the frequency of the transition $b \leftarrow a$; E_a is the energy of the low state; k is the Boltzmann constant; h is the Plank constant; c is the speed of light; $Q(T)$ is the partition function and $W_{b\leftarrow a}$, i.e., the probability of the molecular transition from the state a to the state b is given by the expression

$$W_{b\leftarrow a} = \sum_{\alpha=X,Y,Z}\ \sum_{MM'} |\langle b\,M'|M_\alpha|a\,M\rangle|^2, \qquad (31)$$

where the summation is carried out over the magnetic quantum numbers M and M' of the high and low states, and over the components of the dipole moment in the laboratory–fixed frame.

The transition probability can be calculated using the eigenfunctions of the effective Hamiltonian:

$$\psi^{\mathrm{ef}}_{NJM\varepsilon} = \sum_{v_1v_2\ell_2v_3} {}^J C^{v_1v_2\ell_2v_3}_{N\varepsilon}\, |v_1\, v_2|\ell_2|\, v_3\, JM\varepsilon\rangle, \qquad (32)$$

where ${}^J C^{v_1v_2\ell_2v_3}_{N\varepsilon}$ are the mixing coefficients. But in the expression (31) the effective dipole moment operator has to be used instead of the dipole moment operator. The effective dipole moment operator is obtained from the dipole moment operator by the same contact transformations

$$M_{\alpha}^{\mathrm{ef}} = e^{iS_{CT}} M_{\alpha} e^{-iS_{CT}}, \qquad (33)$$

as the effective Hamiltonian from the vibrational–rotational Hamiltonian

$$H^{\mathrm{ef}} = e^{iS_{CT}} H_{VR} e^{-iS_{CT}}. \qquad (34)$$

Thus:

$$W_{N'J'\varepsilon' \leftarrow NJ\varepsilon} = \sum_{\alpha=X,Y,Z} \sum_{MM'} |< \psi^{\mathrm{ef}}_{N'J'M'\varepsilon'} | M_{\alpha}^{\mathrm{ef}} | \psi^{\mathrm{ef}}_{NJM\varepsilon} >|^2. \qquad (35)$$

After several algebraic transformations, the calculations of the matrix elements and summations performed in Eq. (35) the probability of the allowed transition between the stationary states of a linear triatomic molecule in the general form can be written as follows[16,18]:

$$W_{N'J'\varepsilon' \leftarrow NJ\varepsilon} = (2J+1) \sum_{v_1v_2\ell_2v_3} \sum_{\substack{\Delta v_1+\Delta v_2+\Delta v_3=\Delta P \\ \Delta\ell_2}} {}^{J}C_{N\varepsilon}^{v_1v_2\ell_2v_3} \; {}^{J'}C_{N'\varepsilon'}^{v_1+\Delta v_1 v_2+\Delta v_2 \ell_2+\Delta\ell_2 v_3+\Delta v_3} \times$$

$$\times M_{\Delta\mathbf{V}}^{|\Delta\ell_2|} \sqrt{f_{\Delta\mathbf{V}}^{\Delta\ell_2}(\mathbf{V}, \ell_2) \, (1 + \delta_{\ell_2,0} + \delta_{\ell_2',0} - 2\,\delta_{\ell_2,0}\,\delta_{\ell_2',0})} \, (1\Delta\ell_2\, J\, \ell_2 | (J+\Delta J)\, (\ell_2+\Delta\ell_2)) \, (1 + \sum_i \varkappa_i^{\Delta\mathbf{V}} v_i + F_{\Delta\ell_2}^{\Delta\mathbf{V}}(\ell_2, J))|^2. \qquad (36)$$

Here $f_{\Delta\mathbf{V}}^{\Delta\ell_2}(\mathbf{V}, \ell_2)$ are known functions of the vibrational quantum numbers, the explicit form of which for small values $\Delta\mathbf{V}$ is given in Ref. 16, (Table I). We use the vector designation $\mathbf{V}$ for a set of vibrational quantum numbers (v_1, v_2, v_3). Similarly, $\Delta\mathbf{V}$ designates the set (Δv_1, Δv_2, Δv_3). The Clebsch–Gordan coefficient, see expression (36), is connected with the Hönl–London coefficient $L_{\Delta J}^{\Delta\ell_2}$ by the following expression:

$$|(1\,\Delta\ell_2\, J\, \ell_2 | (J+\Delta J)(\ell_2+\Delta\ell_2))|^2 = L_{\Delta J}^{\Delta\ell_2} / (2J+1). \qquad (37)$$

The function $F_{\Delta\ell_2}^{\Delta\mathbf{V}}(\ell_2, J)$ for the parallel bands has the form

$$F_0^{\Delta\mathbf{V}}(\ell_2, J) = b_J^{\Delta\mathbf{V}} m + d_J^{\Delta\mathbf{V}} [J(J+1) + m - \ell_2^2], \qquad (38)$$

where $m = -J, 0, J+1$ for P–, Q– and R–branches, respectively. This function for Q–branches of the perpendicular bands can be written in the form

$$F_{\Delta\ell_2}^{\Delta\mathbf{V}}(\ell_2, J) = -\frac{1}{2} b_J^{\Delta\mathbf{V}} (2\,\ell_2\,\Delta\ell_2 + 1) +$$

$$+ d_{JQ}^{\Delta\mathbf{V}} \left[J(J+1) - \ell_2^2 - \Delta\ell_2 \left(\ell_2 + \frac{\Delta\ell_2}{2} \right) \right], \qquad (39)$$

and for P– and R–branches in the form

$$F_{\Delta\ell_2}^{\Delta\mathbf{V}}(\ell_2, J) = -\frac{1}{4} (d_{JQ}^{\Delta\mathbf{V}} - d_J^{\Delta\mathbf{V}}) -$$

$$-\frac{1}{2} (b_J^{\Delta\mathbf{V}} + d_{JQ}^{\Delta\mathbf{V}})(2\,\ell_2\,\Delta\ell_2 + 1) - d_{JQ}^{\Delta\mathbf{V}} \ell_2^2 +$$

$$+ b_J^{\Delta\mathbf{V}} m + d_J^{\Delta\mathbf{V}} m^2 + (d_{JQ}^{\Delta\mathbf{V}} - d_J^{\Delta\mathbf{V}})\, m \left(\ell_2\,\Delta\ell_2 + \frac{1}{2} \right). \qquad (40)$$

The combination of the Kronecker symbols in the equation (36) is a consequence of the transition to Wang basis for the wave functions. Parameters of the matrix elements of the effective dipole moment operator $M_{\Delta\mathbf{V}}^{|\Delta\ell_2|}$, $\varkappa_i^{\Delta\mathbf{V}}$ ($i = 1, 2, 3$), $b_J^{\Delta\mathbf{V}}$, $d_J^{\Delta\mathbf{V}}$ and $d_{JQ}^{\Delta\mathbf{V}}$ simultaneously describe the line intensities of the cold and hot bands, belonging to the series of transitions with a given value ΔP (see Fig. 1). In our approach these parameters are determined by the least squares fitting of the experimental line intensities. They can also be calculated with the help of the contact transformation method, using the known force field and the dipole moment function of a molecule.

The CO_2 molecule

The equilibrium configuration of this molecule in the ground electronic state has $D_{\infty h}$ symmetry, that leads to the following selection rules for the absorption and emission spectra:

$$\Delta v_3 + \Delta\ell_2 \text{ is odd}, \qquad (41)$$

$$e \to f,\ f \to e \text{ for } \Delta J = 0,$$
$$e \to e,\ f \to f \text{ for } \Delta J = \pm 1. \qquad (42)$$

The transitions with $\Delta\ell_2 = 0, \pm 1$ are called "allowed transitions" and those with $\Delta\ell_2 = \pm 2, \ldots$ are called "forbidden transitions". The latter are initiated by the vibrational–rotational interactions, and the corresponding lines have very low intensities. Because of the equality to zero of the oxygen atom spin the part of the vibrational–rotational energy levels of the CO_2 molecule is forbidden by nuclear statistics. The quantum numbers of the allowed energy levels satisfy the following equation:

$$\varepsilon(-1)^{J+\ell_2+v_3} = 1. \qquad (43)$$

To demonstrate the potentialities of our approach below we present the results of simultaneous fittings of the hot and cold bands, of two series of transitions with $\Delta P = 1$ and $\Delta P = 3$, Refs 56. The bands of the series with $\Delta P = 1$ lie in two spectral regions. In the region of the fundamental band ν_2 about 15 μm and in the region of laser transition $\nu_3 - \nu_1$ about 10 μm. The bands of the series with $\Delta P = 3$, lie in the region of the fundamental band ν_3 and combination band $\nu_1 + \nu_2$ at about 4 μm. In the fitting of the line intensities by the least squares method the eigenfunctions of the effective Hamiltonian were used, the parameters of which have been determined by fitting the experimental values of the spectroscopic constants G_v, B_v and D_v (see Section 2).

In the case of $\Delta P = 1$ the series of transitions into the fitting, were involved the intensities of 743 lines of 13 bands of the principal isotope of the CO_2 molecule, lying in the region of the fundamental band ν_2: 01101 ← 00001, 10001 ← 01101, 02201 ← 01101, 10002 ← 01101, 11101 ← 10002, 11101 ← 02201, 11101 ← 10001, 03301 ← 02201, 11102 ← 10002, 11102 ← 02201, 11102 ← 10001, 20002 ← 11102, 12201 ← 03301, measured by Johns and Vander Auwera,[57] and intensities of 161 lines of 4 bands, lying in the region of band $\nu_3 - \nu_1$: 00011 ← 10001, 00011 ← 10002, 01111 ← 11102, 01111 ← 11101, measured by Dana et al.[58] In the former paper the measurement accuracy was reported to be 4%, and at the latter it was 6%.

For the dimensionless weighted standard deviation of fitting:

$$\chi = \sqrt{\sum_i \left(\frac{o_i - c_i}{\delta_i}\right)^2 \Big/ (m-n)}, \qquad (44)$$

where o_i and c_i are the experimental (observed) and calculated intensity values; δ_i is an experimental error; m is the number of fitted intensities and n is the number of adjusted parameters, we managed to reach the value of 0.965. This means, that the fitting has been performed with the experimental accuracy. The statistical analysis of the fitting is shown in Table VIII, and the set of fitted parameters of the matrix elements of the effective dipole moment operator is given in Table IX.

TABLE VIII. The statistical analysis of the fitting of line intensities of the bands, from the $\Delta P = 1$ series of $^{12}C^{16}O_2$ molecule.

$d = \frac{o. - c.}{o.} \times 100$ %	Number of lines	% lines
$0 \le d < 3$	686	75.9
$3 \le d < 6$	187	20.7
$6 \le d$	31	3.4

For the comparison Table IX also gives the calculated values for some effective dipole moment parameters. These values have been obtained using formulas, derived by means of contact transformations in Refs. 16, 56, on the basis of force field and using dipole moment function by Wattson and Rothman.[10]

The extrapolation abilities of our approach are demonstrated in Table X, where a comparison between the predicted and experimental[59] values of the line intensities of the band 0001←11101 of $^{12}C^{16}O_2$ molecule is given. This band has not been involved into the fitting of the effective dipole moment matrix element parameters. It is necessary to emphasize, that the predicted values of the intensities are within the experimental error.

TABLE IX. The parameters of the matrix elements of the effective dipole moment operator (series $\Delta P = 1$).

Parameter *	Δv_1	Δv_2	Δv_3	CT	Simultaneous fitting
M	0	1	0		−0.12744 (13)**
k_2	0	1	0	−0.0064	−0.00331 (29)
b_J	0	1	0	0.942	0.922 (25)
d_J	0	1	0		0.00312 (84)
d_{JQ}	0	1	0		0.00216 (98)
M	1	−1	0	−0.0037	−0.003951 (58)
b_J	1	−1	0	1.58	1.50 (88)
M	−1	0	1	0.0514	0.05075 (12)
b_J	−1	0	1		−1.010 (77)
M	0	−2	1		−0.001326 (50)
b_J	0	−2	1		−9.68 (135)
χ					0.965

*The parameters $\bar{M}_{\Delta V}$ are given in Debye; the parameters b_J, d_J and d_J^Q are dimensionless and are multiplied by 10^3.

**The numbers in parentheses are one standard deviation in the units of the last digit.

In the case of $\Delta P = 3$ series of transitions 510 lines belonging to 22 parallel bands,[43,60–66] and 810 lines belonging to 20 perpendicular bands[42–44,67] have been fitted simultaneously. We have found that in order to accurately describe the intensities of the perpendicular bands, lying in this region, without the use of matrix element of the effective dipole moment for $\Delta v_3 = 1$ giving its contribution to the line intensities of the perpendicular bands due to resonance Coriolis interaction, is practically impossible. For the weighted standard deviation of the fitting we have obtained the value $\chi = 1.36$. This means, that the fitting has been performed practically with the experimental accuracy. It should be noted that the accuracy of the line intensity measurements is not always clearly presented with the experimental results. In the cases when we did not managed to find estimates of the accuracy of the line intensity measurements, this accuracy was assumed to be 10%. But, as was shown in our analysis such accuracy is too optimistic.

In Table XI is given a set of fitted parameters of the matrix elements of the effective dipole moment operator for $\Delta P = 3$ series, and the values for some parameters, calculated by the method of contact transformations.

TABLE X. The comparison of the predicted and experimental line intensities, cm/molecule, for the band 20001 ← 11101 *of* $^{12}C^{16}O_2$ *molecule.*

Line	Center	S (predicted)	S (observed) Ref. 59	Δ, %*
*P*19	705.5135	6.786D−24	7.228D−24	−6.1
*P*21	703.9700	6.343D−24	7.179D−24	−12
*P*25	700.8906	5.168D−24	5.677D−24	−8.9
*Q*42	719.0339	2.282D−24	2.249D−24	1.5
*R*5	724.9681	3.556D−24	3.592D−24	−1.0
*R*7	726.5356	4.762D−24	4.873D−24	−2.2
*R*9	728.1046	5.767D−24	5.664D−24	1.8
*R*13	731.2475	7.058D−24	6.904D−24	2.2
*R*17	734.3973	7.354D−24	7.381D−24	−0.4
*R*19	735.9748	7.170D−24	6.907D−24	3.8
*R*23	739.1358	6.305D−24	6.175D−24	2.1
*R*25	740.7193	5.708D−24	5.629D−24	1.4
*R*37	750.2731	2.039D−24	2.043D−24	−0.2

$$^{*}\Delta = \frac{\text{c.} - \text{o.}}{\text{o.}} \times 100\ \%.$$

The approach used well reproduces all effects manifested themselves in the line intensities and connected with the intramolecular resonance interactions. Figure 2 shows that our calculations reproduce a significant asymmetry of *P*– and *R*– branches of $\nu_1 + \nu_2$ band, connected with the resonance Coriolis interaction.

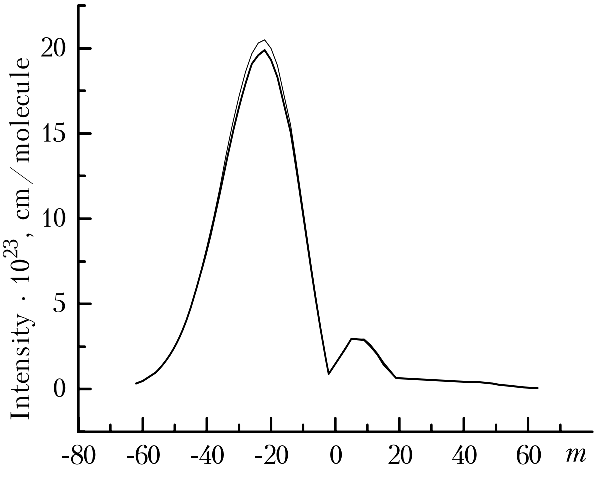

FIG. 2. Calculated (—) and experimental (- - - -) line intensities for the band 11101 ← 00001 *of* $^{12}C^{16}O_2$ *molecule.*

TABLE XI. Parameters of the matrix elements of the effective dipole moment operator for $^{12}C^{16}O_2$ *molecule (Series ΔP = 3).*

Parameter *	Δv_1	Δv_2	Δv_3	CT	Simultaneous fitting
M	0	0	1		−0.3219 (7)**
$\varkappa_1$	0	0	1	−0.0181	−0.029 (2)
$\varkappa_2$	0	0	1	−0.0026	−0.0077 (12)
b_J	0	0	1	−0.150	−0.160 (40)
d_J	0	0	1		−0.0031 (10)
M	−1	2	1		−0.00090 (3)
M	1	1	0	0.00136	0.001474 (3)
$\varkappa_1$	1	1	0		0.0247 (53)
b_J	1	1	0	7.56	0.53 (13)
d_{JQ}	1	1	0		−0.0056 (21)
d_J	1	1	0		0.0045 (30)
M	2	−1	0		−0.000393 (60)
$\varkappa_2$	2	−1	0		−0.068 (12)
b_J	2	−1	0		4.94 (27)
d_{JQ}	2	−1	0		−0.021 (6)
d_J	2	−1	0		−0.021 (8)
M	0	3	0		−0.000285 (15)
k_2	0	3	0		−0.0241 (35)
b_J	0	3	0		−7.86 (13)
d_{JQ}	0	3	0		−0.0137 (29)
$10^5\,M$	−1	5	0		0.23 (8)
χ					1.359

*The parameters $M_{\Delta\mathbf{V}}$ are given in Debye; parameters b_J, d_J, b_{JQ}, $\varkappa_1$ and $\varkappa_2$ are dimensionless; the parameters b_J, d_J and b_{JQ} are multiplied by 10^3.

**The numbers in parentheses are standard deviations in the units of the last digit.

The N_2O molecule.

The equilibrium configuration of this molecule in the ground electronic state is of $C_{\infty V}$ symmetry. Therefore, in contrast to CO_2 molecule, all vibrational transitions are allowed for N_2O molecule. The nuclear statistics does not forbid any vibrational–rotational energy levels, and gives the same statistical weight, equal to 1 for all the vibrational–rotational states. The selection rules with respect to rotational quantum numbers and parity ε are given by the expression (42).

To demonstrate the capabilities of the effective operator method we give here the results of simultaneous fitting[18] of the line intensities of cold and hot bands of N_2O molecule, lying in the region near 4 μm and recorded by Rachet and coauthors, Refs. 68–70. The authors of Refs. 68–70 estimate the measurement accuracy to be 3%. By means of the least–square method the intensities of the 612 lines, from *P*– and *R*– branches of 10 parallel bands:

0001 ← 0000, 2000 ← 0000, 1200 ← 0000, 1310 ← 0110, 2110 ← 0110, 1400 ← 0200, 3000 ← 1000, 2200 ← 1000, 2200 ← 0200 and 3000 ← 0200, have been fitted to 12 parameters of the matrix elements of the effective dipole moment operator which entering into the equations (36) and (38). In this case the eigenfunctions were used of a partly reduced effective Hamiltonian corresponding to the fitting, the results of which are given in Table VI. The set of fitted parameters and weighted standard deviations of fitting are given in Table XII. The statistical analysis of the fitting is given in Table XIII. As follows from this table and from the value of the weighted standard deviation $\chi = 0.35$, we have reached the experimental accuracy in the line intensity reproduction.

TABLE XII. Parameters of the matrix elements of the effective dipole moment operator for $^{14}N_2{}^{16}O$ molecule. (Series $\Delta P = 4$).

Parameter *	Δv_1	Δv_2	Δv_3	Value
M	0	0	1	0.2487 (2)**
b_J	0	0	1	−0.125 (17)
M	2	0	0	0.02755 (2)
$\varkappa_1$	2	0	0	0.0228 (9)
$\varkappa_2$	2	0	0	0.0044 (7)
d_J	2	0	0	0.0105 (3)
M	1	2	0	−0.00210 (2)
d_J	1	2	0	0.0187 (21)
M	0	4	0	−0.000079 (6)
b_J	0	4	0	4.22 (45)
M	1	−2	1	−0.0115 (9)
M	3	−2	0	−0.000177 (5)
χ				0.35

*The values of the parameters are given in Debye, except the parameters b_J, d_J, $\varkappa_1$ and $\varkappa_2$, which are dimensionless. The parameters b_J, d_J are multiplied by 10^3.

**The numbers in parentheses are standard deviations in the units of the last digit; χ is the weighted standard deviation.

TABLE XIII. The statistical analysis of the fitting of Rachet et al. experimental data, Refs. 68–70.

$d = \left\lvert \frac{\text{c.}-\text{o.}}{\text{o.}} \right\rvert \times 100\%$	Number of lines	% of lines
$0 \le d < 1$	445	68
$1 \le d < 2$	172	26
$2 \le d < 3$	29	5
$3 \le d \le 5$	6	1

Very often, no data on line intensities are published in papers on experimental studies. Instead such papers give intensities of bands or vibrational moments of transitions and Herman–Wallis parameters of bands. The intensity of the absorption band $S_V(T)$, cm^{-2}/atm, at temperature T, K, is defined as follows, (see, for example, Ref. 57):

$$S_V(T) = \frac{8\pi^3}{3\,hc}\, n\, \frac{273.15}{T}\, C\, \nu_0\, \frac{\exp(-\,hc\,E_V/kT)}{Q_V(T)} |R_V|^2, \quad (45)$$

where ν_0 is the band center, E_V is the energy of the low vibrational state, and $Q_V(T)$ is the vibrational partition function. The square of the vibrational moment of the transition between the levels N and N', which does not depend on the rotational quantum number, is given by the expression (Ref. 16)

$$|R^{\Delta\ell_2}_{N'\leftarrow N}|^2 = \Big| \sum_{v_1v_2v_3} \sum_{\Delta v_1+\Delta v_2+\Delta v_3=\Delta P} C^{v_1v_2v_3}_{N|\ell_2|}\, C^{v_1+\Delta v_1 v_2+\Delta v_2 v_3+\Delta v_3}_{N'|\ell_2'|} \times$$
$$\times M^{|\Delta\ell_2|}_{\Delta\mathbf{V}} \sqrt{f^{\Delta\ell_2}_{\Delta\mathbf{V}}(\mathbf{V}, \ell_2)\,(1 + \delta_{\ell_2,0}+\delta_{\ell_2',0} - 2\,\delta_{\ell_2,0}\,\delta_{\ell_2',0})} \times$$
$$\times\Big(1+\sum_i \kappa_i^{\Delta\mathbf{V}}\, v_1 - \Delta\ell_2\, a_k^{\Delta\mathbf{V}}\,(2\,\ell_2 + \Delta\ell_2) - d_{JQ}^{\Delta\mathbf{V}}\,\ell_2^2\Big)\Big|^2. \quad (46)$$

The mixing coefficients $C^{v_1v_2v_3}_{N|\ell_2|}$ in this formula are taken at $J = \ell_2$, and parameter $a_k^{\Delta\mathbf{V}}$ is approximately equal to $\frac{1}{2}\, b_J^{\Delta\mathbf{V}}$.

Using expression (46) (see Ref. 17) we have successfully carried out the fitting of the experimental values of the vibrational transition moments, published by Toth,[71] to the parameters of matrix elements of the effective dipole moment operator. The series of transitions in $^{14}N_2{}^{16}O$ molecule for $\Delta P = 2$, $\Delta P = 3$, $\Delta P = 4$, $\Delta P = 5$ and $\Delta P = 6$ have been considered. As an example we present in this review the result of fitting of the vibrational transition moments for $\Delta P = 2$ series. The set of fitted parameters of the matrix elements of the effective dipole moment operator for this series and the value of weighted standard deviation of the fitting are given in Table XIV. The comparison of the calculated and experimental values of the vibrational transition moments is shown in Table XV. Several fittings have been performed. In all fittings the calculated values of the vibrational transition moments for the transitions 0001 ← 1000 and 0001 ← 0200 strongly differ from the experimental ones. Therefore, these transitions have not been involved into the final fitting, the results of which are shown in Table XIV and Table XV. Table XV gives predicted values of the vibrational transition moments for these transitions. They differ considerably from Toth data.[71] But our predicted value for the vibrational transition moment of the transition

0001←1000 is in a very good agreement with the value $|R_{0001-1000}| = 5.658 \cdot 10^{-2}$ Debye, published by Lacome et al.[27]

TABLE XIV. Parameters of the effective dipole moment, 10^{-2} Debye, *for* $^{14}N^{16}O_2$ *molecule. (Series* $\Delta P = 2$*).*

$M_{\Delta v_1 \Delta v_2 \Delta v_3}$			Value
1	0	0	13.592 (44)
−1	0	1	−5.566 (247)
0	2	0	−0.867 (11)
0	−2	1	0.173 (50)
2	−2	0	−0.040 (6)
χ			2.88

TABLE XV. Calculated and experimental values of the vibrational transition moments of $^{14}N_2{}^{16}O$ *molecule. (Series* $\Delta P = 2$*).*

Transition		$\lvert R_v \rvert \times 10^2$, Debye		
$v_1'\ v_2'\ \ell_2\ v_3'\ \varepsilon'$	$\leftarrow v_1 v_2 \ell_2 v_3\ \varepsilon$	Calculation	Experiment, Ref. 71	$\frac{\text{c. − o.}}{\text{o.}}$ × 100%
0111e	← 1110e	5.21	5.16(13)*	1.0
0111f	← 1110f	5.21	5.18(13)	0.6
0111e	← 0310e	2.06	2.07(5)	−0.3
0111f	← 0310f	2.07	2.06(5)	0.3
0200	← 0000	2.54	2.57(1)	−1.1
1000	← 0000	13.46	13.36(2)	0.8
0310e	← 0110e	3.16	3.26(3)	−3.2
0310f	← 0110f	3.16	3.23(3)	−2.2
1110e	← 0110e	13.45	13.66(4)	−1.6
1110f	← 0110f	13.45	13.68(5)	−1.7
1200	← 1000	3.48	3.30(2)	5.4
0400	← 0200	4.04	4.06(3)	−0.6
0420f	← 0220f	3.47	3.49(6)	−0.6
1200	← 0200	13.44	13.80(10)	−2.6
1220f	← 0220f	13.48	13.79(14)	−2.2
2000	← 1000	18.95	18.76(14)	1.0
2000	← 0200	0.891	0.894(5)	−0.3
0510e	← 0310e	4.51	4.52 (8)	−0.2
1310e	← 0310e	13.46	13.75(46)	−2.1
2110e	← 1110e	19.0	18.6 (4)	1.9
2110f	← 1110f	19.0	18.5 (7)	2.5
1001	← 0001	13.5	13.9 (6)	−3.0
1400	← 0400	13.5	13.4 (4)	0.4
1420f	← 0420f	13.5	13.3 (4)	1.6
0001	← 1000	5.37**	3.48 (2)	54.3
0001	← 0200	1.62**	1.42 (3)	14.1

*The numbers in parentheses are standard deviations in the units of the last digit.

**The value predicted.

The values of the parameters of the matrix elements of the effective dipole moment operator obtained can be used for estimating intensities of the forbidden bands with $\Delta\ell_2 = \pm 2$, because in the case with N_2O molecule the main contribution to the line intensities of forbidden transitions comes from the ℓ–type interaction, which may be due to the Fermi resonance $\omega_1 \approx 2\omega_2$. In our paper[17] for the vibrational moments of the forbidden transitions $v_1\ v_2\ 2\ v_3 \leftarrow 0000$, published by Toth,[71] we have derived the following approximate expression:

$$|R_{\Delta \mathbf{V}}^{\Delta_2=2}| = [J'\,(J'+1)]^{-1} \times$$

$$\times \left| \sum_{2\Delta v_1+\Delta v_2=0} {}^{J'}C^{v_1+\Delta v_1,\, v_2+\Delta v_2,\, 0,\, v_3}_{v_1 v_2\, 2 v_3 \varepsilon'}\ M_{\Delta \mathbf{V}}^{\Delta_2=0} \sqrt{f_{\Delta \mathbf{V}}^{\Delta_2=0}(\mathbf{V}, \ell_2)} \right|, \tag{47}$$

where J' and ε' are the quantum numbers of the upper vibrational–rotational state. Using the mixing coefficients ${}^{J'}C^{v_1+\Delta v_1,\, v_2+\Delta v_2,\, 0,\, v_3}_{v_1 v_2\, 2 v_3 \varepsilon'}$, obtained from the fitting of the vibrational–rotational energy levels, and parameters $M_{\Delta \mathbf{V}}^{\Delta\ell_2=0}$, obtained from the fitting of the band intensities of the allowed bands, we have estimated the band intensities of some forbidden bands.

The results of a comparison made between the predicted values for the band intensities of some forbidden bands and those measured by Toth[71] are given in Table XVI.

Table XVI shows a good agreement between the predicted and experimental intensities for all forbidden bands, except for a very weak band 0620←0000. It should be noted that Toth in his paper[71] does not publish even the accuracy of this band intensity measurements.

TABLE XVI. The values of the vibrational transition moment predicted for the forbidden bands of $^{14}N_2{}^{16}O$ *molecule.*

ν_0, cm^{-1}	Transition		$\lvert R_v \rvert \times 10^6$, Debye		
	$v_1'\ v_2'\ \ell_2'\ v_3'\ \varepsilon'$	$\leftarrow v_1 v_2 \ell_2 v_3$	Calculation	Experiment, Ref. 71*	$\frac{\text{c. − o.}}{\text{o.}}$ × 100 %
1177.745	0220	← 0000	2.66	2.28 (1)	16.7
2331.122	0420	← 0000	0.915	0.851(22)	7.5
2474.799	1220	← 0000	1.38	1.26 (4)	9.5
3373.141	0221	← 0000	0.839	0.763 (9)	10.0
3474.450	0620	← 0000	0.1271	0.0659	92.9

*The numbers in parentheses are standard deviations in the units of the last digit.

4. CONCLUSION

This review demonstrates the potentialities of the effective operator approach in application to the problem of the global treatment of high resolution spectra of linear triatomic molecules. The examples with CO_2 and N_2O molecules show, that with the help of this method it is possible to reach the accuracy of the spectra description, comparable with the experimental accuracy. Good extrapolation properties of the models proposed for both the effective Hamiltonian and effective dipole moment operators have been demonstrated. The calculations in the frame of the effective operator method do not require powerful computers. In our case this method is realized on a personal computer with a Pentium processor. The main result series of the papers reviewed is the foundation laid for the development of a database on the high–temperature spectra of CO_2 and N_2O molecules.

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