

PARAMETERS OF INDIVIDUAL MULTIPLET COMPONENTS IN THE SPECTRUM OF MOLECULAR OXYGEN WITH ^{17}O ISOTOPE

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A method for constructing effective Hamiltonian in the subspace of the functions total angular momentum F (including the nuclear spin I) is considered in the paper. The effective Hamiltonian is presented for a diatomic molecule having the nuclear spin $I = 5/2$ in the state $^3\Sigma$. The calculational results for isotopic modifications $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ of the oxygen molecule based on the Hamiltonian obtained are analyzed. The reliability of the effective Hamiltonian formulation proposed was checked by a comparison of line centers computed with the experimental ones and it was assessed to be satisfactory.

A great advance in the experimental instrumentation has made it possible to record high-resolution molecular spectra which require for their theoretical interpretation the intramolecular interactions of higher orders to be considered. This fact shows that new demands to the physical models of intramolecular interactions and mathematics are to be formulated.

Processing of molecular spectra with a hyperfine structure caused by electron-nucleus spin interaction is especially complicated. No analytical relations can be found in the literature that make it possible to calculate parameters of some components of multiplets in the absorption spectra and to describe experiment well enough.

From the practical point of view the most important representative of molecules of the type discussed is the molecular oxygen containing the ^{17}O isotope. Despite of low intensity of the isotopic multiplets, the role of the latter in the microwave propagation may be essential because the oxygen concentration in the atmosphere is high.

The account for absorption by this isotope will probably allow the nonresonance absorption of the microwaves in oxygen to be explained. Therefore, development of the techniques and algorithms for calculations of the parameters of lines of the hyperfine structure in the paramagnetic molecules is an urgent task.

1. PECULIARITIES OF THE MOLECULAR OXYGEN ISOTOPIC MODIFICATIONS $^{16}\text{O}^{17}\text{O}$ AND $^{17}\text{O}^{18}\text{O}$

The molecular oxygen in the ground electronic state $^3\Sigma$ has a zero projection of the electron orbital angular momentum ($\Lambda = 0$). Owing to the interaction of the orbital momentum with uncompensated spin of electrons equal to $1h$ ($S = 1$), each line in the vibrational-rotational spectrum is a triplet (the fine structure of the spectrum). The molecule has a constant magnetic moment equal to two Bohr magnetons. The nuclear spin of the oxygen molecule in the basic isotopic modification $^{16}\text{O}_2$ equals zero, while the nuclear spin of the isotope ^{17}O equals $5/2$ what considerably complicates the spectrum (the hyperfine structure appears). Because of symmetry the molecule has no constant electric dipole moment, and optical transitions in it occur due to nonzero magnetic-dipole and quadrupole moments.

In this paper we consider the oxygen molecule in the ground electronic state ($^3\Sigma_g^-$).

Use of the Hund schemes for diatomic molecules is justified by sufficiently high accuracy in the spectrum description.³ However, certain complications arise for the oxygen molecule because in low energy states the molecule is described as the case (a) according to Hund, whereas in the upper energy states it is described as the case (b) according to Hund.^{4,5}

For definiteness we consider here only the case (b) because the rotational energy of the atmospheric oxygen is sufficiently large. Moreover, in Refs. 1, 2, 6–8 the calculations based on the Hund scheme agreed the experiment better. To assign the spectra of the isotopic modifications $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$, the case b_{pj} according to Hund⁴ is used. The nuclear spin ($I = 5/2$) of the isotope ^{17}O is taken into account in this case.

Up to now the calculations for the case of oxygen isotopic modifications $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ were carried out in Refs. 1 and 2. In Ref. 1 only qualitative analysis of these isotopic modifications has been carried out aimed at determination of the nuclear spin of ^{17}O , and in Ref. 2 the matrix elements of Hamiltonian were calculated in the subspace of the total angular momentum functions J ignoring the nuclear spin I . In this approach the isotopic modifications of the molecular oxygen, whose spectra do not have hyperfine structure, are described with a block-diagonal matrix of the effective Hamiltonian (isolated block for one J), and for the isotopic modifications $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ we have three-diagonal matrix with an accuracy of diagonalization depending on the maximum value of J accepted in calculations.

Thus, for example, calculation of the parameters of transitions between energy levels with $J = 50$ and $J = 49$ requires diagonalization of a rather large matrix (about 100×100). Moreover, the vector \mathbf{J} equal to the composition of \mathbf{N} and \mathbf{S} vectors was assumed^{2,4} to be the motion vector being conserved. However, the absence of commutation between \mathbf{N}^2 and \mathbf{S}_ξ , \mathbf{N}^2 and \mathbf{J}_ξ (ξ is an axis in the molecular coordinate system) makes it difficult, when allowing for the nuclear spin, to use the traditional approach to forming the Hamiltonian matrix. In our approach, since the vector of total momentum, \mathbf{F} , is the motion vector being conserved, the formation of the Hamiltonian matrix is carried out

according to scheme $\mathbf{F} = \mathbf{J} + \mathbf{I}$ which is more adequate to the vector composition rules and to the general physical sense of vector interactions in the molecule O_2 including ^{17}O isotope. Analogous approach was used in Ref. 12 for the state $^2\Sigma$ with the electron spin $S = 1/2$ and the nuclear one $I = 3/2$.

For the oxygen molecules having the isotope ^{17}O the effective Hamiltonian matrix for given F in the absence of external actions (magnetic or electrical field) has the block-diagonal structure that essentially simplifies the calculation of its eigenvalues.

2. CONSTRUCTION OF THE EFFECTIVE HAMILTONIAN

Let us construct the effective Hamiltonian based on the Hund scheme of composition of vectors of momentum, the case $b_{\beta\gamma}$ (see Ref. 4).

The components of the effective Hamiltonian corresponding to rotation, spin-rotation and spin-spin interactions (the electron spin is meant) are the same for all isotopic modifications of oxygen, and for the molecules without the ^{17}O isotope they completely describe the spectrum.

Interactions, including the nuclear spin angular momentum, cause hyperfine splitting of spectra. It is usually very small and can only be observed at spectral resolution of several megahertz. The Hamiltonian written in the general form is as follows²:

$$H^{\text{eff}} = BN^2 + DN^4 + \gamma(\mathbf{NS}) + \gamma_d(\mathbf{NS})N^2 + \gamma_{dd}(\mathbf{NS})N^4 + 2/3\lambda(3S_z^2 - S^2) + 1/3\lambda_d[(3S_z^2 - S^2), N^2]_+ + b(\mathbf{IS}) + c(3I_z S_z - \mathbf{IS}) + \chi/(4I(2I-1))(3I_z^2 - I^2), \quad (2.1)$$

where

$$BN^2 + DN^4 = H_R \quad (2.2)$$

is the rotational term allowing also for the centrifugal distortion,

$$\gamma(\mathbf{NS}) + \gamma_d(\mathbf{NS})N^2 + \gamma_{dd}(\mathbf{NS})N^2 = H_{SR} \quad (2.3)$$

is the term allowing for the spin-rotation interaction,

$$2/3\lambda(3S_z^2 - S^2) + 1/3\lambda_d[(3S_z^2 - S^2), N^2]_+ = H_{SS} \quad (2.4)$$

is the term allowing for the spin-spin interaction,

$$b(\mathbf{IS}) = H_{FC} \quad (2.5)$$

is the term allowing for the Fermi-contact interaction,

$$c(3I_z S_z - \mathbf{IS}) = H_{DD} \quad (2.6)$$

is the term allowing for the dipole-dipole interaction,

$$(3I_z^2 - I^2) \chi / (4I(2I-1)) = H_Q \quad (2.7)$$

is the term allowing for the quadrupole interaction.

Using Eq. (2.1) for the matrix of the effective Hamiltonian the energy structure of all isotopic modifications of the oxygen molecule can be calculated.

In this paper the values of constants entering into the effective Hamiltonian are taken from Refs. 2, 6, 8. But for $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ modification the Fermi-contact and dipole-dipole interactions are determined differently² that leads to the necessity of using the formulas of transition from Refs. 12: $b = b' + c'/3$; $c = c'/3$. The constants used in our calculations are given in Table 1.

We propose to construct the effective Hamiltonian in the subspace of functions with the fixed total angular momentum

\mathbf{F} ($\mathbf{F} = \mathbf{J} + \mathbf{I}$). Naturally, the Hamiltonian matrix has the block-diagonal form too, since all matrix elements for $F' \neq F$ equal zero. Dimension of a single block of the matrix does not exceed 18×18 (see the figure), and diagonalization of the matrix, for example, with the Jacobi method¹³ is quite easy.

The matrix elements of the effective Hamiltonian interactions in the general form, i.e. in terms of $6-j$ and $9-j$ symbols, can be found in Refs. 9 and 12, and they differ only by constant factors. Analytical expressions for these elements in terms of quantum numbers are presented in Ref. 9. Unfortunately, not all necessary matrix elements are presented there and, moreover, the book has many misprints. Therefore the formulas for the matrix elements were obtained all over again.

TABLE I.

Constant	Value, MHz	
	$^{16}\text{O}^{17}\text{O}$	$^{17}\text{O}^{18}\text{O}$
B	41830.6	39437.4
D	-0.138	-0.123
γ	-245.114	-231.049
γ_d	-0.00024	-0.00027
γ_{dd}	0.00000031489	0.0000002769
b	-54.863	-54.89
λ	59500.09	59497.80
λ_d	0.0575	0.054
c	46.57	46.56
χ	-8.3	-7.8

J		1	2	3	4	5	6
	N	0 1 2	1 2 3	2 3 4	3 4 5	5 6 7	5 6 7
1	0	A D	E	G			
	1	A	B E	G			
	2	D A	B	C G			
2	1	B	A D	E	G		
	2	E B	A	B E	G		
	3	E	D A	B	C G		
3	2	G C	B	A D	E	G	
	3	G	E B	A	B E	G	
	4	G	E	D A	B	C G	
4	3		G C	B	A D	E	G
	4		G	E B	A	B E	G
	5		G	E	D A	B	C G
5	4			G C	B	A D	E
	5			G	E B	A	B E
	6			G	E	D A	B
6	5				G C	B	A D
	6				G	E B	A
	7				G	E	D A

FIG. 1.

$A = \langle NSJIF | H^{\text{eff}} | NSJIF \rangle$ is the sum of nonzero matrix elements for the transition $N \rightarrow N, J \rightarrow J$;
 $B = \langle NSJ \mp 1 IF | H_{FC} + H_{DD} + H_Q | NSJIF \rangle$ is the sum of nonzero matrix elements for the transition $N \rightarrow N, J \rightarrow J \mp 1$;
 $C = \langle NSJ \mp 2 IF | H_Q | NSJIF \rangle$ is the sum of nonzero matrix elements for the transition $N \rightarrow N, J \rightarrow J \mp 2$;
 $D = \langle N \mp 2 SJIF | H_{SS} + H_{DD} + H_Q | NSJIF \rangle$ is the sum of nonzero matrix elements for the transition $N \rightarrow N \mp 2, J \rightarrow J$;
 $E = \langle N \mp 2 SJ \mp 1 IF | H_{DD} + H_Q | NSJIF \rangle$ is the sum of the nonzero matrix elements for transition $N \rightarrow N \mp 2, J \rightarrow J \mp 1$;
 $G = \langle N \mp 2 SJ \mp 2 IF | H_Q | NSJIF \rangle$ is the sum of the nonzero matrix elements for transition $N \rightarrow N \mp 2, J \rightarrow J \mp 2$;
 For H^{eff} see Eq. (2.1), H_{FC} and H_{DD} - Eqs. (2.5) and (2.6), H_Q - Eq. (2.7), H_{SS} - Eq. (2.4).

3. ANALYSIS OF RESULTS

The results on the multiplet energy values obtained for $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ are sufficiently close to the experimental ones (see Table 2). The average deviation for $^{16}\text{O}^{17}\text{O}$ in our case was about 0.051 MHz that looks like a good result taking into account that experimental accuracy was 0.020 MHz (Ref. 2) and average standard deviation for calculations of the spectral line centers is 0.022 MHz (Ref. 2). The same is valid for $^{17}\text{O}^{18}\text{O}$: the average deviation (0.058 mHz) that moderately exceeds the sum of experimented error (0.020 mHz) and the average standard deviation (0.036 mHz) (Ref. 2).

Thus, the method of effective Hamiltonian with the fixed F we used allows quite accurate description of experimental data. To obtain more accurate results, the inverse spectroscopic problem for determination of molecular constants should be solved.

TABLE II.

Number of lines and their deviations from the experiment	$^{16}\text{O}^{17}\text{O}$		$^{17}\text{O}^{18}\text{O}$	
	Ref. 2	This paper	Ref. 2	This paper
Number of lines total:	59	59	30	30
with deviation, MHz				
up to 0.022	17	14	10	8
up to 0.042	28	32	15	18
more than 0.0	31	27	15	12
Deviation, MHz:				
maximum	0.144	0.161	0.127	0.135
minimum	0.002	0.005	0.004	0.005
average	0.047	0.051	0.052	0.058

CONCLUSION

It is shown that in order to calculate parameters of the isotopic modifications of oxygen molecule the block-diagonal form of the effective Hamiltonian matrix may be

used. This form simplifies the calculations significantly while not causing the loss of accuracy. Calculation of the probability of transition in multiplets is planned for the next stage.

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