Theoretical treatment of the vibrational-rotational spectra of stable diatomic radicals in the $^2\Pi$ state

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The paper summarizes models of the effective operators (Hamiltonian and dipole moment operators) presented in the literature. These models are used for theoretical treatment of spectra of diatomic molecules in the nonsinglet $^2\Pi$ state. Matrix elements are presented of the effective operators calculated in the basis of a set of wave functions corresponding to Hund's case (a).

Introduction

In this paper I consider the problems, which arise in a study of the energy levels and line intensities of diatomic molecules in nonsinglet $^2\Pi$ state. This state is the ground state of the nitric oxide molecule and stable radicals like OH and ClO, which play an important role in the photochemistry of the troposphere and stratosphere. The interaction of electron motions with the molecular rotation and vibration determines specific features of the spectra of these molecules and, accordingly, of the theoretical treatment. Therefore, to create a global treatment model of the vibrational-rotational spectra of stable diatomic radicals analysis of theoretical models considered in the literature has been performed.

The $^2\Pi$ electronic state is characterized by a unity projection of the orbital angular momentum on the molecular axis and by the total spin of 1/2. The designations of the momenta used and corresponding quantum numbers are given in Table 1.

Since $\Lambda \neq 0$, the state is twice degenerate relative to Λ and thus the projection of the spin Σ can take both positive and negative values. The $^2\Pi$ state is a multiplet comprising two components, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. These two components correspond to different values of the projection of the total electronic angular momentum on the molecular axis Ω, $\Omega = |\Lambda + \Sigma|$, equal to 1/2 and 3/2, respectively. Splitting into two components is due to spin-orbital interaction. Each of the components, in its turn, remains degenerate relative to Λ, the so-called Λ-doubling.

Table 1. The designations of the angular momenta

The type of angular momentum	Operator	Quantum numbers	
		Total	Projection
Electronic orbital	L	L	Λ
Electronic spin	S	S	Σ
Rotational	R	R	...
Total	$J = R + L + S$	J	$\Omega = \Lambda + \Sigma$
Total–Spin	$N = R + S$	N	Λ

The vibrational-rotational spectrum of such a molecule consists of two subbands as if corresponding to the vibrational-rotational spectra of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components, respectively. As long as L electronic orbital angular momentum and S spin angular momentum precess about the molecular axis, quantum numbers Λ, Σ shall remain "good". This means that the quantum number Ω is also "good" and the transitions between the components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are forbidden by the selection rule $\Delta\Sigma = 0$. This case is referred to as Hund's case (a) when the spin-orbit split $\Delta E \sim A\Lambda\Sigma$ is large compared with the rotational energy and the interaction between molecular rotation and electron motions is weak. The constant of spin-orbit interaction A may take both positive and negative values. If $A > 0$ (ordinary situation) the energy of the $^2\Pi_{1/2}$ state is lower than that of the $^2\Pi_{3/2}$ state. For the $A < 0$ the situation is the opposite.

With the increasing rotational energy of a molecule, the interaction between molecular rotation and orbital motion increases, the spin selection rule may be violated and, as a result, gradual transition of the molecule from the state characterized as Hund's case (a) to Hund's case (b) occurs. Therefore, in addition to the $^2\Pi_{1/2} \to {}^2\Pi_{1/2,}$ and $^2\Pi_{3/2} \to {}^2\Pi_{3/2}$ subbands, $^2\Pi_{1/2} \rightleftarrows {}^2\Pi_{3/2}$ transitions will take place. Thus the vibrational-rotational spectrum comprises two subbands $^2\Pi_{1/2} \to {}^2\Pi_{1/2,}$ and $^2\Pi_{3/2} \to {}^2\Pi_{3/2}$ the so-called main subbands, and two weak satellite subbands $^2\Pi_{1/2} \rightleftarrows {}^2\Pi_{3/2}$. Intensity of the satellite subbands is 10^4 lower than the intensity of the main subbands.[1]

The interaction between $^2\Pi$ state with other Σ electronic states (singlet states) lifts the $\pm\Lambda$ degeneracy and leads to doubling of the levels. The interaction between the rotational and orbit motion yields Λ doubling for any angular momentum J and it increases with increase of the total angular momentum J.

Thus, all the specific features in the spectra of diatomic molecules in the ground nonsinglet $^2\Pi$ state are accounted for in the models that are used in calculations of the line centers and intensities.

Effective Hamiltonian for diatomic molecule in $^2\Pi$ state

The problem of constructing an effective Hamiltonian for multiplet electronic states have been discussed by many authors.[1–11] In processing infrared spectra a phenomenological Hamiltonian with a variable number of interactions and accordingly parameters is used.[12]

For a diatomic molecule in the absence of external field the Hamiltonian for the electronic and nuclear motions can be written[10,11] in the following form:

$$H = H_\mathrm{e} + \frac{1}{2\mu} P_r^2 + B(r)\mathbf{R}^2 + \frac{1}{2M}\Pi^2 + H_\mathrm{SO} + H_\mathrm{SR} + H_\mathrm{SS}, \tag{1}$$

in the system of coordinates with the origin in the center of mass of the molecule. In Eq. (1) $\mu = M_\mathrm{a}M_\mathrm{b}/(M_\mathrm{a} + M_\mathrm{b})$ and $M = M_\mathrm{a} + M_\mathrm{b}$ are, respectively, the reduced and total mass of the nuclei.

$$B(r) = \hbar^2/2hc\mu r^2; \ \Pi = \sum_i p_i$$

is the total momentum of the electrons; H_e includes both the kinetic energy of the electrons and the complete Coulomb potential energy. The second term in Eq. (1) is the vibrational kinetic energy, the third one is the rotational energy:

$$\begin{aligned} H_\mathrm{R} &= B(r)\mathbf{R}^2 = B(r)(\mathbf{J} - \mathbf{L} - \mathbf{S})^2 = \\ &= B(r)\{(J^2 - J_z^2) + (L^2 - L_z^2) + (S^2 - S_z^2) - \\ &-(J_+L_- + L_+J_-) - (J_+S_- + S_+J_-) + (S_+L_- + L_+S_-)\}; \end{aligned} \tag{2}$$

$$H_\mathrm{SO} = A(r)\,\mathbf{LS} = A(r)\{L_zS_z + \frac{1}{2}(L_+S_- + L_-S_+)\} \tag{3}$$

is the operator of the spin-orbit interaction;

$$H_\mathrm{SS} = \lambda(r)(3S_z^2 - S^2) \tag{4}$$

is the operator of the spin-spin interaction;

$$H_\mathrm{SR} = \gamma(r)\mathbf{NS} \tag{5}$$

is the operator of the spin-rotation interaction. Some authors (Refs. 8 and 13) use the phenomenological form of the spin-rotation operator (5) $H_\mathrm{SR} = \gamma(r)\mathbf{RS}$:

$$\begin{aligned} H_\mathrm{SR} &= \gamma(r)\mathbf{RS} = \gamma(r)(\mathbf{J} - \mathbf{L} - \mathbf{S})\mathbf{S} = \\ &= \gamma(r)\{(J_zS_z - L_zS_z - S^2) + \frac{1}{2}(J_+S_- + J_-S_+) - \\ &- \frac{1}{2}(L_+S_- + L_-S_+)\}. \end{aligned} \tag{5a}$$

Representation the spin-rotation operator in such a form simulate an additional term in the spin-orbit interaction. This term gives small corrections to spin-orbit constant $A(r)$. As a rule, this correction is neglected in calculating the matrix elements. Various representations of the spin-orbit operator give rise to difference in matrix elements of the effective Hamiltonian.

In the above formulas $B(r)$ is rotational constant, $A(r)$, $\gamma(r)$, $\lambda(r)$ are parameters associated with the spin-orbit, spin-rotation, and spin-spin interactions.

To derive an effective rotational Hamiltonian for a degenerate state of a diatomic molecule one uses three-stage scheme of transformation to separate "electronic," "vibrational," and "rotational" parts. Quite often, to separate the variables in the Hamiltonian, the Van Vleck transformation is used,[14] which is a particular case of the generalized contact transformations.[11] Following Refs. 6 and 8, consider the scheme of formulation of the effective Hamiltonian.

The zero-order approximation is defined as $H_0^\mathrm{e} = H_\mathrm{e}$, and the other terms from the complete electron-nuclei Hamiltonian determine the perturbation operator:

$$H = H_0^\mathrm{e} + \lambda V,$$

where

$$V = \frac{1}{2\mu} P_r^2 + B(r)\mathbf{R}^2 + \frac{1}{2M}\Pi^2 + H_\mathrm{SO} + H_\mathrm{SR} + H_\mathrm{SS}. \tag{6}$$

We assume that the electronic states are located far enough from each other, the spin-orbit coupling is weak compared with the electronic energy intervals and can be considered as perturbation. The choice of a set of basic functions is arbitrary, however under the assumptions made, one chooses the wave functions corresponding to Hund's case (a) coupling. The case (a) wave functions are denoted by $|n\Lambda S\Sigma, r\rangle$ as functions of the internuclear distance r. The solution of electronic Schrödinger equation with the H_0^e Hamiltonian gives us the electronic energy, which depends on the internuclear distance and represents the Born-Oppenheimer potential for the motion of the nuclei in the nth electronic state. This state with the basic vector $|n\Lambda S\Sigma, r\rangle$ is degenerate, since for a given electronic quantum number n there are $2S+1$ possible spin projections $-S, -S+1, \ldots, S$ and two possible orbital angular momentum projections $-\Lambda$, Λ for $\Lambda \neq 0$.

The electronic contact transformations are being chosen such that they enable one to remove the off-diagonal relative to n matrix elements from the Hamiltonian. As a rule, one uses for that perturbation theory in terms of projectors (Refs. 8, 10, 11). The projector on the electronic state n is constructed $P_n^{(r)} = |n\rangle\langle n|$, where index (r) means the dependence on the internuclear distance. The explicit form of the perturbation operator may be written in the following form:

$$V = \frac{1}{2M}\Pi^2 + \frac{1}{2\mu}P_r^2 + B(r)(L^2 - L_z^2) +$$
$$+B(r)\{(J^2 - J_z^2) + (S^2 - S_z^2)\} + A(r)L_zS_z +$$
$$+\lambda(r)(3S_z^2 - S^2) + \gamma(r)(J_zS_z - S^2) -$$
$$-(B(r) - \gamma(r)/2)(J_+S_- + S_+J_-) - B(r)(J_+L_- + L_+J_-) +$$
$$+\frac{1}{2}\{A(r) + 2B(r) - \gamma(r)\}(L_+S_- + L_-S_+). \quad (7)$$

It must be noted, that the perturbation operator is nondiagonal in quantum numbers n and Λ. After separation of the electronic variables an effective Hamiltonian for nonsinglet electronic state n, treated up to the second order of perturbation theory, is presented in the form[10,11]:

$$H_n = \tilde{W}_n(r) + \frac{1}{2\mu}P_r^2 + B_n(r)\{(J^2 - J_z^2) +$$
$$+(S^2 - S_z^2)\} + A_n(r)L_zS_z + \lambda_n(r)(3S_z^2 - S^2) +$$
$$+\gamma_n(r)(J_zS_z - S^2) - (B_n(r) - \gamma_n(r)/2)(J_+S_- + S_+J_-) +$$
$$+\{O_{n+}(r)S_-^2 + O_{n-}(r)S_+^2\} - \{P_{n+}(r)J_-S_- + P_{n-}(r)J_+S_+\} +$$
$$+\{Q_{n+}(r)J_-^2 + Q_{n-}(r)J_+^2\}, \quad (8)$$

where $\tilde{W}_n$ is the effective potential,

$$\tilde{W}_n = W_n(r) + W_n^{\mathrm{ad}}(r) + W_n^{\mathrm{n.ad}}(r) + W_n^{(\mathrm{s})}(r). \quad (9)$$

First term provides the Born-Oppenheimer potential, the second term arisen from the first order of the perturbation is the adiabatic correction to this potential:

$$W_n^{\mathrm{ad}}(r) = \frac{1}{2\mu}\langle n|P_r^2|n\rangle + \frac{1}{2M}\langle n|\Pi^2|n\rangle + B(r)\langle n|(L^2 - L_z^2)|n\rangle. \quad (10)$$

The nonadiabatic correction $W_n^{\mathrm{n.ad}}$ appears in the second order of perturbation and includes the nondiagonal matrix elements of electronic operators. The quantity $W_n^{(\mathrm{s})}$ represents the correction to the potential due to spin-spin interactions. The last three terms in Eq. (8) produce Λ-doubling effects. The index n indicate the electronic state with quantum number n for which the effective Hamiltonian and its parameters are written. Formulas for the parameters of the effective Hamiltonian (8) are given in Refs. 6 and 10. Thus, the equation (8) offers the effective Hamiltonian for nuclear motion in nonsinglet electronic state.

In the literature, the unit-perturbation method (Refs. 6 and 9) is frequently employed for derivation of such a Hamiltonian. In this approach, the account for interactions with other electronic states is restricted to the interaction with one state. So, the interaction with other electronic state is replaced by second order corrections, which are found by Van Vleck transformation.[6,8] The relations between parameters obtained using the unit-perturbation approximation and the parameters resulting from full contact transformation can be found in Ref. 10.

After separating the electron variables the effective Hamiltonian (8) undergoes vibrational contact transformation. This provides an effective spin-rotational Hamiltonian for each vibronic state with the quantum numbers n and v. As a rule,[6,8,10,12] the effective Hamiltonian is developed in the Born-Oppenheimer approximation neglecting the corrections in Eq. (9). However, it is possible to perform the contact transformation of the effective Hamiltonian (8) with the account of the deviations from the Born-Oppenheimer approximation. The consideration of adiabatic and nonadiabatic corrections in Eq. (8) do not affect the form of the vibrational and rotational energy but it gives small correction to the spectroscopic parameters.[10,11,15,16]

In order to calculate energy in an analytical form one has to use certain parameterization of the potential function.[11,17] More often the potential function of a diatomic molecule is presented by a power series expansion in the Dunham coordinate $\xi = (r - r_\mathrm{e})/r_\mathrm{e}$ or in non-dimensional normal coordinate $q = \beta^{-1}(r - r_\mathrm{e})/r_\mathrm{e}$.

The expansion of the potential function may be presented in the following way

$$W(q) = \omega(\frac{1}{2}q^2 + \alpha_1 q^3 + \alpha_2 q^4 + \ldots + \alpha_n q^n), \quad (11)$$

where $\omega \equiv \omega_\mathrm{e}$ is the fundamental vibrational frequency (cm^{-1}); $\alpha_n = K_{n+2}/\omega$ are the reduced anharmonic potential constants (non-dimensional); $\beta = (2B_{n\mathrm{e}}/\omega_\mathrm{e})^{1/2}$ is the reduced rotational constant. The radial dependence of the constants $A_n(r)$, $\gamma_n(r)$, $\lambda_n(r)$, $B_n(r)$, $O_n(r)$, $P_n(r)$, $Q_n(r)$ in the effective Hamiltonian (8) yields the appearance of the off-diagonal, relative to the vibrational quantum number v, matrix elements. Therefore, the vibrational contact transformations are chosen so that they remove the off-diagonal matrix elements. As zero-order approximation the harmonic oscillator $H_{n\mathrm{e}}^{\mathrm{V}}$ and the rigid rotor H_{n0}^{R} are used

$$H_{n0} = \frac{\omega}{2}(p^2 + q^2) + B_{n\mathrm{e}}\{(J^2 - J_z^2) + (S^2 - S_z^2)\}. \quad (12)$$

The remaining terms are treated as a perturbation, which is considered weak compared to the vibrational energy. After separation of the vibrational variables the resultant effective Hamiltonian for the spin-rotation structure is generally presented by its matrix elements in the set of basis functions corresponding to Hund's case (a) coupling. These functions are denoted by $|nv\Lambda S\Sigma\, J\Omega M\rangle$, where $|nv\rangle$ is the vibrational part; $|\Lambda\Sigma\rangle$ is the electronic part, and $|J\Omega M\rangle$ is the rotational part of the function. These wave functions are the eigenfunctions of the operators J^2, S^2, J_Z, S_Z, and L_Z with the corresponding eigenvalues $J(J + 1)$, $S(S + 1)$, Ω, Σ, and Λ. However, the operator L^2 is not diagonal in this representation. The phase conventions are chosen so that the matrix elements of the ladder operators $J_\pm$ and $S_\pm$ are defined as follows:

$$\langle J\Omega \pm 1|\mathbf{J}_{\pm}|J\Omega\rangle = \left[J(J+1) - \Omega(\Omega \pm 1)\right]^{1/2}, \quad (13)$$

$$\langle S\Sigma \pm 1|\mathbf{S}_{\pm}|S\Sigma\rangle = \left[S(S+1) - \Sigma(\Sigma \pm 1)\right]^{1/2}. \quad (14)$$

Note, that different authors use different phase conventions for the spin function (Refs. 6, 8, 13, 18, and 19). The matrix of the effective Hamiltonian for $^2\Pi$ state evaluated in the set of basis functions corresponding to Hund's case (a) coupling will have 4 × 4 dimension. As known, the calculation of energy levels significantly depends on the choice of the basis set parity. Each of the wave functions may be classified as even or odd according to whether it remains unchanged or changes its sign upon inverting the space. The molecular Hamiltonian is invariant under inversion, and only the transitions between the states of the same parity will have nonvanishing matrix elements. In thus symmetrized basis set the matrix of effective Hamiltonian will consist of two non-interacting blocks, one for even and the other for odd-parity functions. If the wave functions of well-defined parity (even or odd) are constructed from Hund's case (a) functions than the matrix of Hamiltonian will be divided in two 2 × 2 blocks.

To classify the states of heteronuclear diatomic molecules the $C_{\infty v}$ molecular symmetry group is used, that consists of two elements, one of which is the inversion $\mathbf{I}(E^*)$. The geometric symmetry operation $\sigma_v(xz)$ (reflection from the xz plane), when it is applied to the electronic, vibrational, and rotational variables, is equivalent to the operation of inversion $\mathbf{I}(E^*)$ in a space-fixed system of coordinates. Inverting the spatial coordinates the wave function $|nv\Lambda S\Sigma J\Omega M\rangle$ for $^2\Pi$ state is transformed as follows[18]:

$$\sigma_v(I)\left|nv\,\Lambda S\Sigma\,J\Omega M\right\rangle = \\ = \pm(-1)^{L-\Lambda+S-\Sigma+J-\Omega}\left|nv - \Lambda S - \Sigma\,J - \Omega M\right\rangle. \quad (15)$$

The expression (15) allows one to construct the basic wave functions of different parity as linear combinations:

$$\left|nv\,\Lambda S\Sigma\,J\Omega M(\pm)\right\rangle = \\ = \frac{1}{\sqrt{2}}\left(\left|nv\,\Lambda S\Sigma\,J\Omega M\right\rangle \pm \left|nv - \Lambda S - \Sigma\,J - \Omega M\right\rangle\right). \quad (16)$$

The wave function $|nv\Lambda S\Sigma J\Omega M+\rangle$ is defined even and corresponds to the sublevel "*e*" (or "*c*"), while the function $|nv\Lambda S\Sigma J\Omega M-\rangle$ is defined odd and corresponds to the sublevels "*f*" (or "*d*"). Therefore, for each value of the quantum number J two wave functions can be constructed for the components $|\Omega| = 1/2$ or $|\Omega| = 3/2$ of the $^2\Pi$ state. One of these functions will have the even parity and the other will have the odd parity. The matrix of the effective Hamiltonian will be split in two blocks for even "*e*" and odd "*f*" wave functions. For simplification the wave function (16) for each of the components $|\Omega| = 1/2$ and $3/2$ of the $^2\Pi$ state will be written as $|nv\,{}^2\Pi_{1/2}JM\rangle^{e,f}$ and $|nv\,{}^2\Pi_{3/2}JM\rangle^{e,f}$ correspondingly.

As a rule, the effective spin-rotational Hamiltonian of the $^2\Pi$ state is represented by its matrix elements in a basis of symmetrized functions. Since different methods are employed in constructing the effective Hamiltonian, the matrix elements may have differences (Refs. 6, 8, 10, 12, and 20). In this paper, we present the matrix elements of the effective Hamiltonian constructed in the unit-perturbation approximation, in which only the interaction with one of the states Σ^+ or Σ^- is taken into account. Such a model is often used in processing the experimental data. Note, that the spin-spin interaction in the $^2\Pi$ states equals zero and thus it is ignored in calculating the matrix elements.

Diagonal matrix elements independent of quantum number J:

$$^{e,f}\langle nv\,{}^2\Pi_{1/2}JM\,|H^{\mathrm{eff}}|\,nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = T_e + G_v - A_v/2 - \gamma_v/2 + o_v, \quad (17)$$

$$^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\,|H^{\mathrm{eff}}|\,nv\,{}^2\Pi_{3/2}JM\rangle^{e,f} = \\ = T_e + G_v + A_v/2 - \gamma_v/2, \quad (18)$$

where T_e is the electronic energy;

$$G_v = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \ldots \quad (19)$$

is the vibrational energy; v is the vibrational quantum number; ω_e, $\omega_e x_e$, $\omega_e y_e$ are the spectroscopic vibrational constants.

Diagonal matrix elements dependent on the quantum number J:

$$^{e,f}\langle nv\,{}^2\Pi_{1/2}JM\,|H^{\mathrm{eff}}|\,nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = (B_v - A_{Jv}/2 - \gamma_{Jv}/2)(x+1) - \\ -D_v\left[(x+1)^2 + x\right] + H_v\left[(x+1)^3 + x(3x+1)\right] + \\ + \frac{1}{2}\{p_v + p_{Jv}(x+1)\}\left[1 \mp (J+1/2)\right] + \\ + \frac{1}{2}\{q_v + q_{Jv}(x+1)\}\left[x + 2 \mp (J+1/2)\right]; \quad (20)$$

$$^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\,|\,H^{\mathrm{eff}}\,|\,nv\,{}^2\Pi_{3/2}JM\rangle^{e,f} = \\ = (B_v - A_{Jv}/2 - \gamma_{Jv}/2)(x-1) - D_v\left[(x-1)^2 + x\right] + \\ + H_v\left[(x-1)^3 + x(3x-1)\right] + \frac{1}{2}\{q_v + q_{Jv}(x-1)\}x. \quad (21)$$

Off-diagonal matrix elements:

$$^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\,|\,H^{\mathrm{eff}}\,|\,nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = \{-B_v + \gamma_v/2 + (1/2)\gamma_{Jv}J(J+1) + 2D_v x - \\ -H_v(3x^2 + x + 1) - (1/4)[p_v + p_{Jv}J(J+1)] + \\ + \frac{1}{2}[q_v + q_{Jv}J(J+1)][-1 \pm (J+1/2)]\}(x)^{1/2}. \quad (22)$$

In all matrix elements the superscripts denote "*e*" levels, while the subscripts denote the "*f*" levels. For the sake of simplicity the following notation is used $x = (J + 1/2)^2 - 1$. All the constants B, D, H, A, γ, p, q, and o are the functions of the vibrational quantum number and thus are supplied with the subscript v:

$$B_v = B_e - \alpha_e(v+1/2) + \ldots .$$

$$D_v = D_e + \beta_e(v+1/2) + \ldots ,\ H_v = H_e + \kappa_e(v+1/2) + \ldots$$

$$A_v = A_e + \chi_e(v+1/2) + \ldots .$$

Parameters p_v, q_v, and o_v are the so-called Λ-doubling constants with their notation being a standard one.[6] These parameters appear in the Hamiltonian if the interactions of $^2\Pi$ state with other electronic states are to be allowed for. Definitions of parameters p_v, q_v, o_v are given in the Appendix 1. It is necessary to emphasize, that the matrix elements of effective Hamiltonian presented by Eqs. (20)–(22) are defined for the positive phase of the spin function (13) and for the model of unit perturbation. Change of the spin function phase and complete account for the interactions among the electronic states will change the formulas (20)–(22). The corresponding matrix elements for the effective Hamiltonian by Brown[10] are given in the Appendix 2.

The effective spin-rotational Hamiltonian for the $^2\Pi$ state, which is presented by its matrix elements (17)–(22), is ambiguous. The ambiguity arises due to the possibility of unitary transformations $\tilde{H} = e^{iS}H^{\mathrm{eff}}e^{-iS}$, which do not change eigenvalues, operator form, but considerably change its parameters. The existing ambiguity leads to strong correlation among the parameters of the effective Hamiltonian, which makes the processing of experimental data by use of this model too difficult. Reduced effective Hamiltonians are free of ambiguities. Different forms of reduced effective Hamiltonians have been used for diatomic molecules in $^2\Pi$ state.[10]

The eigenvalues of the effective spin-rotational Hamiltonian presented by Eqs. (17)–(22) are obtained by means of diagonalization of two matrices for even and odd states, which difference is caused by Λ-doubling. For each of the $^2\Pi$ state components the rotational levels will be doublets with the subscripts "e" (+) and "f" (–). Since the matrices of the effective Hamiltonian are of 2×2 dimension, then the diagonalization can be made analytically and the resulting expressions for the vibration-rotation energies of diatomic molecule in the $^2\Pi$ state can be written in explicit form[21]:

$$E_i(\Omega_i,v,J) = T_e + G_v + B_v[(J+1/2)^2 - \Lambda^2] +$$
$$+B_v[L(L+1) - \Lambda^2] - D_v[(J+1/2)^4 - (J+1/2)^2 + 1] +$$
$$+(-1)^{i+1}[B_v^2(J+1/2)^2 + (1/4)A_v(A_v - 4B_v)\Lambda^2]^{1/2} \pm$$
$$\pm E_i^{\Lambda}(v,J), \qquad (23)$$

where $i = 1, 2$ denotes the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$ states, respectively. The Λ-doubling energy terms $E_i^{\Lambda}(v,J)$ are approximated by[21]:

$$E_1^{\Lambda}(v,J) = -2p(J+1/2) - E_2^{\Lambda}(v,J), \qquad (24)$$

$$E_2^{\Lambda}(v,J) = -\left[4q\Big/\left(\frac{A_v}{B_v}-2\right) + 2p\Big/\left(\frac{A_v}{B_v}-2\right)^2\right]z, \qquad (25)$$

$$z = (J-1/2)(J+1/2)(J+3/2).$$

The parameters A_v, p, and q in equations (23)–(25) are assumed independent of J and the effective spin-rotational constant γ_v is zero.

Line intensities

The intensity of an absorption spectral line S_a^b, corresponding to a transition between the states $a = \{nv\Lambda S\Sigma\ J\Omega_i M\}$ and $b = \{n'v'\Lambda'S'\Sigma'\ J'\Omega_k M'\}$ is proportional, in the dipole approximation, to the transition probability $W_{a\to b}$, which is defined as follows:

$$W_{a\to b} = |\langle\Psi_b|\mu_Z|\Psi_a\rangle^2, \qquad (26)$$

where Ψ_a and Ψ_b are the wave functions of the lower and upper states; $\boldsymbol{\mu}_Z$ is the dipole moment of the molecule in the space-fixed coordinate system. Since we consider vibrational-rotational transitions inside a degenerate $^2\Pi$ electronic state, the conditions $\Delta\Lambda = 0$, $\Delta S = 0$ hold for the transitions between "a" and "b" states. The interaction of the molecular rotation with the electronic motions lifts the prohibition for the spin projections ($\Delta\Sigma = 0$) and makes allowed the transitions between the components $^2\Pi_{3/2} \leftrightarrow {}^2\Pi_{1/2}$. In the case of transitions between rotational levels the following selection rules should hold: $\Delta J = 0, \pm 1$ and $+ \leftrightarrow -$ or "e" $\leftrightarrow$ "f" or "c" $\leftrightarrow$ "d".

The component $\boldsymbol{\mu}_Z$ of the molecular dipole moment in the space-fixed coordinate system is related to the dipole moment $\mu(q)$ oriented along the molecular axis via the direction cosine φ_Z:

$$\mu_Z = \varphi_Z\mu(q). \qquad (27)$$

One can see that for evaluating the transition probability defined by Eq. (26), it is necessary to know the correct wave functions of lower and upper states and the dipole moment function of the molecule. The projection of the dipole moment in the molecular-fixed system is usually presented as a power series over normal coordinates. Therefore, the calculation of transition probabilities is quite a complicated problem, in which different formulations of perturbation theory are used to take into account the intramolecular interactions. As a rule, the so called Hönl-London factor S_R is separated out in Eq. (26). This factor represents squared matrix elements of a direction cosine calculated with the account for summation over the magnetic quantum number. Often the Hönl-London factor is called the rotational line strength. The transition probability (26) may be written in the following form[22]:

$$W_{a\to b} = S_R M^2(v, J, \Omega_i \to v', J', \Omega_k),$$

where $M(v,\ J,\ \Omega_i \to v',\ J',\ \Omega_k)$ is radial matrix element of the dipole moment in the molecular-fixed coordinate system:

$$M(v,J,\Omega_i \to v',J',\Omega_k) = \langle vJ\Omega_i|\mu(q)|v'J'\Omega_k\rangle. \quad (28)$$

Now two methods are realized for the calculating the transition probabilities of diatomic molecules in the $^2\Pi$ state. Chronologically the first method realizes the formalism of effective operators: Hamiltonian and the operator of dipole moment. It allows one to relate, based on theory of perturbations, the parameters of the initial models of effective dipole moment deduced from fitting of experimental intensities to those of molecular dipole moment function. The transition probability (26) in such a method can be written[22]:

$$W_{\mathrm{a}\to\mathrm{b}} = S_R\, M^2(v \to v')\, F^2_{v\to v'}(m), \quad (29)$$

where $M(v \to v')$ is the matrix element of the dipole moment over vibrational wave functions; $F_{v\to v'}(m)$ is the factor that allows for the vibrational-rotational interaction, or the so-called Herman-Wallis factor[22–25]:

$$F_{v\to v'}(m) = 1 + Cm + Dm^2 + \ldots, \quad (30)$$

where

$m = J' = J + 1$ for the R-branch,
$m = -J' = J - 1 = -J$ for the P-branch.

Here C, D, and so on are the functions depending on the molecular constants and they are called the Herman-Wallis coefficients. We emphasize that with the increase of the difference between the upper and lower vibrational quantum numbers $\Delta v = v' - v$, the order numbers of the contributions to be accounted for in the perturbation theory in calculating the transition probabilities also increases.

For the diatomic molecules in singlet states the analytical relations for calculating the transition probabilities with different Δv have been obtained and realized in calculation algorithms for any overtones.[17] Such an algorithm can be applied if the dipole moment function and the potential function of the molecule are known.

Equation (29) is usually applied for data reduction while the parameters $M(v \to v')$, C, and D are determined from experimental intensities using the least-squares fitting.

In the case of molecules in the $^2\Pi$ state the main $^2\Pi_{1/2} \to {}^2\Pi_{1/2}$ and $^2\Pi_{3/2} \to {}^2\Pi_{3/2}$ and satellite $^2\Pi_{1/2}$ $^2\Pi_{3/2}$ transitions are observed. In practice, to determine the intensities of both type of the transitions, Eq. (29) is used. The rotational line strengths are calculated in a basis set of wave functions of the effective spin-rotational Hamiltonian (Refs. 1, 21 and 26); the expressions for them are given in Table 2.

To evaluate the radial matrix elements of the dipole moment the relations applicable to Σ state of the molecule can be used. Such an approximation is applied when spin-orbit interactions has negligible effect on the transition moment.[27–28] The expressions (29) and (30) are also valid for fitting the experimental data while parameters of the Herman-Wallis factor are sought for each of the main transitions separately.[29–32]

The neglect of influence of the orbital motion on the transition moments is justified for the quantum number $J \approx 15$ because interaction between vibration and rotation is strong, but this influence can be important for low J values, like it was observed for OH molecule. The equations for the moments of the transition with $\Delta v = 1, 2$ were first presented in Refs. 26 and 33. Consider in a more detail the application of formalism of the effective operators to evaluation of the transition probabilities for diatomic molecules in the $^2\Pi$ state.

It is well known that the method of effective dipole moment[24,34] significantly simplifies the calculation of the transition probabilities, because of replacing the calculation of matrix elements of the molecular dipole moment (26) over the exact wave function:

$$\langle\Psi_{\mathrm{a}}|\mu_Z|\Psi_{\mathrm{b}}\rangle = {}^{\mathrm{eff}}\langle\Psi_{\mathrm{a}}|\tilde{\mu}_Z\,|\Psi_{\mathrm{b}}\rangle^{\mathrm{eff}} \quad (31)$$

by calculating matrix elements of the transformed dipole moment over the effective wave function. In the case considered here $|\Psi(\Omega_i, J)|\rangle^{\mathrm{eff}}$ are the eigenfunctions of effective spin-rotational Hamiltonian presented by Eqs. (17)–(22) for $^2\Pi$ state. The latter are written as expansion over wave functions of the state $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$:

$$|\Psi(\Omega_i, J)|\rangle^{\mathrm{eff}} = |v\Omega_i J\,{}^{e}_{f}\rangle^{\mathrm{eff}} = \sum_i {}_iC^J_v({}^{e}_{f})\,|v\rangle\,|\,{}^2\Pi_i J\Omega_i\,{}^{e}_{f}\rangle. \quad (32)$$

Table 2. Hönl-London factor, or rotational line strength factor S_R

Vibrational-rotational transitions	Main subbands $^2\Pi_{3/2} \to {}^2\Pi_{3/2}$ $^2\Pi_{1/2} \to {}^2\Pi_{1/2}$ $\Omega_i \to \Omega_i$	Satellite subbands $^2\Pi_{1/2} \rightleftarrows {}^2\Pi_{3/2}$, $\Omega_i \rightleftarrows \Omega_k$
$vJ \to v'J + 1$ R-branch	$\dfrac{(J+1)^2-\Omega_i^2}{J+1}$	$\dfrac{1}{J+1}\left\{{}_1C^{J+1}_{v'}\,{}_2C^J_v\left[(J+1)^2-\Omega_k^2\right]^{1/2} - {}_1C^J_v\,{}_2C^{J+1}_{v'}\left[(J+1)^2-\Omega_i^2\right]^{1/2}\right\}^2$
$vJ \to v'J - 1$ P-branch	$\dfrac{J^2-\Omega_i^2}{J}$	$\dfrac{1}{J}\left\{{}_1C^{J-1}_{v'}\,{}_2C^J_v\left[J^2-\Omega_k^2\right]^{1/2} - {}_1C^J_v\,{}_2C^{J-1}_{v'}\left[J^2-\Omega_i^2\right]^{1/2}\right\}^2$
$vJ \to v'J$ Q-branch	$\dfrac{(2J+1)\Omega_i^2}{J(J+1)}$	$\dfrac{2J+1}{J(J+1)}\left\{{}_1C^J_{v'}\,{}_2C^J_v\left[\Omega_k\right] - {}_1C^J_v\,{}_2C^J_{v'}\left[\Omega_i\right]\right\}^2$

Indices $\binom{e}{f}$ correspond to notation of the even and odd functions; $|v\rangle$ are the wave functions of the harmonic oscillator; $|^2\Pi_i J\Omega_i \, {}^{e}_{f}\rangle$ are the symmetrized rotational wave functions; ${}_iC_v^J\binom{e}{f}$ are the eigenvector coefficients appearing in the expansion of the wave functions derived from the diagonalization of the matrix of an effective Hamiltonian, i.e., from fitting of either line position or energy levels. Usually, Λ-doubling is ignored in calculating the eigenvectors therefore no indices "*e*" or "*f*" is used for the eigenvectors.

The explicit expressions for the effective wave functions have the following form:

$$|\Psi(\Omega = 3/2, J)\rangle^{\text{eff}} =$$
$${}_1C_v^J\,|v\rangle\,|\,{}^2\Pi_{3/2}J\,\Omega = 3/2\rangle + {}_2C_v^J\,|v\rangle\,|\,{}^2\Pi_{1/2}J\,\Omega = 1/2\rangle, \tag{33}$$
$$|\Psi(\Omega = 1/2, J)\rangle^{\text{eff}} =$$
$$= {}_1C_v^J\,|v\rangle\,|\,{}^2\Pi_{1/2}J\,\Omega = 1/2\rangle - {}_2C_v^J\,|v\rangle\,|\,{}^2\Pi_{3/2}J\,\Omega = 3/2\rangle.$$

Analytical diagonalization of the effective Hamiltonian matrix allows one to obtain explicit expressions for the eigenvectors of this matrix, in which Λ-doubling is neglected[1,21]:

$${}_1C_v^J = \left[(X_v - 2 + A_v/B_v)/2X_v\right]^{1/2},$$
$${}_2C_v^J = \left[(X_v + 2 - A_v/B_v)/2X_v\right]^{1/2}, \tag{34}$$
$$X_v = \left[4(J + 1/2)^2 + A_v/B_v\left(A_v/B_v - 4\right)\right]^{1/2}.$$

The effective dipole moment operator $\tilde{\mu}_Z$ in Eq. (31) is related to the projection of the dipole moment $\boldsymbol{\mu}_Z$ by the same unitary transformation as those applied to the vibrational-rotational Hamiltonian of the molecule H:

$$\tilde{\mu}_Z = \ldots\, e^{iS_2}\, e^{iS_1}\, \mu_Z\, e^{-iS_1}\, e^{-iS_2} \ldots\, . \tag{35}$$

Here the generators S_1 and S_2 are the transformation operators. Since the transition probability for diatomic molecules can be separated in the rotational line strength and radial matrix element (28), it is possible to apply the transformation to radial matrix element evaluation to avoid a complicated commutation of rotational operators with direction cosines.

Thus, the evaluation of radial matrix element is replaced by an evaluation of the matrix elements of an effective dipole moment over the wave functions of the harmonic oscillator

$$M(v, J, \Omega_i \to v', J', \Omega_k) = {}_0\langle v\,|\tilde{\mu}(J, J', \Omega_i|\,v'\rangle_0.$$

Like for the Hamiltonian one considers *k*-times transformed dipole moment operator and recovers terms of different order according to the ordering scheme. The effective dipole moment operator is expanded in a series over powers of the small parameter λ:

$$\tilde{\mu}(J, J', \Omega_i) = M_0 + \lambda\tilde{M}_1(J, J', \Omega_i) +$$
$$+ \lambda^2\tilde{M}_2(J, J', \Omega_i) + \ldots + \lambda^n\tilde{M}_n(J, J', \Omega_i). \tag{36}$$

The use of the contact transformation in the representation of creation $\mathbf{a}^+$ and annihilation $\mathbf{a}$ operators for the normal mode vibrational modes allows one to present Eq. (35) in a form of "overtone" expansion[17,24], where each operator for "overtone" number n has nonvanishing matrix elements with the fixed difference $\Delta v = n$. So, to obtain the radial matrix elements for transitions $(vJ\Omega_i) \to (v + \Delta vJ'\Omega_i)$ it is quite sufficient to construct the operator of the *n*th "overtone."

The one-time transformed dipole moment operator $\tilde{\mu}(J, J', \Omega_i)$ for $^2\Pi$ state was considered in Ref. 26 and the formulas for radial matrix elements for the bands with $\Delta v = 1, 2$ were written. The spin-orbit interactions were taken into account in the calculations (Appendix 3). Relations presented in Ref. 26 for radial matrix elements could be easily presented as the transition moment for the band under study and Herman-Wallis factor with the re-determined values of m.

The second method used for evaluation of the transition probabilities is realized through numerical calculations.[35,36] The exact wave functions for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states are determined by numerically integrating two coupled Schrödinger equations.[37,38] In this scheme different presentations of the potential function can be used. It was found that the most precise rovibrational wave functions are derived by use of the vibrational RKR potential (Rydberg–Klein-Rees).[28] In addition, the *ab initio* dipole moment surfaces or Pade representation of the dipole moment function ensure the calculations of transition probabilities.[28] Such numerical calculations of line position and intensities for diatomic molecules in the $^2\Pi$ state are included in well-known databases HITRAN and HITEMP.

Conclusion

In this paper known methods and models used for theoretical treatment of vibrational-rotational spectra of diatomic molecules in the $^2\Pi$ state have briefly been reviewed. The author was not intended to point out the best of them, since the specific character of a problem and a molecule determines the choice of a proper model. It should be noted, that available model of the effective Hamiltonian allows one to determine the energy levels with the experimental accuracy including Λ-doubling for $v = 0$ ($J \approx 60, 5$) and $v = 22$ ($J \approx 35, 5$) for the NO molecule, while for the OH molecule the range is up to $v = 10$ and $J \approx 35, 5$. The main problem in the line intensity calculations remains the dipole moment function. It is known, that up to now the *ab initio* calculations of the dipole moment surfaces did not allow one to reproduce the intensity values with the experimental accuracy. Therefore, in fitting the observed intensities the model presented by expression (28) is used, which provides experimental accuracy of the presentation and physically clear interpretation of the interactions occurring in the molecule.

Appendix 1

Λ-doubling parameters caused by interactions between $^2\Pi$ and $^2\Sigma^{\pm}$-states

$$o_v^{\Pi} = \frac{1}{2}\sum_{n',v'}\frac{\langle n^2\Pi vJ\,|A(r)L_+|\,n'^2\Sigma v'J\rangle^2}{E_{nvJ}-E_{n'v'J}};$$

$$p_v^{\Pi} = 2\sum_{n',v'}\frac{\langle n^2\Pi vJ|A(r)L_+|n'^2\Sigma vJ\rangle\langle n^2\Pi vJ|B(r)L_+|n'^2\Sigma vJ\rangle}{E_{nvJ}-E_{n'v'J}};$$

$$q_v^{\Pi} = 2\sum_{n',v'}\frac{\langle n^2\Pi vJ\mid B(r)L_+\mid n'^2\Sigma v'J\rangle^2}{E_{nvJ}-E_{n'v'J}}.$$

Appendix 2

Matrix elements of the effective spin-rotational Hamiltonian by Brown[10]

Diagonal matrix elements independent of quantum number J:

$$\begin{gathered} {}^{e,f}\langle nv\,{}^2\Pi_{1/2}JM\,|H^{\text{eff}}|\,nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = T_e + G_v - \frac{A_v}{2} - \gamma_v; \end{gathered}$$

$$\begin{gathered} {}^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\mid H^{\text{eff}}\mid nv\,{}^2\Pi_{3/2}JM\rangle^{e,f} = \\ = T_e + G_v + A_v/2. \end{gathered}$$

Diagonal matrix elements, which depend on the quantum number J:

$$\begin{gathered} {}^{e,f}\langle nv\,{}^2\Pi_{1/2}JM\mid H^{\text{eff}}\mid nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = (B_v - A_{Jv}/2)(x+2) - (\gamma_{Jv}/2)(3x+4) - \\ - D_v[(x+1)(x+4)] + H_v[(x+1)(x^2+8x+8)] \mp \\ \mp \frac{1}{2}\{p_v + p_{Jv}(x+2)\}(J+1/2) \mp \\ \mp \frac{1}{2}\{q_v + q_{Jv}(3x+4)\}(J+1/2); \end{gathered}$$

$$\begin{gathered} {}^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\mid H^{\text{eff}}\mid nv\,{}^2\Pi_{3/2}JM\rangle^{e,f} = \\ = (B_v - A_{Jv}/2 - \gamma_{Jv}/2)x - D_v[(x+1)x] + \\ + H_v[x(x+1)(x+2)] \mp \frac{1}{2}\{q_{Jv}x(J+1/2)\}. \end{gathered}$$

Off-diagonal matrix elements:

$$\begin{gathered} {}^{e,f}\langle nv\,{}^2\Pi_{3/2}JM\,|H^{\text{eff}}|\,nv\,{}^2\Pi_{1/2}JM\rangle^{e,f} = \\ = \{-B_v + \gamma_v/2 + (1/2)\gamma_{Jv}(x+2) + 2D_v(x+1) - \\ - H_v(x+1)(3x+4) \pm (1/4)p_{Jv}(J+1/2) \pm \\ \pm (1/2)[q_v + q_{Jv}(x+2)](J+1/2)\}(x)^{1/2}. \end{gathered}$$

Designations are the same as in the text. The superscript corresponds to "*e*" levels, the subscript is for "*f*" levels.

Appendix 3

Radial matrix elements for transitions between $^2\Pi_i$ and $^2\Pi_k$ components of $^2\Pi$ state

$$M(v,J,\Omega_i \to v+1,J',\Omega_i) = \sqrt{\frac{(v+1)}{2}}\{\mu_1 + \mu_0\beta^3(F_i - F_i')\},$$

$$\begin{gathered} M(v,J,\Omega_i \to v+1,J',\Omega_k) = \\ = \sqrt{\frac{(v+1)}{2}}\{\mu_1 + \mu_0\beta^3(F_i - F_k') + \mu_0(-1)^i A_1/2\omega\}, \end{gathered}$$

$$\begin{gathered} M(v,J,\Omega_i \to v+2,J',\Omega_i) = \\ = \frac{1}{2}\sqrt{(v+1)(v+2)}\{\mu_2 + \mu_1[\alpha_1 + \beta^3(F_i - F_i')] - \\ - (\mu_0/2)[(\frac{3}{2}\beta^4 - \alpha_1\beta^3)(F_i - F_i') + \beta^6(F_i - F_i')^2]\}, \end{gathered}$$

$$\begin{gathered} M(v,J,\Omega_i \to v+2,J',\Omega_k) = \\ = \frac{1}{2}\sqrt{(v+1)(v+2)}\{\mu_2 + \mu_1[\alpha_1 + \beta^3(F_i - F_k')] - \\ -(\mu_0/2)[(\frac{3}{2}\beta^4 - \alpha_1\beta^3)(F_i - F_k') + \beta^6(F_i - F_k')^2] - \\ - \frac{(-1)^i\mu_0}{2\omega}[A_2 + A_1\alpha_1 - A_1\beta^3(F_i - F_k')]\}, \end{gathered}$$

where

$$F_i = f - \Omega_i + 1/2, \quad f = J(J+1),$$

$$i = 1, \ \ \Omega_i = 3/2, \ \ i = 2, \ \ \Omega_i = 1/2.$$

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