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Influence of non-adiabatic interactions on the Lande g-factors of the $X^2\Sigma^+ \sim A^2\Pi \sim B^2\Sigma^+$ complex of the CN radical

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The effect of the electron-rotational interaction induced by an external magnetic field on the values of Lande g-factors is systematically investigated within the quantum mechanical model of coupled radial Schrėdinger equations for locally and regularly perturbed electronic-vibrational-rotational (rovibronic) levels of nonadiabatically coupled $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of the CN radical, whose isotopomers are of persistent astronomical interest due to their wide use in optical diagnostics of various regions of the interstellar and near-stellar medium.

Keywords: Lande g-factor, non-adiabatic interaction, CN radical.

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Introduction

The splitting and shift of rotational levels of an isolated molecule under the effect of a static magnetic field [1] is a well-known physical phenomenon (known as the „molecular Zeeman effect“), which serves as a fundamental basis for the development of optical (non-contact) methods for measurement of external magnetic field strength H (optical magnetometers [2]). In particular, Zeeman splitting of lines in the molecular spectra of light transition metal hydrides (such as for example FeH(D) and NiH(D) [3]) with a spectrally resolved rotational structure at low temperatures and a relatively large magnetic moment (Lande factor or g-factor) are extensively used in astrophysical studies of the spatiotemporal evolution of magnetic field strength in various areas of the outer space, including the atmosphere of exoplanets, cold stars, and brown dwarts [4].

It is obvious that the observed spectrum of any (paramagnetic) molecule with a non-zero magnetic moment can in principle be used for remote measurement of magnetic field strength. The CN radical is not an exception, which has intense emission and absorption lines in the microwave, infrared, and visible parts of the spectrum, widely observed in the atmospheres of exoplanets [5], as well as in various regions of the interstellar medium and circumstellar envelopes.

It should be reminded that the modern accuracy of laboratory measurements and quantum mechanical calculations of the magnetic characteristics (primarily that of Lande factors) of atoms and molecules in the gaseous phase is very high in a very wide range of their absolute changes, which makes the sign and absolute value of g-factors the most important characteristic of atomic-molecular levels along with their energy and radiation properties [6].

It is well known that the fundamental feature of the Zeeman operator is that it is determined by the total rotational angular momentum of the molecule $\mathbf{J}$, as well as the orbital $\mathbf{L}_t$ and spin $\mathbf{S}_t$ angular momenta of electrons, and, therefore, for its calculation it is not necessary to know additional intramolecular matrix elements compared to the Hamiltonian of an isolated (without external field) molecule. Moreover, in the limiting situations, which are so-called pure Hund's coupling cases (**a**), (**b**), and (**c**), the magnetic structure of the rovibronic levels of diatomic molecules can be calculated rather simply (as a rule, even in an analytical form) provided that most of the quantum numbers characterizing the molecular states under consideration are conserved (i. e. they are *good*). However, when intramolecular (nonadiabatic) interactions are taken into account, almost all quantum numbers used for adiabatic states (with the exception of the magnetic quantum number M) cease to be *good* (i. e. they are not conserved). In this case, the quantitative description of the molecular Zeeman effect ceases to be a trivial problem but represents an independent and very sensitive test for correctness of the quantum mechanical model used for the nonadiabatic description of the structural (energy) properties of an isolated molecule [7].

An important advantage of observing and interpreting the field-linear Zeeman effect in diamagnetic (zero magnetic moment) states is that its associated splittings and shifts are a direct manifestation of the nonadiabatic effect caused by intramolecular interactions with neighboring paramagnetic states of the molecule [8]. The nonadiabatic effect is especially pronounced in the case of energy resonances, when almost degenerate (in the adiabatic approximation) rovibronic (electron-vibrational-rotational) states of the molecule interact with each other due to spin-orbital, spin-rotational and electron-rotational interactions [9]. It is obvious that when estimating molecular g-factors for intermediate cases of Hund's coupling and in the presence of intramolecular perturbations, it is necessary to explicitly take into account the mixing of adiabatic states, based on the knowledge of corresponding nonadiabatic electronic matrix elements [10,11].

In this study, a rigorous quantum mechanical modeling of g-factors of rovibronic levels of the complex of doublet states $X^2\Sigma^+ \sim A^2\Pi \sim B^2\Sigma^+$ of the CN molecule was carried out, taking into account spin-rotational and electron-rotational interactions induced by an external magnetic field, as well as local and regular intramolecular perturbations caused by the competition between spin-orbital, spin-rotational, and electron-rotational nonadiabatic interactions in an isolated molecule.

Linear Zeeman effect in a diatomic molecule

In the case of a spatially uniform magnetic field directed along the Z axis of the laboratory coordinate system (LCS), the Zeeman operator $\mathbf{H}_{Ze}$ can be represented as follows [12]:

$$\mathbf{H}_{Ze} = -\mu_B H \sum_{t=0,\pm1} (-1)^t D^1_{0-t}\left[g_L \mathbf{L}_t + g_S \mathbf{S}_t\right]. \tag{1}$$

where μ_B is Bohr magneton; $g_L = 1$ and $g_S = 2.00232$ are orbital and spin g-factors of electron, and D^1_{0-t} is matrix of the rotation from molecular coordinate system to laboratory coordinate system, acting on the rotational functions of the $|J\Omega M\rangle$ molecule and having non-zero matrix elements according to the selection rules: $\Delta J = 0, \pm1$ and $\Delta\Omega = 0, \pm1$. In this case, only the magnetic quantum number M remains *good*. On the contrary, operators of orbital $\mathbf{L}_t$ and spin $\mathbf{S}_t$ angular momentum of electrons act on the electronic part $|\Omega; L\Lambda S\Sigma\rangle$ of the total electron-vibrational-rotational (rovibronic) wave function of the molecule. It should be reminded that in an isolated linear molecule the projection $\Omega = \Lambda + \Sigma$ of the total angular momentum J onto the internuclear axis in the molecular coordinate system (MCS) is always a *good* quantum number, and the projections of the orbital Λ and spin Σ angular momentum of electrons are good only in the so-called pure Hund's coupling case (**a**) with the corresponding selection rules $\Delta\Lambda = 0, \pm1$ and $\Delta\Sigma = 0, \pm1$.

The total (non-adiabatic) wave function of the interacting rovibronic states of a diatomic molecule Ψ^{CC}_J can be represented as a linear combination of basic electron-rotational wave functions corresponding to the pure Hund's coupling case (**a**):

$$\Psi^{CC}_J = \sum_{i=1}^{N} \phi^J_i(R)|\Omega^\pm_i; L\Lambda S\Sigma\rangle|J\Omega_i M>, \tag{2}$$

where subscript i means the serial number of the electronic state included explicitly in the non-adiabatic consideration; sign ± denotes the use of a symmetrized electron-rotational basis, where levels have a certain (e/f) symmetry, and expansion coefficients $\phi^J_i(R)$ are multicomponent vibrational wave functions, which are a solution to N coupled radial Schrëdinger equations:

$$\left(-\mathbf{I}\frac{\hbar^2 d^2}{2\mu dR^2} + \mathbf{V}_{e/f}(R;\mu, J) - \mathbf{I}E^{CC}_J\right)\Phi^{CC}_J(R) = 0, \tag{3}$$

with the usual boundary conditions for discrete (bound) states of a molecule: $\Phi^{CC}_J(0) = \Phi^{CC}_J(+\infty) = 0$. Here $\mathbf{I}$ is diagonal unit matrix, μ is reduced mass of the molecule, and $\mathbf{V}_{e/f}(R;\mu, J)$ is symmetric $N \times N$ matrix of potential energy, which is an explicit function of the internuclear distance R and parametrically dependent on μ and the rotational quantum number J.

The Zeeman Hamiltonian (1) is an even operator, therefore it can only mix molecular states of the same symmetry, just like the operators of intramolecular (non-adiabatic) perturbations. Consequently, in $\mathbf{H}_{Ze}$ only diagonal matrix elements will be non-zero for certain J and M:

$$\Delta E^{(1)}_J(M) = \langle\Psi^{CC}_J|\mathbf{H}_{Ze}|\Psi^{CC}_J\rangle = -g_J\mu_B HM, \tag{4}$$

Then, taking into account representations (1) and (2), the desired dimensionless g-factor of the non-adiabatic state of an isolated molecule can be represented as a sum of products of matrix elements of angular momentum:

$$g_J = \left[\frac{2J+1}{J(J+1)}\right]^{\frac{1}{2}} \times \left[\sum_t (-1)^t \sum_{ij} \begin{pmatrix} J & 1 & J \\ -\Omega_i & t & \Omega_j \end{pmatrix} \left[g_L \mathbb{L}_{ij} + g_S \mathbb{S}_{ij}\right]\right], \tag{5}$$

where $\mathbb{L}_{ij}$ and $\mathbb{S}_{ij}$ are electron-vibrational matrix elements:

$$\mathbb{L}_{ij} = \delta_{S_i S_j}\delta_{\Sigma_i\Sigma_j}\langle\phi_i|\langle\Lambda_i|\mathbf{L}_t|\Lambda_j\rangle_{\mathrm{r}}|\phi_j\rangle_R; \tag{6}$$

$$\mathbb{S}_{ij} = \delta_{\Lambda_i\Lambda_j}\langle\phi_i|\langle\Sigma_i|\mathbf{S}_t|\Sigma_j\rangle_{\mathrm{r}}|\phi_j\rangle_R, \tag{7}$$

and δ_{ij} are Kronecker symbols that define the selection rules for the Zeeman operator based on the spin $S_i = S_j$, its projection $\Sigma_i = \Sigma_j$, and the value of $\Lambda_i = \Lambda_j$ in the pure Hund's coupling case (**a**) .

Taking into account also the selection rules for non-zero $3j$-symbols included in expression (5), the following can be written explicitly:

$$\left[\frac{2J+1}{J(J+1)}\right]^{\frac{1}{2}} (-1)^t \begin{pmatrix} J & 1 & J \\ -\Omega_i & t & \Omega_j \end{pmatrix} = \begin{cases} \frac{\Omega_i}{J(J+1)}, & t = 0 \\ \pm\frac{\sqrt{[J(J+1)-\Omega_i(\Omega_i\pm1)]/2}}{J(J+1)}, & t = \pm1 \end{cases} \tag{8}$$

Similarly, for diagonal and off-diagonal electron matrix elements of the operators of orbital and spin angular momenta of electrons of the molecule the following can be written, respectively:

$$\langle\Lambda_i|\mathbf{L}_t|\Lambda_j\rangle_{\mathrm{r}} = \begin{cases} \Lambda_i, & \Lambda_i = \Lambda_j \\ \pm L_{ij}(R)/\sqrt{2}, & \Lambda_i - \Lambda_j = \pm1, \end{cases} \tag{9}$$

$$\langle \Sigma_i|\mathbf{S}_t|\Sigma_j\rangle_{\mathrm{r}} = \begin{cases} \Sigma_i, \ \Sigma_i = \Sigma_j \\ \pm S_{ij}(R)/\sqrt{2}, \ \Sigma_i - \Sigma_j = \pm 1, \end{cases} \tag{10}$$

In the case when the orbital L and/or spin S angular momentum of the molecule is conserved, the off-diagonal matrix elements $L_{ij}(R)$ and $S_{ij}(R)$ can be evaluated analytically:

$$S_{ij} = \sqrt{S(S+1) - \Sigma_i(\Sigma_i \pm 1)}, \tag{11}$$

$$L_{ij} = \sqrt{L(L+1) - \Lambda_i(\Lambda_i \pm 1)}, \tag{12}$$

Equation (12) reflects the validity of the hypothesis of the so-called pure precession of Van Vleck [7], which is relatively rarely fulfilled in practice for the vast majority of molecular states. The exception is the Rydberg states of light molecules, primarily hydrides. On the contrary, the conservation of the total spin of the molecule S and, accordingly, the validity of expression (11) is typical for most pure Hund's coupling cases, except, of course, the case (**c**). Thus, it is easy to see that even when taking into account non-adiabatic interactions, the g-factors of molecular states can be calculated based only on the wave functions of an isolated molecule (in the absence of an external magnetic field) and the corresponding diagonal and off-diagonal electron matrix elements of the angular operators momenta.

It should be reminded that in the limiting cases of the Hund's coupling, g-factors can be represented analytically. For example, for the states of pure coupling cases (**a**) and (**c**) they have the simplest form:

$$g_J^{(a)} = \Omega \frac{g_L\Lambda + g_S\Sigma}{J(J+1)}, \Omega = \Lambda + \Sigma, \tag{13}$$

$$g_J^{(c)} = \Omega \frac{g_L\Omega + (g_S - g_L)\langle\Omega|\mathbf{S}_0|\Omega\rangle_{\mathrm{r}}}{J(J+1)}, \tag{14}$$

whereas for the pure coupling case (**b**) they become noticeably more complicated:

$$g_J^{(b)} = \frac{g_L}{2J(J+1)}\left[\frac{\Lambda^2[J(J+1) + N(N+1) - S(S+1)]}{N(N+1)}\right] + g_S\frac{J(J+1) - N(N+1) + S(S+1)}{2J(J+1)}, \tag{15}$$

where $N = J \pm S$.

g-factors of the $X^2\Sigma^+ \sim A^2\Pi \sim B^2\Sigma^+$ complex of CN molecule

Quantum mechanical calculation of g-factors of rovibronic levels of the low-lying doublet states $X^2\Sigma^+$, $A^2\Pi_\Omega$, and $B^2\Sigma^+$ of the CN radical was based on a strict non-adiabatic model of coupled vibrational channels (CC) [13], within which the matrix of potential energy $\mathbf{V}_{e/f}(R;\mu,J)$ for the $X \sim A \sim B$ complex of mutually-perturbing states included in an explicit form the spin-orbital, spin-rotational, and electron-rotational intramolecular interactions between all three states of the complex [14], as well as second-order corrections of non-degenerate perturbation theory, effectively taking into account non-adibatic interactions with distant doublet states using Van Vleck contact transformations [15]. Necessary non-adiabatic vibrational wave functions $\phi_i^J(R)$ for all rovibronic levels of the $X \sim A \sim B$ complex within the range of excitation energy of 0−60000 cm^{-1} and rotational quantum number $J \in [0.5, 120.5]$, were found from the numerical solution to the system of four coupled radial equations (3) of the CC method. For this purpose, a five-point finite-difference scheme [16] was used to replace the kinetic energy operator in equation (3), and the resulting band matrix was diagonalized using the FEAST library program [17]. The partial contribution of each electronic state to the resulting multicomponent vibrational wave functions of the $\Phi_J^{CC}(R)$ complex was determined from the conditions for normalizing the wave functions of bound molecular states:

$$p_i = \langle\phi_i^J|\phi_i^J\rangle_R, \qquad \sum_{i=1}^{N} p_i = 1, \tag{16}$$

where $i \in [X^2\Sigma^+, A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+]$.

Based on equation (5) and auxiliary expressions (8)-(10), it is easy to show that in the g_J-factor of the $X \sim A \sim B$ complex under consideration the following terms will make non-zero contributions:

$$g^{^2\Sigma^+} = g_S\frac{1 \pm (J+1/2)}{2J(J+1)}p_{X/B}, \tag{17}$$

$$g^{^2\Pi_{1/2}} = \frac{g_L - g_S/2}{2J(J+1)}p_{A_{1/2}}, \tag{18}$$

$$g^{^2\Pi_{3/2}} = \frac{3[g_L + g_S/2]}{2J(J+1)}p_{A_{3/2}}, \tag{19}$$

$$g^{^2\Pi_{1/2}-^2\Pi_{3/2}} = g_S\frac{\sqrt{J(J+1) - 3/4}}{2J(J+1)}\langle\phi_{A_{1/2}}^J|\phi_{A_{3/2}}^J\rangle_R, \tag{20}$$

$$g^{^2\Pi_{1/2}-^2\Sigma^+} = \pm g_L\frac{J+1/2}{2J(J+1)}\langle\phi_{A_{1/2}}^J|L_{\Pi\Sigma}|\phi_{X/B}^J\rangle_R, \tag{21}$$

$$g^{^2\Pi_{3/2}-^2\Sigma^+} = g_L\frac{\sqrt{J(J+1) - 3/4}}{2J(J+1)}\langle\phi_{A_{3/2}}^J|L_{\Pi\Sigma}|\phi_{X/B}^J\rangle_R, \tag{22}$$

where the signs ± refer to the symmetry levels e/f, respectively.

The electronic matrix element of the spin-rotation interaction S_{ij} between the components $\Omega = \frac{3}{2}$ and $\Omega = \frac{1}{2}$ of the state $A^2\Pi_\Omega$ included in equation (20) was estimated analytically according to formula (11), under the assumption that the molecular spin S remains a *good* quantum number.

The non-adiabatic matrix elements of the electron-rotational coupling $L_{\Pi\Sigma}(R)$ between $A^2\Pi_\Omega$ and the states $X/B^2\Sigma^+$ included in the expressions (21−22) are known in a point-wise form, obtained earlier within the *ab initio* quantum chemical calculation of the electronic structure of the $X \sim A \sim B$ complex [14]. It should be reminded that it was these intramolecular matrix elements that were used

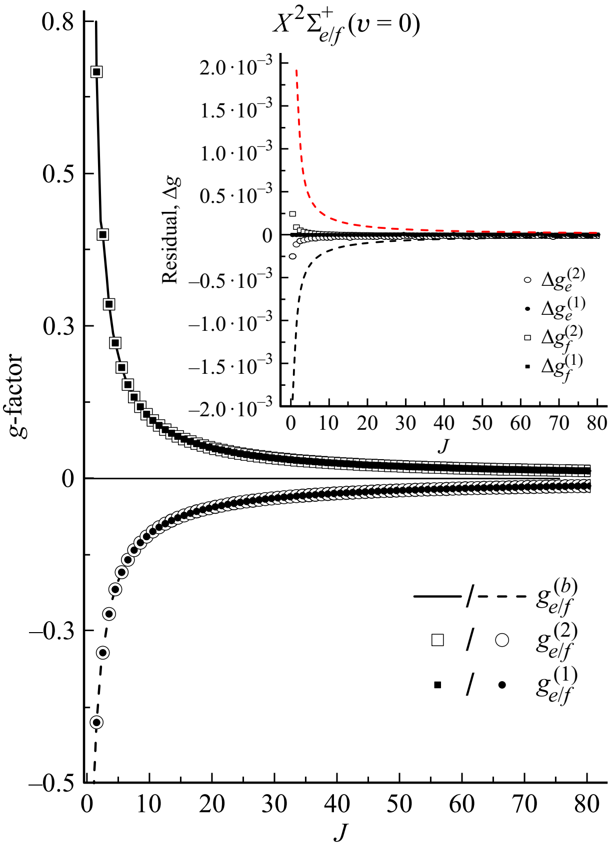

Figure 1. Lande factors of weakly perturbed rotational levels of the ground vibrational state $X^2\Sigma_{e/f}(v=0)$ of the CN molecule, calculated within the pure Hund's coupling case (**b**), $g^{(\mathrm{b})}$, as well as taking into account only intramolecular, $g^{(1)}$, and magnetic field-induced, $g^{(2)}$, non-adiabatic interactions. The insert shows the deviations of non-adiabatic g-factors from predictions for the pure Hund's coupling case (**b**). Dashed lines correspond to corrections of the 2-nd order of smallness $g^{(2)}_{^2\Sigma^+}$, calculated according to equation (24).

in the non-adiabatic analysis of the rovibronic energy levels of the complex under study [13], but at the same time they were completely ignored in the calculation of its magnetic g-factors in [18].

On the contrary, in this study we calculated the g-factors of rovibronic levels of the $X\sim A\sim B$ complex in a wide range of its vibrational-rotational excitation with the explicitly taken into account contribution of the electron-rotational interaction according to equations (21) and (22). In addition, to estimate the required multicomponent vibrational wave functions $\Phi^{CC}_J(R)$ from equation (3), a precision non-adiabatic model [13] was used, which allows reproducing (unlike the study of [18]) energies of both locally and regularly perturbed levels of an isolated CN molecule at an almost spectroscopic (experimental) level of accuracy.

However, it should be emphasized that although the non-adiabatic model used effectively takes into account regular interactions with an infinite number of distant doublet states using Van Vleck contact transformations, to assess the effect of these states on the Lande factors of the $X\sim A\sim B$ complex in question, it is necessary to additionally take into account the magnetic field-linear corrections of the order of non-degenerate perturbation theory of the following type:

$$\Delta E_i^{(2)} = \sum_{j\neq i}\frac{\langle\Psi_i^{ad}|\mathbf{V}_{pert}|\Psi_j^{ad}\rangle}{E_i^{ad}-E_j^{ad}}\langle\Psi_j^{ad}|\mathbf{H}_{Ze}|\Psi_i^{ad}\rangle \qquad (23)$$

where E_j^{ad}, Ψ_j^{ad} are adiabatic (unperturbed) energies and wave functions of the molecule, and $\mathbf{V}_{pert}$ is the operator of spin-orbital and/or electron-rotational intramolecular interaction.

Within the purely *ab initio* technique, it is quite difficult to perform summation over states according to equation (23), because it is necessary to know all the corresponding electronic matrix elements and energies. However, fortunately, the situation is significantly simplified when making use of the approximate relationship between the desired second-order corrections to g-factors, $g_i^{(2)}$, and the so-called effective constants of Λ- doubling of the doublet states of the molecule. Thus, for example, for the state $^2\Sigma^+$ the following

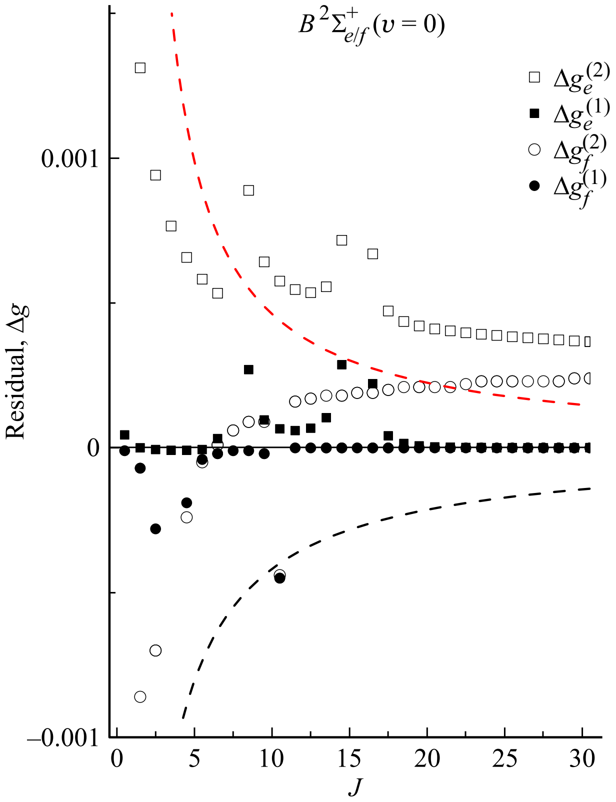

Figure 2. Non-adiabatic contributions $g^{\mathrm{Calc}}-g^{(\mathrm{b})}$ to the Lande factors of the rotational levels e/f of the vibrational state $B^2\Sigma^+(v=0)$ of the CN molecule, calculated with and without taking into account the magnetically induced electron-rotational interaction. Dashed lines show the contribution of the second order of smallness to the g-factor estimated according to approximate relationship (24).

can be written using the Curl formula [19]:

$$g^{(2)}_{^2\Sigma^+} \approx \mp g_L \frac{J+1/2}{J(J+1)} \left(\frac{\gamma}{2B}\right), \qquad (24)$$

where γ is experimental γ-doubling constant, and B is rotational constant of the state $^2\Sigma^+$ under consideration. Similarly, the correction to the g-factor of the diamagnetic state $^2\Pi_{\Omega=1/2}$ can be expressed through the experimental Λ-doubling constants p and q, as well as the rotational constant B as follows:

$$g^{(2)}_{^2\Pi} \approx \pm g_L \frac{J+1/2}{J(J+1)} \left(\frac{p}{2B}\right) + g_L \left(\frac{q}{B^2}\right), \qquad (25)$$

Results and discussion

Systematic non-adiabatic analysis of numerous spectroscopic (experimental) data corresponding to the low-lying states $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ of the CN radical, carried out in [13,20] made it possible to conveniently classify all rovibronic levels of the $X \sim A \sim B$ complex in question into three groups:

1. Almost „pure" (very weakly perturbed) levels that can be described in the approximation of an isolated electronic state, obeying the pure Hund's coupling case. These include, for example, several low-lying vibrational ($v = 0 - 3$) levels of the ground electronic state $X^2\Sigma^+$, obeying the pure Hund's coupling case (**b**).

2. Regularly perturbed levels that make up the bulk of the experimental terms of the CN molecule. The intramolecular perturbation of these levels is determined by the severe competition of spin-orbit and electron-rotational interactions between all three states of the complex, as well as regular interaction with distant electronically excited states of the molecule.

3. A few locally perturbed levels that correspond to the position of energy resonances and appear only in very narrow intervals of electron-vibrational-rotational excitation of the molecule. Among them, the pairs of quasi-degenerate terms $B^2\Sigma^+(v=0) \sim A^2\Pi(v=10)$, $B^2\Sigma^+(v=5) \sim A^2\Pi(v=17)$, and $A^2\Pi(v=7) \sim X^2\Sigma^+(v=11)$ are the most studied.

From the analysis of expressions for g-factors (17–19) it follows that among all the under-consideration states of the complex, only the $\Omega = \frac{1}{2}$ component of the $A^2\Pi_\Omega$ state is diamagnetic in the adiabatic approximation. The $A^2\Pi_{3/2}$ component, as well as the $X^2\Sigma^+$ and $B^2\Sigma^+$ states are paramagnetic and, therefore, the dominant contribution to their g-factors can be obtained on the basis of analytical expressions (13) and (15) corresponding to the Hund's coupling cases (**a**) and (**b**), respectively. However, it should be emphasized that the $A^2\Pi_{1/2}$ component of the doublet is strictly diamagnetic only if the magnetic moment of the electron g_S is identically equal to two (according to expression (13)). In the real case of an anomalous magnetic moment of electron, the $A^2\Pi_{1/2}$ component remains weakly paramagnetic even within pure Hund's coupling case (**a**).

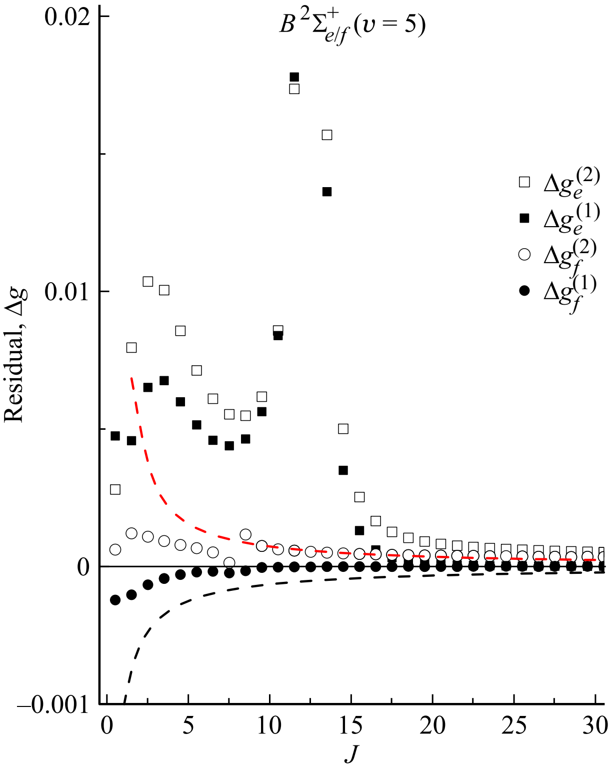

Figure 3. Non-adiabatic contributions $g^{\text{Calc}} - g^{(\text{b})}$ to the Lande factors of the rotational levels e/f of the vibrational state $B^2\Sigma^+(v=5)$ of the CN molecule, calculated with and without taking into account the magnetically induced electron-rotational interaction. Dashed lines show the contribution of the 2-nd order of smallness to the g-factor estimated according to relationship (24).

Consequently, to obtain corrections to the g-factors of paramagnetic states at the level of hundredths of a percent, it becomes absolutely necessary to take into account the quantum electrodynamic (QED) correction for the magnetic moment of the electron.

From a comparison of expression (20) with (21) and (22), an assumption can also be made that the contribution of the electron-rotational interaction to the g-factors of doublet states induced by an external magnetic field is significantly less than that of the spin-rotational interaction, and will be most effectively manifested only in the case of strong local perturbations. To confirm this conclusion, two calculation options were carried out.

1. Taking into account only the spin contribution (20) to the g-factors ($g^{(1)}$). This calculation does not require knowledge of non-adiabatic matrix elements $L_{ij}(R)$ and is similar to the approach implemented in [18] based on the DUO program [6,21].

2. Taking into account the additional electron-rotational contribution of the g-factors ($g^{(2)}$) based on expressions (21) and (22).

Fig. 1 shows the g-factors of the rotational levels of the ground vibrational state $X^2\Sigma^+(v=0)$ of the CN molecule, calculated in various approximations. As expected, the Lande factors of a given regularly and very weakly perturbed level are described almost perfectly (within hundredths of a percent) according to equation (15) within the pure Hund's coupling case (**b**). In this case, the difference between the results obtained taking into account only intramolecular and magnetic field-induced non-adiabatic interactions turned out to be minimal, and a significant role is played by corrections of the second order of smallness calculated according to equation (24).

Fig. 2 and 3 present the results of calculations of the contributions of regular non-adiabatic interactions to the Lande factors of the rotational e/f-levels of the $B^2\Sigma^+(v=0)$ and $B^2\Sigma^+(v=5)$ states of the CN molecule, both taking into account and without taking into account the magnetic field-induced electron-rotational interaction, estimated according to equations (21) and (22). The contribution of regular perturbations to the level $v=0$ is obviously significantly less than that to $v=5$, and is comparable to the contribution of the second order of smallness $g^{(2)}_{^2\Sigma^+}$. The contribution of magnetically induced interactions to g-factors does not exceed 0.005.

The table, as well as Figs. 4 and 5, present the g-factors calculated for the rovibronic levels of the $X \sim A \sim B$ complex, for which strong local intramolecular perturbations are observed. As was expected, these are the levels, for which the largest deviation from the adiabatic model is observed. Moreover, the maximum contribution of the magnetically induced interaction is also observed here, which is caused by a significant deviation of the non-adiabatic CC-models [13] and [18], which, in particular, manifests in the accuracy of the description of the energies of these levels [13]. Thus, in this case, although the effect of taking into account terms (21) and (22) is amounted to a few percent, the influence of magnetically induced perturbations turns out to be noticeable in terms of absolute value.

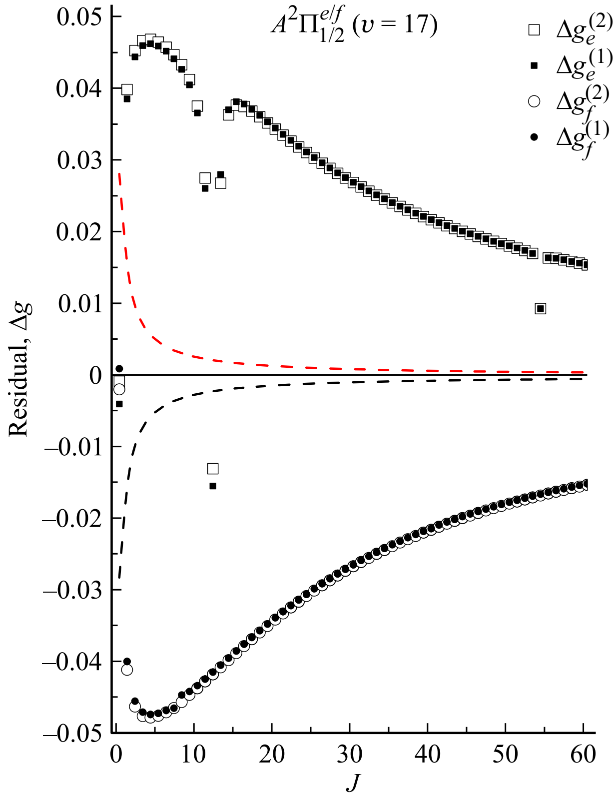

Figure 4. Non-adiabatic contributions $g^{\mathrm{Calc}} - g^{(\mathrm{a})}$ to the Lande factors of rotational e/f-levels of the $A^2\Pi_{1/2}(v=17)$ state of the CN molecule, calculated taking into account intramolecular and magnetic field-induced non-adiabatic interactions. Dashed lines show the contribution of the second order of smallness to the g-factor estimated from relationship (25).

Contribution of $\Delta g = g^{Calc} - g^{(a/b)}$ intramolecular and field-induced non-adiabatic interactions to g-factors of *locally* perturbed rovibronic levels $X \sim A \sim B$ of the CN molecule complex

J	$\Delta g^{(2)}$	$\Delta g^{(1)}$	p_X	$p_{A_{1/2}}$	$p_{A_{3/2}}$	p_B
$X^2\Sigma_e^+(v=11)$						
24.5	-0.00039	0.00032	70.8	8.5	20.7	0
25.5	0.00343	0.00286	59.6	6.6	33.8	0
45.5	0.01889	0.01881	54.5	32.4	13.1	0
$X^2\Sigma_f^+(v=11)$						
13.5	-0.03738	-0.03799	67.0	1.7	31.3	0
26.5	-0.00094	-0.00152	67.2	24.0	8.8	0
27.5	-0.00293	-0.00232	68.8	25.0	6.2	0
$B^2\Sigma_e^+(v=0)$						
7.5	0.00437	0.00445	0	0.7	12.5	86.8
15.5	0.02293	0.02276	0	18.4	3	78.6
$B^2\Sigma_e^+(v=5)$						
11.5	0.01735	0.01778	0	9.2	2.6	88.2
12.5	0.05673	0.05821	0	38.4	6.2	55.4
13.5	0.01568	0.01361	0	13.5	0.4	86.1
$A^2\Pi^e_{1/2}(v=17)$						
11.5	0.02749	0.02604	0	82.8	6.0	11.2
12.5	-0.0131	-0.0155	0	52.5	3.4	44.1
13.5	0.02678	0.02798	0	76.4	10.1	13.5
$A^2\Pi^e_{3/2}(v=7)$						
24.5	0.00648	0.00598	28.7	13.1	58.1	0
25.5	0.00211	0.00288	40.1	15.7	44.2	0
$A^2\Pi^f_{3/2}(v=7)$						
13.5	-0.09484	-0.09434	32.5	9.6	57.9	0

Conclusion

The calculations carried out in this study allow making the following conclusions.

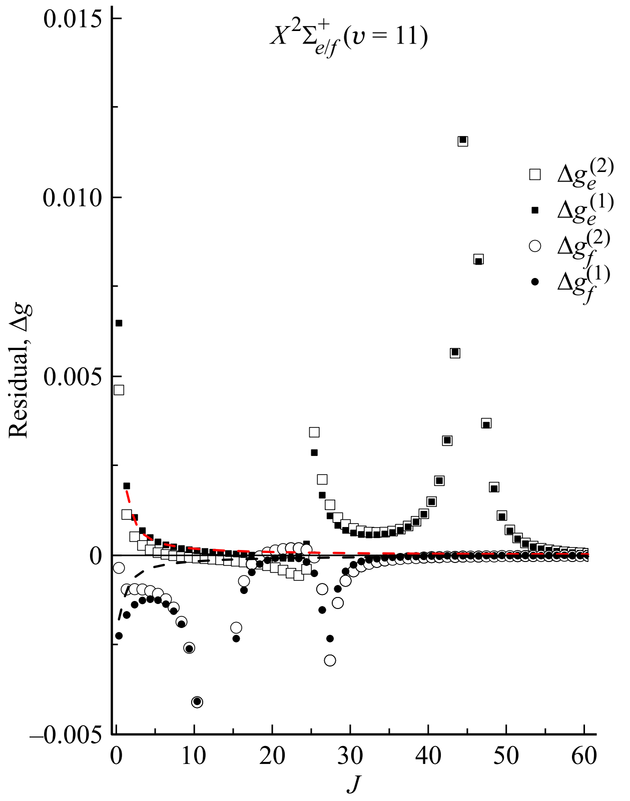

Figure 5. The contribution of local non-adiabatic interactions to the Lande factors of vibrational-rotational levels of the ground state $X^2\Sigma^+(v = 11)$ of the CN molecule, calculated with and without taking into account the magnetically induced electron-rotational interaction. Dashed lines show the contribution of the second order of smallness to the g-factor estimated according to approximate relationship (24).

1. Magnetic g-factors for the overwhelming number of rovibronic levels of the considered $X^2\Sigma^+ \sim A^2\Pi \sim B^2\Sigma^+$ complex of CN radical can be described with a very good accuracy in terms of the simplest (limiting) Hund's coupling cases (**a**) and (**b**).

2. Only for a small number of locally perturbed levels of the complex a non-adiabatic model is actually required, and exactly the same as for describing the energy levels of an isolated molecule in the absence of an external field. Thus, the use of a simplified model for describing g-factors proposed in [6] seems completely justified, at least in the case of this complex.

3. The inclusion of electron-rotational interactions induced by an external field in the Zeeman Hamiltonian insignificantly affects the observed g-factors and is therefore necessary only in the case of particularly precise magnetic measurements.

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Conflict of interest

The authors declare that they have no conflict of interest.

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