

INFLUENCE OF INTERACTIONS OF EXCITED VIBRATIONS ON THE MOLECULAR PARAMETERS

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The interaction of vibrations is studied by the algebraic method of perturbation theory. Formulas are derived that take into account the influence of interactions on the anharmonic spectroscopic parameters of excited vibrations with compound frequencies.

INTRODUCTION

The present work studies the excited states of molecules for transitions for which several vibrational quantum numbers change. They are called compound transitions [1, 2] and are subdivided into vibrations with summed and difference frequencies ($\omega_a + \omega_b$) and ($\omega_a - \omega_b$), where a and b are the serial numbers of vibrations ($a, b = 1, 3N - 6$) and N is the number of atoms in the molecule. Such vibrations together with overtones give rise to additional absorption bands in the IR spectra of molecules. However, difficulties caused by the special features of the dynamics of atoms in molecules in the excited states, the influence of interaction of vibrations forming transitions with compound frequencies that are manifested through the anharmonicity of the spectroscopic parameters and resonances of vibrational states with energies close in values to these excited states and forming polyads of the examined bands arise in an analysis and identification of spectra in experimental spectroscopy.

The above-listed problems explain the necessity of application and development of various methods, including matrix theory [3, 4], for the determination of the molecular parameters in the IR absorption spectra. The present work is aimed at the derivation of an equation for excited vibrations with compound frequencies by means of transformation of the basic equation of normal vibrations. To this end, the operation of direct multiplication of matrices is used together with its properties for eigenvalues and eigenvectors of matrices-multipliers in the context of the matrix theory of perturbations [3]. A solution of the equation yields vibration types and their changes in the first order of the perturbation theory. The formulas derived allow the influence of perturbations on the structural and electrooptical parameters, centrifugal distortion coefficients, and Coriolis interactions to be investigated.

EQUATION FOR EXCITED VIBRATIONS

The theoretical study of integral intensities of IR compound vibration bands based on the valence-optical scheme of molecular vibration theory [1, 2] and quantum-mechanical method of contact transformations [5] demonstrates that the key parameters in computational formulas are the second-order derivatives of the dipole moment with respect to the normal coordinates and the coefficients of rotational-vibrational interaction. The method of direct calculations of the anharmonic electrooptical parameters was described in [6]. It is based on semi-empirical quantum-chemical CNDO/2 method with the use of the method of numerical differentiation of the dipole moment function by cubic splines and is implemented in the program complex whose algorithm and description can be found in [7].

Calculations by the developed method with the use of the program complex allow redistribution of electric charges and dipole moment coordinates accompanying the displacement of atoms calculated by solving the direct

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mechanical problem for normal vibrations to be determined as well as changes of these structural parameters accompanying the subsequent vibrations. A numerical experiment allows vibrations with $(\omega_a \pm \omega_b)$ compound frequencies to be modeled considering that atoms first undergo vibrations with frequencies ω_a ($a = 1, 3N - 6$) accompanied by changes of all intramolecular parameters and then vibrations occur with the other frequency. We note that the atomic vibrations with the second frequency occur for the intermolecular bond lengths, valence sites, and dipole moment coordinates that have already been changed as a result of the first vibrations rather than from the equilibrium position. The frequencies ω'_b ($b = 1, 3N - 6$) of the subsequent vibrations calculated by solving the direct mechanical problem with allowance for changes in the matrix of the kinematic coefficients differ from the frequencies of normal vibrations ω_b ($b = 1, 3N - 6$) by $\Delta\omega_b = \omega'_b - \omega_b$. Therefore, the frequencies of compound vibrations $(\omega_a \pm \omega'_b)$ differ from the summed or difference frequencies of two normal vibrations by $\Delta\omega_b$ whose values change from several tens to several hundreds of reciprocal centimeters. This is confirmed by experimental measurements of the band centers of compound vibrations, for example, for the water molecule and its isotopes that have been much studied from the spectroscopic point of view and presented in [8]. Hence, the second compound vibration can be considered excited, and the algebraic method of the matrix theory of perturbations [3] can be used to investigate it.

Let us derive the equation for vibrations at compound frequencies. We first write down the basic equation for normal vibrations [1, 2]

$$DZ = \Lambda Z, \quad (1)$$

in which the matrix of the dynamic coefficients D is the product of matrices of kinematic interaction G and force constants F : $D = GF$, the matrix of normal vibration types is designated by Z , and the components of the diagonal matrix Λ are numbers proportional to the squared frequencies of normal vibrations: $\lambda_i = 4\pi^2 c^2 \omega_i^2$ ($i = 1, 3N - 6$).

After grouping terms with analogous normal vibration symmetry types in Eq. (1), the matrix D is transformed into the block-diagonal matrix with quadratic submatrices along its diagonal. We now write down the matrix D as a direct sum of these quadratic submatrices:

$$D = D_1 \oplus D_2 \oplus \dots \oplus D_n. \quad (2)$$

Such transformation reduces the order of Eq. (1) and allows us to proceed to a solution of lower-order matrix equations of fixed symmetry type. The matrix Z of vibration type components can be expressed analogously:

$$Z = Z_1 \oplus Z_2 \oplus \dots \oplus Z_n. \quad (3)$$

Based on Eqs. (1)–(3), we now write down the matrix equation for one of the symmetry types of normal vibrations

$$D_a Z_a = \Lambda_a Z_a. \quad (4)$$

Here Λ_a is the diagonal matrix with the components $\lambda_{a_i} = 4\pi^2 c^2 \omega_{a_i}^2$ ($i = 1, a$). For vibrations with other symmetry type, the equation will be analogous to Eq. (4); however, taking into account perturbations of vibrations in the context of the matrix theory for eigenvalues and eigenvectors [4], we obtain

$$D'_b Z'_b = \Lambda'_b Z'_b. \quad (5)$$

The components of the diagonal matrix Λ'_b are numbers $\lambda'_{b_j} = 4\pi^2 c^2 (\omega'_{b_j})^2$, where $j = 1, b$.

In [4] it was proved that if the analytical representation

$$\Lambda'_b = \Lambda_b + \varepsilon \Delta \Lambda_b \quad (6)$$

exists in the first-order approximation of the perturbation theory for the matrix of eigenvalues Λ'_b given by Eq. (5), it also exists for other matrices

$$D'_b = D_b + \varepsilon \Delta D_b, \quad (7)$$

$$Z'_b = Z_b + \varepsilon \Delta Z_b, \quad (8)$$

where ε is the order of smallness. The normal vibrations with frequencies ω_{b_j} ($j = 1, b$) are determined from a solution of the equation

$$D_b Z_b = \Lambda_b Z_b. \quad (9)$$

The components of the matrix ΔD_b in Eq. (7) are equal to changes of the dynamic coefficients, and the matrix ΔZ_b in Eq. (8) comprises the components describing the change of the vibration type. The diagonal matrix $\Delta \Lambda_b$ from Eq. (6) is set by the components $\Delta \lambda_{b_j} = 4\pi^2 c^2 (\Delta \omega_{b_j})^2$, $j = 1, b$.

To derive the equation for vibrations at compound frequencies, we apply the operation of direct multiplication of matrices and use its properties for eigenvalues and eigenvectors which follow from theoretical considerations [4]. If there exists a matrix polynomial $\varphi(A, B) = \sum c_{ij} A^i \otimes B^j$ formed from matrices $A_{m \times m}$ and $B_{n \times n}$ with real coefficients c_{ij} , mn numbers $\varphi(\lambda_i, \sigma_j)$ will be the eigenvalues of the matrix $\varphi(A, B)$, where λ_i ($i = 1, m$) are the eigenvalues of the matrix A and σ_j ($j = 1, n$) are the eigenvalues of the matrix B .

Let us multiply directly both parts of Eq. (4) by the unit diagonal matrix $I_{b \times b}$ from the right and Eq. (5) by $I_{a \times a}$ from the left. Taking into account the property of noncommutativity of the direct product, we obtain two equations

$$(D_a \otimes I_b)(Z_a \otimes I_b) = (\Lambda_a \otimes I_b)(Z_a \otimes I_b), \quad (10)$$

$$(I_a \otimes D'_b)(I_a \otimes Z'_b) = (I_a \otimes \Lambda'_b)(I_a \otimes Z'_b). \quad (11)$$

After multiplication of Eq. (10) from the right by the matrix expression $(I_a \otimes Z'_b)$ and Eq. (11) by $(Z_a \otimes I_b)$ and application of the property of the direct product $(A \otimes B)(C \otimes D) = AC \otimes BD$, we obtain the transformed equations:

$$(D_a \otimes I_b)(Z_a \otimes Z'_b) = (\Lambda_a \otimes I_b)(Z_a \otimes Z'_b), \quad (12)$$

$$(I_a \otimes D'_b)(Z_a \otimes Z'_b) = (I_a \otimes \Lambda'_b)(Z_a \otimes Z'_b). \quad (13)$$

Subtraction of Eq. (13) from Eq. (12) yields the matrix equation

$$(D_a \otimes I_b - I_a \otimes D'_b)(Z_a \otimes Z'_b) = (\Lambda_a \otimes I_b - I_a \otimes \Lambda'_b)(Z_a \otimes Z'_b) \quad (14)$$

with eigenvalues determined by the diagonal components of the matrix $(\Lambda_a \otimes I_b - I_a \otimes \Lambda'_b)$. They are equal to the difference between the numbers $(\lambda_{a_i} - \lambda'_{b_j})$ ($i = 1, a$ and $b = 1, j$). We express them through the frequencies of normal vibrations:

$$\lambda_{a_i} - \lambda'_{b_j} = 4\pi^2 c^2 \left(\omega_{a_i}^2 - (\omega'_{b_j})^2 \right). \quad (15)$$

Let us square both parts of equality (15); we obtain the expression

$$\left(\lambda_{a_i} - \lambda'_{b_j}\right)^2 = \left(4\pi^2 c^2 \left(\omega_{a_i} + \omega'_{b_j}\right)^2\right) \left(4\pi^2 c^2 \left(\omega_{a_i} - \omega'_{b_j}\right)^2\right), \quad (16)$$

from which it follows that to derive the matrix equation with the eigenvalues determined by Eq. (16), the direct product of both parts of Eq. (14) must be squared. Using designations $A^{[2]} = A \otimes A$, we finally obtain the equation for vibrations at compound frequencies:

$$(D_a \otimes I_b - I_a \otimes D'_b)^{[2]} (Z_a \otimes Z'_b)^{[2]} = (\Lambda_a \otimes I_b - I_a \otimes \Lambda'_b)^{[2]} (Z_a \otimes Z'_b)^{[2]}. \quad (17)$$

We note that among the diagonal elements of the matrix of eigenvalues in Eq. (17) there are components that differ from expression (16). They have no physical meaning and are omitted. The inequality $\omega_{a_i} > \omega'_{b_j}$ ($i = 1, a$ and $j = 1, b$) should also be satisfied for the frequencies. Cases are possible when $a = b$, that is, vibrations have the same symmetry type; then the serial numbers of vibrations should not coincide ($i \neq j$).

MOLECULAR PARAMETERS

In the theory of matrices [4], equation (17) belongs to the important class of equations solving the fundamental problem of determining the eigenvalues and corresponding eigenvectors. From its solution it follows that the matrix of vibrations with summed or difference frequencies is determined by the direct product of the submatrices:

$$Z_{ab} = Z_a \otimes Z'_b. \quad (18)$$

Taking into account Eq. (8), we can write the above equation in the form

$$Z_{ab} = Z_a \otimes (Z_b + \varepsilon \Delta Z_b). \quad (19)$$

The column components of the matrix Z_{ab} in Eq. (19) at frequencies $(\omega_{a_i} \pm \omega'_{b_j})$ coincide with the coordinates of vectors:

$$Z_{a_i, b_j} = Z_{a_i} \otimes Z'_{b_j} = Z_{a_i} \otimes (Z_{b_j} + \varepsilon \Delta Z_{b_j}), \quad (i = 1, a; j = 1, b). \quad (20)$$

We now analyze the dependence of ΔZ_{b_j} on changes in the frequencies $\Delta \omega_{b_j}$ ($j = 1, b$). We take advantage of the results obtained in [9] where formulas for the eigenvalues and eigenvectors, determining changes in ΔZ_{b_j} versus $\Delta \omega_{b_j}$, were derived in the context of the matrix theory of perturbations up to the n th perturbation order. For the compound vibrations, we take advantage of the formula for the first-order approximation:

$$\Delta Z_{b_j} = \sum_{\substack{i=1 \\ i \neq j}}^b \frac{\beta_{ij}}{(\lambda_{b_j} - \lambda_{b_i}) s_i} Z_{b_i}, \quad (21)$$

in which s_i are calculated as a scalar product of the left transposed eigenvector of the matrix D_b from Eq. (9) by its right eigenvector Z_{b_i} . The coordinates of the left transposed eigenvector coincide with the components of the i th row of the inverse matrix Z_b^{-1} . Because these vectors are orthonormalized, all s_i ($i = 1, b$) are equal to unity. According to [3], the components β_{ij} are given by the expression

$$\beta_{ij} = (\mathbf{Y}_{b_i})^T \Delta \Lambda_b \mathbf{Z}_{b_j}. \quad (22)$$

After simple transformations, we write down Eq. (22) in terms of frequencies of normal vibrations

$$\Delta \mathbf{Z}_{b_j} = \sum_{\substack{i=1 \\ i \neq j}}^b \frac{\beta'_{ij}}{\omega_{b_j}^2 - \omega_{b_i}^2} \mathbf{Z}_{b_i} \quad (23)$$

with components

$$\beta'_{ij} = \sum_{k=1}^b Y_{bk,i} \Delta \omega_k \mathbf{Z}_{b_j,k}. \quad (24)$$

Formulas (23) and (24) specify the coordinates of vectors $\Delta \mathbf{Z}_{b_j}$ ($j = 1, b$) and hence the components of the matrix $\Delta \mathbf{Z}_b$.

After substitution of Eq. (23) into Eq. (20), we obtain the expression

$$\mathbf{Z}_{a_i,b_j} = \mathbf{Z}_{a_i} \otimes \left(\mathbf{Z}_{b_j} + \varepsilon \sum_{\substack{i=1 \\ i \neq j}}^b \frac{\beta'_{ij}}{\omega_{b_j}^2 - \omega_{b_i}^2} \mathbf{Z}_{b_i} \right), \quad (25)$$

in which the coordinates of the vector \mathbf{Z}_{a_i,b_j} and hence the components of the vibration type matrix Z_{ab} given by Eq. (19) depend explicitly on the change of frequencies caused by the interaction of vibrations.

The displacements of atoms with normal vibrations at the frequency ω_{a_i} ($i = 1, a$) are determined by the relation $X_a = l_a Q_a$, where $l_a = M^{-1} B_a^T (Z_a^{-1})^T Q_a$ according to [2], $X_a = (\Delta r_1, \Delta r_2, \dots, \Delta r_a)$, M^{-1} is the diagonal matrix of the reciprocal atomic masses, B_a^T is the transposed matrix of the Wilson s -vectors, $(Z_a^{-1})^T$ is the transposed inverse matrix of the vibration type Z_a given by Eq. (4), and $Q_a = (Q_{a1}, Q_{a2}, \dots, Q_{aa})^T$ is the column of the normal coordinates.

For the second perturbed vibration at the frequency ω'_{b_j} ($j = 1, b$), the atomic displacements are written down with allowance for changes:

$$X'_b = l'_b Q_b = (l_b + \varepsilon \Delta l_b) Q_b, \quad (26)$$

$$X'_b = M^{-1} B_b^T ((Z'_b)^{-1})^T Q_b. \quad (27)$$

In Eq. (27), the matrix $((Z'_b)^{-1})^T$ is the transposed inverse matrix $(Z'_b)^{-1}$. In the matrix theory of perturbations [4], the following assertion was proved: if Eq. (6) is obeyed, then together with Eq. (8), the following analytical expression can be written for the inverse matrix:

$$(Z'_b)^{-1} = Z_b^{-1} + \varepsilon \Delta Z_b^{-1}. \quad (28)$$

After transformations of the left eigenvectors by the algebraic method of the theory of perturbations [3] analogous to the transformations described in [9], we obtain the following formula for the components of the j th row of the matrix ΔZ_b^{-1} :

$$\Delta \mathbf{Y}_{b_j}^T = \sum_{\substack{i=1 \\ i \neq j}}^b \frac{\beta'_{ij}}{\omega_{b_j}^2 - \omega_{b_i}^2} \mathbf{Y}_{b_i}^T, j = 1, b. \quad (29)$$

Having substituted Eq. (28) into Eq. (27), we derive the expression for the displacement of atoms with excited vibrations:

$$\mathbf{X}'_b = M^{-1} B_b^T \left(\left((\mathbf{Z}'_b)^{-1} \right)^T + \varepsilon \Delta \left((\mathbf{Z}'_b)^{-1} \right)^T \right) \mathbf{Q}_b. \quad (30)$$

The second term in Eq. (30) determines the change of displacements caused by the interaction of vibrations. It should be taken into account in direct calculations of the spectroscopic parameters of molecules. Therefore, the anharmonic coefficients of centrifugal distortion are determined by the relations

$$A_{ab}^{(\alpha\alpha)} = \sum_{i=1}^N \left(l_{a_i}^{(\beta)} (l'_{b_i})^{(\beta)} + l_{a_i}^{(\gamma)} (l'_{b_i})^{(\gamma)} \right) = \sum_{i=1}^N \left(l_{a_i}^{(\beta)} l_{b_i}^{(\beta)} + l_{a_i}^{(\gamma)} l_{b_i}^{(\gamma)} \right) + \sum_{i=1}^N \left(l_{a_i}^{(\beta)} \Delta l_{b_i}^{(\beta)} + l_{a_i}^{(\gamma)} \Delta l_{b_i}^{(\gamma)} \right), \quad (31)$$

$$A_{ab}^{(\alpha\beta)} = -\sum_{i=1}^N l_{a_i}^{(\alpha)} (l'_{b_i})^{(\beta)} = -\sum_{i=1}^N l_{a_i}^{(\alpha)} \left(l_{b_i}^{(\beta)} + \Delta l_{b_i}^{(\beta)} \right), \quad (\alpha, \beta, \gamma = x, y, z), \quad (32)$$

which comprise the terms determined by the interaction of vibrations.

The Coriolis coefficients that characterize coupling of two vibrations are determined by the coordinates of vectors

$$\zeta_{ab} = \sum_{i=1}^N [l_{a_i} l'_{b_i}] = \sum_{i=1}^N [l_{a_i} (l_{b_i} + \Delta l_{b_i})]. \quad (33)$$

Calculations were performed for the H₂¹⁶O water molecule and its two heavy isotopes H₂¹⁷O and H₂¹⁸O from formulas (31)–(33) using the program for solving the direct mechanical problem taken from [7]. They have demonstrated that the terms determining changes of $\Delta A_{ab}^{(\alpha\alpha)}$, $\Delta A_{ab}^{(\alpha\beta)}$, and $\Delta \zeta_{ab}$ caused by the interaction of excited vibrations at compound frequencies are \varkappa^2 times smaller than the unperturbed values of the corresponding parameters presented, for example, in [8] (here \varkappa is the Born–Oppenheimer parameter). These results are in agreement with the estimates obtained by different methods in [3, 4, 8] in the first order of the perturbation theory.

The important spectroscopic parameters for vibrations at compound frequencies are the second-order derivatives of the dipole moment with respect to the normal coordinates:

$$\frac{\partial^2 \bar{\mu}}{\partial Q_a \partial Q_b} = \sum_{k,n=1}^{3N-6} \frac{\partial^2 \bar{\mu}}{\partial S_{a_i,k} \partial S_{b_j,n}} Z_{a_i,k} Z'_{b_j,n} = \sum_{k,n=1}^{3N-6} \frac{\partial^2 \bar{\mu}}{\partial S_{a_i,k} \partial S_{b_j,n}} Z_{a_i,k} (Z_{b_j,n} + \Delta Z_{b_j,n}). \quad (34)$$

Here $S_{a_i,k}$ and $S_{b_j,n}$ are the coordinates of symmetry of the corresponding vibration types.

Let us give an example of calculations of the second-order derivative of the x -component of the dipole moment $\mu_{12}^x = \frac{\partial^2 \mu_x}{\partial Q_1 \partial Q_2}$ and its change $\Delta \mu_{12}^x$ determined by the second term of Eq. (34). Calculations were performed by the method described in [6] with the use of the program complex described in [7]. For the H₂¹⁶O water molecule, we obtained the following values: $\mu_{12}^x = -0.9998 \cdot 10^{-2}$ D and $\mu_{12}^x = -0.35 \cdot 10^{-4}$ D. They are in agreement with the experimental value $(\mu_{12}^x)_{\text{exp}} = -(0.843 \pm 0.18) \cdot 10^{-2}$ D [10]. For the H₂¹⁷O isotope, we obtained $\mu_{12}^x = -0.9973 \cdot 10^{-2}$ D and $\Delta \mu_{12}^x = -0.28 \cdot 10^{-4}$ D. For the other H₂¹⁸O isotope, we obtained $\mu_{12}^x = -0.9945 \cdot 10^{-2}$ D and $\Delta \mu_{12}^x = -0.25 \cdot 10^{-4}$ D.

However, we failed to find in the literature a comparative experiment for both isotopes. Analyzing the results obtained, we note that μ_{12}^x and $\Delta\mu_{12}^x$ have the same signs, and their contributions to values of the anharmonic electrooptical parameters are comparable with changes of the derivatives caused by the effect of isotopic substitution. Therefore, μ_{12}^x and $\Delta\mu_{12}^x$ must be taken into account in direct calculations of the anharmonic electrooptical parameters.

In conclusion, we note that the main theoretical results are formulas (17)–(21), (23), (25), and (27)–(34). They allow one to substantiate the interaction of vibrations and to investigate its influence on the spectroscopic parameters of molecules vibrating at the compound frequencies.

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