# Effect of isotopic substitution on spectra of linear XY$_2$-type molecules (D$_{\infty h}$)

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The effect of symmetric isotopic substitution in linear XY$_2$-type molecules having the D$_{\infty h}$ symmetry is considered, and approximate equations for isotopic shifts of rotation-vibration lines are proposed.

## Introduction

The isotopic substitution in molecules is usually considered based on the Born—Oppenheimer approximation.[1] In this approximation, some molecular characteristics, for example, the intramolecular potential function, equilibrium configuration, dipole moment of the molecule, and others, depend only on properties of the electron shell and are independent of atomic masses. The availability of isotope-invariant characteristics allows derivation of relations between molecular and spectroscopic parameters of isotopic species, namely, the isotopic relations, which appear to be quite useful in analysis of molecular spectra.

The results of investigations of the isotopic substitution in vibrational and rotational spectra have been considered in detail in the literature.[2–10] A number of various isotopic rules and relations for molecular and spectroscopic parameters, as well as methods for calculation of spectra of isotopically substituted molecules were proposed. A feature of the method proposed in Ref. 10 is that it allows determination of isotopic relations for any molecular constants without explicitly transforming the Hamiltonian of the isotopic species. The analysis of relations between the Hamiltonians: $H(x)$ (2.19), "intermediate" Hamiltonian $h$ (3.8), and the Wilson—Howard—Watson Hamiltonian $H^{\text{W}}$ (1.57), allowed the authors to study the isotopic relations for harmonic frequencies and anharmonic parameters of the potential energy function, Coriolis constants, and derivatives of the tensor of inertia with respect to the normal coordinates, as well as the spectroscopic constants: rotational and centrifugal distortion parameters, first and second derivatives of the dipole moment.[10]

It was shown[10] that the problem can be solved based on the possibility of constructing the effective rotational-vibrational (RV) operators of the parent molecule and the isotopically substituted molecule both in the Born—Oppenheimer approximation and with allowance for deviations from this approximation.

With the advent of spectrometers of new type and the use of laser equipment, the accuracy of experimental data on positions and intensities of spectral lines has increased drastically. This circumstance requires the deviations from the Born—Oppenheimer approximation to be taken into account as well when considering the structural parameters of the molecule and the harmonic frequencies of vibrations. Watson[11] considered the effect of deviation from this approximation for diatomic molecules. He has thoroughly analyzed different isotopic species of the LiH molecule using the available experimental data. This work is devoted to analysis of the effect of isotopic substitution on RV spectra of linear triatomic XY$_2$-type molecules having the D$_{\infty h}$ symmetry in the case of symmetric substitution of heavy atoms.

## 1. General equations

In molecular spectra, the strongest effect is associated with substitution of hydrogen nuclei, for example, the shift of vibrational frequencies can amount to hundreds of reciprocal centimeters. The substitution of heavier atoms, such as boron, carbon, nitrogen, and others causes a "moderate" isotopic effect. In this case, the shifts of lines and bands are mostly within tens of reciprocal centimeters. The substitution of very heavy atoms (for example, Os, Ge, U) only slightly changes the spectrum, which leads to certain difficulties in studying the spectra of mixtures of different isotopic modifications of such molecules.[2]

The "moderate" isotopic effect, that is, the isotopic substitution of heavy atoms in a molecule, is characterized by relatively small change of the mass, which can be described by some small parameter. This allows us to use the perturbation theory methods and not only to find the isotopic relations between the molecular or spectroscopic parameters,[10] but also to determine line shifts and changes in the line intensities in RV spectra of the substituted molecule. Further we use the method proposed in Ref. 10, applying the scheme of contact transformations and the corresponding transformations of the Hamiltonian and dipole moment of the molecule. The Hamiltonian of the substituted molecule $h$ can be represented in the form

$$h = H^{\mathrm{p}} + \Delta h. \qquad (1)$$

Here $H^{\mathrm{p}}$ is the Hamiltonian of the parent molecule; $\Delta h$ is an addition due to the isotopic substitution.

The order of terms in the expansion of the operator $\Delta h$ will be described by two parameters: the mass parameter $\varepsilon = \max|\varepsilon_N|$ and the Born−Oppenheimer parameter $\kappa = \sqrt{m_{\mathrm{e}}/M}$, where $\varepsilon_N = (m'_N - m_N)/m'_N$, $m'_N$ and $m_N$ are the masses of the $N$th atom of the substituted and parent molecules, respectively; $m_{\mathrm{e}}$ is the electron mass; $M$ is the magnitude of the order of the average mass of nuclei. It is obvious that $H^{\mathrm{p}}$ and $\Delta h$ are functions of parameters of the parent molecule.

In the general form, $\Delta h$ can be written through the dimensionless operators of coordinates $q_\lambda$, momenta $p_\lambda$, and components of the operator of the total angular momentum $J_\alpha$ as a sum of products of these operators:

$$\Delta h = \sum_{\alpha\beta\lambda\mu\nu\tau} {}^{\alpha\beta\dots}h_{\lambda\mu\dots}^{\nu\tau\dots}\, q_\lambda q_\mu \dots p_\nu p_\tau \dots J_\alpha J_\beta \dots \; . \qquad (2)$$

The explicit operator form of these terms can be derived either from the symmetry conditions or through the expansion of $\Delta h$ into power series in terms of normal coordinates.

The deviation from the Born−Oppenheimer equation will be taken into account with the aid of the perturbation theory,[10] through writing the Hamiltonians of the substituted and the parent molecules in the form

$$H(X,Y) = H_0^{\mathrm{B-O}}(X) + \Delta H^{\mathrm{B-O}}(X,Y), \qquad (3)$$

where $X$ and $Y$ are two sets of variables, and the second term is considered as a small perturbation of the first one. Here $H_0^{\mathrm{B-O}}(X)$ is the molecular Hamiltonian, which is usually determined by the perturbation theory with the Born−Oppenheimer parameter of smallness. Hamiltonian (3) differs from the commonly used Hamiltonian, but describes the same physical system. This allows us to solve the problem for eigenvalues, determine energy levels, transition frequencies and intensities of the substituted molecule, expressing them through the parameters of the parent molecule.

The dipole moment operator of the substituted molecule $\mu'$ can also be represented as a sum of the dipole moment of the parent molecule $\mu_\alpha^{\mathrm{p}}$ and some additions $\Delta\mu$ due to the isotopic substitution:

$$\mu'_\alpha = \mu_\alpha^{\mathrm{p}} + \Delta\mu_\alpha. \qquad (4)$$

The components of the dipole moment operator are usually written in the form of a series in terms of the normal vibrations

$$\mu_\alpha = \sum_\beta {}_{\alpha\beta}\left\{ \mu_\beta^0 + \sum_\lambda \mu_\beta^\lambda Q_\lambda + \sum_{\lambda\nu} \mu_\beta^{\lambda\nu} Q_\lambda Q_\nu + \dots \right\}.$$

The explicit form of $\Delta\mu$ is also derived from the symmetry requirements or through expansion into series. In Ref. 10, it is shown that the difference in

the dipole moment of the substituted and the parent molecules is caused only by a change of the orientation of the molecule-fixed coordinate system:

$$\mu'^0_\alpha = \sum_\beta {}_{\beta\alpha}^{\prime 0}\, \mu_\beta^{\mathrm{p}\,0}.$$

Here ${}_{\beta\alpha}^{\prime 0}$ is the matrix corresponding to the rotation of the coordinate system of the parent molecule to the coordinate system of the substituted molecule (direction cosine matrix). For the first and second derivatives of the dipole moment of linear molecules, this difference is also connected with the difference in orientation of coordinate axes of the parent and substituted molecules with configurations of nuclei different from the equilibrium ones:

$$\mu'^\lambda_\alpha = \sum_\beta {}_{\beta\alpha}^{\prime 0}\, \sum_\nu \mu_\beta^{\mathrm{p}\,\nu}\, \alpha_{\lambda\nu},$$

$$\mu'^{\lambda\nu}_\alpha = \sum_\beta {}_{\beta\alpha}^{\prime 0}\, \sum_{\gamma\leq\kappa} \mu_\beta^{\mathrm{p}\,\gamma\kappa} (\alpha_{\gamma\lambda}\,\alpha_{\kappa\nu} + \alpha_{\gamma\nu}\,\alpha_{\kappa\lambda}). \qquad (5)$$

Here $\alpha_{\lambda\nu}$ are parameters of transformation of normal coordinates, depending on atomic masses:

$$Q_\lambda = \sum_\nu \alpha_{\lambda\nu}\, Q'_\nu + \sum_{\nu\kappa} \alpha_{\nu\kappa}^\lambda\, Q'_\nu Q'_\kappa + \dots \; .$$

## 2. Isotopic shifts

To determine the isotopic shifts of molecular anharmonic, rotational, and centrifugal distortion parameters, it was proposed[10] to use a two-stage transformation scheme for Hamiltonian (1). First, a series of small unitary transformations is carried out, which reduces the operator $H^{\mathrm{p}}$ to the block-diagonal form − the effective rotational Hamiltonian. Then, through the expansion in series in terms of the parameter $\varepsilon$, the addition associated with the isotopic substitution is taken into account in the transformed Hamiltonian.

However, because of the need to perform two contact transformations, this scheme appears to be rather complicated and cumbersome. The calculations of line positions and intensities of linear molecules within the "global" approach in the method of effective Hamiltonians involve the terms corresponding to high orders of the perturbation theory. In this case, the form of the effective Hamiltonian and the spectroscopic constants are determined from symmetry considerations, that is, without contact transformations in the explicit form. The Hamiltonian parameters, such as high centrifugal distortion corrections, resonance terms, and others, are determined by fitting to the measured values of line positions.

To obtain the analogous equations for isotopic shifts of RV lines, it is more convenient to use the general scheme of the Rayleigh−Schrödinger perturbation theory. The wave functions of the substituted molecule and its energy levels can be represented in the form

$$\Psi'_n = \Psi_n + \sum_m \frac{\langle \Psi_n | \Delta h | \Psi_m \rangle}{E_n - E_m} \Psi_m + \ldots; \qquad (6)$$

$$E'_n = E_n + \varepsilon \langle \Psi_n | \Delta h | \Psi_n \rangle + \varepsilon^2 \sum_{m \neq n} \frac{|\langle \Psi_n | \Delta h | \Psi_m \rangle|^2}{E_n - E_m} + \ldots . \quad (7)$$

Here $\psi_n$ and $E_n$ are the wave functions and the energy levels of RV states of the parent molecule, and $\Delta h$ is determined from Eq. (2). It is also assumed that the isotopic substitution does not cause a strong mixing of levels, therefore we can establish one-to-one correspondence between stationary states of isotopic species.

When calculating matrix elements in Eqs. (6) and (7), it is possible to use zero-approximation functions $\tilde{\Psi}_n$, introducing simultaneously the correction factors depending on the vibrational and rotational quantum numbers. In this case

$$E'_n = E_n +$$

$$+ \varepsilon \sum_{\alpha\beta\lambda\mu\nu\tau} {}^{\alpha\beta\ldots}h^{\nu\tau\ldots}_{\lambda\mu\ldots} \left\langle \tilde{\Psi}_n \left| q_\lambda q_\mu \ldots p_\nu p_\tau \ldots J_\alpha J_\beta \ldots \right| \tilde{\Psi}_n \right\rangle \times$$

$$\times \left\{ 1 + {}^{\alpha\beta\ldots}\eta^{\nu\tau\ldots}_{\lambda\mu\ldots}(n) + \ldots \right\} +$$

$$+ \varepsilon^2 \sum_{\alpha\beta\lambda\mu\nu} \sum_{\alpha'\beta'\lambda'\mu'\nu'} {}^{\alpha\beta\ldots}h^{\nu\tau\ldots}_{\lambda\mu\ldots} {}^{\alpha'\beta'\ldots}h^{\nu'\tau'\ldots}_{\lambda'\mu'\ldots} \times$$

$$\times \sum_{m \neq n} \left\langle \tilde{\Psi}_n \left| q_\lambda q_\mu \ldots p_\nu p_\tau \ldots J_\alpha J_\beta \ldots \right| \tilde{\Psi}_m \right\rangle \times$$

$$\times \left\langle \tilde{\Psi}_m \left| q_\lambda q_{\mu'} \ldots p_{\nu'} p_{\tau'} \ldots J_{\alpha'} J_{\beta'} \ldots \right| \tilde{\Psi}_n \right\rangle \times$$

$$\times \frac{1}{E_n - E_m} \left\{ 1 + {}^{\alpha\beta\alpha'\beta'\ldots}\mu^{\nu\tau\nu'\tau'\ldots}_{\lambda\lambda'\mu\mu'\ldots}(n,m) + \ldots \right\} + \ldots . \quad (8)$$

Terms in braces in the right-hand side of Eq. (8) are the corrections to be determined through fitting to the measured values of isotopic shifts. Other parameters in Eq. (8) are obviously the main contributors to isotopic shifts of the levels:

$$\Delta\nu_{n \leftarrow 0} = (E'_n - E'_0) - (E_n - E_0) =$$

$$= \varepsilon \left\{ \left\langle \tilde{\Psi}_n | \Delta h | \tilde{\Psi}_n \right\rangle - \left\langle \tilde{\Psi}_0 | \Delta h | \tilde{\Psi}_0 \right\rangle \right\} + \ldots . \quad (9)$$

The determination of matrix elements by the zero-approximation functions — harmonic oscillator and rigid top — presents no difficulties, because we can use the same equations as for the parent molecule.

The analysis has shown that the spectroscopic parameters and derivatives of the dipole moment of the substituted molecule can be determined as functions of the constants of the parent molecule and $\varepsilon$:

$$^{\alpha\beta\ldots}h^{\nu\tau\ldots}_{\lambda\mu\ldots \text{subst}} = f(\varepsilon)\,^{\alpha\beta\ldots}h^{\nu\tau\ldots}_{\lambda\mu\ldots}; \qquad (10)$$

$$\mu'^{\lambda\kappa\ldots}_\alpha = \sum_\beta \,^0_{\beta\alpha} \sum_{\nu\gamma\ldots} f(\varepsilon)\mu_\beta^{p\,\nu\gamma\ldots}. \qquad (11)$$

## 3. Molecules of XY$_2$ (D$_{\infty h}$) type

Consider the case of symmetric isotopic substitution in XY$_2$-type molecules having the symmetry D$_{\infty h}$. The carbon dioxide molecule, which is a good example of such molecules, will be analyzed in detail by the following reasons. First, according to the classification accepted in spectroscopy, both atoms: carbon and oxygen, fall in the category of heavy atoms, and it is possible to consider the substitution of one, two, or three atoms simultaneously. Second, there is extensive experimental and theoretical information on the high-resolution RV spectra of different isotopic species for this molecule. Third, the study of the isotopic effect in this molecule is very important for atmospheric applications.

The CO$_2$ molecule has three harmonic oscillations: two with non-degenerated frequencies $\omega_1$, $\omega_3$ and one with doubly degenerated frequency $\omega_2$. These frequencies are related to each other as $\omega_1 \approx 2\omega_2$ and $\omega_3 \approx 3\omega_2$, due to which the matrix of the considered Hamiltonian has a polyad structure. Each polyad includes vibrational states with quantum numbers $V_i$, belonging to the set determined by the relationship $P = 2V_1 + V_2 + 3V_3$. The polyads can be numbered by the integer $P$, and the sets of transitions — by $\Delta P$ [Ref. 12].

Denote the relative change in the mass of the oxygen and carbon atoms as

$$\varepsilon_O = (m_{O_{isotope}} - m_O)/m_{O_{isotope}},$$

$$\varepsilon_C = (m_{C_{isotope}} - m_C)/m_{C_{isotope}},$$

in order to consider the simultaneous substitution of the three atoms. Several first coefficients for $\Delta h$ of this molecule can be written in the explicit form:

$$h^{11} = \omega_1 \varepsilon_O, \quad h^{2_1 2_1} = h^{2_2 2_2} = -\omega_2 \frac{\varepsilon_O m_C + \varepsilon_C 2m_O}{m_{CO_2}},$$

$$h^{33} = -\omega_3 \frac{\varepsilon_O m_C + \varepsilon_C 2m_O}{m_{CO_2}},$$

$$h^{13}_{2_1} = h^{13}_{2_2} = -\frac{1}{2} \frac{\varepsilon_O}{\sqrt{2mr^2}} \sqrt{\frac{\omega_1 \omega_3}{\omega_2}},$$

$$h^{12_1}_3 = h^{12_2}_3 = \frac{1}{2} \frac{\varepsilon_O}{\sqrt{2mr^2}} \sqrt{\frac{\omega_1 \omega_2}{\omega_3}},$$

$$h^{2_1 3}_{2_1 3} = h^{2_2 3}_{2_2 3} = \frac{1}{4} \frac{2\varepsilon_O + \varepsilon_C}{2mr^2} \frac{\omega_3}{\omega_2},$$

$$h^{32_1}_{32_1} = h^{32_2}_{32_2} = \frac{1}{4} \frac{2\varepsilon_O + \varepsilon_C}{2mr^2} \frac{\omega_2}{\omega_3},$$

$$h^{32_1}_{2_1 3} = h^{32_2}_{2_2 3} = h^{2_1 3}_{32_1} = h^{2_2 3}_{32_2} = -\frac{1}{4} \frac{2\varepsilon_O + \varepsilon_C}{2mr^2},$$

$$h = -\frac{1}{4} \frac{2\varepsilon_O + \varepsilon_C}{2mr^2}, \quad {}^x h^1 = -{}^y h^1 = -\varepsilon_O \frac{\sqrt{\omega_1}}{\sqrt{2mr^2}},$$

$$^{xx}h = {}^{yy}h = -\frac{1}{2}\frac{2\varepsilon_O + \varepsilon_C}{2mr^2},$$

$$^{x}h_{2_2}^3 = -{}^{y}h_{2_1}^3 = -\frac{1}{2}\frac{2\varepsilon_O + \varepsilon_C}{2mr^2}\sqrt{\frac{\omega_3}{\omega_2}},$$

$$^{x}h_3^{2_2} = -{}^{y}h_3^{2_1} = \frac{1}{2}\frac{2\varepsilon_O + \varepsilon_C}{2mr^2}\sqrt{\frac{\omega_2}{\omega_3}}. \qquad (12)$$

The general case of symmetric substitution of the atoms is described as

$$\Delta B_{\alpha\beta}(\varepsilon) = \frac{h}{8\pi^2 c}\Delta\mu_{\alpha\beta}^0, \quad \Delta B_{\alpha\beta}(\varepsilon^2) = -4\sum_\lambda \theta_{\alpha\lambda}^0\theta_{\beta\lambda}^0. \qquad (13)$$

For the case of symmetric substitution of oxygen atoms:

$$\Delta B_{\alpha\alpha}(\varepsilon) = -\varepsilon_O B_{\alpha\alpha}^0; \qquad (14)$$

$$\Delta\tau_{\alpha\beta\gamma\delta}(\varepsilon) = -2\varepsilon_O \tau_{\alpha\beta\gamma\delta}; \qquad (15)$$

$$\Delta B_{\beta\beta}(\varepsilon\kappa^2) = \frac{3}{2}\varepsilon_O \sum_\lambda \alpha_\lambda^\beta\left(v_\lambda + \frac{g_\lambda}{2}\right), \qquad (16)$$

where $\alpha_\lambda^\beta$ is the RV constant; $v_\lambda$ is the vibrational quantum number; $g_\lambda$ is the degree of degeneration of the harmonic frequency $\lambda$; $\Delta B_{\beta\beta}(\varepsilon^2) = 0$.

The main part of the rotational constant is

$$B_\beta^{B-O} = \left\{\sum_N m_N\left(r_{N\gamma}^{0\ 2} + r_{N\delta}^{0\ 2}\right)\right\}^{-1},$$

where $\beta$, $\gamma$, $\delta$ are cyclic permutations of the indices $x$, $y$, $z$.

These relationships are the isotopic relations directly between the energy levels, obtained in the framework of the Born—Oppenheimer approximation for the case of symmetric isotopic substitution. The application of these relations in determination of the effective Hamiltonian from spectra (see, for example, Ref. 2) likely presents no difficulties. At the same time, the use of isotopic relations and experimental data on the isotopically substituted molecules improves the stability of inverse problems.

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