

Centrifugal distortion and HEL-resonances in the rovibrational spectra of triatomic molecules

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Simple, one-dimensional model of bending-rotation motion in a triatomic molecule is used to estimate the off-diagonal Hamiltonian matrix elements related to the high-order resonances in water molecule. It is shown that the resonances of this type arise due to strong centrifugal distortion near the linear configuration in a triatomic molecule having low barrier to linearity. The off-diagonal matrix elements are quite large, if the wave functions are near the linear configuration.

Introduction

The study of absorption spectra of gaseous atmospheric constituents and pollutants in the near-IR and visible spectral regions are of certain interest for atmospheric spectroscopy. As known, weak molecular absorption lines due to transitions to higher vibrational states affect the global Earth's radiation budget.

High-excited rotational-vibrational states of molecules are connected with strong resonance effects. Besides Coriolis, Fermi, and Darling–Dennison resonances typical of triatomic molecules, higher-order resonances, in particular, the so-called HEL (Highly Excited Local) resonances occur at a rather strong excitation.¹ These resonances connect the states belonging to different resonance polyads, and they are caused by strong centrifugal distortion near the linear configuration. Earlier, in Ref. 2, in analyzing the water vapor spectra it was shown that the HEL-resonances lead to appearance of a lot of lines associated with transitions to high bending states (050), (060), (070), (080), and (0 10 0) in the spectra.

The aim of this work was to assess the off-diagonal matrix elements of the Hamiltonian that are related to the HEL-resonances. The H₂O molecule is considered as an example, but this effect may manifest itself in other triatomic molecules having a relatively low barrier to linearity, such as, CH₂, H₃⁺ and others. The Hamiltonian of a triatomic molecule in natural coordinates is used, what allows the calculations to be performed for high-excited vibrational states lying above the barrier of the linear configuration.

1. Hamiltonian of a triatomic molecule

For describing the high-excited rotational-vibrational states of triatomic molecules, it is convenient to use the natural coordinates: lengths of the bonds and the angles between them. The molecular Hamiltonian in the natural coordinates has the form³:

$$H = h_s(\rho_1) + h_s(\rho_2) + 2b_0 z p_1 p_2 + h_{tb}(\rho_1, \rho_2, z) + h_M(\rho_1, \rho_2, z) + h_y J_y + h_{xz} \{J_x, J_z\} + U(\rho_1, \rho_2, z), \quad (1)$$

where

$$h_s(\rho_i) = p_i^2 + U_s(\rho_i); \quad (2)$$

$p_i = -i\partial/\partial\rho_i$, $\rho_i = r_i/r_e$, $z = \cos\theta$, ($0 \leq \rho_i \leq \infty$, $-1 \leq z \leq 1$) are dimensionless vibrational coordinates; r_i is the length of the i th bond ($i = 1, 2$); r_e is the equilibrium value of the bond length; θ is the angle between the bonds; $\{A, B\} = AB + BA$ is the anticommutator;

$$h_{tb}(\rho_1, \rho_2, z) = \left[\frac{b_1}{\rho_1^2} + \frac{b_2}{\rho_2^2} \right] \times \left[p_z(1-z^2)p_z + \frac{J_z^2}{2(1+z)} + \frac{J_x^2}{2(1-z)} + \frac{J_y^2}{8} \right] + U_b(z),$$

$$h_y = \frac{1}{2} \left[\frac{b_1}{\rho_1^2} - \frac{b_2}{\rho_2^2} \right] \left\{ \sqrt{1-z^2}, p_z \right\}, \quad (4)$$

$$h_{xz} = -\frac{1}{2} \left[\frac{b_1}{\rho_1^2} - \frac{b_2}{\rho_2^2} \right] \frac{1}{\sqrt{1-z^2}}, \quad (5)$$

$$h_M(\rho_1, \rho_2, z) = \frac{b_0}{\rho_1 \rho_2} \times \left[\left\{ z, p_z(z^2 - 1)p_z \right\} + \frac{J_z^2}{(1+z)} - \frac{J^2/2 - J_z^2/2}{(1-z)} + z \frac{J_y^2}{2} \right] + b_0 \left(\frac{1}{\rho_2} p_1 + \frac{1}{\rho_1} p_2 \right) \left\{ 1 - z^2, p_z \right\} - b_0 \sqrt{1-z^2} \left(\frac{1}{\rho_2} p_1 - \frac{1}{\rho_1} p_2 \right) J_y. \quad (6)$$

The parameters b_1 , b_2 , b_0 are determined by the following equations:

$$b_i = \frac{h}{8\pi^2 c \mu_i r_e^2}, \quad \frac{1}{\mu_i} = \frac{1}{m_i} + \frac{1}{M}, \quad b_0 = \frac{h}{8\pi^2 c M r_e^2}. \quad (7)$$

where μ_i is reduced mass of i th bond; M is mass of a “central” atom; m_i are masses of the “end” atoms.

The system of coordinates fixed in the molecule is defined as follows. The molecule lies in the xz plane, the axis x is directed along the bisector of the angle HOH and is the second-order symmetry axis in the equilibrium configuration.

The potential energy function can be presented as

$$V(\rho_1, \rho_2, z) = U_s(\rho_1) + U_s(\rho_2) + U_b(z) + U(\rho_1, \rho_2, z). \quad (8)$$

2. Calculation of resonance matrix elements

The effective Hamiltonian \tilde{H}_Γ is defined as usually:

$$\tilde{H}_\Gamma = \sum_{i,j \in \Gamma} h_{ij} |i\rangle \langle j|; \quad (9)$$

$$h_{ij} = \langle \psi_i^0 | H | \psi_j^0 \rangle + \frac{1}{2} \sum_{k \in \Gamma} \langle \psi_i^0 | H | \psi_k^0 \rangle \langle \psi_k^0 | H | \psi_j^0 \rangle \left[\frac{1}{E_i^0 - E_k^0} + \frac{1}{E_j^0 - E_k^0} \right] + \dots, \quad (10)$$

where Γ is the set of states considered together. The polyad Γ is assumed large enough, so that it incorporates all the resonance interactions significant for the formation of the energy spectrum. In this case, the denominators in the right-hand side of Eq. (10) are assumed large enough, and second-order additions are small.

Our task is to assess the contributions from different terms of Eq. (1) into the off-diagonal elements connected with the HEL-resonances. It is necessary to determine which terms of the Hamiltonian give the largest contribution to the HEL-resonances. The last term in Eq. (1), namely, the separation between the bending and stretching potentials from the total intramolecular potential can be considered small, because of the representation (8). The direct calculation has shown that the contribution of $U(\rho_1, \rho_2, z)$ is smaller by an order of magnitude. Consequently, we should analyze only a part of the Hamiltonian that is connected with the molecular rotation. The third ($2b_0 z p_1 p_2$) and fifth $h_M(\rho_1, \rho_2, z)$ terms in Eq. (1) are proportional to $1/M$, and, consequently, give small contributions, while the sixth and seventh terms contribute only to the resonances between the states of different symmetry.

For estimation we use the model Hamiltonian for the bending-rotational problem that follows from the Hamiltonian (1). In this case, we take into account the rotation around all the three axes of inertia.

In the approximation of the frozen stretching coordinates, the model Hamiltonian has the form:

$$\frac{H_{rb}}{2b_e} = p_z(1-z^2)p_z + \left[\frac{1}{2(1+z)} - \frac{1}{2} \left(\frac{1}{2(1-z)} + \frac{1}{4} \right) \right] J_z^2 + \frac{1}{2} \left(\frac{1}{2(1-z)} + \frac{1}{4} \right) J^2 + \frac{1}{2} \left[\frac{1}{2(1-z)} - \frac{1}{4} \right] J_{xy}^2 + 2b_e U_b(z - z_e),$$

(11)

where $b_e = h/8\pi^2 c \mu r_e^2$. The operator (11) describes the bending vibration and rotation of the molecule around all the three molecule-fixed axes.

For determination of the effective rotational Hamiltonian, let us use the vibrational part of the Hamiltonian (11) as a zero-approximation operator:

$$H_0 = p_z(1-z^2)p_z + 2b_e U_b(z - z_e) \quad (12)$$

and the following operator as a perturbation

$$V = \left[\frac{1}{2(1+z)} - \frac{1}{2} \left(\frac{1}{2(1-z)} + \frac{1}{4} \right) \right] J_z^2 + \frac{1}{2} \left(\frac{1}{2(1-z)} + \frac{1}{4} \right) J^2 + \frac{1}{2} \left[\frac{1}{2(1-z)} - \frac{1}{4} \right] J_{xy}^2. \quad (13)$$

The problem on eigenvalues cannot be solved exactly with the Hamiltonian (12). For determination of zero-approximation energy levels and wave functions, we use the direct variational method with the basis functions:

$$\phi_V^{(\alpha,\beta)}(z) = N_V(\alpha,\beta)(1-z)^{\alpha/2}(1+z)^{\beta/2} P_V^{(\alpha,\beta)}(z), \quad (14)$$

where $P_V^{(\alpha,\beta)}(z)$ are the Jacobi polynomials and

$$N_V(\alpha,\beta) = \left\{ \frac{V!(2V+\alpha+\beta+1)\Gamma(V+\alpha+\beta+1)}{2^{\alpha+\beta+1}\Gamma(V+\alpha+1)\Gamma(V+\beta+1)} \right\}^{1/2}$$

is the normalized factor. The zero-approximation wave functions $\psi_V^0(z)$ are determined as a linear combination

$$\psi_V^0(z) = \sum_{n=0}^N c_{Vn} \phi_n^{(\alpha,\beta)}(z), \quad (15)$$

and the energy levels E_V^2 are obtained as eigenvalues of the matrix calculated with the basis functions (14). The potential energy function of the bending vibration can be presented in the form

$$U_b(z - z_0) = a_2(z - z_e)^2 + a_3(z - z_e)^3 + a_4(z - z_e)^4 + \dots$$

For estimation of the permanent HEL-resonances, it is necessary to calculate the off-diagonal matrix elements of the perturbation operator that relates the states with $|\Delta V_2| = 1, 2, 3, 4$. To cause rather strong mixing of wave functions, the off-diagonal matrix elements should be comparable with the energy difference between the resonant levels, that is, $\sim 10 \text{ cm}^{-1}$. Thus, the problem consists in calculation of matrix elements of the operator (13) with the zero-approximation functions (15).

The first-order correction

$$\langle n | W | m \rangle = f_k^{nm} J_z^2 + f_J^{nm} J^2 + f_{xy}^{nm} J_{xy}^2,$$

where

$$f_k^{nm} = b_e^{nm} \langle \psi_n^0 | \frac{1}{1+z} | \psi_m^0 \rangle$$

(for f_J^{nm}, f_{xy}^{nm} the equations are quite similar) determines the rotational constants at $n = m$ and the resonance constants at $n \neq m$. Note that here we do not consider the HEL-resonances between vibrational states of the same symmetry.

For calculation we used the following parameters: $r_e = 0.95843$, $\angle\theta_e = 104.4^\circ$, $a_2 = 18975$, $a_3 = 1728$, $a_4 = 5154 \text{ cm}^{-1}$, $\alpha = 1.1$, $\beta = 1.1$, the basis dimension $N = 20$; all these data have been borrowed from Ref. 4.

The wave functions $\psi_V^0(z)$ are shown in Fig. 1. Note that as the excitation increases, the values of the wave function near the linear configuration increase, and, as a consequence, the contribution of the linear configuration to the diagonal and off-diagonal matrix elements increases as well.

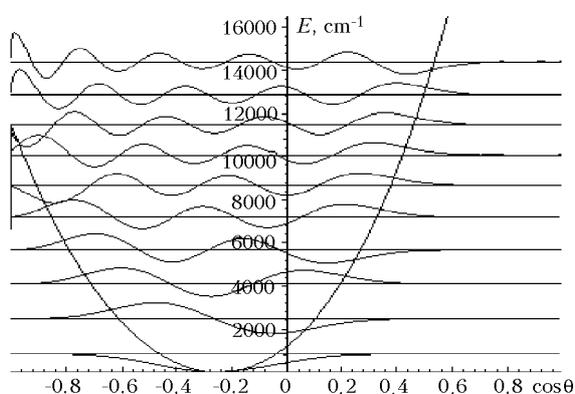


Fig. 1. Wave functions of the (0V0) states.

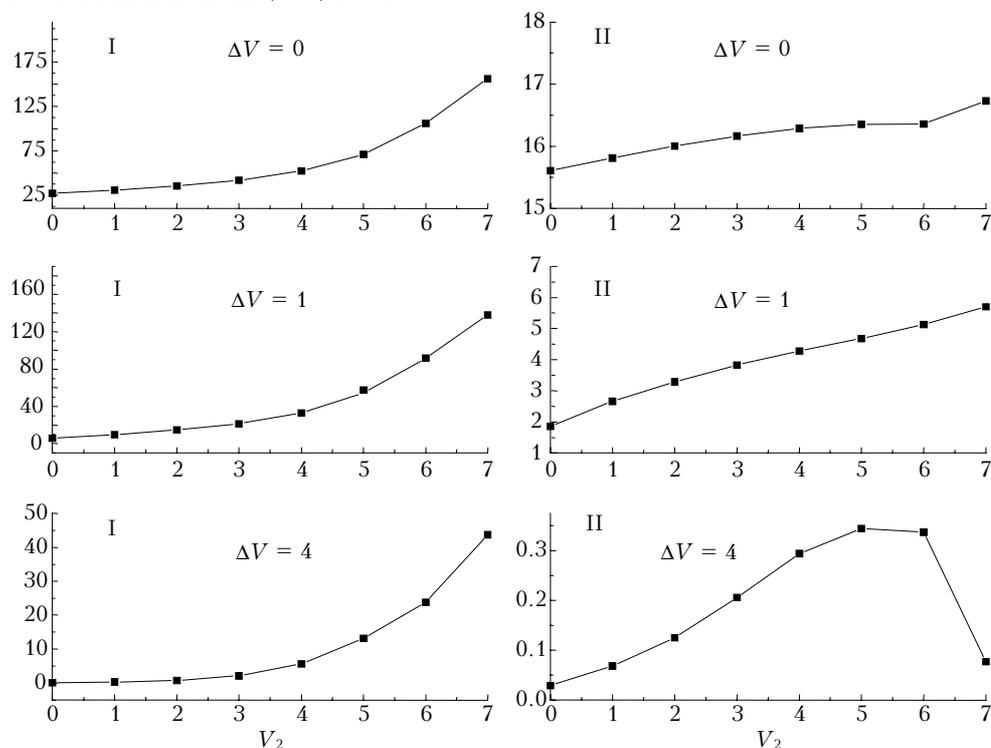


Fig. 2. The values of the matrix elements $|\langle\psi_V^0|(1+z)^{-1}|\psi_{V+\Delta V}^0\rangle|$ (I) and $|\langle\psi_V^0|(1-z)^{-1}|\psi_{V+\Delta V}^0\rangle|$ (II).

Figure 2 depicts the dependence of the matrix elements $|\langle\psi_V^0|(1+z)^{-1}|\psi_{V+\Delta V}^0\rangle|$ (I) on the quantum number V_2 . Note that these matrix elements grow rather fast with the increase of V_2 and become comparable with the differences between the rotational levels. At the same time, the matrix elements of the operator $|\langle\psi_V^0|(1-z)^{-1}|\psi_{V+\Delta V}^0\rangle|$ (II) vary only slightly. Thus, it can be concluded that it is just the centrifugal distortion associated with the linear configuration H–O–H and the resonance parameters f_k^{nm} that determine the HEL-resonances, while the contributions of the parameters f_J^{nm}, f_{xy}^{nm} must be small.

Conclusions

In conclusion, it should be noted that here we present only the general estimate of the V_2 -dependence of the constants of the HEL-resonances, and for more accurate calculation it is necessary to use more accurate potential energy function and to take into account the relation between the stretching and bending vibrations. Despite the numerical estimates we have obtained in this paper for water molecule, it can be suggested, in general, that centrifugal distortion in any triatomic molecule having a rather low energy barrier for the linear configuration must manifest itself as mixing of the states, whose wave functions are located just near the linear configuration. It should be noted that earlier the constants of the resonance operators of the effective Hamiltonian of the H_2O molecule were presented in Ref. 5.

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