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Variational calculation of the vibronic spectrum in the $X^2\Pi_u$ electronic state of C_6^-

MARKO MITIĆ[1*#], MILAN MILOVANOVIĆ[1#], RADOMIR RANKOVIĆ[1#], STANKA JEROSIMIĆ[1#] and MILJENKO PERIĆ[1,2]

[1]*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, P. O. Box 47, PAK 105305, 11158 Belgrade, Serbia and* [2]*Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11158 Belgrade, Serbia*

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Abstract: A variational approach for *ab initio* handling of the Renner–Teller effect in six-atomic molecules with linear equilibrium geometry is elaborated. A very simple model Hamiltonian suitable for the description of small-amplitude bending vibrations in Π electronic states of arbitrary spin multiplicity was employed. The computer program developed within the framework of the present study was tested on the example of the $X^2\Pi_u$ state of C_6^-. The results are compared with those generated in corresponding perturbative calculations.

Keywords: Renner–Teller effect; *ab initio* calculations; variational approach; C_6^-.

INTRODUCTION

For a long time, the Renner–Teller (R–T) effect[1] was investigated only in triatomic molecules. The first theoretical study of this kind of vibronic coupling in Π electronic states of molecules with linear equilibrium geometry was performed by Petelin and Kiselev.[2] A simple model for *ab initio* handling of the R–T effect, accompanied by spin–orbit coupling in Π and Δ electronic species has been developed and tested on a number of examples.[3–13] In these studies, the vibronic Schrödinger equation was solved using both variational and perturbative approaches. Perturbative calculations of the vibronic spectra in five-[14] and six-atomic[15,16] molecules were also realized. A method for handling the R–T effect in molecules with an arbitrary number of nuclei was sketched and perturbative formulae for several particular coupling schemes were derived.[17] For an exhaustive literature survey of this topic, the reader is referred to the papers cited above.

In two recent studies,[13,18] it was explicitly shown that the vibronic coupling in molecules with more than three nuclei could be understood as a combination

* Corresponding author. E-mail: marko.mitic@ffh.bg.ac.rs
# Serbian Chemical Society member.
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of the classical R–T effect, arising as a consequence of the interaction between two components of an electronic state spatially degenerate at the linear geometry and split upon bending, and unavoidable (avoided) crossings of the corresponding potential surfaces at non-linear nuclear arrangements, similar to those in the classical Jahn–Teller effect.[19] In the second of these papers,[18] a variational method for calculating the vibronic spectrum in five-atomic molecules was elaborated and applied to calculate the low-energy vibronic spectrum in the $X^2\Pi_u$ state of C_5^-. In the present study, for the first time variational *ab initio* calculations of vibronic levels in a six-atomic molecule, namely in the $X^2\Pi_u$ state of C_6^-, were realized. This system was handled in a previous study using the perturbative formulae derived therein. One of the aims of the present study is to check the reliability of this second-order perturbative treatment and to cover the coupling cases for which the perturbative formulae are not available.

THE MODEL HAMILTONIAN

The model Hamiltonian used herein for *ab initio* handling of the Renner–Teller effect and spin–orbit coupling in Π electronic states of six-atomic molecules is subject to the following restrictions:[18] the equilibrium molecular geometry is linear; the harmonic approximation is applied; the coupling between the bending and stretching vibrational modes is neglected; the end-over-end rotations are not considered; the spin–orbit operator is assumed in the phenomenological form and the asymptotic (linear limit) electronic wave functions are used in matrix representation of the kinetic energy operator. Thus, the model Hamiltonian has the form:

$$\hat{H} = \hat{H}_e + \hat{T}_b + \hat{H}_{SO} \tag{1}$$

where $\hat{H}_e$ is the electronic Hamiltonian, $\hat{T}_b$ is the kinetic energy operator for bending motions of the nuclei, and $\hat{H}_{SO}$ is the electronic spin–orbit operator.

A six-atomic molecule with linear equilibrium geometry, whose nuclei have the masses m_1, m_2,…, m_6, is considered in general. The equilibrium distances between the nuclei are denoted by r_1, r_2,…, r_5. The z-axis was chosen to coincide with the molecular axis at the equilibrium nuclear arrangement (see Fig. 1 of Ref. 17). Infinitesimal bending vibrations were considered herein. To describe the four doubly degenerate bending modes, the Cartesian bending coordinates ρ_{1x}, ρ_{2x}, ρ_{3x}, ρ_{4x} and ρ_{1y}, ρ_{2y}, ρ_{3y}, ρ_{4y} were introduced.[15,16] In terms of the derivatives of these coordinates, the kinetic energy operator (in atomic units) for infinitesimal bending vibrations is represented by a sum of x- and y- contributions:

$$\hat{T}_b = \hat{T}_b(x) + \hat{T}_b(y) \tag{2}$$

where

$$\begin{aligned}\hat{T}(x) = -\frac{\hbar^2}{2}\Bigg\{&\sum_{i=1}^{4}\left(\frac{m_i+m_{i+1}}{m_i m_{i+1} r_i^2} + \frac{2}{m_{i+1} r_i r_{i+1}} + \frac{m_{i+1}+m_{i+2}}{m_{i+1} m_{i+2} r_{i+1}^2}\right)\frac{\partial^2}{\partial\rho_{ix}^2} - \\ &-2\sum_{i=1}^{3}\left(\frac{1}{m_{i+1} r_i r_{i+1}} + \frac{m_{i+1}+m_{i+2}}{m_{i+1} m_{i+2} r_{i+1}^2} + \frac{1}{m_{i+2} r_{i+1} r_{i+2}}\right)\frac{\partial^2}{\partial\rho_{ix}\partial\rho_{i+1,x}} + \\ &+\sum_{i=1}^{2}\frac{1}{m_{i+2} r_{i+1} r_{i+2}}\frac{\partial^2}{\partial\rho_{ix}\partial\rho_{i+2,x}}\Bigg\}\end{aligned} \tag{3}$$

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and with a completely analogous form for $\hat{T}_{\mathrm{b}}(y)$. For the handling of symmetric six-atomic molecule of the type ABCCBA, when $m_4 = m_3$, $m_5 = m_2$, $m_6 = m_1$, it is convenient to introduce the symmetrized Cartesian bending coordinates $\rho_{\mathrm{C}1x}$, $\rho_{\mathrm{C}2x}$, $\rho_{\mathrm{T}1x}$, $\rho_{\mathrm{T}2x}$ and $\rho_{\mathrm{C}1y}$, $\rho_{\mathrm{C}2y}$, $\rho_{\mathrm{T}1y}$, $\rho_{\mathrm{T}2y}$, defined as:

$$\begin{aligned} \rho_{\mathrm{C}1x} &= \frac{1}{\sqrt{2}}(\rho_{4x} + \rho_{1x}), \quad \rho_{\mathrm{C}2x} = \frac{1}{\sqrt{2}}(\rho_{3x} + \rho_{2x}), \\ \rho_{\mathrm{T}1x} &= \frac{1}{\sqrt{2}}(\rho_{4x} - \rho_{1x}), \quad \rho_{\mathrm{T}2x} = \frac{1}{\sqrt{2}}(\rho_{3x} - \rho_{2x}) \end{aligned} \tag{4}$$

and analogously for the *y*-coordinates. The new coordinates describe two collective *cis*- and two *trans*-bending vibrations in the planes *xz* and *yz*. A straightforward transformation of expression (3), as well as of its *y*-counterpart, results in:

$$\begin{aligned} \hat{T}_{\mathrm{b}} = \hat{T}_{\mathrm{C}} + \hat{T}_{\mathrm{T}} = &-\frac{1}{2\mu_{\mathrm{C}1}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{C}1x}^2} + \frac{\partial^2}{\partial\rho_{\mathrm{C}1y}^2}\right) - \frac{1}{2\mu_{\mathrm{C}2}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{C}2x}^2} + \frac{\partial^2}{\partial\rho_{\mathrm{C}2y}^2}\right) + \\ &+\frac{1}{2\mu_{\mathrm{C}12}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{C}1x}\rho_{\mathrm{C}2x}} + \frac{\partial^2}{\partial\rho_{\mathrm{C}1y}\rho_{\mathrm{C}2y}}\right) - \frac{1}{2\mu_{\mathrm{T}1}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{T}1x}^2} + \frac{\partial^2}{\partial\rho_{\mathrm{T}1y}^2}\right) - \\ &-\frac{1}{2\mu_{\mathrm{T}2}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{T}2x}^2} + \frac{\partial^2}{\partial\rho_{\mathrm{T}2y}^2}\right) + \frac{1}{2\mu_{\mathrm{T}12}}\left(\frac{\partial^2}{\partial\rho_{\mathrm{T}1x}\rho_{\mathrm{T}2x}} + \frac{\partial^2}{\partial\rho_{\mathrm{T}1y}\rho_{\mathrm{T}2y}}\right) \end{aligned} \tag{5}$$

where

$$\begin{aligned} &\mu_{\mathrm{C}1} = \frac{m_1 m_2 m_3 r_1^2 r_2^2}{m_1 m_2 r_1^2 + m_1 m_3 (r_1 + r_2)^2 + m_2 m_3 r_2^2}, \quad \mu_{\mathrm{C}2} = \frac{m_2 m_3 r_2^2}{m_2 + m_3}, \\ &\mu_{\mathrm{C}12} = \frac{m_2 m_3 r_1 r_2^2}{m_2 r_1 + m_3 (r_1 + r_2)}, \quad \mu_{\mathrm{T}1} = \frac{m_1 m_2 m_3 r_1^2 r_2^2}{m_1 m_2 r_1^2 + m_1 m_3 (r_1 + r_2)^2 + m_2 m_3 r_2^2}, \\ &\mu_{\mathrm{T}2} = \frac{m_2 m_3 r_2^2 r_3^2}{4\left[m_2 (r_2 + r_3/2)^2 + m_3 (r_3/2)^2\right]}, \quad \mu_{\mathrm{T}12} = \frac{m_2 m_3 r_1 r_2^2 r_3}{2 m_2 r_1 (r_2 + r_3/2) + m_3 r_3 (r_1 + r_2)} \end{aligned} \tag{6}$$

The kinetic energy operator is equivalent to that derived in Ref. 15; the only difference is that now the factors $1/\sqrt{2}$ were used in Eqs. (4) instead of $1/2$, having been employed before.

When the coupling of the two components of the Π electronic state is neglected, the potential energy part of the bending Hamiltonian in the harmonic approximation has the form:

$$\begin{aligned} V = V_{\mathrm{C}} + V_{\mathrm{T}} = &\frac{1}{2}k_{\mathrm{C}1}\left(\rho_{\mathrm{C}1x}^2 + \rho_{\mathrm{C}1y}^2\right) + \frac{1}{2}k_{\mathrm{C}2}\left(\rho_{\mathrm{C}2x}^2 + \rho_{\mathrm{C}2y}^2\right) + \\ &+k_{\mathrm{C}12}\left(\rho_{\mathrm{C}1x}\rho_{\mathrm{C}2x} + \rho_{\mathrm{C}1y}\rho_{\mathrm{C}2y}\right) + \frac{1}{2}k_{\mathrm{T}1}\left(\rho_{\mathrm{T}1x}^2 + \rho_{\mathrm{T}1y}^2\right) + \\ &+\frac{1}{2}k_{\mathrm{T}2}\left(\rho_{\mathrm{T}2x}^2 + \rho_{\mathrm{T}2y}^2\right) + k_{\mathrm{T}12}\left(\rho_{\mathrm{CT}x}\rho_{\mathrm{T}2x} + \rho_{\mathrm{T}1y}\rho_{\mathrm{T}2y}\right) \end{aligned} \tag{7}$$

Note that also the potential energy operator is separated (besides into a *cis*- and a *trans*--part) into *x*- and *y*-contributions.

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In the next step, the bending normal coordinates are introduced in a way presented in the literature,[15] and finally, the kinetic and potential energy are expressed in terms of the polar components (q_i, ϕ_i) of the dimensionless normal coordinates. In this way, relations (5) and (7) are transformed into:

$$\hat{T}_{\mathrm{b}} = -\frac{1}{2}\sum_{i=1}^{4}\left(\frac{\partial^2}{\partial q_i^2} + \frac{1}{q_i}\frac{\partial}{\partial q_i} + \frac{1}{q_i^2}\frac{\partial^2}{\partial \phi_i^2}\right)\omega_i \tag{8}$$

where ω_i are the bending vibrational frequencies.

The potential energy part of the Hamiltonian becomes:

$$V = \frac{1}{2}\sum_{i=1}^{4}\omega_i q_i^2 \tag{9}$$

The spin–orbit (S–O) operator in the phenomenological form is:

$$\hat{H}_{\mathrm{SO}} = A_{\mathrm{SO}}\hat{L}_z\hat{S}_z \tag{10}$$

where A_{SO} is the spin–orbit constant, and $\hat{L}_z$ and $\hat{S}_z$ are the components of the electronic orbital and spin angular momentum along the molecular axis.

The model Hamiltonian (1) is represented in the two-dimensional electronic space spanned by the "diabatic" electronic eigenfunctions ψ^{Λ} and $\psi^{-\Lambda}$ defined as:

$$\psi^{\Lambda} = \frac{1}{\sqrt{2}}e^{i\tau}\left(\psi' + i\psi''\right), \quad \psi^{-\Lambda} = \frac{1}{\sqrt{2}}e^{-i\tau}\left(\psi' - i\psi''\right) \tag{11}$$

where ψ' and ψ'' are the eigenfunctions of the electronic operator $\hat{H}_{\mathrm{e}}$ obtained within the framework of the Born–Oppenheimer approximation ("adiabatic" electronic functions) for the two components of the Π state, and τ is an angle defined as:[4]

$$\tau = \frac{1}{2}\arctan\left\{\frac{\sum_{i=1}^{4}\sum_{j=1}^{4}\varepsilon_{ij}\sqrt{\omega_i\omega_j}\,q_i q_j \sin\left(\phi_i + \phi_j\right)}{\sum_{i=1}^{4}\sum_{j=1}^{4}\varepsilon_{ij}\sqrt{\omega_i\omega_j}\,q_i q_j \cos\left(\phi_i + \phi_j\right)}\right\} \tag{12}$$

with the quantities ε_{ij} determined by the energy difference of the adiabatic potentials at planar geometries. The sense of τ is that it defines the plane with the property that one of the adiabatic electronic wave functions (ψ') is invariant when reflected on it, and the other (ψ'') changes its sign upon the reflection. On this basis, the electronic operator has the matrix elements:

$$\left\langle \psi^{\Lambda}\middle|\hat{H}_e\middle|\psi^{\Lambda}\right\rangle = \frac{V' + V''}{2} = \left\langle \psi^{-\Lambda}\middle|\hat{H}_e\middle|\psi^{-\Lambda}\right\rangle \tag{13}$$

$$\left\langle \psi^{\Lambda}\middle|\hat{H}_e\middle|\psi^{-\Lambda}\right\rangle = \frac{V' - V''}{2}e^{-2i\tau}, \quad \left\langle \psi^{-\Lambda}\middle|\hat{H}_e\middle|\psi^{\Lambda}\right\rangle = \frac{V' - V''}{2}e^{2i\tau} \tag{14}$$

where V' and V'' are the eigenvalues of the electronic Hamiltonian corresponding to the adiabatic wave functions ψ' and ψ'', respectively. The off-diagonal matrix elements (14) are responsible for the vibronic coupling of the components of the Π electronic state.

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The matrix of the nuclear kinetic energy operator can be computed by using the asymptotic forms (corresponding to the linear molecular geometry) of the basis functions (11) and then it is diagonal.[4] The matrix elements of the S–O operator (10) are

$$\left\langle \psi_1 \middle| \hat{H}_{\mathrm{SO}} \middle| \psi_1 \right\rangle = A_{\mathrm{SO}} \Lambda \Sigma, \quad \left\langle \psi_2 \middle| \hat{H}_{\mathrm{SO}} \middle| \psi_2 \right\rangle = -A_{\mathrm{SO}} \Lambda \Sigma, \\ \left\langle \psi_1 \middle| \hat{H}_{\mathrm{SO}} \middle| \psi_2 \right\rangle = 0 = \left\langle \psi_2 \middle| \hat{H}_{\mathrm{SO}} \middle| \psi_1 \right\rangle \tag{15}$$

where Λ (= 1 in the present case of a Π electronic state) and Σ (= ±½ for doublet states) are the eigenvalues of the z-components of the spatial and spin electronic angular momentum, respectively.

The electronic matrix elements act as operators onto vibrational basis functions. As complete basis functions for the matrix representation of the Hamiltonian (1) were used:

$$\left| v_1 l_1, v_2 l_2, v_3 l_3, \pm\Lambda, \Sigma \right\rangle \equiv \psi^{\pm\Lambda} \prod_{i=1}^{4} \frac{1}{\sqrt{2\pi}} e^{i l_i \phi_i} R_{v_i l_i}(q_i) \tag{16}$$

where l_i is the eigenvalue of the vibrational angular momentum $\hat{R}_{iz} = -i\partial / \partial\phi_i$, and $R_{v_i l_i}(q_i)$ is the solution of the radial equation for the ith two-dimensional harmonic oscillator.

For the quantum numbers l_i, taking for a given bending quantum number v_i, the values $-v_i$, $-v_i + 2$, …, v_i are subject to the constraint:

$$\sum_{i=1}^{S-2} l_i \pm \Lambda = K \tag{17}$$

where K is the eigenvalue of the z-component if the total angular momentum excludes spin, $\hat{N}_z$. The quantum number $P = K + \Sigma$, being the eigenvalue of the z-component of the total angular momentum, $\hat{J}_z$, was also defined. The Hamiltonian (1) commutes with both $\hat{N}_z$ and $\hat{J}_z$, and thus K and P are good quantum numbers within the framework of the resent model. For this reason, the vibronic levels and wave functions can be calculated for each K and P (or Σ) separately. For more details, the reader is referred, *e.g.*, to a recent study.[18]

RESULTS AND DISCUSSION

In calculations of the low-energy part of the vibronic spectrum in the $X^2\Pi_u$ state of C_6^-, the set of parameters obtained by *ab initio* calculations in a previous study[15] were used (Table I). These computations were realized by means of the Gaussian program package[20] at the UB3LYP/aug-cc-pVTZ level of theory.[21] It was found that the equilibrium geometry of the molecule (as well as of the neutral C_6 and the positive ion C_6^+) is linear.[16] For the equilibrium bond lengths, the values C_1–C_2 = C_5–C_6 = 1.267 Å, C_2–C_3 = C_4 –C_5 = 1.323 Å, and C_2–C_3 = = 1.248 Å were obtained. The harmonic vibrational frequencies (expressed in wave numbers) for the two *cis*-bending modes were found to be 430.92 and 117.94 cm^{-1}, whereas their *trans*-counterparts are 543.50 and 259.29 cm^{-1}. The parameters entering in the proposed model Hamiltonian were extracted from adiabatic potential energy values for both components of the $X^2\Pi_u$ electronic state, calculated at 13 planar geometries. For both pure C_1 and C_2 *cis*-bending vibrations at planar nuclear arrangement the B_1 (A" in terms of the C*s* point

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group irreducible representations), potential curve lies above its A_1 (A') counterpart and thus, according to the convention assumed,[11] the splitting parameters ε_{C1} and ε_{C2} are negative. The third *cis*-splitting parameter, ε_{C12}, was found to be negative, too. At one of the *trans*-bending modes, the A_2 (A'' in the C_S nomenclature), potential curve is above the B_2 (A') one, and at the other the ordering is reversed. Note that the ε values presented in Eq. 71 of Ref. 15 are dimensionless – to obtain the input parameters for the present program, they were multiplied by the corresponding quadratic force constants and additionally by 1/2, due to the new definition of the symmetrized bending coordinates. The spin–orbit constant was computed using the MOLPRO 2006.1 program package[22] at the MRCI level of sophistication. At the equilibrium molecular geometry, the value of 25.16 cm^{-1} was obtained.

TABLE I. Low-lying part of the vibronic spectrum in the $X^2\Pi_u$ state of C_6^-. $E^{(0)}$: bending vibrational levels when the R–T and S–O coupling are neglected. Pert: results of second-order perturbative calculations. Var.: results of variational calculations. In parentheses are given discrepancies between variational and perturbative results

$v_{T1},v_{T2},v_{C1},v_{C2}$	K	$E^{(0)}$	Pert.		Var.	
			$\Sigma=-1/2$	$\Sigma=1/2$	$\Sigma=-1/2$	$\Sigma=1/2$
0,0,0,0	1*u*	1352	1334	1359	1334 (0)	1359 (0)
1,0,0,0	2*u*	1895	1873	1898	1873 (0)	1898 (0)
	0*u*		1837	1837	1839 (+2)	1839 (+2)
			1955	1955	1954 (–1)	1954 (–1)
0,1,0,0	2*u*	1611	1591	1617	1592 (+1)	1616 (–1)
	0*u*		1584	1584	1585 (+1)	1585 (+1)
			1617	1617	1616 (–1)	1616 (–1)
0,0,1,0	2*g*	1783	1763	1789	1764 (+1)	1788 (–1)
	0*g*		1737	1737	1737 (0)	1737 (0)
			1819	1819	1819 (0)	1819 (0)
0,0,0,1	2*g*	1470	1452	1477	1452 (0)	1477 (0)
	0*g*		1452	1452	1452 (0)	1452 (0)
			1478	1478	1478 (0)	1478 (0)
2,0,0,0	3*u*	2439	2410	2435	2410 (0)	2434 (–1)
	1*u*		2357	2359	2360 (+3)	2362 (+3)
			2524	2522	2522 (–2)	2520 (–2)
0,2,0,0	3*u*	1870	1848	1874	1849 (+1)	1873 (–1)
	1*u*		1837	1835	1839 (+2)	1837 (+2)
			1875	1877	1872 (–3)	1875 (–2)
0,0,2,0	3*u*	2213	2192	2217	2192 (0)	2216 (–1)
	1*u*		2152	2152	2152 (0)	2153 (+1)
			2265	2265	2266 (+1)	2264 (–1)
0,0,0,2	3*u*	1588	1570	1595	1570 (0)	1595 (0)
	1*u*		1569	1569	1569 (0)	1569 (0)
			1596	1596	1596 (0)	1596 (0)
1,1,0,0	3*u*	2154	2128	2153	2128 (0)	2152 (–1)
	1*u*		2095	2094	2098 (+3)	2097 (+3)

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TABLE I. Continued

$v_{T1},v_{T2},v_{C1},v_{C2}$	K	$E^{(0)}$	Pert.		Var.	
			$\Sigma=-1/2$	$\Sigma=1/2$	$\Sigma=-1/2$	$\Sigma=1/2$
1,1,0,0			2122	2147	2123 (+1)	2144 (–3)
			2214	2216	2211 (–3)	2213 (–3)
1,0,1,0	3*g*	2326	2302	2327	2302 (0)	2327 (0)
	1*g*		2254	2254	2255 (+1)	2256 (0)
			2307	2332	2307 (0)	2331 (–1)
			2396	2395	2395 (–1)	2394 (–1)
1,0,0,1	3*g*	2013	1991	2016	1991 (0)	2015 (–1)
	1*g*		1955	1955	1956 (+1)	1956 (+1)
			1991	2016	1991 (0)	2015 (–1)
			2073	2073	2072 (–1)	2072 (–1)
0,1,1,0	3*g*	2042	2020	2046	2021 (+1)	2045 (–1)
	1*g*		1991	1990	1992 (+1)	1991 (+1)
			2017	2043	2018 (+1)	2042 (–1)
			2075	2076	2074 (–1)	2075 (–1)
0,1,0,1	3*g*	1729	1709	1734	1709 (0)	1734 (0)
	1*g*		1702	1701	1703 (+1)	1702 (+1)
			1709	1734	1709 (0)	1732 (–2)
			1736	1736	1734 (–2)	1735 (–1)
0,0,1,1	3*u*	1901	1881	1906	1881 (0)	1906 (0)
	1*u*		1855	1855	1855 (0)	1855 (0)
			1881	1906	1881 (0)	1906 (0)
			1937	1937	1937 (0)	1937 (0)
1,1,1,0	4*g*	2585	2557	2582	2557 (0)	2581 (–1)
	2*g*		2514	2514	2514 (0)	2514 (0)
			2550	2575	2551 (+1)	2574 (–1)
			2564	2589	2565 (+1)	2589 (0)
			2657	2657	2650 (+7)	2651 (–6)
	0*g*				2510	2510
					2519	2519
					2555	2555
					2584	2584
					2648	2648
					2652	2652
1,1,0,1	4*g*	2272	2246	2271	2246 (0)	2270 (–1)
	2*g*		2213	2211	2216 (+3)	2215 (+4)
			2239	2265	2240 (+1)	2263 (–2)
			2246	2271	2246 (0)	2270 (–1)
			2332	2333	2329 (–3)	2330 (–3)
	0*g*				2214	2214
					2216	2216
					2240	2240
					2263	2263
					2328	2328
					2330	2330
1,0,1,1	4*u*	2444	2420	2445	2420 (0)	2444 (–1)

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TABLE I. Continued

$v_{T1},v_{T2},v_{C1},v_{C2}$	K	$E^{(0)}$	Pert.		Var.	
			$\Sigma=-1/2$	$\Sigma=1/2$	$\Sigma=-1/2$	$\Sigma=1/2$
1,0,1,1	2*u*		2373	2373	2373 (0)	2374 (–1)
			2419	2445	2420 (+1)	2444 (–1)
			2425	2450	2425 (0)	2449 (–1)
			2515	2514	2513 (–2)	2512 (–2)
	0*u*				2371	2371
					2376	2376
					2424	2424
					2450	2450
					2510	2510
					2514	2514
0,1,1,1	4*u*	2160	2138	2163	2138 (0)	2163 (0)
	2*u*		2117	2117	2110 (–7)	2109 (–8)
			2135	2160	2136 (+1)	2159 (–1)
			2138	2163	2138 (0)	2163 (0)
			2202	2203	2192 (–10)	2193 (–10)
	0*u*				2108	2108
					2110	2110
					2135	2135
					2159	2159
					2191	2191
					2193	2193
1,1,1,1	5*u*	2703	2675	2700	2675 (0)	2699 (–1)
	3*u*		2629	2629	2631 (+2)	2632 (+3)
			2668	2693	2669 (+1)	2691 (–2)
			2675	2700	2675 (0)	2699 (–1)
			2682	2707	2683 (+1)	2706 (–1)
			2772	2772	2768 (–4)	2769 (–3)
	1*u*				2627	2627
					2632	2632
					2637	2637
					2669	2673
					2673	2691
					2683	2701
					2702	2707
					2765	2766
					2769	2768
					2770	2771

The program for the variational treatment of the R–T effect in six-atomic molecules is written in the Python programming language using the Numpy package. The basis for the variational calculations consisted of the functions (16) with $v_{C1} = v_{C2} = v_{T1} = v_{T2} \leq 8$ and $l_{C1} = l_{C2} = l_{T1} = l_{T2} \leq 8$. The dimensions of the constructed vibronic Hamiltonian matrices (for quantum number K= 0–5) were ≈ 400000×400000. Diagonalization of a matrix of these dimensions takes about

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1.5 h on the available machine with an Intel Xeon processor E5-1620 v3 (10M Cache, 3.50 GHz, 4 cores) when NumPy is linked against Intel MKL.

The levels obtained when both the vibronic- and spin–coupling were neglected are given in column $E^{(0)}$ of Table I. The vibronic levels are labeled by the subscript *g* or *u*. The electronic state is of *u*-symmetry, the *trans*-bending vibrational states are all *gerade*, and the *cis*-bending vibrational species corresponding to odd vibrational quantum numbers are *ungerade*, whereas those for even vibrational quantum numbers are *gerade*. Thus, a vibronic level is of *g*-symmetry when the sum of the quantum numbers v_{C1} and v_{C2} is odd, and of *u*-symmetry if this sum is even.

In Table I are presented all vibronic levels with the sum of the vibrational quantum number (v_{C1}, v_{C2}, v_{T1}, v_{T2}) ≤ 3, and additionally the vibronic levels for $v_{C1} = v_{C2} = v_{T1} = v_{T2} = 1$. Many of them could be calculated by means of the derived second-order perturbative formulae,[15] but the number of levels that are not covered by these formulae (blue colored levels in Table I), strongly increases with increasing vibrational quantum numbers. As predicted in a previous study,[15] the discrepancy between the results of the variational and perturbative calculations is in the low-energy part of the vibronic spectrum, not larger than 10 cm^{-1}. For a more detailed analysis, see the previous study.[15]

CONCLUSIONS

Within the framework of this study, a variational *ab initio* approach for handling the vibronic and spin–orbit structure in Π electronic states of six-atomic molecules with linear equilibrium geometry was developed. The numerical results for the $X^2\Pi_u$ state of C_6^- are in good agreement with those obtained within the framework of the second-order perturbation theory. However, while the perturbative approach covers only the cases with particular combinations of vibrational quantum numbers, the present variational method ensures calculation of all vibronic species. The model Hamiltonian employed in this study is extremely simple, but it involves all the most important effects, when one is restricted to the lowest-energy part of vibronic spectra. Handling of the R–T effect in molecules with more than three nuclei would hardly be possible at a higher level of sophistication. However, it is frequently the case that the vibronic spectrum of a molecule with larger number of nuclei reflects the excitation of only one or two of the bending modes. In such a situation, the vibronic problem is effectively reduced to that of a triatomic or tetraatomic species.

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ИЗВОД

ВАРИЈАЦИОНО РАЧУНАЊЕ ВИБРОНСКОГ СПЕКТРА У $X\,^2\Pi_u$ ЕЛЕКТРОНСКОМ СТАЊУ C_6^-

МАРКО МИТИЋ[1], МИЛАН МИЛОВАНОВИЋ[1], РАДОМИР РАНКОВИЋ[1], СТАНКА ЈЕРОСИМИЋ[1] и МИЉЕНКО ПЕРИЋ[1,2]

[1]*Факултет за физичку хемију Универзитета у Београду и* [2]*Српска академија наука и уметности*

Разрађен је варијациони поступак за *ab initio* третирање Ренер–Телеровог ефекта у шестоатомским молекулима с линеарном равнотежном геометријом. Коришћен је веома једноставан моделни хамилтонијан, погодан за описивање савијајућих вибрација малих амплитуда у П електронским стањима с произвољном спинском мултиплетношћу. Рачунарски програм разрађен у оквиру овог рада тестиран је на примеру $X\,^2\Pi_u$ стања молекула C_6^-. Резултати су упоређени са онима који се добијају у одговарајућим пертурбационим рачунањима.

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