Study of the vibronic coupling in the first excited state of MgCH$_3$ radical

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Abstract

A methodology based on the crude adiabatic approximation is used to study the complete linear and quadratic vibronic coupling in the first excited state of MgCH$_3$ radical. Firstly we evaluate 30 integrals intervening in the formulation of the vibronic coupling and which are used to build the representation of the hamiltonian. Secondly, we diagonalize this representation to evaluate the vibronic levels. For the lowest excited vibronic states, the implied modes are $Q_1$ (symmetric C-Mg stretching) and $Q_4$ (CH$_3$ rocking). Energy gaps $A_1-A_2$ and $A_2-\epsilon$ resulting of the splitting due to the Jahn-Teller coupling $E \otimes \epsilon = A_1 + A_2 + \epsilon$ are evaluated to 126 and 208 cm$^{-1}$, respectively. Finally we surround essential coupling parameters to simplify the study of highly excited vibronic states. In these states, the involved modes are $Q_5$ (antisymmetric C-H stretching) and $Q_6$ (antisymmetric C-H bending). The energy gaps are evaluated to 22 cm$^{-1}$ ($A_2-A_1$) and 34 cm$^{-1}$ ($A_2-\epsilon$) for $Q_5$ mode, 9 cm$^{-1}$ ($A_1-A_2$) and 16 cm$^{-1}$ ($A_2-\epsilon$) for $Q_6$ mode.

Keywords: Vibronic coupling; Emission spectrum; First excited state; Methyl-magnesium radical; Crude adiabatic

1. Introduction

Considering their physical, chemical and spectroscopic properties, the organometallic radicals play an important role in several areas. They intervene as initiation or propagation agents (polymerization, biological phenomena, organic and organometallic syntheses) and in the analysis and the identification of species containing metallic elements as witness molecules (in astrophysics). However, considering their electronic structures, these radicals are liable, in their first excited states, to two types of phenomena which in some cases are competitive: it concerns the spin-orbit coupling and the vibronic coupling.

In a previous paper [1], we have performed a structural and vibrational study of the methyl-magnesium radical in its ground state (3s orbital of magnesium) and first excited state (p valence orbital: 40%; Rhydberg orbital: 60%). We have concluded that geometrical deformations by the Jahn-Teller effect are very weak, in agreement with the strong Rhydberg character of the p orbital and with the non-bonding character of the electron occupying this orbital. The raising of the two potential energy surfaces degeneracy near the Jahn-Teller point can induce a non-negligible dynamic Jahn-Teller (vibronic coupling) whose evaluation by
means of the vibronic states calculation necessitates a theoretical processing beyond the Born-Oppenheimer approximation. A numerical tractable model, which permits taking into account all the nuclear vibrations up to second-order terms in the nuclear displacements, uses as the electronic basis set the adiabatic wave functions for a reference nuclear configuration. That is the well-known crude adiabatic approximation [2,3].

In the framework of this approximation, Marinelli and Roch [4] have formally treated the $T_2 \otimes (a_1 + e + 2t_2)$ coupling problem with all linear and quadratic parameters in the case of Jahn-Teller instability for $XY_4$ molecules with $T_d$ configuration. Numerical applications have been done for $NH_4$ in a type p Rhydberg $^2T_2$ excited state[5] and for $CH_4^+$ in the $^2T_2$ state[6] formed by the removal of $1t_2$ electron from the methane ground state. In the first case theoretical results confirm the assignment by Herzberg of the emission spectrum of the ammonium radical. In the second case theoretical results lead to a calculated photoelectron spectrum of $CH_4$ in agreement with the experimental one.

In a previous work, A. P. Salzberg et al. [7] have recorded the laser excitation and dispersed fluorescence spectra of the $\tilde{A}^2E \rightarrow \tilde{X}^2A_1$ transition of the jet-cooled $\text{MgCH}_3$ radical. Analysis of spectrum yield the rotational constants and values of the Coriolis and the spin-orbit coupling constant for the radical’s $\tilde{A}^2E$ state. Stakhursky, Vadim, et al. [8] have done simulations of vibronic levels in degenerate electronic states in the presence of Jahn-Teller coupling. They have used the C++/Fortran hybrid to simulate vibronic spectra of Jahn-Teller distorted molecules in the presence of spin-orbit coupling. The multimode calculations include the interaction of up to 3 degenerate vibrational modes and up to 3 symmetric modes. This new computational package was used in a study of PES parameters of the methoxy ($CH_3O$) radical [9].

In a recent study, H. Kayi et al. [10] have investigated in detail, the electronic structure and vibronic coupling in radical $C_3H_3$ and anion $C_3H^-_3$ in ground and excited states, to show how their equilibrium structures, in deviation from the Born–Oppenheimer approximation, originate from the vibronic mixing of at least two electronic states, producing the Jahn–Teller (JT), pseudo JT (PJT), and hidden PJT effects.

In this paper, using a methodology [11] based on the crude adiabatic approximation we study the vibronic coupling in the first excited state of $MgCH_3$ radical. Thus, to build the representation of the Hamiltonian, we evaluate the electronic parameters intervening in the formulation of the vibronic coupling, and we calculate the vibronic states by diagonalization of this representation.

2. Computational details

2.1. Construction of the Hamiltonian representation

The vibronic stationary states may be obtained by solving the Schrödinger equation

$$H \varphi_i(q, Q) = \varepsilon_i \varphi_i(q, Q) \quad \text{with} \quad H = T(Q) + H_e(q, Q)$$

where $q$ and $Q$ are respectively the electronic and the nuclear coordinates for the vibrational motions. $T(Q)$ is the kinetic energy operator for the nuclear and $H_e(q, Q)$ is the electronic Hamiltonian, which includes the Kinetic energy operator for the electrons and all the columatic interactions. The vibronic wave functions $\varphi_i(q, Q)$ may, in principle, be expanded in any complete vibronic basis set. In practice, this basis is severely truncated by keeping only a few electronic wave functions corresponding to the states that are degenerate (Jahn-Teller case) or quasi-degenerate (pseudo-Jahn-Teller case) at some $Q=Q_0$.

Currently $H_e(q, Q)$ is expanded to second-order near the reference nuclear configuration $Q_0$.

$$H_e(q, Q) = H_e(q, Q_0) + \sum_{k=1}^{3N-6} \alpha_k^{\text{e}}(q)Q_k + \frac{1}{2} \sum_{k,l=1}^{3N-6} \beta_k^{\text{e}}(q)Q_k Q_l$$
The chosen model to process the vibronic coupling implies, therefore, two preliminary choices: The geometry of reference and coordinates of displacement which will allow tending the space around the reference point.

- **Choice of the reference structure**

We can a priori choose any structure of the potential surface. But the choice, which seems the most logical considering the necessity to curtail the basis of electronic functions of manner to reduce the dimension of the problem, consists of choosing the Jahn-Teller point ($C_{3v}$ structure of the first excited state [1]) where cross the two potential surfaces $A'$ and $A^"$. The excitation allowing to describe this structure is built with ground state SCF molecular orbitals. This reference is shown as the one which assures the continuity of the potential energy surface near the Jahn-Teller point.

- **Choice of displacement coordinates.**

We have determined the displacement coordinates as follows:

At the $C_{3v}$ Jahn-Teller instability point (reference point) to which corresponds a certain matrix $G$ in the Wilson’s method [12], we associate a matrix $F$ respecting the $C_{3v}$ group properties of symmetry. In this work, this matrix $F$ has been built by regrouping on the one hand, the matrix of force constants linked to the block of $a_1$ symmetry calculated for the first excited state (since the instability concerns only $e$ symmetry modes) and on the other hand that of the $e$ symmetry block of the $C_{3v}$ symmetry ground state. The diagonalization of the matrix ($GF$) defines a system of normal coordinates: $Q_1, Q_2, Q_3$ ($a_1$ symmetry) and ($Q_{4x}, Q_{4y}$), ($Q_{5x}, Q_{5y}$), ($Q_{6x}, Q_{6y}$) ($e$ symmetry). The normal coordinates, thus described, define a reference potential $V_0$ supposed harmonic, centered on Jahn-Teller point:

$$V_0 = \frac{1}{2} k_1 Q_1^2 + \frac{1}{2} k_2 Q_2^2 + \frac{1}{2} k_3 Q_3^2 + \frac{1}{2} k_4 (Q_{4x}^2 + Q_{4y}^2) + \frac{1}{2} k_5 (Q_{5x}^2 + Q_{5y}^2) + \frac{1}{2} k_6 (Q_{6x}^2 + Q_{6y}^2)$$

where $k_i$ (a.u.) = 4,56. $10^{-6} v_i$ (cm$^-1$)

In Table 1, we have summarized the vibration frequencies [1] associated with different modes, together with the corresponding constants intervening in the definition of the reference potential $V_0$.

In the crude adiabatic approximation, the matrix elements of $H$ can be expressed as follows:

$$H_{nm,ij} = \langle X_j(Q)|\delta_{mn}E_n(Q_0) + \Delta U_{nm}(Q)|X_i(Q)\rangle_Q$$

limiting the electronic functions basis to degenerate functions $\Psi^0_x$ and $\Psi^0_y$ at the reference point.

The vibrational $X_j(Q)$ are taken as the Eigenfunctions of an arbitrary $C_{3v}$ harmonic Hamiltonian $T(Q)+V_0$.

### Table 1. Definition of harmonic reference potential $V_0$

<table>
<thead>
<tr>
<th>$Q_i$</th>
<th>$Q_1$</th>
<th>$Q_2$</th>
<th>$Q_3$</th>
<th>$Q_{4x}, Q_{4y}$</th>
<th>$Q_{5x}, Q_{5y}$</th>
<th>$Q_{6x}, Q_{6y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_i$ (cm$^{-1}$)</td>
<td>499</td>
<td>1065</td>
<td>3161</td>
<td>539</td>
<td>1539</td>
<td>3196</td>
</tr>
<tr>
<td>$k_i$ (a.u.)</td>
<td>0,2275.10$^{-2}$</td>
<td>0,4856.10$^{-2}$</td>
<td>0,1441.10$^{-2}$</td>
<td>0,2458.10$^{-2}$</td>
<td>0,7017.10$^{-2}$</td>
<td>0,1457.10$^{-2}$</td>
</tr>
</tbody>
</table>
The evaluation of matrix elements $H_{nm,ij}$ requires, therefore, only the elementary integrals $\langle X_i(Q)|Q_k|X_j(Q)\rangle$, $\langle X_i(Q)|Q_k|X_j(Q)\rangle$, $\langle X_i(Q)|Q_k|X_j(Q)\rangle$. For this we need the terms $\Delta U_{nm}(Q)$ which we rewrite:

$$\Delta U_{nm}(Q) = \Sigma_k \alpha_{nm}^k Q_k + \frac{1}{2} \Sigma_{kl} \beta_{kl}^{nm} Q_k Q_l$$

with $\alpha_{nm}^k = \langle \varphi^0_n(q, Q_0) | \xi_k(q) | \varphi^0_m(q, Q_0) \rangle$ (first-order parameters)

$$\beta_{kl}^{nm} = \langle \varphi^0_n(q, Q_0) | \varphi^0_m(q, Q_0) \rangle$$

(quadratic and bilinear parameters)

In the present case there are a priori 162 integrals to be evaluated.

The application of group theory and $C_{3v}$ symmetry of the reference configuration proves that there are only 30 integrals [10], distributed as follow:

- First-order parameters: $\beta_1, \beta_2$ and $\beta_3$ ($\beta_i = \alpha_{ij}^{xx} = -\alpha_{ij}^{yy} = \alpha_{ij}^{xy}$, $i=1,2,3, j=4,5,6$)

- Non-crossed second-order parameters: $k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_8, k_9, k_{10}, k_{11}$, and $k_{12}$

($k_i = \beta_{ij}^{xx} = \beta_{ij}^{yy}$, $i = j = 1, 2, 3$; $k_i = \beta_{ij}^{xx} = \beta_{ij}^{yy}$, $i = j = 4, 5, 6$).

- Crossed second-order parameters: $\gamma_{14}, \gamma_{15}, \gamma_{16}, \gamma_{24}, \gamma_{25}, \gamma_{26}, \gamma_{34}, \gamma_{35}, \gamma_{36}, \gamma_{45}, \gamma_{46}, \gamma_{56}, \gamma_{44}$, $\gamma_{55}$, $\gamma_{66}$

($\gamma_{ij} = \beta_{ij}^{xx} = -\beta_{ij}^{yy} = \beta_{ij}^{xy}$, $i = j = 4, 5, 6$).

These integrals may be considered as adjustable parameters so that the two model potential surfaces $E_1$ and $E_2$ which obey to the equation $\text{det} |\Delta U_{nm} - B_\delta_{mn}| = 0$ fit to the same potential surfaces derived from some quantum mechanical electronic energy calculations.

### 2.2. Evaluation of the integrals intervening in the formulation of vibronic coupling

The used procedure can be summarized in three points:

- Choice of a cup in the potential surface (activation of the mode). This choice is guided by the aimed parameters.

- Calculation, at MP2 level, of $A'$ and $A''$ states in a number of points of the direction in the potential surface defined by the activated modes. We built the excitation allowing to describe the two structures with SCF ground state M.O.

- Simultaneous adjustment, by a less square method, of $H_q(Q, Q_0)$ representation, on the two calculated surfaces.

**Table 2.** Values of parameters intervening in the formulation of vibronic coupling

<table>
<thead>
<tr>
<th>$K_1$ (10^3)</th>
<th>$K_2$ (10^3)</th>
<th>$K_3$ (10^3)</th>
<th>$K_4$ (10^3)</th>
<th>$K_5$ (10^3)</th>
<th>$K_6$ (10^3)</th>
<th>$K'_6$ (10^3)</th>
<th>$K''_6$ (10^3)</th>
<th>$K'_6$ (10^3)</th>
<th>$K''_6$ (10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2236</td>
<td>0.4889</td>
<td>0.1433</td>
<td>0.7016</td>
<td>0.1457</td>
<td>0.4149</td>
<td>0.4975</td>
<td>0.6917</td>
<td>0.6622</td>
<td>0.2458</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$K'_6$ (10^3)</th>
<th>$K''_6$ (10^3)</th>
<th>$\beta_1$ (10^3)</th>
<th>$\beta_2$ (10^3)</th>
<th>$\beta_3$ (10^3)</th>
<th>$\gamma_{24}(10^3)$</th>
<th>$\gamma_{25}(10^3)$</th>
<th>$\gamma_{26}(10^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1575</td>
<td>0.1560</td>
<td>0.7524</td>
<td>0.4753</td>
<td>0.4030</td>
<td>-0.7011</td>
<td>-0.3695</td>
<td>-0.3240</td>
</tr>
<tr>
<td>0.5623</td>
<td>0.5566</td>
<td>0.3721</td>
<td>0.5103</td>
<td>0.1986</td>
<td>0.2337</td>
<td>0.3365</td>
<td>-0.1343</td>
</tr>
</tbody>
</table>
Table 2 shows the values of the 30 parameters. We have carried the values resulting from an arithmetic mean when different determinations were possible and which are kept for the calculation of vibronic coupling. The obtained results show that:

- At the level of first-order parameters, the parameter $\beta_1$ is the most important.
- The gap $|k'_4 - k^*_4|$ is greater than gaps $|k'_\epsilon - k^*_\epsilon|$ and $|k'_\epsilon - k^*_\epsilon|$ at the level of non-crossed second-order terms.
- Probably, the crossed second-order parameters, $\gamma_{ij}$, will not have any effect on the vibronic coupling.

2.3. Calculation of vibronic coupling in MgCH$_3$ radical’s first excited state $^2E$ : Diagonalization of the Hamiltonian

Computer codes

A first code gives matrices containing the coefficients of symmetric vibronics $[\Gamma]$ and $[\Gamma]^+$ for an arbitrary choice of maximal vibrational quantum members $V_i (i=1,2,...,9)$ and for each irreducible representation of $C_{3v}$. A second code constructs the matrix $[H]$ and a third code gives the representation of the Hamiltonian in the adapted symmetry basis set $[HS] = [\Gamma]^+[H][\Gamma]$ for each irreducible representation.

Finally the three different blocks of $[HS]$ are diagonalized by the Davidson algorithm [13].

2.3.1. Limitation of the problem to $e$ symmetry normal modes

In a first time, we have activated only normal modes of $e$ symmetry ($Q_4$, $Q_5$ and $Q_6$), assets in Jhan-Teller effect [1], by exciting them equally ($V=V_4=V_5=V_6$). The vibrational excitation number of $a_1$ symmetry modes are posed equal to zero ($V_i=V_2=V_3=0$). Then, we have varied the vibrational quantum number $V$ from 1 to 5, therefore $NT$ from 3 to 15 where $NT = \Sigma_{i=1}^6 V_i$. The obtained results are recorded in Table 3 (for each symmetry we have carried the three lowest vibronic states).

<p>| Table 3. Study of the three first excited vibronics levels convergence |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|</p>
<table>
<thead>
<tr>
<th>NT</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibronics $A_1$</td>
<td>0.039308</td>
<td>0.039031</td>
<td>0.038900</td>
<td>0.038859</td>
<td>0.038854</td>
</tr>
<tr>
<td></td>
<td>0.043134</td>
<td>0.042923</td>
<td>0.042923</td>
<td>0.042828</td>
<td>0.042779</td>
</tr>
<tr>
<td></td>
<td>0.046854</td>
<td>0.043475</td>
<td>0.043127</td>
<td>0.042929</td>
<td>0.042925</td>
</tr>
<tr>
<td>Vibronics $A_2$</td>
<td>0.040112</td>
<td>0.039777</td>
<td>0.039493</td>
<td>0.039447</td>
<td>0.039428</td>
</tr>
<tr>
<td></td>
<td>0.042857</td>
<td>0.042643</td>
<td>0.042620</td>
<td>0.042602</td>
<td>0.042598</td>
</tr>
<tr>
<td></td>
<td>0.046817</td>
<td>0.043536</td>
<td>0.043223</td>
<td>0.042910</td>
<td>0.042856</td>
</tr>
<tr>
<td>Vibronics $\epsilon$</td>
<td>0.036057</td>
<td>0.035929</td>
<td>0.035914</td>
<td>0.035910</td>
<td>0.035909</td>
</tr>
<tr>
<td></td>
<td>0.040988</td>
<td>0.040736</td>
<td>0.040520</td>
<td>0.040487</td>
<td>0.040475</td>
</tr>
<tr>
<td></td>
<td>0.043015</td>
<td>0.042746</td>
<td>0.042366</td>
<td>0.042144</td>
<td>0.042085</td>
</tr>
</tbody>
</table>

From the analysis of this table, we can notice that whatever the value of considered $NT$, the hierarchy of vibronic levels is the same: firstly an $\epsilon$ symmetry state corresponding to Zero Point Energy (Z.P.E.) level,
then an $A_1$ symmetry state, then a state of symmetry $A_2$, finally an $\epsilon$ symmetry state. This result is in agreement with that of a previous work [7].

2.3.2. Taking into account of $a_1$ and $e$ modes: study of the interaction between these two types of modes

To better account for the effect of $a_1$ mode on the energies of states studied previously, we have activated simultaneously the $a_1$ and $e$ modes with: $V_1=V_2=V_3=2$ and $V_4=V_5=V_6=5$. Also in this case ($NT=21; Q_1^2, Q_2^2, Q_3^2, Q_4^2, Q_5^2, Q_6^2$), the convergence reached in the first levels is in the order of $10^{-6}$ a.u.

Figures 1, 2 and 3 gathering these results for the $A_1$, $A_2$, and $\epsilon$ vibronics, allow by simple comparison of the two application $NT=15$ and $NT=21$ to well visualize the interactions of $a_1$ and $e$ modes. On these figures, we have carried on the one hand the stabilization energies of $e$ levels, and on the other hand the gap, in relation to the first level, of two other levels which appear around 524 cm$^{-1}$ and 1045 cm$^{-1}$. We can observe that these two values are very close to vibration frequencies calculated [1] in the first excited state for $C-Mg$ stretching mode $Q_1$ (499 cm$^{-1}$) and symmetric $C-H$ bending $Q_2$ (1065 cm$^{-1}$), respectively.

**Figure 1.** Interaction of $a_1$-$e$ modes: $A_1$ symmetry vibronics.

**Figure 2.** Interaction of $a_1$-$e$ modes: $A_2$ symmetry vibronics.
Figure 3. Interaction of $a_1$-e modes : $\varepsilon$ symmetry vibronics.

On Figure 4, we have carried the relative position of the different vibronic levels of symmetry $A_1$, $A_2$, $\varepsilon$ calculated in the framework of the application $NT=21$. We have adopted for the vibronic levels the following notation: $n X(x)$, where : $n$: the number of state in each Irreducible representation (states are classified by ascendat order of the energy), $X$: the symmetry of the vibronic state and $x$: the symmetry of the implied vibration mode. A priori, we can note particularly that the first vibronic excited state $2\varepsilon(a_1)$ involves an $a_1$ symmetry mode, while the second $1A_1(e)$, the third $1A_2(e)$, and the fourth $3\varepsilon(e)$ excited vibronic states involve as for them an $e$ symmetry mode. To specify the nature of these implied modes, it is necessary to analyze the vibronic function of each state.

Figure 4. Relative position of the different vibronic states $A_1$, $A_2$ and $\varepsilon$ (calculated for $NT=21$ application)

2.3.3. Analysis of the vibronic function of the first four excited states
To simplify notations, we have reduced the writing of the vibrational functions, product of nine polynomial of Hermite, to only the active modes with in exponent the value of the vibrational quantum number associated with each mode and the symbol (*) to be able to differentiate, thereafter, the basis of the modes for the excited state from that of the ground state.

- Vibronic function of the first excited state $2\varepsilon(a_1)$
\[ \varphi_{2\varepsilon(a_2)} = -0.968(Q_{1x}^0 \psi_x^0) + 0.183 \left[ \frac{1}{\sqrt{2}} Q_{1x}^* Q_{2x}^0 \psi_x^0 + \frac{1}{\sqrt{2}} Q_{1x}^* Q_{3x}^0 \psi_x^0 \right] \]

This development carries essentially on the \( Q_1 \) mode with a weak contribution of \( Q_{4x} \) and \( Q_{4y} \) modes. Therefore the vibration movement implied in this state is that of \( C-Mg \) stretching.

- Vibronic functions of excited states \( 1A_1(e), 1A_2(e) \) and \( 3\varepsilon(e) \)
- State \( 1A_1(e) \)
  \[ \varphi_{1A_1(e)} = -0.952 \left[ \frac{1}{\sqrt{2}} Q_{4y}^0 \psi_y^0 + \frac{1}{\sqrt{2}} Q_{3x}^* \psi_x^0 \right] - 0.233 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* Q_{4x}^0 \psi_y^0 - \frac{1}{2} Q_{4x}^* \psi_y^0 \right] \]
- State \( 1A_2(e) \)
  \[ \varphi_{1A_2(e)} = -0.932 \left[ \frac{1}{\sqrt{2}} Q_{4y}^0 \psi_y^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \psi_x^0 \right] + 0.250 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* Q_{4x}^0 \psi_y^0 - \frac{1}{2} Q_{4x}^* \psi_y^0 \right] \]
- State \( 3\varepsilon(e) \)
  \[ \varphi_{3\varepsilon(e)} = -0.899 \left[ \frac{1}{\sqrt{2}} Q_{4y}^0 \psi_y^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \psi_x^0 \right] + 0.201 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* Q_{4x}^0 \psi_y^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \psi_y^0 \right] \]

The analysis of these three vibronic functions shows that the implied vibration modes in each of corresponding states are the same namely \( Q_{4x} \) and \( Q_{4y} \). Consequently, the active vibration movement is the methyl-rocking one.

We can therefore conclude that these three states result from the coupling of \( Q_{4x} \) and \( Q_{4y} \) modes (\( e \) modes) by means of electrons movement (electronic state \( E \)). Therefore a coupling of type:

\[ B \otimes e = A_1 + A_2 + \varepsilon \]

schematized in Figure 5.

\[ \Delta_2 - \Delta_1 = 539 \text{ cm}^{-1} \]

\[ \Delta_2^{(1)} - \Delta_1 = 638 \text{ cm}^{-1} \]

\[ \Delta_2^{(2)} - \Delta_1 = 764 \text{ cm}^{-1} \]

\[ \Delta_2^{(3)} - \Delta_1 = 972 \text{ cm}^{-1} \]

(a) Without coupling

(b) With coupling

Figure 5. Raising of \( Q_{4x} \) and \( Q_{4y} \) modes degeneracy by vibronic coupling.

In the case where the vibronic coupling is neglected (part a of Figure 5), we have represented transitions, towards the lowest vibrational level \( a_1 \) of the ground state, on the one hand from the lowest vibrational level \( a_1(A_1) \) of the first excited state and on the other hand from the vibrational level \( e (A_2) \) implying \( Q_{4x} \) and \( Q_{4y} \).
modes of this same state. The value of the frequency \(\nu_d\) associated with \(Q_{ds}\) and \(Q_{dy}\) modes, deduced experimentally by emission spectroscopy from the difference (\(A_2-A_1\)), is estimated in this work at 539 cm\(^{-1}\) [1]. The raising of degeneracy of these modes (\(Q_{ds}\) and \(Q_{dy}\)) by vibronic coupling (part b of Figure 5) leads respectively to three equivalents transitions of energies \(\Delta\varepsilon^{(1)}_2\), \(\Delta\varepsilon^{(2)}_2\) and \(\Delta\varepsilon^{(3)}_2\), from \(1A_1(e)\), \(1A_2(e)\) and \(3\varepsilon(e)\) levels implying these modes. We predict, therefore, in the emission spectrum three bands around 638, 764 and 972 cm\(^{-1}\). In summary, beside transitions from \(1A_1(e)\), we predict equivalent transitions from \(1A_2(e)\) and \(3\varepsilon(e)\) levels which will be distant of 126 cm\(^{-1}\) (764-638) and 208 cm\(^{-1}\) (972-764), respectively.

### 2.3.4. Put in evidence the essential coupling parameters

In the preceding paragraph, we have analyzed the vibronic functions for the lowest excited states \(1A_1(e)\), \(1A_2(e)\), \(2\varepsilon(a_1)\) and \(3\varepsilon(e)\). This analysis has shown that these states involve \(Q_i\), \(Q_{ds}\) and \(Q_{dy}\) modes. We can, therefore, hope to reduce the dimension of the vibrational basis and to take into account only these modes. For this, we consider the applications \(NT=2,4,6,8,10,12\) of \(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6\) type in which the \(Q_i\) and \(Q_d\) modes are activated of the same manner. The results of the Hamiltonian diagonalization relative to the application \(NT=14\), for which we have obtained a convergence of \(2.10^{-6}\) a.u., are summarized in Table 4.

#### Table 4. Reduction of the vibrational basis to \(Q_1\) and \(Q_4\) modes

<table>
<thead>
<tr>
<th>Symmetry of the considered state</th>
<th>Energies (a.u.)</th>
<th>(\Delta\varepsilon^{(14)}) (cm(^{-1}))</th>
<th>(\Delta\varepsilon^{(21)}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\varepsilon(a_1)) (Z.P.E. state)</td>
<td>0.035969</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>(2\varepsilon(a_1))</td>
<td>0.038371</td>
<td>(\Delta\varepsilon^{14}_{01} = 527)</td>
<td>(\Delta\varepsilon^{21}_{01} = 523)</td>
</tr>
<tr>
<td>(1A_1(e))</td>
<td>0.038901</td>
<td>(\Delta\varepsilon^{14}_{02} = 643)</td>
<td>(\Delta\varepsilon^{21}_{02} = 638)</td>
</tr>
<tr>
<td>(1A_2(e))</td>
<td>0.039468</td>
<td>(\Delta\varepsilon^{14}_{03} = 768)</td>
<td>(\Delta\varepsilon^{21}_{03} = 764)</td>
</tr>
<tr>
<td>(3\varepsilon(e))</td>
<td>0.040430</td>
<td>(\Delta\varepsilon^{14}_{04} = 979)</td>
<td>(\Delta\varepsilon^{21}_{04} = 972)</td>
</tr>
</tbody>
</table>

These results show that, by report to \(1\varepsilon(a_1)\) (Z.P.E.) level, the energy gaps \(\Delta\varepsilon^{14}_{01}, \Delta\varepsilon^{14}_{02}, \Delta\varepsilon^{14}_{03}\) and \(\Delta\varepsilon^{14}_{04}\) of the lowest four excited states \(1A_1(e), 1A_2(e), 2\varepsilon(a_1)\) and \(3\varepsilon(e)\) are equal to those obtained previously for the application \(NT=21\).

We can therefore conclude that the vibrational basis \((Q_1, Q_4)\) is sufficient for the determination of the lowest vibronic levels.

At this level, we can easily list parameters that appear essential for the calculation of these states. These parameters are as follows:

- Parameters \(k_1, k_2, k_3, k_4, k_5\) and \(k_6\) intervening in the definition of the reference harmonic potential \(V_0\).
- The first-order parameter corresponding to \(Q_d\), namely \(\beta_1\).
- The second-order parameters \(k'_{1}, k'_{2}, k'_{3}, k'_{5}, k'_{6}\) and \(\gamma_{14}\) (coupling term since \(Q_1\) and \(Q_4\) modes are active).

In these conditions, the results of the Hamiltonian diagonalization are regrouped in Table 5. We verify obviously that the first obtained states as well as the corresponding energy values are rigorously the same as those of Table 4. It is convenient therefore to note that the taken fourteen parameters are well adapted to the calculation of the first vibronic levels involving \(Q_1\) and \(Q_4\) modes.
Table 5. Put in evidence the essential coupling parameters

<table>
<thead>
<tr>
<th>Symmetry of the considered state</th>
<th>Energies (a.u.)</th>
<th>ΔE(^{(14)}) (cm(^{-1}))</th>
<th>ΔE(^{(21)}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\varepsilon(a_1)) (Z.P.E. state)</td>
<td>0.035969</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>(2\varepsilon(a_1))</td>
<td>0.038371</td>
<td>(\Delta E_{21}^{(14)} = 527)</td>
<td>(\Delta E_{21}^{(21)} = 523)</td>
</tr>
<tr>
<td>(1A_1(e))</td>
<td>0.038901</td>
<td>(\Delta E_{22}^{(14)} = 643)</td>
<td>(\Delta E_{22}^{(21)} = 638)</td>
</tr>
<tr>
<td>(1A_2(e))</td>
<td>0.039468</td>
<td>(\Delta E_{23}^{(14)} = 768)</td>
<td>(\Delta E_{23}^{(21)} = 764)</td>
</tr>
<tr>
<td>(3\varepsilon(e))</td>
<td>0.040430</td>
<td>(\Delta E_{24}^{(14)} = 979)</td>
<td>(\Delta E_{24}^{(21)} = 972)</td>
</tr>
</tbody>
</table>

2.3.5. Vibronic coupling study of \(Q_4\) and \(Q_5\) modes by means of electron movement

In the preceding paragraph, we have shown that the vibrational basis \(\{Q_i, Q_4\}\) is sufficient to the study of \(Q_4\) mode coupling. In the following, we take into account only \(Q_1\) and \(Q_5\) modes to the coupling study of \(Q_5\) mode and only \(Q_1\) and \(Q_6\) modes to that of \(Q_6\) mode.

○ Case of the vibrational basis \(\{Q_1, Q_5\}\)

We have considered applications \(NT=2,4,6,8,10,12,14\) of \(Q_1^7, Q_2^6, Q_3^5, Q_4^4, Q_5^3, Q_6^2\) type in which this time, only \(Q_1\) and \(Q_5\) modes are excited with quantum number \(V\) (varying from 1 to 7).

To the extent where the vibrational functions basis is limited to \(Q_1\) and \(Q_5\) modes, the new list of coupling parameters, which seems to be compatible with this basis, is as follows:

- \(k_1, k_2, k_3, k_4, k_5\) and \(k_6\) parameters defining the reference potential \(V_0\).
- Parameter of first-order corresponding to \(Q_5\) (\(\beta_5\)).
- Parameters of second-order \(k_4', k_4'', k_5', k_5'', k_6', k_6''\) and \(\gamma_{15}\).

A satisfying convergence of the order of \(10^{-6}\) a.u. is obtained for the application \(NT=14\) \((Q_1^7, Q_2^6, Q_3^5, Q_4^4, Q_5^3, Q_6^2)\), the results of which are presented in Table 6.

Table 6. Study of \(Q_5\) coupling

<table>
<thead>
<tr>
<th>Symmetry of the considered state</th>
<th>Energies (a.u.)</th>
<th>ΔE (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon(a_1)) (Z.P.E. state)</td>
<td>0.036169</td>
<td>------</td>
</tr>
<tr>
<td>(\varepsilon(a_1))</td>
<td>0.038547</td>
<td>(\Delta E_{01} = 522)</td>
</tr>
<tr>
<td>(A_1(e))</td>
<td>0.043309</td>
<td>(\Delta E_{02} = 1567)</td>
</tr>
<tr>
<td>(A_2(e))</td>
<td>0.043408</td>
<td>(\Delta E_{23} = 22)</td>
</tr>
<tr>
<td>(\varepsilon(e))</td>
<td>0.044364</td>
<td>(\Delta E_{24} = 34)</td>
</tr>
</tbody>
</table>

The energy gap, \(\Delta E_{01}\) (522 cm\(^{-1}\)) of the first excited level involving the \(Q_1\) mode, by report to Z.P.E. level, is the same as that obtained in the case of the activation of all modes (524 cm\(^{-1}\) for the application \(NT=21\)).

Furthermore, the analysis of the vibronic function of the three other obtained excited levels \(A_1(e), A_2(e)\) and \(\varepsilon(e)\) shows the implication of \(Q_5\) and \(Q_5\) modes (antisymmetric C-H stretching).

These states are therefore the result of the coupling of these modes by means of electrons movement (coupling of type \(E \otimes e = A_1 + A_2 + \varepsilon\) )

If \(\Delta E_{02}\), \(\Delta E_{23}\) and \(\Delta E_{24}\) designate energy gaps, respectively, between:
• Z.P.E. state and A₂(e) state.
• A₂(e) and A₁(e).
• A₂(e) and ε(e).

We expect, beside transitions from A₂(e) level at 1567 cm⁻¹ (ΔE₂), to equivalent transitions from A₁(e) and ε(e) levels and which will be distant of 22 cm⁻¹ (ΔE₂₃) and 34 cm⁻¹ (ΔE₂₄) respectively.

- Case of the vibrational basis (Q₇, Q₆)

In this case, the vibrational functions basis is limited to Q₁ and Q₆ modes and the adapted parameters are as follows:
• Parameters defining the reference potential V₀.
• The first-order parameter corresponding to Q₆ (β₁).
• Second-order parameters k’₄, k”₄, k’₅, k”₅, k’₆, k”₆ and γ₁₆.

The obtained results are summarized in Table 7.

<table>
<thead>
<tr>
<th>Symmetry of the considered state</th>
<th>Energies (a.u.)</th>
<th>ΔE (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε(a₁) (Z.P.E. state)</td>
<td>0.036225</td>
<td>----------</td>
</tr>
<tr>
<td>ε(a₁)</td>
<td>0.038613</td>
<td>ΔE₂₁ = 524</td>
</tr>
<tr>
<td>A₁(e)</td>
<td>0.050874</td>
<td>ΔE₂₂ = 3215</td>
</tr>
<tr>
<td>A₂(e)</td>
<td>0.050915</td>
<td>ΔE₂₃ = 9</td>
</tr>
<tr>
<td>ε(e)</td>
<td>0.050947</td>
<td>ΔE₂₄ = 16</td>
</tr>
</tbody>
</table>

We signal that we have obtained a convergence of the order of 10⁻⁶ a.u. for the application NT=14 (Q₁⁶, Q₂⁶, Q₃⁶, Q₄⁶, Q₅⁶, Q₆⁶).

Considering ΔE₂₁, ΔE₂₂, ΔE₂₃ and ΔE₂₄ the energy gaps respectively between:
• The Z.P.E. level and the first excited level ε(a₁) implying the Q₁ mode.
• The Z.P.E. level and the second level A₁(e) involving the Q₆ mode (antisymmetric C-H bending).
• Vibronic states A₁(e) and A₂(e) (implying also the Q₆ mode).
• Vibronic states A₁(e) and ε(e) (implying the same mode Q₆).

The last three excited levels are therefore obtained by coupling of the Q₆ mode by means of the electrons movement (coupling E ⊗ e = A₁ + A₂ + ε). We expect therefore, for each transition from A₁(e) level at 3215 cm⁻¹, to analogous transition from the two other levels A₂(e) and ε(e) and which will be distant of 9 and 16 cm⁻¹, respectively.

3. Conclusion

In this paper, we have performed a vibronic coupling study in the first excited state of MgCH₃ radical using a methodology based on the crude adiabatic approximation. Firstly we have evaluated the electronic integrals intervening in the formulation of the vibronic coupling and which are used to build the Hamiltonian. The obtained results show that:
• At the level of first-order parameters, the parameter β₁ is the most important.
The gap $|k'_4 - k''_4|$ is greater than gaps $|k'_5 - k''_5|$ and $|k'_6 - k''_6|$ at the level of non-crossed second-order terms.

We have then diagonalized the representation of the Hamiltonian. This diagonalization allowed to determine the nature of first vibronic levels, therefore the implied modes in this coupling ($Q_1$, $Q_{4x}$ and $Q_{4y}$), and to surround essential coupling parameters.

Energy gaps, $A_1-A_2$ and $A_2-\epsilon$, resulting of splitting of the level $e$ ($Q_{4x}$ and $Q_{4y}$ modes) by means of electrons movement, have been evaluated at 126 and 208 cm$^{-1}$, respectively.

Concerning the high excited vibronic states implying the $Q_5$ and $Q_6$ modes, the revealed splitting due to the Jahn-Teller coupling $E \otimes e = A_1+A_2+\epsilon$, are in this case weaker. The corresponding energy gaps are evaluated to 22 cm$^{-1}$ ($A_2-A_1$), and 34 cm$^{-1}$ ($A_2-\epsilon$) for $Q_5$ mode, 9 cm$^{-1}$ ($A_2-A_1$) and 16 cm$^{-1}$ ($A_2-\epsilon$) for $Q_6$ mode.

References