Study of the vibronic coupling in the ground state of Methylthio radical

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Using a methodology based on the crude adiabatic approximation, we study the complete linear and quadratic vibronic coupling in the ground state of SCH3 radical. In order to build the representation of the hamiltonian, we evaluated 30 integrals intervening in the formulation of the vibronic coupling. Diagonalization of this representation gives the vibronic levels. For the lowest vibronic states, the implied modes are Q1 (symmetric C-S stretching) and Q4 (CH3 rocking). Energy gaps A1-A2 and A2-ε resulting from the splitting due to the Jahn-Teller coupling \( E \otimes \varepsilon = A_1 + A_2 + \varepsilon \) are evaluated to 250 and 169 cm\(^{-1}\), respectively. Essential coupling parameters are surrounded to simplify the study of highly vibronic states.

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Capsule Summary: The linear and quadratic vibronic coupling in the ground state of SCH3 radical was studied using adiabatic approximation, the first-order parameters, \( \beta_1 \) is the most important and diagonalization allowed to determine the nature of first vibronic levels.

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INTRODUCTION

The development of analytical methods, mainly the laser-induced fluorescence, significantly reduced the analysis time while providing emission spectra well resolved vibrationally. The study of short-lived species has been considered. Thus, a number of studies on simple organic and organometallic radicals have been published (Kochi, 1978; Reilly et al., 2008; Murakami et al., 2007; Fu et al., 2005; Gravel et al., 2004). The precise interpretation of the results requires methods appropriate to the calculations of open layers species. Pankratov (2004; 2005; 2012) reported scientific bases of the analytical characteristics prediction for azo coupling reactions.

This work focuses on the organic radical CH3S. This radical is an important chemical intermediate in the environmental chemistry. It has been suggested that it may be an intermediate in the atmospheric oxidation by OH and NO3 (Mellouki et al., 1977) of organic sulfides such as CH3SCH3, CH3SSCH3 and CH3SH. It has been the subject of numerous spectroscopic studies, such as emission (Ohbayashi et al., 1977), the laser photodetachment (Janousek et al., 1980; Engelking et al., 1978), the electron paramagnetic resonance (EPR) (Gillbro, 1974), the IR matrix (Jacox, 1983), the laser-induced fluorescence (Chiang et al., 1991; Hsu et al., 1989; Suzuki et al., 1984) and the microwave (Endo et al., 1986).

In a previous paper (El Bouzaidi et al., 2000), we carried out a structural and vibrational study of CH3S radical in the ground state and in the first excited state. It turned out
that the static Jahn-Teller effect in the ground state was low, in the order of 84 cm⁻¹. The relaxation of the C₃ᵥ symmetry structure, in the same state, led to two C₃ symmetry structures, A’ and A”’. A’ is slightly more stable than A”’. The lifting of degeneracy of the two potential energy surfaces may cause a significant vibronic coupling. In this work, taking into account all modes of vibration, we used the approximation “crude adiabatic” to determine the first vibronic states and the nature of the modes involved in each state.

In the framework of this approximation, Marinelli and Roch (1986) have formally treated the T₂ ⊗ (a₁ + e + 2T₂) coupling problem with all linear and quadratic parameters in the case of Jahn-Teller instability for XY₄ molecules with T₂ configuration. Numerical applications have been done for NH₂ in a type p Rydberg 2T₂ excited state (Cardy et al., 1988) and for CH₄ in the 2T₂ state (Marinelli and Roche, 1990) formed by the removal of 1t₂ 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 led to a calculated photoelectron spectrum of CH₄ in agreement with the experimental one. Recently, El Bouzaidi et al. (2015) have studied the complete linear and quadratic vibronic coupling in the first excited state of MgCH₃ radical.

**COMPUTATIONAL PROCEDURE**

**Construction of the Hamiltonian representation**

The vibronic stationary states may be obtained by solving the Schrödinger equation $H\phi_i(q, Q) = e_i\phi_i(q, Q)$ with $H = T(Q) + H_e(q, Q)$.

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 nucler and $H_e(q, Q)$ is the electronic Hamiltonian which includes the Kinetic energy operator for the electrons and all the coupling interactions. The vibronic wavefunctions $\phi_i(q, Q)$ may, in principle, be expanded in any complete vibronic basis set. In practice, this basis is severely truncated by keeping only a few electronic wavefunctions 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 $Q_0$.

$$H_e(q, Q) = H_e(q, Q_0) + \sum_{k=1}^{3N-6} \tilde{\alpha}_k(q)Q_k + \frac{1}{2} \sum_{k,l=1}^{3N-6} \tilde{\beta}_{kl}(q)Q_kQ_l$$

with $\tilde{\alpha}_k(q) = \left( \frac{\partial H_e(q,Q)}{\partial q_k} \right)_{Q_0}$

and $\tilde{\beta}_{kl}(q) = \left( \frac{\partial^2 H_e(q,Q)}{\partial q_k\partial q_l} \right)_{Q_0}$

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 ground state (El Bouzaidi et al., 2000) where cross the two potential surfaces A’ and A”’. The excitation allowing describing this structure is built with SCF molecular orbitals of the ground state. 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), which correspond to a certain matrix $G$ in the Wilson’s method (Wilson et al., 1955), 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 ground 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 first excited state.

The diagonalization of the matrix $(GF)$ defines a system of normal coordinates: $Q_1, Q_2, Q_3$ ($a_1$ symmetry) and $(Q_{4a}, Q_{4b})$, $(Q_{5a}, Q_{5b})$, $(Q_{6a}, Q_{6b})$ ($e$ symmetry). The normal coordinates, thus described, define a reference potential $V_0$ supposed harmonic, centered on Jahn-Teller point.

In Table 1, we have summarized the vibration frequencies (El Bouzaidi et al., 2000) 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:

$$H_{nm,ij} = \langle X_i(Q) | \delta_{mn} E_n(Q_0) + \Delta U_{nm}(Q) | X_j(Q) \rangle_Q \quad (m,n=1,2)$$

Limiting the electronic functions basis to degenerate functions $\Psi_0^+$ and $\Psi_0^-$ at the reference point. The vibrational $X_j(Q)$ are taken as the Eigen functions of an arbitrary $C_{3v}$ harmonic Hamiltonian $T(Q)+V_0$. The evaluation of matrix elements $H_{nm,ij}$ requires, therefore, only the elementary integrals.

$$\langle X_i(Q) | Q_k | X_j(Q) \rangle , \langle X_i(Q) | Q_k^2 | X_j(Q) \rangle , \langle X_i(Q) | Q_k Q_l | X_j(Q) \rangle$$

For this we need the terms $\Delta U_{nm}(Q)$ which we rewrite:

$$\Delta U_{nm}(Q) = \sum_k \alpha_{nm}^{k} Q_k + \frac{1}{2} \sum_{k,l} \beta_{kl}^{nm} Q_k Q_l$$

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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>738</td>
<td>1149</td>
<td>3030</td>
<td>605</td>
<td>1485</td>
<td>3198</td>
</tr>
<tr>
<td>$k_i$ (a.u.)</td>
<td>0.336510$^{-2}$</td>
<td>0.523910$^{-2}$</td>
<td>0.138110$^{-1}$</td>
<td>0.275910$^{-2}$</td>
<td>0.677210$^{-2}$</td>
<td>0.146110$^{-1}$</td>
</tr>
</tbody>
</table>

Table 2: Values of parameters intervening in the formulation of vibronic coupling

<table>
<thead>
<tr>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_3$</th>
<th>$K_4$</th>
<th>$K_5$</th>
<th>$K_6$</th>
<th>$K'_6$</th>
<th>$K'_5$</th>
<th>$K'_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.348410$^{-2}$</td>
<td>0.529910$^{-2}$</td>
<td>0.138410$^{-1}$</td>
<td>0.275910$^{-2}$</td>
<td>0.677210$^{-2}$</td>
<td>0.146110$^{-1}$</td>
<td>0.362810$^{-2}$</td>
<td>0.670410$^{-2}$</td>
<td>0.458010$^{-2}$</td>
</tr>
</tbody>
</table>

Table 3: Study of the three first excited vibronics levels convergence

<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>$(Q_1^0Q_2^0Q_3^0Q_4^0Q_5^0Q_6^0)$</td>
<td>$(Q_1^0Q_2^0Q_3^0Q_4^0Q_5^0Q_6^0)$</td>
<td>$(Q_1^0Q_2^0Q_3^0Q_4^0Q_5^0Q_6^0)$</td>
<td>$(Q_1^0Q_2^0Q_3^0Q_4^0Q_5^0Q_6^0)$</td>
<td>$(Q_1^0Q_2^0Q_3^0Q_4^0Q_5^0Q_6^0)$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{nm}^{(i)} = \langle \psi_{nm}^0(q, Q_0)</td>
<td>\hat{a}_k(q)</td>
<td>\psi_{nm}^0(q, Q_0) \rangle$</td>
<td>$\beta_{nm}^{(i)} = \langle \psi_{nm}^0(q, Q_0)</td>
<td>\hat{b}_k(q)</td>
<td>\psi_{nm}^0(q, Q_0) \rangle$</td>
</tr>
</tbody>
</table>

(First-order parameters)

($\alpha_{nm}^{(i)}$ | $\beta_{nm}^{(i)}$ |
| (quadratic and bilinear parameters) |

In the present case there are a priori 162 integrals to be evaluated. The application of group theory and $G_3$ symmetry of the reference configuration proves that there are only 30 integrals (Cardy et al., 1988), distributed as follow:

First-order parameters: $\beta_1$, $\beta_2$ and $\beta_3$ ($\beta_i = \alpha_{ij} = -\alpha_{ji} = \nu_{ij}$, $i, j = 1, 2, 3$)  

Non-crossed second-order parameters: $k_1$, $k_2$, $k_3$, $k_4$, $k_5$, $k_6$, $k'_4$, $k'_5$, $k'_6$ and $k''_6$  

Crossed second-order parameters: $\gamma_{14}$, $\gamma_{15}$, $\gamma_{16}$, $\gamma_{24}$, $\gamma_{25}$, $\gamma_{26}$, $\gamma_{34}$, $\gamma_{35}$, $\gamma_{36}$, $\gamma_{45}$, $\gamma_{46}$, $\gamma_{56}$, $\gamma_{56}$ and $\gamma''_{56}$ ($\gamma_{ij} = \beta_{ij}^{(x)} = -\beta_{ij}^{(y)}$)

First-order parameters: $\beta_1$, $\beta_2$ and $\beta_3$ ($\beta_i = \alpha_{ij} = -\alpha_{ji} = \nu_{ij}$, $i, j = 1, 2, 3$)  

Non-crossed second-order parameters: $k_1$, $k_2$, $k_3$, $k_4$, $k_5$, $k_6$, $k'_4$, $k'_5$, $k'_6$ and $k''_6$  

Crossed second-order parameters: $\gamma_{14}$, $\gamma_{15}$, $\gamma_{16}$, $\gamma_{24}$, $\gamma_{25}$, $\gamma_{26}$, $\gamma_{34}$, $\gamma_{35}$, $\gamma_{36}$, $\gamma_{45}$, $\gamma_{46}$, $\gamma_{56}$, $\gamma_{56}$ and $\gamma''_{56}$ ($\gamma_{ij} = \beta_{ij}^{(x)} = -\beta_{ij}^{(y)}$)
These integrals may be considered as adjustable parameters so that the two model potential surfaces $E_1$ and $E_2$ which obey the equation $\det|\Delta U_{mn} - E \delta_{mn}| = 0$ fit to the same potential surfaces derived from some quantum mechanical electronic energy calculations.

**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 of vibronic coupling in SCH: radical’s ground state \(2E\): Diagonalization of the hamiltonian

Computer codes: A first code gives matrices containing the coefficients of symmetric vibronics \(\Gamma\) and \(\Gamma^\dagger\) for an arbitrary choice of maximal vibrational quantum numbers \(V_i\) \((i=1,2,...9)\) and for each irreducible representation of \(\mathcal{C}_v\).

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 (Davidson, 1975).

RESULTS AND DISCUSSION

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. (ii) 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. (iii) Probably, the crossed second-order parameters \(\gamma_{ij}\) will not have any effect on the vibronic coupling.

Limitation of the problem to e symmetry normal modes

In a first time, we have activated only normal modes of e symmetry (\(Q_6, Q_5, Q_3\), and \(Q_2\), in Jahn-Teller effect (El Bouzaidi et al., 2000), by exciting them equally \((V=V_6=V_5=V_3=0)\). Then, we varied the vibrational quantum number \(V\) from 1 to 5, therefore \(\text{NT}\) from 3 to 15 where, \(\text{NT} = \sum_{i=1}^{5} V_i\).

The obtained results are recorded in Table 3 (for each symmetry we have carried the three lowest vibronic states).

From the analysis of this table, it was observed that whatever the value of \(\text{NT}\) considered, the hierarchy of vibronic levels was the same. This result was in agreement with that of a previous work (El Bouzaidi et al., 2015).

As shown in Figure 1, we carried the relative position of the different vibronic levels of symmetry \(A_1, A_2, \epsilon\) calculated in the framework of the application \(\text{NT}=21\). We adopted for the vibronic levels the following notation: \(n X(\epsilon)\)

Where, \(n\) the number of state in each Irreducible representation (states are classified by ascending order of the energy), \(X\) the symmetry of the vibronic state, \(\epsilon\) the symmetry of the implied vibration mode.

A priori, particularly it was noted that the second vibronic excited state \(2\epsilon(a_1)\) involves an \(a_1\) symmetry mode, while the first \(1A_1(e)\), the third \(1A_2(e)\), and the fourth \(3\epsilon(e)\) excited vibronic states involve as through an \(e\) symmetry mode. To specify the nature of these implied modes, it is necessary to analyze the vibronic function of each state.

Analysis of the vibronic function of the first four excited states

To simplify notations, we 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 \(\Gamma\) 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 state \(2\epsilon(a_1)\): This development carries essentially on the \(Q_1\) mode with a weak contribution of \(Q_6\) and \(Q_8\) modes. Therefore the vibration movement implied in this state is that of C-S stretching.

Vibronic functions of excited states \(1A_1(e), 1A_2(e)\) and \(3\epsilon(e)\): The analysis of these vibronic functions shows that the implied vibration modes in each of corresponding states are the same namely \(Q_6\) and \(Q_8\). Consequently, the active vibration movement is the methyl-rocking one.

We can therefore conclude that these three states result from the coupling of \(Q_6\) and \(Q_8\) modes (modes \(e\) by means of electrons movement (electronic state \(E\)). Therefore a coupling of type:

\[ E \otimes e = A_1 + A_2 + \epsilon \] (schematized in Fig. 2).

In the case where the vibronic coupling is neglected (part a of Figure 2), we represented transitions, towards the lowest vibrational level \(a_1\) of the ground state, on the one hand from the lowest vibrational level \(a_1(\Delta_1)\) of the first excited state and on the other hand from the vibrational level \(e(\Delta_3)\) implying \(Q_6\) and \(Q_8\) modes of this same state. The value of the frequency \(\nu_4\) associated with \(Q_6\) and \(Q_8\) modes, deduced experimentally by emission spectroscopy from the difference \((\Delta_2-\Delta_1)\), is estimated in this work at 605 cm\(^{-1}\). The raising of degeneracy of these modes \((Q_6\) and \(Q_8\)) by vibronic coupling (part b of Figure 2) leads respectively to three equivalents transitions of energies \(\Delta_2^{(1)}, \Delta_2^{(2)}, \) and \(\Delta_1^{(2)}\), from \(1A_1(e), 1A_2(e)\) and \(3\epsilon(e)\) levels implying these modes. Therefore, we predicted that there are three bands around 572, 822 and 994 cm\(^{-1}\) in the emission spectrum.

In summary, beside transitions from \(1A_1(e)\), we predicted equivalent transitions from \(1A_2(e)\) and \(3\epsilon(e)\) levels which will be distant of 250 cm\(^{-1}\) (822-572) and 172 cm\(^{-1}\) (994-822), respectively.

Put in evidence the essential coupling parameters
In the preceding paragraph, we analyzed the vibronic functions for the lowest four excited states $1A_1(e), 1A_2(e), 2\epsilon(a_1)$ and $3\epsilon(e)$. This analysis has shown that these states involve $Q_1, Q_6$ and $Q_{5y}$ 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 \( Q_1^2 Q_6^2 Q_{5y}^2 Q_{5}^2 Q_{5y}^2 \) type in which the $Q_1$ and $Q_6$ 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 \( 10^{-6} \) a.u., are summarized in Table 4.

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

We can therefore conclude that the vibrational basis \( \{Q_1, Q_6\} \) 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 $Q_6$, namely $\beta_1$.
- The second-order parameters $k'_{q_6}, k''_{q_6}, k'_{s_6}, k''_{s_6}, k'_{e_6}$ and $k''_{e_6}$ and $\gamma_{15}$ (coupling term since $Q_1$ and $Q_4$ mode are active).

In these conditions, the results of the Hamiltonian diagonalization are regrouped in Table 5. We obviously verified that the first obtained states as well as the corresponding energy values are rigorously the same as those of Table 4. It was 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 7: Study of $Q_6$ coupling

<table>
<thead>
<tr>
<th>Symmetry of the considered state</th>
<th>Energies ($\epsilon(a_1)$) (Z.P.E. state)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
<th>$\Delta E_{exp}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon(a_1)$ (Z.P.E. state)</td>
<td>0.035897</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>$\epsilon(a_1)$</td>
<td>0.039223</td>
<td>$\Delta E_{01} = 730$</td>
<td>$\Delta E_{01} = 727$</td>
</tr>
<tr>
<td>$A_1(e)$</td>
<td>0.048659</td>
<td>$\Delta E_{02} = 2801$</td>
<td>$\Delta E_{02} = 2706$</td>
</tr>
<tr>
<td>$A_2(e)$</td>
<td>0.048718</td>
<td>$\Delta E_{23} = 13$</td>
<td>-----</td>
</tr>
<tr>
<td>$e(e)$</td>
<td>0.048750</td>
<td>$\Delta E_{24} = 7$</td>
<td>-----</td>
</tr>
</tbody>
</table>

### 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 \( \{Q_1, Q_6\} \) is sufficient to the study of $Q_4$ mode coupling. In the following, we take into account only $Q_1$ and $Q_6$ modes to the coupling study of $Q_5$ mode and only $Q_1$ and $Q_6$ modes to that of $Q_4$ mode.

Case of the vibrational basis \( \{Q_1, Q_6\} \): We have considered applications \( NT=2,4,6,8,10,12,14 \) of \( Q_1^1 Q_2^0 Q_3^0 Q_4^0 Q_5^1 Q_6^0 \) type in which this time, only $Q_1$ and $Q_6$ 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 $Q_6$ modes, the new list of coupling parameters, which seems to be compatible with this basis, is as follows:

- $k_4, k_5, k_6, k_7$ and $k_8$ parameters defining the reference potential $V_0$.
- Parameter of first-order corresponding to $Q_5$ ($\beta_3$).
- Parameters of second-order $k'_{q_4}, k''_{q_4}, k'_{s_4}, k''_{s_4}, k'_{e_4}$ and $k''_{e_4}$ and $\gamma_{15}$.

A satisfying convergence of the order of \( 10^{-6} \) a.u. is obtained for the application \( NT=14 \) \( (Q_1^1, Q_2^0, Q_3^0, Q_4^0, Q_5^1, Q_6^0) \), the results of which are presented in Table 6.

The energy gap, $\Delta E_{01}$ (730 cm$^{-1}$) of the first excited level involving the $Q_1$ mode, by report to Z.P.E. level, was in good agreement with the experimental frequency of C-S stretching mode (727 cm$^{-1}$) (Chiang and Lee, 1991). Similarly the gap (\( \Delta E_{02} \)) between Z.P.E. level and $1A_1(e)$ state is very close to the measured frequency of C-H a-bending (1496 cm$^{-1}$). Furthermore, the analysis of the vibronic function of the three other obtained excited levels $A_1(e), A_2(e)$ and $e(e)$ shows the implication of $Q_{5x}$ and $Q_{5y}$ 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 \( E \otimes e = A_1 + A_2 + \epsilon \). If \( \Delta E_{02}, \Delta E_{23} \) and \( \Delta E_{24} \) designate energy gaps, respectively, between:
- Z.P.E. state and \( A_2(e) \) state.
- \( A_1(e) \) and \( A_1(e) \).
- \( A_1(e) \) and \( \epsilon(e) \).

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

where \( k_i \text{ (a. u.)} = 4.56 \times 10^{-6} v_i \text{ (cm}^{-1} \text{)} \)

\[ \varphi_{2\epsilon(a_1)} = -0.836 (Q_1^* \psi_0^0) + 0.285 \left[ \frac{1}{\sqrt{2}} Q_1^* Q_{4y} \psi_0^0 + \frac{1}{\sqrt{2}} Q_1^* Q_{4x} \psi_0^0 \right] \]  (Eq. 2)

- State \( IA_1(e) \)

\[ \varphi_{1A_1(e)} = -0.843 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 - \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 \right] + 0.396 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 - \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 - \frac{1}{2} Q_{4x}^2 \psi_0^0 \right] \]

- State \( IA_2(e) \)

\[ \varphi_{1A_2(e)} = -0.865 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 - \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 \right] - 0.283 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 - \frac{1}{2} Q_{4x}^2 \psi_0^0 \right] \]

- State \( 3\epsilon(e) \)

\[ \varphi_{3\epsilon(e)} = -0.746 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 - \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 \right] + 0.488 \left[ \frac{1}{\sqrt{2}} Q_{4y}^* \psi_0^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \psi_0^0 \right] \]  (Eq. 3)

Beside transitions from \( A_2(e) \) level at 1567 cm\(^{-1}\) (\( \Delta E_{02} \)), we expected an equivalent transitions from \( A_1(e) \) and \( \epsilon(e) \) levels and which will be distant of 22 cm\(^{-1}\) (\( \Delta E_{23} \)) and 34 cm\(^{-1}\) (\( \Delta E_{24} \)), respectively.

Case of the vibrational basis \((Q_i, Q_6)\): In this case, the vibrational basis functions was limited to \( Q_1 \) and \( Q_6 \) modes and the adapted parameters are as follows:
- Parameters defining the reference potential \( V_0 \)
- The first-order parameter corresponding to \( Q_6 \) (\( \beta_3 \)).
- Second-order parameters \( k'4, k''4, k'5, k''5, k'6, k''6 \) and \( \gamma_{16} \).

The obtained results are summarized in Table 7. We signal that we have obtained a convergence of the order of 10\(^{-6}\) a.u. for the application \( NT=14 \) (\( Q_1^1, Q_2^2, Q_3^3, Q_4^4, Q_5^5, Q_6^6 \)). Considering \( \Delta E_{01}, \Delta E_{02}, \Delta E_{23} \) and \( \Delta E_{24} \) the energy gaps respectively between:
- The Z.P.E. level and the first excited level \( \epsilon(a_1) \) implying the \( Q_1 \) mode.
- The Z.P.E. level and the second level \( A_1(e) \) involving the \( Q_6 \) mode (antisymmetric \( C-H \) bending).
- Vibronic states \( A_1(e) \) and \( A_2(e) \) (implying also the \( Q_6 \) mode).

In this paper, we have performed a vibronic coupling study in the ground state of \( SCH_3 \) radical using a methodology based on the crude adiabatic approximation. Firstly, we evaluated the electronic integrals intervening in the formulation of the vibronic coupling and which are used to build the Hamiltonian. Results revealed that;
Fig. 1: Relative position of the different vibronic states $A_1$, $A_2$ and $e$ (calculated for application NT=21)

Without coupling
\[ \Delta_2 - \Delta_1 = 605 \text{ cm}^{-1} \]
\[ \Delta_2^{(2)} - \Delta_1 = 822 \text{ cm}^{-1} \]  
(a)

With coupling
\[ \Delta_2^{(1)} - \Delta_1 = 572 \text{ cm}^{-1} \]
\[ \Delta_2^{(3)} - \Delta_1 = 994 \text{ cm}^{-1} \]  
(b)

Fig. 2: Raising of $Q_x$ and $Q_y$ modes degeneracy by vibronic coupling
At the level of first-order parameters, the parameter $\beta_1$ was the most important.

The gap $|k'_{4} - k''_{4}|$ was greater than gaps $|k'_{5} - k''_{5}|$ and $|k'_{6} - k''_{6}|$ at the level of non-crossed second-order terms.

We 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 ($Q_6$, $Q_6$, and $Q_6$), and to surround essential coupling parameters.

Energy gaps, $A_x$,$A_z$ and $A_z - \varepsilon$, resulting of splitting of the level $e$ ($Q_6$ and $Q_6$ modes) by means of electrons movement, have been evaluated at 250 and 169 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 $E \otimes e = A_1 + A_2 + \varepsilon$, are in this case weaker. The corresponding energy gaps are evaluated to 38 cm$^{-1}$ ($A_2 - A_1$), and 17 cm$^{-1}$ ($A_2 - \varepsilon$) for $Q_5$ mode, 13 cm$^{-1}$ ($A_2 - A_1$) and 7 cm$^{-1}$ ($A_2 - \varepsilon$) for $Q_6$ mode.

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