



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

R. Drissi El Bouzaidi^{1,2,*} and A. El Gridani¹

¹Laboratoire de chimie physique, Faculté des Sciences, B.P. 8106, Université Ibn Zohr, 80000, Agadir, Maroc.

²Centre Régional des Métiers de L'Éducation et de Formation (CRMEF), Souss Massa Daraa, Inezgane, Maroc.

*Corresponding author's E. mail: drissi.rachid1@hotmail.fr, Tel.: 21267222253, Fax: 212524882123

ARTICLE INFO

Article type:

Research article

Article history:

Received July 2015

Accepted September 2015

April 2016 Issue

Keywords:

Vibronic coupling

Emission spectrum

Ground state

Methylthio radical

Crude adiabatic

ABSTRACT

Using a methodology based on the crude adiabatic approximation, we study the complete linear and quadratic vibronic coupling in the ground state of SCH_3 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 Q_1 (symmetric C-S stretching) and Q_4 (CH_3 rocking). Energy gaps A_1-A_2 and $A_2-\varepsilon$ resulting from the splitting due to the Jahn-Teller coupling $E \otimes e = A_1 + A_2 + \varepsilon$ are evaluated to 250 and 169 cm^{-1} , respectively. Essential coupling parameters are surrounded to simplify the study of highly vibronic states.

© 2016 International Scientific Organization: All rights reserved.

Capsule Summary: The linear and quadratic vibronic coupling in the ground state of SCH_3 radical was studied using adiabatic approximation, the first-order parameters, β_1 is the most important and diagonalization allowed to determine the nature of first vibronic levels.

Cite This Article As: R. Drissi El Bouzaidi and A. El Gridani. 2016. Study of the vibronic coupling in the ground state of Methylthio radical. Chemistry International 2(2) 70-79

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.

Our work focuses on the organic radical CH_3S . 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 NO_3 (Mellouki et al., 1977)

of organic sulfides such as CH_3SCH_3 , CH_3SSCH_3 and CH_3SH . 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 CH_3S 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 C_{3v} symmetry structure, in the same state, led to two C_s 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

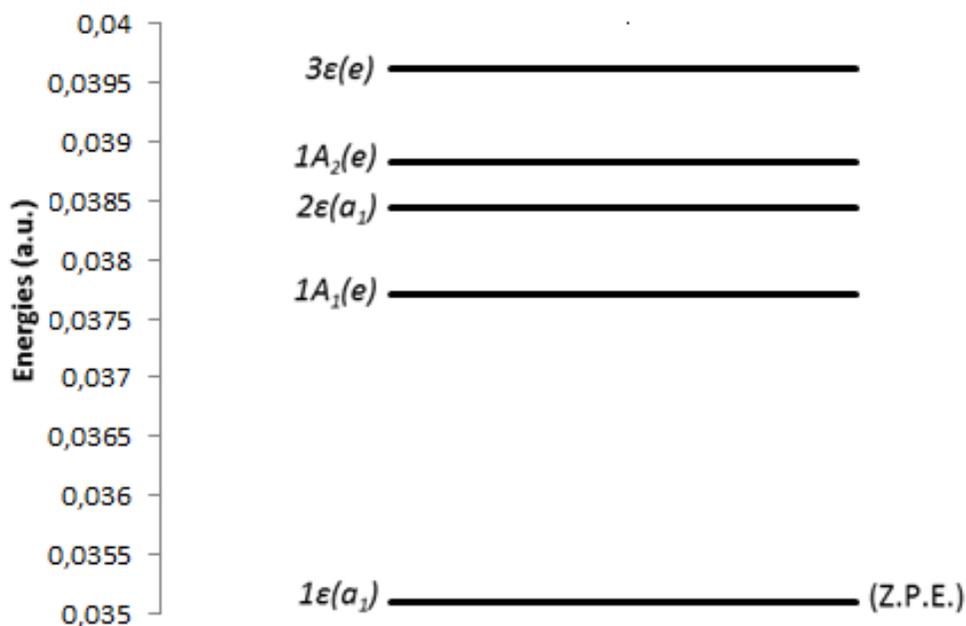


Fig. 1: Relative position of the different vibronic states A1, A2 and ϵ (calculated for application NT=21)

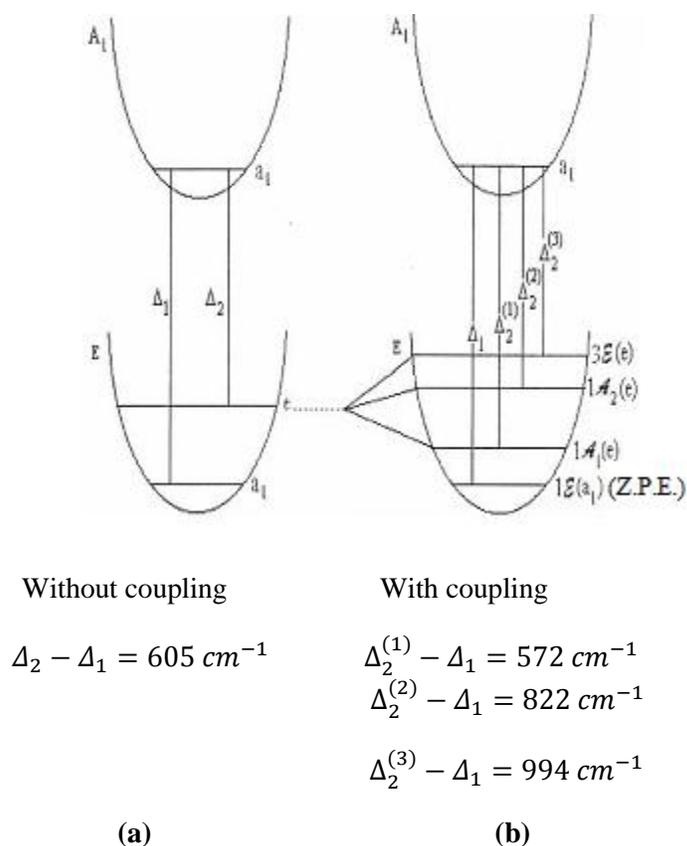


Fig. 2: Raising of Q_{4x} and Q_{4y} modes degeneracy by vibronic coupling.

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 $T_2 \otimes (a_1 + e + 2t_2)$ 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 (Cardy et al., 1988) and for CH_4^+ in

the 2T_2 state (Marinelli and Roche, 1990) 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 led to a calculated photoelectron spectrum of CH_4 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 $MgCH_3$ radical

COMPUTATIONAL DETAILS

Construction of the Hamiltonian representation

The vibronic stationary states may be obtained by solving the Schrödinger equation $H\varphi_i(q, Q) = \varepsilon_i\varphi_i(q, Q)$ 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 nuclei and $H_e(q, Q)$ is the electronic Hamiltonian, which includes the Kinetic energy operator for the electrons and all the coulombic interactions. The vibronic wavefunctions $\varphi_i(q, Q)$ may, in principle, be expanded in any complete vibronic basis set. In practice, this basis is severely truncated by keeping only a few electronic 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 .

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

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

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

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 $(Q_{4x}, Q_{4y}), (Q_{5x}, Q_{5y}), (Q_{6x}, Q_{6y})$ (e symmetry). The normal coordinates, thus described, define a reference potential V_0 supposed harmonic, centered on Jahn-Teller point.

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:

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

limiting the electronic functions basis to degenerate functions Ψ_x^0 and Ψ_y^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:

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

$$\text{with } \alpha_k^{nm} = \langle \Psi_n^0(q, Q_0) | \tilde{\alpha}_k(q) | \Psi_m^0(q, Q_0) \rangle$$

(first-order parameters)

$$\beta_{kl}^{nm} = \langle \Psi_n^0(q, Q_0) | \tilde{\beta}_{kl}(q) | \Psi_m^0(q, Q_0) \rangle$$

(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 (Cardy et al., 1988), distributed as follow:

- First-order parameters: β_1, β_2 and β_3 ($\beta_i = \alpha_{jy}^{xx} = -\alpha_{jy}^{yy} = \alpha_{jx}^{xy}$, $i=1,2,3$ $j=4,5,6$)
- Non-crossed second-order parameters: $k_1, k_2, k_3, k_4, k_5, k_6, k'_4, k''_4, k'_5, k''_5, k'_6$ and k''_6

Table 1: Definition of harmonic reference potential V_0

Q_i	Q_1	Q_2	Q_3	Q_{4x}, Q_{4y}	Q_{5x}, Q_{5y}	Q_{6x}, Q_{6y}
ν_i (cm ⁻¹)	738	1149	3030	605	1485	3198
k_i (a.u.)	$0,3365.10^{-2}$	$0,5239.10^{-2}$	$0,1381.10^{-1}$	$0,2759.10^{-2}$	$0,6772.10^{-2}$	$0,1461.10^{-1}$

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

K_1	K_2	K_3	K_4	K_5	K_6	K'_4	K''_4	K'_5	K''_5
$0,3484.10^{-2}$	$0,5299.10^{-2}$	$0,1384.10^{-1}$	$0,2759.10^{-2}$	$0,6772.10^{-2}$	$0,1461.10^{-1}$	$0,3628.10^{-2}$	$0,6704.10^{-2}$	$0,4580.10^{-2}$	$0,5328.10^{-2}$
K'_6	K''_6	β_1	β_2	β_3	γ_{14}	γ_{15}	γ_{16}	γ_{24}	γ_{25}
$0,1429.10^{-1}$	$0,1421.10^{-1}$	$-0,1145.10^{-2}$	$0,4128.10^{-3}$	$0,3100.10^{-3}$	$0,3548.10^{-3}$	$-0,6156.10^{-4}$	$-0,4744.10^{-3}$	$-0,2962.10^{-3}$	$0,4820.10^{-3}$
γ_{26}	γ_{34}	γ_{35}	γ_{36}	γ'_{45}	γ'_{46}	γ'_{56}	γ''_{45}	γ''_{46}	γ''_{56}
$0,3423.10^{-4}$	$0,2237.10^{-3}$	$0,1272.10^{-3}$	$0,3179.10^{-4}$	$0,3155.10^{-3}$	$-0,3178.10^{-5}$	$-0,1282.10^{-3}$	$0,1406.10^{-3}$	$-0,1891.10^{-3}$	$-0,1390.10^{-3}$

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

NT	3	6	9	12	15
$(Q_1^0 Q_2^0 Q_3^0 Q_4^y Q_5^y Q_6^y)$	$(Q_1^0 Q_2^0 Q_3^0 Q_4^1 Q_5^1 Q_6^1)$	$(Q_1^0 Q_2^0 Q_3^0 Q_4^2 Q_5^2 Q_6^2)$	$(Q_1^0 Q_2^0 Q_3^0 Q_4^3 Q_5^3 Q_6^3)$	$(Q_1^0 Q_2^0 Q_3^0 Q_4^4 Q_5^4 Q_6^4)$	$(Q_1^y Q_2^0 Q_3^0 Q_4^y Q_5^y Q_6^0)$
Vibronics A_1	0.038547 0.041381 0.046143	0.038005 0.041128 0.044269	0.037986 0.040883 0.043162	0.037929 0.040885 0.042682	0.037928 0.040876 0.042662
Vibronics A_2	0.040159 0.041861 0.046107	0.039215 0.041576 0.044540	0.039084 0.041435 0.043870	0.039055 0.041418 0.043161	0.039051 0.041413 0.043111
Vibronics ε	0.035571 0.041205 0.041505	0.035306 0.040329 0.041287	0.035267 0.039916 0.041072	0.035255 0.039749 0.041058	0.035252 0.039710 0.041017

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, 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 describing the two structures with SCF ground state M.O.

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

- Crossed second-order parameters: $\gamma_{14}, \gamma_{15}, \gamma_{16}, \gamma_{24}, \gamma_{25}, \gamma_{26}, \gamma_{34}, \gamma_{35}, \gamma_{36}, \gamma'_{45}, \gamma'_{46}, \gamma'_{56}, \gamma''_{45}, \gamma''_{46}$ and γ''_{56} ($\gamma_{ij} = \beta_{ij}^{xx} = -\beta_{ij}^{yy} = \beta_{ij}^{xy}, i = 1,2,3 \quad j = 4,5,6$;

$$\gamma'_{ij} = \beta_{ixjx}^{xx} = \beta_{iyjy}^{yy}, \quad \gamma''_{ij} = \beta_{ijjy}^{xx} = \beta_{ixjx}^{yy}, \quad i = 4,5 \quad j = 5,6 \quad i \neq j).$$

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

Table 4: Reduction of the vibrational basis to Q_1 and Q_4 modes

Symmetry of the considered state	Energies	$\Delta E^{(14)}$
	(a.u.)	(cm^{-1})
$1\varepsilon(a_1)$ (Z.P.E. state)	0.035589	-----
$2\varepsilon(a_1)$	0.038177	$\Delta E_{01}^{14} = 568$
$1A_1(e)$	0.038917	$\Delta E_{02}^{14} = 730$
$1A_2(e)$	0.039318	$\Delta E_{03}^{14} = 250$
$3\varepsilon(e)$	0.040330	$\Delta E_{04}^{14} = 169$

Table 5: Put in evidence the essential coupling parameters

Symmetry of the considered state	Energies	$\Delta E^{(14)}$	$\Delta E^{(21)}$
	(a.u.)	(cm^{-1})	(cm^{-1})
$1\varepsilon(a_1)$ (Z.P.E. state)	0.035589	-----	-----
$2\varepsilon(a_1)$	0.038177	$\Delta E_{01}^{14} = 568$	$\Delta E_{01}^{21} = 586$
$1A_1(e)$	0.038917	$\Delta E_{02}^{14} = 730$	$\Delta E_{02}^{21} = 727$
$1A_2(e)$	0.039318	$\Delta E_{03}^{14} = 250$	-----
$3\varepsilon(e)$	0.040330	$\Delta E_{04}^{14} = 169$	-----

Table 6: Study of Q_5 coupling

Symmetry of the considered state	Energies	ΔE	ΔE_{exp}
	(a.u.)	(cm^{-1})	(cm^{-1}) (Chiang and Lee, 1991)
$\varepsilon(a_1)$ (Z.P.E. state)	0.035802	-----	-----
$\varepsilon(a_1)$	0.039128	$\Delta E_{01} = 730$	$\Delta E_{01} = 727$
$A_2(e)$	0.042576	$\Delta E_{02} = 1487$	$\Delta E_{02} = 1496$
$A_1(e)$	0.042749	$\Delta E_{23} = 38$	-----
$\varepsilon(e)$	0.042826	$\Delta E_{24} = 34$	-----

- Simultaneous adjustment, by a least square method, of $H_e(q, Q_0)$ representation, on the two calculated surfaces.

Calculation of vibronic coupling in SCH_3 radical's ground state 2E : Diagonalization of the hamiltonian

Computer codes

A first code gives matrices containing the coefficients of symmetric vibronics $[\Gamma]$ and $[\Gamma]^+$ for an arbitrary choice of

maximal vibrational quantum members V_i ($i=1,2,\dots,9$) 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 (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:

- (i) At the level of first-order parameters, the parameter β_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, γ_{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_4 , Q_5 and Q_6), assets in Jhan-Teller effect (El Bouzaidi et al., 2000), 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 ($V_1=V_2=V_3=0$). Then, we varied the vibrational quantum number V from 1 to 5, therefore NT from 3 to 15 where $NT = \sum_{i=1}^6 V_i$

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 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).

On Figure 1, we carried the relative position of the different vibronic levels of symmetry A_1 , A_2 , ε calculated in the framework of the application $NT=2I$. We 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 ascendant order of the energy).

X : the symmetry of the vibronic state.

x : the symmetry of the implied vibration mode.

A priori, particularly it was noted that the second vibronic excited state $2\varepsilon(a_1)$ involves an a_1 symmetry mode, while the first $1A_1(e)$, the third $1A_2(e)$, and the fourth $3\varepsilon(e)$ 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 ($\overset{\circ}{\circ}$) 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 $2\varepsilon(a_1)$

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-S stretching.

- Vibronic functions of excited states $1A_1(e)$, $1A_2(e)$ and $3\varepsilon(e)$

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:

$$E \otimes e = A_1 + A_2 + \varepsilon$$

and schematized in Figure 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 $a_1(A_1)$ 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 ν_4 associated with Q_{4x} and Q_{4y} modes, deduced experimentally by emission spectroscopy from the difference ($A_2 - A_1$), is estimated in this work at 605 cm^{-1} . The raising of degeneracy of these modes (Q_{4x} and Q_{4y}) by vibronic coupling (part b of Figure 2) leads respectively to three equivalents transitions of energies $\Delta_2^{(1)}$, $\Delta_2^{(2)}$ and $\Delta_2^{(3)}$, from $1A_1(e)$, $1A_2(e)$ and $3\varepsilon(e)$ 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 $3\varepsilon(e)$ 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 $1A_1(e)$, $1A_2(e)$, $2\varepsilon(a_1)$ and $3\varepsilon(e)$. This analysis has shown that these states involve Q_1 , Q_{4x} and Q_{4y} modes. We can, therefore, hope to reduce the dimension of the vibrational basis and to take into account only these modes.

Table 4: Study of Q_6 coupling

Symmetry of the considered state	Energies (a.u.)	ΔE (cm ⁻¹)	ΔE_{exp} (cm ⁻¹) (Chiang and Lee, 1991)
$\varepsilon(a_1)$ (Z.P.E. state)	0.035897	-----	-----
$\varepsilon(a_1)$	0.039223	$\Delta E_{01} = 730$	$\Delta E_{01} = 727$
$A_1(e)$	0.048659	$\Delta E_{02} = 2801$	$\Delta E_{02} = 2706$
$A_2(e)$	0.048718	$\Delta E_{23} = 13$	-----
$\varepsilon(e)$	0.048750	$\Delta E_{24} = 7$	-----

For this, we consider the applications $NT=2,4,6,8,10,12$ of $Q_1^V Q_2^0 Q_3^0 Q_4^V Q_5^0 Q_6^0$ type in which the Q_1 and Q_4 mode 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 $I\varepsilon(a_1)$ (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 $IA_1(e)$, $IA_2(e)$, $2\varepsilon(a_1)$ 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_4 , namely β_1 .
- The second-order parameters k'_4 , k''_4 , k'_5 , k''_5 , k'_6 , k''_6 and γ_{14} (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.

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_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.

- o Case of the vibrational basis (Q_1 , Q_5)

We have considered applications $NT=2,4,6,8,10,12,14$ of $Q_1^V Q_2^0 Q_3^0 Q_4^0 Q_5^V Q_6^0$ 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 (β_2).
- Parameters of second-order k'_4 , k''_4 , k'_5 , k''_5 , k'_6 , k''_6 and γ_{15} .

A satisfying convergence of the order of 10^{-6} a.u. is obtained for the application $NT=14$ ($Q_1^7, Q_2^0, Q_3^0, Q_4^0, Q_5^7, Q_6^0$), the results of which are presented in Table 6.

The energy gap, ΔE_{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 s-stretching mode (727cm⁻¹) (Chiang and Lee, 1991). Similarly the gap (ΔE_{02}) between Z.P.E. level and $IA_1(e)$ 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 $\varepsilon(e)$ 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 $E \otimes e = A_1 + A_2 + \varepsilon$)

If ΔE_{02} , ΔE_{23} and ΔE_{24} designate energy gaps, respectively, between:

- Z.P.E. state and $A_2(e)$ state.
- $A_2(e)$ and $A_1(e)$.
- $A_2(e)$ and $\varepsilon(e)$.

$$V_0 = \frac{1}{2}k_1Q_1^2 + \frac{1}{2}k_2Q_2^2 + \frac{1}{2}k_3Q_3^2 + \frac{1}{2}k_4(Q_{4x}^2 + Q_{4y}^2) + \frac{1}{2}k_5(Q_{5x}^2 + Q_{5y}^2) + \frac{1}{2}k_6(Q_{6x}^2 + Q_{6y}^2) \quad (\text{Eq. 1})$$

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

$$\varphi_{2\varepsilon(a_1)} = -0.836(Q_1^* \Psi_x^0) + 0.285 \left[\frac{1}{\sqrt{2}} Q_1^* Q_{4y}^* \Psi_x^0 + \frac{1}{\sqrt{2}} Q_1^* Q_{4x}^* \Psi_y^0 \right] \quad (\text{Eq. 2})$$

- State $1A_1(e)$

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

- State $1A_2(e)$

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

- State $3\varepsilon(e)$

$$\varphi_{3\varepsilon(e)} = -0.746 \left[\frac{1}{\sqrt{2}} Q_{4y}^* \Psi_x^0 + \frac{1}{\sqrt{2}} Q_{4x}^* \Psi_y^0 \right] + 0.488 \left[\frac{1}{\sqrt{2}} Q_{4y}^{*2} \Psi_x^0 + \frac{1}{\sqrt{2}} Q_{4x}^{*2} \Psi_x^0 \right] \quad (\text{Eq. 3})$$

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

o Case of the vibrational basis (Q_I, Q_6)

In this case, the vibrational functions basis was limited to Q_I 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 (β_3).
- Second-order parameters $k'_4, k''_4, k'_5, k''_5, k'_6, k''_6$ and γ_{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 $NT=14$ ($Q_1^7, Q_2^0, Q_3^0, Q_4^0, Q_5^0, Q_6^7$).

Considering $\Delta E_{01}, \Delta E_{02}, \Delta E_{23}$ and ΔE_{24} the energy gaps respectively between:

- The Z.P.E. level and the first excited level $\varepsilon(a_1)$ implying the Q_I 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).

- Vibronic states $A_1(e)$ and $\varepsilon(e)$ (implying the same mode Q_6).

The gaps (ΔE_{01}) and (ΔE_{02}) are close to observed frequencies of C-S s-stretching (727 cm^{-1}) and C-H a-bending (2706 cm^{-1}) respectively.

The last three excited levels are therefore obtained by coupling of the Q_6 mode by means of the electrons movement (coupling $E \otimes e = A_1 + A_2 + \varepsilon$). Therefore, we expected that for each transition from $A_1(e)$ level at 2801 cm^{-1} , to analogous transition from the two other levels $A_2(e)$ and $\varepsilon(e)$ and which will be distant of 13 and 7 cm^{-1} , respectively.

CONCLUSION

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. The obtained results showed that:

- At the level of first-order parameters, the parameter β_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_1 , Q_{4x} and Q_{4y}), and to surround essential coupling parameters.

Energy gaps, A_1-A_2 and $A_2-\varepsilon$, resulting of splitting of the level e (Q_{4x} and Q_{4y} 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.

REFERENCES

- Cardy, H., Liotard, D., Dargelos, A., Marinelli, F., & Roche, M. 1988. Ab initio CI study of the emission spectrum and the vibronic coupling in the $3p\ 2\ T\ 2$ state of the ammonium radical. *Chemical physics* 123(1), 73-83.
- Chiang, S.Y., Lee, Y.P., 1991. Vibronic analysis of the $\tilde{A}\ 2A_1-\tilde{X}\ 2E$ laser-induced fluorescence of jet-cooled CH_3S . *The Journal of Chemical Physics* 95(1), 66-72.
- Davidson, E.R., 1975. The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices. *Journal of Computational Physics*, 17(1), 87-94.
- El Bouzaidi, R.D., El Hammadi, A., Boutalib, A., El Mouhtadi, M. 2000. Ab initio-CI study of SCH 3 radical: analysis of the Jahn-Teller effect in the ground state. *Journal of Molecular Structure: THEOCHEM* 497(1), 197-203.
- El Bouzaidi, R.D., El Merbouh, B., Bourjila, M., Tijjar, R., El Gridani, A., 2015. Study of the vibronic coupling in the first excited state of MgCH_3 radical. *Moroccan Journal of Chemistry* 3(2), 190-201.
- Endo, Y., Saito, S., Hirota, E., 1986. The microwave spectrum of the thiomethoxy radical CH_3S . *The Journal of Chemical Physics* 85(4), 1770-1777.
- Engelking, P.C., Ellison, G.B., Lineberger, W.C., 1978. Laser photodetachment electron spectrometry of methoxide, deuteromethoxide, and thiomethoxide: Electron affinities and vibrational structure of CH_3O , CD_3O , and CH_3S . *The Journal of Chemical Physics* 69(5), 1826-1832.
- Fu, Y., Liu, L., Yu, H.Z., Wang, Y.M., Guo, Q.X. 2005. Quantum-chemical predictions of absolute standard redox potentials of diverse organic molecules and free radicals in acetonitrile. *Journal of the American Chemical Society* 127(19), 7227-7234.
- Gillbro, T., 1974. ESR and structure of sulfur-centered radicals and radical ions. γ -Irradiated dimethyl disulfide and methane thiol single crystals at 77° K. *Chemical Physics* 4(3), 476-482.
- Gravel, J.F., Luo, Q., Boudreau, D., Tang, X.P., Chin, S.L. 2004. Sensing of halocarbons using femtosecond laser-induced fluorescence. *Analytical chemistry* 76(16), 4799-4805.
- Hsu, Y.C., Liu, X., & Miller, T.A., 1989. Rotational analysis of $\tilde{A}\ 2A_1 \leftrightarrow \tilde{X}\ 2E$ electronic transition of the jet-cooled methylthio radical. *The Journal of Chemical Physics* 90(12), 6852-6857.
- Jacox, M.E., 1983. The reaction of F atoms with CH_3SH . Vibrational spectroscopy and photochemistry of CH_3S and CH_2SH hydrogen-bonded to HF. *Canadian Journal of Chemistry* 61(5), 1036-1043.
- Janousek, B.K., Brauman, J.I. 1980. Electron photodetachment of thiomethoxyl and deuteriothiomethoxyl anions: Electron affinities, vibrational frequencies, and spin-orbit splitting in CH_3S^- and CD_3S^- . *The Journal of Chemical Physics* 72(1), 694-700.
- Kochi, J., 1978. Organometallic mechanisms and catalysis: the role of reactive intermediates in organic processes. Academic Press, New York, pp. 65-68
- Marinelli, F., & Roche, M. 1986. Vibronic wavefunctions for XY 4 molecules in a T 2 electronic state. *Chemical Physics Letters* 130(5), 384-389.
- Marinelli, F., Roche, M., 1990. A crude adiabatic computation of the photoelectron spectrum of CH_3S . *Chemical Physics* 146(1), 219-223.
- Mellouki, A., Jourdain, J.L., Le Bras, G., 1977. *Chemical Physics Letters* 48, 231.
- Murakami, Y., Endo, K., Ohta, I., Nosaka, A. Y., Nosaka, Y. 2007. Can OH radicals diffuse from the UV-irradiated photocatalytic TiO_2 surfaces? Laser-induced-fluorescence study. *The Journal of Physical Chemistry C* 111(30), 11339-11346.
- Ohbayashi, K., Akimoto, H., Tanaka, I., 1977. Emission spectrum of CH_3S radical. *Chemical Physics Letters* 52(1), 47-49.
- Pankratov, A.N., 2004. Azo-Coupling Reactions Used in Analytical Chemistry: The Role of Reactants, Intermediates, and Aqueous Medium. *Helvetica Chimica Acta* 87(6), 1561-1573.
- Pankratov, A.N., 2005. Analytical Azo Coupling Reactions: An Insight from the Viewpoint of Quantum Chemistry” (in Russian). *Journal of Analytical Chemistry (in Russian: Zhurnal Analiticheskoi Khimii)* 60, No. 10, 1036-1046. English Translation: Pankratov, A.N., 2005. Analytical Azo Coupling Reactions: A Quantum-Chemical Consideration. *Journal of Analytical Chemistry* 60(10), 920-929.

- Pankratov, A.N., 2012. Mechanism of the Griess Analytical Reaction: A Quantum Chemical Substantiation of Some Stages for Diazotization and Azo Coupling (in Russian). Applied Analytical Chemistry (in Russian: Prikladnaya Analiticheskaya Khimiya) 3, No. 2 (8), 36-51.
- Reilly, N.J., Kokkin, D.L., Nakajima, M., Nauta, K., Kable, S. H., Schmidt, T.W., 2008. Spectroscopic observation of the resonance-stabilized 1-phenylpropargyl radical. Journal of the American Chemical Society 130(10), 3137-3142.
- Suzuki, M., Inoue, G., & Akimoto, H. 1984. Laser induced fluorescence of CH3S and CD3S radicals. The Journal of Chemical Physics 81(12), 5405-5412.
- Wilson, E.B., Decius, J.C., Cross, P.C., 1955. Molecular Vibrations: the theory of infrared and Raman spectra. McGraw-Hill.

Visit us at: <http://bosajournals.com/chemint/>

Submissions are accepted at: editorci@bosajournals.com OR
bosajournals@gmail.com