Theor Chem Acc (2010) 126:109–116
DOI 10.1007/s00214-009-0574-4

REGULAR ARTICLE

Avoided crossings in metal (M)–gas (X) reactions ($M = Hg$, and $X = SiH_4, GeH_4$)

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Received: 26 February 2009 / Accepted: 17 April 2009 / Published online: 29 May 2009

Abstract A study of nonadiabatic transitions through avoided crossings between two potential energy curves, associated to the approach of a mercury atom to an organic gas molecule (silane or germane) is presented. We study the Si–H and Ge–H bond breaking in the molecules SiH_4 and GeH_4, which are an important subject in the production of hydrogenated amorphous thin films. We here emphasize the importance of the excited states, the avoided crossings generated during the molecule–metal approach and the nonadiabatic transition probabilities. We have developed a model to extend the Landau–Zener theory utilizing the angle instead of the distance as the main parameter of the reaction, which is particularly adapted for tetrahedral molecules (as silane and germane). The activation process of these molecules requires several stages; first, we solve the Schrödinger equation (within the Born-Oppenheimer approximation) for the metal–molecule system during interaction. We always take into account all those states that can play a role in the reaction, even those that because of their energetic separation from the ground state are forgotten by other groups. The calculations begin at a LCAO-MO approximation and thenceforth variational and perturbative CI including of the order of a million determinants are carried out. Usually, some states of the metal repel the gas molecule and others attract it. This produces a series of avoided crossings among the curves, demanding that the nonadiabatic transition probabilities are obtained. This is the ultimate goal of the present study.

Keywords Nonadiabatic transition probability · Avoided crossing · Excited states · Reaction parameter · Potential energy surfaces

1 Introduction

Avoided crossings in the reactions of mercury (Hg) and silane (SiH_4), and mercury and germane (GeH_4) are the main aim in this paper. The potential energy surfaces (PES) were previously obtained [1, 2] by means of PSHONDO-IJKL-GMCP-FOCK-CIPSI code developed by Daudey et al. [3–6]. In this case, we use the Landau–Zener theory for avoided crossings previously extended by Pacheco et al. [7] to use the angle θ between reactants as the reaction coordinate. As is well known, states of the same symmetry cannot cross over but rather repel each other and a descending curve of interaction of a high state will approach an ascending curve of a lower one only to repel each other before they meet. This phenomenon is known as an "avoided crossing". Von Neumann and Wigner [8] quantitatively formulated the non-crossing rule in 1929 proving a theorem initially proposed by Hund [9]. Non-adiabatic transitions between potential energy curves have applications in physics, chemistry, biology and even social sciences [10]. We have recently [11] generalized the Landau–Zener Theory [12, 13] to the interaction between tetrahedral molecules and metal atoms.

We used nonadiabatic potentials that allow the system to pass from one potential curve to the other through its

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Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

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tangent line. In our case, the theory for avoided crossings was extended not only to use the distance *r* between reactants as the reaction coordinate, but also to use the angle θ as the reaction coordinate as well. This is applied to obtain the transition probabilities for the lowest Mercury–Silane and Mercury–Germane excited states. The general research to obtain transition probabilities for predicting quenching of metals in collision with a gas has been an aim for a long time [14–16].

The equation developed by Pacheco-Sánchez et al. [17] based on Zener [13] to calculate the transition probabilities for a molecular system to pass from one potential surface to another in the region of avoided crossings allows the gas molecule to orbit around the metal with a very slow angular velocity, so the translational energy is therefore irrelevant. The theoretical results for the nonadiabatic transition probability depending on the angular velocity allow the determination of the inertia moment, and such inertia moments are calculated through our approximation.

The process of finding the potential energy curve versus the angle θ has been widely applied to atom–molecule interactions [1, 2, 16–37]. But, there have been few calculations [7, 11, 17] of nonadiabatic crossing among energy levels when the energy is a function of the angle. The potential energy curves for the $M + XH_4$ systems are determined by means of Hartree-Fock self-consistent field (HF-SCF) ab initio calculations where relativistic effective potentials are used to describe the atomic cores. These calculations are accomplished using the PSHF program [4]. From these initial calculations, multiconfigurational self-consistent field calculations (MCSCF) are accomplished, providing the optimal sets of molecular orbitals (MO) to be used in the configuration interaction (CI) scheme. The contribution to the electronic correlation energy is obtained by means of interaction calculations of multireferential configurations at a variational and perturbative theory of a second-order Möller-Plesset (MP2) level through an iterative algorithm CIPSI in its second version [3].

A first approximation for the energy value is established using the geometry of Chaquin et al. [38] in a C_s symmetry (Fig. 1) and assuming arbitrary initial values for seven (4 angles and 3 distances) of its eight parameters. The following step is to change the value of the angle θ and to adjust six of the seven remaining parameters until the optimal value of the energy is found through SCF approximations. The other parameter value is obtained simply by reflection due to the symmetry C_s. The internuclear distance *r* corresponds to the distance *d* (as it will be shown in Fig. 3). The first calculation gives the energy value when metal and gas are very distant from each other. This is achieved by assigning a very large internuclear distance (essentially equivalent to infinity) between the molecule and the atom. The next calculation varies the specific value of the angle θ by changing the internuclear distance between metal and gas until an approximate distance of insertion of the metal atom in an X–H bond of methane molecule is reached. The metal atom does not directly affect the other bonds of the gas. Figure 1 exhibits lines joining hydrogen metal, which represent distance vectors. The remaining calculations are accomplished by varying uniformly the angle θ by 10° steps. During each step, the other parameters are again optimized as described before. In this way, the procedures established in the Landau–Zener [12, 13] theory are still valid and applicable to the present case.

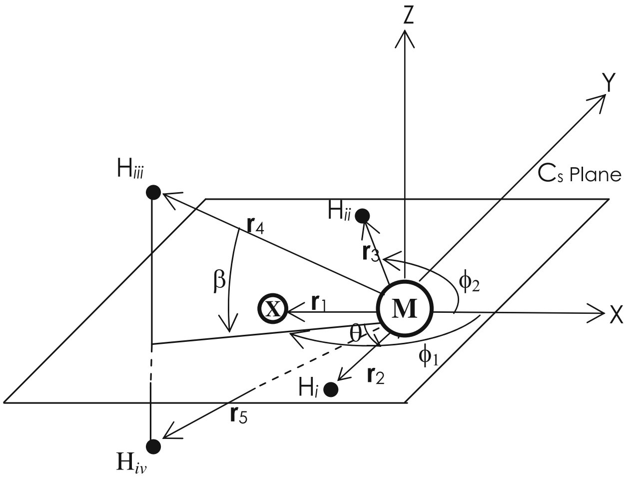

Fig. 1 Schematization of the geometrical parameters varied to obtain the reaction pathway for the M + X interactions, θ is determining the reaction coordinate. In this figure, the main axis is located on the metal atom. The metal M, nucleus X (X = Ge, Si), and two hydrogen atoms H_i and H_{ii} are located in the same plane of C_s symmetry; the other two hydrogen atoms are outside of the plane, one reflecting the other. (i) Ge–H = 1.54Å; (ii) Si–H = 1.49Å

The PES of the $Hg(^1S,^1P) + SiH_4$ and $Hg(^1S,^1P) + GeH_4$ reactions were previously reported by Luna-García et al. [1, 2]. The transition probabilities (TPs) between these reactions pathways are calculated in the present work. These TPs calculated for the lowest energy levels of the corresponding reactions were obtained through nonadiabatic crossings using an extension of the Landau–Zener (L–Z) theory toward an angular reaction coordinate. Thus, the nonadiabatic crossings depend on both the angular velocity and the moment of inertia, among other things. The transition probabilities of the systems $HHgSiH_3$ and $HHgGeH_3$ leading from one energy level to another are calculated through avoided crossings.

2 Methodology to build the potential energy curves

The minimum energy trajectory points corresponding to each electronic state are determined by Hartree-Fock self-consistent field ab initio calculations, these points are obtained by the PSHF code [4], using relativistic effective core potentials (RECP) method of Durand and Barthelat [39]. The calculations have been made with a neon-type RECP for silicon [40], an argon-type RECP for germane [40] and a xenon-type RECP for mercury [41] augmented by 14 4f electrons [1, 2], because said 14 4f electrons are close to the nucleus and much lower in energy than the actual valence electrons. We are explicitly correlating 20 electrons, 12 from mercury ($5d^{10}6s^2$), 4 valence electrons from silane or germane and 1 for each of the 4 hydrogens. These calculations are followed by calculations called MCSCF [6], which provide the optimal sets of molecular orbitals and of the integrals used in the configuration interaction scheme (CI).

The valence Gaussian basis set of the silicon atom was also taken from [40] with a triple-ζ(4s4p/3s3p) contraction scheme; this basis set was augmented with the *d*-type polarization function (exponent = 0.45) from Francl [42]. The Gaussian basis set of the mercury atom are taken from [41]. This basis set is also contracted to a triple-ζ+2pol scheme (3s3p4d/3s2p3d). The Gaussian basis set of the germane atom are taken from [40]. The basis set is contracted to a double-ζ scheme (3s3p1d/2s2p1d); this basis set was augmented with the *d*-type polarization function (exponent = 0.2) from Dingguo and Balasubramanian [43]. The hydrogen 1s double-ζ basis set was taken from [44] and was augmented with the two p-polarization orbitals of [22].

The initial SCF orbitals and integrals (at all calculated geometries) of either the Hg(^{1}S) + SiH_4 or Hg(^{1}S) + GeH_4 potential curves were used as input for the MCSCF calculations [6], which included up to three of the most important configurations describing each electronic state. This step is of particular interest to obtain the two open-shell orbitals of the $1^3A'$ and the $2^1A'$ molecular states arising from either Hg(^{3,1}P) + SiH_4 or Hg(^{3,1}P) + GeH_4 asymptotes. However, through previous multireference configuration interaction calculations, a single configuration for the triplet and singlet states was enough to optimize the molecular orbital (MO) sets of these excited states, since the CI coefficients of these configurations were always greater than 0.95 in the overall correlated wave functions (using the intermediate normalization), for the mercury atom.

The dynamic electronic correlation effects were taken into account using the two-step configuration interaction, starting with a multireference configurational zeroth-order variational wave function, followed by second-order multireference Möller-Plesset (MP2) perturbation with the CIPSI algorithm in its two-class version [3]. The reference (S) spaces used for the variational CI of the molecular states arising from the three M(^{1}S,^{3}P,^{1}P) + SiH_4 or M(^{1}S,^{3}P,^{1}P) + GeH_4 asymptotes contained between 184 and 262 determinants, which generated between 32 and 51 million perturbed MP2 determinants near the region of the reactants and the equilibrium geometry of the silyl-metal-hydride or germanyl-metal-hydride intermediate, respectively.

First, we calculate the coordinates $\theta, \varphi_1, \varphi_2, \beta, d, d_1, d_2, d_3$ for a C_s plane of symmetry where the metal is not at the center of the geometry. This is because the original coordinates obtained from the literature are given in a symmetry where the nuclear atom of the gas molecule is at the center of the geometry. However, the metal atom must be at the center of the symmetry because this is the heaviest part of the intermediary molecule, and the center of the angle θ, which is the natural coordinate for the reaction parameter. The second step is to translate these coordinates into Cartesian coordinates that the PSHONDO program will recognize. Once the initial data is modified to fit the above requirements we run the PSHONDO program. Then, we run the IJKL program, after that we run the GMCP program, then we run the FOCK program and lastly the CIPSI program. The applied methodology corresponds to the coupled programs PSHONDO-IJKL-GMCP-FOCK-CIPSI, which have allowed us to perform a wide variety of studies for reactions between metallic atoms and gases, like the ones studied here.

3 Transition probability theory

In Fig. 2, Ψ_1 is defined as the electronic eigenfunction of the energy state E_1 and Ψ_2 as the electronic eigenfunction of the energy state E_2. For $\theta \gg \theta_0$ Ψ_1 has a $6s^2$ character, but for $\theta \ll \theta_0$ Ψ_1 is of $6p^1$ character. Analogously, if $\theta \gg \theta_0$ Ψ_2 is of $6p^1$ character, but if $\theta \ll \theta_0$ Ψ_2 is of $6s^2$ character. However, if θ changes with a finite velocity,

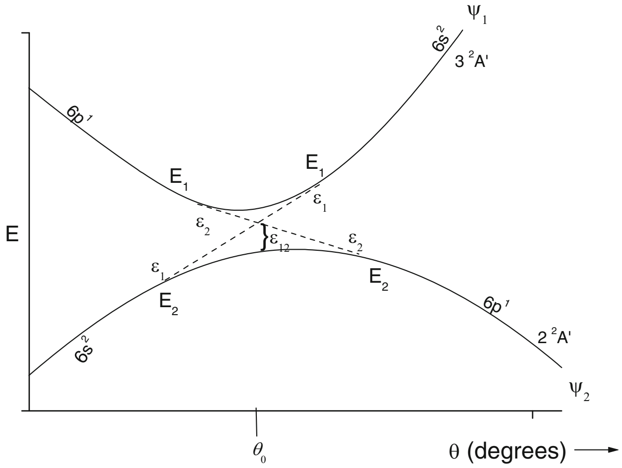

Fig. 2 Typical graph of energy as a function of the insertion angle θ, where the two *solid lines* correspond to the avoided crossing at θ_0, and the *dashed lines* correspond to the probable transitions between the potential energy curves

there is a finite probability that the molecule changes state and goes from Ψ_2 to Ψ_1 as it passes the crossing point at $\theta = \theta_0$, therefore, its final electronic state will be represented by a linear combination [11].

$$\psi = A_1(\theta)\psi_1 + A_2(\theta)\psi_2 \tag{1}$$

It is convenient to express Ψ_1 and Ψ_2 in terms of two other wave functions φ_1 and φ_2 for the calculation of A_1 and A_2. The particularity of these new wave functions is that they will respect the original character or configuration they had throughout the whole pathway (curve), i.e., φ_1 is equal to Ψ_1 for $\theta \gg \theta_0$, which in this case is of $6s^2$ character and for $\theta \ll \theta_0$ it remains of the same $6s^2$ character. Analogously, φ_2 is equal to Ψ_2 ($6p^1$ character) for large values of θ and it maintains the $6p^1$ character for all θ. The energies ε_1 and ε_2 corresponding to φ_1 and φ_2 intersect as they are functions of the internuclear angle θ (Fig. 2). Consequently φ_1 and φ_2 are not exact eigenfunctions of the complete Hamiltonian for the system, and their eigenvalues ε_1 and ε_2 are only approximate; actually they are eigenvalues for the Hamiltonian which does not include the interaction energy ε_{12}, which is the difference between the exact eigenvalues E_1, E_2 and the approximate eigenvalues ε_1, ε_2.

Zener [13] found TP from one potential curve to another as shown in Fig. 2, albeit using the distance r as reaction coordinate. For this coordinate, the electronic wave eigenfunction of the energy state E is the following linear combination $\Psi = A_1(r)\Psi_1 + A_2(r)\Psi_2$. Evidently, if the angle θ is the reaction coordinate, as in Eq. 1, then all the developments established by Zener are still valid, given that the time dependent Schrödinger equation is the right equation to find the TP. Therefore, the developments will take the reaction coordinate as a constant. So that, the nonadiabatic transition probability P is still.

$$P = \mathrm{e}^{-2\pi\gamma} \tag{2}$$

for

$$\gamma = \frac{2\pi}{h} \frac{\varepsilon_{12}^2}{\left|\frac{\mathrm{d}}{\mathrm{dt}}(\varepsilon_1 - \varepsilon_2)\right|} \tag{3}$$

where $s_1 = \frac{\mathrm{d}\in_1}{\mathrm{d}\theta}, \quad s_2 = \frac{\mathrm{d}\in_2}{\mathrm{d}\theta}$. Due to the fact that the angle θ is the reaction parameter, the velocity is no longer linear but angular $\omega = \frac{\mathrm{d}\theta}{\mathrm{d}t}$ for a system crossing $\theta = \theta_0$; and $|s_1 - s_2|$ is the difference of the two slopes (of the two surfaces of potential) that cross in $\theta = \theta_0$. We obtained the slopes by drawing two lines that are tangent to the curves and unite the crossing point. Finally, we have the transition probability.

$$P = \mathrm{e}^{-\frac{4\pi^2 \in_{12}^2}{h\omega|s_1 - s_2|}} \tag{4}$$

which is of nonadiabatic nature.

For the calculation of transition probabilities of nonadiabatic behavior using Eq. 4, we must obtain the angular velocity ω, the energy $\in_{12}$, and the corresponding slopes s_1 and s_2 crossing in the transition point, given that the other values are constants of known value. The energy $\in_{12}$ at the crossing point where $\in_1 = \in_2$ is determined by the equation:

$$\in_{12}(\theta_0) = \frac{E_1(\theta_0) - E_2(\theta_0)}{2} \tag{5}$$

in which E_1 and E_2 must be directly read of the graphs of E versus θ.

Considering the intermediary molecule $HMCH_3$ as a rigid body formed at the adsorption point of the potential energy curve, the energy is given by

$$E = \frac{1}{2} I\omega^2 \tag{6}$$

where ω is the angular velocity and I is the moment of inertia of the intermediary molecule. This is expressed of the following way

$$\omega = \sqrt{\frac{2E}{I}} \tag{7}$$

where the moment of inertia of this molecule is given by $I = \sum_i m_i r_i^2$ with $m = \frac{W}{N_0}$ in which W is the molecular weight and N_0 is the Avogadro number in [molecules/gr mol] units. The energy at Eq. 7 is directly calculated through the difference between the energy of the reference excited state and the minimum of the potential energy well in which the avoided crossing occurs. Thus, we have obtained the equation for calculating the transition probability between energy surfaces, based on the angular velocity and consequently of the moment of inertia. The probability calculated with this methodology must be compared with the magnitude of the branching fraction measured by experiments of the quenching of excited metal atoms. Next, we apply this equation to calculate the avoided crossings obtained in the mercury–silane and mercury–germane reactions.

4 Results of the transition probabilities on Hg + GeH_4 and Hg + SiH_4 reactions

Now, the avoided crossing found for the PES of the Hg + XH_4 (X = Ge, Si) reaction reported by Luna-García et al. [1, 2] will be analyzed. The intermediary molecules $HHgXH_3$ formed in the point of adsorption of the potential energy curve is considered as a rigid body throughout the trajectory. We recognize that the rigid body model is not always valid when gas phase molecules approach the metal rapidly, which is not our case, because in the interaction we restricted our study to those molecules captured by the metal, thus eliminating any translational freedom.

The moment of inertia is calculated using the atomic masses of Hg (3.33×10^{-25} kg), Ge (1.21×10^{-25} kg), Si (4.66×10^{-26} kg) and H (1.67×10^{-27} kg) as the geometry of the most stable $HHgXH_3$ intermediary molecule in the Hg (^1P:$5d^{10}6s^16p^1$) + XH_4 interaction, when the main axis is located at X (Fig. 3).

This geometry corresponds to the values of the parameters reported in Tables IV and V of References [1] and [2], respectively. Figures 4 and 5 exhibit avoided crossings taking place between the potential energy curve $2^1A'$ [which comes from the Hg (^1P:$5d^{10}6s^16p^1$) + XH_4 interaction] and the potential energy curve X^1A' [the one that similarly originates from the Hg ^1S ($5d^{10}6s^2$) + XH_4 interaction]. These potential energy curves are given as a function of the angle of insertion H–Hg–X. The avoided crossing is due to the left segment of the superior curve having a $6p^1$ character and that one of the right inferior curve also having a $6p^1$ character, whereas the segment of the left inferior curve has a $6s^2$ character and that of the right superior curve also has a $6s^2$ character. From curves of Figs. 4 and 5, the calculations of the transition probabilities $2^1A' \rightarrow X^1A'$ are obtained through an avoided crossing in each case.

Nevertheless, we propose that the correct value of the moment of inertia is calculated by setting the main axis Z at the Hg metal atom. This is because previously [22–24] to fix the main axis to the metal atom has been found to give better theoretical results in comparison with experiment. The values for the new geometry and the Cartesian coordinates of the intermediary product are given in Tables 1 and 2.

Therefore, the moments of inertia are

$$I = m_{\mathrm{Ge}} r_1^2 + m_{\mathrm{H}}(r_2^2 + r_3^2 + r_4^2 + r_5^2)$$
$$= 3.65 \times 10^{-24}\,\mathrm{kg\ (a.u.)}^2 = 9.94 \times 10^{-25}\,\mathrm{kg\ Å}^2.$$

$$I = m_{\mathrm{Si}} r_1^2 + m_{\mathrm{H}}(r_2^2 + r_3^2 + r_4^2 + r_5^2)$$
$$= 1.31 \times 10^{-24}\,\mathrm{kg(a.u.)}^2 = 3.56 \times 10^{-25}\,\mathrm{kg\ Å}^2.$$

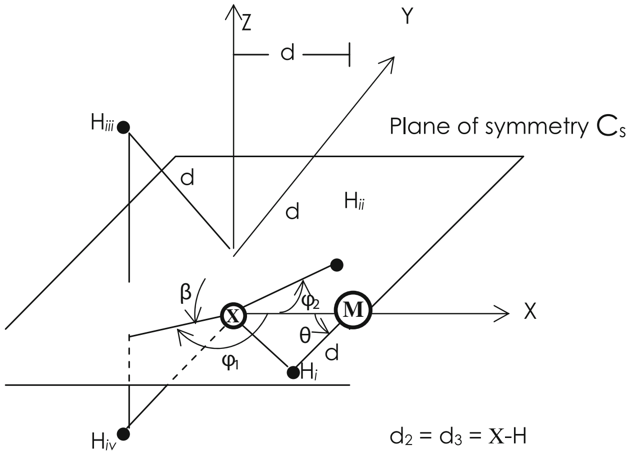

Fig. 3 Geometry configuration with the main axis located at the center X. (i) Ge–H = 1.54 Å; (ii) Si–H = 1.49 Å

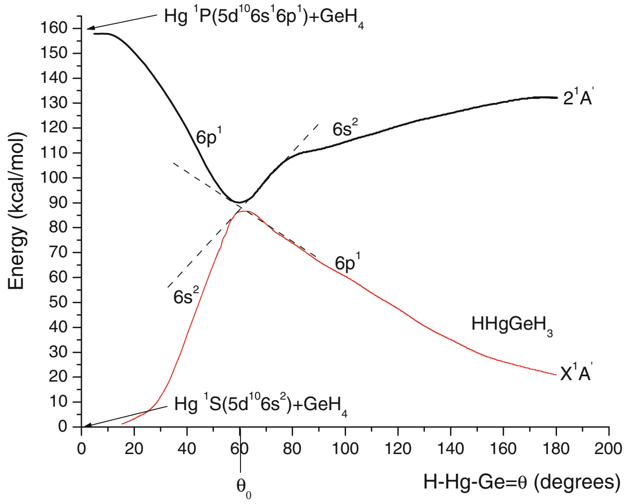

Fig. 4 Crossing of energy surfaces on the Hg + GeH_4 reaction

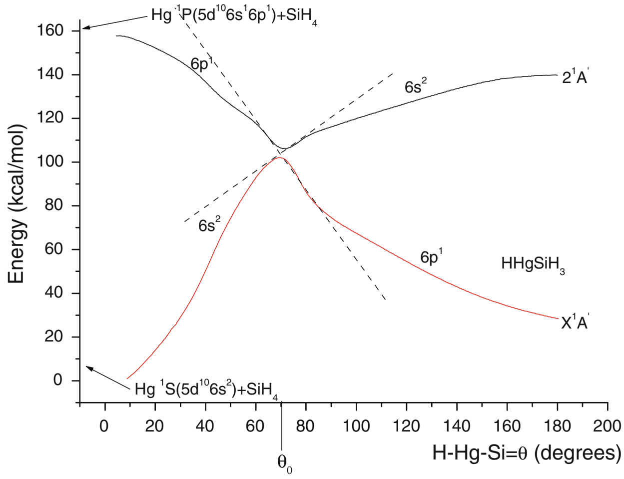

Fig. 5 Crossing of energy surfaces on the Hg + SiH_4 reaction

Table 1 New geometry (angstroms and deg) of the transition states of the X^1A' $HHgXH_3$ surfaces

Geometry	X = Ge	X = Si
d(Hg–X)	2.8	2.48
d_1(Hg–H_i)	2.55	2.15
d_2(X–H_{ii})	3.72	3.4
d_3(X–H_{iii})	3.53	3.29
θ = H_i–X–M angle	60	70
φ_2 = H_{ii}–X–M angle	138.78	136.82
φ_1 = angle	168.26	168.16
2β = H_{iii}–X–H_{iv} angle	44.30	45.08

The main axis is at the mercury atom in columns X = Ge, Si

Proceeding in this way and using the crossing straight lines (dashed lines) on Fig. 4, the calculation of the transition probability from curve $2^1A'$ to curve X^1A' in the

Table 2 Cartesian coordinates in a.u. of the intermediary product $HHgXH_3$ of the transition states of the X^1A' surfaces

Ge	X	Y	Z	$\|r\|$	Si	X	Y	Z	$\|r\|$
r_1 = Hg–Ge	−5.29	0.0	0.0	5.29	r_1	−5.29	0.0	0.0	4.69
r_2 = Hg–H_i	2.88	−4.17	0.0	5.07	r_2	2.88	−4.17	0.0	5.04
r_3 = Hg–H_{ii}	−5.29	4.63	0.0	7.03	r_3	−5.29	4.63	0.0	6.42
r_4 = Hg–H_{iii}	−6.05	−1.26	2.51	6.67	r_4	−6.05	−1.26	2.51	6.22
r_5 = Hg–H_{iv}	−6.05	−1.26	−2.51	6.67	r_5	−6.05	−1.26	−2.51	6.22

The main axis is at the mercury atom as in Fig. 1

Table 3 Transition probabilities from $2^1A'$ to X^1A' potential energy surfaces

	P	P'
Hg $^1P(5d^{10}6s^16p^1)$ + GeH_4 → Hg $^1S(5d^{10}6s^2)$ + GeH_4	$e^{-0.184} = 0.832$	0.168
Hg ^1P $(5d^{10}6s^16p^1)$ + SiH_4 → Hg ^1S $(5d^{10}6s^2)$ + SiH_4	$e^{-0.236} = 0.7897$	0.2103

numerator of the exponent in Eq. 4 is found to be: $E_1 = 87.804$, $E_2 = 87.607$; and due to Eq. 5 the following value is obtained: $\in_{12}^2 = 0.00965$. The calculation of the transition probability from curve $2^1A'$ to curve X^1A' in Fig. 5 is found when $E_1 = 104.641$, $E_2 = 104.332$; and due to Eq. 5 the following value is obtained: $\in_{12}^2 = 0.02387$. The way we found E_1 and E_2 consists on locating the crossing point $\in_{12}$ and taking the value from the superior point in the curve as E_1 and the inferior point in the curve as E_2, exactly as shown in Figs. 2 and 5.

The energy in Eq. 7 is $E = 157.143 - 87.804$ in the graph of Fig. 4, with the resultant angular velocity value $\omega = 1.181 \times 10^{13}$; and $E = 157.79 - 104.74$ in the graph of Fig. 5, with the consequent resultant angular velocity $\omega = 1.726 \times 10^{13}$.

On the other hand, directly from the graph of Fig. 4, we read the following values for the slopes of the dashed lines that mark the crossing: $s_1 = \frac{115.598-61.58}{85.741-38.272}$, $s_2 = \frac{67.277-105.58}{89.364-38.272}$, from these values we get $|s_1 - s_2| = 1.839$. And from the graph of Fig. 5, we read the following values for the slopes: $s_1 = \frac{162.219-38.617}{33.063-110.128}$, $s_2 = \frac{73.431-139.353}{32.43-112.724}$, from these values we get $|s_1 - s_2| = 2.425$. Replacing all the values, the results in Table 3 correspond to the probability of crossing from the curve $2^1A'$ to X^1A'.

The transition probability between the PES $2^1A' \rightarrow X^1A'$ has been obtained for the reaction: Hg $^1P(5d^{10}6s^16p^1)$ + XH_4 → Hg $^1S(5d^{10}6s^2)$ + XH_4. Through the avoided crossing shown in Figs. 4 and 5 the products H, $HgXH_3$, HgH y XH_3 of the reaction were obtained [1, 2]. This happens when mercury is photoexcited to the Hg (^1P:$5d^{10}6s^16p^1$) excited state, allowing the mercury atom to be inserted in germane or silane (XH_4) molecule. This effect is observed in the minimum of the curve $2^1A'$ in which the intermediate product $HHgXH_3$ is formed. When $HHgGeH_3$ continues its way, it has a probability of $P = 0.83$ of crossing toward curve X^1A' and a probability of $P = 0.17$ of continuing by the same curve $2^1A'$. When continuing in the direction of the state X^1A', the breaking of the intermediary product occurs in the minimum of the curve, consequently, we have the formation of the final products. While in case of the intermediate $HHgSiH_3$, when continuing its way has a probability $P = 0.79$ of crossing toward curve X^1A and a probability of $P = 0.21$ of continuing in the same curve $2^1A'$. When going toward the X^1A' state, it carries out the formation of the product at the minimum of the curve.

The transition probabilities must be compared with the magnitude of the branching fraction measured by means of quenching experiments of excited mercury atoms; up to now measurements have been accomplished only for triplet states of mercury [45, 46]; singlet states are still waiting for experiments. In a previous paper [7], our results of the transition probabilities among the three lowest states of the gallium–methane interaction agree with branching fractions obtained by quenching experiments.

5 Discussion

Our ab initio PSHONDO-IJKL-GMCP-FOCK-CIPSI methodology developed by Daudey [3–6] to construct the PES remain in the Born-Oppenheimer (BO) approximation, which is the previous work necessary to know about the possible transitions from the excited states to the ground state. The next step is to use such PES for calculating transition probabilities among the avoided crossings. As known, in BO the nuclear motion is supposed to be much slower than the electron motion; however, at the point of an avoided crossing the nuclear motion may not be slow enough when compared with the electronic motion due to the sudden change of nuclear conformations. In this context, the application of the BO approximation breaks up, and the electronic wave function depends of the nuclear coordinates, and in addition, of the nuclear velocities. This is one of the reasons for achieving a sequence of calculations from which finally we get a reliable potential energy curve. In practice, it is hard working to get the calculations near to the avoided crossing points. Our methodology has been successfully applied in many reactions and compared with experimental results. Examples of constructing the PES in agreement with experimental measurements of triplet states [45, 46] are the previous papers [1, 2] used in this work. In those cases presented here, our predictions on singlet states are still waiting for experimental measurements; furthermore, avoided crossings are only present in singlet states. In addition, using our methodology we got agreement between our transition probabilities and the experiment in gallium–methane reactions [7]. The actual problem deals with the theory of atom–molecule collisions, which is one of the basic fields in chemical physics [47]. As one example among many, reference [48] is about reactions of triplet states of mercury with diatomic molecules, it seems there is not experimental interest in singlet states of mercury until now.

6 Conclusions

We here report the probabilities leading to products of the $Hg + GeH_4$ and $Hg + SiH_4$ reactions, via a modified version of the Landau–Zener theory of avoided crossings for nonadiabatic transitions. The transition probabilities from a potential curve to the next one were obtained for the lowest states of mercury–germane and mercury–silane by using the Landau–Zener theory extended to permit the use of the angular reaction coordinate. In both cases, mercury–germane and mercury–silane, we obtain an avoided crossing and the transition probabilities for the avoided crossing between the surfaces $2^1A' \rightarrow 1^1X'$ are $P = 0.832$ and $P = 0.7897$, respectively. These results are predictions awaiting experimental confirmation.

Two eigenstates of a system approach very closely when the reaction parameter varies adiabatically, and afterward they mutually repel, while interchanging the character the corresponding eigenfunctions possess. If this parameter is varied with finite speed, the system passes from one state to another one without being subject to a change of character.

A graph-geometric methodology has been proposed and applied to obtain predictions of the mercury–germane and mercury–silane interactions. This methodology is based on both ab initio calculations and the Landau–Zener theory.

The Hg atom in its ground state ^1S (ns^2) is not capable of activating the SiH_4 and GeH_4 molecules spontaneously. The mercury atom in its $^1P(ns^1np^1)$ state was found responsible for either the Ge–H or Si–H bond activation and the relaxation processes involved in the formation of the $HHgGeH_3$ or $HHgSiH_3$ intermediate complex. The formation of these intermediate products takes place through an avoided crossing of the two lowest lying A' surfaces. The calculated molecular transition probabilities in these cases give certainty that the intermediate complexes can dissociate through an activation barrier toward $HgH + SiH_3$ and $H + HgSiH_3$ or $HgH + GeH_3$ and $H + HgGeH_3$ products.

It must be also stated that experiments confirm that the $^3P(ns^1np^1)$ excited state reaches the $HgH + XH_3$ (X = Si, Ge) products with no barrier to the breaking of the Si–H [45] or Ge–H [46] bonds. Nevertheless, the Hg $^3P(5d^{10}6s^16p^1) + CH_4$ reaction cannot activate the Si–H or Ge–H bond of silane or germane in matrix isolation experiments, because it presents an excited state that is forbidden by absorption through dipolar transitions by spin multiplicity. The activation of such bonds was confirmed previously by theoretical research [1, 2].

This work through nonadiabatic transitions probabilities confirms that the Hg atom in its ^1P (ns^1np^1) excited state in the presence of either silane or germane molecules in the gaseous phase leads to the formation of SiH_3 or GeH_3 radicals and H atoms. We may also see some HgH molecules, and silicide or germanide of mercury molecules as the case may be. On the other hand, experiments for the activation of SiH_4 or GeH_4 by atoms of Hg might predict the formation of the products $HHgSiH_3$ and $HHgGeH_3$, respectively. In fact, this is exactly what was obtained in experimental and theoretical studies on the $Cu + CH_4$ reactions [19, 29].

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