Multibody effects in intermolecular interactions and reaction pathways for catalytic processes. Part II the contributions of Sidonio Castillo

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We here continue the review on the work of Octavio Novaro and collaborators in the important field of nonadditivity of intermolecular interactions and catalysis, with special interest in the work that Sidonio Castillo contributed to this effort before his demise. His early work with Polish coauthors on methane and ammonia trimers and with British coauthors on N_3, P_3, N_4 and P_4 are highlighted. Then our focus will shift mainly to his work on the activation of methane, silane and germane starting with his Ph.D. thesis under O. Novaro and ending in his last papers with the present authors which marked the end of his short but brilliant career.

Keywords: Theoretical catalysis; multibody effects; nonadditivity; Sidonio Castillo´s, contributions.

Aquí continuaremos la revisión del trabajo de Octavio Novaro y sus colaboradores en los importantes campos de la no aditividad de las interacciones intermoleculares y de la catálisis, enfatizando las contribuciones de Sidonio Castillo que resultaron altamente útiles en este esfuerzo conjunto, antes de su prematuro fallecimiento. Sus primeros trabajos, con reconocidos científico polacos en los trímeros de metano y amoniaco y con coautores ingleses en trímeros y tetrámeros de fósforo y nitrógeno, serán presentados primero, seguidos de sus estudios sobre la activación catalítica de moléculas de metáno, silano y germano (de alto potencial en aplicaciones valiosas). Sus primeros trabajos en catálisis formaron parte de su tesis doctoral dirigida por O. Novaro y los últimos fueron consecuencia de las tesis doctorales que el Dr. Castillo dirigió a los otros dos coautores de esta revisión. Esta labor fue desgraciadamente interrumpida por la muerte de Sidonio. Así concluyó su corta pero brillante carrera.

Descriptores: Catálisis teórica; efectos de multicuerpos; no-aditividad; contribución de Sidonio Castillo.

PACS: 31.5. Ar; 31.25.-v; 31.50.-x

1. Introduction

This is the second part of a Review for Revista Mexicana de Física on the work developed by O. Novaro and his students on the subjects indicated in the title. Therefore the emphasis of this Part II, devoted to the contributions of Sidonio Castillo to the Mexican School of Theoretical Catalysis, is not wholly representative of each of Castillo's ideas, nor does it pretend to provide a faithful review of all of his work. For instance his papers on metal alloys will not be included here, nor others that do not involve the personal participation of the present authors. We will include about fiftee of Castillo's papers, and just as many therefore will not be included. Even those reviewed here will often be mentioned briefl , thus lacking some details. We feel however that they will invite the reader to learn more about Castillo's important work. For this journal (RMF) we will therefore produce the second chapter of this Review of the Mexican School of Theoretical Catalysis and nonadditive effects. This other important subject, nonadditivity, is discussed in Sec. 3 which will be self-contained

in the sense of being self-introductory, so we will devote this Introduction section solely to the main subject of the theses of Sidonio Castillo and his Ph.D. students: the activation of tetrahedral molecules by metal catalysts.

His interest in the activation of methane sprang from a chapter by O. Novaro [1] in a book published by the American Chemical Society. In it a preliminary explanation was given of a striking discovery [2] by another of Novaro's students, García Prieto, then in Toronto where he was occupying a post doctoral position. This discovery caught Castillo's eye and he decided to ask Novaro to guide his Ph.D. thesis on precisely this theme. They then worked together [3-4] and published a couple of papers on this subject which will be reviewed in Sec. 4.

The great interest in methane lies in the fact that it is the main component of natural gas and the most conspicuous product of the decomposition of organic matter. Its energy content is quite high, making it an ideal fuel, albeit with certain drawbacks. One is the resistance it presents to activating any of its CH bonds (the energy cost is higher than

100 kcal/mol) thus requiring the use of costly noble metal catalysts to achieve it. García-Prieto's discovery in the Lash Miller Laboratory in Toronto [2], showing that a cheap metal like copper did activate methane at temperatures of a few degrees Kelvin, fille Prof. Ozin, head of the Laboratory, with enthusiasm and encouraged him to contact the Mexican theoretical catalysis group to provide a quantum mechanical explanation, as we had done before for other of his cryogenic experiments. As for us, knowing that in Mexico natural gas is mostly found associated with the oil extracted in petroleum wells, where it is often burnt *in situ* due to problems of storage, lack of transport and others we enthusiastically accepted Ozin's invitation. The possibility of producing valuable products (*e.g.* ethylene) from methane with a low-cost catalyst like Cu was very tempting.

The main advance achieved by Ozin and García-Prieto [2] stemmed from the use of photoactivation of the copper atoms captured in methane matrices at temperatures below 10 Kelvin. As soon as light strikes Cu atoms, previously completely inactive, they attack the C-H bonds in methane with almost unbelievable efficien y. Sidonio Castillo's thesis was aimed [3,4] at explaining this spectacular effect. This will be addressed in Sec. 4, where Sidonio's study of photoactivated zinc, aimed at explaining Billup and his coworkers experiments [5] (which were also included in his Ph.D. thesis) will be reviewed [6].

Thereafter Castillo directed his own Ph.D. students, Hector Luna and Horacio Pacheco, in the study of other tetrahedral molecules such as silane and germane, and other metal photocatalysts such as cadmium, mercury and gallium (Refs. 7 and 9). When Novaro saw these theses, he suggested that avoided crossings stemming from the attractive excited states of the metal atoms as they descend due to the interactions with the molecules were crucial, implying a need to study the nonadiabatic transition probabilities.

Horacio Pacheco immediately took this suggestion and generalized the Landau-Zener theory to apply to these (M) metal-gas (X) molecule systems (with M=Cu,Zn,Cd,Ga,Hg and X=methane, silane and germane). We wrote two papers [10,11] that would be the last produced by Sidonio Castillo. All of these papers will be presented, albeit briefl , in Secs. 4 and 5.

2. Method

Over a period spanning three decades, the work of Castillo with our group has utilized a diversity of methods to attack these problems, all basically within the SCF-LCAO-MO approximation and in most cases adding extensive configuratio interaction corrections, beyond the Hartree-Fock level. The specifi programs used, however, are varied, namely GAUSSIAN including UHF procedures for the nonadditivity studies [12]. Regarding Castillo's studies on the activation of H-H and C-H bonds by metallic catalysts [3-4], use was made of a sequence of programs: PSHF [13] for the Hartree-Fock SCF calculations that help establish the minimum trajectory points

(MTP) corresponding to each of the metal-molecule states. The ground and all relevant excited states were obtained via the PSHF code [14], using relativistic effective potentials by the methods of Durand and Barthelat [15]. These calculations are then followed by multiconfigurationa (variational and perturbational) calculations (MCSF) [16] which provide the optimal set of molecular orbitals and of the integrals used in the configuratio interaction scheme. The basis set used for all of the different metals and molecules are too many to be given here; the interested reader should go to the original references [7-11].

The dynamic correlation effects are taken into account using the two-step configuratio interaction, starting from a multireference configurationa zeroth-order variational wave function, followed by second-order multireference Möller-Plesset (MPT) perturbations using the CIPSI algorithm in its two-class version [17]. Typically several hundred determinants appear in the variational configuratio interaction (CI)
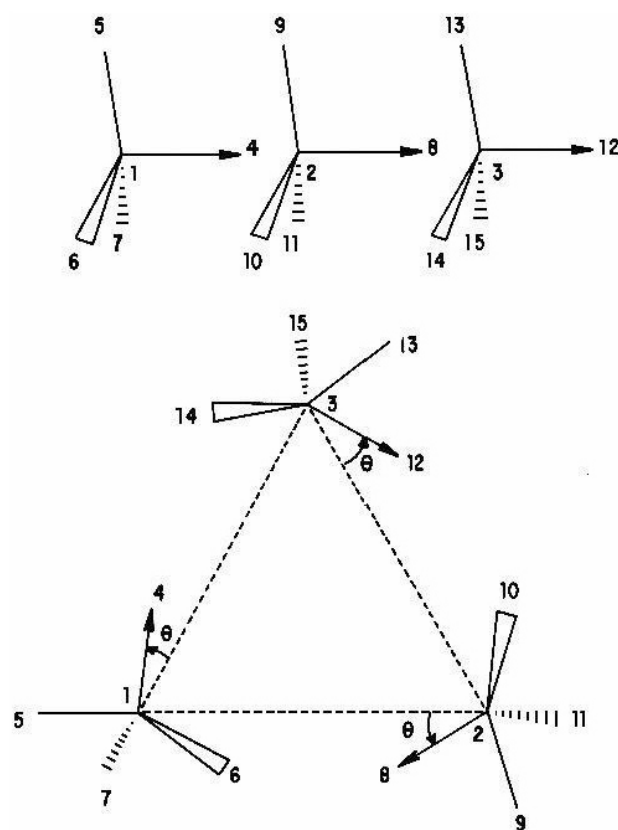

FIGURE 1. Linear and equilateral equilibrium configuration of the methane trimers as established by obtaining the three-body nonadditive corrections to the interaction energies. Notice that two C-H bonds of the CH_4 tetrahedra lie in the plane of the carbon atoms. For the linear case, a CH bond points towards a neighboring C center. Most remarkable is the equilateral case where the CH...C interaction has the proton pointing away ($\theta=14°$) from the C-C line, a measure of the inability of the tree-body attractions to overtake the pairwise repulsions. This makes methane quite similar to noble gases, a fact that may relate to the similar behavior of cryogenic CH_4 and noble gas matrices.
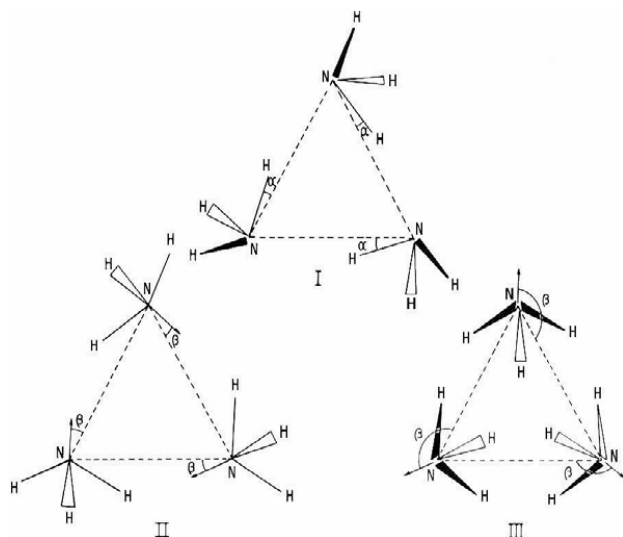
FIGURE 2. Equilibrium geometries of the cyclic ammonia trimers containing one, two or none of the N-H bonds, in the N-N-N plane, respectively. Notice that the angle α is that between the sides of the N-N-N triangle, while β is the angle between the sides of the triangle. Of the three the most stable structure is I, the one having a single N-H bond on the N-N-N plane, due to its high nonadditive attraction.

scheme, then of the order of some 50 million determinants occur in the perturbational CI scheme. Sometimes even more determinants have to be included, especially in the region where the metal catalyst induces bond weakening and new bond formation in the activated molecules.

In short the following sequence of programs is utilized: firs the PSHONDO, then the IJKL, then the GMCP, then the FOCK, and finall the CIPSI program. In the last two papers of Sidonio Castillo, a new equation developed by Pacheco-Sánchez, following a suggestion by Novaro for obtaining the transition probabilities from one excited-state interaction curve to another is used, but again the reader is kindly referred to the original papers [10,11], to learn the details.

3. Nonadditivity and the activation of hydrogen by metal atoms

The f rst collaboration of Sidonio Castillo with our group, also allowed him to meet and work with two visiting Polish scientists, W. Kolos and A. Leś. Wlodek Kolos especially had enormous renown, being the very firs scientist in the world to theoretically obtain the precise values for the energies and bonds of a real molecule, thus justifying the bold phrase of Dirac "with the establishment of modern quantum chemistry, the whole of Chemistry can in principle be solved". With them we obtained the three-body correction to the interaction energy between methane [18] and ammonia trimers [19]. Figures 1 to 3 present the optimal orientations of the bonds between these molecules. In Fig. 1, the linear and equilateral configuration of $(CH_4)_3$ trimers remind us of the same configuration of noble gas trimers and in fact their nonaddi-

tive energies are remarkably similar for methane trimers and for Ne_3 and Ar_3. This may be considered a cause for the observed [2] fact that methane matrices at near $0°K$ temperatures may replace the noble gas matrices in cryogenic photocatalitic experiments. Figures 2 and 3 represent 6 different configuration of the ammonia molecule trimers, of which the most stable ones are the cyclic configuratio I in Fig. 2 and the chain configuratio (a) in Fig. 3. These two configurations fi quite well [19] with the experimental geometries for ammonia crystals and polymers, although reasons of space preclude our giving more details of each possible configuration of these trimers (which the reader can fin in the original references [18-19]). Wlodek was quite happy with the results and Sidonio's work.

Slightly latter, another famous chemist (John N. Murrell, author of several books on nonadditivity) also visited Mexico, and we studied the nitrogen and phosphorus trimers. Some of the calculations were done by Vernon Saunders in Great Britain, but the bulk of the work was done here by Castillo [20]. Our British visitor was very impressed by the
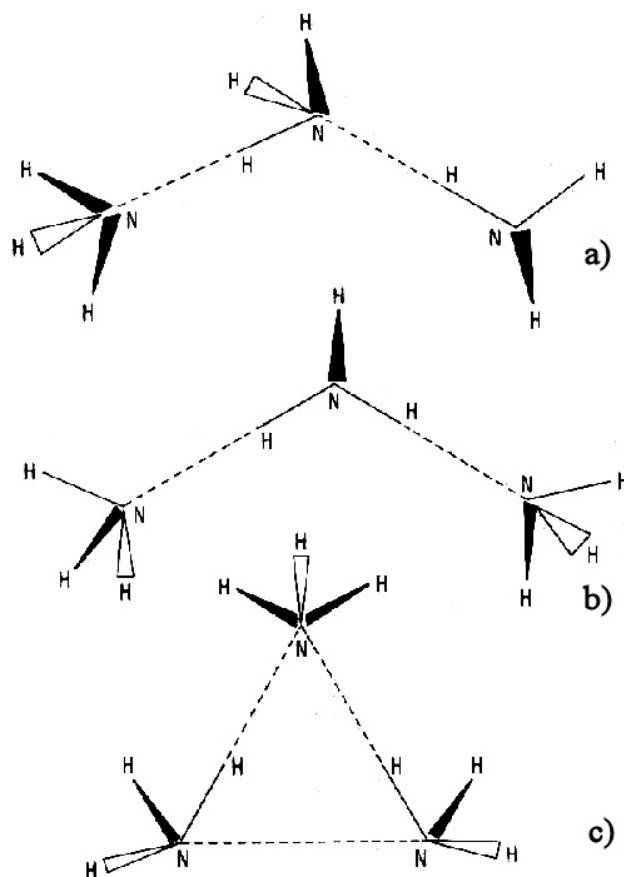

FIGURE 3. Equilibrium geometries of the chain (a), double donor (b) and double acceptor (c) configuration of the ammonia trimer. Notably the separations are virtually identical to those of the ammonia crystal. The chain configuratio (a) is the most stable one with a 5-6 Kcal/mol binding energy. This and I, the cyclic config uration of Fig. 2, actually coincide with the experimentally known geometries of ammonia polymers.
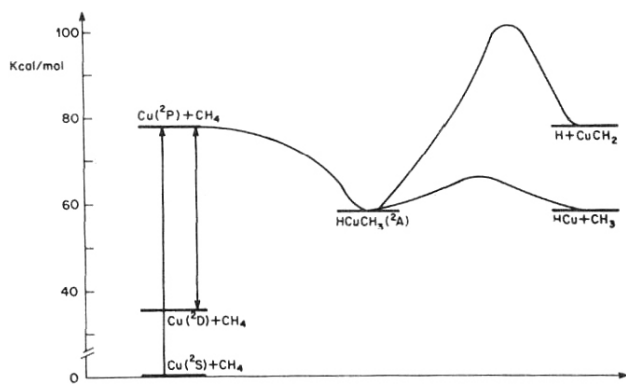
FIGURE 4. Potential energy curves for the attack of photoexcited copper, captured in a cryogenic matrix of frozen methane, onto one of the CH_4 molecules. The intermediate complex H Cu CH$_3$ is subject to a second photon to reach the fina products: H+CuCH$_3$ or HCu+CH$_3$.
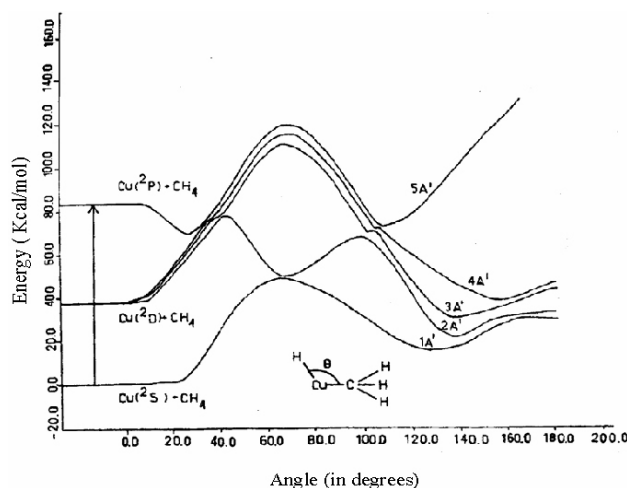

FIGURE 5. Insertion mechanism of the three lowest states of the Cu atom (^{2}S, ^{2}P and ^{2}D) into a C-H bond of methane.

latter's work in showing that N_3 was linear, while P_3 was a quasi-equilateral triangle [20], and even more so when he received, back in Brighton, a copy of another paper by us on the phosphorus tetramers, which were tetrahedral, while N_4 was proven to be unstable [21]. John Murrell was very impressed with our pioneering calculations, especially because they supported his qualitative speculation of a Jahn-Teller instability on these systems in one of his books [22]. He insisted that Sidonio Castillo should go to Sussex University to work with him, but this being a very early stage in his career we decided against his going either to England or to Poland. There would always be time, we thought... alas it was not to be.

Later Castillo joined our studies on the activation of the internal bond of the H_2 molecule using several metals: nickel, platinum, rhodium and ruthenium [23]. The two younger members of the team became particularly interested in ruthenium; Castillo helped me solve a practical question, the control of this metal to avoid its volatilization [24], which led to a new patent which attempted to replace the three-way catalyst

still used in the auto industry, and to Colmenares' findin a path to his Ph.D. thesis [25]. The latter led to what I consider one of the major discoveries of the Mexican school of theoretical catalysis, which was recently published in *Foundations of Chemistry* [26], which postulates that the most active metals involved in the catalytic phenomenon, do so through their closed d-shell (or maximal-occupancy d-shell), thus establishing a new chemical paradigm: the closed s- and p-shells are chemically inactive (case of the rare gases), but closed d-shells in contrast have a maximal catalytic activity. Following a different route from Colmenares, Castillo estimated that the patent [27] that would derive from [24] would not be appreciated- he was absolutely right, by the way - and set out to defin another path towards his Ph.D. His choice was brilliant: he began studies on the catalytic activation of tetrahedral molecules, methane, silane and germane. This will be reviewed in the following section.

4. Activation of methane, silane and germane

As mentioned in the Introduction, the experiments carried out by Jaime García-Prieto in the Lash Miller Lab of the University of Toronto [2] (which were considered by the Institute for Science Information in Current Contents as the technologically most promising discovery of the year 1985) were the main inspiration for the theoretical studies in Castillo's Ph.D. thesis [3,4]. He aimed at solving the following questions: how understand the reaction mechanism and the determination of the electronic and geometrical factors that govern the C-H bond activation at the copper sites, highlighting the participation of the electronic states of the reactants, then of the intermediates and finall of the reaction products. We determined precisely the activation barriers (which it must be said become almost nil after the photoactivation shown in Fig. 4 (from Ref. 1), and also the participation of the σ and σ* orbitals of the C-H bond attacked by the photoactivated Cu atom through its own orbitals and finall the nature of the metal catalytic site, the charge-transfer mechanisms and the geometry associated with the intermediate complexes and of course of the fina products. This is partially depicted in Fig. 5 (see Ref. 4) which explains the original inactivity of the copper atoms contained in the methane matrix (notice the high barrier for the Cu(^{2}S') atom attack on methane). After photoactivation up to the Cu(^{2}P) state, an evident attraction of methane occurs and the potential energy curve drops steeply until it encounters an avoided crossing with the firs excited state ^{2}D, which was originally nonbonding, but now forced by the curves' repulsion to descend until a second avoided crossing with the repulsive ^{2}S ground state of copper occurs. This bends the ground state curve, which then begins its own descent. This was the original explanation by Novaro in the chapter of his book [1] on the striking experimental finding of García-Prieto [2]. He explained that after photoactivation of Cu, a successful attack on the methane was inevitable, whether the Cu stayed in its excited state ^{2}P descending towards the two avoided crossings where non-adiabatic transi-

tions would lead to the products, or decayed to the ^{2}D intermediate state with a negligible barrier that would also allow an easy methane capture by copper. Even if state ^{2}P decayed, by emitting a photon, towards the ground state ^{2}S with its high barrier, the conversion of the original luminous energy used to excite Cu would become a purely kinetic energy of this atom, as can be seen in Fig. 5; there is obviously enough energy to surpass the activation barrier depicted there (see Refs. 3 and 4).

The last part of Castillo's Ph.D. thesis contains the activation of methane by photoexcited zinc atoms [6], aimed at explaining the experiments of Billup *et al.* [5]. For the theoretical explanations, the lowest three states of Zn (^{1}S, ^{3}P y ^{1}P) were studied. Calculations were carried out to obtain the reaction pathways towards the products, making it possible to establish the thermodynamics involved, as well as the
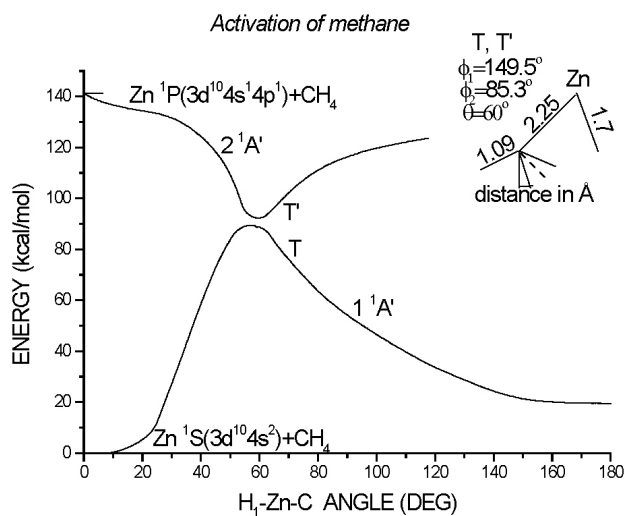
FIGURE 8. Slope lines of the energies corresponding to the avoided crossings between the three lowest states of Ga+CH$_4$. The nonadiabatic transition probability between the 3 ^{2}A'→2 ^{2}A' curves takes the value: P=e$^{-0.34}$=0.715 (see Ref. 10), a rather high "jump" probability, which fit quite well with experimental quenching data [28,29].

FIGURE 6. Insertion mechanism of the two lowest states of the Zn atom (^{1}S and ^{1}P) into a C-H bond of methane, to reach the HZnCH$_3$.
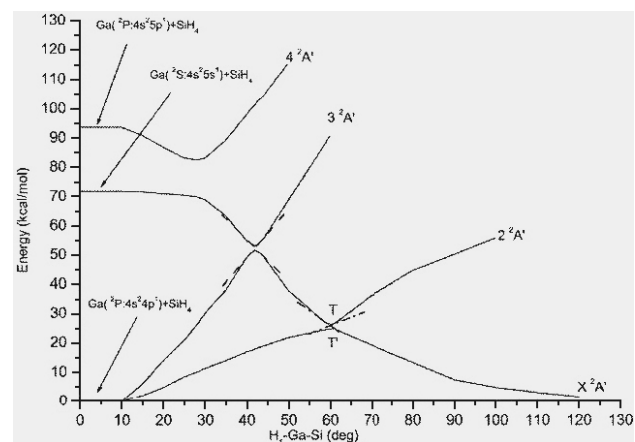
FIGURE 9. Slope lines shown at each avoided crossing of the Ga+SiH$_4$ reaction. The nonadiabatic transition probability 3 ^{2}A'→2 ^{2}A' is: P=0.701. On the other hand the corresponding probability to the 2 ^{2}A'→X ^{2}A' is: P=0.685. Unfortunately no quenching data for the gallium-silane reaction yet exist, so our predictions await experimental confirmation

geometrical and electronic configurationa aspects of the ground and lowest excited states of Zn. They are represented in Fig. 6 where the ground state Zn(^{1}S) presents a high activation barrier, while the second excited state (^{1}P) is attractive from the outset until these states collide at the avoided crossing region (the firs excited state ^{3}P is of a different symmetry and does not mix in this curve repulsion situation). The high barrier of the ground state ($\sim$85 kcal/mol, see Fig. 6), is easily overcome because the photoexciting energy of over 140 kcal/mol will convert to kinetic energy of the ground state Zn as it attacks the methane. If the atom remains in its ^{1}P state, activation of the methane will still occur by means of
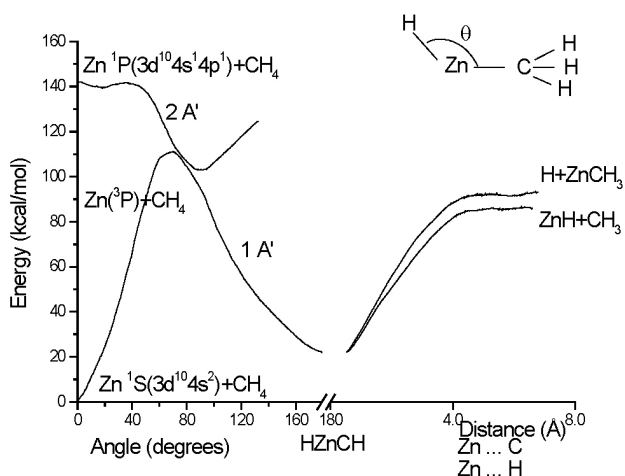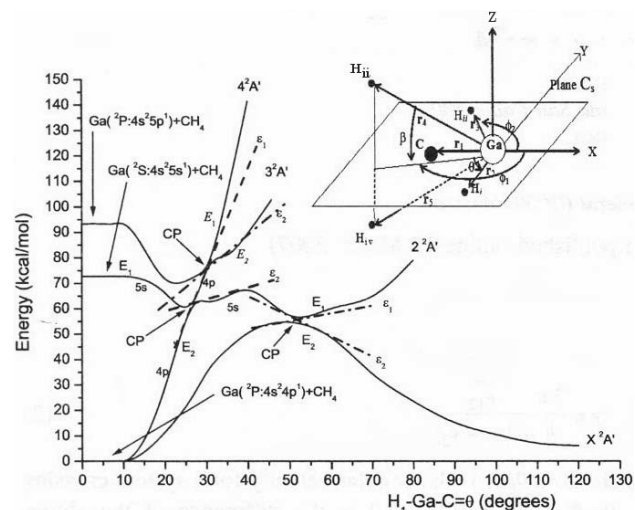
FIGURE 7. Potential energy curves of the interaction of Zn(^{1}S) and Zn(^{1}P) with methane, *i.e.* the complete reaction coordinate leading to the products.

a non-adiabatic transition at the avoided crossing, as we shall show in the following section. The main result is that both intermediate structures $ZnCH_3$ and ZnH are reached easily after the zinc photoactivation, albeit with a slightly higher probability for the latter, as shown in Fig. 7. The whole reaction coordinate of Zn with methane, leading to the $ZnCH_3$+H and ZnH+CH_3 products, is depicted.

Sidonio Castillo continued this line of research with his students. Hector Luna-García studied metal reactions with silane and germane [7] in his Ph.D. thesis, and Horacio Pacheco [8,9] the photoactivation of methane and silane by gallium. Figure 8 represents the interaction of the ground state of $Ga(^2P:4s^24p^1)$ and the firs two excited states of $Ga(^2S:4s^25s^1)$ and $(^2P:4s^25p^1)$ respectively, with methane Ref. 8. In Fig. 9 we see that the firs excited state $(^2S:4s^25s^1)$ of gallium inserts into and eventually breaks a Si-H bond in silane, after the photoactivation of the ground state with a photon with an energy E=hυ ~72 kcal/mol, enough to overcome a ground-state barrier of around 49 kcal/mol. This leads to an intermediate molecule $HGaSiH_3$ which then breaks, evolving to the fina products $GaSi_3$+H and HGa+SiH_3; all of this is well documented in Ref. 9. All in all, Castillo led his Ph.D. students, coauthors of this review, into this particular line of research of the Mexican School of catalysis founded by the lead coauthor. All three of us deeply appreciate Sidonio's contributions to our collective work and will miss him dearly.

5. The final works of Sidonio Castillo with our group

When Novaro read the material of the Ph.D. thesis of Horacio Pacheco, especially the curves represented in Figs. 6 and 7, just depicted at the end of the previous section, he could not help but notice the odd shapes of the reaction coordinate curves. He told Horacio that they apparently were overlooking symmetry avoided crossings, as shown in Fig. 9. The whole reaction coordinate of Ga with methane, leading

to the $GaCH_3$+H and GaH+CH_3 products, is depicted crossings that were the real cause of the efficien reaction. This meant that the calculation of the nonadiabatic transition from the upper to the lower curves had to be obtained. Horacio got to add a comment about this possibility in his thesis, but only after obtaining his Ph.D. did he devote his time to developing an interesting modificatio of the Landau-Zener theory of nonadiabatic transitions adapted to the special geometries involved in the activation of tetrahedral molecules like methane, silane and germane by metal atoms in cryogenic conditions, aided by photoactivation. This was reported and applied to the Ga reactions from his thesis. We have depicted these avoided crossings in Fig. 8 for Ga + CH_4 and Fig. 9 for Ga + SiH_4 taken from references [10,11]. Clearly the correct explanation of the photoactivation of Zn, Cu and Ga of these tetrahedral molecules is finall achieved by the same mechanism originally advanced by Novaro in the chapter of his book from 20 years ago. These were in fact the main conclusions of Sidonio Castillo posthumous work [10,11]: the nonadiabatic transition probability between 3A'$\rightarrow$ 2A' is 0.715, well within the range of the experimental quenching data [28,29] for the gallium-methane reaction. For the case of silane we predicted two nonadiabatic transition values: 0.701 for the probability of transition between the firs two excited states and 0.685 for the transition to the ground state. These last two results still await experimental confirmation

6. Final remarks

Sidonio Castillo always told his collaborators that a potential energy surface for any state may be sketched using Wigner's theory. His former students feel an obligation to follow this profound suggestion, which is a useful example of the theory of molecular collisions at slow velocities utilizing transition probability calculations for transitions between excited states. This will be of value for our future work in these metal-molecule reactions.

∗ Member of El Colegio Nacional.

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