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An *ab initio* study of platinum hydrogen interaction

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Potential energy surfaces of the ground state $^3D(5d^96s^1)$ and the first excited state $^1S(5d^{10})$ of the Pt-H_2 interaction are calculated by using variational and perturbative MRCI and pseudopotential relativistic methodologies in order to obtain the distances and the energies of adsorption. Reaction mechanisms between Pt and H_2 are established. Hydrogen H_2 and oxygen O_2 are the fuels used in a commercial fuel cell, where the proper mechanism of hydrogen storage is actually a process that is complicated to find. Thus, theoretical calculations can be very useful in these designs. The potential energy surfaces involved in these processes are obtained, and the probability of transition between them is obtained by means of Landau-Zener Theory. Futhermore, the physisorption of the hydrogen molecule H_2 on platinum Pt metal atom, and the chemisorption of the two hydrogen atoms on Pt are obtained and explained.

Keywords: Nonadiabatic transition probability; avoided crossing; hydrogen chemisorpton; hydrogen physisorption.

Se calculan superficies de energía potencial del estado base $^3D(5D^96s^1)$ y del primer estado excitado $^1S(5d^{10})$ de la interacción Pt-H_2 usando metodologías MRCI variacionales y perturbativas, junto con el uso de seudopotenciales relativistas, para obtener las energías de adsorción. Se establecen mecanismos de reacción. Los combustibles hidrógeno H_2 y oxígeno O_2 son directamente usados en una celda de combustible, donde el mecanismo adecuado de almacenamiento de hidrógeno realmente es un proceso bastante complicado de encontrar. Entonces, cálculos téoricos pueden ser muy útiles en estos diseños. Se obtienen las superficies de energía potencial involucradas en estos procesos, y la probabilidad de transición entre ellas es obtenida por medio de la Teoría de Landau-Zener. Además, la fisisorción de la molécula de hidrógeno H_2 sobre un átomo metálico de platino Pt, y la quimisorción de los dos átomos de hidrógeno en Pt son obtenidas y explicadas.

Descriptores: Probabilidad de transición no-adiabatica; cruce evitado; quimisorción de hidrógeno; fisisorción de hidrógeno.

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1. Introduction

The electronic features and the reactivity of metal transition clusters have been widely investigated [1-9]. Theoretical studies of the interaction of platinum with hydrogen and small clusters of platinum-metal with hydrogen provide information such as adsorption and desorption [10], which might be useful for experimental hydrogen chemisorption studies [11-27]. Detailed investigations of the interaction between platinum and platinum clusters with hydrogen can contribute to the design of useful hydrogen storage devices propitious for fuel cells. Hydrogen chemisorption is achieved on the metallic Pt surface and it has very localized features. In the case that hydrogen is chemisorbed on platinum, a real bond between Pt and atomic H is formed, *i.e.* two electrons are located in a bonding orbital between Pt and H or H_2. In the case that hydrogen is molecularly physisorbed, the interaction between Pt and molecular H_2 is electrostatic, *i.e.* no electrons are shared in a Pt-H bond and no dissociation takes place.

One of the first *ab initio* theoretical studies with relativistic corrections and electronic correlation of the interaction of one hydrogen molecule with an atom of platinum was developed by Poulain *et al.* [4], within the group of research and development led by Novaro. They postulated that the singlet excited electronic state $^1S(d^{10})$ of Pt closed shell is responsible for H_2 capture. This state is correlated to the closed shell $^1A_1$ molecular state of the Pt-H_2 system. Recently, Novaro [28] reported the activity of closed d-shells in noble metal atoms, proposing more generally that closed d-shells are responsible for a good catalyst, which before it can chemisorb and activate a molecule, must physisorb it efficiently. More details of physisorption and chemisorption in agreement with the proposal of Novaro will be explained throughout this paper. The electronic mechanism for hydrogen added to the Pt atom in this system is essentially the same as for small clusters of platinum atom.

Reaction mechanisms between the Pt metal atom and one of the fuels (H_2) were found by means of DFT-B3LYP calculation [7], which represents a bridge bond between the theoretical calculations and the processes of fuel transformation in the fuel cells. The closed shell energies involved in the process were obtained, starting when the platinum and the hydrogen are completely separated and ending until the hydrogen atoms separate and remain bound to platinum, thus forming a new product. The equilibrium geometry of the latter system was reached at an HPtH angle of about 82.764°

for a broken H-H bond. The latter was obtained using the DFT-B3LYP method.

The reason we need to calculate over and over the Pt-H_2 interaction thus studied is that we need to understand more clearly the most possible part of its reaction mechanisms. This is pursued with the intention to design fuel cells, as we have been to do trying recently [7,29]. *Ab initio* theoretical calculations provide slightly more useful information for designing processes of fuel transformation in the fuel cells than DFT calculations. For example, the DFT calculations carried out in a previous paper [7] only give a range 2.5-3.5 Å of activation distances by means of Mulliken population calculations, and a range 2-3 Å also by means of HOMO-LUMO calculations. This is due to the limitations of DFT methodology, one of them being its limited ability to calculate excited states. The best result calculated in Ref. 7 for the activation distance is 1.97 Å, and it was obtained by means of Moller Plesset *ab initio* calculations, a result which is very close to the 2.05 Å value proposed by Nakatsuji *et al.* [10]. This distance is observed in Fig. 8d of Ref. 7, where a bond between the hydrogen atoms is still present instead of the expected molecule, very similar geometrically to a water molecule.

Physisorption and chemisorption energies are calculated in this paper, and will be compared with theoretical and experimental data.

2. Methodology

The energy surface is determined by means of *ab initio* Hartree Fock self-consistent field (HF-SCF) calculations [30] with configuration interaction (CI). Calculations at the *ab initio* level were also carried out, where the electrons were taken into account by means of the use of an effective core potential [31]. The contribution of the energy of dynamic electronic correlation is obtained by means of interaction calculations of multireferential configurations using variational and perturbative levels. The latter is of the second order in the Moller-Plesset (MP2) scheme through an iterative algorithm CIPSI in its second version [32].

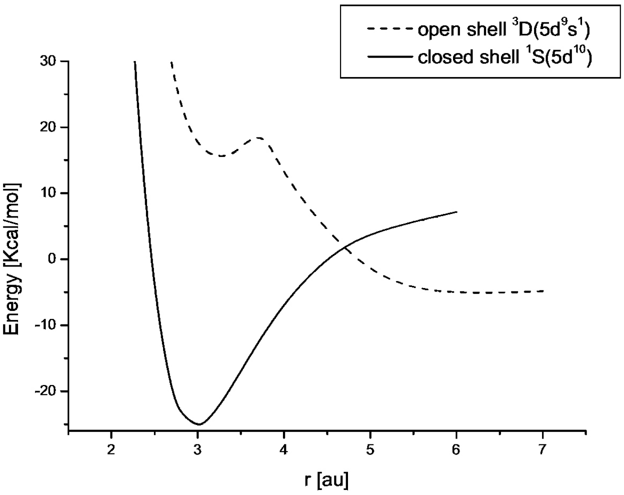

FIGURE 1. The crossing point is located at 1.85 kcal/mol and at 4.7 au, while the minimum of the well potential is located at –25.03 kcal/mol and at 3.00 au.

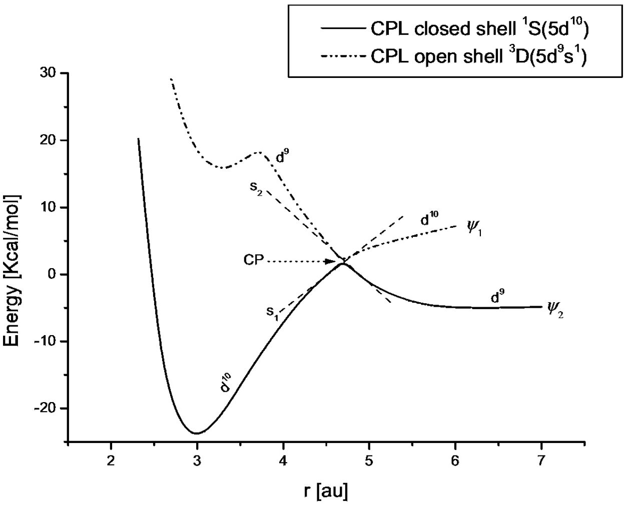

FIGURE 2. Avoided crossing illustrating the values at the end of the dashed lines and at the crossing point (CP). CPL means left side of the crossing point.

In order to describe the valence electrons of the platinum atom, a (3s, 1p, 4d) Gaussian basis contracted to (2s, 1p, 3d) was used where the p function refers to polarization. The hydrogen atoms were treated by using a (5s, 1p) basis set contracted to (3s, 1p). This is to say, for hydrogen atoms the Van Duijneveldt [33] (5s/3s) set plus a p polarization function with an optimum exponent of 0.68 were used. These bases are the same used in some previous studies [4-7].

The main equation obtained by Landau-Zener Theory is the nonadiabatic transition probability

$$P = e^{-\frac{4\pi^2 \epsilon_{12}^2}{hv|s_1 - s_2|}}$$

where h is the Planck constant, v is the velocity of the intermediary product, s_1 and s_2 are the slopes at the avoided crossing, and $\epsilon_{12} = \epsilon_{12}\,(r_0)$ where

$$\epsilon_{12}\,(r_0) = \frac{E_1\,(r_0) - E_2\,(r_0)}{2},$$

where r_0 is the distance at the crossing point and $E_1 \; and$ E_2 are the energies above and below the crossing point r_0 at the corresponding wave function ψ_1 and ψ_2 respectively, as shown in Fig. 2.

3. Results

The platinum atom is placed at the origin of the geometry, and the two hydrogen atoms are located one as a reflection of the other with a separation of 1.41 au between them. This indicates that a plane passes perpendicularly between the middle of the line that unites the two hydrogen atoms and also passes through the center of the platinum atom, which corresponds to the plane of symmetry C_{2v}. Taking the geometry already mentioned and using *ab initio* calculations with the coupled programs PSHONDO-IJKL-FOK-CIPSI in C^{nv} symmetry,

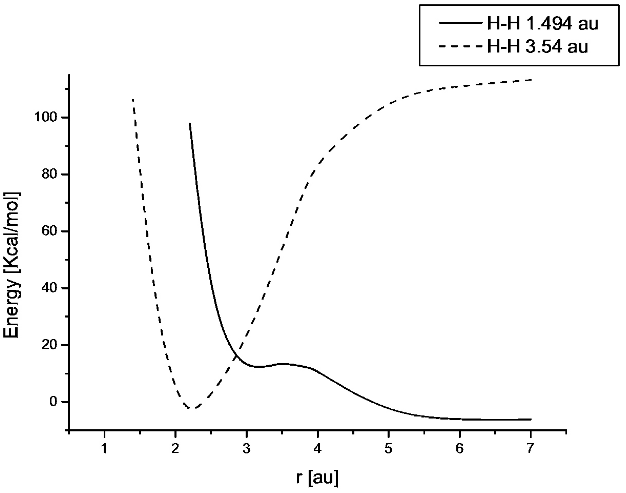

FIGURE 3. Two curves of potential energy calculated from the ground state ^{3}D(5d^{9}s^{1}), the gray line at 1.494 au and the black line at 3.54 au separation distances of the hydrogen atoms. The crossing point is located at 15.91 kcal/mol and at -2.87 au, while the minimum of the well potential is located at -1.93 kcal/mol and at 2.24 au.

a relative binding energy of –25.03 kcal/mol to a distance of 3 (au) for ^{1}S(5d^{10}) closed shell state was obtained. Thus, the adsorption process is given by the whole well of potential energy exhibited in the graph of Fig. 1 and corresponds to the attraction effect. The repulsive effect corresponds to the ground state ^{3}D(5d^{9}s^{1}) open shell in Fig. 1, and exhibits a small barrier located at 3.7 au, indicating a possible avoided crossing at this peak. These potential curves were calculated for an improvement of 200-450 determinants.

After these calculations, it can be stated that the singlet excited electronic state ^{1}S(5d^{10}) of the Pt closed shell is responsible for H_2 capture. The adsorption process in the well of potential corresponds to a physisorption where the two hydrogen atoms still form a hydrogen molecule. The state ^{1}S(5d$_{10}$) is correlated to the molecular state of closed shell ^{1}A$_{1}$ of the Pt-H_2 system. The calculations here were carried out by improving the number of determinants; however, in Ref. 7, no improvement was made. It should be mentioned first that the energy at the crossing point 0.08 eV (1.85 kcal/mol) is near the anti-bonding state 0.3 eV for hydrogen strongly adsorbed on Pt; and second, the energy from the crossing point to the minimum point in the well of potential is 26.88 Kcal/mol, which matches very well with the quenching experimental value 26.52 Kcal/mol (1.15 eV) measured by Emrick [34]. Furthermore, the distance 4.7 au (2.487 Å) at the crossing point is comparable with the experimental 2.07 Å value of the hydrogen dissociation. Thus, the crossing point corresponds to the chemisoption process of the reaction Pt-H_2.

On a close approach, two potential curves of states with the same properties of symmetry and spin (known as states of the same species) intersect. Nevertheless, in agreement with the noncrossing rule between two very close curves [35], such an intersection is avoided when a great approach between such curves exists. Thus, the crossing point in Fig. 1 corresponds to an avoided crossing as shown in Fig. 2, where the character changes from d^{9} on the left side to d^{10} on the right side of the crossing point for the wave function ψ_1, and the character changes from d^{10} to d^{9} after the crossing point in ψ_2, similar to the Landau-Zener (L-Z) theory.

The nonadiabatic transition probability at the avoided crossing can be obtained from the L-Z theory by taking r as the reaction parameter. The rotational energy is irrelevant in this case, and so the energy of the system is given by $E = (1/2)mv^2$. Thus, the velocity is obtained by choosing $E = 28.09$ kcal/mol. The slopes $s_1 = 9.94$ and $s_2 = -11.69$, and the difference of energies at the crossing point $\epsilon_{12} = 0.127$ were obtained by reading values from the graph in Fig. 2. Then, taking the mass of the intermediary product HPtH $m_{HPtH} = 3.27 \times 10^{-25} Kgr$, the probability of transition from state d^{9} in ψ_1 to state d^{9} in ψ_2 in this case is $P = e^{-0.023}$, so $P = 0.977$.

As the reaction proceeds, the two curves of potential energy shown in Fig. 3 were calculated one at 3.54 au H-H distance, and the other at 1.494 au near the H-H equilibrium distance. The crossing point located at 15.91 Kcal/mol and 2.87 au as shown in the graph of Fig. 3 reveals the dissociation process of the hydrogen molecule into two hydrogen atoms. The energy from the crossing point to the minimum point in the well of potential is 17.84 Kcal/mol agrees with the fact that in this dissociating process the Pt atom prefers the d^{9}s^{1} configurations by 17.5 Kcal/mol, to the d^{10} configuration [7,36]. The distance 2.87 au (1.519 Å) agrees very well with the experimental Pt-H bond value [4,37]. The reaction Pt-H_2 leading to the product HPtH corresponds to a chemisorption process for hydrogen atoms on Pt, and this product looks geometrically like a water molecule.

In the case of Fig. 3, the well of potential corresponds to a physisorption of every hydrogen atom on the Pt atom. And the crossing point does not corresponds to an avoided crossing because both curves were calculated at the same ground state ^{3}D(5d^{9}s^{1}) by fixing a different distance between the two hydrogen atoms for each curve.

4. Conclusion

The singlet excited electronic state ^{1}S(5d^{10}) of Pt closed shell is responsible for H_2 capture (physisorption), and the triplet ground state ^{3}D(5d^{9}s^{1}) is responsible of the dissociation for the hydrogen molecule (chemisorption). The ^{1}S(5d^{10}) state is correlated to the molecular state of closed shell ^{1}A$_{1}$ of the Pt-H_2 system, and the ^{3}D(5d^{9}s^{1}) state is correlated to the open shell ^{1}A$_{1}$ of the Pt-H_2 reaction.

There is a transition from state d^{9} in the wave function ψ_1 to state d^{9} in the wave function ψ_2, calculated through the crossing point as an avoided crossing using the Landau-Zener Theory. The probability of transition is 0.9768.

The crossing point obtained at the same ground state ^{3}D(5d^{9}s^{1}) drawn in Fig. 3 agrees very well with the experimental data.

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