

Computational Reaction Design (CRD): Controlling the Dynamics of Hydrogen-Surface Reactions, A Case Study

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1. Introduction

Hydrogen is probably the most important of all elements, both for its abundance in the universe and for its theoretical interest¹⁾. It is the only stable neutral two-body system, and its energy levels can be calculated with accuracy far higher than for any other element (currently of the order of 10^{-11} cm⁻¹). In addition, atomic hydrogen possesses a rich spectrum of resonances ranging from the radio to the ultraviolet frequency. Thus, serving as a fertile ground for experimentalists. Several of its absorption frequencies are particularly sharp, and thus very suitable for metrology. For these reasons, hydrogen has played a central role in the development of modern physics. With hydrogen, one could, by performing measurements of its energy level separations, make precise tests of current theories.

The understanding of how hydrogen interacts with different materials is also of broad interest. From a technological point-of-view^{2,4)}, the interactions of hydrogen with solids are influential in a number of industrial processes, and, in energy and power systems. An outstanding technological problem concerns the degradation in the mechanical, electrical, and magnetic properties of these materials upon interaction with hydrogen^{5,6)}. From an environmental point-of-view, hydrogen has also been attracting a lot of attention, esp., with recent growing concern for the environment. With WATER as the only EMISSION from hydrogen combustion, hydrogen is being promoted as the POWER SOURCE of the future. In order to support this developing hydrogen economy⁷⁾, infrastructures have to be built. Development of efficient processes for hydrogen extraction, and efficient processes and materials for hydrogen storage⁸⁾ would also be necessary. Thus, from an economics point-of-view, the transition to an economy based on hydrogen (energy) could, in the long run, also serve as key to solving the problems we are currently facing. From an academic point-of-view, hydrogen is the simplest possible adsorbate. Thus, an understanding of how hydrogen behaves, when it approaches and subsequently comes into contact with some surface, should give us the most fundamental view of gas-surface interaction.

2. What do we know about Hydrogen-Surface Reactions?

The understanding of how hydrogen interacts with surfaces entails an atomic level understanding of fundamental principles (elementary processes) underlying, among others, the bond-making and bond-breaking at surfaces⁹⁾. Questions, such as—Which physical factors (degrees-of-freedom: DOF) most affect the outcome of a reaction?—, have to be answered. Our current understanding has gained significantly from systematic experimental and theoretical studies on such benchmark systems as the interaction of hydrogen with metal surfaces. For the rest of this contribution, we will pay particular attention to the inherent feature of H₂ (D₂)–solid surface reactions (and, in general, any reaction) to be strongly orientation-dependent¹⁰⁾.

The orientation of a molecule¹¹⁾ during its interaction with the surface determines the ground-state energy of the molecule-surface electron system, which, in turn, serves as the effective/relevant potential energy (hyper-) surface (PES) that determines the dynamics of the molecule-surface reaction. One consequence of this strong orientation dependence is the

concept of *steering*¹⁰. *Steering* pertains to the dynamical reorientation of the impinging molecule, with respect to the surface components, in an attempt to follow the *path of least resistance*, i.e., to assume an orientation with the least potential. We could also say that this pertains to the capability of the orientation-sensitive PES to reorient the molecule from an initially *unfavorable* orientation to a *favorable* one, or vice-versa. By taking into account *steering* (which allows for the dynamical reorientation¹⁰ of the impinging H₂ (D₂) to a more favorable orientation, thus enabling it to undergo some desired reaction, e.g., dissociation on Cu(111)), one could explain the non-monotonic initial rotational state dependence of the H₂ (D₂) dissociation dynamics on solid surfaces (e.g., Cu(111))^{10,12-18}. It has been shown that *steering* is a general feature/concept that is present regardless of whether the system is activated or not¹⁹. Its efficacy, however, strongly depends on the translational energy of the impinging H₂ (D₂)^{20,21}. It was demonstrated later on how the concept of *steering* could also explain the non-monotonic initial translational energy dependence of H₂ dissociation on Pd(100)²². Another feature of the H₂ (D₂)–solid surface reaction, which can also be inferred from its inherently strong dependence on the H₂ (D₂) orientation, is the possibility of dynamically filtering²³⁻²⁵ H₂ (D₂), so that we get rotating H₂ (D₂) whose rotational axes are at particular orientations with respect to the surface. Thus, in principle, it would be possible to prepare H₂ (D₂) such that we can have a beam of molecules all doing helicopter-like or cartwheel-like rotations.

3. Controlling the Dynamics of Hydrogen-Surface Reactions—Probing Local Surface Reactivity with H₂ (D₂)

From the discussions above, one could immediately infer that H₂ (D₂) is very sensitive to even the slightest variations in the *local* properties of the surface. To verify this, we have recently investigated^{26,27} the interaction of H₂ with two different alloy surfaces, viz., Cu₃Pt(111) (which was observed to have no barrier for the dissociative adsorption of H₂^{28,29}) and NiAl(110) (which was observed to have an H₂ dissociative adsorption barrier^{30,31}). In particular, we considered the dynamics of H₂ scattering along Cu₃Pt(111)[1 $\bar{2}$ 1] and along NiAl(110)[1 $\bar{1}$ 0], and compared them with the corresponding H₂ scattering dynamics on single component surfaces, viz., Cu(001)[100]³²⁻³⁴ and Ni(110)[1 $\bar{1}$ 0]^{32,35}. Based on the calculation results obtained, we found that the H₂ (D₂) does actually know whether it is dealing with a single component solid surface or a multi-component (in this case, a two-component) solid surface, and the discernible (by H₂ (D₂)) differences between the different sites eventually turn up as measurable/observable transitions in the internal states of the scattered H₂ (D₂)^{26,27}.

To continue with our task of answering the question—*Can we and how do we control the dynamics of hydrogen molecules in surface reactions?*³⁶—, and consider the feasibility of exploring the sensitivity of H₂ (D₂)–solid surface reaction to the *local features* of the surface to realize the control of H₂ (D₂) dynamics, and possibly the use of H₂ (D₂) as probes that will provide us with information regarding various interesting processes occurring at surfaces (e.g., adsorbate-surface interaction and *local/site-specific* surface reactivity, the salient features of the corresponding effective PES, and the surface structure), we consider and compare the dynamics of an H₂ impinging along Cu₃Pt(111)[1 $\bar{2}$ 1] and NiAl(110)[1 $\bar{1}$ 0]. By varying the angle of incidence θ of the impinging H₂, with respect to the surface normal, we investigate how (and whether or not) the dissociative adsorption/sticking probability *vs.* incidence translational energy (*S vs. E_t*) profile correspondingly changes.

Cu₃Pt and NiAl are examples of binary alloys consisting of metals *A* and *B*, where *A* is some metal on whose surface H₂ dissociation is activated (e.g., Al, Cu, Ag, and Au), and *B* is some metal on whose surface H₂ dissociation is non-activated (e.g., Fe, Ni, Pd, and Pt). Cu and Pt are known^{28,29} to form series of miscible and well-ordered alloys over a large concentration range. The resulting alloy Cu₃Pt has the FCC structure of Cu₃Au–type with

the Pt atoms situated at the corners while the Cu atoms are located at the face centers of the unit cell. The corresponding $\text{Cu}_3\text{Pt}(111)$ surface is well ordered, with the Cu atoms completely surrounding the Pt atoms. NiAl in turn forms an ordered alloy with a CsCl structure^{30,31}, and its (110) surface is terminated by 50% Ni and 50% Al. To obtain information regarding the form of the H–H bond orientation (with respect to the surface) and site-dependent PES for H_2 dissociation, we have performed density-functional-theory (DFT)⁴¹–PES calculations (DFT–PES calculations)^{26,36-40} using the Gaussian 94 programs⁴², adopting Becke's 3-parameter functional⁴³, Perdew and Wang's gradient-corrected correlation functional⁴⁴, and Dunning and Hay's⁴⁵ and Hay and Wadt's basis sets⁴⁶. We considered the CuH_2Pt_2 , CuH_2Pt , and $\text{Cu}_2\text{H}_2\text{Pt}$ systems to approximate the three different sites along $\text{Cu}_3\text{Pt}(111)[1\bar{2}1]$, where the Cu and Pt atoms alternate, viz., the atop–Cu, the Cu–Pt bridge, and the atop–Pt sites, respectively. For the two different sites along $\text{NiAl}(110)[1\bar{1}0]$, viz., the atop–Ni and Ni–Ni bridge sites, we considered the NiAl_4H_2 and $\text{Ni}_2\text{Al}_2\text{H}_2$ systems, respectively. We constrain the H_2 to dissociate over the aforementioned sites in a planar geometry^{26,36-40}. The calculations were carried out with the intention of getting a basic idea of the qualitative features of the PES and should not be interpreted too literally. The resulting qualitative features agree with earlier calculations using a repeated slab geometry to describe the dissociation of a parallel-oriented H_2 on a Pt and a Cu on $\text{Cu}_3\text{Pt}(111)$ ⁴⁷, and on Ni and Al on $\text{NiAl}(110)$ ^{30,48}. More detailed discussion of the DFT–PES calculation results can be found elsewhere^{26,36-40}.

We then performed quantum mechanical calculations^{10,19,20,23-25,49-52} for the dissociative adsorption/sticking probability by solving the time-independent Schrödinger equation for an H_2 , in the rovibrational ground state ($\nu = 0$, $J = 0$), moving along the reaction path, and under the influence of an orientationally anisotropic PES, using the coupled-channel method⁴⁹⁻⁵². The dynamical variables we considered include the H_2 center-of-mass (CM) distance Z from the surface, the H_2 bond-length r , the polar and azimuthal angular orientation of the H–H bond with respect to the surface, θ and ϕ , respectively, and the position of the H_2 CM X , along the $\text{Cu}_3\text{Pt}(111)[1\bar{2}1]$, and along the $\text{NiAl}(110)[1\bar{1}0]$ direction. To solve the corresponding time-independent Schrödinger equation which describes dissociative adsorption, it is convenient to make the coordinate transformation $(Z,r) \rightarrow (s,\rho)$, where (s,ρ) are *reaction path* coordinates⁴⁹. s gives the position of the H_2 CM along the *reaction path*, and ρ is a coordinate perpendicular to s . (We refer the readers to Refs. 26, 36-40, for more details regarding the functional form of the orientation θ - and reaction path coordinate⁴⁹ s -dependent PES.) Although it is possible to carry out fully quantum mechanical, six-dimensional (6D) dynamics calculations^{22,34,53,55-57}, the complexity of 6D dynamics makes it rather difficult to disentangle the contributions of the different quantum effects due to each of the different degrees-of-freedom (DOF) involved. Thus, here, we carry out a more systematic approach where the influence of certain DOF is minimized, keeping only the essential physics.

In Fig. 1 we show the calculated E_t - and Θ -dependent sticking probability results for an H_2 , in the rovibrational ground state ($\nu = 0$, $J = 0$), impinging along $\text{Cu}_3\text{Pt}(111)[1\bar{2}1]$ (Fig. 1, lower panel). We see that the sticking probability vs. incidence translational energy (S vs. E_t) profile strongly depends on the angle of incidence Θ of the impinging H_2 with respect to the surface normal. For normal incidence ($\Theta = 0^\circ$) of the impinging H_2 , the sticking probability $S_{J=0}^{\nu=0}(\Theta = 0^\circ, E_t)$ initially decreases, and then finally increases as we increase the incidence energy E_t . Note that activated and non-activated sites/pathways exist along $\text{Cu}_3\text{Pt}(111)[1\bar{2}1]$ ^{26,36-40} (cf., Fig. 2). Because of the small initial incidence energy E_t of the impinging H_2 (effectively the total energy E_{tot} , with $E_{\text{tot}} = E_t + E_J$, and $E_J = 0$), *steering* (Fig. 2) will initially dominate. Most of the impinging H_2 will be steered to more favorable

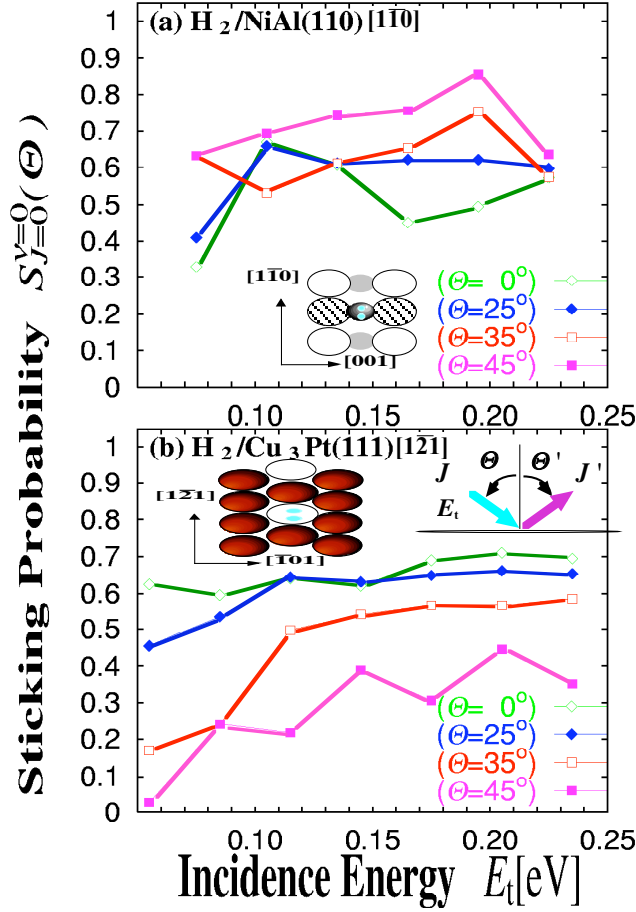


Fig. 1 Calculated incident translational energy E_t -dependent sticking probabilities $S_{J=0}^{v=0}$ for an H_2 in the vibrational ground state $v = 0$, and initial rotational states $J = 0$, impinging along (a) the $\text{NiAl}(110)[110]$ direction, and (b) the $\text{Cu}_3\text{Pt}(111)[121]$ direction (where the atop-Cu, Cu-Pt bridge, and atop-Pt sites alternate), at incident angles (cf., (b), **Right Inset**) $\Theta = 0^\circ$ (\diamond), 25° (\blacklozenge), 35° (\square), 45° (\blacksquare) with respect to the surface normal. ((a), **Inset**) A depiction of the $\text{NiAl}(110)[110]$, with the $[110]$ and $[001]$ directions indicated. The big, white circles indicate 1st layer Al, and the big, hatched circles indicate 2nd layer Al. The smaller, solid circles indicate a 1st layer Ni, and the shaded circles indicate 2nd layer Ni. ((b), **Left Inset**) A depiction of the $\text{Cu}_3\text{Pt}(111)[121]$, with the $[121]$ and $[101]$ directions indicated. The big red circles indicate Cu, and the big white circles indicate Pt. Again, the two smallest circles indicate the H_2 . These are all m -averaged sticking probabilities, $-J \leq m \leq J$.

orientations/sites and stick to the surface (cf., e.g., Refs. 10, 12, 19, 20, 22, 53, 55, 57, and references found therein). Thus, for normal incidence ($\Theta = 0^\circ$) and low E_t , the nonactivated sites become easily accessible to the impinging H_2 , and we observe a relatively high $S_{J=0}^{v=0}(\Theta = 0^\circ, E_t)$ value (Fig. 2, upper panel). However, on increasing E_t , there is a corresponding decrease in the amount of time that the H_2 stays under the influence of the anisotropic PES (cf., e.g., Refs. 10, 20, and references found therein). This reduces the probability of the impinging H_2 to be steered/reoriented to more favorable sites/orientations along the surface. We thus observe an initial decrease in $S_{J=0}^{v=0}(\Theta = 0^\circ, E_t)$. As we further increase E_t , eventually, we observe again a corresponding increase in $S_{J=0}^{v=0}(\Theta = 0^\circ, E_t)$. Thus, under these conditions, the non-activated sites dominate, and we observe an S vs. E_t profile characteristic of non-activated systems (cf., e.g., Ref. 10 and references found therein). Upon increasing Θ , we see a corresponding decrease in the sticking probability $S_{J=0}^{v=0}(\Theta = 0^\circ, E_t)$, for small E_t . A kind of *shadowing effect* occurs (Fig. 2, lower panel), with the results

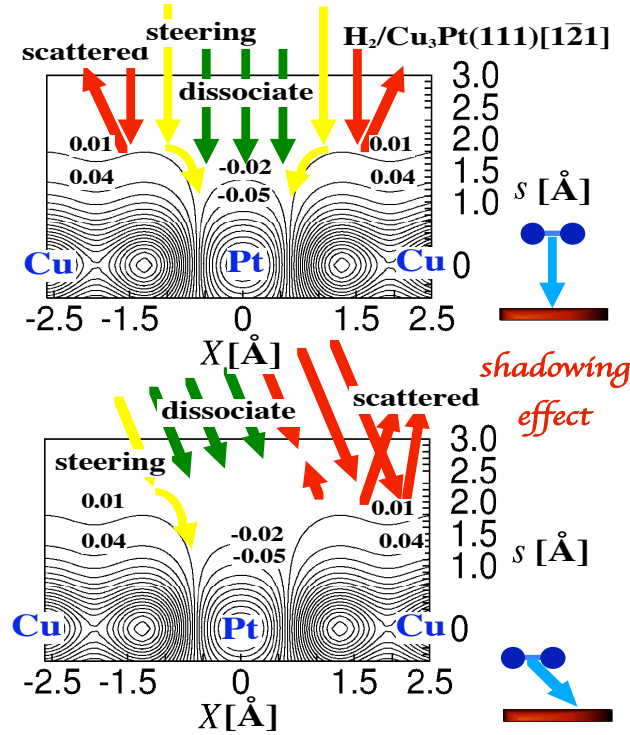


Fig. 2 A cut through the effective potential energy (hyper-) surface (PES)^{26,36-40} for H₂ impinging along Cu₃Pt(111)[1 $\bar{2}$ 1] at (**upper panel**) normal incidence $\Theta = 0^\circ$, and (**lower panel**) at an angle $\Theta > 0^\circ$. The Cu and Pt sites are as indicated. A considerable barrier exists at the atop-Cu and the Cu-Pt bridge sites, and an attractive well at the vicinity of Pt. Contour spacing is 0.03 eV.

determined by the local features of the surface. Along Cu₃Pt(111)[1-21], the non-activated regions/sites are smaller in spatial extent compared to the activated sites (Fig. 2). As we increase Θ , the non-activated sites fall under the shadow of the activated sites, and become less accessible to the impinging H₂, despite *steering*. Thus, under these conditions, the activated sites dominate, and we observe an S vs. E_i profile characteristic of activated systems (cf., e.g., Ref. 10 and references found therein).

Next, we compare the calculated E_i - and Θ -dependent sticking probability results for an H₂, in the rovibrational ground state ($v = 0$, $J = 0$), impinging along Cu₃Pt(111)[1 $\bar{2}$ 1] (Fig. 1, lower panel), with those for H₂ impinging along NiAl(110)[1 $\bar{1}$ 0] (Fig. 1, upper panel). The most striking thing we can immediately notice about the S vs. E_i profile for H₂ impinging along NiAl(110)[1 $\bar{1}$ 0] is that it does not change much with variations in the angle of incidence $\Theta : [0^\circ, 45^\circ]$. A comparison of the spatial extent of the activated and non-activated regions/sites along NiAl(110)[1 $\bar{1}$ 0] provides us with the answer.

From Fig. 3, we can see that along NiAl(110)[1 $\bar{1}$ 0], the activated and non-activated region/sites are almost equally distributed, whereas along Cu₃Pt(111)[1 $\bar{2}$ 1], the non-activated regions/sites are smaller in spatial extent compared to the activated sites. Thus, we would immediately expect, upon inspection of Figs. 3 and 4, that the dissociation dynamics of H₂ along NiAl(110)[1 $\bar{1}$ 0] would be less susceptible to *shadowing effects* than along Cu₃Pt(111)[1 $\bar{2}$ 1]. This complements the results we have found earlier for the scattering dynamics of H₂ along Cu₃Pt(111)[1 $\bar{2}$ 1] and NiAl(110)[1 $\bar{1}$ 0].

4. Summary and Conclusions

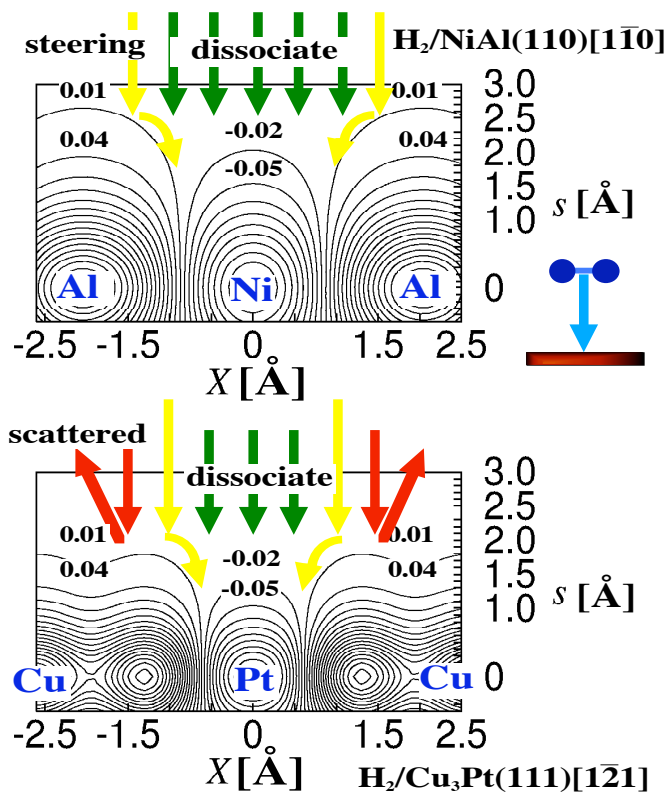


Fig. 3 A cut through the effective potential energy (hyper-) surface (PES)^{26,36-40} for H₂ impinging at normal incidence $\theta = 0^\circ$ along (upper panel) NiAl(110)[110] and (lower panel) Cu₃Pt(111)[121]. The Ni, Al, Cu, and Pt sites are as indicated. As it is for Cu₃Pt(111)[121], a considerable barrier exists at the atop-Al site, and an attractive well at the vicinity of Ni. Contour spacing is 0.03 eV.

In summary, we explore the feasibility of controlling the dynamics of hydrogen-surface reactions. At the same time, we also found that it would be feasible to utilize hydrogen to probe adsorbate-surface interaction, surface structures, and the effective potential energy (hyper-) surface relevant to the reaction considered. To demonstrate, we consider the dissociative adsorption dynamics of H₂, in the rovibrational ground state ($v = 0, J = 0$), on Cu₃Pt(111) (where experimentally there was no barrier observed for the dissociative adsorption of H₂^{28,29}) and on NiAl(110) (where experimentally an H₂ dissociative adsorption barrier was observed^{30,31}). Based on calculation results presented here, we conclude that because of the inherently strong dependence of hydrogen-solid surface interactions on the H-H orientation (with respect to the surface), not only was hydrogen able to distinguish the difference between various components on the surface, but also how the components are distributed. These discernible (by hydrogen) differences turn up as measurable/observable strong dependence of the corresponding dissociative adsorption/sticking probability *vs.* incidence translational energy (S *vs.* E_i) profile on the angle of incidence of the impinging H₂. With further, more detailed investigation, we could, from these information, infer the salient features of the effective potential energy (hyper-) surface (PES) relevant to the reaction (e.g., the relative extent of activated and non-activated regions/sites on surfaces, etc.). Thus, it would not be long before we could actually utilize H₂ (D₂) as probes to study adsorbate-surface interaction (*local/site-specific* surface reactivity), surface structures, and the effective potential energy (hyper-) surface relevant to the reaction considered. With recent developments in laser and molecular beam technology, it should not be difficult to experimentally verify the results presented here. Although it would be

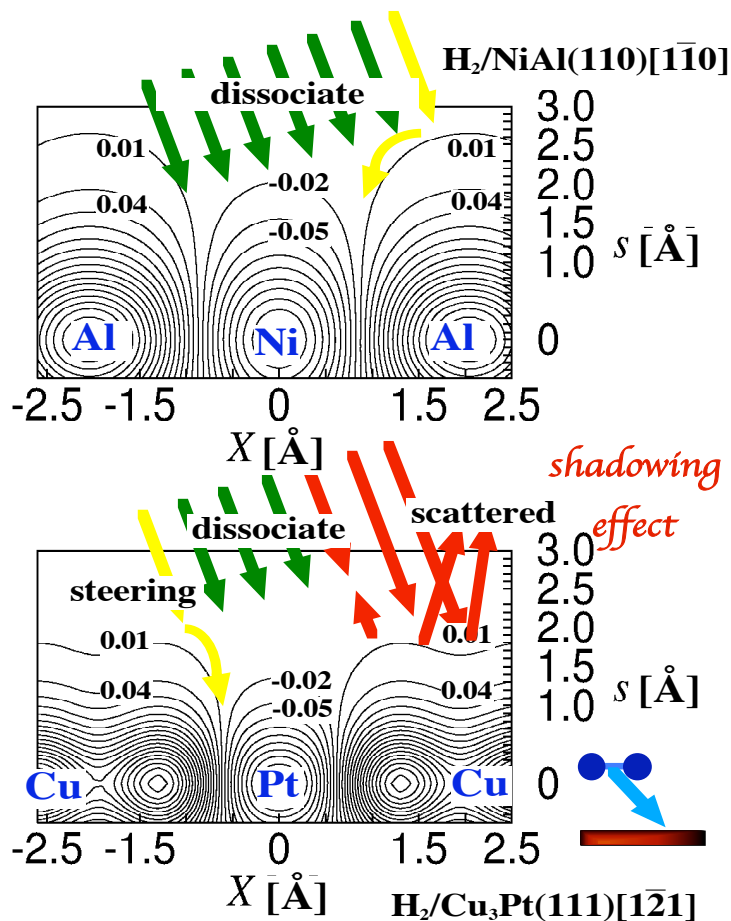


Fig. 4 A cut through the effective potential energy (hyper-) surface (PES)^{26,36-40} for H₂ impinging at incidence angle $\theta > 0^\circ$ along (**upper panel**) NiAl(110)[110] and (**lower panel**) Cu₃Pt(111)[121]. Contour spacing is 0.03 eV.

necessary to carry out ($\nu = 0, J, m$)-resolved scattering and detection^{21,58-66} of H₂, on the corresponding alloy surfaces mentioned above, and applying a variation of the shadowing approach introduced by Rettner (as cited in Ref. 21). Further information could also be available once it is possible to determine⁶⁷ whether those that dissociated as H (D) eventually reside on or near the surface, or somewhere in the bulk.

We hope that we have convincingly demonstrated that by Computational Reaction Design (CRD), we have at our grasp a relatively simple, cost-effective method for solving a timely and urgent problem such as that of controlling the dynamics of hydrogen-surface reactions. One immediate use we have for this would be, e.g., to solve the problem of how we could increase the orthohydrogen-parahydrogen conversion yield⁶⁸. Another, more directly related problem would be how we could simulate the catalytic reactivity of Platinum, through the design of *local surface features*, having a priori knowledge of hydrogen dynamics. This should lead to the design of more cost effective and, yet still, environmental- and user-friendly, novel hydrogen-related industrial processes.

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