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Can we probe local surface reactivity with hydrogen molecules?

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Abstract

To explore the feasibility of using hydrogen molecules to probe local surface reactivity, we consider the dissociation dynamics of H_2/$Cu_3Pt(111)[1\bar{2}1]$, as an example. Calculation results show that as we increase the incidence angle Θ_i (measured with respect to the surface normal) of the impinging H_2, thereby changing the apparent surface features, the corresponding dissociative adsorption/sticking probability S versus incidence translational energy E_t profile changes. Noting that the hydrogen is sensitive to the local features of the solid surface that it is interacting with, and that it distinguishes among them, we were able to account for these results.

In this brief communication, we explore the feasibility of using using H_2 (D_2) as probes, thus providing 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 potential energy (hyper)surface (PES), and the surface structure). One of the driving forces behind this idea is an already well-known inherent feature of H_2 (D_2)–solid surface reactions (and, in general, any reaction) of being strongly dependent on the orientation of H_2 (D_2) with respect to the surface [1]. One consequence of this strong orientation dependence of the H_2 (D_2)–surface reaction is the concept of steering (see [1] and references therein). 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, which is due to the strong molecular orientation dependence of the PES. We could also say that this pertains to the capability of the orientation-sensitive PES of reorienting the molecule from an initially *unfavourable* orientation to a *favourable* one, or vice versa. The orientation of the molecule upon encountering the surface determines the ground-state energy of the molecule–surface electron system, which, in turn, serves as the effective/relevant PES that determines the dynamics of the molecule–surface reaction. By taking into account steering (which allows for the dynamical reorientation [1] of the impinging H_2 (D_2) to a more favourable orientation, thus enabling it to undergo some desired

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reaction, e.g., dissociation on Cu(111)), one can explain the non-monotonic initial rotational state dependence of the H_2 (D_2) dissociation dynamics on solid surfaces (e.g., Cu(111)) [1–8]. It has also been shown that steering is a general feature/concept, and that is present regardless of whether the system is activated or not [9]. Its efficacy, however, strongly depends on the translational energy of the impinging H_2 (D_2) [10, 11]. Later on, it was demonstrated how the concept of steering could also explain the non-monotonic initial translational energy dependence of H_2 dissociation on Pd(100) [12]. Another feature of the H_2 (D_2)–solid surface reaction, which can also be inferred from its inherently strong dependence on the H_2 (D_2) orientation, is the possibility of dynamically filtering [13, 14] H_2 (D_2), so that we get rotating H_2 (D_2) whose rotational axes are at particular orientations with respect to the surface. Thus, in principle, it would be possible to prepare H_2 (D_2) such that we can have a beam of molecules all doing helicopter-like or cartwheel-like rotations.

From the discussions above, one could immediately infer that H_2 (D_2) is very sensitive to even the slightest variations in the *local* properties of the surface. To verify this, we have recently investigated [15] the interaction of H_2 with two different alloy surfaces, namely, $Cu_3Pt(111)$ (which was observed to have no barrier to the dissociative adsorption of H_2 [16,17]) and NiAl(110) (which was observed to have an H_2 dissociative adsorption barrier [18, 19]). In particular, we considered the dynamics of H_2 scattering along $Cu_3Pt(111)[1\bar{2}1]$ and along $NiAl(110)[1\bar{1}0]$, and compared them with the corresponding H_2 scattering dynamics on single-component surfaces, namely, Cu(001)[100] [20–22] and Ni(110)[001] [20, 23]. From the calculation results obtained, we found that the H_2 (D_2) 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 H_2 (D_2)) differences between the various sites eventually turn up as measurable/observable transitions in the internal states of the scattered H_2 (D_2) [15].

Here, we present another example suggesting the feasibility of exploring the sensitivity of H_2 (D_2)–solid surface reaction to the *local features* of the surface. We consider an H_2 impinging along $Cu_3Pt(111)[1\bar{2}1]$. By varying the angle of incidence Θ_i of the impinging H_2, with respect to the surface normal, we investigate how (and whether or not) the dissociative adsorption/sticking probability versus incidence translational energy (S versus E_t) profile changes correspondingly.

$Cu_3Pt(111)$ is an example of a binary alloy surface consisting of metals A and B, where A is some metal on whose surface H_2 dissociation is activated (e.g., Al, Cu, Ag, and Au), and B is some metal on whose surface H_2 dissociation is non-activated (e.g., Fe, Ni, Pd, and Pt). Cu and Pt are known [16, 17] to form series of miscible and well-ordered alloys over a large concentration range. The resulting alloy Cu_3Pt has the fcc structure of Cu_3Au type with the Pt atoms situated at the corners while the Cu atoms are located at the face centres of the unit cell. The corresponding $Cu_3Pt(111)$ surface is well ordered, with the Cu atoms completely surrounding the Pt atoms. 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) [28] PES calculations (DFT-PES calculations) [15, 24–27] using the Gaussian94 programs [29], adopting Becke's three-parameter functional [30], Perdew and Wang's gradient-corrected correlation functional [31], and Dunning and Hay's [32] and Hay and Wadt's basis sets [33]. We considered the CuH_2Pt_2, CuH_2Pt, and Cu_2H_2Pt systems to approximate the three different sites along $Cu_3Pt(111)[1\bar{2}1]$, where the Cu and Pt atoms alternate, namely, the atop-Cu, the Cu–Pt bridge, and the atop-Pt sites, respectively. We constrain the H_2 to dissociate over the aforementioned sites in a planar geometry [15, 24–27]. 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 parallel-oriented H_2 on Pt and Cu on $Cu_3Pt(111)$ [34]. More detailed discussion of the DFT-PES calculation results can be found elsewhere [15,24–27].

We perform quantum mechanical calculations [1, 13, 14, 35–38] 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 method [35–38]. The dynamical variables that we considered include the H_2 centre-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 $Cu_3Pt(111)$ direction where Cu and Pt alternate. 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* coordinates [35]. s gives the position of the H_2 CM along the *reaction path*, and ρ is a coordinate perpendicular to s.

To describe H_2 dissociation at each of the aforementioned sites, we have adopted the following functional form for the (orientation) θ-dependent and (reaction path coordinate [35]) s-dependent PES:

$$V(s,\theta) = \frac{V_0}{\cosh^2(\alpha s)}(1-\beta\cos^2\theta) + \frac{[1+\tanh(\alpha s)]}{2}\{V_1\cos^2\theta + V_2\sin^2 2\theta\}. \tag{1}$$

For the effective PES $V_{\mathrm{aC}}(s,\theta)$ that describes the activated H_2 dissociation at the atop-Cu site we take $V_0 \approx 0.5$ eV, $V_1 \approx 1.0$ eV, $V_2 \approx 0.0$ eV, $\alpha = 1.5$ Å^{-1}, and $\beta = 0.25$ in equation (1) [1,13,14,24–27].

For the activated dissociation across the Cu–Pt bridge site, V_{CP}, we take $V_0 \approx 0.5$ eV, $V_1 \approx 0.6$ eV, $V_2 \approx 0.7$ eV, $\alpha = 1.5$ Å^{-1}, and $\beta = 0.50$ in equation (1) [24–27].

For the non-activated atop-Pt site, $V_{\mathrm{aP}}(s,\theta)$, we take $V_0 \approx -0.4$ eV, $V_1 \approx 0.8$ eV, $V_2 = 0.0$ eV, $\alpha = 1.5$ Å^{-1}, and $\beta = 0.25$ in equation (1) [1,24–27].

We were then able to construct the effective s-, θ-, and X-dependent PES, by connecting the potentials at each site, as follows:

$$\begin{aligned} V_{\mathrm{Cu_3Pt(111)[1\bar{2}1]}}(X,s,\theta) = {}& \frac{V_{\mathrm{CP}}(s,\theta)}{2}F_{-2}(gX)\sin^2(gX) + \frac{V_{\mathrm{aP}}(s,\theta)}{4}F_{+2}(gX)F_{+1}(gX) \\ &+ \frac{V_{\mathrm{aC}}(s,\theta)}{4}F_{+2}(gX)F_{-1}(gX), \end{aligned} \tag{2}$$

where $F_{\pm n}(gX) = 1 \pm \cos(ngX)$. The reciprocal-lattice vector $g = 2\pi/a_X$, and X gives the surface lateral coordinate of the H_2 CM. $Cu_3Pt(111)$ has a lattice constant of $a_X = 5.22$ Å [17].

Although it is possible to carry out fully quantum mechanical, six-dimensional dynamics calculations [12, 22, 39–43], the complexity of six-dimensional 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 take a more systematic approach where the influence of certain DOF is minimized, keeping only the essential physics.

In figure 1 we show the calculated E_{t}- and Θ_{i}-dependent sticking probability results for an H_2, in the rovibrational ground state ($\nu = 0$, $J = 0$), impinging along $Cu_3Pt(111)[1\bar{2}1]$. We see that the sticking probability versus incidence translational energy (S versus E_{t}) profile strongly depends on the angle of incidence Θ_{i} of the impinging H_2 with respect to the surface normal. For normal incidence ($\Theta_{\mathrm{i}} = 0°$) of the impinging H_2, the sticking probability $S_{J=0}^{\nu=0}$ ($\Theta_{\mathrm{i}} = 0°$, 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 $Cu_3Pt(111)[1\bar{2}1]$ [15,24–27]. Because of the small initial incidence energy E_{t} of the impinging H_2 (effectively the total energy E_{tot},

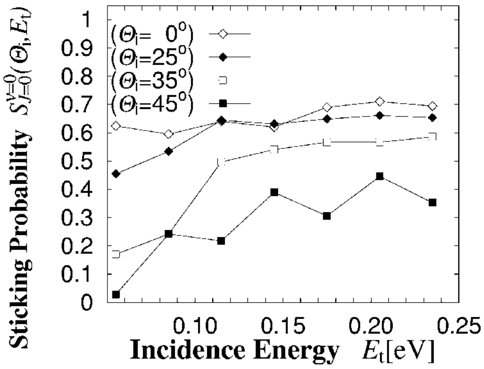

Figure 1. Calculated (incident translational energy) E_t-dependent sticking probabilities S^{ν}_{J} for an H_2 in the vibrational ground state $\nu = 0$, and initial rotational states $J = 0$, impinging along $Cu_3Pt(111)[1\bar{2}1]$ (where the atop-Cu, Cu–Pt bridge, and atop-Pt sites alternate) at incident angles $\Theta_i = 0^\circ, 25^\circ, 35^\circ, 45^\circ$ with respect to the surface normal. These are all m-averaged sticking probabilities, $-J \leqslant m \leqslant J$. The parameters are as given in the text. The H_2 gas-phase rotational constant $B \approx 7.6$ meV.

with $E_{tot} = E_t + E_J$, and $E_J = 0$), steering will initially dominate. Most of the impinging H_2 will be steered, instead of scattered, to more favourable orientations/sites and stick to the surface (cf, e.g., [1,2,9,10,12,39,41,43] and references therein). Thus, for normal incidence ($\Theta_i = 0^\circ$) and low E_t, the non-activated sites become easily accessible to the impinging H_2, and we observe a relatively high $S^{\nu=0}_{J=0}(\Theta_i = 0^\circ, E_t)$ value. 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., [1, 10] and references therein). This reduces the probability of the impinging H_2 being steered/reoriented to more favourable sites/orientations along the surface. We thus observe an initial decrease in $S^{\nu=0}_{J=0}(\Theta_i = 0^\circ, E_t)$. As we further increase E_t, eventually we observe again a corresponding increase in $S^{\nu=0}_{J=0}(\Theta_i = 0^\circ, E_t)$. Thus, under these conditions, the non-activated sites dominate, and we observe an S versus E_t profile characteristic of non-activated systems (cf, e.g., [1] and references therein).

Upon increasing Θ_i, we see a corresponding decrease in the sticking probability $S^{\nu=0}_{J=0}(\Theta_i, E_t)$, for small E_t. A kind of *shadowing effect* occurs, with the results determined by the local features of the surface. Along $Cu_3Pt(111)[1\bar{2}1]$, the non-activated regions/sites are smaller in spatial extent compared to the activated sites (equation (2)). As we increase Θ_i, the non-activated sites fall under the shadow of the activated sites, and become less accessible to the impinging H_2, despite steering. Thus, under these conditions, the activated sites dominate, and we observe an S versus E_t profile characteristic of activated systems (cf, e.g., [1] and references therein).

In summary, we explore the feasibility of utilizing hydrogen molecules to probe adsorbate–surface interaction, surface structures, and the effective potential energy (hyper)surface (PES) relevant to the reaction considered. To give a demonstration, we consider the dissociative adsorption dynamics of H_2, in the rovibrational ground state ($\nu = 0$, $J = 0$), on $Cu_3Pt(111)$ (where experimentally there was no observed barrier to the dissociative adsorption of H_2 [16, 17]). On the basis of 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), hydrogen is able to distinguish the difference between various components on the surface. These discernible (by hydrogen) differences eventually turn up as measurable/observable strong dependence of the corresponding dissociative adsorption/sticking probability versus incidence translational energy (S versus E_t) profile on the angle of incidence of the impinging H_2. From this information, we can then infer the salient features of the effective PES relevant to the reaction (e.g., the relative extent of activated and non-activated regions/sites on surfaces, etc). Thus, it should not be long before we can actually utilize H_2 (D_2) as probes to study adsorbate–surface interaction (*local*/site-specific surface reactivity), surface structures, and the effective PES relevant to the reaction considered. Note that the results presented here could be verified experimentally, with recent developments in laser and molecular beam technology, by carrying out ($\nu = 0, J, m$)-resolved scattering and detection [11, 44–52] of H_2, on the corresponding alloy surfaces mentioned above, and applying a variation of the shadowing approach introduced by Rettner (as cited in [11]). Further information could also be available once it is possible to determine [53] whether those entities that dissociated as H (D) eventually reside on or near the surface, or somewhere in the bulk.

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