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The fight for a reactive site

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Chapter 5

A theoretical study of H₂ dissociation on ($\sqrt{3} \times \sqrt{3}$)R30° CO/Ru(0001)

This chapter is based on:

I. M. N. Groot, J. C. Juanes-Marcos, R. A. Olsen and G. J. Kroes,
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Abstract

We have studied the influence of pre-adsorbed CO on the dissociative adsorption of H₂ on Ru(0001) with density functional theory calculations. For a coverage of 1/3 monolayer CO we investigated different possible reaction paths for hydrogen dissociation. One reaction path was studied in detail through an energy decomposition and molecular orbital type of analysis. The minimum barrier for H₂ dissociation is found to be 0.29 eV. At the barrier the H-H bond is hardly stretched. Behind this barrier a molecular chemisorption minimum is present. To dissociate, the molecules have to overcome a second, lower barrier of 0.23 eV. To move along the reaction path from reactants to products, the hydrogen molecule needs to rotate while moving along the reaction path. The dissociative chemisorption of H₂ on CO/Ru(0001) is endoergic, in contrast to the case of H₂ on bare Ru(0001). The presence of CO on the surface increases the barrier height to dissociation compared to bare Ru(0001). Based on an energy decomposition and molecular orbital analysis we attribute the presence of a barrier mainly to an occupied-occupied interaction between the bonding H₂ σ_g orbital and the (surface-hybridized) CO 1π orbitals. There is a small repulsive contribution to the barrier from the interaction between the H₂ molecule and the Ru part of the CO covered Ru surface, but it is smaller than one might expect based on the calculations of H₂ interacting with a clean Ru surface. Actually, the analysis suggests that the Ru surface as a subsystem is (slightly) *more* reactive for the reaction path studied *with* CO pre-adsorbed on it than *without* it. Thus, the results indicate that the influence of CO on H₂ dissociation on Ru is more than a simple site-blocking effect, the electronic structure of the underlying Ru is changed.

5.1 Introduction

A very important type of heterogeneous catalysis involves the interaction of gas phase molecules with solid surfaces. This interaction can lead to reflection of the molecules back into the gas phase, or (dissociative) adsorption of the molecules, possibly followed by a chemical reaction between different adsorbates. One of the processes investigated in great

detail is the dissociative adsorption of hydrogen on different metal surfaces (for reviews see Refs. [1–5]), which has been recognized as an elementary step in many industrial processes, *e.g.* the production of ammonia [6].

To get more insight into chemical reactions occurring at surfaces, the co-adsorption of hydrogen and different other adsorbates has also been studied (see *e.g.* Refs. [7–26]). Examples of these studies involve the so-called ‘poisoning’ of hydrogen dissociation on Pt(533) by O_2 [23], on Pt(111) by K [14], on Ni(100) by S [8–11], on Pd(111) by S and Cl [21], on Pd(100) by S [11, 12, 15, 17–20, 22], and on Ru(0001) by S [7]. Different effects of poisoning can be observed: Dissociation sites for hydrogen can be completely blocked by the adsorbate at the experimentally relevant conditions, additional energy barriers can be built up along the dissociation pathway of hydrogen, and the heights of energy barriers can be changed. Theoretical studies on $H_2 + S/Pd(100)$ claim that the poisoning gives rise to the build-up of energy barriers on the potential energy surface (PES) [15, 17–20, 22], while experiments on the same system observe site-blocking effects [12]. Experiments of D_2 dissociation on CO/Ru(0001) observe both effects [27]. Possible poisoning mechanisms include a change in the density of states at the Fermi level [28–30] and an adlayer induced electrostatic field [31, 32].

The poisoning of hydrogen adsorption by CO on different metal surfaces has also been studied under high pressure conditions [33]. The authors find an H-D exchange rate that varies more strongly with CO coverage than would be expected from a simple site-blocking mechanism. The addition of 10 ppm CO has a significant effect on the reaction probability of H_2 . The metal most sensitive to this influence is Ir, followed by Pt. Palladium is found to be the least sensitive to the presence of CO.

The process investigated in this paper, the dissociative adsorption of H_2 on CO-precovered Ru(0001), is particularly interesting for the methanation reaction [34–37], and for Fischer-Tropsch synthesis [38–40].

The individual adsorption of CO and H_2 on Ru(0001) has been studied in detail. Carbon monoxide adsorbs non-dissociatively [41–44], preferentially at the on-top position for coverages up to 1/3 monolayer (ML), oriented perpendicular to the surface [45–49]. The C-end is bound to the surface, with the O atom facing the vacuum [41, 50, 51]. Different experimental low energy electron diffraction (LEED) structures have been found for several coverages of CO. At 1/3 ML a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is observed [45, 52–54]. At 1/2 ML a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure is assigned, with either equal populations of top, hcp hollow and fcc hollow sites [55], or exclusively top sites [56]. A $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure has also been observed at 7/12 ML [52, 55]. A saturated $(5\sqrt{3} \times 5\sqrt{3})R30^\circ$ structure (assigned coverage of 49/75 ML) was observed by LEED [52] and helium scattering experiments [57]. For coverages below 1/3 ML a lattice gas in equilibrium with $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ islands is observed [54].

Molecular hydrogen adsorbs dissociatively on the Ru(0001) surface, and the H atoms bind preferentially in the fcc hollow sites [58]. Both experiment [59, 60] and theory [61] observe direct, activated adsorption, with a suggestion of non-activated adsorption occurring at low collision energies in experiment [59, 60]. No isotope effect is seen over a wide range of kinetic energies, and normal energy scaling is obeyed [60]. The saturation coverage equals 1 ML with respect to the Ru surface atoms [62].

The co-adsorption of hydrogen and CO on Ru(0001) has been studied both experimentally [27, 33, 57, 63–67] and theoretically [42, 65]. The interaction between CO and H/D is

repulsive, as is found from temperature programmed desorption (TPD) [67], He atom scattering (HAS) [57], thermal energy He atom scattering (TEAS) [67] and density functional theory (DFT) studies [65]. No chemical reaction between CO and H/D was found [63].

In this paper we present a study of different possible hydrogen dissociation pathways at the CO-precovered Ru(0001) surface. By using (adaptive) nudged elastic band calculations we find the barrier geometries for different paths in which all 6 degrees of freedom of the H₂ molecule have been optimized. In addition, we present 2D (r, Z) cuts through the 6D PES. One possible reaction path of hydrogen dissociation is studied in more detail by two-center projected density of states calculations and an energy decomposition analysis.

The rest of the paper is organized as follows. Section 5.2 describes the details of the computational methods used. Results are given and discussed in Section 5.3. Finally, Section 5.4 summarizes our main conclusions.

5.2 Theory

5.2.1 H₂ + CO/Ru(0001) system

For carbon monoxide adsorbed on the Ru(0001) surface, a coverage of 1/3 ML is considered, with the CO molecules bound at the on-top sites, perpendicularly to the surface with the C atom closest to it. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface unit cell is used, as this is the structure experimentally seen by LEED of 1/3 ML CO on Ru(0001) [45, 52–54]. A schematic top view of the unit cell is shown in Fig. 5.1 (left panel). Note that the unit cell contains two threefold rotational axes and a mirror plane, as indicated in the figure.

The H₂ molecular configuration is described by considering all six degrees of freedom ($X, Y, Z, r, \theta, \varphi$). Here, r is the H-H distance, Z the distance from the center-of-mass of H₂ to the surface, X and Y represent the center-of-mass motion parallel to the surface, and θ and φ are the polar and azimuthal angles defining the orientation of the H-H molecular axis. This coordinate system is displayed in Fig. 5.1 (right panel).

5.2.2 Electronic structure calculations

The electronic structure calculations are done applying DFT [68, 69] as implemented in the DACAPO code [70]. The exchange-correlation functional is described within the generalized gradient approximation, using a revised Perdew-Burke-Ernzerhof (RPBE) functional [71]. This functional is known to give rather accurate chemisorption energies for CO on a range of flat metal surfaces, including Ru(0001) [72]. Comparison of experiment [60] to earlier predictive six-dimensional quantum dynamics calculations [61] suggests that the PW91 functional overestimates the reactivity of H₂ on Ru(0001), whereas the RPBE functional underestimates it. However, there is no systematic proof yet that other standard GGA functionals perform better for H₂-metal surface reactions. The ionic cores are modeled using ultrasoft pseudo-potentials [73], and a plane-wave basis set is used for the electronic orbitals.

The CO/Ru(0001) system is modeled using a three-layer slab of Ru-atoms and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface unit cell. To check whether the relatively small amount of three layers in the Ru slab is enough, we calculated the height of the dissociation barrier for slabs with 3 to 9 layers of Ru atoms. The difference in barrier height between the lowest and highest value calculated is 0.016 eV. This difference is small enough that the number of 3 layers is

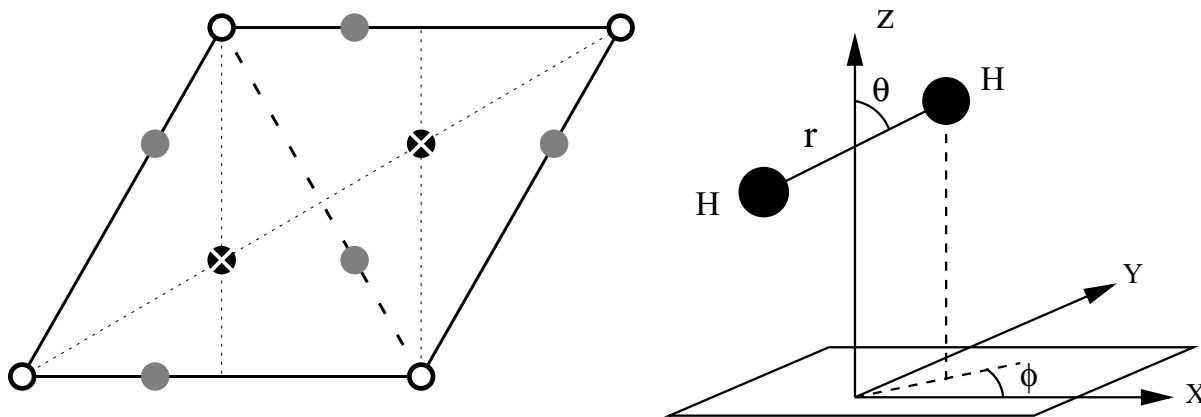


Figure 5.1: (Left panel) A schematic top view of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell used to model the CO/Ru(0001) surface. The length of the unit cell is $\sqrt{3}a = 4.75 \text{ \AA}$. The white circles represent CO molecules adsorbed perpendicular to the surface. The black and gray circles represent Ru atoms in the first (top) and second layers, respectively. Only the top two Ru layers are shown. In the structure of Ru(0001), the third layer is directly below the first layer. The mirror plane is indicated by a black, dashed thick line and the 3-fold rotation axes are indicated by white crosses. (Right panel) The six-dimensional $(X, Y, Z, r, \theta, \phi)$ coordinate system used to describe the interaction of H_2 with the CO/Ru(0001) surface. For simplicity the CO molecules and Ru atoms are not explicitly shown.

acceptable. To avoid artifacts caused by the use of periodic boundary conditions along Z , we placed a vacuum layer of $15 \text{ \AA}$ between the slabs in this direction (the vacuum distance being defined as the distance from the O-atom of adsorbed CO to the bottom of the periodic image of the Ru slab). The total height of the unit cell is thus $22.3 \text{ \AA}$, and the distance between the top of the Ru slab and the bottom of its periodic image is $18.1 \text{ \AA}$. The Brillouin zone is sampled by a set of $(8,8,1)$ Monkhorst-Pack k -points [74]. The kinetic energy cut-off of the plane wave basis used for the electronic orbitals is set at 400 eV , whereas an 800 eV cut-off is used for the density grid. The electronic smearing energy we use is 0.1 eV and the calculations are performed spin-unpolarized. It was checked whether spin-polarized calculations were necessary, but no significant difference was observed when comparing those to the results of spin-unpolarized calculations.

All Ru atoms and the CO adsorbate are taken as frozen, after allowing the atoms to relax in the Z -direction. This approximation is reasonable, as the reaction probability for hydrogen found in experiments for the clean Ru(0001) and for the CO/Ru(0001) system is independent of surface temperature [27, 60]. For the clean Ru(0001) slab a relaxed interlayer distance of $2.12 \text{ \AA}$ was found for both the distance between layer 1 and 2, and between layer 2 and 3, compared to $2.18 \text{ \AA}$ for bulk Ru [61]. For the lattice parameter a we use $a = 2.745 \text{ \AA}$. The Ru interlayer distance was relaxed using the quasi-Newton method in the presence of relaxed CO, and a value of $2.11 \text{ \AA}$ was obtained for both layers, which is slightly compressed with respect to the Ru slab without CO present ($2.12 \text{ \AA}$). The Ru atoms on which the CO molecules reside are slightly lifted from the surface, by $0.11 \text{ \AA}$. This agrees with earlier calculations done with the VASP code and the PW91 functional [49]. The CO molecule is found to be non-dissociatively adsorbed perpendicular to the surface, as was found previously both theoretically [42–44]

and experimentally [41]. The C-end is attached to the Ru atom, and the calculated C-Ru distance is 1.93 Å. The C-O distance we find is 1.18 Å, compared to 1.16 Å for the gas phase. These values compare well to other calculations [42, 44, 47–49] and experimental results [45, 75] (see Table 5.1). Several high-symmetry adsorption sites were explored for CO on the Ru(0001) surface. The adsorption energy is defined as $E_{ads} = E_{CO} + E_{Ru} - E_{CO/Ru}$. The on-top site is found to be the most stable adsorption site with an adsorption energy of 1.85 eV, comparing well to earlier calculations [42, 47, 76, 77] and experiments [77–79], with experimental results ranging from 1.49 to 1.81 eV. Assuming that the most recent experimental value (1.49 eV [77]) of the adsorption energy is the most accurate one, our theoretical RPBE result (1.85 eV) overestimates the adsorption energy, in accordance with the observation that this GGA still overbinds for molecule-metal surface interactions [71]. For the other high-symmetry sites we find the following adsorption energies: 1.66 eV for the bridge site, 1.65 eV for the hcp hollow site, and 1.57 eV for the fcc hollow site. For an overview of our results and results from the literature, see Table 5.1.

5.2.3 Locating barriers along different H₂ dissociation paths

Different H₂ + CO/Ru(0001) reaction paths and the corresponding barrier heights and transition states were determined. By a reaction path we mean a path from hydrogen in the gas phase to two H atoms chemisorbed atomically on the surface, and proceeding through stationary points. This was done using two different methods: i) Adaptive nudged elastic band (ANEb) [81] calculations where the hydrogen molecule is free to move in all six degrees of freedom; and ii) determination of the minimum energy path in two-dimensional (2D) cuts through the full 6D PES, by exploring the two coordinates r and Z , and fixing the remaining ones (X, Y, θ, φ). To obtain the 2D (r, Z) cuts single point DFT calculations were done for at least four different values of r and at least twelve different values of Z . The results were interpolated using cubic splines, and the energy barriers were found from the 2D spline fits.

The ANEB calculations are done in the following way. For different high symmetry sites of an H atom at the CO/Ru(0001) surface, the relaxed energy minimum is calculated using the quasi-Newton method. For the configuration with the lowest energy a second H atom at a high symmetry site is added and again the energy is minimized. This is done for four different configurations. These four configurations are used as the final configurations (chemisorbed atoms) in four calculations with the ANEB method. The initial configuration (H₂ in gas phase) is then calculated by using the same center-of-mass X and Y coordinates as used in the initial geometries employed to compute the geometry and energy of the dissociated molecule, but with a bond length $r = 0.75$ Å, and a height Z (8.45 Å) that corresponds to a molecule-surface distance where the molecule-surface interaction is negligible. Three images are linearly interpolated and equally spaced between the initial and final configurations. Between adjacent images, artificial spring forces are added, in order to keep the images equally spaced along the band. The images are moved by minimizing with the quasi-Newton method both the real (electrostatic) force acting on them perpendicular to the band, and the artificial spring force parallel to the band. The barrier is found by taking the two images around the local maximum as the new initial and final configurations, and applying the same procedure iteratively until no more significant changes in the maximum are found. The highest energy image gives then a good estimate of the transition state.

For the four reaction paths studied the reaction paths were explored in additional detail

Table 5.1: Overview of our results and results from literature for the C-Ru, and the C-O distance, and the absolute value of the adsorption energy E_{ads} for different CO adsorption sites. Distances are in Å and energies in eV. T = theory, E = experiment.

Reference	Adsorption site	C-Ru	C-O	E_{ads}	T/E	Functional
This paper	Top	1.93	1.18	1.85	T	RPBE
	Bridge			1.66	T	RPBE
	hcp hollow			1.65	T	RPBE
	fcc hollow			1.57	T	RPBE
Stroppa 2008 [80]	Top			1.99	T	PBE
				2.14	T	HSE
				1.50	T	BLYP
				1.78	T	B3LYP
	fcc hollow			1.82	T	PBE
				1.77	T	HSE
				1.08	T	BLYP
				1.17	T	B3LYP
McEwen 2007 [49]	Top	1.894	1.165		T	PW91
Gajdos 2004 [44]	Top	2.03	1.166		T	PZ
Ciobica 2003 [43]	Top			1.96	T	PW91
	Bridge			1.72	T	PW91
	hcp hollow			1.83	T	PW91
	fcc hollow			1.76	T	PW91
Ciobica 2003 [42]	Top	1.90	1.17	1.81	T	PW91
Christoffersen 2002 [72]				1.65	T	RPBE
Mortensen 1997 [47]	Top	1.92	1.17	1.90	T	PW91
	Bridge			1.70	T	PW91
	hcp hollow			1.78	T	PW91
Hammer 1996 [76]	Top			1.80	T	PW91
Abild-Pedersen 2007 [77]	Top			1.49±0.22	E	
Over 1993 [75]	Top	1.93±0.04	1.10±0.05		E	
Michalk 1983 [45]	Top	2.00±0.1	1.10±0.10		E	
Pfnür 1983 [79]	Top			1.81	E	
Pfnür 1978 [78]	Top			1.66	E	

using the NEB method to refine stretches of the reaction path. The initial and final configurations used were the same as in one of the ANEB calculations. Then 10 images were linearly interpolated and equally spaced in between. These 10 configurations were moved applying the same method described above for the ANEB calculations. These calculations were performed to verify the existence of additional saddle points. We also performed additional energy minimizations to characterize local minima in the reaction paths.

5.2.4 Two-center projected density of states calculations

We calculate the two-center projected density of states (PDOS) for several H₂ configurations along the reaction path studied by NEB. Together with an energy decomposition analysis it is then possible to develop a molecular orbital based description of the repulsive and attractive interactions, and thereby obtain a qualitative understanding of the dissociation mechanism of H₂ on CO/Ru(0001).

The two-center PDOS is calculated at energies ϵ of the localized orbital ϕ_a as

$$n_a(\epsilon) = \sum_i \sum_k |\langle \phi_a | \psi_{ik} \rangle|^2 \delta(\epsilon - \epsilon_{ik}), \quad (5.1)$$

where i runs over all electronic bands, and k labels the k -points used for sampling the Brillouin zone. The ψ_{ik} are the Kohn-Sham wave functions and the ϵ_{ik} are the corresponding energies. The Fermi level is set to zero on the energy scale. The δ -function is represented by a Gaussian function with a width of 0.1 eV. In Eq. 5.1 ϕ_a was chosen as either the H₂ molecular bonding (σ_g) or antibonding (σ_u) orbital, which are constructed by the normalized linear combinations of hydrogen s orbitals, ϕ_s^H , centered at the positions of the two H atoms $\mathbf{R}_1$ and $\mathbf{R}_2$:

$$\begin{aligned} \phi_{\sigma_g}(\mathbf{r}) &= c_1 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) + \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}, \\ \phi_{\sigma_u}(\mathbf{r}) &= c_2 \{ \phi_s^H(\mathbf{r} - \mathbf{R}_1) - \phi_s^H(\mathbf{r} - \mathbf{R}_2) \}. \end{aligned} \quad (5.2)$$

Here $c_1 = 1/\sqrt{2(1+S)}$ and $c_2 = 1/\sqrt{2(1-S)}$ are the normalization coefficients. Furthermore, S is the overlap term given by $S = \int \phi_s^{H*}(\mathbf{r} - \mathbf{R}_1) \phi_s^H(\mathbf{r} - \mathbf{R}_2) d\tau$, which is analytically calculated by [82]:

$$S = \left\{ 1 + \frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} + \frac{1}{3} \left(\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a_0} \right)^2 \right\} \exp(-|\mathbf{R}_1 - \mathbf{R}_2|/a_0), \quad (5.3)$$

where a_0 is the Bohr radius.

5.3 Results and discussion

5.3.1 Barrier heights and locations

To study the dissociation of H₂ on CO-precovered Ru(0001), six different constrained reaction paths were studied by creating 2D cuts through the PES. Of these six, four (with the center-of-mass at or close to the CO 'hollow' sites, *i.e.* on top of a free Ru atom) were investigated further by adaptive nudged elastic band calculations, which put no constraint

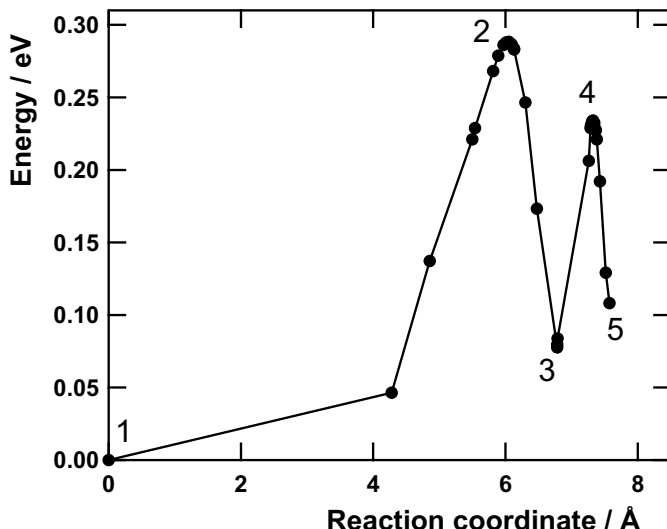


Figure 5.2: Energy versus reaction coordinate for one of the four different reaction paths studied by ANEB calculations. The energy of the gas phase is taken to be zero, and the definition of the reaction coordinate is given in the text (see Eq. 5.4).

on the intermediate values of X , Y , θ and φ . The 2D reaction paths and the ANEB reaction paths that correspond to the same initial configuration are labeled with the same number in Table 5.2. The 2 other reaction paths (5 and 6) that are studied either have their center-of-mass halfway between two CO molecules (5) or on top of a CO molecule (6). Additionally, we further investigate stretches of one of these reaction paths ('ANEB 2' in Table 5.2) with nudged elastic band calculations, as described in Sec. 5.2.3. The barrier heights and locations for these different reaction paths are shown in Table 5.2.

All four reaction paths studied show a complex energy landscape, with more than one barrier and minimum present. We choose to discuss one representative reaction path in more detail (the one labeled 'ANEB 3' in Table 5.2), because it contains features that are generic to other reaction paths as well. Figure 5.2 shows the plot of the energy versus the reaction coordinate. The energy of the gas phase is taken as zero and the reaction coordinate is defined as

$$R_i = \sum_0^i \sqrt{(X_i - X_0)^2 + (Y_i - Y_0)^2 + (Z_i - Z_0)^2 + (r_i - r_0)^2}, \quad (5.4)$$

where '0' corresponds to the gas phase configuration.

From this figure we observe a barrier (labeled '2' in Fig. 5.2) with a height of 0.29 eV (all energies quoted are relative to $H_2 + CO/Ru$, with H_2 in the gas phase). The same barrier is found for all four reaction paths studied with ANEB calculations. In addition, we observe a local molecular chemisorption minimum with an energy of 0.078 eV (labeled '3' in Fig. 5.2), which is also observed for all four reaction paths. Here, the H-H distance is only 0.84 Å, hardly larger than the gas phase H-H bond distance of 0.75 Å. When proceeding along the reaction coordinate, we then observe a second, lower barrier, of 0.23 eV (labeled '4' in Fig. 5.2). The presence of a second barrier is also characteristic for other reaction

Table 5.2: Barrier heights and configurations of the transition states (X_b , Y_b , Z_b , r_b , θ_b , φ_b) and final states for the separated H-atoms (x_1 , y_1 , z_1 , x_2 , y_2 , z_2) found for the different reaction paths studied. The barriers are obtained from 2D (r , Z) cuts through the PES with X , Y , θ and φ fixed, and from adaptive nudged elastic band (ANEb) calculations where the H_2 molecule is free to move in all 6 degrees of freedom. $Z = 0$ is defined as the average Z -coordinate of the first layer Ru atoms.

Calculation	$X_b/\text{\AA}$	$Y_b/\text{\AA}$	$r_b/\text{\AA}$	$Z_b/\text{\AA}$	θ_b/deg	φ_b/deg	Height/eV	$x_1/\text{\AA}$	$y_1/\text{\AA}$	$z_1/\text{\AA}$	$x_2/\text{\AA}$	$y_2/\text{\AA}$	$z_2/\text{\AA}$
2D (r, Z) cut 1	3.17	1.37	0.80	1.94	90	60	0.92						
ANEb 1	2.40	1.33	0.75	2.50	77	65	0.29	2.29	0.00	1.09	3.61	1.99	1.10
2D (r, Z) cut 2	2.18	0.34	0.81	1.86	90	30	0.86						
ANEb 2	2.38	1.29	0.76	2.40	65	96	0.29	2.53	1.65	1.54	1.89	0.07	0.98
2D (r, Z) cut 3	4.56	1.72	0.80	2.23	90	30	1.30						
ANEb 3	4.77	2.76	0.76	2.40	69	73	0.29	2.56	1.10	1.54	1.47	2.40	1.00
2D (r, Z) cut 4	3.96	1.37	0.66	2.93	90	30	2.70						
ANEb 4	3.93	2.15	1.77	1.46	83	26	0.43	1.23	2.12	1.10	2.30	0.00	1.10
2D (r, Z) cut 5	3.57	2.06	1.02	4.67	90	30	0.87						

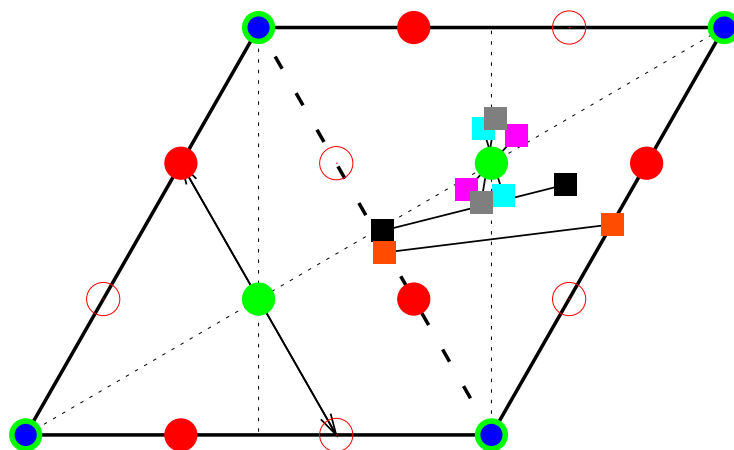


Figure 5.3: For one of the four different reaction paths studied by ANEB calculations (ANEB3, see text) the positions of the hydrogen atoms in the initial state (pink), in the first barrier configuration (light blue), in the molecular chemisorption minimum (gray), in the second barrier configuration (black) and in the final state (orange) are shown in the $CO/Ru(0001)$ unit cell. The CO molecules and Ru atoms are displayed as in Fig. 5.1. The fcc hollow sites are indicated by open red circles. The arrow corresponds to the minimum energy path for H_2 dissociating on the bare Ru surface.

paths, although for one of the four reaction paths studied this barrier was higher rather than lower than the first barrier encountered (0.29 eV). Finally the molecule dissociates to an atomic chemisorption minimum with an energy of 0.11 eV (labeled '5' in Fig. 5.2). The dissociation described by reaction path '3' is endoergic: The energy of the final state lies above 0, the energy of the gas phase. The same is observed for the other three reaction paths studied. This is in contrast with H_2 dissociation on bare $Ru(0001)$, which is observed to be exoergic [83]. Hence, the endoergicity must be caused by the presence of the CO molecules. For some of the other reaction paths dissociative chemisorption minima that are slightly lower (by a few meV) are present, but the calculations suggest that the molecules need to overcome a barrier that is higher than 0.3 eV to get there.

For the configurations discussed above the position of the separate H atoms is shown in the unit cell in Fig. 5.3. The initial, barrier and molecular chemisorption configuration are all on top of a bare Ru atom, and the $H-H$ bond is hardly stretched. Upon overcoming the second barrier the $H-H$ bond starts to stretch, and when the molecule is finally dissociated, the H atoms are 2.34 Å apart.

Figure 5.4, left panel shows another visualization of the dissociation process. The same five configurations as labeled in Fig. 5.2 and shown in Fig. 5.3 are also shown here. From Fig. 5.4 it can be observed that the $H-H$ bond first starts stretching considerably when moving towards the second barrier. The molecule rotates considerably while moving along this reaction path towards dissociation.

At the bare $Ru(0001)$ surface, the lowest barrier to dissociation is located at the top site [83], and the H_2 molecule subsequently dissociates with the H atoms moving to the threefold hollow sites [58, 83] (see Fig. 5.3). For the $CO/Ru(0001)$ system the first barrier is also present at the top site, but in this case the H atoms cannot be accommodated in the threefold hollow sites, since then they come too close to the CO molecules present at the surface (see Fig. 5.3). Because the H atoms cannot move to the hcp and fcc site towards

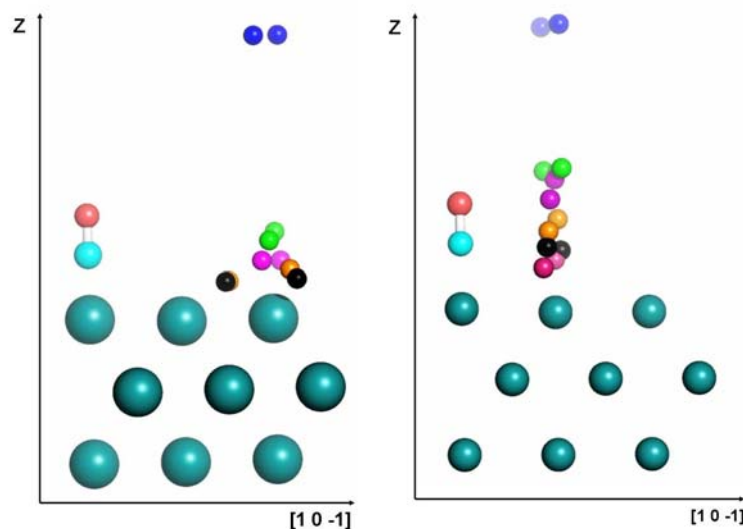


Figure 5.4: Left: Visualization of five configurations along a reaction path studied by ANEB calculations. The configurations shown are numbered in Fig. 5.2. Blue: gas phase; green: first barrier; pink: molecular chemisorption minimum; orange: second barrier; black: dissociated molecule. Right: Visualization of six configurations along the minimum energy reaction path for $\text{H}_2 + \text{CO}/\text{Ru}(0001)$ as found from NEB calculations. These 6 configurations are the same that are studied with projected density of states calculations (see text for details).

which they are directed in the first barrier geometry, after going through the molecular chemisorption minimum the center-of-mass of the molecule has to move away from the top site to stay on the (local) minimum energy path. The system then has to overcome a second barrier to allow the H atoms to move to atomic chemisorption sites close to the threefold hollow sites, but further removed from the adsorbed CO molecules than these sites. The poisoning of the threefold hollow atomic chemisorption sites by CO also explains why the H_2 dissociation process is endoergic, while H_2 dissociation at bare $\text{Ru}(0001)$ is exoergic.

The barriers found in the 2D cuts are considerably higher than found in the corresponding ANEB paths (see Table 5.2), due to the fact that X , Y , θ and φ are fixed in the 2D cuts. To overcome the minimum barrier, the molecule needs to rotate away from its initial orientation parallel to the surface (change of θ). Also the azimuthal angle φ changes upon overcoming the barrier, especially between the molecular chemisorption minimum and the second barrier. For the 2D reaction path where H_2 is placed directly above a CO molecule (reaction path 6) very high energies are found, indicating that this is not a favorable route to dissociation. The incoming H_2 molecule experiences a large repulsion on top of the CO and does not dissociate: Neither a barrier nor an exit channel are observed in the 2D cut.

Stretches of reaction path 2 are studied in more detail by NEB calculations (see Sec. 5.2.3) to get a global idea of the important configurations along the minimum energy path. The coordinates of 6 selected configurations along this path are given in Table 5.3. Figure 5.4 (right panel) shows a visualization of these 6 configurations along the minimum energy path. We observe that the H_2 molecule rotates to achieve a geometry that closely corresponds to the transition state (orange configuration in Fig. 5.4, right panel) and to chemisorb on the surface as separated atoms (pink configuration).

Table 5.3: Coordinates for the H_2 molecule in 6 selected configurations along one reaction path for H_2 dissociation on CO-precovered Ru(0001). See text and Fig. 5.4, right panel.

Configuration	$X/\text{\AA}$	$Y/\text{\AA}$	$r/\text{\AA}$	$Z/\text{\AA}$	θ/deg	φ/deg
0	2.38	1.38	0.75	8.45	90	160
1	2.38	1.38	0.75	4.17	90	160
2	2.36	1.36	0.75	3.58	29	93
3	2.38	1.32	0.76	2.51	55	90
4	2.36	1.37	0.81	1.81	90	86
5	2.44	0.87	1.72	1.30	73	104

Table 5.4: Energies in eV for 6 selected configurations along one reaction path for H_2 dissociation on CO-precovered Ru(0001). See text and Fig. 5.4, right panel. The gas phase energy is taken to be zero. The energies are compared for $H_2 + \text{CO/Ru(0001)}$, $H_2 + \text{Ru(0001)}$, H_2 with the CO overlayer only, and H_2 only. The coordinates of the configurations are given in Table 5.3.

Configuration	$H_2 + \text{CO/Ru}$	$H_2 + \text{Ru}$	$H_2 + \text{CO}$	H_2
0	0.00	0.00	0.00	0.00
1	0.09	-0.01	0.11	0.00
2	0.14	0.01	0.14	0.00
3	0.29	0.14	0.24	0.00
4	0.10	-0.14	0.26	0.06
5	0.21	-0.28	3.87	3.73

5.3.2 An energy decomposition and a molecular orbital analysis of the H_2 approach to the surface and the subsequent dissociation

To understand the mechanism of H_2 dissociation on CO-precovered Ru(0001) two-center projected density of states calculations are done for the total system and 3 subsystems: H_2 with pre-adsorbed CO on the Ru surface (Fig. 5.5), H_2 interacting with a clean Ru surface (Fig. 5.6), H_2 with only the CO overlayer (Fig. 5.7) and H_2 only (Fig. 5.8). The projected density of states plots are shown for the six configurations along reaction path 2 given in Table 5.3 and shown in Fig 5.4, right panel. The corresponding energy profiles are given in Table 5.4 and Fig. 5.9.

If the H_2 molecule is far from the surface only the H_2 σ_g bonding state is occupied (Fig. 5.5A, Fig. 5.6A and Fig. 5.7A). It is essentially a molecular state that is slightly broadened due to the interaction with its periodic images, as can be seen in the two-center projected density of states where only H_2 is present in the unit cell (Fig. 5.8A). But one should note that a part of the broadening seen in Figs. 5.5A through 5.8A is due to the finite width used to represent the δ -function in Eq. 5.1.

When moving the H_2 molecule closer to the CO/Ru surface (to the configuration labeled 1) a repulsion of 0.09 eV is encountered (Table 5.4 and Fig. 5.9). Table 5.4 and Fig. 5.9 clearly show this to be dominated by a direct repulsion between H_2 and CO. The repulsion is mainly due to an occupied-occupied interaction between the bonding H_2 σ_g orbital and the (surface-hybridized) CO 1π orbitals. [The occupied-occupied repulsion between H_2 σ_g

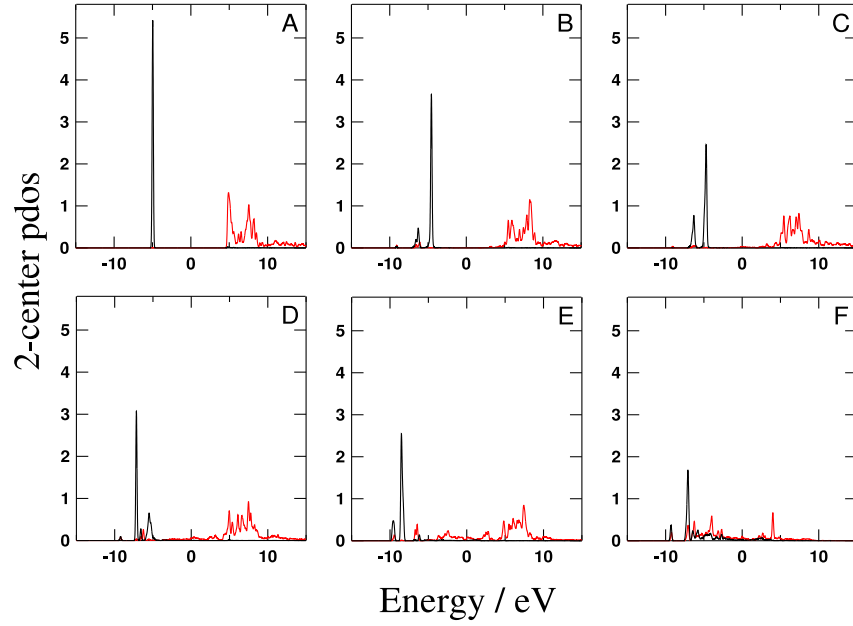


Figure 5.5: Two-center projected density of states (arb.units) for the full system, H_2 with the $\text{CO}/\text{Ru}(0001)$ surface, for 6 selected configurations (shown in Fig. 5.4, right panel) along one reaction path: A) gas phase; B) entrance channel 1; C) entrance channel 2; D) barrier; E) molecular chemisorption minimum; F) exit channel. Black: H_2 bonding state; red: H_2 antibonding state. The coordinates of the configurations are given in Table 5.3. The Fermi level is set at zero energy.

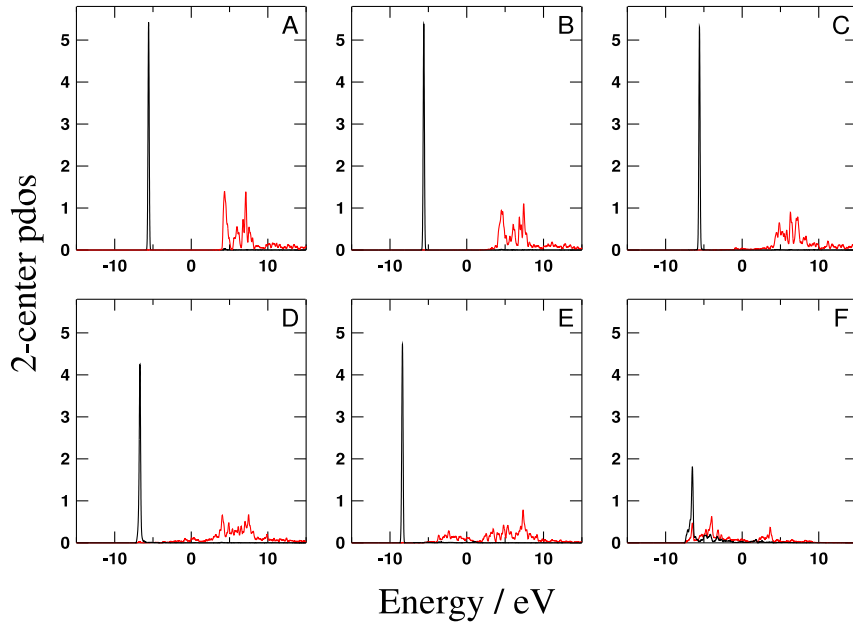


Figure 5.6: The same as Fig. 5.5, but now for the subsystem H_2 with the clean $\text{Ru}(0001)$ surface.

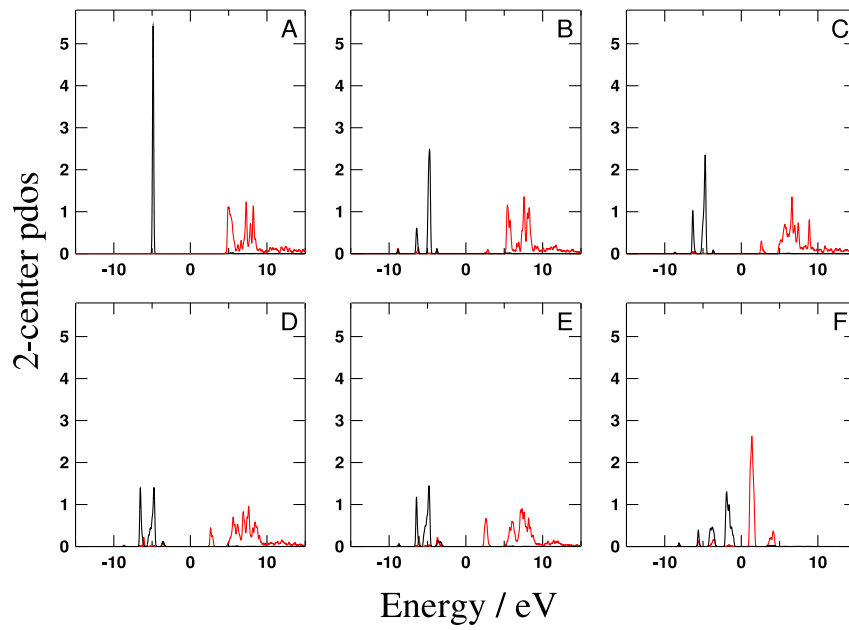


Figure 5.7: The same as Fig. 5.5, but now for the subsystem H_2 with the CO overlayer.

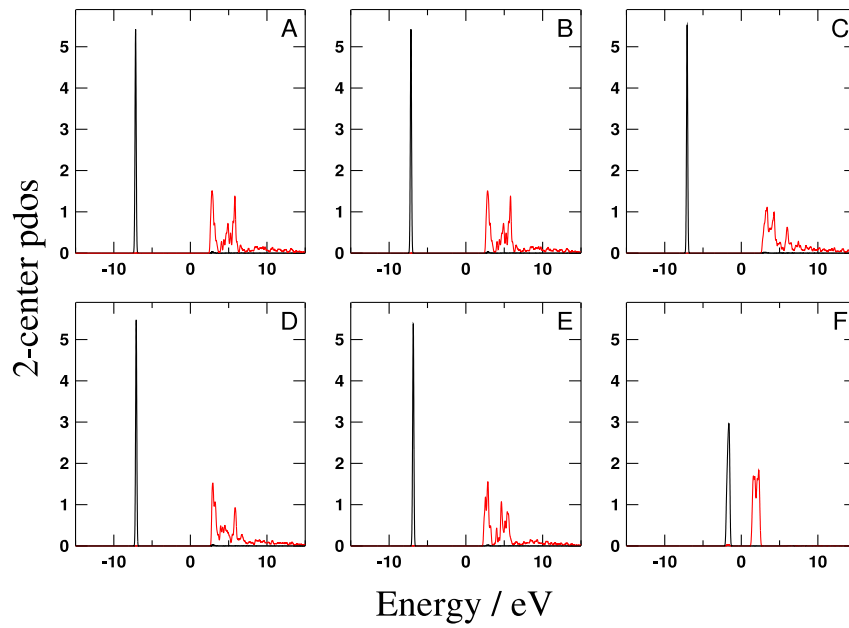


Figure 5.8: The same as Fig. 5.5, but now for the subsystem H_2 only.

and (surface-hybridized) CO 4σ and 5σ is very small, which is easily explained by the spatial extent of the occupied (surface-hybridized) CO orbitals: Both 4σ and 5σ are mainly extended along the CO bond axis (perpendicular to the surface) while the 1π orbitals are mainly extended parallel to the surface, creating larger overlaps with σ_g of the H_2 approaching the surface between the CO molecules.]

Moving the H_2 molecule even closer to the CO/Ru surface (to the configuration labeled 2) a repulsion of 0.14 eV is encountered (Table 5.4 and Fig. 5.9). Based on Table 5.4 and Figs. 5.5C through 5.8C and Fig. 5.9 exactly the same interpretation can be given as in the B case: The repulsion is mainly due to a direct occupied-occupied interaction between the H_2 σ_g orbital and the (surface-hybridized) CO 1π orbitals.

When reaching the barrier configuration the picture is slightly more complicated. A large part of the repulsive energy of 0.29 eV for CO/Ru (Table 5.4) appears to be due to the occupied-occupied repulsion between the H_2 σ_g orbital and the (surface-hybridized) CO 1π orbitals (0.24 eV, Table 5.4). This is understood based on the above arguments. But there is also a repulsive contribution from the interaction between the H_2 molecule and the Ru surface. Note, however, that if we take this contribution to be equal to the repulsive energy for $H_2 + \text{CO/Ru}$ minus that of $H_2 + \text{CO}$ (*i.e.* as 0.05 eV), then it appears to be smaller than one might expect based on the calculations of H_2 interacting with a clean Ru surface (0.14 eV, Table 5.4). The fact that the barrier (0.29 eV) is smaller than the sum of the repulsive energies obtained for the $H_2 + \text{CO}$ and $H_2 + \text{Ru}$ subsystems ($0.24 + 0.14 = 0.38$ eV, Table 5.4) suggests an interpretation in which the Ru surface as a subsystem is (slightly) *more* reactive for this approach geometry *with* CO pre-adsorbed than *without* it. To explain this we need to consider the interaction of H_2 with the clean Ru surface in some detail. But first we should note that we do not think the alternative explanation to be correct, that adsorbing CO onto the surface makes it *less* repulsive than the overlayer by itself. The reason is that the repulsion from the CO overlayer fully accounts for the repulsion on the approach to the barrier in $H_2 + \text{CO/Ru}$ (configurations 1 and 2, Table 5.4), since the energies for H_2 interacting with the CO/Ru(0001) and with the CO overlayer are almost the same. If adsorbing CO onto the surface makes it *less* repulsive than the overlayer by itself, we believe this would not have been the case.

In general, the height of the barrier to H_2 dissociation on top of a d -metal atom can, to a large extent, be understood as resulting from a competition between increasing overlap of the H_2 σ_u orbital and the metal d_{xz} -orbital (or a linear combination of d_{xz} and d_{yz} orbitals), decreasing overlap of the H_2 σ_g orbital and the metal d_{z^2} -orbital, and from the degree of occupation of the metal d -orbitals involved in the interactions (see *e.g.* Ref. [84]). In the case of H_2 approaching the clean Ru surface a part of the σ_g - d_{z^2} interaction can be seen as the lowering of the most intense σ_g peak in Fig. 5.6D (located at -6.7 eV), as compared to the situation when the H_2 molecule is further from the surface (peak located at -5.6 eV, Figs. 5.6A through 5.6C). This part of the σ_g - d_{z^2} interaction is molecule-surface bonding. However, since the d -band to a large degree is filled for Ru, there is a considerable population of the molecule-surface antibonding part from the same orbital interaction (this is not visible in Fig. 5.6D because it has predominantly metal- d character and does not show up in the H_2 σ_g projected density of states plots). The net effect of the σ_g - d_{z^2} interaction is therefore molecule-surface antibonding. The σ_u - d_{xz} interaction leads to a slight occupation of the H_2 σ_u orbital, as can be seen from the small bond elongation in Table 5.3 for configuration 3. The interaction is molecule-surface bonding, but the occupation of the resulting orbitals

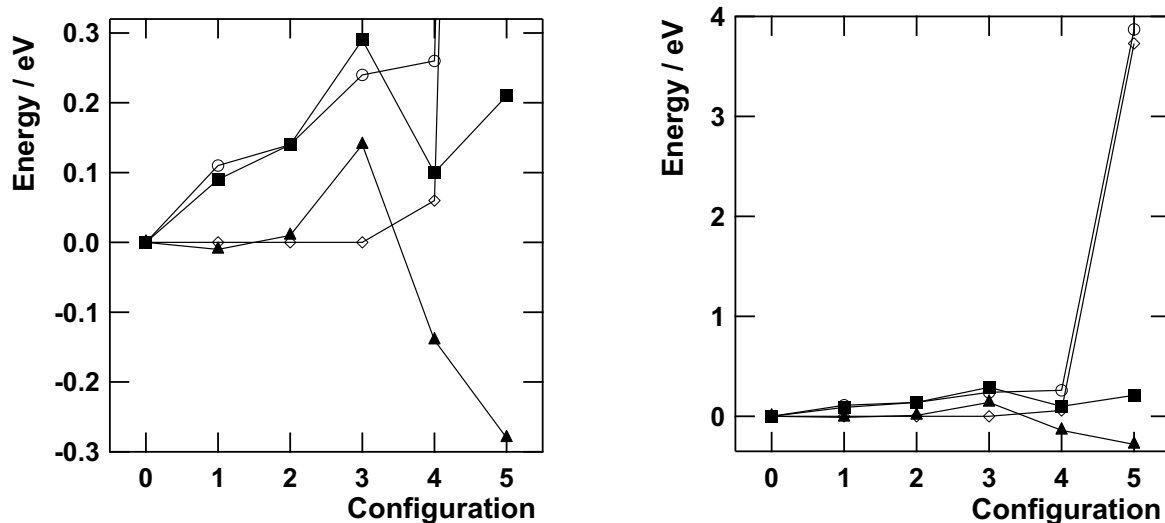


Figure 5.9: Energy profiles for 6 selected configurations (shown in Fig. 5.4, right panel) along one reaction path of H_2 dissociation on CO-precovered Ru(0001). The gas phase energy is taken to be zero. The profiles are compared for $H_2+CO/Ru(0001)$ (squares), $H_2+Ru(0001)$ (triangles), H_2 with the CO overlayer (circles), and H_2 only (diamonds). (Left panel) Plotted between -0.30 and 0.32 eV. (Right panel) Plotted between -0.35 and 4 eV. The coordinates of the configurations are given in Table 5.3.

is not large enough to counter the repulsive $\sigma_g-d_{z^2}$ interaction. Thus, the net effect of the $\sigma_g-d_{z^2}$ and σ_u-d_{xz} interactions is to create a barrier to H_2 dissociation along this path of 0.14 eV.

As already indicated, the numbers from Table 5.4 suggest that the contribution to the overall barrier of 0.29 eV from the Ru surface itself is only 0.05 eV. This is 0.09 eV lower than the corresponding barrier on clean Ru (note that the path considered is not exactly the minimum energy path for the $H_2 + Ru$ system [83]). The reason can clearly be seen in Fig. 5.10: Upon CO adsorption the d -orbitals of the surface Ru atoms with no adsorbed CO on them show a clear (small) shift upwards with respect to the Fermi level (the d -orbitals of the surface Ru atoms with adsorbed CO on them show a downward shift as expected [results not shown]). This reduces the repulsion due to a smaller occupation of the molecule-surface antibonding part of the $\sigma_g-d_{z^2}$ interaction. Although we here use a language from a localized molecular orbital interpretation picture, it is fully consistent with what would have been deduced from the much used d -band model: The center of the d -band of the reaction ensemble (i.e., the surface Ru atoms without adsorbed CO) moves towards the Fermi level upon CO adsorption, and therefore becomes more reactive [85]. It is important to stress that this discussion pertains to the Ru surface subsystem (and as such is rather academical although interesting), the total effect of CO adsorption on the Ru surface is to increase the hydrogen dissociation barrier.

The reduction in repulsion just after the first barrier [at the configuration labeled 5 (which is the molecular chemisorption configuration discussed earlier) and relative to barrier configuration 4] is seen to be caused mainly by the attraction towards the Ru surface, as

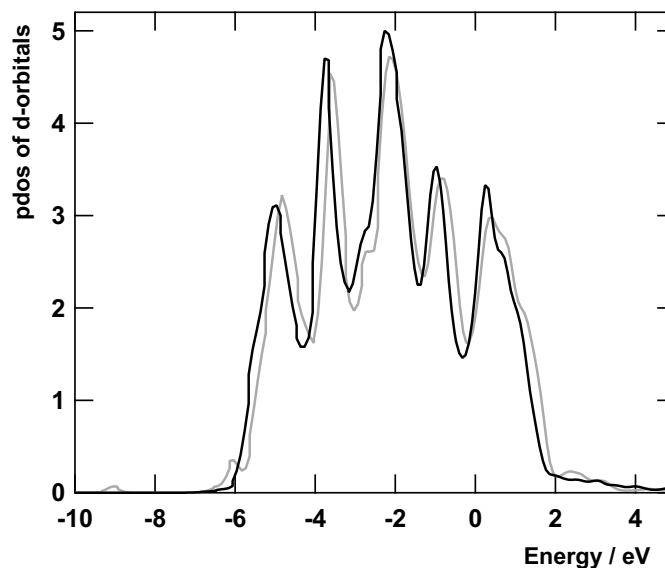


Figure 5.10: The projected density of states shows the d -orbitals with (gray) and without (black) CO adsorbed on the surface. The d -orbitals are displayed for the free Ru surface atoms, *i.e.* the green Ru atoms in Fig. 5.3 above which the first barrier to dissociation is crossed.

there is little change in the interaction with the CO overlayer from the barrier configuration (Table 5.4). This can be explained by the increasing population of the molecule-surface bonding molecular orbitals originating from the σ_u - d_{xy} interaction (compare Figs. 5.5E and 5.6E to Fig. 5.7). Thus, it is the σ_u - d_{xy} interaction that gives rise to the local minimum. The final step is the complete breaking of the H_2 bond (configuration labeled 5; this configuration corresponds to a stable dissociative chemisorption minimum, although the energy is higher than the dissociative chemisorption energy for ANEB 3) where all H_2 molecular properties are lost and separate bonds between the two hydrogen atoms and the Ru surface are formed (Table 5.4 and Figs. 5.5F through 5.8F).

5.4 Conclusions

We studied different reaction paths for the dissociative adsorption of hydrogen on a Ru(0001) surface pre-covered with 1/3 ML CO with DFT calculations. One reaction path was investigated in more detail by an energy decomposition analysis and by projected density of states calculations.

All reaction paths show a complex energy landscape. The minimum barrier to dissociation is 0.29 eV. At this barrier, the H-H bond is hardly stretched. In all reaction paths we studied, the system then moves to a molecular chemisorption minimum. This minimum is due to the molecule-surface bonding interaction of the d_{xy} orbital with the σ_u orbital. To fully dissociate, the molecule has to overcome a second barrier, which may either be lower or higher than the first barrier of 0.29 eV. The existence of the second barrier is caused by the fact that due to the presence of CO, H_2 cannot dissociate to the threefold hollow sites, as it does on bare Ru(0001). As a result, the dissociation is endoergic, as opposed to bare

Ru(0001) where H_2 dissociation is exoergic [83].

The barriers to dissociation found from the 2D (r, Z) cuts through the potential energy surface are all significantly higher than the ones found from the ANEB calculations. The reason is that the molecule has to rotate (*i.e.* change θ and/or φ) and to change its center-of-mass position in order to reach the minimum barrier geometry and dissociate, as allowed in the ANEB calculations.

The presence of CO on the surface increases the barrier to dissociation compared to the barrier for bare Ru(0001) (0.085 eV for the minimum energy path [83]). The results of the applied energy decomposition and molecular orbital analysis suggest that the increase of the barrier is mainly due to an occupied-occupied interaction between the bonding H_2 σ_g orbital and the (surface-hybridized) CO 1π orbitals. A small repulsive contribution to the barrier from the interaction between the H_2 molecule and the Ru part of the CO covered Ru surface is found, but it is smaller than one might expect based on the calculations of H_2 interacting with a clean Ru surface. Counter to intuition, the analysis suggests that the Ru surface as a subsystem is (slightly) *more* reactive for the reaction path studied *with* CO pre-adsorbed than *without* it. Thus, the results indicate that the influence of CO on H_2 dissociation on Ru is more than a simple site-blocking effect, the electronic structure of the underlying Ru (in particular the d -orbitals on the free Ru atoms) is changed.

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