Supporting Information: Anomalous Dependence of the Reactivity on the Presence of Steps: Dissociation of D₂ on Cu(211)

Gernot Füchsl,†,§ Kun Cao,†,§ Süleyman Er,‡ Egidius W. F. Smeets,† Aart W. Kleyn,¶ Ludo B. F. Juurlink,∗,† and Geert-Jan Kroes∗,†

†Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
‡Center for Computational Energy Research, Dutch Institute For Fundamental Energy Research, De Zaale 20, 5612 AJ Eindhoven, The Netherlands
¶Center of Interface Dynamics for Sustainability, Institute of Materials, CAEP,— 596 Yinhe Road 7th Section, Shuangliu,Chengdu, Sichuan 610200, Peoples Republic of China

§These authors contributed equally.

E-mail: l.juurlink@chem.leidenuniv.nl; g.j.kroes@chem.leidenuniv.nl
Phone: +31 (0)71 527 4221; +31 (0)71 527 4396
1. Potential Energy Surface

1.1 Computational Setup

To map out the potential energy surface for \( D_2(H_2) \) on Cu(211) we used the specific reaction parameter (SRP) approach to density functional theory (DFT). The DFT calculations employed the generalized gradient approximation (GGA) in the form of the SRP48 functional, that was build using a mixture of 48% RPBE and 52% PBE functionals. The validity of the SRP(48) functional for the description of the \( H_2 + Cu(111) \) interaction was previously established in Refs.\(^1\)\textsuperscript{-3} The calculations were carried out using ultra-soft pseudopotentials (US)\(^4\textsuperscript{,}5\) and a plane-wave basis as implemented in the \textit{Vienna Ab Initio Simulation Package} (VASP).\(^6\textsuperscript{-9}\) Since the simulation cells were repeated periodically, a vacuum spacing of 15 Å was included along the metal surface normal in order to prevent artificial interactions between periodic images. The Cu(211) surface was modeled using a \((1 \times 2)\) surface unit cell, with the bottom two layers of a five layer thick supercell kept fixed at their bulk lattice positions. The remaining three uppermost layers were allowed to relaxed before the \( H_2 + Cu(211) \) interaction potential was computed under the condition that the Cu(211) surface obeys the symmetry of the \( p1m1 \) space group, that is, the mirror axis is preserved, see below. The kinetic energy cutoff for the plane-wave expansion of electron wave functions was set at 370 eV. Brillouin zone integrations were carried out with \( \Gamma \)-centered \( 8 \times 8 \times 1 \) regular \( k \)-point grids that were generated using the Monkhorst-Pack scheme.\(^{10}\) Fermi smearing was used with a smearing width of 0.01 eV. The convergence criterion for self-consistency was set to 0.1 meV between two consecutive electronic steps. The structural optimizations of the periodic slab structures were assumed to be completed when the total remaining forces on the atoms were lower than 0.01 eV/Å. For PW91 calculations, we applied the same computational setup. Density of states (DOS) calculations are performed with a smearing width of 0.1 eV.
Figure S1: Coordinate system of H$_2$(D$_2$) on Cu(211). Left: top view onto a Cu(211)(1×1) unit cell with sampling points (blue dots) used to represent the 6D PES on the irreducible wedge (IW). Shown are the azimuth $\phi \in [0, 2\pi]$ and the lateral coordinates $X, Y$ of the center of mass of H$_2$ in units of $L_X = 6.373$ Å and $L_Y = 2.602$ Å. Right: side view on three layers of Cu(211) with definition of the molecule-surface distance $Z$ and the polar angle $\theta \in [0, \pi]$ between the macroscopic surface normal (black solid line) and the molecular axis (red dashed line). Also indicated is the terrace coordinate system (blue lines) which was rotated by $\chi = 18.7^\circ$ in the $X, Z$ plane in order to get its $Z'$ axis aligned with the normal to the terrace. This coordinate system is used to define the internal angular coordinates $\{\theta', \phi'\}$ as applied in the interpolation scheme, see also the text.

1.2 Construction of the Potential Energy Surface

For the presented dynamics study, we have constructed a potential energy surface (PES) incorporating the six molecular degrees of freedom (DOF) of the hydrogen molecule by interpolating a set of 115,830 DFT energy points calculated for different configurations of D$_2$(H$_2$) on a rigid Cu(211) surface. The molecular DOF are given by the center of mass position $X, Y, Z$ of H$_2$ relative to a Cu reference atom at the step edge, where $X$ and $Y$ describe the lateral position and $Z$ the molecule-surface distance. Also included are the H-H distance $r$, the azimuthal angle $\phi$ and the polar angle $\theta$ measured relative to the macroscopic surface plane, see Fig. S1 for more details.

An accurate interpolation is achieved by employing the corrugation reducing procedure
(CRP)\textsuperscript{11} which has previously been used to represent PESs of many other gas-surface systems with small interpolation errors.\textsuperscript{12–15} The CRP method exploits the fact that interpolation techniques are less error-prone for data that vary only modestly within the interpolation range. This is typically not a common feature of realistic global interaction potentials whose values can indeed be dramatically altered by small changes of the molecular position. Therefore, the raw potential data - denoted by $V^{DFT}$ in the following - need to be modified before they are interpolated. For that, a set of $V^{DFT}$ data is at first calculated for discrete positions $\{Q_i\}$ of the molecule (where $i$ is a multidimensional index and the position vector is defined as $Q_i = [X_{i1}, Y_{i2}, Z_{i3}, r_{i4}, \theta_{i5}, \phi_{i6}]^T$) and then reduced by the (mainly repulsive) contributions of the atomic H(D)+Cu interaction potentials $V_{at}$:

$$I(Q_i) = V^{DFT}(Q_i) - V_{at}(q^{(1)}_i) - V_{at}(q^{(2)}_i).$$

The new data set $\{I(Q_i)\}$ is significantly less corrugated and suitable for the interpolations subsequently applied to the discrete representation. This results in a continuous and smooth function $I(Q)$, and a well described and continuous function $V(Q)$ valid for arbitrary positions $Q$ within the interpolation range:

$$V(Q) = I(Q) + V_{at}(q^{(1)}) + V_{at}(q^{(2)}).$$

The atomic potential $V_{at}$ is a function of the position of the $k$th hydrogen atom defined by the vector $q^{(k=1,2)} = [x^{(k)}, y^{(k)}, z^{(k)}]^T$ and is itself constructed by using the CRP method:\textsuperscript{11}

$$I_{at}(q_i) = V_{at}^{DFT}(q_i) - V_{ref}(q_i)$$

and, after interpolation of $I_{at}$, 

$$V_{at}(q) = I_{at}(q) + V_{ref}(q).$$
The reference potential $V_{\text{ref}}$ must be provided as continuous function of $q$ and is obtained by a simplistic force field Ansatz:

$$V_{\text{ref}}(x, y, z) = \sum_{n}^{N_{\text{clus}}} V_{\text{top}}(r_n) = \sqrt{(x-x_n)^2 + (y-y_n)^2 + (z-z_n)^2}, \quad (5)$$

where $V_{\text{top}}(r_n)$ is a simple representation of the H-Cu interaction potential, here calculated at the top site ($x = y = 0$) along the atom surface distance $z$. For the evaluation of eq. (5) it is convenient to replace the coordinate $z$ at which $V_{\text{top}}$ was calculated by the distances $r_n$ that an H atom assumes relative to the $n$th Cu atom of a reference cluster.

### Table S1: DFT grid representation of the irreducible wedge (IW) of the (1\times1) Cu(211) unit cell used to interpolate the three-dimensional atomic potential for the H(D)+Cu(211) system. The IW is indicated in Fig. S1.

| quantity                          | value          | unit | remark         |
|-----------------------------------|----------------|------|----------------|
| grid range along $x$ on IW        | [0,$L_X$]      | Å    |                |
| grid range along $y$ on IW        | [0,$L_Y/2$]    | Å    |                |
| grid range along $z$              | [-3.627, 6.372]| Å    |                |
| $N_x$ number of grid points in $x$ on IW | 18             |      | equidistant   |
| $N_y$ number of grid points in $y$ on IW | 3              |      | equidistant   |
| $N_z$ number of grid points in $z$ | 101            |      | equidistant   |
| $\Delta x$ grid spacing along $x$ | $L_X/18$       | Å    |                |
| $\Delta y$ grid spacing along $y$ | $L_Y/4$        | Å    |                |
| $\Delta z$ grid spacing along $z$ | 0.1            | Å    |                |
| representation of $V_{\text{top}}$ reference potential grid range along $z$ | [0, 6.372] | Å | non-equidistant |
| $N_{z_{\text{top}}}$ number of grid points in $z$ | 537            |      |                |

We proceed as follows to represent the atomic potential. We calculate the H-Cu(211) interaction potential along $z$ on 54 different impact sites $(x, y)$, sampling equidistantly the irreducible wedge of the (1\times1) surface plane. The irreducible wedge corresponds to the surface area sampled by the blue dots in Fig. S1. (Since a mirror plane exists parallel to $x$ at the brg line, there are two indistinguishable irreducible wedges corresponding to either the upper or the lower half of the total surface unit cell, see Fig. S1 for further information.) Details on
the grid representation are listed in Table S1. (We did not perform spin polarized calculations as it is not needed for our purposes). To properly describe the repulsive interaction given by the \( V^{top} \) reference potential \((x = 0 \text{ and } y = 0)\), we chose a dense, but non-equidistant, grid along \( z \). Altogether, about 6000 DFT points were calculated to construct the three-dimensional atomic potential of the H+Cu(211) system. The atomic corrugation reduced potential \( I_{at} \) as well as the top site reference potential \( V^{top} \) are interpolated along \( z \) by using a one-dimensional natural cubic spline interpolation. For the interpolation along the \( x, y \) direction, we adopt a Fourier interpolation that accounts for the translational invariance of the potential (periodicity along \( x \) and \( y \)) and the local \( C_S \) point group symmetry of the surface. The symmetry-adapted Fourier basis corresponds to the \( A_1 \) irreducible representation of the \( C_S \) point group and was obtained by applying the procedure presented in Ref.\(^{16}\)

### Table S2: DFT grid representation of the irreducible wedge (IW) of the (1×1) Cu(211) unit cell used to interpolate the six-dimensional interaction potential of H\(_2\)(D\(_2\)) on Cu(211).

| quantity                        | value   | unit | remark        |
|---------------------------------|---------|------|---------------|
| grid range along \( X \) on IW  | [0, \( L_X \)] | Å    |               |
| grid range along \( Y \) on IW  | [0,\( L_Y/2 \)] | Å    |               |
| grid range along \( Z \)        | [-2, 4.6] | Å    |               |
| grid range along \( r \)        | [0.4, 2.5] | Å    |               |
| grid range along \( \theta' \)  | [0, \( \pi/2 \)] | rad |               |
| grid range along \( \phi' \)    | [-\( \pi/4 \), \( \pi/2 \)] | rad |               |
| \( N_X \) number of grid points in \( X \) on IW | 9       |      | equidistant   |
| \( N_Y \) number of grid points in \( Y \) on IW | 3       |      | equidistant   |
| \( N_Z \) number of grid points in \( Z \) | 45      |      | equidistant   |
| \( N_r \) number of grid points in \( r \) | 22      |      | equidistant   |
| \( N_{\theta'} \) number of grid points in \( \theta' \) | 2       |      | equidistant   |
| \( N_{\phi'} \) number of grid points in \( \phi' \) | 3-4     |      | equidistant   |
| \( \Delta X \) grid spacing along \( X \) | \( L_X/9 \) | Å    |               |
| \( \Delta Y \) grid spacing along \( Y \) | \( L_Y/4 \) | Å    |               |
| \( \Delta Z \) grid spacing along \( Z \) | 0.15    | Å    |               |
| \( \Delta r \) grid spacing along \( r \) | 0.1     | Å    |               |
| \( \Delta \theta' \) grid spacing along \( \theta' \) | \( \pi/2 \) | rad |               |
| \( \Delta \phi' \) grid spacing along \( \phi' \) | \( \pi/4 \) | rad |               |
With the 3D atomic potentials in hand, we are able to construct the 6D PES for the D$_2$(H$_2$) + Cu(211) system in the following manner.$^{11}$ We calculate a number of two-dimensional potential (2D) cuts at different impact sites ($X, Y$) and different orientations of the molecule ($\theta, \phi$) defined with respect to the macroscopic surface normal. During this work, it turned out that a proper choice of selected angular orientations needs to be made, which allows us to avoid large oscillations in the DFT potential values and to simultaneously reduce the amount of \{\theta, \phi\} grid points used in the construction. Rather than working with \theta and \phi directly, we first introduce new coordinates $\theta'$ and $\phi'$ that are defined with respect to the normal of the (111) terrace. The coordinate transformation \{\theta, \phi\} → \{\theta', \phi'\} reads:

\[
\begin{align*}
\cos \theta' &= -\cos \phi \sin \chi \sin \theta + \cos \theta \cos \chi \\
\cos \phi' \sin \theta' &= \cos \phi \cos \chi \sin \theta + \cos \theta \sin \chi
\end{align*}
\]

and the back transformation \{\theta', \phi'\} → \{\theta, \phi\} is given by:

\[
\begin{align*}
\cos \theta &= \cos \theta' \cos \chi + \cos \phi' \sin \theta' \sin \chi \\
\cos \phi \sin \theta &= \sin \theta' \cos \phi' \cos \chi - \cos \theta' \sin \chi
\end{align*}
\]

Here, $\chi = 18.7^\circ$ is the angle assumed between the normal to the terrace and the normal to the macroscopic surface of Cu(211), see Fig. S1. For the potential representation, we choose the grid points \{\theta', \phi'\} = \{0^\circ, 0^\circ\}, \{90^\circ, 0^\circ\}, \{90^\circ, 45^\circ\}, \{90^\circ, 90^\circ\} and, in the case that the center of mass of D$_2$(H$_2$) is located on the top-to-bridge ($t2b$) line where no mirror plane exists, we also consider the angular orientation of \{90^\circ, -45^\circ\}. Note, that the orientation given by \{\theta' = 0^\circ, \phi' = 0^\circ\} describes the molecular axis perpendicular to the (111) terrace.

We apply the following interpolation order: (i) interpolation of all 117 2D cuts along $r$ and $Z$ using a 2D spline interpolation, (ii) interpolation along $\theta'$ using a one-dimensional trigonometric interpolation, (iii) interpolation along $X, Y, \phi'$ using a coupled three-dimensional
symmetry-adapted Fourier interpolation.

Finally, to make the PES global toward arbitrarily large values of \( Z \), we take advantage of the property that the PES must match the gas phase potential of the free \( \text{H}_2 \) molecule, which is only dependent on the H-H distance \( r \). We therefore switch the interpolated 6D PES to the gas phase potential \( V_{\text{gas}}(r) \) of \( \text{H}_2 \), when a certain distance \( Z_{\text{min}} \) is reached. The switching is done before the atomic potentials are added to the corrugation reduced 6D potential:

\[
I_{\text{sw}}(Q) = \begin{cases} 
I(Q)(1 - f(Z)) + I_{\text{gas}}(r)f(Z), & \text{if } Z_{\text{min}} \leq Z \leq Z_{\text{max}} \\
I_{\text{gas}}(r), & \text{if } Z > Z_{\text{max}},
\end{cases}
\]

where \( f(Z) = \left[ 1 + \cos\left(\frac{Z_{\text{max}} - Z_{\text{min}} - Z}{Z_{\text{max}} - Z_{\text{min}}}\pi\right) \right] / 2 \) and \( I_{\text{gas}}(r) = V_{\text{gas}}(r) - V_{\text{at}}(\vec{q}^{(1)}) - V_{\text{at}}(\vec{q}^{(2)}) \). (We note that \( V_{\text{at}}(x, y, z) \) is zero for large values of \( z \)). The switching boundaries are \( Z_{\text{min}} = 4.5 \ \text{Å} \) and \( Z_{\text{max}} = 4.6 \ \text{Å} \). The resulting PES and forces are smooth and fast to evaluate.

1.3 Accuracy of the Potential Energy Surface

Before performing dynamics calculations, we have carefully evaluated the accuracy of our PES by comparing its values with two different DFT data sets, not used in the construction of the PES. The first data set consists of \( N = 2000 \) DFT energy points calculated for randomly selected geometries of \( \text{D}_2 \) on \( \text{Cu}(211) \). In Fig S2, we plot the root mean square error

\[
\text{RMSE}(V_{\text{max}}) = \left( \frac{\sum_{i=1}^{N(V_{\text{max}})} (V_{\text{DFT}}(Q_i) - V_{\text{PES}}(Q_i))^2}{N(V_{\text{max}})} \right)^{1/2}, \text{ if } V_{\text{PES}}(Q_i) \leq V_{\text{max}} \quad (11)
\]

as function of the maximum potential energy \( V_{\text{max}} \) (meaning that the RMSE is evaluated over the number of data points \( N(V_{\text{max}}) \) for which the condition \( V_{\text{PES}}(Q_i) \leq V_{\text{max}} \) is fulfilled). For potential energy values of up to 10.0 eV (measured relative to the potential value at which \( \text{D}_2 \) assumes its classical equilibrium distance in the gas phase), the RMSE is below
43.4 meV (1 kcal/mol). The dynamically relevant part of the PES ($V_{\text{max}} < 2$ eV) is even better represented (RMSE $< 35$ meV).

Figure S2: Accuracy of the 6D PES in comparison to DFT calculations. Plotted is the root mean square error (RMSE) as function of the maximum potential energy. The RMSE values were determined using a data set consisting of up to 2000 randomly selected geometries for $\text{D}_2$ on Cu(211). The dashed horizontal line indicates chemical accuracy, that is, an RMSE value of 43.4 meV (1 kcal/mol). Also indicated is the number of points $N(V_{\text{max}})$ used to evaluate the RMSE, see text.

The maximum absolute error found at $V_{\text{max}} \leq 2.7$ eV is $\Delta = 160$ meV on the random data set. We therefore test the accuracy of the PES in the dynamically relevant region. The second data set we compared with consists of $N = 1564$ DFT energy points that were calculated for $\text{H}_2$ geometries selected from QCT calculations. This allows us to explore the accuracy of the PES in more detail for reactant configurations (region I), reactive configurations of $\text{H}_2(\text{D}_2)$ near the barriers (region II) and dissociative configurations (region III). The corresponding RMSE values are listed in Table S3. We achieve an overall very good agreement and a low RMSE of only 24.5 meV on all energy points. This is also supported by the comparison with
seven different transition state energies obtained from nudged elastic band calculations using VASP, as discussed in the next section. We therefore expect that results obtained from QCT calculations using the 6D PES are comparable to results that would have been obtained by far more expensive ab initio molecular dynamics (AIMD) calculations addressing the same conditions.

Table S3: Accuracy of the 6D PES in comparison to DFT calculations. RMSE values in meV for different regions of the dynamically relevant part of the PES. The test points were randomly selected from QCT calculations which sample PES values of up to 2.2 eV.

| region I | region II | region III | all |
|----------|-----------|------------|-----|
| Z > 1.5Å | Z ≤ 1.5Å, 0.9 ≤ r ≤ 1.5Å | Z ≤ 1.5Å, r > 1.5Å |     |
| RMSE     | RMSE      | RMSE       | RMSE |
| 21.8    | 28.8   | 25.6       | 24.5 |
| 1063    | 197   | 181        | 1564 |
1.4 Reaction Barriers of D₂ on Cu(211) and Influence of the DFT Functional

In the following, additional information on the reaction barriers computed with the nudged elastic band\(^{17,18}\) (NEB) algorithm are provided. (Specifically, we used the climbing image NEB algorithm). In Tab. S4, the coordinates of \{X, Y, Z, r, θ, φ\} of H\(_2\)(D\(_2\)) at the different barriers are specified. The geometries are also depicted in Fig. S3. Note, that θ, φ are here defined with respect to the macroscopic surface normal. The lateral positions X, Y are given in units of the surface lattice constants. In case of Cu(211), these are \(L_X = 6.373\) Å (6.308 Å) and \(L_Y = 2.602\) Å (2.575 Å) for SRP48 (PW91) calculations. In case of Cu(111), \(L_X = L = 2.602\) Å (2.575 Å) for SRP48 (PW91) calculations, and for Cu(100), \(L_X = L_Y = 2.602\) Å. The presented barriers are 1\(^{st}\) order saddle points, except at \(t_1\) which is a 2\(^{nd}\) order saddle point. We verified this by vibrational frequency analyses.

Table S4: Reaction barrier geometries for H\(_2\)(D\(_2\)) on Cu(211) at different impact sites obtained from NEB calculations using the SRP48 and PW91 (values in brackets) functionals. The lateral positions (X, Y) of the center of mass is defined in units of \(L_X\) and \(L_Y\), see text.

| Site | X[\(L_X\)] | Y[\(L_Y\)] | Z [Å] | r [Å] | θ [°] | φ [°] |
|------|------------|------------|--------|--------|--------|--------|
| \(b_1\) | 0.958(0.961) | 0.500(0.500) | 0.98(0.98) | 1.17(1.16) | 76.5(77.5) | 0.0(0.0) |
| \(b_2\) | 0.806(0.814) | 0.252(0.242) | 0.89(0.93) | 1.06(1.06) | 85.5(87.0) | 62.2(63.2) |
| \(b_3\) | 0.621(0.621) | 0.000(0.001) | 0.48(0.52) | 1.04(1.01) | 71.8(72.1) | 0.0(0.0) |
| \(b_4\) | 0.466(0.470) | 0.255(0.259) | 0.17(0.22) | 1.04(1.02) | 97.2(97.3) | 120.3(120.5) |
| \(t_1\) | 0.983(0.979) | 0.000(0.000) | 1.37(1.36) | 1.43(1.41) | 90.0(90.0) | 90.0(90.0) |
| \(t_2\) | 0.375(0.374) | 0.000(0.000) | 0.26(0.29) | 1.13(1.09) | 97.8(97.6) | 0.0(0.0) |
| \(t_2b\) | 0.962(0.971) | 0.168(0.168) | 1.31(1.31) | 1.41(1.40) | 105.7(105.7) | 86.5(87.2) |

Cu(111)\(^{1,3}\) | 0.500(0.500) | 0.000(0.000) | 1.17(1.16) | 1.03(1.01) | 90.0(90.0) | 90.0(90.0) |
| Cu(100)\(^{19}\) | 0.500 | 0.000 | 0.99 | 1.24 | 90.0 | 90.0 |

Barrier energies \(E^\dagger\) calculated with the PW91 and SRP48 functional are given in Tab. S5. Values \(E^\dagger_{\text{PES,SRP48}}\) denote the PES values at the SRP48-NEB geometries. PW91 calculations included a new bulk and slab optimization.
Table S5: Reaction barrier energies $D_2(H_2)$ on Cu(211) with geometries specified in Table S4 according to SRP48 and PW91 calculations. Energies $E^\dagger_{\text{PES,SRP48}}$ from our PES are obtained for the NEB-SRP48 geometries. Deviations $\Delta$ between NEB and PES are also listed for comparison. All energies are in meV relative to the classical minimum energy value of $D_2(H_2)$ in gas phase.

| Path | $E^\dagger_{\text{PW91}}$ | $E^\dagger_{\text{SRP48}}$ | $E^\dagger_{\text{PES,SRP48}}$ | $\Delta$ [meV] |
|------|----------------|----------------|----------------|--------------|
| b$_1$ | 546.0 | 726.9 | 715.3 | -11.6 |
| b$_2$ | 508.6 | 672.8 | 671.9 | -0.9 |
| b$_3$ | 571.0 | 725.7 | 725.9 | 0.2 |
| b$_4$ | 646.0 | 800.4 | 817.6 | 17.2 |
| t$_1$ | 507.9 | 694.1 | 692.9 | -1.2 |
| t$_2$ | 564.7 | 726.7 | 727.0 | 0.3 |
| t$_2$b | 476.0 | 662.8 | 678.8 | 16.0 |
| Cu(111)$^{1,3}$ | 485.5 | 636.0 | 636.0 | — |
| Cu(100)$^{19}$ | — | — | 742.0 | — |

The geometries associated with the barrier indicate that molecules most likely dissociate for parallel alignments of the molecular axis relative to the macroscopic surface. PW91-barriers are generally lower than SRP48-barriers. According to PW91 calculations, the lowest barrier on Cu(211) (t$_2$b position) is by about 9 meV smaller than that on Cu(111). This suggests that an SRP approach is necessary to properly describe the $H_2 + Cu(211)$ interaction, as the PW91 finding of the lower barrier for Cu(111) seems incompatible with the experimental evidence in Fig. 1.
Figure S3: Top view on to the $(1 \times 1)$ unit cell of Cu(211) and molecular hydrogen assuming different geometries at the first order saddle points as obtained from NEB calculations and the SRP48 functional.
2. Dynamics Calculations and Molecular Beam Parameters

The dissociation dynamics of D$_2$ is theoretically studied by performing quasi-classical trajectory simulations that account for the experimental molecular beam conditions, that is, the ro-vibrational state and translational energy distribution of the molecules in the beam. At a given nozzle temperature $T_n$, the probability of finding a hydrogen molecule in the beam with a velocity $v + dv$ and in a particular ro-vibrational state characterized by the vibrational quantum number $\nu$ and the angular momentum quantum number $j$ is here given by:

$$P(v, \nu, j, T_n)dv = P_{vel}(v; T_n)dv \times P_B(\nu, j, T_n)$$

$$= A(v^3) \exp\left(-\frac{(v - v_0)^2}{\alpha^2}\right)dv \times P_B(\nu, j, T_n)$$

(12)

where $A$ is a normalization constant. The probability function reflecting the population of the ro-vibrational states associated with the eigenenergies $E_{\nu,j}$ at $T_n$ is given by:

$$P_B(\nu, j, T_n) = \frac{w(j)f(\nu, j, T_n)}{\sum_{\nu', j' \equiv j \mod 2} f(\nu', j', T_n)}$$

(14)

with

$$f(\nu, j, T_n) = (2J + 1)\exp\left(-\frac{(E_{\nu,0} - E_{0,0})}{k_BT_n}\right)\exp\left(-\frac{(E_{\nu,j} - E_{\nu,0})}{0.8k_BT_n}\right)$$

(15)

The factor $w(j)$ accounts for ortho- and para-hydrogen molecules present in the beam. In the case of H$_2$, $w(j)$ assumes a value of 1/4 (3/4) for even (odd) values of $j$, and in the case of D$_2$, $w(j) = 2/3 (1/3)$ for even (odd) values of $j$. The probability distributions $P(v, \nu, j, T_n)$ is sampled for the molecular beam parameters listed in Table S6 by a Monte-Carlo method described in Ref. 21.
Table S6: Molecular beam parameters, experimental and theoretical results on the sticking coefficients $S_0$ for D$_2$ on Cu(111) and Cu(211). Experimental values on sticking were determined from ten different measurements. Theoretical results are obtained from $5 \times 10^4$ - $10^6$ trajectory calculations simulating the experimental beam conditions.

| ($E_i$) [kJ/mol] | $\alpha$ [m/s] | $v_0$ [m/s] | $T_n$ [K] | Experiment $S_0 \pm \sigma$ [$\times 10^{-2}$] | Theory - QCT $S_0 \pm \sigma$ [$\times 10^{-2}$] |
|------------------|----------------|-------------|----------|----------------------------------|----------------------------------|
| D$_2$ + Cu(111)  |                |             |          |                                  |                                  |
| 29.8             | 1155.6         | 3217        | 1328     | 1.18 ± 0.21                      | 0.56 ± 0.03                      |
| 32.4             | 1150.8         | 3409        | 1441     | 1.38 ± 0.28                      | 1.03 ± 0.05                      |
| 34.8             | 1228.0         | 3497        | 1550     | 2.08 ± 0.23                      | 1.77 ± 0.06                      |
| 39.2             | 1463.9         | 3519        | 1744     | 2.38 ± 0.29                      | 4.45 ± 0.09                      |
| D$_2$ + Cu(211)  |                |             |          |                                  |                                  |
| 29.0             | 1136.6         | 3173        | 1290     | 0.69 ± 0.09                      | 0.21 ± 0.01                      |
| 29.0             | 1092.3         | 3221        | 1290     | 0.91 ± 0.18                      | 0.20 ± 0.01                      |
| 31.7             | 1281.8         | 3212        | 1413     | 0.82 ± 0.08                      | 0.53 ± 0.01                      |
| 33.7             | 1315.6         | 3315        | 1500     | 0.91 ± 0.06                      | 0.82 ± 0.01                      |

For simplicity, we work within the Born-Oppenheimer static surface (BOSS) approximation in the QCT calculations and solve Newton’s equation of motion:

$$m_i \frac{d^2 q_i}{dt^2} = -\frac{\partial V(q)}{\partial q_i}. \tag{16}$$

For practical reasons, we chose to propagate in cartesian (atomic) coordinates $q_i$, and the mass $m_i$ is the mass of a D atom. (The forces resulting from the potential (rhs of eq.(16)) are transformed from molecular to cartesian coordinates). For the propagation of the dynamics, we used a the velocity-verlet algorithm with a time step of $0.5 \hbar/E_h \ (\approx 0.0121 \text{ fs})$ allowing for an energy conservation error of smaller than 1 meV. The maximum propagation time is 4 ps. All trajectories start at a molecule-surface distance of $Z = 7.0 \text{ Å}$. Dynamically calculated probabilities $P_i$ are computed as ratio of the number of results $N_i$ in the specific outcome considered and the total number $N$ of calculated trajectories:

$$P_i = N_i/N. \tag{17}$$
Here, $P_i$ can be the sticking ($S_0$) or the scattering probability ($\sigma$). For Cu(211), $N$ is usually $10^6$ and for calculations on Cu(111) $N = 5 \times 10^4$. Molecules are counted as scattered, if they reach a molecule-surface distance of $Z = 7.1$ Å after collision with the surface, and as adsorbed, if a D-D distance of $r \geq 2.45$ Å is observed. We note that $\sigma = 1 - S_0$ is fulfilled suggesting that molecular trapping is unimportant for the dynamics.
3. Reactive Sites for D$_2$ Dissociation on Cu(211)

In the following, we analyse QCT calculations in order to reveal the reactive sites on Cu(211) for bond cleavage of D$_2$ at an incidence energy of $\langle E_i \rangle = 33.67$ kJ/mol, according to beam parameters given in Tab. S6. We therefore determined the reaction density on the Cu(211)(1×1) unit cell by computing the probability density of finding reacting molecules per surface area once the molecule that goes on to react has assumed a particular interatomic distance $r_a$ in the dynamics. (A molecule is considered as reacted once it takes on an interatomic distance of $r = 2.45$ Å, $r_a$ is only used for analysis purposes.) In Fig S4c), the corresponding plot for D$_2$ at $r_a = 1.1$ Å is shown. For a better guidance of the eye, we also included a top view onto the Cu(211) surface in Fig S4a) and a plot of the optimized reaction barrier energies as function of the impact site in Fig S4b). We observe that reaction predominantly takes place near the t$_2$b TS geometry in an area ranging from the step edge atoms to the b$_2$ site and, clearly separated from that, at the t$_2$ site on top of the highest coordinated Cu atom located at the bottom of the step. This picture remains qualitatively unchanged during the entire reaction dynamics in the sense that it is independent of the precise interatomic distance $r_a$ at which the analysis is performed. This suggests that the reaction assumes a direct mechanism and does not involve long-lived molecular trapped states before dissociation occurs.

As discussed in the main paper, the high efficacy of the t$_2$ site for reaction is a consequence of configurational effects associated with the bond length $r^\dagger$ assumed at the barrier and the ability of a surface area to be “azimuthally open”. At the TS state geometry, that is, at the t$_2$b site, the molecule assumes a larger interatomic distance than at the t$_2$ site. The t$_2$ site appears also to be the site that is azimuthally most open. For more details, see the geometries specified in Tab. S4 and and azimuthally averaged barriers listed in Tab.1 of the main paper.
Figure S4: a) Top view onto the Cu(211)(1×1) surface, b) lowest reaction barriers as function of the impact site X, Y, and c) reaction density as function of X, Y calculated for D$_2$ incident with $\langle E_i \rangle = 33.67$ kJ/mol on Cu(211). The reaction density plot was resolved over 290 000 reactive trajectories in the moment they assume an analysis distance of $r_a = 1.1$ Å.
4. Molecular Beam Experiments

4.1 King and Wells Technique

The sticking probability of D$_2$ on Cu(111) and Cu(211) is determined using the King and Wells (KW) technique.$^{22}$ Our supersonic molecular beam-UHV system has been described before.$^{23}$ Briefly, two flags and a valve intersect a double differentially-pumped molecular beam on its path toward the UHV-housed sample. The valve separates the first and second differential stages. Closing the valve allows us to determine the residual effusive load from our 1-4 bar expansion of the pure gases in the expansion chamber through a 25 µm orifice, laser-drilled through a tungsten nozzle. The first flag is located in the first differential chamber. It blocks the entire beam from entering the second differentially-pumped chamber and the UHV chamber. The second flag is located inside the main chamber and blocks the beam from impinging onto the single crystal surface.

The KW technique used with a single measurement can be applied when the sticking probability, $S$, is larger than $\sim$0.01-0.03 as the dip in the partial pressure trace that appears when opening the second flag needs to be discernable within the noise-level. To improve our detection limit, the opening and closing of the two flags is computer-controlled with accurate, but variable time intervals for both flags. The sticking probability is measured repeatedly under identical conditions and we average the resulting KW-traces. Hence, we improve our detection limit by (approximately) the square root of the number of repetitions of the measurement. Fig. S5a) shows an example of our data from ten repeated measurements. Note that it only shows the upper tenth part of the vertical axis’ full scale. The data clearly show the dip in the partial pressure when opening the second flag 16 sec after the first flag. It also shows a slowly increasing background, which we account for by fitting and extrapolating the data prior to opening the second flag and by comparison to results when the second flag was not opened at all during the 40 sec experiment. Note that accounting for this modest change
Figure S5: a) Example of using repeated KW measurements to improve the detection limit. The red curves are ten repeated measurements, whereas the black curve is the average of those. The inset graph I) shows the full range of a single measurement, from which the drop in the QMS signal can not be distinguished. The inset graph II) shows the average signal after the slow time-dependent increase in the background pressure has been removed. b) Example of the time-dependent sticking (red) and a double-exponential fit (black) obtained from normalizing and inverting the KW trace as shown in inset II). The fit is used to determine $S_0$.

in background for the duration of the experiment (on the order of a couple of percent only) is relevant to accurate determination of the time-dependence of sticking. The slow increase in background likely results from extremities of the UHV system being pumped less efficiently and/or a change in the QMS channeltron’s sensitivity by exposure to hydrogen.24 Fig. S5b) illustrates how we extract an accurate initial sticking coefficient, $S_0$, from the averaged data.

We fit the time-dependent sticking obtained through normalizing and inverting the averaged KW trace by a linear functional form through the first couple of seconds and a double exponential functional form when reliable data is available for longer exposures, and extrapolating to the exact time of opening the second flag. This removes the convolution of the QMS partial pressure measurement at 4-5 Hz with the time constant from opening the second flag.

Fig. S6 shows for nearly identical conditions a direct comparison of the coverage-dependent sticking probabilities obtained in this way for Cu(111) (red) and Cu(211) (blue). Although the kinetic energy for Cu(211) is higher, the (initial) sticking probability is clearly considerably lower.
4.2 Time of Flight Technique

The velocity distribution of the beam can be described by a shifted Maxwell-Boltzmann distribution:\textsuperscript{25}

\[ P_{\text{vel}}(v; T_n) = A v^3 \exp\left(\frac{-(v - v_0)^2}{\alpha^2}\right) \]  

(18)

where \( v_0 \) is the flow velocity, \( \alpha \) a measure for the velocity spread, and \( A \) a normalization factor. This distribution folds into the probability of finding a hydrogen molecule in the beam with a velocity \( v + dv \) as described by equation 12. We use time-of-flight (TOF) methods to measure the molecular beam’s velocity distribution. The continuous molecular beam is chopped into short pulses by a chopper wheel with a duty cycle of 0.5\%. The chopper wheel is spun at a frequency of \( \sim 170 \text{Hz} \), resulting in convolution of the TOF distribution with a gating function.
The total measured flight time, \( t_{\text{total}} \), is composed of the following contributions:

\[
t_{\text{total}} = t_{\text{TOF}} + \Delta t_{\text{trig}} + \Delta t_{\text{elec}} + \Delta t_{\text{QMS}}
\]  

(19)

where \( t_{\text{TOF}} \) is the flight time of the neutral species from chopper wheel to the QMS ionizer over a distance \( L \). \( \Delta t_{\text{trig}} \) captures the offset between the signal of the optical sensor triggering our multi-channel scalar (MCS) card and the center time of release of the gas pulse. \( \Delta t_{\text{QMS}} \) captures the flight time of the ionized species from ionizer to the QMS channeltron. \( \Delta t_{\text{elec}} \) captures the electronic delay difference for the optical pulse and channeltron pulse to arrive at the MCS card.

Our QMS, with its cross-beam ionizer, is mounted inside a differentially pumped stage, which can be moved by an \( x, y, z \) manipulator along the beam axis over a distance, \( d \), of 200 mm. By doing so, we vary only \( L \), i.e. the flight length of the neutral, hence \( t_{\text{TOF}} \). Through linear extrapolation of \( t_{\text{total}} \) to \( L=0 \) mm, we derive the sum of all other time delays, i.e. \( \Delta t_{\text{trig}} + \Delta t_{\text{elec}} + \Delta t_{\text{QMS}} \). These offsetting values are required for fitting procedures in the time-domain, as described below. Simultaneously, the slope in a graph plotting the most probable arrival time for different values of \( d \) yields the most probable velocity. This is not identical to \( v_0 \), though.

To obtain the beam’s velocity distribution, we convert equation (19) to the time-domain:

\[
\int P_{\text{vel}}(v; T_n) dv = \int g(t; T_n) dt
\]

(20)

Using \( v = L/t \) and \( dv \sim t^{-2} \) the function can be rewritten as:

\[
g(t; T_n) \sim \left( \frac{L}{t} \right)^5 \cdot \exp \left( - \left( \frac{L}{t} - \frac{L}{t_0} \right)^2 \frac{1}{\alpha} \right)
\]

(21)
Figure S7: a) A typical TOF spectrum (red) and fit (black) in the time domain. b) The corresponding molecular beam’s energy distribution. The dashed blue line indicated the full width at half maximum.

The time $t$ in this equation corresponds to the time-of-flight for the neutral species, $t_{TOF}$. Prior to fitting in the time domain, we correct the measured time, $t_{total}$, for all delays and offsets as determined by the procedure described above. Then we fit each TOF spectrum for its specific neutral flight path length, $L$, taking into account that our density sensitive detector modulates the signal by a factor of $1/v$, hence fitting $g_{dens}(t)$ with a pre-exponential factor proportional to $(L/t)^4$. We also include a gating function by adding nine of the $g_{dens}(t)$ functions, each separated by 3 $\mu$s and scaled with the appropriate amplitude. We verify that the flow velocity, $v_0$, and distribution as characterized by $\alpha$ for spectra taken for identical expansion conditions, but varying $L$, yield consistent values.

We average values for $v_0$ and $\alpha$ for identical beam conditions and calculate the kinetic energy distribution by converting the velocity distribution to the energy domain:

$$g(E; T_n) = \frac{1}{m\sqrt{2E/m}}P_{vel}(v; T_n)$$  \hspace{1cm} (22)

where $E = mv^2/2$. Figure S7 shows a typical result of our TOF analysis for a pure D$_2$ beam. The reported molecular beam energy in Fig. 1 (and Tab. S6) represent average kinetic energy calculated from eq. (22). The horizontal dashed line in Fig. S7b) shows that
the energy width in our beam in a typical experiment is substantial. The beam parameters, \( v_0 \) and \( \alpha \), as determined by our fitting procedure in the time domain are reported in Tab. S6. The nozzle temperatures \( T_n \) were calculated from \( \langle E_i \rangle = 2.7 \times k_B T_n \) assuming 20\% rotational cooling and no vibrational cooling Ref.\(^\text{26}\). Comparison to temperatures measured 10-20 mm downstream the nozzle confirmed that, as expected, in most cases the nozzle temperatures determined from the relation stated above exceed the measured lower bounds, by values in the range 50 - 470 K. Nozzle temperatures were computed from the accurately determined average translational energies because physical constraints made it impossible to measure the nozzle temperature in our beam machine at the tip of our gas expansion tube. For the measurements reported here, as we noted, the thermocouple was attached 10-20 mm toward a cooling block and, therefore, it provided values significantly lower than the actual expansion temperatures. As the tip of the expansion tube is also hidden from view by heat shields, we could not use an optical pyrometer to measure the actual temperature near the nozzle’s orifice. In previous experiments from nearly a decade ago, where the thermocouple was located significantly closer to the tip of a previous design, we measured \( \sim 1800 \) K as the maximum obtainable temperature for nearly identical heating conditions. This maximum value is consistent with the maximum achieved nozzle temperature we determined from the average translational energies (1744 K, see Tab. S6).
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