Dynamical Quantum Filtering via Enhanced Scattering of \( \text{para-H}_2 \) on the Orientationally Anisotropic Potential of SrTiO\(_3\)(001)

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Quantum dynamics calculation, performed on top of density functional theory (DFT)-based total energy calculations, show dynamical quantum filtering via enhanced scattering of \( \text{para-H}_2 \) on SrTiO\(_3\)(001). We attribute this to the strongly orientation-dependent (electrostatic) interaction potential between the \( \text{H}_2 \) (induced) quadrupole moment and the surface electric field gradient of ionic SrTiO\(_3\)(001). These results suggest that ionic surfaces could function as a scattering/filtering media to realize rotationally state-resolved \( \text{H}_2 \). This could find significant applications not only in \( \text{H}_2 \) storage and transport, but also in realizing materials with pre-determined characteristic properties.

The behavior/dynamics of \( \text{H}_2 \) on surfaces strongly depend on the \( \text{H}_2 \) molecular orientation/rotational states (rotational quantum number \( J \), magnetic quantum number \( m \)) (cf., e.g., ref. 1 and references therein). On transition metal surfaces such as copper (Cu) and palladium (Pd), \( \text{H}_2 \) exhibits rotational alignment (cf., e.g., refs. 1,2 and references therein). One could then tune or design the structure of the metal (alloy) surfaces to dynamically filter the quantum rotational states of desorbing or scattered \( \text{H}_2 \) (dynamical quantum filtering), and control the \( \text{H}_2 \) dynamics (cf., e.g., refs. 1–7 and references therein). The resulting \( \text{H}_2 \) dynamics could, in turn, be used to probe local surface reactivity\(^8,9\) (e.g., via the \( \text{H}_2(\text{D}_2) \) diffraction spectra\(^10–12\)). On ionic crystal surfaces, the \( \text{H}_2 \) quadrupole moment interacts with the surface local electric field gradient to couple the translational and rotational degrees-of-freedom\(^13\). On SrTiO\(_3\)(001) (STO(001)), an ionic crystal material\(^14–21\) with tunable surface terminations (cf., e.g., refs. 22–23), \( \text{H}_2 \) adsorbs with the H-H bond oriented parallel (polar coordinate \( \theta = \pi/2 \)) to the TiO\(_2\)-terminated surface at the Ti-site, and perpendicular (\( \theta = 0 \)) to the SrO-terminated surface on top of the O-site (cf., Fig. 1)\(^24\). The strong orientationally anisotropic potential (\( \Delta E_{\text{anisotropy}} = |E_{\theta=0} - E_{\theta=\pi/2}| \)) results in adsorbed \( \text{H}_2 \) with (hindered) rotational states (\( J, m \)) different from that of gas phase \( \text{H}_2 \). These strongly hindered adsorption states lead to (\( J, m \))-dependent thermal desorption energies\(^24–30\), suggesting the possibility of separating \( \text{H}_2 \) [(\( p\)-\( \text{H}_2, J = 0, m = 0 \)) and \( \text{ortho-} \text{H}_2, \{ o-\text{H}_2, (J = 1, m = \pm 1) \}] \) through an adsorption-desorption process. This could find significant applications not only in \( \text{H}_2 \) storage and transport applications, but also in realizing materials with pre-determined characteristic properties.

As with metal (alloy) surfaces\(^5,8,9\), the \( \text{H}_2 \) dynamics would be susceptible to the positive and negative charges that corrugate ionic crystal surfaces. In the following, we will show that on STO(001), under the influence of the orientationally anisotropic potential, on top of the surface lateral corrugation, \( p\)-\( \text{H}_2 \) scatter strongly at specific angles from the TiO\(_2\)-terminated and SrO-terminated STO(001). This dynamical filtering/scattering selectivity allows for more economical (less heat consumption) and more efficient means to rotationally separate \( o\)-\( \text{H}_2 \) and \( p\)-\( \text{H}_2 \), than the usual adsorption-desorption process\(^1–5,24–30\).

Results and Discussion

\( \text{H}_2/\text{SrTiO}_3(001) \) System. Figure 1 shows a \( \text{H}_2 \) interacting with STO(001). \( X \) gives the surface lateral coordinate of the \( \text{H}_2 \) center-of-mass (CM) along the most corrugated directions on the two STO(001) terminations, viz., along [100] for TiO\(_2\)-termination (Ti-O-Ti row) and along [110] for SrO-termination (Sr-O-Sr row), respectively.
becomes of finding H2(80 meV). This corresponds to the surface lateral position of the H2 CM along the (a) [100] and (b) [110] direction on the TiO2- and SrO-terminated SrTiO3(001), respectively.

Figure 1. A depiction of H2 adsorption (a) atop the Ti-site and (b) atop the O-site on the TiO2- and SrO-terminated SrTiO3(001), with corresponding preferential orientations \( \theta = \pi/2 \) and 0, respectively. The lower left panel shows which colored balls correspond to which element. (c) A depiction of H2 with the H2 center-of-mass (CM) at a distance Z from the surface, and the H-H bond at an orientation \( \phi \) with respect to the surface normal. (d) A depiction of H2 scattering on SrTiO3(001) with angle of incidence \( \theta_i \) and scattering angle \( \theta_f \). 

(c.f., Fig. 1(a,b)). Z gives the normal distance of the H2 CM from the surface. \( \phi \) (not shown) gives the azimuthal angular orientation of the H-H bond with respect to the surface normal. \( \phi \) (not shown) gives the azimuthal angular orientation of the H-H bond with respect to the surface normal, with respect to the X-axis, at each site on STO(001). \( \phi \) gives H2 incidence (scattering) angle measured with respect to the surface normal (c.f., Fig. 1(c,d)). In the following, given \( \frac{H_2}{(f)} \) with initial rotational state \( (J_i, m_i) \), we determine the probability of finding \( \frac{H_2}{(f)} \) with final rotational state \( (J_f, m_f) \) scattered from STO(001) with a final translational energy \( E_f \), at an incidence angle \( \theta_i \) with respect to the surface normal. \( \frac{H_2}{(f)} \) scattered as \( \frac{H_2}{(m)} \) indicates a H2 with final rotational state \( (J_f, m_f) \), scattered from STO(001) with a final translational energy \( E_f \) and at a scattering angle \( \theta_f \) with respect to the surface normal.

Orientationally anisotropic electrostatic potential. In Figs. 2 and 3, we plot the (electrostatic interaction energies) dot products of the (induced) dipole moment with the surface electric field \( U_i \) and the (induced) quadrupole moment with the gradient of the surface electric field \( V_{ij} \) for the TiO2-terminated and SrO-terminated surfaces, respectively. We can see that the orientational \( (\theta) \) anisotropy \( \Delta E^{\theta}_{\text{anisotropy}} \) becomes important when the impinging H2 comes sufficiently near the surface, viz., at \( Z \leq 2.4 \) Å above the Ti-site and \( Z \leq 2.6 \) Å above the O-site on the TiO2- and SrO-terminated surfaces, respectively. On the other hand, far from the surface, viz., at \( Z \geq 3.2 \) Å above the O-site and \( Z \geq 3.0 \) Å above the Sr-site of the TiO2- and SrO-terminated surfaces, respectively, only a small \( \Delta E^{\theta}_{\text{anisotropy}} \) can be observed. This orientational anisotropy \( \Delta E^{\theta}_{\text{anisotropy}} \) on top of the surface lateral corrugation, would prove to be useful in our attempt to control the H2 scattering dynamics, as we will discuss in detail in the next sections.

H2 Scattering along STO(001)[100] on TiO2-terminated STO(001). In Fig. 4(a–c), we show the calculated (scattering) probabilities/spectra \( P^{\text{scat}}_{h=0, m_h}(E_i = 80 \text{ meV}, E_f, \theta_i = 15.9^\circ, \phi_h) \) of finding \( \frac{H_2}{(f)} \) at \( E_i = 80 \text{ meV}, \theta_i = 15.9^\circ \) scattered as \( \frac{H_2}{(m)} \) at \( \theta_f \) along the [100] direction of a TiO2-terminated STO(001). The corresponding initial surface perpendicular translational energy \( E_i \times \cos^2 \theta_i = 80 \text{ meV} \times \cos^2(15.9^\circ) \sim 74.0 \text{ meV} \) and initial surface lateral translational energy \( E_i \times \sin^2 \theta_i = 80 \text{ meV} \times \sin^2(15.9^\circ) \sim 6.00 \text{ meV} \). This corresponds to the maximum \( p-H_2 \) to \( o-H_2 \) ratio \( R_p/o_{H_2}(E_i = 80 \text{ meV}, \theta_i = 15.9^\circ, \phi_h) \) on a TiO2-terminated STO(001) (c.f., Table 1). The resulting trends can be explained by inspecting the corresponding orientational anisotropy and surface lateral corrugation of the potential encountered by the impinging \( \frac{H_2}{(f)} \) at \( E_i = 80 \text{ meV}, \theta_i = 15.9^\circ \) (i.e., \( \langle V^m_{ij} \rangle V(Z, \theta, \phi) \rangle \langle V^m_{ij} \rangle \), cf., Fig. 4(d)). Note that along STO(001)[100], \( \frac{H_2}{(f)} \) encounters a strongly corrugated and orientationally anisotropic PES (c.f., solid curve in Fig. 4(d)), that favors molecular
Adsorption atop the Ti-site, with H-H bond oriented parallel to the surface, and an adsorption energy $E_{\text{ads}} = -191$ meV. Atop the O-site, $H_2$ preferentially adsorbs with the H-H bond oriented perpendicular to the surface, with $E_{\text{ads}} = -72.5$ meV. As a result, in Fig. 4(a), we find a corresponding spectra dominated by off-specularly scattered $H_2$ with dominant components coming from backscattering. Most of the $H_2(\vec{j}_i = 0, m_i = 0)$ would be
molecularly adsorbed (due to reorientation/steering\textsuperscript{31,32}), and only a small fraction would be elastically scattered (due to shadow effect\textsuperscript{9}). Considering the angle of incidence, the inelastically scattered $\text{H}_2$ would come from those hitting the repulsive part of the potential well near the O-site (shadow effect, cf., solid curve in Fig. 4(d)), resulting in a change in surface lateral momentum and off-specular scattering angles. Energy transfer from the

Figure 3. Calculated electrostatic potential contributions from (a) the induced dipole moment $\Delta D_i$ with the surface electric field $U_i$, (b) the induced quadrupole moment $\Delta Q_{ij}$ and (c) the $\text{H}_2$ quadrupole moment $Q_{ij}$ with the gradient of the surface electric field $V_{ij}$, on the Sr-site (squares) and the O-site (circles) with $\theta = 0$ (open symbols) and $\theta = \pi/2$ (filled symbols) for the SrO-terminated STO(001). (d) The sum of the contributions (a–c). $i,j = (x,y,z)$. The dotted vertical lines intercepting the abscissas indicate the locations of the corresponding potential energy minima ($\text{H}_2$–surface equilibrium distance) at each respective surface site.
Figure 4. (a–c) Calculated H\textsubscript{2} scattering probability \((J_i, |m_i|) \rightarrow (J_f, |m_f|)\) from initial rotational state \((J_i, |m_i|)\) to final rotational state \((J_f, |m_f|)\) on the TiO\textsubscript{2}-terminated STO(001) as a function of the scattering angle \(\Theta_f\) for incident energy \(E_i = 80\) meV and incident angle \(\Theta_i = 15.9^\circ\). The dotted vertical lines intercepting the abscissas indicate specular scattering. (d) Solid, dotted, and dash-dot lines indicate constant energy surfaces of \(\left\langle Y_{\theta YV}^{\Theta} \right\rangle \left(\theta, \Theta, X\right)\left|Y_{\theta Z}^{\Theta}\right\rangle\) (with 80 [meV] \(\times \cos^2\Theta\); corresponding to H\textsubscript{2} surface normal translational energy) encountered by a H\textsubscript{2} impinging with initial rotational states \((J_i, m_i)\); \{(0, 0), (1, 0), (1, 1)\}, respectively. Same scales used for \(X\)- and \(Z\)-coordinates. The arrows indicate the direction of incidence of the impinging H\textsubscript{2}.

Table 1. Calculated \(R_{J=0/1}^{(E_i, \Theta_i, \Theta_f)}\) and \(\overline{R}_{J=0/1}^{(E_i, \Theta_i, \Theta_f)}\) on TiO\textsubscript{2}-terminated STO(001) at the incident energy range \(10\) meV \(\leq E_i \leq 80\) meV. For each incident energy, we list only the maximum \(R_{J=0/1}^{(E_i, \Theta_i, \Theta_f)}\) with the corresponding incident and scattering angles.
translational degree-of-freedom (DOF) to the rotational DOF allows the molecule more time to sample the anisotropic surface through reorientation/steering. Those that succeed would molecularly adsorb. Those that fail, would be rotationally de-excited on the way back to the gas phase, because of the smaller anisotropic potential further (out in the vacuum) from the surface. Thus, the scattering spectra shows negligible rotationally excited H2, i.e., H2\((J_f = 2, m_f = 0)\). H2\((J_i = 1, m_i = \pm 1)\) also encounters a strongly anisotropic PES (cf., dash-dot curve in Fig. 4(d)). Thus, we see the same trend in Fig. 4(c), i.e., a corresponding spectra dominated by off-specularly scattered H2, with dominant components coming from backscattering. On the other hand, H2\((J_i = 1, m_i = 0)\) encounters an almost flat PES (cf., dotted curve in Fig. 4(b)). As a result, we see strong (dominant) specular scattering of H2\((J_f = 1, m_f = 0)\) (Fig. 4(b)). Finally, we could observe a p-H2 to o-H2 ratio as large as ca. 4.96 (cf., Table 1) compared to that of normal-H2 (n-H2) (i.e., >1/3 at 300 K) at scattering angle \(\Theta_f = 5.26^\circ\) (Fig. 4).

**H2 Scattering along STO(001)[110] on SrO-terminated STO(001).** In Fig. 5(a–c), we show the calculated (scattering) probabilities/spectra corresponding to the maximum \(para\)-to-\(ortho\) ratio \(R_{\text{p-o}}\)\((E_i = 60 \text{ meV}, \Theta_i = 76.5^\circ, \Theta_f)\) along the [110] direction of a SrO-terminated STO(001) (cf., Table 2). (The initial surface perpendicular translational energy \(E_i \times \cos^2\Theta_i = 60 \text{ meV} \times \cos^2(76.5^\circ) \approx 3.27 \text{ meV}\) and the initial surface lateral translational energy \(E_i \times \sin^2\Theta_i = 60 \text{ meV} \times \sin^2(76.5^\circ) \approx 56.7 \text{ meV}\).) Again, the resulting trends can be explained by inspecting the corresponding orientational anisotropy and surface lateral corrugation of the surface.
potential encountered by the impinging H₂ (\(E_i, m_i, E_i = 60 \text{ meV}, \Theta_i = 76.5^\circ\)) (i.e., \(\{Y^m_{\theta_i}[V(Z, \theta, X)]Y^m_{\phi_i}\}\), cf., Fig. 5(d)). Note that along STO(001)[110] on the SrO-terminated STO(001), H₂ (\(j_f = 0, m_i = 0\)) encounters a strongly corrugated and orientationally anisotropic PES (cf., solid curve in Fig. 5(d)), that now favors molecular adsorption atop the O-site, with H-H bond oriented perpendicular to the surface, and an adsorption energy \(E_{ad} = -151 \text{ meV}\) \(^{24}\). Atop the Sr-site, H₂ adsorbs with the H-H bond oriented parallel to the surface, and \(E_{ad} = -111 \text{ meV}\) \(^{24}\). As a result, in Fig. 5(a), we find a corresponding spectra dominated by off-specularly scattered H₂ with dominant components coming from backscattering. Again, most of the H₂ (\(j_f = 0, m_i = 0\)) would be molecularly adsorbed (due to reorientation/steering\(^{12,32}\)), and only a small fraction would be elastically scattered (possibly due to shadow effect\(^{9}\)). Considering the angle of incidence, the inelastically scattered H₂ would come from those hitting the repulsive part of the potential well near the Sr-site (shadowing effect, cf., solid curve in Fig. 4(d)), resulting in a change in surface lateral momentum and off-specular scattering angles. Note that the impinging H₂ has a larger surface lateral momentum as compared to the corresponding surface perpendicular component. This allows the impinging H₂ more time to explore the anisotropic surface. Those that succeed would molecularly adsorb via reorientation/steering. Those that fail, would be rotationally de-excited on the way back to the gas phase, because of the smaller anisotropic potential further (out in the vacuum) from the surface. Thus, the scattering spectra shows negligible rotationally excited H₂, i.e., H₂ (\(j_f = 2, m_i = 0\)). H₂ (\(j_f = 1, m_i = \pm 1\)) also encounters a strongly anisotropic PES (cf., dash-dot curve in Fig. 5(d)). But now recall that the preferred adsorption site is at the O-site, with the H-H bond oriented perpendicular to the surface. Thus, we see strong specular scattering in Fig. 5(c). H₂ (\(j_f = 1, m_i = 0\)) shows higher backscattering probabilities (cf., Fig. 5(b)) due to the larger surface anisotropy along X, making it more susceptible to reorientation/steering. Finally, we could observe a p-H₂ to o-H₂ ratio as large as ca. 16.1 (cf., Table 2) compared to that of n-H₂ (i.e., >1/3 at 300 K) at scattering angle \(\Theta_i = -76.5^\circ\) (Fig. 5).

### Table 2. Calculated \(R_{j_f=0/1}(E_i, \Theta_i, \Theta_f)\) and \(R_{j_f=0/1}(E_i, \Theta_i, \Theta_f)\) on SrO-terminated STO(001) at the incident energy range 10 meV \(\leq E_i \leq 80 \text{ meV}\). For each incident energy, we list only the maximum \(R_{e=0/1}(E_i, \Theta_i, \Theta_f)\) with the corresponding incident and scattering angles.

| \(E_i [\text{meV}]\) | \(\Theta_i [^\circ]\) | \(\Theta_f [^\circ]\) | \(R_{j_f=0/1}\) | \(R_{j_f=0/1}\) |
|----------------------|-------------------|-------------------|----------------|----------------|
| 10.0                 | 0.00              | 47.1              | 1.32           | 0.124          |
| 20.0                 | 7.44              | 22.9              | 5.97           | 0.496          |
| 30.0                 | 47.8              | 47.8              | 11.4           | 0.529          |
| 40.0                 | 15.9              | 55.5              | 4.06           | 0.137          |
| 50.0                 | 47.5              | 47.5              | 2.90           | 0.541          |
| 60.0                 | 76.5              | 76.5              | 16.1           | 0.0294         |
| 70.0                 | 7.96              | 56.2              | 1.57           | 0.0194         |
| 80.0                 | 57.3              | 57.3              | 1.73           | 0.00328        |

### Conclusion

Here, we reported increased para-H₂ (p-H₂) to ortho-H₂ (o-H₂) ratio of H₂ scattered from SrTiO₃(001) (viz., ca. 4.96 and 16.1 along the SrTiO₃(001)[100] and SrTiO₃(001)[110] of the TiO₂- and SrO-terminated SrTiO₃(001), respectively). For reference, normal-H₂ (n-H₂) have a p-H₂ to o-H₂ ratio of 1/3, at room temperature (\(T = 300 \text{ K}\)). We attribute this to the strongly orientation-dependent (electrostatic) interaction potential between the H₂ (induced) quadrupole moment and the surface electric field of ionic SrTiO₃(001). These results suggest that ionic surfaces (with tunable surface terminations) could function as a scattering/filtering media to realize rotationally state-resolved H₂. This could find significant applications not only in H₂ storage and transport, but also in realizing materials with pre-determined characteristic properties.

We can compare the present results to previous reports for the inelastic scattering of H₂ on LiF(001), at normal incidence (\(\Theta_i = 0^\circ\)) and incident energy of \(E_i = 100 \text{ meV}\) \(^{34}\). From the scattering probability data \(^{35}\), we estimate a maximum \(p-H₂\) to \(o-H₂\) ratio \(R_{j_f=0/1}\) of ca. 2 (as compared to ca. 4.96 and 16.1 along SrTiO₃(001)[100] and SrTiO₃(001)[110] of the TiO₂- and SrO-terminated SrTiO₃(001), respectively). (Note that the results of ref. \(^{34}\) have since been confirmed experimentally\(^{36}\)).

Considering the Debye temperature of SrTiO₃ (ca. 413.3 K\(^{35}\)), we may expect some thermal modulation/attenuation. With Ti having a smaller mass than Sr, we would expect more pronounced effect (modulation/attenuation) on TiO₂-terminated SrTiO₃(001), as compared to SrO-terminated SrTiO₃(001). Consider for example a...
surface temperature of 100 K and incidence angle $\Theta_i$ [0°, 66°]. For TiO$_2$-terminated SrTiO$_3$(001), we estimated Debye-Waller factor values (cf., e.g., ref. 13 for more details) ranging from ca. 0.3 to 0.6, increasing with increasing incidence angle $\Theta_i$. In comparison, for SrO-terminated SrTiO$_3$(001), we estimated 13 Debye-Waller factor values ranging from ca. 0.6 to 0.8, increasing in value with increasing incidence angle $\Theta_i$. The modulation/attenuation would become more pronounced with increased temperature. However, regardless of the degree of modulation/attenuation, the maximum $p$-H$_2$ to $o$-H$_2$ ratio for each surface termination remained almost the same (viz., ca. 4.48 and 16.7 along the SrTiO$_3$(001)[100] and SrTiO$_3$(001)[110] of the TiO$_2$- and SrO-terminated SrTiO$_3$(001), respectively, at 100 K).

Finally, because of the wide spread of the scattering angle, we could expect small scattering probabilities at each particular scattering angle. Furthermore, the larger the (surface lateral) incident energy, the more number of (surface lateral) diffraction channels (would be) involved (excited). As a result, the normalized $p$-H$_2$ to $o$-H$_2$ ratio $R_{p/o}$ shows small values (cf., Tables 1 and 2). Thus, so far, we can collect only a small amount of H$_2$ through any given scattering event. (But with high purity!) For engineering applications, scattering at optimum surface angles should resolve this problem.

Methods

Model Hamiltonian. To study the dynamics of H$_2$ scattering on STO(001) (Fig. 1), we performed quantum dynamical calculations (cf., e.g., refs. 1,3,5,6,8,9,24,31,32) by solving the corresponding time-independent Schrödinger equation for H$_2$ in the vibrational ground state ($\nu = 0$), under the influence of an orientationally anisotropic potential energy (hyper-) surface (PES), using the coupled-channel method 36–42. The dynamical variables we considered include the H$_2$ center-of-mass (CM) distance $Z$ from the surface, the H$_2$ bond-length $r$, the polar and azimuthal angular orientations of the H–H bond with respect to the surface, $\theta$ and $\phi$, respectively, and the position of the H$_2$, CM X, along STO[001][100] and STO[001][110] of the TiO$_2$- and SrO-terminated STO(001), respectively. Considering that the energy scale of the H$_2$ molecular vibration ($h\nu = 516$ meV) exceeds the energy range relevant to our current study (i.e., $E_i$ [10, 80] meV), we can neglect the molecular vibrational excitations, and fix the H$_2$ interatomic distance at $r = 0.74$ Å. The small variation of the potential energy with respect to $\phi$ allows us to further neglect the $\phi$-dependence 34. Thus, we can reduce the original 6-Dimensional (6-D) Hamiltonian (for the diatomic molecule-surface system) to the following simplified 3-D form:

$$H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial Z^2} + \frac{\partial^2}{\partial X^2} \right) - \frac{\hbar^2}{2m} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + V(Z, \theta, X).$$

(1)

$m$ and $I$ correspond to the H$_2$ total mass and moment of inertia, respectively.

Potential Energy (Hyper-) Surface: PES. The 3-D PES $V(Z, \theta, X)$ in Eq. (1) comes from previously performed density functional theory (DFT)-based total energy calculations 43–45 for H$_2$ adsorption at the Ti and O surface sites on the TiO$_2$-terminated STO(001), the Sr and O surface sites on the SrO-terminated STO(001), and H$_2$ polar orientations $\theta = 0$ and $\pi/2$. We fitted the potential energy curves for each configuration using Morse potentials:

$$V_{A(B),\theta} = D_{A(B),\theta} \times \{\exp \left[ -2\alpha_{A(B),\theta}(Z - Z_{eq}^{A(B),\theta}) \right] - 2\exp[\alpha_{A(B),\theta}(Z - Z_{eq}^{A(B),\theta})] \},$$

(2)

and connected the Morse potentials for $\theta = 0$ and $\pi/2$ at each surface site for different surface sites to get

$$V(Z, \theta, X) = [V_{A,\theta = \pi/2}\sin \theta + V_{A,\theta = \pi/2}\cos \theta \cos^2 \theta \cos^2 \phi + V_{A,\theta = 0}\cos \theta + V_{B,\theta = 0}\sin \theta \sin^2 \phi + V_{B,\theta = 0}\sin \theta \sin^2 \phi].$$

(3)

$$D_{A(B),\theta} \propto \alpha_{A(B),\theta} Z_{eq}^{A(B),\theta}$$

give the corresponding potential depth, potential width, and equilibrium (normal/perpendicular) distance of H$_2$ from the surface cation sites (A:[Ti, Sr]) and oxygen site (B), at H–H bond angle $\theta$, respectively. The reciprocal lattice constant $a'_x(=\pi/a_x)$, with corresponding direct lattice constants $a'_x(100) = 3.91$ Å and $a'_x(110) = 5.52$ Å along [100] and [110] of the TiO$_2$- and SrO-terminated STO(001), respectively 46. Table 3 shows the fitted parameters for each configuration. We used spherical harmonics and plane waves as basis sets for the translational motion and the translational motion (perpendicular to the surface and along the surface direction X), respectively.

To extract the contribution of the electrostatic interaction between the H$_2$ quadrupole moment and the surface local electric field, as discussed above, we used the charge density distribution obtained from previous DFT-based total energy calculations 44. We calculated the induced dipole $\Delta D_i(=\Delta \rho_i)$ and quadrupole moments $\Delta Q_i(=\Delta \rho_i)$ from the charge density difference $\Delta \rho_i(Z) = \rho_{H_2/STO}(Z) - \rho_{H_2 - STO}$ as a function of Z for the Ti and O sites (TiO$_2$-termination) and Sr and O sites (SrO-termination) with $\theta = 0$ and $\pi/2$. We also calculated the H$_2$ quadrupole moment $Q_{ij}$ from the charge density distribution of the isolated system. We used the pristine STO(001) to calculate the surface electric field and its gradient.

Scattering probability. Consider a H$_2$ impinging with an initial rotational state ($j_i, m_i$), incident energy $E_i$, and angle of incidence with respect to the surface normal $\Theta_i$ (cf., e.g., Fig. 1(c,d), and Table 4). Using the coupled-channel method 36–42, we calculated the probability $P_{m_{ij}}^{m_{ij}}(E_i, \Theta_i, \Theta_i)$ of finding the H$_2$ scattered with a final rotational state ($j_f, m_f$), final kinetic energy $E_f$, scattering at an angle of $\Theta_f$ with respect to the surface normal. (We carefully checked the convergence for calculations with maximum quantum numbers $I_{max} = 10$ and $|\Theta_{max}| = 30$). From the calculated scattering probability $P_{m_{ij}}^{m_{ij}}(E_i, \Theta_i, \Theta_i)$ of H$_2$ on STO(001), we evaluated
The corresponding \( p-H_2 \) to \( o-H_2 \) ratio \( R_{j=0/1} = \frac{\int \rho_{j=0}(E_\nu, \Theta_\nu, \Theta_j) \, dE_\nu \, \rho_{o-H_2}(E_\nu, \Theta_\nu, \Theta_j)}{\int \rho_{j=1}(E_\nu, \Theta_\nu, \Theta_j) \, dE_\nu \, \rho_{o-H_2}(E_\nu, \Theta_\nu, \Theta_j)} \) given the incident energy \( E_\nu \), incident angle \( \Theta_\nu \), and scattering angle \( \Theta_j \), i.e.,

\[
R_{j=0/1}(E_\nu, \Theta_\nu, \Theta_j) = \frac{\int dE_\nu P_{j=0, \Theta_\nu, \Theta_j}(E_\nu, \Theta_\nu, \Theta_j)}{\int dE_\nu \sum_{m=-1}^{1} P_{j=1, \Theta_\nu, \Theta_j}(E_\nu, \Theta_\nu, \Theta_j)} = \frac{P_{0, \Theta_\nu, \Theta_j}(E_\nu, \Theta_\nu, \Theta_j)}{\sum_{m=-1}^{1} P_{1, \Theta_\nu, \Theta_j}(E_\nu, \Theta_\nu, \Theta_j)}. \tag{4}
\]

Note that

\[
\int dE_\nu \sum_{m=-j}^{j} P_{j,m}(E_\nu, \Theta_\nu, \Theta_j) = 1. \tag{5}
\]

And since we are considering the case when \( j = J \) and \( m = m_j \), in Eq. (4) we have

\[
P_{j,m}(E_\nu, \Theta_\nu, \Theta_j) = \frac{\int dE_\nu P_{j,m}(E_\nu, \Theta_\nu, \Theta_j)}{\int dE_\nu \sum_{m=-j}^{j} P_{j,m}(E_\nu, \Theta_\nu, \Theta_j)} = P_{J,m}(E_\nu, \Theta_\nu, \Theta_j). \tag{6}
\]

### Table 3

Fitted values of the potential depth \( D \), potential width \( \alpha \), and equilibrium distance from the surface \( Z^{eq} \), at each surface site, in Eq. (3).

| Termination | adsorption site | \( \theta \) [rad] | \( D \) [eV] | \( \alpha \) [Å⁻¹] | \( Z^{eq} \) [Å] |
|-------------|-----------------|-------------------|---------|----------------|-------------|
| TiO\(_2\)    | Ti site-A       | 0                 | 0.0350  | 1.40           | 3.18        |
|              |                 | \( \pi/2 \)       | 0.172   | 1.47           | 2.37        |
|              | O site-B        | 0                 | 0.0665  | 1.30           | 2.97        |
|              |                 | \( \pi/2 \)       | 0.0486  | 1.24           | 3.14        |
| SrO         | Sr site-A       | 0                 | 0.0409  | 1.21           | 3.57        |
|              |                 | \( \pi/2 \)       | 0.108   | 1.39           | 2.93        |
|              | O site-B        | 0                 | 0.152   | 1.18           | 2.55        |
|              |                 | \( \pi/2 \)       | 0.0322  | 0.755          | 3.70        |

### Table 4

Some relevant physical values corresponding to \( H_2(E_\nu, J_\nu, m_\nu, \Theta_\nu) \) impinging a TiO\(_2\)- and SrO-terminated SrTiO\(_3\)(001). Incident angles presented in this work doubly underlined.

|                | \( \alpha \) [Å] | \( E_\parallel \) [meV] | \( E_\perp \) [meV] | \( E_{\text{init}} \) [meV] | \( G_{ij} \) [Å] |
|----------------|-----------------|------------------------|-------------------|-----------------------------|----------------|
| TiO\(_2\)-termination |                  |                        |                  |                             |               |
| \( a_\parallel \) [001] | 3.91            | \( a_\parallel \) [110] | 5.52              |                             |               |
| \( E_\parallel \) [001] | 80              | \( E_\parallel \) [001] | 60                |                             |               |
| \( E_{\text{init}} \) [001] | 80              | \( E_{\text{init}} \) [001] | 60                |                             |               |
| SrO-termination    |                  |                        |                  |                             |               |
| \( \Theta \) [°] |                   |                        |                  |                             |               |
| 0                | 0.00            |                        |                  |                             |               |
| 1                | 5.26            |                        |                  |                             |               |
| 2                | 10.6            |                        |                  |                             |               |
| 3                | 15.9            |                        |                  |                             |               |
| 4                | 21.5            |                        |                  |                             |               |
| 5                | 27.3            |                        |                  |                             |               |
| 6                | 33.3            |                        |                  |                             |               |
| 7                | 39.9            |                        |                  |                             |               |
| 8                | 47.1            |                        |                  |                             |               |
| 9                | 55.5            |                        |                  |                             |               |
| 10               | 66.3            |                        |                  |                             |               |
| 11               | 115.5           |                        |                  |                             |               |
| 12               | 123.8           |                        |                  |                             |               |
| 13               | 176.5           |                        |                  |                             |               |

Note that

\[
\int dE_\nu \sum_{m=-j}^{j} P_{j,m}(E_\nu, \Theta_\nu, \Theta_j) = 1. \tag{5}
\]

And since we are considering the case when \( j = J \) and \( m = m_j \), in Eq. (4) we have

\[
P_{j,m}(E_\nu, \Theta_\nu, \Theta_j) = P_{J,m}(E_\nu, \Theta_\nu, \Theta_j). \tag{6}
\]
We also calculated the normalized p-H₂ to o-H₂ ratio $R_{\text{p-o}}(E_p, \Theta_1, \Theta_2)$, i.e.,

$$R_{\text{p-o}}(E_p, \Theta_1, \Theta_2) = \frac{P_{\text{p}}^1(E_p, \Theta_1, \Theta_2) + \sum_{m=-1}^{1} P_{\text{p}}^m(E_p, \Theta_1, \Theta_2)}{\sum_{m=-1}^{1} P_{\text{o}}^m(E_p, \Theta_1, \Theta_2)}.$$  (7)

In Eq. (7), we multiplied the angle specific p-H₂ to o-H₂ ratio by a normalization factor, so as to evaluate the efficiency of rotational state separation with respect to the incident n-H₂. Note that the p-H₂ to o-H₂ ratio of n-H₂ corresponds to 0.333 (1/3) at room temperature ($T = 300$ K).

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**Author contributions**
K.S., W.A.D., H.N., K.F., and H.K. conceived the model and performed the calculation. All authors contributed to the discussion, analyses, and writing the manuscript.

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A.Y. is an employee of Kawasaki Heavy Industries, Ltd. The other authors declare no competing interests.

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