SUPPLEMENTARY MATERIALS

for

Quantifying the interplay between fine structure and geometry of an individual molecule on a surface

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SUPPLEMENTARY TEXT

S1 – STM/STS sample characterization

We characterized the properties of Fe and TiH, as well as the MgO film with STM/STS. A typical constant-current image is shown in Fig. S1(a). MgO islands on top of Ag(100) can be identified by a lower apparent height compared to the bare Ag surface. Fe atoms and TiH molecules adsorbed on the oxygen sites were distinguished by their different apparent heights. A histogram of numerous measurements for both species is shown in Fig. S1(b) resulting in average heights of 103 ± 8 pm for TiH and 151 ± 8 pm for Fe, in agreement with previously reports [37,44].

We identified the adsorption sites by imaging the oxygen atoms of the MgO lattice and creating a reference grid (Fig. S2). Utilizing this grid (white lines), we ascertained that both TiH and Fe adsorbates that exhibit the aforementioned apparent heights resided on top of an oxygen atom. Additionally, TiH can be identified by two particular spectroscopic fingerprints, namely the potential orbital excitation observed at ≈ ±90 mV (Fig. S3), as well as the spin excitation (see section S6). The position of the orbital excitation varied by several mV dependent on the tip, stabilization parameters or investigated molecule and was not observed for bridge-site TiH molecules.

We identified the thickness of the MgO film by using point-contact measurements, as previously reported [44]. Fig. S4 shows the results measured on two different Fe atoms adsorbed on two and three monolayers (ML) of MgO. Point contact was defined as the z-piezo position with the highest measured current and was set to be 0 pm in the plot. For 2 ML films, we measured $I_t = 11.1$ nA at point-contact, corresponding to a conductance of $G = 0.143 G_0$. This is in agreement with previous work [44]. For Fe adsorbed on 3 ML films, we measured $I_t = 1.78$ nA. This corresponded to $G = 0.023 G_0$, manifesting the expected strong reduction of conductance for thicker layers of MgO. All experiments reported in the main manuscript were performed on 2 ML films.

S2 – RF transmission measurement and compensation

Prior to all f-sweep mode measurements, we corrected for the frequency-dependent variations in transmission due to the transfer function [45]. Fig. S5 illustrates an example of the frequency-dependent transmission in a wide range of 1 – 22 GHz as measured on the non-linearity at $V_{DC} = -78$ meV of a TiH spectrum with constant $\tilde{P}_{RF}$. To compensate for this frequency-dependent transmission and achieve a constant $V_{RF}$, $\tilde{P}_{RF}$ was adjusted accordingly via the generator. Fig. S6 shows an example of compensation in a frequency range of 7.9 – 8.5 GHz. The blue/red curve shows $V_{RF}$ for a constant/adjusted $\tilde{P}_{RF}$ before/after compensation.

S3 – Additional ESR raw data

In this section, we present ESR raw data sets supplementary to Fig. 2 of the main manuscript and that were later used in the analysis in Fig. 3 and supplementary section S4. The data set presented in Fig. S7 was taken with the same micro tip and on the same molecule as the data shown in the $B_r$-sweep as well as both f-sweeps of Fig. 2. Further data sets on another TiH molecule are presented in Fig. S8 and S9 for the $B$-sweep and f-sweep mode, respectively.

S4 – ESR of TiH molecules for different stabilization parameters

All the 31 data sets used for the g-tensor analysis in Fig. 3(b) are plotted in Fig. S10. We found that different tip-sample distances did not significantly affect the extracted g-
factors, although this did result in different horizontal and vertical offsets due to variable influence of the tip stray field. The corresponding measurement parameters for all data sets are indicated in the figure legend, with \( V_{\text{DC}} = 50 \text{ mV} \) for all sets. To analyze the \( g \)-tensor for these data sets, we excluded non-linear data points in the low frequency region around zero-field. For this, we first fitted the data with a hyperbolic function to mimic the stray field effect that was subsequently modeled thoroughly in section S4:

\[
f(x) = \frac{b}{a} \sqrt{(x - c)^2 + a^2} + d,
\]

where \( c \) is the center of the hyperbola, \( d \) a vertical offset and \( b/a \) denotes the slope \( k_A \) of the corresponding linear asymptotes. Via the minima and maxima of the third derivative, we found \( x_{\text{min,max}} = c \pm \frac{1}{2} a \). Using a scaling factor \( S \) we moved from these positions along the \( x \)-axis to \( x_{1,2} = c \pm \frac{1}{2} a S \). We related the algebraic expression for the hyperbola’s slope \( k_H \) at \( x_{1,2} \) as a function of \( S \) with respect to \( k_A \):

\[
k_H = \frac{S}{\sqrt{4 + S^2}} \cdot k_A = F \cdot k_A.
\]

In our analysis, we considered the slope \( k_H \) to be within 95% of \( k_A \) (\( F = 0.95 \)) and neglect experimental data not fulfilling this criterion.

S5 – Modeling the tip stray field

Probing low frequency bands requires the application of only small magnetic field values, while maintaining a magnetically stable tip. It has been shown previously, that Cr bulk tips retain a stable magnetization from zero to several Tesla [46]. Furthermore, despite the antiferromagnetic layering of the Cr, such magnetic tips also exhibit magnetic stray fields on the order of 50-200 mT, which is a common observation in the literature [21,47-50]. As the value of the externally applied magnetic field \( B_{\text{ext}} \) is reduced, it can become comparable to this stray field \( B_{\text{tip}} \), making it a non-negligible component of the total field \( B_{\text{tot}} \). We constructed a classical model that includes both \( B_{\text{ext}} \) and \( B_{\text{tip}} \), in order to calculate the expected Zeeman splitting for a classical TiH spin. We note that variations of the quantization axis in the low-field limit is not captured by this treatment. Furthermore, temperature-related effects were neglected. The externally applied magnetic field, \( \vec{B}_{\text{ext}} \), is oriented in the \( yz \)-plane:

\[
\vec{B}_{\text{ext}} = \begin{pmatrix} 0 \\ B_{y,\text{ext}} \\ B_{z,\text{ext}} \end{pmatrix}.
\]

Here, we define \( B_{y,\text{ext}} = B_t \) and \( B_{z,\text{ext}} = B_{\perp} \). During the experiment, one of the components (\( B_{y,\text{ext}} \) or \( B_{z,\text{ext}} \)) was varied while the other component is held at a constant value. We consider an arbitrary \( \vec{B}_{\text{tip}} \) toward a total applied magnetic field \( \vec{B}_{\text{tot}} \):

\[
\vec{B}_{\text{tip}} = \begin{pmatrix} B_{x,\text{tip}} \\ B_{y,\text{tip}} \\ B_{z,\text{tip}} \end{pmatrix},
\]

\[
\vec{B}_{\text{tot}} = \vec{B}_{\text{ext}} + \vec{B}_{\text{tip}} = \begin{pmatrix} B_{x,\text{tip}} \\ B_{y,\text{ext}} + B_{y,\text{tip}} \\ B_{z,\text{ext}} + B_{z,\text{tip}} \end{pmatrix}.
\]
We consider the spin of the TiH molecule as $|\vec{S}| = 1/2$ with its orientation parallel to the total magnetic field, $\vec{B}_{\text{tot}} \parallel \vec{S}$, hence:

$$\vec{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix} = \begin{pmatrix} B_{x,\text{tot}} / |\vec{B}_{\text{tot}}| * |\vec{S}| \\ B_{y,\text{tot}} / |\vec{B}_{\text{tot}}| * |\vec{S}| \\ B_{z,\text{tot}} / |\vec{B}_{\text{tot}}| * |\vec{S}| \end{pmatrix}.$$  

Lastly, we define a $g$-tensor that allows for anisotropy in axial symmetry ($g_x = g_y \neq g_z$) by

$$\vec{g} = \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} = \begin{pmatrix} g_{||} & 0 & 0 \\ 0 & g_{||} & 0 \\ 0 & 0 & g_{\perp} \end{pmatrix}.$$  

With these components, the Hamiltonian for the Zeeman interaction can be described as:

$$\mathcal{H}_{\text{Zeeman}} = \mu_B \vec{B}_{\text{tot}} \cdot (\vec{g} \cdot \vec{S})$$

$$\begin{align*}
\mathcal{H}_{\text{Zeeman}} &= \mu_B |\vec{S}| \frac{g_{||} (B_{x,\text{tot}}^2 + B_{y,\text{tot}}^2) + g_{\perp} (B_{z,\text{tot}}^2)}{|\vec{B}_{\text{tot}}|} \\
&= \mu_B |\vec{S}| \frac{g_{||} (B_{x,\text{tip}}^2 + (B_{y,\text{ext}} + B_{y,\text{tip}})^2) + g_{\perp} ((B_{z,\text{ext}} + B_{z,\text{tip}})^2)}{\sqrt{(B_{x,\text{tip}}^2 + (B_{y,\text{ext}} + B_{y,\text{tip}})^2 + (B_{z,\text{ext}} + B_{z,\text{tip}})^2)}}.
\end{align*}$$  

Fig. S11(a) depicts how $\vec{B}_{\text{tot}}$ varies as $\vec{B}_{\text{ext}}$ is swept in one direction, and how the spin $\vec{S}$ is reoriented as a result. Note, that only the $\vec{B}_{\text{tip}}$ component parallel to $\vec{B}_{\text{ext}}$ can be compensated, while the remaining part provides a constant offset field. This latter point is what leads to non-linearity in the data in the low field limit. In Fig. S11(b), two example data sets with strong plateau-like deviations are shown. The measurement conditions were identical, except for a difference in $\vec{B}_{\text{tip}}$ for the two different measurements. The observed difference in this non-linear behavior for the same atom measured with distinct micro tips rules out that the non-linear behavior results from intrinsic effects from the atom, such as the crystal field. This was further substantiated as we observed measurements with a linear trend down to smaller frequencies for other tips. Modeling the data sets with equation (2) (solid lines in Fig. S11(b), fit performed within the global fit of Fig. S12), we found tip magnetic fields (see figure legend) with an expected magnitude, as discussed within this section.

In Fig. S12, we fitted all data sets of Fig. S10 simultaneously with equation (2) by using $g_{||}$ and $g_{\perp}$ as global fitting parameters, and allowing for a unique $\vec{B}_{\text{tip}}$ for every data set. Two additional data sets with strong plateau-like behavior of the peak shifts were included compared to section S3. We found $g_{||} = 1.896$ and $g_{\perp} = 0.638$. Note, that the perfect
agreement with a S=1/2 system and keep in mind that the fitting procedure does not capture variations in g-factors.

The average magnitude $|\vec{B}_{\text{tip}}|$ for $I_t = 2$ pA is $\approx 44$ mT, in line with expectations for stray fields of Cr bulk tips of around 50 mT [21,47]. As expected, by reducing the tip-sample distance, i.e. for a larger value of $I_t$ the extracted $\vec{B}_{\text{tip}}$ values increased ($\approx 123$ mT for $I_t = 5$ pA, $\approx 229$ mT for $I_t = 10$ pA). The average angle of $\vec{B}_{\text{tip}}$ with respect to the z-axis is $\approx 54^\circ$ (with decreasing angle for larger $I_t$).

Furthermore, via simple arguments one can rule out that the observed non-linearities are a result of an unsaturated tip magnetization. Firstly, we observe these non-linearities for different tips, even though they were all prepared with Fe clusters at the apex. Secondly, for a magnetic moment of 3µB (assuming Fe with a spin of 2 at the apex), a paramagnetic tip at 40 mK should saturate below 25 mT. Since we observe the non-linearities typically at even larger fields and the stray fields we find are on the order of what is reported in literature (see above), the stray field assumption is the most likely explanation in the experimental observations.

S6 – ESR of a TiH molecule at elevated temperature

As shown in Fig. S3 and below in section S7, we see no signature of a Kondo-like resonance in STS. To further rule out Kondo-related effects, we performed ESR experiments at 1.1 K in $f$-sweep mode in Fig. S13. This allows a comparison of the measured g-tensor at a temperature where previous experiments were performed. We observed the renormalized g-factors of $g_\parallel = 1.57 \pm 0.04$ and $g_\perp = 0.55 \pm 0.01$, comparable to what was observed at 30-50 mK. This further rules out that the anisotropy in the g-tensor results from Kondo screening at mK temperatures, since the magnetization should strongly change as a function of temperature near $T_K$.

S7 – ISTS of TiH molecules and Fe atoms

We investigated ISTS of TiH and Fe with inelastic scanning tunneling spectroscopy (ISTS), to complement the observation of the g-tensor anisotropy. Magnetic field dependent ISTS measurements, with a non-magnetic tip, in a very small energy window of $\pm 1.5$ meV on a TiH molecule are plotted in Fig. S14(a,b). There is no zero-field splitting (ZFS) observed in the case of zero magnetic field, further corroborating that the TiH molecule on the surface of MgO resides in a spin doublet ground state as previously reported [22].

We observed an inelastic spin excitation in variable magnetic field, for both $B_\parallel$ (Fig. S14(a)) and $B_\perp$ (Fig. S14(b)). For both orientations, the inelastic step shifts toward higher energy in increasing field, as expected for a spin doublet. The magnitude of the shifts differed for the two applied magnetic field directions, with the change in magnetic field being smaller for $B_\perp$. The ISTS measurements were done on four different TiH molecules and the extracted averaged step position is plotted in Fig. S14(c). We obtained $g_\parallel = 1.84 \pm 0.01$ and $g_\perp = 0.50 \pm 0.01$, confirming the anisotropic g-tensor found in our ESR-STM measurements. We note that in STS, there was no $V_{RF}$ applied. This illustrates the anisotropic g-tensor results from an intrinsic property of the TiH molecule, and not from the ESR method.
In order to calibrate the applied magnetic field, we also performed magnetic field-dependent ISTS measurements on individual Fe atoms. Two Fe atoms were investigated as shown in the inset of Fig. S14(c). A spin-excitation step at zero field was observed at \( \approx 14.4 \text{ meV} \), in agreement with literature [15,51]. As previously reported [51], the inelastic step energy increases linearly with \( B_{\perp} \). We extracted an effective \( g \)-factor of \( g_{\perp}^* = 2.48 \pm 0.18 \).

When the ISTS measurements were done with a spin-polarized tip, the inelastic spin excitation steps of Fe showed spin pumping features [51] that were used to confirm that the tip was spin polarized. Additionally, the emerging asymmetry of the spin excitation steps around \( E_F \) of the TiH molecules (Fig. S3) was also used for this purpose [22].

S8 – DFT+U calculations

We calculated the electronic and crystal structure of the TiH molecule on the MgO surface using density-functional theory (DFT) methods. We considered a \( 3 \times 3 \) unit cell of bilayer MgO with periodic boundary conditions and 18 Å vacuum space along the \( z \) direction. The TiH molecule was placed on top of the central oxygen atom, as depicted in Fig. S15(a). The DFT calculations were performed within generalized gradient approximation (GGA-PBE) of exchange-correlation functionals [52] as implemented in the projector augmented wave based Vienna ab initio simulation package (VASP) [53]. In these calculations, we set the energy cutoff to 500 eV and the energy convergence criteria to \( 10^{-6} \text{ eV} \). For the Brillouin zone integration, a \( 8 \times 8 \times 1 \) \( \Gamma \)-centered Monkhorst-Pack mesh was used. Electronic correlations were taken into account in a mean field way using the DFT+U method in rotationally invariant form [54]. In this approach, the intra-atomic exchange interaction \( J_H \) was set to 0.9 eV, while \( U \) was varied within the calculations. All atoms of the constructed unit cell were allowed to relax until all the residual force components of each atom were less than \( 5 \times 10^{-3} \text{ eV/Å} \). In agreement with ref. [31], the resulting unit cell oxygen atom was distorted upwards to the TiH molecule, while the bottom Mg atom relaxed downwards due to weakening of the Mg-O bond. For DFT, without the \( U \) correction, we found the optimized distances: \( d(\text{Ti-H}) = 1.79 \text{ Å}, d(\text{Ti-O}) = 1.93 \text{ Å} \) and \( d(\text{O-MgO}) = 0.46 \text{ Å} \). Small changes in bond distances were observed with DFT+U, e.g. for \( U = 4 \text{ eV} \): \( d(\text{Ti-H}) = 1.80 \text{ Å}, d(\text{Ti-O}) = 1.99 \text{ Å} \) and \( d(\text{O-MgO}) = 0.49 \text{ Å} \).

The MgO substrate with \( C_4v \) point group symmetry causes a crystal field splitting of the Ti(\( d \)) states, which can be seen in the DFT (\( U = 0 \)) band structure and densities of states in Fig. S15(b,c). Since the titanium \( d_\z \) orbital is oriented towards the hydrogen atom, it leads to a strong hybridization of the Ti(\( d_\z \)) and H(s) states, transferring a valence electron from titanium to H(s), filling the s shell. From the band structure point of view, Ti(\( d_\z \)) has a finite bandwidth due to the hybridization, while the rest of the titanium states appear as flat energy levels. Another valence electron occupies the orbital of \( d_{x^2-y^2} \) symmetry, which is oriented in the direction of positively charged magnesium atoms, giving an unpaired spin \( S = \frac{1}{2} \) in the system. The obtained energy spectra were in good agreement with earlier calculations [22,31].

The orbital contribution to energy bands near the Fermi energy is represented in Table S1. Due to the geometry of orbitals, the hydrogen s state is hybridized with the titanium \( d_\z \) and bottom oxygen p\_z states. At the same time, doubly degenerated energy bands are mainly composed of titanium \( d_{xz} \) and \( d_{yz} \) states and bottom oxygen states with different symmetry.
combinations. Finally, bands close to the Fermi energy are composed of purely atomic titanium $d_{xy}$ and $d_{x^2-y^2}$ states.

The projected densities of states for different values of $U$ are represented in Fig. S16. The spin up channel of $d_{x^2-y^2}$ states is fully occupied, while the spin down one is unoccupied, yielding $S = \frac{1}{2}$. The variation of the $U$ parameter leads to a stronger splitting of spin up and down channels of the $d_{x^2-y^2}$ states and shifts the titanium $d$ states to higher energies. The hydrogen $s$ state was not influenced by this variation.

Within these DFT calculations, we computed the orbital moment in the presence of spin-orbit coupling. However, the resulting orbital moment on the titanium atom was found to be very small and only amounts to $\approx 0.05 \mu_B$ and nearly independent of the $U$ parameter (Table S2). The calculations also predict that the orbital moment is oppositely oriented to the spin moment. Thus, the DFT+$U$ calculations predict that the orbital moment is quenched in this system, which contradicts the experimental and QC observations.

Finally, we calculated the potential energy landscape of the TiH molecule by rotating the hydrogen atom around the Ti at a fixed Ti-H distance. We found that this landscape depended strongly on the choice of $U$, with multiple solutions. This reveals a strong dependence on the on-site Coulomb interaction parameter. For large enough $U$, the energy minimum corresponds to the situation, where hydrogen sits on the top of the titanium atom. A smaller $U$ changes the favorable position of H, which is then tilted off the $z$-axis towards the MgO surface. The $C_4v$ symmetry of the substrate then allows four energy minimum positions, forming a multi-well potential as shown in Fig. S17. However, this requires a significant lowering of the $U$ parameter (down to $U = 3$ eV) than is commonly used for titanium systems ($U \geq 5$ eV).

S9 – Quantum chemistry modeling

To compute the $g$-factors of TiH on the MgO surface in the presence of a magnetic field, we use two models: a static model, in which we assume the center of mass of the TiH molecule as well as the orientation of the internuclear axis to be fixed with respect to the crystal surface and the magnetic field, and a dynamic model, in which we still keep the center of mass of the molecule fixed, but include the (hindered) rotation of the internuclear axis quantum mechanically.

The static model is described in section S9.1. It requires an interaction potential between the surface and the molecule, which is described in section S9.1.3. The dynamic model is described in section S9.2. The models are approximate, but have no empirical parameters. Instead, the parameters are obtained from $ab$ initio quantum chemistry calculations described in section S9.3 (see also Fig. 1 of the main paper). The results are given in section S9.4 and in Fig. 4 of the main paper.

S9.1 The static model

The $^2\Delta$ electronic state of TiH can be described by Hund’s case (a) wave functions $|\Lambda S \Sigma \rangle$ [55], where the electron spin quantum number $S = 1/2$, the projection of the orbital angular momentum onto the internuclear axis (the $z$-axis) is $\Lambda \hbar = \pm 2\hbar$, and the projection of
the electron spin angular momentum is \( \Sigma h = \pm 1/2 \ h \). In the static model, the electronic wave function is a linear combination of these four functions:

\[
\Psi = \sum_{\Lambda=\pm2} \sum_{\Sigma=\pm1/2} |\Lambda \Sigma \Sigma \rangle c_{\Lambda \Sigma}.
\]  

S9.1.1 Zeeman Hamiltonian

The interaction with the magnetic field is described by the Zeeman Hamiltonian

\[
\hat{H}_Z = -\mu \cdot \mathbf{B} = \frac{\mu_B}{h} \left( \hat{L} + g_\mu \hat{S} \right) \cdot \mathbf{B},
\]

where \( g_\mu \approx 2.0023 \) is the electron spin \( g \)-factor, \( \mu_B = \frac{e h}{2m_e} \) is the Bohr magneton, \( \mu \) the magnetic moment of the molecule, \( \mathbf{B} \) the magnetic field, and \( e \) and \( m_e \) are the electron charge and mass, respectively. In atomic units we have \( e = m_e = \hbar = 1 \) and \( \mu_B = 1/2 \).

Furthermore, a magnetic field of 1 tesla has a strength of \( 4.254 \cdot 10^{-6} \) in atomic units. Only the \( z \)-component \( \hat{L}_z \) of the orbital angular momentum operator has nonzero matrix elements and it is diagonal in the case (a) basis:

\[
\langle \Lambda' \Sigma' \Sigma \rangle \hat{L}_z |\Lambda \Sigma \Sigma \rangle = \delta_{\Lambda' \Lambda} \delta_{\Sigma' \Sigma} \Delta \hbar.
\]  

The \( z \)-component of the spin operator has diagonal elements

\[
\langle \Lambda' \Sigma' \Sigma \rangle \hat{S}_z |\Lambda \Sigma \Sigma \rangle = \delta_{\Lambda' \Lambda} \delta_{\Sigma' \Sigma} \Sigma \hbar.
\]

The spin-operator, however, also has off-diagonal elements. They are most easily expressed for the ladder operators \( \hat{S}_\pm \) by

\[
\langle \Lambda' \Sigma' \Sigma \rangle \hat{S}_\pm |\Lambda \Sigma \Sigma \rangle = \delta_{\Lambda' \Lambda} \delta_{\Sigma' \Sigma} \pm \hbar.
\]

The same transformation can be used for vectors, such as \( \mathbf{B} \). The spherical components of the magnetic moment operator are given by

\[
\hat{\mu}_0 = -\frac{\mu_B}{\hbar} (\hat{L}_z + g_\mu \hat{S}_z)
\]

\[
\hat{\mu}_{\pm 1} = \pm \frac{\mu_B g_\mu}{\hbar \sqrt{2}} \hat{S}_\pm.
\]

We consider two additional terms in the Hamiltonian: the spin-orbit coupling and the electrostatic interaction between the \( \Lambda = 2 \) and \( \Lambda = -2 \) components due to the crystal field.

S9.1.2 Spin-orbit Hamiltonian

The spin-orbit Hamiltonian is given by

\[
\hat{H}_{SO} = A \hat{L} \cdot \hat{S}.
\]
In our ab initio calculations described below, we find a spin-orbit coupling constant $A = 110.05$ cm$^{-1}$. In the case (a) basis, this operator has only diagonal elements

$$
\langle \Lambda' \Sigma' | \hat{H}_{SO} | \Lambda \Sigma \rangle = \delta_{\Lambda' \Lambda} \delta_{\Sigma' \Sigma} A \Lambda \Sigma. \quad (10)
$$

Before we include the crystal field and present the full calculation, it is instructive to consider four special cases:

(i) If we only consider the $S = 1/2$ electron spin, i.e., for a $^2\Sigma$ state, the Zeeman Hamiltonian has eigenvalues $\pm \mu_B g_e B / 2$, which are independent of the angle between the internuclear axis and the direction of the magnetic field. The $g$-factor is reported as the energy of the upper level minus the energy of the lower level, divided by the Bohr magneton and the magnetic field $B$, i.e., it is $g_e (\approx 2.0023)$.

(ii) If we only consider the orbital angular momentum, i.e., for a $^1\Delta$ state, the $g$-factor, which is non-negative by definition, is $2|\Lambda| = 4$ when the magnetic field is parallel to the internuclear axis, and it is zero when they are perpendicular.

(iii) When the magnetic field is parallel to the internuclear axis, and we ignore the crystal field, the case (a) wave functions are eigenfunctions of the Hamiltonian consisting of the Zeeman interaction and the spin-orbit coupling, and the four eigenvalues are

$$
\langle \Lambda \Sigma \Sigma | \hat{H}_{SO} + \hat{H}_Z | \Lambda \Sigma \Sigma \rangle = A \Lambda \Sigma + \mu_B (\Lambda + g_e \Sigma) B. \quad (11)
$$

We assume the observed transition involves the lowest two levels. Since the Zeeman interaction is much weaker than the spin-orbit coupling, the lowest two energy levels have $A \Lambda \Sigma < 0$, and since $A > 0$ we also have $\Lambda \Sigma < 0$. This means that the magnetic moments due to orbital angular momentum and spin angular momentum have opposite signs. Since $2|\Lambda| > g_e$, the $g$-factor is $2|\Lambda| - g_e \approx 1.9977$.

Thus, for a $^2\Delta$ state with a positive spin-orbit coupling constant, with the magnetic field parallel to the internuclear axis and no crystal field interaction, we expect a $g$-factor of about 2, just as for a $^2\Sigma$ state.

(iv) The last limiting case we consider is where the spin-orbit coupling is negligible and the crystal field is strong. When the crystal field is cylindrically symmetric around the internuclear axis it will have no effect on the mixing of the case (a) functions and the $g$-factor, but when it has a Fourier component $c_0 \cos(4\phi)$ or $c_0 \sin(4\phi)$, where $\phi$ is the azimuthal angle, it will mix the $\Lambda = 2$ and $\Lambda = -2$ functions. When the mixing is 50/50, the orbital angular momentum will be completely quenched, i.e., the matrix elements of $\hat{L}_z$ (and also the other components), will be zero. In this case, the $g$-factor will again be equal to $g_e$ due to the electron spin.

Thus, perhaps somewhat surprisingly, we expect a $g$-factor of about two for the $^2\Delta$ state when either the orbital angular momentum is quenched by the crystal field, or when instead the spin-orbit interaction dominates, and the magnetic field is parallel to the internuclear axis. However, in intermediate coupling cases and when the magnetic field is not parallel to the axis, which we consider below, we expect $g$-factors between 0 and 2.

S9.1.3 Crystal Field

We adopt a phase convention for the $|\Lambda\rangle$ states with $\Lambda = \pm 2$ that matches the symmetry of one-electron functions with $e^{i\Lambda \varphi}$ dependence on the azimuthal angle $\varphi$ of the electron. Thus, we define real wave functions by
\[
\Delta_{x^2-y^2} = |\Lambda = 2\rangle + |\Lambda = -2\rangle\quad (12)
\]
\[
\Delta_{xy} = \frac{|\Lambda = 2\rangle - |\Lambda = -2\rangle}{i\sqrt{2}}\quad (13)
\]
i.e.,
\[
|\Lambda = \pm 2\rangle = \frac{\Delta_{x^2-y^2} \pm i\Delta_{xy}}{\sqrt{2}}.\quad (14)
\]
Thus, the matrix elements of the surface potential operator \(\hat{V}_s\) in the complex basis are related to the real matrix elements as
\[
\langle \Lambda = \pm 2 | \hat{V}_s | \Lambda = \pm 2 \rangle = \frac{1}{2} \left[ \langle \Delta_{x^2-y^2} | \hat{V}_s | \Delta_{x^2-y^2} \rangle + \langle \Delta_{xy} | \hat{V}_s | \Delta_{xy} \rangle \right] + i \langle \Delta_{x^2-y^2} | \hat{V}_s | \Delta_{xy} \rangle.\quad (15)
\]
\[
\langle \Lambda = \pm 2 | \hat{V}_s | \Lambda = \mp 2 \rangle = \frac{1}{2} \left[ \langle \Delta_{x^2-y^2} | \hat{V}_s | \Delta_{x^2-y^2} \rangle - \langle \Delta_{xy} | \hat{V}_s | \Delta_{xy} \rangle \right] - i \langle \Delta_{x^2-y^2} | \hat{V}_s | \Delta_{xy} \rangle.\quad (16)
\]
A direct calculation of the lowest two electronic states of the TiH molecule near the surface would give the eigenvalues of the \(\hat{V}_s\) operator and the corresponding adiabatic states, which would be a linear combination of \(|\Delta_{x^2-y^2}\rangle\) and \(|\Delta_{xy}\rangle\). Since these two electronic states are degenerate in the free TiH molecule and their splitting by the crystal-field remains relatively small, one may expect the Born-Oppenheimer or adiabatic approximation to break down. Therefore, some kind of diabatization procedure is required to obtain the \(2 \times 2\) interaction matrix. We determine the real adiabatic states \(|\Delta_{x^2-y^2}\rangle\) and \(|\Delta_{xy}\rangle\) in an ab initio calculation that does not include the surface, and we include the Coulomb interaction in the surface potential \(\hat{V}_s\).

Initially, we used a multipole expansion of the electric field of the crystal at the position of the TiH molecule. Since for the \(^2\Delta\) state \(\Lambda = 2\), the first moment that couples \(\Lambda = 2\) and \(\Lambda = -2\) is of rank \(l = 2|\Lambda| = 4\) because of angular momentum constraints. This moment couples through the transition hexadecapole multipole moment between the \(\Delta_{x^2-y^2}\) and \(\Delta_{xy}\) states. The ranks of other terms that contribute are multiples of four because of the four-fold symmetry. However, we found that the multipole starts to diverge before it reaches a stable value. This is not too surprising, since the electron clouds of the crystal and the molecule must overlap at the equilibrium height: the Coulomb interaction is attractive, and the Pauli exchange repulsion between the electron clouds result in a stable equilibrium. Thus, instead we calculated the electrostatic interaction between the crystal, with the ions modeled by point charges, and the molecule exactly. With \(|1\rangle\) denoting the \(\Delta_{x^2-y^2}\) state and \(|2\rangle\) denoting the \(\Delta_{xy}\) state, we compute the diagonal elements of the operator \(\hat{V}_s\)
\[
V_{i,i} = \langle i | \hat{V}_s | i \rangle = \sum_k q_k \int \int \frac{-\rho_i(r)}{|r - R_k|} \, dr + \sum_A \frac{Z_A}{|R_A - R_k|}.\quad (17)
\]
for \(i = 1\) and \(i = 2\). The sum over \(k\) is a sum over the ions in the crystal with charges \(q_k\) and Cartesian positions \(r\), the sum over \(A\) is over the two nuclei of the TiH molecule, with Cartesian positions \(R\) and nuclear charges \(Z_A\) (i.e., \(Z_H = 1\) and \(Z_{Ti} = 22\)). The electron densities \(\rho_i(r)\) for the two states are computed ab initio as described in section S9.4.

The off-diagonal element of \(\hat{V}_s\) in the real basis is given by
\[
V_{1,2} = V_{2,1} = \sum_k q_k \int \int \frac{-\rho_{1,2}(r)}{|r - R_k|} \, dr,\quad (18)
\]
where again we have a sum over the ions in the crystal, but there is no contribution from the molecular nuclei because of the orthogonality of the molecular states. The transition density \( \rho_{1,2}(r) \) is the product of the wave functions of the two states.

Since both expressions consist of sums over the ions, and all terms are linear in the ionic charges \( q_k \), we can write the potential matrix elements as

\[
V_{i,j} = \sum_k q_k V_{i,j}^{(+)}(R_k),
\]

(19)

where \( V_{i,j}^{(+)}(R) \) is the interaction potential for the molecule and a single ion with charge \(+e\) at position \( R \).

The functional form of the potentials \( V_{i,j}^{(+)}(R) \) is well known, since they correspond to the potentials of a complex consisting of an atom (or ion) and a diatomic molecule in a spatially degenerate state [56]. These potentials are most easily described in a frame with the \( z \)-axis along the molecular axis and the origin at the center of mass of the molecule. With \( R \) as the Cartesian coordinates of the ion in this frame and \( R = |R| \), we express the unit vector \( \hat{R} \) along the vector \( R \) in spherical polar coordinates \((\beta, \alpha)\), i.e.,

\[
\hat{R} = R_z(\alpha) R_y(\beta) e_z,
\]

(20)

where \( e_z \) is the unit vector along the \( z \)-axis, and \( R_z(\alpha) \) and \( R_y(\beta) \) are \( 3 \times 3 \) matrices representing rotations around the \( z \)- and \( y \)-axes, respectively. Note that the potentials \( V_{i,j}^{(+)}(R, \beta, \alpha) \) depend not only on the distance \( R \) and Jacobi “bending” coordinate \( \beta \), but also on the azimuthal angle \( \alpha \). For a molecule in a \( \Sigma \) state, the electron density would be cylindrically symmetric, and the potential would be independent of \( \alpha \). Since the sum of the electron densities of the \( \Delta_x \Delta_y^2 \) and \( \Delta_{xy} \) also has cylinder symmetry, the sum of \( V_{1,1}^{(+)}(R, \beta, \alpha) \) and \( V_{2,2}^{(+)}(R, \beta, \alpha) \) is also independent of \( \alpha \). For the one-electron \( \Delta_x \Delta_y^2 \) state, the azimuthal angle \((\varphi)\)-dependence of the wave function is \( \cos(2\varphi) \) and for \( \Delta_{xy} \) it is \( \sin(2\varphi) \), so the transition density \( \rho_{1,2} \) depends on

\[
\cos(2\varphi) \sin(2\varphi) = \frac{1}{2} \sin(4\varphi).
\]

(21)

As a result, the off-diagonal element depends on \( \alpha \) as

\[
V_{1,2}^{(+)}(R, \beta, \alpha) = V^{(+)}(R, \beta) \sin(4\alpha).
\]

(22)

The eigenvalues of the \( 2 \times 2 \) interaction matrix \( V^{(+)} \), with elements \( V_{i,j}^{(+)}(R, \beta, \alpha) \) are

\[
\epsilon_{\pm} = \frac{V_{1,1}^{(+)} + V_{2,2}^{(+)}}{2} \pm \sqrt{\left| V_{1,1}^{(+)} - V_{2,2}^{(+)} \right|^2 + \left| V_{1,2}^{(+)} \right|^2}.
\]

(23)

and since they clearly must be independent of \( \alpha \), the difference potential, \( V_{2,2}^{(+)} - V_{1,1}^{(+)} \), should be

\[
V_{1,2}^{(+)}(R, \beta, \alpha) = V^{(+)}(R, \beta) \cos(4\alpha).
\]

(24)

Since the \( \alpha \)-dependence is known, and the off-diagonal element is related to the difference of the diagonal elements, we can restrict the \textit{ab initio} calculations to \( \alpha = 0 \), and determine \( V^{(+)}(R, \beta) \) from the difference potential. Since the sum potential is also independent of \( \alpha \), we only need to compute the \( \Delta_x \Delta_y^2 \) and \( \Delta_{xy} \) states with the molecule along the \( z \)-axis and the point charge in the \( xy \)-plane (i.e., for \( \alpha = 0 \)).

Note that this derivation does not give the relative sign of the difference potential and the off-diagonal potential. Since the off-diagonal potential depends on a phase convention for the wave-functions, this is unimportant in the static model. In the diabatic dynamic model, discussed in the next section, the phase convention for the electronic wave function must be consistent for different orientations of the molecule.
The derivation above seems to depend on the explicit angular dependence of a one-electron $\Delta$ wave function. However, a slightly more formal derivation [56] only uses the rotational symmetry of the complex states

$$\hat{R}_z(\alpha) |\Lambda\rangle = e^{-i\frac{\alpha}{2}\hat{L}_z} |\Lambda\rangle = e^{-i\alpha \Lambda} |\Lambda\rangle,$$

which also holds for arbitrary $N$-electron $\Delta$ states. The symmetry-based derivation also clearly shows why no higher Fourier components such as $\cos(4n\alpha)$ or $\sin(4n\alpha)$ for $n = 2, 3, \ldots$ appear in the potential and it solves the phase convention issue. Specifically, it shows that the matrix elements of the interaction potential for a single point charge in the complex basis can be expanded as

$$\langle \Lambda'\Sigma\Sigma' | \hat{V}(\pm) |\Lambda\Sigma\Sigma\rangle = \delta_{\Sigma\Sigma'} \sum_{l=|\Lambda-\Lambda'|}^{\infty} C_{l,\Lambda-\Lambda'}(\beta, \alpha) c_{l,\Lambda-\Lambda'}(R),$$

where $C_{l,\Lambda-\Lambda'}$ are Racah normalized spherical harmonics, which depend on $\alpha$ through $e^{i(\Lambda-\Lambda')\alpha}$. We can relate the potentials in the complex basis to the matrix element for the real components of the $2\Delta$ function with Eqs. (12)-(13), and we can easily re-derive the $\alpha$ dependence of the diagonal and off-diagonal matrix elements in the real basis. Before we can take the sum of Eq. (19) to obtain the potential for the entire crystal, we transform Eq. (26) to a “crystal-fixed” coordinate system, in which the $z$-axis is the normal of the MgO crystal surface, and the origin is on the oxygen ion of the unperturbed crystal underlying the TiH molecule. The $x$-axis points from the origin to one of the nearest Mg ions. We denote the spherical polar coordinates of ion $k$ in this frame by $(R_k, \theta_k, \phi_k)$, while the unit vector along the TiH axis has polar angles $(\theta, \phi)$. The Racah spherical harmonics in Eq. (26) can be expressed in these new coordinates by [56]

$$C_{l,\Lambda-\Lambda'}(\beta, \alpha) = \sum_{m=-l}^{l} C_{l,m}(\theta_k, \phi_k) D^{(i)}_{m,\Lambda-\Lambda'}(\phi, \theta, 0),$$

where $D^{(i)}_{m,\Lambda-\Lambda'}$ is a Wigner D-matrix element. Thus, the matrix elements of the interaction potential for the crystal and the molecule in the case (a) basis are

$$\langle \Lambda'\Sigma'\Sigma' | \hat{V}_s |\Lambda\Sigma\Sigma\rangle = \delta_{\Sigma\Sigma'} \sum_{l=|\Lambda-\Lambda'|}^{\infty} \sum_{m=-l}^{l} D^{(i)}_{m,\Lambda-\Lambda'}(\phi, \theta, 0) \times \sum_{k} q_k C_{l,m}(\theta_k, \phi_k) c_{l,\Lambda-\Lambda'}(R_k).$$

S9.1.4 Computation of the $g$-factor in the static model

The Hamiltonian consists of the Zeeman Hamiltonian [Eq. (2)], the spin-orbit coupling [Eq. (9)], and the crystal field $\hat{V}_s$,

$$\hat{H}_{\text{static}} = \hat{H}_Z + \hat{H}_{\text{SO}} + \hat{V}_s.$$ (29)

The wave function is expanded in a basis of four Hund’s case (a) functions [Eq. (1)]. The matrix elements of the Hamiltonian are computed with Eqs. (3), (4), (10), (17) and (18). We compute the energies as the eigenvalues of the Hamiltonian matrix for a magnetic field of $B = 1$ T, and compute the $g$-factor as

$$g_{\perp/\parallel} = \frac{E_1 - E_0}{\mu_B B_{\perp/\parallel}}.$$ (30)

For a derivation of the analytic expressions of both $g$-factors as provided in the main text, we refer to section S9.3.
S9.2 Dynamical model

In the dynamical model, the polar angles $\theta$ and $\phi$ of the TiH internuclear axis are no longer fixed, but we still keep the center of mass of the molecule at a fixed position above the surface. We expand the wave function in a free rotor Hund’s case (a) dynamical basis

$$|\Lambda S J M \Omega \rangle = \sqrt{\frac{2J + 1}{4\pi}} D^J_{M,\Omega}(\phi, \theta, 0) \hat{R}(\phi, \theta, 0)|\Lambda S \rangle_{\perp}.$$ (31)

The electronic wave function $|\Lambda S \rangle_{\perp}$ is the case (a) wave function as in the static model, with the TiH internuclear axis perpendicular to the surface. It is rotated by the rotation operator $\hat{R}(\phi, \theta, 0)$ so that the axis has spherical polar angles $\theta$ and $\phi$. The rotation operator is defined by

$$\hat{R}(\phi, \theta, 0) = \hat{R}_x(\phi) \hat{R}_y(\theta) = e^{-\frac{i}{\hbar} \phi \hat{J}_x} e^{-\frac{i}{\hbar} \theta \hat{J}_y},$$ (32)

where the $\hat{J}_x$ and $\hat{J}_y$ are the components of the total angular momentum operator in the crystal frame. This somewhat formal notation simplifies the computation of matrix elements below.

The Hamiltonian consists of $\hat{H}_{\text{static}}$ with two additional terms, the rotational kinetic energy $\hat{T}_R$ and an extra term in the potential $\hat{V}_r$,

$$\hat{H} = \hat{T}_R + \hat{H}_S + \hat{H}_Z + \hat{V}_s + \hat{V}_r.$$ (33)

S9.2.1 Rotational kinetic energy

The rotational kinetic energy is given by

$$\hat{T}_R = B_{\text{Tih}} \hat{R}^2 = B_{\text{Tih}} (\hat{R}_x^2 + \hat{R}_y^2),$$ (34)

where $\hat{R} = \hat{J} - L - S$ is the nuclear angular momentum, which only has contributions perpendicular to the molecular axis. The rotational constant of TiH is $B_{\text{Tih}} = 1/(2\mu r^2)$, with reduced mass $\mu$ and bond length $r$. Using the $ab$ initio bond distance from section S9.4, we find a rotational constant of $B_{\text{Tih}} = 5.4434$ cm$^{-1}$. The rotational term can be rewritten to

$$\hat{T}_R = B_{\text{Tih}} (J^2 - \tilde{J}_z^2 + S^2 - \tilde{S}_z^2 + \tilde{L}^2$$

$$- \tilde{L}_z^2 + \tilde{L}_+ \tilde{S}_- + \tilde{L}_- \tilde{S}_+ - \tilde{J}_+ \tilde{L}_- - \tilde{J}_- \tilde{L}_+ - \tilde{J}_+ \tilde{S}_- - \tilde{J}_- \tilde{S}_+).$$ (35)

Some of these terms only result in an overall shift in energy and may be neglected (assuming a doublet state, this also holds for $\tilde{S}_z$). Furthermore, the ladder operators $\tilde{L}_\pm$ only couple other electronic states, which we assume to be far apart in energy. The last two terms give rise to a Coriolis effect and couple nearby $\Omega$, which we also assume to be separated more in energy than states with different $J$. We can then greatly simplify Eq. (35) to

$$\hat{T}_R \approx B_{\text{Tih}} (J^2 - \tilde{J}_z^2).$$ (36)

The matrix elements of this operator are diagonal in the dynamic basis and are given by

$$\langle \Lambda' S' \Sigma' J' M' \Omega' | \hat{T}_R | \Lambda S \Sigma J M \Omega \rangle = \delta_{\Lambda \Lambda'} \delta_{S S'} \delta_{\Sigma \Sigma'} \delta_{J J'} \delta_{M M'} \delta_{\Omega \Omega'} B_{\text{Tih}} [J(J + 1) - \Omega^2].$$ (37)

Note, that the operator $\hat{J}_z$ is a body-fixed operator and therefore yields a factor $\Omega$ instead of $M$. 

\[14\]
S9.2.2 Repulsive potential

A crystal surface modeled by point charges completely lacks the Pauli repulsion between the electrons of the molecule and the electrons of the ions. This leads to unphysically strong interactions between, e.g., the partly charged hydrogen atom and the negative oxygen ions at large values of $\theta$. To mimic the Pauli repulsion we include a repulsive potential, which increases the energy for spatial orientations in the downward direction without modifying the potential for small $\theta$. This potential therefore does not affect the energy at small $\theta$ and is mainly used to avoid nonphysical local minima at larger inclination angles. For computational convenience, we expand the repulsive potential in Legendre polynomials, which are related to Racah normalized spherical harmonics,

$$V_r(\theta) = \sum_{\ell=0}^{\ell_{\text{max}}} c_\ell P_\ell(\cos \theta) = \sum_{\ell=0}^{\ell_{\text{max}}} c_\ell C_{\ell,0}(\theta, 0).$$  \hspace{1cm} (38)

The coefficients $c_\ell$ are chosen such that the potential is zero for $\theta = 0$ and has some maximal value $V_{r_{\text{max}}}$ for $\theta = \pi$, and such that its derivatives up to some order $n_{\text{max}}$ for $\theta = 0$ and $m_{\text{max}}$ for $\theta = \pi$ are zero as well. These conditions give rise to a system of $2 + n_{\text{max}} + m_{\text{max}}$ equations for which evaluation of the Legendre polynomials and its derivatives for $\cos \theta = -1$ and $\cos \theta = 1$ are needed. These can be calculated by the explicit representation of Legendre polynomials:

$$P_\ell(z) = \frac{1}{2\ell} \sum_{k=0}^{[\ell/2]} (-1)^k \binom{l}{k} \binom{2l-2k}{l} z^{l-2k}. \hspace{1cm} (39)$$

The repulsive potential is taken the same for both electronic states, so the matrix elements are given by

$$\langle \Lambda'\Sigma'|\hat{V}_r|\Lambda\Sigma\rangle = \delta_{\Lambda'\Lambda} \delta_{\Sigma'\Sigma} \sum_{\ell=0}^{\ell_{\text{max}}} c_\ell C_{\ell,0}(\theta, \phi). \hspace{1cm} (40)$$

This repulsive potential is only of importance for the dynamical model. From the static model we determine the value of $V_{r_{\text{max}}}$ needed to remove the unphysical minima for large $\theta$. In our calculations we have used $V_{r_{\text{max}}} = 0.06$ atomic units, $n_{\text{max}} = 2$ and $m_{\text{max}} = 4$.

S9.2.3 Matrix elements of the spin-orbit Hamiltonian

Since the spin orbit Hamiltonian only acts on the electronic wave functions, and the normalized Wigner rotation matrix elements constitute an orthonormal basis, the matrix elements are given by

$$\langle \Lambda'\Sigma'|\hat{H}_{SO}|\Lambda\Sigma\rangle = \delta_{\Lambda'\Lambda} \delta_{\Sigma'\Sigma} \sum_{J=1}^{J_{\text{max}}} \sum_{M=1}^{M_{\text{max}}} \langle J' M' | \hat{H}_{SO} | J M \rangle \mu_m \langle \Lambda J M | \Lambda' J' M' \rangle.$$

S9.2.4 Matrix elements of the Zeeman Hamiltonian

The Zeeman Hamiltonian is the same as for the static model [Eq. (2)]. Using the spherical representation of the dot product we find for the matrix elements

$$\langle \Lambda'\Sigma'\Omega'|\hat{H}_Z|\Lambda\Sigma\Omega\rangle = \frac{\sqrt{(2J' + 1)(2J + 1)}}{4\pi} \sum_{m=-1}^{1} (-1)^{m+1} B_m$$

$$\times \int \int D_{M',J'}^\ell(\phi, \theta, 0) \perp \langle \Lambda'\Sigma'\Omega'|\hat{R}_m \hat{R}|\Lambda\Sigma\rangle \perp D_{M,J}^{\ell*}(\phi, \theta, 0) \cos \theta.$$  \hspace{1cm} (42)

The spherical components of the magnetic moment transform as rank one tensor operators.
Rotating the magnetic moments is done using Eq. (43). For the integral we introduce the third Euler angle by multiplying the equation with
\[ 1 = \frac{1}{2\pi} \int_0^{2\pi} e^{i\chi(-\Omega + m' + \Omega)} d\chi. \] (44)

This relation holds, since the matrix element of the magnetic moment \( \hat{\mu}_{m' m} \) gives \( \Omega' = m' + \Omega \). The integral then evaluates to
\[ \frac{1}{2\pi} \int_0^{2\pi} \int_0^{2\pi} D_{M', \Omega}^{J'}(\phi, \theta, \chi) D_{m, m'}^{J, *}(\phi, \theta, \chi) d\phi d\cos \theta d\chi = 4\pi(-1)^{M' - \Omega'} \left( \begin{array}{cc} J' & 1 \\ -M' & M \end{array} \right) \left( \begin{array}{cc} J' & 1 \\ -\Omega' & m' \end{array} \right), \] (45)
where we have introduced the 3-\( j \) symbols resulting from the coupling of angular momenta. Moreover, these coefficients restrict the values for \( r_{rr} \) and \( m' \) to \( m = M' - M \) and \( m' = \Omega' - \Omega \), both attaining integer values of -1 to 1. Due to these constraints, the summations over \( r_{rr} \) and \( m' \) will only yield a value for one specific term. Evaluating the matrix elements for \( \hat{\mu}_{m' m} \) in the same way as for the static case then results in the following matrix elements for the Zeeman Hamiltonian:
\[ \langle \Lambda' S' \Sigma' J' M' \Omega' | \hat{H}_Z | \Lambda S \Sigma J M \Omega \rangle = \delta_{\Lambda', \Lambda} \left[ J', J \right] \frac{1}{2} (-1)^{M' - \Omega'} \times \left( \begin{array}{cc} J' & 1 \\ -M' & M' - M \end{array} \right) \left( \begin{array}{cc} J' & 1 \\ -\Omega' & \Omega' - \Omega \end{array} \right) \times \left[ \frac{1}{\sqrt{2}} (B_x + iB_y) \delta_{M', M - 1} + B_z \delta_{M', M} - \frac{1}{\sqrt{2}} (B_x - iB_y) \delta_{M', M + 1} \right] \times \mu_B \left( \frac{g_e}{\sqrt{2}} C_-(S, \Sigma) \delta_{\Sigma, \Sigma - 1} + (\Lambda + g_e \Sigma) \delta_{\Sigma', \Sigma} - \frac{g_e}{\sqrt{2}} C_+(S, \Sigma) \delta_{\Sigma', \Sigma + 1} \right). \] (46)

S9.2.5 Matrix elements of the surface potential

Using the matrix elements for the Coulomb interactions from Eq. (28), we find for the dynamic matrix elements that
\[ \langle \Lambda' S' \Sigma' J' M' \Omega' | \hat{V}_d | \Lambda S \Sigma J M \Omega \rangle = \delta_{\Sigma', \Sigma} \left[ J', J \right] \frac{1}{4\pi} \sum_k q_k \sum_{\ell, m} c_{\ell, \Lambda - \Lambda'} (r_k) C_{\ell, m}(\theta_k, \phi_k) \times \int \int D_{M', \Omega'}^{J'}(\phi, \theta, 0) D_{m, M', -M'}^{J, *}(\phi, \theta, 0) D_{M, \Omega}^{J, *}(\phi, \theta, 0) d\phi d\cos \theta. \] (48)

The integral is evaluated in the same way as before. We now find the restrictions \( m = M - M' \) and \( \Lambda' - \Lambda = \Omega' - \Omega \). The final matrix elements are then given by
\[ \langle \Lambda' S' \Sigma' J' M' \Omega' | \hat{V}_d | \Lambda S \Sigma J M \Omega \rangle = \delta_{\Sigma', \Sigma} (-1)^{M' - \Omega'} \left[ J', J' \right] \times \sum_{\ell} \left( \begin{array}{cc} J' & \ell \\ -M' & M' - M \end{array} \right) \left( \begin{array}{cc} J' & \ell \\ -\Omega' & \Lambda' - \Lambda \end{array} \right) \times \sum_k q_k C_{\ell, \Lambda - \Lambda'} C_{\ell, M - M'}(\theta_k, \phi_k). \] (49)
S9.2.6 Matrix elements of the repulsive potential

The repulsive potential is given by Eq. (38). It is the same for both electronic states. The matrix elements are

$$\langle \Lambda' \Sigma' J'M' \Omega' | \hat{V}_r | \Lambda \Sigma J M \Omega \rangle = \delta_{N',N} \delta_{\Sigma',\Sigma} [J',J] \frac{4\pi}{\ell_{\text{max}}} \times \sum_{\ell=0}^\ell c_\ell \int D_{M'\Omega'}(\phi,\theta,0) C_{\ell,0}(\theta,\phi) D_{J'J,\Omega}(\phi,\theta,0) \, d\phi \, d\cos \theta .$$

(Eq. 50)

Evaluating the integral as before then yields the matrix elements

$$\langle \Lambda' \Sigma' J'M' \Omega' | \hat{V}_r | \Lambda \Sigma J M \Omega \rangle = \delta_{N',N} \delta_{\Sigma',\Sigma} \delta_{J',J} \delta_{M',M} \delta_{\Omega',\Omega} (-1)^{M'-M} [J',J] \times \sum_{\ell=0}^\ell c_\ell \begin{pmatrix} J' & \ell & J \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} J' & \ell & J \\ -\Omega & 0 & \Omega \end{pmatrix} .$$

(Eq. 51)

The coefficients $c_\ell$ are determined by the procedure as given in the static case, such that only a finite number of coefficients is non-zero.

S9.2.7 Computation of the $g$-factor in the dynamic model

Using Eqs. (37), (41), (46), (49) and (51), the matrix elements for the total Hamiltonian (33) can now be calculated. In all calculations, a basis is used containing elements with $J = 1.5$ up to 20.5. Diagonalizing this Hamiltonian then yields the eigenenergies and the eigenfunctions as linear combinations of the complex basis $|\Lambda \Sigma J M \Omega \rangle$. The $g$-factor is then again determined by Eq. (30).

S9.2.8 Adding an external electric field

In the dynamic model we can also incorporate an external electric field in any direction and induce a Stark effect. This interaction is given by

$$\hat{H}_S = -\vec{E} \cdot \hat{\mu} ,$$

(Eq. 52)

where $\vec{E}$ is the electric field and $\hat{\mu}$ is the electric dipole moment. The derivation of the matrix elements is analogous to the one for the Zeeman Hamiltonian with the magnetic dipole moment, where we note that only $\langle \Lambda | \hat{\mu}_z | \Lambda \rangle$ remains and is equal for both states. We then find the matrix elements

$$\langle \Lambda' \Sigma' J'M' \Omega' | \hat{H}_S | \Lambda \Sigma J M \Omega \rangle = \delta_{N',N} \delta_{\Sigma',\Sigma} \delta_{J',J} \delta_{\Omega',\Omega} (-1)^{M'-M} [J',J] \times \begin{pmatrix} J' & 1 & J \\ -M' & M' - M & J \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega & 0 & \Omega \end{pmatrix} \times \left( \frac{-1}{\sqrt{2}} (E_x + iE_y) \delta_{M',M-1} - E_z \delta_{M',M} + \frac{1}{\sqrt{2}} (E_x - iE_y) \delta_{M',M+1} \right) .$$

(Eq. 53)

S9.3 Derivation of analytic expression for the $g$-tensor

Here, we provide a derivation of the analytic expressions for both $g$-factors as given in the main text. For both time-reversal symmetries, the lower eigenvalue of the Hamiltonian matrix is

$$E_0 = -\sqrt{A_{s0}^2 + \left(\frac{1}{2} V_c \right)^2}$$

(Eq. 54)
and the upper eigenvalue is $E_1 = -E_0$. Rewrite the Hamiltonian matrices (in the bases $\{\Psi_\pm(2, -1/2), \Psi_\pm(2, 1/2)\}$, assuming $A_{SO} \geq 0$),
\[
H_\pm = E_1 \begin{pmatrix} -\cos \alpha & \pm \sin \alpha \\ \pm \sin \alpha & \cos \alpha \end{pmatrix},
\]
where
\[
\tan \alpha = \frac{V_c}{2A_{SO}}.
\]
The eigenvector with the lower eigenvalue ($E_0$) is
\[
u_\pm = \begin{pmatrix} -\cos(\alpha/2) \\ \pm \sin(\alpha/2) \end{pmatrix},
\]
so that the relative sign of the components of the eigenvector depends on the time-reversal symmetry. It is obviously true for $\alpha = 0$. When $\alpha$ goes from zero to $2\pi$, the eigenvector changes sign. This is the famous geometric phase you get when you go around a conical intersection.

To determine $g_\parallel$ consider the effect of $\hat{S}_x$: it couples to the fine-structure states, but the sign of the coupling depends on the time-reversal symmetry:
\[
\langle \Psi_\pm(2, 1/2) | \hat{S}_x | \Psi_\pm(2, -1/2) \rangle = \pm \frac{1}{2}.
\]
Thus, the lower eigenvalue $E_0$ splits due to the Zeeman interaction as
\[
E_0^{(\pm)} = -E_1 \left(1 \pm \frac{\mu_B g e V_c B}{4E_1^2} \right).
\]
To first order in $B$ this gives, using $\sqrt{1 + \epsilon} = 1 + \epsilon/2 + O(\epsilon^2)$ for small $\epsilon$,
\[
E_0^{(\pm)} = -E_1 \left(1 \pm \frac{\mu_B g e V_c B}{4E_1^2} \right).
\]
The $g$-factor is the derivative of the energy difference with respect to $B$, divided by $\mu_B$, and so the $g_\parallel$-factor is
\[
g_\parallel = \frac{g e V_c}{2E_1} = g_e \frac{r}{\sqrt{1 + r^2}},
\]
with $\mu_B = 1/2$ in atomic units and where
\[
r = \frac{V_c}{2A_{SO}}.
\]
When the field is perpendicular to the surface, the degeneracy is lifted by the $z$-component of the Zeeman Hamiltonian which breaks time-reversal symmetry, see Eq. (3) of the main text. The contribution of the fine-structure states are determined by the eigenvectors $\nu_\pm$, so we find
\[
g_\perp = \langle u_1^- \Psi_-(2, -1/2) + u_2^- \Psi_-(2, 1/2) | \hat{L}_z + g_e \hat{S}_z | u_1^+ \Psi_+(2, -1/2) + u_2^+ \Psi_+(2, 1/2) \rangle
\]
\[
= |u_1|^2 (4 - g_e) - |u_2|^2 (4 + g_e)
\]
\[
= 4(|u_1|^2 - |u_2|^2) - g_e.
\]
The eigenvector dependent part can be written as

\[ |u_1|^2 - |u_2|^2 = \cos(\alpha/2)^2 - \sin(\alpha/2)^2 = \cos \alpha = \frac{A_{\text{SO}}}{E_1} = \frac{1}{\sqrt{1 + r^2}}, \tag{66} \]

where in the before last step we used the expression for \( H_{1,1} \) of Eq. (55), so we find

\[ g_\perp = \frac{4}{\sqrt{1 + r^2}} - g_e. \tag{67} \]

**S9.4 Ab initio calculations**

For the \textit{ab initio} electronic structure calculations we used the Molpro [40] program package. Using this software, we determined the electronic ground state of TiH in the adsorbed phase. Moreover, for use in the model we computed molecular properties of TiH in the gas phase, in particular: the spin-orbit coupling constant and the molecular electrostatic potential for calculations of the Coulomb interaction with the surface.

Two electronic states of the TiH molecule are of special interest: \( ^4\Phi \) and \( ^2\Delta \). In the gas phase they are the lowest quartet and doublet spin states, respectively. The former is also the overall ground state of free TiH. Decreasing the distance between the TiH and the surface changes the order of electronic states and, as shown in Fig. 1 of the main text, the \( ^2\Delta \) state becomes the ground state at smaller heights above the MgO surface.

**S9.4.1 Gas phase**

For the gas-phase calculations the actual symmetry of the diatomic TiH molecule is \( C_{\infty v} \), but Molpro adopts \( C_2 \) symmetry. This group has irreducible representations (irreps) \( A_1, B_1, B_2 \) and \( A_2 \), and the two components of the \( ^2\Delta \) state belong to the \( A_1 \) and \( A_2 \) irreps. We denote these by \( ^2\Delta_{x^2-y^2} \) and \( ^2\Delta_{3p} \), respectively, since they represent the character of the corresponding occupied \( d \)-orbitals. In the gas phase, these are degenerate, but they will split upon introduction of the surface with its four-fold symmetry. The degenerate \( ^4\Phi \) states belong to the \( B_1 \) and \( B_2 \) irreps, but are not split in energy in this system.

All calculations have been performed using an aug-cc-pVTZ basis set [57]. A first orbital guess is generated by Hartree-Fock (HF) calculations, which are followed by a complete-active-space self-consistent field (CASSCF) [58,59] calculation with irrep occupation 9,3,3,1 (\( A_1, B_1, B_2, A_2 \)) and closed orbitals 5,2,2,0 for both electronic states. To obtain the correct states, however, a prior CASSCF calculation was needed with a larger number of active orbitals in the \( A_1 \) irrep, i.e., occupied orbitals 13,3,3,1 and closed orbitals 6,2,2,0. Following these CASSCF calculations, a multireference configuration interaction (MRCI) [60-62] calculation was made in each case to obtain the final energy. The wavefunction definition remained the same as in the CASSCF calculations.

With the final wave function thus obtained we calculated the spin-orbit coupling constant, as well as the molecular electronic potential using the one-electron operator ‘pot’.
S9.4.2 Adsorbed phase

For the MgO lattice we used the parameters resulting from DFT calculations. The in-plane lattice constant was set to 2.04 Å and the out-of-plane constant to 2.20 Å. Moreover, the oxygen atom directly below the TiH molecule is vertically displaced by 0.48 Å relative to the rest of the surface. For all calculations we used a finite lattice consisting of two layers and stretching 21 atoms along both in-plane directions, after which the total \textit{ab initio} energy in atomic units had converged up to 6 decimals.

The adsorbed phase calculations were used to optimize the TiH bond length, as well as its height above the surface. In addition to TiH, we explicitly included the Mg and O atoms directly underneath. The other atoms in the finite surface were modeled as point charges using the lattice parameters listed above and charges $+\frac{2}{3}$ and $-\frac{2}{3}$ for the Mg and O atoms, respectively.

Initially only the MgO-TiH linear complex was included in the Molpro calculations with some Ti-H bond distance $R$ and some height $h$ above the surface. We started by choosing $h$ to be large such that TiH is essentially in the gas phase, in order to produce the correct electronic state in $C_{2v}$ symmetry. Then including MgO, we used irrep occupation 20,5,5,1 and closed orbitals 13,4,4,0 in the first CASSCF calculation, followed by one with occupation 16,5,5,1 and closed orbitals 12,4,4,0. Once the correct state was established from these CASSCF calculations, we added point charges and turned off the symmetry. Then, the height is decreased, CASSCF and MRCI are performed for each value of $h$. The energies from the MRCI calculations then provide the potential as a function of $h$, as given in Fig. 1. At the minimum of this function, we optimized the bond distance $R$. Since the optimal height $h^*$ and bond distance $R^*$ depend on each other, this process was repeated to arrive at optimal $h^*$ and $R^*$ values for each state to within a reasonable error estimate. For both electronic states, the optimal height and distance as well as the energy difference between the components are given in Table S3. These values are then used as inputs for the diabatic models.

In addition to these calculations, we performed embedded cluster calculations with TiH adsorbed on clusters as large as Mg$_9$O$_9$ embedded in a crystal represented by point charges. These are described in Appendix B of the main article.

S9.5 Supplementary results

S9.5.1 Molecular orbital diagrams

The molecular orbital diagrams of the electronic $^2\Delta$ and $^4\Phi$ states of the gas-phase TiH molecule are given in Fig. S18. The molecular orbitals are also given in a visual representation by performing \textit{ab initio} calculations as described in S9.4.1. The visualization is done using Molden [63,64]. As can be seen, a bonding-antibonding orbital pair is formed between the Ti and H atoms. The highest occupied molecular orbitals are given by almost pure Ti d-orbitals.

To show the negligible hybridization of TiH in the $^2\Delta$ state with the surface, we provide the molecular orbitals in Fig. S19. We performed \textit{ab initio} calculations by converging TiH towards a Mg$_9$O$_9$ cluster and then visualized them using Molden.

S9.5.2 Crystal field
To give an idea of the contribution of the Coulomb interactions experienced from the surface, Fig. S20 shows the potential energy. The left picture illustrates the average energy $V_{s,\text{avg}}(\theta, \phi)$ of the two real orbitals, the righthand one the difference $V_{s,\text{diff}}(\theta, \phi)$ between the two energy levels. This difference is defined as the energy of the eigenstate with $^2\Delta_x^2-\Delta_y^2$ as the major component minus the energy of the state with $^2\Delta_x\Delta_y$ as the major component. When $\phi$ is a multiple of 45°, these are pure states, while for other angles the states get mixed by the rotation around the internuclear axis.

S9.5.3 $g$-factors upon rotating TiH

In Fig. S20, one can see that the average potential is cylindrically symmetric. For $\theta = 90^\circ$, the orbitals get much closer to the underlying O atom and therefore have a higher energy. The difference potential clearly shows four-fold symmetry. For $\phi = 0^\circ$, at $\theta = 0^\circ$, the $^2\Delta_x^2-\Delta_y^2$ state has a lower energy due to its lobes pointing towards the positive Mg point charges. Eventually, at larger $\theta$, the ground state switches to $^2\Delta_x\Delta_y$, since the negatively charged O point charge below TiH increases the energy for the $^2\Delta_x^2-\Delta_y^2$ state, which points towards this charge. For $\phi = 45^\circ$, the lowest state is always $^2\Delta_x\Delta_y$.

In the main paper, $g$-factors have been given for $\theta = \phi = 0^\circ$, since this is the most favorable position. Fig. S21 shows the $g$-factors for different orientations of TiH. At most orientations, the determining factor for the eigenstates is the Coulomb interaction. Only at the four ‘dots’, where $V_{s,\text{diff}}(\theta, \phi) = 0$, the spin-orbit coupling takes over.

S9.5.4 Sensitivity of the $g$-tensor to static electric fields

As the ESR-STM experiments are extremely precise, we can consider how perturbations due to changes in local electric fields can alter the $g$-factor of the TiH molecule. The scatter of the experimental data in Fig. 3(b) could not solely be mapped to quantities like different atoms, measurement parameters or microtips. To investigate the response of the TiH molecule to electrostatic field perturbations, we employed the dynamical model and considered an additional external electric field in atomic units ($E = 1$ a.u. = 5.14·10¹¹ Vm⁻¹) interacting with the TiH dipole moment. The resulting $g$-factors for a static electric field parallel ($E_\parallel$) and perpendicular ($E_\perp$) to the MgO surface are depicted in Tables S4 and S5.

We find that the $g$-tensor of the TiH molecule is more sensitive to $E_\parallel$ than it is to $E_\perp$. Considering a single charge defect ($\pm 1e$ instead of $\pm 2e$) at one lattice site distance to the TiH, the electric field the TiH experiences is $E_\parallel \approx 1.5\cdot10^{10}$ Vm⁻¹ = 0.03 a.u. Accordingly, $g_\parallel$ and $g_\perp$ change by ≈ 5 and 15 %, respectively. Potentially, such changes could stem from embedded defects in the crystal, vicinity to the edges of the MgO islands but also other undetected variations of the electrostatic environment. For perpendicular electric fields, the $g$-tensor remains almost unaffected, even for $E_\perp = -0.1$ a.u. Therefore, even changes of the tip work function or the electric field induced by the measurement parameters assuming a simple plate capacitor model ($d$(tip-sample) ≈ 0.7 nm, $V_{\text{DC}}$ = 50 mV, $I = 2$ pA and $V_{\text{RF}}$ = 8 mV, $E_\parallel \approx 0.00016$ a.u.) do not affect the measured $g$-tensor, as they are orders of magnitudes smaller as would be needed according to the calculations.

We conclude that we are not measuring an artificial effect from the tip on the TiH but changes in the local electrostatic environment might cause measurable variations in the $g$-
tensor. We speculate, this might explain the scatter of the data we observe in Fig. 3(b), that could not be matched to any other obvious parameters.

**S9.5.5 Gas-phase and adsorbed spin-orbit coupling**

The gas-phase spin orbit coupling constant as calculated from *ab initio* calculations is 110.05 cm⁻¹. This value has been used throughout the calculations. After convergence to the point charge surface with MgO explicitly taken into account along the z-axis, the spin-orbit constant is found to only change by -0.3 cm⁻¹ and so it only changes negligibly.

**S9.5.6 Sensitivity of charges in point charge model**

We have investigated the stability of our model under changes in the charges of the surface atoms for which we had used +2 and -2 for Mg and O, respectively, for all calculations. When Bader charge analysis in DFT is considered, where we find charges of +1.7 and -1.7 for Mg and O, one might wonder how this will affect the results from the model. As it turns out, the TiH system is quite insensitive to such changes of the charges.

We carried out calculations in a similar manner as in Fig. 1 of the main text, but up to the CASSCF level. The energy splitting of the two ²Δ states as a function of the height above the surface for charges $q = \pm 2$ and $q = \pm 1.7$ is given in the Fig. S22. For different charges, the optimal height above the surface changes. This is mainly due to Coulomb repulsion as higher charges lead to more repulsion and thus a larger height. However, larger charges also give rise to a larger energy splitting of the two ²Δ states. These effects roughly cancel as can be seen by the colored bars along the x- and y-axes. Our model is therefore rather insensitive to the exact charges of the atoms in the ionic surface.
FIG. S1. STM characterization. (a) Constant-current STM image of a representative sample with MgO patches grown on Ag(100) and co-deposited Fe and TiH ($V_{DC} = 100$ mV, $I_t = 10$ pA). (b) Histogram representation of numerous measured apparent heights of TiH molecules (green) and Fe atoms (yellow) at $V_{DC} = 30$ mV and $I_t = 10$ pA. TiH molecules can easily be distinguished by their lower apparent height of $103 \pm 8$ pm compared to $151 \pm 8$ pm for Fe atoms (dashed lines represent the average value).
FIG. S2. Adsorption site determination. Constant-current image of a typical 2 ML MgO film with adsorbed TiH and Fe. Superimposed atomic resolution image on the indicated region of the patch was recorded at $V_{DC} = -5$ mV and $I_t = 15$ nA. The corresponding larger scale image was recorded at $V_{DC} = -5$ mV and $I_t = 20$ pA. The grid formed by the white lines reference the oxygen sites, based on the atomic lattice image.
FIG. S3. Spectroscopic fingerprints of TiH. STS recorded on top of the same TiH molecule adsorbed on an oxygen site of the MgO surface, with and without a spin-polarized tip. We observe the orbital excitation at $\approx \pm 90$ meV, as well as signatures of spin pumping for both this excitation and the low energy spin excitation (stabilized at $V_{DC} = 100$ mV, $I_t = 200$ pA; $B_{\perp} = 150$ mT, $f_{mod} = 809$ Hz, $V_{mod} = 1$ mV).
FIG. S4. MgO thickness determination. Point-contact measurements with switched off feedback loop on two different Fe atoms adsorbed on two (red) and three (blue) ML MgO (stabilized at $V_{DC} = 10$ mV, $I_t = 20$ pA).
FIG. S5. Transmission of the ESR-STM. Measurement of the frequency-dependent transmission with the RF voltage applied on the tip. The recorded signal was rectified over the non-linearity in the TiH spectrum (Fig. S3) at $V_{\text{DC}} = -78$ mV. The absolute $V_{\text{RF}}$ at the junction was not calibrated for this measurement, and therefore the signal was normalized with respect to the highest peak.
FIG. S6. Flattening of $V_{RF}$. Measured $V_{RF}$ in a region of 7.9 – 8.5 GHz before (blue) and after (red) compensating for the frequency-dependent transmission. A constant $V_{RF}$ was achieved by adjusting the output power of the generator $\tilde{P}_{RF}$ according to the frequency-dependent transmission.
FIG. S7. Complementary ESR raw data for $B$-sweep mode. ESR $B$-sweeps on the same molecule with the same microtip complementary to Fig. 2 of the main manuscript in both field directions $B_\parallel$ (blue) and $B_\perp$ (red). The same molecule as in the $B_\parallel$-sweep and both $f$-sweeps of Fig. 2 was probed. After fitting each peak with a Lorentzian and linearly fitting the ESR peak positions, we obtain $g_\parallel = 1.80 \pm 0.01$ and $g_\perp = 0.49 \pm 0.01$. Note, these values were obtained prior application of the linearity criterion introduced in section S4.
FIG. S8. Additional ESR raw data for $B$-sweep mode. Recorded in both field directions $B_l$ (blue) and $B_\perp$ (red) on the same molecule and micro tip. After fitting each peak with a Lorentzian and linearly fitting the ESR peak positions, we obtain $g_l = 1.82 \pm 0.02$ and $g_\perp = 0.63 \pm 0.01$. 
FIG. S9. Additional ESR raw data for f-sweep mode. Recorded in both field directions $B_\parallel$ (blue) and $B_\perp$ (red) on the same molecule and micro tip. After fitting each peak with a Lorentzian and linearly fitting the ESR peak positions (see insets), we obtain $g_\parallel = 1.33 \pm 0.14$ and $g_\perp = 0.64 \pm 0.04$. 
FIG. S10. ESR data sets with various stabilization parameters. Extracted ESR peak positions for the data sets used for the $g$-tensor analysis in Fig. 3B. The tip was stabilized at $V_{DC} = 50$ mV for all measurements, and the values of $I_t$ and $V_{RF}$ are indicated in the table. For $B$-sweeps in data sets #12 and #30, $V_{RF}$ was not calibrated and $P_{RF}$ set to 23 dBm. In the plot, different symbols correspond to different atoms, filled or open symbols represent $B$-, or $f$-sweeps and blue or red colors represent the external magnetic field direction (ǁ or ┴ to the sample surface).
FIG. S11. Tip stray field influence on ESR-STM. (a) Illustration of the TiH molecule influenced by the stray magnetic field of the tip, $\vec{B}_{\text{tip}}$, indicated by yellow dashed field lines. Vector arrows illustrate the variation of the total magnetic field $\vec{B}_{\text{tot}}$ at the TiH spin and its vector decomposition in $\vec{B}_{\text{ext}}$ and $\vec{B}_{\text{tip}}$. The spin ($\vec{S}$) of TiH follows the direction of $\vec{B}_{\text{tot}}$. (b) ESR peak positions (dots) extracted from two data sets with identical measurement parameters ($V_{\text{DC}} = 50$ mV, $I_t = 2$ pA, $V_{\text{RF}} = 8$ mV), but with a different micro-tip. $\vec{B}_{\text{tip}} = (B_x, B_y, B_z)$ for each data set (legend) is extracted from a global fit of all available data sets (see Fig. S12) and reveals $B_x$ and $B_y$ components that cannot be compensated with $B_{z,\text{ext}}$. 
FIG. S12. Fitting measured ESR spectra considering the tip stray field. (a) Extracted ESR peaks from experimental data sets in different $B_{\text{ext}}$ directions $Z$ (red) or $Y$ (blue), fitted with an arbitrary tip stray field $\vec{B}_{\text{tip}}$. The data sets include different tips, atoms, stabilization parameters and $V_{\text{RF}}$. We obtained $g_{\parallel} = 1.896$ and $g_{\perp} = 0.638$. (b) Enlarged section of (a) (indicated with a rectangular frame) showing the non-linear trends as captured by the fit equation.
FIG. S13. ESR f-sweeps at 1.1 K. (a,b) ESR f-sweep measurements in \( \perp \) (A) and \( \parallel \)-direction (B) on TiH at \( T = 1.1 \) K (stabilized at \( V_{\text{DC}} = 50 \) mV, \( I_t = 5 \) pA; \( V_{\text{RF}} = 8 \) mV). An additional static field of \( B_\parallel = 30 \) mT and \( B_\perp = 150 \) mT was applied in (a) and (b), respectively. Peak positions were extracted from Lorentzian fits (gray lines). (c) Extracted resonance peak positions (circles) and linear fits (dashed line) to the data. Resulting \( g \)-factors of \( g_\parallel = 1.57 \pm 0.04 \) ([21.90 ± 0.60] GHz/T) and \( g_\perp = 0.55 \pm 0.05 \) ([7.69 ± 0.68] GHz/T) agree well with the observations at lower temperatures.
FIG. S14. ISTS of TiH and Fe measured in a vector magnetic field. ISTS of a TiH molecule in (a): in-plane field, and (b): out-of-plane field. The spin-excitation shifts linearly to higher energies for increasing fields, but with different slopes depending on the magnetic field orientation (stabilized at $V_{DC} = 3$ mV, $I_t = 100$ pA; $V_{mod} = 25$ µeV, $f_{mod} = 809$ Hz). C Extracted spin-excitation step position, averaged for four different TiH molecules for the out-of-plane (red) and in plane (blue) direction (error bars are smaller than the marker size). The corresponding $g$-factors are extracted from linear fits to the data and result in $g_\parallel = 1.84 \pm 0.01$ and $g_\perp = 0.50 \pm 0.01$. The inset shows the same measurements for (two averaged) Fe atoms, where $g_\perp = 2.48 \pm 0.18$. 
FIG. S15. Geometric and electronic structure from DFT of TiH. (a) Optimized crystal structure illustrated as ball-stick model for TiH adsorbed on the oxygen site of the MgO surface. (b) DFT ($U = 0$) band structure of the TiH/MgO system. Ti($d$) states are split in energy due to the crystal field of the $C_4v$-symmetric surface. Indices 1 to 6 label the Ti and H states as used in Table S1. (c) Density of states as a function of energy. Color corresponds to the various atomic orbital contributions for the energy bands of the TiH molecule to the LDOS.
FIG. S16. DFT+U density of states for various values of U. Evolution of projected densities of states of TiH/MgO for different values of the U parameter within the DFT+U calculations. For increasing U (a-c), the spin up and spin down channels of the Ti($d_{x^2-y^2}$) state show a stronger splitting and all Ti($d$) states shift to higher energies. The hydrogen $s$ state remains unaffected.
FIG. S17. Potential energy landscape for rotated H obtained from DFT+$U$. (a) 3D potential energy landscape (normal scale) for the TiH molecule adsorbed on MgO obtained by rotating the hydrogen atom around the Ti atom at a fixed Ti-H distance. Corresponding x- and y-axes are oriented towards the Mg atoms. (b) Same as in (a) but plotted on a logarithmic scale for better visualization of the energy minima.
FIG. S18. Molecular orbital diagrams of the gas-phase electronic $^2\Delta$ and $^4\Phi$ states of TiH, accompanied by visual representations of the molecular orbitals.
FIG. S19. Highest occupied molecular orbital of the adsorbed TiH molecule in the $^2\Delta$ state on a Mg$_9$O$_9$ cluster. There is negligible hybridization between the TiH and the MgO surface.
FIG. S20 Potential energy landscape for rotated H from QC. Polar plots of $V_s, \text{avg}(\theta, \varphi)$ (a) and $V_s, \text{diff}(\theta, \varphi)$ (b) at a height of 2.42 Å. The azimuth is represented by the angle $\varphi$, where $\varphi = 0, 90, 180$ and $270^\circ$ is the rotation towards a Mg atom. The radius is given by $\sin \theta$, with $\theta$ spanning the sphere in the out-of-plane direction with $\theta = 0^\circ$ in the center and $\theta = 90^\circ$ at the edge.
FIG. S21. Calculated g-factors for different orientations of TiH from QC. Polar plots of $|g_\perp|$ (a) and $|g_\parallel|$ (b) at a height of 2.42 Å. The azimuth is represented by the angle $\phi$, where $\phi = 0, 90, 180$ and 270° is the rotation towards a Mg atom. The radius is given by $\sin \theta$, with $\theta$ spanning the sphere in the out-of-plane direction with $\theta = 0^\circ$ in the center and $\theta = 90^\circ$ at the edge. For $g_\parallel$, the magnetic field is at an angle of $\phi = 21.2^\circ$. 
FIG. S22. Splitting of the two Δ-states for different charges. The plots show the calculated energy splitting of the two Δ-states for point charges of ±2e (purple) or ±1.7e (orange) on the Mg and O sites with respect to the TiH molecule’s adsorption height above the surface. As the bars indicate, the changes resulting from a lower adsorption height for the ±1.7e charges, results in the same splitting of the states as for the original calculation and charges or ±2e.
TABLE S1. Main atomic contributions to energy bands near $E_F$ from DFT. The band index (1 to 6) corresponds to the notation in Fig. S15. The decimal numbers indicate the contribution of each orbital state to the indicated energy band.

|     | Hydrogen |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     | $s$      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 1   | 0.60     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 2   | 0.01     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 3   | -        |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 4   | -        |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 5   | -        |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 6   | -        |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

|     | Titanium |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | 0.08     | 0.10 | 0.12 | -   | -   | -   | -   | -   | -   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 2   | 0.17     | -    | 0.70 | -   | -   | -   | -   | -   | -   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 3   | -        | -    | -    | -    | -   | -   | -   | -   | 0.99 | -   | -   | -   | -   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 4   | -        | -    | -    | -    | -   | -   | -   | -   | 0.99 | 0.32 | 0.63 | -   | -   | -   | -   | -   | -   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 5   | -        | -    | -    | -    | -   | -   | -   | 0.32 | 0.63 | -   | -   | -   | -   | -   | 0.02 | 0.03 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 6   | -        | -    | -    | -    | -   | -   | -   | 0.63 | 0.32 | -   | -   | -   | -   | -   | 0.03 | 0.02 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
TABLE S2. Calculated spin and orbital angular momentums of TiH with DFT+U. The orbital moment is found to be very small and independent of the chosen $U$ parameter, which does not reflect the experimental observation.

| $U$ (eV) | moments along $Y (\mu_B)$ | moments along $Z (\mu_B)$ |
|----------|---------------------------|---------------------------|
|          | $m_S$ | $m_L$ | $m_S$ | $m_L$ | $m_S$ | $m_L$ |
| 3        | 0.81  | -0.04 | 0.82  | -0.04 |       |       |
| 4        | 0.84  | -0.04 | 0.83  | -0.04 |       |       |
| 5        | 0.88  | -0.04 | 0.85  | -0.04 |       |       |
TABLE S3. Optimized values for the different states in the adsorbed phase. Optimal height $h^*$, bond length $R^*$, and energy difference $\Delta E$ between different components for the $^2\Delta$ and $^4\Phi$ states.

|                | $^2\Delta$         | $^4\Phi$         |
|----------------|---------------------|------------------|
| $h^*$ (Å)      | 2.42 ± 0.01         | 2.60 ± 0.01      |
| $R^*$ (Å)      | 1.774 ± 0.001       | 1.834 ± 0.003    |
| $\Delta E$ (meV) | 46.26               | 0                |
TABLE S4. Calculated $g$-factors with applied parallel static electric field $E_i$. For the calculation of $g_i (g_{\perp})$, the magnetic field was applied in [1,0,0] ([0,0,1])-direction. The [x, 0, 0]- and [0, y, 0]-directions point towards the neighboring Mg atoms. $E_i = [0.03, 0, 0]$ compares to a single charge defect of a neighboring site to the TiH molecule and causes changes in $g_i (g_{\perp})$ on the order of $\approx 5 \% (15 \%)$.

| $E_i$ (a.u.)  | $g_i$  | $g_{\perp}$ |
|--------------|--------|-------------|
| [0, 0, 0]    | 1.838  | 0.478       |
| [0.01, 0, 0] | 1.828  | 0.506       |
| [0, 0.01, 0] | 1.827  | 0.506       |
| [0.03, 0, 0] | 1.775  | 0.558       |
TABLE S5. Calculated $g$-factors with applied parallel static electric field $E_\perp$. For the calculation of $g_\parallel$ ($g_\perp$), the magnetic field was applied in [1,0,0] ([0,0,1])-direction. The [x, 0, 0]- and [0, y, 0]-directions point towards the neighboring Mg atoms. Compared to an applied $E_\parallel$, the $g$-tensor is less sensitive to changes in $E_\perp$.

| $E_\perp$ (a.u.) | $g_\parallel$ | $g_\perp$ |
|------------------|---------------|------------|
| [0, 0, 0]        | 1.838         | 0.478      |
| [0, 0, -0.01]    | 1.839         | 0.478      |
| [0, 0, -0.1]     | 1.844         | 0.491      |
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See Supplemental Material at http://link.aps.org/supplemental/ further details, including Secs. 1-9, Figs. S1–S22, Tables S1–S5, and Refs. [44–64].

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