

## Supporting Information

### 1 Simulated system

The tip-surface system is simulated as an Fe cluster interacting with a magnetic Fe overlayer on a W(001). The cluster is represented as a square based pyramid with variable number of atomic layers. The surface is represented with periodic boundary conditions applied in the surface plane. The atoms in the Fe monolayer are included explicitly in the calculations, whereas the effect of underlying W(001) surface is modeled effectively via the renormalization of the NCAA model parameters, as explained in Refs<sup>15,16</sup>. The simulated system is illustrated in Fig. 2. The Hamiltonian of the system includes four terms describing the cluster at the tip, the antiferromagnetic surface overlayer, the cluster-surface interaction and the interaction with the external magnetic field

$$H = H_t + H_s + H_{int} + H_z \quad (1)$$

The Hamiltonians for the cluster and the surface are

$$H_t = H_t^{NCAA} - K_t \sum_{i_t} (\vec{M}_i \cdot \vec{e}_z)^2, \quad (2)$$

$$H_s = H_s^{NCAA} - K_s \sum_{i_s} (\vec{M}_i \cdot \vec{e}_z)^2, \quad (3)$$

where the subscripts  $t$  and  $s$  refer to tip cluster and surface, and  $H^{NCAA}$  stands for NCAA part of the Hamiltonian. The  $K$  denotes easy axis parameters,  $i$  the atom index,  $\vec{M}_i$  magnetic moment of atom  $i$ , and  $\vec{e}_z$  the easy axis. The interaction of the cluster at the tip with the surface is included through the hopping between the lowest cluster atom and the underlying surface atom

$$H_{int} = \sum_{\alpha} V_{ts} \left( d_{t\alpha}^{\dagger} d_{s\alpha} + d_{s\alpha}^{\dagger} d_{t\alpha} \right). \quad (4)$$

Here,  $V_{ts}$  is the  $d$ -electron hopping parameter between the lowest cluster atom on the tip (t) and the underlying atom on the surface (s) and  $d_{t\alpha}^{\dagger}, d_{t\alpha}, d_{s\alpha}^{\dagger}, d_{s\alpha}$  are creation and annihilation operators for  $d$ -electrons with spin projection  $\alpha$ . Interaction with an external magnetic field applied perpendicular to the surface plane is included in the model as

$$H_z = -B^z \sum_{i,\alpha,\beta} d_{i\alpha}^{\dagger} \sigma_{\alpha\beta}^z d_{i\beta}, \quad (5)$$

where  $B^z$  is the magnetic field strength and the sum is over all atoms of the cluster at the tip and the surface monolayer.

### 2 Rate calculations

The rate of magnetic transitions in the tip was calculated using an extension of the harmonic transition state theory (HTST) for magnetic degrees of freedom<sup>22,23</sup>. First, the minimum energy paths (MEP) between the P and AP alignment of

the magnetization in the cluster at the tip and the underlying surface atom were found using the Geodesic Nudged Elastic Band (GNEB) method.<sup>21</sup> The maximum along the MEP gives an estimate for the activation energy,  $E_a$ , within the HTST approximation. However, in the present case, a magnetic cluster with uniaxial anisotropy, there is a zero-mode at the saddle point corresponding to rotation of the total magnetic moments of the system around the easy axis. Such a mode cannot be approximated with a harmonic approximation, so the HTST expression for the rate constant needs to be modified. In order to do so, it is necessary to start from the full transition state theory expression for the rate constant

$$k^{TST} = \frac{1}{C} \int_R e^{-\frac{E(\mathbf{x})}{k_B T}} \delta(f(\mathbf{x})) v_{\perp}(\mathbf{x}) \chi[v_{\perp}(\mathbf{x})] d\mathbf{x} \quad (6)$$

where  $R$  denotes the configuration space corresponding to the initial state of the system, including the dividing surface, and

$$C = \int_R e^{-\frac{E(\mathbf{x})}{k_B T}} d\mathbf{x}. \quad (7)$$

Here,  $\mathbf{x}$  represents all variables describing the system and  $f(\mathbf{x})$  is a transition state dividing surface which is chosen so as to represent the tightest bottleneck for transitions out of the initial state.  $v_{\perp}(\mathbf{x})$  is the component of the velocity normal to the dividing surface and  $\chi$  is the Heaviside function equal to unity if the starting velocity  $v_{\perp}$  points away from the initial state, but zero otherwise.

When zero modes are present, the dividing surface should be chosen in such a way that it contains those degrees of freedom. That is, the zero modes should lie within the dividing surface. The integration along the zero modes in 6 can then be performed to obtain the entropy associated with the zero modes. In particular, the integration gives the volume of the subspace corresponding to the zero-modes. The harmonic approximation can be applied to the remaining degrees of freedom analogous to what has been done previously for magnetic systems without zero modes.<sup>22,23,35</sup> This leads to the following extended HTST expression for the rate constant

$$k^{HTST} = \frac{(2\pi k_B T)^{\frac{nm-n_s}{2}} V_s}{2\pi V_m} \sqrt{\frac{\det H^m}{\det' H^s}} \sqrt{\prod_{j=2+n_s}^D \frac{a_j^2}{\epsilon_{s,j}}} \exp\left(-\frac{E_a}{k_B T}\right) \quad (8)$$

where the subscript  $m$  refers to the minimum and  $s$  refers to the saddle point,  $V$  is the volume,  $n$  is the number of zero-modes, and  $H$  is the Hessian in a subspace excluding the zero-mode subspace. The prime means that the negative eigenvalue is excluded in the determinant corresponding to the saddle point. The  $a_j$  are coefficients of the velocity,  $v_{\perp}$ , represented in normal mode coordinates, the  $\epsilon$  are eigenvalues of the Hessian,  $D$  is the number of degrees of freedom in the system and  $E_a$  is the activation energy. Note the temperature dependence in the pre-exponential factor that is introduced by the zero modes.

### 3 Computational details

The surface is simulated with periodic boundary conditions in the plane of the surface. A total of 50 magnetic atoms were included in the Fe overlayer. The

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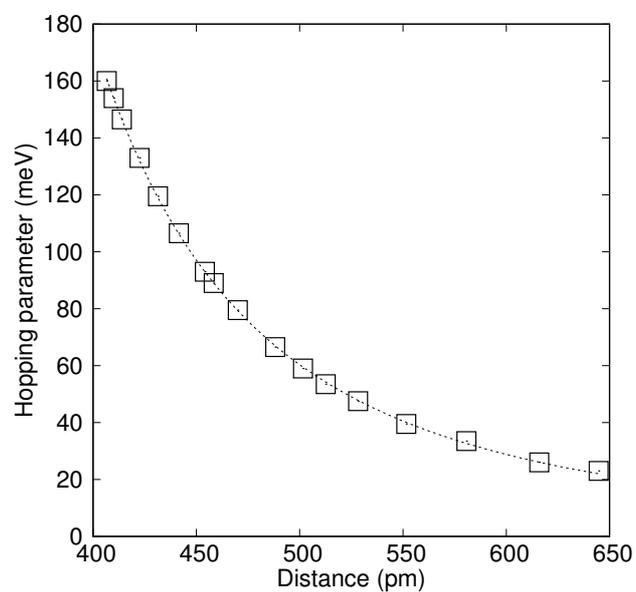
parameters of the NCAA model are  $E_0 = -11.8\Gamma$ ,  $U = 13.0\Gamma$ , where  $\Gamma$  is the width of the d-band. These values are 2.5% different from the values used to model  $\alpha$ -iron crystal<sup>18,19</sup>. The Fe atoms are commensurate with the underlying W(100) surface and, therefore, every Fe atom has four W atom nearest neighbors (see Fig.1). The closest Fe atoms are second nearest neighbors and hopping of electrons between the Fe atoms passes through the conductivity band. Therefore, not only is effective interaction between first-neighbor magnetic atoms included but also the second-neighbor interaction between magnetic atoms (as illustrated in Fig. 1). Due to the fact that there are twice as many paths to the first-neighbor magnetic atom as compared with the second-neighbor magnetic atom, the effective hopping parameter between the second-neighbors is less than the effective hopping parameter between first-neighbors by a factor of  $\sqrt{2}$ ,  $V_{\text{surf}}^{(2)} = V_{\text{surf}}^{(1)}/\sqrt{2}$ . The hopping to first-neighbor magnetic atom is taken to be  $V_{\text{surf}}^{(1)} = 0.45\Gamma$ . With these parameter values, the Fe atoms in the surface overlayer are antiferromagnetically ordered in the ground state, with  $d$ -electron number of 6.62 and magnetic moment per atom of  $2.81\mu_b$ , which is close to the results of DFT calculations,  $2.67\mu_b$ <sup>20</sup>.

For the square-based pyramidal cluster at the tip, the value of  $E_0$  and  $U$  were chosen to be the same as those for the surface. For  $V_{\text{tip}} = 0.6\Gamma$  ferromagnetic state is found to be a ground state where the number of  $d$ -electrons per Fe atom is 6.61 and the magnitude of the magnetic moment of the apex atom of a 14 atom cluster is  $M_t = 2.91\mu_b$ , which is similar to the results of DFT calculations ( $M_t = 2.85\mu_b$  from Ref.<sup>11</sup>).

The value of the parameter  $\Gamma$ , which is determined by the s-d hybridization, needs to be specified in order to obtain an absolute value of the lifetime. Typically,  $\Gamma$  lies in the range from 0.1 to 1.0 eV<sup>13,15,19</sup> and in our calculation, we used  $\Gamma = 0.5$  eV. The value of the anisotropy parameter,  $K_s = 6.24 \times 10^{-4}\Gamma$ , for the surface gives 2.4 meV/atom magneto-crystalline anisotropy energy in agreement with the value from Ref<sup>20</sup>. The value of the anisotropy parameter,  $K_t = 2.6 \times 10^{-4}\Gamma$ , for the Fe cluster at the tip gives anisotropy of about 1.0 meV/atom, the same value as was used in Ref.<sup>10</sup>.

The magnetic exchange energy can be calculated within the NCAA model as the energy difference between P and A states. The value is a strong function of the hopping parameter  $V_{ts}$  which in turn depends on the tip-surface distance,  $d$ . The curve shown in Fig. 2 for  $E_{ex}(d)$  is obtained from the experimental measurement<sup>10</sup> after assigning the absolute value of the distance by comparison with DFT calculations.<sup>12</sup> This curve is used to parametrize the hopping parameter which describes the interaction between cluster and surface as a function of the distance,  $V_{ts}(d)$ . The fit is shown in Fig. 7.

In the experiment, it is not possible to determine the sign of exchange energy between the cluster at the tip and the underlying surface atom. DFT calculations within the generalized gradient approximation have indicated that the A ordering is lower in energy.<sup>12</sup> The NCAA model, however, shows P having lower energy. We tested to see whether the inclusion of hopping between the lowest cluster atom and second neighbor surface atoms could change the sign of the exchange energy, but the P orientation was still favored. There are well documented examples where DFT/GGA calculations do not predict correctly the preference between ferromagnetic and antiferromagnetic states, the Mn<sub>2</sub> dimer being one such



**Fig. 1** Distance dependence of the hopping parameter  $V_{ts}(d)$  describing the interaction between cluster and surface. The parametrization was carried out to fit the exchange energy reported by Schmidt *et al.*<sup>10</sup> as a function of distance, shown in Fig. 3.

case.<sup>36</sup> It is, therefore, not of particular concern that the results of the NCAA calculations are not in agreement with the DFT/GGA calculations in this respect.