Suplemental material: Microscopic theory of spin-relaxation of a single Fe adatom coupled to substrate vibrations

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DETAILS OF DFT CALCULATIONS

We have used relativistic density functional theory (DFT) calculations to compute the electronic and vibrational structures of the Fe/MgO/Ag(100) system and calculate the electron-phonon matrix elements. The vibrational frequencies and the potential induced by the atomic displacements were calculated using the so-called direct method, employing symmetries to reduce computational costs, as explained in Ref. [S1]. The calculations were done using the non-colinear off-site formalism for the spin-orbit coupling implemented in SIESTA [S2, S3]. The unit cell consisted of a $4\times4\times1$ super cell of a MgO/Ag(100) slab, with an iron adatom adsorbed on top of an oxygen site. The MgO/Ag(100) slab is modeled by 11 Ag layers and an overlayer of 2 to 4 monolayers of MgO in both terminations. We optimized the geometry of the system keeping fixed the positions of the inner 5 layers of silver. The generalized gradient approximation parametrized by Perdew, Burke, and Ernzerhof [S4] (PBE-GGA) has been used for the exchange-correlation functional. Core electrons are represented using separable [S5] norm-conserving Pseudo-Potentials (PPs) and valence electrons are expanded using optimized basis sets for silver and oxygen, a triple-zeta plus 2 polarization orbitals for magnesium and a triple-zeta plus 3 polarization orbitals for iron. The Γ-point was used for integration of the Brillouin zone, and real space integrals were computed using a mesh cutoff of 600 Ry. together with the Grid.CellSampling parameter to mitigate the egg-box effect on atomic forces and properly determine the soft modes of the adatom. A Fermi-Dirac distribution function for an electronic temperature of 300 K was used to compute the occupations.

STEVENS OPERATORS

The Stevens operators used on this work are the following:

$$\hat{O}_2^0(\mathbf{L}) = 3L_z^2 - X, \tag{S1}$$

$$\hat{O}_4^0(\mathbf{L}) = 35L_z^4 - (30X - 25)L_z^2 + 3X^2 - 6X \tag{S2}$$

and

$$\hat{O}_4^4(\mathbf{L}) = \frac{1}{2}(L_+^4 + L_-^4). \tag{S3}$$

Where $X = L(L+1)$.

For a extended table of Stevens operators visit https://easyspin.org/easyspin/documentation/stevensoperators.html.

BASIS STATES IN SECOND QUANTIZATION

To obtain the second quantization expression of the basis states $|M_\mathrm{S}, M_\mathrm{L}\rangle$ of the ^5D term ($S = 2$ and $L = 2$), we have started from the trivial maximum $M_L = 2$ and $M_S = 2$ state given by

$$|2,2\rangle = c_{2\downarrow}^\dagger c_{-2\uparrow}^\dagger c_{-1\uparrow}^\dagger c_{0\uparrow}^\dagger c_{1\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle, \tag{S4}$$

where subindices denote orbital angular momentum z-projection and spin, respectively, and $|0\rangle$ denotes the state with no d electrons. The order for the operators chosen along the work is placing spin majority operators on the right, with highest orbital angular momentum z-projection on the right.

The remaining states can be obtained by applying S_- and L_- operators. All the states are listed below:

$$
\begin{aligned}
&|M_L, M_S\rangle \\
&|\;\;2,\;\;\;2\rangle = c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
&|\;\;2,\;\;\;1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;2,\;\;\;0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow}\right. \\
&\qquad\qquad \left. + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;2,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;2,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \\
&|\;\;1,\;\;\;2\rangle = c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
&|\;\;1,\;\;\;1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;1,\;\;\;0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}\right. \\
&\qquad\qquad \left. + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;1,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;1,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{1\uparrow}|0\rangle \\
&|\;\;0,\;\;\;2\rangle = c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
&|\;\;0,\;\;\;1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;0,\;\;\;0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}\right. \\
&\qquad\qquad \left. + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;0,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|\;\;0,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}|0\rangle \\
&|-1,\;\;\;2\rangle = c^\dagger_{-1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
&|-1,\;\;\;1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|-1,\;\;\;0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}\right. \\
&\qquad\qquad \left. + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|-1,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle \\
&|-1,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}|0\rangle \\
&|-2,\;\;\;2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}|0\rangle \\
&|-2,\;\;\;1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-2\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle
\end{aligned}
\tag{S5}
$$

$$|-2,\quad 0\rangle = \frac{1}{\sqrt{6}}\left(c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}\right.$$
$$\left. + c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle$$
$$|-2,-1\rangle = \frac{1}{\sqrt{4}}\left(c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle$$
$$|-2,-2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}|0\rangle$$

MASTER EQUATION AND FERMI'S GOLDEN RULE

The Hamiltonian describing the Fe adatom deposited on MgO/Ag(100) coupled to a phonon bath is

$$H = \sum_i E_i C_i^\dagger C_i + \sum_\eta \omega_\eta b_\eta^\dagger b_\eta + \sum_{i,f,\eta} G_{if}^\eta\, C_f^\dagger C_i\,(b_\eta^\dagger + b_\eta), \tag{S6}$$

where E_i are the energies of the states obtained from the Stevens Hamiltonian presented on the main text (Eq. (4)), ω_η are the phonon frequencies obtained from DFT calculations and G_{if}^η are the electron-phonon matrix elements between the adatom multiplet states. $c^\dagger$ ($b^\dagger$) and c (b) are the electron (phonon) creation and annihilation operators, respectively. The first term, H_A, descirbes the electronic structure of the adatom and the second one, H_B, the phonon bath. The last term, V, represents the interaction between the adatom electronic states and the phonon bath.

Using the density matrix formalism, the time evolution of the whole system is given by the Liouville-von-Neumann equation in the interaction picture

$$\frac{d\rho(t)}{dt} = -i\,[V,\rho(t)]\,. \tag{S7}$$

However, as the system of interest is the adatom itself, and not the phonon bath, the problem can be simplified making use of the theory of open quantum systems [S6]. The state of the adatom system (S) can then be obtained from a partial trace over the phonon bath degrees of freedom (B), introducing the so called reduced density matrix:

$$\rho_A(t) = \mathrm{Tr}_B\rho(t). \tag{S8}$$

In pump probe experiments preformed to measure spin-flip lifetimes, an excited state of the adatom is populated by a pump pulse, and then the evolution towards the ground states is measured with probe pulses. In the density matrix formalism, the evolution of the occupations of the electronic states of the adatom, is given by the diagonal elements of the reduced density matrix, ρ from now on. Expanding the Liouville-von-Neumann equation and after several approximations, known as the Born-Markov approximations, we obtain the master equation for the diagonal elements of the density matrix of the adatom:

$$\begin{aligned}\frac{d\rho_{ii}(t)}{dt} =& +2\pi\sum_{j,\eta}|G_{ij}^\eta|^2\rho_{jj}(t)\,[n_{BE}^\eta\delta(E_j-E_i+\omega_\eta)+(n_{BE}^\eta+1)\delta(E_j-E_i-\omega_\eta)]\\ &-2\pi\sum_{j,\eta}|G_{ij}^\eta|^2\rho_{ii}(t)\,[n_{BE}^\eta\delta(E_i-E_j+\omega_\eta)+(n_{BE}^\eta+1)\delta(E_i-E_j-\omega_\eta)]\,.\end{aligned} \tag{S9}$$

Here n_{BE}^η represents the thermal occupation of a phonon ω_η given by the Bose–Einstein distribution function.

At low temperatures it is a safe assumption to consider only the initial excited state $\Psi_i = \Psi_1$ and final ground state $\Psi_f = \Psi_0$, with $E_i - E_f = \Delta E > 0$:

$$\begin{pmatrix} d\rho_{11}/dt \\ d\rho_{00}/dt\end{pmatrix} = \begin{pmatrix} -(\Gamma_0+\Gamma_T) & +\Gamma_T \\ +(\Gamma_0+\Gamma_T) & -\Gamma_T\end{pmatrix}\cdot\begin{pmatrix}\rho_{11}\\ \rho_{00}\end{pmatrix}, \tag{S10}$$

where we have defined the temperature independent rate

$$\Gamma_0 = 2\pi\sum_\eta |G_{1,0}^\eta|^2\delta(\Delta E-\omega_\eta), \tag{S11}$$

and the temperature dependent rate

$$\Gamma_T = 2\pi \sum_\eta |G^\eta_{1,0}|^2 n^\eta_{BE} \delta(\Delta E - \omega_\eta). \tag{S12}$$

This set of coupled differential equations has a simple solution in the basis of eigenvectors that diagonalizes the matrix above:

$$\begin{pmatrix} \rho_{11}(t) \\ \rho_{00}(t) \end{pmatrix} = C_1 \begin{pmatrix} \Gamma_T/(\Gamma_0 + \Gamma_T) \\ 1 \end{pmatrix} + C_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(\Gamma_0 + 2\Gamma_T)t}. \tag{S13}$$

Where C_1 and C_2 are constants to be determined by the initial conditions of the system. If the adatom is prepared tp be in the excited state Ψ_1, then $\rho_{11}(0) = 1$ and $\rho_{00}(0) = 0$, thus the evolution of the density matrix is given by

$$\rho_{11}(t) = \frac{\Gamma_T}{\Gamma_0 + 2\Gamma_T} + \frac{\Gamma_0 + \Gamma_T}{\Gamma_0 + 2\Gamma_T} e^{-(\Gamma_0 + 2\Gamma_T)t}, \tag{S14}$$

and

$$\rho_{00}(t) = \frac{\Gamma_0 + \Gamma_T}{\Gamma_0 + 2\Gamma_T} - \frac{\Gamma_0 + \Gamma_T}{\Gamma_0 + 2\Gamma_T} e^{-(\Gamma_0 + 2\Gamma_T)t}. \tag{S15}$$

Thus, the Fermi's Golden Rule rate equation presented on the main text (Eq. (6)) can be inferred from these equations:

$$\Gamma_{1\to 0} = \Gamma_0 + 2\Gamma_T = 2\pi \sum_\eta |G^\eta_{1,0}|^2 \left[2n_{BE}(\omega_\eta) + 1\right] \delta(E_1 - E_0 - \omega_\eta). \tag{S16}$$

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