Supplementary information: Magnetic-State Controlled Molecular Vibrational Dynamics at Buried Molecular-Metal Interfaces

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I. EXPERIMENTAL DATA

A. Comparison of the bias-dependent noise power at two different low temperatures

Decreasing temperature from 10 K to 0.3 K opens low bias gap of about 20 mV for RTN excitation and generally reduces amplitude of LFN anomalies without qualitative changes relative to the data obtained at 10 K as shown in Fig. S1.



FIG. S1. Experimental power spectral noise in P state ($S_{\rm P}$) measured on the 1.2 nm thick PTCDA sample at a) T = 0.3 K and b) T = 10 K.

B. Reproducibility of the low-frequency noise measurements

We have tested the reproducibility of the bias dependent noise through the multiple (up to four) bias sweeps (see Fig. S3). To understand qualitatively the effect, the noise power data has been analyzed through bias dependent Hooge factor plots. Our results point out towards generally reproducible effects with small deviations which should not affect the interpretation.



FIG. S2. Reproducibility of the bias dependent noise measurements analysed using Hooge factor. Measurements are done in the P state at T = 10 K for the OMTJs with 1.2 nm thick PTCDA.

C. Bias-dependent conductance in the P and AP states

Typical bias dependent conductance in two different magnetic states of our OMTJs with PTCDA barrier (Fig. S5).

II. THEORETICAL MODEL FOR REACTIONS DRIVEN BY INELASTIC EXCITATIONS BY SPIN-POLARIZED CURRENTS

We follow the theoretical framework of Refs.³⁻⁵.



FIG. S3. Comparison between bias dependence of conductance measured at 10 K for the OMTJs with 1.2 nm PTCDA in the P and AP states.

A. Hamiltonian

We consider the standard adsorbate resonance model Hamiltonian for a metal-molecule-metal tunnel junction:

$$H_{0} = \varepsilon_{0} |M\rangle \langle M| + \sum_{L} \varepsilon_{L} |L\rangle \langle L| + \sum_{R} \varepsilon_{R} |R\rangle \langle R|$$
$$+ \sum_{L} (V_{LM} |L\rangle \langle M| + h.c.)$$
$$+ \sum_{R} (V_{RM} |R\rangle \langle M| + h.c.)$$
$$+ \hbar \Omega (b^{\dagger}b + 1/2), \qquad (S1)$$

written in terms of the one-particle electron states $|M\rangle$, $|L\rangle$, $|R\rangle$ of molecule and left/right electrode, respectively, and their corresponding one-electron energies ε_0 , ε_L , and ε_R . V_{LM} (V_{RM}) describes the hopping integrals between the left L and right R electrodes and the molecular level, respectively. The vibrational energy quantum is $\hbar\Omega$.

We further consider that the vibrational mode that couples linearly to the central resonance

$$H' = \chi(b^{\dagger} + b)|M\rangle\langle M|, \qquad (S2)$$

where χ is the electron-vibration coupling matrix element and is b (b^{\dagger}) the corresponding vibration annihilation (creation) operator.

The system is therefore described by the following Hamiltonian

$$H = H_0 + H'. \tag{S3}$$

B. Vibrational excitation/deexcitation rates

With Fermi's Golden Rule (FGR) we can express the vibrational excitation rates $\Gamma^{\alpha\beta}_{\uparrow,\downarrow}$ in terms of electrons initially in a state in electrode $\alpha \in \{L, R\}$ and ending up in

a final state in electrode $\beta \in \{L,R\}$ as

$$\Gamma_{\uparrow}^{\alpha\beta} = \frac{2\pi}{\hbar} \sum_{\sigma} \sum_{i \in \alpha} \sum_{f \in \beta} |\langle f\sigma; 1 | H' | i\sigma; 0 \rangle|^2 \\ \times n_{\rm F}(\varepsilon_i - \mu_\alpha) [1 - n_{\rm F}(\varepsilon_f - \mu_\beta)]) \, \delta_{\varepsilon_i,\varepsilon_f + \hbar\Omega} \\ = \frac{2\pi}{\hbar} \chi^2 \iint d\varepsilon_i d\varepsilon_f \sum_{\sigma} \rho_{\sigma,\alpha}(\varepsilon_i) \rho_{\sigma,\beta}(\varepsilon_f) \\ \times n_{\rm F}(\varepsilon_i - \mu_\alpha) [1 - n_{\rm F}(\varepsilon_f - \mu_\beta)] \, \delta(\varepsilon_f + \hbar\Omega - \varepsilon_i) \\ = \frac{2\pi}{\hbar} \chi^2 \int d\varepsilon \sum_{\sigma} \rho_{\sigma,\alpha}(\varepsilon) \rho_{\sigma,\beta}(\varepsilon - \hbar\Omega) \\ \times n_{\rm F}(\varepsilon - \mu_\alpha) [1 - n_{\rm F}(\varepsilon - \hbar\Omega - \mu_\beta)]$$
(S4)

and

$$\Gamma_{\downarrow}^{\alpha\beta} = \frac{2\pi}{\hbar} \sum_{\sigma} \sum_{i \in \alpha} \sum_{f \in \beta} |\langle f\sigma; 0 | H' | i\sigma; 1 \rangle|^2 \\ \times n_{\rm F}(\varepsilon_i - \mu_\alpha) [1 - n_{\rm F}(\varepsilon_f - \mu_\beta)]) \,\delta_{\varepsilon_i, \varepsilon_f - \hbar\Omega} \\ = \frac{2\pi}{\hbar} \chi^2 \int d\varepsilon \sum_{\sigma} \rho_{\sigma, \alpha}(\varepsilon) \rho_{\sigma, \beta}(\varepsilon + \hbar\Omega) \\ \times n_{\rm F}(\varepsilon - \mu_\alpha) [1 - n_{\rm F}(\varepsilon + \hbar\Omega - \mu_\beta)], \tag{S5}$$

where we write the partial density of states $\rho_{\sigma,\alpha}$ from electrode α and spin channel σ as

$$\rho_{\sigma,\alpha}(\varepsilon) = \frac{1}{2\pi} \frac{\gamma_{\sigma,\alpha}}{(\varepsilon - \varepsilon_0)^2 + (\gamma_\sigma/2)^2}$$
(S6)

and the total density of states as $\gamma_{\sigma} = \gamma_{\sigma,L} + \gamma_{\sigma,R}$ in the wide-band approximation.

C. Zero-temperature limit

In the low-temperature limit the Fermi-Dirac occupation function $n_{\rm F}(\varepsilon)$ becomes a step function and one has

$$\Gamma_{\uparrow}^{\alpha\beta} = \frac{2\pi}{\hbar} \chi^2 \int_{\mu_{\beta}+\hbar\Omega}^{\mu_{\alpha}} d\varepsilon \sum_{\sigma} \rho_{\sigma,\alpha}(\varepsilon) \rho_{\sigma,\beta}(\varepsilon - \hbar\Omega)$$
(S7)
$$= \sum_{\sigma} \mathcal{D}_{\alpha\beta}^{\sigma} [\mathcal{I}_{-}(\mu_{\alpha},\gamma_{\sigma}) - \mathcal{I}_{-}(\mu_{\beta} + \hbar\Omega,\gamma_{\sigma})] \times \theta(\mu_{\alpha} - \mu_{\beta} - \hbar\Omega)$$
(S8)

and

$$\Gamma_{\downarrow}^{\alpha\beta} = \frac{2\pi}{\hbar} \chi^2 \int_{\mu_{\beta}-\hbar\Omega}^{\mu_{\alpha}} d\varepsilon \sum_{\sigma} \rho_{\sigma,\alpha}(\varepsilon) \rho_{\sigma,\beta}(\varepsilon + \hbar\Omega)$$
(S9)
$$= \sum_{\sigma} \mathcal{D}_{\alpha\beta}^{\sigma} [\mathcal{I}_{+}(\mu_{\alpha},\gamma_{\sigma}) - \mathcal{I}_{+}(\mu_{\beta} - \hbar\Omega,\gamma_{\sigma})] \\\times \theta(\mu_{\alpha} - \mu_{\beta} + \hbar\Omega),$$
(S10)

where we have defined

$$\mathcal{D}^{\sigma}_{\alpha\beta} = \frac{\chi^2}{\pi\hbar} \frac{\gamma_{\sigma,\alpha}\gamma_{\sigma,\beta}}{\gamma_{\sigma}[\gamma^2_{\sigma} + (\hbar\Omega)^2]},$$
 (S11)

and

$$\mathcal{I}_{\pm}(\mu, \gamma_{\sigma}) = \arctan \frac{2(\mu - \varepsilon_0 \pm \hbar\Omega)}{\gamma_{\sigma}} + \arctan \frac{2(\mu - \varepsilon_0)}{\gamma_{\sigma}} \\ \pm \frac{\gamma}{2\hbar\Omega} \ln \frac{(\mu - \varepsilon_0 \pm \hbar\Omega)^2 + (\gamma_{\sigma}/2)^2}{(\mu - \varepsilon_0)^2 + (\gamma_{\sigma}/2)^2}.$$
 (S12)

D. Total excitation and relaxation rates

The total vibrational excitation and deexcitation rates, Γ_{\uparrow} and Γ_{\downarrow} , respectively, are obtained by summation over the two leads $\alpha \in \{L, R\}$ and $\beta \in \{L, R\}$:

$$\Gamma_{\uparrow}(\mu_L,\mu_R) = \Gamma_{\uparrow}^{LR} + \Gamma_{\uparrow}^{RL}, \qquad (S13)$$

$$\Gamma_{\downarrow}(\mu_L,\mu_R) = \Gamma_{\downarrow}^{LR} + \Gamma_{\downarrow}^{RL} + \Gamma_{\downarrow}^{LL} + \Gamma_{\downarrow}^{RR}.$$
 (S14)

E. Electrode spin polarization

Let us further define the spin-averaged density of states $\bar{\gamma}_{\alpha}$ of electrode α via

$$2\bar{\gamma}_{\alpha} = \gamma_{\uparrow,\alpha} + \gamma_{\downarrow,\alpha} \tag{S15}$$

and the electrode polarization \mathcal{P}_{α} as

$$\mathcal{P}_{\alpha} = \frac{\gamma_{\uparrow,\alpha} - \gamma_{\downarrow,\alpha}}{2\bar{\gamma}_{\alpha}}.$$
 (S16)

In this way $\mathcal{P}_{\alpha} = 0$ when $\gamma_{\uparrow,\alpha} = \gamma_{\downarrow,\alpha}, \mathcal{P}_{\alpha} \to 1$ when $\gamma_{\uparrow,\alpha} \gg \gamma_{\downarrow,\alpha}$, and $\mathcal{P}_{\alpha} \to -1$ when $\gamma_{\uparrow,\alpha} \ll \gamma_{\downarrow,\alpha}$.

Conversely, we can express the spin components in terms of γ_{α} and \mathcal{P}_{α} as

$$\gamma_{\uparrow,\alpha} = \bar{\gamma}_{\alpha} (1 + \mathcal{P}_{\alpha}), \tag{S17}$$

$$\gamma_{\downarrow,\alpha} = \bar{\gamma}_{\alpha} (1 - \mathcal{P}_{\alpha}). \tag{S18}$$

F. Switching rate

The switching rate R out of a given atomic configuration is given by the product of the quasi-stationary population P_{n-1} for the vibrational level n-1 and the excitation rate out of this state $(n\Gamma_{\uparrow})$, that is³

$$R = n\Gamma_{\uparrow} \left(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}}\right)^{n-1}.$$
 (S19)

It is evident that the switching rate scales as $R \propto \chi^2$.

G. Elastic electron current

Inelastic corrections to the tunnel current are typically small and we can thus here approximate the total current by computing just the noninteracting component. At zero temperature the (elastic) electronic current through the single level is given by

$$I = \frac{e}{h} \sum_{\sigma} \int_{\mu_L}^{\mu_R} T_{\sigma}(E) dE$$
(S20)
$$e \sum_{\sigma} \gamma_{\sigma} L \gamma_{\sigma} R$$

$$= \frac{c}{h} \sum_{\sigma} 2 \frac{\gamma_{\sigma,L} \gamma_{\sigma,R}}{\gamma_{\sigma}}$$
(S21)

$$\times \left(\arctan \frac{2(\mu_L - \varepsilon_0)}{\gamma_{\sigma}} - \arctan \frac{2(\mu_R - \varepsilon_0)}{\gamma_{\sigma}} \right).$$

The tunneling magneto resistance (TMR) is defined as

$$TMR(V) = \frac{|I_{\rm P} - I_{\rm AP}|}{\min(|I_{\rm P}|, |I_{\rm AP}|)}.$$
 (S22)



FIG. S4. Modelling of magnetic state dependent LFN for electrode spin polarization $\mathcal{P} = 0.50$: a) Model for the biasdependent polarization (dotted line) and TMR (solid line) with the parameters defined in Sec. SIII. b) Switching rate in P (dotted red line) and AP (full blue line) and without spin polarization (full grey line). c) Power noise spectrum in P state. d) Power noise spectrum difference between P and AP states in absolute value.

H. Noise power

Following Machlup⁶ the noise power of a twoparameter random signal ($\tau_1 = 1/R_1$ and $\tau_2 = 1/R_2$) is given by

$$S(\omega) = \frac{1}{\pi} \frac{\tau_1 \tau_2}{(\tau_1 + \tau_2)^2} \frac{1/\tau_1 + 1/\tau_2}{\omega^2 + (1/\tau_1 + 1/\tau_2)^2}$$
(S23)

$$= \frac{1}{\pi} \frac{R_1 R_2}{(R_1 + R_2)^3 + (R_1 + R_2)\omega^2}.$$
 (S24)

Assuming $\tau_1 = \tau_2 = 1/R$ this reduces to

$$S(\omega) = \frac{1}{\pi} \frac{R}{8R^2 + 2\omega^2},$$
 (S25)

as well as in frequency notation $(f = \omega/2\pi)$ to

$$S(f) = \frac{2\pi R}{(4\pi R)^2 + f^2}.$$
 (S26)

I. Numerical results

The numerical results shown in Fig. 4 (main text) and Fig. S4 were obtained with the following model parameters: $\varepsilon_0 = 10\gamma_L = 10\gamma_R = 1$ eV, n = 20 and $\chi = 1$ meV. The molecular vibrations were described by a set of modes characterized by energies being multiples of

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FIG. S5. Ratio of the reaction yields Y_P and Y_{AP} for the parallel and antiparallel electrode configurations of a symmetrically coupled single-level junction and varying electrode polarizations: (a) $\mathcal{P} = 0.3$, (b,c) $\mathcal{P} = 0.5$. The differently colored curves correspond to different level positions (with respect to the Fermi energy $\varepsilon_F = 0$) spanning both on-resonant and off-resonant tunneling conditions: $\varepsilon_0 = 0$ (red), $\varepsilon_0 = \Omega$ (blue), $\varepsilon_0 = 5\Omega$ (green), $\varepsilon_0 = 10\Omega$ (dark green), $\varepsilon_0 = 1000\Omega$ (gray). The variation with the other model parameters (bias voltage V and reaction order n) is very weak as seen by comparing panels (b) and (c). Most importantly, the ratio is larger than one. This shows that the probability for a tunneling electron to induce the reaction is significantly *enhanced* in the parallel (AP) configuration.

 $\hbar\Omega = 20$ meV. The electrode polarization was described phenomenologically as $\mathcal{P}_L = \pm \mathcal{P}_R = \mathcal{P}_0 - 0.5 \mathrm{V}^{-1} |V|$, with $\mathcal{P}_0 = 0.32$ in Fig. 4 (main text) and $\mathcal{P}_0 = 0.50$ in Fig. S4.

To understand the origin of increased vibrational heating in the P state compared to AP, we show in Fig. S5 an analysis of the ratio of the reaction yields $Y_{\rm P}$ and $Y_{\rm AP}$ as a function of all essential model parameters. The results clearly illustrate that $Y_{\rm P} \geq Y_{\rm AP}$, i.e., that the probability for an electron exciting a vibrational mode during the tunneling process is larger in the P (than AP) configuration. The origin of this effect can be understood in terms of the available phase space (initial and final states) for the inelastic tunneling process which is larger in P than in AP. This is analogous to the TMR effect where the elastic transmission of electrons is also larger in P than AP.

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- ¹ Li K.-S.; Chang Y.-M.; Agilan S.; Hong J.-Y.; Tai J.-C.; Chiang W.-C.; Fukutani K.; Dowben P. A.; Lin M.-T. Organic Spin Valves with Inelastic Tunneling Characteristics, *Phys. Rev. B*, **2011**, *83*, 172404.
- ² Hong J.-Y.; Ou Yang K.-H.; Wang B.-Y.; Li K.-S.; Shiu H.-W.; Chen C.-H.; Chan Y.-L.; Wei D.-H.; Chang F.-H.; Lin H.-J.; Chiang W.-C.; Lin M.-T. Interfacial Spectroscopic Characterization of Organic/Ferromagnet Hetero-junction of 3,4,9,10-perylene-teracarboxylic dianhydride-based Organic Spin Valves, *Appl. Phys. Lett.* **2014**, *104*, 083301
- ³ Shiwu G.; Persson M.; Lundqvist B. I. Theory of Atom Transfer with a Scanning Tunneling Microscope, *Phys. Rev.*

B, 1997, 55, 4825-4836.

- ⁴ Frederiksen T.; Paulsson M.; Ueba H. Theory of Action Spectroscopy for Single-molecule Reactions induced by Vibrational Excitations with STM, *Phys. Rev. B*, **2014**, *89*, 035427.
- ⁵ Brumme T.; Gutierrez R.; Cuniberti G. Vibrational Heating in Single-molecule Switches: an Energy-dependent Density-of-states approach, J. Phys.: Condens. Matter, 2012, 24, 394003.
- ⁶ Machlup S. Noise in Semiconductors: Spectrum of a Two-Parameter Random Signal, *Journal of Applied Physics*, **1954**, 25, 341-343.