Electronically Mediated Magnetic Anisotropy in Vibrating Magnetic Molecules

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ABSTRACT: We address the electronically induced anisotropy field acting on a spin moment in a vibrating magnetic molecule located in the junction between ferromagnetic metals. Under weak coupling between the electrons and molecular vibrations, the nature of the anisotropy can be changed from favoring a high spin (easy-axis) magnetic moment to a low spin (easy plane) by applying a temperature difference or a voltage bias across the junction. For unequal spin polarizations in ferromagnetic metals, it is shown that the character of the anisotropy is essentially determined by the properties of the weaker ferromagnet. By increasing the temperature in this metal or introducing a voltage bias, its influence can be suppressed such that the dominant contribution to the anisotropy is interchanged to the stronger ferromagnet. With increasing coupling strength between the molecular vibrations and the electrons, the nature of the anisotropy is locked into favoring easy-plane magnetism.

INTRODUCTION

Magnetic interactions and anisotropies are fundamentally important for magnetic ordering and magnetic properties of both materials, and molecular complexes. Recent demonstrations of stabilized ordered magnetic configurations in clusters of magnetic adatoms deposited on metallic surface, low-frequency switching between degenerate ground states, and magnetic remanence of single atoms open for atomic and molecular scale magnetism. Reports of electrical control of the amplitude of the magnetic anisotropy show versatile functionality. Moreover, the sign of the anisotropy is fundamentally important for whether the spin assumes a high (easy-axis) or a low (easy-plane) spin ground state. The general mechanisms that control the sign of the anisotropy remain, nonetheless, an open question.

Crucial for the demonstrations, for example, in refs is that the effective anisotropy field acting on the local magnetic moments is sufficiently strong to suppress rapid fluctuations between degenerate and nearly degenerate magnetic configurations. However, experiments of this kind are often performed at low temperatures because the energy scale of the pertinent magnetic anisotropies is on the order of submillielectronvolt and, thus, are not effective at high temperatures.

Another aspect of low-temperature measurements is that ionic displacements and vibrations can be subdued, thus quenching undesired configurational fluctuations which may transfer angular momentum into the spin degrees of freedom. It is well-known, however, that molecular vibrations may have a severe influence on the electronic and magnetic properties of molecular structures. The resulting modifications of the internal properties are then conveyed over to, for example, the transport properties, which has been shown both experimentally and theoretically.

Thus far, issues related to ionic displacements and vibrations have been studied separately from questions concerning magnetically relevant quantities in molecular structures. At a phenomenological level, however, there have been several studies in which effective coupling rates between vibrational and spin degrees of freedom have been employed to account for thermal fluctuations through molecular vibrations (see, e.g., refs ). On the other hand, the coupling rates have been inserted by hand in an ad hoc fashion and do not relate to the real microscopic nature of the system. In this article, we consider the magnetic anisotropy acting on a local magnetic moment, embedded in a molecular environment, which is induced by the molecular electronic structure. In order to go beyond the simple electronic picture of the anisotropy, we include a weak coupling between electrons and molecular vibrations. We make contact with a possible experimental setup by considering the molecular compound to be inserted in the junction between ferromagnetic metallic electrodes, as studied, for example, in ref . It is important to notice that the anisotropy crucially depends not only on the molecular electronic and magnetic structure near the chemical potential in the setup but also on the occupied electronic density. The interplay between these components and of the spin polarizations in the ferromagnets determines the sign of the anisotropy. We, furthermore, find that the electronically induced magnetic anisotropy strongly, in addition to the spin polarizations of the leads, depends on the temperature.
difference and voltage bias across the junction. In particular, the sign of the anisotropy field can be deliberately switched, in junctions with different spin polarizations in the two ferromagnets, by increasing the temperature in the ferromagnet with weaker spin polarization. Furthermore, when inferring nonequilibrium conditions by applying a voltage bias across the junction, the polarity of the voltage determines the sign of the anisotropy. Of major importance is that our results remain robust under the presence of molecular vibrations weakly coupled to the electrons. This may not be expected because the molecular vibrations tend to broaden the distribution of the electronic density. However, because the contribution associated with the electronic density at the chemical potential can be tuned by external gating, it is feasible to vary both the sign and the amplitude by external forces. For sufficiently strong electron–vibron coupling, the sign of the anisotropy is locked into favoring easy-plane ground state only.

Here, we build on the previous predictions made in refs 38,40 for dimers of magnetic molecules in which the effective spin–interaction amplitudes are mediated by the properties of the delocalized electrons, especially addressing the magnetic self-interactions or magnetic anisotropy acting on the localized spin moment. Our setup pertains to, for instance, M-phthalocyanine (MPC), M-porphyrins, where M denotes a transition-metal atom,11,41 for example, Cr, Mn, Fe, Co, Ni, and Cu, and also bis(phthalocyaninato)R (TPC),42,43 where R denotes a rare earth element, for example, Tb. Such molecules can be investigated in, for example, mechanically controlled break junctions,44 carbon nanotube assemblies,44 and scanning tunneling microscopy.11,42 Vibrational modes ranging from 0.1 to 100 meV have been observed for various types of magnetic molecular compounds.21,26

**RESULTS AND DISCUSSION**

**Model.** We consider the electronically mediated magnetic anisotropy in a single magnetic molecule embedded in the junction between ferromagnetic or normal metallic leads (see Figure 1 for a sketch of the setup). The molecule comprises a ligand structure, which provides the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) close to the Fermi level of the system as a whole, which is connected to the leads via tunneling. Henceforth, we shall refer to the HOMO/LUMO levels as the localized level. Located in the molecular structure is a spin moment which interacts via local exchange (Kondo coupling) with the localized level. Molecular vibrations are, moreover, coupled to the localized level. All in all, the structure is modeled using the Hamiltonian

\[ \mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_T + \mathcal{H}_{mol} \]  

(1)

Here, the energies of the metallic leads are given by \( \mathcal{H}_L = \sum_{\nu \in \mathcal{E}_L} \epsilon_{\nu L} c_{\nu L}^\dagger c_{\nu L} \) and \( \mathcal{H}_R = \sum_{\nu \in \mathcal{E}_R} \epsilon_{\nu R} c_{\nu R}^\dagger c_{\nu R} \), where \( \mathcal{E}_L \) is the set of states with the left (L) and right (R) leads, in which electrons are created ( annihilated) by the operator \( c_{\nu L}^\dagger(c_{\nu L}) \) at the energy \( \epsilon_{\nu L} \) with momentum \( \mathbf{k} \) and spin \( \sigma \). For convenience, we denote electrons in the left (right) lead with the momentum \( \mathbf{k} = \mathbf{p} \) (\( \mathbf{k} = \mathbf{q} \)). Tunneling between the leads and the localized level is described in terms of \( \mathcal{H}_T = \sum_{\nu \in \mathcal{E}_L} \mathcal{T}_{\nu L} c_{\nu L}^\dagger c_{\nu R} + \text{H.c.} \), where \( \mathcal{T}_{\nu L} \) defines the spin-dependent tunneling rate, whereas \( \mathcal{H}_{mol} \) denotes the electron annihilation in the localized level. The molecular complex is, finally, described through the Hamiltonian

\[ \mathcal{H}_{mol} = \sum_{\nu} (\tilde{\epsilon}_{\nu} + U n_{\nu}/2) n_{\nu} - \mathbf{S} \cdot \mathbf{S} + \omega_0 b^\dagger b \]  

(2)

where \( \tilde{\epsilon}_{\nu} \) denotes the spin-independent energy of the localized level, \( U \) is the local Coulomb repulsion, and \( n_{\nu} = d_{\nu}^\dagger d_{\nu} \). The electron spin \( \mathbf{s} = \sum_{\nu \sigma} d_{\nu \sigma}^\dagger d_{\nu \sigma} / 2 \) in the localized level interacts with the local spin with rate \( \lambda \), where \( \sigma \) is the vector of Pauli matrices. The local vibrational mode is described by the bosonic operators \( b^\dagger \) and \( b \) and energy \( \omega_0 \) and is coupled to electrons in the localized level with rate \( \lambda \).

The coupling between the electronic and vibrational degrees of freedom is considered to be weak such that the local electronic structure is only weakly modified by the vibrations. Although this assumption limits the applicability of our conclusions, it nevertheless provides qualitative information about some expected influences from the vibrations on the local magnetic moment. For stronger couplings and more general conclusions, one would have to employ self-consistent methods or coupled spin and lattice dynamics. However, under the assumption of weak coupling, we can employ the Lang–Firsov transformation, which leads to a diagonal formulation of \( \mathcal{H}_{mol} \) with respect to the effective fermionic and bosonic degrees of freedom.

The Lang–Firsov transformation is performed through the canonical transformation \( \mathcal{H} = \mathcal{e}^S \mathcal{H} \mathcal{e}^{-S} \), with the generating functional \( \mathcal{S} = -(\lambda/\omega_0)(b - b^\dagger) \sum_{\nu \sigma} n_{\nu \sigma} \). The transformation leads to the localized energy levels that are shifted into \( \tilde{\epsilon}_{\nu} = \tilde{\epsilon}_{\nu} - \lambda^2/\omega_0 \), where the renormalized charging energy \( U = U - 2\lambda^2/\omega_0 \). The Hamiltonian for the molecular structure is, accordingly, reduced to

\[ \mathcal{H}_{mol} = \sum_{\nu} (\tilde{\epsilon}_{\nu} + U n_{\nu}/2) n_{\nu} - \mathbf{S} \cdot \mathbf{S} + \omega_0 b^\dagger b \]  

(3)

The tunneling rates in \( \mathcal{H}_T \) are changed into \( \mathcal{T}_{\nu} X \), where \( X = \exp\{\lambda(\mathbf{S} \cdot \mathbf{S})/2\} \). However, considering only weakly coupled electrons and vibrations, the factor \( X \approx 1 \) such

Figure 1. Sketch of the vibrating magnetic molecule mounted in the junction between ferromagnetic leads with different temperatures. Electrons in the molecules, subject to the Coulomb repulsion \( U \), are coupled to the vibrations with rate \( \lambda \), the localized spin moment with rate \( \gamma \), and the electrodes with tunneling rates \( t_L, t_R \). The applied voltage \( V \) across the junction shifts the (electro)chemical potentials \( \mu_L, \mu_R \) of the leads from the equilibrium chemical potential \( \mu \).

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that we can replace the tunneling rates by $t_{\text{eff}}$. Hence, the remaining three contributions in the Hamiltonian are considered to be unaffected by the transformation. We also assume that the renormalization is considered to be instantaneous equilibrating,\textsuperscript{51–53} which is justified because we are merely interested in how the magnetic anisotropy modifies with the presence of vibrations. The back action of both the spin and the electrons on the vibrational degrees of freedom is a topic which is beyond the present study.

Green Function Approach. We calculate physical quantities, such as the electronically induced magnetic anisotropy acting on the local spin moment and the density of electron states of the localized level, in terms of the single-electron Green function $G(t,t') = \{(-i)\langle T_d^\dagger(t)d(t') \rangle \}_\text{ee}$, which is a $2 \times 2$-matrix in the spin $1/2$ space. For later purposes, we note that the Green function can be decomposed into its charge and magnetic components $G_0$ and $G_\mu$, respectively, according to $G = G_0\sigma^0 + G_\mu\sigma$, where $\sigma^0$ is the identity matrix. Hence, the nonequilibrium density of electron states and the corresponding spin polarization are obtained from

$$\rho(\omega) = \frac{i}{2\pi} \text{tr} (G^\dagger(\omega) - G(\omega)) = \frac{i}{\pi} (G^0(\omega) - G_0^\dagger(\omega)) \quad (4a)$$

$$\rho_s(\omega) = \frac{i}{2\pi} \text{tr} \sigma (G^\dagger(\omega) - G(\omega)) = \frac{i}{\pi} (G^0_s(\omega) - G_0^\dagger_s(\omega)) \quad (4b)$$

respectively.

Given that the leads are aligned in either parallel or antiparallel to one another, we can introduce a global spin-quantization axis, say, $z$, along which all magnetic properties are given. It is, thus, justified to assume that $G_z = G_z\vec{z}$ such that we can define $G_0(\omega) = \sum_{\sigma}G_{0\sigma}(\omega)p_\sigma/2$, where $G_\sigma$ is the spin-projected Green function. Finally, we notice that because we are interested in nonequilibrium properties, we calculate all quantities in terms of the lesser and greater propagators $G^\langle/\rangle$. For simplicity, however, and because we view the leads as source and drain reservoirs for electrons, the lesser/greater Green functions will be calculated using the relation $G^\langle/\rangle = G^\dagger \sum_{\sigma}G_{\sigma}^\langle/\rangle G_{\sigma}/G_{\sigma}^\dagger$, where $G_\sigma^\langle/\rangle$ is the retarded/advanced forms of the Green function, whereas $\sum_{\sigma}^\langle/\rangle$ is the lesser/greater self-energy. Here, we shall merely include the couplings $G^\langle/\rangle$ to the reservoirs in this self-energy such that we can write $\sum_{\sigma}^\langle/\rangle(\omega) = (\pm i)\sum_{\sigma} f_\sigma(\pm\omega)\Gamma^\langle/\rangle$, where $f_\sigma(\omega) = f(\omega - \mu_\sigma)$ is the Fermi distribution function for the electrons in the lead $\chi$ with (electro)chemical potential $\mu_{\chi}$. The spin-resolved coupling parameters $\Gamma^\langle/\rangle = 2\pi \sum_{\sigma} f_\sigma(\pm\omega)\delta(\omega - \varepsilon_{\chi})$ are parameterized such that $\Gamma^\langle\rangle = \Gamma(1 + \sigma_z\eta_{\chi})/4$, $-1 \leq \eta_{\chi} \leq 1$, where $\Gamma = \sum_{\chi} \Gamma_{\chi}$, $\Gamma^\langle = \sum_{\chi} \Gamma^\langle_{\chi}$, and $\Gamma^\rangle = \sum_{\chi} \Gamma^\rangle_{\chi}$.

From the Lang–Firsov transformation, it also follows that the single electron Green function

$$G_{\sigma\rho}(t,t') = \langle -i \langle T_d^\dagger(t)d(t') \rangle \rangle = \tilde{G}_{\sigma\rho}(t,t')\langle X(t)X(t') \rangle \quad (5)$$

where the propagators $\tilde{G}_{\sigma\rho}(t,t') = \langle -i \langle T_d^\dagger(t)d(t') \rangle \rangle$ and $\langle X(t)X(t') \rangle$ are defined in the model Hamiltonian $\hat{H}$ such that $\tilde{d}(t) = \exp\{i\hat{H}_{\text{electron}}t\}d_\sigma$, $\tilde{d}(t) = \exp\{i\hat{H}_{\text{electron}}t\}d^\dagger_\sigma$, and $X(t) = \exp\{i\hat{H}_{\text{vibration}}t\}X \exp\{-i\hat{H}_{\text{vibration}}t\}$. The renormalization factor caused by the coupling between the electrons and the vibrations is calculated through $\langle X(t)X'(t') \rangle = \exp\{-\Phi(t,t')\}$, where\textsuperscript{54} $t = t' - \tau$

$$\Phi(t) = \left(\frac{\lambda}{\omega_0}\right)^2 (n_\text{B}[1 - e^{-\omega_0t}] + (1 + n_\text{B}[1 - e^{-\omega_0t}]) \quad (6)$$

Here, $n_\text{B} = \exp\{\beta\omega_0\} - 1^{-1}$ is the Bose–Einstein distribution with the inverse temperature $\beta = 1/k_B T$ in terms of the Boltzmann constant $k_B$. Furthermore, we calculate the electronic propagator $\tilde{G}$ in the mean-field approximation, where the retarded components are given by $\tilde{G}_\sigma' = \delta_{\sigma\rho}\tilde{G}_{\rho\sigma}'$ with

$$\tilde{G}_\sigma'(\omega) = \omega - \epsilon_0 - (1 - \langle n_\sigma \rangle)\tilde{U} - \langle n_\sigma \rangle\tilde{U}\tilde{\Gamma}_\sigma'/2 \quad (7)$$

and $\langle n_\sigma \rangle = \langle -i \int \tilde{G}_\sigma'(\omega) d\omega \rangle/2\pi$. This construction of the Green function requires a self-consistent treatment, except for effectively noninteracting conditions, $\tilde{U} = 0$. Here, we restrict our investigation to this limit, in which the expression in eq 7 simplifies to

$$\tilde{G}_\sigma'(\omega) = \frac{1}{\omega - \epsilon_0 + i\tilde{\varphi}_\sigma'/2} \quad (8)$$

It is a straightforward calculation to obtain

$$G_{\sigma \rho}(\omega) = e^{-\lambda/(2\omega_0^2)} \sum_n I_n(z) e^{-\lambda n(\omega - \omega_0)} \quad (9)$$

where $I_n(z)$ is the $n$th modified Bessel function and $z = 2(\lambda/\omega_0)^2\sqrt{n(n + 1)}$.

We infer the limitations of the present approximations\textsuperscript{39} on $\lambda$, $\omega_0$, and $\Gamma$, given by $\lambda/\omega_0 < 1 < (\Gamma/2\omega_0) \exp(-\lambda/\omega_0^2)$, $\omega_0 < \epsilon_0 - \lambda^2/\omega_0$, and $2\lambda^2/\omega_0 < \Gamma$. In order to fulfill these restrictions, we require that $\lambda/\Gamma \leq 1/6$ and $1/5 < \omega_0/\Gamma < 6/5$.

We comment that the only source of spin imbalance in the localized level is generated by the spin-dependent coupling parameters $\Gamma_\sigma^\langle$ to the left and right leads. While it is possible to imagine an induced Zeeman split from the ferromagnetic leads, by assuming that the tunnel junction is formed by, for example, a quantum point contact between the leads, we can omit stray and fringing fields that otherwise may generate this splitting.

Anisotropy Parameter. The influence of the electronic motion on the localized spin moment has been considered previously in studies of, for example, the spin and transport dynamics in single magnetic molecules\textsuperscript{35,56} and the interplay between magnetic interactions, configurations, and transport in dimers of magnetic molecules\textsuperscript{38–40} as well as in general materials structures.\textsuperscript{38} Following the prescription formulated in these publications, we here write the electronically induced magnetic anisotropy acting on the localized spin moment according to\textsuperscript{38} $I_{zz} = \nu^2 \int_{\omega_0}^{\infty} \langle \delta_{\text{zz}}(t)\delta_{\text{zz}}(t') \rangle \exp\{i\omega(t - t')\} d\omega'$. However, for the general interacting model in the present setup, this propagator cannot be decoupled to the form given in ref 38 but has to be treated with an additional care. Nevertheless, because we restrict ourselves to effective noninteracting conditions, $\tilde{U} = 0$, the expression

$$I_{zz} = \nu^2 \int_{\omega_0}^{\infty} \frac{G_{\sigma \rho}^\langle(\omega)G_{\sigma \rho}^\gamma(\omega') - G_{\sigma \rho}^\gamma(\omega)G_{\sigma \rho}^\langle(\omega')}{\omega - \omega'} \frac{d\omega}{d\omega'} \frac{2\pi}{2\pi} \quad (10)$$
remains valid. While the anisotropy is generally formulated as a second-rank tensor, it is here reduced to the zz-component only because all magnetic properties are aligned with the global ζ-direction. In the framework of an effective model for the localized spin, where the surrounding environment is parameterized into local interactions and anisotropies, we write the spin Hamiltonian as

$$\mathcal{H}_s = D S_z^2 + E (S_z^2 - S_x^2)$$  \hspace{1cm} (11)$$

where $D$ and $E$ are the uniaxial and transverse anisotropy parameters, respectively. In the present setup, where the spin direction is given along $\zeta$, the transverse anisotropy $E = 0$, whereas the uniaxial anisotropy $D \equiv I_\zeta$. Within the scheme presented above, we can derive a simplified expression for the anisotropy parameter $D$ in terms of the retarded Green function for the localized level and the coupling parameters to the leads. After some straightforward algebra, we obtain

$$D = -D_0^r + D_0^T$$  \hspace{1cm} (13)$$

where we have introduced the components

$$D_0^r = \frac{\nu}{2} \sum_x \sum_{\sigma \sigma'} \sigma_x^{\sigma \sigma'} \Gamma_0^{\sigma \sigma'} \sum_{f \in L/R} \left. G_{\sigma}^{f}(\omega) \right|^{2}$$  \hspace{1cm} (14a)$$

and

$$D_0^T = \frac{\nu}{2} \sum_x \sum_{\sigma \sigma'} \sigma_x^{\sigma \sigma'} \Gamma_0^{\sigma \sigma'} \sum_{f \in L/R} \left. G_{\sigma}^{f}(\omega) \right|^{2}$$  \hspace{1cm} (14b)$$

From this expression, it can be understood that the anisotropy crucially depends on the spin imbalance $\ln\left(G_{\uparrow}^{f}(\omega) - G_{\downarrow}^{f}(\omega)\right)$ in the molecular electronic structure. The specific details of the electronic structure near the chemical potentials $\mu_\sigma$ of the leads are provided through the contribution $D_0^r$ because it involves the derivative $-\partial G_{\sigma}^{f}(\omega)/\partial \mu$. The strength as well as the sign of the anisotropy energy is determined by the interplay between the contributions $D_0^r$ and $D_0^T$, manifest through their opposite signs. The former component is large whenever there is a simultaneous large local electron density and large local spin imbalance at the chemical potentials $\mu_\sigma$. This follows from the presence of the derivatives of the Fermi function, which pick out the value of the spin-resolved density of electron states, $-\text{Im} G_{\sigma}^{f}$ at these energies. The amplitude of the latter component $(D_0^T)$ depends, in addition to the magnitude of the spin imbalance, on the electronic occupation. Trivially, this component vanishes identically when the electronic density is completely empty, that is, in the limit $\mu_\sigma \rightarrow -\infty$, for all $x$. In the opposite limit, however, there may be a finite value caused by, for example, distinct occupation numbers of the molecular spin states. The amplitude of the contribution $D_0^T$ is, nevertheless, maximal when the localized level is resonant with the chemical potentials. Henceforth, we shall refer to $D_0^T$ as Fermi surface effect and $D_0^r$ as the volume or Fermi sea effect—in correspondence to a terminology often employed in condensed matter physics. We thereby allude to their intrinsic dependences on the electronic structure at the chemical potentials and on the occupied electron density.

Concerning the realistic values of the parameters pertaining to the molecular compounds for this modeling, the local (Kondo) exchange coupling may vary in the range $\nu \approx 0.5$–20 meV,\textsuperscript{27,28} molecular vibrations $\omega_0 \approx 0.1$–100 meV,\textsuperscript{21,26} the on-site Coulomb repulsion is often not known but can be, to a good approximation, often taken as small, or negligible, for the s- and p-orbitals that constitute the localized level. Therefore, we consider the case with vanishing bare Coulomb repulsion in the absence of coupling between the vibrations and the electrons and vanishing effective Coulomb repulsion whenever this coupling is finite.

**Zero Voltage Bias.** The anisotropy has a nontrivial dependence on the spin polarization both in the leads and locally in the molecular structure as well as on the external conditions which may, or may not, plunge the system into nonequilibrium. However, in a simple setup with a spin-degenerate localized level, where the only spin dependence is provided from the spin-dependent coupling parameters $\Gamma_0^{\sigma \sigma'}$, the anisotropy is expected to be positive and large near resonance $(\epsilon_0 - \mu_\sigma \approx 0)$ while it is negative and small away from resonance. This behavior is verified in Figure 2a, where we plot $D_0$ as function of the localized level $\epsilon_0$ with respect to the equilibrium chemical potential $\mu = 0$ ($\mu_\sigma = \mu$). In the simulations, we assumed $p_L = 0.6$ and $p_R \in \{0.6, 0.3, 0, -0.3\}$, $T_{L/R} = 3$ K. The behavior of the anisotropy, varying between negative and positive, opens for the possibility to switch the localized spin moment between high and low spin configurations, where a positive (negative) anisotropy leads to a low (high) spin ground state.

Upon increasing the temperature in the right lead, the influence of the thermal broadening becomes asymmetric, which has a dramatic influence on the resulting anisotropy. In Figure 2b,c, we plot the corresponding $D_0$ for two finite temperature differences (5 and 10 K, respectively) at different spin polarizations $p_R$. The most notable feature is that the sign of $D_0$ changes in all setups with asymmetric spin polarizations ($p_L \neq p_R$) when the temperature difference increases.

We analyze this property by resolving the Fermi surface and Fermi sea effects into left and right components according to $D_0^{\text{LS}L} = D_0^{\text{LS}L} + D_0^{\text{LS}R}$, which is a natural partitioning given the summation over the left and right electrodes in eq 14. In Figure 3a, the total anisotropy $D_0$ (black) is plotted along with its components (see the figure for details), for spin polarizations $p_L = 2p_R = 0.6$ and vanishing temperature difference between the
leads. It is clear from the plots that the left and right contributions are strongly asymmetric and that the right components dominate the total anisotropy, in this case. Here, \( D_{0R} > 0 \) and \( D_{0R}^T < 0 \) near resonance, and because the amplitude of the former is the larger one, the result is \( D_0 > 0 \). This condition remains true under an increase of the temperature \( T_L \) (see Figure 3b) because the increased thermal broadening of the components \( D_{0R}^2 > 0 \) and \( D_{0L}^2 < 0 \) induced from the left lead tends to equalize the sizes of their amplitudes such that \( D_{0L}^2 + D_{0R}^2 \approx 0 \). However, by increasing the temperature \( T_R \) on the other hand, likewise, the increased thermal broadening tends to equalize the amplitudes of \( D_{0R}^2 > 0 \) and \( D_{0R}^2 < 0 \) instead such that the overall effect from the right lead vanishes (see Figure 3c). Hence, the properties induced from the left lead begin to dominate, and in the setup depicted in Figure 3, the negative amplitude \( D_{0L}^T \) is larger than the positive amplitude of \( D_{0L}^2 \), which leads to an overall negative anisotropy.

Furthermore, consider the simplified expression of the surface component to the anisotropy in eq 14a at \( \lambda = 0 \), \( U = 0 \), and let the temperature \( T_X \rightarrow 0 \) such that the energy derivative of the Fermi function can be replaced by the Dirac delta function \( \delta(\omega - \mu_X) \). Then, the value of the integrand is picked out at the chemical potential \( \mu_R \) which enables an analysis of the voltage-dependent sign of the anisotropy at \( \mu_X \). In fact, it is straightforward to show that this contribution is positive whenever the spin polarization \( p_X \) satisfies the condition

\[
|p_X| > 4 \frac{|p_L| + p_R|}{4 + (p_L + p_R)^2}
\]

Using this relation gives a tool to design and engineer the structure in terms of the ferromagnetic leads such that the nature or sign of the anisotropy can be predicted.

The conclusion regarding the anisotropy at zero voltage bias is, hence, that its sign can be switched under the application of a thermal difference across the molecular junction provided that the spin polarizations in the leads are unequal. This feature is strongly enhanced the stronger the asymmetry of the spin polarizations of the leads is along with a large temperature difference between the leads. The properties of the anisotropy are dominated by the properties of the lead with the lowest temperature. If both temperatures are equal or nearly equal, the lead with the weaker spin polarization has the strongest influence. In the asymmetric setup, the stronger spin polarization tends to generate a negative anisotropy near resonance, whereas the weaker generates a positive. Because the latter typically has the larger amplitude, the overall anisotropy becomes positive. By increasing the temperature in the lead with weaker (stronger) spin polarization, the effect of the lead with the stronger (weaker) becomes increasingly important.

A compelling issue regarding the sign changes of the anisotropy is whether these features remain under the influence of molecular vibrations. In particular, one concern might be that the sign change at resonance is suppressed by the broadening of the electron density caused when vibrational fluctuations modify the electronic structure. However, by investigating the anisotropy in the presence of the molecular vibrations (\( \lambda > 0 \)), we find that most of the features that were obtained in the absence of the vibrations are quite robust in the sense that these are retained also when the coupling to the vibrations is finite. In Figure 4, we plot the anisotropy for the spin polarizations and temperature differences used in Figure 2. The most noticeable difference compared to the case without molecular vibrations is the general decrease in amplitude near resonance. Associated with this decrease is also a slight broadening of the anisotropy around resonance. We attribute these features to the emergence of several resonances in the electronic density caused by the coupling between the electrons and the vibrations, which is visualized in Figure 5. In this figure, we have plotted the spin-resolved densities of electron states for varying coupling \( \lambda \) and temperature difference across the junction. In particular, the emergence of vibrational side resonances with increasing \( \lambda \), and the temperature difference is clearly seen in the spin channel corresponding to smaller couplings to the leads. The energy shift of the resonant conditions, both in the anisotropy and the densities of electron states, seen for finite \( \lambda \) is due to the energy renormalization \( \tilde{E}_0 = \tilde{\epsilon}_0 - \lambda / \omega_0 \) invoked by the Lang–Firsov transformation.

These observations for the anisotropy at zero voltage bias and finite temperature difference solidify our previous conclusion in that the possibility to switch the anisotropy between negative and positive values near resonance remains
couplings the left. Other parameters are as in Figure 4.

In the left, are as in Figure 2. (c) $T_R = 3 K$, $T_L = 13 K$, and (d) $T_R = 23 K$, at constant temperature $T_L = 3 K$ in the left, $\epsilon_0 = 0.8 mV$, $\lambda = \Gamma/8$, and $U = 2\lambda^2/\epsilon_0$. Other parameters are as in Figure 2.

Figure 4. Anisotropy as a function of the localized energy level $\epsilon_0$ for different spin polarizations $p_R = 0.6, 0.3, 0, -0.3$ at constant $p_L = 0.6$ and different temperatures in the right lead: (a) $T_R = 3 K$, (b) $T_R = 8 K$, (c) $T_R = 13$, and (d) $T_R = 23 K$, at constant temperature $T_L = 3 K$ in the left, $\epsilon_0 = 0.8 mV$, $\lambda = \Gamma/8$, and $U = 2\lambda^2/\epsilon_0$. Other parameters are as in Figure 2.

$T e$ the case of equal spin polarizations in the leads. We discuss this tendency to lock the sign of the anisotropy, which is striking in also important to notice that the coupling to vibrations has a increased broadening around resonance makes it less susceptible to fluctuations in the molecular environment. It is also important to notice that the coupling to vibrations has a tendency to lock the sign of the anisotropy, which is striking in the case of equal spin polarizations in the leads. We discuss this effect in more detail below.

Finite Voltage Bias. At zero bias, the amplitude and sign of the anisotropy field results from a nontrivial interplay between the Fermi surface and volume effects, on the one hand, and the relation between the spin polarizations in the two leads, on the other. Under finite temperature differences, the latter led to a ceased net contribution to the anisotropy from the lead with higher temperatures. Under finite bias voltages, the situation is slightly analogous, in the sense that the anisotropy is dominated by the properties, for example, spin polarization and temperature, of the lead that is resonant with the molecular level, whereas the portion emerging from the other lead is negligible.

The result of this behavior is that the anisotropy can become positive for one voltage bias polarity and negative for the opposite, which may particularly occur under asymmetric spin polarizations in the leads. This prediction is manifest in Figure 6, where the anisotropy is shown as a function of the molecular level position for different couplings $\lambda$ and voltage biases (see the figure caption for details).

Low voltage biases only slightly alter the shape and nature of the anisotropy from its zero voltage bias characteristics (see Figure 6a), which would be expected from a linear response consideration. At higher voltage biases, however, the individual properties of the ferromagnetic leads become legible (see Figure 6b,c) in the signatures of the anisotropy. This behavior underscores that it is the electronic density and spin polarization, as well as their corresponding occupations, near the chemical potential that determine the nature of the anisotropy. In the situations displayed in Figure 6, the left lead has the stronger spin polarization, $|p_L| > |p_R|$, and following the results from zero voltage bias, one would expect that the influence from this lead is negative and weaker than the one from the right. A positive voltage bias shifts the left (right) chemical potential $\mu_L (\mu_R)$ to a higher (lower) energy by $eV/2 > 0$ ($-eV/2 < 0$), which leads to different resonant conditions between the molecular level $\epsilon_0$ and the left and right chemical potentials. As $\epsilon_0$ approaches $\mu_L (\mu_R)$, only the spin polarization in the left (right) lead matters to the resulting anisotropy, which, in the present case, becomes negative (positive). The same, but opposite, characteristics are obtained for negative polarity of the voltage bias, which can be seen in Figure 6d, which shows the anisotropy as a function of the molecular level energy and voltage bias. Finally, increasing the strength of the coupling $\lambda$ tends to lock the sign of the anisotropy to favor the
low spin ground state, analogous to the situation at zero voltage bias. The vibrationally induced broadening of the density of electron states as well as lowering its amplitude decreases the electron occupation, which quenches the volume contribution and opens for the surface contribution to become dominant. Hence, the net anisotropy assumes a positive sign for a wide range of voltage biases.

### CONCLUSIONS

We have studied the electronically induced magnetic anisotropy acting on a localized moment embedded in a molecular structure and placed in the junction between ferromagnetic leads. The spin polarization of the leads allows for a uniaxial structure and placed in the junction between ferromagnetic leads. The spin polarization of the leads allows for a uniaxial structure and placed in the junction between ferromagnetic leads. By the influence of a temperature difference across the junction, the anisotropy can, however, change its sign provided that it is the temperature of the lead with lower spin polarization that is increased. Under finite voltage bias and unequal spin polarizations in the leads, we notice that the lead with the weaker spin polarization tends to have the stronger influence on the resulting sign of the anisotropy. The influence of a temperature difference across the junction, the anisotropy can, however, change its sign provided that it is the temperature of the lead with lower spin polarization that is increased. Under finite voltage bias and unequal spin polarizations in the leads, we notice that the lead with the weaker spin polarization tends to have the stronger influence on the resulting sign of the anisotropy. The influence of a temperature difference across the junction, the anisotropy can, however, change its sign provided that it is the temperature of the lead with lower spin polarization that is increased. Under finite voltage bias and unequal spin polarizations in the leads, we notice that the lead with the weaker spin polarization tends to have the stronger influence on the resulting sign of the anisotropy.

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