

## Tunnel magnetoresistance of magnetic molecules with spin-vibron coupling

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The effect of molecular vibrations on the tunnel magnetoresistance (TMR) of a magnetic tunnel junction with a single spin-anisotropic molecule interconnecting its electrodes is investigated theoretically. We demonstrate that if these vibrations couple at the same time to the charge of tunneling electrons and to the spin of the molecule, the spin anisotropy of such a molecule becomes enhanced. This has, in turn, a profound impact on the TMR of such a device showing that molecular vibrations lead to a significant change of spin-polarized transport, differing for the parallel and antiparallel magnetic configuration of the junction. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4974285>]

### I. INTRODUCTION

The driving force behind the growing interest in nano-electronic devices based on single molecules is the prospect of harnessing their inherent functional properties,<sup>1</sup> e.g., mechanical, optical or magnetic ones. Here, especially large-spin molecules are attractive as suitable candidates for applications in information-storing and -processing devices.<sup>2</sup> In this context, magnetic anisotropy of such molecules is crucial to ensure their magnetic bistability—a key prerequisite for a system to be considered as a memory element. Consequently, much efforts have been devoted to control this by synthesis,<sup>2</sup> mechanical straining<sup>3</sup> or electrical gating.<sup>4</sup> Yet, another unique feature of many molecules is their ability to vibrate. Interestingly, these vibrations of a single molecule captured in a junction can couple to the charge of tunneling electrons which can result, e.g., in modification of spectroscopic signatures of a molecular device<sup>5,6</sup> or even suppression of transport.<sup>7,8</sup> Although such effects have been experimentally addressed in various molecular systems,<sup>9–12</sup> only recently these have been investigated in spin-anisotropic molecules.<sup>13–16</sup>

In this Communication we address the problem of how vibrations of a magnetic molecule bridged between electrodes of a magnetic tunnel junction affect the tunnel magnetoresistance (TMR) of such a device. For this purpose, we consider a spin-anisotropic model molecule in which vibrations couple to the charge of tunneling electrons as well as to the spin of the molecule. We show that the interplay of these two types of couplings leads to renormalization of magnetic anisotropy of the molecule, and this effect can be clearly observed in transport spectroscopy. Importantly, such mechanism provides a new means of enhancing magnetic anisotropy of a molecule, which essentially corresponds to increasing an energy barrier for molecular spin reversal, and thus, to improving the performance of a molecule as a memory switch. We calculate spin-dependent transport for two magnetic configurations of the junction, that is, when the relative orientation of spin moments of electrodes is parallel and antiparallel, demonstrating that molecular vibrations lead to non-monotonic variations of the TMR.

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## II. THEORETICAL DESCRIPTION

### A. Model

The essential physical properties of a device consisting of a magnetic tunnel junction (MTJ) with a single *magnetic* molecule embedded in it are modeled by the Hamiltonian  $\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{mol}} + \hat{\mathcal{H}}_{\text{MTJ}}$ , with the first (second) term standing for the molecule (MTJ).

We consider here a generic molecule whose magnetic features at low temperatures are fully accountable for by the *giant-spin approach*,<sup>17</sup> within which the molecule in a specific charge state  $n$  is simply treated as an effective large spin  $\hat{S}_n$ . In the following we assume that the molecule is capable of accepting only a single extra electron, and thus, it can be either *neutral* ( $n = N$ ) or *charged* ( $n = N + 1$ ) —for notational brevity we set  $N = 0$ . In the static case, i.e., in the absence of vibrations, the molecule is described by  $\hat{\mathcal{H}}_{\text{mol}} \equiv \hat{\mathcal{H}}_{\text{mol}}^{\text{stat}} = \hat{\mathcal{H}}_{\text{mag}} + \hat{\mathcal{H}}_{\text{g}}$ , where the magnetic properties are captured by

$$\hat{\mathcal{H}}_{\text{mag}} = \sum_n \left\{ -D_n (\hat{S}_n^z)^2 + E_n [(\hat{S}_n^x)^2 - (\hat{S}_n^y)^2] \right\}. \quad (1)$$

The first and second terms of  $\hat{\mathcal{H}}_{\text{mag}}$  represent, respectively, the *uniaxial* and *transverse* component of magnetic anisotropy, with  $D_n$  and  $E_n$  denoting the corresponding relevant anisotropy constants. On the other hand,  $\hat{\mathcal{H}}_{\text{g}} = \varepsilon(V_{\text{g}})\hat{n}$  takes into account the effect of capacitive coupling of the molecule to a gate electrode. Note that for conceptual simplicity we include here only one conducting molecular orbital, with  $\hat{n}$  being its occupation operator. Consequently, the molecular magnetic eigenstates,  $|\chi_n\rangle = \sum_{S_n, M_n} C_{S_n, M_n}^{\chi_n} |S_n, M_n\rangle$ , are superpositions of angular momentum (spin) states  $|S_n, M_n\rangle$ , with  $\hat{S}_n^z |S_n, M_n\rangle = M_n |S_n, M_n\rangle$ , and  $C_{S_n, M_n}^{\chi_n}$  denoting the linear expansion coefficients.

The situation becomes more complex if the molecule can support vibrations, which might couple to the charge of tunneling electrons.<sup>5–8</sup> This so-called *charge-vibron* interaction can be incorporated into the present discussion using an Anderson-Holstein-like model,<sup>18</sup> which approximates vibrations by means of a harmonic oscillator,  $\hat{\mathcal{H}}_{\text{vib}} = \hbar\omega \hat{b}^\dagger \hat{b}$ . Oscillator states  $|q\rangle_{\text{v}}$  are characterized by the number of vibrons  $q$  (i.e., quanta of molecular vibrations) with the ground state  $|0\rangle_{\text{v}}$  denoting the absence of vibrations. This oscillator is coupled to a molecular charge state,  $\hat{\mathcal{H}}_{\text{ch-vib}} = \lambda \hbar\omega (\hat{b}^\dagger + \hat{b})\hat{n}$ . To keep the model simple, but still without losing its generic nature, we consider only a single vibrating mode of energy  $\hbar\omega$ , which is created (annihilated) by the operator  $\hat{b}^\dagger$  ( $\hat{b}$ ). The charge-vibron coupling is quantified by a dimensionless parameter  $\lambda$ . However, if the molecule is magnetic, one expects that also its spin can couple to vibrations, which is the main subject of this Communication. This *spin-vibron* coupling can be written as<sup>19,20</sup>

$$\hat{\mathcal{H}}_{\text{sp-vib}} = \sum_n \hbar\omega \left\{ \Lambda_n^{\text{u}} (\hat{S}_n^z)^2 + \Lambda_n^{\text{t}} [(\hat{S}_n^x)^2 - (\hat{S}_n^y)^2] \right\} (\hat{b}^\dagger + \hat{b}), \quad (2)$$

where  $\Lambda_n^{\text{u(t)}}$  is the dimensionless coupling strength of vibrations to the uniaxial (transverse) component of the molecular spin. As a result, the molecule is described by the total Hamiltonian  $\hat{\mathcal{H}}_{\text{mol}} = \hat{\mathcal{H}}_{\text{mol}}^{\text{stat}} + \hat{\mathcal{H}}_{\text{vib}} + \hat{\mathcal{H}}_{\text{ch-vib}} + \hat{\mathcal{H}}_{\text{sp-vib}}$ , and a new basis of molecular states  $\{|\chi_n\rangle \otimes |q\rangle_{\text{v}}\}$  has to be used, including both magnetic and vibronic degrees of freedom. Obviously,  $\hat{\mathcal{H}}_{\text{mol}}$  is not diagonal in this basis owing to the presence of the charge- ( $\hat{\mathcal{H}}_{\text{ch-vib}}$ ) and spin-vibron ( $\hat{\mathcal{H}}_{\text{sp-vib}}$ ) couplings. Whereas the former coupling can be eliminated by application of the Lang-Firsov transformation,<sup>21</sup> the latter one cannot be removed in general.<sup>22</sup> Nevertheless, an appropriate canonical transformation<sup>22</sup> can be found for a specific case of a molecule characterized by  $S_0 = 1/2$  and  $S_1 = 1$ , to which we limit our considerations henceforth. The contribution  $(\hat{\mathcal{H}}_{\text{mol}}^{\text{stat}})'$  to the canonically transformed molecular Hamiltonian,  $\hat{\mathcal{H}}'_{\text{mol}} = (\hat{\mathcal{H}}_{\text{mol}}^{\text{stat}})' + \hat{\mathcal{H}}_{\text{vib}}$ , has essentially the same form as  $\hat{\mathcal{H}}_{\text{mol}}^{\text{stat}}$ ; however, it incorporates new effective anisotropy constants  $D'_n$  and  $E'_n$ , see Eq. (1), which depend on  $\lambda$  and  $\Lambda_n^{\text{u(t)}}$  —for details see Ref. 22. The key achievement of this procedure is that  $\hat{\mathcal{H}}'_{\text{mol}}$  is diagonal in the basis  $\{\hat{\mathcal{H}}'_{\text{mol}}|\xi\rangle = \mathcal{E}_\xi|\xi\rangle; |\xi\rangle \equiv |\chi_n\rangle \otimes |q\rangle_{\text{v}}\}$ , which allows for tracking down easily the transitions between different molecular vibronic states due to charge transport, as we discuss below.

To complete the model necessary to study spin-polarized transport, such a molecule is next inserted into a MTJ. This junction is represented by the Hamiltonian  $\hat{\mathcal{H}}_{\text{MTJ}} = \hat{\mathcal{H}}_{\text{el}} + \hat{\mathcal{H}}_{\text{tun}}$  describing both the electrodes ( $\hat{\mathcal{H}}_{\text{el}}$ ) as well as electron tunneling process through the junction *via* the molecule

( $\hat{\mathcal{H}}_{\text{tun}}$ ). Essentially, the junction is formed by two metallic ferromagnetic electrodes, referred to as *source* ( $r = s$ ) and *drain* ( $r = d$ ), characterized by collinear—parallel (P) or antiparallel (AP)—relative orientations of their spin moments, which are also collinear with respect to the easy ( $z$ ) axis of the molecule. These serve as reservoirs of non-interacting, itinerant and spin-polarized electrons, and are described by  $\hat{\mathcal{H}}_{\text{el}} = \sum_{rk\sigma} \varepsilon_{k\sigma}^r \hat{a}_{k\sigma}^{r\dagger} \hat{a}_{k\sigma}^r$ . Here, the operator  $\hat{a}_{k\sigma}^{r\dagger}$  ( $\hat{a}_{k\sigma}^r$ ) creates (annihilates) an electron with orbital quantum number  $k$  and spin  $\sigma$  in the  $r$ th electrode. The magnetic properties of the  $r$ th electrode are fully parametrized by the total DOS,  $\rho_r = \rho_r^+ + \rho_r^-$ , with  $\rho_{+(-)}^r(\varepsilon) = \rho_{+(-)}^r$  denoting the density of states (DOS) of spin-majority (-minority) electrons in the flat-band limit, and by the *spin-polarization coefficient*,  $P_r = (\rho_r^+ - \rho_r^-)/(\rho_r^+ + \rho_r^-)$ .

The processes of electron tunneling are captured by<sup>23</sup>

$$\hat{\mathcal{H}}_{\text{tun}} = \sum_{rk\sigma} \sum_{\chi_1\chi_0} \mathbb{T}_r \mathcal{T}_{\chi_1\chi_0}^\sigma \hat{X}^\dagger |\chi_1\rangle \langle \chi_0| \hat{a}_{k\sigma}^r + \text{H.c.} \quad (3)$$

The parameter  $\mathbb{T}_r$  is used here to quantify the strength of electron tunneling between the  $r$ th electrode and the molecule,  $\hat{X}^\dagger = \exp[\lambda(\hat{b}^\dagger - \hat{b})]$ , and

$$\mathcal{T}_{\chi_1\chi_0}^\sigma = \sum_{M_0M_1} C_{S_1M_1}^{\chi_1^*} C_{S_0M_0}^{\chi_0} \langle S_0, M_0; \frac{1}{2}, \sigma | S_1, M_1 \rangle. \quad (4)$$

The third factor on the right-hand side stands for the Clebsch-Gordon coefficient for adding spins  $S_0$  and  $1/2$  to get  $S_1$  and imposes spin-selection rules on the charge transport *via* the molecule. Finally, one can write spin-dependent broadening of molecular levels due to tunneling of electrons as  $\Gamma_\pm^r = (\Gamma_r/2)(1 \pm P_r)$  with  $\Gamma_r = 2\pi\rho_r|\mathbb{T}_r|^2$ . Assuming that both electrodes are made of the same material ( $\rho_s = \rho_d$ ) and the molecule is symmetrically coupled to electrodes ( $\mathbb{T}_s = \mathbb{T}_d$ ), we obtain a single parameter  $\Gamma = \Gamma_s = \Gamma_d$  determining the strength of electron tunneling. If  $\Gamma \ll k_B T$ , with temperature  $T$ , a perturbative approach can be used to study charge transport through the system under consideration.

## B. Transport calculation

Here, we concentrate on the limit of weakly coupled molecules, where stationary transport in *first-order* ( $\propto \Gamma$ ) is of interest. We furthermore focus on the case of a collinear magnetic configuration of the MTJ, and assume that the energy separation of molecular states is sizable (i.e.,  $|\mathcal{E}_\xi - \mathcal{E}_{\xi'}| \gg \Gamma$ , for all  $|\xi\rangle \neq |\xi'\rangle$ ). It is then convenient to describe transport properties in terms of occupation probabilities  $\mathcal{P}_\xi$  of the molecular states  $|\xi\rangle$ ,<sup>22,24</sup> whose time-evolution is found from the master equation:

$$\frac{d\mathcal{P}_\xi}{dt} = 0 = \sum_{\xi'} \Sigma_{\xi\xi'} \mathcal{P}_{\xi'}. \quad (5)$$

The self-energies  $\Sigma_{\xi\xi'}$ , describing tunneling transitions between molecular states, can be derived by means of Fermi's golden rule or a standard diagrammatic technique.<sup>25</sup> The average tunneling current through the junction via a molecule is defined as  $I = (I_d - I_s)/2$ , and

$$I = -\frac{ie}{2\hbar} \text{Tr}[\Sigma^I \mathcal{P}]. \quad (6)$$

To keep compact notation, the occupation probabilities are written in vector form,  $\mathcal{P}$ , whereas the matrix  $\Sigma^I$  consists of the current self-energies which are evaluated diagrammatically,<sup>25</sup> similarly to the self-energies.

## III. DISCUSSION OF NUMERICAL RESULTS

We consider a model molecule with spin values  $S_0 = 1/2$  and  $S_1 = 1$ , so that the notion of magnetic anisotropy in the neutral charge state becomes obsolete, and we assume  $D_1 \equiv D = 0.1$  meV and  $E_1 \equiv E = 0.2D$ . Despite its simplicity, this model proves to be physically very insightful, as we show below. The molecule is characterized by the following spin states, see the inset in Fig. 1(a): the spin doublet  $|\chi_0^\pm\rangle = |1/2, \pm 1/2\rangle$  for the *neutral charge* state is degenerate, whereas the states  $|\chi_1^0\rangle = |1, 0\rangle$  and  $|\chi_1^\pm\rangle = (|1, 1\rangle \pm |1, -1\rangle)/\sqrt{2}$  for the *charged* state are split in energy due to magnetic anisotropy.

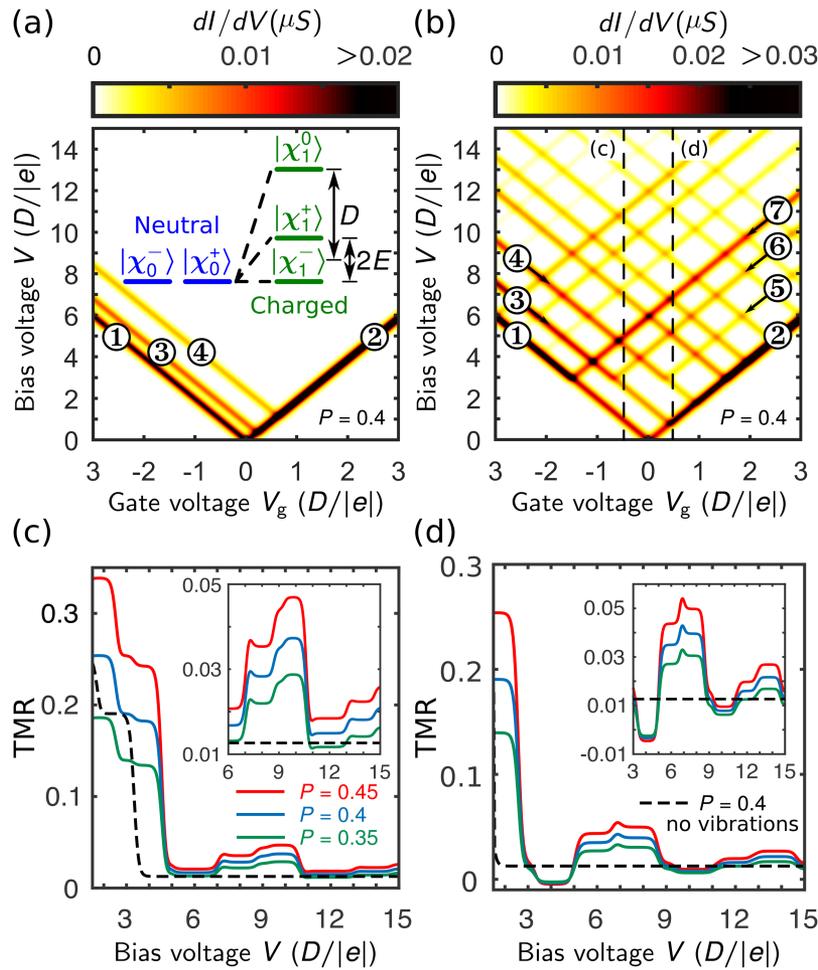


FIG. 1. *Top panel*: Differential conductance  $dI/dV$  shown as a function of gate  $V_g$  and bias  $V$  voltages for the system without (a) and with (b) molecular vibrations included in the *parallel* magnetic configuration of the MTJ for  $P_s = P_d \equiv P = 0.4$  [ $\hbar\omega/D = 3$ ,  $\lambda = 1.3$  and  $\Lambda_1^u = (4/3)\Lambda_1^l = 0.05$ ]. Inset in (a): Schematic of the energy spectrum of the model molecule at  $V_g = 0$ . *Bottom panel*: Tunnel magnetoresistance,  $TMR = (I_P - I_{AP})/I_{AP}$ , cross-sections for: (c)  $|e|V_g/D = -0.5$  and (d)  $|e|V_g/D = 0.5$ —see the dashed lines in (b). Other parameters:  $k_B T/D = 0.05$ , and  $\Gamma/D = 0.001$ .

## A. Transport through a static molecule

In the absence of molecular vibrations, spectroscopic features in transport through a molecule are determined by spin transitions allowed by the selection rules (4). One easily concludes that sequential tunneling of electrons should lead to all possible transitions between the two spin manifolds corresponding to different molecular charge states. Indeed, this can be observed as distinct resonances in Fig. 1(a): ① and ② result from the ground-to-ground-state transitions  $|\chi_0^\pm\rangle \rightarrow |\chi_1^\mp\rangle$  and  $|\chi_1^\mp\rangle \rightarrow |\chi_0^\pm\rangle$ , respectively, while ③ and ④ are associated with the ground-to-excited-state transitions  $|\chi_0^\pm\rangle \rightarrow |\chi_1^\pm\rangle$  and  $|\chi_0^\pm\rangle \rightarrow |\chi_1^0\rangle$ . Transitions between ground and excited states can only occur when the molecule becomes reduced, i.e., when it accepts an additional electron. They are absent for the reverse process (oxidation) since the neutral charge state involves only a degenerate spin doublet. Finally, the position of ③ and ④ with respect to ① allows for deducing the spin anisotropy parameters  $D$  and  $E$ , as indicated in Fig. 1(a).

## B. Effect of molecular vibrations

The situation gets more complex when a molecule can vibrate, as molecular vibrations usually result in strong spectroscopic signatures in transport,<sup>9–16</sup> see Fig. 1(b). Basically, in such a case the

spin spectrum shown in Fig. 1(a) is duplicated at energies  $q\hbar\omega$  (for  $q = 1, 2, 3, \dots$ ) corresponding to excited vibrational states  $|q\rangle_v$  of the molecule. Here, the spin-vibron coupling leads also to exchange of the relative position of states  $|\chi_1^\pm\rangle$ . Transitions between different vibrational states are governed by Franck-Condon factors,<sup>8</sup> which in combination with the spin selection rules (4) allow one to understand the mechanism behind the resonance pattern in Fig. 1(b).

To begin with, due to the presence of vibrationally excited spin states  $|\chi_0^\pm\rangle \otimes |q\rangle_v$ , more transitions upon oxidation of the molecule become visible, see resonances parallel to ② in Fig. 1(b). One particular feature worthy of note is that the first two of these resonances do not continue to ①, which indicates that they originate from excited-to-excited-state transitions. Specifically, resonance ⑤ arises owing to  $|\chi_1^0\rangle \otimes |0\rangle_v \rightarrow |\chi_0^\pm\rangle \otimes |1\rangle_v$ , whereas ⑥ is due to  $|\chi_1^\pm\rangle \otimes |0\rangle_v \rightarrow |\chi_0^\pm\rangle \otimes |1\rangle_v$  transitions. The next pronounced resonance ⑦ represents transitions between ground spin states of two neighboring vibrational states, i.e.,  $|\chi_1^\pm\rangle \otimes |q\rangle_v \rightarrow |\chi_0^\pm\rangle \otimes |q'\rangle_v$  for  $q' - q = 1$ , with dominating equilibrium contribution from  $q = 0$ , and hence, this resonance extends to ①. In general, the higher-voltage resonances occur as a result of spin-allowed transition between vibronic states with  $|\Delta q| > 1$ , and are characterized by lower intensities due to decreasing Franck-Condon factors.

Another crucial feature that can be spotted in Fig. 1(b) is the renormalization of the anisotropy constants, Eq. (1), which manifests as a shift of resonances ③ and ④ as compared to Fig. 1(a). These resonances move towards larger bias-voltage values, meaning that the molecule's spin anisotropy increases. A large spin anisotropy is desirable for a bistable system to be utilized as a memory element: in the presence of the uniaxial term of magnetic anisotropy only, it corresponds to an increasing energy barrier for molecular spin reversal.

### C. Tunnel magnetoresistance (TMR)

Molecular vibrations significantly affect the TMR of the considered spin-anisotropic device leading to a rich gate- and bias-dependence, as illustrated in Figs. 1(c)–(d).

First, transverse magnetic anisotropy [see the second term in Eq. (1)] leads to a mixing of molecular spin states, such that the picture of two independent spin-channels for describing transport through the molecule does not hold any longer. This is clearly visible from the fact that the asymptotic (high-voltage) value of the  $\text{TMR} = P^2/(1 - P^2)$ , characteristic to the sequential tunneling regime when all molecular states participate in transport,<sup>26</sup> is never reached, neither in the absence nor in the presence of molecular vibrations.

Furthermore, the effect of the vibrationally induced enhancement of the magnetic anisotropy can be observed. To visualize this, we compare the case of a static molecule (black dashed line) to a vibrating molecule at different electrode spin-polarization strengths in panel (c) of Fig. 1. As a result, large steps in the TMR at low bias voltage that can be associated with transitions between different molecular spin states within the vibronic ground state (③ and ④) are shifted towards larger bias voltages.

Finally, opening of new transport channels due to ground-to-excited-state transitions enabled by the presence of excited vibrational states, is distinctly reflected as new, more subtle, features in the TMR as a function of the bias voltage. Overall, the TMR is tendentially increased by molecular vibrations. However, interestingly, once transitions between different vibronic states come into play at a sufficiently large bias voltage, these lead to non-monotonic changes of the TMR. Here the behavior is strongly asymmetric with respect to the gate voltage: Only for  $V_g > 0$ , small regions occur, where the TMR can be reduced with respect to the static molecule or even almost completely canceled, see Fig. 1(d). In these regions, a major contribution to transport stems from transitions between the spin-degenerate neutral state,  $|\chi_0^\pm\rangle$ , and the zero-spin charged state,  $|\chi_1^0\rangle$ , which show high symmetry with respect to spin-dependent tunneling processes. This is followed by an increase of the TMR when also transitions between  $|\chi_1^\pm\rangle$  to the neutral (vibrationally excited) neutral state contribute. This sequence of features in the TMR reduction/increase is repeated (less pronouncedly) with every new vibronic excitation state entering the bias window. Consequently, it can be seen that molecular vibrations can be employed to improve the electrical tunability of the TMR of a molecular device.

#### IV. CONCLUSIONS

In this Communication, we demonstrated that, due to the presence of molecular vibrations and their interplay with the magnetic anisotropy of the molecule, the TMR of the device is more variegated and more susceptible to electrical tuning either by the application a bias or a gate voltage. This property, which manifests in the occurrence of subtle, non-monotonic changes in the TMR, can be explained by the impact of the charge- and spin-vibron coupling on the magnetic anisotropy, as well as by the contribution of excited-to-excited state transitions within the vibrational spectrum of the molecule.

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