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# Electron Transfer Assisted by Vibronic Coupling from Multiple Modes

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**Supporting Information** 

**ABSTRACT:** Understanding the effect of vibronic coupling on electron transfer (ET) rates is a challenge common to a wide range of applications, from electrochemical synthesis and catalysis to biochemical reactions and solar energy conversion. The Marcus–Jortner–Levich (MJL) theory offers a model of ET rates based on a simple analytic expression with a few adjustable parameters. However, the MJL equation in conjunction with density functional theory (DFT) has yet to be established as a predictive first-principles methodology. A framework is presented for calculating transfer rates modulated



by molecular vibrations, that circumvents the steep computational cost which has previously necessitated approximations such as condensing the vibrational manifold into a single empirical frequency. Our DFT-MJL approach provides robust and accurate predictions of ET rates spanning over 4 orders of magnitude in the  $10^6-10^{10}$  s<sup>-1</sup> range. We evaluate the full MJL equation with a Monte Carlo sampling of the entire active space of thermally accessible vibrational modes, while using no empirical parameters. The contribution to the rate of individual modes is illustrated, providing insight into the interplay between vibrational degrees of freedom and changes in electronic state. The reported findings are valuable for understanding ET rates modulated by multiple vibrational modes, relevant to a broad range of systems within the chemical sciences.

# INTRODUCTION

Electron transfer (ET) reactions are paramount in many fields of the chemical, physical, and biological sciences.<sup>1–8</sup> Controlling the movement of charges between weakly coupled donors (D) and acceptors (A) is pivotal for a host of applications, e.g. photocatalytic processes,<sup>9–11</sup> dye-sensitized solar cells,<sup>12,13</sup> and organic photovoltaics,<sup>14,15</sup> in photosystem II<sup>16–18</sup> and in other redox-driven catalytic processes.<sup>19–21</sup> The ability to describe the mechanisms and rates of charge transfer in the weakly coupled regime is thus essential for understanding a wide range of systems and mechanisms as well as for the design and characterization of molecular components for solar energy conversion and catalytic applications.

The semiclassical Marcus theory has become a standard tool for modeling ET processes.<sup>1,22</sup> The theory models the ET rates according to a simple equation

$$k_{\rm ET,Marcus} = \frac{2\pi |H_{\rm AD}|^2}{\hbar \sqrt{4\pi \lambda k_{\rm B} T}} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\rm B} T}\right)$$
(1)

by approximating the reactants and products as harmonic states at temperature *T*. Here,  $k_{\rm B}$  is the Boltzmann constant,  $H_{\rm AD}$  is the electronic coupling between donor and acceptor,  $\lambda$  is the reorganization energy, and  $\Delta G^0$  is the free energy change of the ET reaction.

Equation 1 shows that the maximum  $k_{\rm ET}$  is obtained when  $\lambda = -\Delta G^0$ , corresponding to an activationless transfer. The rate then decreases when  $\Delta G^0$  becomes more negative in the so-called Marcus *inverted region*, despite the reaction being more thermodynamically favorable. The resulting parabolic functional form of  $\log(k_{\rm ET})$  as a function of  $-\Delta G^0$  is schematically shown in Figure 1b. The inverted region was experimentally confirmed for a homologous series of donor-spacer-acceptor (D-Sp-A) dyads, with the same D and a rigid saturated hydrocarbon spacer (Sp) to ensure weak coupling and uniform D-A separation (10 Å) for all dyads, while changing A to have increasing thermodynamic driving potential  $(-\Delta G^0)$  for charge transfer, as represented in Figure 1.<sup>23,24</sup>

The Marcus equation, eq 1, has been extensively applied as a 3-parameter model for ET to fit experimental data.<sup>1,25-28</sup> The reorganization of the system due to ET is modeled in eq 1 by a single parameter that effectively accounts for both the outersphere (solvent) and inner-sphere (solute) reorganization

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Figure 1. (a) The donor(D)-spacer(Sp) structure is coupled to 9 different acceptors (A1-A9), forming dyads 1–9. (b) Schematic depiction of a symmetric parabolic curve of ET rates (log scale) as a function of  $-\Delta G^0$ , as predicted by Marcus theory, eq. 1. (c) Corresponding schematic representation of rates based on the Marcus–Jortner–Levich theory, where consideration of vibronic couplings yields an asymmetric curve with higher predicted rates in the inverted region ( $-\Delta G^0 > \lambda$ ).

energies. Predictions based on eq 1 typically underestimate the  $k_{\rm ET}$  values in the inverted region and fail to capture the asymmetric shape of the curve of  $\log(k_{\rm ET})$  vs  $-\Delta G^{0.29-31}$  The Marcus–Jortner–Levich (MJL) theory, described by eqs 2 and 4,<sup>32–34</sup> overcomes some of the limitations of the original Marcus model by separating the outer-sphere reorganization energy  $\lambda_{\rm S}$ , from the inner-sphere reorganization energy  $\lambda_{\rm V}$ , and by explicitly including the contribution from the vibronic coupling between reactant and product state, while still approximating those states as harmonic. The resulting MJL framework predicts higher ET rates in the inverted region, and thus  $k_{\rm ET}$  vs  $\Delta G^0$  parabolas that agree with the asymmetric shape observed in experimental measurements (Figure 1c).<sup>2</sup>

Closs et al. measured the intramolecular ET rates for dyads **2–9** after reduction of the donor moiety.<sup>23,24</sup> The parameters  $\lambda_{\rm V}$ ,  $\lambda_{\rm S}$ , and  $H_{\rm AD}$  were fitted to the experimental rates using literature values for  $\Delta G^0$  and assuming a single effective vibrational mode of the aryl system with frequency  $\omega = \omega_{\rm eff} = 1500 \text{ cm}^{-1}$ , according to the one-mode version of the MJL equation<sup>23,24</sup>

$$k_{\rm ET,MJL, leff} = \frac{\pi |H_{\rm AD}|^2}{\hbar \sqrt{\pi \lambda_{\rm S} k_{\rm B} T}} \sum_{\nu=0}^{\infty} e^{-S} \frac{S^{\nu}}{\nu!} \exp\left(-\frac{(\Delta G^0 + \lambda_{\rm S} + \nu \hbar \omega_{\rm eff})^2}{4 \lambda_{\rm S} k_{\rm B} T}\right)$$
(2)

where

$$S = \frac{\lambda_{\rm V}}{\hbar\omega_{\rm eff}} \tag{3}$$

The one-mode model has been used for modeling photoinduced  $\text{ET}^{35}$  as well as triplet—triplet energy and electron transfer.<sup>36,37</sup> Many other studies have also adopted the single effective mode model with a typical frequency of 1500–1600 cm<sup>-1</sup>,<sup>38–40</sup> corresponding to an average stretching mode of an organic conjugated system. The outstanding question is whether MJL theory can be used as a truly predictive theory at the density functional theory level, without relying on adjustable parameters or simplified vibronic models.

Here, we implement a scheme for calculations based on the full active space of vibrational modes, as described by eq 4, moving beyond the one-effective-mode approximation<sup>32</sup>

$$k_{\text{ET,MJL,expl}} = \frac{\pi |H_{\text{AD}}|^2}{\hbar \sqrt{\pi \lambda_S k_B T}} \exp\left(\sum_{i=1}^N -S_i\right) \sum_{\nu_1=0}^\infty \cdots \sum_{\nu_i=0}^\infty \cdots \sum_{\nu_N=0}^\infty \times \left(\prod_{i=1}^N \left(\frac{S_i^{\nu_i}}{\nu_i!}\right) \exp\left(-\frac{(\Delta G^0 + \lambda_S + \sum_{i=1}^N \hbar \omega_i \nu_i)^2}{4\lambda_S k_B T}\right)\right)$$
(4)

where

$$S_i = \frac{\Delta Q_i^2 \mu_i \omega_i}{(2\hbar)} \tag{5}$$

Here the index *i* runs over all *N* normal modes *i* with quantum numbers  $v_{ij}$  frequencies  $\omega_{ij}$  and reduced masses  $\mu_{ij}$  and the prefactor and first exponential can be evaluated separately from the succeeding nested sum. This form of the MJL equation explicitly and quantum mechanically considers the complete manifold of intrasolute states, whereas solvent-polarizing modes, typically with frequencies  $\hbar\omega \ll k_{\rm B}T$ , are implicit as derived by Ulstrup and Jortner.<sup>32,41</sup> The ET reaction causes displacements in nuclear coordinates Q, often entailing partial changes in bond order, which is reflected in different minimumenergy geometries of reactant and product. The resulting reaction coordinate displacements are projected onto the nuclear displacement associated with the *i*th vibrational mode to obtain  $\Delta Q_i$ . The unitless reduced displacements  $\Delta Q_i (\mu_i \omega_i / \omega_i)$  $(\hbar)^{1/2}$  are directly related to the Huang–Rhys factors  $S_i$  as per eq 5. Thus, the  $S_i$  constitute a measure of the reactionvibration overlap and the contribution of mode *i* to the ET rate constant.

The DFT-MJL model, based on eq 4, describes electronic (vibronic) state transitions semiclassically within the Golden

rule approximation of first-order time-dependent perturbation theory. It is practical since it requires no explicit dynamical simulations and is comparable to other approaches to model ET beyond the simple Marcus approximation.<sup>36,42–44</sup> The consideration of all intramolecular vibrational modes constitutes an improvement compared to prevailing theoretical descriptions of ET rates. Other recently proposed strategies to refine this picture concern local temperature differences between reactant and product,<sup>45</sup> the temperature dependence of  $\Delta G^0$  and  $\lambda$ ,<sup>46</sup> and the more general effect of a nonequilibrated thermal bath.<sup>47</sup>

We find that eq 4 can be efficiently evaluated by Monte Carlo sampling of vibrational quantum numbers  $v_{ij}$  bypassing the need for reducing the dimensionality of the vibronic manifold or employing empirical parameters. All vibrational modes, within the  $\hbar \omega \gg k_{\rm B}T$  approximation, are considered; which is particularly helpful for molecules where the ET is in the inverted region. The parameters  $\Delta G^0$ ,  $\lambda_{\rm V}$ ,  $\lambda_{\rm S}$ ,  $\omega$ , and  $H_{\rm AD}$  can be computed directly at the DFT level or at a higher level of quantum chemistry if desired. In the following section, we show that the resulting approach yields first-principles rate predictions in agreement with experiments over a wide range of values of ET rates and provides insights on the modulation of ET rates by couplings to multiple vibrational modes.

#### METHODS

Free Energies and Frequencies. Electronic structure calculations of free energies  $\Delta G^0$  and harmonic frequencies  $\omega$ were carried out using the Gaussian0948 software, at the  $B3LYP^{49}/6-31+G(2d,p)$  level of theory, using an ultrafine integration grid, and the SMD implicit solvent model for tetrahydrofuran (THF).<sup>50,51</sup> Comparisons to the M062X<sup>52</sup> and  $\omega$ B97XD<sup>53</sup> functionals and the 6-311+G(2d,p) basis set show consistent results for the free energies, see Table S3 in the Supporting Information (SI). The  $\Delta G^0$  were computed by fragmenting the dyads into three separate units, including the donor (D), spacer, and acceptor (A) (see Figure S4 in the SI for details on the fragmentation scheme). Since the spacer is a redox-inactive, rigid hydrocarbon fragment, systematic analysis of the trends in  $\Delta G^0$ ,  $\lambda$ , and  $\Delta Q$  across the whole series of dyads is performed considering D and A only, disregarding the spacer.3

The free energies of the fragments D and A in their neutral and reduced forms (i.e.,  $G_D$ ,  $G_A$ ,  $G_{D-}$ ,  $G_{A-}$ ) are obtained in terms of the electronic energies plus thermal corrections to the Gibbs free energy based on the ideal-gas, rigid-rotor, harmonic-oscillator approximation in conjunction with the SMD implicit solvent model, <sup>51,54,55</sup> as follows:

$$\Delta G0 = G_{\text{prod}} - G_{\text{react}} = (G_{\text{D}} + G_{\text{A}^{-}}) - (G_{\text{D}^{-}} + G_{\text{A}}) \quad (6)$$

The Dushin code<sup>56</sup> was used to align the geometries of reactant and product and to project the reaction coordinate difference vectors on the vibrational mode displacement vectors to obtain the reduced displacements  $\Delta Q_i$ .

**Reorganization Energies.** The reorganization energies were computed separately for each fragment, corresponding to infinite D–A distance at the same level of theory as  $\Delta G^0$ , but without thermal contributions since vibrational free energies are reliably calculated only at stationary points. The total reorganization energies  $\lambda_{T\infty}$ , including the reorganization of both solute (inner-sphere) and solvent (outer-sphere),<sup>57,58</sup> were obtained as the averages of the reorganizations of reactants  $\lambda_{T\infty,R}$  and products  $\lambda_{T\infty,P}$  as follows:

$$\lambda_{T\infty,R} = E(3) - E(2), \quad \lambda_{T\infty,P} = E(4) - E(1),$$
$$\lambda_{T\infty} = \frac{\lambda_{T\infty,R} + \lambda_{T\infty,P}}{2}$$
(7)

This is a variant of Nelsen's four-point method,<sup>59</sup> where E(1)-E(4) correspond to the energies of states 1–4 on the potential energy surfaces (PES) of reactant and products (Figure 2).



**Figure 2.** Reactant and product potential energy surfaces. Computed energies of states 1-4 are used to obtain total reorganization energies  $\lambda_{T\infty}$ .

Such deviations from the Marcus–Hush formalism through introduction of different reorganization energies for forward and backward ET transitions have also been studied extensively by Matyushov.<sup>60</sup> The total reorganization energies  $\lambda_{T,\infty}$  are calculated without relaxing the "slow" reaction field corresponding to the solvent nuclear motion during fast ET.<sup>57,61,62</sup> Accordingly, the reaction fields associated with states 1 and 2 are used for the nonequilibrium-reaction-field energy calculations of states 3 and 4 (see the SI for example input files).

The inner-sphere reorganization energy  $\lambda_V$  does not enter explicitly in eq 4, but this parameter is inferred as the sum of contributions from each mode *i* as follows:<sup>63,64</sup>

$$\lambda_{\rm V} = \sum_{i=1}^{N} S_i \hbar \omega_i \tag{8}$$

The outer-sphere (solvent) reorganization energies  $\lambda_{S,\infty}$  are obtained by subtracting the inner-sphere  $\lambda_V$  from the total reorganization energy  $\lambda_{T,\infty}$  as follows:

$$\lambda_{\mathrm{S},\infty} = \lambda_{\mathrm{T},\infty} - \lambda_{\mathrm{V}} \tag{9}$$

The Marcus expression for outer-sphere reorganization energies  $\lambda_{S,R}$  depends explicitly on the D–A distance *R* as follows:<sup>65</sup>



**Figure 3.** (a) Decomposition of rate contributions from individual modes. The Huang–Rhys factors  $S_i$  and wave numbers  $\omega_i$  of the most important modes *i* (with  $S_i > 0.03$ ) of representative fragments (A2, A5, and A7). Heat map showing the contributions to the rates from each mode *i* as a function of  $v_i$  assuming  $v_{i\neq i} = 0$  for the other modes [see eq 16]. (b) Displacement vectors upon reduction, scaled by a factor of 30 for visibility. (c) Displacement vectors of the vibrational mode with the largest  $S_{ij}$  i.e. the largest overlap between vibrational mode displacement and changes in reaction coordinates upon ET.

$$\lambda_{\rm S,R}^{\rm Marcus} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{\varepsilon_{\rm op}} - \frac{1}{\varepsilon_{\rm S}}\right) \left(\frac{1}{2a_{\rm D}} + \frac{1}{2a_{\rm A}} - \frac{1}{R}\right)$$
(10)

This expression is used to correct our fragment-based calculations of  $\lambda_S$  for finite D–A distances

$$\lambda_{\rm S} = \lambda_{\rm S,\infty} \frac{\lambda_{\rm S,R}^{\rm Marcus}}{\lambda_{\rm S,\infty}^{\rm Marcus}} = \lambda_{\rm S,\infty} \frac{\left(\frac{1}{2a_{\rm D}} + \frac{1}{2a_{\rm A}} - \frac{1}{R}\right)}{\left(\frac{1}{2a_{\rm D}} + \frac{1}{2a_{\rm A}}\right)} \tag{11}$$

where *R* is the average of the shortest and largest atom-to-atom distance between D and A of each dyad. The donor and acceptor effective solvation radii  $a_D$  and  $a_A$  are obtained from the implicit solvation cavity volumes or surface areas, assuming spherical fragments. Finally, the total reorganization energy  $\lambda_T$  is corrected for finite D–A distances as follows:

$$\lambda_{\rm T} = \lambda_{\rm S} + \lambda_{\rm V} \tag{12}$$

The reorganization energies were calculated in a dielectric continuum solvation model. While existing studies hint toward variations in reorganization energies calculated using such models in viscous,<sup>66,67</sup> polar,<sup>68–71</sup> and soft condensed media,<sup>72</sup> the computed energies typically agree within 10% of experimental values, as pointed out by Buda.<sup>73</sup>

**Electronic Couplings.** The electronic couplings  $H_{AD}$  between the lowest unoccupied molecular orbital (LUMO) of the donor and the LUMO of the acceptor were calculated at the B3LYP<sup>49</sup>/TZ2P level of theory, using the ADF<sup>74,75</sup> package and the charge transfer integral (CTI) method:<sup>76–78</sup>

$$H_{\rm AD} = \frac{J_{\rm AD} - \frac{1}{2}S_{\rm AD}(e_{\rm D} + e_{\rm A})}{\sqrt{1 - S_{\rm AD}^2}}$$
(13)

Here,  $J_{\rm DA}$  is the off-diagonal element of the Fock matrix corresponding to the donor and acceptor orbitals.  $S_{\rm DA}$  is the overlap integral of the two orbitals, and  $e_{\rm D}$  and  $e_{\rm A}$  are the energies of the system bearing the electron on the donor or acceptor, respectively. Electronic couplings, and thus  $k_{\rm ET}$ , depend strongly on the distance and relative orientation between the donor and acceptor.<sup>79,80</sup> Because of the rigidity of the steroid spacer, however, the distance between donor and acceptor in these dyads is fixed. Nevertheless, the single bonds connecting the donor and acceptor units to the spacer can rotate. The strength of electronic coupling is modulated by the coplanarity between the donor and acceptor aryl groups, <sup>81,82</sup> as defined by a dihedral angle  $\varphi$  of rotation. Therefore, we construct a Boltzmann average of the electronic couplings to include the effect of thermal fluctuations as follows

$$|H_{AD}(T)|^{2} = \frac{\int |H_{DA}(\varphi)|^{2} e^{\frac{-\Delta E(\varphi)}{RT}} d\varphi}{\int e^{\frac{-\Delta E(\varphi)}{RT}} d\varphi}$$
$$\approx \frac{\sum_{\varphi=0^{\circ}}^{345^{\circ}} (|H_{AD}(\varphi)|^{2} e^{\frac{-\Delta E(\varphi)}{RT}})}{\sum_{\varphi=0^{\circ}}^{345^{\circ}} e^{\frac{-\Delta E(\varphi)}{RT}}}$$
(14)

where  $H_{\rm AD}({\rm T})$  is the conformationally averaged coupling, and  $\Delta E(\varphi)$  is the energy of each dyad relative to its global minimum. The  $\Delta E(\varphi)$  were calculated using relaxed scans over  $\varphi$  using Gaussian09 and B3LYP/6-31g(d) in implicit THF solvent. The integrals in eq 14 are evaluated by quadrature in  $\varphi$  intervals of 15°.

Monte Carlo Rate Calculations. To solve the full MJL expression eq 4, we implement an importance-sampling Monte Carlo (MC) scheme to avoid explicit evaluation of all terms in

the nested sum, instead focusing on sampling those sets of  $v_i$  that contribute to the rate. The MC routine samples vibrational quanta in the  $v_i = 0-11$  range for all contributing ( $S_i > 1 \times 10^{-6}$ ) vibrational modes N of each dyad, up to N = 77 for dyad 5. The evaluations of  $k_{\text{ET,eq 4}}$  are fully converged within  $10^8$  MC iterations, which constitutes a tremendous efficiency improvement compared to the  $\sim 10^{22}$  evaluations necessary for explicitly computing all possible sets of  $v_i$  in the same 0-11 range. The SI includes a thorough description of the MC algorithm, including the analysis of convergence and comparisons to benchmark calculations, sampling function form, and other technical details.

#### RESULTS AND DISCUSSION

**Vibrational Modes.** Eq 2 provides the simplest possible model for vibronic effects on ET rates based on the MJL formalism, assuming that vibrations influence the rate as a single effective mode with frequency  $\omega_{\text{eff}}$  Previous studies have implemented the one-mode model by fitting or assuming  $\omega_{\text{eff}}$  to approximately match the observed rates.<sup>23,24,38-40</sup> More rigorously,  $\omega_{\text{eff}}$  can be computed in terms of the DFT frequencies  $\omega_i$  and Huang–Rhys factors  $S_i$  as follows:<sup>83</sup>

$$\omega_{\text{eff}} = \frac{\sum_{i=1}^{N} S_i \omega_i}{\sum_{i=1}^{N} S_i} \tag{15}$$

Since the spacer of dyads 1-9 is structurally rigid, only the modes of the redox-active D and A moieties change upon ET and, therefore, require consideration in eq 15.<sup>84</sup> The DFT values of  $\omega_{\text{eff}}$  for dyads 1-9 range from 835 cm<sup>-1</sup> for 5 to 992 cm<sup>-1</sup> for 2. Interestingly, those effective frequencies are considerably lower than the 1500 cm<sup>-1</sup> value empirically fitted by Closs et al.,<sup>23</sup> who assumed that the ET is mostly coupled to an aryl breathing mode.

Due to the Poissonian-like dependence of the rates with  $S_i$ and  $v_i$ , modes with small  $S_i$  contribute mostly with  $v_i = 0$ . Conversely, vibrational excitations in modes with larger  $S_i$ couple to the ET, making these modes contribute with higher vibrational quantum numbers  $v_i$  in the inverted region, as shown in Figure 3. Figure 3a shows the distribution of values of  $S_i$  and  $\omega_i$  for modes with  $S_i > 0.03$  in three representative dyads, including results in the normal, near-activationless, and inverted regions. Figure 3a also depicts the contributions to the rates as a function of  $v_i$  for the same modes, when all other modes are in the ground state with  $v_i = 0$  as follows:

$$Z(S_i, v_i) = e^{-S_i} \left( \frac{S_i^{v_i}}{v_i!} \right) \exp\left( -\frac{\left( \Delta G^0 + \lambda_S + \hbar \omega_i v_i \right)^2}{4\lambda_S k_B T} \right)$$
(16)

The heat map of Z in Figure 3a shows that multiple modes couple to ET and unavoidably modulate the rates. Most modes have associated Huang–Rhys factors  $S_i < 1.0$ , for which  $v_i = 0$ dominates the rate contribution in the normal region. However, all acceptors exhibit multiple modes with sufficiently large  $S_i$  to significantly affect the rate. The modes with larger  $S_i$  involve stretching of the aryl rings, due to delocalization of the transferred electron across the whole conjugated system (see Figures S14–S22 in the SI for the displacement vectors of all modes in all donors and acceptors with  $S_i > 0.03$ ). This signifies that the aryl stretching modes are critical for ET, and efforts to alter vibronic transfer rates should focus on tuning such modes.

Figure 3b shows the atomic displacements induced by ET in A2, A5 and A7, as compared to the displacement vector

components of the vibrational mode with the largest  $S_i$  (i.e., the mode with the largest overlap with the reaction coordinate change) shown in Figure 3c. The modes shown for benzoquinonyl (A7) and naphthyl (A2) both exhibit displacement vectors strikingly similar to the overall nuclear displacements induced by ET (Figure 3b). However, this similarity is not necessarily immediately obvious for any fragment or mode, as seen for example for hexahydronaphthoquinonyl (A5) shown in Figures 3b and 3c. The lack of apparent agreement for A5 is because the vibration-reaction overlaps are calculated in curvilinear internal coordinates, making the 2D projection illustrated in Cartesian coordinates as shown in Figure 3b incapable of providing a good representation of the internalcoordinate changes in this case. Overall, the results from Figure 3 highlight the importance of systematic evaluation of the Huang-Rhys factors for all modes with significant contributions to the rates, and the precariousness of neglecting contributions from the complete set of modes that couple to ET. This is most significant for the inverted region, where several modes of large  $S_i$  often contribute significantly.

**Electron-Transfer Free Energies.** The ET free-energy changes  $\Delta G^0$  are negative for the entire set, except for the practically symmetric dyad 1 for which  $\Delta G^0 = 0$ . Figure 4



**Figure 4.** Correlation between calculated and experimental<sup>23</sup> ET free energy changes  $-\Delta G^0$  for dyads **1–9**.

compares the DFT-calculated values of  $\Delta G^0$  to the corresponding experimental values (see Table S3 in the SI), showing remarkable agreement with a mean absolute deviation of only 0.037 eV, over the complete set of dyads 1–9. Accurate and efficient calculations of  $\Delta G^0$  are essential for reliable predictions of ET rates, since  $\Delta G^0$  is squared in the exponential of eq 4, therefore affecting the rates considerably.

**Reorganization Energies.** Table 1 reports the calculated values of reorganization energies. The mean inner-sphere  $\lambda_{\rm V} = 0.56$  eV obtained from our first-principles calculations is larger than the corresponding experimentally fitted dyad-wide value ( $\lambda_{\rm V} = 0.45$  eV), whereas our mean outer-sphere  $\lambda_{\rm S} = 0.79$  eV is in close agreement with the experimental estimate ( $\lambda_{\rm S} = 0.75$  eV).<sup>23,24</sup> The smallest  $\lambda_{\rm V}$  corresponds to the pyrenyl dyad 4 where the added electron is extensively delocalized and therefore does not polarize or distort the structure significantly, whereas the largest  $\lambda_{\rm V}$  corresponds to the hexahydronaphto-

#### Table 1. Reorganization Energies of All Dyads

dyad	$\lambda_{ m V} \; [{ m eV}]$	$\lambda_{ m S} \; [ m eV]$
1	0.66	0.72
2	0.45	0.79
3	0.48	0.79
4	0.43	0.82
5	0.69	0.83
6	0.56	0.81
7	0.58	0.80
8	0.59	0.80
9	0.59	0.79
mean	0.56	0.79

quinonyl dyad **5** where the conjugation is disrupted by two saturated carbons. The  $\lambda_{\rm S}$  values exhibit a very narrow spread due to the similar radii of the D and A fragments. The radii are in the 3.2–3.7 Å range as obtained from the implicit solvent cavity volume. This increases to 3.6–4.2 if instead obtaining the radii from the cavity surface area, with the difference stemming from the fragments not being perfectly spherical. Nevertheless,  $\lambda_{\rm S}$  remains unchanged to within 3% if instead using the latter radii.

The good agreement with experimentally fitted  $\lambda$  values yields similar curvatures of the log( $k_{\rm ET}$ ) vs  $\Delta G^0$  curves (Figure 6), providing partial validation of our distance-correction scheme based on relatively simple geometric arguments.

**Electronic Couplings.** Figure 5 illustrates the dependency of  $H_{AD}(\varphi)$  and  $\Delta E(\varphi)$  on  $\varphi$ , for dyads 2 and 8, showing that the estimation of  $H_{AD}$  based only on the minimum energy conformation would typically neglect important contributions



**Figure 5.** Relative energies  $\Delta E$  (red) and electronic couplings  $|H_{AD}|$  (black), as a function of the dihedral angle  $\varphi$  between the fixed donor-spacer (D-Sp) and the acceptor (A) for (a) dyad 2 and (b) dyad 8.

from thermally accessible conformations. Similar results for the other dyads are included in the SI (Figures S5-S13). This shows clearly that the minimum-energy conformation typically is not the one with the strongest D–A electronic coupling.

Table 2 compares the ensemble-average couplings  $H_{AD}(T)$ and the electronic couplings  $H_{AD,opt}$  of the minimum-energy

Table 2.  $LUMO_D - LUMO_A$  Electronic Couplings Calculated at the Minimum Energy Geometry As Compared to the Thermal Ensemble Average at Room Temperature T

dyad	$ H_{AD,opt} $ [eV]	$ H_{\rm AD}(T) $ [eV]
1	$4.86 \times 10^{-4}$	$6.88 \times 10^{-4}$
2	$5.29 \times 10^{-4}$	$5.42 \times 10^{-4}$
3	$5.40 \times 10^{-4}$	$8.33 \times 10^{-4}$
4	$2.73 \times 10^{-4}$	$1.00 \times 10^{-3}$
5	$4.53 \times 10^{-5}$	$9.73 \times 10^{-4}$
6	$2.53 \times 10^{-4}$	$4.53 \times 10^{-4}$
7	$8.83 \times 10^{-5}$	$4.84 \times 10^{-4}$
8	$1.31 \times 10^{-4}$	$5.40 \times 10^{-4}$
9	$1.16 \times 10^{-4}$	$4.39 \times 10^{-4}$
mean	$2.74 \times 10^{-4}$	$6.62 \times 10^{-4}$

conformations. For dyads A1-A4 with a polyaromatic hydrocarbon acceptor, the couplings of the minimum-energy conformation largely determine the value of the ensemble average. However, for dyads 5-9 the ensemble average includes important contributions from twisted conformations partly due to steric hindrance caused by proximal carbonyl oxygen atoms. The mean value of the rotationally averaged DFT couplings  $6.62 \times 10^{-4}$  eV agrees well with the empirical value  $(7.7 \times 10^{-4} \text{ eV})$  obtained by fitting to measured rates according to eq 2.<sup>23</sup> We note, however, that rather than a uniform value for the couplings, DFT calculations show that  $|H_{AD}(T)|$  varies by more than a factor of 2 across the set of dyads investigated, and  $H_{AD}(T)^2$  varies by more than a factor of 5. Furthermore, the use of only minimum-energy conformations  $(H_{AD,opt})$  would underestimate  $k_{ET}$  by up to 2 orders of magnitude compared to the ensemble average  $(H_{AD}(T))$ . It is, therefore, clear that the conformational-averaging procedure is essential for proper modeling of ET rates.

Estimating electronic coupling strengths from quantum chemistry calculations is challenging, although various methodological developments have been made recently.<sup>85–92</sup> Our method of estimating the coupling for ET with DFT is based on the single-orbital approximation, i.e. that the coupling between reactant and product state is described by the coupling between only LUMO<sub>donor</sub> and LUMO<sub>acceptor</sub>, see Table S6 in the SI for elaboration. This method is straightforward while somewhat crude and, like any DFT method, likely involves shortcomings with respect to the level of theory, e.g. overdelocalization of charge, which is only partly remedied by the employment of hybrid exchange–correlation functionals.<sup>90</sup> Hence, the good agreement of our calculated rates to those reported experimentally is expected to involve some cancellations of error.

The process investigated here corresponds to an ET from the LUMO of the donor to the LUMO of the acceptor. However, the methodology is readily applied to ET between other orbitals, e.g. highest occupied molecular orbital (HOMO) to HOMO transfers, which are relevant to the oxygen-evolving half-cell in photocatalytic water-splitting dye cells, or LUMO– HOMO which dominate the recombination process in dye-

sensitized solar cells. Therefore, the reported findings on the participation of multiple vibrational states and the influence of thermal fluctuations on the average electron couplings should be valuable for theoretical modeling ET in a wide range of systems and applications.

**Electron Transfer Rates.** Figure 6 compares the experimental ET rates,  $k_{\text{ET}}$ , for dyads 1–9 to those obtained



**Figure 6.** Electron transfer rates  $k_{\rm ET}$  as reported experimentally (black)<sup>23</sup> and calculated with eq 1 (green), eq 2 (blue), and eq 4 (red) plotted versus the free energy change  $-\Delta G^0$  of the ET reaction. The experimental rate estimate for dyad **5** is a lower-bound instrument-limited value.

with DFT-MJL theory, according to eqs 1, 2, and 4. Clearly, eq 4 provides a better agreement with experimental data than calculations based on the more approximate models (see Table S1 in the SI for all tabulated rates), enabling predictions with no adjustable parameters or effective vibrational approximations. We note that the experimental rate for **5** is a lower-bound instrument-limited value,<sup>23</sup> so the actual rate is most likely in better agreement with theory than is apparent from Figure 6.

Using the full MJL expression eq 4, the rate ratio  $k_{\rm ET,eq} 4/k_{\rm ET,exp}$  ranges between 0.20 and 5.13, corresponding to dyads 9 and 5, respectively, resulting in a very small mean absolute error (MAE) on the logarithmic scale of 0.35 log(s<sup>-1</sup>). The one-effective mode ratio  $k_{\rm ET,eq} 2/k_{\rm ET,exp}$  ranges from 0.06 to 5.69, corresponding to the same dyads, with MAE = 0.52 log(s<sup>-1</sup>). Overall, the correlation is remarkably good, considering the sensitivity of  $k_{\rm ET}$  to the parameters of the model and the several orders of magnitude wide span of absolute rate constants across the homologous set of dyads.

## CONCLUSIONS

The Marcus–Jortner–Levich (MJL) theory based on one effective vibrational mode, introduced by eq 2, has been extensively used for fitting experimental ET rates with an analytic model that involves a few adjustable parameters including the reaction free energy  $\Delta G^0$ , the electronic coupling  $H_{\rm AD}$ , solute and solvent reorganization energies  $\lambda_{\rm V}$  and  $\lambda_{\rm S}$ , and the frequency  $\omega_{\rm eff}$  of a single effective vibrational mode. Here,

we have shown that the theory can be used in conjunction with DFT beyond the single effective vibrational mode model, as a predictive method without empirical parameters, including the complete active space of vibrational modes as introduced by eq 4. Implementation of the resulting all-mode MJL framework as per eq 4 is based on a Monte Carlo scheme to efficiently sample the ensemble of quantum numbers for all vibrational modes. The explicit consideration of all modes allows us to improve prediction of rates by an order of magnitude in the inverted region where tunneling and nuclear effects are prominent, while also permitting a decomposition of the rate contribution from individual modes, providing physical insight unavailable under the one-effective-mode approximation. In all of the studied moieties, delocalized aryl stretching modes show the strongest coupling to the ET process and are thus worthy of particular attention when developing systems with improved transfer rates.

Direct comparisons with experimental data illustrate the importance of considering the complete active space of vibrational modes that unavoidably couples to ET, the donor–acceptor relative orientations, and the solvent exclusion volume due to the proximity of the electron donor and acceptor partners. By addressing all of these important effects, MJL theory based on DFT calculations is able to predict ET rates for the whole set of nine dyads spanning over 4 orders of magnitude in the  $10^6-10^{10}$  s<sup>-1</sup> range. It is, therefore, expected that the reported methodology should be particularly useful for reliable descriptions of charge-transfer rates in a wide range of applications, including solar photovoltaic and photocatalytic processes.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.7b00513.

Details on the computational methodology; results from testing of other computational methods; details on  $k_{\rm ET}$ calculated with eqs 1, 2, and 4 and from experiments; details on the MC algorithm used to solve eq 4; example input files for calculations of  $\Delta G^0$ ,  $\lambda_{\rm T}$ , and  $H_{\rm AD}$ ; optimized coordinates of the molecules (PDF)

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#### Notes

The authors declare no competing financial interest.

The Fortran source code for the Monte Carlo program for this article is available upon request from the corresponding authors.

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