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Electron Transfer Rates in Solution: Toward a Predictive First Principle Approach

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Abstract: Using a very recently proposed theoretical model, electron transfer rates in solution are calculated from first principles for different donor-acceptor pairs in tetrahydrofuran. We show that this approach, which integrates tunneling effects into a classical treatment of solvent motion, is able to provide reliable rate constants and their temperature dependence, even in the case of highly exergonic reactions, where Marcus' theory usually fails.

Keywords: electron transfer; solvation effects; reorganization energy; temperature dependence

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1. Introduction

Electron transfer (ET) reactions are at foundation of modern chemistry, being exploited in numerous applications (e.g., photovoltaics, biosensing, molecular electronics), and are still the subject of active and vibrant research. The seminal work of Marcus paved the way to the development of this vast field [1–3]. Marcus' theory relates the kinetics of ET process to two well-defined physical quantities: (i) the ΔG^0 of the whole ET reaction and (ii) the reorganization energy associated with the motions of both solvent λ_{solv} and reactants λ_{int}. While this elegant theory is still successfully used to address ET phenomena, as for instance the rational design of organic molecules to be used in technological devices, its classical treatment of nuclear quantum motion does not allow to explore regimes in which tunneling is crucial [4–6], and drammatically fails in reproducing ET rates of strongly exothermic reactions [7].

Alternative theories have been formulated [8], and several papers have focused on implementing quantum effects arising from high frequency vibrational modes into Marcus' theory [9–16], but only recently the task of including the whole heat bath provided by intramolecular coordinates of the redox pair—which represented the real breakthrough for understanding the unusual temperature dependence of an early ET step occurring in bacterial photosynthetic reaction center [17–19]—has been undertaken [20]. That objective has been achieved by introducing a multistep kinetic model of ET reactions, described in refs. [21,22], in which the motion of the solvent is separated from that of the redox pair [23,24]. That separation of motion makes it possible the employment of an effective treatment of tunnelling effects, which incorporates the whole set of nuclear coordinates of the redox pair and takes into account changes of both the equilibrium nuclear positions and of vibrational frequencies upon electronic transition, allowing to include effects due to normal mode mixing too [17,25,26]. The approach has been tested on different D-A pairs in both polar and non-polar solvents: it proved to provide ET rates in excellent agreement with measurements [27,28] and to reproduce the expected temperature dependence [20]. The achievement of such a satisfactory result was however subdued to the use of solvent reorganization energy as extrapolated from available experimental data. Nevertheless, to make the model predictive, an ab initio determination of such a quantity would be highly desirable. The evaluation of the solvent reorganization energy based on molecular dynamics with an explicit treatment of solvent molecules [29–32] is certainly a possible choice, but it might be unaffordable for high-throughput screening procedures. Therefore, the use of implicit solvent methods would be desirable, provided that their accuracy is properly tested. Herein, we show that the simple non-equilibrium Marcus' approach for the evaluation of solvent reorganization energy is extremely effective and leads to calculated ET rates which are in excellent agreement with the observed ones, yielding also the correct temperature dependence.

2. Theory

2.1. The Kinetic Model

For a given donor-acceptor system, the multistep mechanism reads as Scheme 1:

$$\mathrm{D^-A} \underset{k_{dact}}{\overset{k_{act}}{\rightleftharpoons}} \{\mathrm{D^-A}\}^* \underset{k_{ET}}{\overset{k_{ET}}{\rightleftharpoons}} \{\mathrm{DA^-}\}^* \underset{k_{act}}{\overset{k_{dact}}{\rightleftharpoons}} \mathrm{DA^-}$$

Scheme 1. The multistep kinetic mechanism of ET.

Where $\mathrm{D^-A}$ and $\mathrm{DA^-}$ represent the initial and the final states, respectively, and $\{\mathrm{D^-A}\}^*$ and $\{\mathrm{DA^-}\}^*$ indicate the ensembles of transient structures in vibronic resonance with each other.

First, we consider the activation step bringing the donor and the acceptor species into electronic degeneracy, which is mandatory when initial and final states are not in vibronic resonance at frozen solvent coordinates. This may typically occur in polar solvents for which $\lambda_{\mathrm{solv}} > \Delta G^0$. The rate constant of this step is hence estimated assuming the sole involvement of the solvent coordinate and a typical Arrhenius dependence on temperature:

$$k_{act} = k_0 \exp\left(-\frac{\Delta G^\#}{k_B T}\right) \tag{1}$$

where k_0 is a transmission coefficient and $\Delta G^\#$ is the standard activation free energy, i.e. the free energy difference of $\{\mathrm{D^-A}\}^*$ with respect to $\mathrm{D^-A}$. Applying Marcus' reasoning to frozen intramolecular coordinates [3], $\Delta G^\#$ is defined as [1,3]:

$$\Delta G^\# = \frac{(\Delta G^0_{fi} + \lambda)^2}{4\lambda_{\mathrm{solv}}}. \tag{2}$$

In Equation (2), ΔG^0_{fi} is the free energy difference between initial and final states, λ is the total reorganization energy, composed by the sum of the solvent and reactants contributions. These in turn may be splitted in the individual contributions pertaining to the donor and the acceptor, e.g., for the solvent $\lambda_{\mathrm{solv}} = \lambda_{\mathrm{solv}}(\mathrm{D}) + \lambda_{\mathrm{solv}}(\mathrm{A})$. Following Ref. [20], k_0 appearing in Equation (1), is defined as:

$$k_0 = k_{dact}\frac{g_{act}}{g_{eq}}, \tag{3}$$

where g_{act} and g_{eq} are the total degeneracies of the activated and the equilibrium states and k_{dact} is the rate constant for deactivation, available from experiments, in consistence with the principle of microscopic reversibility [33].

The second step is the elementary ET process in resonant conditions, for which the rate can be calculated within the framework of the Fermi Golden Rule, considering a non-radiative transition between two electronic states $|i\rangle$ and $|f\rangle$:

$$k_{i\to f} = \frac{2\pi}{\hbar} F(\Delta E_{fi}, T), \tag{4}$$

where $F(\Delta E_{fi}, T)$ is:

$$\begin{aligned} F(\Delta E_{fi}, T) &= |\langle f|\,\mathcal{H}'\,|i\rangle|^2 \sum_{\mathbf{v}'}\sum_{\mathbf{v}''} w_{\mathbf{v}'}(T)|\langle \mathbf{v}''|\mathbf{v}'\rangle|^2 \delta(E_{i\mathbf{v}'} - E_{f\mathbf{v}''} - \Delta E_{fi}) \\ &= |V_{fi}|^2 \rho(\Delta E_{fi}, T) \end{aligned} \tag{5}$$

where $\mathcal{H}'$ is the electronic coupling element for ET reaction, assumed to be independent of the vibrational coordinates, $\mathbf{v}'$ and $\mathbf{v}''$ indicate the vectors of the vibrational quantum states of the $|i\rangle$ and $|f\rangle$, respectively, $E_{i\mathbf{v}'}$ and $E_{f\mathbf{v}''}$ are the vibronic energies of $|i\mathbf{v}'\rangle$ and $|f\mathbf{v}''\rangle$, respectively, and $w_{\mathbf{v}'}$ is the equilibrium (Boltzmann) population of $|i\mathbf{v}'\rangle$. Overall, $F(\Delta E_{fi}, T)$ consists of an electronic coupling term V_{fi} and of $\rho(\Delta E_{fi}, T)$, the Franck-Condon weighted density of states of the elementary $|i\rangle \rightarrow |f\rangle$ transition at the ΔE of the reaction, averaged over a thermal equilibrium distribution of initial vibrational states. For weakly interacting molecules, the vibrational motions of each molecular site upon electron transfer can be assumed to be independent from each other. It follows that:

$$\rho(\Delta E, T) = \int_{-\infty}^{\infty} dE \mathcal{D}(E)\mathcal{A}(\Delta E - E). \tag{6}$$

where $\mathcal{D}(E)$ and $\mathcal{A}(E)$ are the spectral distributions of the donor photoelectronic and of the acceptor electron attachment spectra [34,35], which can be measured [36–38] and reliably estimated from ab initio calculations [17,35,39–45].

From the description of the kinetic scheme, it is clear that the determination of the solvent reorganization energy is apical in the model. In fact, while ET reactions are exothermic when both solvent (Q) and molecular ($\vec{q}$) nuclear coordinates are in their equilibrium conditions, we here assume the elementary ET step to occur at fixed Q. In particular, we define:

$$\Delta G^0_{eff} = \Delta G^0_{fi} + \lambda_{\text{solv}}, \tag{7}$$

and consider two cases: (i) $\Delta G^0_{eff} < 0$, for which ET occurs at $Q = Q_{0i}$, the equilibrium solvent coordinate of the initial state, without thus requiring any solvent activation; (ii) $\Delta G^0_{eff} > 0$, for which ET occurs at $Q = Q_c$, the point at which the potential energy surfaces of the initial and final states cross each other when intramolecular coordinates are kept fixed at their initial equilibrium value. From Equation (7), it follows that λ_{solv} determines the occurrence and the rate of the activation step. Furthermore, even in cases when ET is exothermic and activation is not required, i.e. the kinetic model is not applied, λ_{solv} still influences the ET rate, inasmuch as the Franck-Condon weighted density of states is evaluated from Equation (4) at $\Delta E_{fi} = \Delta G^0_{eff}$, which in turns depend on λ_{solv}, Equation (7).

2.2. Solvent Reorganization Energy

In a previous study [20], λ_{solv} in tetrahydrofuran (THF) has been directly estimated from the experimental rate constants of the extremely exothermic BIP-BQO or BIP-NQO pairs, see Figure 1, and from the electronic coupling elements reported in ref. [29]. However, this approach provides values of λ_{solv} independent of the chemical nature of the acceptor, an approximation which works well for the A/D pairs of Figure 1 [29], but likely impracticable in other cases, and, more importantly, restricts the feasibility of the model to the study of cases in which λ_{solv} can be extrapolated from measurements, thus limiting its predictive power.

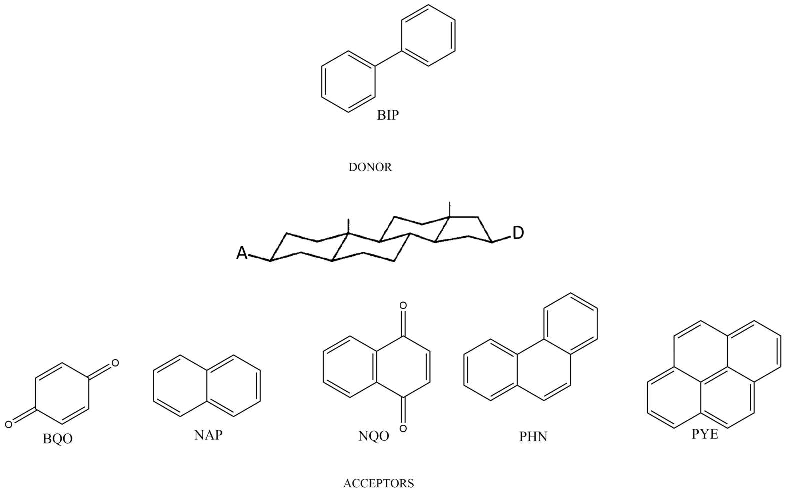

Figure 1. Chemical structures of the donor and the acceptors considered in this study. BIP = 1,1-biphenyl, BQO = 2-benzoquinonyl, NAP = 2-naphthyl, NQO = 2-naphtoquinonyl, PHN = 9-phenanthryl, PYE = 1-pyrenyl.

Here, we calculate λ_{solv} in THF using Marcus' non-equilibrium approach, according to which [1,46]:

$$\lambda_{\mathrm{solv}} = (ne)^2\Big(\frac{1}{2r_{\mathrm{A}}} + \frac{1}{2r_{\mathrm{D}}} - \frac{1}{R}\Big)\Big(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\Big), \tag{8}$$

where n is the number of exchanged electrons, e is the electron charge, r_{A} and r_{D} are the radii of cavity accommodating the donor and acceptor, respectively, R the intermolecular distance, ϵ_∞ and ϵ_0 the high-frequency and static dielectric constants of the solvent, respectively.

Since solvent reorganization energies are sensitive to the chosen radii of the dielectric cavities, only for comparison purposes, we have also employed a nonlocal response function theory, formulated in the inverted-space representation of the electrostatic fields, in which the cavity is determined from the atomic radii of A/D pair and solvent [47]. Within this theory, the solvent reorganization is given by two contributions [47]:

$$\lambda_{\mathrm{solv}} = \lambda_p + \lambda_d. \tag{9}$$

where λ_p is the usual orientational reorganization energy, associated with the energetic strength of anisotropic fluctuations of the solvent polarization, and λ_d the density reorganization energy, which describes how the translational motion of the solvent alters its response by locally changing solvent density around the solute. We will not consider here the latter effect, which is not included in Marcus' theory.

3. Computational Details

Equilibrium geometries, normal coordinates and vibrational frequencies of the neutral and anionic species are calculated at the density functional theory (DFT) using Gaussian 16 [48]. We employ the B3LYP (Becke [49], 3-parameter [50], Lee–Yang–Parr) [51] functional with the 6-31+G(d,p) basis set. In all the calculations, solvent effect was included by using the continuum polarizable medium (PCM) approach [52,53]. To determine λ_{solv} in Equation (8), the radii of cavities have been obtained from the computed PCM cavity volumes, assuming spherical shapes, whereas R has been evaluated as the sum of r_A, r_D and the androstane spacer length, the latter taken from geometry optimization of the whole molecules.

Solvent reorganization energies from nonlocal response theory are evaluated employing the freely available SOLVMOL package [54]; for each redox state, ESP charges evaluated by Gaussian 16 at the same level of the theory cited above have been employed [55].

Franck-Condon weighted density of states (FCWDs) are calculated using a development version of the MolFC package, available on request. The internal (curvilinear) representation of normal coordinates have been adopted in all the cases [56]. The electronic coupling elements reported in ref. [29] have been employed throughout. When activation step is not necessary, ET rates are calculated by Equation (4) with the FCWD evaluated at ΔG^0_{eff}. In the other case, the kinetic scheme is used and the set of coupled ordinary differential equations (ODEs) is solved by using the Dormand-Prince method of order 4, a member of the Runge-Kutta family of ODE solvers, as implemented in MATLAB package [57] with k_{act} from Equation (1) and k_{ET} from Equation (4) but with the FCWD evaluated at $\Delta G = 0$.

4. Results and Discussion

Calculated values of ΔG^0_{fi}s and λ_{solv}s for each A/D pair in THF are listed in Table 1, along with values of $\Delta G^{\#}$s, the standard activation free energy (c.f. Equation (2)), and the calculated and the observed rate constants. Solvent reorganization energies calculated by Marcus' solvent treatment and by nonlocal response theory function are very similar each other, when only solvent polarization effects are considered; we have thus considered only the former ones for computing ET rates. Herein, assuming that the entropy of reaction due to intramolecular vibrations is negligible, we consider the calculated energy differences as free energies. The extremely exergonic ET reactions involving BIP-BQO and BIP-NQO pairs do not require an activation step because they retain exergonicity also at frozen solvent coordinates (see Table 1), so that their rate constants can be directly evaluated by Equations (4)–(6), using $\rho(\Delta G_{eff}, T)$. Vice versa, all the other A/D pairs require a solvent activation step, so that their rates have been obtained by numerically solving the systems of ordinary differential equations associated to the multistep kinetic ET mechanism, c.f. Scheme 1. The rate of the solvent response to a nonequilibrium charge distribution of the solute (k_{dact}) has been taken from time dependent spectroscopic measurements (Stokes shifts) [58], and the transmission coefficient k_0 has been set to 5×10^{12} s^{-1} for all species, as in previous work [20]. Table 1 shows that for all systems considered here the calculated rates differ from the experimental ones by a factor 2–3, the order of magnitude being well reproduced in all the cases.

Table 1. Calculated equilibrium energy changes (ΔG^0_{fi}), reorganization energies (λ_{solv}), activation free energy ($\Delta G^{\#}$), and rate constants (k) for ET of each BIP-bridge-A pair. All energies are in eV. Experimental rate constants from ref. [27].

		λ_{solv}			k(s^{-1})	
Acceptor	ΔG^0_{fi}	**Equation (8)**	**SolvMol**	$\Delta G^{\#}$	**Theo**	**Exp**
BQO	−2.4	0.78	0.71	-	1.2×10^8	$(2.5 \pm 0.3) \times 10^8$
NAP	−0.03	0.74	0.71	0.2	4.4×10^6	$(1.5 \pm 0.5) \times 10^6$
NQO	−2.1	0.73	0.64	-	6.7×10^8	$(3.8 \pm 1) \times 10^8$
PHN	−0.1	0.71	0.68	0.2	1.3×10^7	$(1.2 \pm 0.2) \times 10^7$
PYE	−0.5	0.66	0.68	0.01	4.0×10^9	$(1.5 \pm 0.5) \times 10^9$

In Figure 2, the temperature dependence of ET for two acceptors, BQO and NAP, the only two for which experimental results are available [59], is reported. ET from BIP to NAP needs activation by solvent motion and therefore the T dependence of ET rate constant is dominated by the Arrenhius exponential factor, and thus ET rates change by over 4 orders of magnitude. Conversely, ET from BIP to BQO occurs by tunneling and it is almost temperature independent. In this case, we have considered that the dielectric constant of THF exhibits a significant temperature dependence, which, in the temperature range −78 to 30 °C, can be expressed by the following relation: $\epsilon(T) = -1.50 + 2650/T$ [60]. It is interesting to remark as $\epsilon(T)$ increases with T, so does solvent reorganization energy. However, since ET rates occurs by tunneling, the larger values of λ_{solv} do not produce an exponentially decrease of the rate. In fact, we observed an increase of the Franck-Condon weighted density of states with a mild effect on ET rates, c.f. Figure 2.

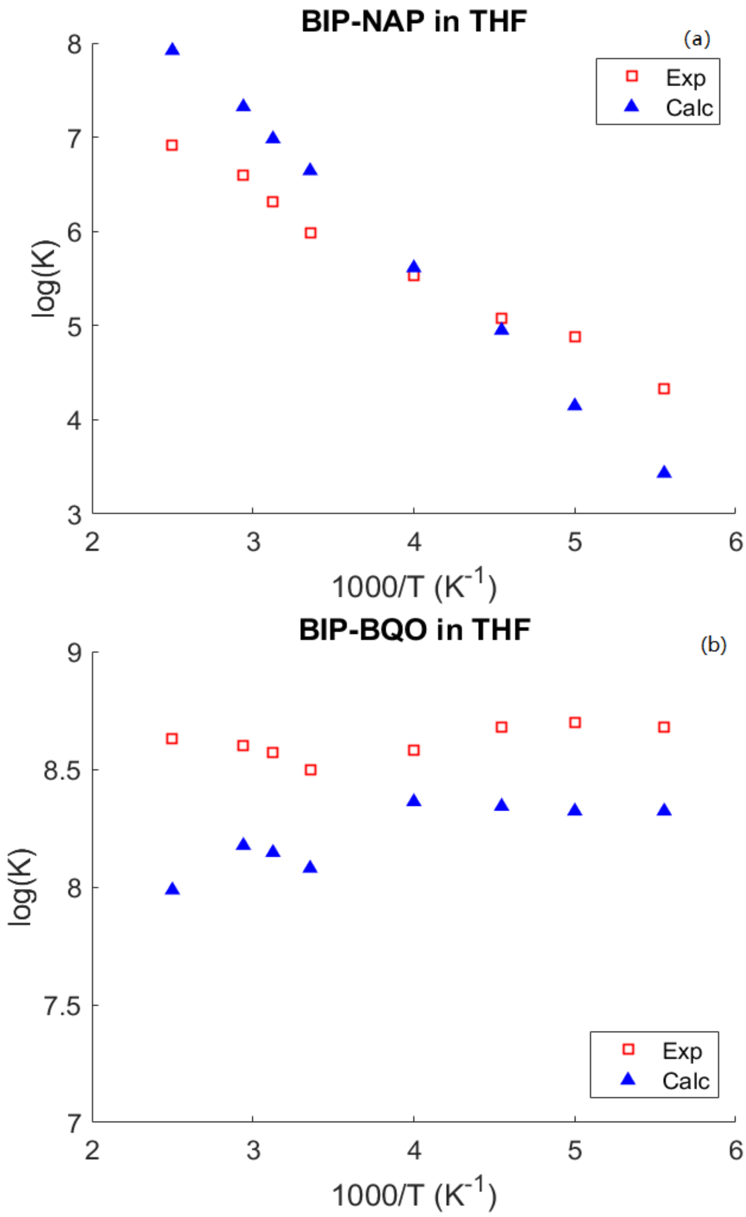

Figure 2. Experimental (red squares) and calculated (blu triangles) temperature dependence of rate constat for BIP-NAP (panel (**a**)) and BIP-BQO (panel (**b**)) pairs in THF.

5. Conclusions

In our approach, we have assumed that elementary ET reactions always occurs by tunneling and that solvent motion modulates the energy condition under which this phenomenon occurs. Herein, at variance with a previous study, we calculate solvent reorganization energy using Marcus' original expression, showing that it yields satisfying results for the systems considered here. That is a significant step toward the development of a predictive first-principles approach for the calculation of ET rates, which ultimately tends to avoid the long and laborious calculations of molecular dynamics, routinely used for determining ET rates in solution. However, the approach still makes use of an adjustable parameter to be set from experimental data, i.e. the transmission coefficient k_0, and this parameter has to be related to solvent properties; work is in progress along this line.

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References

1. Marcus, R.A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* **1956**, *24*, 966–978. [CrossRef]
2. Marcus, R.A. Chemical and Electrochemical Electron-Transfer Theory. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.
3. Sumi, H.; Marcus, R.A. Dinamical Effects in Electron Transfer Reactions. *J. Chem. Phys.* **1986**, *84*, 4894. [CrossRef]
4. Landi, A.; Borrelli, R.; Capobianco, A.; Velardo, A.; Peluso, A. Hole Hopping Rates in Organic Semiconductors: A Second-Order Cumulant Approach. *J. Chem. Theory Comput.* **2018**, *14*, 1594–1601.
5. Landi, A. Charge Mobility Prediction in Organic Semiconductors: Comparison of Second-Order Cumulant Approximation and Transient Localization Theory. *J. Phys. Chem. C* **2019**, *123*, 18804–18812.
6. Landi, A.; Borrelli, R.; Capobianco, A.; Velardo, A.; Peluso, A. Second-Order Cumulant Approach for the Evaluation of Anisotropic Hole Mobility in Organic Semiconductors. *J. Phys. Chem. C* **2018**, *122*, 25849–25857.
7. Akesson, E.; Walker, G.C.; Barbara, P.F. Dinamical Solvent Effects on Electron Transfer Rates in the Inverted Regime: Ultrafast Studies on the Betaines. *J. Chem. Phys.* **1991**, *95*, 4188. [CrossRef]
8. Formosinho, S.J.; Arnaut, L.G.; Fausto, R. A Critical Assessment of Classical and Semi-classical Models for Electron Transfer Reactions in Solution. *Prog. React. Kinet* **1998**, *23*, 1–90.
9. Levich, V.G. *Present State of the Theory of Oxidation-Reduction in Solution*; Interscience: New York, NY, USA, 1965; Volume 4.
10. Dogonadze, R.; Kuznetsov, A.; Margishvili, T. The Present State of the Theory of Charge Transfer Processes in Condensed Phase. *Electrochim. Acta* **1980**, *25*, 1–28. [CrossRef]
11. Kestner, N.; Logan, J.; Jortner, J. Thermal Electron Transfer Reactions in Polar Solvents. *J. Phys. Chem.* **1974**, *78*, 2148. [CrossRef]
12. Jortner, J.; Bixon, M. Intramolecular Vibrational Excitations Accompanying Solvent-Controlled Electron Transfer Reactions. *J. Chem. Phys.* **1988**, *88*, 167. [CrossRef]
13. Bixon, M.; Jortner, J. *Electron Transfer—From Isolated Molecules to Biomolecules, Part One*; John Wiley & Sons: New York, NY, USA, 1999; Volume 106.
14. Zusman, L.D. Outer-Sphere Electron Transfer in Polar Solvents. *Chem. Phys.* **1980**, *49*, 295. [CrossRef]
15. Sparpaglione, M.; Mukamel, S. Adiabatic vs. Nonadiabatic Electron Transfer and Longitudinal Solvent Dielectric Relaxation: Beyond the Debye Model. *J. Phys. Chem.* **1987**, *91*, 15. [CrossRef]
16. Ovchinnikova, M.Y. Teor. Eksp. Kim. *Theor. Exper. Chem.* **1982**, *17*, 507. [CrossRef]
17. Borrelli, R.; Peluso, A. The Temperature Dependence of Radiationless Transition Rates from Ab Initio Computations. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4420–4426. [CrossRef]
18. Schenck, C.; Parson, W.; Holten, D.; Windsor, M.W.; Sarai, A. Temperature Dependence of Electron Transfer Between Bacteriopheophytin and Ubiquinone in Protonated and Deuterated Reaction Centers of *Rhodopseudomonas shaeroides*. *Biophys. J.* **1981**, *36*, 479–489. [CrossRef]
19. Kirmaier, C.; Holten, D.; Parson, W.W. Temperature and Detection-Wevelenght Dependence of the Picosecond Electron-Transfer Kinetics Mesured in *Rhodopseudomonas shaeroides* Reaction Centers. Resolution of New Spectral and Kinetic Components in the Primary Charge-Separation Process. *Biochim. Biophys. Acta Bioenerg.* **1985**, *810*, 33–48. [CrossRef]
20. Leo, A.; Peluso, A. Electron Transfer Rate in Polar and Non-Polar Environments: A Generalization of Marcus' Theory to Include an Effective Treatment of Tunneling Effects. *J. Phys. Chem. Lett.* **2022**, *13*, 9148–9155. [CrossRef]
21. Landi, A.; Borrelli, R.; Capobianco, A.; Peluso, A. Transient and Enduring Electronic Resonances Drive Coherent Long Distance Charge Transport in Molecular Wires. *J. Phys. Chem. Lett.* **2019**, *10*, 1845–1851.
22. Landi, A.; Capobianco, A.; Peluso, A. Coherent Effects in Charge Transport in Molecular Wires: Toward a Unifying Picture of Long-Range Hole Transfer in DNA. *J. Phys. Chem. Lett.* **2020**, *11*, 7769–7775.
23. Peluso, A.; Caruso, T.; Landi, A.; Capobianco, A. The Dynamics of Hole Transfer in DNA. *Molecules* **2019**, *24*, 4044. [CrossRef]
24. Landi, A.; Capobianco, A.; Peluso, A. The Time Scale of Electronic Resonance in Oxidized DNA as Modulated by Solvent Response: An MD/QM-MM Study. *Molecules* **2021**, *26*, 5497. [CrossRef]
25. Kubo, R.; Toyozawa, Y. Application of the Method of Generating Function to Radiative and Non-Radiative Transitions of a Trapped Electron in a Crystal. *Prog. Theor. Phys.* **1955**, *13*, 160–182. [CrossRef]
26. Lax, M. The Franck-Condon Principle and Its Application to Crystals. *J. Chem. Phys.* **1952**, *20*, 1752–1760. [CrossRef]

27. Closs, G.L.; Calcaterra, L.T.; Green, N.J.; Penfield, K.W.; Miller, J.R. Distance, Stereoelectronic Effects, and the Marcus Inverted Region in Intramolecular Electron Transfer in Organic Radical Anions. *J. Chem. Phys.* **1989**, *90*, 3673–3683. [CrossRef]
28. Liang, N.; Miller, J.R.; Closs, G.L. Correlating Temperature Dependence to Free Energy Dependence of Intramolecular Long-Range Electron Transfer. *J. Am. Chem. Soc.* **1989**, *11*, 8740–8741. [CrossRef]
29. Parson, W.W. Effects of Free Energy and Solvent on Rates of Intramolecular Electron Transfer in Organic Radical Anions. *J. Phys. Chem. A* **2017**, *121*, 7297–7306.
30. Parson, W.W. Vibrational Relaxations and Dephasing in Electron-Transfer Reactions. *J. Phys. Chem.* **2016**, *120*, 11412–11418.
31. Parson, W.W. Electron-Transfer Dynamics in a Zn-Porphyrin-Quinone Cyclophane: Effects of Solvent, Vibrational Relaxations, and Conical Intersections. *J. Phys. Chem. B* **2018**, *122*, 3854–3863.
32. Parson, W.W. Temperature Dependence of the Rate of Intramolecular Electron Transfer. *J. Phys. Chem. B* **2018**, *122*, 8824–8833.
33. Mahan, B.H. Microscopic Reversibility and Detailed Balance. *J. Chem. Educ.* **1975**, *52*, 299–302. [CrossRef]
34. Hopfield, J.J. Electron transfer between biological molecules by thermal activated tunneling. *Proc. Natl. Acad. Sci. USA* **1974**, *71*, 3640–3644. [CrossRef] [PubMed]
35. Borrelli, R.; Peluso, A. Elementary Electron Transfer Reactions: From Basic Concepts to Recent Computational Advances. *WIREs: Comput. Mol. Sci.* **2013**, *3*, 542–559. [CrossRef]
36. Rabalais, J.W.; Karlsson, L.; Werme, L.O.; Bergmark, T.; Siegbahn, K. Analysis of Vibrational Structure and Jahn-Teller Effects in the Electron Spectrum of Ammonia. *J. Chem. Phys.* **1973**, *58*, 3370–3372.
37. Wang, X.B.; Woo, H.K.; Wang, L.S. Vibrational Cooling in a Cold Ion Trap: Vibrationally Resolved Photoelectron Spectroscopy of Cold $C60^-$ Anions. *J. Chem. Phys.* **2005**, *123*, 051106.
38. Capobianco, A.; Carotenuto, M.; Caruso, T.; Peluso, A. The Charge-Transfer Band of an Oxidized Watson-Crick Guanosine-Cytidine Complex. *Angew. Chem. Int. Ed.* **2009**, *48*, 9526–9528. [CrossRef]
39. Niu, Y.; Peng, Q.; Deng, C.; Gao, X.; Shuai, Z. Theory of Excited State Decays and Optical Spectra: Application to Polyatomic Molecules. *J. Phys. Chem. A* **2010**, *114*, 7817–7831. [CrossRef] [PubMed]
40. Santoro, F.; Lami, A.; Improta, R.; Bloino, J.; Barone, V. Effective Method for the Computation of Optical Spectra of Large Molecules at Finite Temperature Including the Duschinsky and Herzberg-Teller Effect: The Q_x Band of Porphyrin as A Case Study. *J. Chem. Phys.* **2008**, *128*, 224311. [CrossRef]
41. Capobianco, A.; Borrelli, R.; Landi, A.; Velardo, A.; Peluso, A. Absorption Band Shapes of a Push-Pull Dye Approaching the Cyanine Limit: A Challenging Case for First Principle Calculations. *J. Phys. Chem. A* **2016**, *120*, 5581–5589. [CrossRef]
42. Peluso, A.; Borrelli, R.; Capobianco, A. Photoelectron Spectrum of Ammonia, a Test Case for the Calculation of Franck–Condon Factors in Molecules Undergoing Large Geometrical Displacements upon Photoionization. *J. Phys. Chem. A* **2009**, *113*, 14831–14837. [CrossRef]
43. Landi, A.; Landi, A.; Velardo, A.; Peluso, A. Efficient Charge Dissociation of Triplet Excitons in Bulk Heterojunction Solar Cells. *ACS Appl. Energy Mater.* **2022**, *5*, 10815–10824. [CrossRef]
44. Landi, A.; Padula, D. Multiple Charge Separation Pathways in New-Generation Non-Fullerene Acceptors: A Computational Study *J. Mater. Chem. A* **2021**, *9*, 24849–24856. [CrossRef]
45. Velardo, A.; Borrelli, R.; Capobianco, A.; Landi, A.; Peluso, A. Disentangling Electronic and Vibrational Effects in the Prediction of Band Shapes for Singlet-Triplet Transitions. *J. Phys. Chem. C* **2019**, *123*, 14173–14179. [CrossRef]
46. Marcus, R.A. Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. II. *J. Chem. Phys.* **1956**, *24*, 979–989.
47. Matyushov, V.D. Solvent Reorganization Energy of Electron-Transfer Reactions in Polar Solvent. *J. Chem. Phys.* **2004**, *120*, 7532–7556. [CrossRef]
48. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16 Revision C.01*; Gaussian Inc.: Wallingford, CT, USA, 2016.
49. Kim, K.; Jordan, K.D. Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer. *J. Phys. Chem.* **1994**, *98*, 10089–10094. [CrossRef]
50. Stephens, P.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627. [CrossRef]
51. Cramer, C.J. *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; John Wiley & Sons: New York, NY, USA, 2004
52. Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic Interaction of a Solute with a Continuum. A Direct Utilization of Ab Initio Molecular Potentials for the Prevision of Solvent effects. *Chem. Phys.* **1981**, *55*, 117–129. [CrossRef]
53. Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999–3094. [CrossRef]
54. Matyushov, D. Software Package for the Solvation Thermodynamics of Biomolecules. 2007. Available online: https://skysonginnovations.com/technology/software-package-for-the-solvation-thermodynamics-of-biomolecules/ (accessed on 16 December 2022).
55. Singh, U.C.; Kollman, P.A. An Approach to Computing Electrostatic Charges for Molecules. *J. Comput. Chem.* **1984**, *5*, 129–145. [CrossRef]
56. Capobianco, A.; Borrelli, R.; Noce, C.; Peluso, A. Franck-Condon Factors in Curvilinear Coordinates: The Photoelectron Spectrum of Ammonia. *Theor. Chem. Acc.* **2012**, *131*, 1181. [CrossRef]

57. Dormand, J.R.; Prince, P.J. A Family of Embedded Runge-Kutta Formulae. *J. Comput. Appl. Math.* **1980**, *6*, 19–26. [CrossRef]
58. Simon, J.D. Time-Resolved Studies of Solvation in Polar Media. *Res. Chem. Acc.* **1988**, *21*, 128–134. [CrossRef]
59. Liang, N.; Miller, J.R.; Closs, G.L. Temperature-Independent Long-Range Electron Transfer Reactions in the Marcus Inverted Region. *J. Am. Chem. Soc.* **1990**, *112*, 5353–5354. [CrossRef]
60. Metz, D.J.; Glines, A. Density, Viscosity and Dielectric Constant of Tetrahydrofuran Between -78 and 30. *J. Chem. Phys.* **1966**, *11973*. [CrossRef]