Anomalous (Exergonic) Behavior in the Transfer of Electrons between Donors and Acceptors: Mobility, Energy, Caloric Capacity, and Entropy

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ABSTRACT: Understanding the kinetics of electron transfer reactions involves active research in physics, chemistry, biology, and nano-tech. Here, we propose a model to apply in a broader framework by establishing a connection between thermodynamics and kinetics. From a purely thermodynamic point of view, electronic transfer Marcus' theory is revisited; consequently, calculations of thermodynamic variables such as mobility, energy, and entropy are provided. More significantly, two different regimes are explicitly established. In the anomalous region, an exergonic process associated with negative heat capacity appears. Further, in the same region, mobility, energy, and entropy decrease when the temperature increases.

Predicted two-regimes behavior of electron transfer

From the standard Marcus-type expression for electron transfer rate:
$$\frac{\hbar}{\tau} = \sqrt{\pi} H^2 \frac{1}{\sqrt{\lambda k_B T}} e^{\frac{-1}{4\lambda k_B T}(G+\lambda)^2},$$
where $K_{ET} = 1/\tau$, by defining a dimensionless temperature,
$$t = 4\lambda k_B T/(G+\lambda)^2$$

We found the well-known two-regimes behavior of Marcus rate for the dimensionless mobility μ/μ_0, energy E, and entropy s/s_0 thermodynamic variables.

$\mu/\mu_0 = \sqrt{t}e^{1/t}$ $E = e^{-1/t}/\sqrt{t}$ $s/s_0 = \frac{2(4+2t+t^2)e^{-2/t}}{t^2}$

1. INTRODUCTION

Electron transfer (ET) occurs in many phenomena in nature, such as the processes of photosynthesis, light harvesting in solar cells, and oxidation−reduction reactions in biology and chemistry.[1−4] Several approaches have been proposed to understand the kinetics of ET-based reactions, and one of the most important is the theory developed by Marcus.[1−14]

Generally, Marcus' phenomenological theory considers ET between electron-donor and electron-acceptor species in a finite system.[1−3] That is, an open system with two sub-systems exchanging charges, while the surrounding environment is reorganized (solvent sheath of ligands and/or adjacent free solvent), and their individualities are retained. Although ET is basically a quantum phenomenon, the environment influences the reaction because it modulates the electron jump. This formulation has been improved and extended gradually to describe a wide variety of reactions, such as reactions between ions or molecules and electrodes, photoelectric emission spectra of ionic solutions, chemiluminescent ETs, ET through frozen media, and ET through thin hydrocarbon-like films on electrodes, among others.[15−19] In fact, it is a transport theory for mesoscopic systems.[20] Marcus' theory allows us to evaluate the rate k_{ET} of reactions, which involves both static and dynamic effects.[5−8] Static effects such as stabilization of reactants, products, and dynamic effects correspond to relaxations of nuclear and solvent modes.

The k_{ET} rate depends on quantities that can be computed or determined experimentally (free energy, reorganizational energy, and electronic coupling). The electronic coupling process becomes a relevant variable because it describes the adiabatic or non-adiabatic nature of the reactions. The non-adiabatic regime corresponds to a small coupling, while large electronic coupling accounts for adiabatic transfer. In this work, from a purely thermodynamic point of view, electronic transfer Marcus' theory is revisited, consequently, calculations of thermodynamic variables such as mobility, energy, entropy, and others are provided. More importantly, two different regimes are explicitly established (normal and anomalous). Novelties such as negative heat capacity or mobility decreasing with temperature, among others, also appear. The paper is structured as follows. Marcus' model is revisited in Section 2. The mobility for the normal and the anomalous region is described in Section 3. In addition, the corresponding threshold separating both regions is explicitly obtained. Provided that for an open quantum system, the lifetime-width is related to the energy through the uncertainty principle, the internal energy (Section 4), the partition function, the free energy, heat capacity, and entropy are calculated in Section 5. These magnitudes likewise display a threshold and split the thermodynamic behavior into a normal and anomalous regime. Finally, Section 6 presents conclusions and scopes.

2. MARCUS' THEORETICAL MODEL FOR ET

This theory can be derived through semiclassical expressions.[21] In this context, the relaxation time τ is given by[1−3]

$$\frac{\hbar}{\tau} = \frac{\sqrt{\pi}H^2}{\sqrt{\lambda k_B T}}e^{-(G+\lambda)^2/4\lambda k_B T} \qquad (1)$$

where the apparition of Planck's constant $\hbar$ and temperature T tells us that the electronic motion is linked to quantum decoherence. The Gibbs free energy G is the driving force for the reaction, and the reorganizational energy λ corresponds to the required rearrangement of the reactants and solvents. The reorganization energy is composed of two terms: internal reorganization energy, λ_i, which accounts for the change in the bond angles and bond lengths, and external reorganization energy, λ_s, which considers the energy of the solvent shell for the required rearrangement.[13] Finally, the superposition between the donor and acceptor wave functions is described by the electronic energy coupling H or degree of quantum mechanical mixing.

Regarding eq 1, the reaction rate, $k_{ET} = 1/\tau$, is maximum when the free energy of activation $E_A \propto (G + \lambda)^2$ is minimum $(G = -\lambda)$. Figure 1a shows the dependence for k_{ET} as a
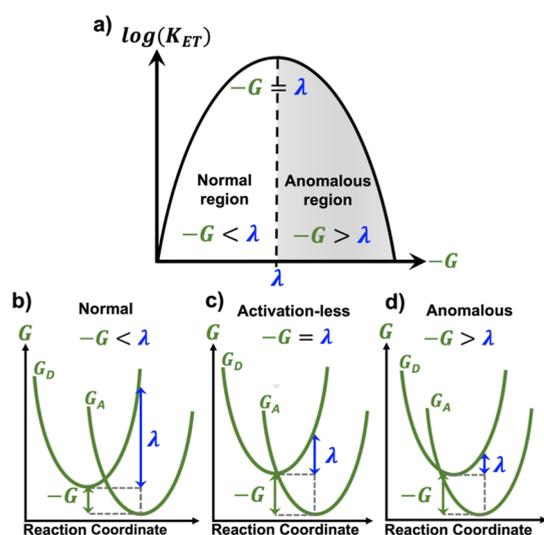
Figure 1. (a) Dependence between the logarithm of the reaction rate k_{ET} as a function of Gibbs free energy G eq 1. The lower panels show the Gibbs free energy curves at (b) the normal region $-G < \lambda$, (c) activationless region $(G = \lambda)$, and (d) anomalous region $-G > \lambda$ with spontaneous energy emission (no barrier between both minimum).

function of free energy G. The magnitudes of G and λ determine three situations for the transfer process. The lower panels represent the Gibbs free energy curves of the donor G_D and the acceptor G_A corresponding to the three expected situations: (b) the normal regime, when $-G < \lambda$, in which k_{ET} increases when the energy $-G$ goes up. (c) The "activation-less" region (maximum k_{ET}) corresponding to the top of the curve of panel (a) satisfies the condition $(G = -\lambda)$. Lastly, (d), an interesting anomalous regime occurs when $-G > \lambda$, in which the reaction becomes slower as $-G$ goes up. This regime, called the Marcus inverted region,[13] has been experimentally verified for long-distance intermolecular ET reactions.[22−24] The reaction coordinate (x axis) takes into account the energy difference between the donor and acceptor structure. The greater the difference in structure, the greater

the displacement of the energy curves. Furthermore, as the energy barrier also increases with the displacement of the energy curves, the slower the reaction.

Finally, estimations based on eq 1 commonly underestimate the rate transfer in the inverted region. The previously proposed model, as Marcus−Jortner−Levich theory, overcame some of the limitations of the original Marcus' model by separating the internal and external reorganization energy and by explicitly including the contribution from the vibronic coupling between the reactant and product state.[25]

3. MOBILITY: NORMAL AND ANOMALOUS BEHAVIOR

Mobility μ is a key factor that characterizes charge transport. Several models have been proposed to describe the carrier drift in materials.[26−29] In the hopping model, which dominates at room temperature, mobility can be connected with the diffusion constant through Einstein's relation.[30] In the standard band theory model, which is suitable for ordered systems at low temperatures, the transport behavior is governed by the Boltzmann equation which can be solved using relaxation-time approximation.[31] In this case, the mobility derived according to first principles[32−42] is $\mu = q\tau/m^*(H)$, where q is the electrical charge, τ is the average relaxation time, and $m^*(H)$ is the effective mass which depends proportionally on the hopping transport.[29,43] Besides, the electronic mobility can be related to the conductivity through the Landauer equation[44,45] by using the Einstein relation between conductivity and diffusion.[46,47] Therefore, from eq 1, the electronic mobility becomes

$$\mu = \frac{q\hbar}{m^*\sqrt{\pi}H^2}\sqrt{\lambda k_B T}\,e^{(G+\lambda)^2/4\lambda k_B T} \qquad (2)$$
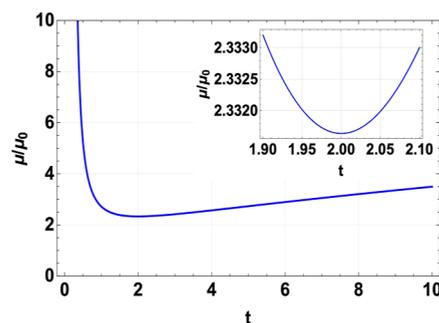
Figure 2. Dimensionless mobility μ/μ_0 as a function of the dimensionless temperature $t = 4\lambda k_B T/(G + \lambda)^2$ and the mobility parameter $\mu_0 = (q\hbar/m^*\sqrt{\pi}H^2)|(G + \lambda)|/2)$. Two regions exist depending on the temperature. In the first one, the mobility drops when the temperature increases (normal regime). In the second, the mobility rises when the temperature grows (anomalous). The inset shows an amplification around the threshold red point $t_c = 2$.

Figure 2 shows the dimensionless mobility μ/μ_0 [where $\mu_0 = (q\hbar/m^*\sqrt{\pi}H^2)|G + \lambda|/2]$ as a function of the dimensionless temperature $t = 4\lambda k_B T/(G + \lambda)^2$. The more relevant topic is the apparition of two regimes depending on temperature. These two behaviors also exist for other quantities such as energy, specific heat, and additional

thermodynamic functions (Sections 4 and 5). Figure 2 inset shows an amplification around the threshold point $t_c = 2$.

In this way, there is a singular point t_c separating two kinds of thermodynamic behaviors:

- For temperatures $t < t_c$ the mobility decreases with the temperature (normal behavior).
- When $t > t_c$ the mobility rises with the temperature (anomalous). Also expected for electronic conductivity.

As mentioned, two regimes will likewise be deducted for other thermodynamic quantities. Chiefly, it will be also true for the specific heat with two branches (positive and negative[48−61]). The negative branch is related to exergonic processes as it will be discussed in detail in the next section.

Finally, the charge transport properties of conjugated small molecules/polymers are relevant parameters to evaluate their performance in organic optoelectronic applications.[62,63] Indeed, the molecular parameters H and λ become of paramount importance for high charge transport ability. Several studies have shown that the combination of density functional theory (DFT), with Marcus' theory and the Einstein−Smoluchowski equation, allows the prediction of the mobility of positive and negative charge carriers in conjugated systems.[64−67] Although comparable results have been obtained between predicted mobilities and experimental measurements, the computational cost of DFT calculations increases significantly as systems become more complex. In this sense, eq 2 allows estimating the charge mobility more simply. As an example, we have estimated the hole mobility μ for two typical π-electronic core organic semiconductors, the pentacene ($C_{22}H_{14}$)[68,69] and the rubrene ($C_{42}H_{28}$).[70−72] These semiconductors present a negative temperature coefficient of the mobility ($d\mu/dT < 0$) under ambient conditions, which can be considered as a fingerprint of the "band-like" transport behavior.[73] The room-temperature hole mobilities obtained by eq 2 gives values of order of units $cm^2/(V\ s)$ (see Supporting Information, Figure S2), which are in good agreement with the reported data for pentacene[69,74−76] and rubrene.[70,72,74] Let us remark that the effective mass is not a quantity that can be easily experimentally determined which makes the estimation of μ_0 complicated. However, the effective mass can be obtained by the analytical description $m^* = -\hbar^2/(\partial^2\epsilon(\mathbf{k})/\partial\mathbf{k}^2)$, where $\epsilon(\mathbf{k})$ are the eigenvalues, and $\mathbf{k}$ is the wavevector.[77−80]

4. INTERNAL ENERGY AND NEGATIVE SPECIFIC HEAT

It is well known that for quantum systems, the lifetime-width, out of the stationary regime, and the representative spread spectrum E (or level width) can be connected through[81−83]

$$\tau E \approx \hbar \tag{3}$$

which can be seen as a fluctuation−dissipation relation.[32−36] Consequently, eqs 1 and 3 give the energy estimation as a function of temperature

$$E = \frac{\sqrt{\pi} H^2}{\sqrt{\lambda k_B T}} e^{-(G+\lambda)^2/4\lambda k_B T} \tag{4}$$

with a two-regime behavior as a function of temperature, as shown in Figure 3. Namely, it is analogous to the mentioned case of mobility. Importantly, from eq 4, we can also obtain the variation of the energy at a constant temperature

$$\frac{\partial E}{\partial G} \propto -(G + \lambda) \tag{5}$$
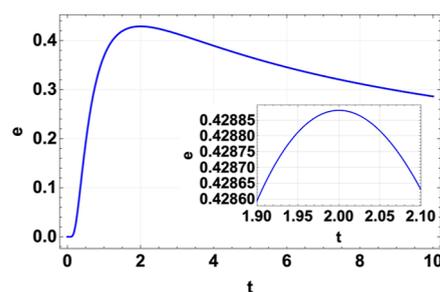
Figure 3. Dimensionless energy $e = E(G + \lambda)/(2\sqrt{\pi} H^2)$ as a function of normalized temperature $t = 4\lambda k_B T/(G + \lambda)^2$ [i.e., $e = \exp(-1/t)/\sqrt{t}$]. There are two behaviors, or regimes, as occurs with mobility (Figure 2). In the anomalous region $t > 2$, the specific heat $c = \partial E \partial T$ becomes negative and compatible with spontaneous energy loss (exergonic process).

hence, in the anomalous regime $(G + \lambda) < 0$ (Figure 1) and for spontaneous process $\Delta G < 0$ there is energy emission $\Delta E < 0$ (exergonic process).

Specific heat $c = \partial E/\partial T$[32−35] presents negative values[48−61] in the anomalous regime ($t > 2$, Figure 3). Usually, a negative specific heat is associated with non-isolated subsystems composing a system.[33,50] Always at the anomalous regime, a diminution of the dimensionless energy $\Delta e < 0$ is encompassed by an augmentation of Δt (Figure 3), but as long as $t = 4\lambda k_B T/(G + \lambda)^2$ a variation $\Delta t \propto -\Delta G$ ensues. Accordingly, if $\Delta t < 0$ then $\Delta G < 0$, also corresponding to the mentioned exergonic behavior in the region of negative specific heat (i.e., the system loses spontaneously energy, $\Delta e < 0$).

5. PARTITION FUNCTION, FREE ENERGY, AND ENTROPY

At this stage, it is convenient to use so-called activation energy E_A[1−3] related to energy E by

$$E_A = \frac{E^2}{2\lambda} \tag{6}$$

which measures transport difficulties through a potential barrier. As long as the activation energy E_A and the partition function Z are connected through $E_A = \partial/\partial\beta \ln(Z)$ [with $\beta = 1/(k_B T)$],[32−35] it follows

$$\ln(Z) = \frac{2\pi H^4}{(G + \lambda)^2}\left(\frac{1}{2\lambda k_B T} + \frac{1}{(G + \lambda)^2}\right)e^{-(G+\lambda)^2/2\lambda k_B T} \tag{7}$$

which, from eq 6, gives the expression for the energy E described by (eq 4). Helmholtz free energy $F = -\ln(Z)/\beta$ becomes related to the entropy S through the usual expression $F = EA - TS$, but in terms of the energy E it must be modified as

$$F = \frac{E^2}{2\lambda} - TS \tag{8}$$

In this way, the entropy $S = \partial F/\partial T$ becomes evaluated as

$$S = k_B \pi H^4\left(\frac{2}{(G + \lambda)^4} + \frac{1}{2\lambda^2 k_B T}\left(\frac{1}{k_B T} + \frac{2\lambda}{(G + \lambda)^2}\right)\right)$$
$$e^{-(G+\lambda)^2/(2\lambda k_B T)} \tag{9}$$

which as Figure 4 shows also presents a two-regime behavior with a singular point at $t_c = 2$.
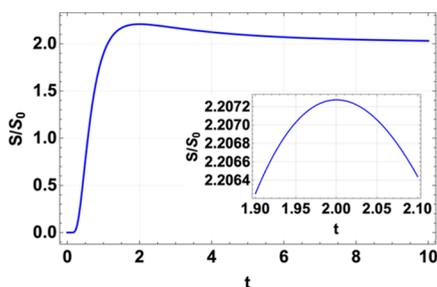
Figure 4. Dimensionless entropy $S = 2S_0((4 + 2t + t^2)/t^2)e^{-2/t}$ as a function of dimensionless temperature $t = 4\lambda k_B T/(G + \lambda)^2$, where $S_0 = \pi H^4 k_B/(G + \lambda)^4$ is an auxiliary parameter. There are two behaviors, or regimes, as occurs with mobility and energy (Figures 2 and 3). In the anomalous regime, encompassed by an exergonic behavior, the system tends to weak order. The inner figure shows the entropy function around $t_c = 2$ corresponding to a maximum.

The importance of the entropy function is related to the second principle of thermodynamics defining irreversibility as it agrees with a dissipative system. The core of the ET mechanism is associated with dissipation and consequently related to conductance or mobility (Section 3). On the other hand, the entropy function can be associated with the degree of the disorder[32-35] and, in the anomalous regime ($t < 2$), it diminishes when the dimensionless temperature rises. Consequently, a (weak) degree of order in this singular regime can be expected.

Figure 4 exhibits the entropy as a function of dimensionless temperature t. In the normal regime ($t < 2$), the entropy grows with temperature. Conversely, in the anomalous regime ($t > 2$), the entropy slightly decreases when the temperature rises. Finally, and formally, when $t \to 0$ the entropy goes to zero (Nernst principle[32]) and at the limit of large temperature $t \to \infty$ the entropy goes to a constant.

6. CONCLUSIONS

Open incoherent/dissipative electronic transport between two sub-systems (donor/acceptor) has been widely discussed through Marcus' theory of ET. This scheme gives the relaxation rate of electronic motion as a function of temperature and appropriate energy parameters (eq 1). It becomes connected to mobility (eq 1, Figure 2) and supports two regimes, normal and anomalous. In the normal regime, mobility decreases with the temperature and likewise the electrical conductivity and, probably, the thermal conduction. Conversely, in the anomalous regime, mobility rises with the temperature. Additionally, the threshold between both regimes was explicitly evaluated. Although comparable results have been obtained between predicted mobilities and experimental measurements, the computational cost of DFT calculations increases significantly as systems become more complex. In this sense, our outcomes allow estimating the charge transport properties in a simpler and less computationally expensive way. From the usual connection between energy and relaxation time eq 3, the thermal energy of the system emerges. It retains clearly, similar to mobility, a two-regime behavior (Figure 3). Even more interesting, in the anomalous regime, the specific heat becomes negative, and spontaneous energy loss exists (exergonic process). Free energy and entropy also were

evaluated showing the same two behaviors. For entropy, Figure 4, the temperature augmentation is encompassed by entropy diminution in the anomalous case. Moreover, always in this region, the system becomes tiny ordered. Entropy, energy, and mobility have (dimensionless) temperature thresholds. Finally, in future works, we expect to connect our results with experiments on electronic transport in more complex organic molecules.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04094.

> Brief connection with experimental and theoretical data and estimation of hole transfer rates k_{ET} and hole mobility μ as a function of the temperature for pentacene ($C_{22}H_{14}$) and rubrene ($C_{42}H_{28}$) (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* **1993**, *65*, 599−610.

(2) Blumberger, J. Recent Advances in the Theory and Molecular Simulation of Biological Electron Transfer Reactions. *Chem. Rev.* **2015**, *115*, 11191−11238.

(3) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y. Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. Photoinduced electron transfer to C60 across extended 3- and 11-bond hydrocarbon bridges: Creation of a long-lived charge-separated state. *J. Org. Chem.* **1996**, *61*, 5055−5062.

(4) Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology: An Introduction to the Theory*; John Wiley & Sons Ltd., 1999.

(5) Jortner, J. Temperature dependent activation energy for electron transfer between biological molecules. *Chem. Phys.* **1976**, *64*, 4860−4867.

(6) Gray, H. B. Long-range electron transfer. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 3534−3539.

(7) Barthel, E. R.; Martini, I. B.; Schwartz, B. J. How Does the Solvent Control Electron Transfer? Experimental and Theoretical

Studies of the Simplest Charge Transfer Reaction. *J. Phys. Chem. B* **2001**, *105*, 12230−12241.

(8) Skourtis, S. S.; Waldeck, D. H.; Beratan, D. N. Fluctuations in Biological and Bioinspired Electron-Transfer Reactions. *J. Electroanal. Chem.* **2010**, *61*, 461−485.

(9) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *Chem. Phys.* **1956**, *24*, 966−978.

(10) Marcus, R. A. Tutorial on rate constants and reorganization energies. *J. Electroanal. Chem.* **2000**, *483*, 2−6.

(11) Marcus, R. A. Exchange reactions and electron transfer reactions including isotopic exchange. Theory of oxidation-reduction reactions involving electron transfer. Part 4.—A statistical-mechanical basis for treating contributions from solvent, ligands, and inert salt. *Annu. Rev. Phys. Chem.* **1960**, *29*, 21−31.

(12) Marcus, R. A. Chemical and Electrochemical Electron-Transfer Theory. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155−196.

(13) Marcus, R. A.; Sutin, N. Electron transfers in chemistry and biology. *Biochim. Biophys. Acta, Rev. Bioenerg.* **1985**, *811*, 265−322.

(14) Peters, B. Common features of extraordinary rate theories. *J. Phys. Chem. B* **2015**, *119*, 6349−6356.

(15) Libby, W. F. Theory of Electron Exchange Reactions in Aqueous Solution. *J. Phys. Chem.* **1952**, *56*, 863−868.

(16) Small, D. W.; Matyushov, D. V.; Voth, G. A. The Theory of Electron Transfer Reactions What May Be Missing. *J. Am. Chem. Soc.* **2003**, *125*, 7470−7478.

(17) Matyushov, D. V.; Voth, G. A. Modeling the free energy surfaces of electron transfer in condensed phases. *Chem. Phys.* **2000**, *113*, 5413−5424.

(18) Matyushov, D. V.; Voth, G. A. New Developments in the Theoretical Description of Charge Transfer Reactions in Condensed Phases. *J. Am. Chem. Soc.* **2003**, *18*, 147−210.

(19) LeBard, D. N.; Matyushov, D. V. Glassy Protein Dynamics and Gigantic Solvent Reorganization Energy of Plastocyanin. *J. Phys. Chem. B* **2008**, *112*, 5218−5227.

(20) Bueno, P. R.; Benites, T. A.; Davis, J. J. The Mesoscopic Electrochemistry of Molecular Junctions. *Sci. Rep.* **2016**, *6*, 18400.

(21) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. Contemporary Issues in Electron Transfer Research. *J. Phys. Chem.* **1996**, *100*, 13148−13168.

(22) Piechota, E. J.; Meyer, G. J. Introduction to Electron Transfer: Theoretical Foundations and Pedagogical Examples. *J. Chem. Educ.* **2019**, *96*, 2450−2466.

(23) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. Intramolecular long distance electron transfer in radical anions. The effects of free energy and solvent on the reaction rates. *J. Am. Chem. Soc.* **1984**, *106*, 3047−3049.

(24) Imahori, H.; Tamaki, K.; Guldi, D.; Luo, C. P.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. Modulating Charge Separation and Charge Recombination Dynamics in Porphyrin-Fullerene Linked Dyads and Triads: Marcus-Normal versus Inverted Region. *J. Am. Chem. Soc.* **2001**, *123*, 2607−2617.

(25) Chaudhuri, S.; Hedström, S.; Méndez-Hernández, D. D.; Hendrickson, H. P.; Jung, K. A.; Ho, J.; Batista, V. S. Electron Transfer Assisted by Vibronic Coupling from Multiple Modes. *J. Chem. Theory Comput.* **2017**, *13*, 6000−6009.

(26) Takeuchi, E.; Muramatsu, M.; Yoneda, Y.; Katayama, T.; Iwamoto, A.; Nagasawa, Y.; Miyasaka, H. Vibrational decoherence induced by ultrafast intramolecular charge separation of an asymmetric bianthryl derivative. *J. Chem. Phys.* **2020**, *153*, 84307.

(27) Deng, W.-Q.; Goddard, W. A. Predictions of Hole Mobilities in Oligoacene Organic Semiconductors from Quantum Mechanical Calculations. *J. Phys. Chem. B* **2004**, *108*, 8614−8621.

(28) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. Charge Transport in Organic Semiconductors. *Chem. Rev.* **2007**, *107*, 926−952.

(29) Zhao, S.; Yu, F.; Yang, G.; Zhang, H.; Su, Z.; Wang, Y. Theoretical study on the charge transport property of Pt(CNtBu)-2(CN)2 nanowires induced by Pt-Pt interactions. *Dalton Trans.* **2012**, *41*, 7272−7277.

(30) Schein, L. B.; McGhie, A. R. Band-hopping mobility transition in naphthalene and deuterated naphthalene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1979**, *20*, 1631−1639.

(31) Bassani, G. F.; Liedl, G. L.; Wyder, P. *Encyclopedia of Condensed Matter Physics*; Elsevier: Amsterdam, 2005.

(32) Huang, K. *Statistical Mechanics*, 2nd ed.; Wiley and Sons, 1987.

(33) Landau, L. D.; Lifschitz, E. M. *Statistical Mechanics*; Elsevier, 2005.

(34) Morikazu, T.; Kubo, R.; Saitô, N. *Statistical Physics I Equilibrium Statistical Mechanics*; Springer Berlin Heidelberg, 1983.

(35) Feynman, R. *Statistical Mechanics*; CRC Press, 1998.

(36) Pathria, R.; Beale, P. D. *Statistical Mechanics*, 4th ed.; Academic Press, 2009.

(37) Economou, E. N. *The Physics of Solids: Essentials and Beyond*; Springer: Berlin, Heidelberg, 2010.

(38) Galbiati, M.; Motta, N.; De Crescenzi, M.; Camilli, L. Group-IV 2D materials beyond graphene on nonmetal substrates: Challenges, recent progress, and future perspectives. *Appl. Phys. Rev.* **2019**, *6*, 41310.

(39) Kittel, C. *Introduction to Solid State Physics*; John Wiley & Sons: New York, 1986.

(40) Madelung, O. *Introduction to Solid State Physics*; Springer Berlin Heidelberg, 1978.

(41) Ashcroft, N. W.; Mermin, N. *Solid State Physics*; Holt, Rinehart & Winston, 2002.

(42) Anderson, P. W. *Concepts in Solids: Lectures on the Theory of Solids*; World Scientific: Singapore, 1997.

(43) Hutchison, G. R.; Zhao, Y.-J.; Delley, B.; Freeman, A. J.; Ratner, M. A.; Marks, T. J. Electronic structure of conducting polymers: Limitations of oligomer extrapolation approximations and effects of heteroatoms. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 35204.

(44) Landauer, R. Electrical resistance of disordered one-dimensional lattices. *The Philosophical Magazine: J. Theor. Appl. Phys.* **1970**, *21*, 863−867.

(45) Economou, E. N.; Soukoulis, C. M. Static Conductance and Scaling Theory of Localization in One Dimension. *Phys. Rev. Lett.* **1981**, *46*, 618−621.

(46) Enz, C. P.; Flores, J. C. Localization and cross-over in linear models of random arrays of barriers. *Helv. Phys. Acta* **1988**, *61*, 1079−1086.

(47) Enz, C. P. A. *Course on Many-Body Theory Applied to Solid-State Physics*; World Scientific, 1992.

(48) Thirring, W. Systems with Negative Specific Heat. *Phys. Z.* **1970**, *235*, 339−352.

(49) Berry, R.; Smirnov, B. Heat capacity of isolated clusters. *J. Exp. Theor. Phys.* **2004**, *98*, 366−373.

(50) Lynden-Bell, D.; Wood, R.; Royal, A. The gravo-thermal catastrophe in isothermal spheres and the onset of red-giant structure for stellar systems. *Mon. Not. Roy. Astron. Soc.* **1968**, *138*, 495−525.

(51) Schmidt, M.; Kusche, R.; Hippler, T.; Donges, J.; Kronmüller, W.; von Issendorff, B.; Haberland, H. Negative Heat Capacity for a Cluster of 147 Sodium Atoms. *Phys. Rev. Lett.* **2001**, *86*, 1191−1194.

(52) Eryurek, M.; Guven, M. H. Thermodynamic Properties of Ar39 Cluster. *AIP Conf. Proc.* **2007**, *899*, 171−172.

(53) Gross, D. H. E.; Kenney, J. F. The microcanonical thermodynamics of finite systems: The microscopic origin of condensation and phase separations, and the conditions for heat flow from lower to higher temperatures. *Chem. Phys.* **2005**, *122*, 224111.

(54) Kinoshita, M.; Yoshidome, T. Molecular origin of the negative heat capacity of hydrophilic hydration. *Chem. Phys.* **2009**, *130*, 144705.

(55) Serra, P.; Carignano, M. A.; Alharbi, F. H.; Kais, S. Quantum confinement and negative heat capacity. *Europhys. Lett.* **2013**, *104*, 16004.

(56) Chomaz, P.; Gulminelli, F. Phase Transition in Small System. *Nucl. Phys. A* **2005**, *749*, 3−13.

(57) Flores, J. C.; Palma-Chilla, L. Theoretical thermodynamics connections between Dual (Left-Handed) and Direct (Right Handed) systems: Entropy, temperature, pressure and heat capacity. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *476*, 88−90.

(58) Palma-Chilla, L.; Flores, J. Negative heat capacity in a left-handed system. *Phys. A* **2017**, *471*, 396−401.

(59) Velázquez, L.; Curilef, S. On the thermodynamic stability of macrostates with negative heat capacities. *J. Stat. Mech.: Theory Exp.* **2009**, *2009*, P03027.

(60) Staniscia, F.; Turchi, A.; Fanelli, D.; Chavanis, P. H.; De Ninno, G. Negative Specific Heat in the Canonical Statistical Ensemble. *Phys. Rev. Lett.* **2010**, *105*, 10601.

(61) Carignano, M. A.; Gladich, I. Negative heat capacity of small systems in the microcanonical ensemble. *Europhys. Lett.* **2010**, *90*, 63001.

(62) Shoaee, S.; Stolterfoht, M.; Neher, D. The Role of Mobility on Charge Generation, Recombination, and Extraction in Polymer-Based Solar Cells. *Org. Electron.* **2018**, *8*, 1703355.

(63) Serdiuk, I. E.; Mońka, M.; Kozakiewicz, K.; Liberek, B.; Bojarski, P.; Park, S. Y. Vibrationally assisted direct intersystem crossing between the same charge-transfer states for thermally activated delayed fluorescence: Analysis by Marcus Hush theory including reorganization energy. *J. Phys. Chem. B* **2021**, *125*, 2696−2706.

(64) Zhang, Y.; Li, Y.; Chen, C.; Wang, L.; Zhang, J. Design new hole transport materials for efficient perovskite solar cells by suitable combination of donor and core groups. *Org. Electron.* **2017**, *49*, 255−261.

(65) Qiu, M.; Pei, W.; Lu, Q.; Li, Z.; Li, Y.; Liang, J. DFT Characteristics of Charge Transport in DBTP-Based Hole Transport Materials. *Appl. Sci.* **2019**, *9*, 2244.

(66) Wang, Q.; Li, Y.; Song, P.; Su, R.; Ma, F.; Yang, Y. Non-Fullerene Acceptor-Based Solar Cells: From Structural Design to Interface Charge Separation and Charge Transport. *Polymers* **2017**, *9*, 692.

(67) Li, S.-B.; Duan, Y.-A.; Geng, Y.; Li, H.-B.; Zhang, J.-Z.; Xu, H.-L.; Zhang, M.; Su, Z.-M. A designed bithiopheneimide-based conjugated polymer for organic photovoltaic with ultrafast charge transfer at donor/PC71BM interface: theoretical study and characterization. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25799−25808.

(68) Zhang, X.; Yang, X.; Geng, H.; Nan, G.; Sun, X.; Xi, J.; Xu, X. Theoretical comparative studies on transport properties of pentacene, pentathienoacene, and 6,13-dichloropentacene. *J. Comput. Chem.* **2015**, *36*, 891−900.

(69) Fan, J.-X.; Chen, X.-K.; Zhang, S.-F.; Ren, A.-M. Theoretical Study on Charge Transport Properties of Intra- and Extra-Ring Substituted Pentacene Derivatives. *J. Phys. Chem. A* **2016**, *120*, 2390−2400.

(70) Delgado, M.; Kim, E. G.; Filho, D. A.; Bredas, J. L. Tuning the charge-transport parameters of perylene diimide single crystals via end and/or core functionalization: A density functional theory investigation. *J. Am. Chem. Soc.* **2010**, *132*, 3375−3387.

(71) da Silva Filho, D. A.; Kim, E. G.; Brédas, J. L. Transport properties in the rubrene crystal: Electronic coupling and vibrational reorganization energy. *Adv. Mater.* **2005**, *17*, 1072−1076.

(72) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. Elastomeric Transistor Stamps: Reversible Probing of Charge Transport in Organic Crystals. *Science* **2004**, *303*, 1644−1646.

(73) Sakanoue, T.; Sirringhaus, H. Band-like temperature dependence of mobility in a solution-processed organic semiconductor. *Synth. Met.* **2010**, *9*, 736−740.

(74) Shuai, Z.; Li, W.; Ren, J.; Jiang, Y.; Geng, H. Applying Marcus theory to describe the carrier transports in organic semiconductors: Limitations and beyond. *Chem. Phys.* **2020**, *153*, 80902.

(75) Geng, H.; Peng, Q.; Wang, L.; Li, H.; Liao, Y.; Ma, Z.; Shuai, Z. Toward quantitative prediction of charge mobility in organic semiconductors: Tunneling enabled hopping model. *Adv. Mater.* **2012**, *24*, 3568−3572.

(76) Harima, Y.; Kubota, K.; Ishiguro, Y.; Ooyama, Y.; Imae, I. Electrical Characteristics of Pentacene Films on Cross-Linked Polymeric Insulators of Varying Thicknesses. *ACS Omega* **2016**, *1*, 784−788.

(77) McKelvey, J. P. *Solid State and Semiconductor Physics*; Harper's Physics Series; Krieger Publishing Company, 1982.

(78) de Wijs, G. A.; Mattheus, C. C.; de Groot, R. A.; Palstra, T. T. Anisotropy of the mobility of pentacene from frustration. *Synth. Met.* **2003**, *139*, 109−114.

(79) Li, Z. Q.; Podzorov, V.; Sai, N.; Martin, M. C.; Gershenson, M. E.; Di Ventra, M.; Basov, D. N. Light quasiparticles dominate electronic transport in molecular crystal field-effect transistors. *Phys. Rev. Lett.* **2007**, *99*, 16403.

(80) Yamamoto, A.; Murata, Y.; Mitsui, C.; Ishii, H.; Yamagishi, M.; Yano, M.; Sato, H.; Yamano, A.; Takeya, J.; Okamoto, T. Zigzag-Elongated Fused π-Electronic Core: A Molecular Design Strategy to Maximize Charge-Carrier Mobility. *Adv. Sci.* **2018**, *5*, 1700317.

(81) Messiah, A. *Quantum Mechanics*; Dover Books on Physics Dover Publications, 2014.

(82) Gasiorowicz, S. *Quantum Physics*; John Wiley: New York, 2003.

(83) Landau, L. D. *Quantum Quantum Mechanics*, 3rd ed.; Pergamon, 1977.