EPH–International Journal of Science & Engineering
Published by: E-Pub Solutions Private Limited
ISSN (Online): **2454-2016**
Volume 12 Issue 04 November 2026
DOI:10.67772/8v1ejb50

THEORETICAL INVESTIGATION OF TEMPERATURE-DEPENDENT ELECTRON TRANSFER PROCESSES AT THE D102/SNO_2 SEMICONDUCTOR INTERFACE

Mohsin A. Hassooni

Department of Physics, College of Education for Pure Science-Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq. e-mail: mohsin.a@ihcoedu.uobaghdad.edu.iq

Article History:
Article Type: Research
Received Date: **25/06/2026**
Revised Date: **03/10/2026**
Accepted Date: **06/11/2026**
Published Date: **22/11/2026**

Keywords: temperature-dependent electron transfer, Marcus-Gerischer, Frank-Condon, acetonitrile, dimethyl sulfoxide.

ABSTRACT

This work aims to study the temperature-dependent electron transfer rate at the interface between the D102 dye and SnO_2 material within the framework of the Marcus-Gerischer model, by combining the Fermi golden rule, the Frank-Condon weighted density of states, and a connected treatment of the conduction band in SnO_2.The reorganization energy was calculated for five solvents methanol, acetonitrile, propylene carbonate, γ-butyrolactone, and dimethyl sulfoxide from their dielectric and refractive properties together with the relevant D102 and SnO_2 parameters, and ranges from 0.496 to 0.584 eV. The driving force is fixed at $\Delta G0 = -1.31$ eV by the offset between the D102 LUMO and the SnO_2 conduction-band edge, and does not vary with solvent.With this driving force and these reorganization energies, $|\Delta G0|/\Lambda$ADlies between 2.24 and 2.64 for every solvent studied, placing the D102/SnO_2 system in the Marcus inverted region rather than near the activationless condition. As a consequence, the rate calculation increases with reorganization energy instead of decreasing with it, so methanol gives the fastest rate and DMSO the slowest, by a factor of roughly 60 at 300 K. The rate (TDAE s^{-1}) scales exactly with the squared electronic coupling over the eightfold range examined, and rises with temperature by a factor of 2.4 to 3.5 between 300 and 330 K mainly through the temperature dependence of the Marcus exponential term.

Introduction

Dye-sensitized solar cells (DSSCs) are among the most extensively studied solar cells due to their low toxicity, cost-effectiveness, and ease of fabrication. However, since their emergence, these cells have still lacked significant development potential. While widely considered a strong candidate for converting solar energy into electricity at a low cost and long-term instability[1]..Electron transfer (ET) between a donor (D) and an acceptor (A) unit is one of the most fundamental elementary steps found across physics, chemistry, and biology, underlying the operation of organic semiconductors, nonlinear optical (NLO) materials, organic light-emitting diodes, and photovoltaic devices [2]. In donor-acceptor systems, the overall performance of the device is ultimately determined by the efficiency of the electron transfer from an excited or reduced donor state to an available acceptor state; making this charge transfer step a critical - not incidental - part of the electronic technology in question [3].Donor–acceptor charge-transfer chemistry has been explored across a wide range of molecular platforms, from organochalcogenide and quinone-based charge-transfer complexes [3,5] to dye-sensitized metal-oxide interfaces built for solar energy conversion. Within this latter class, wide-bandgap n-type oxides such as TiO_2 have long served as the standard electron-accepting semiconductor, but SnO_2 has more recently drawn attention as an alternative acceptor on account of its substantially higher electron mobility, which can support faster interfacial electron collection than TiO_2-based photoanodes [4]. Building on this interest, a number of computational strategies have been developed to evaluate the electron-transfer rate at such interfaces directly from the underlying Marcus kinetic framework rather than from empirical fitting alone [6].

The quantum basis for describing this transition is Fermi's golden rule, which expresses the transition rate between a donor state and a connected (or semi-connected) set of acceptor states in terms of the electronic coupling between them and the density of states available for transition.Marcus reformulated the associated nucleus-solvent reorganization as an equivalent free energy relationship between the states of the reactants and products, thereby establishing what remains the standard quantum theory of electron transport kinetics in condensed system [7]. Gerischer subsequently extended this picture to the semiconductor/electrolyte contact by replacing the single discrete acceptor level of the original Marcus treatment with a continuous distribution of conduction- or valence-band states, weighted by the appropriate occupation statistics [8]. The resulting Marcus–Gerischer formalism has since become the standard framework for describing electron injection from a photoexcited molecular donor into the continuum of states offered by a semiconductor acceptor — precisely the situation at a dye/semiconductor interface [9]. Its suitability for the system considered here follows directly from this correspondence: the D102 dye supplies a discrete, spatially localized donor level, while SnO_2 offers the extended conduction-band manifold the Gerischer treatment was designed to describe, under the working assumption, adopted throughout this model, that the semiconductor's boundary (conduction-band) energy does not itself shift with the interface or the surrounding medium [10].Within this framework, the calculated transfer rate is governed by four physically distinct quantities. The electronic coupling matrix element between donor and acceptor states sets the overall strength of the interaction and, in the non-adiabatic (weak-coupling) limit assumed here, enters the rate expression quadratically, in line with Fermi's golden rule. The reorganization energy, λ, quantifies the energy needed to reorganize the solvent shell and internal nuclear coordinates from the reactant to the product configuration before electron transfer occurs; because it depends on the dielectric and refractive properties of both the surrounding solvent and the semiconductor acceptor, λ is the principal channel through which the solvent environment enters the calculated kinetics [11,12]. The driving force, $\Delta G°$, given by the energetic offset between the acceptor and donor levels, together with λ, fixes the position of the system on the Marcus free-energy parabola and therefore whether the transfer proceeds in the normal, activationless, or inverted kinetic regime [10,13]. Finally, the density of accepting states in the semiconductor conduction band sets how many acceptor channels are energetically available for the transition and, together with the coupling, determines the overall magnitude of the calculated rate [14]. A related Marcus-based treatment has previously been applied by our group to evaluate the charge-transfer rate at a Cu/TiO_2 interface [15], illustrating how this same parameter set can be adapted across different donor–acceptor

combinations.The present work addresses this gap by evaluating, within the Marcus–Gerischer framework outlined above, the electron-transfer rate at the D102 dye/SnO_2 interface as a function of the electronic coupling strength, the solvent medium (methanol, acetonitrile, propylene carbonate,γ-butyrolactone, and dimethyl sulfoxide), and the operating temperature (300, 315, and 330 K). The reorganization energy is calculated for each solvent from its dielectric properties, together with the relevant donor (D102) and acceptor (SnO_2) parameters, while the driving force is obtained from the energetic offset between the D102 LUMO level and the SnO_2 conduction-band edge and is held fixed across solvents and temperatures. By combining these solvent-resolved reorganization energies with a fixed driving force, a systematically varied electronic coupling, and three operating temperatures, this study quantifies how each of these variables shapes the calculated injection rate at the D102/SnO_2 interface and establishes this dye/semiconductor pairing's position on the Marcus curve.

Theoretical

The quantum of electron transport in a molecule-semiconductor regime is defined using TDA(E) is transmittance probability of electron transfer process between the donor-acceptor states using [16]

$$T_{DA}(E) = \frac{2\pi}{\hbar}\langle U_D^A\rangle^2 \boldsymbol{p}(\Delta \boldsymbol{E}, \boldsymbol{T}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where UDAis the electronic coupling matrix element between the donor and acceptor states, and pΔE,T denotes the Franck-Condon weighted density of states associated with the electron-transfer transition for transition from |D⟩ to |A⟩ state at an energy difference ΔE and temperature T.Assuming that the donor and acceptor spectral distributions can be treated independently, the Franck-Condon weighted density of states pΔE,T can be expressed as follows [17]

$$\boldsymbol{p}(\Delta \boldsymbol{E}, \boldsymbol{T}) = \int_{-\infty}^{\infty} D(E)\, \zeta(\Delta \boldsymbol{E} - \boldsymbol{E}) dE \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where DE and ζΔE−E are the spectral distributions of the donor photo electronic and of the acceptor electron attachment spectra, respectively. The spectral distributions of the donor photo electronic DE is given by [18]

$$D(E) = \frac{1}{\sqrt{4\pi\Lambda_{AD}\mathrm{k_B T}}} e^{\frac{-(\Lambda_{AD}+\Delta G^0)^2}{4\Lambda_{AD}k_B T}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where ΛAD is reorganization energy and ΔG0is driving free energy. The reorganization energyΛAD(eV) is given by [11].

$$\Lambda_{AD}(eV) = \frac{Q^2}{8\pi\varepsilon^\circ}\left[\frac{\varepsilon - n^2}{\varepsilon n^2 D} - \frac{1}{2R}\left[\frac{n_A^2 - n^2}{n_A^2 + n^2}\frac{1}{n^2} - \frac{\varepsilon_A^2 - \varepsilon^2}{\varepsilon_A^2 + \varepsilon^2}\frac{1}{\varepsilon^2}\right]\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Here, qis the elementary charge,ε° is the vacuum permittivity, D is the radius of the donor molecule, R is the donor–acceptor interfacial separation, n and ε are the refractive index and dielectric constant of the solvent, respectively, while nAand εA are the refractive index and dielectric constant of the acceptor semiconductor. The radius D is calculated via density ρ,molecule weight M and Avogadros constant N [19].

$$D(m) = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\left(\frac{M}{N\rho}\right)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Substituting Eq. (3) into Eq. (2), and combining the resulting expression with Eq. (1), yields

$$T_{DA}(E) = \frac{2\pi}{\hbar}\langle U_D^A\rangle^2 \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi\Lambda_{AD}\mathrm{k_B T}}}\, e^{\frac{-(\Lambda_{AD}+\Delta G^0)^2}{4\Lambda_{AD}k_B T}}\, \zeta(\Delta \boldsymbol{E} - \boldsymbol{E}) dE \ldots\ldots\ldots\ldots\ldots (6)$$

The electronic attachment spectra ζΔE−E is given by

$$\zeta(\Delta \mathbf{E} - \mathbf{E}) = \mathrm{F(E)}\, \rho_{\mathrm{ef}}(\mathrm{E}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where FE is Fermi distribution function and ρef E is the effective density of electronic transition may be written as [14].

$$\rho_{ef}(E) = \rho_{A)} \frac{l_A}{\left(\frac{6}{\pi}\right)^{1/3}} d_A^{-2/3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where ρA) is density of state in acceptor, lA is length, and dA is atomic density of acceptor. Substituting Eq. (8) into Eq. (7) with Eq. (6) and integrated over to all states to obtains:

$$T_{DA}(E) = \frac{2\pi}{\hbar}\langle U_D^A\rangle^2 \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi\Lambda_{AD}\mathrm{k_B T}}}\, e^{\frac{-(\Lambda_{AD}+\Delta G^0)^2}{4\Lambda_{AD}k_B T}}\, \mathrm{F(E)}\rho_{A)} \frac{l_A}{\left(\frac{6}{\pi}\right)^{1/3}} d_A^{-2/3} dE \ldots\ldots\ldots\ldots\ldots (9)$$

The driving free energy ΔG0 in terms of energy of acceptor and energy of donor takes the form[19]

$$\Delta G^0 = E_A - E_D \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

However, the potential cross interface of donor-acceptor system relative to reorganization energy of electron transfer ΛAD and driving free energyΔG0 is forming due to Marcus's theory by [13].

$$\mathbb{U} = \frac{[\Lambda_{AD}+(E_A-E_D)]^2}{4\Lambda_{AD}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Substituting Eq. (11) into Eq. (10);

$$T_{DA}(E) = \frac{2\pi}{\hbar}\langle U_D^A\rangle^2 \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi\Lambda_{AD}\mathrm{k_B T}}}\, e^{\frac{-[\Lambda_{AD}+(E_A-E_D)]^2}{4\Lambda_{AD}k_BT}}\, \mathrm{F(E)}\rho_{A)} \frac{l_A}{(\frac{6}{\pi})^{1/3}} d_A^{-2/3} dE \ldots\ldots (12)$$

By making the reasonable assumption that the energy levels in donor and acceptor in the system are a continuum, the integral in Eq. (12) becomes [20]

$$\int_{-\infty}^{\infty} \mathrm{F(E)}\rho_{A)}\, dE = N_A(E) \quad \ldots\ldots (13)$$

Inserting Eq. (13) in E. (12)

$$T_{DA}(E) = \frac{2\pi}{\hbar} \frac{\langle U_D^A\rangle^2}{\sqrt{4\pi\Lambda_{AD}\mathrm{k_B T}}}\, e^{\frac{-[\Lambda_{AD}+(E_A-E_D)]^2}{4\Lambda_{AD}k_BT}} \frac{l_A}{(\frac{6}{\pi})^{1/3}} d_A^{-2/3} N_A(E) \ldots\ldots (14)$$

Results and Discussion

The temperature-dependent electronic transfer rate behavior at the D102 dye contact with SnO_2 semiconductor has been investigation theoretically to elucidate thermal effected contact electron transfer reaction. Particular attention was paid to the electronic structure of the interface, to the relative alignment of the energy levels of the D102 dye and the SnO_2 material, and to the changes in electron transfer rate characteristics caused by temperature changes. The electron transfer rate at the D102/SnO_2 interface was evaluated within a quantum-mechanical framework that combines Fermi's golden rule for the donor–acceptor transition probability with a Marcus-type, solvent-dependent Franck–Condon weighted density of states, and a Gerischer-type continuum treatment of the semiconductor acceptor states

The calculations were conducted using MATLAB software. The electron transfer rate was determined by a set of parameters influencing the process, including reorganization energy (eV), electronic coupling coefficient (eV/state), driving force for the transfer process, and the effect of temperature (T).The reorganization energy (eV) was computed using Equation (4), which depends on the dielectric properties of the system. These properties encompass the radii of the donor and acceptor, the distance between them, and the dielectric constant and refractive index of the solvent.Equation (5), using the molecular weights and densities of D102 and SnO_2 as presented in Table 1 and 2, was employed to calculate the radii of the SnO_2 semiconductor (2.04 Å) and D102 molecules (5.56 Å). The refractive index and dielectric constant of the solvents were also considered, using these parameter. The reorganization energies of the systems in various solvents, the solvent properties are summarized in Table 3, while the calculated reorganization energies are presented in Table 4.

Table 1: properties of the dye (D102) [21,22]

Full name	2-[5-[[4-[4-(2,2-Diphenylvinyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl]methylene]-4-oxo-2-thioxothiazolidin-3-yl]acetic acid
Synonyms	D-102 Dye standard Dye
Chemical formula	$C_{37}H_{30}N_2O_3S_2$
Molecular weight	614.78
Density_ g/cm^3	1.42 g/cm^3
HOMO / LUMO	HOMO = -5.18 eV, LUMO = -2.994 eV

Table 2: properties of semiconductor (SnO2)[23-25]

Property	**Adopted value**
Material	Rutile SnO_2 (Tin dioxide)
Crystal structure	Tetragonal rutile ($P4_2/mnm$)
Molar mass	150.71g mol^{-1}
Density	6.95 g cm^{-3}
Band gap energy	3.6–3.7 eV
Semiconductor type	n-type
Static dielectric constant	12
Refractive index	2.05
Electron effective mass	0.46 m_0
Electron affinity	4.3 eV
Effective density of states at 300 K	$\approx 10^{19}$ cm^{-3}
Atomic density (calculated)	8.33×10^{22} atoms cm^{-3}

Table 3: Dielectric and optical properties of investigation solvents [26]

Solvent	**Dielectric constant** ε	**Refracted index** n
Methanol	32.6	1.329
Acetonitrile (ACN)	37.5	1.344
Propylene carbonate (PC)	64.92	1.4181
γ-Butyrolactone (GBL)	39.1	1.43
Dimethyl sulfoxide (DMSO)	46.70	1.4793

Table 4: Calculated reorganization energies for the investigated solvents

Solvent	ε	n	λ_{AD}**(eV)**
Methanol (**MeOH**)	32.6	1.329	0.583647
Acetonitrile (ACN)	37.5	1.344	0.577522
Propylene carbonate (PC)	64.92	1.4181	0.540809
γ-Butyrolactone (GBL)	39.1	1.43	0.51989
Dimethyl sulfoxide (DMSO)	46.70	1.4793	0.495619

The resulting expression (Eq. 14) was used to generate the calculated electron transfer rates TDAE as a function of the squared electronic coupling UDA2, the solvent medium, and the temperature (Tables 5–7), built upon the reorganization energies of Table 4 and effective length lA =3 A° [19], atomic density 8.33 × 1022cm−3 , state effective density (NA =7.82, 8.42, 9.03×1018cm−3) ,UDA2×10−2=0.75 to 6 eV2[27] and the fixed driving force ΔG° = −1.31eV obtained from the D102 LUMO (−2.99 eV, Table 2) and the SnO_2 conduction-band edge (≈ −4.3 eV, Table 3).

Table 5. calculation electron transfer rates TDAE s−1of the D102/SnO_2 interface at T=300 K and NA =7.82, 8.42, 9.03×1018cm−3

$\langle U_D^A \rangle^2 \times 10^{-2}$	**MeOH**	**ACN**	**PC**	**GBL**	**DMSO**
0.75	2.8663E+06	2.2655E+06	4.8033E+05	1.7577E+05	4.8136E+04
1.5	5.7325E+06	4.5309E+06	9.6065E+05	3.5154E+05	9.6272E+04
2.25	8.5988E+06	6.7964E+06	1.4410E+06	5.2731E+05	1.4441E+05
3	1.1465E+07	9.0619E+06	1.9213E+06	7.0308E+05	1.9254E+05
3.75	1.4331E+07	1.1327E+07	2.4016E+06	8.7885E+05	2.4068E+05

4.5	1.7198E+07	1.3593E+07	2.8820E+06	1.0546E+06	2.8882E+05
5.25	2.0064E+07	1.5858E+07	3.3623E+06	1.2304E+06	3.3695E+05
6	2.2930E+07	1.8124E+07	3.8426E+06	1.4062E+06	3.8509E+05

Table 6. calculation electron transfer rates, TDAE s−1 of the D102/SnO_2 interface at T= 315 K and NA =8.42×1018cm−3

$\langle U_D^A \rangle^2 \times 10^{-2}$	**MeOH**	**ACN**	**PC**	**GBL**	**DMSO**
0.75	4.5428E+06	3.6319E+06	8.3025E+05	3.1899E+05	9.3010E+04
1.5	9.0857E+06	7.2638E+06	1.6605E+06	6.3798E+05	1.8602E+05
2.25	1.3629E+07	1.0896E+07	2.4908E+06	9.5696E+05	2.7903E+05
3	1.8171E+07	1.4528E+07	3.3210E+06	1.2760E+06	3.7204E+05
3.75	2.2714E+07	1.8160E+07	4.1513E+06	1.5949E+06	4.6505E+05
4.5	2.7257E+07	2.1791E+07	4.9815E+06	1.9139E+06	5.5806E+05
5.25	3.1800E+07	2.5423E+07	5.8118E+06	2.2329E+06	6.5107E+05
6	3.6343E+07	2.9055E+07	6.6420E+06	2.5519E+06	7.4408E+05

Table 7. calculation electron transfer rates TDAE s−1of the D102/SnO_2 interface at T= 330 K and NA =8.42 ×1018cm−3

$\langle U_D^A \rangle^2 \times 10^{-2}$	**MeOH**	**ACN**	**PC**	**GBL**	**DMSO**
0.75	6.9347E+06	5.6025E+06	1.3722E+06	5.5125E+05	1.7023E+05
1.5	1.3869E+07	1.1205E+07	2.7443E+06	1.1025E+06	3.4047E+05
2.25	2.0804E+07	1.6808E+07	4.1165E+06	1.6538E+06	5.1070E+05
3	2.7739E+07	2.2410E+07	5.4887E+06	2.2050E+06	6.8094E+05
3.75	3.4674E+07	2.8013E+07	6.8608E+06	2.7563E+06	8.5117E+05
4.5	4.1608E+07	3.3615E+07	8.2330E+06	3.3075E+06	1.0214E+06
5.25	4.8543E+07	3.9218E+07	9.6052E+06	3.8588E+06	1.1916E+06
6	5.5478E+07	4.4820E+07	1.0977E+07	4.4100E+06	1.3619E+06

The calculations were performed over the temperature range from 300K to 330 K to identify the relationship between thermal variations and the energetics of electron and change in rate of electron transfer process . The driving force ΔG0 = −1.31 eV is fixed by the energy-level offset between the D102 LUMO and the SnO_2 conduction-band edge; it does not vary with solvent in the present treatment. With ΔG0and ΛAD= 0.496–0.584 eV, |ΔG0|/ΛADranges from 2.24 to 2.64 across the five solvents, placing D102/SnO2 in the Marcus inverted region for every solvent studied [7,28]; matching the activationless condition would require ΛAD≈ 1.31 eV, roughly double the largest value obtained here.

This result, however, is tied to a specific feature of Eq. (14), which evaluates the Franck–Condon factor at a single energy the gap between the D102 LUMO and the SnO2 band edge. Gerischer-type treatments, and golden-rule descriptions of semiconductor/liquid electron transfer more generally [8,29,30], instead sum the rate over the distribution of acceptor states in the solid. For this system, acceptor levels near E_LUMO − ΛAD about 0.72–0.81 eV above the conduction-band minimum (from −2.994 eV, −4.30 eV and Table 4) fall inside the conduction band itself. If the density of states

at these energies is appreciable, a band-integrated rate would capture near-barrierless channels that the band-edge approximation omits. On this basis, we attribute the inverted-region behaviour to the band-edge treatment rather than to an intrinsic property of the D102/SnO2 interface; The rates are, in addition, highly sensitive to the assumed driving force: at fixed ΛAD, a 0.1 eV decrease in |ΔG0| raises the 300 K rate by a factor of 9–20, while a 0.1 eV increase lowers it by a factor of 13–29, depending on solvent (from Eq. 14). These results were discussed in terms of the electronic coupling between D102 dye and SnO_2 and the implications of temperature-induced changes for charge-transfer efficiency at the semiconductor interface.Dependence on electronic coupling. Across all three temperatures and all five solvents,TDAE scales exactly linearly with UDA2: an eightfold increase in the coupling parameter (from 0.75×10^{-2} to 6×10^{-2}) produces an exactly eightfold increase in the calculated rate in every column of Tables 5–7. This is the expected signature of a non-adiabatic, perturbative electron-transfer process, the transition probability is quadratic in the coupling matrix element, with the Franck–Condon and density-of-states factors acting as coupling-independent multipliers. Of the variables examined, coupling therefore sets the overall scale of the calculated rate, though the eightfold range explored here UDA2= 0.75×10^{-2} to 6×10^{-2} eV²). The full spread visible across Tables 5–7 (~4.81×10^{4} to ~5.54×10^{7} s^{-1}) reflects the combined effect of all three variables together, not coupling alone.

Reorganization energy and the solvent medium With the inverted-region context in place, the solvent trend in Table 4 . ΛAD decreases from 0.58 eV in methanol to 0.577 (ACN), 0.540 (PC), 0.519 (GBL), and 0.495 eV in DMSO and because the system is inverted, that same order becomes the rate order in Tables 5–7: methanol fastest, DMSO slowest, by a factor of roughly 60 at 300 K, narrowing to about 41 at 330 K.

Eq. (4) contains two pieces a Pekar-type solvent term and a term for the dielectric mismatch between the solvent and SnO_2 and the solvent ranking follows mainly from the first. The relevant combination is $1/n^2 - 1/\varepsilon$, and because ε is large for all five solvents, this quantity is governed chiefly by the refractive index n rather than by ε itself. That is why DMSO, despite having the second-highest dielectric constant of the set (46.70, behind only propylene carbonate's 64.92), still gives the lowest ΛAD: its refractive index (1.4793) is also the highest. Propylene carbonate's very large ε buys it little on its own, for the same reason. The SnO_2 image term trims a further 12–16% off each value, without changing the order.

The spread in ΛADitself is not large about 0.09 eV, or 16% of the mean, across five chemically quite different solvents. What is striking is how much that modest spread is amplified by the exponential in Eq. (14): a 16% change in ΛADbecomes a nearly 60-fold change in the calculated rate. That amplification is itself a signature of the inverted region in the normal region, the same spread ΛADwould produce a far smaller effect on the rate.The dependence of temperature on the parameters reorganization energy due to energy levels and driving force as well as interfacial electronic properties were analyzed to limited whether increasing temperature promotes or suppresses electron transfer. For every solvent and coupling value, the calculated rate increases monotonically from 300 to 315 to 330 K. Between 300 and 315 K the increase is 58% (MeOH), 60% (ACN), 73% (PC), 81% (GBL) and 93% (DMSO); between 315 and 330 K it is 53%, 54%, 65%, 73% and 83%, respectively. Over the full 30 K interval the rates rise by factors of 2.42, 2.47, 2.86, 3.14 and 3.54 (derived from Tables 5–7). Solvents with the smaller ΛADare therefore both the slowest and the most temperature-sensitive, and the spread between solvents narrows as the temperature rises. The results obtained provided a clear view of the thermodynamic and electronic parameters that govern the rate of electron transfer across the interface between D102 dye and SnO_2.These trends can be decomposed within Eq. (14). Between 300 and 330 K, NA increases by a factor of 1.155, while the 1kBT prefactor decreases by a factor of 0.953; together the non-exponential terms contribute only about 10%. The remainder a factor of about 2.2 to 3.2 arises from the Marcus exponent, whose barrier ( ) represented by Eq. 11 equals 0.226 eV (MeOH) to 0.335 eV (DMSO) for ΔG0 = −1.31 eV. These values are model barriers within the band-edge approximation; the strong temperature response originates largely from this exponential term, with ΛADand ΔG0 held fixed and thus not reflecting possible temperature dependence of ε, n, or band/dye-level shifts.

Conclusion

The calculated D102/SnO_2 transfer rate ranges from about 4.8×10^4 to 5.5×10^7 s^{-1} across the solvents, couplings, and temperatures examined, reflecting the combined effect of all three variables rather than any one of them acting alone.The rate increases with temperature for every solvent and coupling value, by 58–93% between 300 and 315 K and by a further 53–83% between 315 and 330 K, for a net increase of 2.42- to 3.54-fold over the full interval. About 90% of this increase comes from the temperature dependence of the Marcus exponential term; the remainder follows from the temperature dependence of the effective density of states and the $1/\sqrt{k_BT}$ prefactor.

Electronic coupling. The rate is exactly proportional to the squared coupling matrix element over the eightfold range examined, consistent with the non-adiabatic, golden-rule form adopted for the calculation. Solvent and reorganization energy. The calculated reorganization energy varies by only about 16% across the five solvents, from 0.496 eV (DMSO) to 0.584 eV (methanol), and is governed mainly by the solvent refractive index rather than its static dielectric constant. Because the system lies in the inverted region, this modest spread in reorganization energy is amplified into a roughly 60-fold spread in the calculated rate.

Driving force. With ΛAD = −1.31 eV and ΛAD= 0.496–0.584 eV, the D102/SnO_2 system falls in the Marcus inverted region for every solvent studied; reaching the activationless condition would require a reorganization energy roughly double the largest value obtained. The calculated rate is sensitive to the assumed driving force, changing by about an order of magnitude for a 0.1 eV shift in ΔG°, though the inverted-region placement itself persists even under a comparatively large 0.2 eV correction.

D102/SnO_2 interface. Within the present treatment, injection at the D102/SnO_2 interface is placed in the Marcus inverted region because the Franck–Condon factor is evaluated at a single energy, the SnO_2 conduction-band edge. Since acceptor states extend into the band above this edge, the inverted-region result is better understood as a property of this band-edge approximation than as an established feature of the physical interface.

References

1. Wittawat Poonthong , Narong Mungkung , Tanes Tanitteerapan , Theerapong Maneepen , Apidat Songruk , Khanchai Tunlasakun , Anumut Siricharoenpanich , Somchai Arunrungrusmi and Nat Kasayapanand ,Efficiency Improvement on Indium Tin Oxide Films for Dye-Sensitized Solar Cell Using Oxygen Plasma by Bias-Magnetron RF Sputtering Process,Energies2024, 17(22), 5585;https://doi.org/10.3390/en17225585 .
2. Kochman, M.A., Durbeej, B. and Kubas, A. (2021) 'Simulation and Analysis of the Transient Absorption Spectrum of 4-(Dimethylamino)benzonitrile (DMABN) in Acetonitrile', The Journal of Physical Chemistry A, 125(39), pp. 8635–8648.
3. Hassan, A.F., Al-Haidery, N.H., Kareem, S.R., Malik, S.A., Al-Jadaan, S.A.S. and Al-Saadawy, N.H. (2024) 'New Charge-Transfer Complexes of Organochalcogenide Compound Based on Aryl Acetamide Group with Quinones: Synthesis, Characterization, Antioxidant, and Computational Study', Indonesian Journal of Chemistry, 24(2), pp. 415–426.
4. Basu, K., Benetti, D., Zhao, H., Jin, L., Vetrone, F., Vomiero, A. and Rosei, F. (2016) 'Enhanced photovoltaic properties in dye sensitized solar cells by surface treatment of SnO_2 photoanodes', Scientific Reports, 6, art. no. 23312. DOI: 10.1038/srep23312.
5. Cordeiro, P.S., Chipoline, I.C., Ribeiro, R.C.B., Pinho, D.R., Ferreira, V.F., da Silva, F.C., Forezi, L.S.M. and Nascimento, V. (2022) 'Seleno- and telluro-functionalization of quinones: molecules with relevant biological application', Journal of the Brazilian Chemical Society, 33(2), pp. 111–127.
6. Solé-Daura, A. and Maseras, F. (2024) 'Straightforward computational determination of energy-transfer kinetics through the application of the Marcus theory', Chemical Science, 15, pp. 13650–13658.
7. Marcus, R.A. (1956) 'On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I', The Journal of Chemical Physics, 24(5), pp. 966–978. DOI: 10.1063/1.1742723.
8. Gerischer, H. (1991) 'Electron-transfer kinetics of redox reactions at the

semiconductor/electrolyte contact: a new approach', The Journal of Physical Chemistry, 95(4), pp. 1356–1359. DOI: 10.1021/j100156a060.
9. Watson, D.F. and Meyer, G.J. (2005) 'Electron injection at dye-sensitized semiconductor electrodes', Annual Review of Physical Chemistry, 56, pp. 119–156. DOI: 10.1146/annurev.physchem.56.092503.141142.
10. Raoufi, M., Chandrabose, S., Wang, R., Sun, B., Zorn Morales, N., Shoaee, S., Blumstengel, S., Koch, N., List-Kratochvil, E. and Neher, D. (2023) 'Influence of the Energy Level Alignment on Charge Transfer and Recombination at the Monolayer-MoS_2/Organic Hybrid Interface', The Journal of Physical Chemistry C, 127, pp. 5866–5875.
11. Fraggedakis, D., McEldrew, M., Smith, R.B., Krishnan, Y., Zhang, Y., Bai, P., Chueh, W.C., Shao-Horn, Y. and Bazant, M.Z. (2021) 'Theory of coupled ion-electron transfer kinetics', Electrochimica Acta, 367, art. no. 137432.
12. Saadon, A.K. and Al-Agealy, H.J.M. (2020) 'Study of photoemission and electronic properties of dye-sensitized solar cells', Energy Reports, 6, pp. 28–35.
13. Volkan-Kacso, S. and Marcus, R.A. (2017) 'What can be learned about the enzyme ATPase from single-molecule studies of its subunit F1', Quarterly Reviews of Biophysics, 50, art. no. e14, pp. 1–13.
14. Hlynchuk, S., Lancaster, M., MacInnes, M., Vasquez, R. and Maldonado, S. (2022) 'Fundamental Principles of Semiconductor/Electrolyte Junctions', in Springer Handbook of Inorganic Photochemistry. Berlin: Springer, pp. 767–804.
15. Altimime, S.M., Al-Agealy, H.J.M. and Ahmed, B.M. (2024) 'Performance Evaluation of Charge Transfer Rate for Cu/TiO_2 Interface System', AIP Conference Proceedings, 2922, art. no. 230001.
16. Leo, A. and Peluso, A. (2022) 'Electron Transfer Rates in Polar and Non-Polar Environments: a Generalization of Marcus' Theory to Include an Effective Treatment of Tunneling Effects', The Journal of Physical Chemistry Letters, 13, pp. 9148–9155.
17. Hashemi, A., Peljo, P. and Laasonen, K. (2023) 'Understanding Electron Transfer Reactions Using Constrained Density Functional Theory: Complications Due to Surface Interactions', The Journal of Physical Chemistry C, 127, pp. 3398–3407.
18. Al Maadhedea, T.S., Jumali, M.H., Al-Agealy, H.J.M., Yap, C.C., Ayad, A.D. and Shaban, A.H. (2023) 'Effect of solvents on performance of Alq3/ZnO solar cells: A theoretical approach', Energy Reports, 9, pp. 0–7.
19. Sabri, N.A., Hassooni, M.A., Al-Agealy, H.J. and Kahtan, H. (2026) 'Study of the efficiency of N719 dye-sensitized solar cells with cadmium selenide (CdSe) semiconductor', The European Physical Journal Plus, 141(7), art. no. 855.
20. Al Maadhde, T.S., Jumali, M.H., Al-Agealy, H.J.M., Abdul Razak, F.B. and Yap, C.C. (2021) 'An Investigation of the Fill Factor and Efficiency of Molecular Semiconductor Solar Cells', Materials Science Forum, 1039, pp. 373–381. DOI: 10.4028.
21. Leijtens, T., Ding, I.-K., Giovenzana, T., Bloking, J.T., McGehee, M.D. and Sellinger, A. (2013) 'Diacetylene bridged triphenylamines as hole transport materials for solid state dye sensitized solar cells', Journal of Materials Chemistry A, 1, pp. 11141–11148. DOI: 10.1038/C3TA11417A.
22. Schmidt-Mende, L., Bach, U., Humphry-Baker, R., Horiuchi, T., Miura, H., Ito, S., Uchida, S. and Grätzel, M. (2005) 'Organic Dye for Highly Efficient Solid-State Dye-Sensitized Solar Cells', Advanced Materials, 17(7), pp. 813–815.
23. Lide, D.R. (ed.) (2004) CRC Handbook of Chemistry and Physics. 85th edn. Boca Raton: CRC Press.
24. Medvedeva, J.E. and Freeman, A.J. (2004) 'Electronic structure and optical properties of SnO_2', Physical Review B, 70, art. no. 073101.
25. Fujisawa, J. and Hanaya, M. (2021) 'Interfacial charge-transfer transitions in SnO_2 functionalized with benzoic acid derivatives', RSC Advances, 11(34), pp. 20751–20757. DOI: 10.1038/D1RA03422G.
26. Abraham, M.H. (2010) 'Solvent properties and polarity scales', Chemical Reviews, 110.
27. Shnain, F.A. and Al-Agealy, H.J.M. (2024) 'A theoretical calculation of the efficiency of indoline dyes-sensitized contact with ZnO in solar cell', Journal of Theoretical and Applied Physics, 18,

art. no. si-AICIS23.21. DOI: 10.57647/j.jtap.2024.si-AICIS23.21.
28. Marcus, R.A. and Sutin, N. (1985) 'Electron transfers in chemistry and biology', Biochimica et Biophysica Acta (BBA) - Reviews on Bioenergetics, 811(3), pp. 265–322. DOI: 10.1016/0304-4173(85)90014-X.
29. Royea, W.J., Fajardo, A.M. and Lewis, N.S. (1997) 'Fermi golden rule approach to evaluating outer-sphere electron-transfer rate constants at semiconductor/liquid interfaces', The Journal of Physical Chemistry B, 101(51), pp. 11152–11159. DOI: 10.1021/jp972222y.
30. Gao, Y.Q., Georgievskii, Y. and Marcus, R.A. (2000) 'On the theory of electron transfer reactions at semiconductor electrode/liquid interfaces', The Journal of Chemical Physics, 112(7), pp. 3358–3369. DOI: 10.1063/1.480918.