The Role of Charge Transfer State on the Reduced Langevin Recombination in Organic Solar Cells: A Theoretical Study

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S.1 The derivation of the Langevin reduction factor from Hilczer's continuum method

According to the theory of Hilczer[1], the Langevin reduction factor is given as:

$$\boldsymbol{\gamma = \frac{1}{1-e^{-\frac{r_c}{R}}+\frac{Dr_c}{k_r R^3}e^{-\frac{r_c}{R}}}} \qquad \text{(Eq. A1)}$$

where the Onsager radius r_c is defined as $q^2/4\pi\varepsilon kT$, R is the reaction radius, D is the sum of the diffusion coefficients of electrons and holes, and k_r is the rate with which a bound electron-hole pair ultimately recombines. In Ref. 1, R is assumed as 1 nm, and at room temperature $r_c \approx 14$ nm when $\varepsilon=4$, $D=5.2\text{x}10^{-6}$ cm^2/s. Guided by the fitting results of the γ-T data of Deibel et al.[2], the temperature range of 180~300 K implies $\frac{Dr_c}{k_r R^3}\boldsymbol{e}^{-\frac{r_c}{R}} \gg 1 \gg \boldsymbol{e}^{-\frac{r_c}{R}}$. Hence, Eq. A1 can be rewritten as:

$$\boldsymbol{\gamma \approx \frac{k_r R^3}{Dr_c}e^{\frac{q^2}{4\pi\varepsilon R}/kT}} \qquad \text{(Eq. A2)}$$

When considering $\boldsymbol{\beta = 4\pi Dr_c}$, $\boldsymbol{N_0=1/R^3}$, $\boldsymbol{E'_b = \frac{q^2}{4\pi\varepsilon R}}$, and formally assigning $\boldsymbol{\tau_{CT} = 1/4\pi k_r}$, the Eq. A2 formally resembles Eq. 11 with $\sigma_{CT}=0$ V.

It is important to note at this point, that $\boldsymbol{\tau_{CT}}$ is defined as the characteristic time with which CT states recombine to the ground state, rather than being the overall decay time (considering also a split of the bound electron-hole pair back into free carriers). Note further, that Hilczer and Tachiya assume that both the recombination rates as well as the diffusion coefficient are temperature-activated. Hence, the factor $\frac{D}{k_r R}$ is set to $A\boldsymbol{e}^{-\Delta E/kT}$, where ΔE is the activation energy difference between D and k_r. Joining the exponential terms yields:

$$\boldsymbol{\gamma \approx \frac{R^2}{r_c A}e^{(E'_b+\Delta E)/kT}} \qquad \text{(Eq. A3)}$$

where r_c in the prefactor is a markedly less dependent on temperature than the exponential term.

Eq. A3 is now assuming a form corresponding to Eq. 11 in this work. Now we can associate $\boldsymbol{\tau_{CT} = Rr_c A/\beta}$, indicating that τ_{CT} itself is negatively temperature dependent. The fitting the γ-T data of Ref. 1 gives ΔE=-0.239 eV for the data of Deibel et al..[2] The comparison between Eq. 11 and Eq. A3 implies that the binding energy $E'_b = \boldsymbol{\frac{q^2}{4\pi\varepsilon R}}$ overestimates the CT state binding energy E_b.

References

(1) Hilczer, M.; Tachiya, M. Unified Theory of Geminate and Bulk Electron−Hole Recombination in Organic Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 6808–6813.

(2) Deibel, C.; Wagenpfahl, A.; Dyakonov, V. Origin of Reduced Polaron Recombination in Organic Semiconductor Devices. *Phys. Rev. B* **2009**, *80*, 075203.