

## Comment on “Observation of the Marcus Inverted Region for Bimolecular Photoinduced Electron-Transfer Reactions in Viscous Media”

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In this comment, we list concerns with the validity of the data analysis and interpretation of the paper by Kumbhakar et al.<sup>1</sup> As we argue in the following, there are three major points that are problematic: (i) the misuse of a multiexponential fitting approach to time-resolved data (ii) a wrong reduction potential for one of the studied coumarins that leads to the spurious observation of the Marcus inverted region and which disappears if the correct potential is used, and (iii) a flawed qualitative interpretation of the data using the Sumi–Marcus model.

The experimental evidence of the existence of the Marcus inverted region (MIR)<sup>2,3</sup> in photoinduced bimolecular electron-transfer reactions has been a major concern in the field of photochemistry for the last 45 years since the publication of the seminal and suggestive paper of Rehm and Weller,<sup>4</sup> which only recently has seen the beginning of closure.<sup>5</sup> Several groups claimed having observed the MIR in highly viscous or diffusion-constrained media over the past decade,<sup>6–8</sup> but doubts about the analysis of the data leading to this affirmation were cast, too.<sup>9</sup> Working under diffusion-influenced conditions requires a proper understanding of the interplay between molecular motion, distance-dependent reactivity and the dynamics of the electronically excited molecules (vibrational relaxation, solvation dynamics, and population decay). Such a framework is provided by modern diffusion–reaction theories like encounter theories.<sup>10</sup> For example, if the excited state lifetime of the fluorophore is of the same order of magnitude as the transient stage of diffusion (the stage before the equilibrium between the material flow of reactants and their intrinsic reaction is reached) the rate constant obtained from a Stern–Volmer plot (time-integrated kinetics or stationary fluorescence data) or from the tail of the time-resolved fluorescence decays will contain different contributions of this transient stage, making comparison between different fluorophores with different lifetimes meaningless. Furthermore, the contribution of the transient stage is enhanced and prolonged with increasing viscosity, which explains why the spurious observation of the inverted region appears only in solvents of high viscosity. This was the message behind our report published in ref 9. The spurious effects in highly viscous solvents arising from an oversimplified Stern–Volmer analysis were therefore compared against the outcome of an analysis accounting for diffusion and the transient effects. With an appropriate analysis, it was found that the MIR is absent from

the set of data studied in ref 9 and those cited therein, and that the obtained rate constants are in excellent agreement with Marcus theory for the normal regime, as expected for this range of driving force.

Recently, Kumbhakar et al. reported on the quenching dynamics of 8 coumarins in the presence of 1 M *N,N*-dimethylaniline (DMA) in two room temperature ionic liquids (RTIL), 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (emim) and 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (hmim).<sup>1</sup> Using subpicosecond fluorescence up-conversion, they concluded to have observed the MIR working under the conditions that were critically reviewed in ref 9. The rate constants were extracted from triexponential fits to the raw fluorescence decays, and the authors argued that molecular diffusion and solvation dynamics were absent during the first 10 ps at the measured viscosities and at the selected emission wavelengths recorded. Consequently, they made a qualitative use of the Sumi–Marcus theory<sup>11</sup> to explain the inversion that was observed when the inverse of the shortest lifetime components was plotted against the free Gibbs energy of the electron-transfer reaction. The maxima of the so obtained parabolas were located at around −0.5 eV. In addition, several shortcomings were pointed out as well, leading to their conclusion that encounter theories and the experimental strategies used in ref 9 were no longer adequate at large viscosities.

We will not comment here extensively the critics made on our previous works. It is, however, important to note that reaction–diffusion theory has been used by many research groups in a wide range of viscosities and its applicability has been quantitatively discussed and censured for a long time. References 12–20 constitute a nonexhaustive list exemplifying the development and use of reaction–diffusion equations. Another major criticism used by Kumbhakar et al. is the use of an organic solvent mixture in ref 9 to change viscosity while keeping other macroscopic solvent parameters constant: a collection of several experiments has been published recently<sup>21</sup> showing that the DMSO/glycerol mixture used in ref 9 does

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not exhibit any unexpected behavior and is well suited for investigating bimolecular electron-transfer reactions.

Furthermore, the data presented in ref 1 at a single emission wavelength could be contaminated with the solvation dynamics of the fluorophores. Using coumarin 153, Maroncelli and colleagues have estimated that the average solvation times for the two RTILs used in ref 1 amount to 150 and 410 ps, respectively.<sup>22–24</sup> We will assume, nevertheless, that it is possible to find a wavelength range at which the intrinsic fluorophore dynamics is completely flat. The kinetics in the presence of 1 M DMA, a concentration high enough to alter the viscosity of the RTILs, were reproduced with triexponential functions. Inspecting Table 1 in ref 1, it can be seen that the data do not reproduce Figure 2 in the main text and Figures S3 and S4 in the Supporting Information (note that, despite the caption, Figure S3 corresponds to emim as a simple comparison with Figure 2 reveals): the amplitudes of the shortest component in Table 1 are too small when compared to the data in the figures (they amount to less than the S/N ratio). (Note also that the data in Figure S5 were obtained using the values listed in Table 1, so they do not correspond to the experimental results).

As the multiexponential fitting is prone to several problems (as discussed in ref 25 because of the mathematical nature of exponentials, the extracted parameters from a multiexponential fit are the unique solution only under quite restrictive conditions), we have reanalyzed the graphical data from ref 1 using a simplified reaction–diffusion model to extract the rate constants of electron transfer. To this end, we have assumed, like the authors, that at the viscosities of these two RTILs (37 and 81 cP), the influence of diffusion during the first 30 ps (insets in Figures S3 and S4) can be neglected (note: we have numerically tested that at 30 ps for 37 cP and found that the deviations of this approach with respect to the one that considers diffusion amount to 5% at most). Under this condition the reaction–diffusion equation simplifies to the equivalent in solid media:<sup>6–8,26</sup>

$$\frac{\partial n(r,t)}{\partial t} = -w(r) n(r,t)$$

in which the derivative of the fluorophore–quencher distribution function,  $n(r,t)$ , with respect to time depends only on the distance-dependent reaction sink,  $w(r)$ . For the latter, we have used a very simple exponential expression, in agreement with the expected spatial dependence of the coupling matrix element:

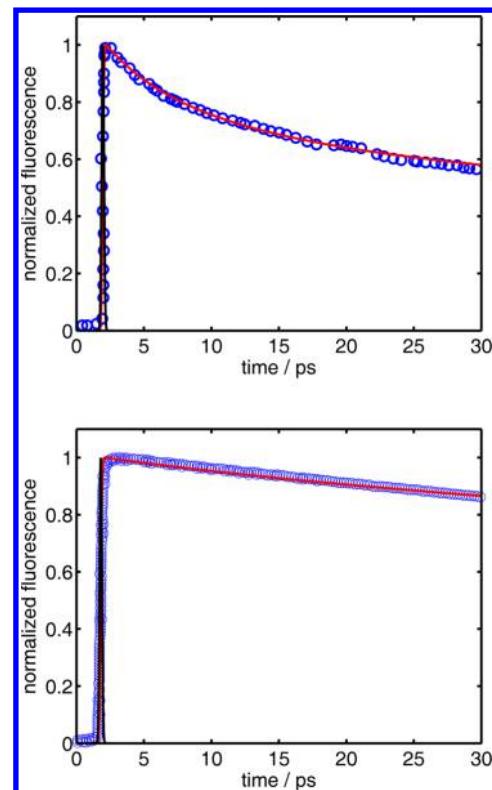
$$w(r) = w(\sigma) \exp\left(-2\frac{r-\sigma}{L}\right)$$

in which  $w(\sigma)$  is the reaction probability for electron transfer at contact distance,  $\sigma$ , and  $L$  is the decay length of the reactivity. We have solved this equation numerically, with homogeneous initial conditions (the liquid solution is homogeneous in the distribution of quenchers before the reaction starts,  $n(r>\sigma,0) = 1$ ) and reflective boundary conditions at contact (the fluorophore and the quencher cannot overlap in space). We have taken the same contact distance for all systems, 7 Å, and adjusted only two parameters:  $w(\sigma)$  and  $L$ . Our goal was not to find the value of these parameters (they contain in fact many dependences on several properties of the solvent and the reacting system, like the solvent relaxation time, reorganization energies and so forth), but to obtain the electron-transfer rate

constant,  $k_0$ . This is given by the value of the rate coefficient at time zero:

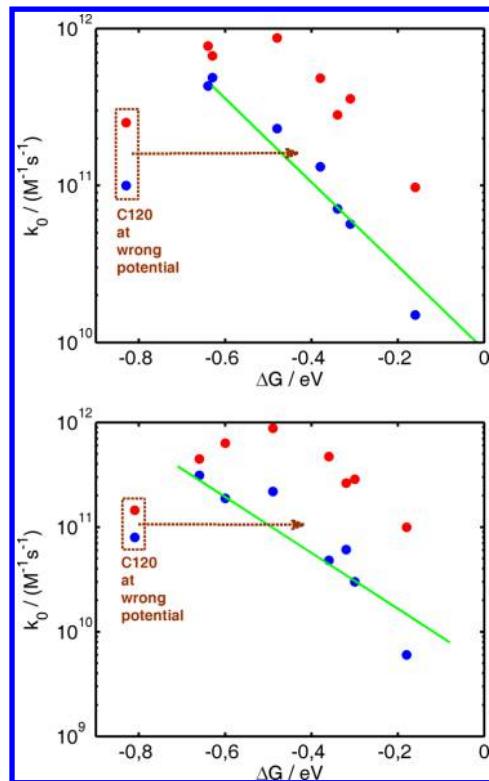
$$k_0 = \int_V w(r) n(r,0) dV$$

We have also taken a Gaussian function of 200 fs fwhm as instrument response function, following the description of the experiments in ref 1. A couple of examples of the results from this procedure are given in Figure 1.



**Figure 1.** Upper panel: C522 + 1 M DMA/emim. Lower panel: C153 + 1 M DMA/hmim. Blue circles: digitized data from ref 1. Black lines: IRF with fwhm of 0.2 ps. Red lines: simulations reported in this comment.

The so-obtained electron-transfer rate constants are plotted in Figure 2 together with the inverse initial lifetimes of ref 1, and the results are listed in Table 1. The  $k_0$  values follow a straight line except for one coumarin, C120, in both solvents. For the inverse lifetimes reported in ref 1, we assume that  $1/\tau = k_0 c$ . With  $c = 1$  M,  $1/\tau$  is numerically identical to  $k_0$ . The  $k_0$  values are in general smaller than in ref 9. However, the trends are very similar and almost identical if a correction for the free enthalpies is allowed, reflecting most likely the change of the solvent dielectric properties. The only point that defines the MIR is the one corresponding to C120. This is also the only coumarin with a CH<sub>3</sub> instead of a CF<sub>3</sub> group in position 3. In the case of the C153/C102 pair, such a change from CF<sub>3</sub> to CH<sub>3</sub> was shown to lead to a strong change in the reduction potential.<sup>27</sup> In ref 1, however, the reduction potential of C120 is very similar to that of C151, the CF<sub>3</sub> analogue, i.e., -1.61 vs -1.57 V. Inspection of the literature reveals that the reduction potential of C120 in ACN has been reported in various sources to be close to -2.1 V vs SCE.<sup>28,29</sup> Taking this value, the driving force for C120/DMA shifts to -0.4 eV, i.e., into the normal



**Figure 2.** Upper panel: electron-transfer rate constants in emim. Lower panel: electron-transfer rate constants in hmim. Red dots: initial inverse lifetimes from ref 1 under the assumption that  $1/\tau = k_0$  as explained in the text. Blue dots: rate constants obtained in this comment from the same experimental results. The arrows mark the horizontal displacement of the C120 values when the redox potential reported in several references is used (see text). The green lines correspond to the trends observed in ref 9 with a correction of 0.2 and 0.1 eV in emim and hmim, respectively.

**Table 1. Simulation Results of the Model Used in This Comment To Reproduce the Kinetics up to 30 ps from Ref 1<sup>a</sup>**

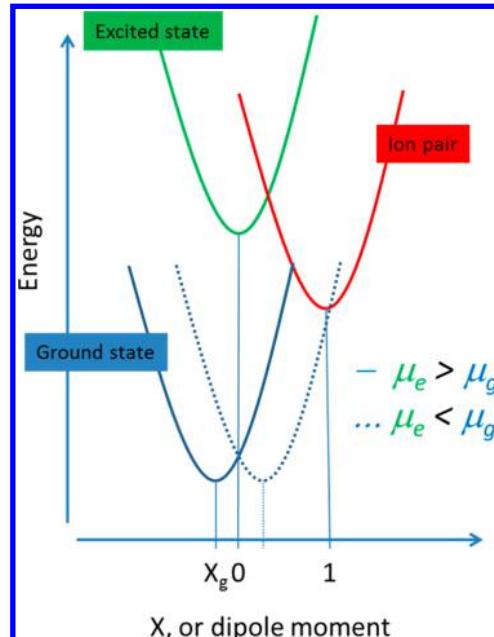
	EMIM			HMIM		
	$w_0/10^3 \text{ ns}^{-1}$	$L/\text{\AA}$	$k_0/10^{11} \text{ M}^{-1} \text{ s}^{-1}$	$w_0/10^3 \text{ ns}^{-1}$	$L/\text{\AA}$	$k_0/10^{11} \text{ M}^{-1} \text{ s}^{-1}$
C120	0.42	1.10	1.00	0.20	1.70	0.80
C151	2.10	0.95	4.30	1.30	1.10	3.12
C152	0.65	0.95	1.32	0.21	1.05	0.48
C153	0.08	0.90	0.15	0.04	0.75	0.06
C307	2.90	0.80	4.88	1.20	0.75	1.88
C481	0.30	1.08	0.71	0.30	0.95	0.61
C500	1.25	0.87	2.31	1.30	0.80	2.19
C522	0.30	0.90	0.57	0.15	0.95	0.30

<sup>a</sup>The notation agrees with that used in ref 1. See text for the meaning of the parameters.

region where the rate constant increases with driving force. As a consequence, the MIR disappears completely.

A final note about the qualitative discussion of the Sumi–Marcus model in ref 1 is necessary. For linked DA systems undergoing intramolecular electron-transfer reactions, the assignment of the initial value of the reaction coordinate can be performed relatively safely. On the contrary, for bimolecular systems, the mutual orientation of the dipole moments of the reactants is not fixed. The orientation of the dipole moments

relative to the axis that passes through the centers of the reactants influences the initial position of the excited state population along the solvent coordinate relative to the crossing region between the reactant and product free-energy potentials. Moreover, this initial position also depends on the excitation excess energy.<sup>30,31</sup> For the systems studied in ref 1, the excess energy is different for each coumarin. It has even been shown theoretically that different coumarins have different sensitivities to the excitation energy and geometry of the encounter complex. Even if the above points are neglected, and only the module of the total dipole moment is to be considered, as implicitly assumed in ref 1, the picture presented there is not correct. As shown in Figure 3, whenever the dipole moment of



**Figure 3.** Initial values for the slow reaction coordinate in the cases of a lower dipole moment in the ground state than in the excited state (continuous blue parabola) and vice versa (dotted blue parabola), assuming that only the module of the dipole moment and not its direction has to be taken into account.

the fluorophore is smaller in the ground state than in the excited state, photoexcitation prepares the system at a position along the reaction coordinate that is smaller than zero. The opposite happens when the dipole moment is larger in the ground than in the excited state. This means that, in the case of coumarins, the first of these two situations is to be expected in this simplified picture, contrary to what is discussed in ref 1. In other words, using the same reasoning as in ref 1, the effective reorganization energy does not decrease with respect to the equilibrium situation, but rather increases. This should shift the MIR to even larger free enthalpies, in accordance with most of the observations reported in the literature of photoinduced electron-transfer reactions.

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### Notes

The authors declare no competing financial interest.

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