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# Theoretical-computational modeling of photo-induced charge separation spectrum and charge recombination kinetics in solution.

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#### Abstract.

In this study we propose a theoretical-computational method, essentially based on Molecular Dynamics simulations and Quantum-Chemical calculations, for modelling the photo-induced Charge Separation (CS) and the subsequent Charge Recombination (CR) processes in solution.

In particular we have reproduced the low-energy UV-Vis spectra of systems composed by an aromatic species (Ar=Benzene or Indene) and Tetracyanoethlyene (TCNE) in chloroform solution, dominated by the formation of  $Ar^+/TCNE^-$  Ion Pair (IP) complex. The kinetics of the Charge Recombination process leading to the regeneration of Ar and TCNE has been also modelled. In both the cases the agreement with the experimental data is satisfactory. Although the presence of systematic deficiencies makes our approach unable to address some key aspects of the above processes (e.g. the ultrafast internal vibrational redistribution), it appears as a rather promising tool for modelling CS-CR process for atomic-molecular systems of very highly complexity. The involvement of the triplet IP complex has been also discussed.

#### Introduction.

Photo-induced charge separation (CS) reactions are a wide class of fundamental processes, underlying many photochemical and photobiological electron transfer (ET) reactions which have represented, and still represent, a topic of great fundamental and practical relevance. <sup>1-12</sup> In these processes, typically occurring in condensed phase, the Acceptor (A) and Donor (D) species undergo an ET reaction with the involvement of an ion-pair  $A^{-}D^{+}$  (IP) species which might be roughly described as either produced by vertical excitation of the electron-donor acceptor complex (EDAC) at a wavelength inactive for infinite dilution solutions of A and D, or generated upon bimolecular fluorescer-quencer association following the A or D excitation.<sup>13-16</sup>

The efficiency of these processes is known to be strongly related to the occurrence of Charge Recombination (CR) reaction which, regenerating the original EDAC from the IP, suppresses the ability of the whole reactive process to promote productive ET reactions.

In the last three decades, because of the impressive technological advancement of the ultrafast spectroscopic techniques, a huge amount of data concerning CS and CR processes has been collected <sup>17-30</sup> hence stimulating several theoretical-computational models as an impelling and indispensable support for their interpretation.

However CS-CR reactions are rather challenging for theoretical-computational chemists as, in general, are characterized by two very different regimes:

i- an ultrafast (femtosecond) regime, essentially dominated by the dynamics of the intramolecular (quantum) relaxations, following the photo-excitations;

ii- a slower domain characterized by the solvent and the intermolecular (semi-classical) relaxation governing the slower (picosecond/nanosecond) kinetics.

As a consequence the modelling of CS-CR events is a tremendously complicated task because it strictly requires the use of mixed quantum-classical dynamical approaches. In the last years a number of elegant models and efficient numerical simulations have been proposed for separately addressing specific aspects ranging from the modelling of the ultrafast relaxations to the EDAC equilibrium photo-excitation.<sup>31-41</sup>

In a number of recent papers we have proposed a theoretical-computational approach, based on Molecular Dynamics (MD) simulations, Quantum-chemical (QM) calculations and Perturbed Matrix Method (PMM)<sup>42-43</sup> for modelling intramolecular <sup>44</sup> and solute-solvent CS-spectra <sup>45</sup> as well as the kinetics of ET reactions <sup>46,47</sup> in liquid state systems. As a natural continuation, we decided to test the validity of our methodology, hereafter termed as MD-PMM, by studying one of the most investigated examples of CS-CR bimolecular reactions involving the photo-excitation of EDAC between an aromatic species (Ar) and Tetracyanoethlyene (TCNE) in solution, according to the Scheme I. <sup>48-54</sup>

Ar<sub>(sol)</sub>+TCNE Ar·TCNE Charge Separation |hv|**Ar**<sup>+</sup>**TCNE**<sup>−</sup> **k**<sub>CR</sub> Charge Recombination (Ar TCNE)

Scheme I

In particular, we selected the prototypical reaction between benzene (Bz) acting as the Donor species and TCNE in  $CH_2Cl_2$  solution. This reaction has been recently reappraised with the use of ultrafast broadband time-resolved fluorescence spectroscopy and all the dynamical and kinetic details have been characterized. This study has revealed that upon the (vertical) formation of IP by photo-excitation, the system undergoes a very fast internal vibrational relaxation (IVR) in the sub-picosecond domain followed by a slower solvent relaxation and the subsequent CR.<sup>55</sup>

In this study we disregard the ultrafast processes taking place within the first femtosecond of the process limiting our attention on the two temporally distinct steps reported in Scheme I and experimentally well characterized: <sup>55</sup>

a- the modelling of the vertical CS-band of EDAC in the UV-Vis range, and

b- the modelling of the kinetics of the CR process taking place on the internally relaxed IP system.

In order to further check the consistency of our results, we repeated the computational procedure on a second example of CS-CR process in which Bz is replaced by Indene (Ind) and showing a sharply different CS spectrum and a much faster CR kinetics. <sup>56</sup> These differences are clearly due to the very different energy domain involved in the ionization process of Ind whose ionization energy is 1.1 eV lower than Bz.

The manuscript is organized as follows. After a first part in which we describe the whole computational procedure, the results related to the modelling of the CS spectrum in solution and the CR kinetics are reported in two distinct sections. The implication of different magnetic states, plausibly involved during the CR process have been also briefly discussed in the last section.

#### **Computational details.**

#### I. Molecular Dynamics simulations and Essential Dynamics analysis.

All the simulations were carried out using the Gromacs package version 4.5.5.<sup>57</sup>

For Bz, Ind, TCNE,  $Bz^+$ ,  $Ind^+$ , and TCNE<sup>-</sup> an all-atoms model has been adapted from the *Gromos* force-field <sup>58</sup> with the atomic point charges obtained by standard QM calculations in vacuum (see next subsection). <sup>59</sup> Details of the force-field are reported in the Supplementary Information. The parameters of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), were taken from the Gromacs library. Different sets of simulations were carried out.

In the simulations hereafter termed as  $MD_{neutral}$  one Ar molecule (Bz or Ind) and one TCNE molecule were inserted in a cubic box of 1167 nm<sup>3</sup> containing CH<sub>2</sub>Cl<sub>2</sub> solvent molecules at its typical density of 1.33 g/cm<sup>3</sup> at 298K and 1.0 bar. These simulations were extended for 120.0 ns.

Another simulation of 40.0 ns, hereafter termed as  $MD_{benzene}$ , was implemented inserting one Bz molecule in a smaller cubic box, 27.0 nm<sup>3</sup>, containing  $CH_2Cl_2$  solvent molecules at the same density. Finally, additional non-equilibrium simulations of the IP system, hereafter termed as  $MD_{IP}$ , were carried out. At this purpose we extracted by the  $MD_{neutral}$  simulations 120 instantaneous EDAC-solvent configurations (coordinates and momenta) corresponding to all the frames in which such species are found to potentially undergo photo-induced CS spectra (see Results section). This ensemble of configurations was then utilized as initial conditions (time zero) for such non-equilibrium  $MD_{IP}$  trajectories of 500.0 ps length in which the  $MD_{neutral}$  force-field was substituted by the corresponding  $Ar^+$  and TCNE<sup>-</sup> parameters.

Note that, obviously, the MD<sub>IP</sub> and MD<sub>neutral</sub> were carried out using the same boxes.

All the equilibrium simulations (MD<sub>benzene</sub> and MD<sub>neutral</sub>) were performed in the NVT ensemble with a time step of 0.001 ps using a standard protocol: after an initial energy minimization, the system was gradually heated from 50 K to 300 K using short (20 *ps*) MD simulations. The temperature was kept constant at 300 K using the Berendsen algorithm <sup>60</sup> with a time constant equal to the time-step used for the integration algorithm, thus being equivalent to the isokinetic coupling ensuring a correct statistical sampling. <sup>61</sup> The LINCS algorithm <sup>62</sup> was employed to constrain all bond lengths and long range electrostatic interactions were computed by the Particle Mesh Ewald method <sup>63</sup> with 34 wave vectors in each dimension and a 4<sup>th</sup> order cubic interpolation.

The MD<sub>IP</sub> simulations were propagated with the previously outlined protocol but, obviously, avoiding the initial equilibration.

All the analysis of the trajectories were performed either using standard tools available in Gromacs or through simple home-made routines.

Essential Dynamics (ED) analysis <sup>64</sup> was utilized for analyzing  $MD_{neutral}$  and  $MD_{benzene}$  (see Results section). More precisely, ED was applied for extracting 10 EDAC structures in both the Ar/TCNE systems from the corresponding  $MD_{neutral}$  simulations, to be used for modelling the equilibrium absorption spectra.

#### II. QM Calculations.

As already mentioned, atomic point charges <sup>59</sup> were calculated for all the simulated solutes using QM calculations, in the framework of Density Functional Theory (DFT) using the CAMB3LYP functional <sup>65-67</sup> in conjunction with the standard 6-311G\* atomic basis set. The same level of theory was used for evaluating the minimum energy positions of the Representative Configurations (RCs) extracted after ED analysis of MD<sub>neutral</sub> and MD<sub>benzene</sub> (see Results section). For this purpose, in order to keep intact as much as possible the RC geometrical features, we only minimized the covalent bond lengths and angles utilizing standard internal-coordinates mode. These locally relaxed structures (LRSs) were used to obtain the electronic unperturbed ground and seven excited states which provides the basis set for the PMM procedure (see below). These calculations were performed in the framework of the Time-Dependent Density Functional Theory (TD-DFT) <sup>68</sup> with the same functional and basis set adopted for the previous optimizations.

The same calculations were also carried out for the Bz,  $Bz^+$ , Ind,  $Ind^+$ , TCNE and TCNE<sup>-</sup> species for modelling of CR kinetics according to the MD-PMM procedure and for analyzing the triplet states of the EDAC, Bz and TCNE. All the QM calculations were carried out using the Dalton <sup>69</sup> suite of programs.

Note that using the same LRSs we also evaluated atomic point charges for all the vertical excited states using the same procedure carried out for the ground state. <sup>59</sup>

Finally for the calculation of the vibronic spectrum of benzene (see below) the evaluation of the intensities of transitions between two vibronic states in gas-phase were obtained by means of a procedure <sup>70</sup> as implemented in Gaussian 09 package. <sup>71</sup>

#### **Results and discussion.**

#### a-Definition and conformational analysis of the Ar-TCNE complexes from MD simulation.

The main aim of the first part of this study is to reproduce the spectral features of the solvated EDAC (Ar·TCNE) associated to the EDAC<sub>(sol)</sub>  $\rightarrow$  IP<sub>(sol)</sub> photo-induced transition This should be

carried out, in principle, by calculating energies and transition moments of the vertical excited states of all the semi-classical configurations accessed by the solvated Ar–TCNE supramolecular system. At this purpose, to generate a significant ensemble of Ar-TCNE-solvent configurations to be utilized in QM calculations, we have performed the  $MD_{neutral}$  simulations, as defined in the previous subsection. Obviously, because of the huge dimension of the Ar-TCNE-solvent configurational space, this operation produces a computationally intractable problem and a number of approximations has to be introduced.

First of all, in line with the typical Quantum-Mechanics/Molecular-Mechanics (QM-MM) approaches, <sup>72</sup> we pre-define a portion of the system, hereafter termed as Quantum Centre (QC) for which we wish to calculate the electronic properties. In the present case the Ar-TCNE system represents the QC. The rest of the system, e.g. the solvent, is treated as an external semi-classical (electrostatic) perturbation hence allowing us to focus our attention limitedly to the more confined conformational space of the Ar-TCNE sub-system. Secondly, although at the expense of a certain methodological strictness, it might be of great computational convenience to define a pre-selected geometrical condition for identify when the Ar-TCNE system has formed the EDAC. At this end we have decided to define as EDAC whatever configuration accessed in solution by Ar and TCNE moieties showing a distance between their centers of mass (c.o.m.) not exceeding 0.50 nm. This value, hereafter termed as r<sub>EDAC</sub>, has been selected on the basis of a simple argument: at distances larger than r<sub>EDAC</sub> we have systematically detected the presence of a few solvent molecules lying between Ar and TCNE moieties. This makes practically impossible the formation of a contact IP by vertical photo-excitation at the investigated energy ranges (see next subsection).

Hence if at a given frame of the  $MD_{neutral}$  simulation we find the TCNE c.o.m. and the Ar c.o.m. at a distance not larger than  $r_{EDAC}$ , all the coordinates of all the atoms of the box are collected into a sub-trajectory hereafter termed as  $MD_{EDAC}$ .



Figure 1. Normalized distribution of the c.o.m. distances between Bz and TCNE from  $MD_{neutral}$  simulation in  $CH_2Cl_2$  and schematic view of the simulation box.

As reported in Figure 1 in the case of Bz and TCNE, the use of the large box makes the formation of the EDAC in the  $MD_{neutral}$  simulation as rather unlikely – less than 1% of the whole frames – in the thermal conditions. Nevertheless the number of configurations, i.e. the number of  $MD_{EDAC}$  frames, turned out to be of the order of 10<sup>4</sup> hence making still impracticable the exhaustive QM calculation of the EDAC excited states.

A third approximation was then introduced, based on Essential Dynamics (ED) analysis following a procedure described in detail in our most recent studies. <sup>44,45</sup>

Briefly: using the  $MD_{EDAC}$  we constructed and diagonalized a covariance matrix of the EDAC atomic positional fluctuations producing a new set of coordinates, i.e. the eigenvectors of the covariance matrix in the  $3N_{atoms}$  dimensional space (where  $N_{atoms}$  is the numer of atoms of EDAC), along which the fluctuations occur. The resulting eigenvalues provide EDAC mean square fluctuation along the above mentioned eigenvectors.

Analysis of the obtained eigenvalues revealed that both in the case of Bz·TCNE (40% of the overall fluctuation) and in the case of Ind·TCNE (42% of the overall fluctuation) the first two eigenvectors (*eig1* and *eig2*), i.e. the directions associated to the highest eigenvalues, could be safely utilized <sup>64</sup> to exhaustively describe the inter-moieties motions and, hence, could be used for carrying out the EDAC inter-partners conformational analysis. In both the simulations we have projected the

MD<sub>EDAC</sub> onto the corresponding *eig1-eig2* planes producing the black points shown in Figure 2. Subsequently we have selected a number of conformational basins, indicated as red circles in the same Figure, at the centre of which we have picked out the related representative configurations (RC) of the EDAC. Note that the values of Root Mean Square Deviation (RMSD) between adjacent RCs do not exceed 0.12 nm. This relatively low value implies that the use of an arbitrary number of basins, of arbitrary dimension, should not severely influence the final result. It is also interesting to note that the selected basins do not show the same density hence indicating that the EDAC conformations are not characterized by the same stability.



Figure 2. Projection of the  $ME_{EDAC}$  sub-trajectories onto their essential planes (black circles) and identification of the conformational basins (red circles).

The coordinates of each of the extracted RCs were then locally relaxed in vacuum using QM calculations for obtaining the LRSs (see Computational Details) to be used for subsequent vertical excited states calculations. Details of the LRSs are reported in the Supplementary Information. Note that hereafter we are referring to j-th RC and LRS for indicating the MD instantaneous configuration falling in the centre of the j-th basin and the corresponding structure minimized using QM calculations, respectively.

A schematic view of the geometries are reported in Figures 3 and 4.



Figure 3. Schematic view of the Representative Configurations extracted from the centre of the basins reported in Figure 2 (for Ar=Bz)



Figure 4. Schematic view of the Representative Configurations extracted from the centre of the basins reported in

Figure 2 (for Ar=Ind)

The same procedure performed using the  $MD_{benzene}$  trajectory, as expected because of the semi-rigid nature of Bz, only produced a single basin which has been taken into account for the evaluation of the related UV spectrum (see below).

b- Modelling of low-energy electronic vertical transitions. Unperturbed QM calculation.

In correspondence of each of the ten LRSs, a collection of 8 vertical gas-phase (unperturbed) electronic states  $\Phi_l^0$  (*l*=ground, 1<sup>st</sup> excited, 2<sup>nd</sup> excited...7<sup>th</sup> excited) were then evaluated using TD/CAMB3LYP/6-311G\* calculations.

In Table 1 we report the relevant information concerning the energy range of interest in this study.

Table 1. Low-energy vertical excitation transitions  $(E_{0-i})$ , norm of the electric dipole expectation values  $(|\mathbf{\mu}_i|)$  for ground state (i=0) first (i=1) and second (i=2) excited states. Transition dipoles  $|\mathbf{\mu}_{0-i}|$  and excitation amplitudes (H stands for HOMO and L stands for LUMO)

Species	$ \mathbf{\mu}_0 $	E0-	Excitation	$ \mathbf{\mu}_1 $	$ \mu_{0-1} $	E <sub>0-</sub>	Excitation	$ \mathbf{\mu}_2 $	$ \mu_{0-2} $
species	(a.u.)	$_1(eV)$	Amplitude	(a.u.)	(a.u.)	$_2(eV)$	Amplitude	(a.u.)	(a.u.)
Bz·TCNE-1	0.55	3.09	H→L 0.5 (H-1)→L -0.8	$\frac{2}{5}$ 5.4	0.12	3.12	H-L -0.5 (H-1)-L -0.8	<sup>2</sup> <sub>5</sub> 5.1	0.75
Bz·TCNE-2	0.35	3.02	H→L -0.7 (H-1)→L -0.7	$\frac{1}{1}$ 5.8	0.18	3.03	H→L -0.7 (H-1)→L -0.7	1 1 5.8	0.37
Bz·TCNE-3	0.28	3.01	H→L 0.9 (H-1)→L -0.3	$\frac{2}{9}$ 7.0	0.12	3.04	H→L -0.9 (H-1)→L -0.3	$\frac{2}{9}$ 7.0	0.49
Bz·TCNE-4	0.41	3.07	H→L 0.1 (H-1)→L -0.9	$\frac{2}{9}$ 4.8	0.060	3.13	H→L -0.1 (H-1)→L -0.9	$\frac{2}{9}$ 4.6	0.70
Bz·TCNE-5	0.40	3.05	H→L 0.2 (H-1)→L -0.9	<sup>7</sup> <sub>6</sub> 5.0	0.042	3.10	H→L -0.2 (H-1)→L -0.9	4.8	0.63
Bz·TCNE-6	0.36	2.99	H→L -0.5 (H-1)→L -0.8	<sup>0</sup> <sub>6</sub> 6.1	0.20	3.02	H→L -0.5 (H-1)→L -0.8	<sup>0</sup> <sub>6</sub> 6.1	0.33
Bz·TCNE-7	0.47	2.95	H→L -0.9 (H-1)→L 0.0	<sup>9</sup> 0 5.4	0.17	3.05	$\begin{array}{cc} H \rightarrow L & 0.9 \\ (H-1) \rightarrow L & 0.0 \end{array}$	5.4	0.48
Bz·TCNE-8	0.36	2.96	H→L -0.9 (H-1)→L -0.3	$\frac{3}{7}$ 5.8	0.10	3.00	H→L 0.9 (H-1)→L -0.3	<sup>3</sup> <sub>7</sub> 5.8	0.27
Bz·TCNE-9	0.50	3.00	H→L -0.9 (H-1)→L -0.0	$^{9}_{0}$ 6.0	0.097	3.07	H→L 0.9 (H-1)→L -0.0	6.0	0.49
Bz·TCNE-10	0.35	3.05	H→L -0.9 (H-1)→L -0.0	<sup>9</sup> 4.6	0.17	3.10	H→L 0.9 (H-1)→L -0.0	4.5	0.63
Ind-TCNE-1	0.34	2.04	H→L -0.9 (H-1)→L -0.0	$\frac{9}{0}$ 6.8	0.050	2.74	H→L 0.0 (H-1)→L -0.9	6.4	0.26
Ind-TCNE-2	0.56	2.02	H→L -0.9 (H-1)→L -0.0	<sup>9</sup> 6.9	0.18	2.73	H→L 0.0 (H-1)→L -0.9	6.4	0.43
Ind-TCNE-3	0.89	2.36	H→L -0.9 (H-1)→L -0.0	<sup>9</sup> <sub>0</sub> 5.3	0.96	2.90	H→L 0.0 (H-1)→L -0.9	5.3	0.31
Ind.TCNE-4	0.57	2.11	$\begin{array}{ccc} H \rightarrow L & -0.9 \\ (H-1) \rightarrow L & -0.0 \end{array}$	<sup>9</sup> 6.3	0.13	2.85	$\begin{array}{ccc} H \rightarrow L & 0.0 \\ (H-1) \rightarrow L & -0.9 \end{array}$	5.9	0.49
Ind-TCNE-5	0.54	2.07	$\begin{array}{c} H \rightarrow L & -0.9 \\ (H-1) \rightarrow L & -0.0 \end{array}$	<sup>9</sup> 6.8	0.25	2.75	$\begin{array}{c} H \rightarrow L & 0.0 \\ (H-1) \rightarrow L & -0.9 \end{array}$	6.3	0.14
Ind-TCNE-6	0.52	2.07	$\begin{array}{ccc} H \rightarrow L & -0.9 \\ (H-1) \rightarrow L & -0.0 \end{array}$	<sup>9</sup> 6.1	0.15	2.81	$\begin{array}{ccc} H \rightarrow L & 0.0 \\ (H-1) \rightarrow L & -0.9 \end{array}$	5.7	0.53
Ind-TCNE-7	0.50	2.05	H→L -0.9	9 6.0	0.69	2.73	H→L 0.0	6.4	0.050

			_	_				_			
			(H <b>-</b> 1)→L	-0.00				(H-1)→L	-0.99		
Ind TONE 9	0.54	1.07	H→L	-0.99	6.0	0.26	2 77	H→L	0.00	68	0.41
IIIQ-ICINE-0	0.54	1.97	(H <b>-</b> 1)→L	-0.00	0.9	0.20	2.11	(H-1)→L	-0.99	0.0	0.41
Led TONE 0	0.66	2.00	H→L	-0.99	6.1	0.61	2.01	H→L	0.00	6.2	0.10
IIIQ-ICINE-9	0.00	2.08	(H <b>-</b> 1)→L	-0.00	0.1	0.01	2.01	(H-1)→L	-0.99	0.5	0.10
Ind TONE 10	0.66	2.00	H→L	-0.99	77	0.26	2 70	H→L	0.00	71	0.41
mu-rCNE-10	0.00	2.00	(H-1)→L	-0.00	1.1	0.20	2.70	(H-1)→L	-0.99	/.1	0.41

In full agreement with literature data, <sup>73-76</sup> essentially for all the EDAC configurations in both the systems the two lowest-energy transitions are characterized by a sharp CS character, as emerged by the drastic increase of the dipole moment upon the excitation as well as by the analysis of the atomic point-charges (see below).

As already inferred in previous computational studies  $^{77,78,55}$  irrespective on the EDAC geometries, both the  $0\rightarrow 1$  and  $0\rightarrow 2$  transitions can be described as an electron excitation from the two nearly degenerate  $\pi$  orbitals localized onto the Ar species to the  $\pi^*$  orbital of the TCNE moiety as pictorially shown in Figure 4.<sup>79</sup>

## **Bz-TCNE**



Figure 4. Schematic picture of the EDA complex frontier orbitals involved in the low-energy transitions (see Table 1). Note that the same picture emerges for each of the investigated RCs.

Nevertheless clear differences do emerge from the comparison between the two systems.

In the case of Ind-TCNE the two transitions are separated by a sharp energy gap which becomes close to zero in the case of Bz-TCNE. This nicely reflects the character of the two transitions in terms of frontier orbitals as reported in Table 1. In fact only in the case of Ind-TCNE complexes the

0-1 and 0-2 transitions, for all the sampled configurations, can be described as pure HOMO/LUMO and HOMO-1/LUMO transitions, respectively.

As a final comment it is also important to remark the values of the low-energy vertical transitions for a single configuration of a system  $Bz \cdot CH_2Cl_2 \cdot TCNE$  (see Figure 5), obtained at the same level of theory. In this three-body complex, as well as in each of the similar systems extracted from the  $MD_{neutral}$  simulation, the A-D distance is well above the previously defined  $r_{EDAC}$ .

The obtained values of 3.5 eV (0-1) and 3.8 eV (0-2) fall in an energy range well above the one found for the contact IP. Moreover none of the above low-energy transitions are characterized by a sharp At-TCNE CS character. This result provides a more quantitative support to the choice of the  $r_{EDAC}$  value of 0.50 nm, as reported in the previous subsection,



Figure 5. Schematic view of the Bz·CH<sub>2</sub>Cl<sub>2</sub>·TCNE complex configuration used to calculate the vertical excitations.

The whole set of  $\Phi_l^0$  unperturbed states of Table 1 has been used for modeling the CS spectrum in solution using the MD-PMM procedure as described in the next subsection.

### iii- Modelling of Charge-Separation UV-Vis spectra in solution. MD-PMM calculations.

Much of the details of the MD-PMM method for reproducing UV-Vis spectra of non-rigid species in solution as well as the comments about the related approximations and limitations, are reported in our recent papers. <sup>44,45,80,81</sup> In this section we only briefly provide the reader with the significant steps herein involved.

In the rest of this section we concisely refer either to EDAC or benzene, i.e. the systems whose UV-Vis spectrum has been investigated, with the acronym QC (Quantum Centre).

At a given p-th frame of the  $MD_{EDAC}$  or  $MD_{benzene}$  we have evaluated the RMSD between the instantaneous QC configuration and each of the RCs previously identified (In the case of EDAC, see Figure 2, 3 and 4). Assuming that at the p-th frame the minimum RMSD corresponds to the j-th RC we construct the corresponding instantaneous perturbed Hamiltonian matrix by using the  $\Phi_l^0$ 

basis set previously determined on the related LRS

$$\widetilde{H}(\mathbf{r}_{n},\mathbf{x}) = \widetilde{H}^{0}(\mathbf{r}_{n}) + q_{T}V(\mathbf{r}_{0},\mathbf{x}) + \widetilde{Z}(\mathbf{E}(\mathbf{r}_{0},\mathbf{x}),\mathbf{r}_{n}) + \Delta U(\mathbf{r}_{n},\mathbf{x})$$
(1)

where  $\mathbf{r}_n$  are the coordinates of the LRS of the j-th EDAC,  $\mathbf{r}_0$  is the QC center of mass position,  $\mathbf{x}$  are the instantaneous coordinates of the solvent atoms at the frame p-th,  $\tilde{H}^0(\mathbf{r}_n)$  and  $q_T$  are the j-th QC unperturbed Hamiltonian operator and the total charge, V and  $\mathbf{E}$  are the instantaneous perturbing electric potential and electric field exerted by the fluctuating atomic charges at the frame p-th onto  $\mathbf{r}_0$ . In equation (1) the perturbation energy matrix (generic element) is given by:

$$Z_{l,l'} = -\mathbf{E} \cdot \left\langle \Phi_l^0 \mid \hat{\boldsymbol{\mu}} \mid \Phi_{l'}^0 \mid \right\rangle \tag{2}$$

Where  $\hat{\mu}$  is the electric dipole operator and, hence  $\Delta U$  approximates all the perturbation higher order terms as a short range potential.

Repeating the above procedure at each frame of  $MD_{EDAC}$  (or  $MD_{benzene}$ ), and then diagonalizing the related perturbed Hamiltonian matrix (1) for each basin accessed by the QC, we obtain a sequence of perturbed Hamiltonian eigenvalues and eigenvectors. These values are then utilized for calculating the 0-i perturbed vertical excitation energies (i.e. the frequencies,  $v_{0-i}$ ) and whatever perturbed properties of QC such as the transition dipoles ( $\mu_{0-i}$ ) and perturbed charges. <sup>44</sup>

From the distribution of the all perturbed transition energies carried out performed with a defined number of bins, using the corresponding perturbed transition dipoles, the spectroscopic signals for each of the j-th QC configuration can be finally obtained.

The peculiarity of the MD-PMM approach, is the possibility of including the perturbation produced by the environment surrounding the QC at each step of the simulation hence allowing the modelling of the spectral shape for each accessed QC conformation without the use of predefined parameters. However the use of a limited number of QC structures, i.e. a limited number of  $\tilde{H}(\mathbf{r}_n, \mathbf{x})$ , inevitably produces a loss of sensitivity of the method. This deficiency has been shown <sup>44,80,81</sup> to be partially recovered by evaluating, for each basin, the variance ( $\sigma$ ) of the transition frequencies ( $v_{0-i}$ ). This latter quantity might be easily calculated by considering different configurations of the QC belonging to the same conformational basin.

The above theoretical framework can be concisely summarized through equation (3)<sup>80,81</sup>

$$\varepsilon_{0,i}(\nu) \cong \lim_{N \to \infty} \frac{1}{N} \sum_{\nu_{ref}} \frac{|\boldsymbol{\mu}_{o,i}|^2_{\nu_{ref}} h\nu}{6c\varepsilon_0 \hbar^2} \frac{n(\nu_{ref})}{N} \frac{e^{-(\nu - \nu_{ref})^2/(2\sigma^2)}}{\sqrt{2\pi\sigma^2}}$$
(3)

which has been used for the low-energy spectra of EDAC and benzene in infinite dilution conditions. Note that for benzene (see previous subsection) the whole procedure makes use of a single RC. In this equation  $\varepsilon_{0,i}$  is the molar extinction coefficient, N is the number of MD<sub>EDAC</sub> or MD<sub>benzene</sub> frames,  $\varepsilon_0$  is the vacuum dielectric constant, c is the vacuum light speed, h is the Planck constant,  $\hbar=h/2\pi$ ,  $|\mu_{0,i}|_{vref}$  is the reference structure mean electronic transition dipole length as obtained by averaging within the frequency bin centered at  $v_{ref}$ ,  $n(v_{ref})$  is the corresponding number of MD<sub>EDAC</sub> frames falling within the bin and  $\sigma$  is the previously defined variance.

The calculation of the latter produced a value of  $1.0*10^{-3}$  a.u. for Ar-TCNE spectra and  $2.0*10^{-4}$  a.u. for benzene spectrum at infinite dilution. Such a low value of  $\sigma$  for Bz is to be ascribed to the extremely confined fluctuation exclusively due to the out of plane semiclassical Bz vibrations.

Note that equation (3) practically provides us with the vertical absorption spectrum within the assumption of treating all the QC internal nuclear coordinates as semi-classical ones <sup>80, 81</sup>

The inclusion of the vibronic transitions, using a methodology described in detail in a recent paper, <sup>82</sup> although important for a semi-rigid species as Benzene, has revealed (see below) as irrelevant for the shape of the CS UV-Vis spectra of EDAC.



Figure 6. MD-PMM low-energy spectra calculated for Bz in  $CH_2Cl_2$ , Bz-TCNE in  $CH_2Cl_2$  and Ind-TCNE in  $CH_2Cl_2$ . The global spectra for Bz-TCNE and Ind-TCNE have been obtained by summing the 0-1 and 0-2 transitions which are also reported in the same Figure.

System	$\lambda_{0-i,max}$ (nm)	$(M^{-1} cm^{-1})$	$\lambda_{0-i,\max}$ (nm)	$(M^{-1} cm^{-1})$
	Calculated	Calculated	Experimental	Experimental
Benzene <sup>a</sup>	207	2	240	40
	209	6	245	90
	214	21	250	160
	220	38	255	180
	225	32	260	100
Bz·TCNE	389 (0-1 and 0-2)	2030	388 <sup>83</sup>	2000 83
Ind·TCNE	550(0-1)	Not available	540 (0-1) 56	Not available
	420(0-2)		420 (0-2) 56	

Table 2. Theoretical (MD-PMM) and experimental data concerning the lowest energy absorption spectra of benzene, Bz·TCNE and Ind·TCNE in solution.

<sup>a</sup> Data in chloroform.

Based on the inspection of the results reported in Figure 6 and Table 2, the following considerations can be derived.

a) First of all the  $\lambda_{MAX}$  are rather well reproduced. The only discrepancy worth of remark, and also expected because of the widely documented limitations of TD-DFT approaches in describing  $\pi - \pi^*$  transitions, is the slight overestimation of the Bz 0-1 vertical transition energy. Also the  $\varepsilon_{0-1}$  values are found in satisfactory agreement even though, again in the case of Bz, it should be remarked a small but significant underestimation of the value in line with our findings recently published on a very similar system as pyrene. <sup>82</sup> Note that the bandwidth (i.e. FWHM) of the Bz·TCNE and Ind·TCNE, not available in the literature and estimated of the order of 1.2-1.5 eV from similar systems, <sup>84</sup> resulted in line with our theoretical estimations which provided values of 1.5 eV (Bz·TCNE) and 1.9 eV (Ind·TCNE including both 0-1 and 0-2).

b) The Bz vibronic spectrum, found to be in good agreement with the experimental data, turned out to be much narrower than the corresponding low-energy spectra of Bz·TCNE and Ind·TCNE, hence indicating the irrelevance of the inclusion of the quantum vibronic effects in the latter spectra whose broadening is exclusively produced by the semiclassical (mainly) inter-partner motions and by perturbation of the fluctuating solvent molecules.

As a final comment on the CS separation spectra it is important to evaluate the extent of the CS occurring wihin the EDAC upon low-energy, 0-1 or 0-2 transitions. This aspect turns out to be of great relevance for the modelling of the kinetic analysis in second part of the present work,.

This analysis has been accomplished by evaluating the perturbed charges on the two moieties on the (vertical) first and second excited perturbed states.

The corresponding average values calculated using the  $MD_{EDAC}$  trajectories for Bz-TCNE and Ind-TCNE systems, are reported in Table 3.

Table 3. Average value of the perturbed point charges (atomic units) on the Ar moiety in the two systems.

System	Ground state	First excited state	Second excited state
Benzene-TCNE	~ 0.0	0.85	0.85
Indene-TCNE	$\sim 0.0$	0.87	0.86

From these results we can conclude that independently from the electronic state actually populated upon photo absorption (0-1 and 0-2), in both the systems we can observe an almost complete, although not pure, ET from Ar to TCNE moiety. This finding clearly indicates the absence of any correlation between the amount of transferred charge and the ionization energy of the Ar moiety and the position of the  $\lambda_{MAX}$ . This result is of crucial importance. In fact the CR process addressed in

this study might be correctly modelled utilizing the recent theoretical-computational procedure, recently developed in our group <sup>46</sup> for treating the kinetics of ET reactions, provided the process under study strongly resembles a genuine ET reaction. In this case it is important to remark that, from Table 3, a certain amount of charge is found to be delocalized on the two EDAC partners. This result makes our approach as affected by a systematic error whose effect on the final result can be evaluated from the comparison with the experimental results.

#### iv) Modelling of Charge Recombination kinetics

The method for modelling ET reactions, inspired by pioneering works in the literature,<sup>85, 86</sup> is based on the reconstruction of the reactive Adiabatic process through the evaluation of the Diabatic Perturbed surfaces, i.e. vibronic energy of  $Ar^+$  and TCNE<sup>-</sup> species in mutual interaction and perturbed by the solvent, whose sampling is evaluated at each frame of the MD<sub>IP</sub> using an observable as below described. This can be schematically visualized in the Figure 7.



Figure 7 Schematic view of the reactants and products Diabatic Perturbed energy surfaces (solid lines) and their relation with the EDAC Adiabatic Energy surfaces (dashed lines). In the figure the chemical states relevant to the CR reaction have been highlighted (see the text). The red line schematically indicates the Diabatic Perturbed energy surface of the EDAC actually followed along the MD<sub>IP</sub> simulation.

In the abscissa of the Figure we report a generic perturbation, concisely indicating the course of the reaction promoted by the inter-partners and solvent motions. In the ordinate we report the energy

and the intersecting lines correspond to the two crossing Diabatic Perturbed surfaces. The dashed lines, on the other hand, identify the Adiabatic Perturbed surfaces which is the route promoting the CR step, i.e. the  $(Ar^+ \cdot TCNE^-)_{II} \rightarrow (Ar \cdot TCNE)_{II}$  transition. The red circle schematically locates the generic initial condition of the non-equilibrium trajectory, i.e. the IP species with the fully relaxed quantum degrees of freedom (optimized bond distances and bond angles of all the involved species, according to the approximations outlined in the Introduction). The semi-classical dynamics of the system  $Ar^+/TCNE^-$ /solvent, in accordance with the force field of the MD<sub>IP</sub>, basically corresponds to the motion along the Diabatic Perturbed energy surface and can be pictorially figured out as a motion along the red line which drives the system into the Transition Region (TR): the necessary condition for the ET to take place.

Actually, although we have decided to follow the evolution of vibrationally relaxed initial species, i.e.  $(Ar^+ \cdot TCNE^-)$  in its vibronic ground state, we do not have any indication about the nature of the Perturbed Diabatic (Ar · TCNE) crossing state. In other words, see red and blue arrows in Figure 8, several crossings between the relaxed (Ar<sup>+</sup> · TCNE<sup>-</sup>) and different vibrationally excited (Ar · TCNE) can be conceived.

Which of two the processes, hereafter concisely termed as  $IP \rightarrow EDAC$  and  $IP \rightarrow EDAC^*$ , is the preferred route, is due to the instantaneous overlap between the corresponding vibronic states.



Figure 8. Schematic representation of IP  $\rightarrow$  EDAC (red line) and IP  $\rightarrow$  EDAC\* (blue line), see text.

In any case to translate the above picture in more quantitative terms, it is necessary to select an observable to follow along the simulation.

According to our method  $^{46}$  we have evaluated at each frame of the MD<sub>IP</sub> simulations the transition energy TE defined as

$$TE \approx \varepsilon_{\text{TCNE},0/(\text{Ar}+)} - \varepsilon_{\text{TCNE},0/(\text{Ar}+)} + \varepsilon_{\text{Ar},0/(\text{TCNE})} - \varepsilon_{\text{Ar}+,0/(\text{TCNE})}$$
(4)

to follow the IP  $\rightarrow$  EDAC (red line in Figure 8) and the vertical Transition Energy (TEv) defined as

$$TEv \approx \varepsilon_{\text{TCNE},v/(\text{Ar}^+)} - \varepsilon_{\text{TCNE},0/(\text{Ar}^+)} + \varepsilon_{\text{Ar},v/(\text{TCNE})} - \varepsilon_{\text{Ar}^+,0/(\text{TCNE})}$$
(5)

to follow the IP  $\rightarrow$  EDAC\* (red line in Figure 8).

In the equations (4) and (5):

a)  $\varepsilon_{\text{TCNE},0/(\text{Ar}^+)}$  and  $\varepsilon_{\text{TCNE},0/(\text{Ar}^+)}$  are the instantaneous eigenvalues of the electronic Hamiltonian (equation 1) calculated for TCNE and TCNE<sup>-</sup> using the unperturbed basis set evaluated in correspondence of their relaxed geometries, i.e. in their vibrational ground state, and using the instantaneous electric field exerted by the solvent and by the Ar<sup>+</sup> species as perturbation.

b)  $\varepsilon_{Ar,0/(TCNE)}$  and  $\varepsilon_{Ar^+,0/(TCNE)}$  are the instantaneous eigenvalues of the electronic Hamiltonian (equation 1) calculated for Ar and Ar<sup>+</sup> using the unperturbed basis set evaluated in correspondence of their relaxed geometries, i.e. in their vibrational ground state, and using the instantaneous electric field exerted by the solvent and by the TCNE species as perturbation

c)  $\varepsilon_{Ar,v/(TCNE)}$  and  $\varepsilon_{TCNE,v/(Ar^+)}$  are the instantaneous eigenvalues of the electronic Hamiltonian (equation 1) calculated for Ar and TCNE using their unperturbed basis set evaluated in correspondence of the geometries of Ar<sup>+</sup> and TCNE<sup>-</sup> relaxed geometries. Within this approximation we assume that the a maximum overlap can be expected when the IP and EDAC geometries are the same.

Within this picture, at the beginning of the process, TE (or TEv) is clearly positive and becomes increasingly close to zero as the system approaches the TR. Hence we consider that a potential ET event occurs when the TE (or TEv) changes its sign for the first time as shown by way of an example in Figure 9



Figure 9. Time course of the TE for two  $MD_{IP}$  trajectories used for the CR kinetics in Bz-TCNE system. In the black trajectory we observe a crossing, i.e. a potential ET event, approximately at 12.0 ps. In the green trajectory we do not observe any crossing in the first 15.0 ps.

As widely discussed in our recent literature, <sup>46</sup> it is important to remark that we adopt the basic approximation of considering the instantaneous relaxation of the electronic Hamiltonian eigenstate, i.e. Adiabatic approximation, and hence we do not take into account any transmission coefficient. The validity of this approximation cannot be assessed in advance but only in the light of a comparison between the theoretical results with the experimental kinetic data.

Therefore, in order to evaluate the rate constant for the CR process, i.e. either IP  $\rightarrow$  EDAC or the IP  $\rightarrow$  EDAC\* Adiabatic routes, it will be sufficient to measure the distribution of the times needed to reach the first *TE* (or *TEv*) change of sign using the whole ensemble of the non-equilibrium (MD<sub>IP</sub>) trajectories.



Figure 10. Kinetic trace for the IP $\rightarrow$ EDAC (red line) and IP $\rightarrow$ EDAC\* (blue line) and the corresponding exponential fitting (black lines), as provided by the ensemble of non-equilibrium MD<sub>IP</sub> trajectories for Bz-TCNE (left panel) and Ind-TCNE in CH<sub>2</sub>Cl<sub>2</sub> solution.

In Figure 10 we have reported the kinetic trace, i.e. the time length distribution, for the CR reactions, both assuming the IP $\rightarrow$ EDAC (red line) and IP $\rightarrow$ EDAC\* (blue line) transitions as provided by the ensemble of the 120 non-equilibrium MDIP trajectories at 298 K. The corresponding exponential fitting curves, also indicated in the same Figure (black lines), provided the mean lifetime values ( $\tau$ ) collected in Table 4 and compared to the corresponding experimental values.

Table 4. Calculated and experimental mean lifetimes (ps).

System

Experimental Bz/TCNE 
$$29.0^{55}$$
  
IP(Bz)  $\rightarrow$ EDAC  $140 \pm 29$ 

$IP(Bz) \rightarrow EDAC^*$	$39 \pm 9$
Experimental Ind/TCNE	1.7 56
$IP(Ind) \rightarrow EDAC$	$1.1 \pm 0.3$
$IP(Ind) \rightarrow EDAC^*$	$0.5 \pm 0.1$

The calculated values and the related error bars reported in the above table are averages and standard errors calculated considering three ensembles of 40 non-equilibrium trajectories.

The above results clearly indicate that:

a- in the case of the process involving Bz, the calculated vertical IP $\rightarrow$ EDAC\* process provides a mean lifetime which, within the standard error, turns out to be in good agreement with the experimental one. A relative error of 20%, well beyond the expected accuracy of our method, <sup>46,47</sup> is probably due to the systematic error of our calculations induced by the initial charge delocalization on the two IP partners, which makes the present CR process not completely coincident with a genuine ET process. On the other hand, the modelling of IP $\rightarrow$ EDAC process seems much less efficient. Hence it is possible to assess, not in disagreement with experimental observations, that in the present case the CR reaction produces a Bz·TCNE complex not completely internally relaxed.

b- In the case of Ind it is slightly more difficult to quantify the discrepancies between the calculated and measured values. In fact, the experimental  $\tau$  value was taken by a work <sup>56</sup> in which the same quantity for Bz-TCNE system turned out to be sharply overestimated by 50 ps with respect to the most recent estimation of 29 ps utilized in the present study. Hence also for Ind-TCNE the experimental  $\tau$  could be expected to be slightly overestimated. Nevertheless our calculations nicely reproduce the order of magnitude of the experimental  $\tau$ , even though it is not possible to definitely discriminate between the IP $\rightarrow$ EDAC\* and IP $\rightarrow$ EDAC processes.

This data have been finally utilized to visualize the configurations related to the CR events, in each oft he 120 MD<sub>IP</sub>. In Figure 11 We have reported the distance between the c.o.m. of the two partners ( $Ar^+$  and TCNE<sup>-</sup>) at the initial IP and at the crossing. This quantity has been then correlated to the angle formed by the planes of symmetry of the two partners evaluated at the same positions (see inset of Figure 11.



Figure 11. Correlation between the interpartners c.o.m. distances (**R**) and V1-V2 angle at the initial IP configurations (black points) and crossing configurations (red points) as obtained by all the  $MD_{IP}$  trajectories for Ind-TCNE (lowe panel) and Bz-TCNE (upper panel) systems.

In the Ind-TCNE system, lower panel of Figure 11, the IP initial configurations (black points) are characterized by an almost coplanar TCNT<sup>-</sup>/Ind<sup>+</sup> arrangement somewhat correlated to the interpartners distances. Because of the very high efficiency of the IP $\rightarrow$ EDAC (or IP $\rightarrow$ EDAC<sup>\*</sup>) process, previously observed, the CR configurations (red points in the lower panel) do not show appreciable differences in the interpartners distances. On the other hand the TCNT<sup>-</sup>/Ind<sup>+</sup> angular arrangement appear as more diffusely distributed suggesting the lack of any sharp relationship between the interpartners mutual arrangement and the potential CR event.

Such a picture is even more evident for Bz-TCNE system. First of all, because of the less pronounced efficient of the IP $\rightarrow$ EDAC\* process, it is interesting to note that we do not observe any potential CR event at interpartners distances below 0.45 nm. Moreover, both the interpartners distances and angular mutual arrangement of the potential CR event appear as completely uncorrelated. We wish to further remark that the above analysis, within the Adiabatic

approximation, only takes into account the *possibility* that a CR event takes place. Extension of the method, with the inclusion of the explicit evaluation of the adiabaticity, is currently under study in our laboratory.

#### v) Analysis of the plausible implication of triplet Ion-Pair complex

In principle the biradical nature of IP species may involve (at least) both the singlet and the triplet magnetic states. <sup>87</sup> In fact, following the formation of the singlet IP (hereafter termed as <sup>1</sup>IP) through photon absorption, the <sup>1</sup>IP-<sup>3</sup>IP interconversion cannot be *a priori* disregarged. In addition the <sup>3</sup>IP, once formed, might undergo a CR recombination process upon crossing with the triplet magnetic state of the EDAC, hereafter termed as <sup>3</sup>EDAC. All these plausible reaction channels can significantly alter the population of the IP, the experimental observable, and consequently the kinetic picture above outlined. Therefore we decided to preliminary investigate this aspect which, because of the many theoretical-computationally implications will be more in depth addressed in forthcoming studies.

First of all it is important to note that QM calculations carried out at the TD/CAM-B3LYP/6-311G\* level on the gaseous EDAC structures of the Bz/TCNE system in the triplet magnetic state, have revealed the systematic presence of a  $T_1$  state (i.e. first excited state on the triplet magnetic state) with charge-transfer character virtually degenerate with the singlet charge-transfer state  $S_1$ . Moreover, analysis of the Mulliken spin population on the  $T_0$  state of <sup>3</sup>EDAC has shown for the Csp<sup>2</sup> atom (0.025 a.u.), C-sp atom (-0.048 a.u.) and N atom (0.010 a.u.) of the TCNE moiety, essentially the same values obtained for the isolated TCNE (0.022 a.u. for C-sp<sup>2</sup>, -0.048 a.u. for Csp and 0.010 for N). As a consequence the <sup>3</sup>EDAC species can be considered as weakly bound complexes between <sup>1</sup>Bz and <sup>3</sup>TCNE.

On the basis of the above findings and using the same procedure previously described, we have calculated at each frame of the  $MD_{IP}$  simulations, the vertical Transition Energy (<sup>3</sup>TEv) defined as

$${}^{3}TEv \approx \varepsilon_{\text{triplet-TCNE},v/(\text{Ar+})} - \varepsilon_{\text{TCNE},0/(\text{Ar+})} + \varepsilon_{\text{Ar},v/(\text{TCNE})} - \varepsilon_{\text{Ar+},0/(\text{TCNE})}$$
(6)

to check the occurrence of the IP  $\rightarrow$  <sup>3</sup>EDAC\* potential crossing.

In the equation (6), similarly to equation (5), we have used the perturbed ground state energy of the triplet TCNE obtained, through PMM, using the unperturbed basis set evaluated using the geometry of the TCNE<sup>-</sup>.

From the result, reported in the Figure 12



Figure 12. Kinetic trace for the IP $\rightarrow$ <sup>3</sup>EDAC\* (blue line) and the corresponding exponential fitting (black lines), as provided by the ensemble of non-equilibrium MD<sub>IP</sub> trajectories for Bz-TCNE in CH<sub>2</sub>Cl<sub>2</sub> solution.

we have obtained a  $\tau=0.29\pm0.05$  ps clearly showing that the crossing process between <sup>3</sup>IP and <sup>3</sup>EDAC energy surfaces is basically completed within one picosecond from the photo-formation of IP species. Hence, given the extremely low efficiency of the <sup>1</sup>IP $\rightarrow$ <sup>3</sup>EDAC process requiring a simultaneous electron and spin transfer, <sup>46</sup> any CR involving the IP species and the <sup>3</sup>EDAC can only take place if the <sup>1</sup>IP $\rightarrow$ <sup>3</sup>IP process is faster than - or comparable to - 0.29 ps.

In order to estimate the efficiency of the  ${}^{1}IP \rightarrow {}^{3}IP$  transition we have adopted a computational methodology, previously reported in a recent paper.  ${}^{88}$ 

Briefly, at each frame of the  $MD_{IP}$  simulations, we have constructed the approximated spin-Hamiltonian operator

$$\widehat{V} = \frac{\mu_0}{4\pi r^3} \left( \widehat{\mu}_1 - \frac{3}{r^2} \widehat{\mu}_1 \cdot \mathbf{rr} \right) \cdot \widehat{\mu}_2$$
(7)

using as basis set, the singlet and the triplet T<sub>0</sub>,T-1 and T<sub>+1</sub> spin eigenstates.

In the equation (7)  $\mu_0$  is the magnetic permeability in vacuum, r is the instantaneous distance between the interacting radicals (1 and 2 in the same formula) and  $\hat{\mu}$  is the magnetic dipole operator equal to

$$\widehat{\boldsymbol{\mu}} = -\frac{g_e e}{2m_e} \widehat{\mathbf{S}}$$
(8)

with  $g_{e}$ , e and  $m_{e}$  the free electron g-factor, the charge and mass of the electron, respectively, and  $\hat{S}$  is the spin operator.

Diagonalization of the above Hamiltonian provides the instantaneous spin Hamiltonian eigenstates consisting of a singlet spin eigenstate, with eigenvalue always equal to zero, and three triplet states. The instantaneous degeneracy of the above eigenvalues, also in this case in the Adiabatic approximation, should hence allow us to estimate the proper condition for the <sup>1</sup>IP  $\rightarrow$ <sup>3</sup>IP transition. The time-course of the eigenvalues for one trajectory is reported, as an example, in the Figure 13.



Figure 13. Time evolution of the four spin eigenvalues during one of the  $MD_{IP}$  trajectories analyzed. The black, red and blue lines correspond to the three triplet states eigenvalues. The green line corresponds to the singlet eigenstate. With black boxes we have highlighted the crossing events occurred in this specific trajectory.

From the definition of the perturbation operator (7), we have one eigenvalue always equal to zero (green line in Fig. 13) corresponding to the singlet state which is the state in which our system (IP) is present at the beginning of the trajectory. The other three eigenvalues different from zero correspond to spin states essentially resembling the  $T_0$  (red line),  $T_{+1}$  (black line) and  $T_{-1}$  (blue line) spin eigenstates. The black and blue lines, two of the triplet eigenstates, never recombine with the singlet state in this case and in none of the other trajectories, indicating that such a transition is not present. On the other hand a few transitions, i.e. energy crossings, are observed for the singlet and for the triplet state (red line) showing that this transition, although not frequent in this case and in all the other trajectories, is possible. In Figure 13 the black boxes indicate the occurrence of crossing events and the potential singlet to triplet conversion. Hence monitoring the relative energies of these two eigenstates and adopting the same procedure utilized in the case of CR process we have obtained the double-exponential decay profile shown in Figure 14.



Figure 14. Kinetic trace for the <sup>1</sup>IP $\rightarrow$ <sup>3</sup>IP as provided by the ensemble of non-equilibrium MD<sub>IP</sub> trajectories for Bz-TCNE in CH<sub>2</sub>Cl<sub>2</sub> solution. The red and black curves are the non-linear fittings.

Moreover, using also all the trajectories and evaluating the sub-population (black-boxes in Figure 13) of frames in which the transition has occurred, we have also estimated the relative triplet/singlet ratio which resulted approximately equal to 0.13.

The result in Figure 14 clearly shows the presence of two sub-populations in the IP ensemble. The first one, characterized by a  $\tau$ =34 ps, and representing the productive fraction of the IP population (approximately the 54% of the whole population) collect the ensemble of all the configurations at

inter-partner distances lower than 0.35 nm. Within such a sub-population the fraction of formed <sup>3</sup>IP is of the order of 13%, therefore less than 6% of the whole IP ensemble. The second one, with a  $\tau$  of the order of tens of nano-seconds, is not able to produce any <sup>3</sup>IP, at least in the timescales of the decay process. These results suggest that for the Bz-TCNE system, assuming a fully Adiabatic behavior, a small but not negligible fraction of the IP ensemble is expected to interconvert into the triplet state. This subpopulation, although essentially unable to promote CR process for kinetic reasons, can produce a small but not irrelevant effect on the whole kinetics of the process. This might be the one of the origins of the overestimation observed for the CR time-constant (39.0 ps vs 29.0 ps). A more quantitative estimation of these effects, under study in our laboratory, will be presented in forthcoming studies.

#### **Conclusions.**

In this study we have reported a theoretical-computational modelling of some of the key events characterizing the photo-induced Charge Separation and the subsequent Donor-to-Acceptor Charge Recombination process. Two experimentally well investigated systems, i.e. Aromatic moiety (Benzene or Indene as Donor) and Tetracyanoethylene in dicholoromethane solution have been selected as case-studies. Our approach, based on a combination of Molecular Dynamics simulations and Quantum-Chemical calculations has revealed a computationally efficient tool for reproducing the spectral features of the Charge Separation spectra of both the systems. Deep analysis of the results has interestingly revealed that the above spectral shape, is essentially dominated by the solvent perturbation and by the inter-partners mutual rearrangements primarily induced by the thermal fluctuations.

The kinetics of the Charge Recombination process, in the picosecond-nanosecond domain, has been also addressed in satisfactory agreement with the experiment (neglecting the ultrafast processes).

The implication of the triplet magnetic state has also addressed at a semi-quantitative level.

Our results indicate that:

a - even for relatively slow processes (order of tens/hundreds picoseconds) the charge transfer event is supposed to generate vibrationally hot Donor-Acceptor complexes;

b - the occurrence of charge transfer event is apparently not strongly dependent to any interpartners specific geometrical arrangement and, hence, the solvent perturbation is supposed to play a key role in the process efficiency as stated, for example, in the model underlying the Marcus equation; c - The not perfect agreement between the calculated and the experimental charge recombination rate constants has also suggested the presence of systematic deficiencies of the method. In particular: (1) the short range interaction between the partners within the Ion Pair complex is not purely semi-classical as witnessed by the presence of 10% of charge separation. This would produce some inadequacy in the conformational repertoire as emerged from MD simulations and, also, in the description of the Charge Recombination process as a genuine Electron Transfer event. (2) The Adiabatic approximation systematically adopted in the present study, deserves further study to be coherently implemented in the outlined methodology. (3) The implication of the triplet state cannot be disregarded a priori. In the case of Bz-TCNE system, the presence of a small but not irrelevant fraction of triplet state, although unable to produce any charge-recombination process, is expected to slightly modify the population of the Ion-Pair and, hence, the whole kinetic picture.

This study has shown, for the first time to the best of our knowledge, that it is possible to satisfactorily modelling some of the key events of the Charge Separation and Charge Recombination process within the same theoretical-computational framework (and a limited computational cost). The good performance of the method makes it a promising tool for future applications on more complex systems.

Some relevant aspects, in particular the validity of the Adiabatic approximation, are currently under investigation in our laboratory.

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