## Supporting Information

## Mobilities of iodide anions in aqueous solutions for applications in natural dye-sensitized solar cells

Giuseppe Cassone<sup>\*1a</sup>, Giuseppe Calogero<sup>2b</sup>, Jiri Sponer<sup>1c</sup>, Franz Saija<sup>2d</sup>
<sup>1</sup> Institute of Biophysics,
Czech Academy of Sciences, Královopolská 135,
61265 Brno, Czech Republic
<sup>2</sup> CNR-IPCF, Viale Ferdinando Stagno d'Alcontres 37,
98158 Messina, Italy

(Dated: April 9, 2018)

<sup>&</sup>lt;sup>a</sup> Email: cassone@ibp.cz

 $<sup>^{\</sup>rm b}$  Email: calogero@ipcf.cnr.it

 $<sup>^{\</sup>rm c}$  Email: <code>sponer@ncbr.muni.cz</code>

<sup>&</sup>lt;sup>d</sup> Email: saija@ipcf.cnr.it

## I. AB INITIO MOLECULAR DYNAMICS SIMULATIONS

The implementation of an external electric field in numerical codes based on density functional theory (DFT) can be achieved by exploiting the modern theory of polarization and Berry's phases [1] (see, e.g., Ref. [2, 3]). The *ab initio* simulations have been carried out at the average temperature of 300 K after an equilibration run of 5 ns performed by means of typical force-fields simulations in order to prepare a suitable initial atomic configuration for *ab initio* molecular dynamics (AIMD). In the zero-field case, we performed a dynamics of almost 12 ps for the biggest samples (*i.e.*, those mimicking a salt molarity of 0.5 M) whereas trajectories almost 24 ps-long have been accumulated for the simulations of the systems at 2.1 M. As far as the 0.5 M samples are concerned, dynamics of about 4 ps have been simulated for each field strength applied (*i.e.*, 0.05 V/Å, 0.075 V/Å, 0.15 V/Å) whereas trajectories of about 8 ps have been gathered for each of the 2.1 M systems and for each field intensity. Thus, each sample at 0.5 M has been simulated for a total dynamics of about 24 ps whereas each system at 2.1 M has been followed for dynamics of about 48 ps. This led to a global computational effort accounting for a total dynamics of about 215 ps which, for such relatively large systems under the effect of electric fields, represents a sort of computational upper-bound for the employed simulation technique. The fictitious electronic mass was set to a value of 300 a.u., with a cutoff energy of 40 Ry for the plane-wave representation of the wavefunctions and of 320 Ry for the charge density, with a timestep of 0.096 fs chosen ad hoc after extensive testing. With such cutoff values the samples are described in a reliable way since the core electronic interaction is being depicted through ultrasoft pseudopotentials (USPP) generated via the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) method. As an approximation of the exchange and correlation functional, we adopted the Perdew-Burke-Ernzerhof (PBE) functional [5], which belongs to the generalized gradient approximation (GGA). The PBE functional and its adequate description of polarization effects [6] is known to provide a reasonably accurate structure for H-bonded systems [7]. Moreover, albeit its employment is justified by the thoroughly tested adherence of some computational results [8– 10] to many experimental data [11], we carefully checked the reliability of the current results by means of a direct comparison with the available experimental data describing the water structure [11]. The dynamics of the nuclei was simulated classically within a constant number, volume, and temperature (NVT) ensemble, using the Verlet algorithm and a Nosé-



FIG. 1. Iodide-oxygen (a) and iodide-hydrogen (b) running coordination numbers of the 2.1 M KI (black curves), NaI (red curves), and LiI (blue curves) water solutions at 300 K.



FIG. 2. Mean square displacement (MSD) along the field direction (*i.e.*, z-axis) of the iodide anions present in the 0.5 M KI (a), NaI (b), and LiI (c) water solutions at different field strengths. Black curves: 0.05 V/Å; red curves: 0.075 V/Å; blue curves: 0.15 V/Å. No field-induced diffusive regimes have been recorded.

Hoover thermostat set at a frequency of 13.5 THz.



FIG. 3. Mean square displacement (MSD) along the field direction (*i.e.*, z-axis) of the cations present in the 2.1 M water solutions at different field strengths. Dashed lines: 0.075 V/Å; continuous lines: 0.15 V/Å. Black:  $K^+$ ; red:  $Na^+$ ; blue:  $Li^+$ .



FIG. 4. Probability distributions of the electric charge assumed by the cations (a) and the iodide anions (b) in the 2.1 M KI (black curves), NaI (red curves), and LiI (blue curves) water solutions at a field strength of 0.15 V/Å.

## **II. EXPERIMENTS**



FIG. 5. Experimental Current Density as a function of the applied voltage for the KI (black curve), the NaI (red curve), and the LiI (blue curve) 2.1 M aqueous solutions.

- [1] M. V. Berry, Proc. R. Soc. Lond. A, 1984, **392**, 45.
- [2] P. Umari and A. Pasquarello, *Phys. Rev. Lett.*, 2002, **89**, 157602.
- [3] N. J. English and C. J. Waldron, Phys. Chem. Chem. Phys., 2015, 17, 12407.
- [4] A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, 44, 13175.
- [5] J. P. Perdew, K. Burke, K. and M. G. Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865 and *Phys. Rev. Lett.*, 1997, 78, 1396.
- [6] N. Marom, A. Tkatchenko, M. Rossi, V. G. Gobre, O. Hod, M. Scheffler and L. D. Kronik, J. Chem. Theo. Comp. 2011, 7, 3944.
- [7] C. Fiolhais, F. Nogueira and M. Marques, A Primer in Density Functional Theory, Springer-Verlag: Berlin Heidelberg, 2010.
- [8] G. Cassone, F. Creazzo, P. V. Giaquinta, F. Saija and A. M. Saitta, Phys. Chem. Chem. Phys., 2016, 18, 23164.
- [9] A. M. Saitta, F. Saija and P. V. Giaquinta, Phys. Rev. Lett., 2012, 108, 207801.
- [10] J. C. Grossman, E. Schwegler, E. W. Draeger, F. Gygi and G. Galli, J. Chem. Phys., 2003, 120, 300.
- [11] A. K. Soper, The Radial Distribution Functions of Water as Derived from Radiation Total Scattering Experiments: Is There Anything we can Say for Sure? Hindawi Publishing Corporation - ISRN Physical Chemistry 2013, 2013, ID 279463.