Vibrational Study of Iodide-Based Room-Temperature Ionic-Liquid Effects on Candidate N719-Chromophore/Titania Interfaces for Dye-Sensitised Solar-Cell Applications from Ab-Initio Based Molecular-Dynamics Simulation

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Abstract: The accurate ab-initio modelling of prototypical and well-representative photo-active interfaces for candidate dye-sensitised solar cells is a challenging problem. To this end, using ab-initio molecular-dynamics (AIMD) simulation based on Density Functional Theory (DFT), the effects of explicit solvation by iodide-based, I$^-$ [bmim]$^+$ room-temperature ionic liquids (RTILs) have been assessed on modelling a N719-chromophore sensitising dye adsorbed onto an anatase-titania (101) surface. In particular, the vibrational spectra for this model photo-active interface were calculated by means of Fourier transformed mass-weighted velocity autocorrelation functions. These were compared with experiment and against each other to gain an understanding of how using iodine-based RTILs as the electrolytic hole acceptor alters the dynamical properties of the widely-used N719 dye. The effect of Perdew-Burke-Ernzerhof (PBE) and Becke-Lee-Yang-Parr (BLYP) functionals on the vibrational spectra were assessed. PBE generally performed best in producing spectra which matched the typically expected experimental frequency modes.

Keywords: dye-sensitised solar cell; ionic liquid; ab-initio molecular dynamics; vibrational spectra

1. Introduction

In the field of dye-sensitised solar cells (DSCs), the optical band gaps of semiconductors are bridged by a light-absorbing, or sensitising, dyes. DSCs need to have their charge replenished continuously, therefore, it is necessary to have some form of redox electrolyte as the third primary component, such as I$^-$/I$^{3-}$ in an organic solvent. This allows for hole transfer from the dye to the electrolyte, with concomitant circulation of electrons injected into the semiconductor through it into the external circuit, with recombination at the cathode; in such a way, a functioning DSC is realised. A vital factor supporting DSCs’ key prospects is that their manufacture does not depend upon high-purity materials. DSC lifetimes may be enhanced greatly by replacing a volatile electrolyte with low-volatility room-temperature ionic liquids (RTILs). Indeed, RTILs’ liquid-like electrical properties and solid-like physical counterparts (e.g., low volatility, toxicity and flammability [1]) means that RTILs constitute an excellent candidate for DSCs. Indeed, there has been a substantial boost of activity in recent years in the study of prototypical N719-chromophore/titania interfaces (with room-temperature ionic liquids), for DSC application. Particularly interesting work has been carried out in references [2–5], which focus, inter alia, on kinetics of dye charge regeneration [2,5] and the details of electron-hole transfer [3], as well as the nanoscale behaviour of titania in such a context [4].
Given the emergence of Density Functional Theory (DFT)-based molecular simulation, particularly AIMD, as a highly useful prototypical design tool in materials science and particularly for DSCs [6–8], we have leveraged AIMD methods in previous work to study rather dramatic dispersion and explicit-RTIL solvation effects on dye structure and adsorption motifs and modes at a DSC’s metal-oxide interface [9,10]. In particular, we applied this extensively to a well-studied photo-active N719-chromophore dye in contact with anatase-titania (101) surface, gauging both structural and vibrational properties [7,10]. However, in references [9,10], we concentrated on a [bmim]+[NTf2]− RTIL; in recent time there has been a growing impetus in DSC research towards embracing iodide-based liquids owing, *inter alia*, to their more favourable viscosity properties vis-à-vis other popular RTIL candidates based on, e.g., [NTf2] anions [1]. To this end, bearing in mind AIMD’s promising performance and outlook for preliminary DSC-design prototyping [6–8,10], in the present study, we seek as a powerful motivator the assessment of DFT functionals for a model iodine-based RTIL—I−[bmim]+—towards the study of vibrational properties of the well-studied N719 dye adsorbed to the anatase-(101) surface, for which reasonable experimental data are available for validation of predictive performance.

In any event, even though the most widely-used DFT functionals towards ionic-liquid simulation are arguably PBE and Becke, 3-parameter, Lee-Yang-Parr (B3LYP), the decision was made to rule out B3LYP in the present study as a potential candidate functional due to the insightful work of Izgorodina et al. [11], which showed that B3LYP tends to lead towards systematic errors in calculating ionic-liquid properties. Therefore, here, we compare two Generalised-Gradient Approximation (GGA) functionals—PBE and BLYP, as has been done in respect of the [bmim]+[NTf2]− RTIL in references [9,10]; we apply these towards the anatase-(101)-adsorbed N719 and compute the resultant vibrational spectra from AIMD, assessing the I−[bmim]+ RTIL effects thereon.

2. Methodology

The structures and computational procedure were adopted from our previous work [9,10] and this is summarized below for the convenience of the reader. The sensitising dye N719 (cis-di(thiocyanato)-bis(2,2′-bipyridl-4-carboxylate-4′-carboxylic acid)-ruthenium(II)) was used in our simulations with no counterions. Two surface-bound protons were also added for charge neutrality. Careful work of Angelis et al. [12], has established this to constitute a realistic representation of N719 adsorbed to anatase-titania. In the initial configuration, the dye was chemisorbed to the anatase surface via two carboxylate groups, namely bidentate and monodentate [6–10]. This adsorbed configuration is similar to the especially stable I1 found by Schiffmann et al. [13], in view of the surface protonation. As mentioned previously, the RTIL used consisted of 16 cation-anion pairs of 1-butyl-3-methylimidazolium iodide, [bmim]+[I]−, composed of 416 atoms. The liquid-state starting configuration was relaxed by classical Molecular Dynamics (MD). The anatase surface, (TiO2)386, comprised 288 atoms and was periodic along the x- and y-laboratory axes, presenting to the RTIL two parallel (101) surfaces; the x- and y-respective surface dimensions were 2.3 and 2.1 nm. The DSC system with explicit solvent was thus composed of 763 atoms and 3554 valence electrons. For a comparative ‘in-vacuo’ state (i.e., bereft of any RTIL), there were 347 atoms and 2530 valence electrons. These systems were simulated via Born-Oppenheimer Molecular Dynamics (BOMD), as implemented in CP2K [14–17], using the parameters of Byrne et al. [9,10] (*vide infra*); for detailed input and parameters, see the Supplementary Information (SI).

To allow for comparison between the *in-vacuo* and explicitly-solvated cases on influencing the structural and vibrational spectra of this interface, four BOMD simulations were run under the conditions described below for ~8–9 ps. For explicit dispersion effects, the Grimme D3 dispersion corrections [18,19] were added to both functionals in all cases, as references [9,10] highlighted the superior performance of this form of dispersion in the case of the system with the [bmim]+[NTf2]− RTIL. The Nosé-Hoover [20] thermostat was used to maintain the temperature with a period of 0.15 ps, and the virial-estimated [21] average pressure was found to be ~1 atm. The four different *ab-initio* trajectory simulations were generated with the systems mentioned below:
Vibrational spectra were generated from the various BOMD trajectories by taking the mass-weighted sum of the Fourier transforms of each individual dye atom’s velocity autocorrelation function. This technique includes temperature effects and anharmonicity in the generated spectra and is capable of reaching into the far-infrared region [22–24], although the presently-studied system is one of the largest reported cases to have its vibrational spectra probed in this way.

3. Results and Discussion

3.1. Structural Features of Relaxed Geometries

The final configuration of the simulated structures of the dye can be seen from Figure 1. Also, some typical trajectory snapshots of PBE system II and BLYP system II are shown in the SI (Figures S1 and S2, respectively). BLYP systems I & II, together with PBE system I, show explicit hydrogen bonding (denoted as dotted lines in Figure 1) to the surface, whilst PBE system I undergoes (in-vacuo) the greatest change to the dye’s initial binding modes. Only the system simulated with PBE system II (Figure 1d) does not show explicit hydrogen bonding towards the surface, as seen in the unsolvated PBE system I and for both BLYP systems (in vacuo and solvated)—cf. Figure 1c.

Figure 1. Relaxed geometries of the systems after ~8–9 ps of BOMD. Carbon is shown in dark grey, nitrogen in blue, oxygen in red, hydrogen in white, titanium in light grey, sulphur in yellow and ruthenium in light green. System types I: unsolvated, II: solvated with [bmim][I]. Solvated systems omit the solvent for ease of viewing.
Also, the only simulation to exhibit a proton-transfer event from the surface to the dye was PBE system I (Figure 1b), simulated using PBE-D in the absence of any ionic liquid. This suggests that this case has the longest-range interactions of the considered systems, owing to a comparative lack of charge shielding by vacuum in comparison to explicit solvent.

3.2. Vibrational Spectra

Each of the plotted mass-weighted VACF (velocity auto-correlation function) spectra in Figure 2 can be interpreted as follows: the continuous coloured line represents the vibrational spectra generated from BOMD in the frequency range from 0 to 2500 cm\(^{-1}\). The dashed vertical grey lines are established experimental modes for the N719 dye, and are at 1230, 1380, 1450, 1540, 1600, 1720 and 2100 cm\(^{-1}\). The two grey spectral insets are experimental results from ref. 25, with the topmost one being spectra for the unsolvated N719 powder, and the bottom one being for unsolvated N719 powder on anatase. These experimental results are meant as a guide only, as the spectra are slightly different in other studies and the two experimental insets themselves are quite different due to the inclusion of the anatase and N719 binding thereon. The presence of a solvent would be expected to alter the spectra, whether it be the more traditional acetonitrile solvent or an RTIL. In addition, the experimental spectra have a reduced frequency window available and represent an amalgamation of the dynamics of multiple dyes in various geometries, whereas our results are for one N719 molecule adsorbed to the surface, and hence results in a sharper signal.

![Figure 2. Vibrational Spectra of (a) BLYP system I, (b) PBE system I, (c) BLYP system II and (d) PBE system II. Within each plot the grey (lower)/(upper) inset corresponds to the experimental ATR-FTIR signal from reference [25] for (dry-N719 adsorbed onto anatase)/(dry-N719 powder). The dashed lines indicate established vibrational modes [26].](image)
A comparison was made between the dynamics of both system I and system II to determine the effect which the addition of solvation has on the dynamics of the unsolvated N719 dye. Overall, the spectra in Figure 2 are in generally in good agreement with each other, and with (at least semi-quantitatively) consistent the experimental modes. The 2100 cm\(^{-1}\) mode associated with the thiocyanato groups is damped and red-shifted to 2000 cm\(^{-1}\); the 1600 cm\(^{-1}\) mode is attenuated vis-à-vis the experimental results, and the 1230 cm\(^{-1}\) mode is at the higher frequency of 1280 cm\(^{-1}\). However, the other modes are generally in very good agreement between the experimental and simulated spectra. However, admittedly, some of the peaks in the far-infrared frequency range (<500 cm\(^{-1}\)) are different: this is probably due to the different binding modes the dyes end up ultimately adopting.

More specifically, for the BLYP case, the system I & II spectra show good agreement with respect to the location of peaks vis-à-vis the experimental results, with the exception of a large peak at ~1500 cm\(^{-1}\). Figure 2a, c show the spectra for the BLYP systems I & II. From these spectra, it is possible to infer what effect the addition of RTIL has on the dynamical properties of the system. There is some shifting of the peaks relative to the experimental results, although this is to be expected as in these simulations the dye was solvated by the RTIL whereas in the experimental results the dye was dry. In any event, the largest solvation-induced shift in a frequency-peak occurs for the 1230 cm\(^{-1}\) mode, which is blue-shifted to 1300 cm\(^{-1}\).

The effect of explicit solvation on the PBE functional is discernible. Both spectra shown have dispersion corrections added to the functional, with the bottom spectra being the one with the RTIL as well (cf. Figure 2). It is readily evident that the enhanced peak around 1750 cm\(^{-1}\) is present in system I and absent in system II. This indicates that solvation enhances the vibrational frequencies of the system only for the unsolvated cases. Figure 2d, for PBE with explicit [bmim][I] solvation shows that the far-infrared part of the spectrum (<1000 cm\(^{-1}\)), is broadly consistent with the unsolvated PBE system (Figure 2a). However, explicit solvation alters what mode is dominant in the rest of the spectrum; the unsolvated system had a dominant mode at 1500 cm\(^{-1}\), whereas the solvated system has its main frequency mode at 1400 cm\(^{-1}\). This is suspected to arise from an altering of the prepared pyridine mode. In addition, the carboxylic-acid mode at 1720 cm\(^{-1}\) is inhibited in the solvated system.

The BLYP system solvated by [bmim][I] is similar to the BLYP in-vacuo system in the regions <1500 and >2000 cm\(^{-1}\) (cf. Figure 2a, c), with the biggest difference being the inhibition of the mode near 1540 cm\(^{-1}\) associated with a mode of the bipyridine rings. Moreover, the solvated system does not exhibit a strong frequency mode at 1100 cm\(^{-1}\).

4. Conclusions

In AIMD simulation of [bmim]-I solvation effects on mass-weighted vibrational spectra of N719 at anatase surfaces, we have compared PBE against another GGA functional, BLYP, using Grimme-D3 dispersion (owing to references [9,10] establishing the greater suitability of this type of dispersion-interaction modelling). With respect to the structure of the titania surface per se, neither the addition of dispersion corrections nor solvation by the strongly ionic solvent has any noticeable effect [10]. This surface is stable throughout the simulations, as is the carbon backbone of the N719 dye, with neither group showing any real differences in their structure upon change of functional. The PBE functional results in some structural peaks being shifted by 0.1 Å closer than for the BLYP functional [10]. The metal complex at the centre of the dye is also largely unaffected by changes to the functional or presence of solvent. The different treatments can be ranked qualitatively in terms of how closely they were able to reproduce the experimental modes, resulting in PBE I being ranked best, followed then by PBE II, BLYP I and with BLYP II last.

Seeing as how the experimental spectra for N719 changes only moderately whether there is any anatase (and hence any subsequent binding modes to the anatase) present at all, it is not that surprising to see PBE I perform well here in spite of the strange binding structure it undertakes due to Grimme-dispersion corrections [9,10]. The lower part of the frequency spectrum is where the binding modes on anatase would have most effect, and yet BLYP I and PBE I are quite similar in their spectra. This lends further proof that it would be feasible for BLYP I to allow bending towards the surface.
For PBE in-vacuo simulation, there is an enhanced peak at 1540 cm$^{-1}$, corresponding to bipyridine stretching; this peak also occurs for the BLYP in-vacuo simulation counterparts, albeit at the lower frequency of 1500 cm$^{-1}$. The unsolvated PBE and BLYP simulations exhibit spectra which are quite similar to each other. There are also similarities in the dynamics of all four of the solvated systems studied. The different binding modes present in the system can result in altered spectra, as can be seen by the relative magnitudes of the carboxylic versus the carboxylate binding modes, which arise from two or three binding sites. Of the solvated systems, PBE performs a better job in producing spectra which match the experimental frequency modes expected, as seen by comparing the number of modes in agreement with experimental data (cf. bottom panel of Figure 2).

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/11/10/2570/s1, Figure S1: Snapshots of a typical trajectory showing some lowest energy structures of PBE system II. Atom labeling can be seen from figure 1. Figure S2: Snapshots of a typical trajectory showing some lowest energy structures of BLYP system II. Atom labeling can be seen from figure 1. Figure S3: Energy conservation graph of BLYP system II (top) and PBE system II (bottom). Figure S4: Snapshots of a typical trajectory showing with I-[bmim]+. Carbon is shown in cyan, nitrogen in blue, oxygen in red, hydrogen in white, titanium in light pink, sulphur in yellow, ruthenium in light cyan surrounded by nitrogen’s and Iodine in purple. Ionic liquid(bmim) shown in wired form for ease of viewing.

Author Contributions: A.B. and N.J.E. formulated the research concept, whilst A.B. prepared the molecular-simulation input files and performed the AIMD simulations. Y.K. and A.B. performed trajectory and vibrational analysis, whilst Y.K., A.B. and N.J.E. also interpreted and discussed results, with Y.K. and N.J.E. finalising the manuscript after a first draft by A.B.

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