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In situ XPS of Competitive CO_2/H_2O Absorption in an Ionic Liquid

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Abstract

Superbasic ionic liquids (SBILs) are being investigated as potential CO_2 gas capture agents, however, the presence of H_2O in the flue stream can inhibit the uptake of CO_2. In this study a thin film of the SBIL trihexyltetradecylphosphonium 1,2,4-triazolide ([P_{66614}][124Triz]) was deposited onto rutile TiO_2 (110) using *in situ* electrospray deposition and studied upon exposure to CO_2 and H_2O using *in situ* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The molar uptake ratio of gas in the electrosprayed SBIL (n_{gas}:n_{IL}) was calculated to be 0.3:1 for CO_2, 0.7:1 for H_2O, and 0.9:1 for a CO_2/H_2O mixture. NAP-XPS taken at two different depths reveals that the competitive absorption of CO_2 and H_2O in [P_{66614}][124Triz] varies with sampling depth. A greater concentration of CO_2 absorbs in the bulk layers, while more H_2O adsorbs/absorbs at the surface. The presence of H_2O in the gas mixture does not inhibit the absorption of CO_2. Measurements taken during exposure and after the removal of gas indicate that CO_2 absorbed in the bulk does so reversibly, whilst CO_2 adsorbed/absorbed at the surface does so irreversibly. This is contrary to the fully reversible CO_2 reaction shown for bulk ILs in literature and suggests that irreversible absorption of CO_2 in our highly-structured thin films is largely attributed to reactions at the surface. This has potential implications on IL gas capture and thin film IL catalysis applications.

Keywords: ionic liquids, carbon capture, x-ray photoelectron spectroscopy, thin films, electrospray

1. Introduction

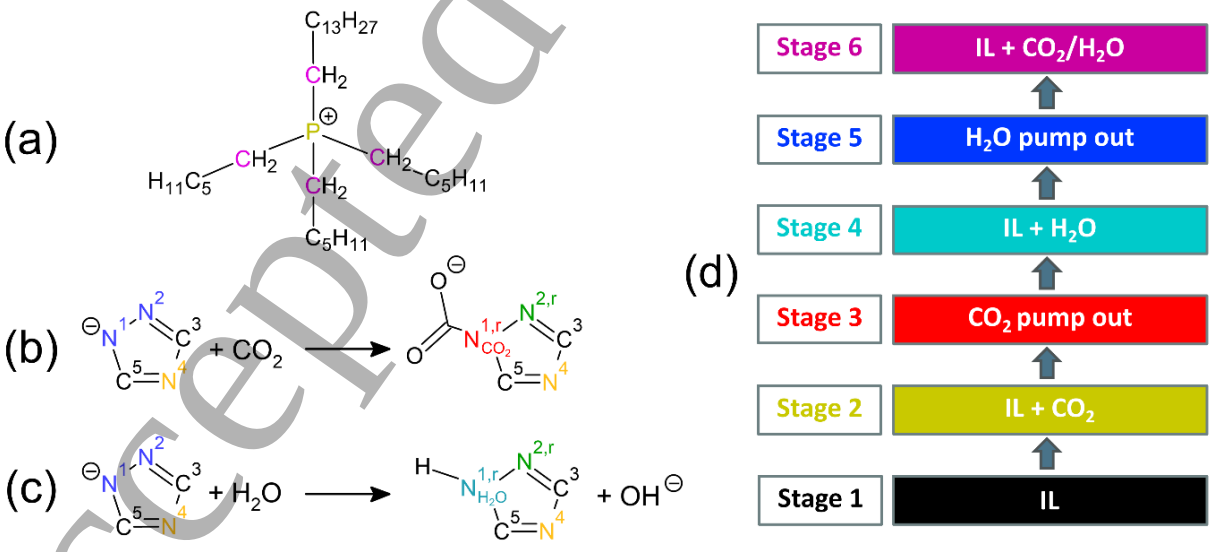
The capture and sequestration of carbon dioxide (CO_2) has been an important process in the reduction of CO_2 emissions in recent years. Currently, fossil fuel-fired power plants use

alkanolamine solvents such as monoethanolamine (MEA) for CO_2 capture. Despite reducing a power plant's CO_2 emissions by as much as 90% [1], these industrial solvents generate problems of their own, with issues such as toxicity and long-term costs challenging their suitability [2]. Ionic liquids (ILs) have seen a recent growth of interest as promising green and non-toxic alternatives to current CO_2 capture solvents. ILs are liquid salts consisting of pairs of bulky anions and cations held together by strong Coulombic forces [3]. The chemical and physical properties of an IL can be fine-tuned via the cation-anion pair. Their high CO_2 capacity, very low volatility, high thermal stability, and lower regeneration temperature compared to MEA make them desirable alternatives [4–6]. The tunability, low melting points and wide electrochemical windows of ILs have led to their use in a wide range of other applications across electrochemistry (electrolytes for batteries [7], nanostructure growth [8,9], and solar cells [10,11]), tribology (lubricants [12,13] and corrosion inhibitors [14]) and catalysis (SCILL and SILP catalysts [15,16]).

An important property for ILs in carbon capture is their selectivity for CO_2. Industrial flue gas contains a complex mixture of gases such as CO_2, H_2O, O_2, N_2, CO, SO_x and NO_x [17,18]. Therefore, it is vital to understand the effect of a mixture of gases on the IL and how they compete for absorption. For conventional ILs with imidazolium-based cations, the anion has been found to be responsible for the solubility of these gases [19,20], but also dictates some of the physical properties of the IL such as its density, viscosity and melting point [21]. Alternatives to conventional physically absorbing ILs came in the way of anime-functionalised task-specific ILs which chemically absorb CO_2, leading to higher CO_2 capacities [6,22]. These ILs, however, suffer increased viscosity upon absorption of CO_2, which consequently hinders further CO_2 absorption and limits their current applicability [23,24]. An emerging class of ILs called superbasic ILs (SBILs) show great promise for CO_2 capture due to their higher CO_2 capacity compared to conventional ILs and the ability to chemically and reversibly absorb CO_2 without significant changes in their viscosity [25].

Commonly, SBILs have phosphonium-based cations and imidazolium-based anions, with anions such as $[benzim]^-$ and $[124Triz]^-$ yielding the highest CO_2 capacities and solubilities [26,27]. In SBILs, the anion chemically reacts with CO_2 in the same way as MEA, forming a carbamate species [22]. In fact, the SBIL $[P_{66614}][124Triz]$ is able to both chemically and physically absorb CO_2 [28]. Mercy *et al.* used DFT simulations to study CO_2 capture in the SBIL $[P_{3333}][124Triz]$ [29]. They found that while the cation plays no direct role in the chemisorption of CO_2, the presence of the cation increases the negative charge of the N^1 nitrogen site in $[124Triz]^-$ (see Scheme 1(b)). This increases the reactivity on N^1, which is considered the most favourable reaction site in the anion. Unlike conventional physically absorbing ILs, SBILs are capable of achieving greater than equimolar amounts of CO_2 absorption. Taylor *et al.* reported a CO_2 uptake of 1.20:1 ($n_{CO_2}:n_{IL}$) in the dry state for the SBIL trihexyltetradecylphosphonium benzimidazolide, $[P_{66614}][benzim]$ [26]. SBILs have been found to only experience minor reductions in CO_2 capacity in the presence of water [26], SO_2 [30], and NO [25], and in some cases preferentially and reversibly absorb CO_2 in the presence of other gases [31].

X-ray photoelectron spectroscopy (XPS) is a technique traditionally carried out at ultra-high vacuum, but advancements in electron optics and the use of synchrotron light and instrumentation have driven development of the technique to near-ambient pressures (up to about 20 mbar) which allows investigations of liquid/gas interfaces [32]. This



Scheme 1. (a) Chemical structure of the $[P_{66614}]^+$ cation with C_{hetero} atoms highlighted in magenta and $C_{aliphatic}$ in black. The reaction scheme for $[124Triz]^-$ with (b) CO_2 and (c) H_2O. Atoms N^1 and N^2 (blue) are equivalent due to resonance effects. Reaction with CO_2 at N^1 results in the formation of carbamate. Reaction with H_2O forms triazole and a hydroxide ion. $N^{1,r}$ (red, light blue) and $N^{2,r}$ (green) denote the N atoms following reaction of the anion with CO_2 or H_2O. (d) Gas exposure regime for the ESD1 $[P_{66614}][124Triz]$ electrosprayed thin film.

technique has been used to study interactions between ILs and gases [31,33–35], including SBILs [31]. For example, a study by Henderson *et al.* revealed that the adsorption of water vapour at the surface of ultra-thin films of $[C_4C_1Im][BF_4]$ induced a reordering of the ions at the IL/gas interface [34]. Water vapour remained trapped at the surface for some time even after the gas was evacuated. Greer *et al*. investigated the competitive absorption of CO_2 and NO in $[P_{66614}]$[benzim] [25]. Although the absorption of NO resulted in irreversible bonding of NONOate species to the $[benzim]^-$ anion, the presence of NO had little effect on the reversibility of CO_2 absorption and the CO_2 capacity of the IL.

There is currently limited information on how interactions between CO_2 molecules and the IL influence structure and ordering at the IL/gas interface, and how these interactions vary through the IL layers. Herein, we report an *in situ* near-ambient pressure XPS study into the ordering and interactions of electrosprayed thin films of the SBIL $[P_{66614}]$[124Triz] on rutile TiO_2 (110) before, during, and after exposure to CO_2 and H_2O. To the best of our knowledge, this will be the first use of NAP-XPS at two different sampling depths to study CO_2 absorption in ILs. These results provide new insights into competitive absorption of CO_2 and H_2O in SBILs and the reversibility of these reactions. Results indicate that more CO_2 absorbs in the bulk layers of the thin film, and this absorption is reversible. However, less CO_2 ad/absorbs at the surface and the ad/absorption is irreversible. Water vapour reversibly ad/absorbs at the surface and does so in greater concentrations compared to the bulk layers.

2. Method

Experimental measurements of the SBIL trihexyltetradecylphosphonium 1,2,4-triazolide ($[P_{66614}]$[124Triz], structure shown in Scheme 1) were carried out at beamline HIPPIE at MAX-IV synchrotron in Sweden (photon energy range 255 – 2200 eV) [36]. The HIPPIE endstation analysis chamber has a hemispherical Scienta-Omicron HiPP-3 electron energy analyser positioned in the plane of the storage ring at 55° to the direction of the incoming X-ray beam [36]. A near-ambient pressure cell is docked to the analyser to carry out near-ambient pressure experiments. All XPS measurements were taken at normal emission (giving a 35° angle between the incident X-ray beam and the sample surface).

A rutile TiO_2 (110) single crystal (PI-KEM) was cleaned via Ar^+ sputter/anneal cycles (sputtering at 1 keV for 10 minutes and annealing at 700°C for 10 minutes) until XPS spectra showed no contamination. $[P_{66614}]$[124Triz] was deposited onto the rutile TiO_2 (110) substrate via electrospray deposition in vacuum using a Molecularspray UHV4 system. The deposition chamber had a base pressure of 2.0×10^{-10} mbar and a deposition pressure of 7.0×10^{-10} mbar. A 0.02 M $[P_{66614}]$[124Triz]/methanol solution was fed into the emitter capillary by a syringe pump delivering a flow rate of 0.3 ml/h. The emitter, syringe and tubing were cleaned prior to use by flushing with the solvent. 3.0 kV was applied to the emitter with respect to the grounded entrance capillary. Two electrospray thin films were deposited, a 2.3 ± 0.6 nm (electrospray deposition 1, ESD1) and a 6.2 ± 1.8 nm (ESD2) thin film. Film thickness calculations are given in the Supplementary Information (SI). A beam damage study showed no degradation of the IL upon prolonged exposure to the beam, but the sample was still moved ~ 0.1 mm between scans to avoid possible charging and degradation of the IL.

The ESD1 thin film of $[P_{66614}]$[124Triz] was characterised using photoemission while exposed to CO_2, H_2O and finally a CO_2/H_2O gas mixture. The IL film was exposed to each of the gases for about 2 hours whilst XPS scans were taken. Gases were leaked into the NAP cell at approximately 1 mbar at room temperature. The molar ratio of CO_2:H_2O in the gas mixture was 1.1:1 ± 0.1, calculated using the areas of the gas-phase peaks in the O 1s spectra. Measurements were taken during exposure and after the gas was pumped out of the NAP cell after each stage in order to study the reversibility of absorption. This exposure procedure is detailed in Scheme 1(d). An XPS study was carried out at two different depths on the $[P_{66614}]$[124Triz] ESD2 thin film by changing the photon energy as summarised in Table 1. These photon energies result in photoelectrons with maximum kinetic energies of 150 and 600 eV, corresponding to surface and bulk sampling depths, respectively. Surface and bulk layers of the ESD2 6.2 nm thin film were probed at sampling depths of 1.6 and 4.0 nm, respectively. Measurements were taken before exposure, during exposure to CO_2, and during exposure to H_2O, both at 1 mbar (2 hour gas exposure time). A summary of the photon energies used for each photoemission region is presented in Table 1.

All XPS peaks have been fitted using 30:70 (Lorentzian:Gaussian) line shapes and a linear background, using the software CasaXPS [37]. The binding energy (BE) scale for all regions has been calibrated to the alkyl C 1s signal at 285.0 eV and all fitted peaks are quoted to ± 0.1 eV BE [38].

3. Results

3.1 $[P_{66614}]$[124Triz] NAP-XPS

NAP-XPS measurements were carried out on an electrosprayed 2.3 nm thin film (ESD1) of the IL $[P_{66614}]$[124Triz]. These were taken as the IL was exposed to CO_2, H_2O, and finally a CO_2/H_2O mixture, all at 1 mbar. Measurements were also taken prior to exposure and after the gas was removed between each exposure stage, as summarised in Scheme 1(d), in order to investigate the reversibility of absorption. Survey spectra taken at each stage of exposure are shown in Figure S1 of the SI.

Region	Photon energy (eV)		
	$[P_{66614}][124Triz]$ ESD1	$[P_{66614}][124Triz]$ ESD2 (surface)	$[P_{66614}][124Triz]$ ESD2 (bulk)
Survey	1000	1000	–
C 1s	435	435	885
N 1s	550	550	1000
O 1s	680	680	1130

Table 1. Photon energies used for each XPS region. ESD1 and ESD2 correspond to the two electrosprayed thin films of $[P_{66614}][124Triz]$, 2.3 and 6.2 nm thick, respectively. Measurements of ESD2 were taken at sampling depths near the surface and in the bulk of the film, achieved by changing the photon energy.

The C 1s region and fitted components are shown in Figure 1 for all stages. The C 1s spectra are intensity normalised to the peak at 285.0 eV. The main C 1s peak at 285 eV can be fitted with two components attributed to the $[P_{66614}]^+$ cation. These occur at 285.0 and 285.7 eV in all stages and are assigned as $C_{aliphatic}$ and C_{hetero}, respectively (see Scheme 1(a)). These agree with previous reports on the $[P_{66614}]^+$ cation [38]. A third component at 287.1 eV is attributed to carbon atoms in positions 3 and 5 in the $[124Triz]^-$ anion ($C^{3,5}$).

Exposing the electrosprayed IL to CO_2 in Stage 2 results in a gas-phase CO_2 peak at 293.3 eV (not shown) and a carbamate peak (see Scheme 1(b)) at 288.3 eV. As expected, there is no carbamate peak present prior to CO_2 exposure in Stage 1. In addition to a chemical shift of −0.2 eV to 286.9 eV, the $C^{3,5}$ component increases in intensity during exposure to CO_2, reverting to its original intensity and BE when the gas is removed in Stage 3. Similarly, the carbamate peak reduces in intensity but does not reduce to zero when CO_2 is removed, indicating that the reaction with CO_2 is not fully reversible. Hereinafter, this will be referred to as residual carbamate. It has been shown that bulk depositions of $[124Triz]^-$ ILs reversibly absorb CO_2 by heating the IL, even in the presence of water [26]. A thick film of a similar SBIL has been shown to reversibly absorb and desorb CO_2 by pumping out the gas [31]. However, as shown here, thin films of $[P_{66614}][124Triz]$ cannot be regenerated through removing the surrounding gas. Only one CO_2 exposure/desorption stage was recorded in our experiment so we do not know how multiple cycles would affect the uptake and reversibility of absorption. However, in previous work, multiple CO_2 exposure/desorption cycles in the similar SBIL $[P_{66614}][benzim]$ were studied using *in situ* attenuated total reflectance-infrared (ATR-IR) spectroscopy as shown in Figures S2 and S3 in the SI. Results show an increase in the carbamate band over multiple exposure/desorption cycles and the presence of small amounts of residual carbamate after desorption, corroborating our XPS data.

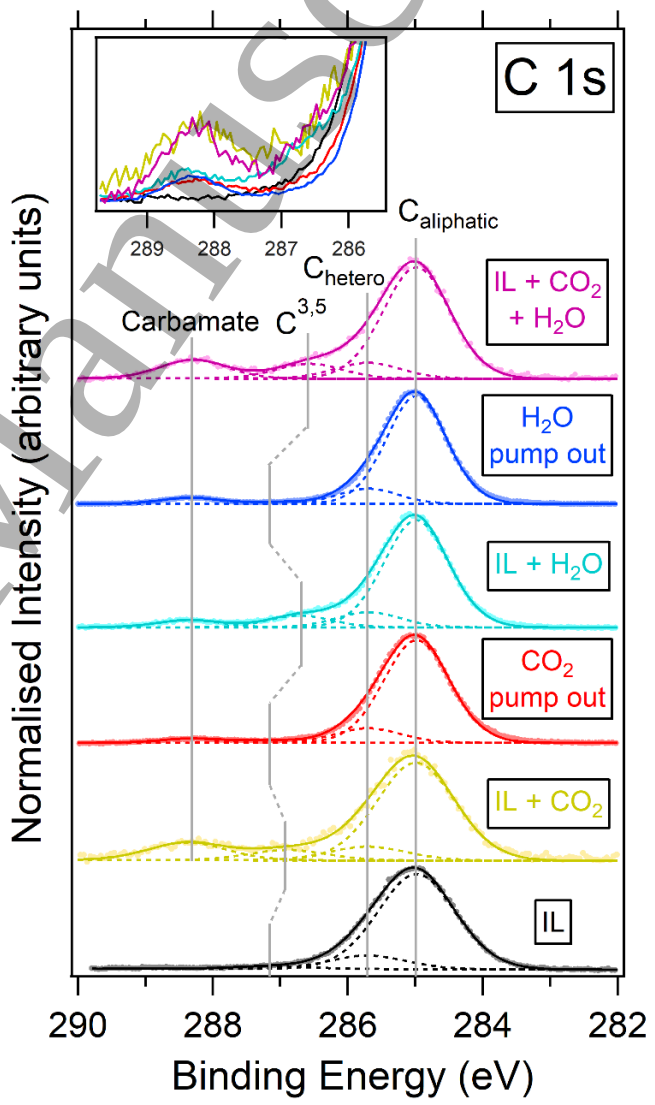


Figure 1. C 1s region recorded at a photon energy of 435 eV for an electrosprayed thin film of $[P_{66614}][124Triz]$ with various exposure regimes of CO_2 and H_2O at 1 mbar. The highlighted lines show common fitted components. The $C^{3,5}$ component shifts downwards in binding energy throughout

the gas exposure stages. The inset shows how the carbamate and $C^{3,5}$ peaks vary in intensity throughout these stages.

When the IL is exposed to H_2O in Stage 4 there is no significant change in intensity of the residual carbamate peak. This would suggest that the absorption of H_2O, which reacts at the same N^1 site as CO_2, does not remove the irreversibly absorbed CO_2. The $C^{3,5}$ component also shifts down to 286.7 eV and increases in intensity, similar behaviour to that found in Stage 2 (IL + CO_2). When the H_2O is removed in Stage 5, the residual carbamate peak persists, suggesting that the absorption and desorption of H_2O has little effect on the absorbed residual carbamate. Overall, the H_2O pump out spectrum closely resembles that of the CO_2 pump out stage, with the $C^{3,5}$ components showing similar intensities and BEs (287.1 eV). This suggests that the IL's reaction with H_2O is reversible.

When the electrosprayed IL is exposed to the CO_2/H_2O mixture in Stage 6, the carbamate peak increases again to a similar intensity to that of Stage 2 (IL + CO_2). This further suggests that the presence of H_2O does not inhibit the absorption of CO_2 and formation of carbamate, which is in agreement with other reports for $[124Triz]^-$-based ILs [26]. Note that the 1 mbar CO_2/H_2O mixture has an approximately equal number of CO_2 and H_2O molecules, therefore one might expect the intensity of the carbamate peak to be lower than the 1 mbar CO_2 exposure. The fact that these intensities are similar suggests that a much greater pressure is needed to fully saturate the IL with CO_2. The $C^{3,5}$ component (which shifts again to 286.6 eV) also increases to a similar intensity as that in Stages 2 and 4, when the IL is exposed to CO_2 and H_2O, respectively. The change in BE and intensity of the $C^{3,5}$ component during gas exposure Stages 2, 4 and 6 is not fully understood. The small BE shifts may be due a change in chemical environment of $C^{3,5}$ upon chemical reaction or physical interaction between the anion and gas. The change in intensity could be explained by a reordering of anions upon exposure to gas. Note that for the CO_2/H_2O mixture, reaction between the two gases may form carbonic acid (H_2CO_3) [39]. It is possible this may interact with the IL thin film, though we find no evidence of carbonic acid (~289 eV) in our spectra. Note that in this experiment we expose the IL to CO_2 first then H_2O. If we were to expose the IL to H_2O first then CO_2, the reversibility of the reactions may be affected. This would make an interesting further study.

Figure 2 shows the N 1s region for all six stages. The spectra have been normalised by peak area between 396 and 404 eV. The N 1s peak can be fitted with three components, the first two of which at 399.1 and 400.1 eV are assigned to nitrogen species inherent to the $[124Triz]^-$ anion. The component at 399.1 eV is attributed to N^4 (C–N–C) while the component at 400.1 eV is assigned to the chemically equivalent N^1 and N^2 atoms ($N^{1,2}$). N^1 and N^2 are chemically equivalent due to resonance effects [40], confirmed by molecular orbital calculations using the software ORCA [41,42]. The IL film was prepared by electrospray in vacuum so we would not expect any significant higher BE peaks attributed to reaction with gas. However, there is a small peak at 401.1 eV which may be due to reactions with trace amounts of gas remaining in the UHV chamber. This peak is assigned to atom $N^{2,r}$ in the reacted anion. We would expect another peak at higher BE attributed to $N^{1,r}$ (atom at which gas reacts), but this cannot be resolved here. It is unclear whether the IL has absorbed CO_2, H_2O, or both in this case because the $N^{2,r}$ component remains at this same BE throughout each of the following exposure stages (the same is also true for the N^4 and $N^{1,2}$ components).

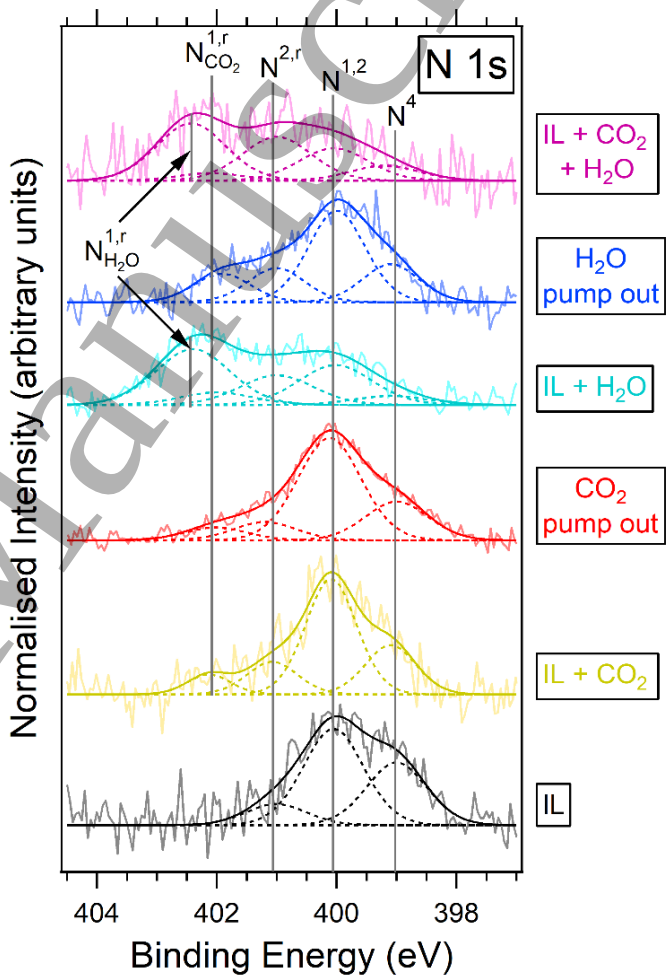


Figure 2. N 1s region recorded at a photon energy of 550 eV for an electrosprayed thin film of $[P_{66614}][124Triz]$ with various exposure regimes of CO_2 and H_2O at 1 mbar. The grey lines show common components fitted through various stages of exposure.

Upon exposure to CO_2 in Stage 2, a peak appears at 402.0 eV. We can assign this to $N^{1,r}$, the atom at which carbamate forms ($N^{1,r}_{CO_2}$). Similar to the C 1s region in Figure 1, this carbamate peak reduces in intensity, but not to zero, when the CO_2 is removed in Stage 3, indicating irreversible CO_2

absorption. This residual carbamate peak appears in all following stages, consistent with the C 1s spectra in Figure 1. During these stages all other components remain at similar BEs and intensities as those in Stage 1. The $C^{3,5}$ component in the C 1s spectra was found to shift upon exposure to CO_2 (and all subsequent exposure stages), however, we do not see any corresponding chemical shifts in the N 1s region. This is likely due to the level of noise in the data.

When the IL is exposed to H_2O in Stage 4, a strong peak occurs at 402.4 eV attributed to protonated $N^{1,r}$ in H_2O-reacted $[124Triz]^-$ ($N^{1,r}_{H_2O}$). In previous work in which $[P_{66614}][benzim]$ was exposed to a CO_2/H_2O mixture, $N^{1,r}_{CO_2}$ and $N^{1,r}_{H_2O}$ occurred at the same or very similar BEs and could not be individually resolved, resulting in a single reaction component [31]. In the case for $[P_{66614}][124Triz]$ in Figure 2, $N^{1,r}_{CO_2}$ and $N^{1,r}_{H_2O}$ occur at different BEs (402.0 and 402.4 eV, respectively). This is most likely due to the different chemical environments of nitrogen atoms in the $[124Triz]^-$ anion compared to $[benzim]^-$. When H_2O is removed in Stage 5, the $N^{1,r}_{H_2O}$ peak at 402.4 eV disappears completely, further indicating that this peak is due to a reversible reaction with H_2O. This supports previous evidence of reversible H_2O absorption discussed above (Figure 1). The $N^{1,r}_{CO_2}$ peak appears to be more intense after the H_2O pump out stage compared to the CO_2 pump out stage. This could indicate a reordering of residual carbamate species to the surface (since measurements were taken at a surface-sensitive photon energy). This is discussed in greater detail below (Figure 4).

Finally, when the IL is exposed to the CO_2/H_2O mixture in Stage 6 the spectrum closely resembles that of Stage 4 (IL + H_2O) except for a more intense $N^{2,r}$ component at 401.1 eV. The pressure in Stage 6 rose slightly higher than 1 mbar (1.3 mbar), therefore resulting in a stronger $N^{2,r}$ component due to a higher relative concentration of reacted anions. Despite an approximately equal CO_2:H_2O molecular ratio in the mixture, the $N^{1,r}_{H_2O}$ component at 402.4 eV is much more intense than the $N^{1,r}_{CO_2}$ component at 402.0 eV. The reason why H_2O absorption appears to dominate over CO_2 absorption in Stage 6 will be explored in detail below (see discussion for Figure 4).

Using the N 1s data in Figure 2, the molar uptake ratio of the gases (n_{gas}:n_{IL}) was calculated to be 0.3:1 for CO_2, 0.7:1 for H_2O, and 0.9:1 for the CO_2/H_2O mixture (each with an uncertainty of ± 0.1). For the CO_2/H_2O gas mixture, the total molar uptake of 0.9 consists of approximately 0.15 for CO_2 and 0.75 for H_2O, further suggesting that H_2O absorption dominates but does not inhibit CO_2 absorption. See the SI for full details of calculations. Looking at the N 1s spectra, we expect less than 1:1 uptake of gas because the unreacted $N^{1,2}$ peak is still present in all spectra. If every anion had reacted then the $N^{1,2}$ peak would not be visible. The uptake of CO_2 is lower in our experiment than that found by Taylor *et al.* for the same IL at atmospheric pressure (0.54:1) [30]. This is to be expected as we are exposing a much thinner film of IL to lower pressures of CO_2.

Another explanation as to why H_2O absoprtion dominates over CO_2 absorption in Figure 2 may be that the timescale over which measurements were taken plays an important role. It has been shown that for the IL [BMIM][OAc] the uptake of water into the bulk takes many hours, yet is much quicker at the IL-gas interfacial layers [43]. Conversely, it has been found by Wang *et al.* that bulk thicknesses of phosphonium-based SBILs with similar anions absorbed CO_2 very quickly, on the order of minutes [44,45]. Admittedly these timescales are likely to change at the mbar pressures used in our study compared to atmospheric pressures used by Wang *et al.* Our measurements were taken over a 30 minute timeframe at a surface sensitive sampling depth. Therefore, if $[P_{66614}][124Triz]$ is similarly behaved to these ILs, then the reason that H_2O absorption dominates over CO_2 absorption may be that there is an abundance of H_2O at the surface due to a slower uptake of the gas into the bulk layers of the IL compared to CO_2.

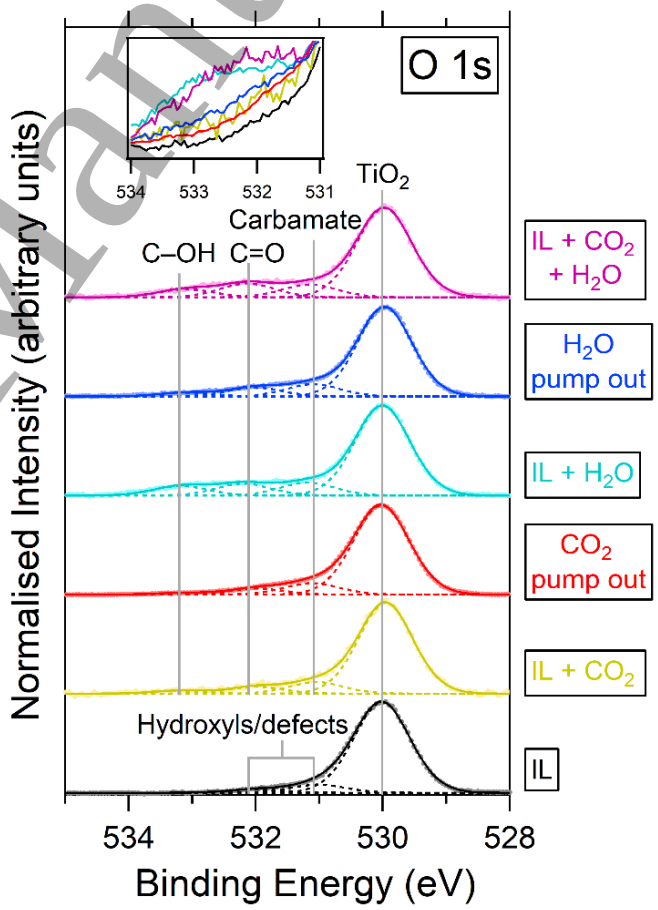


Figure 3. O 1s region recorded at a photon energy of 680 eV for an electrosprayed thin film of $[P_{6614}][124Triz]$ with various exposure regimes of CO_2 and H_2O at 1 mbar. The grey lines show common components fitted through various stages

of exposure. The inset shows how the broad reaction peak at ~533 eV varies in intensity throughout these stages.

In the O 1s region in Figure 3 there is a common peak at 530.0 eV for all stages, attributed to O atoms in the TiO_2 substrate lattice [46]. The electrosprayed IL (black line) can be fitted with two more components at 531.1 and 532.1 eV. Since there are no oxygen atoms in the IL and we do not see any carbamate species in the C 1s region in Stage 1, we assign these to hydroxyls/defects at the TiO_2 surface [47].

When the electrosprayed IL is exposed to CO_2 (gold line) peaks are fitted at 530.1, 531.1, 532.1, 533.2, and 535.6 eV. These are assigned to TiO_2, carbamate, C=O in protonated carbamate, C–OH in protonated carbamate, and gas-phase CO_2 (not shown), respectively. Carbamate species formed upon reaction with CO_2 can be protonated and it is likely that there is a mixture of protonated and unprotonated carbamate species present here [48]. The 531.1 and 532.1 eV peaks in Stages 2 – 6 will also contain contributions from the hydroxyl species/defects at the TiO_2 surface. All fitted components in the O 1s region are summarised in Table 2. When the CO_2 gas is removed in Stage 3 the broad reaction shoulder does not return to the original intensity from Stage 1. This provides further evidence of irreversible CO_2 absorption and reordering in the IL, shown previously in the C 1s and N 1s regions in Figures 1 and 2, respectively.

When the IL is exposed to H_2O in Stage 4, we see a significant increase in intensity of the reaction components. This would support our assumption that components at 532.1 and 533.2 eV are attributed to interactions with water vapour (C=O and C–OH in protonated carbamate species, respectively). Upon exposure to the CO_2/H_2O mixture in the final stage, the broad reaction peak has a similar intensity to that when exposed to H_2O alone. This suggests that the presence of CO_2 does not inhibit the ad/absorption of H_2O. The reason why H_2O absorption appears to dominate over CO_2 absorption in Figure 3 can be explained by exploring absorption at different depths.

Region	Binding Energy (eV) ± 0.1 eV	Assignment
C 1s	285.0	$C_{aliphatic}$
	285.7	C_{hetero}
	287.1[a] → 286.9 → 286.7 → 286.6	$C^{3,5}$
	288.3	Carbamate
	293.3	Gas-phase CO_2
N 1s	399.1	N^4
	400.1	$N^{1,2}$
	401.1	$N^{2,r}$
	402.0	$N^{1,r}_{CO_2}$
	402.4	$N^{1,r}_{H_2O}$
O 1s	530.0	TiO_2 lattice O
	531.1	Carbamate[c]
	532.1	C = O[b,c]
	533.2	C – OH[b]
	535.6	Gas-phase H_2O
	537.0	Gas-phase CO_2

Table 2. Assignments and corresponding BEs of fitted components in the C 1s, N 1s and O 1s regions for $[P_{66614}][124Triz]$ for various gas exposure stages. The arrows (→) denote chemical shifts of the $C^{3,5}$ component between the following exposure stages: IL → IL + CO_2 → IL + H_2O → IL + CO_2 + H_2O. [a] $C^{3,5}$ component returns to this BE during the CO_2 and H_2O pump out stages. [b] Within the protonated carbamate group. [c] These peaks are assigned to hydroxyl species and defects at the TiO_2 surface in Stage 1.

3.2 [P_{66614}][124Triz] NAP-XPS Depth Study

NAP-XPS was carried out on an electrosprayed 6.2 nm thin film of [P_{66614}][124Triz] (ESD2) by probing two sampling depths: 4.0 nm to probe the bulk layers of the IL, and 1.6 nm to probe the surface layers. Photoemission measurements were taken for the electrosprayed IL, the IL exposed to 1 mbar CO_2, and the IL exposed to 1 mbar H_2O, for both bulk and surface sampling depths. Note that these sampling depths are expected to alter slightly during gas exposure stages due to attenuation of electrons through the gas. Since the ESD2 film is formed by depositing more IL on top of the previously measured ESD1 film, we expect some subtle differences in the spectra of the two films. All components remain fitted at approximately the same BEs as those in the previous section.

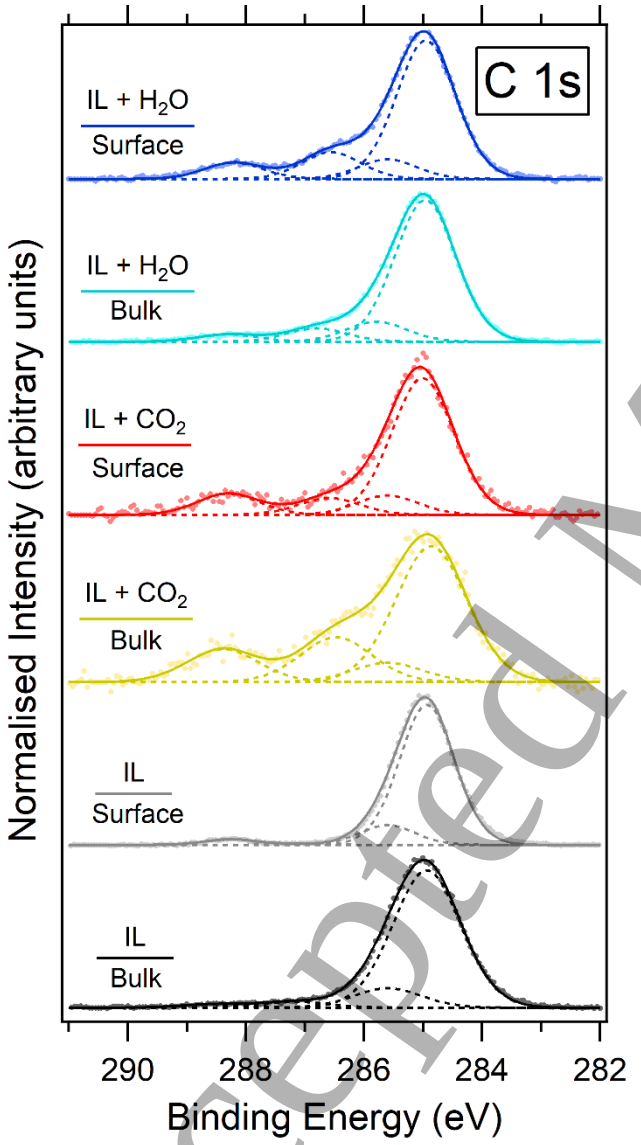


Figure 4. XPS of the C 1s region for an electrosprayed [P_{66614}][124Triz] thin film before exposure, during exposure to CO_2, and during exposure to H_2O. The 6.2 nm thick sample was probed at two sampling depths: 4.0 nm to sample the bulk layers (denoted "Bulk") and 1.6 nm to sample the surface layers (denoted "Surface"). Surface and bulk sampling depths were recorded at photon energies of 435 and 885 eV, respectively.

Figure 4 shows measurements in the C 1s region, with spectra normalised to the peak at 285.0 eV. For the electrosprayed IL, even before exposure to CO_2 there is a small carbamate feature at 288.3 eV for the surface sampling depth (grey line) which may be due to trace amounts of residual CO_2 in the chamber. Alternatively, it could indicate irreversibly absorbed CO_2 from previous exposures (since the ESD2 film was deposited over ESD1), which would further suggest that irreversibly absorbed CO_2 moves to the surface. There has been evidence of irreversible CO_2 absorption in multilayer thin films of the similar IL [P_{66614}][benzim] in a previous study [48].

When the IL is exposed to CO_2, the resulting carbamate peak is more intense for the bulk sampling depth (gold line) compared to the surface (red line). This implies that a greater concentration of carbamate species occurs in the bulk compared to the surface. Lewis *et al*. have reported similar behaviour for aqueous MEA solutions treated with CO_2 [49]. Greater concentrations of CO_2-reacted MEA were found in the bulk of the solution while unreacted MEA was more concentrated at the surface.

When CO_2 is removed and the IL is exposed to H_2O alone, a smaller residual carbamate peak remains in the IL + H_2O spectra (blue lines) at 288.3 eV in Figure 4. Similar evidence of irreversible CO_2 absorption was seen earlier in Figure 1. The residual carbamate peak here is stronger when probed at the surface sampling depth (dark blue line) rather than in the bulk (light blue line), suggesting that more residual carbamate resides at the IL surface than in its bulk layers. In fact, the residual carbamate peak at the surface (dark blue line) is a similar intensity to the carbamate peak at the surface when exposed to CO_2 (red line). This implies that most of the CO_2 that absorbs within the surface layers of the IL does so irreversibly, remaining absorbed when the surrounding gas is pumped out. However, carbamate formed in the bulk (gold line) dramatically reduces in concentration when CO_2 is removed and H_2O introduced (light blue line). This suggests that the irreversible nature of CO_2 absorption in this IL is largely attributed to reactions at the surface.

To summarise, more CO_2 absorption appears to occur in the bulk of the IL, and this absorption is largely reversible. Less CO_2 ad/absorbs at the surface and this is irreversible. These results show that both the concentration of carbamate and the level of reversibility varies with depth into the sample.

XPS measurements taken in the N 1s region are shown in Figure 5. The spectra have been normalised by peak area between 396 and 404 eV. For the electrosprayed IL, the N 1s peaks are similar at the two sampling depths. As discussed in

Figure 2, $N^{1,2}$ atoms in the unreacted anion are largely responsible for the main peak centred on 400 eV, implying that the concentration of unreacted anions does not vary significantly through the IL layers prior to exposure.

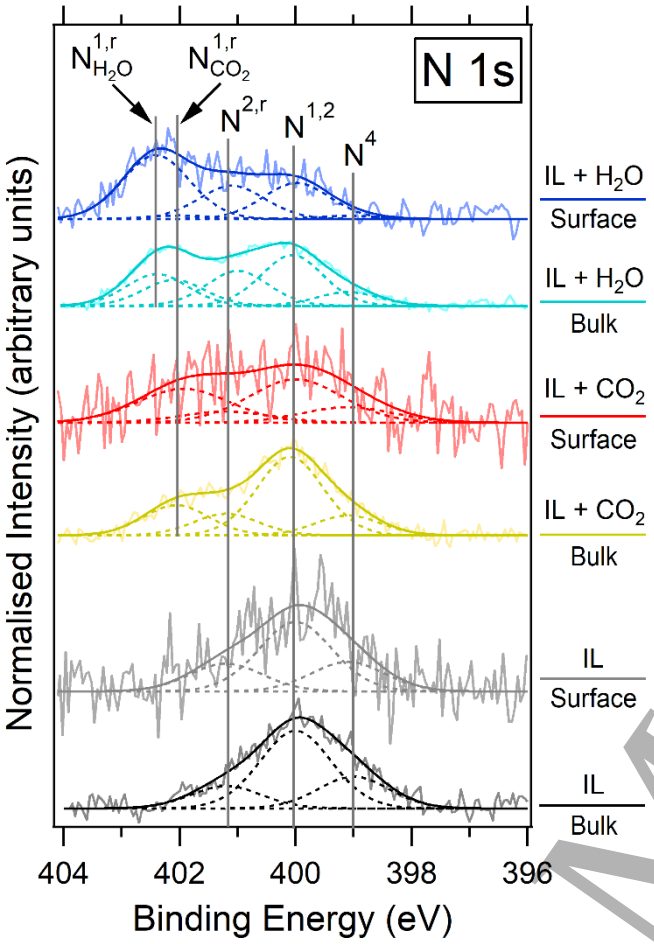


Figure 5. XPS of the N 1s region for an electrosprayed $[P_{66614}][124Triz]$ thin film before exposure, during exposure to CO_2, and during exposure to H_2O. The 6.2 nm thick sample was probed at two sampling depths: 4.0 nm to sample the bulk layers (denoted "Bulk") and 1.6 nm to sample the surface layers (denoted "Surface"). Surface and bulk sampling depths were recorded at photon energies of 550 and 1000 eV, respectively.

Upon absorption of CO_2, a carbamate $N^{1,r}_{CO_2}$ peak appears at 402.0 eV for both sampling depths. The $N^{1,r}_{CO_2}$ peak is of higher relative intensity for the surface sampling depth (red line) compared to the bulk (gold line) However, comparing the two is tenuous given the very noisy nature of the surface sampling depth spectrum. This is most likely due to attenuation of photoelectrons through the CO_2 gas, considering they have low kinetic energies (maximum of 150 eV).

The absorption of H_2O results in protonation of N^1 in $[124Triz]^-$, denoted $N^{1,r}_{H_2O}$, manifesting as a feature at 402.4 eV. Relative to the main $N^{1,2}$ peak and the irreversibly absorbed CO_2 $N^{1,r}_{CO_2}$ peak, the intensity of $N^{1,r}_{H_2O}$ is greater when probed at the surface (dark blue line) than in the bulk (light blue line). This suggests that there is a greater concentration of protonated N atoms at the surface than in the bulk. This is also supported by the more intense $C^{3,5}$ (C atoms in the reacted anion) component at the surface when exposed to H_2O in Figure 4. Results from Figures 4 and 5 suggest that more H_2O-reacted species remain at the surface of the IL film, and more CO_2-reacted species diffuse through the surface to the bulk. This would explain why there is little evidence of CO_2 absorption in Figure 3 (O 1s) and why H_2O absorption appeared to dominate over CO_2 absorption when the IL was exposed to a CO_2/H_2O mixture in Figure 2 (N 1s), because these spectra were taken at surface-sensitive photon energies of 680 eV and 550 eV, respectively.

In a previous study of the similar IL $[P_{66614}][benzim]$, it was found that the presence of H_2O did not significantly inhibit CO_2 absorption in thin films of the IL at near-ambient pressures [31]. This behaviour could be explained by the results presented here. Reactions between the IL and the two different gases may occur primarily at different depths in the IL film. Additionally, the timescale over which the gases absorb in the IL may play an important role here, as these timescales have been shown to vary significantly for CO_2 and H_2O in ILs [43,44] (although, these studies used different ILs and atmospheric pressures as opposed to mbar used in our study).

Discussion

Ordering of IL thin and thick films on solid surfaces has been investigated using a range of other experimental surface-sensitive techniques including angle-resolved NEXAFS [50,51], sum frequency generation (SFG) [52,53], neutron scattering [54,55], atomic force microscopy (AFM) [56], and X-ray reflectivity [57]. Our approach of using XPS at two sampling depths has proven to be another useful tool in analysing the interfacial behaviour of IL thin films on solid surfaces, as well as their interaction with gases. The study presented here is largely qualitative due to limitations of the technique, for example, the high levels of noise as a result of attenuation of photoelectrons through the gas combined with low counts from the use of thin films.

In our thin films, the IL/vacuum and IL/TiO_2 interfaces are likely to have a greater influence than they do in bulk ILs. The ordered structure of ILs at these interfaces is likely to influence specific interactions with CO_2/H_2O and affect how these gases diffuse from the vacuum interface into the bulk. N^1 and N^2 are equivalent in isolated anions, and we would still expect N^1 and N^2 to remain equivalent at the IL/vacuum interface, however, we expect different ordering at the interface compared to the bulk. The charged parts of the ions in imidazolium-based ILs have been found to form an underlayer near the IL/vacuum interface, with the alkyl chains

of the cations pointing out towards the vacuum [58]. SBILs, such as those used in our experiment, have not been studied as widely in this context. In a previous XPS study of the related SBIL $[P_{66614}]$[benzim], C 1s spectra showed a relatively more intense peak associated with the $[benzim]^-$ anion at grazing emission compared to normal emission, suggesting a higher concentration of $[benzim]^-$ anions at the IL/vacuum interface compared to the alkyl chains in the $[P_{66614}]^+$ cation [59]. This study provides evidence of SBILs forming an ordered structure at the IL/vacuum interface.

Fundamental studies of ILs at TiO_2 surfaces are sparse so there is very little literature for comparison [16]. Wagstaffe *et al.* studied 4 Å and 30 Å thick films of an imidazolium-based IL at the anatase TiO_2 (101) surface using XPS [51]. They found that in both films the two nitrogen atoms in the imidazolium ring are chemically equivalent and were assigned to a single peak in the N 1s spectra. However, this shifted by 0.2 eV to a lower binding energy in the thinner film due to the interaction of the imidazolium cation with the TiO_2 surface. It is possible that the N^1 and N^2 nitrogen atoms in $[124Triz]^-$ may react differently with the TiO_2 surface, and this may in turn affect how these anions react with CO_2 or H_2O. If the anions were to react with the TiO_2 surface this could make them unavailable for reaction with CO_2/H_2O. A comprehensive computational study would be required to gain insights into these complex interfacial interactions.

In this study we used electrospray deposition (ESD) to obtain thin films of $[P_{66614}]$[124Triz]. It is likely the film is not completely homogeneous and it is possible the IL could form islands on the surface rather than forming layers. However, we are unable to verify the growth mode from our data. Other methods have been used to deposit thin films of ILs, namely physical vapour deposition (PVD) [34,51,60] and dip-coating [56,61]. Each have their own advantages and disadvantages; for example, PVD requires thermally stable ILs while ESD does not. ESD allows thin films of large molecules to be deposited *in situ* in ultra-high vacuum [62]. However, electrosprayed thin films can have an unequal concentration of cations and anions compared to PVD due to the increased diffusion of cations and anions with positive and negative tip biases, respectively [63]. ESD of ILs is comparatively underutilised, and prior to this study has not been used to deposit large IL molecules or used alongside NAP-XPS to investigate gas capture in thin films of ILs, to the best of our knowledge.

The results presented here have implications for thin film IL-based technologies. For example, thin films of ILs have been used to modify conventional supported catalysts, allowing the selectivity of the solid catalyst to be fine-tuned and improved (SCILL and SILP catalysis) [64]. A problem these technologies face is their sensitivity to changes at the IL/gas phase and IL/solid support interfaces [65]. Therefore, adsorption of gaseous/liquid reactants, products or contaminants in SCILL/SILP catalysts may induce changes in the surface structure of the IL thin film, potentially impacting the diffusion and selectivity for intermediate products in these catalysts [15].

Conclusion

The competitive absorption between CO_2 and H_2O in electrosprayed thin films of the superbasic IL $[P_{66614}]$[124Triz] has been characterised using *in situ* NAP-XPS. To the best of our knowledge, $[P_{66614}]^+$ is the largest IL ion to be successfully deposited via electrospray. Results suggest that both reacted and unreacted $[124Triz]^-$ anions reorder and diffuse through the IL thin film upon exposure to CO_2 and/or H_2O. The NAP-XPS depth study revealed that greater concentrations of CO_2-reacted species appear in the bulk layers of an electrosprayed IL thin film, reversibly forming carbamate on the anion. However, fewer CO_2-reacted species appear at the surface layers, and this reaction is irreversible. H_2O vapour ad/absorbs in greater concentrations at the surface rather than the bulk but does not inhibit the absorption of CO_2. The molar uptake ratio of gases (n_{gas}:n_{IL}) in the electrosprayed IL was calculated to be 0.3:1 for CO_2, 0.7:1 for H_2O, and 0.9:1 for the CO_2/H_2O mixture (each with an uncertainty of ± 0.1). To the best of our knowledge, this is the first use of a NAP-XPS at different depths to study gas absorption in ILs. Reordering of IL thin films upon contamination with air and water vapour may also affect the performance of IL thin film-based technologies such as SCILL/SILP catalysis, IL lubricants and corrosion inhibitors.

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