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In situ XPS of competitive CO₂/H₂O absorption in an ionic liquid

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PAPER

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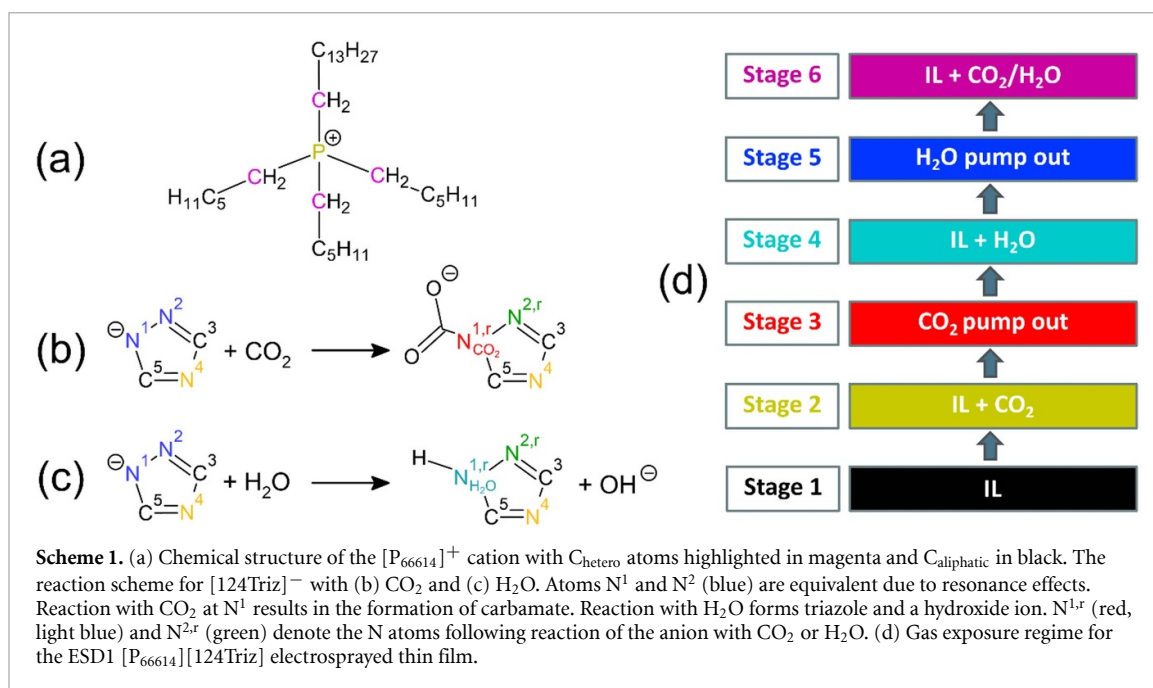
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E-mail: JCole4@uclan.ac.uk and KSyres@uclan.ac.uk**Keywords:** ionic liquids, carbon capture, x-ray photoelectron spectroscopy, thin films, electro spraySupplementary material for this article is available [online](#)**Abstract**

Superbasic ionic liquids (SBILs) are being investigated as potential carbon dioxide (CO₂) gas capture agents, however, the presence of H₂O in the flue stream can inhibit the uptake of CO₂. In this study a thin film of the SBIL trihexyltetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz]) was deposited onto rutile TiO₂ (110) using *in situ* electro spray deposition and studied upon exposure to CO₂ and H₂O using *in situ* near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS). The molar uptake ratio of gas in the electro sprayed SBIL ($n_{\text{gas}}:n_{\text{IL}}$) was calculated to be 0.3:1 for CO₂, 0.7:1 for H₂O, and 0.9:1 for a CO₂/H₂O mixture. NAP-XPS taken at two different depths reveals that the competitive absorption of CO₂ and H₂O in [P₆₆₆₁₄][124Triz] varies with sampling depth. A greater concentration of CO₂ absorbs in the bulk layers, while more H₂O adsorbs/absorbs at the surface. The presence of H₂O in the gas mixture does not inhibit the absorption of CO₂. Measurements taken during exposure and after the removal of gas indicate that CO₂ absorbed in the bulk does so reversibly, whilst CO₂ adsorbed/absorbed at the surface does so irreversibly. This is contrary to the fully reversible CO₂ reaction shown for bulk ionic liquids (ILs) in literature and suggests that irreversible absorption of CO₂ 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.

1. Introduction

The capture and sequestration of carbon dioxide (CO₂) has been an important process in the reduction of CO₂ emissions in recent years. Currently, fossil fuel-fired power plants use alkanolamine solvents such as monoethanolamine (MEA) for CO₂ capture. Despite reducing a power plant's CO₂ 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 CO₂ 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 CO₂ 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 (solid catalysts with an IL layer (SCILL) and supported IL phase (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 density functional theory (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 benzimidazole, $[P_{66614}][benzim]$ [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 (UHV), but advancements in electron optics and the use of synchrotron light and instrumentation have driven development of the technique to near-ambient pressure (NAP) (up to about 20 mbar) which allows investigations of liquid/gas interfaces [32]. This technique has been used to study interactions between ILs and gases [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 CO₂ absorption and the CO₂ capacity of the IL.

There is currently limited information on how interactions between CO₂ 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* NAP-XPS study into the ordering and interactions of electro sprayed thin films of the SBIL [P₆₆₆₁₄][124Triz] on rutile TiO₂ (110) before, during, and after exposure to CO₂ and H₂O. To the best of our knowledge, this will be the first use of NAP-XPS at two different sampling depths to study CO₂ absorption in ILs. These results provide new insights into competitive absorption of CO₂ and H₂O in SBILs and the reversibility of these reactions. Results indicate that more CO₂ absorbs in the bulk layers of the thin film, and this absorption is reversible. However, less CO₂ adsorbs at the surface and the adsorption is irreversible. Water vapour reversibly adsorbs 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 ([P₆₆₆₁₄][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 NAP cell is docked to the analyser to carry out NAP 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 TiO₂ (110) single crystal (PI-KEM) was cleaned via Ar⁺ sputter/anneal cycles (sputtering at 1 keV for 10 min and annealing at 700 °C for 10 min) until XPS spectra showed no contamination. [P₆₆₆₁₄][124Triz] was deposited onto the rutile TiO₂ (110) substrate via electro spray deposition (ESD) in vacuum using a Molecular spray 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 [P₆₆₆₁₄][124Triz]/methanol solution was fed into the emitter capillary by a syringe pump delivering a flow rate of 0.3 ml h⁻¹. 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 electro spray thin films were deposited, a 2.3 ± 0.6 nm (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 [P₆₆₆₁₄][124Triz] was characterised using photoemission while exposed to CO₂, H₂O and finally a CO₂/H₂O gas mixture. The IL film was exposed to each of the gases for about 2 h whilst XPS scans were taken. Gases were leaked into the NAP cell at approximately 1 mbar at room temperature. The molar ratio of CO₂:H₂O in the gas mixture was $1.1:1 \pm 0.1$, 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 [P₆₆₆₁₄][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 CO₂, and during exposure to H₂O, both at 1 mbar (2 h gas exposure time). A summary of the photon energies used for each photoemission region is presented in table 1.

All XPS peaks [37] have been fitted using 30:70 (Lorentzian:Gaussian) line shapes and a linear background, using the software CasaXPS [38]. 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 [39].

3. Results

3.1. [P₆₆₆₁₄][124Triz] NAP-XPS

NAP-XPS measurements were carried out on an electro sprayed 2.3 nm thin film (ESD1) of the IL [P₆₆₆₁₄][124Triz]. These were taken as the IL was exposed to CO₂, H₂O, and finally a CO₂/H₂O 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.

Table 1. Photon energies used for each XPS region. ESD1 and ESD2 correspond to the two electro sprayed 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.

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

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 [39]. 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 electro sprayed 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 0.2 eV chemical shift down 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 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.

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 electro sprayed 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) [40]. 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

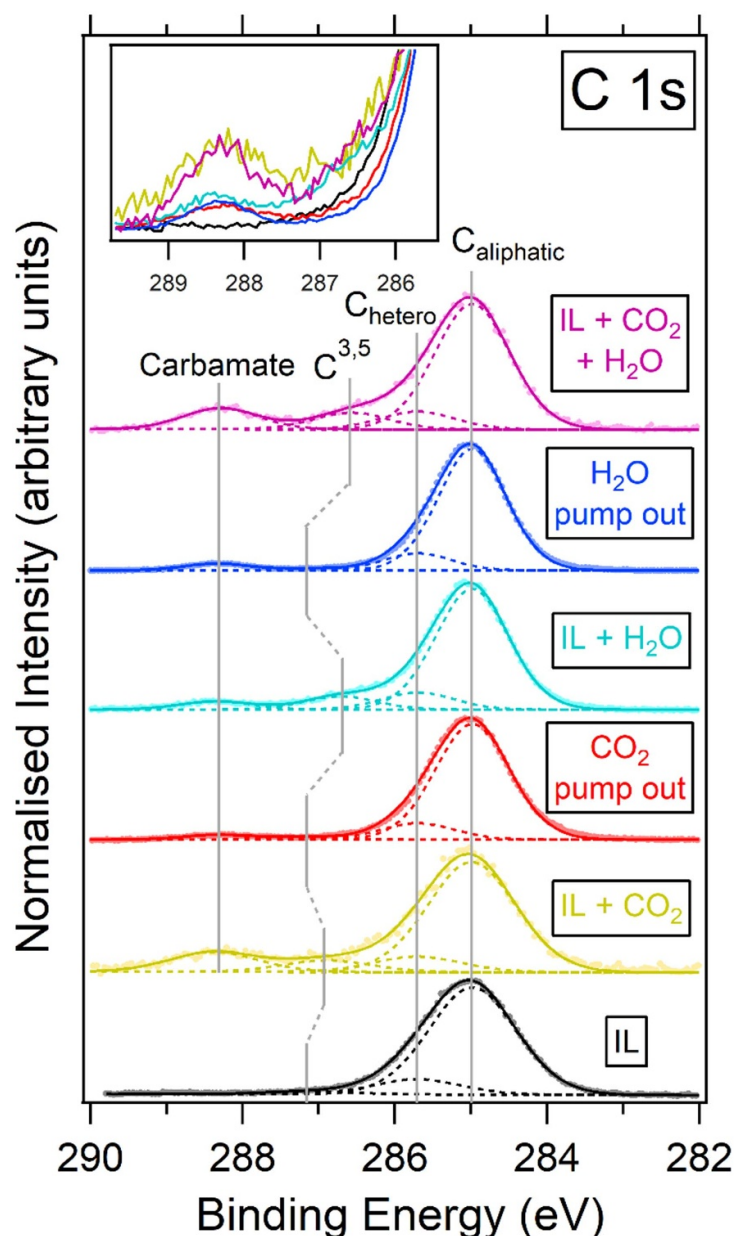
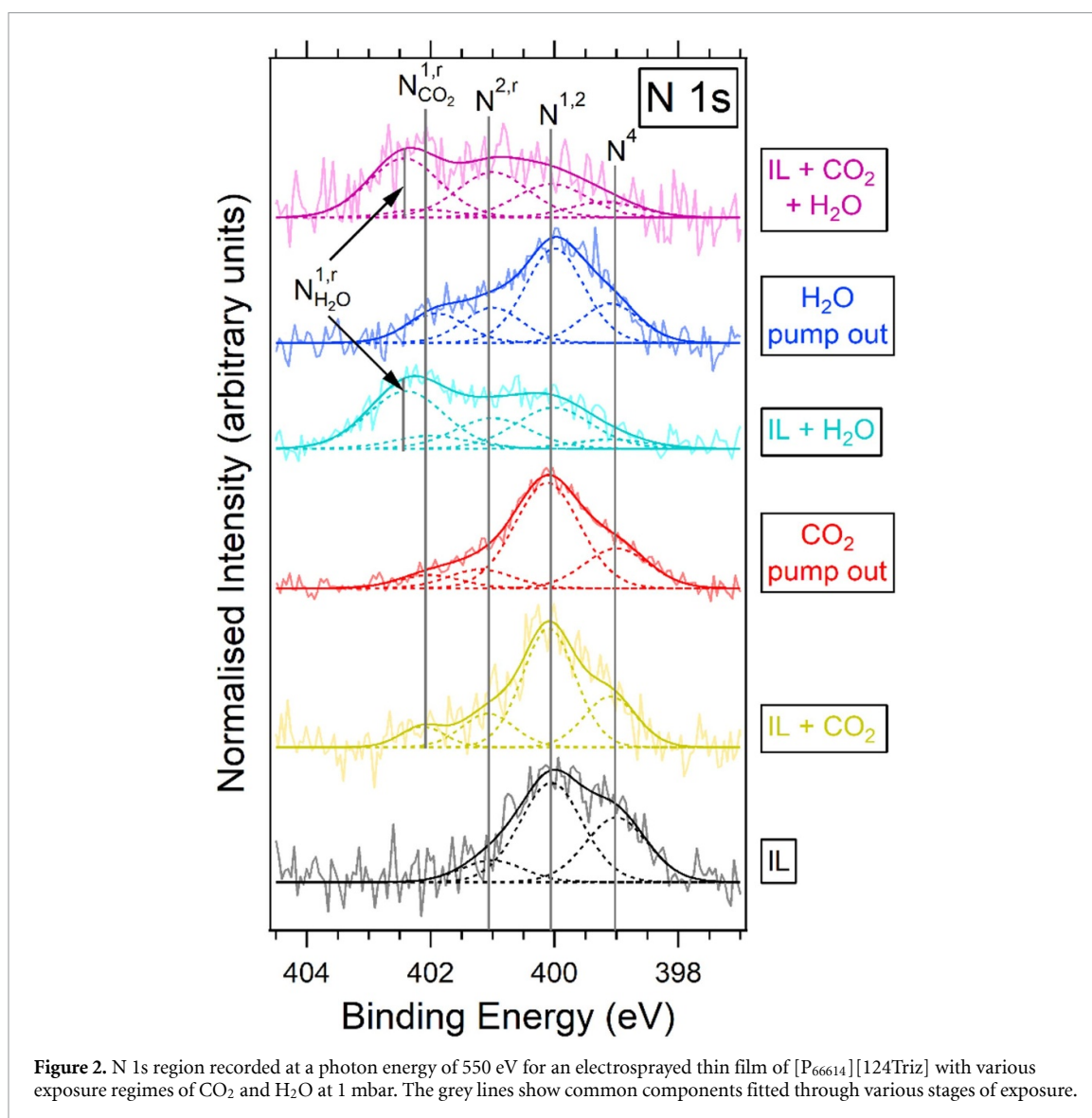


Figure 1. C 1s region recorded at a photon energy of 435 eV for an electrospayed thin film of [P₆₆₆₁₄][124Triz] with various exposure regimes of CO₂ and H₂O at 1 mbar. The highlighted lines show common fitted components. The C^{3,5} component shifts downwards in binding energy throughout the gas exposure stages. The inset shows how the carbamate and C^{3,5} peaks vary in intensity throughout these stages.

400.1 eV are assigned to nitrogen species inherent to the [124Triz]⁻ anion. The component at 399.1 eV is attributed to N⁴ (C–N–C) while the component at 400.1 eV is assigned to the chemically equivalent N¹ and N² atoms (N^{1,2}). N¹ and N² are chemically equivalent due to resonance effects [41], confirmed by molecular orbital calculations using the software ORCA [42, 43]. 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 CO₂, H₂O, 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 N⁴ and N^{1,2} components).

Upon exposure to CO₂ 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}_{CO₂}). Similar to the C 1s region in figure 1, this carbamate peak reduces in intensity, but not to zero, when the CO₂ is removed in Stage 3, indicating irreversible CO₂ 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 CO₂ (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 H₂O in Stage 4, a strong peak occurs at 402.4 eV attributed to protonated N^{1,r} in H₂O-reacted [124Triz]⁻ (N_{H₂O}^{1,r}). In previous work in which [P₆₆₆₁₄][benzim] was exposed to a CO₂/H₂O mixture, N_{CO₂}^{1,r} and N_{H₂O}^{1,r} 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 [P₆₆₆₁₄][124Triz] in figure 2, N_{CO₂}^{1,r} and N_{H₂O}^{1,r} 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 H₂O is removed in Stage 5, the N_{H₂O}^{1,r} peak at 402.4 eV disappears completely, further indicating that this peak is due to a reversible reaction with H₂O. This supports previous evidence of reversible H₂O absorption discussed above (figure 1). The N_{CO₂}^{1,r} peak appears to be more intense after the H₂O pump out stage compared to the CO₂ 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 CO₂/H₂O mixture in Stage 6 the spectrum closely resembles that of Stage 4 (IL + H₂O) 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 CO₂:H₂O molecular ratio in the mixture, the N_{H₂O}^{1,r} component at 402.4 eV is much more intense than the N_{CO₂}^{1,r} component at 402.0 eV. The

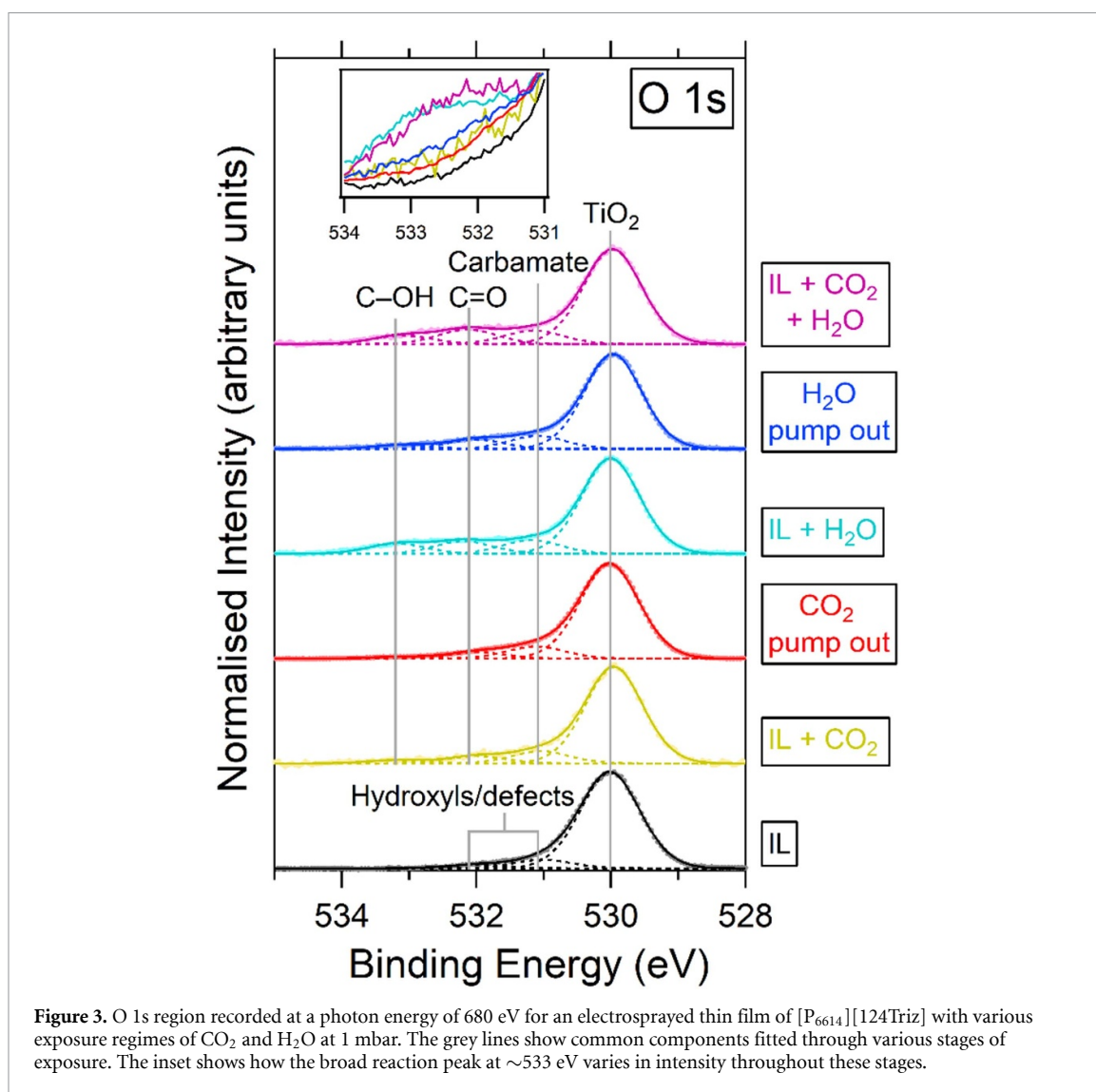


Figure 3. O 1s region recorded at a photon energy of 680 eV for an electro sprayed thin film of [P₆₆₁₄][124Triz] with various exposure regimes of CO₂ and H₂O at 1 mbar. The grey lines show common components fitted throughout various stages of exposure. The inset shows how the broad reaction peak at ~533 eV varies in intensity throughout these stages.

reason why H₂O absorption appears to dominate over CO₂ 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 ($n_{\text{gas}}:n_{\text{IL}}$) was calculated to be 0.3:1 for CO₂, 0.7:1 for H₂O, and 0.9:1 for the CO₂/H₂O mixture (each with an uncertainty of ± 0.1). For the CO₂/H₂O gas mixture, the total molar uptake of 0.9 consists of approximately 0.15 for CO₂ and 0.75 for H₂O, further suggesting that H₂O absorption dominates but does not inhibit CO₂ 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 CO₂ 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 CO₂.

Another explanation as to why H₂O absorption dominates over CO₂ 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 [44]. Conversely, it has been found by Wang *et al* that bulk thicknesses of phosphonium-based SBILs with similar anions absorbed CO₂ very quickly, on the order of minutes [45, 46]. 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 min timeframe at a surface sensitive sampling depth. Therefore, if [P₆₆₁₄][124Triz] is similarly behaved to these ILs, then the reason that H₂O absorption dominates over CO₂ absorption may be that there is an abundance of H₂O at the surface due to a slower uptake of the gas into the bulk layers of the IL compared to CO₂.

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 TiO₂ substrate lattice [47]. The electro sprayed IL (black line) can be fitted with two more components at

Table 2. Assignments and corresponding BEs of fitted components in the C 1s, N 1s and O 1s regions for [P₆₆₆₁₄][124Triz] for various gas exposure stages. The arrows (→) denote chemical shifts of the C^{3,5} component between the following exposure stages: IL → IL + CO₂ → IL + H₂O → IL + CO₂ + H₂O.

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} _{CO₂}
	402.4	N ^{1,r} _{H₂O}
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 ₂ O
	537.0	Gas-phase CO ₂

^a C^{3,5} component returns to this BE during the CO₂ and H₂O pump out stages.

^b Within the protonated carbamate group.

^c These peaks are assigned to hydroxyl species and defects at the TiO₂ surface in Stage 1.

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 TiO₂ surface [48].

When the electro sprayed IL is exposed to CO₂ (gold line) peaks are fitted at 530.1, 531.1, 532.1, 533.2, and 535.6 eV. These are assigned to TiO₂, carbamate, C=O in protonated carbamate, C–OH in protonated carbamate, and gas-phase CO₂ (not shown), respectively. Carbamate species formed upon reaction with CO₂ can be protonated and it is likely that there is a mixture of protonated and unprotonated carbamate species present here [49]. The 531.1 and 532.1 eV peaks in Stages 2–6 will also contain contributions from the hydroxyl species/defects at the TiO₂ surface. All fitted components in the O 1s region are summarised in table 2. When the CO₂ 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 CO₂ 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 H₂O 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 CO₂/H₂O mixture in the final stage, the broad reaction peak has a similar intensity to that when exposed to H₂O alone. This suggests that the presence of CO₂ does not inhibit the ad/absorption of H₂O. The reason why H₂O absorption appears to dominate over CO₂ absorption in figure 3 can be explained by exploring absorption at different depths.

3.2. [P₆₆₆₁₄][124Triz] NAP-XPS depth study

NAP-XPS was carried out on an electro sprayed 6.2 nm thin film of [P₆₆₆₁₄][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 electro sprayed IL, the IL exposed to 1 mbar CO₂, and the IL exposed to 1 mbar H₂O, 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 shows measurements in the C 1s region, with spectra normalised to the peak at 285.0 eV. For the electro sprayed IL, even before exposure to CO₂ 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 CO₂ in the chamber. Alternatively, it could indicate irreversibly absorbed CO₂ from previous exposures (since the ESD2 film was deposited over ESD1), which would further suggest that irreversibly absorbed CO₂ moves to the surface. There has been

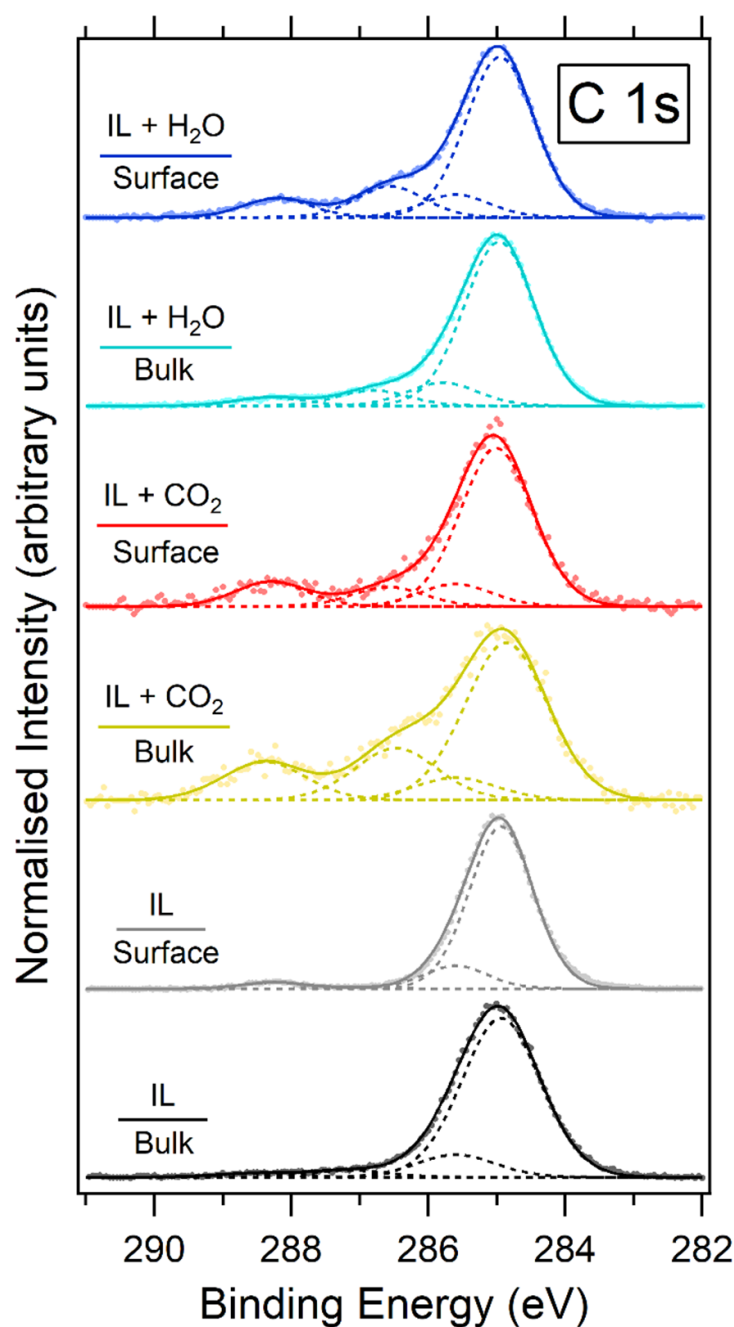


Figure 4. XPS of the C 1s region for an electro sprayed [P₆₆₁₄][124Triz] thin film before exposure, during exposure to CO₂, and during exposure to H₂O. The 6.2 nm thick sample was probed at two sampling depths: 4.0 nm to sample the bulk layers (denoted ‘Bulk’) and 1.6 nm to sample the surface layers (denoted ‘Surface’). Surface and bulk sampling depths were recorded at photon energies of 435 and 885 eV, respectively.

evidence of irreversible CO₂ absorption in multilayer thin films of the similar IL [P₆₆₁₄][benzim] in a previous study [49].

When the IL is exposed to CO₂, 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 CO₂ [50]. Greater concentrations of CO₂-reacted MEA were found in the bulk of the solution while unreacted MEA was more concentrated at the surface.

When CO₂ is removed and the IL is exposed to H₂O alone, a smaller residual carbamate peak remains in the IL + H₂O spectra (blue lines) at 288.3 eV in figure 4. Similar evidence of irreversible CO₂ 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

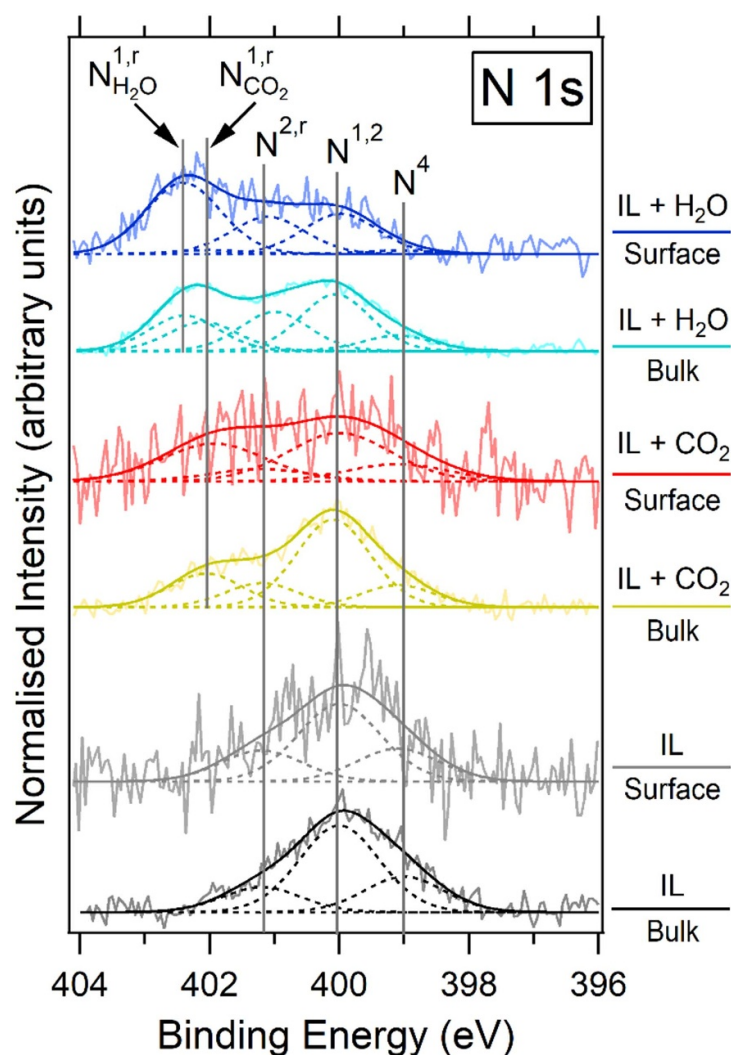


Figure 5. XPS of the N 1s region for an electrospayed [P₆₆₆₁₄][124Triz] thin film before exposure, during exposure to CO₂, and during exposure to H₂O. The 6.2 nm thick sample was probed at two sampling depths: 4.0 nm to sample the bulk layers (denoted ‘Bulk’) and 1.6 nm to sample the surface layers (denoted ‘Surface’). Surface and bulk sampling depths were recorded at photon energies of 550 and 1000 eV, respectively.

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 CO₂ (red line). This implies that most of the CO₂ 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 CO₂ is removed and H₂O introduced (light blue line). This suggests that the irreversible nature of CO₂ absorption in this IL is largely attributed to reactions at the surface.

To summarise, more CO₂ absorption appears to occur in the bulk of the IL, and this absorption is largely reversible. Less CO₂ adsorbs 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 electrospayed 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.

Upon absorption of CO₂, a carbamate N^{1,r} peak appears at 402.0 eV for both sampling depths. The N^{1,r} 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 CO₂ gas, considering they have low kinetic energies (maximum of 150 eV).

The absorption of H₂O results in protonation of N¹ in [124Triz][−], denoted N^{1,r}_{H₂O}, manifesting as a feature at 402.4 eV. Relative to the main N^{1,2} peak and the irreversibly absorbed CO₂ N^{1,r}_{CO₂} peak, the intensity of N^{1,r}_{H₂O} 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 H₂O in figure 4. Results from figures 4 and 5 suggest that more H₂O-reacted species remain at the surface of the IL film, and more CO₂-reacted species diffuse through the surface to the bulk. This would explain why there is little evidence of CO₂ absorption in figure 3 (O 1s) and why H₂O absorption appeared to dominate over CO₂ absorption when the IL was exposed to a CO₂/H₂O mixture in figure 2 (N 1s), because these spectra were taken at surface-sensitive photon energies of 680 eV and 550 eV, respectively.

In our previous study of the similar IL [P₆₆₆₁₄][benzim], it was found that the presence of H₂O did not significantly inhibit CO₂ 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 CO₂ and H₂O in ILs [44, 45] (although, these studies used different ILs and atmospheric pressures as opposed to mbar used in our study).

4. 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 [51, 52], sum frequency generation [53, 54], neutron reflectometry [55], atomic force microscopy [56, 57], and x-ray reflectivity [58]. 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/TiO₂ 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 CO₂/H₂O and affect how these gases diffuse from the vacuum interface into the bulk. N¹ and N² are equivalent in isolated anions, and we would still expect N¹ and N² 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 [59]. SBILs, such as those used in our experiment, have not been studied as widely in this context. In our previous XPS study of the related SBIL [P₆₆₆₁₄][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 [P₆₆₆₁₄]⁺ cation [49]. This study provides evidence of SBILs forming an ordered structure at the IL/vacuum interface.

Fundamental studies of ILs at TiO₂ 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 TiO₂ (101) surface using XPS [52]. 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 BE in the thinner film due to the interaction of the imidazolium cation with the TiO₂ surface. It is possible that the N¹ and N² nitrogen atoms in [124Triz][−] may react differently with the TiO₂ surface, and this may in turn affect how these anions react with CO₂ or H₂O. If the anions were to react with the TiO₂ surface this could make them unavailable for reaction with CO₂/H₂O. A comprehensive computational study would be required to gain insights into these complex interfacial interactions.

In this study we used ESD to obtain thin films of [P₆₆₆₁₄][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, 52, 60] and dip-coating [57, 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].

5. Conclusion

The competitive absorption between CO₂ and H₂O in electrosprayed thin films of the superbasic IL [P₆₆₆₁₄][124Triz] has been characterised using *in situ* NAP-XPS. To the best of our knowledge, [P₆₆₆₁₄]⁺ 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 CO₂ and/or H₂O. The NAP-XPS depth study revealed that greater concentrations of CO₂-reacted species appear in the bulk layers of an electrosprayed IL thin film, reversibly forming carbamate on the anion. However, fewer CO₂-reacted species appear at the surface layers, and this reaction is irreversible. H₂O vapour adsorbs in greater concentrations at the surface rather than the bulk but does not inhibit the absorption of CO₂. The molar uptake ratio of gases ($n_{\text{gas}}:n_{\text{IL}}$) in the electrosprayed IL was calculated to be 0.3:1 for CO₂, 0.7:1 for H₂O, and 0.9:1 for the CO₂/H₂O 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.

Data availability statement


The data that support the findings of this study are openly available at the following URL/DOI: <https://uclandata.uclan.ac.uk/id/eprint/386>.

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References

- [1] Rao A B and Rubin E S 2006 Identifying cost-effective CO₂ control levels for amine-based CO₂ capture systems *Ind. Eng. Chem. Res.* **45** 2421–9
- [2] Cuéllar-Franca R M and Azapagic A 2015 Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts *J. CO₂ Util.* **9** 82–102
- [3] Welton T 2018 Ionic liquids: a brief history *Biophys. Rev.* **10** 691–706
- [4] Yu C H, Huang C H and Tan C S 2012 A review of CO₂ capture by absorption and adsorption *Aerosol Air Qual. Res.* **12** 745–69
- [5] Cuéllar-Franca R M, García-Gutiérrez P, Taylor S F R, Hardacre C and Azapagic A 2016 A novel methodology for assessing the environmental sustainability of ionic liquids used for CO₂ capture *Faraday Discuss.* **192** 283–301
- [6] Bates E D, Mayton R D, Ntai I and Davis J H 2002 CO₂ capture by a task-specific ionic liquid *J. Am. Chem. Soc.* **124** 926–7
- [7] Macfarlane D R, Tachikawa N, Forsyth M, Pringle J M, Howlett P C, Elliott G D, Davis J H, Watanabe M, Simon P and Angell C A 2014 Energy applications of ionic liquids *Energy Environ. Sci.* **7** 232–50

- [8] Li H, Qu J, Cui Q, Xu H, Luo H, Chi M, Meisner R A, Wang W and Dai S 2011 TiO₂ nanotube arrays grown in ionic liquids: high-efficiency in photocatalysis and pore-widening *J. Mater. Chem.* **21** 9487
- [9] Li X, Zhao Z and Pan C 2016 Ionic liquid-assisted electrochemical exfoliation of carbon dots of different size for fluorescent imaging of bacteria by tuning the water fraction in electrolyte *Microchim. Acta* **183** 2525–32
- [10] Roy P, Kim D, Lee K, Spiecker E and Schmuki P 2010 TiO₂ nanotubes and their application in dye-sensitized solar cells *Nanoscale* **2** 45–59
- [11] Bai S et al 2019 Planar perovskite solar cells with long-term stability using ionic liquid additives *Nature* **571** 245–50
- [12] Minami I 2009 Ionic liquids in tribology *Molecules* **14** 2286–305
- [13] Somers A E, Howlett P C, MacFarlane D R and Forsyth M 2013 A review of ionic liquid lubricants *Lubricants* **1** 3–21
- [14] Zhou F, Liang Y and Liu W 2009 Ionic liquid lubricants: designed chemistry for engineering applications *Chem. Soc. Rev.* **38** 2590–9
- [15] Steinrück H P and Wasserscheid P 2015 Ionic liquids in catalysis *Catal. Lett.* **145** 380–97
- [16] Cole J and Syres K L 2022 Ionic liquids on oxide surfaces *J. Phys.: Condens. Matter* **34** 213002
- [17] Porter R T J, Fairweather M, Pourkashanian M and Woolley R M 2015 The range and level of impurities in CO₂ streams from different carbon capture sources *Int. J. Greenh. Gas Control* **36** 161–74
- [18] Xu X, Song C, Wincek R, Andresen J M, Miller B G and Scaroni A W 2003 Separation of CO₂ from power plant flue gas using a novel CO₂ “molecular basket” adsorbent *Fuel Chem. Div. Prepr.* **48** 162–3
- [19] Lei Z, Dai C and Chen B 2014 Gas solubility in ionic liquids *Chem. Rev.* **114** 1289–326
- [20] Boot-Handford M E et al 2014 Carbon capture and storage update *Energy Environ. Sci.* **7** 130–89
- [21] Grishina E P, Ramenskaya L M, Gruzdev M S and Kraeva O V 2013 Water effect on physicochemical properties of 1-butyl-3-methylimidazolium based ionic liquids with inorganic anions *J. Mol. Liq.* **177** 267–72
- [22] Zhang X, Zhang X, Dong H, Zhao Z, Zhang S and Huang Y 2012 Carbon capture with ionic liquids: overview and progress *Energy Environ. Sci.* **5** 6668–81
- [23] Liang Z et al 2015 Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents *Int. J. Greenh. Gas Control* **40** 26–54
- [24] Babamohammadi S, Shamiri A and Aroua M K 2015 A review of CO₂ capture by absorption in ionic liquid-based solvents *Rev. Chem. Eng.* **31** 383–412
- [25] Greer A J, Taylor S F R, Daly H, Quesne M, Catlow C R A, Jacquemin J and Hardacre C 2019 Investigating the effect of NO on the capture of CO₂ using superbase ionic liquids for flue gas applications *ACS Sustain. Chem. Eng.* **7** 3567–74
- [26] Taylor S F R, McCrellis C, McStay C, Jacquemin J, Hardacre C, Mercy M, Bell R G and de Leeuw N H 2015 CO₂ capture in wet and dry superbase ionic liquids *J. Solut. Chem.* **44** 511–27
- [27] McCrellis C, Taylor S F R, Jacquemin J and Hardacre C 2016 Effect of the presence of MEA on the CO₂ capture ability of superbase ionic liquids *J. Chem. Eng. Data* **61** 1092–100
- [28] Hollingsworth N, Taylor S F R, Galante M T, Jacquemin J, Longo C, Holt K B, de Leeuw N H and Hardacre C 2015 CO₂ capture and electrochemical conversion using superbasic [P₆₆₆₁₄][124Triz] *Faraday Discuss.* **183** 389–400
- [29] Mercy M, Rebecca Taylor S F, Jacquemin J, Hardacre C, Bell R G and de Leeuw N H 2015 The addition of CO₂ to four superbase ionic liquids: a DFT study *Phys. Chem. Chem. Phys.* **17** 28674–82
- [30] Taylor S F R, McClung M, McReynolds C, Daly H, Greer A J, Jacquemin J and Hardacre C 2018 Understanding the competitive gas absorption of CO₂ and SO₂ in superbase ionic liquids *Ind. Eng. Chem. Res.* **57** 17033–42
- [31] Henderson Z, Thomas A G, Wagstaffe M, Taylor S F R, Hardacre C and Syres K L 2019 Reversible reaction of CO₂ with superbasic ionic liquid [P₆₆₆₁₄][benzim] studied with *in situ* photoelectron spectroscopy *J. Phys. Chem. C* **123** 7134–41
- [32] Schnadt J, Knudsen J and Johansson N 2020 Present and new frontiers in materials research by ambient pressure x-ray photoelectron spectroscopy *J. Phys.: Condens. Matter* **32** 413003
- [33] Khalifa Y, Broderick A and Newberg J T 2018 Surface enhancement of water at the ionic liquid-gas interface of [HMIM][Cl] under ambient water vapor *J. Phys.: Condens. Matter* **30** 325001
- [34] Henderson Z, Walton A S, Thomas A G and Syres K L 2018 Water-induced reordering in ultrathin ionic liquid films *J. Phys.: Condens. Matter* **30** 334003
- [35] Niedermaier I et al 2014 Carbon dioxide capture by an amine functionalized ionic liquid: fundamental differences of surface and bulk behavior *J. Am. Chem. Soc.* **136** 436–41
- [36] Zhu S et al 2021 HIPPIE: a new platform for ambient-pressure x-ray photoelectron spectroscopy at the MAX IV Laboratory *J. Synchrotron Radiat.* **28** 624–36
- [37] Karen Syres 2023 *Near ambient pressure XPS measurements of CO₂/H₂O absorption in [P66614] Repository* (<https://doi.org/10.17030/uclan.data.00000386>)
- [38] Fairely N et al 2021 Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy *Appl. Surf. Sci. Adv.* **5** 100112
- [39] Blundell R K and Licence P 2014 Quaternary ammonium and phosphonium based ionic liquids: a comparison of common anions *Phys. Chem. Chem. Phys.* **16** 15278–88
- [40] Hollingsworth N, Taylor S F R, Galante M T, Jacquemin J, Longo C, Holt K B, de Leeuw N H and Hardacre C 2015 Reduction of carbon dioxide to formate at low overpotential using a superbase ionic liquid *Angew. Chem.* **127** 14370–4
- [41] Lovelock K R J, Smith E F, Deyko A, Villar-Garcia I J, Licence P and Jones R G 2007 Water adsorption on a liquid surface *Chem. Commun.* 4866–8
- [42] Neese F 2012 The ORCA program system *Wiley Interdiscip. Rev.-Comput. Mol. Sci.* **2** 73–78
- [43] Neese F 2018 Software update: the ORCA program system, version 4.0 *Wiley Interdiscip. Rev.-Comput. Mol. Sci.* **8** 4–9
- [44] Broderick A, Khalifa Y, Shiflett M B and Newberg J T 2017 Water at the ionic liquid-gas interface examined by ambient pressure x-ray photoelectron spectroscopy *J. Phys. Chem. C* **121** 7337–43
- [45] Wang C, Luo X, Luo H, Jiang D, Li H and Dai S 2011 Tuning the basicity of ionic liquids for equimolar CO₂ capture *Angew. Chem.* **123** 5020–4
- [46] Zeng S, Zhang X, Bai L, Zhang X, Wang H, Wang J, Bao D, Li M, Liu X and Zhang S 2017 Ionic-liquid-based CO₂ capture systems: structure, interaction and process *Chem. Rev.* **117** 9625–73
- [47] Syres K L, Thomas A G, Flavell W R, Spencer B F, Bondino F, Malvestuto M, Preobrajenski A and Grätzel M 2012 Adsorbate-induced modification of surface electronic structure: pyrocatechol adsorption on the anatase TiO₂ (101) and rutile TiO₂ (110) surfaces *J. Phys. Chem. C* **116** 23515–25
- [48] Jackman M J, Thomas A G and Murny C 2015 Photoelectron spectroscopy study of stoichiometric and reduced anatase TiO₂ (101) surfaces: the effect of subsurface defects on water adsorption at near-ambient pressures *J. Phys. Chem. C* **119** 13682–90

- [49] Cole J et al 2021 Near-ambient pressure XPS and NEXAFS study of a superbasic ionic liquid with CO₂ *J. Phys. Chem. C* **125** 22778–85
- [50] Lewis T, Faubel M, Winter B and Hemminger J C 2011 CO₂ capture in amine-based aqueous solution: role of the gas-solution interface *Angew. Chem., Int. Ed.* **50** 10178–81
- [51] Walsh J F, Dhariwal H S, Gutiérrez-Sosa A, Finetti P, Muryn C A, Brookes N B, Oldman R J and Thornton G 1998 Probing molecular orientation in corrosion inhibition via a NEXAFS study of benzotriazole and related molecules on Cu(100) *Surf. Sci.* **415** 423–32
- [52] Wagstaffe M, Jackman M J, Syres K L, Generalov A and Thomas A G 2016 Ionic liquid ordering at an oxide surface *ChemPhysChem* **17** 3430–4
- [53] Rivera-Rubero S and Baldelli S 2004 Influence of water on the surface of hydrophilic and hydrophobic room-temperature ionic liquids *J. Am. Chem. Soc.* **126** 11788–9
- [54] Baldelli S 2008 Surface structure at the ionic liquid-electrified metal interface *Acc. Chem. Res.* **41** 421–31
- [55] Bowers J, Vergara-Gutierrez M C and Webster J R P 2004 Surface ordering of amphiphilic ionic liquids *Langmuir* **20** 309–12
- [56] Bovio S, Podestà A, Lenardi C and Milani P 2009 Evidence of extended solidlike layering in [Bmim][NTf₂] ionic liquid thin films at room-temperature *J. Phys. Chem. B* **113** 6600–3
- [57] Zhao W, Zhu M, Mo Y and Bai M 2009 Effect of anion on micro/nano-tribological properties of ultra-thin imidazolium ionic liquid films on silicon wafer *Colloids Surf. A* **332** 78–83
- [58] Solutskin E, Ocko B M, Taman L, Kuzmenko I, Gog T and Deutsch M 2005 Surface layering in ionic liquids: an x-ray reflectivity study *J. Am. Chem. Soc.* **127** 7796–804
- [59] Lockett V, Sedev R, Bassell C and Ralston J 2008 Angle-resolved x-ray photoelectron spectroscopy of the surface of imidazolium ionic liquids *Phys. Chem. Chem. Phys.* **10** 1330–5
- [60] Cremer T, Killian M, Gottfried J M, Paape N, Wasserscheid P, Maier F and Steinrück H P 2008 Physical vapor deposition of [EMIM][Tf₂N]: a new approach to the modification of surface properties with ultrathin ionic liquid films *ChemPhysChem* **9** 2185–90
- [61] Palacio M and Bhushan B 2008 Ultrathin wear-resistant ionic liquid films for novel MEMS/NEMS applications *Adv. Mater.* **20** 1194–8
- [62] Swarbrick J C, Taylor J B and O'Shea J N 2006 Electrospray deposition in vacuum *Appl. Surf. Sci.* **252** 5622–6
- [63] Rietzler F, Piermaier M, Deyko A, Steinrück H P and Maier F 2014 Electrospray ionization deposition of ultrathin ionic liquid films: [C₈C₁Im]Cl and [C₈C₁Im][Tf₂N] on Au(111) *Langmuir* **30** 1063–71
- [64] Steinrück H P, Libuda J, Wasserscheid P, Cremer T, Kolbeck C, Laurin M, Maier F, Sobota M, Schulz P S and Stark M 2011 Surface science and model catalysis with ionic liquid-modified materials *Adv. Mater.* **23** 2571–87
- [65] Fehrmann R, Riisager A and Haumann M 2014 *Supported Ionic Liquids: Fundamentals and Applications* ed R Fehrmann, A Riisager and M Haumann (Wiley)