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## SO<sub>2</sub> capture by ionic liquid and spectroscopic speciation of sulfur(IV) therein†

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The absorption of equimolar sulfur dioxide (SO<sub>2</sub>) by tributyloctylphosphonium bicarbonate ([P<sub>4448</sub>][HCO<sub>3</sub>]) resulted in the formation of a corresponding bisulfite ionic liquid ([P<sub>4448</sub>][bisulfite]) accompanied by carbon dioxide (CO<sub>2</sub>) release. The liquid formed absorbed an additional 0.6 equivalents of SO<sub>2</sub>. The speciation of sulfur(IV) in the SO<sub>2</sub>-loaded ionic liquid was performed using Raman and NMR spectroscopies. The two known isomeric forms of bisulfite ion in aqueous systems were identified while the condensation of bisulfite anion was suppressed in [P<sub>4448</sub>][bisulfite]. The isomer with the proton bonded to the sulfur atom (HSO<sub>3</sub><sup>-</sup>) was more abundant than the one with the proton bonded to the oxygen atom (HOSO<sub>2</sub><sup>-</sup>). The isomeric exchange rate was much slower in the IL than in water as distinguished by <sup>1</sup>H NMR. When excess SO<sub>2</sub> was absorbed by [P<sub>4448</sub>][bisulfite], the presence of molecular SO<sub>2</sub> and HS<sub>2</sub>O<sub>5</sub><sup>-</sup> were suggested by Raman bands as an indication of concerted physisorption and chemisorption.

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### Introduction

Sulfur dioxide is an environmental pollutant emitted in large amounts wherever petroleum is burnt. The onsite capture of sulfur dioxide by a liquid absorbent is an option to address the pollution issue. Ionic liquids (ILs) are liquid salts that are derived from organic cations. They are practically nonvolatile and can capture various gases.<sup>1</sup> Although there are numerous studies on the carbon dioxide (CO<sub>2</sub>) capture by ILs,<sup>1–19</sup> the studies on the SO<sub>2</sub> capture by ILs are rather limited. The physisorption of SO<sub>2</sub> by ILs has been demonstrated by J. L. Anderson *et al.*<sup>20</sup> for 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-*n*-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imides. These two ILs absorb nearly equimolar SO<sub>2</sub> at 25 °C and 0.1 MPa. Interestingly, the absorption capacity of SO<sub>2</sub> and CO<sub>2</sub> as a function of pressure can be roughly scaled by the reduced pressure, which is the actual pressure divided by the saturation pressure of each gas at the measurement temperature.<sup>20</sup> In attempt to attain even

higher absorption capacity (especially in weight basis) and/or in targeting absorptions at lower SO<sub>2</sub> pressures, a number of “functionalized ILs” have been developed.<sup>21–29</sup> It has been found that several functional groups are in particular effective for enhancing SO<sub>2</sub> absorption. These include X<sup>-</sup> (X = halogen),<sup>21</sup> –NH<sub>2</sub> (amino),<sup>22,23</sup> –O<sup>-</sup> (alkoxide and phenoxide),<sup>24</sup> –COO<sup>-</sup> (carboxylate),<sup>25–28</sup> –SO<sub>3</sub><sup>-</sup> (sulfonate),<sup>26</sup> –N–CO– (acylamide)<sup>29</sup> groups, all of which have electron-rich atoms. Actual chemical forms of sulfur in these absorbents are not well understood. Based on the vibrational spectral shift of SO<sub>2</sub> and the colour change of the solution by absorption, it is argued that charge-transfer interaction is operating when SO<sub>2</sub> is absorbed by 1-butyl-3-methylimidazolium bromide.<sup>21</sup>

SO<sub>2</sub> is an acid oxide and thus can be captured by bases, as is done in wet limestone scrubbing process. The usage of ILs with basic anion component is especially attractive for capturing SO<sub>2</sub>. In the present study we demonstrate SO<sub>2</sub> absorption by a newly synthesized IL, tributyloctylphosphonium bicarbonate ([P<sub>4448</sub>][HCO<sub>3</sub>]). From spectroscopic analysis we show that this IL absorbs an equimolar of SO<sub>2</sub> *via* “gas exchange” reaction (eqn (1)).



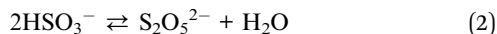
Interestingly we also find that the IL can capture additional SO<sub>2</sub>, after completion of eqn (1). It is quite an interesting issue how SO<sub>2</sub> molecules are dissolved in the IL.

It has been known that bisulfite ion is subject to complicated equilibria in aqueous solutions.<sup>30–32</sup> Raman spectroscopy has provided evidence of condensation (eqn (2)) and isomerization (eqn (3)) equilibria for bisulfite ions.<sup>30–39</sup>

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† Electronic supplementary information (ESI) available: Tables of thermal energies, geometries of the optimized structures of monomers and clusters by DFT calculations, table of experimentally observed Raman shifts, tables of calculated Raman shift and assignments of anions, H NMR, <sup>13</sup>C NMR, IR, and HR-MS spectra of [P<sub>4448</sub>][HCO<sub>3</sub>], <sup>13</sup>C NMR of SO<sub>2</sub> loaded [P<sub>4448</sub>][HCO<sub>3</sub>], figures of images for the optimized structures of monomers and clusters by DFT calculations, explanations of the multi-peak fitting, figures of calculated Raman activities of anions in SCRF water, and of dimers of HOSO<sub>2</sub><sup>-</sup>, and of complexes of bisulfite with SO<sub>2</sub>, temperature dependence of the H NMR. See DOI: 10.1039/c6ra25528k





The hydrogen atom is directly bonded with the sulfur atom in the left-hand side of eqn (3), while the hydrogen atom is bonded with the oxygen atom in the right hand side of eqn (3). Note that the isomer on the right in eqn (3) is present only in solution and its identity is not fully determined. The assignment of sulfur Raman bands in water have been debated for several decades. The coexistence of many structurally different but somewhat similar chemical species often induced confusions about overlapped and closely placed bands. The  $\text{HSO}_3^-$  isomer is identified by combined Raman/X-ray<sup>33</sup> and Raman/neutron<sup>34</sup> analysis of solid  $\text{CsDSO}_3$ . It is characterized in aqueous solution as well by vibrational spectroscopy owing to the well resolved band of the SH stretching mode at  $2530\text{ cm}^{-1}$  ( $\nu_{\text{SH}}$ ). The disulfite ion can be also isolated as a crystalline compound<sup>40</sup> and strong Raman bands have been unambiguously assigned.<sup>35</sup> For other species, they are metastable and are always accompanied by equilibrium “contaminants”. The presence of  $\text{HOSO}_2^-$  isomer in aqueous solution has been deduced from Raman spectroscopic observation<sup>36</sup> and later supported by NMR,<sup>41</sup> XANES,<sup>34</sup> and computational studies.<sup>42–44</sup> There are also several speculative discussions on the existence of the dimers of sulfite anion,<sup>37,45</sup> and several bands remain unassigned. In the present study, analysis of the sulfite Raman bands in the IL is carried out, which in turn aids in confirming the band assignments in aqueous systems.

NMR spectroscopy is complementary to Raman spectroscopy, particularly for quantification. A series of  $^{17}\text{O}$  NMR spectroscopic studies have been carried out by Horner *et al.* to investigate the equilibrium constants and the rates of eqn (2) and (3) in aqueous solutions.<sup>41,46</sup> Although  $^{17}\text{O}$  NMR spectroscopy is straightforward for sulfur(IV) oxoanions, it gives limited information regarding the IL due to severe line broadening. Alternatively,  $^1\text{H}$  NMR provides direct evidence for the bisulfite isomerization in eqn (3) owing to the slowdown of the chemical exchange. In this work, we performed combined NMR and Raman spectroscopic investigations on the sulfur(IV) speciation in ILs to shed light on the absorption mechanism of  $\text{SO}_2$  by ILs.

## Experimental

### Sample preparation

The IL, tributylphosphonium bicarbonate ( $[\text{P}_{4448}]\text{HCO}_3$ ) was obtained as follows. Bromooctane (Wako Chemicals) was reacted with 0.9 equiv. of tributylphosphine (Wako Chemicals) at  $108\text{ }^\circ\text{C}$  for 24 h. The obtained liquid (crude  $[\text{P}_{4448}]\text{Br}$ ) was shaken vigorously with 1.1 equiv. of aqueous  $\text{KPF}_6$  (Aldrich) and dichloromethane. The separation of two phases yielded dichloromethane solution of  $[\text{P}_{4448}]\text{PF}_6$ . Upon evaporation of dichloromethane, the crude  $[\text{P}_{4448}]\text{PF}_6$  was recrystallized 3 times from methanol at  $-40\text{ }^\circ\text{C}$ . The purified and dried  $[\text{P}_{4448}]\text{PF}_6$  showed its melting point of  $36\text{ }^\circ\text{C}$ . The 2-propanol solution of  $[\text{P}_{4448}]\text{PF}_6$  was mixed with 1.1 equiv. of 2-propanol solution of  $\text{CsOH}$  (Nacalai Tesque) and hexane (30 wt%). The precipitates

( $\text{CsPF}_6$ ) were filtered twice at  $-80\text{ }^\circ\text{C}$ . To the filtrate, excess  $\text{CO}_2$  was bubbled in and the resultant solution was stirred with active carbon overnight. After filtration, the filtrate was evacuated at  $30\text{ }^\circ\text{C}$  for solvent removal. The residue was diluted with benzene, and then filtered and evacuated to yield  $[\text{P}_{4448}]\text{HCO}_3$  as highly viscous and almost colourless liquid. The compound was characterized by NMR, IR, and HR-MS which are given at the footnote<sup>‡</sup> and in Fig. S1 of the ESI.<sup>†</sup>

The  $\text{SO}_2$  gas was prepared by the action of concentrated sulfuric acid (Nacalai Tesque) to  $\text{Na}_2\text{S}_2\text{O}_5$  (Nacalai Tesque). The evolved  $\text{SO}_2$  was transferred to a syringe (100 mL) and then injected into an evacuated 300 mL flask containing 10 g of  $[\text{P}_{4448}]\text{HCO}_3$ . The IL was stirred for 30 min to ensure uptake of  $\text{SO}_2$ . Then approximately 0.7 g of the liquid was withdrawn to an NMR tube for NMR and Raman spectroscopic measurements. To the rest of the liquid, additional injections of  $\text{SO}_2$  were performed in a similar manner to obtain samples at higher  $\text{SO}_2$  loadings.

In the present work,  $\text{SO}_2$  loadings in the IL is reported by the mole ratio  $q_{\text{SO}_2}$ , which is defined by the mole of  $\text{SO}_2$  absorbed by the liquid divided by the mole of the  $[\text{P}_{4448}]$  cation. Specifically,  $q_{\text{SO}_2} = 1$  corresponds to “pure”  $[\text{P}_{4448}][\text{bisulfite}]$ . We use the notation [bisulfite] for including all plausible isomers of  $\text{HSO}_3^-$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for  $[\text{P}_{4448}][\text{bisulfite}]$  are given at the footnote.<sup>§</sup> The  $q_{\text{SO}_2}$  of each sample was calculated by the volume of  $\text{SO}_2$  injected to the reactor vessel. Nevertheless, this may overestimate the actual loading when part of  $\text{SO}_2$  injected remained in the gas phase of the reactor at equilibrium. Thus we checked the  $q_{\text{SO}_2}$  directly by wet titration method for selected samples as follows. After the spectroscopic measurements were finished, the sample was dissolved in water and immediately oxidized by the action of excess  $\text{KMnO}_4$ . The excess  $\text{KMnO}_4$  was reduced by oxalic acid until the purple colour disappears. To the solution, ammonia solution was added to precipitate  $\text{Mn}^{2+}$  from the solution. The moles of  $\text{SO}_4^{2-}$  (which is equal to the loading of  $\text{SO}_2$ ) was determined by the standard back titration method using aqueous  $\text{BaCl}_2$  and disodium salts of EDTA as titrants and phthalein complex as an indicator. On the other hand, the mole of the  $[\text{P}_{4448}]$  cation was determined by the integral of  $^{31}\text{P}$  NMR peak (34 ppm) within an accuracy of 2%. Thus obtained values of  $q_{\text{SO}_2}$  was consistent ( $\pm 10\%$ ) with that determined by the injected volume, indicating that injected  $\text{SO}_2$  was quantitatively absorbed by the IL up to  $q_{\text{SO}_2} \sim 1.6$  at atmospheric pressure.

### NMR measurements

NMR spectra were obtained using a JEOL ECA300 (8.4 T) magnet equipped with a standard 5 mm probe (TH5AT). The  $^1\text{H}$  NMR spectra were scanned > 8 times with a repetition time of 60 s.

<sup>‡</sup>  $[\text{P}_{4448}]\text{HCO}_3$ :  $^1\text{H}$  NMR:  $\delta$  0.8 (br), 1.2–1.6(br), 2.6(br), ( $\delta$  0.8–2.6 44H), 11.3(br),  $1.01 \pm 0.03\text{H}$ ).  $^1\text{H}$  NMR ( $\text{H}_2\text{O}$  with 0.20% w/w STSP):  $\delta$  0.85–0.93 (m, 12H), 1.23–1.33 (m, 8H), 1.40–1.60 (m, 16H), 2.13 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{H}_2\text{O}$ ):  $\delta$  12.88 (3C), 13.85 (1C), 17.95 (d,  $J_{\text{CP}} = 190\text{ Hz}$ , 4C), 20.88 (d,  $J_{\text{CP}} = 18\text{ Hz}$ , 1C), 22.41 (1C), 23.00 (d,  $J_{\text{CP}} = 18\text{ Hz}$ , 3C), 23.51 (d,  $J_{\text{CP}} = 60\text{ Hz}$ , 3C), 28.25 (1C), 18.47 (1C), 30.06 (d,  $J_{\text{CP}} = 60\text{ Hz}$ , 1C), 31.47 (1C), 160.49 (1C).

<sup>§</sup>  $[\text{P}_{4448}][\text{bisulfite}]$  (no solvent):  $\delta$  0.8(br), 1.2–1.6(br), 2.6(br) ( $\delta$  0.8–2.6 44H), 4.06(s, 0.47H), 9.85(s, 0.53H).



The  $^{13}\text{C}$  NMR spectra were scanned >256 times with a repetition time of 30 s; the  $T_1$  of the  $\text{HCO}_3^-$  was 3 s at 25 °C and shorter at lower temperatures. The overlapped  $^1\text{H}$  NMR peaks due to the  $\text{HSO}_3^-$  isomer and the coalesced hydroxyl protons were decomposed by a double Lorentzian function to obtain peak integrals of each component. Due to the high viscosity of the IL and the resultant line broadening, we could not obtain useful information from  $^{17}\text{O}$  NMR.<sup>47</sup>

### Raman measurements

Raman spectra were measured at the back scattering geometry by using a doubled output of a Nd:YAG laser (Spectra Physics, Excelsior-532-300) as a probing beam. The scattering light was detected by a Peltier-cooled CCD camera attached to the spectrometer (Princeton Instruments, Insight 256E). The Raman shift was calibrated by the Raman spectra of cyclohexane and benzene in the finger print region, and by the line spectra of a neon lamp at the CH-stretching region. Generally, the sample was enclosed in the NMR tube and the Raman scattering was measured at the room temperature. For the measurement at the low temperature, the temperature was regulated by circulating the temperature controlled water and methanol mixture through the cell holder. The sample was yellowish at  $q_{\text{SO}_2} > 1$  and turned green at the laser spot while the Raman spectra were collected. The background signals in the Raman measurement were slightly dependent on the  $\text{SO}_2$  loading, which were subtracted by making proper baseline signals by connecting the signal points where no Raman signal detected.

### Electronic state calculations

DFT calculations were performed using the basis set of 6-311G+(d,p) or aug-cc-pVTZ and the B3PW91 functional by gaussian-09.<sup>48</sup>

## Results and discussion

### NMR spectroscopic analysis

We prepared an IL containing sulfur(IV) species by loading various amounts of  $\text{SO}_2$  into a dried bicarbonate IL,  $[\text{P}_{4448}]\text{HCO}_3^-$ . Since  $\text{SO}_2$  is a stronger acid than  $\text{CO}_2$ , we expect the anion exchange reaction in eqn (1) to occur. In fact, when the bicarbonate IL was brought in contact with  $\text{SO}_2$ , evolution of bubbles was observed. To confirm the progress of eqn (1),  $^{13}\text{C}$  NMR spectra were collected for each sample. The spectra are shown in Fig. S2.† The bicarbonate anion was observed at 159 ppm in pure  $[\text{P}_{4448}]\text{HCO}_3^-$ . The peak integral monotonously decreased as the  $\text{SO}_2$  injection was repeated, indicating the escape of the bicarbonate anion as gaseous  $\text{CO}_2$ . Molecular  $\text{CO}_2$  in the IL (which would appear at 125 ppm, if present) was not detected. The cation peak significantly sharpened with the  $\text{SO}_2$  uptake which is related to the decrease in viscosity.

$^1\text{H}$  NMR spectra for the samples are shown in Fig. 1. In  $^1\text{H}$  NMR spectra, a peak emerged at 10 ppm. This peak has not been reported by NMR studies on aqueous bisulfite salts. The chemical shift was insensitive to temperature (Fig. S3†), which indicates that the peak is not of a hydroxyl proton. As

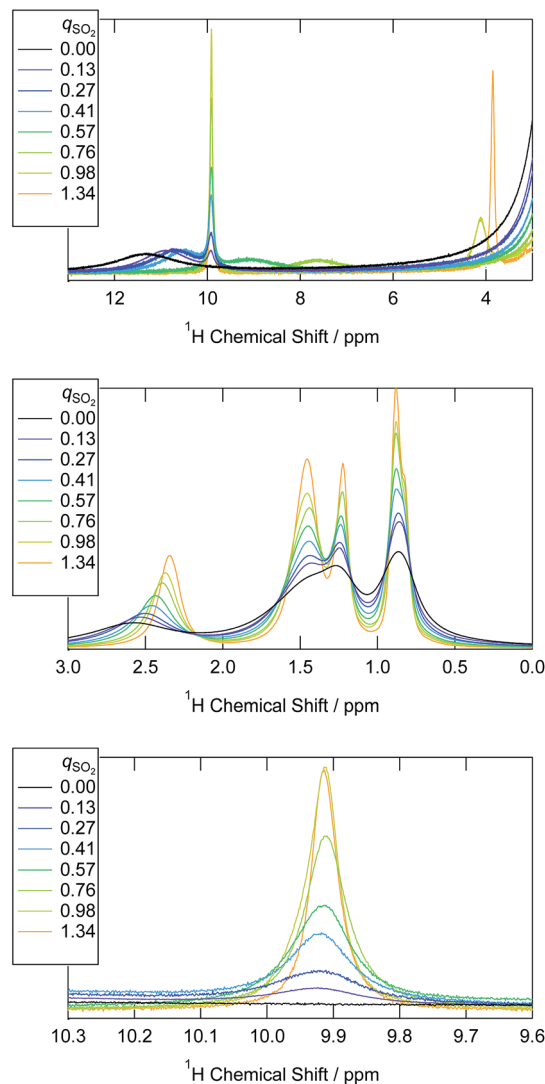


Fig. 1  $^1\text{H}$  NMR spectra of the  $[\text{P}_{4448}]\text{HCO}_3^-$  and the ILs that have absorbed  $\text{SO}_2$  by various mole ratios ( $q_{\text{SO}_2}$ ) at 298 K.

mentioned in the Introduction, two isomers are proposed for the bisulfite anion (eqn (3)). We elucidate that the peak is due to  $\text{HSO}_3^-$ , the isomer without the hydroxyl proton. A broad peak was observed spanning from 13 to 10 ppm in  $[\text{P}_{4448}]\text{HCO}_3^-$  ( $q_{\text{SO}_2} = 0$ ) and it moved towards 4 ppm as  $\text{SO}_2$  loading increased. The peak shifted rightwards at an elevated temperature (Fig. S3†), which indicates hydrogen bonding. Thus we attribute this peak to the species that have hydroxyl protons, namely  $\text{HCO}_3^-$  and  $\text{HOSO}_2^-$ . It is presumable that they exchange their protons rapidly and give a single but broad coalesced NMR signal. The drastic chemical shift change with increasing  $\text{SO}_2$  loading is ascribed to the decrease of  $\text{HCO}_3^-$  and the concomitant increase of  $\text{HOSO}_2^-$ ; the chemical shift of a coalesced peak is the weighted average of the intrinsic chemical shifts of individual components. As established from Fig. 1, these are 12 and 4 ppm for  $\text{HCO}_3^-$  and  $\text{HOSO}_2^-$ , respectively. The large chemical shift value of  $\text{HCO}_3^-$  implies the presence of tight hydrogen bonds, such as those found in the carboxylic acid dimer. The



chemical shift value of  $\text{HOSO}_2^-$  is typical for a hydrogen-bonded OH group.

The fact that we observe separate  $^1\text{H}$  NMR peaks for the two bisulfite isomers  $\text{HSO}_3^-$  and  $\text{HOSO}_2^-$  implies that the proton exchanges between the two isomers are relatively slow ( $>1$  s). Such a situation is very different from that in water; in aqueous bisulfite solution, no  $^1\text{H}$  NMR peaks other than water is observed. This implies that the two bisulfite isomers rapidly exchange the protons and it is probably mediated by water.

The chemical shift of the  $\alpha$  proton (proton attached to the carbon bonded to the P atom) decreased, indicating stronger cation–bicarbonate interactions replaced by weaker cation–bisulfite interactions.

Based on the above peak assignments, we integrated each of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks and compared the peak integrals with those of the  $[\text{P}_{4448}]$  cation. Whenever overlapped peaks were observed, they were decomposed by Lorentzian functions. This allowed us to evaluate the concentration of chemical species  $i$  in terms of the mole ratio ( $q_i$ ) relative to the  $[\text{P}_{4448}]$  cation (Fig. 2). The  $\text{HCO}_3^-$  was quantified by the  $^{13}\text{C}$  NMR peak integral (159 ppm). As can be seen from Fig. 2, eqn (1) proceeded quantitatively until the  $q_{\text{SO}_2}$  reached 1. The  $\text{HSO}_3^-$  isomer was quantified by the  $^1\text{H}$  NMR peak integral (10 ppm). The other isomer was quantified by the coalesced peak for the hydroxyl proton (chemical shift varies) after the  $\text{HCO}_3^-$  contribution was subtracted. One needs to consider the possibility of the two bisulfite ions condensing to form  $\text{S}_2\text{O}_5^{2-}$  as in eqn (2). When this would be the case, 1 equiv. of water may also contribute to the coalesced hydroxyl proton peak. As we will see later,  $\text{S}_2\text{O}_5^{2-}$  was not present in samples when  $q_{\text{SO}_2} < 1$  according to Raman spectroscopy. Thus, we could safely quantify the  $\text{HOSO}_2^-$  isomer from the  $^1\text{H}$  NMR spectra for  $q_{\text{SO}_2} < 1$  as in Fig. 2.

When  $q_{\text{SO}_2}$  exceeded 1,  $q_{\text{HSO}_3^-}$  started to decrease, indicating that  $\text{HSO}_3^-$  is consumed to form new sulfur(IV) species. These species were not detected by  $^1\text{H}$  NMR. In view of high sulfur concentrations, the formation of disulfite ion is plausible. Key

information on the sulfur speciation at  $q_{\text{SO}_2} > 1$  is provided by Raman spectroscopy in the next section.

As can be seen from Fig. 2,  $\text{HSO}_3^-$  is the more abundant of the two bisulfite isomers. The equilibrium quotient of the two isomers ( $Q = [\text{HOSO}_2^-]/[\text{HSO}_3^-]$ ) was in the range of  $0.5 \pm 0.1$  for the 5 samples whose  $q_{\text{SO}_2}$  was less than 0.8. Knowing that the corresponding equilibrium quotient is reported to be 3–4 for water,<sup>34,41</sup> the isomer population is reversed in the two solvents.

We consider several plausible reasons for the difference. The first is the absence of hydrogen-bonding in ILs. In an aqueous solution, water molecules form hydrogen bonds more strongly with the isomer that has a hydroxyl group than with one that does not. Thus, the former is more favoured in water than the latter.

The second critical difference is the existence of the Coulomb interactions with cations in ILs. The difference in interactions between bisulfite and phosphonium cation may result in different stabilities of the isomer in ILs. In order to test how the interaction with the cation affects the energetic stability of the isomer, we carried out DFT calculations for  $\text{HSO}_3^-$  and  $\text{HOSO}_2^-$  in vapour, in SCRF water, and as a cluster with one  $[\text{P}_{4448}]^+$  cation. DFT calculations were done using the basis set aug-cc-pVTZ and B3PW91 functional for the isolated anion in vapour and in SCRF water. For the cluster calculations, we used the 6-311G+(d,p) basis set owing to limitations in computational resources. The optimized structures of the anions and the clusters are shown in Fig. S4 and S5.† Although the cation has conformational flexibility, we limited the calculations for all *trans* and all *gauche* conformations (Fig. S5(a) and (b)†). The energies for the optimized structures are listed in Tables S1 and S2,† and the geometrical parameters are listed in Table S3.† According to the calculations, the  $\text{HOSO}_2^-$  isomer was stable compared to the  $\text{HSO}_3^-$  isomer by  $10 \text{ kJ mol}^{-1}$  in vapour when the aug-cc-pVTZ basis set was used. A similar energy value was calculated for that in SCRF water ( $10 \text{ kJ mol}^{-1}$ ) as the model does not include the hydrogen-bonding effect. When we used the 6-311G+(d,p) basis set, the energy difference became somewhat larger ( $32 \text{ kJ mol}^{-1}$ ). According to the theoretical estimations of the energy difference between  $\text{HOSO}_2^-$  and  $\text{HSO}_3^-$  performed by several groups using MP2 or DFT calculations, the energy difference between these isomers is quite subtle even for the isolated state in vapour, and depends on the basis sets.<sup>42,43</sup> Our calculation results are consistent with previous estimations<sup>42</sup> using similar basis sets. The determination of the absolute value at the present level calculation remains challenging. By making clusters with cations, the energy difference between the isomers became somewhat large ( $41 \text{ kJ mol}^{-1}$  for all *trans*,  $46 \text{ kJ mol}^{-1}$  for all *gauche*). Therefore, by pairing with a cation, the  $\text{HOSO}_2^-$  isomer is energetically more stable than the  $\text{HSO}_3^-$  isomer, in contradiction to the expectation from the experimental result. One point to be considered is that the dihedral angles of  $\text{HO}_1\text{SO}_2$  and  $\text{HO}_1\text{SO}_3$  of  $\text{HOSO}_2^-$  (Fig. S4 and S5†) dramatically changed through the complexation with a cation. On the other hand, no significant structure change was calculated for  $\text{HSO}_3^-$ . This kind of

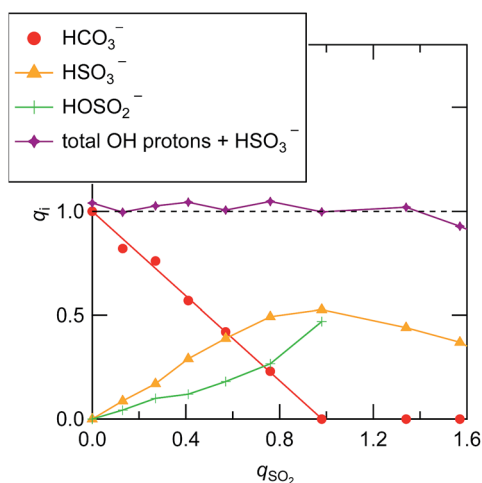


Fig. 2 The abundance of bisulfite isomers and the bicarbonate ion in the ILs with the progress of  $\text{SO}_2$  absorption. The vertical axis denotes to the mole ratio with respect to the  $[\text{P}_{4448}]$  cation.



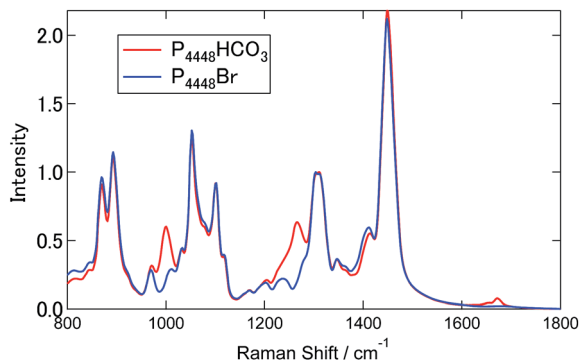


Fig. 3 Raman spectra of  $[P_{4448}]Br$  and  $[P_{4448}]HCO_3$ , respectively.

difference may contribute to isomer stability if more cation molecules surround the anion.

### Anion speciation based on Raman spectra

Fig. 3 shows the Raman spectra for  $[P_{4448}]Br$  and  $[P_{4448}]HCO_3$  in the finger print region. Table S4<sup>†</sup> summarizes the Raman shifts of the bands observed for these ILs together with those following  $SO_2$  loading on  $[P_{4448}]HCO_3$ . The following Raman bands in Fig. 3 appeared only for the  $[P_{4448}]HCO_3$  sample: 996, 1267, 1655, and 1672  $cm^{-1}$ . In reference to the assignments in aqueous solution,<sup>49</sup> these bands are  $\nu_{C-OH}$ ,  $\nu_s CO_2$ , and  $\nu_{as} CO_2$  vibrational modes of  $HCO_3^-$ . The other bands are assigned to the vibrational modes of  $[P_{4448}]^+$ , and they do not seem to be affected by the anion exchange from  $Br^-$  to  $HCO_3^-$ . In the ESI,<sup>†</sup> DFT calculations are presented for the  $[P_{4448}]^+$  vibrational Raman spectra in all *trans* or all *gauche* alkyl-chain conformations using the 6-311G+(d,p) basis set and B3PW91 functional (Fig. S6<sup>†</sup>). The calculated Raman bands are presented to give the half width at half height of 4  $cm^{-1}$ . The calculation captured majority of the features found in the experimental Raman spectrum. When we used the scaling factor of 0.976 for the horizontal scale, the coincidence between the theory and experiment became much better. The bands could be assigned as follows: (1) the band around 670  $cm^{-1}$  is due to the symmetric stretching mode of the centre P with four connected carbon atoms; (2) the bands around 900  $cm^{-1}$  are mostly in-plane-bending of C-C-H at the terminal  $CH_3$ ; (3) the bands around 1100  $cm^{-1}$  are the bending motions of alkyl-chains; (4) the bands around 1300  $cm^{-1}$  are the wagging motions of C-C-H<sub>2</sub> in the methylene carbons of the alkyl-chain; (5) and the bands around 1450  $cm^{-1}$  are the scissoring motion of HCH.

Fig. 4 shows the Raman spectra of  $[P_{4448}]HCO_3$  following  $SO_2$  absorption. The inset figures are the magnifications around 1050  $cm^{-1}$ . Each spectrum is normalized by the band at 1449  $cm^{-1}$  (one of the  $[P_{4448}]^+$  vibrations). As the amount of  $SO_2$  increased, several new bands appeared while the  $HCO_3^-$  bands (621  $cm^{-1}$ , 996 and 1267  $cm^{-1}$ ) diminished. Fig. 5 shows difference spectra from the pure  $[P_{4448}]HCO_3$ . From  $q_{SO_2} = 0$  to 0.98, several new bands (315, 505, and 725  $cm^{-1}$  in Fig. 5(a); 1029, 1048, 1079, and 1120  $cm^{-1}$  in Fig. 5(b)) appeared and their intensities increased with increasing  $q_{SO_2}$ . On the other hand,

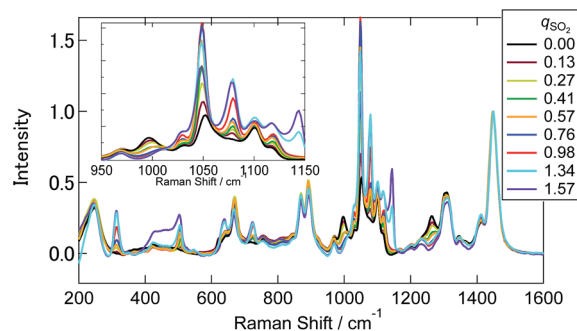


Fig. 4 Raman spectra of  $[P_{4448}]HCO_3$  with different  $q_{SO_2}$ . The inset figure is the magnification around 1050  $cm^{-1}$ . Each spectrum is normalized by the band at 1449  $cm^{-1}$ .

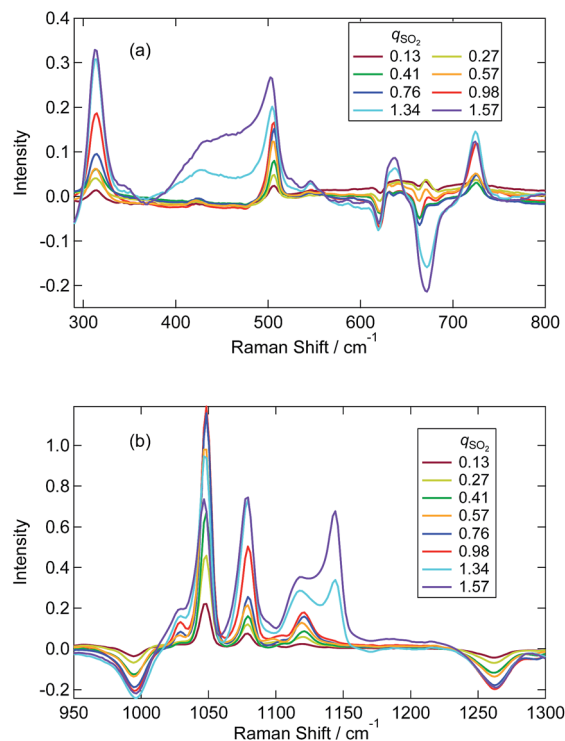


Fig. 5 Difference Raman spectra of  $[P_{4448}]HCO_3$  with different  $q_{SO_2}$  from neat  $[P_{4448}]HCO_3$ . (a) From 300 to 800  $cm^{-1}$ . (b) From 950 to 1300  $cm^{-1}$ .

the  $HCO_3^-$  bands were shown as dips, which gradually deepened with  $q_{SO_2}$ . Further increase of  $q_{SO_2}$  from 0.98 to 1.57 resulted in the emergence of a broad band in the 430–500  $cm^{-1}$  range in addition to narrower bands at 635 and 1144  $cm^{-1}$ . A large negative dip appeared around 670  $cm^{-1}$ , suggesting a structural change in the cation.

Raman spectra at the SH and CH stretching vibrations are shown in Fig. 6. The spectrum was normalized by the CH stretching region band center of the  $[P_{4448}]^+$  cation (2918  $cm^{-1}$ ). A characteristic SH stretching band was found at 2440  $cm^{-1}$ . This assignment is confirmed by the Raman shift in aqueous media ( $\sim 2530$   $cm^{-1}$ )<sup>34,36,38,39</sup> and DFT calculations (see below). The intensity of this band increased with increasing  $q_{SO_2}$  from



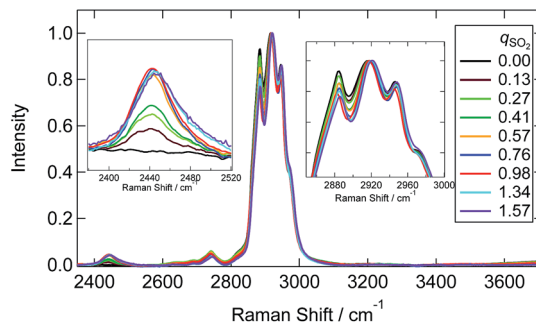


Fig. 6 Raman spectra of  $[P_{4448}]HCO_3^-$  with different  $q_{SO_2}$  for the SH and CH stretching region. The inset figures are the magnifications around  $2450\text{ cm}^{-1}$  and  $2920\text{ cm}^{-1}$  respectively. Each spectrum is normalized by the band at  $2918\text{ cm}^{-1}$ .

0 to 0.98 and then showed a slight decrease for  $q_{SO_2} > 1$ . The frequency of this band showed an increase with increasing  $q_{SO_2}$ . Interestingly, the lower frequency side band shape of the CH stretching band ( $2800\text{--}3000\text{ cm}^{-1}$ ) changed as the  $q_{SO_2}$  increased from 0 to 0.98 and then became almost invariant at higher  $SO_2$  loadings. A slight change of the intensity at the higher frequency side was also noted.

We attempted to assign the characteristic Raman bands particularly seen below  $1300\text{ cm}^{-1}$  by tracking the band intensity changes with  $SO_2$  absorption. Based on previous works in aqueous solutions, the following species are plausible: the two bisulfite isomers ( $HSO_3^-$ ,  $HOSO_2^-$ ), disulfite (pyrosulfite) ion ( $S_2O_5^{2-}$ ), and molecular  $SO_2$ . In water, the disulfite anion is formed by the dehydration of 2 bisulfite anions (eqn (2)). We started by assigning those bands that appear only at  $q_{SO_2} > 1$ ; these are the broad bands around  $430\text{--}470\text{ cm}^{-1}$  and two narrower bands at  $635$  and  $1140\text{ cm}^{-1}$ . The band at  $1140\text{ cm}^{-1}$  was assigned to  $SO_2$  (physisorption) according to ref. 24 and 26. The bands at  $430$  and  $635\text{ cm}^{-1}$  could be assigned to the vibrations of  $S_2O_5^{2-}$  according to ref. 25, which determined corresponding strong bands at  $424$  and  $655\text{ cm}^{-1}$  in water. Later in Sec. 3.3, we will discuss the possibility of  $HS_2O_5^-$  instead of  $S_2O_5^{2-}$  for  $q_{SO_2} > 1$  in more detail. In any case, due to the absence of the marker bands at  $1140\text{ cm}^{-1}$  of  $SO_2$  and at  $430\text{ cm}^{-1}$  of disulfite for  $q_{SO_2} < 1$ , we concluded that molecular  $SO_2$  and disulfite were absent for  $q_{SO_2} < 1$ .

From the above discussion, the plausible origins of the new Raman bands observed at  $q_{SO_2} < 1$  are the bisulfite isomers ( $HSO_3^-$ ,  $HOSO_2^-$ ). The appearance of the SH stretching vibration clearly indicates that the  $HSO_3^-$  isomer is present, while we could not detect a clear Raman band for the HO vibration of the other isomer. The HO vibration has been observed by one IR study of aqueous sulfite solutions at  $3620\text{ cm}^{-1}$ ,<sup>37</sup> and one Raman spectroscopic study at  $3145\text{ cm}^{-1}$ .<sup>34</sup> The band could be weak, broad or overlapped with C-H vibrations in the IL. The bands at  $505$  and  $1120\text{ cm}^{-1}$  correspond to the aqueous bands observed at  $496\text{--}508\text{ cm}^{-1}$  and  $1126\text{--}1128\text{ cm}^{-1}$ ,<sup>34,36,38</sup> both of which have been assigned to the  $HSO_3^-$  in ref. 34. Similarly, we assign the bands at  $1079$  and  $725\text{ cm}^{-1}$  to  $HOSO_2^-$  using ref. 34 and 36, respectively, although other reports have not mentioned these bands. The bands near  $315\text{ cm}^{-1}$  and  $1079\text{ cm}^{-1}$  are

assigned to the vibrations of  $S_2O_5^{2-}$  in some publications.<sup>33,36,39</sup> As discussed in the previous paragraph, however, we have eliminated the presence of  $S_2O_5^{2-}$  at  $q_{SO_2} < 1$ .

We evaluated intensities of Raman bands that appear at different  $SO_2$  loadings by making a multi-peak fit to the difference spectra (Fig. 5(a) and (b)). The detail of the fitting procedure is described in the ESI† and typical examples are shown in Fig. S7(a).† Note that the  $996\text{ cm}^{-1}$  dip of  $HCO_3^-$  was taken into account by assuming a negative component. Fig. 7 shows the variation of the band intensities as a function of  $q_{SO_2}$ . The vibrational frequencies of decomposed bands were almost independent of  $q_{SO_2}$ , and the variations were within *ca.*  $1\text{ cm}^{-1}$  except for the band assigned to the SH vibration (Fig. S7(b)†). To track the band intensity change, the intensities were normalized to unity at equimolar  $SO_2$  loading ( $q_{SO_2} = 0.98$ ).  $HCO_3^-$  was quantified using the negative integral area of the  $HCO_3^-$  band ( $996\text{ cm}^{-1}$ ) in the difference spectra. When this negative area is normalized, it is the portion ( $x$ ) of  $HCO_3^-$  consumed upon  $SO_2$  absorption. Thus the value was converted to the portion of  $HCO_3^-$  that is remaining by  $1 - x$ . The concentrations of the two bisulfite isomers and  $HCO_3^-$  as estimated by NMR in Sec. 3.1 are also shown after the normalization.

As shown in the Fig. 7 the fraction of  $HCO_3^-$  as estimated by NMR and Raman agreed quite well. The sulfur-related Raman bands shown in Fig. 7 are divided into two groups based on their  $q_{SO_2}$  dependences. The first group includes bands at  $505$ ,  $1048$ ,  $1120$ , and  $2440\text{ cm}^{-1}$ , while the second group includes bands at  $315$ ,  $725$ ,  $1029$ , and  $1079\text{ cm}^{-1}$ . We elucidated that each group of bands arises from one of the two bisulfite isomers. On the basis of NMR spectroscopic abundances, we assigned the first group to the  $HSO_3^-$  isomer and the second to the  $HOSO_2^-$  isomer. The assignments of the two bisulfite Raman bands at  $1029$  and  $1048\text{ cm}^{-1}$  in aqueous solutions have been ambiguous for decades. In this work, we identified the band at  $1048\text{ cm}^{-1}$  as the  $HSO_3^-$  vibration and the band at  $1029\text{ cm}^{-1}$  as the  $HOSO_2^-$  vibration in the IL. The assignment is

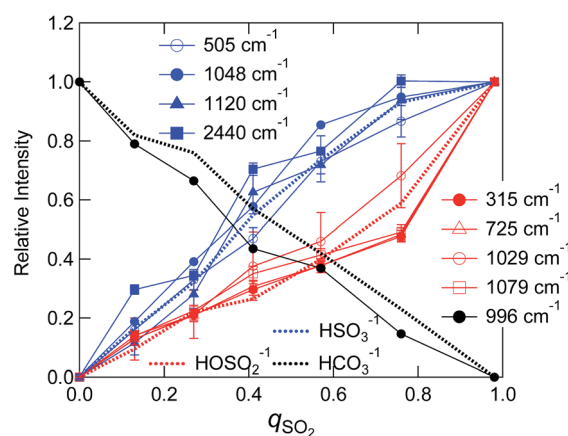


Fig. 7 Dependence of the relative intensity of Raman band on  $q_{SO_2}$ . The black broken line represents the relative concentration of  $HCO_3^-$  to that at  $q_{SO_2} = 0$ , and blue and red ones represent the relative concentrations of  $HSO_3^-$  and the species having hydroxyl group determined by NMR measurement, respectively.



further confirmed by the fact that the intensity of the 1048  $\text{cm}^{-1}$  band corresponded to the NMR measurement above  $q_{\text{SO}_2} = 1$  (slight decrease with increasing  $q_{\text{SO}_2}$ ) (not shown in Fig. 7).

The comparison between the experimental difference spectra and the DFT calculations is shown in Fig. 8, and the assignments of bands by the DFT calculations are listed in Table S5.† Although the coincidence between theory and experiment is not so good, it gives us some hints for band assignments. By comparing the calculations, the band at 505  $\text{cm}^{-1}$  observed experimentally is the bending mode of  $\text{SO}_2$  in  $\text{HSO}_3^-$ , the band at 1048  $\text{cm}^{-1}$  is the symmetric stretching mode of  $\text{SO}_2$  in  $\text{HSO}_3^-$ , and the band at 1120  $\text{cm}^{-1}$  is the bending mode of OSH. As for the  $\text{HOSO}_2^-$  vibrations, the band at 315  $\text{cm}^{-1}$  is the bending mode of OS(OH), and the bands at 1029 and 1079  $\text{cm}^{-1}$  are the combinations of the bending band of SOH with SO stretching vibration and  $\text{SO}_2$  symmetric stretching vibration, respectively.

A few remarks must be made regarding band assignments. First, the intensity of the band at 1120  $\text{cm}^{-1}$  assigned to the  $\text{HSO}_3^-$  vibration remarkably increased above  $q_{\text{SO}_2} = 1$ , although the concentration of  $\text{HSO}_3^-$  decreased according to the NMR result. This may be due to the overlapping with sulfur species that forms above  $q_{\text{SO}_2} = 1$ . Second, the  $\nu_{\text{SH}}$  band at 2440  $\text{cm}^{-1}$  in the IL shows a significant lower frequency shift relative to the corresponding band in the aqueous solution (2530  $\text{cm}^{-1}$ ).<sup>34,36,38,39</sup> The S–H bonding may be weakened in the IL due to the interaction with the surrounding cations. The SH frequency shows an increase with increasing  $q_{\text{SO}_2}$  (Fig. S7(b)†). This suggests that not only is the interaction with the cation important for SH frequency, but so is the one with the anion.

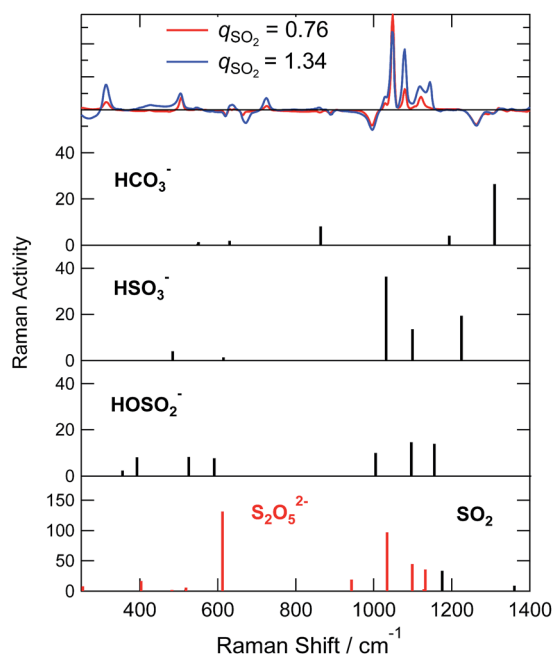


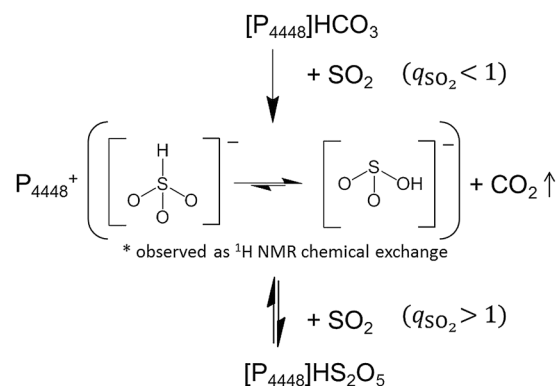
Fig. 8 Vibrational spectra of different anions calculated by DFT using aug-cc-pVTZ basis set and B3PW91 functional. The upper panel shows difference Raman spectra of  $[\text{P}_{4448}]\text{HCO}_3$  with different  $q_{\text{SO}_2}$  from neat  $[\text{P}_{4448}]\text{HCO}_3$ .

Third, our DFT calculations did not reproduce the band at 725  $\text{cm}^{-1}$ . As previously reported, a difficulty exists in the calculation for the S–O(H) mode<sup>43</sup> and a theoretical model inadequacy may be the reason. As for another plausible reason for the lack of band reproduction, at first we considered that the complexation with cation may produce a shift of the band. As shown in the calculated spectra in Fig. S8,† the computational Raman spectra of  $\text{HCO}_3^-$  and  $\text{HOSO}_2^-$  with a cation showed a relatively large shift probably due to the nature of asymmetric complex formation. However, we could not identify a band at 725  $\text{cm}^{-1}$  for these complexes. Zhang and Ewing proposed the existence of the  $\text{HOSO}_2^-$  dimer.<sup>37</sup> Although we performed the calculation for this species in vapour, it was not stable. The calculation in water (SCRf model) converged and two stable isomers of the  $\text{HOSO}_2^-$  dimer were calculated. The optimized structures are shown in Fig. S9(a) (symmetric dimer) and (b) (asymmetric dimer).† The geometrical parameters are listed in Table S6.† Calculated Raman spectra are shown in Fig. S9(c).† The vibrational band around 700  $\text{cm}^{-1}$  was calculated by making a dimer in either symmetric or asymmetric conformation. This band is due to the vibration of S(OH) symmetric stretching in both sides. The calculations suggest the possibility of  $\text{HOSO}_2^-$  dimer formation. The quadratic dependence of  $\text{HCO}_3^-$  and  $\text{HOSO}_2^-$  concentrations on  $q_{\text{SO}_2}$  in Fig. 7 may be due to the  $\text{HOSO}_2^-$  dimer formation.

### SO<sub>2</sub> absorption mechanism

Based on the spectroscopic observations, the  $\text{SO}_2$  absorption by  $[\text{P}_{4448}]\text{HCO}_3$  consists of two phases; see Scheme 1. In the first phase (below  $q_{\text{SO}_2} = 1$ ), the bicarbonate anion is quantitatively replaced by  $\text{SO}_2$  as in eqn (1) until the mole of absorbed  $\text{SO}_2$  reaches the initial mole of bicarbonate ( $q_{\text{SO}_2} = 1$ ). The absorbed  $\text{SO}_2$  is present either as  $\text{HSO}_3^-$  or  $\text{HOSO}_2^-$  (eqn (3)), which are in equilibrium. Condensation of bisulfite to form disulfite (eqn (2)) is negligible within the first phase. At  $q_{\text{SO}_2} = 1$ , the ionic liquid turns into pure  $[\text{P}_{4448}][\text{bisulfite}]$  by complete “gas exchange”. Above  $q_{\text{SO}_2} = 1$  (the second phase),  $\text{SO}_2$  is absorbed by another mechanism which will be discussed in the followings.

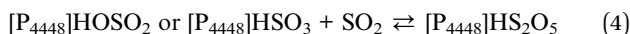
The  $[\text{P}_{4448}][\text{bisulfite}]$  liquid can further absorb  $\text{SO}_2$  and the  $q_{\text{SO}_2}$  nearly reaches 1.6 at  $\text{SO}_2$  partial pressure less than 0.1 MPa.



Scheme 1 Proposed  $\text{SO}_2$  chemisorption mechanism by the bicarbonate ionic liquid  $[\text{P}_{4448}]\text{HCO}_3$ .



It is argued here what is the actual chemical form of the newly absorbed  $\text{SO}_2$ . We postulate the following Lewis acid–base reaction.



We have no information on which of the two bisulfite isomers is more reactive. Molecular  $\text{SO}_2$  has Lewis basic character as well as Lewis acidic character.<sup>50</sup> The adducts of  $\text{SO}_2$  with electron-rich species such as amines and halide ions are well known.<sup>50,51</sup> As is mentioned in the Introduction, bromide in 1-butyl-3-methylimidazolium bromide ionic liquid can capture  $\text{SO}_2$  by a charge-transfer interaction.<sup>21</sup> The charge-transfer interaction is evidenced by a yellowish or orange colour of the solution and the low frequency shift of the  $\nu_s(\text{SO}_2)$  Raman band. In our system, both a colour change (colourless at  $q_{\text{SO}_2} < 1$  and turned into bright yellow at  $q_{\text{SO}_2} > 1$ ) and a Raman band shift (from  $1152 \text{ cm}^{-1}$  in water<sup>38</sup> to  $1144 \text{ cm}^{-1}$  in the IL) were observed.

In the  $q_{\text{SO}_2} > 1$  absorption phase, three intense Raman bands have emerged ( $\sim 430$ ,  $635$ ,  $\sim 1050 \text{ cm}^{-1}$ ). These Raman bands nearly coincide with some of the strongest bands of  $\text{S}_2\text{O}_5^{2-}$ . On the other hand the Raman bands for  $\text{HS}_2\text{O}_5^-$  has not been reported. Given the structural similarity, these two ionic species may not be distinguished only from Raman spectra.

The  $\text{S}_2\text{O}_5^{2-}$  can form *via* the condensation of two bisulfite ions as in eqn (2). We have shown that this reaction does not occur below  $q_{\text{SO}_2} = 1$ . Then, it seems unreasonable to imagine the reaction abruptly switched on above  $q_{\text{SO}_2} = 1$ . Thus we may assign the observed Raman bands to  $\text{HS}_2\text{O}_5^-$ , which has been formed *via* eqn (4).

In order to test the above idea, we completed DFT calculations for  $\text{HS}_2\text{O}_5^-$ . The calculations showed that both  $\text{HOSO}_2^-$  and  $\text{HSO}_3^-$  make stable complexes with  $\text{SO}_2$  to form  $\text{HS}_2\text{O}_5^-$  with stabilization energies of  $68 \text{ kJ mol}^{-1}$  and  $60 \text{ kJ mol}^{-1}$ , respectively, at the aug-cc-pVTZ and B3PW91 level calculations in vacuum (Table S1†). Fig. S10(a) and (b)† show the structure of the optimized cluster and Table S7† summarizes the geometrical parameters. The Mulliken charge of  $\text{SO}_2$  was  $-0.55$  for the complex with  $\text{HOSO}_2^-$ , and  $-0.20$  for the complex with  $\text{HSO}_3^-$ . This clearly indicates that the complexation is due to the charge transfer process. The extent of the charge transfer was more significant for the former complex. The vibrational Raman spectra are compared for  $\text{S}_2\text{O}_5^{2-}$  and the complex between  $\text{SO}_2$  and bisulfite in Fig. S7(e)†. The intense band at  $400 \text{ cm}^{-1}$  for  $\text{S}_2\text{O}_5^{2-}$  is the combination of the wagging motion of the  $\text{SO}_2$  side and the bending motions of  $\text{SO}_2$  in the  $\text{SO}_3$  side, the band at  $612 \text{ cm}^{-1}$  is the umbrella mode of  $\text{SO}_3$ , the band at  $1034 \text{ cm}^{-1}$  is the symmetric vibration of  $\text{S}_2\text{O}_5$ , and the band at  $1099 \text{ cm}^{-1}$  is the asymmetric vibration of  $\text{S}_2\text{O}_5$ . For the complex of  $\text{HOSO}_2^-$  or  $\text{HSO}_3^-$  with  $\text{SO}_2$ , similar vibrational modes were calculated as split bands near the frequencies for  $\text{S}_2\text{O}_5^{2-}$ . Based on these results, chemisorption of eqn (4) is consistent with experimental observations as the  $\text{SO}_2$  absorption mechanism for  $q_{\text{SO}_2} > 1$ .

In summary the absorption scheme of  $\text{SO}_2$  by  $[\text{P}_{4448}]\text{HCO}_3^-$  is illustrated in Scheme 1. Below  $q_{\text{SO}_2} = 1$ ,  $\text{SO}_2$  is absorbed by the

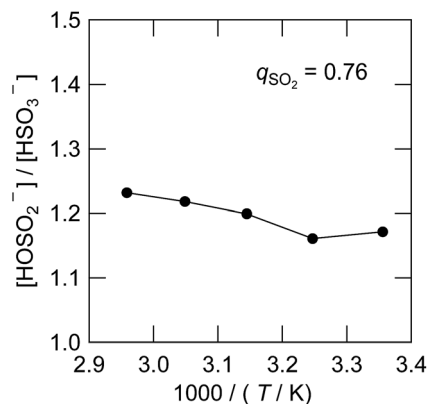


Fig. 9 Temperature dependence of the isomeric equilibrium quotient between  $\text{HSO}_3^-$  and  $\text{HOSO}_2^-$  at  $q_{\text{SO}_2} = 0.76$ .

IL in replacement with  $\text{CO}_2$  as  $\text{HSO}_3^-$  or  $\text{HOSO}_2^-$ , where they are in equilibrium. Above  $q_{\text{SO}_2} = 1$ ,  $\text{SO}_2$  is absorbed by the IL making the charge transfer complexes with  $\text{HSO}_3^-$  or  $\text{HOSO}_2^-$ .

### Isomerization equilibrium and kinetics

The equilibrium quotient of the bisulfite isomers is reported to be dependent on temperature in water by  $^{17}\text{O-NMR}$ <sup>41</sup> and XANES<sup>34</sup> studies. The quotient changes by a factor of 2 with the temperature change of 40 K,<sup>41</sup> with the  $\text{HOSO}_2^-$  isomer favoured more at lower temperatures. In Fig. 9, we determined the corresponding value in the IL using the  $^1\text{H NMR}$  spectra presented in Fig. S3.† As can be seen, the value changed only by 5% with the temperature change of 40 K. The striking difference between water and the IL solvent can be interpreted by the solvation of the  $\text{HOSO}_2^-$  isomer. Only in water is the  $\text{HOSO}_2^-$  isomer hydrogen-bonded to the solvent. Since the hydrogen bond is stronger at lower temperature, we expect the  $\text{HOSO}_2^-$  isomer to be more abundant in low temperature water but such a temperature effect is not expected in the IL. We have also

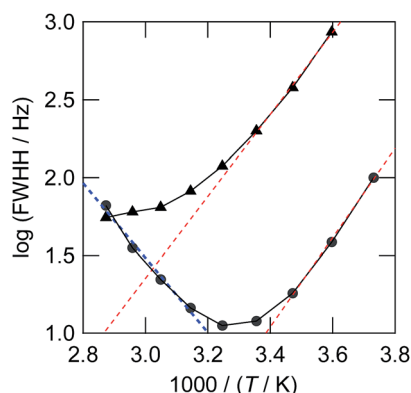


Fig. 10  $^1\text{H NMR}$  full width at half height (FWHH) at 268–348 K. The FWHH for the  $\text{HSO}_3^-$  isomer and the coalesced hydroxyl protons ( $\text{HOSO}_2^-$  and  $\text{HCO}_3^-$ ) are shown by circles and triangles, respectively. The red thin dashed lines show the natural width. The thick blue dashed line shows the line broadening of the  $\text{HSO}_3^-$  peak due to the isomer exchange of eqn (3).





confirmed that the Raman spectra were not dependent on temperature from 296 K to 253 K for the sample of  $q_{\text{SO}_2} = 0.76$ .

In order to detect any proton exchanges between the two bisulfite isomers, we plotted the width (full width at half height or FWHH) of the  $^1\text{H}$  NMR peaks for the  $\text{HSO}_3^-$  and hydroxyl protons against temperature in Fig. 10. The FWHH in the low temperature region could be fitted to an exponential function (red dashed lines). In this region, the FWHH is controlled by the solvent viscosity. It is remarkable that the FWHH's of  $\text{HSO}_3^-$  and hydroxyl protons deviate from the viscosity trend at higher temperatures. This is reasoned by a line broadening due to the chemical exchange, the rate of which exponentially increases with temperature (blue dashed line). The spin dynamics theory states that the FWHH in the Hz unit is proportional to the first order rate constant of the proton exchange reaction  $k$ . At 320 K, the value of  $k$  is estimated to be  $\sim 10 \text{ s}^{-1}$ . The blue dashed lines demonstrate that the FWHH follows the Arrhenius-type temperature dependence. From the slope, we determined the activation energy of the bisulfite anion exchange to be  $46 \pm 4 \text{ kJ mol}^{-1}$ .

## Conclusions

Herein, for the first time, we have reported NMR and Raman spectroscopic observations for bisulfite IL, which is prepared via "gas exchange" of bicarbonate ionic liquid. Both Raman and NMR spectra have indicated that the bisulfite anion is subject to isomerization. One of the isomers has an SH bond ( $\text{HSO}_3^-$ ) that is characterized by a signal at 10 ppm by  $^1\text{H}$  NMR and the Raman bands at 506, 1048, 1120 and  $2440 \text{ cm}^{-1}$ . The other isomer has an OH bond ( $\text{HOSO}_2^-$ ) that is characterized by the Raman bands at 314, 725, 1029 and  $1079 \text{ cm}^{-1}$ . The isomerization equilibrium in the IL is shifted to the  $\text{HSO}_3^-$  side compared to that in water. The bisulfite IL absorbs excess  $\text{SO}_2$  by making the charge transfer complex with bisulfite anions as elucidated by Raman bands at 430–500 (broad), 635, and  $1140 \text{ cm}^{-1}$ .

## Acknowledgements

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