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ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · FEBRUARY 2012

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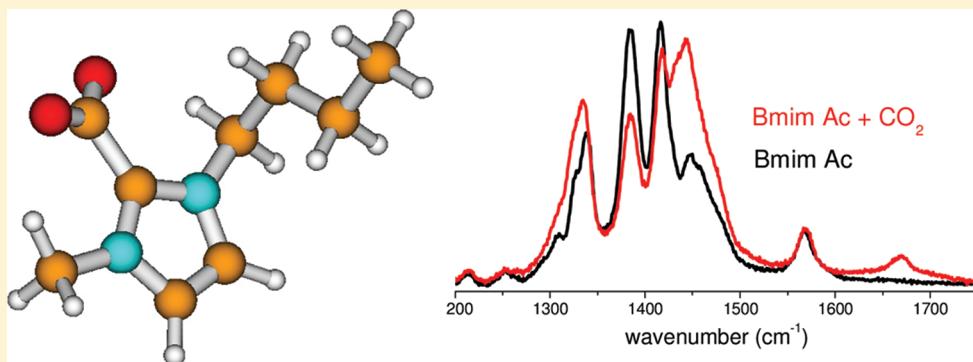
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S Supporting Information



ABSTRACT: The unusual solubility of carbon dioxide in 1-butyl-3-methylimidazolium acetate (Bmim Ac) has been studied by Raman spectroscopy and DFT calculations. It is shown that the solubility results from the existence of two distinct solvation regimes. In the first one (CO_2 mole fraction ≤ 0.35), the usual Fermi dyad is not observed, a fact never reported before for binary mixtures with organic liquids or ionic liquids (IL). Strong experimental evidence complemented by effective DFT modeling shows that this regime is dominated by a chemical reaction leading to the carboxylation of the imidazolium ring accompanied by acetic acid formation. The reactive scheme proposed involves two concerted mechanisms, which are a proton exchange process between the imidazolium cation and the acetate anion and the carboxylation process itself initiated from the formation of “transient” CO_2 -1-butyl-3-methylimidazole 2-ylidene carbene species. In that sense, CO_2 triggers the carboxylation reaction. Moreover, this dynamic picture circumvents consideration of a long-lived carbene formation in dense phase. The second regime is characterized by the detection of the CO_2 Fermi dyad showing that the carboxylation reaction has been strongly moderated. This finding has been interpreted as due to the interaction of the acetic acid molecules with the COO group of acetate anions involved in monodentate forms with the cation. The observation of the Fermi doublet allows us to infer that CO_2 essentially preserves its linear geometry and that the nature and strength of the interactions with its environment should be comparable to those existing in organic liquids and other IL as well. These results have been supported by DFT calculations showing that the CO_2 molecule interacts with energetically equivalent coexisting structures and that its geometry departs only slightly from the linearity. Finally, we find that the CO_2 solvation in Bmim Ac and 1-butyl-3-methylimidazolium trifluoroacetate (Bmim TFA) cannot be straightforwardly compared neither in the first regime due to the existence of a chemical reaction nor in the second regime because CO_2 interacts with a variety of environments not only consisting of ion pairs like in Bmim TFA but also with carboxylate and acetic acid molecule.

1. INTRODUCTION

Understanding, at the molecular level, the solvation of CO_2 in organic solvents is a subject of current interest motivated by the promising perspective offered by this compound as an alternative solvent in the context of green chemistry. Theoretical and experimental investigations have shed light on the basic interactions existing between CO_2 and solute molecules. It was established that the solvation process of this nonpolar molecule can be rationalized considering that CO_2 is a

charge-separated molecule with significant nonzero bond dipoles moments.¹ In this “chemical approach”, the electron-deficient carbon atom of CO_2 acts a Lewis acid (LA) and interacts with Lewis base (LB) groups leading to the formation of LA-LB complexes. Moreover, it was also shown that the

Received: November 21, 2011

Revised: January 10, 2012

Published: January 13, 2012

oxygen atom of CO_2 could be involved in an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond interaction with the hydrogen atom of a hydroxyl group, for instance,² or in a more subtle manner as with aldehydes.^{3–5} In this latter case, the previous LA–LB interaction is accompanied by a cooperative intermolecular C–H \cdots O interaction formed between an oxygen atom of CO_2 and the hydrogen atom of the proton or the methyl group of aldehyde leading to the formation of so-called “nonconventional” hydrogen bonding.^{6–8} Most of these studies concerned solutions in which the solute was very diluted in the CO_2 . Other investigations have been performed on binary mixtures of CO_2 with organic liquids, obtained by introducing supercritical CO_2 under increasing pressure allowing variation of the state of CO_2 from solute to solvent. In these binary mixtures, it was also confirmed that during the time scale of the spectroscopic observation carbon dioxide forms transient LA–LB heterodimers with the organic molecules and that CO_2 mostly interacts nonspecifically either with itself (concentrated mixtures in CO_2) or with the organic molecules (diluted mixtures in CO_2).^{9–12}

The difference of solubility of CO_2 in alkanes and perfluoroalkanes is still a matter of debate.^{12–22} On one hand, it was shown that the interactions of CO_2 in these two classes of systems involve a specific interaction having a different nature, namely that CO_2 interacts through its oxygen atoms with alkanes whereas it interacts through its carbon atom with perfluoroalkanes.¹⁷ The exploration by ab initio methods of the CO_2 -philicity of fluorocarbon through stepwise fluorination of methane showed that an optimal density of fluorine atoms in an alkyl chain yields a maximum of the CO_2 -philicity.^{17,23} On the other hand, there is also evidence that electrostatic interactions play a minor role in these systems and that the interaction with nonpolar solvents is due to dispersion forces.^{22,24} All these investigations have provided valuable insights on the solvation at the molecular level of CO_2 in organic liquids by considering mostly the role of the energetic (enthalpic) contributions restricted to the solute–solvent interactions. However, assessing the relative importance of the entropic contribution^{1,12,17,19,25–34} as well as the time scales involved in the interactions³⁵ and their connection with the spectroscopic techniques in the study of the complexation of CO_2 ^{9–12} have to be considered to understand the CO_2 solubility in each particular organic liquid and in the comparison between hydrogenated liquids and their fluorinated homologues. Clearly, these studies are of particular relevance to attempt to understand a new class of materials constituted by ionic liquids (ILs) in which the study of the solvation of CO_2 has become increasingly important. Such investigations have been prompted by the need to capture and sequester CO_2 to convert it into stable useful adducts, a theme of paramount importance in the context of environmental studies. Fundamental and applied investigations of IL– CO_2 biphasic systems have been extensively discussed in a number of reviews.^{31,36–39} At the molecular scale, the high solubility of CO_2 in ionic liquids has been investigated mainly on dialkylimidazolium-based ILs.³² To date, much evidence has been obtained experimentally and theoretically that allows rationalization of the CO_2 solubility in these ILs. It was established that the nature of the anions plays a central role and that CO_2 interacts with the anion through LA–LB interactions.^{40–42} In contrast, the cations have relatively little influence although increasing the length of the alkyl chain has been found to slightly increase the solubility. It was established on a number of systems,

involving tetrafluoroborate ($[\text{BF}_4^-]$), hexafluorophosphate ($[\text{PF}_6^-]$), and bis(trifluoromethylsulfonyl)imide ($[\text{Tf}_2\text{N}^+]$) as the anion, that the CO_2 molecule can be intercalated in the cavities of the IL perturbing only slightly the structure of the IL and the conformation of the cation.^{23,32,34,43–45} The strength of CO_2 –anion interactions cannot be solely responsible for the solubility of CO_2 because the strength of the anion–cation interaction also affects the available free volume contribution, due to strong Coulombic interaction as was shown, for instance, from the comparison of CO_2 diluted in Bmim BF_4^- and in Bmim PF_6^- .^{25,31,40,46} A comparative study of mixtures of CO_2 in ILs with anions containing fluoroalkyl groups (trifluoromethanesulfonate [TfO^-], $[\text{Tf}_2\text{N}^+]$, and tris(trifluoromethylsulfonyl) methide [methide]) showed that the solubility of CO_2 is higher than when the IL contains non-fluorinated anions.²⁷ This enhanced solubility has been attributed to favorable interactions between CO_2 and the fluoroalkyl substituent.

The view that the high solubility of CO_2 in ionic liquids is dominated by enthalpic effects and special interactions between the solute and the ions has been repeatedly questioned. During the past decade, several authors^{40,42} showed that though weak complexes between CO_2 and ionic liquid anions were observed, their intensity did not follow the solubility trend, nor were they strong enough to account for the large solubility of CO_2 observed in ionic liquids. Coutinho et al. results³³ indicate that the solubility of CO_2 in nonvolatile solvents, of which ionic liquids are a particular case, was entropically controlled and that a universal correlation for the solubility of CO_2 in these compounds was possible to derive. Based on these results, they postulate a dependency of the solubility on the molar volume of the ionic liquid, thus explaining the effects of fluorination and increasing chain length. The same authors later showed that the solubility of other gases in ionic liquids were also entropically driven with the solute–solvent interactions present playing a minor role in the solubility.⁴⁷ Mounting evidence supporting these conclusions has been put forward lately by other authors as well,^{48,49} it now being clear that the physisorption of CO_2 in ionic liquids is controlled by their size with the interactions playing a minor role in this process. This is not however true when some sort of chemisorption takes place in the process as happens for 1-butyl-3-methylimidazolium acetate (Bmim Ac).

The solubility of CO_2 in 1-butyl-3-methylimidazolium acetate (Bmim Ac) has been measured by Maginn et al.,⁵⁰ Shiflett et al.,⁵¹ and Carvalho et al.⁵² It was found that this system presents an unusual phase behavior characterized by a very large CO_2 solubility, about 0.25 mole fraction under very low vapor pressure (0.05 MPa) at 298 K. It has been demonstrated using several experimental methods including infrared spectroscopy that a molecular complex was formed between CO_2 and Bmim Ac. The complex formation was shown to be reversible as CO_2 evolved from the Bmim Ac mixture at elevated temperature (352 K).⁵¹ The eventuality of a chemical reaction leading to the carboxylation of the imidazolium cation by CO_2 as proposed by Maginn⁵⁰ was ruled out by Shiflett et al.⁵¹ and Carvalho et al.⁵² Subsequently, Shiflett et al.⁵³ studied the solubility of CO_2 in a large number of imidazolium-based ILs, particularly Bmim Ac and Bmim TFA, at 298 K and under a pressure less than about 2 MPa. Using thermodynamic considerations, these authors classified the interaction of CO_2 with the ILs as belonging to the so-called “chemical” or “physical absorption” type of association. The criteria is based upon the deviation from Raoult’s law; large

negative deviation characterizing chemical absorption, that is, chemical complex formation. The high solubility of CO₂ in Bmim Ac has been interpreted as resulting from the formation of a 1:2 molecular complex (in which 1 is the CO₂ and 2 the IL molecule) whereas the interaction between CO₂ and Bmim TFA has been considered as an ordinary physical absorption.

Recently, using electrochemical methods, it was shown that CO₂ is almost irreversibly absorbed by Bmim Ac at room temperature and undergoes a chemically irreversible one-electron reduction.⁵⁴ The value of the diffusion coefficient of CO₂ was found to be unusually low (more than an order of magnitude lower than that in Bmim BF₄ and Bmim PF₆) and interpreted as evidence of an irreversible complexation of CO₂ with the IL.

A comparative study of the solubility of carbon dioxide in these two ionic liquids has been reported⁵² (Figure 1), and

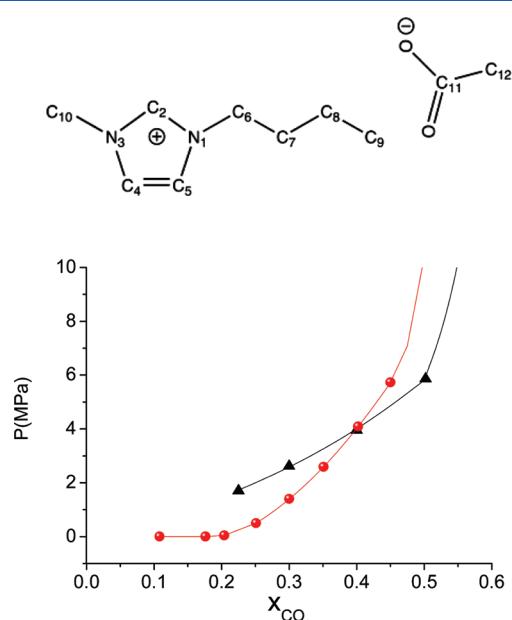


Figure 1. Comparison of the solubility of carbon dioxide at 313 K in Bmim Ac (●, red) and in Bmim TFA (▲, black). The schematic representation of the Bmim Ac molecule is presented (top).

solubility was found to be greater in the hydrogenated system than in the fluorinated homologue up to 0.4 mole fraction (313 K) of CO₂. At this particular value, a crossover is observed, and at higher concentration the solubility of carbon dioxide becomes greater in the fluorinated compound. This finding is in marked contrast with the trend previously reported for the solubility of CO₂ in hydrogenated versus fluorinated ILs and organic liquids.^{19,27}

In previous work, we have performed a Raman and ab initio study of the CO₂-Bmim TFA mixture.⁵⁵ We found that this ionic liquid is capable of hosting a large amount of carbon dioxide (up to 0.54 mole fraction at 313 K) without significant disturbance of its local structure. It was concluded that the CO₂ molecules reside in two different environments. In the first one, CO₂ molecules interact with themselves, whereas in a second environment, the CO₂ molecules coexisting dynamically with the molecules of the first site interact with the anion via a charge transfer mechanism taking place between the carbon atom of carbon dioxide (LA) and the negatively charged carboxyl group of the TFA anion (LB). Moreover the evolution

of the local ordering of the IL upon dilution presents similarity with a microsegregation phenomenon reported for ILs upon increasing alkyl chain length.³⁴ It is noteworthy that although a specific interaction occurs between the CO₂ and the anion, leading to the formation of a complex, the solubility observed in this system follows an almost ideal behavior. Due to the unusual solubility of CO₂ in Bmim Ac and its higher value compared with that in Bmim TFA (up to 0.4 CO₂ mole fraction), we have undertaken a study of the CO₂-Bmim Ac mixtures considered here as a model system to get insight on the solvation at the molecular level of CO₂ using Raman spectroscopy combined with DFT modeling.

One of the main goals of this paper is to provide evidence at the molecular level of the mechanisms at the origin of the solvation process. Can the “unusual” solubility explained as being due to the formation of a transient molecular complex as it has been proposed or is there a more complex process, involving a chemical reaction as proposed by Maginn⁵⁰ (see section 5) that occurs in this mixture? In a recent communication, experimental evidence has been reported from the X-ray structure of the solid-state products resulting from the reaction of CO₂ with acetate ionic liquids, in particular 1-ethyl-3-methylimidazolium acetate.⁵⁶ These authors also characterized by ¹H and ¹³C NMR spectra the adduct products of a chemisorption obtained bubbling CO₂ through the IL. In a very recent letter, we have also reported evidence of the formation of 1-butyl-3-methylimidazolium-2-carboxylate in the mixture of CO₂ with Bmim Ac under mild conditions (298 K, 0.1 MPa) in the liquid phase using ¹H, ¹³C, and ¹⁵N NMR, Raman and infrared spectroscopy measurements complemented by DFT calculations.⁵⁷ This study showed that the main features observed in the liquid mixture (carboxylate and acetic acid formation) are also observed in the solid state.

The purpose of this paper is now to discuss in depth the interactions existing in the CO₂-Bmim Ac mixture, which have been only briefly presented in the above-mentioned communications.^{56,57} We will also show that the existence of several different solvation regimes of CO₂ depending on its concentration in the mixture needs to be considered, results that have never been addressed until now.

2. EXPERIMENTAL SECTION

2.1.1. Experimental Conditions. Raman Spectroscopy.

The experimental conditions are identical to those previously reported and will be only briefly summarized here.⁵⁵ The polarized and depolarized Raman spectra were measured with a resolution of 1.8 cm⁻¹ in the spectral range 200–3400 cm⁻¹ on a Jobin-Yvon HR800 spectrometer with a Spectra Physics krypton-ion laser source operating at a wavelength of 752.5 nm with a power of 6 mW using a backscattering geometry. Typical spectra have been collected during 60 s and accumulated 100 times to improve the signal-to-noise ratio. In order to take accurate line positions, the spectrometer has been calibrated by recording different emission lines of a neon bulb. We have used the pressure bench and the Raman cell equipped with fused silica windows previously described⁵⁸ to work in the 0.1–10 MPa pressure range at T = 313 K. The ionic liquid originated from Solvionic (purity greater than 98%) and the CO₂ from Air Liquide (purity 99.995%). The pure IL was put in a glass container connected to a vacuum line and dried at 353 K under primary vacuum during more than 48 h with continuous stirring performed with a magnetic rotating agitator. The water content was measured by Karl Fischer titration and found to be

530 ppm, a value much lower than that measured for the undried ionic liquid (≤ 5000 ppm corresponding to about 5% in water mole fraction). The preparation of the binary mixtures and the precautions taken for their equilibration have been previously detailed.⁵⁵ The selected pressure and the corresponding mole fraction of CO₂ in the mixtures have been calculated from thermodynamic data reported previously^{51,52} (Table 1). We have also performed some experiments with

Table 1. Concentration of CO₂ in the Dense Phase of the Mixtures with Bmim Ac as a Function of the Pressure at 313 K Interpolated from Refs 51 and 52

pressure (MPa)	CO ₂ mole fraction
0.2	0.23 ^a
0.5	0.25
0.8	0.27
1.5	0.30
2.6	0.35
4.0	0.41
6.0	0.45
8.5	0.49

^aValue interpolated at 313 K from ref 51.

Bmim Ac for which the water content has been varied up to 5% in mole fraction. Complementary Raman and infrared experiments have been performed on mixtures at low carbon dioxide pressure using both natural and ¹³C-labeled CO₂ (Aldrich origin, 99 atom %) under a pressure of 0.1 MPa, at 298 K. Infrared absorption and ATR spectra have been measured on a Nicolet-Thermo Optek 6700 interferometer with a 4 cm⁻¹ resolution in the spectral range 400–4000 cm⁻¹ after collecting 50 scans. We use KRS5 windows for the absorption cell and a lead spacer to have a path length of 25 μm, which has been controlled on the empty cell using the standard method based upon interferences fringes.

Further Raman experiments with acetic acid (Riedel-de Haën origin, purity >99.8%) diluted in Bmim Ac have been also performed.

2.1.2. DFT Calculations. The DFT calculations have been carried out using the Gaussian 03 suite.⁵⁹ The optimized structures of the ion pair dimer (IP)₂ {Bmim⁺ CH₃COO⁻}₂ (with and without CO₂) have been achieved from the DFT procedure using the B3LYP functional using the 6-31+G(d,p) basis set. We emphasize that ion pair dimer (IP)₂ constitutes the minimal size of a cluster able to consider the influence of the cooperative effects between ions and therefore lead to a more realistic depiction (even if undoubtedly remaining oversimplified) of the interaction processes taking place in ILs.^{60,61} Recent spectroscopic investigations about ILs combined with quantum chemistry calculations seem to reinforce this point.^{62–64}

The optimized geometries have been obtained using a very tight criterion of convergence. The interaction energy (ΔE_{int}) has been evaluated and corrected from the basis set superposition error (BSSE) according to the site-site function (SSFC) scheme.^{65–69} Then, the vibrational analysis has been carried out from the calculated structures using the standard Wilson FG matrix formalism based on the harmonic force field approximation.⁷⁰

2.2. Experimental Results. The Raman spectra of the pure IL and its assignment based upon a comparison with the

spectra of Bmim BF₄ and Bmim PF₆ are described in the Supporting Information (Table S11).

2.2.1. Spectra of the Mixture CO₂–Bmim Acetate. We have reported in Figure 2 the polarized Raman spectra of pure Bmim Ac and Bmim Ac submitted to CO₂ pressures increasing from 0.5 to 8.5 MPa ($x_{\text{CO}_2} = 0.25$ –0.49 mole fraction in the dense phase of the mixture). It is readily apparent that sizable perturbations of the spectrum of the ionic liquid are observed as soon as carbon dioxide is mixed with the IL at low pressure (0.5 MPa, $x_{\text{CO}_2} = 0.25$, bottom of Figure 2a–c). At higher pressure, up to 4.0 MPa ($x_{\text{CO}_2} = 0.41$, top of Figure 2a–c), these perturbations still develop but with a lesser extent and, finally, upon increasing the pressure up to 8.5 MPa, it is only in the 1200–1800 cm⁻¹ spectral domain in which weak perturbations are still detected. Considering now carbon dioxide, we observed that its characteristic signature constituted by the strongly active $2\nu_2 - \nu_1$ Fermi dyad (centered at about 1280 and 1380 cm⁻¹) is only detected for rather concentrated solution ($x_{\text{CO}_2} > 0.35$). The Fermi doublet displays a narrow band (at about 1380 cm⁻¹) and a broad composite one (at about 1280 cm⁻¹) whose intensity increases with the concentration (Figure 2b, top). We may infer from these observations that the solvation of carbon dioxide in Bmim Ac will certainly involve two regimes. The first takes place as soon as carbon dioxide is mixed with Bmim Ac and is characterized by a profound perturbation of both Bmim Ac and CO₂ spectra. In the second regime, taking place at CO₂ mole fraction greater than about 0.35, the observation of the Fermi doublet of carbon dioxide having an increasing intensity with the pressure, together with the fact that only faint perturbations of the Bmim Ac spectrum are observed, could suggest that this regime of solvation appears similar to that reported for the Bmim TFA system. The detailed description of the perturbations observed in the spectra of the mixtures compared with that of the pure IL is presented in the Supporting Information. We should emphasize that the Raman spectra obtained with mixtures with undried Bmim Ac ($x_{\text{H}_2\text{O}} \leq 0.05$) show the same spectral signatures that those performed on the mixtures with dried IL.

In conclusion, the more remarkable perturbations are encountered in the first regime as soon as the CO₂ is introduced in the IL, and concern four main findings: the absence of the CO₂ Fermi dyad, the appearance of three new bands (794, 1323, and 1672 cm⁻¹) (Table 2, Figure 3), the strong intensity increase observed at about 1450 cm⁻¹, and the strong perturbation of the band centered at about 900 cm⁻¹. To better characterize the perturbations observed on the IL at low CO₂ concentration, we have performed further experiments at lower CO₂ pressure. These experiments showed that the referred perturbations persist after degassing the mixture and even after heating (up to 363 K) and are described in the Supporting Information (Figure S17).

3. ANALYSIS OF THE CO₂ SOLVATION

3.1.1. First Solvation Regime. Perturbation of the CO₂. One of the characteristic features of the Raman spectra of carbon dioxide diluted in organic^{11,12} and in ionic liquids^{55,71} is the presence of the intense and narrow peaks assigned to the Fermi dyad. Surprisingly, as we have shown before, the appearance of such specific signature is absent in the spectrum of the solution of Bmim Ac even at quite high mole fraction ($x_{\text{CO}_2} < 0.35$). Obviously, carbon dioxide is present in the

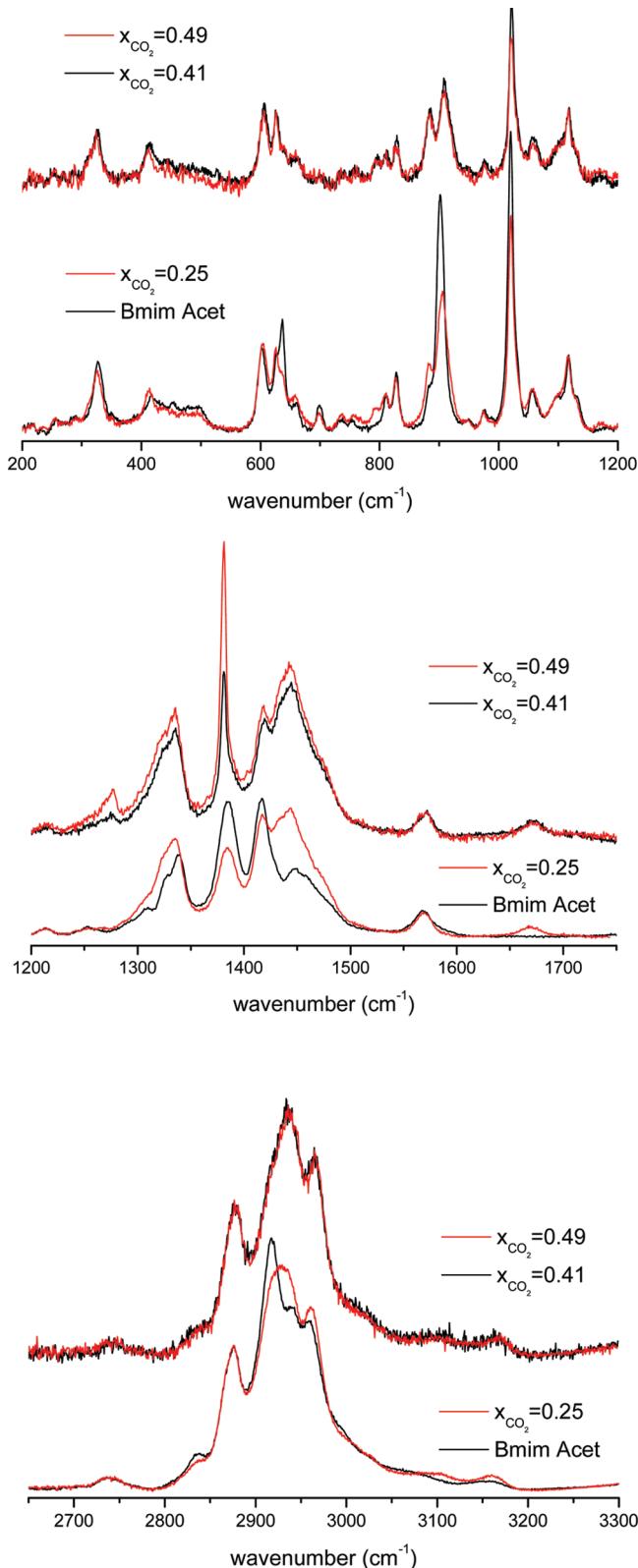


Figure 2. Comparison of the polarized Raman spectrum of pure Bmim Ac with the spectra of its binary mixture with carbon dioxide at different mole fractions. For clarity, the spectral domain has been split in three regions.

mixture, and we must conclude that the coupling between the $2\nu_2$ and ν_1 modes leading to the Fermi resonance is so strongly affected by the solvent that the dyad peaks are no longer

observed. The absence of the Fermi dyad and the concomitant observation of the three new bands pushed us to suspect that these bands are associated with the vibrations of a strongly perturbed carbon dioxide. To judge about this statement, we have performed additional experiments using $^{13}\text{CO}_2$. Because all the sizable perturbations reported previously for the mixture are observed at low pressure, we performed these experiments at 0.1 MPa and 298 K ($x_{\text{CO}_2} \leq 0.3$). We have observed that the main perturbation due to the isotopic substitution is a red shift of the three new bands, which are now detected at 783, 1294, and 1631 cm^{-1} . This is clearly seen in Figure 3 (top) in which the Raman spectra of the neat IL and its mixtures with natural and $^{13}\text{CO}_2$ are compared. In infrared spectroscopy, the frequency of the bands detected in CO_2 and $^{13}\text{CO}_2$ are found to be very close to those observed in Raman (Figure 3 bottom, Table 2).

The linear CO_2 molecule has four vibrational modes, which are the doubly degenerated bending (660 cm^{-1} Raman inactive), the OCO symmetric stretch (1337 cm^{-1} , infrared active giving rise in Raman to the Fermi doublet), and the OCO asymmetric stretch (2349 cm^{-1} , infrared active) (Table 2). In marked contrast, the three new bands have been found active in both spectroscopies with frequency very different for the bending and the asymmetric modes and without the presence of the Fermi dyad observed in Raman spectroscopy. Hence, we conclude that the CO_2 molecule is strongly perturbed, and a tentative assignment is given in Table 2. The reported findings are characteristic of a carbon dioxide molecule that has lost its $D_{\infty h}$ symmetry to become bent with a C_{2v} symmetry. A simple estimation based upon a valence force field for a symmetrical triangular molecule (YX_2) using the values of the symmetric and asymmetric stretching vibrations allows calculation of a bending angle of about 114° for both CO_2 and $^{13}\text{CO}_2$ molecules.⁷² Although, such a calculation is certainly crude, it nevertheless confirms the viewpoint that the configuration taken by the molecule strongly departs from the linear one when it is isolated.

Indeed, the activation of CO_2 (highly inert) through the formation of complexes is a subject of considerable interest in the field of the coordination of CO_2 by metal atoms and metal ions; a number of investigations⁷³ have shown that the CO_2 molecule as a ligand in metal complexes loses the linear configuration that it has in an isolated state to become bent with a typical OCO angle always ranging between 130° to 140° . Vibrational spectroscopic studies using isotopically enriched ^{13}C and ^{18}O carbon dioxide have shown that the frequency shifts observed for these molecules allow one to distinguish among the different possible mode of bonding.^{74,75} More precisely, it has been found that the different modes of coordination such as end-on (C_s), side-on (C_s) and C-coordinated (C_{2v}) of CO_2 to the metal can be characterized by the magnitude of the difference $\nu_{\text{asym}} - \nu_{\text{sym}}$ between the asymmetric and symmetric frequency values. An additional criterion has been provided by the comparison of the sum of the frequency shifts observed for the symmetric and asymmetric vibrations of the ^{13}C -labeled compounds. The difference $\nu_{\text{asym}} - \nu_{\text{sym}}$ ($\sim 350\text{ cm}^{-1}$ for CO_2 and $\sim 340\text{ cm}^{-1}$ for $^{13}\text{CO}_2$) indicates that carbon dioxide is C-bonded. The sum of the frequency shifts for the ^{13}C -labeled compound is here about 60 cm^{-1} , a value again compatible with the literature for the so-called C-bonding. It comes out that the criteria proposed in the literature to characterize the coordination of carbon dioxide in

Table 2. New Bands Detected in CO₂-Bmim Ac Mixtures by Raman and IR Spectroscopies in Comparison with Those of Pure CO₂^a

	Raman		IR				CO ₂ ^c	¹³ CO ₂ ^c
	CO ₂ -Bmim Ac	¹³ CO ₂ -Bmim Ac	CO ₂ -Bmim Ac	¹³ CO ₂ -Bmim Ac	Bmim carboxylate ^b			
δ OCO	794	783	792	781	794	667	649	
ν sym COO	1323	1294	1323	1293	1323	1337 ^d	1317 ^d	
ν asym COO	1672	1631	1665	1622	1662	2349	2284	

^aThe units of frequency are cm⁻¹. ^bValues reported for 1-butyl-3-methyl-imidazolium-2-carboxylate.⁷⁶ ^cValues reported by Nakamoto.⁹³ ^dAverage of the frequency values of the Fermi dyad observed in Raman.⁹⁴

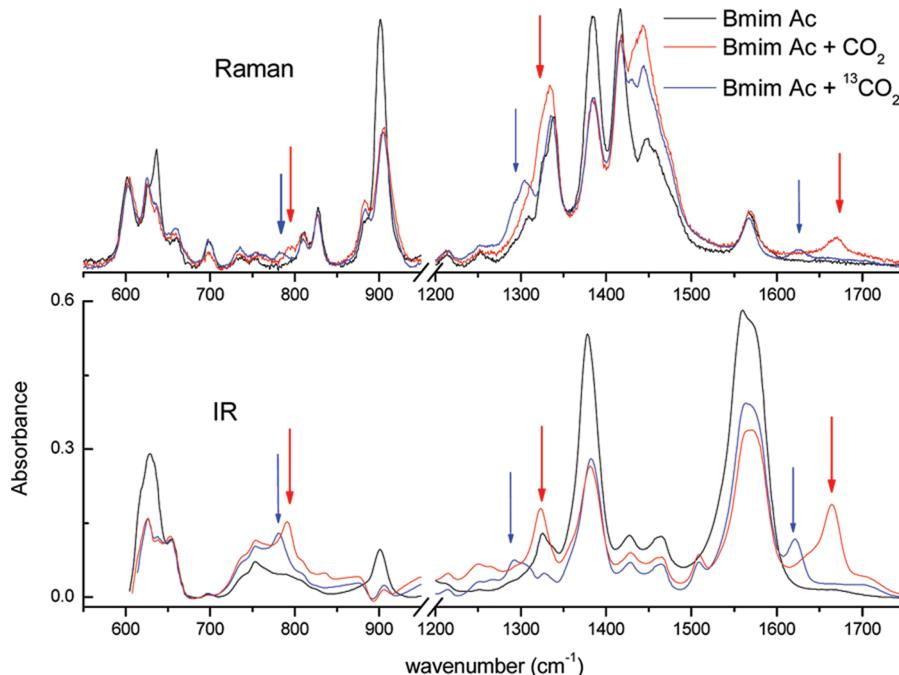


Figure 3. Comparison of the Raman (top) and infrared (bottom) spectra of Bmim Ac and its mixtures with CO₂ (red) and ¹³CO₂ (blue) (mole fraction less than ca. 0.3). The arrows pinpoint the three new bands (see text and Table 2).

the specific context of organometallic chemistry supports the viewpoint that the perturbation observed on carbon dioxide should result from its C-coordination. This result raises the issue about the origin of the center to which the carbon atom of CO₂ is bonded. At this level, it is noteworthy to remember that the hypothesis of the carboxylation of the imidazolium ring by CO₂ has been proposed by Maginn.⁵⁰ Recently, the direct carboxylation of 1,3-dialkylimidazolium chlorides with CO₂ has been reported and shown to provide a new procedure for the synthesis of organic carboxylate anions without using strong bases. In this context, the synthesis of the 1,3-dialkylimidazolium-2-carboxylates has been performed, and these new molecules have been characterized using standard laboratory techniques including in particular infrared spectroscopy.⁷⁶ The frequencies of the new Raman and IR bands measured in our study are compared with the corresponding ones reported by Tommasi et al.⁷⁶ for the 1-butyl-3-methylimidazolium-2-carboxylate (Table 2). We find that there is a perfect agreement between these two data sets which allows us to conclude that carbon dioxide is bonded on the imidazolium ring after substitution of the hydrogen atom of its carbon 2. Therefore, the new vibrations should not be considered as those of a CO₂ molecule interacting with the IL but correspond to the group vibration of the functional COO group of the carboxylate molecule. We note that this allows assignment of the vibrations

of the COO group reported by Tommasi et al.⁷⁶ These authors have also reported the vibrational frequency of the other modes of the carboxylate molecule. All these modes have been observed in Raman or IR or both in this study, and we have assigned them and others not reported to those of the Bmim cation (Supporting Information, Table SI1). Other authors have previously performed a study on the unexpected synthesis of the 1,3-dimethylimidazolium-2-carboxylate and presented the characteristic IR bands of this molecule.⁷⁷ Their results confirm the existence of the bands that we have found and not previously reported.

Recently, the factors influencing the decarboxylation of imidazolium carboxylates with different alkyl groups have been systematically investigated.⁷⁸ It was shown that the decarboxylation temperature can be correlated with the frequency of the COO asymmetric vibration and the dihedral angle between the planes of the COO group and the imidazolium ring. The values of the frequency of the asymmetric ν_{COO} (Table 2) and of the dihedral angle (42°, section 4) of the 1-butyl-3-methylimidazolium-2-carboxylate detected in our study allow estimation that the decarboxylation temperature falls in the range 413–433 K. Upon the basis of this estimation, we conclude that the characteristic bands of the COO group of the 1-butyl-3-methylimidazolium-2-carboxylate molecule should be present in our system at a temperature of 363 K, in agreement with the

results obtained at very low CO_2 pressure presented in Supporting Information.

3.1.2. Perturbation of the IL. A glance at Figure 2 and at the assignment of the bands of Bmim Ac (Table SI1, Supporting Information) shows that upon dilution with CO_2 , the vibrations of the cation are almost unaffected with the exception of the spectral region centered at about 1450 cm^{-1} , whereas all the vibrations of the anion are found to be perturbed.

3.1.2.1. Perturbation of the Cation. The broad, composite, and almost structure-less band centered at about 1450 cm^{-1} results from the overlapping of four ring modes assigned to vibrations involving the ring and ring vibration coupled to the methyl group bonded to the nitrogen atom 3 (see scheme in Figure 1).

This strong perturbation may be interpreted as a consequence of the carboxylation of the carbon atom in position 2 by CO_2 . Indeed, the role of the C_2 position in interionic interactions of imidazolium-based ILs has been recently investigated using, in particular, vibrational spectroscopy.⁷⁹ It was found that the methylation of the C_2 position of 1,3-dialkylimidazolium $[\text{Tf}_2\text{N}]$ led to distinct differences with the non-methylated IL. In particular, the existence of a strong Raman active band centered at 1499 cm^{-1} , not reported before in the literature, was assigned to a $\text{NC}(\text{CH}_3)\text{N CCH}_3$ stretching mode.⁷⁹ The nature of this vibration and the value of its frequency, which is close to the perturbation reported before ($\sim 1450\text{ cm}^{-1}$), support the previous inference on the carboxylation of the ring in C_2 position.

3.1.2.2. Perturbation of the Anion. It is readily apparent that upon dilution of the IL by carbon dioxide, all the vibrational modes of the anion, namely, the stretching (symmetric 1382 cm^{-1} and asymmetric 1582 cm^{-1}) and bending vibration (637 cm^{-1}) of the COO group of the acetate, the methyl vibration (2917 cm^{-1}), and the ν_{CC} vibration (902 cm^{-1}), are perturbed (Figure 2).

The ν_{CC} vibration, which gives rise to an intense Raman band, well isolated from other modes, is the best adapted for an analysis. Let us remember that the ν_{CC} vibration has been extensively studied by Raman spectroscopy for acetate salts in aqueous solutions.^{80,81} It has been shown that this mode is a particularly good probe of the complexation of the carboxylate group, with sometimes more sensitivity than the vibrations of the COO group itself. As a matter of fact, the presence of "free" and mono- and bicomplexed forms of acetate ions in solutions has been observed either directly from the partially resolved structure due the presence of the different "complexes" or indirectly from the band shape analysis associated with this mode. In such solutions, the Raman bands associated with the ν_{CC} vibration have been observed for the so-called "free" acetate ion (CH_3CO_2^-) in solution at about 930 cm^{-1} and, at increasing frequency, for mono- and bicomplexed forms (typically 940 and 950 cm^{-1} , respectively).

As far as we know, the only study in Raman spectroscopy concerning the behavior of the ν_{CC} mode of acetate ions in ionic liquids has been reported by us on the Bmim TFA system and its solutions in carbon dioxide.⁵⁵ In marked contrast with aqueous solution, we found that the band shape of the ν_{CC} mode for this neat IL is always constituted by a single Gaussian profile that keeps its spectral characteristics (width and band center) upon dilution in the broad CO_2 concentration range investigated. We have thus performed a band shape analysis of the profile associated with the ν_{CC} vibration in Bmim Ac. In the pure liquid, we found that the profile is composite and can be

nicely fitted by a weighted sum of three Gaussian profiles centered at about 883 , 902 , and 909 cm^{-1} . The first one is assigned to a symmetric mode of the cation (Supporting Information, Table SI1) and the others to the ν_{CC} modes of the anion. The intensity of the band at 902 cm^{-1} is about twice that centered at 909 cm^{-1} (Figure 4). Upon dilution of the IL by

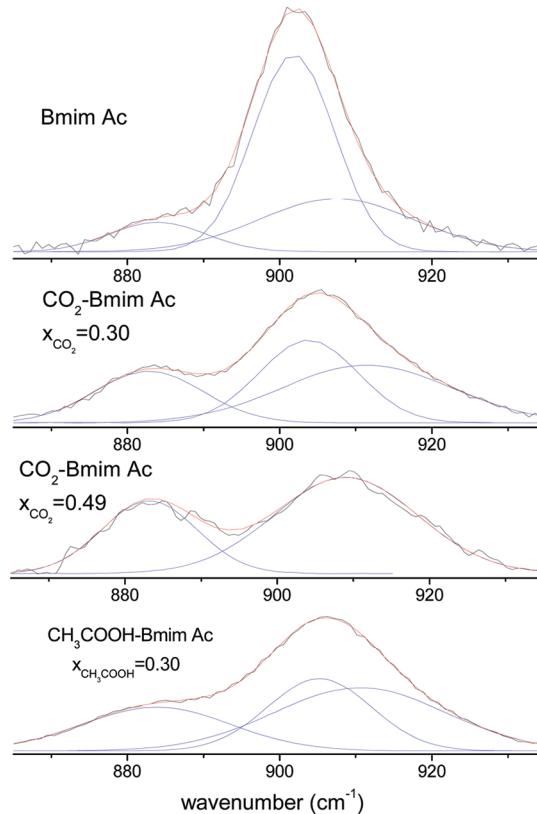


Figure 4. Band-shape analysis of the ν_{CC} vibration in Bmim Ac, CO_2 -Bmim Ac mixtures, and CH_3COOH -Bmim Ac mixture using Gaussian profiles.

carbon dioxide ($x_{\text{CO}_2} = 0.30$) the band centers of the two Gaussians are slightly blue-shifted (by about 2 cm^{-1}) and the intensity of the higher frequency component increases relative to the lower one (the intensity ratio decreases from about 2 to 0.85). Finally, at concentration equal to or greater than 0.41, the profiles merge and can be fitted by a single Gaussian line. The observation in the first regime of two Gaussian profiles having different but rather close band center wavenumbers indicates the existence of two distinct distributions associated with the ν_{CC} mode in Bmim Ac. Hence, we are led to infer that the carboxylate groups of the anions can be partitioned in two distinct populations interacting differently with the Bmim cations. For the sake of this discussion, we will label the corresponding distributions D1 and D2, the former being associated with the band observed at lower frequency. The decrease of the intensity ratio of the band associated with D1 at the expense of the other one upon dilution of the IL shows that the presence of carbon dioxide disturbs the equilibrium existing between the two distributions and that the D2 species are favored upon dilution (up to 0.35 mole fraction). At higher carbon dioxide mole fraction, the observation of a single line can be correlated with the occurrence of the second regime.

The structural organization of Emim Ac has been recently investigated by MD and neutron diffraction.⁸² It has been shown that the local ordering of the first shell of anions around a central cation is dominated by the interaction between the oxygen acetate atoms of the anion and the ring hydrogen of the Bmim cation. The anions form like a “bilayer” structure with charged carboxylate groups oriented toward the cation ring hydrogens (polar domain), while their methyl groups are led to be gathered in a so-called “pocket of hydrophobicity” (nonpolar domain). The average coordination number of acetate oxygen around the cation is close to one. A further analysis of the calculated radial distribution functions have provided a classification of the possible types of the cation–anion coordination in single, bidentate, bifurcated, and bridging interactions. It comes out from this structural analysis that the two most probable short-ranged interactions involve mainly one oxygen atom coordinated with the most acidic proton of the imidazolium ring (monodentate) and then both acetate oxygens interacting with one hydrogen atom (bidentate). On this basis, we may tentatively assign the D1 distribution to acetate anion involving a single interaction, that is, monodentate, whereas D2 could be assigned to bidentate and other geometries in which the oxygen atoms are interacting with the protons of the ring. It comes out that for each distribution (D1 or D2), the sites accessible to the corresponding carboxylate population should not be very different on the Raman time scale of observation, leading to frequencies relatively close to each other. We notice that the use of frequency distribution and therefore of distance distribution brought by the analysis of the Raman profiles extends on the short time scale and short spatial range probed by this spectroscopy, the tentative analysis of Bowron et al.,⁸² which considers specific distances to characterize the different geometries of the “complexes”. In the condensed phase, the characteristic distances involved in the different geometric forms of the acetate complexes should be distributed.⁸³

3.2.1. Second Solvation Regime. Perturbation of the CO₂. As the CO₂ concentration increases and reaches a mole fraction close to about 0.35, the “usual” Fermi dyad signature situated at about 1270 and 1380 cm⁻¹ is recovered, an observation that is more and more sizable as the dilution increases (Figure 2b). This “usual” behavior is confirmed from the comparison of the spectrum of the dyad with those measured in Bmim TFA and in pure CO₂ (at comparable density 766 kg m⁻³). We note that the two components are red-shifted and broader in Bmim Ac (Figure 5). As the CO₂ concentration increases, we do not observe significant variations of the position and broadening of the lines. This is not surprising in view of the restricted domain of mole fraction investigated in the second regime (0.4 < x < 0.49).

For this reason and because the highest frequency component of the dyad overlaps with a Bmim cation mode, we have not attempted to perform such a detailed band shape analysis as we did for Bmim TFA.⁵⁵ Nevertheless, we found that the lower frequency component could be fitted by three Lorentzian profiles situated at about 1256, 1270, and 1277 cm⁻¹ having a relative intensity ratio close to 1:4:3 and broadening 6, 12, and 8 cm⁻¹, respectively. The higher component of the dyad was fitted by a simple Lorentzian centered at about 1380 cm⁻¹ with a full width of 6 cm⁻¹. The ratio of the intensity of the higher versus the lower component of the dyad is close to 4. These features show that the values of the shift of band center position, bandwidths, and intensity

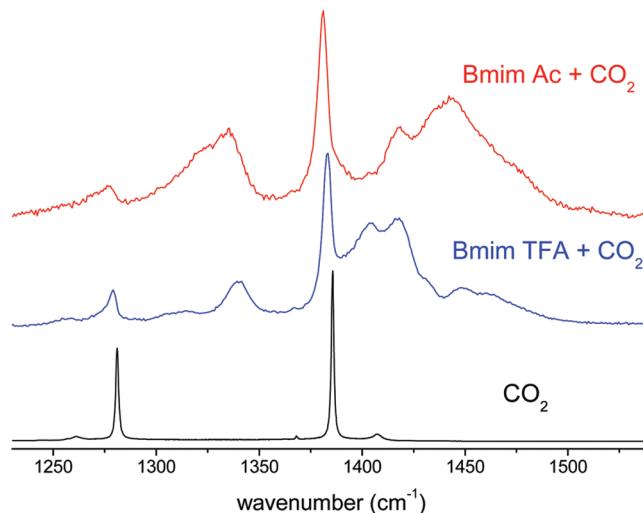


Figure 5. Raman spectra in the region of the Fermi dyad of the most concentrated mixture of CO₂ in Bmim Ac ($x_{\text{CO}_2} = 0.49$) and Bmim TFA ($x_{\text{CO}_2} = 0.54$). The spectrum of pure CO₂ (14.1 MPa, $\rho = 765.09 \text{ kg m}^{-3}$, 313 K) is displayed for comparison.

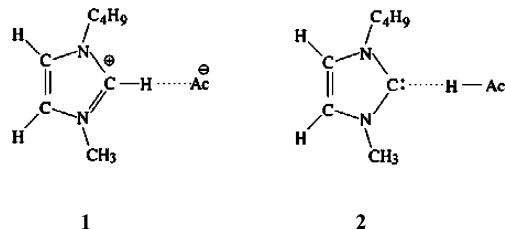
ratio are greater than those observed for Bmim TFA revealing a greater strength of the perturbation of the CO₂ molecule in Bmim Ac.

3.2.2. Perturbation of the Anion. The main perturbations of the anion are assessed from the evolution of the ν_{CC} mode. The fact that at the end of the first solvation regime the two distributions D1 and D2 merge into a single one indicates that the vibration probes a great variety of environments that are no longer distinguishable on the Raman time scale of observation. We note that a single distribution has been also found in the CO₂–Bmim TFA system in the neat IL and its dilution. The apparent similarity of the behavior of CO₂ in Bmim TFA and Bmim Ac in the second regime will be discussed in section 5.

4. VIBRATIONAL MODELING USING DFT CALCULATIONS

We have first determined the global energy minimum structures for the pure ionic liquid modeled as a ion pair dimer, (IP)₂ {Bmim⁺ CH₃COO⁻}₂ (structure I) (Supporting Information, Figure SI8) and of the mixture represented by a CO₂ molecule interacting with the (IP)₂ (structure II) (Supporting Information, Figure SI9). The detailed description of these structures, as well as their calculated total interaction energy (and the relevant contributions) is reported in Supporting Information (Table SI2). The vibrational analysis has been carried out, and the main calculated (harmonic) fundamental transitions, the IR and Raman Intensities (as well as the depolarization ratios) are reported in Supporting Information (Table SI3). This analysis shows that the vibrations of the IL are only slightly perturbed by the presence of CO₂ and that the vibrations of CO₂ are found to be significantly different from those detected in the first solvation regime. Therefore, a theoretical treatment that does not consider explicitly the carboxylation reaction appears inadequate for providing a realistic description of the first solvation regime. For this reason, we have tackled the question of the carboxylation in a more effective way. We have supposed that the carboxylate product results from a chemical reaction involving CO₂ and the imidazolium ring after deprotonation of

its C₂ atom leading to the formation of 1-butyl-3-methylimidazolium-2-carboxylate. Indeed, a recent study has provided evidence in a dialkylimidazolium-based IL with acetate (though under very low pressure conditions) of the coexistence of two conformers through an exchange process of the acidic proton (C₂), which are (1) the imidazolium cation interacting with the acetate anion and (2) the N-heterocyclic carbene (NHC)-acetic acid complex with an energy barrier of isomerization about 3.6 kcal/mol (Figure 6).⁸⁴ Although, the



1

2

Figure 6. Conformers coexisting in the CO₂-Bmim Ac mixture: (1) {Bmim⁺ CH₃COO⁻} ion pair and (2) N-heterocyclic carbene (NHC)-acetic acid complex.

formation of an N-heterocyclic carbene species is certainly questionable in liquid phase, the formation of transient 1-butyl-3-methylimidazole 2-ylidene carbene species in CO₂-BmimAc solutions (on a subpicosecond time scale) could lead to a specific interaction with a nearest CO₂ (step 1 of the reactive scheme given in Figure 7). Such a “transient” association can be

Step 1:

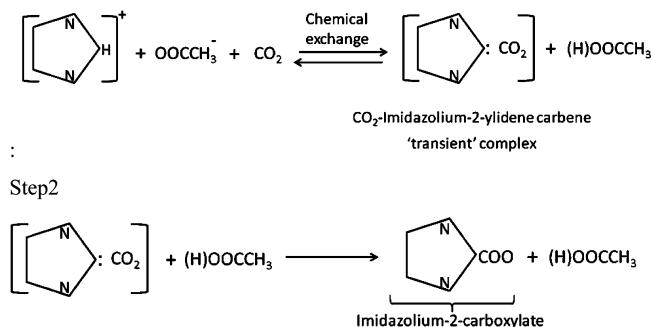


Figure 7. Concerted mechanisms for the formation of 1-butyl-3-methylimidazolium-2-carboxylate involving the isomerization process and the formation of a “transient” CO₂-carbene complex.

considered as another intermediate precursor step (step 2 of the reaction in Figure 7) toward a definitive CO₂ capture by imidazole 2-ylidene carbene species. In that sense, CO₂ triggers the carboxylation reaction through two concerted mechanisms, which are the isomerization process and the formation of a “transient” CO₂-carbene as displayed in Figure 7.

From DFT calculations, we can define the last step of the carboxylation mechanism from the “transient” CO₂-carbene complex, the isomerization process having been discussed.⁸⁴ For this purpose, we have evaluated the potential energy surface (in gas phase) from such a CO₂-carbene association leading to the formation of a stable 1-butyl-3-methyl-imidazolium-2-carboxylate species (step 2) in order to determine the intrinsic reaction path crossing a unique transition state (Figure 8). The activation barrier is evaluated at 1.5 kcal/mol. This value is found to be sufficiently small to suppose that the carboxylation reaction from a CO₂-carbene association is highly probable

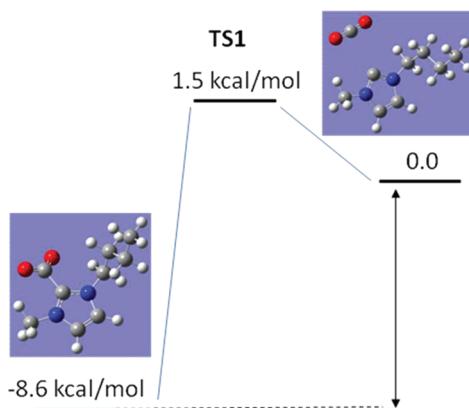


Figure 8. Reactive (step 2) scheme associated with the formation of the 1-butyl-3-methylimidazolium-2-carboxylate species from the CO₂ complexed with the “transient” 1-butyl-3-methylimidazole-2-ylidene carbene determined at the B3LYP/6-31+G** level.

especially because the barrier is certainly lower in dense phase. Moreover, the carboxylate product is found to be more stable than the initial CO₂-carbene association by about 8.6 kcal/mol, leading to a calculated value of the formation enthalpy, $\Delta H_f \approx -7.9$ kcal/mol in the gas phase at 298 K.

On this basis, we have in the following determined minimum energy structures in which the product of the carboxylation reaction, that is, the 1-butyl-3-methylimidazolium-2-carboxylate, is explicitly involved and interacts with the anion-cation couple (Figure 9). In a first structure (structure III), we found that the bond length connecting the carboxylate group COO to the imidazolium ring is 1.553 Å and the bond lengths d_{OC} associated with the COO group are 1.242 and 1.255 Å with a bond angle α_{OCO} about 132.3°. The dihedral angle between the planes of the COO group and the imidazolium ring has a value of 42°, whereas it is 28° for the isolated molecule. The BSSE-corrected interaction energy between the interacting species is -113.0 kcal/mol (Table 3).

In a second step, we have considered the influence upon this structure of both acetic acid and CO₂ molecules. For this purpose, we have determined two other minimum energy structures. In structure IV, a CO₂ molecule interacts with the COO group of the acetate anion interacting with the imidazolium cation while a second CO₂ molecule interacts with the imidazolium carboxylate, the CO₂ molecule being oriented perpendicularly to the COO group (Figure 9). We have reported the calculated values of the total interaction energy as well as the different interaction energy contributions associated with these structures in Table 3. The pair interaction energy of CO₂ with the acetate anion is found to be close to that obtained in structure II (interaction energy -4.9 kcal/mol and distance $R_{C\cdots O} \approx 2.66$ Å) whereas for CO₂ with the carboxylate species the interaction energy is -3.6 kcal/mol (distance $R_{C\cdots O} \approx 3.30$ Å).

In structure V, we consider explicitly the influence of acetic acid resulting from the carboxylation reaction. In this structure, the acetic acid molecule interacts with the COO group of the acetate anion through a strong O-H...O hydrogen-bond (distance $R_{O-H\cdots O} \approx 1.43$ Å). The interaction energy is evaluated at about -20.5 kcal (Table 3). The CO₂ molecule interacts with the COO group of imidazolium carboxylate according to a configuration close to that obtained for CO₂ interacting with the carboxylate species in structure IV (Figure 9).

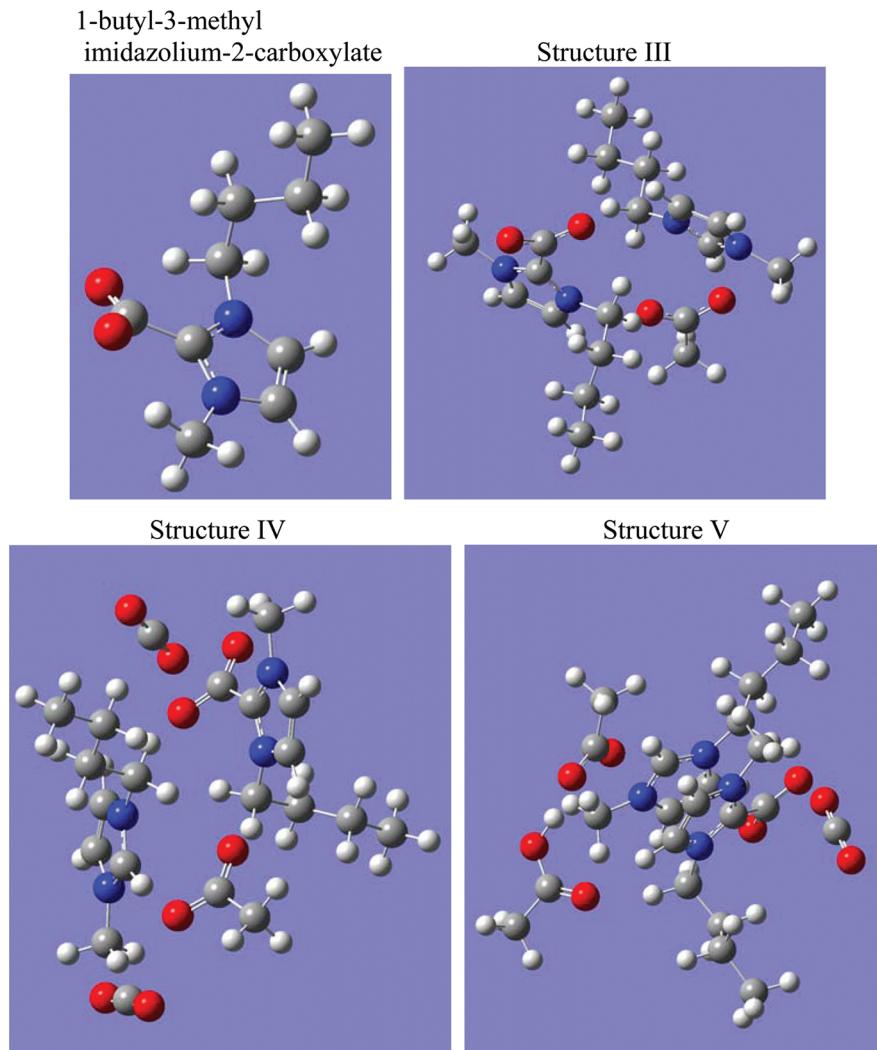


Figure 9. Structures calculated at the B3LYP/6-31+G** level: (III) for a single 1-butyl-3-methylimidazolium-2-carboxylate molecule with the ion pair dimer, (IV) for a CO_2 molecule interacting with the COO group of the 1-butyl-3-methylimidazolium-2-carboxylate and another CO_2 molecule interacting with the COO group of the Ac anion engaged within a Bmim Ac ion pair, and (V) for a CO_2 molecule interacting with the COO group of the 1-butyl-3-methylimidazolium-2-carboxylate and an acetic acid molecule interacting with the COO group of the Ac anion engaged within a $\{\text{Bmim}^+ \text{CH}_3\text{COO}^-\}$ ion pair.

In both structures IV and V, the interactions of CO_2 with its environment do not lead to a significant departure from the linearity of this molecule (deviation lower than 5°). Such CO_2 associations are quite representative of situations that should be encountered in the second solvation regime of CO_2 diluted in IL (concomitantly with the observation of the Fermi dyad). Nevertheless, we notice that in structure V, the interaction existing between acetic acid and the acetate anion reinforces the interaction energy of CO_2 with the imidazolium carboxylate by about 1 kcal/mol (cf. values in Table 3) even if structurally only small deviations are found comparatively with the CO_2 association in structure IV (distance $R_{\text{C}..\text{O}} \approx 3.31 \text{ \AA}$ instead of 3.30 \AA). This additional attractive interaction energy enhancement of CO_2 with the carboxylate species originates from a cooperative effect leading to significant changes in the electron distribution on all the species. Indeed, in structure V, the acetic acid molecule is hydrogen-bonded to one of the oxygen atoms of the acetate anion, while the other oxygen atom of the acetate is H-bonded to the acidic proton of the imidazolium carboxylate ring (Figure 9). In other terms, the interaction between acetic acid and acetate anion forms H-

bonded bridge between the two imidazolium rings (Bmim cation and carboxylate). Such a structural organization induces significant perturbations in the charge distribution of all the species involved (Figure 9).

The vibrational analysis carried out from these predicted structures (III–V) shows that the main calculated vibrational transitions compare reasonably well with the values observed in the mixture (Table 4). In particular, the calculated vibrations of the imidazolium carboxylate group (either COO or with ^{13}COO groups), namely, the bending and the symmetric and asymmetric stretches, are in fairly good agreement with the experimental values.

This analysis provides a strong indication that the 1-butyl-3-methylimidazolium-2-carboxylate species likely exists in the CO_2 –Bmim Ac mixtures. Moreover, it is noteworthy that in structure V, the calculated vibrational transitions associated with the three modes of the imidazolium carboxylate are found in better agreement with the measured ones compared with values calculated from structure III and IV. Thus, it clearly appears that the significant charge redistribution in the different species involved in structure V due to the interaction of acetic

Table 3. BSSE-Corrected Values of the Interaction Energy Obtained for the Calculated Structures of the IP {Bmim⁺ CH₃COO⁻} and 1-Butyl-3-methylimidazolium-2-carboxylate and with Interacting CO₂ Molecules with Acetate Anion (S1) and with 1-Butyl-3-methylimidazolium-2-carboxylate (S2) at the B3LYP/6-31+G(p,d) Level^a

	IP{Bmim ⁺ CH ₃ COO ⁻ } + 1-butyl-3-methylimidazolium-2-carboxylate		
	structure III	+ 2CO ₂ structure IV	CO ₂ + CH ₃ COOH structure V
ionic interactions			
ΔE _{int} (ions +ImidCOO)	-113.2	-112.7	-111.4
acet. acid–ion interactions			
ΔE _{int} (Acet Acid-(S1))			-20.5
CO₂–ion interactions			
ΔE _{int} (CO ₂ -(S1))		-4.9	
ΔE _{int} (CO ₂ -(S2))		-3.6	-4.6
total interaction energy			
ΔE ^(cor) _{int} (TOT)	-113.2	-121.2	-136.5
ΔE _f (CO ₂)		-8.0	
ΔH _f (T _{298K})		-6.6	+3.2

^aEnergy unit is kcal/mol. Site (S1): COO group of anion acetate interacting with Bmim⁺. Site (S2): COO group of 1-butyl-3-methylimidazolium-2-carboxylate interacting with the ion pair {Bmim⁺ CH₃COO⁻}. ΔE_f(CO₂) is the predicted “gas phase” value of the association energy of CO₂ (and acetic acid) with the ion pair {Bmim⁺ CH₃COO⁻} and the 1-butyl-3-methylimidazolium-2-carboxylate. ΔH_f(T_{298K}) is the corresponding enthalpy of formation calculated at T = 298 K.

acid with the acetate anion improve significantly the agreement between theoretical and experimental values of the spectral signatures of the carboxylate species engaged in a complex structure involving cooperative effects. This provides final evidence that a carboxylation reaction takes place as CO₂ is diluted in Bmim Ac and is accompanied with the formation of “nascent” acetic acid in agreement with the conclusions experimentally drawn from the Raman spectral signatures observed in the first solvation regime.

5. DISCUSSION

5.1.1. First Regime. Carboxylation Reaction. We have shown that as soon as CO₂ is diluted in Bmim Ac a carboxylation reaction occurs and continues until a mole fraction greater than 0.35 is reached. This conclusion is grounded upon a number of observations. First of all, the absence of the CO₂ Fermi dyad with the consequent appearance of three new bands observed in both Raman and infrared spectroscopy with CO₂ and ¹³CO₂. These bands have been assigned to the vibrations of a C-coordinated CO₂ molecule (having a C_{2v} geometry) to the carbon 2 of the imidazolium ring. Major evidence of the formation of the 1-butyl-3-methylimidazolium-2-carboxylate came out from the comparison of our observations with the infrared bands characterizing the synthesized 1,3-dialkylimidazolium-2-carboxylate.^{76,77,85} Indeed, a perfect matching of the frequencies of the vibrations of the carboxylate group and of perturbed modes of the imidazolium ring (domain centered at about 1450 cm⁻¹)

has been obtained allowing the assignment of these modes partially done before.⁷⁶

We found that the carboxylation reaction is irreversible and that the carboxylate is still present at temperature as high as 363 K, a fact that we have rationalized using a recent systematic work correlating the geometry of the carboxylate and its decarboxylation temperature.⁷⁸ The carboxylate molecule is formed as a stable product lasting long time periods (>6 months) as observed by spectroscopy. Finally, all the results observed on mixtures prepared using dried Bmim Ac are still obtained using the undried IL with traces of water. Clearly, on the basis of all these experimental facts, we must conclude that carbon dioxide has reacted with Bmim Ac to form a carboxylate molecule. The success of the “effective” modeling (section 4) is a further strong indication that a carboxylate molecule is present in the IL and interacts with the ions.

5.1.2. Acetic Acid Production. Due to the formation of the carboxylate molecule, the proton interacting with the acetate anion is released and then reacts with this anion to form acetic acid (AA).⁵⁰ The “nascent” AA is then expected to interact with the acetate anion of neighboring ion pairs of the IL. The interaction will take place between the OH group of the AA and the non-coordinated oxygen atom of the monodentate species. Hence, the relative population of bidentate should grow at the expense of the monodentate forms. Since the vibrations of the acetate groups in these species should not be very different, the discrimination between the vibrations of the “nascent” acetic acid and those of the acetate anion involved in the ion pair of the IL is not an easy task.

Nevertheless, we have compared the spectrum of the neat IL with the spectrum of the mixture Bmim Ac with glacial acetic acid (AA) in which the acid mole fraction is about 0.3 and corresponds approximately to the mole fraction of CO₂ before the appearance of the second solvation regime (Figure 10a).

The main perturbations are mostly observed in the spectral domains of the ν_{CC}, the symmetric and asymmetric COO stretching vibrations, and the ν_{CH} vibrations, and no new bands are detected upon mixing. Because the vibrations of the imidazolium ring are dominant in the COO stretching vibration domain and badly overlap, we will only focus our discussion on the ν_{CC} and ν_{CH} spectral domains. In the CH region, the new band centered at about 2936 cm⁻¹ when CO₂ is diluted in the IL (assigned to the CH vibration of the methyl group of the acetate) is also observed in the acidic mixture (Figure 10b). In the ν_{CC} region, the profiles observed in the acidic mixture and in the CO₂–Bmim Ac mixture are almost identical (Figure 10c). A band shape analysis of the profile in the acidic mixture confirms that two Gaussian components are needed to nicely describe the ν_{CC} profile (Figure 4, bottom) having values of the parameters very close to those obtained for CO₂–Bmim Ac mixture (CO₂ mole fraction 0.3, section 3.1.2.2).

The similarity of the trends observed on the ν_{CC} and ν_{CH} vibrations of the acidic mixture with those in the CO₂–Bmim Ac mixture in the first regime shows that these two spectral domains are influenced by the presence of the acetic acid, added or formed, respectively. Thus the ν_{CC} vibration probes the evolution of the local ordering of the acetate anions due to the production of the acetic acid concomitant with the introduction of CO₂ in the IL. Therefore, we can conclude that the formed bidentate acetates originate from the nascent acetic acid interacting with the acetate anions, which were mainly monodentate in the pure IL. This situation continues

Table 4. Vibrational Transitions, IR and Raman Intensities Associated with the Main Vibrational Transitions of the Calculated Structures {Bmim⁺ CH₃COO⁻} + 1-Butyl-3-methylimidazolium-2-carboxylate (Structures III, IV, and V^a) at the B3LYP/6-31+G Level^b**

	1-butyl-3-methylimidazolium-2-carboxylate ^c + {Bmim ⁺ CH ₃ COO ⁻ } (structure III)				1-butyl-3-methylimidazolium-2-carboxylate ^c + {Bmim ⁺ CH ₃ COO ⁻ } + CO ₂ (structure IV)				1-butyl-3-methylimidazolium-2-carboxylate ^c + {Bmim ⁺ CH ₃ COO ⁻ } + acetic acid (structure V)				exptl Raman
	ν_{calc}	I_{IR}	I_{Ran}	ρ_{dep}	ν_{calc}	I_{IR}	I_{Ran}	ρ_{dep}	ν_{calc}	I_{IR}	I_{Ran}	ρ_{dep}	
b OCO (CO ₂)					605.9 (603.3)	60.5	13.6	0.152	601.4 (600.3)	79.5	14.0	0.178	
					624.2 (610.0)	27.0	3.7	0.509	635.8 (633.4)	19.1	0.1	0.679	
					634.8 (633.5)	17.6	0.5	0.610					
					652.1 (639.8)	26.8	0.1	0.140					
b OCO \otimes ν_{CC} (carboxylate)	777.8 ^c (768) (767.1)	73.6	2.2	0.104	787.5 ^c (776.5)	72.9	2.2	0.099	795.6 ^c (776.5) (785.7)	81.2	2.2	0.140	794 ^c (783)
b OCO (Ac)	644.0	26.2	5.3	0.233	649.3	31.5	5.2	0.202	656.5	45.8	3.8	0.447	637
ν_{CC} (Ac)	909.1	37.4	11.5	0.175	914.2	26.5	10.0	0.087	899.8	64.2	11.7	0.216	
ν sym CO (CO ₂)					1358.0 (1357.9)	10.9	40.6	0.097	920.4	2.3	17.0	0.092	910
					1361.3 (1361.2)	2.2	25.3	0.068	1360.8 (1360.5)	2.1	25.2	0.100	
sym ip ring	1356.4 ^c (1356.4)	1.8	27.7	0.189	1356.4 ^c (1356.2)	2.5	27.8	0.199	1360.2 ^c (1359.0)	11.7	36.6	0.095	1336
	1358.6	7.7	15.6	0.147	1354.8	12.9	14.2	0.167	1356.8	6.3	17.1	0.250	
ν sym COO (Ac)	1326.1 ^c (1315) (1315.4)	197.6	30.2	0.094	1339.1 ^c (1318.5)	183.8	25.6	0.095	1329.8 ^c (1323.4)	228.4	27.7	0.111	1323 ^c (1304)
	1424.9	281.6	16.4	0.702	1427.5	278.2	26.2	0.578	1437.6	209.4	20.6	0.414	
sym ip ring	1470.0 ^c (1470) (1469.8)	31.0	58.1	0.171	1472.5 ^c (1472.1)	2.1	48.2	0.234	1457.5 ^c (1456.9)	19.8	64.6	0.251	1445
	1371.7	3.9	7.8	0.255	1369.9	4.6	8.3	0.415	1356.8	6.3	17.1	0.250	
ν asym C(CN) ring	1540.8 ^c (1540.6) (1540.2)	51.4	5.6	0.725	1542.3 ^c (1542.0)	58.6	4.6	0.734	1536.6 ^c (1536.3)	75.8	2.9	0.719	1568
	1600.3	315.7	6.7	0.098	1604.9	243.8	6.2	0.120	1608.3	217.6	2.4	0.715	
ν sym. C(CN) ring	1609.9 ^c (1609.9) (1610.5)	36.8	14.9	0.154	1610.5 ^c (1610.5)	37.5	12.9	0.137	1615.8 ^c (1615.8)	4.1	10.3	0.209	
	1612	190.3	1.1	0.577	1612.9	189.7	1.4	0.457	1611.2	8.7	7.6	0.271	
ν asym COO (Ac)	1620.8	149.9	3.5	0.696	1616.2	309.0	2.9	0.651	1587.7	780.1	27.7	0.639	1672 ^c
	1748 ^c (1700) (1700.8)	653.4	19.2	0.741	1738.8 ^c (1692.0)	555.5	14.1	0.723	1716.1 ^c (1691.5) (1675.3)	351.8	9.4	0.721	(1631)
ν C=O (acetic acid)									1722.3	523.9	17.4	0.111	
ν asym CO (CO ₂)					2400.0 (2331.5)	564.9	0.6	0.742	2405.1 (2336.5)	622.0	0.2	0.713	

^aIn structure IV, CO₂ molecules interact with the COO group (site S1) of anion acetate and with COO group (site S2) of 1-butyl-3-methylimidazolium-2-carboxylate. In structure V, acetic acid interacts with site S1 of anion acetate and CO₂ with site S2 of 1-butyl-3-methylimidazolium-2-carboxylate. ^bExperimental frequency values (Raman) are displayed for comparison. Only some Raman bands are reported here for comparison with the calculated ones. The Raman bands observed are described with their assignment in Supporting Information and Table SI1. The units of frequency, IR activity, and Raman intensity are cm⁻¹, Km/mol and Å⁴/amu, respectively. ^cVibrational transition of the COO group of the 1-butyl-3-methylimidazolium-2-carboxylate. Values for labeled ¹³C are reported in parentheses.

until the end of the first solvation regime in which a single distribution of acetate forms is found.

Our pragmatic approach consisting of adding acid to the IL to “mimic” the formation of AA due to the proton release by the carboxylation reaction has another implication. Indeed, the state of aggregation of acetic acid molecules in the pure liquid consists of coexisting species such as monomer, linear chains,

and predominantly cyclic dimers. In contrast, the “nascent” acid in the IL is under monomeric form at the very instant of its formation and will subsequently interact with the acetate environment. Apparently, adding AA to the IL is not equivalent to having a “nascent” isolated molecule. However, the dilution of AA in the IL will strongly perturb the acid local ordering modifying the relative distributions of the aggregated forms,

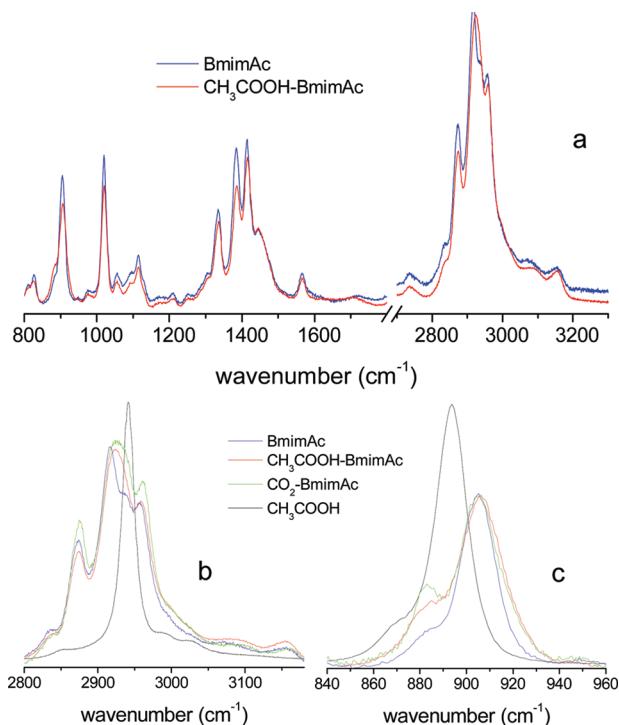


Figure 10. Comparison of the Raman spectra of pure Bmim Ac (blue), CH_3COOH -Bmim Ac (red, $x_{\text{CH}_3\text{COOH}} = 0.30$); CO_2 -Bmim Ac (green, $x_{\text{CO}_2} = 0.30$), and pure CH_3COOH (black). The spectral domains of ν_{CH} vibration of the methyl group of the acetate and the ν_{CC} of the acetate are displayed in panels b and c, respectively.

favoring the appearance of monomeric and linear chains at the expense of cyclic dimers. This is confirmed by comparing the spectra of the acidic mixture and of the pure acid. In the mixture, the bands in the ν_{CC} and ν_{CH} regions are blue-shifted ($>15 \text{ cm}^{-1}$) and red-shifted ($>20 \text{ cm}^{-1}$), respectively, from those observed in the pure acid (Figures 10b,c). Moreover in the pure acid, the band-shape analysis of the ν_{CC} profile is very different from that obtained in the diluted mixture in the IL because at least four Gaussian components are needed to get a good description.

This modification of the state of aggregation of carboxylic acids, in particular, acetic acid, upon dilution in organic liquids is well documented.^{86–90} In mixtures with polar solvents, the population of cyclic dimers decreases in favor of monomers and linear forms, which may form complexes with the solvent. In particular, Burneau et al. reached the same conclusion from the analysis of the ν_{CC} profile in aqueous solutions (D_2O).⁹⁰ A similar finding has been made in studies of water diluted in imidazolium-based ILs. Upon dilution in the IL, the water network structure is broken to lead to the formation of monomers interacting with the anions and small aggregates even at rather high water concentration.^{91,92} From this conclusion, we emphasize that the existence of monomeric “nascent” acetic acid molecules and their subsequent interaction with the acetate anion was able to capture the physical–chemical implications of the release of the proton and the interaction of the formed acetic acid with its environments in CO_2 -Bmim Ac mixture.

5.1.3. On the Reactive Scheme. It is worthwhile to consider the reactive scheme proposed by Maginn⁵⁰ who is the first to have envisaged the possibility of a carboxylation reaction in the CO_2 -Bmim Ac mixture. His chemical scheme predicts the

formation of imidazolium carboxylate accompanied by the formation of acetic acid. In a first step, the proton attached to the carbon C_2 of the imidazolium ring is released and reacts with the acetate anion of the IL leading to the formation of a carbene molecule together with an acetic acid molecule. In a second step, the carbon atom of the CO_2 reacts with the carbene to form the carboxylate molecule. Our previous analysis shows that a chemical reaction not only occurs in the CO_2 -Bmim Ac mixture, which cannot be considered as minor, but also leads to the final products, the carboxylate molecule and the acetic acid, as predicted.⁵⁰ Although there is an agreement concerning the final products of the reaction, the discussion of the two steps of the reactive scheme should be considered. According to the first step, we would expect that carbene and acetic acid are present in the IL and coexist with the ion pairs. These species, if they are formed and have lifetime adapted to the detection by spectroscopic methods, should be observed in the pure IL. We emphasize that neutron diffraction,⁸² as well as the present study, has not detected acetic acid in the pure IL. Moreover, the existence of an isolated carbene is also questionable. Indeed, as mentioned before, the signature of this species has been recently reported in Emim Ac under very stringent thermodynamic conditions (423 K, 1 Pa)⁸⁴ which are very different from those considered here in dense phase. Finally, we have shown that the introduction of CO_2 in the IL strongly disturbs the existing equilibrium between the Bmim and acetate ions to initiate from the very beginning the carboxylation process. Clearly, the relevance of the role played by CO_2 in triggering the reaction has to be considered according to a transient complexation step as proposed in section 4.

However, until now we have considered a static picture keeping aside the fact that the dynamics of the molecular interactions should be taken into account. Considering the pure IL, we may suppose that the proton (C_2) of the ring, which is hydrogen bonded to the oxygen atom of the acetate anion, could perform an exchange process between these two sites. Due to this exchange, two conformers may coexist, namely, the Bmim Ac ion pair (1) and the so-called N-heterocyclic carbene (NHC)-acetic acid complex (2) (Figure 6). As CO_2 is diluted in the IL and the proton has jumped from site 1 to site 2, we may envisage that the CO_2 molecule (still interacting with the anion) takes advantage of this situation to interact with the deprotonated carbon 2 and form the carboxylate. This picture could be viewed as a cooperative process between carbon dioxide and the moieties constituting the IL. This concerted process will take place obviously on a very short time scale during which the deprotonated C_2 site could be considered as belonging to a carbene molecule. Considering that the time scale of this elementary process (certainly in the subpicosecond range) avoids the need to suppose that a long-lived carbene has been formed in the mixture. This scenario is not unrealistic considering the order of magnitude of the values of the energy barriers of the isomerization process (step 1) and of the carboxylation reaction involving the transient CO_2 carbene species proposed here (step 2) (Figures 7 and 8), which are even lower in dense phase due to the stabilization by the environment.⁸⁵

5.2. Second Regime. The existence of the second regime is characterized by the appearance of the Fermi dyad in the Raman spectra. This is an experimental fact implying two main issues. The first one is that the carboxylation reaction should be largely moderated if not stopped; otherwise the reaction will

proceed, and consequently the Fermi dyad will be still unobserved. This result can be understood by noting that part of the imidazolium cations have been transformed into carboxylate molecules and that an equivalent amount of acetic acid has been formed. The study of the ν_{CC} vibration indicates that the acetic acid formed interacts with the monodentate acetate leading to an increasing population of bidentate acetate. The structural study of Emim Ac showed that the dominant forms are monodentate acetate anions hydrogen bonded to protons attached to carbon 2 of the ring.⁸² It can be inferred that a similar situation prevails in Bmim Ac. Therefore, it is very likely that the acetic acid molecules interact with the available oxygen atom of the acetate COO groups. As a consequence of the steric hindrance of these groups, it is likely that these sites are no longer easily available to interact with more CO₂ molecules. This mechanism might be at the basis of the moderation of the carboxylation reaction ending the first regime and preparing the second one.

The second issue is that the observation of the Fermi dyad has been always reported for carbon dioxide diluted in organic liquids and in ionic liquids. The analysis of the spectral perturbations of this doublet (band center shifts and perturbation of the line shapes) allows characterization of the nature of the interactions of CO₂ with its environment, which slightly distort the geometry of the molecule (say by 10° at most) from its linear configuration as it exists in an isolated state. The distortion of the geometry of the CO₂ molecule in relation to the perturbation of the Fermi dyad constitutes then a criterion to assess the strength of the interaction. Clearly, upon a strong coordination or reaction of CO₂, the signature of the Fermi dyad is lost, whereas it is present with "softer" interactions such as those involved in the formation of transient molecular complexes as reported in the literature. Thus, in the second regime, we are forced to admit that CO₂ interacts in a softer way with its environment consisting of ions pairs, carboxylate molecules, acetic acid, and even CO₂. This diversity of environment as a consequence of a chemical reaction is not found in the majority of CO₂ in imidazolium-based ILs containing anions such as [BF₄]⁻, [PF₆]⁻, [Tf₂N]⁻, and [TFA]⁻.

To support this view, let us remember that from our DFT calculations we determined a structure IV involving a carboxylate interacting with a single Bmim Ac ion pair in which it may exist two possible stable configurations of CO₂ (cf. section 4). It was shown that, indeed, a diversity of sites is offered to the CO₂ molecule in which to reside while keeping an almost linear structure, for which the Fermi dyad is active. This conclusion is consistent with the experimental observation of the Fermi dyad. The diversity and number of accessible "nonreactive" sites (including those offered by the alkyl nonpolar domains) compared with the presumably hindered reactive ones as a consequence of acid production is at the basis of this experimental observation.

As this level, it is worthwhile to compare the solubility of CO₂ in Bmim Ac and Bmim TFA. It is clear that the existence of a reactive regime is at the basis of the major difference between these two systems. The greater solubility observed in the hydrogenated system versus the fluorinated one in the first regime is due to the existence of a chemical reaction. In Bmim TFA, the nonexistence of this reactive regime is likely a consequence of the electron-withdrawing effect of the fluorinated atoms acting on the charge distribution of the COO group of the anion. Hence, the interaction taking place between the carbon atom (LA center) of CO₂ and the oxygen

atom (LB center) of the [TFA] anion is weakened. Concomitantly, the hydrogen bond existing between the oxygen atom of the anion COO group and the hydrogen atom of the ring (bonded to C₂) is also weakened. As a consequence of these cumulated effects, the probability of the ring deprotonation followed by the carboxylation reaction in the fluorinated compound should be reduced in comparison with the hydrogenated one. It is only in the second regime that one might be tempted to make a crude comparison based upon the presence of the Fermi dyad and the almost absence of the perturbation in both IL spectra with increasing concentration. However, the CO₂-Bmim Ac system is a complex system (quaternary mixture), which is obviously different from the binary CO₂-Bmim TFA. Therefore, the CO₂ solvation in these two systems cannot be straightforwardly compared.

6. CONCLUSION

The main issue addressed in this work is the interpretation of the unusual solubility of CO₂ in Bmim Ac. This solubility results from the existence of two distinct solvation regimes. The first regime, corresponding to a CO₂ mole fraction less than about 0.35, is dominated by an irreversible chemical reaction leading to the carboxylation of the imidazolium ring accompanied by acetic acid formation. We provided here much strong experimental evidence complemented by an effective DFT modeling to support this assertion. The second regime is characterized by the detection of the CO₂ Fermi dyad and corresponds to a physical absorption of the CO₂. This shows that the carboxylation reaction has been strongly moderated and even stopped as soon as the second regime is reached. This finding has been interpreted as due to the interaction of the acetic acid molecules with the acetate anions involved in monodentate forms with the cation of the ion pair.

Another issue is the solubility of CO₂ in Bmim Ac and Bmim TFA. The greater solubility observed in the hydrogenated system versus the fluorinated one, before the cross over (Figure 1), is due to the existence of a chemical reaction. Although a physical absorption is involved in the second regime in both systems, the CO₂-Bmim Ac one becomes a complex system (quaternary mixture), which is obviously different from the binary CO₂-Bmim TFA. Therefore, the CO₂ solvation in these two systems cannot be straightforwardly compared.

The unique behavior of the CO₂-Bmim Ac system is of great interest and offers unique possibilities of investigations. Indeed, the carboxylation reaction observed in this study marks a great contrast with the general behavior reported for ionic liquids. Understanding the mechanism of the reaction has challenging aspects. We have suggested that in the dense phase, this scheme could be understood by considering the role of CO₂ in concerted interactions having in mind a dynamic picture. The elucidation of this scheme will open the way to interesting experimental kinetics investigations involving possibly time-resolved spectroscopy. From the theoretical point of view, we argue that investigations devoted to elucidating the reactive scheme are still needed to understand the current system.

Finally, we note that the results presented here have also some interest in the context of green chemistry, which is the solute recovery from ILs using supercritical CO₂.³¹ Clearly, this study indicates that due to the reaction between CO₂ and the IL, solute recovery is not always feasible. At last, we emphasize that efforts in understanding at the molecular level the subtle interactions existing between CO₂ in its ionic environments

should be pursued as providing a better understanding and therefore a mastering of the solvation process.

■ ASSOCIATED CONTENT

Supporting Information

Raman spectra of the pure IL and its assignment based upon a comparison with the spectra of Bmim BF₄⁻ and Bmim PF₆⁻, detailed description of the perturbations observed in the spectra of the mixtures compared with that of the pure IL, structures for the pure ionic liquid modeled as a ion pair dimer and the mixture represented by a CO₂ molecule interacting with the (IP)₂, detailed description of these structures and their calculated total interaction energy, and calculated (harmonic) fundamental transitions, the IR and Raman Intensities, and the depolarization ratios. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are pleased to thank Drs. Jean Luc Bruneel and David Talaga for their help in the Raman experiments. The authors are also indebted to Dr. Joëlle Mascetti for providing facilities and help in the preparation of very diluted solutions of CO₂ in the IL. We are also pleased to acknowledge Dr. G. Le Bourdon and Dr. T. Buffeteau for their help in ATR measurements. We gratefully acknowledge the support provided by the M3PEC computer centre of the DRIMM (Direction des Resources Informatiques et Multimédia Mutualisée, Talence, France) of the University of Bordeaux I and the IDRIS computer centre of the CNRS (Institut du Développement et des Resources en Informatique Scientifique, Orsay, France) for allocating computing time and providing facilities. This work was partly founded by FCT under project PTDC/EQU/FTT-102166/2008.

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