Ab initio studies on [bmim][PF$_6$]–CO$_2$ mixture and CO$_2$ clusters

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Abstract. *Ab initio* molecular dynamics studies have been carried out on the room temperature ionic liquid, 1,*n*-butyl,3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) and supercritical carbon dioxide mixture at room temperature and experimental density. Partial radial distribution functions (RDF) for different sites have been computed to see the organization of CO$_2$ molecules around the ionic liquid. Several partial RDFs around the carbon atom of CO$_2$ molecule are compared to find out that the CO$_2$ has specific interaction with a carbon atom present in the imidazolium ring. The CO$_2$ is also found to be very well organized around the terminal carbon atom of the butyl chain. The partial RDFs for the oxygen atoms around oxygen and carbon atoms of the CO$_2$ suggests that there is very good organization of CO$_2$ molecules around themselves even in the [bmim][PF$_6$] – CO$_2$ mixture. The instantaneous quadrupole moment tensor has been calculated for the anion and the cation. The ensemble average of diagonal components of quadrupole moment tensor of the cation have finite values, whereas the off-diagonal components of the cation and both the diagonal and off-diagonal components of the anion have the value of zero with a large standard deviation. The CPMD studies performed on CO$_2$ clusters reveals the greater tendency of the clusters with more CO$_2$ units, to deviate from the linear geometry.

Keywords. Ionic liquids; supercritical carbon dioxide; *ab initio*; molecular dynamics.

1. Introduction

The increase in the pollution level due to the solvents used currently in industries demands alternative solvents which are not harmful to the environment. The quest for such solvents has given rise to two types of green solvents, viz. supercritical carbon dioxide and a class of compounds called the room temperature ionic liquids.

Supercritical CO$_2$ (scCO$_2$) with its unique property of liquid-like density and gas-like transport (Senapati *et al* 2004), combined with its non-toxicity, recyclability, high diffusivity and tunability of solvent properties is an environmentally benign solvent (Leitner 2000; Poliakoff and King 2001; Wells and DeSimone 2001; DeSimone 2002) for various solutes (DeSimone *et al* 1992; Li *et al* 2003; Ribeiro and Bernardo-Gil 1995). Unlike conventional liquids, the density of the supercritical fluid can even be doubled by doubling the pressure (Clifford 1999) which is a characteristic feature of compressible fluids. scCO$_2$ has been widely studied by researchers (Clarke *et al* 1997; Nagashima *et al* 2003) as also simulations in the pure state (Chen *et al* 2001; Salaniwal *et al* 1999, 2001; Senapati *et al* 2004; Saharay and Balasubramanian 2004a, 2006b, 2007) and in the mixture (Saharay and Balasubramanian 2006).

Room temperature ionic liquids (RTILs), on the other hand, are a class of compounds comprising solely of ions

and they are liquids at room temperature. These compounds have negligibly low vapour pressure, are non-toxic and have a wide liquid range. The reason for the low melting point of these compounds is that they are composed of bulky asymmetric organic cations and organic or inorganic anions which cause frustration in packing. These compounds which are polar solvents have been demonstrated to be good solvents for synthesis (Welton 1999; Earle and Seddon 2000). They are also widely used in catalysis, electrochemical cells and also for energy storage. Using a combination of different anion, cation and the substituent on the cation, compounds can be prepared with desired physical and chemical properties which can suit a particular application. All these properties and applications of these compounds have attracted the interest of academia and industry. These compounds have been studied extensively in recent years (Seddon *et al* 2000; Huddleston *et al* 2001; Every *et al* 2004). A number of computational studies have also been undertaken to obtain an insight into the atomic level interactions in these systems (Hanke *et al* 2001; de Andrade *et al* 2002; Del Pópolo and Voth 2004; Lopes *et al* 2004; Bhargava and Balasubramanian 2005, 2006; Del Pópolo *et al* 2005; Urahata and Rebeiro 2005).

Among the ionic liquids, 1,*n*-butyl,3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) is one of the most studied compounds. Several experimental and computational studies have been reported on these compounds so far. It has been demonstrated to be a good solvent in syn-

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thesis. Although the viscosity of this compound is very high (around 200 cP), the compound has generated immense interest of the chemists as its melting point is below room temperature (283 K).

As RTILs have low vapour pressure, the products of a chemical reaction conducted in such ILs cannot be extracted through a distillation process. However, CO_2 in supercritical form has been demonstrated to extract such products from ILs. It has been observed that CO_2 is highly soluble in RTILs, but RTILs are almost insoluble in CO_2. Several experimental studies have been carried out to study the solubility of CO_2 in RTILs so far to determine the phase behaviour of CO_2 in these compounds. In addition to these studies, X-ray diffraction studies as well as ATR–IR spectroscopic studies have also been reported which aim at probing the specific interactions between the CO_2 and RTILs which can give possible clues for the high solubility of CO_2 in these compounds.

With these applications in mind, several groups have studied the phase behaviour of CO_2 in different RTILs. There have been numerous reports on the solubility of CO_2 in different RTILs as a function of pressure. It has been found that the solubility of CO_2 in some of the ionic liquids is extraordinarily high. Eventhough the reason for this high solubility is not clear, there have been several explanations for this behaviour. It has also been observed that the volume expansion of RTILs upon addition of CO_2 is very less. Reports from experiments suggest that up to 80 mole % of CO_2 is soluble in some of the ionic liquids, with only around 30% increase in the volume of the liquid. Recently, there have been experiments to study the specific interactions between the CO_2 and the ions of the RTIL. X-ray diffraction experiments have concluded that the anion is responsible for the high solubility of CO_2 in [bmim][PF$_6$]. Recent ATR–IR spectroscopic studies have probed the effect of different anions on the solubility of CO_2 and have found that BF_4 ion interacts strongly with CO_2 when compared with PF_6. However, the solubility of CO_2 in [bmim][PF$_6$] is higher than that in [bmim][BF$_4$], which suggests that the interaction between anion and CO_2 plays a key role in the solubility.

The solvation of a solute not only depends on the solute–solvent interactions but also on the relative strength of solvent–solvent and solute–solute interactions. This necessitates a detailed investigation on the nature of solute–solute (in this case, CO_2) interactions in its pristine state. In our earlier studies on neat scCO$_2$ and scCO$_2$ with co-solvents, we have shown that CO_2 can act either as a Lewis acid or base depending on its environment. The isotropic polarizability of CO_2 is around $2 \cdot 6$ Å^3 which is comparable to that of HCl. Also, the anisotropic polarizability (i.e. the difference between the components that are parallel and perpendicular to the CO_2 backbone) of CO_2 is also much larger than, say, that of HCl. Thus, near neighbour interactions in a inhomogeneous solvation shell can induce an instantaneous dipole moment in CO_2

(Saharay and Balasubramanian 2004a). Several experimental and simulation studies have been carried out to estimate the extent of this type of interaction on the stabilization energies of CO_2 clusters (Illies *et al* 1987; Jucks *et al* 1987; Nesbitt 1988; Weida and Nesbitt 1996; Tsuzuki *et al* 1999). Here, we report the evolution of instantaneous geometry of CO_2 with respect to the size of CO_2 clusters.

Computational studies by Berne *et al* (Huang *et al* 2005) have thrown some light on the reasons for the high solubility of CO_2 in imidazolium based ionic liquids. They have found that the large number of small voids present in the ILs easily rearrange to accommodate CO_2. The solubility curve which rises steeply after a certain mole fraction of CO_2 corresponding to the highest solubility hints that this may be due to the reason that all the voids which can accommodate CO_2 have been exhausted. Although this is one of the explanations for the high solubility of CO_2 in ILs, it is not clear why the solubility differs very much between the compounds with the same cation and different anions. Extensive studies at the molecular level are required to obtain a clear picture of solubility of CO_2 in ILs and its dependence on the different anions and cations involved.

This paper describes our efforts to understand the interactions between the [bmim][PF$_6$] and CO_2 and complements our recent work in this area (Bhargava and Balasubramanian 2007).

2. Methodology and simulation details

A mixture of CO_2 and room temperature ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, was studied using *ab initio* molecular dynamics simulations. The simulated system consisted of 12 units each of [bmim] and [PF$_6$] ions and 28 CO_2 molecules, amounting to 70 mole % of CO_2 in the mixture. The simulations were carried out at 298 K at extrapolated experimental density (Blanchard *et al* 2001; Aki *et al* 2004; Kanakubo *et al* 2005) using the CPMD (Car and Parrinello 1985; Hutter *et al* 1990) code. The solubility data of CO_2 in [bmim][PF$_6$] obtained from Aki *et al*'s (2004) studies was fitted to a second order polynomial, which yielded the volume expansion to be $1 \cdot 312$ for the 70 mole % (CO_2) mixture of CO_2 – [bmim][PF$_6$] relative to pure [bmim][PF$_6$]. A value of $1 \cdot 30$ was chosen to arrive at the simulation density which agrees with the value that is used in Kanakubo *et al* (2006) studies. This system with a total of 468 atoms was simulated in a cubic box of edge length, $17 \cdot 56$ Å. Norm conserving pseudopotentials of the Troullier–Martins form (Troullier and Martins 1991) were employed to take into account the effect of the core electrons and the nuclei. Gradient corrected exchange and correlation functionals prescribed by Becke (1988) and Lee *et al* (1988) were employed. The initial configuration for the

CPMD run was obtained from a classical MD simulation of 8 ns duration. A plane wave basis set with an energy cutoff of 90 Ry was used to expand the electronic orbitals. This value of the cutoff was chosen after checking for the convergence of the forces on ions as a function of increasing energy cutoff. Three-dimensional periodic boundary conditions were applied to obtain bulk behaviour. All the hydrogens in the system were substituted by deuterium, in order to enable the use of a larger time step of integration. Prior to the CPMD run, the electronic degrees of freedom were quenched to the Born–Oppenheimer surface. During the CPMD simulations, a fictitious electron mass of 700 a.u. was employed. The kinetic energy of the ions was controlled by using the Nosé–Hoover chain thermostat (Martyna *et al* 1992). The equations of motion were integrated with a time step of 5 a.u. (around 0·12 fs) over a length of 13·9 ps out of which the last 10·4 ps data was used for analysis. The conservation in total energy was 8 parts in 10^9 over a duration of 7 ps.

In order to study the differences in the structure and dynamics upon addition of CO_2 to [bmim][PF₆], an additional CPMD simulation of pure [bmim][PF₆] containing 12 ion pairs was carried out at room temperature and at a density of 1·36 g/cc. This system consisted of a total of 384 atoms within a cubic box of edge length, 16·09 Å. The CPMD trajectory length was 11 ps, out of which the last segment of 7·9 ps duration was used for analysis. Other details of the run are the same as that for the mixture.

We have also carried out gas phase calculations of CO_2 clusters of size ranging from monomer to quadrumer. The initial configurations for the clusters were taken from the geometry optimized structures (Sommerfeld and Posset 2003). CPMD simulations of each of these clusters were performed in cubic supercells of box length, 10 Å at 318·15 K. The fictitious mass of electrons was set to 500 a.u. and the equations of motion were integrated with a time step of 5 a.u. (around 0·12 fs). Temperature control for the ions was achieved by the use of a Nosé–Hoover chain thermostat (Martyna *et al* 1992). The total run length for each of the clusters was around 5 ps.

A band width of 0·1 Å is used in the calculation of radial distribution functions in bulk systems. For the calculation of molecular quadrupole moments, 34 instantaneous configurations each of the pure [bmim][PF₆] system and of the mixture were selected and the centres of maximally localized Wannier orbitals (Wannier 1937; Boys 1960; Resta 1994; Resta and Sorella 1999; Berghold *et al* 2000) were obtained using the CPMD code. The quadrupole moment of molecules or ions were calculated by assigning a charge of $-2e$ for the Wannier centres and atomic valence charges for the ion centres. The dipole moment for a charged system depends on the choice of the origin of the coordinate system. Here, we follow the earlier work of Lynden-Bell and coworkers (Resende Prado *et al* 2006).

3. Results and discussion

3.1 *CO_2 cluster*

Although CO_2 is a non-dipolar compound due to its molecular symmetry ($D_{\infty h}$), the partial charges on the individual atoms result in non-zero bond dipole moments which produce a significant quadrupole moment, making scCO_2 a 'quadrupolar' solvent (Reynolds *et al* 1996; Kauffman 2001). Raveendran and Wallen have demonstrated that CO_2 can be considered as a charge separated polar molecule to its near neighbour while the resultant dipole moment is zero for distant molecules (Raveendran and Wallen 2003; Raveendran *et al* 2005). This can be well understood from an analysis of its electronic polarizability (α), which is a measure of the 'softness' of the charge cloud around a molecule. The polarizability of neutral CO_2 (2·63 Å³) in its ground state is much higher than that of CO (1·98 Å³) and is comparable with that of HCl (2·6 Å³). The overall higher anisotropy in polarizability of CO_2 with respect to CO and HCl indicates the possibility of distortion in its geometry due to solvent–solvent and solute–solvent interactions. The absence of a permanent dipole moment in CO_2 makes it Raman inactive in the isolated state despite the strong Fermi-coupled v_1 (symmetric stretching) and $2v_2$ (first overtone of bending mode) doublet. Interestingly, this doublet can be observed in pressurized CO_2 (Gebbie and Stone 1963) due to collision induced absorption (CIA). Based on the CIA spectra of CO_2, Vigasin *et al* (Baranov and Vigasin 1999; Vigasin 2000; Vigasin *et al* 2001) demonstrated that the thermally averaged rotational constants in CO_2 dimer are different from the ground state.

The arrangement of CO_2 molecules in the first coordination shell have been discussed in our earlier studies on neat supercritical CO_2 at varying solvent densities (Saharay and Balasubramanian 2007). Our results on the radial distribution functions and the angle of inclination of CO_2 back bone vectors with respect to a central molecule indicate that the nearest neighbours prefer distorted T-shaped geometry whereas the distant molecules prefer slipped parallel geometry with respect to a central CO_2 in bulk system. In contrast, gas phase calculations have shown that slipped parallel geometry of CO_2 dimer is energetically more favourable than the T-shaped configuration. *Ab initio* (Tsuzuki *et al* 1999) and high resolution IR spectroscopic data (Weida and Nesbitt 1996) indicate that the ring like structure of a CO_2 trimer is most stable as it enhances the number of possible Lewis acid–Lewis base interactions between the CO_2 molecules. Thus, in the present study, we have taken CO_2 dimer in the slipped parallel and trimer in the ring like configurations.

The instantaneous intramolecular $O\widehat{C}O$ angle distributions in different clusters of $(CO_2)_n$ ($n = 1, 4$) have been shown in figure 1. The distribution for CO_2 monomer shows a sharp peak at $\cos(\theta) = -1$ with a short tail up to

$\cos(\theta) = -0.985$. Note that the probability at $\cos(\theta) = -1$ gradually decreases with increasing cluster size. However, a slower decay in the distributions can be observed as the cluster size increases, i.e. the propensity to deviate from a linear geometry in the instantaneous configurations is larger in bigger clusters. In our previous study on neat $scCO_2$, we have pointed out that this deviation from linear geometry occurs due to the inhomogeneous molecular arrangement in the vicinity of a central CO_2 molecule. For comparison, we have shown the same plot obtained for bulk CO_2 at 1·4 g/cc in figure 1. As the neighbouring environment in bulk is more homogeneous than in a cluster, CO_2 obtains greater tendency towards linear geometry in the former situation.

3.2 *Radial distribution functions*

The schematic of [bmim][PF$_6$] along with the atom numbering scheme and the directions employed in the calculation of the quadrupole moment of the cation is provided in figure 2 in order to aid the discussion.

The partial radial distribution function of carbon and oxygen atoms of CO_2 around the carbon atoms on the imidazolium ring of the cation are presented in figure 3. The first peak of the C3–C(CO_2) $g(r)$ is present at 4·15 Å with a coordination number of 2·5 up to the first minimum at 5·15 Å. The C4–5–C(CO_2) $g(r)$ also exhibits a peak at 4·15 Å but the coordination number in this case is slightly lower i.e. 2·2 up to the first minimum which is present at 5·05 Å. It can be noticed that the peak height in the case of C3 is marginally higher when compared to that of C4 or C5. The C3–O(CO_2) $g(r)$ peak is found nearer to that of C3–C(CO_2) position which is 3·35/AA. This suggests that CO_2 is not oriented in a tangential to

the ring, rather it is close to a radial orientation. However, it should be noted that it is also not a perfect radial orientation which is evident from the first peak position of C3–C(CO_2) $g(r)$ and C3–O(CO_2) $g(r)$. The coordination number of CO_2 around C3 up to the first minimum in its $g(r)$ is 2·3 which can be compared to the coordination number of C4–5 around CO_2 which is 2·1 eventhough the latter has the first peak position and the first minimum at the same positions as the former. This small increase in the coordination can be rationalized as due to the slightly higher interaction of the hydrogen attached to the carbon C3, when compared to the hydrogens on the other two ring carbon atoms. The hydrogen attached to C3 is slightly acidic and has the tendency to form weak hydrogen bond with the oxygen atom of the CO_2 molecule.
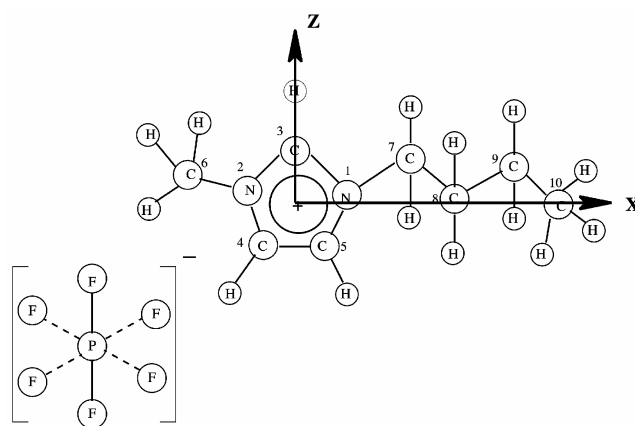

Figure 2. Schematic representation of [bmim][PF$_6$] along with the atom numbering scheme. The axes define the coordinate system employed in the calculation of the quadrupole moment of the cation. *Y*-axis is perpendicular to the plane of the imidazolium ring.
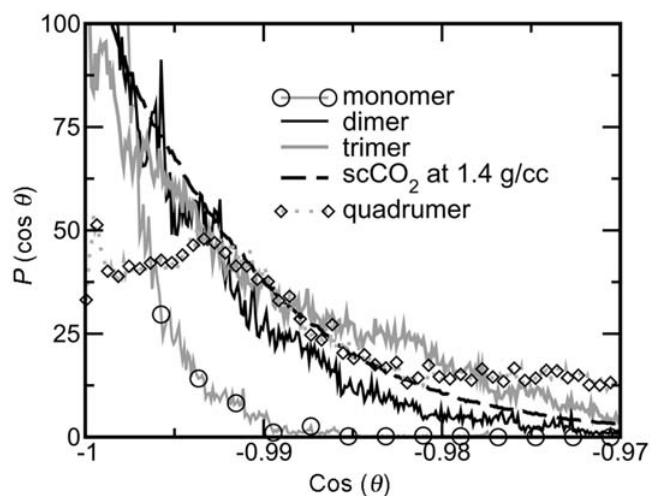

Figure 1. Intramolecular O–C–O angle distributions of CO_2 in bulk under supercritical conditions and in small clusters. Symbols are shown infrequently for clarity.
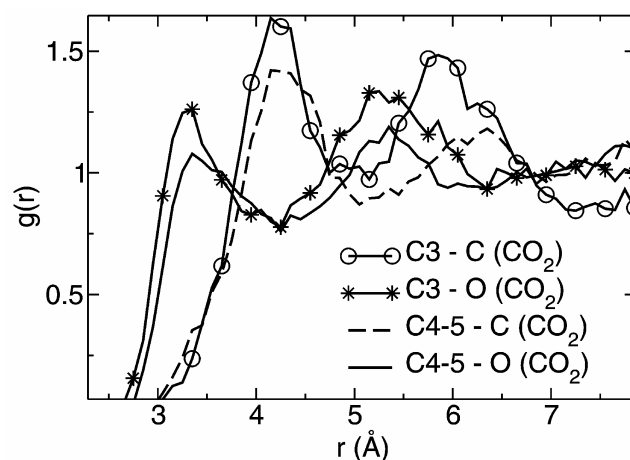

Figure 3. Radial distribution function of carbon and oxygen atoms of CO_2 around the carbon atoms present on the imidazolium ring. Symbols are shown infrequently for clarity.

The radial distribution function of carbon atom of CO_2 around different carbon atoms of the cation are presented in figure 4. It can be noticed that the CO_2 is well organized around the terminal carbon atom of the butyl chain attached to the imidazolium ring, when compared to that around other carbon atoms of the cation and it is least organized around the carbon atom, C8. From these observations we can conclude the organization of CO_2 around the central carbon atoms of the butyl chain. The radial distribution function of CO_2 around C3 shows two peaks of comparable heights, one due to the CO_2 molecules directly interacting with the C3, and the other due to those CO_2 molecules which are interacting with C4 or C5 carbon atoms of the ring. The RDFs of CO_2 are around C3, C7, C8, C9 and C10 peaks at 4·15, 4·35, 4·45, 4·25 and 3·95 Å, respectively. Eventhough there is not much dif-

ference between the first peak position of the RDFs of CO_2 around these atoms, one thing which can immediately be noticed is that the nearest peak occurs for C10 followed by that of C3. Even the highest peak intensity occurs for C10 suggesting that the organization of CO_2 is pretty well around this terminal carbon atom of the butyl chain. The first minimum in the above mentioned order is 5·15, 6·95, 7·35, 6·45 and 5·75 Å. Again here we can notice that the first minimum is nearest in the case of C3, which suggests that the CO_2 has some specific interactions with either the C3 atom or the hydrogen atom attached to it. The second nearest is in the case of C10, which makes a narrow first peak in its case also. However, for C7 and C8, the first minimum occurs at very large distances resulting in broader first peak in their cases, which hints about the non-specific interaction of CO_2 with these atoms.

The running coordination number of CO_2 around different atoms of the cation is defined as the average number of CO_2 molecules in a shell of radius, r, around the particular atom. In figure 5, the running coordination numbers for the atoms, C3, C7, C8, C9, C10, have been presented up to 6 Å. The number of CO_2 molecules is more in the vicinity of C10 followed by C9 in the immediate neighbourhood of these atoms which is evident from the figure. However, with the increase in the distance almost all the curves overlap at around 6 Å, where the number of carbon atoms surrounding each of these atoms is almost the same. The coordination number which is defined as the number of atoms in the first coordination shell varies widely, since the first minimum for the different atoms plotted in the figure themselves varies widely from 5·15–7·35 Å. Since the volume varies as the cube of the radius, it is expected that the coordination number for the atoms with larger first minimum to be quite high compared to those with first minimum at smaller radial distance. The coordination numbers are found to be 2·4, 7·3, 8·8, 6·1
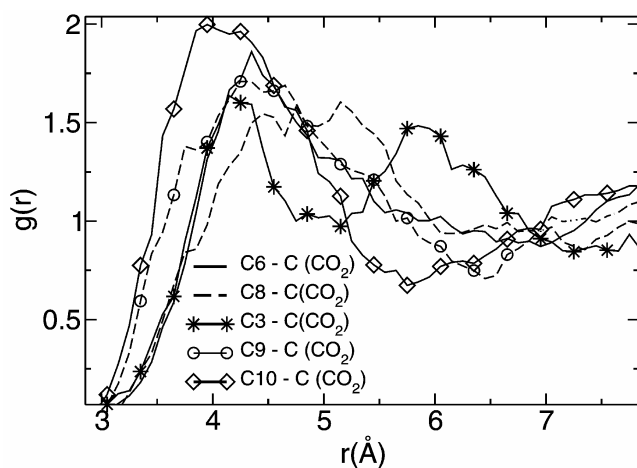

Figure 4. Radial distribution function of different carbon atoms of the cation with the carbon atom of CO_2 molecule. Symbols are shown infrequently for clarity.
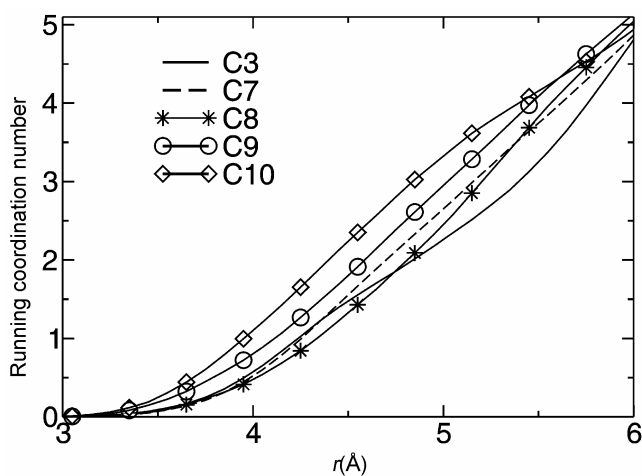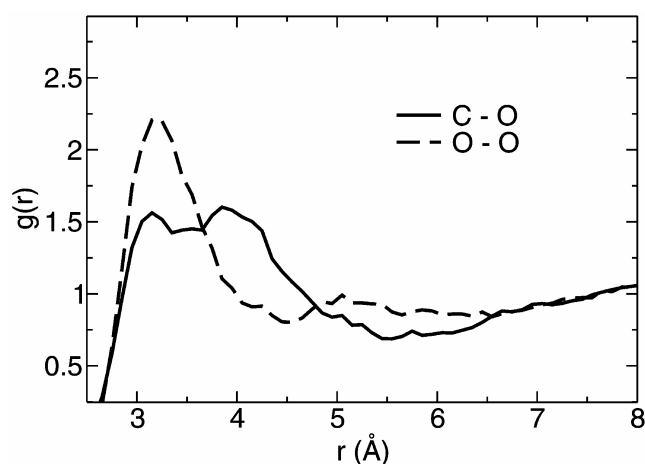

Figure 5. Running coordination number of carbon dioxide molecules around different carbon atoms of the cation. Symbols are shown infrequently for clarity.

Figure 6. Radial distribution function of oxygen atoms of CO_2 around the carbon and oxygen atoms of CO_2.

and 4·5 for C3, C7, C8, C9 and C10, respectively which directly varies as the location of the corresponding first minimum.

The radial distribution functions of oxygen atoms of CO_2 molecule around carbon and oxygen atoms of CO_2 are presented in figure 6. The peak arising due to the intramolecular contribution is not shown. The O–O RDF peaks at 3·15 Å with its first minimum at 4·55 Å followed by a small broad peak. The $C(CO_2)$–$O(CO_2)$ RDF has two similar peaks with comparable intensity at 3·15 Å and 3·85 Å separated by a small valley. This RDF has its first minimum at 5·55 Å. The coordination number of oxygen atoms around carbon up to the first minimum is 7·3 and oxygen atoms around oxygen atom of CO_2 is 4·2. In calculating these coordination numbers the intramolecular contribution has been subtracted. The high coordination number of 7·3 oxygen atoms around the carbon atom of CO_2 molecule suggests that carbon dioxide exhibits a good structure around itself.

3.3 *Quadrupole moments*

The ensemble average of the diagonal components of instantaneous quadrupole moment tensor of the cation are
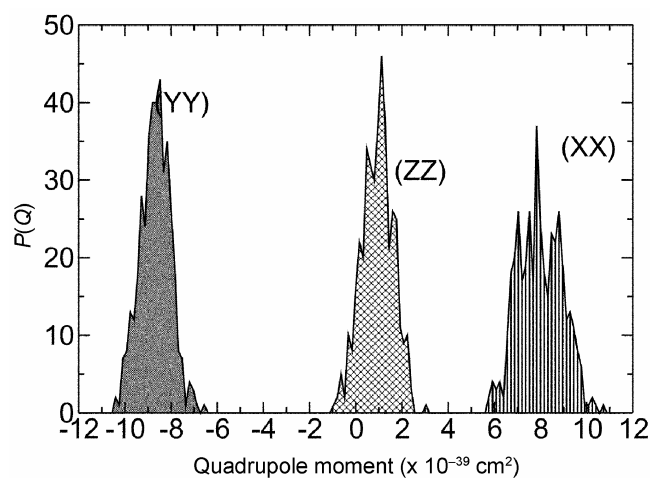

Figure 7. Distribution of diagonal components of instantaneous quadrupole moment of the cation along the directions defined in figure 2.

Table 1. The ensemble average of components of instantaneous quadrupole moment tensor in the case of cation and anion obtained from the CPMD simulations.

Component	Cation ($\times 10^{-39}$ cm^2)	Anion ($\times 10^{-39}$ cm^2)
XX	7·90 ± 0·94	0·00 ± 0·13
YY	−8·77 ± 0·66	0·02 ± 0·13
ZZ	0·86 ± 0·67	0·02 ± 0·11
XY	−0·08 ± 1·26	−0·02 ± 0·34
XZ	0·18 ± 0·83	0·05 ± 0·34
YZ	−0·03 ± 0·54	−0·03 ± 0·34

presented in figure 7. The components are along the directions defined in figure 2. It can be immediately noticed from the figure that the XX and YY components have positive and negative values, whereas the ZZ component is very small when compared to the other two components. The quadrupole moment depends on the definition of the coordinate system. The present definition of the coordinate axes, is in accordance with that defined by Lynden-Bell and coworkers (Resende Prado *et al* 2006), which would make the components of dipole moment along X and Y axes to be zero, thus making the Z-component of dipole moment to be equal in its magnitude. Since the cation considered is non-spherical, it is obvious that the charge distribution cannot be spherical and thus gives rise to a finite quadrupole moment.

However, the ensemble average for the off-diagonal components were closer to zero with a large deviation. In case of anion, the ensemble average of both diagonal and off-diagonal components of instantaneous quadrupole moment were zero with an intermediate deviation when compared to that of the deviations in the values of off-diagonal components of cation. This can be rationalized as the anion considered is the spherical PF_6 ion, which has near spherical charge distribution. For the sake of completion, the values of the ensemble average of the components of quadrupole moment tensor are presented in table 1.

3.4 *Vibrational dynamics*

The vibrational density of states obtained from the fourier transform of velocity auto correlation function for the atoms H(C3), H(C4) and H(C5) of the cation is shown in figure 8. The peaks corresponding to the stretching vibrations of the ring hydrogen atoms with the carbon appears
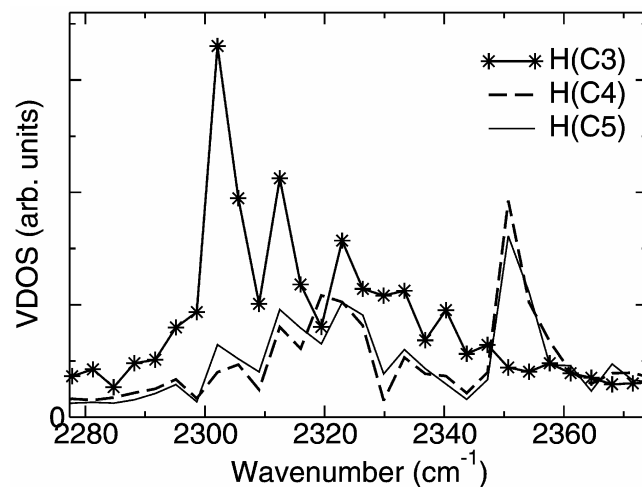

Figure 8. Vibrational density of states corresponding to the C–D stretching mode for the atoms, H(C3), H(C4) and H(C5).

here in the range 2300–2400 cm^{-1} since deuterium is used instead of hydrogen in the study. It can be noted that the wavenumber corresponding to H(C3) has been red shifted compared to H(C4) and H(C5) which are almost similar. Such a red shift in the stretching mode has also been observed previously in the case of [dmim][Cl] (Bhargava and Balasubramanian 2005). The reason for this shift is the weakening of the C–D stretching interaction due to the formation of a hydrogen bond between the H(C3) atom and the fluorine atoms of the anion.

4. Conclusions

Ab initio molecular dynamics studies have been carried out on [bmim][PF₆]–CO₂ mixture at 70 mole fraction concentration of CO₂. Partial radial distributions have been calculated to look at the structure of CO₂ molecules around the specific sites of the cation, which can give hint towards understanding the high solubility of CO₂ in room temperature ionic liquids. A slightly increased interaction of CO₂ with one of the carbon atoms attached to the ring over the other two is noticed. This can be due to specific interaction between the hydrogen atom which is slightly acidic, attached to C3 carbon atom of the imidazolium ring. The interaction of CO₂ with the cation of [bmim][PF₆] is consistent with the results observed in CO₂ clusters. In the current work, we have characterized the CO₂–CO₂ interactions and their effect on the CO₂ geometry through a study of instantaneous intramolecular O–C–O angle distributions in clusters and in bulk. The anisotropy in the polarizability due to inhomogeneous near neighbour arrangement makes the CO₂ molecules to deviate from the linear geometry.

Comparison of RDFs of carbon atom of CO₂ with different carbon atoms of the cation illustrates the specific interaction of CO₂ with either C3 or the hydrogen atom attached to it, with a narrow first peak in its RDF. There is better organization of CO₂ around the terminal carbon atom of the butyl chain attached to the ring which is evident from the peak intensity in its RDF. However, the organization is very poor around C8 which suggests that the CO₂ interacts with both the ring atoms as well as the tail, but not the atoms in between. The partial radial distribution of oxygen atoms of CO₂ around the carbon and oxygen atoms of CO₂ suggests that the CO₂ is structured around itself even in the [bmim][PF₆] mixture just as in the pure supercritical CO₂.

The instantaneous quadrupole moments of the cation and anion have been calculated from the localized charge centres. It is found that the ensemble average of the diagonal components of the instantaneous quadrupole moment have a finite value along two directions but the value along the third direction is small compared to the other two. The off-diagonal components average out to zero with fluctuations. The finite value for the quadrupole

moment of the cation is not difficult to rationalize, having known the structure of the cation. The spherical PF₆ anion has all its components of quadrupole moment tensor to be zero, which is evident since the instantaneous polarization can occur in any direction of the space in bulk liquid.

Acknowledgements

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