

# Hydrogen Bond Stabilization in 1,3-Dimethylimidazolium Methyl Sulfate and 1-Butyl-3-Methylimidazolium Hexafluorophosphate Probed by High Pressure: The Role of Charge-Enhanced C–H···O Interactions in the Room-Temperature Ionic Liquid

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The hydrogen bonding structures of room-temperature ionic liquids 1,3-dimethylimidazolium methyl sulfate and 1-butyl-3-methylimidazolium hexafluorophosphate have been studied by infrared spectroscopy. High-pressure infrared spectral profiles and theoretical calculations allow us to make a vibrational assignment of these compounds. The imidazolium C–H bands of 1,3-dimethylimidazolium methyl sulfate display anomalous non-monotonic pressure-induced frequency shifts. This discontinuity in frequency shift is related to enhanced C–H···O hydrogen bonding. This behavior is in contrast with the trend of blue shifts in frequency for the methyl C–H stretching mode at ca. 2960 cm<sup>−1</sup>. Our results indicated that the imidazolium C–H groups are more favorable sites for hydrogen bonding than the methyl C–H groups in the pure 1,3-dimethylimidazolium methyl sulfate. Nevertheless, both methyl C–H and imidazolium C–H groups are favorable sites for C–H···O hydrogen bonding in a dilute 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O mixture. Hydrogen bond-like C–H···F interactions were observed between PF<sub>6</sub><sup>−</sup> and H atoms on the alkyl side chains and imidazolium ring for 1-butyl-3-methylimidazolium hexafluorophosphate.

## Introduction

Room-temperature ionic liquids have found widespread application in the chemical industry as a nonvolatile, recyclable alternative to the traditional volatile organic solvents.<sup>1,2</sup> Ionic liquids exhibit an almost vanishing vapor pressure, the characteristic electrical conductivity of an ionic conductor, and a considerable gap between the melting point and the temperature of decomposition. The most extensively studied ionic liquids are the 1-alkyl-3-methylimidazolium salts.<sup>3–10</sup> The physical–chemical properties of these ionic liquids are strongly influenced by the nature of the *N*-alkyl imidazolium substituents and that of the counteranions. Nevertheless, little has been known for liquid structures of ionic liquids. Ionic liquids have a melting temperature around room temperature generally achieved by employing a bulky asymmetric organic cation to prevent ions from packing easily. The structure of ionic liquids results from a competition between screening and packing. This means a balance between long-range electrostatic forces and geometric factors. Various studies have been made to elucidate the role of weak hydrogen bonds, such as C–H···O and C–H···X, in the structure of ionic liquids.<sup>3–8</sup> Whereas the results of crystal structures are highly informative on the relative geometry changes, crystallography is silent on the question of whether C–H···O interactions are attractive or appear merely as a result of steric constraints. Thus, the observation of the C–H stretching

vibration is one of keys to characterize the presence of such a weak hydrogen bond and to evaluate the strength of the bond.

The increased understanding of weak interactions, such as C–H···O bonding, has required an expansion of the classical definition of hydrogen bonding. A wealth of recent work has transformed the notion of a C–H···O hydrogen bond from a sketchy hypothesis into a well-documented common observation. One of the intriguing aspects of weak hydrogen bonds is that the C–H covalent bond tends to shorten as a result of formation of a hydrogen bond with a Lewis base.<sup>11–13</sup> Despite the rather large number of papers devoted to the phenomenon of blue-shifting hydrogen bonds, the mechanism by which C–H bonds are strengthened by a C–H···O interactions is still the subject of debate.<sup>11–15</sup> As suggested by Hobza et al.,<sup>12</sup> the blue-shifting C–H···O may be attributed to the electron density transfer from the proton acceptor to the remote part of the proton donor.<sup>2</sup> Therefore, the strengthened C–H bond originates from a new mechanism, i.e., anti-hydrogen bond, in which a secondary effect or structural reorganization of the proton donor framework occurs. However, Scheiner<sup>13</sup> and Dannenberg<sup>15</sup> et al. have concluded, from a set of theoretical calculations, that anti-hydrogen bonds do not differ fundamentally from conventional hydrogen bonds. According to their results, the electron density redistribution upon hydrogen bond formation is similar for both the C–H···O and O–H···O interactions. The controversy is mainly caused by the inherent weakness of the C–H···O interactions.<sup>12–16</sup> Therefore, the study of methods that enhance C–H···O interactions is crucial if we are to obtain a clear and unified view of this important phenomenon. Several studies have shown the potential significant effect that pressure

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has on controlling the strength of C—H···O interactions.<sup>17–20</sup> Strengths of the C—H···O interactions can also be enhanced in molecular aggregates containing charges.<sup>18,19</sup> Our present study is an attempt to provide the experimental spectroscopic evidence of charge-enhanced C—H···O interactions.

Ionic liquids are distinguished from molten salts by virtue of their low melting points and effectively zero vapor pressure. These features arise because of their composition of a large organic cation, which in many cases is based upon 1,3-dialkylimidazolium cations, normally coupled with large, weakly coordinating anions.<sup>21–26</sup> With three hydrogen atoms bound to the imidazolium ring, two or three resolved absorption bands are observed with 1-alkyl-3-methylimidazolium salts in the IR spectral region between 3000 and 3200 cm<sup>−1</sup>.<sup>6</sup> These can be attributed to coupled aromatic C—H stretching vibrations. Several authors have observed the existence of hydrogen bonds between these aromatic C—H and basic counterions.<sup>3–8</sup> One of the main contributions to the hydrogen bond energy is the Coulombic interaction between the positive and negative partial charges on the hydrogen atom and the acceptor atom, respectively. This contribution will be especially strong for charge-assisted hydrogen bonds, which are present in ionic liquids. In this work, we demonstrate that C—H···O hydrogen bonding is one of the dominating forces in 1,3-dimethylimidazolium methyl sulfate. The observed pressure-dependent C—H infrared shift supports the proposed structures.

The use of pressure as a variable allows one to change, in a controlled way, the intermolecular interactions without encountering the major perturbations produced by changes in temperature and chemical composition.<sup>27,28</sup> Under high-pressure conditions, the relative weights of the strong intramolecular interactions responsible for molecular bonding, and of the weaker intermolecular forces defining the aggregation state, are altered, and the repulsive side of the intermolecular potential is explored. Nevertheless, the pressures used to investigate chemical systems typically range from ambient to several gigapascals.<sup>28</sup> As pressure is applied at ambient temperature, liquid water transforms at around 1 GPa to tetragonal ice VI, and at around 2 GPa to cubic ice VII. In the results and discussion section, we show that the high-pressure infrared technique is a sensitive method to probe the charge-enhanced hydrophobic structures in aqueous ionic liquids.

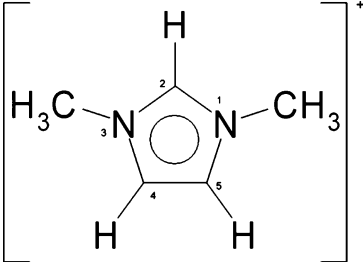
## Experimental Section

Samples were prepared using 1,3-dimethylimidazolium methyl sulfate (>97%), 1-butyl-3-methylimidazolium hexafluorophosphate (>96%), supplied by Fluka, and 99.97% D<sub>2</sub>O, supplied by Merck. 1,3-Dimethylimidazolium methyl sulfate is water soluble. A 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O mixture (mole fraction of ionic liquid: 0.1) was prepared by mixing. A diamond anvil cell (DAC) of Merrill-Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to ca. 3 GPa. Two type-IIa diamonds were used for mid-infrared measurements. The sample was contained in a 0.3-mm-diameter hole in a 0.25-mm-thick stainless steel gasket mounted on the diamond anvil cell. To reduce the absorbance of the samples, CaF<sub>2</sub> crystals (prepared from a CaF<sub>2</sub> optical window) were placed into the hole and compressed firmly prior to inserting the sample. A droplet of a sample filled the empty space of the entire hole of the gasket in the DAC, which was subsequently sealed when the opposed anvils were pushed toward one another.

Infrared spectra of the samples were measured on a Perkin-Elmer Fourier transform spectrophotometer (model Spectrum

**TABLE 1: DFT-Calculated C—H Stretching Frequencies (cm<sup>−1</sup>) and Infrared Intensities (km/mol)<sup>a</sup>**

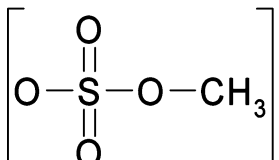
1,3-Dimethylimidazolium Cation



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calcd frequencies (intensities)	assignment
2954 (1)	sym. CH <sub>3</sub> stretch
2954 (8)	sym. CH <sub>3</sub> stretch
3034 (0)	asym. CH <sub>3</sub> stretch
3034 (0)	asym. CH <sub>3</sub> stretch
3048 (1)	asym. CH <sub>3</sub> stretch
3048 (0)	asym. CH <sub>3</sub> stretch
3152 (16)	asym. C(4,5)—H stretch
3157 (32)	C(2)—H stretch
3167 (8)	sym. C(4,5)—H stretch

Methyl Sulfate Anion



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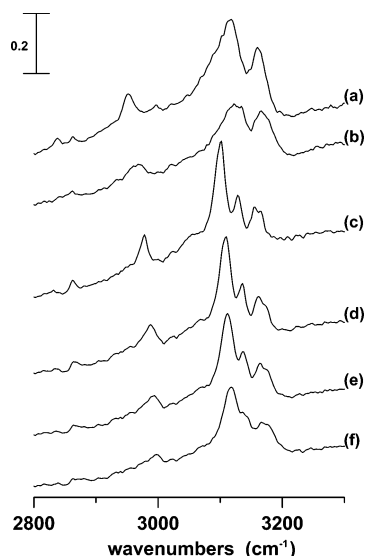
calcd frequencies (intensities)	assignment
2876 (100)	sym. CH <sub>3</sub> stretch
2933 (44)	asym. CH <sub>3</sub> stretch
2948 (54)	asym. CH <sub>3</sub> stretch

<sup>a</sup> Frequencies scaled by 0.955.

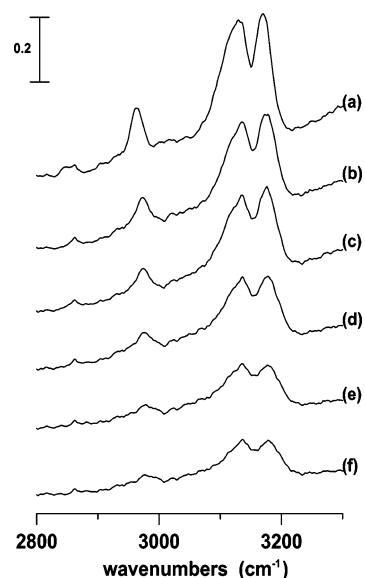
RXI) equipped with a LITA (lithium tantalite) mid-infrared detector. The infrared beam was condensed through a 5× beam condenser (Perkin-Elmer) onto the sample in the diamond anvil cell. Typically, we chose a resolution of 4 cm<sup>−1</sup> (data point resolution of 2 cm<sup>−1</sup>). For each spectrum, typically 1000 scans were compiled. To remove the absorption of the diamond anvils, the absorption spectra of DAC were measured first and subtracted from those of the samples. All experiments were performed at room temperature (ca. 25 °C).

## Results and Discussion

We performed density functional theory (DFT) calculations using the *Gaussian 98* program package;<sup>29</sup> Table 1 displays the predicted C—H stretching frequencies of the 1,3-dimethylimidazolium cation and the methyl sulfate anion. Harmonic vibrational frequencies were obtained from analytical second derivatives at the B3LYP/6-31+G\* level. The scaling factor for the calculated frequencies is 0.955.<sup>17–20</sup> Figure 1 presents infrared spectra of pure 1,3-dimethylimidazolium methyl sulfate obtained under ambient pressure (curve a), and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). As indicated in Figure 1a, the infrared spectrum of pure 1,3-dimethylimidazolium methyl sulfate exhibits three bands at 2953, 3114, and 3161 cm<sup>−1</sup> corresponding to C—H stretching modes. By comparing Figure 1a and Table 1, we found that



**Figure 1.** IR spectra displaying the C–H stretching region of pure 1,3-dimethylimidazolium methyl sulfate under (a) ambient pressure and at (b) 0.3, (c) 0.9, (d) 1.5, (e) 1.9, and (f) 2.3 GPa.



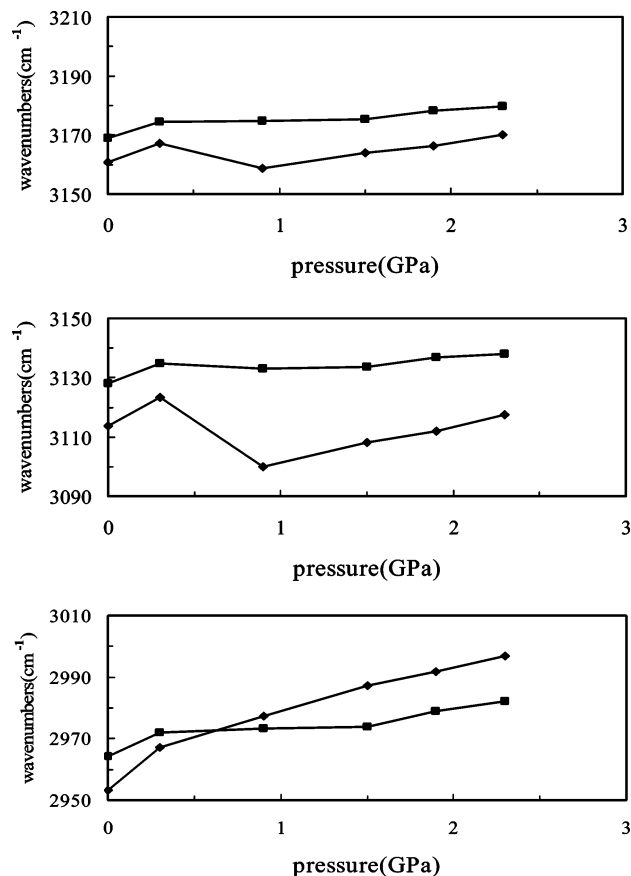
**Figure 2.** Pressure dependence of the IR spectra in the C–H stretching region of a 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O mixture having its mole fraction of 1,3-dimethylimidazolium methyl sulfate equal to 0.1 under the following pressures: (a) ambient, (b) 0.3 GPa, (c) 0.9 GPa, (d) 1.5 GPa, (e) 1.9 GPa, and (f) 2.3 GPa.

the 3114 and 3161  $\text{cm}^{-1}$  bands can be attributed to coupled imidazolium C–H stretching vibrations. The absorption band at 2953  $\text{cm}^{-1}$  should be attributed to C–H stretching modes of the methyl groups. As revealed in Figure 1b, the pressure dependence of the C–H stretches yielded a blue frequency shift. The C–H stretches were blue-shifted to 2967, 3123, and 3167  $\text{cm}^{-1}$  in Figure 2b. The imidazolium C–H stretching modes in the region 3050–3200  $\text{cm}^{-1}$  underwent dramatic changes in their spectral profiles as the pressure was elevated to 0.9 GPa in Figure 1c. Spectral changes were observed in Figure 1c, as the imidazolium C–H stretching bands became separated into three bands at 3100, 3128, and 3158  $\text{cm}^{-1}$ . As the sample was compressed, i.e., increasing the pressure from ambient (Figure 1a) to 2.3 GPa (Figure 1f), we observed a monotonic blue shift in frequency for the methyl C–H stretching mode at ca. 2960  $\text{cm}^{-1}$ . The blue shift may originate from the combined effect of the overlap repulsion enhanced by hydrostatic pressure,

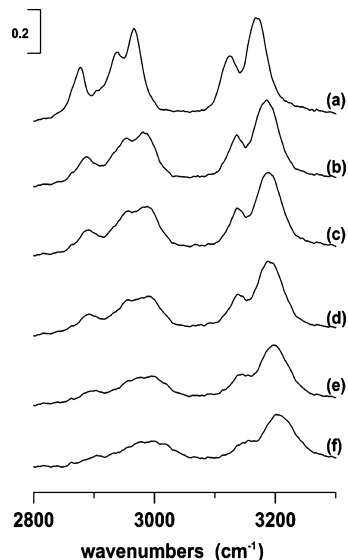
C–H $\cdots$ O contacts, and so forth. Pressure might also change the anharmonic nature of the potential well for C–H stretching in such a way as to increase the observed frequency.

It is interesting to note that the imidazolium C–H bands in Figure 1 display anomalous non-monotonic pressure-induced frequency shifts. Analysis of the pressure dependence of the imidazolium C–H absorption peaks yield blue frequency shifts at pressure below 0.3 GPa (Figure 1a,b), but a further increase in pressure leads to a red frequency shift of the dominant imidazolium C–H bands (Figure 1c). This discontinuity in frequency shift should be related to the mechanism of C–H $\cdots$ O hydrogen bonding. From the point of view of fundamental studies, the nature of C–H $\cdots$ O interactions continues to be an important and controversial subject. Dannenberg et al. have illustrated that electric fields can affect the strength of C–H $\cdots$ O interactions.<sup>15</sup> For example, in weak electric fields, the C–H bond of a methane–water complex shortens by up to 0.02 au as the electric field strength increases, and then, it lengthens as the field strength increases.<sup>15</sup> In light of this finding, we may be able to attribute the red shift observed in Figure 1c to strengthening of the imidazolium C–H $\cdots$ O contacts upon compression, i.e., a switch to imidazolium C–H $\cdots$ O hydrogen bond-like.

Figure 2 displays the infrared spectra of a 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O mixture (mole fraction of 1,3-dimethylimidazolium methyl sulfate: 0.1) obtained under ambient pressure (curve a), and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). The C–H stretching overlaps with the O–H stretching bands of H<sub>2</sub>O, so we studied C–H stretching vibrations in a solution of D<sub>2</sub>O rather than H<sub>2</sub>O. As the mixture was compressed, i.e., increasing the pressure from ambient (Figure 2a) to 0.3 GPa (Figure 2b), we observed a blue shift in frequency for the methyl C–H stretching band at ca. 2965  $\text{cm}^{-1}$ . We noticed, however, that no appreciable changes in the band frequency of the methyl C–H stretching band occurred upon further compression (cf. Figure 2b–d). This result is remarkably different from the monotonic blue shift in frequency that is revealed in Figure 1. A possible explanation for this effect is the hydrophobic hydration, i.e., hydrogen bond-like C–H $\cdots$ O, between methyl C–H groups and D<sub>2</sub>O under high-pressure conditions. To illustrate the frequency shift, the pressure dependence of the maximum positions of the C–H groups was plotted (Figure 3). To determine the correct band center, the peaks were analyzed by Gaussian functions. We see that the peak frequencies of the methyl and imidazolium C–H stretching bands in a dilute D<sub>2</sub>O solution have an unusual non-monotonic pressure dependence. Figure 3 demonstrates that it blue-shifts initially, then undergoes no change, and then blue-shifts again upon increasing the pressure. Our results indicate that both methyl C–H and imidazolium C–H groups are favorable sites for C–H $\cdots$ O hydrogen bonding in a dilute 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O mixture. Nevertheless, the imidazolium C–H groups are more favorable sites for hydrogen bonding than the methyl C–H groups in the pure 1,3-dimethylimidazolium methyl sulfate. In other words, water can be added to change the structure of pure 1,3-dimethylimidazolium methyl sulfate by introducing water–ionic liquid interactions. The presence of water makes the ionic liquid–ionic liquid associations looser. The single-crystal X-ray structure of pure 1,3-dimethylimidazolium methyl sulfate has been determined by Holbrey et al. and showed the formation of discrete ribbons comprising two anion–cation hydrogen-bonded chains aligned in opposite directions.<sup>22</sup> The only significant hydrogen bonds present are short contacts between the imidazolium ring



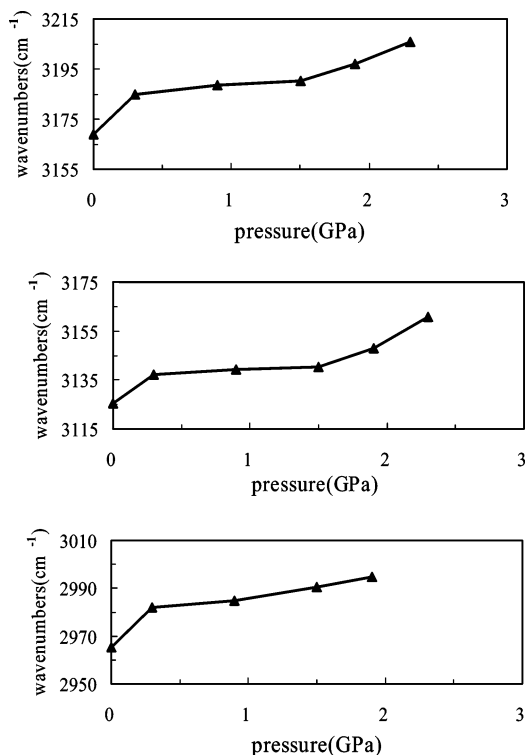
**Figure 3.** The C–H stretching frequencies of pure 1,3-dimethylimidazolium methyl sulfate (diamond) and 1,3-dimethylimidazolium methyl sulfate/D<sub>2</sub>O (square) vs the pressure.



**Figure 4.** IR spectra displaying the C–H stretching region of pure 1-butyl-3-methylimidazolium hexafluorophosphate under (a) ambient pressure and at (b) 0.3, (c) 0.9, (d) 1.5, (e) 1.9, and (f) 2.3 GPa.

hydrogens C(2), C(4), and C(5) and the three terminal oxygen atoms of the sulfate anion.<sup>22</sup> In the lack of crystal structure obtained at high hydrostatic pressure, we do not know whether the pressure-induced transformation in structure should be excluded or not.

We obtained a complementary insight into the C–H stretching spectral features revealed in Figure 4 by measuring the pressure-dependent variations in the infrared spectra of pure 1-butyl-3-methylimidazolium hexafluorophosphate. Figure 4

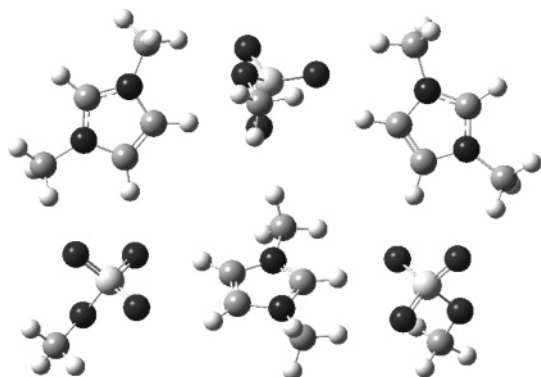


**Figure 5.** The C–H stretching frequencies of pure 1-butyl-3-methylimidazolium hexafluorophosphate vs the pressure.

presents infrared spectra of pure 1-butyl-3-methylimidazolium hexafluorophosphate obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). The absorption bands at 2850–3050  $\text{cm}^{-1}$  are assigned to C–H stretching vibrations of alkyl side chains. It is likely that these IR bands consist of multiple vibrations, although no attempt was made to deconvolute them. The coupled imidazolium C–H stretching vibrations exhibit two bands centered at ca. 3125 and 3170  $\text{cm}^{-1}$  in Figure 4a. As revealed in Figure 4 and Figure 5, the pressure-dependent results indicate that the peak frequencies of the alkyl and imidazolium C–H stretching bands have a non-monotonic pressure dependence. They blue-shifts initially (Figure 4a,b), then undergoes no change (Figure 4b–d), and then blue-shifts again upon increasing the pressure (Figure 4d–f). This discontinuity in frequency shift in Figure 4 is similar to the trend revealed in Figure 2. Our results indicate C–H $\cdots$ F interactions between the fluorine atoms of the  $\text{PF}_6^-$  anion and the imidazolium C–H. Additional hydrogen bond-like interactions were also observed between  $\text{PF}_6^-$  and the H atoms on the alkyl side chains in pure 1-butyl-3-methylimidazolium hexafluorophosphate. The aliphatic C–H stretching bands overlap each other and become one major broad peak and one minor peak at pressure above 1.9 GPa (Figure 4f,g). These results correlate with a recent *ab initio* calculation study of pure 1-butyl-3-methylimidazolium hexafluorophosphate that supports a strong interaction between the C(2) hydrogen and the fluorine atoms in  $\text{PF}_6^-$ .<sup>6</sup> An additional hydrogen bond was also predicted between the methylene group and  $\text{PF}_6^-$  in pure 1-butyl-3-methylimidazolium hexafluorophosphate.<sup>6</sup>

Figure 6 displays the optimized DFT-calculated structure of (1,3-dimethylimidazolium methyl sulfate)<sub>3</sub> complex with the participation of C–H $\cdots$ O interactions. The geometry optimization and vibrational frequencies of the cluster were calculated by using the Becke3LYP level with the 6-31+G\* basis set. Harmonic vibrational frequencies were obtained with a single





**Figure 6.** Optimized structures of (1,3-dimethylimidazolium methyl sulfate)<sub>3</sub>.

**TABLE 2: DFT-Calculated C–H Stretching Frequencies (cm<sup>-1</sup>), Infrared Intensities (km/mol), C–H Bond Lengths (Å), and C–H···O Lengths (Å) Involving the Bridging Hydrogen of (1,3-Dimethylimidazolium Methyl Sulfate)<sub>3</sub><sup>a</sup>**

calcd frequencies <sup>b</sup>	intensities	<i>r</i> (C–H)	<i>D</i> (C–H···O)	assignment
3049	481	1.0869	2.0343	bonded asym. C(4,5)–H
3076	482	1.0857	2.0574	bonded C(2)–H
3106	178	1.0835	2.0898	bonded sym. C(4,5)–H

<sup>a</sup> Structure illustrated in Figure 5. <sup>b</sup> Frequencies scaled by 0.955.

**TABLE 3: Changes in Mulliken Atomic Charge (me), Changes in C–H Stretching Frequencies (cm<sup>-1</sup>), and Changes in C–H Band Lengths (Å) Involving the Bridging Hydrogen<sup>a</sup>**

$\Delta Q$ (me)	$\Delta \nu$ (cm <sup>-1</sup> ) <sup>b</sup>	$\Delta r$ (C–H) (Å)	assignment <sup>a</sup>
76	–103	0.0071	bonded asym. C(4,5)–H
67	–81	0.0056	bonded C(2)–H
66	–61	0.0037	bonded sym. C(4,5)–H

<sup>a</sup> Structures illustrated in Figure 5. <sup>b</sup> Frequencies scaled by 0.955.

factor of 0.955. As revealed in Table 2, the characteristic bonded C–H is red-shifted to lower frequencies at 3049, 3076, and 3106 cm<sup>-1</sup> for bonded asymmetric C(4,5)–H, bonded C(2)–H, and bonded symmetric C(4,5)–H, respectively. It is instructive to note that the calculated results may only provide qualitative support for the suggested C–H···O interactions, since the calculations are based on gas-phase structure of the trimer complex. Table 3 indicates electron density loss from the bridging hydrogen atom as the result of C–H···O hydrogen bond formation. It is known that the bridging proton becomes more positively charged as the result of hydrogen bond formation. This trend is characteristic of conventional hydrogen bonds as well as C–H···O hydrogen bonds.<sup>30</sup> As shown in Table 3, the bridging C–H bond elongations are accompanied by a red shift of the associated C–H stretching frequency. The changes in Mulliken atomic charges of the C(2)–H bridging hydrogen are less than that of the asymmetric C(4,5)–H bridging hydrogen. This observation may indicate the steric effect of the methyl groups adjacent to the C(2)–H. Table 4 shows the calculated imidazolium C–H frequencies of the (1,3-dimethylimidazolium methyl sulfate)<sub>2</sub> complex. As revealed in Table 4, the frequency values of free C(2)–H and free C(4)–H for the dimer are similar to those for the isolated species (see Table 1). We note that the calculated bonded C(2)–H is located at higher frequency (3132 cm<sup>-1</sup>) in Table 4 than it is in Table 2. The results suggest that the reorganization of geometry and cluster size may enhance C–H···O hydrogen bonds as the high pressures are applied. Finally, the possibility of pressure-induced crystal polymorphism<sup>31</sup> may not be excluded in this study. In

**TABLE 4: DFT-Calculated C–H Stretching Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol) of (1,3-Dimethylimidazolium Methyl Sulfate)<sub>2</sub>**

calcd frequencies <sup>a</sup>	intensities	assignment
3038	329	bonded C(4,5)–H <sup>b</sup>
3068	248	bonded C(4,5)–H <sup>b</sup>
3070	336	bonded C(5)–H <sup>c</sup>
3132	189	bonded C(2)–H <sup>c</sup>
3158	7	free C(2)–H <sup>b</sup>
3160	2	free C(4)–H <sup>c</sup>

<sup>a</sup> Frequencies scaled by 0.955. <sup>b</sup> Imidazolium #1. <sup>c</sup> Imidazolium #2.

the lack of crystal structure at high hydrostatic pressure, we do not know how significant this effect is.

## Conclusions

The pressure-dependent IR bands in the C–H stretching region may prove useful as potential spectroscopic probes for studies of molecular interactions in ionic liquids. The imidazolium C–H bands display anomalous non-monotonic pressure-induced frequency shifts. This discontinuity in frequency shift is related to enhanced C–H···O hydrogen bonding. The high-pressure approach made it possible for us to detect intermolecular contacts of two types: ionic liquid–ionic liquid and water–ionic liquid. In the pure 1,3-dimethylimidazolium methyl sulfate, the imidazolium C–H groups are more favorable sites for hydrogen bonding. However, both methyl C–H and imidazolium C–H groups are favorable hydrogen bonding sites in a dilute aqueous mixture. Increasing water content was found to appreciably change the structure of pure 1,3-dimethylimidazolium methyl sulfate through the participation of water in imidazolium C–H and methyl C–H mediated hydrogen bonds.

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