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Synthesis, NMR, IR, Raman spectra and DFT calculations of 1-octyl-1,4-diazabicyclo [2.2.2] octan-1-ium bis(trifluoromethylsulfonyl)imide

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Journal of Molecular Structure

Synthesis, NMR, FT-IR, FT-Raman spectra and thermal studies of Choline bis(trifluoromethylsulfonyl)imide Ionic Liquid combined with DFT Calculations. --Manuscript Draft--

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Abstract:	<p>In an environmentally friendly manner, the reaction of choline chloride ($[\text{CHOL}^+][\text{Cl}^-]$) with lithium bis(trifluoromethanesulfonyl)imide ($[\text{Li}^+][\text{CF}_3\text{SO}_2)_2\text{N}^-]$) in water leads to the formation of the ionic liquid (IL) choline bis(trifluoromethanesulfonyl)imide ($[\text{CHOL}^+][\text{CF}_3\text{SO}_2)_2\text{N}^-]$). The ionic liquid IL have been characterized by using ^1H, ^{13}C and ^{19}F-NMR, FT-IR and FT-Raman spectroscopies. The experimental spectra have been combined with B3LYP/6-311++G** calculations to obtain complete assignments of vibrational spectra of IL and its cation by using the scaled mechanical quantum force field (SQMFF) methodology and the Molvib program. Here, we reported the 102 vibration modes of IL and the 36 of cation together with the scaled force constants for both species. The predicted structure shows the formation of the S-O...H interaction in agreement with experiments. Very good correlations evidence the comparisons among the experimental and theoretical NMR, FT-IR and FT-Raman spectra. The existence of the strong S-O...H interaction and other weak H bonds interactions are supported by NBO and AIM calculations. The analyses of gap values suggest a higher reactivity of IL in gas phase and a higher stability in aqueous solution. The comparison of this IL with $[\text{C}_8\text{DABCO}^+][\text{CF}_3\text{SO}_2)_2\text{N}^-]$ reveal that the $[\text{C}_8\text{DABCO}^+]$ cation increases the reactivity of latter IL in solution. Besides a detailed characterization of its thermal (TGA/DSC) is presented. Investigation of the thermal properties demonstrated that the investigated IL can be classified as an ionic liquid, as the melting temperature is near room temperature. A glass transition and a cold crystallization were revealed at -75 and -26 °C.</p>
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To

Editor J. Molecular Structure

Dear Editor;

I send the article for consideration to publication in Journal of Molecular Structure, "**Synthesis, NMR, FT-IR, FT-Raman spectra and thermal studies of Choline bis(trifluoromethylsulfonyl)imide Ionic Liquid combined with DFT Calculations.**", by Boumediene Haddad, Silvia Antonia Brandán, María V. Castillo, Touil Aya Khadidja, Annalisa Paolone, Bekhaled Fetouhi, Nathalie Bar, Didier Villemin, Mustapha Rahmouni, Serge Bresson

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With my best regards,

Sincerely yours,

Corresponding author.

(Pr. Boumediene HADDAD)



- **MANUSCRIPT TITLE AND AUTHORS:** " **Synthesis, NMR, FT-IR, FT-Raman spectra and thermal studies of Choline bis(trifluoromethylsulfonyl)imide Ionic Liquid combined with DFT Calculations** ", by Boumediene Haddad, Silvia Antonia Brandán, María V. Castillo, Touil Aya Khadidja, Annalisa Paolone, Bekhaled Fetouhi, Nathalie Bar, Villemin, Mustapha Rahmouni, Serge Bresson

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- **MANUSCRIPT'S SCIENTIFIC MOTIVATION:** In an environmentally friendly manner, the reaction of choline chloride ($[\text{CHOL}^+][\text{Cl}^-]$) with lithium bis(trifluoromethanesulfonyl)imide ($[\text{Li}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) in water leads to the formation of the ionic liquid (IL) choline bis(trifluoromethanesulfonyl)imide ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$). The ionic liquid IL have been characterized by using ^1H , ^{13}C and, ^{19}F -NMR, FT-IR and FT-Raman spectroscopies. The experimental spectra have been combined with B3LYP/6-311++G** calculations to obtain complete assignments of vibrational spectra of IL and its cation by using the scaled mechanical quantum force field (SQMFF) methodology and the Molvib program. Here, we reported the 102 vibration modes of IL and the 36 of cation together with the scaled force constants for both species. The predicted structure shows the formation of the S-O...H interaction in agreement with experiments. Very good correlations evidence the comparisons among the experimental and theoretical NMR, FT-IR and FT-Raman spectra. The existence of the strong S-O...H interaction and other weak H bonds interactions are supported by NBO and AIM calculations. The analyses of gap values suggest a higher reactivity of IL in gas phase and a higher stability in aqueous solution. The comparison of this IL with $[\text{C}_8\text{DABCO}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ reveal that the $[\text{C}_8\text{DABCO}^+]$ cation increases the reactivity of latter IL in solution. Besides a detailed characterization of its thermal (TGA/DSC) is presented. Investigation of the thermal properties demonstrated that the investigated IL can be classified as an ionic liquid, as the melting temperature is near room temperature. A glass transition and a cold crystallization were revealed at -75 and -26 °C.

Pr. Boumediene HADDAD

HIGHLIGHTS

- ✓ Choline bis(trifluoromethanesulfonyl)imide ionic liquid was synthesized.
- ✓ Characterization by NMR, FT-IR and FT-Raman spectroscopies.
- ✓ The 102 vibration modes of IL and the 36 of cation are reported.
- ✓ NBO and AIM calculations support the existence of strong S-O···H interactions.
- ✓ Thermal (TGA/DSC) properties are presented.

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Synthesis, NMR, FT-IR, FT-Raman spectra and thermal studies of Choline bis(trifluoromethylsulfonyl)imide Ionic Liquid combined with DFT Calculations.

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Abstract

In an environmentally friendly manner, the reaction of choline chloride ($[\text{CHOL}^+][\text{Cl}^-]$) with lithium bis(trifluoromethanesulfonyl)imide ($[\text{Li}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) in water leads to the formation of the ionic liquid (IL) choline bis(trifluoromethanesulfonyl)imide ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$). The ionic liquid IL have been characterized by using ^1H , ^{13}C and, ^{19}F -NMR, FT-IR and FT-Raman spectroscopies. The experimental spectra have been combined with B3LYP/6-311++G** calculations to obtain complete assignments of vibrational spectra of IL and its cation by using the scaled mechanical quantum force field (SQMFF) methodology and the Molvib program. Here, we reported the 102 vibration modes of IL and the 36 of cation together with the scaled force constants for both species. The predicted structure shows the formation of the S-O \cdots H interaction in agreement with experiments. Very good correlations evidence the comparisons among the experimental and theoretical NMR, FT-IR and FT-Raman spectra. The existence of the strong S-O \cdots H interaction and other weak H bonds interactions are supported by NBO and AIM calculations. The analyses of gap values suggest a higher reactivity of IL in gas phase and a higher stability in aqueous solution. The comparison of this IL with $[\text{C}_8\text{DABCO}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ reveal that the $[\text{C}_8\text{DABCO}^+]$ cation increases the reactivity of latter IL in solution. Besides a detailed characterization of its thermal (TGA/DSC) is presented. Investigation of the thermal properties demonstrated that the investigated IL can be classified as an ionic liquid, as the melting temperature is near room temperature. A glass transition and a cold crystallization were revealed at -75 and -26 $^\circ\text{C}$.

KEYWORDS: Choline-ionic liquids; bis(trifluoromethylsulfonyl)imide, NMR; Raman/IR vibrational spectra; TGA /DTA thermal analysis; DFT calculations.

1. Introduction

For several years, there has been an increasing concern in the development of new solvents, in particular ionic liquids (ILs) and deep eutectic solvents (DES) [1] meeting certain green chemistry criteria and considering as potential environmentally friendly alternative solvents [2]. Both categories of solvents present attractive characteristics since they have a negligible saturated vapor pressure, are non-flammable and have good thermal and chemical stability [3]. These solvents can have very good ionic conduction when ionic molecules are integrated into the mixture [4] opening the possibility of using them in energy-related fields. In addition, the specific properties of ILs, modulated by the appropriate choice of couple anion–cation [5], justify their use in many fields such as the chemical industry [6], medicine [7], nanotechnologies [8], the field of energy [9] and in particular electrochemistry [10] or even in renewable energies [11]. Now, most of researchers have been focusing their attention on the synthesis of new DES and in the study of their properties for device applications. Thus, choline derivatives have been the subjects of numerous studies and play an essential role in the evolution of green chemistry. Therefore, the quaternary ammonium salt choline, also known as hepacholine, biocolina and lipotril and cholonium, has shown interesting and unique physico-chemical properties in various processes extraction [12]. Some metal-free choline-based ionic liquids (ILs) were developed by Liu et al [13], with the aim to use them as catalysts in the glycolysis of PET. Rabhi et al. [14] evaluated a choline bis(trifluoromethylsulfonyl)imide based ionic liquid for the extraction of o-xylene, o-cresol and acetonitrile from the aqueous solution showing a good potential. Domanska et al. [15] found that $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ strongly interact with pyridene, leading to high heptane/pyridine selectivity, while Cesari et al. [16] demonstrated that $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ is an appropriate solvent to recover phenolic compounds from water. Ribeiro et al. [17] have investigated choline oxyanions salts attached with the acetate and dihydrogen phosphate anions by using the IR and Raman spectra. These authors evidenced the spectral marks of the H-bonds interactions and intramolecular motions of the ions. In other study, Ludwig et al. have revealed the effect of structural and dynamical behaviour of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ on melting temperatures, viscosities and conductivities [18]. Nockemann et al. [19] reported binary mixtures of water with temperature effect on the thermophysical, and thermomorphic properties, as well as the optical properties of choline bis(trifluoromethanesulfonyl)imide, while Zhuravlev et al. [20] studied the electronic and vibrational properties of ILs synthesized with choline halides. To date, the experimental structure of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ was determined by Nockemann et al. [19] by XRD but there are no studies reported on

1 topological, electronic and vibrational properties of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ nor any detailed
2 assignments of its vibrational spectra. Hence, the present work aims to synthesize the
3 $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL through a simple metathesis reaction, and to characterize it by
4 using ^1H , ^{13}C and ^{19}F -NMR, infrared, Raman spectroscopy combined with computational
5 techniques in order to perform the complete vibrational assignments. Hence, its scaled
6 harmonic force constants are reported. Moreover, the physical properties were investigated
7 by DSC and TGA while the inter- and intra-molecular interactions are analyzed utilizing
8 natural bond orbital (NBO) and atoms in molecules (AIM) calculations in addition to the IR
9 and Raman spectra. Reactivities and behaviours of IL in different media are also predicted.
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17 **2. Experimental**

18 **2.1. Materials and methods**

19 In the current work, all materials used had analytical grades and were not purified before
20 being utilized. Choline chloride ($[\text{CHOL}^+][\text{Cl}^-]$) (purity: 98%), and lithium
21 bis(trifluoromethanesulfonyl)imide ($[\text{Li}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) were commercially available from
22 Fluka. Deionized H_2O was obtained by means of a Millipore ion-exchange resin deionizer.
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25 Choline bis(trifluoromethanesulfonyl)imide, ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was synthesized at the
26 LCMT *Molecular and Thio-organic Chemistry Laboratory*. Ionic liquid of
27 ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) is prepared following our previous works [21-23], and was
28 characterized by intermediary of NMR, IR and Raman spectroscopy. Firstly, the NMR
29 analysis include ^1H -NMR (600 MHz), ^{13}C -NMR (150.87 MHz) decoupled only from ^1H
30 and ^{19}F . ^{19}F -NMR (564.04 MHz) spectra were acquired on a Bruker-Neo 600MHz
31 instrument; the chemical shifts were referenced to TMS as external standard. The spectra were
32 measured in dimethylsulfoxide ($\text{DMSO-}d_6$), and the $\text{DMSO-}d_6$ residual peak was used as the ^1H
33 internal reference (quintuplet $\delta = 2.5$ ppm), while the $\text{DMSO-}d_6$ central peak at $\delta = 39.5$ ppm
34 was used as the ^{13}C reference. The Raman spectrum of ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was
35 acquired by a Vertex 70-RAM II Bruker FT-Raman spectrometer in the $4000\text{-}45$ cm^{-1} range
36 (resolution = 1 cm^{-1} , 128 scans for each spectrum) at room temperature. The FT-IR spectrum
37 of ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was recorded by on a Bruker Vertex II-70RAM Spectrometer
38 between 600 and 4000 cm^{-1} (resolution = 1 cm^{-1} , 64 scans per spectrum).
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51 The thermal stability of ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was examined by thermogravimetric
52 analysis (TGA) between 25 and 700 $^\circ\text{C}$, while the phase transition were examined by
53 differential scanning calorimeter (DSC) between -80 and 200 $^\circ\text{C}$. A Mettler Toledo DSC3 and
54 a Setaram Setsys Evolution 1200 TGA system were used for DSC and TGA measurements,
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2 which were both performed in an inert (argon) helium flux of 60 mL/min. The temperature
3 rate for the measurements were 5 (DSC) or 10 °C/min (TGA).

4 In the present study, the choline bis(trifluoromethanesulfonyl)imide ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$)
5 was synthesized through a simple anion exchange reactions as shown in **Scheme 1**. A solution
6 of 2.87g (0.1M) of lithium bis(trifluoromethylsulfonyl)imide ($[\text{Li}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) in 15 mL of
7 distilled water and a solution of 1.32g (0.1M) of Choline chloride ($[\text{CHOL}^+][\text{Cl}^-]$) in 15 mL
8 of distilled water were mixed in a flask with stirring for 1 hour at room temperature. After
9 isolation of ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) (bottom) from lithium chloride (top) by centrifugation
10 for 60 min in the aqueous phase, the obtained ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was washed a few times
11 by deionized water in order to remove chloride impurities and then dried in a vacuum better
12 than 1 mbar for 12 h, to obtain a colorless liquid. Finally, ($[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$) was dried
13 in Ca_2Cl_2 to remove water traces. Coulometric Karl Fischer titration, performed by a
14 Metrohm 831 instrument, found a water content lower than 523 ppm.
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27 **Scheme 1.** General synthesis of Choline bis(trifluoromethylsulfonyl)imide.
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31 **2.2. Computational details**

32 The starting initial structures of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL and its cation were extracted from
33 the CIF file of Ref [19] while the anion was removed from the IL using *GaussView*[26]. The
34 structures of the cation and of the IL were optimized both in vacuum and in an aqueous
35 solution at the B3LYP/6-311++G** level of theory/basis set, by means of Gaussian 16
36 [24,25,27]. The structure of $[(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ anion was taken from that previously reported at
37 the same level of theory [21,22]. The integral equation-formalism polarizable continuum
38 model (IEF-PCM) and universal solvation method (SMD) calculations were used for all
39 calculations in solution [28-30]. The MOLDRAW program was applied for the volume
40 calculations [31]. A calculation of the vibration frequencies was performed for all optimized
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52 The NBO and AIM2000 programs were employed to calculate atomic charges, bond orders
53 stabilization energies, and topological properties [32-35]. The reactivity of the species was
54 calculated based on frontier orbitals [21,22,36-37]. Harmonic force fields of the species were
55 calculated and the assignment of the vibrations was performed accordingly. For that purpose,
56 the scaled quantum mechanical force field (SQMFF) methodology was employed using
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MOLVIB [38-40]. The Raman spectra predicted for the three species in activities were transformed to intensities [41]. The electronic spectra in aqueous solution were investigated using time-dependent DFT calculations (TD-DFT) performed by Gaussian 16 [24,25,27]. The NMR spectra were calculated applying the Gauge-Independent Atomic Orbital (GIAO) method [42].

3. Results and discussion

3.1. NMR spectra analysis

The synthesized $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL was characterized by using ^1H , ^{13}C and ^{19}F -NMR spectroscopy technique. The experimental ^1H , ^{13}C and ^{19}F -NMR are given respectively in **Figs. 1, 2 and 3**. The NMR spectra show the following signals. **^1H -NMR** (600 MHz, $\text{DMSO-}d_6$) δ_{H} (ppm): 3.10 (s, CH_3 , 9H), 3.40 (t, NCH_2 , 2H, $J=1.8$ Hz), 3.83 (tt, CH_2 , 2H, $J=5.4$ and 1.4 Hz), 5.29 (t, OH, $J_{\text{H,OH}}=5.4$ Hz). **^{13}C -NMR** (150.87) MHz, decoupled with ^1H , coupled with ^{19}F , DMSO) δ_{C} (ppm): 52.9, 55.2, 66.8, 116.1, 118.3, 120.12, 122.36. **^{19}F -NMR** (564.04 MHz, DMSO) δ_{F} (ppm): -78.97 (s, (CF_3)).

In the ^1H -NMR spectrum, the single intense peak at 3.10 ppm corresponds to nine protons (H_a) of three methyl groups bounded to the nitrogen atom $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]$ with an integration of around 9.00 which have the same chemical and magnetic equivalence. The triplet at 3.40 ppm indicates protons (H_b) of methylene groups $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]$, while the methylene protons (H_c) $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]$ are centred at 3.83 ppm. Both triplets have an integration of around 2.00. On the other hand, the signal at $\delta=5.29$ ppm with an integration of around 1.00 can be attributed to the proton (H_d) of hydroxyl group in the choline cation $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]$. The appearance of this signal as a triplet indicates that the $-\text{OH}$ group of $([\text{CHOL}^+])$ was coupled with adjacent protons of the CH_2 through the C-O-H. The agreement of these integration values evidence the structure of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ and its high purity. Note that the experimental ^{13}C -NMR spectrum decoupled with ^1H but not decoupled with ^{19}F also further corroborate the structure of $([\text{CHOL}^+])$ cation. Moreover, one finds a quartet (intensity 1,3,3,1) at 116.1, 118.3, 120.1, 122.4 ppm, consistently with the expected signals of the $([\text{NTf}_2^-])$ anion, $\delta=119.21$ ppm with $J_{\text{C-F}}\approx 312$ Hz [43]. Furthermore, ^{19}F -NMR spectrum presents a singlet at $\delta=-78.97$ ppm, in agreement with the presence of F atoms. This demonstrates the effectiveness of the anionic reaction.

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Figure 1. Experimental Hydrogen atom labeling and ^1H -NMR spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

Figure 2. Experimental ^{13}C -NMR spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

Figure 3. Experimental ^{19}F -NMR spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

The computed ^1H , ^{13}C and ^{19}F -NMR chemical shifts are reported in Tables 1, 2 and 3, where they are compared with the experimental values. The predicted values for the F atoms of anion and IL were obtained using $\text{CCl}_3\text{-F}$ as reference. The optimized structures of cation, anion and IL are reported in **Figure 4**.

Figure 4. Optimized structures of cation, anion and $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ionic liquid in gas phase by using the B3LYP/6-311G** level of theory showing the formation of intra-molecular H bond between an O atom of S=O group and the H atom of OH group.

Experimental and computed values show better agreement for the ^1H and ^{19}F nuclei of the IL (0.57 and 21.62 ppm) than of the cation (1.01 and 32.75 ppm) while, on the contrary, for the ^{13}C nucleus a higher RMSD value is observed for IL (7.16 ppm) as compared to value of cation (4.32 ppm). From the good concordances observed for the ^1H and ^{13}C nucleus the molecular structure of IL was confirmed despite the lower correlations observed for the ^{19}F nucleus, as also was observed for the same anion in ILs with different cations [21,22]. The high RMSD observed for the ^{19}F nucleus could be justified by the predicted C-F...H interactions, as we will see in the next section. In general, the observed variations could be ascribed to different solvent used and to other types of interactions in solution not considered in the calculations.

3.2. Optimizations in gas phase and aqueous solution

Figure 4 shows the optimized structure of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL in which one can note an intra-molecular H bond between the O atom of a SO_2 group of $[(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ and hydrogen atom of OH group of $[\text{CHOL}^+]$. **Table 4** shows the calculated total energies, volume (V) and dipole moment (μ) of the IL, anion and cation in different media. The anion presents higher μ and V in the two media than the cation and both species increase these values in the IL. Higher μ and V values are observed for the IL in solution (24.19 D and 317.6 \AA^3), as compared to the gas phase (14.22 D and 311.5 \AA^3). In solution, the cation and IL show a volume expansion, as a consequence of the increase in their μ values, while the anion decreases its V in water. **Figure S1** shows the different magnitudes, directions and orientations of the μ vectors of the three species. The vectors of cation and anion are shown

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in gas phase while for the IL they are reported in both media. In the IL the vector is oriented from the N of anion to the N of cation changing the direction and orientation in solution. Moreover, one can note that the values of total energies corrected by the Zero-point vibrational energy (ZPVE) are less negative than the non corrected ones, as observed in other ILs [21,22]. The difference between the uncorrected energy of the IL (-2156.5257 Hartrees) and the sum of the energies of the isolated cation and anions (-328.7894 and -1827.6092 = -2156.3986 Hartrees) is the interaction energy between the ions.

Table 5 shows some predicted distances in the IL: the closest distances between anion and cation involve S2-O3...H18 (1.832 Å) and S9-O10...H25 (2.160 Å) in the gas phase while in solution the closest distance is that of the former groups (1.948 Å). In Table 5 it is possible to observe short C-F...H distances, which can justify the high ¹⁹F chemical shifts predicted for IL.

In **Table 6** the geometrical parameters for the IL calculated in the two media are compared with the corresponding experimental ones reported in Ref [19] in the solid state. A better agreement is found for distances (0.055-0.029 Å) than for angles (1.8-1.3 °). The values calculated in solution display in general a lower agreement with the experiments. Regarding the values, it is observed that the predicted bond O3-H18 lengths in both media (1.832, 1.948 Å) are different from the experimental one (1.703 Å), possibly because of the formation of hydrogen bonds in the real system. Also, as a consequence of cation-anion interactions the bond S2-O3-H18 angles change from 137.4 ° in gas phase to 130.0 ° in solution while the experimental value is slight lower (127.8 °). Thus, from Fig. 4 we observed the formation of S2-O3...H18 interaction and, for this reason, the related parameter (N1-S2-O3) changes notably in both media. On the other hand, few change is observed in the S2=O3 bond length (1.473 Å) in gas phase; however, a lower value (1.469 Å) than the experimental one (1.475 Å) is observed in solution. Obviously, the heavier S and O atoms are more difficult to modify than lighter H ones. The parameters related to CF₃ groups of anion and the quaternary N16 atoms of cation have extremely small changes in both media. However, in solution, the geometrical parameters of N1 atoms change probably because the lone pairs could be hydrated.

3.3. Atomic charges, molecular electrostatic potentials and bond orders

The Mulliken, Merck-Kollman (MK) and atomic natural population analysis (NPA) charges for all atoms of IL are compared in **Table S1**. The graphic comparison of the charges of N, C, O and F atoms are displayed in **Figure S3**. The variations of MK and NPA charges on those atoms follow practically the same behaviours in both media. Small values of Mulliken

1 changes are calculated in a vacuum, while, on the contrary, some changes in these values
2 occur in solution. The Mulliken charges on S2 increases in gas phase while it decreases on
3 S9. The MK charge on quaternary N16 is positive in both media, as expected for the cation,
4 while NPA and Mulliken charge is negative. The values of NPA and MK charges of O, C and
5 F show little change with the medium. In this study, the three types of charges in the two
6 media show on N1 negative values, which are expected since that atom belongs to the anion.
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8 To analyse the reaction sites in the IL and, also the strength of different bonds, the bond
9 orders (BO) expressed as Wiberg indexes and the molecular electrostatic potentials
10 (MEP) have been studied in both media. **Table S2** shows the two parameters for the
11 [CHOL⁺][(CF₃SO₂)₂N⁻]IL in the two media. The MEP values change as expected considering
12 the electronegativity of the atoms in the order F > O > S > N > C > H. The O atoms of the
13 anion display the higher variations (0.055-0.019 a.u.) passing from vacuum to solution, while
14 for the S (0.023 a.u.) and C (0.017-0.015 a.u.) atoms, lower values are predicted. Moreover,
15 the lowest MEP values are calculated for the most labile atoms in both media (H18); hence, it
16 is clear that this atom forms an H bond with the O3 atom of SO₂ group belonging to anion.
17 Figure S3 reports the MEP surfaces of IL in the two media and one can visualize (i) the
18 various electrophilic and nucleophilic sites of reaction and, (ii) the notable reduction of the
19 energy in solution. The value decreases from 0.074 a.u. in vacuum to 0.011 a.u. in solution.
20 From figure S3 it is observed that the regions corresponding to cation presents blue colours
21 and are electrophilic, which is expected because it is positively charged, while the red colours
22 corresponding to anion are located on the O atoms and are the nucleophilic sites.
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24 The bond orders (BO) by atom, expressed as Wiberg indexes, for the IL in the two media are
25 displayed in Table S2: the values of all the atoms change in solution, with the exception of S2
26 and H36 atoms that have similar values independently of the medium. The slight differences
27 observed in these values could be related to the formation of hydrogen bonds in solution.
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29 **3.4. NBO and AIM calculations**

30 The investigation of stability of [CHOL⁺][(CF₃SO₂)₂N⁻] in the two media is highly important,
31 especially considering the hydrogen bond network which develops in the IL. Here, the
32 stabilities of IL have been studied by using: (i) the acceptor-donor interactions energies (E2)
33 calculated with the Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
34 [32] and (ii) by using the Bader's theory of atoms in molecules with the AIM 2000 program
35 [33,34]. **Table S3** reports the E2 values [32]. Two different types of interactions are expected
36 for the IL, as previously observed in other ILs [21,22]. The first one is the $n \rightarrow \sigma^*$ interaction
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1 between the lone pairs of O, N and F atoms of $[(CF_3SO_2)_2N^-]$ to various anti bonding S-O, S-
2 N, S-C, and C-F orbitals. The second type of interaction is the $\sigma^* \rightarrow \sigma^*$ one that involves the
3 anti bonding S-O orbitals (see Table S3). The total energy is 1762.0 kJ/mol in vacuum and
4 1950.1 kJ/mol in solution. The similarity of these values point towards a similar stability of
5 the IL in the two media, even though it seems slightly more stable in solution.
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9 The AIM 2000 program [33,34] was used to investigate the topological properties of the IL in
10 the various critical points. Table S4 reports the main interactions while Table S5 summarize
11 the main values of the topological properties found both in gas and in solution phases. Figure
12 S4 reports the location of the critical points. The new interactions S9-O10...H25 and C19-
13 H22...N1 in gas phase and, C12-F13...H25 in solution are shown in **Table S6**. Both NBO
14 and AIM investigations suggest a good stability of $[CHOL^+][(CF_3SO_2)_2N^-]$, independently of
15 the medium.
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21 **3.5. Frontier Orbitals calculations**

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23 The frontier orbitals and their differences are calculated to obtain the gap values and the
24 reactivity of the IL. The global softness (S), hardness (η), and electrophilicity (ω) were
25 calculated (see **Table S7**). For comparison, the same parameters were computed for the
26 isolated ions. The gap of the cation largely exceeds that of the anion, while in the ionic
27 couple one has an intermediate value, which is higher in solution (7.4640 eV) than in the gas
28 phase (6.5360 eV); therefore, the IL is more reactive in vacuum and more stable in solution.
29 Comparing the gap values of $[CHOL^+][(CF_3SO_2)_2N^-]$ IL with those reported for
30 $[C_8DABCO^+][(CF_3SO_2)_2N^-]$ (6.7756 eV in gas phase and 5.7389 eV in solution) it is clear
31 that this latter IL is more reactive in solution while the former is more reactive in gas phase
32 [22]. Here, the $[C_8DABCO^+]$ cation increases the reactivity of $[C_8DABCO^+][(CF_3SO_2)_2N^-]$ in
33 solution while $[CHOL^+]$ increases the reactivity of $[CHOL^+][(CF_3SO_2)_2N^-]$ in gas phase. The
34 frontier orbitals of $[CHOL^+][(CF_3SO_2)_2N^-]$ in the two media are reported in **Figure S5**; one
35 can observe that the anion orbitals participate in the HOMO in gas phase but not in solution
36 while the contrary is observed in the LUMO. The cation is involved in the HOMO in
37 solution. Evidently, the different participations of HOMO and LUMO in the media justifies
38 the higher reactivity of IL in vacuum and its higher stability (< reactivity) in solution.
39 Consistently, the global electrophilicity index ω (3.1743 eV) is higher in the gas phase.
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3.6. Vibrational study

We used calculation to optimize the structure of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL with C_1 symmetry, with the SO_2 groups in opposite positions and with the CF_3 groups in *Trans* positions, as shown in Figure 4. In this IL, the presence of 36 atoms generates a total of 102 normal vibration modes, all a of them both Raman and infrared active. The experimental infrared and Raman spectra in the solid phase are compared respectively in **Figures 5** and **6** with the spectra calculated for the ionic couple, the cation and anion in vacuum. Calculated and experimental spectra show a good correlation, especially the Raman one. Clearly, Figure 5 displays that the observed IR bands of IL in the region of higher wavenumbers are due to cation while the bands between 2000 and 10 cm^{-1} are due to cation and anion species. The theoretical infrared spectrum of IL, cation and anion are reported in **Figure S6**. The scaled quantum mechanical force field (SQMFF) method allowed to obtain the harmonic force fields of the ionic couple in the two media, by means of the MOLVIB suite [38-40]. For the IL and the cation the normal internal coordinates and transferable scaling factors were used while for the anion the normal internal coordinates of anion were obtained from the literature [22]. A good agreement between the calculated and measured bands is observable in Table 7, where also the assignment of the vibrations is reported. One can note in Table 7, that due to the formation of hydrogen bonds between the two ions, the cation vibrational bands are displaced toward lower frequencies in the IL. The main assignments of the vibrational bands are reported in the following.

Figure 5. Experimental FT-IR spectrum of IL in the solid phase compared with the corresponding predicted for IL and its cation and anion in the gas phase by using the hybrid B3LYP/6-311++G** level of theory.

3.6.1. Vibrational band Assignment

3.6.1.1. 4000-2000 cm^{-1} region. The OH stretching and the symmetric and antisymmetric stretching of CH_2 and CH_3 groups of the cations are expected [21,22] in this region. Calculations predict that the bands of the IL can be found at lower wavenumbers with respect to those of the cation, due to the interaction between the ions, as it was observed in other IL [22]. Moreover, the SQM calculations predict different assignments for the cation and the IL, due to the interaction between the ions, as previously investigated by NBO and AIM calculations. The assignment of the infrared and Raman bands observed in this region are displayed in Table 7. It can be noted that this IL does not possess intense Raman bands;

1 therefore, hence, the symmetric CH₂ and CH₃ stretching modes are assigned in the expected
2 positions according to the SQM calculations.

3 **3.6.1.2. 2000-1000 cm⁻¹ spectral range.** In this spectral range, the vibration modes of cation
4 and IL, such as CH₃ and CH₂ deformation, OH deformation, CH₂ wagging, CH₃ and CH₂
5 rocking modes are expected in addition to SO₂ and CF₃ stretching modes of anion [21,22].
6 According to SQM calculations, the observed bands in the range 1507-1058 cm⁻¹ are ascribed
7 to CH₃ and CH₂ deformation, CH₂ wagging, CH₃ and CH₂ rocking modes of the cation. Then,
8 the interaction of cation with the anion leads to the shifting toward lower wavenumber of SO₂
9 stretching modes involved in the H bond interaction. Hence, in the anion the symmetric
10 stretching mode ν_s SO₂ (S2) is expected at 1056 cm⁻¹ while in the IL that mode is calculated at
11 1029 cm⁻¹. Also, the antisymmetric mode in the anion is predicted at 1236 cm⁻¹ while in the
12 IL at 1234 cm⁻¹. However, the stretching modes of CF₃ groups remain practically in the same
13 positions because these groups are involved in weak H bond interactions. The OH
14 deformation mode in the cation is expected at 1164 cm⁻¹; on the contrary in the IL this mode
15 is predicted in different positions and coupled with other modes due to participation of this
16 group to strong S2-O3...H18 interactions. The very strong infrared active bands centered at
17 1197 and 1149 cm⁻¹ are ascribed to deformation and torsion of OH group, as well as to the
18 stretching modes of CF₃ groups (see Table 7). Finally, the very strong IR band at 1071 cm⁻¹ is
19 assigned to C-O and C-C stretching modes of cation and IL.

20 **3.6.1.3. 1000-10 cm⁻¹ region.** In this region, one can observe the CH₂ and CH₃ twisting and
21 C-C, C-N and S-N stretching, as well as and CCC, CCN, skeletal modes of cation together
22 with vibration modes of anion [21,22]. The CH₂ twisting modes are poorly influenced by the
23 anion and are expected in the cation between 1053 and 843 cm⁻¹ while in the IL between 960
24 and 847 cm⁻¹. Here, it is observed that the SO₂ wagging, rocking and twisting modes related to
25 the S2-O3...H18 interaction are predicted in the IL at a higher wavenumber than in the
26 cation due to H bond. The vibration modes of CF₃ groups are poorly influenced by the cation
27 and, thus, these modes in the IL are observed in the same regions observed for the anion.

28 **Figure 6.** Experimental FT-Raman spectrum of IL in the solid phase compared with the corresponding predicted
29 for IL and its cation and anion in the gas phase by using the hybrid B3LYP/6-311++G** level of theory.

30 **3.7. Scaled force constants**

31 Scaled force constants for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid and its cation and anion in
32 vacuum and solution were calculated at the B3LYP/6-311++G** level of theory/basis set

1 because these parameters show how the interactions influence the geometrical parameters and
2 vibration modes. These factors have been obtained from the corresponding harmonic force
3 fields previously reported [38-40].
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5 In **Table 8** were reported the main scaled internal force constants for the ionic liquid and the cation
6 in the two media while for the $[(CF_3SO_2)_2N^-]$ anion the values in vacuum have been taken
7 from previous literature at the same level of theory [22]. Comparing the $f(\nu_{OH})$ force
8 constants of IL and cation, it is observed the decreasing of the values in the IL in the two
9 media due to the formation of S2-O3...H18 interaction where that group is involved. Note
10 that all force constants of cation change in the IL as a consequence of interactions, with the
11 exception of $f(\delta_{CH3})$ and $f(\delta_{CH2})$ force constants that show the same values. Hence, the effect
12 of anion on the cation is clearly observed in these parameters. While the values of IL and
13 anion are compared between them, it is observed that the force constants related to SO₂
14 groups demonstrate higher changes than to those corresponding to CF₃ groups. The observed
15 changes here are attributed to the different interactions predicted by NBO and AIM
16 calculations (see Tables 5, S3 and S4 and Figure S4).
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28 **4. Thermal analysis**

29 The thermogravimetric analysis (TGA) of ILs is a powerful means which provides access to
30 information linked to thermal behaviour, namely the degradation temperature [45]. On the
31 other hand, low temperature analysis by Differential Scanning Calorimetry (DSC) also makes
32 it possible to determine phase transitions: Freezing, melting, glass transition, cold
33 crystallisation and solid-solid transition temperatures. The curves measured for the mass
34 variation and the heat flux as a function of temperature are presented in Figures 7 and
35 8. During the rise in temperature, a glass transition around -75°C and three endothermic peaks
36 at 3, 27 and 31°C is observed. The first peak is ascribed to a solid-solid transition of
37 $[(CHOL^+)[(CF_3SO_2)_2N^-]$, the other two peaks at 27 and 31°C were associated to the melting
38 process. This result agrees with previous study of Villanueva et al. [46].
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48 **Figure 7:** DSC curve of $[(CHOL^+)[(CF_3SO_2)_2N^-]$.
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51 The TGA curve reported in Figure 8 suggests that $[(CHOL^+)[(CF_3SO_2)_2N^-]$ decomposes in
52 one step, the T_d value of $[(CHOL^+)[(CF_3SO_2)_2N^-]$ was higher than 400 °C with weight loss
53 was observed starting from T_{id}= 360 °C and was completed at T_{fd}=475°C. The introduction of
54 a bis(trifluoromethanesulfonyl)imide anion resulted in higher T_d values for
55 $[(CHOL^+)[(CF_3SO_2)_2N^-]$. This result indicates that the thermal stability of the IL is strictly
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connected to that of the anion. In addition, it can be noted that the investigated IL exhibited better thermal stability than the halide analogues, containing the Cl or Br anion, thanks to the strong ionic linkage between the cation ([CHOL⁺]) and the anion ([CF₃SO₂)₂N⁻][47].

Figure 8: TGA curve of [CHOL⁺][CF₃SO₂)₂N⁻].

5. Conclusions

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2 In summary, the synthesis and experimental characterisation of [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid NMR,
3 infrared and Raman spectroscopy was reported. Structural, topological, electronic and reactivity of IL in
4 vacuum and aqueous solution have been predicted by using B3LYP/6-311++G** calculations. Studies on
5 atomic MK, NPA and Mulliken charges and MEP, NBO and AIM, frontier orbitals have evidenced that the
6 strong S-O...H interaction and other weak H bonds interactions play a very important role in determining the
7 properties of this new IL. The MEP surfaces evidenced that the main reactive sites are located on positively
8 charged N⁺ of the cation and on the SO₂ groups of the anions. Good agreement is observed between the
9 predicted IR, ¹H-NMR and ¹³C-NMR, and Raman spectra and the experimental ones. A complete assignment of
10 all vibration modes for the IL and its cation is suggested, together with the scaled force constants. In addition,
11 the IL showed its melting temperature near at 30°C while a glass transition and a cold crystallization have been
12 revealed at 3 and -26 °C.
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33 fruitful support.
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39 **Supporting Information Available: Tables S1-S4 and Figures S1-S11.**

Conflicts of interest

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43 All authors declare that there are no conflicts of interest.
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Figure Captions

Scheme 1. General synthesis of Choline bis(trifluoromethylsulfonyl)imide

Figure 1. Experimental Hydrogen atom labeling and $^1\text{H-NMR}$ spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

Figure 2. Experimental $^{13}\text{C-NMR}$ spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

Figure 3. Experimental $^{19}\text{F-NMR}$ spectrum of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

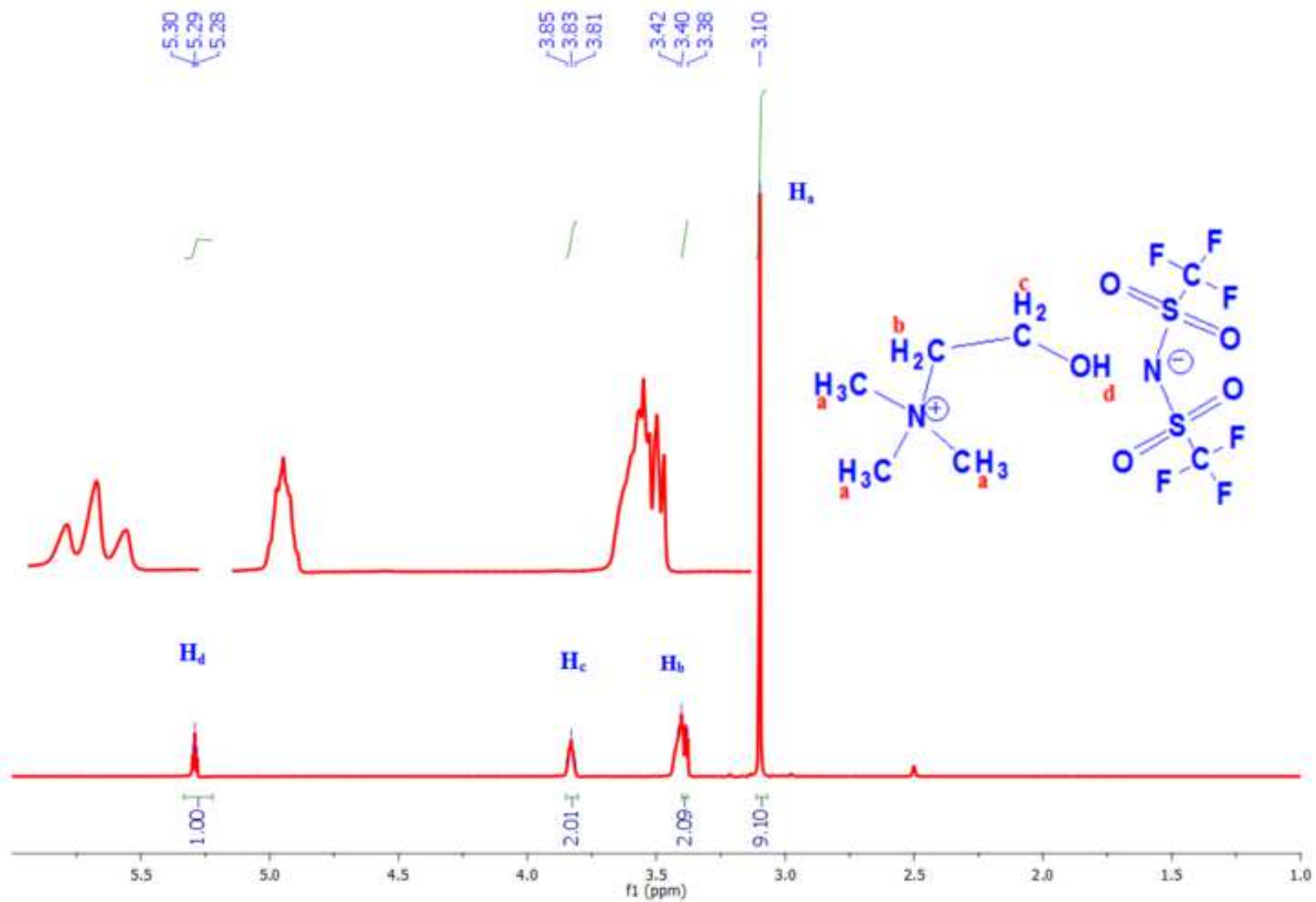
Figure 4. Optimized structures of cation anion and IL by using the hybrid B3LYP/6-311++G** level of theory.

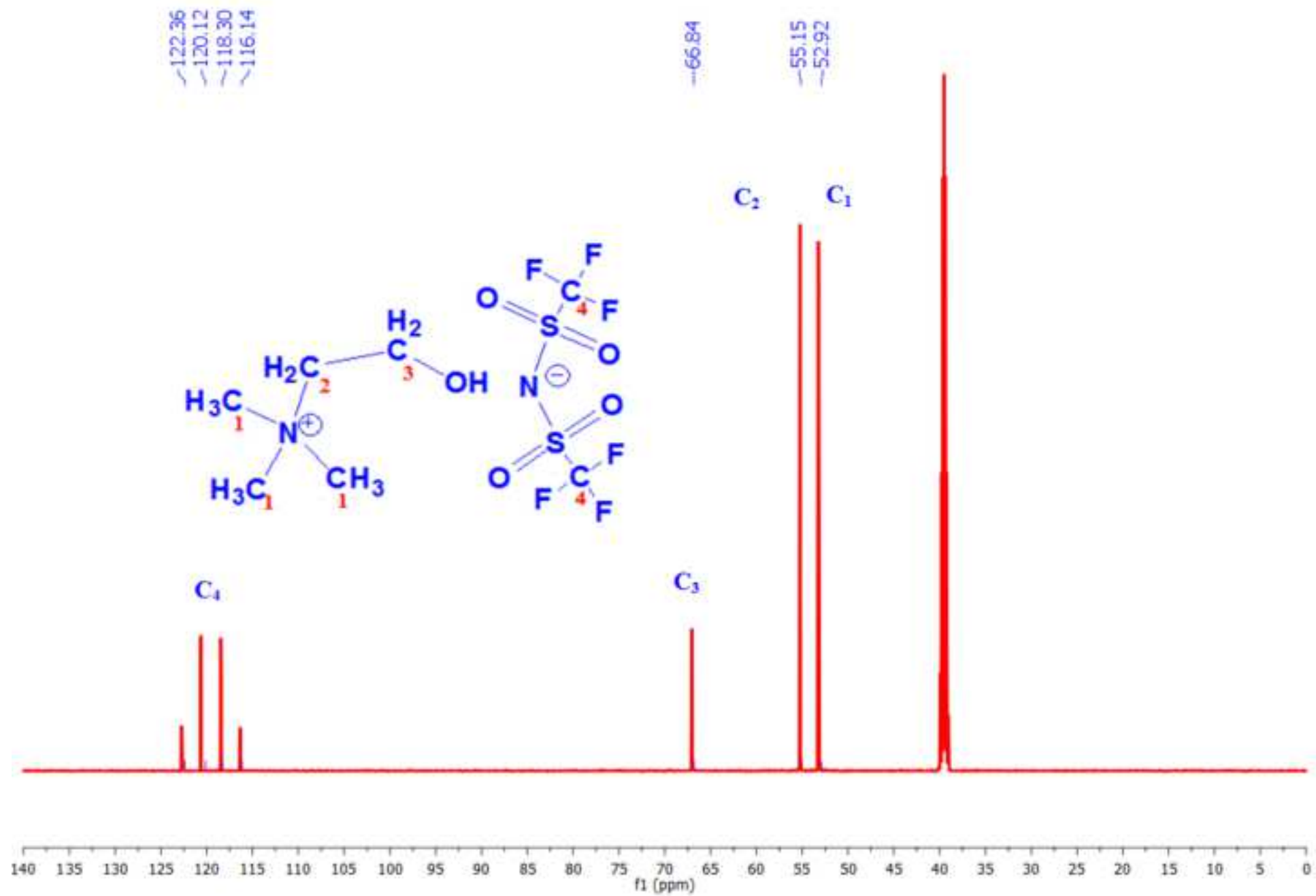
Figure 5. Experimental FT-IR spectrum of IL in the solid phase compared with the corresponding predicted for IL and its cation and anion in the gas phase by using the hybrid B3LYP/6-311++G** level of theory.

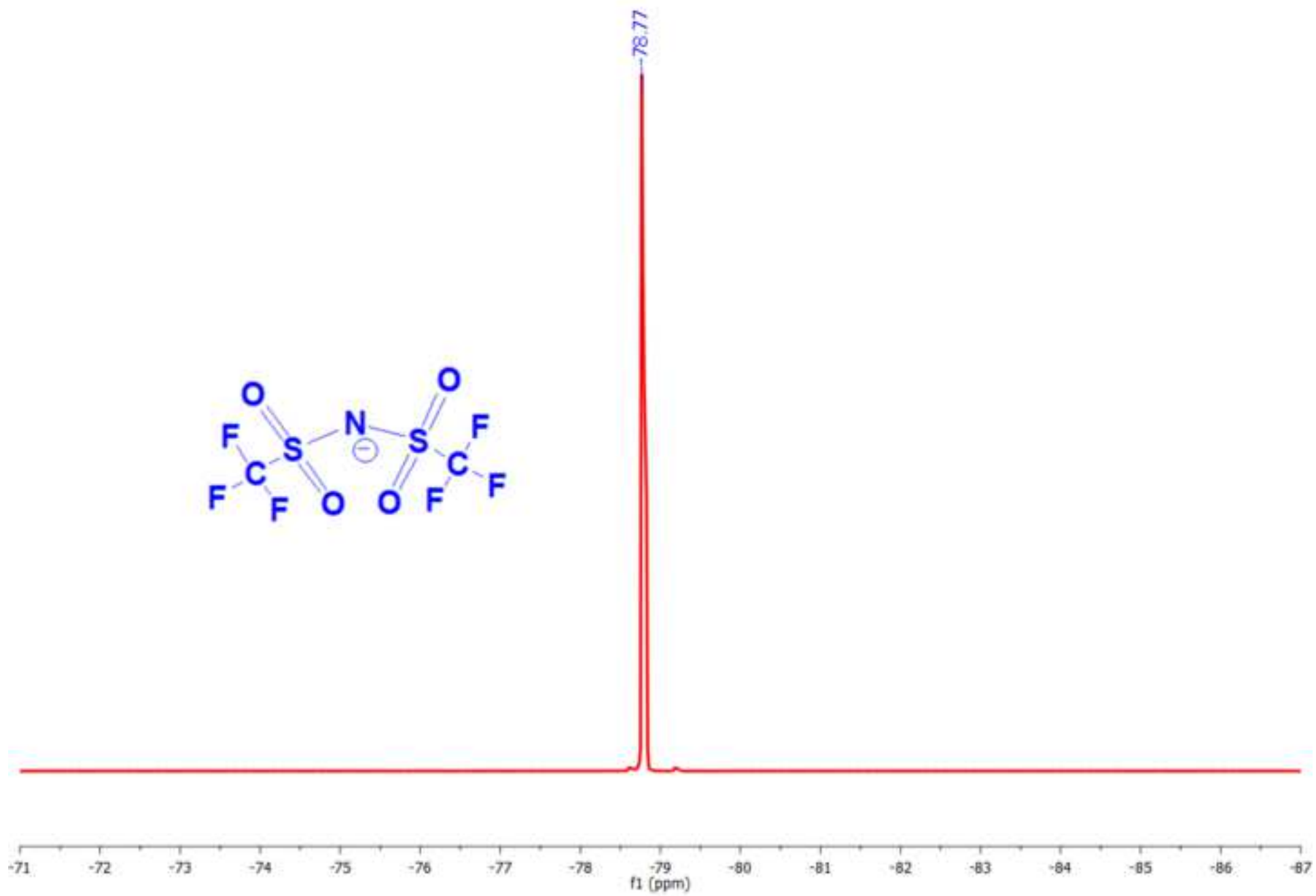
Figure 6. Experimental FT-Raman spectrum of IL in the solid phase compared with the corresponding predicted for IL and its cation and anion in the gas phase by using the hybrid B3LYP/6-311++G** level of theory.

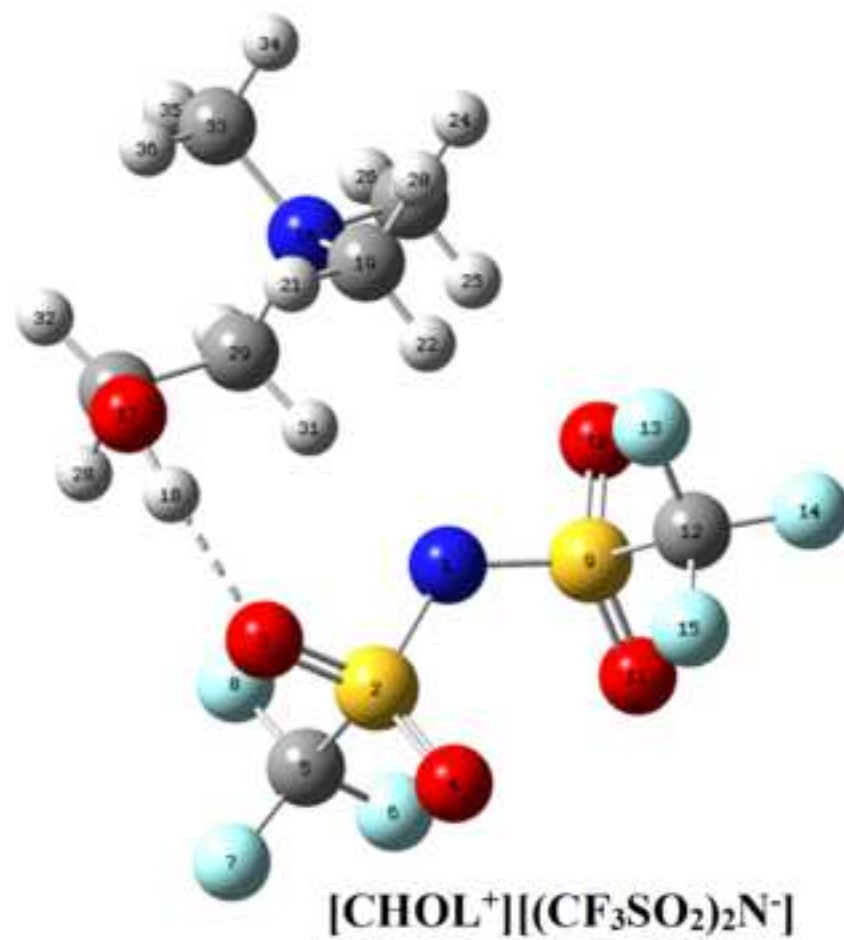
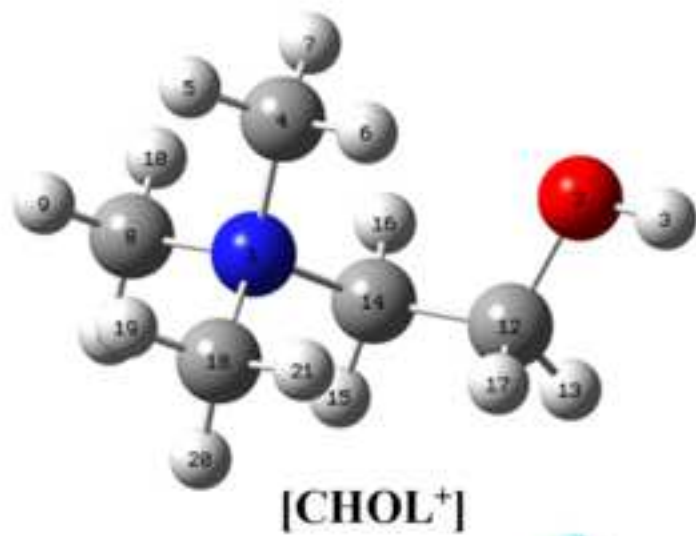
Figure 7: DSC curve of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

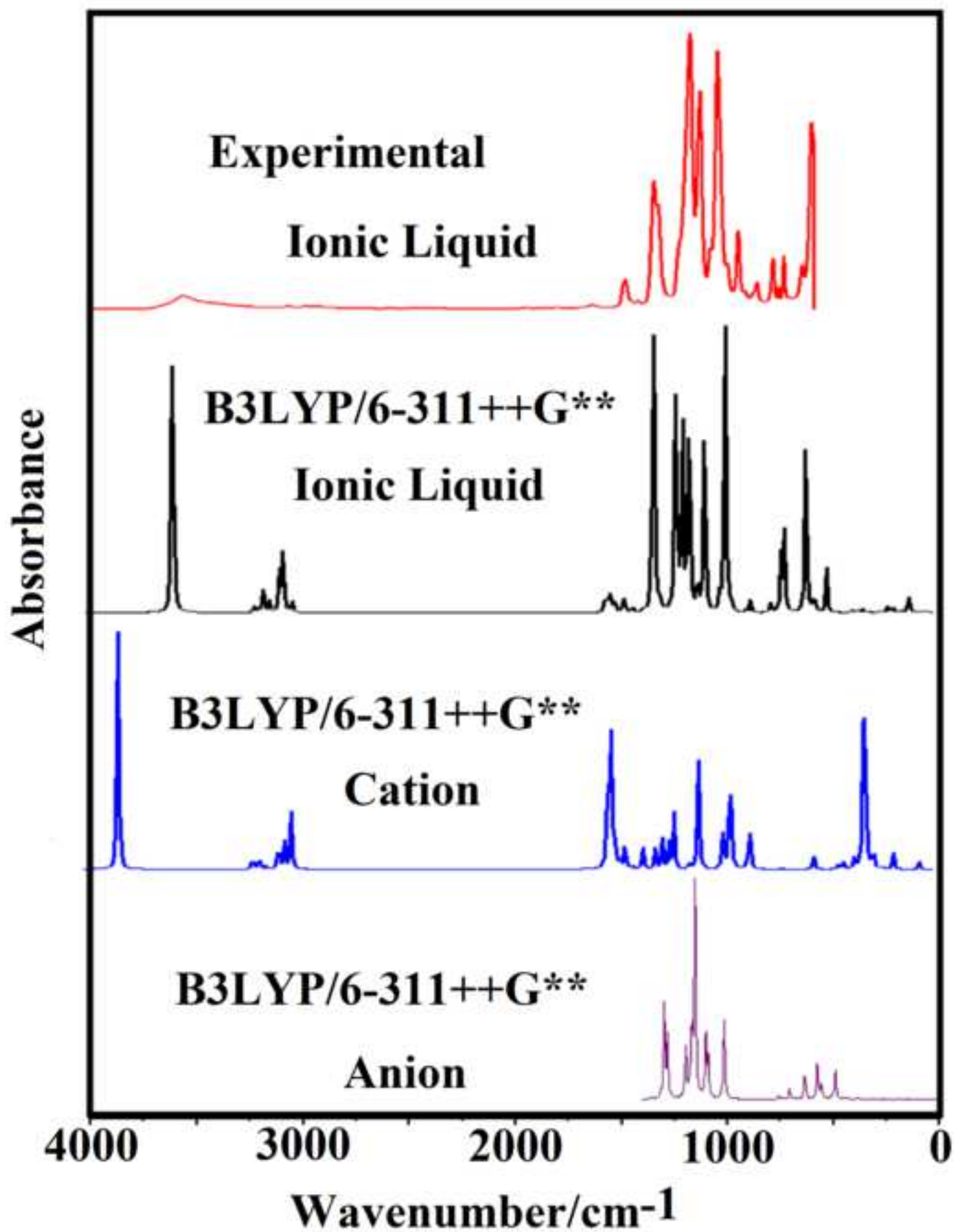
Figure 8: TGA curve of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

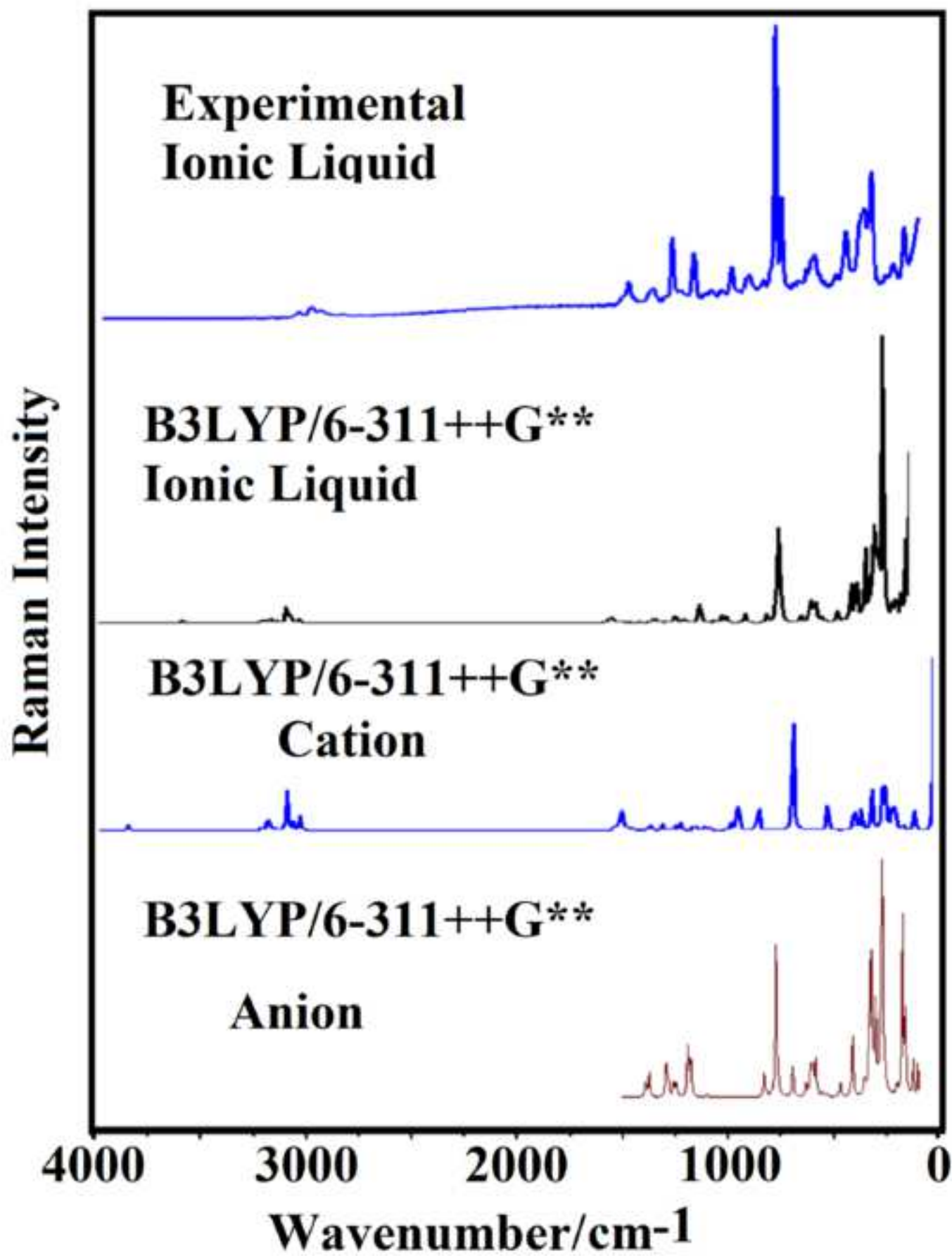


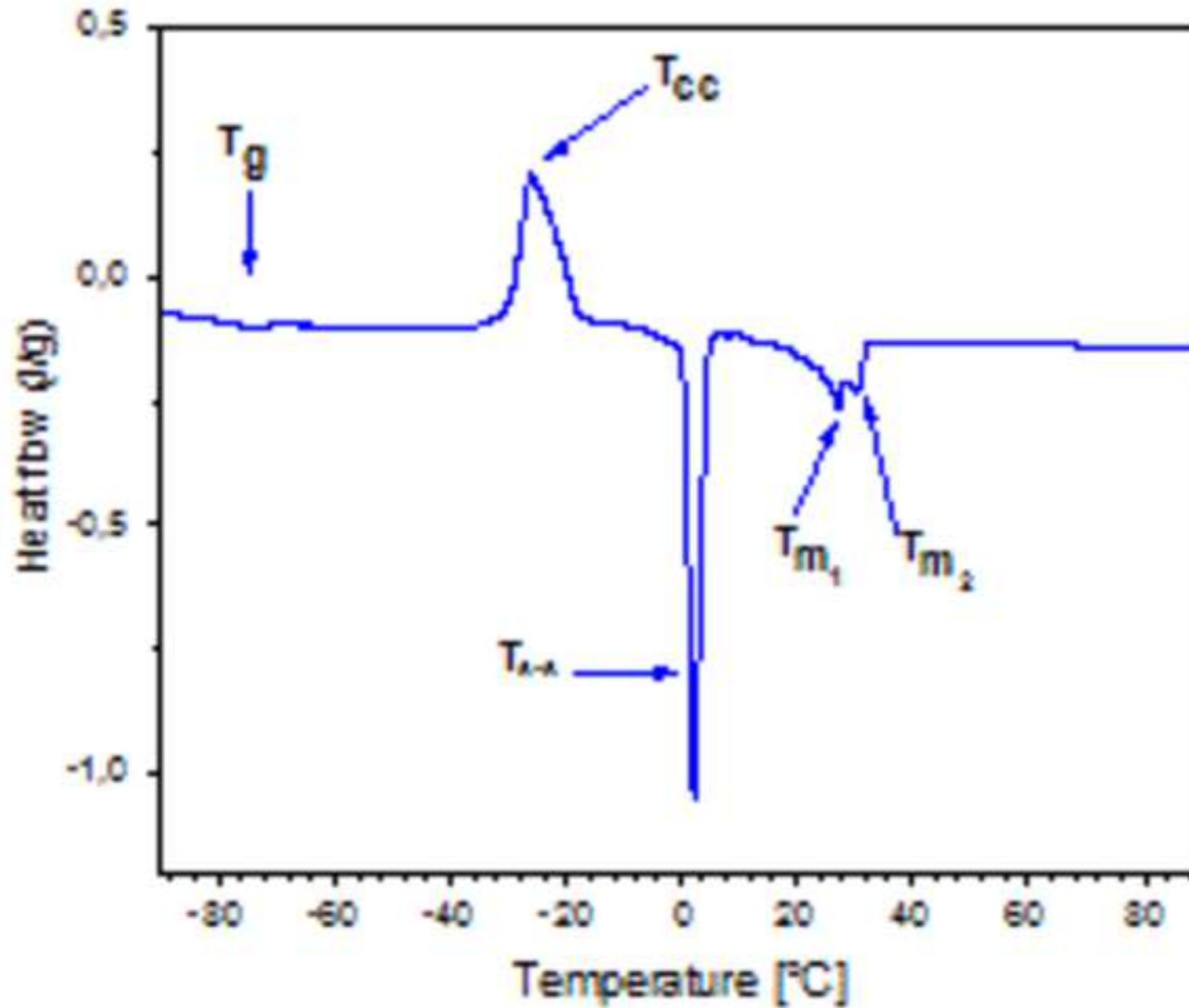


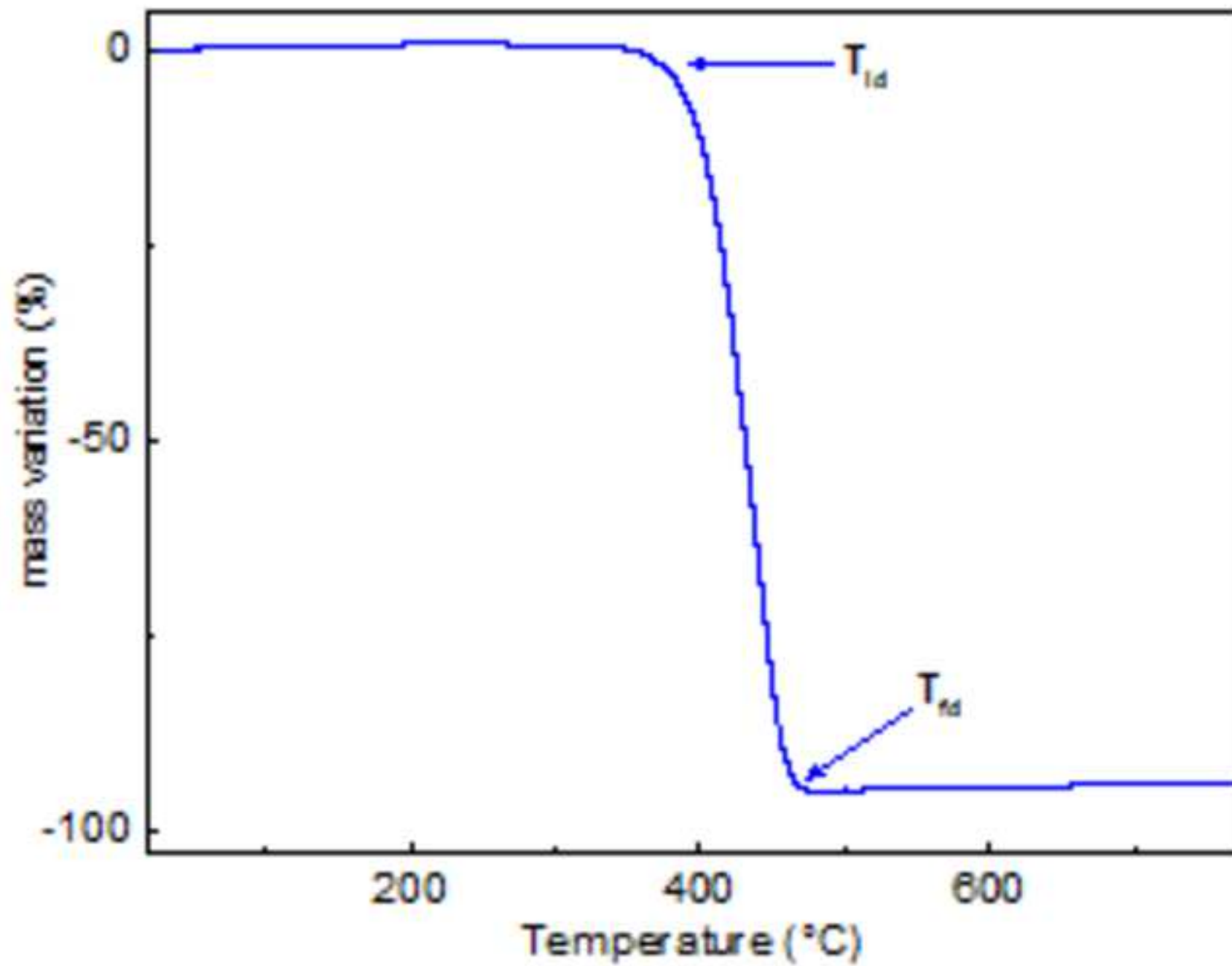


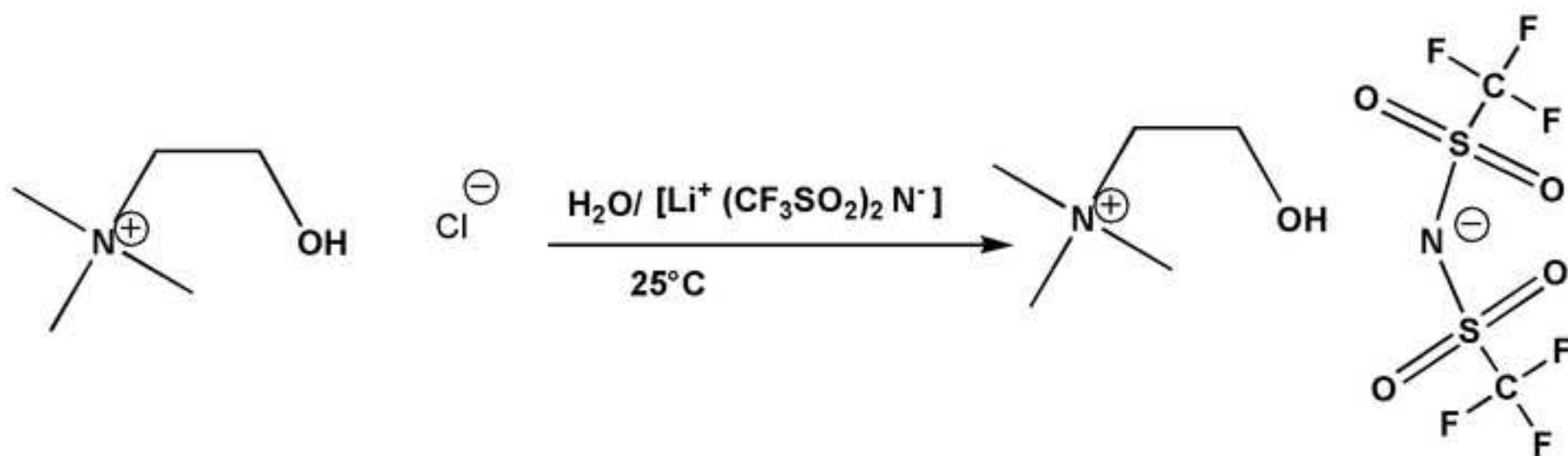












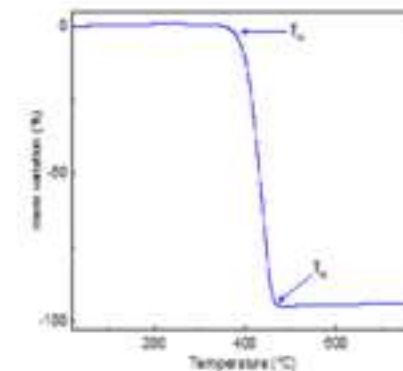
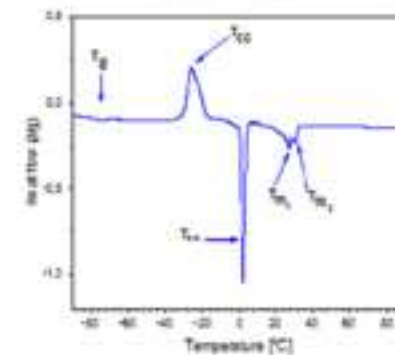
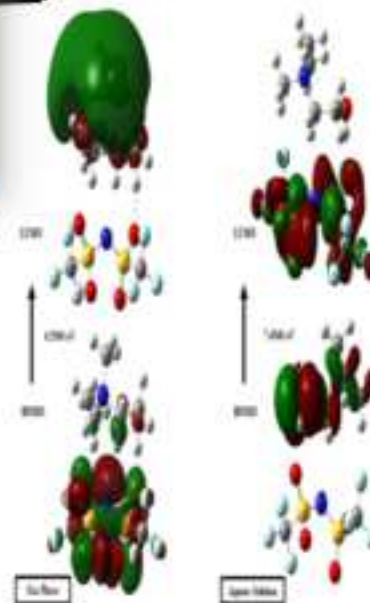
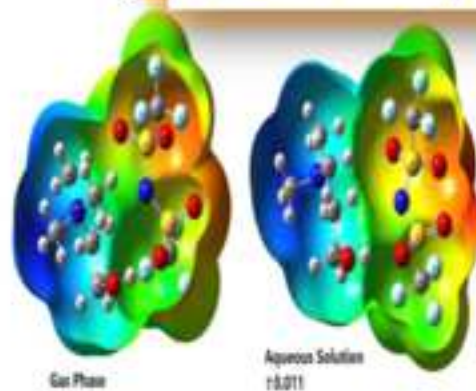
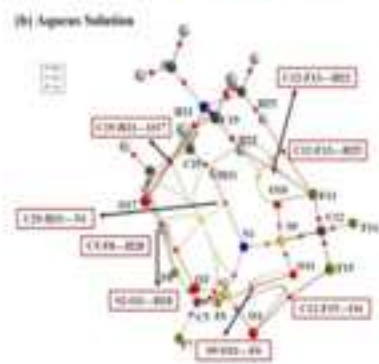
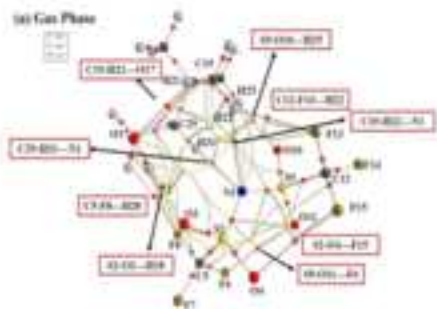
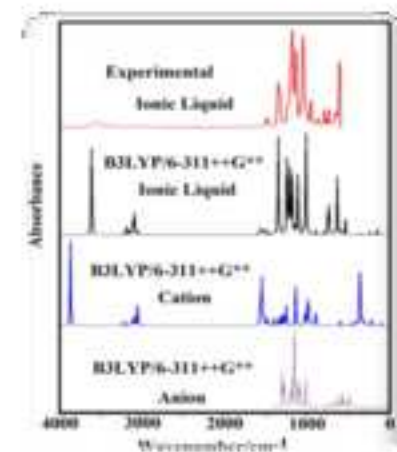
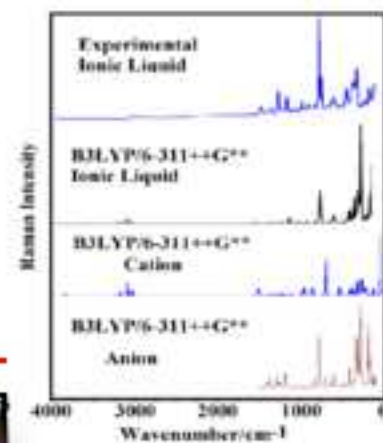
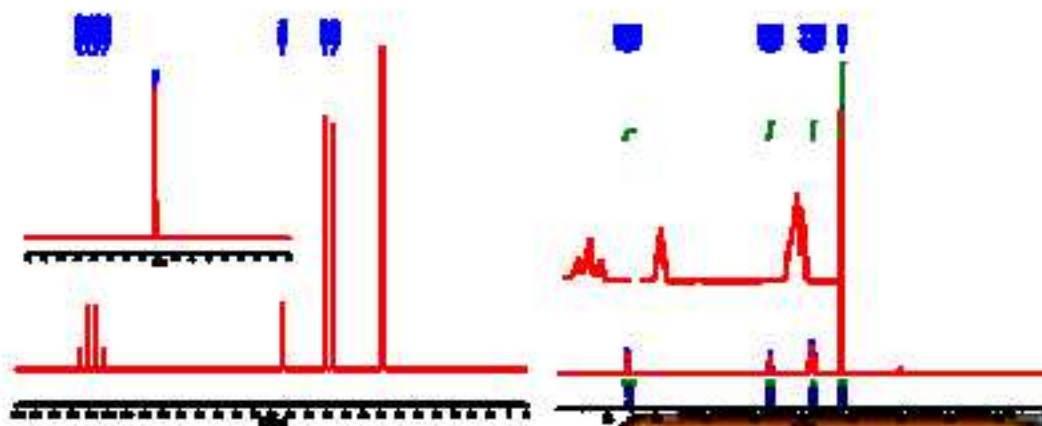


Table 1. Observed and calculated ^1H chemical shifts (δ in ppm) of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL and its cation in aqueous solution by using the hybrid B3LYP/6-311++G**method.

Atoms	B3LYP/6-311++G**method		Exp. ^a
	$[\text{CHOL}^+]$	$[\text{CHOL}^+]\text{NTFS}_2^-]^a$	
18-H	1.65	3.50	5.29
20-H	2.93	2.91	3.10
21-H	3.34	3.56	3.10
22-H	2.94	2.98	3.10
24-H	2.99	2.94	3.10
25-H	3.08	3.11	3.10
26-H	3.01	2.94	3.10
28-H	4.06	4.08	3.83
30-H	3.29	3.05	3.40
31-H	3.57	4.02	3.40
32-H	4.52	4.21	3.83
34-H	2.96	2.97	3.10
35-H	2.64	2.68	3.10
36-H	3.34	3.53	3.10
RMSD	1.01	0.57	

^aThis work.

Table 2. Observed and calculated ^{13}C chemical shifts (δ in ppm) of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL and its cation in gas phase by using the hybrid B3LYP/6-311++G**method

Atoms	B3LYP/6-311++G**method		Exp. ^a	
	$[\text{CHOL}^+]$	$[\text{CHOL}^+]\text{NTFS}_2^-]^a$		
5-C	Anion	130.34	119.23	
12-C	Anion	130.34	119.23	
19-C		53.71	54.36	52.92
23-C		57.67	58.01	52.92
27-C		61.97	61.94	55.15
29-C		71.34	72.62	66.84
33-C		51.09	50.69	52.92
RMSD	4.32	7.16		

^aThis work.

Table 3. Observed and calculated ^{19}F chemical shifts (δ in ppm) of $[\text{CHOL}^+][(\text{NTFS}_2)^-]$ IL and its cation in gas phase by using the hybrid B3LYP method.

Atoms	B3LYP/6-311++G**method		Exp. ^a
	$[\text{NTFS}_2]^-$ ^b	$[\text{CHOL}^+]\text{NTFS}_2^-$ ^a	
6-F	-108.45	-101.19	-78.97
7-F	-112.64	-102.79	-78.97
8-F	-113.82	-98.1	-78.97
13-F	-108.45	-96.85	-78.97
14-F	-112.64	-103.12	-78.97
15-F	-113.82	-100.78	-78.97
RMSD	32.75	21.62	

^aThis work.

Table 4. Calculated uncorrected and corrected by ZPVE total energies (E and E_{ZPVE}), dipole moments (μ) and volumes (V) of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ionic liquid and its cation and anion in gas phase and aqueous solution by using the B3LYP/6-311++G** method.

B3LYP/6-311++G** Method				
[CHOL ⁺]				
Species	E (Hartrees)	E_{ZPVE} (Hartrees)	μ (D)	V (\AA^3)
Gas Phase	-328.7894	-328.5924	1.95	136.1
Aqueous Solution	-328.8820	-328.6852	3.69	137.7
[(CF ₃ SO ₂) ₂ N ⁻]				
Gas Phase	-1827.6092	-1827.5572	4.36	183.1
Aqueous Solution	-1827.6810	-1827.5620	7.04	180.4
[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻]				
Gas Phase	-2156.5257	-2156.2746	14.22	311.5
Aqueous Solution	-2156.5699	-2156.3202	24.19	317.6

Zero point vibrational energy (ZPVE)

Table 5. Calculated distances (in Å) of interactions predicted for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid in gas phase and aqueous solution by using the B3LYP/6-311++G** Method.

Interactions	Gas Phase	Aqueous solution
S2-O3...H18	1.832	1.948
S2-O4...F15	3.046	3.221
S9-O11...F6	3.015	3.234
S9-O10...H25	2.160	-----
C5-F8...H28	2.882	3.292
C12-F13...H22	2.790	3.098
C12-F13...H25	----	2.838
C19-H21...O17	2.283	2.508
C19-H22...N1	2.519	----
C29-H31...N1	2.224	2.664

^aThis work; Letters bold, shorter distances.

Table 6. Calculated geometrical parameters of [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid in gas phase and aqueous solution by using the B3LYP/6-311++G**method compared with the corresponding experimental ones [19].

B3LYP Method 6-311++G**			
Parameters	[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻] ^a		Exp ^b
	Gas Phase	Solution	
Bond lengths (Å)			
N1-S2	1.621	1.608	1.620
N1-S9	1.627	1.612	1.616
S2-O3	1.473	1.469	1.475
S2-O4	1.452	1.465	1.458
S2-C5	1.897	1.892	1.870
O3-H18	1.832	1.948	1.703
C5-F6	1.327	1.334	1.333
C5-F7	1.334	1.335	1.334
C5-F8	1.349	1.334	1.343
S9-O10	1.469	1.464	1.477
S9-O11	1.453	1.466	1.457
S9-C12	1.896	1.892	1.875
C12-F13	1.348	1.334	1.345
C12-F14	1.335	1.335	1.336
C12-F15	1.328	1.334	1.332
N16-C19	1.514	1.503	1.515
N16-C23	1.508	1.504	1.508
N16-C29	1.533	1.525	1.540
N16-C33	1.497	1.502	1.501
O17-H18	0.977	0.971	0.980
O17-C27	1.409	1.428	1.406
RMSD	0.029	0.055	
Bond angles (°)			
S2-N1-S9	126.2	125.7	127.4
N1-S2-O3	105.6	107.7	103.0
N1-S2-O4	117.2	117.1	117.7
N1-S2-C5	104.5	103.4	104.5
O3-S2-O4	119.3	117.9	120.2
O3-S2-C5	102.4	103.9	103.4
O4-S2-C5	105.9	104.9	105.8
S2-O3-H18	137.4	130.0	127.8
S2-C5-F6	111.7	110.1	111.0
S2-C5-F7	109.2	109.1	110.5
S2-C5-F8	109.6	110.3	109.2
F6-C5-F7	109.4	109.1	108.8
F6-C5-F8	108.6	109.1	108.8
F7-C5-F8	108.4	109.1	108.2

N1-S9-O10	105.3	107.8	103.8
N1-S9-O11	116.9	116.6	118.0
N1-S9-C12	104.0	102.9	105.5
O10-S9-O11	120.0	118.4	119.4
O10-S9-C12	102.9	104.2	102.5
O11-S9-C12	105.8	104.9	105.5
S9-C12-F13	109.8	110.3	109.8
S9-C12-F14	109.1	109.2	109.4
S9-C12-F15	111.6	110.2	111.1
F13-C12-F14	108.3	109.0	108.4
F13-C12-F15	108.6	109.1	108.8
F14-C12-F15	109.3	109.1	109.1
C19-N16-C23	108.2	108.4	108.1
C19-N16-C29	110.9	111.8	110.5
C19-N16-C33	109.3	109.4	109.4
C23-N16-C29	107.4	107.2	107.6
C23-N16-C33	109.5	108.5	109.6
C29-N16-C33	111.5	111.3	111.2
H18-O17-C27	108.8	108.5	110.0
O17-C27-C29	114.7	115.1	118.5
N16-C29-C27	116.3	117.6	115.7
RMSD	1.8	1.3	

^aThis work, ^bFrom Ref [19].

Table 7. Observed and calculated wavenumbers (cm^{-1}) and assignments for $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ionic liquid and its cation and anion in gas phase by using the hybrid B3LYP/6-311++G** Method.

Experimental ^a		B3LYP/6-311++G**					
		[CHOL ⁺] ^a		[(CF ₃ SO ₂) ₂ N ⁻] ^c		[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻] ^a	
IR	Raman	SQM ^b	Assignments ^a	SQM ^c	Assignments ^c	SQM ^b	Assignments ^a
3555w		3672	vO2-H3			3426	vO17-H18
3068vw		3064	v _a CH ₃ (C4)			3059	v _a CH ₃ (C19)
		3044	v _a CH ₃ (C18)			3039	v _a CH ₃ (C19)
		3035	v _a CH ₃ (C8)			3036	v _a CH ₃ (C33)
		3032	v _a CH ₃ (C8)			3021	v _a CH ₃ (C33)
		3029	v _a CH ₃ (C4)			3017	v _a CH ₃ (C23)
	3021w	3027	v _a CH ₃ (C18)			3014	v _a CH ₃ (C23)
2988vw		3003	v _a CH ₂ (C14)			2988	v _a CH ₂ (C29)
2958vw	2965w	2953	v _s CH ₂ (C14)			2946	v _s CH ₃ (C19)
		2948	v _s CH ₃ (C4)			2941	v _a CH ₂ (C27)
		2944	v _s CH ₃ (C18)			2937	v _s CH ₃ (C33)
		2940	v _s CH ₃ (C8)			2928	v _s CH ₂ (C29)
2908vw	2917w	2921	v _a CH ₂ (C12)			2921	v _s CH ₃ (C23)
	2813w	2890	v _s CH ₂ (C12)			2888	v _s CH ₂ (C27)
1652w	1530vw	1522	δCH ₂ (C12)			1507	δCH ₂ (C27)
1497w						1500	δCH ₂ (C29)
1485sh		1487	δCH ₂ (C14)			1473	δ _a CH ₃ (C19)
	1463sh	1464	δ _a CH ₃ (C4)			1462	δ _a CH ₃ (C23)
	1454sh	1452	δ _a CH ₃ (C8), δ _a CH ₃ (C18)			1443	δ _a CH ₃ (C33)
1438w	1441w	1445	δ _a CH ₃ (C18)			1438	δ _a CH ₃ (C23)
		1431	δ _a CH ₃ (C4), δ _a CH ₃ (C18)			1433	δ _a CH ₃ (C33)
		1426	δ _a CH ₃ (C18), δ _a CH ₃ (C8)			1429	δ _s CH ₃ (C23), δ _s CH ₃ (C19)
	1419sh	1424	δ _a CH ₃ (C8)			1411	δ _a CH ₃ (C19)
		1414	δ _a CH ₃ (C4)			1398	δO5-H18-O17, δOH
1396sh		1397	wagCH ₂ (C12)			1395	wagCH ₂ (C29), δ _s CH ₃ (C33)
1382sh		1383	δ _s CH ₃ (C4)			1388	δ _s CH ₃ (C23), δ _s CH ₃ (C19)
1361s		1381	δ _s CH ₃ (C18), δ _s CH ₃ (C8)			1379	δ _s CH ₃ (C33)
	1350sh	1352	wagCH ₂ (C14)			1350	wagCH ₂ (C27), wagCH ₂ (C29)
1331sh	1324w	1335	ρCH ₂ (C14)			1325	ρCH ₂ (C29)
1265sh		1276	ρCH ₂ (C12)			1266	ρCH ₂ (C27)
						1261	δO5-H18-O17, τO5-H18
1240sh	1248sh	1259	ρ'CH ₃ (C18), ρCH ₃ (C8)	1236	v _a SO ₂ (S2)	1258	v _a SO ₂ (S3)
	1230m			1221	v _a SO ₂ (S3)	1234	v _a SO ₂ (S2)
1227sh	1215sh	1228	ρCH ₃ (C4), ρCH ₃ (C18)			1223	δO5-H18-O17, ρ'CH ₃ (C19)
1197vs		1208	ρ'CH ₃ (C8), ρCH ₂ (C14)			1204	δO5-H18-O17, τO5-H18
1197vs	1189w	1164	δOH			1166	v _a CF ₃ (C8)
				1157	v _a CF ₃ (C9)	1157	v _a CF ₃ (C9)
1149s				1150	v _s CF ₃ (C8)	1149	v _a CF ₃ (C8), v _s CF ₃ (C8)
						1139	v _s CF ₃ (C8)
1134sh	1124m	1124	ρ'CH ₃ (C18)	1124	v _a CF ₃ (C9)	1122	ρCH ₃ (C23), ρCH ₃ (C19)
		1112	ρCH ₃ (C8), ρ'CH ₃ (C4)	1120	v _a CF ₃ (C8)	1116	ρ'CH ₃ (C33)
1103sh	1106sh			1108	v _a CF ₃ (C9)	1107	v _a CF ₃ (C9)

1071vs	1073sh	1059	vC12-O2	1104	$\nu_a\text{CF}_3(\text{C8})$	1104	$\nu_a\text{CF}_3(\text{C8})$
1056sh		1053	$\tau_w\text{CH}_2(\text{C12})$	1056	$\nu\text{SO}_2(\text{S2})$	1065	$\nu\text{C27-O17}, \nu\text{C27-C29}$
1040sh	1041w	1050	$\rho'\text{CH}_3(\text{C8}), \rho\text{CH}_3(\text{C18})$ $\rho\text{CH}_3(\text{C4})$	1041	$\nu\text{SO}_2(\text{S3})$	1058	$\rho'\text{CH}_3(\text{C23}), \rho'\text{CH}_3(\text{C19})$ $\rho\text{CH}_3(\text{C33})$
1038sh						1039	$\delta\text{O5-H18-O17}, \tau\text{O5-H18}$
1026sh	993w					1036	$\nu\text{SO}_2(\text{S3})$
972m	968sh			970	$\nu\text{S2-N1}$	1029	$\nu\text{SO}_2(\text{S2})$
940w	948w	946	vC12-C14			960	$\tau_w\text{CH}_2(\text{C27})$
		923	$\nu\text{N1-C8}$			940	$\nu\text{S2-N1}, \nu\text{S3-N1}$
899sh	887sh	915	$\nu\text{N1-C4}, \nu\text{N1-C18}$			932	$\nu\text{N16-C33}$
885w	858w	843	$\tau_w\text{CH}_2(\text{C14}), \nu\text{N1-C8}$			914	$\nu\text{N16-C23}$
808m		828	$\nu\text{N1-C14}, \nu\text{N1-C4}$			847	$\tau_w\text{CH}_2(\text{C29})$
760m	750sh	792w		732	$\nu_s\text{CF}_3(\text{C9})$	827	$\nu\text{N16-C19}$
736w	735vs			723	$\delta_s\text{CF}_3(\text{C8})$	737	$\nu_s\text{CF}_3(\text{C9})$
674m	705sh			684	$\nu\text{S3-N1}$	729	$\delta_s\text{CF}_3(\text{C8}), \delta_s\text{CF}_3(\text{C9})$
674m		678	$\nu\text{N1-C14}$			688	$\tau\text{O5-H18}, \tau\text{H18-O17}$
649sh						679	$\nu\text{N16-C29}$
628s	626w			616	$\text{wagSO}_2(\text{S3})$	644	$\tau\text{H18-O17}$
	581sh					590	$\text{wagSO}_2(\text{S2}), \text{wagSO}_2(\text{S3})$
						582	δS2N1S3
				568	$\text{wagSO}_2(\text{S2})$	559	$\tau\text{O5-H18}, \delta\text{SO}_2(\text{S2})$
	550w			550	$\delta_a\text{CF}_3(\text{C9})$	552	$\delta_a\text{CF}_3(\text{C9})$
				540	$\delta_a\text{CF}_3(\text{C9})$	539	$\delta_a\text{CF}_3(\text{C9})$
	533sh			538	$\delta_a\text{CF}_3(\text{C8})$	535	$\delta_a\text{CF}_3(\text{C8})$
		528	$\delta\text{N1C14C12}, \delta\text{O2C12C14}$	528	$\delta_a\text{CF}_3(\text{C8})$	534	$\delta\text{N16C29C27}$
	515sh			497	$\delta\text{SO}_2(\text{S3})$	515	$\delta_a\text{CF}_3(\text{C8})$
	509sh			483	$\delta\text{SO}_2(\text{S2})$	496	$\delta\text{SO}_2(\text{S3}), \delta\text{SO}_2(\text{S2})$
	446w	443	$\delta\text{C8N1C18}$			449	$\delta\text{C23N16C19}$
		435	$\delta\text{C18N1C4}$			440	$\delta\text{C33N16C19}$
	416sh	405	$\delta\text{O2C12C14}$	409	$\tau_w\text{SO}_2(\text{S3})$	414	$\delta\text{C23N16C33}, \delta\text{O17C27C29}$
	398m					369	$\tau_w\text{SO}_2(\text{S2}), \tau_w\text{SO}_2(\text{S3}), \rho\text{CF}_3(\text{C8})$
		363	$\rho'\text{N1-C14}, \delta\text{C8N1C4}$	366	$\tau_w\text{SO}_2(\text{S2})$	365	$\rho'\text{N16-C29}$
	354sh					358	$\delta\text{S2-O5-H18}$
	346sh			331	$\rho\text{SO}_2(\text{S3})$	344	$\delta\text{N1S3C9}, \delta\text{N1S2C8}$
	333sh			310	$\rho\text{CF}_3(\text{C9})$	326	$\delta\text{S2-O5-H18}$
	314m	301	$\rho\text{N1-C14}$	303	$\rho\text{CF}_3(\text{C8})$	301	$\rho\text{N16-C29}$
		293	τOH			293	$\delta\text{S2O5H18}, \rho\text{SO}_2(\text{S2})$
	280sh					290	$\delta\text{O5H18O17}, \tau\text{O5-H18}$
	275s	282	$\tau_w\text{CH}_3(\text{C18})$			289	$\tau\text{O5-H18}, \delta\text{S2-O5-H18}$
				284	$\rho\text{SO}_2(\text{S2})$	274	$\tau_w\text{CH}_3(\text{C23})$
	257sh	259	$\tau_w\text{CH}_3(\text{C4}), \tau_w\text{CH}_3(\text{C8})$	259	$\nu\text{S3-C9}$	274	$\rho\text{SO}_2(\text{S2}), \rho\text{SO}_2(\text{S3})$
	242sh	250	$\delta\text{N1C14C12}$	252	$\nu\text{S2-C8}$	255	$\tau\text{O5-H18}, \tau\text{H18-O17}$
		210	$\tau_w\text{CH}_3(\text{C4}), \tau_w\text{CH}_3(\text{C8})$			250	$\nu\text{S2-C8}, \rho'\text{CF}_3(\text{C8}), \nu\text{S3-C9}$ $\rho'\text{CF}_3(\text{C9})$
	211sh					218	$\tau_w\text{CH}_3(\text{C33}), \tau_w\text{CH}_3(\text{C19})$
	192sh			187	$\rho'\text{CF}_3(\text{C9})$	207	$\delta\text{N1S3C9}, \delta\text{N1S2C8}$
				186	$\rho'\text{CF}_3(\text{C8})$	191	$\tau\text{O5-H18}, \tau\text{H18-O17}$
	168w	162	$\tau\text{C12-C14}$	163	δN1S3C9	189	$\rho\text{CF}_3(\text{C9})$
						173	$\tau\text{O5-H18}, \tau\text{H18-O17}$

155sh			149	δ N1S2C8	154	τ O5-H18, τ H18-O17
133sh					136	ν O5-H18
118m					112	τ O5-H18, τ H18-O17
105sh			100	δ S2N1S3	103	δ N1S3C9, δ N1S2C8
83sh					82	τ O5-H18, δ O5H18O17
70sh					65	τ wC29-N16, τ C27-C29
50m	57	τ wC14-N1	60	τ S2-N1	54	τ S2-N1, τ S3-N1
					41	δ S2O5H18, δ O5H18O17
			38	τ wCF ₃ (C9)	37	δ S2O5H18, τ OH, τ wCF ₃ (C8) τ wCF ₃ (C9)
			30	τ wCF ₃ (C8)	28	δ S2O5H18, τ O5-H18
					23	τ wO5-S2
					19	τ O5-H18, τ H18-O17
			5	τ S3-N1	15	τ O5-H18

Abbreviations: ν , stretching; β , deformation in the plane; γ ,deformation out of plane; wag, wagging; τ , torsion; ρ ,rocking; τ w,twisting; δ ,deformation; a, antisymmetric; s, symmetric; ^aThis work, ^bFrom scaled quantum mechanics force field with B3LYP/6-311++G** method, ^bFrom scaled quantum mechanics force field with B3LYP/6-311++G** method from Ref [22].

Table 8. Scaled internal force constants for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid and its cation and anion in gas phase and aqueous solution by using the hybrid B3LYP/6-311++G** method.

Force constants	B3LYP method				
	6-311++G**				
	[CHOL ⁺] ^a		[(CF ₃ SO ₂) ₂ N ⁻] ^b		[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻] ^a
	Gas	Aqueous Solution	Gas	Gas	Aqueous Solution
<i>f</i> (<i>ν</i> OH)	7.54	7.41		7.13	7.17
<i>f</i> (<i>ν</i> C-O)	4.96	4.52		5.19	4.66
<i>f</i> (<i>ν</i> N-C)	3.76	3.90		3.82	3.91
<i>f</i> (<i>ν</i> CH ₂)	4.77	4.83		4.75	4.86
<i>f</i> (<i>ν</i> CH ₃)	4.98	5.00		4.96	5.01
<i>f</i> (<i>δ</i> CH ₂)	0.87	0.83		0.88	0.83
<i>f</i> (<i>δ</i> CH ₃)	0.55	0.54		0.55	0.54
<i>f</i> (<i>δ</i> OH)	0.67	0.67		1.96	0.92
<i>f</i> (<i>ν</i> SO ₂)			8.20	8.36	7.91
<i>f</i> (<i>ν</i> CF ₃)			5.31	5.49	5.43
<i>f</i> (<i>ν</i> N-S)			4.56	4.17	4.43
<i>f</i> (<i>ν</i> S-C)			2.17	2.17	2.25
<i>f</i> (<i>δ</i> SO ₂)			1.90	1.93	1.82
<i>f</i> (<i>δ</i> CF ₃)			1.51	1.49	1.44

Units are mdyne Å⁻¹ for stretching and mdyne Å rad⁻² for angle deformations. ^aThis work, ^bFrom Ref [22].

MATERIAL SUPPORTING TO**Synthesis, NMR, FT-IR, FT-Raman spectra and thermal studies of
Choline bis(trifluoromethylsulfonyl)imide Ionic Liquid combined with
DFT Calculations.**

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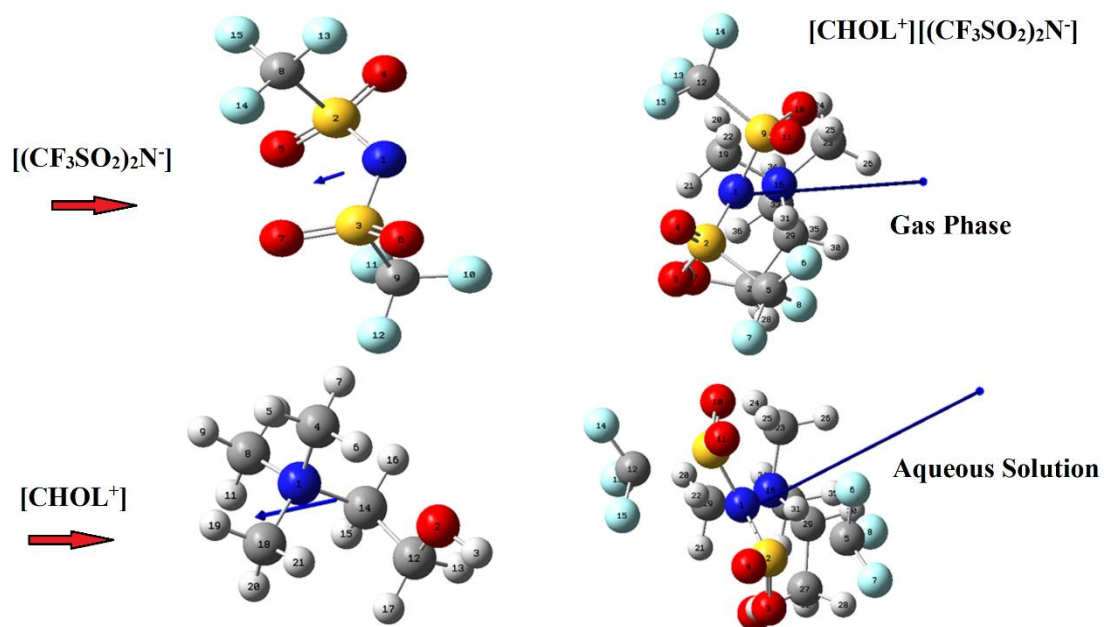


Figure S1. Orientations and directions of dipole moment vectors for $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL in both media and its $[\text{CHOL}^+]$ cation and $[(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ anion in gas phase by using the hybrid B3LYP/6-311++G** level of theory.

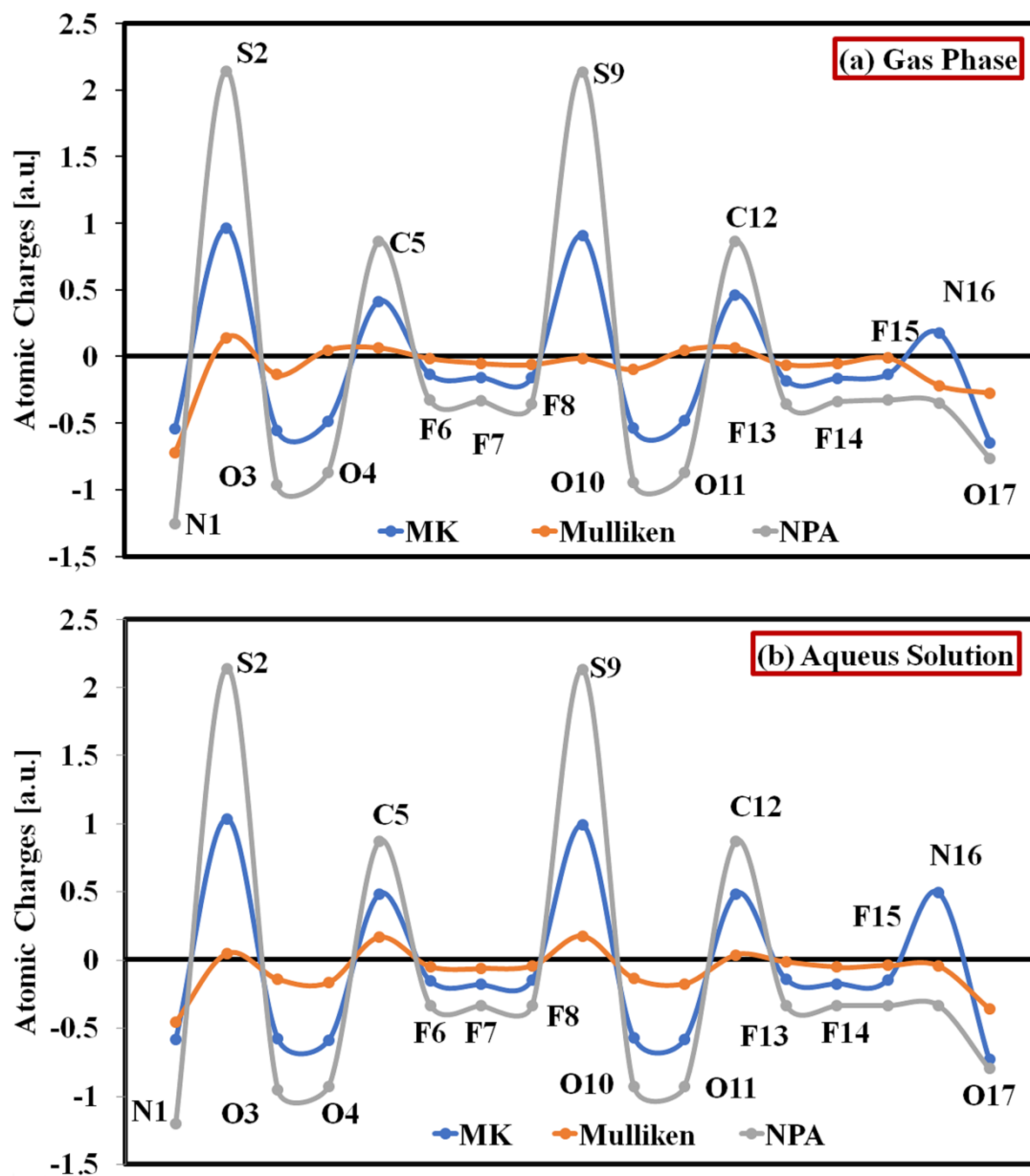


Figure S2. Calculated atomic MK, Mulliken and NPA charges on the N, C, and F atoms of [CHOL⁺][(CF₃SO₂)₂N⁻] IL, (a) in gas phase and (b) in aqueous solution by using the B3LYP/6-311++G** level of theory.

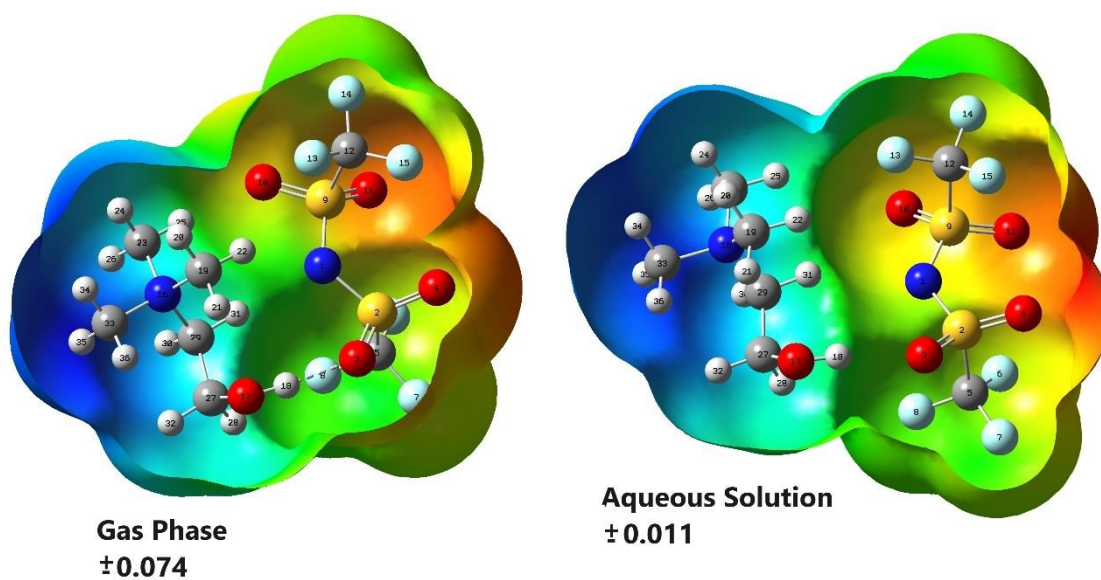


Figure S3. Calculated electrostatic potential surfaces on the molecular surface of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL in gas phase and in aqueous solution by using the B3LYP/6-311++G** level of theory. Isodensity value of 0.004.

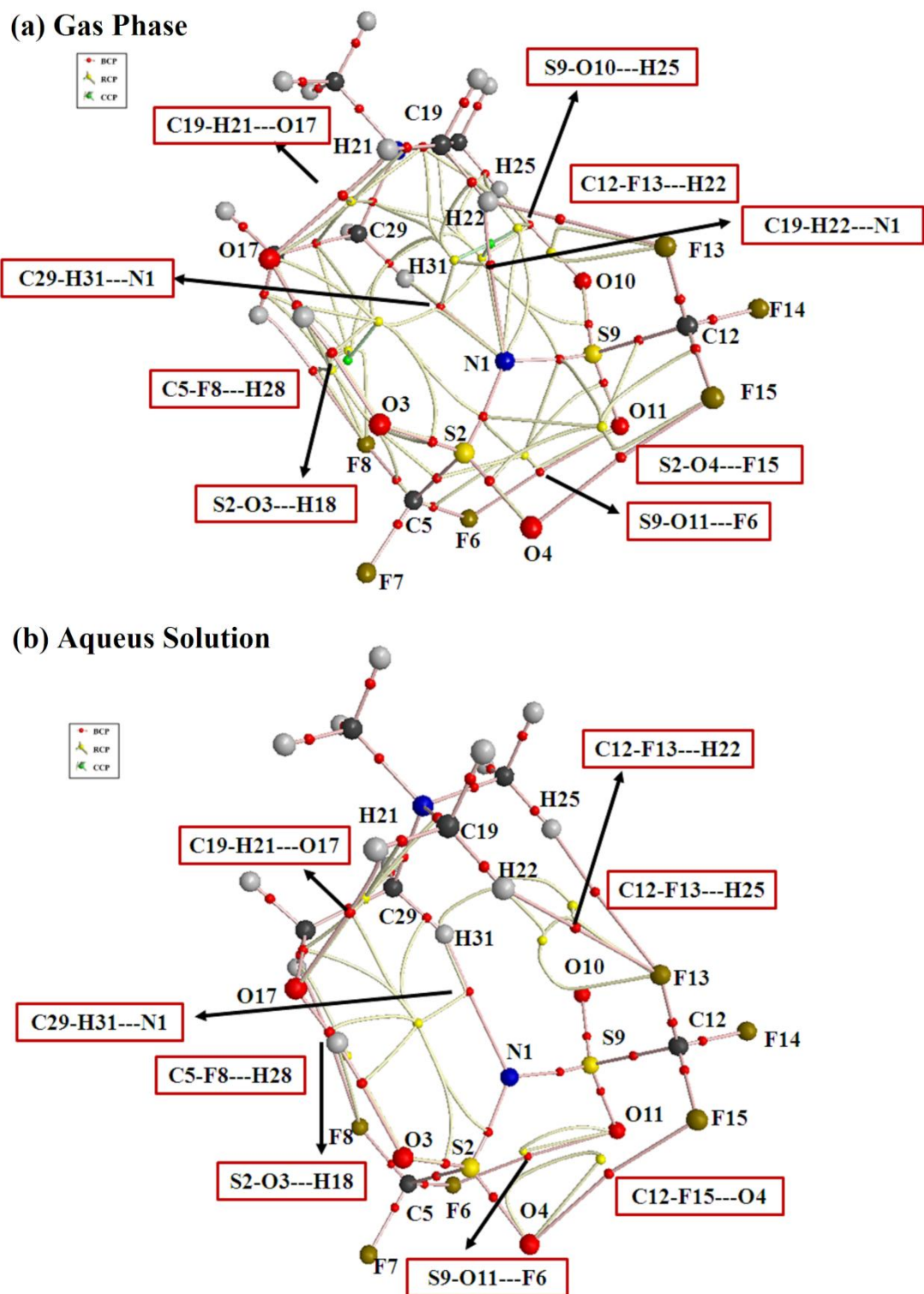


Figure S4. Molecular graphics for $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL, (a) in gas phase and (b) in aqueous solution by using the B3LYP/6-311++G** level of theory.

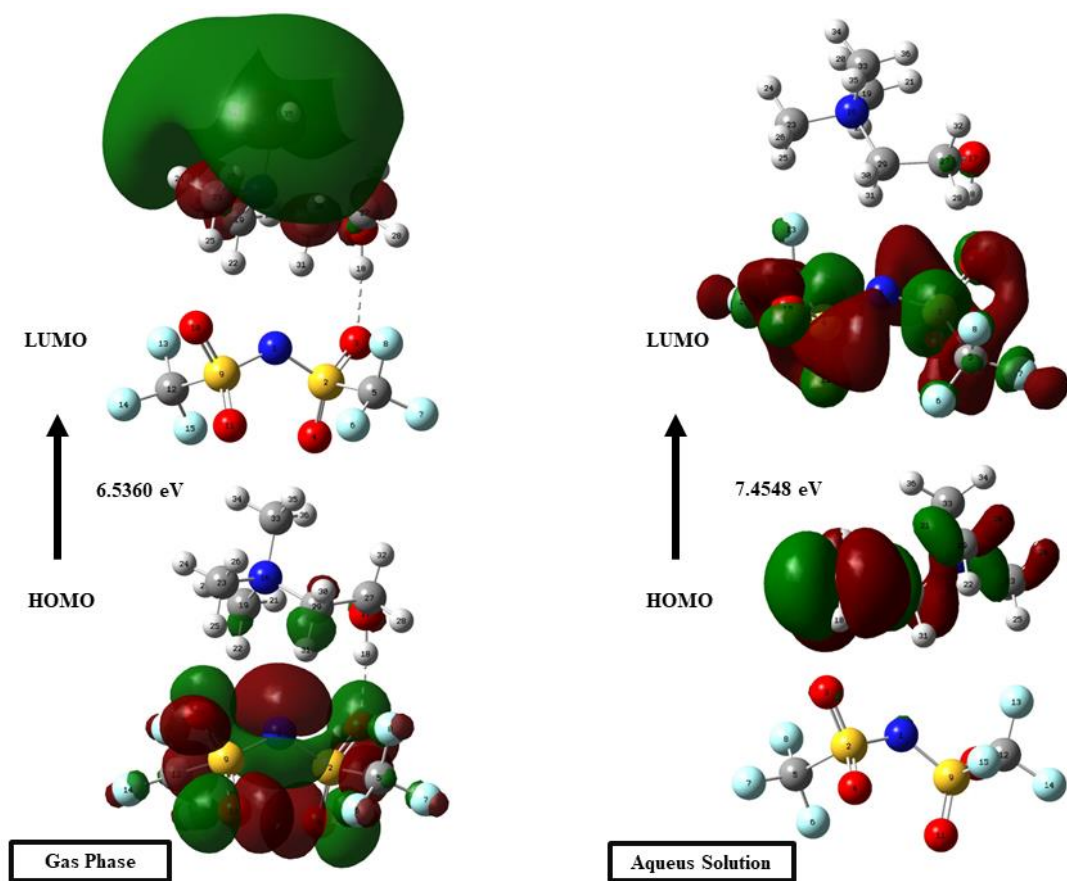


Figure S5. Characteristics of HOMO-LUMO orbitals for [CHOL⁺] [(CF₃SO₂)₂N⁻] IL showing the gap values in gas phase and aqueous solution by using the B3LYP/6-311++G** level of theory.

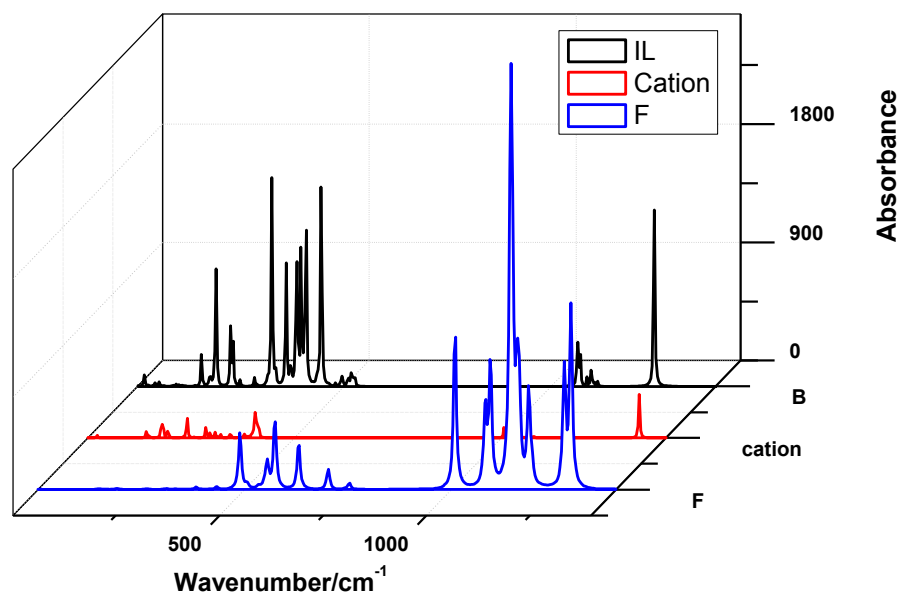


Figure S6.Theoretical FT-IR spectrum of ionic liquid in the gas phase (black colour) compared with the corresponding predicted for the cation (red colour) and anion(blue colour) by using the B3LYP/6-311++G** level of theory.

Table S1. Calculated atomic MK, Mulliken and NPA charges on the atoms of [CHOL⁺][(CF₃SO₂)₂N⁻] IL in gas phase and in aqueous solution by using the B3LYP/6-311++G** level of theory.

B3LYP/6-311G**METHOD						
[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻]						
Atoms	Gas Phase			AqueousSolution		
	MK	Mulliken	NPA	MK	Mulliken	NPA
1 N	-0.540	-0.722	-1.254	-0.589	-0.457	-1.206
2 S	0.961	0.139	2.140	1.031	0.047	2.134
3 O	-0.556	-0.134	-0.961	-0.583	-0.144	-0.954
4 O	-0.485	0.049	-0.868	-0.595	-0.168	-0.931
5 C	0.414	0.063	0.862	0.483	0.166	0.871
6 F	-0.132	-0.016	-0.325	-0.154	-0.050	-0.338
7 F	-0.157	-0.051	-0.334	-0.182	-0.067	-0.337
8 F	-0.158	-0.061	-0.359	-0.148	-0.046	-0.336
9 S	0.908	-0.014	2.132	0.987	0.174	2.128
10 O	-0.539	-0.095	-0.943	-0.576	-0.136	-0.935
11 O	-0.478	0.049	-0.872	-0.588	-0.178	-0.935
12 C	0.460	0.067	0.861	0.483	0.034	0.869
13 F	-0.182	-0.064	-0.356	-0.146	-0.018	-0.335
14 F	-0.167	-0.055	-0.336	-0.178	-0.054	-0.337
15 F	-0.135	-0.011	-0.326	-0.152	-0.041	-0.339
16 N	0.177	-0.218	-0.348	0.493	-0.045	-0.339
17 O	-0.647	-0.273	-0.765	-0.731	-0.365	-0.797
18 H	0.463	0.392	0.509	0.462	0.416	0.501
19 C	-0.278	-0.493	-0.359	-0.450	-0.414	-0.352
20 H	0.150	0.182	0.199	0.184	0.234	0.224
21 H	0.177	0.244	0.243	0.205	0.222	0.231
22 H	0.125	0.249	0.248	0.194	0.231	0.227
23 C	-0.382	-0.228	-0.358	-0.412	-0.306	-0.350
24 H	0.172	0.179	0.207	0.191	0.212	0.228
25 H	0.222	0.325	0.268	0.161	0.227	0.228
26 H	0.172	0.181	0.205	0.186	0.214	0.227
27 C	0.161	-0.619	-0.048	0.110	-0.630	-0.053
28 H	0.055	0.219	0.195	0.076	0.242	0.196
29 C	-0.202	-0.422	-0.201	-0.204	-0.388	-0.192
30 H	0.133	0.166	0.207	0.153	0.222	0.237
31 H	0.102	0.504	0.262	0.090	0.380	0.238
32 H	0.068	0.160	0.171	0.111	0.198	0.198
33 C	-0.594	-0.296	-0.350	-0.647	-0.360	-0.355
34 H	0.218	0.182	0.214	0.234	0.210	0.229
35 H	0.223	0.204	0.212	0.232	0.228	0.228
36 H	0.268	0.219	0.228	0.270	0.210	0.228

Table S2. Molecular electrostatic potentials (MEP) and Bond orders (BO) expressed as Wiberg bond index, totals by atom for the [CHOL⁺][(CF₃SO₂)₂N⁻] IL in gas phase and in aqueous solution by using the B3LYP/6-311++G** level of theory.

Atoms	MEP (a.u.)		Bond Orders	
	Gas	AqueousSolution	Gas	AqueousSolution
1 N	-18.393	-18.401	2.476	2.531
2 S	-59.004	-59.027	4.280	4.280
3 O	-22.369	-22.388	1.605	1.609
4 O	-22.375	-22.430	1.723	1.634
5 C	-14.493	-14.508	3.645	3.655
6 F	-26.551	-26.576	1.074	1.057
7 F	-26.550	-26.569	1.058	1.054
8 F	-26.547	-26.550	1.026	1.059
9 S	-59.007	-59.030	4.286	4.287
10 O	-22.373	-22.402	1.620	1.624
11 O	-22.376	-22.433	1.718	1.629
12 C	-14.494	-14.496	3.644	3.655
13 F	-26.548	-26.524	1.028	1.058
14 F	-26.551	-26.559	1.056	1.053
15 F	-26.552	-26.565	1.073	1.057
16 N	-18.222	-18.174	3.567	3.570
17 O	-22.353	-22.359	1.793	1.751
18 H	-0.991	-1.001	0.745	0.753
19 C	-14.696	-14.653	3.740	3.758
20 H	-1.051	-1.000	0.962	0.951
21 H	-1.059	-1.031	0.943	0.949
22 H	-1.060	-1.024	0.945	0.951
23 C	-14.686	-14.638	3.750	3.755
24 H	-1.043	-0.990	0.959	0.950
25 H	-1.052	-1.015	0.930	0.950
26 H	-1.043	-0.996	0.959	0.950
27 C	-14.684	-14.665	3.865	3.838
28 H	-1.080	-1.065	0.965	0.964
29 C	-14.688	-14.650	3.803	3.820
30 H	-1.049	-1.005	0.959	0.946
31 H	-1.062	-1.038	0.941	0.947
32 H	-1.080	-1.044	0.974	0.964
33 C	-14.670	-14.627	3.784	3.759
34 H	-1.030	-0.982	0.956	0.949
35 H	-1.030	-0.983	0.957	0.949
36 H	-1.034	-0.993	0.950	0.950

Table S3. Main delocalization energy (in kJ/mol) of $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ IL in gas phase and in aqueous solution by using the B3LYP/6-311++G** level of theory.

B3LYP/6-311G**METHOD		
[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻]		
Delocalization	Gas	PCM
<i>LP(2)N1</i> → σ^* <i>S2-C5</i>	69.1	73.3
<i>LP(2)N1</i> → σ^* <i>S9-C12</i>	67.2	70.7
<i>LP(2)O3</i> → σ^* <i>N1-S2</i>	67.0	72.1
<i>LP(3)O3</i> → σ^* <i>S2-O4</i>	67.8	66.2
<i>LP(3)O3</i> → σ^* <i>S2-C5</i>	53.2	60.2
<i>LP(2)O4</i> → σ^* <i>N1-S2</i>	101.7	94.4
<i>LP(3)O4</i> → σ^* <i>S2-O3</i>	72.1	60.2
<i>LP(3)O4</i> → σ^* <i>S2-C5</i>	76.2	74.7
<i>LP(2)F6</i> → σ^* <i>S2-C5</i>	44.4	42.3
<i>LP(3)F6</i> → σ^* <i>C5-F8</i>	58.2	
<i>LP(3)F6</i> → σ^* <i>C5-F7</i>		54.0
<i>LP(2)F7</i> → σ^* <i>C5-F6</i>	41.8	
<i>LP(2)F7</i> → σ^* <i>S2-C5</i>		42.1
<i>LP(3)F7</i> → σ^* <i>C5-F6</i>		47.7
<i>LP(3)F7</i> → σ^* <i>C5-F8</i>	63.2	42.1
<i>LP(3)F7</i> → σ^* <i>C5-F7</i>	55.1	
<i>LP(2)F8</i> → σ^* <i>S2-C5</i>		44.8
<i>LP(3)F8</i> → σ^* <i>C5-F6</i>		43.1
<i>LP(3)F8</i> → σ^* <i>C5-F7</i>		47.2
<i>LP(2)O10</i> → σ^* <i>N1-S9</i>	72.9	77.5
<i>LP(3)O10</i> → σ^* <i>S9-O11</i>	64.5	63.7
<i>LP(3)O10</i> → σ^* <i>S9-C12</i>	63.2	68.5
<i>LP(2)O11</i> → σ^* <i>N1-S9</i>	103.9	94.8
<i>LP(3)O11</i> → σ^* <i>S9-O10</i>	67.5	54.3
<i>LP(3)O11</i> → σ^* <i>S9-C12</i>	81.4	79.0
<i>LP(2)F13</i> → σ^* <i>C12-F15</i>	46.7	
<i>LP(2)F13</i> → σ^* <i>S9-C12</i>		44.4
<i>LP(3)F13</i> → σ^* <i>C12-F14</i>	57.3	47.3
<i>LP(3)F13</i> → σ^* <i>C12-F15</i>		42.9
<i>LP(2)F14</i> → σ^* <i>S9-C12</i>		41.8
<i>LP(3)F14</i> → σ^* <i>C12-F13</i>	62.0	42.8
<i>LP(3)F14</i> → σ^* <i>C12-F15</i>		47
<i>LP(2)F15</i> → σ^* <i>S9-C12</i>	45.2	41.8
<i>LP(3)F15</i> → σ^* <i>C12-F13</i>	54.7	
<i>LP(3)F15</i> → σ^* <i>C12-F14</i>		55.0
$\Delta ET_{LP \rightarrow \sigma^*}$	1556.4	1735.8
σ^* <i>S2-O3</i> → σ^* <i>S2-O4</i>	87.2	214.3
σ^* <i>S9-O10</i> → σ^* <i>S9-O11</i>	118.3	
$\Delta ET_{\sigma^* \rightarrow \sigma^*}$	205.5	214.3
ΔET_{TOTAL}	1762.0	1950.1

Table S4. Predicted intramolecular interactions for the $[\text{CHOL}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ionic liquid in gas phase and aqueous solution by using the topological properties and the B3LYP/6-311G** Method.

Interactions ^a	
Gas Phase	Aqueous solution
S2-O3...H18	S2-O3...H18
S2-O4...F15	S2-O4...F15
S9-O11...F6	S9-O11...F6
S9-O10...H25	
C5-F8...H28	C5-F8...H28
C12-F13...H22	C12-F13...H22
	C12-F13...H25
C19-H21...O17	C19-H21...O17
C19-H22...N1	
C29-H31...N1	C29-H31...N1

^aThis work; Letters bold, shorter distances.

Table S5. Analysis of the topological properties for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid in gas phase and aqueous solution by using the B3LYP/6-311++G** Method.

Parameter (a.u.)	Gas Phase						
	S2-O3...H18	S2-O4...F15	S9-O11...F6	C5-F8...H28	C12-F13...H22	C19-H21...O17	C29-H31...N1
$\rho(r_c)$	0.0296	0.0063	0.0067	0.0032	0.0052	0.0162	0.0181
$\nabla^2\rho(r_c)$	0.1128	0.0251	0.0265	0.0142	0.0208	0.0537	0.0561
λ_1	-0.0432	-0.0051	-0.0056	-0.0028	-0.0048	-0.0172	-0.0205
λ_2	-0.0418	-0.0050	-0.0054	-0.0023	-0.0041	-0.0150	-0.0188
λ_3	0.1978	0.0352	0.0375	0.0193	0.0296	0.0859	0.0954
$ \lambda_1/\lambda_3$	0.2184	0.1451	0.1483	0.1437	0.1608	0.2004	0.2146
Distance (Å)	1.821	2.989	2.951	2.585	2.593	2.193	2.224
Parameter (a.u.)	Aqueussolution						
	S2-O3...H18	S2-O4...F15	S9-O11...F6	C5-F8...H28	C12-F13...H22	C19-H21...O17	C29-H31...N1
$\rho(r_c)$	0.0217	0.0048	0.0047	0.0012	0.0018	0.0114	0.0079
$\nabla^2\rho(r_c)$	0.0874	0.0200	0.0197	0.0060	0.0087	0.0378	0.0235
λ_1	-0.0292	-0.0033	-0.0032	-0.0009	-0.0015	-0.0106	-0.0072
λ_2	-0.0275	-0.0020	-0.0017	-0.0008	-0.0012	-0.0086	-0.0067
λ_3	0.1441	0.0253	0.0246	0.0077	0.0114	0.0570	0.0374
$ \lambda_1/\lambda_3$	0.2028	0.1294	0.1283	0.1196	0.1291	0.1860	0.1918
Distance (Å)	1.955	3.210	3.223	3.274	3.043	2.482	2.622

Table S6. Analysis of the topological properties for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid in gas phase and aqueous solution by using the B3LYP/6-311++G** Method.

Parameter (a.u.)	Gas Phase		
	S9-O10...H25	C19-H22...N1	C12-F13...H25
$\rho(r_c)$	0.0160	0.0104	-----
$\nabla^2\rho(r_c)$	0.0576	0.0306	-----
λ_1	-0.0183	-0.0097	-----
λ_2	-0.0174	-0.0086	-----
λ_3	0.0933	0.0490	-----
$ \lambda_1 /\lambda_3$	0.1957	0.1988	-----
Distance (Å)	2.215	2.678	
Parameter (a.u.)	Aqueussolution		
	S9-O10...H25	C19-H22...N1	C12-F13...H25
$\rho(r_c)$	-----	-----	0.0030
$\nabla^2\rho(r_c)$	-----	-----	0.0132
λ_1	-----	-----	-0.0027
λ_2	-----	-----	-0.0026
λ_3	-----	-----	0.0185
$ \lambda_1 /\lambda_3$	-----	-----	0.1464
Distance (Å)			2.838

Table S7. Calculated HOMO and LUMO orbitals, energy band gap, global hardness (η), global softness (S) and global electrophilicity index (ω) for the [CHOL⁺][(CF₃SO₂)₂N⁻] ionic liquid in gas phase and aqueous solution by using the B3LYP/6-311++G** method. The parameters for cation and anion in gas phase are also presented by using the B3LYP/6-311++G** method.

Frontierorbitals (eV)	Gas Phase		6-311++G**	
	6-311++G**	6-311++G**	[CHOL ⁺][(CF ₃ SO ₂) ₂ N ⁻] ^a	
	[CHOL ⁺]	[(CF ₃ SO ₂) ₂ N ⁻]	Gas Phase	AqueousSolution
HOMO	-12.1197	-6.0443	-7.8229	-7.8824
LUMO	-4.0861	-1.8039	-1.2869	-0.4184
GAP	8.0337	4.2404	6.5360	7.4640
	Descriptors			
X	8.1029	3.9241	4.5549	4.1504
μ	-8.1029	-3.9241	-4.5549	-4.1504
η	4.0168	2.1202	3.2680	3.7320
S	0.1245	0.2358	0.1530	0.1340
ω	8.1727	3.6314	3.1743	2.3079

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors declare no conflict of interest.

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