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Density Functional Theory Study of EmimBF4 Ionic Liquid Monomer and their Interaction with CO_2 in Ionic Liquid Environments: Insights from Vibrational Spectra Analysis

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Abstract

In order to improve our knowledge of cation-anion interactions in ionic liquids, we optimized the 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMImBF4]), and their interactions with CO_2, with a focus on structural properties and vibrational behavior relevant to chemical applications such as carbon capture. By using density functional theory (DFT), the structures of the cation, anions, and cation-anion ion pairs of [EMImBF4] with CO_2 were optimized. Vibrational spectroscopy was employed to emphasize structural properties, and vibrational frequencies of EMImBF4 and EMImBF4-CO_2 (monomer) compounds were calculated. The scaled values were compared to experimental far-infrared and far-infrared Raman spectra to validate the theoretical findings.The study identified the most stable geometries of [EMImBF4] and [EMImBF4]-CO_2 interactions, showing specific vibrational modes upon interaction with CO_2 that align well with experimental data. These insights highlight the potential of [EMImBF4] in gas separation and capture, demonstrating its unique physicochemical properties and reinforcing the importance of understanding IL-CO_2 interactions for developing efficient carbon capture technologies.

Keywords: Density functional calculations; Ionic liquids; Monomer; EMImBF4-CO_2; Vibrational spectra; Computational protocol.

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1. Introduction

Ionic liquids (ILs) have garnered significant attention in recent times due to their unique properties, such as high thermal stability, low volatility, and configurable physicochemical aspects [1]. Among them, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm-BF4) has become particularly well-known for its adaptable properties, low volatility, and thermal stability [2]. This IL has been extensively studied for various applications, including electrochemistry and catalysis [3]. Carbon dioxide (CO_2), a major greenhouse gas, poses significant environmental challenges due to its contribution to global climate change. Industrial sources must effectively absorb and store CO_2 emissions to mitigate these

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detrimental impacts [4]. ILs, due to their high selectivity, capacity, and reversible absorption properties, have significant potential for CO_2 storage [5]. EMIm-BF4, as a prototype IL, is noted for its stability and adaptability across a broad range of applications, including catalysis, electrochemistry, and gas separation [6].

Understanding the vibrational dynamics of EMIm-BF4 and its interaction with CO_2 is crucial for elucidating their molecular interactions and developing effective separation techniques for ecologically relevant gases. The unique characteristics of ILs, such as good thermal stability, low vapor pressure, and effective solvency for various chemicals, enhance their utility as process electrolytes [7]. The tetrafluoroborate anion ([BF4]−) and 1-ethyl-3-methylimidazolium cation ([EMIm]+) in EMIm-BF4 contribute to its low viscosity, thermal stability, and superior solvation abilities, forming a stable ionic network through hydrogen bonding and electrostatic interactions [8]. The versatility of EMIm-BF4 is attributed to its ability to undergo various molecular motions—rotation, translation, and vibration—that influence its physicochemical behavior and applications. Understanding the interaction between ILs and CO_2 at the molecular level is essential for designing efficient separation processes and developing new materials for carbon capture technologies. The solution's characteristics can be tailored by altering the cations and anions, with the possibility of modulating physico-chemical properties (e.g., hydrophobicity) through precise mixing [9]. These attributes make ILs promising candidates for various applications, including green chemistry, catalysis, and electrochemistry. In this study, we explore the vibrational frequencies of EMIm-BF4 IL and its interaction with CO_2 to gain insights into their molecular structure and potential applications in gas separation and capture. Vibrational spectroscopy plays a fundamental role in characterizing ionic liquids and understanding their interactions, underscoring its continued importance as a powerful tool in this field [10]. While extensive research has been conducted on ILs, our work focuses on the vibrational properties of EMIm-BF4 and its CO_2 interaction, an area that remains less explored. By providing detailed insights into these interactions, our study offers novel contributions to the understanding of IL-CO_2 systems by using DFT and Vibrational Spectrocopy, crucial for advancing carbon capture technologies and environmental remediation efforts.In this study, we propose a new approach of using ionic liquid with CO_2 based on the successive density fuctional method for enhancing our understanding in the microsocopic point of view .

2. Materials and Method: Computational Method

Density functional calculations (DFT) were utilized to establish the minimum energy structures, interaction energies, and binding energies of complexes [11]. The B3LYP hybrid functional, a three-parameter functional designed by Becke that combines the Becke gradient-corrected exchange functional with the Lee-Yang-Parr functional for exchange and correlation, was employed for quantum chemical calculations [12]. The vibrational frequencies were measured in terms of wavelength (cm^{-1}) for various vibrations, including

BF4 twist, scissors, wag, symmetric stretching, umbrella, and CO_2 bending, symmetric stretch, and asymmetric stretch.

The vibrational frequencies of the EMIM-BF4 IL and EMIMBF4-CO_2 systems were investigated by spectroscopy, a powerful analytical technique for probing molecular vibrations and elucidating chemical structures. The corresponding vibrational frequencies were analyzed to identify characteristic modes and assess the impact of CO2 on the vibrational behavior of the IL. The minimum relative interaction energy and atomic charges were determined using DFT. The 6-31+G(d,p) basis set was selected for its accuracy and computational efficiency. The gas-phase and liquid-phase optimized architectures and their corresponding vibrational frequencies were examined [13]. The liquid-phase structures and vibrational frequencies were calculated using the IEF-PCM at 298 K and 1 atmosphere pressure.

The NBOs and ESPs of all optimized structures were estimated at the B3LYP/6-31+G(d,p) level. All graphical illustrations in this article were created with Avogadro software packages [14]. All simulations were conducted using the Gaussian 09 quantum chemistry software [15].

3. Results and Discussion

3.1. *IL complexes: 1-Ethyl-3-methylimidazolium-tetra-fluoroborate [EMIMBF4] and [EMIMBF4-CO_2]*

Comparing the vibrational frequencies of the EMIM-BF4 IL and EMIMBF4-CO_2 systems reveals interesting new details on their molecular interactions. The vibrational modes seen in both systems may be categorized into many forms of molecular motion, including twisting, bending, stretching, and wagging.

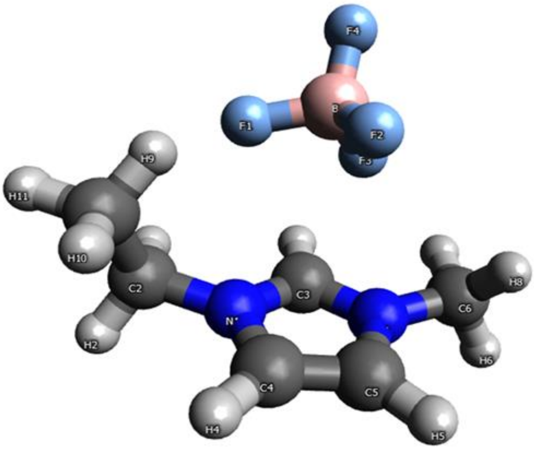

Fig. 1. The locations of the minimum energy structures found for [EMIM] + [BF4] - in terms of [EMIM].

As shown in Fig. 1, ion pair concentrations in water are estimated using the PCM implicit model, with calculations done at the B3LYP/6- 31+g (d,p) level. The graphics shown in this article were created using Avogardo Software, a visualization program In EMIM-BF4 IL, the BF4 ion vibrates in the following modes: twist, scissors, wag, and symmetric stretching. These modes are seen at wavelengths of 339 cm^{-1}, 341 cm^{-1}, 499.8 cm^{-1}, and 750.5 cm^{-1}, respectively. The BF4 ion is stable and physically intact inside the IL matrix, as indicated by these vibrations. When the [EMIM][BF4] liquid changed the vibrational and configuration state of the [EMIM][BF4] IL, Takashi Makino et al. noticed a slight symmetric stretching vibration of the BF4 anion (experimental Raman research). It is noteworthy, therefore, that neither the IL nor the CO_2-EMIMBF4 systems exhibit any appreciable anion (vibrational symmetric stretching) difference in the structures where BF4 symmetric stretching takes place. This is probably because figuring out the vibrational frequencies of an actual IL requires more than just modeling the IL as an ion pair in a continuum.

Table 1. Shows a comparative comparison of vibrational frequencies. Both the methyl and ethyl chains have high structural flexibility with regard to the IMIM ring, according to vibrational frequency calculations.

Vibrations	Wavelength(cm^{-1}) System EMIM BF4
BF4	
Twist	339
Scissors	341
	499.8
Wag	500.5
	501.5
Symmetric stretching	750.5
	1004
Umbrella	1009
	1012
CO_2	
Bending	637.3
	637.3
Symmetric Stretch	1359.5
Asymmetric Stretch	2340.2

CO_2 bending and symmetric stretching modes have wavelengths of 637.3 cm^{-1} and 1359.5 cm^{-1}, respectively, while the asymmetric stretching mode emerges at 2340.2 cm^{-1}. These frequencies suggest the existence of CO_2 molecules in the IL environment and shed light on the nature of CO-IL interactions. Interestingly, the symmetric stretching mode of CO_2 displays a blue shift when compared to its frequency in the gas phase, indicating that the CO_2 molecule's electronic environment is perturbed by contact with the IL. This change might be explained by electrostatic interactions between CO_2 and the charged species found in the IL, such as the BF4 ion.

There are also ample literature which are also similar to our finding [16,17]. Anion [BF4]- interaction energies and lowest stable energy structures in EMIMBF4 ionic liquid are investigated in this paper through the use of VF analysis in conjunction with other methods of investigation.

3.2. *1-Ethyl-3-methylimidazolium-tetra-fluoroborate and Carbon dioxide [EMIMBF4-CO_2]*

Upon interaction with CO_2, additional vibrational modes emerge in the EMIMBF4-CO_2 system, corresponding to the bending and stretching motions of CO_2 molecule. Nevertheless, our calculations indicate that the change in vibrational frequencies seen in the experiment is not caused by the creation of a CO_2 and BF4 link, but rather by a more intricate alteration of the ionic liquid structure. It is important to note that this mode, which includes the BF4 anion twisting at a distance of around 339 cm^{-1}, illustrates the IL's flexibility and rotational freedom.

This mode is associated with the BF4 anion's scissoring motion at around 341 cm^{-1}, indicating that it can experience symmetric deformation.The BF4 anion's wagging motion, which ranges from 499.8 to 501.5 cm^{-1}, shows how dynamic and sensitive it is to outside stimuli. This mode, which is located at about 750.5 cm^{-1}, indicates the symmetric stretching of the BF4 anion and emphasizes its structural stability in the IL. The BF4 anion's umbrella motion, which ranges from 1009 to 1012 cm^{-1}, illustrates its capacity for asymmetric deformation and adds to the ILs overall flexibility. As can be seen, we expect that the CO_2 vibrational frequencies will fluctuate as well, even though the quantity of CO_2 in the IL has no influence on any of the BF4 frequencies. Both a little rise in the symmetric stretching frequency and an increase in the bending frequencies are estimated**.**

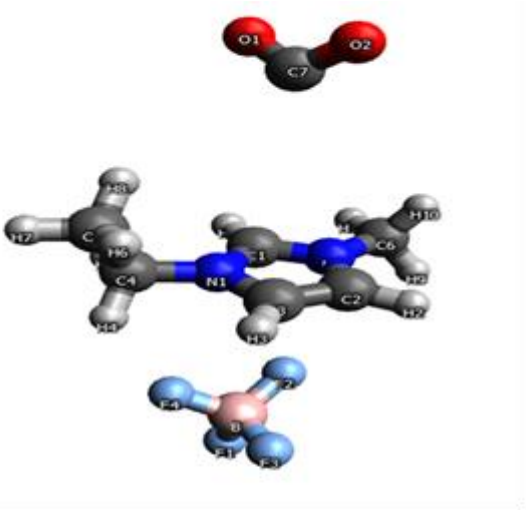

Fig. 2. Energy structures of the [EMIM][BF4]- CO_2 ion pair.

Table 2. A comparative comparison of vibrational frequencies. Both the methyl and ethyl chains have high structural flexibility with regard to the IMIM ring, according to vibrational frequency calculations.

Vibrations	Wavelength(cm^{-1}) System EMIM BF4 CO_2
BF4	
Twist	338.3
Scissors	341.6
	499.0
Wag	500.1
	502.3
Symmetric stretching	750.6
	1000.2
Umbrella	1008.5
	1019.8
CO_2	
Bending	666.6
	640.9
Symmetric Stretch	1362.6
Asymmetric Stretch	2343.0

This mode, which varies between 640.9 and 666.6 cm^{-1}, represents the bending motion of CO_2 and shows how it interacts with its surroundings. Symmetric. This mode, which is located between 1359.5 and 1362.6 cm^{-1}, represents the symmetric stretching of CO2 and its confinement inside the IL matrix. The asymmetric stretching of CO_2 shows that it may interact directionally with the molecules around it, with a range of 2340.2 to 2343.0 cm^{-1}. The BF4 anion's umbrella motion, which is seen between 1009 and 1012 cm^{-1}, highlights its capacity for asymmetric deformation, which is essential in determining the structural dynamics and interactions of the IL[18].

While vibrational spectroscopy gives useful information on the general dynamics of IL-CO_2 systems. Furthermore, the existing literature is mostly concerned with static vibrational spectra acquired under ambient circumstances. There is a knowledge gap regarding the dynamic behavior of IL-CO_2 systems at various temperatures, pressures, and compositions. The influence of these factors on vibrational frequencies and molecular dynamics might reveal important information about the thermodynamic and kinetic aspects of CO_2 collection and release mechanisms in ILs. The study gap in the realm of IL-CO_2 interactions creates an intriguing opportunity for future research into the molecular design, dynamic behavior, and practical applications of ILs in CO_2 capture and use. Addressing these gaps might pave the path for the development of sustainable solutions to combat climate change and accelerate the transition to a carbon-neutral society. Looking ahead, further study on EMIM-BF4 vibrational frequencies (VFs) and their interaction with CO_2 offers a plethora of chances to expand our understanding and realize the promise of these molecular systems.The comparison of vibrational frequencies in EMIM-BF4 IL and the EMIMBF4-CO_2 system reveals important information about their molecular dynamics and interaction processes. These discoveries have significance for a wide range of applications, including gas separation, storage, and catalytic processes. Future research efforts may concentrate on understanding the unique nature of CO_2-IL interactions and investigating innovative IL systems for improved CO_2 collection and utilization techniques. We have studied several literature and almost all of the experimental data from these literatures simply coincide to our finding [19,20]. When the vibrational frequencies of the EMIM-BF4 IL and EMIMBF4-CO_2 systems are compared, unique spectrum characteristics that reflect various molecular interactions and movements are revealed. Typical vibrational modes linked to [EMIM]+ and [BF4]-ions are seen in the pure EMIM-BF4 IL, which represent the kinetics and structural configuration of the IL matrix. These modes' vibrational frequencies shed light on the nature of the interactions between [BF4] and ions as well as the solvation behavior of these interactions in EMIM-BF4 IL. The EMIMBF4-CO_2 system exhibits new vibrational modes upon contact with CO_2, which are indicative of the CO_2 molecules present in the IL environment and their interactions with the surrounding ions.The vibrational modes associated with CO_2 bending, symmetric stretching, and asymmetric stretching are detected, indicating the production of CO2-IL complexes and the disruption of CO_2 molecule vibrations in the IL matrix. The frequencies and intensities of these modes reveal information on the intensity and type of CO_2-IL interactions, which is critical for developing effective CO_2 capture materials and procedures. Understanding the frequency at which CO_2 is absorbed by the ionic liquid is critical because it indicates the interaction intensity and kind of bonding between the CO_2 molecule and the ionic liquid. The barrier height for collecting CO_2 has been determined for both gas phase and aqueous solution, revealing the major effect of solvent polarity on the reaction processes.

4. Conclusion

The investigation of vibrational frequencies of EMImBF4 ionic liquid and its interaction with CO_2 using DFT and vibrational spectroscopy revealed specific vibrational modes and spectral features characteristic of these systems. The identified vibrational modes provide valuable insights into the microscopic point of view and interactions between EMImBF4 and CO_2. The computational vibrational spectral data from the calculation align well with experimental observations, confirming the accuracy of our theoretical models. The study highlights the strong potential of EMImBF4 in applications related to gas separation and carbon capture. Understanding the specific vibrational modes and molecular interactions in IL-CO_2 complexes is crucial for developing efficient carbon capture technologies and novel IL-based materials for environmental remediation.These results underscore the importance of understanding the molecular interactions in IL-CO_2 complexes for environmental applications. Further research into the structure-property relationships of IL-CO_2 systems is essential to fully exploit their capabilities in addressing CO_2 emissions and related environmental challenges.

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