JSR Publications

Available Online

J. Sci. Res. **17** (2), 561-567 (2025)

JOURNAL OF
SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Density Functional Theory-Based Study of CO_2 Vibrational Frequencies in Dimer Ionic Liquids

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Received 12 September 2024, accepted in final revised form 21 February 2025

Abstract

The vibrational frequency analysis of ionic liquids (ILs) interacting with CO_2 represents a rapidly emerging field, yet significant gaps persist in understanding microscopic interactions at the molecular level, particularly regarding solvation dynamics and structural relaxation. In this study, density functional theory (DFT) was employed to optimize the structures of the cation, anion, and cation–anion ion pairs of 1-ethyl-3-methylimidazolium tetrafluoroborate ([$EMImBF_4$]), focusing on stable geometries. The structural properties and vibrational frequencies of the [$EMImBF_4$]$_2$ dimer were systematically investigated, followed by an analysis of the [$EMImBF_4$]$_2$-CO_2 complex. Scaled vibrational frequencies were compared with experimental far-infrared and Raman spectra, revealing critical insights into the ν_3 asymmetric stretching mode of CO_2. The dimer model demonstrated superior accuracy in representing CO_2 interactions compared to monomeric systems, with energy differences of 2.8 kcal·mol^{-1} observed in the liquid phase. These findings enhance the understanding of CO_2 behavior in IL environments, offering implications for CO_2 capture technologies and spectroscopic interpretation.

Keywords: Density functional theory; Ionic liquids; Dimer; EMImBF4-CO_2; Vibrational spectra.

doi: https://dx.doi.org/10.3329/jsr.v17i2.76119 J. Sci. Res. **17** (2), 561-567 (2025)

1. Introduction

Ionic liquids (ILs) have garnered significant attention due to their unique properties, including low vapor pressure, thermal stability, and tunable solvation dynamics [1-3]. Their application in CO_2 capture has become a focal point, driven by environmental concerns and

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the need for efficient carbon sequestration technologies [4,5]. Despite progress, the molecular-level interactions between ILs and CO_2, particularly the role of solvation dynamics and structural relaxation, remain poorly understood [6,7].

This study addresses these gaps by investigating the vibrational behavior of CO_2 in the [EMImBF$_4$] IL system. The ν_3 asymmetric stretching mode of CO_2 serves as a vibrational chromophore, sensitive to local solvation environments [8]. Prior studies on imidazolium-based ILs, such as [C_4C_1im][X] (X = BF_4^-, PF_6^-, Tf_2N^-), have highlighted the influence of anion identity on CO_2 vibrational frequencies by using different methods and functional as well as molecular dynamic simulation [9,10]. However, the role of IL aggregation (e.g., dimers) in modulating CO_2 interactions remains underexplored. The novelty of this work lies in its focus on the [EMImBF$_4$]$_2$ dimer as a model system, which better replicates the bulk IL environment compared to monomeric ion pairs. By combining DFT calculations with vibrational spectroscopy, this study elucidates how charge transfer and geometric distortions between CO_2 and ILs impact the ν_3 frequency. The objectives are twofold: (1) to establish a computational framework for modeling CO_2-IL interactions and (2) to correlate theoretical predictions with experimental vibrational spectra, advancing the design of ILs for CO_2 capture.

2. Materials and Methods: Computational Methods

Density functional theory (DFT) was used to optimize the minimum energy structures, interaction energies, and binding energies of the complexes [11]. The B3LYP hybrid functional, combining Becke's gradient-corrected exchange functional with the Lee-Yang-Parr correlation functional, was applied for quantum chemical calculations [12].

The vibrational spectra of the EMIM-BF4 dimer and its interaction with CO_2 were investigated using spectroscopy. This analysis helped identify characteristic vibrational modes and assess the impact of CO_2 on the IL's vibrational behavior. Interaction energies and atomic charges were calculated using DFT. The 6-31+G(d,p) basis set was chosen for its accuracy and computational efficiency. Gas-phase and liquid-phase optimized structures and vibrational frequencies were examined, with liquid-phase calculations performed using the IEF-PCM model at 298 K and 1 atm pressure [13].

Natural bond orbitals (NBOs) and electrostatic potentials (ESPs) of all optimized structures were evaluated at the B3LYP/6-31+G(d,p) level. Graphical illustrations were created using Avogadro and Molden software [14], and simulations were performed with Gaussian 09 software [15].

3. Results and Discussion

3.1. *Structural optimization*

The optimized geometries of the [EMImBF$_4$] monomer and dimer are depicted in Figs. 1a and 1b respectively. In the dimer, parallel alignment of imidazolium rings facilitated anion sharing between H4 and H5 sites, stabilizing the structure through hydrogen bonding. CO_2 binding in the dimer system (Fig. 2b) involved multiple anion contacts, contrasting with the monomer (Fig. 2a), where CO_2 adopted a coplanar orientation relative to the imidazolium ring.

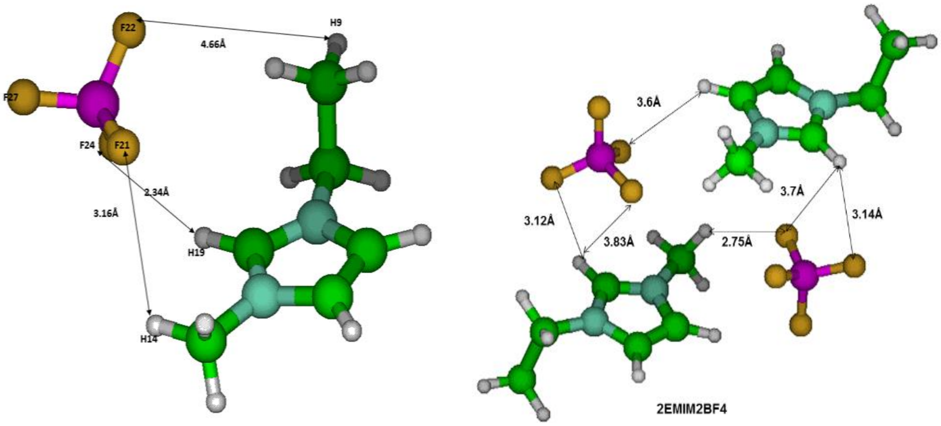
3.2. *Vibrational frequency analysis*

The observed vibrational shifts in CO_2 upon interaction with $[EMIm][BF_4]$ provide critical insights into the mechanism of CO_2 capture in ionic liquids. The red shift in the asymmetric stretching mode of CO_2 indicates a weakening of the C=O bond, suggesting strong interactions between CO_2 and the ionic liquid components. This shift is primarily attributed to the stabilization of CO_2 by the BF_4^- anion, which facilitates charge delocalization and lowers the activation energy for capture.in different ILs. Vibrational frequencies for $[EMImBF_4]_2$ and $[EMImBF_4]_2$-CO_2 are summarized in Table 1.

Table 1. Comparison of the vibrational frequency of $[EMImBF_4]_2$ IL and $[EMImBF4]_2$- CO_2 in ionic liquid (At 298 K and 1atmospheric pressure, the vibrational frequencies, measured in centimeters per second, are presented for comparison).

Vibrations	Wavelength System $[EMImBF_4]_2$	Wavelength System $[EMImBF_4\ ]_2$-CO_2
BF_4 Twist	340.346	339.310
	340.698	339.540
Scissors	341.659	340.065
	341.920	340.654
	436.197	499.949
	499.800	500.046
Wag	499.542	501.327
	500.221	501.450
Symmetric stretching	500.907	500.539
	501.961	504.053
	749.958	749.659
	750.545	751.322
	1004.446	1005.986
	1006.689	1006.176
Umbrella	1009.099	1010.148
	1009.876	1008.898
	1010.081	1010.611
	1010.611	1013.311
CO_2 Bending		637.878
		657.730
Symmetric stretch		1362.683
Asymmetric stretch		2346.683

The key observations include: CO_2 bending modes: 637.9 cm^{-1} and 657.7 cm^{-1}, reflecting sensitivity to solvation-induced distortions. Symmetric stretch (ν_1): 1362.7 cm^{-1}, consistent with experimental values [16,17]. Asymmetric stretch (ν_3): 2346.7 cm^{-1}, shifted by +3.7 cm^{-1} compared to gas-phase CO_2 due to anion charge transfer. The dimer exhibited greater stabilization ($\Delta E = 2.8$ kcal·mol^{-1}) than the monomer, attributed to enhanced intermolecular interactions. This aligns with prior reports on IL clustering effects [18-20].

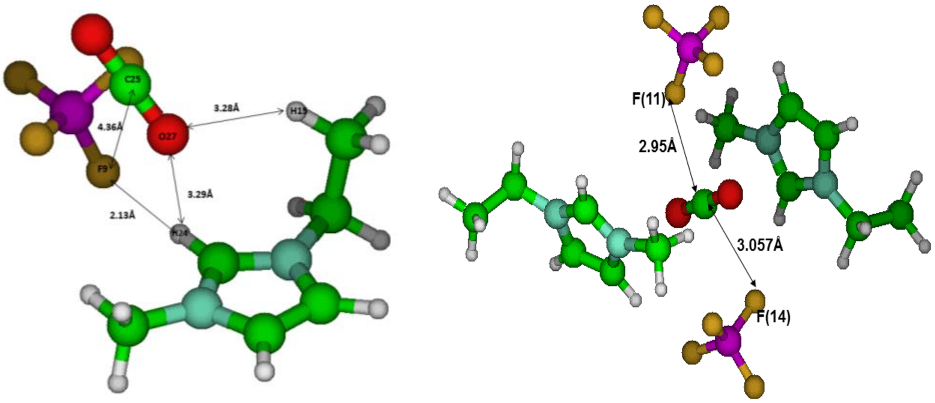


(a) (b)

Fig. 1. In the liquid phase, an optimized ion pair monomer (a) and dimer (b) and their minimal energy structure has been developed. Some key distances are reported. H(19)-F(24) distance 2.34 Å. All distances are reported in Angstrom.

A detailed description of the $EMImBF_4$, $EMImBF_4 – CO_2$ Monomer and its vibrational frequencies is presented briefly elsewhere in our previous article [21] confirming that all structures are both highly stable and thoroughly optimized. Notably, monomer CO_2 systems are less stable compared to dimer CO_2 systems, with energy differences of 2.06 and 2.8 kcal mol^{-1}, respectively, in the liquid phase. In the dimer CO_2-$EMImBF_4$ system, the two imidazolium rings are aligned in parallel, with each anion shared between the H5 side of one cation and the H4 side of the other, a characteristic feature of this conformer.

As a result, the two ion pairs serve as an excellent model for CO_2 absorption in this system. By carefully examining vibrational frequencies, small but important differences across chemical systems were revealed. Variations in vibrational modes reflect different bonding patterns, intermolecular interactions, and structural configurations, providing insight into the complex system influencing molecular activity. Minor but important differences across chemical systems were discovered by meticulously analyzing vibrational frequencies. Precisely simulating the potential energy surfaces and comprehending the impact of charge transfer on the vibrational modes of CO_2 when solvated in different ILs is required [22]. Furthermore, little is known about the harmonic coupling of normal modes and how it affects the vibrational spectra [23].



(a) (b)

Fig. 2. Depicts the complex structure of the [EMIMBF$_4$]-CO$_2$ monomer (a) and dimer (b) in the liquid phase of the reaction. Complex 1 (monomer) and the probable binding site for the CO$_2$ molecules are shown in this illustration. Optimized ion pair monomer and dimer in the presence of CO$_2$ in the liquid phase.

The CO$_2$-dimer system exhibits unique vibrational properties. The bending mode of CO$_2$ shows frequencies of 637.878 cm^{-1} and 657.730 cm^{-1}, indicating its flexibility and sensitivity to bending motions. The molecule resonates strongly at 1362.683 cm^{-1} in the symmetric stretch mode, highlighting the uniform elongation and contraction of its carbon-oxygen bonds. Additionally, the asymmetric stretch mode displays a significant frequency of 2346.683 cm^{-1}, reflecting the non-uniform stretching of CO$_2$ molecular structure. The examination of vibrational frequencies reveals small but important differences across chemical systems. These variations in vibrational modes reflect different bonding patterns, intermolecular interactions, and structural configurations, providing valuable insights into the complex dynamics influencing molecular activity. Minor variances in these values could be attributed to experimental errors or differing conditions under which measurements were made [24]. Vibrational frequencies of CO$_2$ are significantly influenced by its molecular structure. The bending vibration involves a change in the angle between the two oxygen atoms relative to the carbon atom. The symmetric stretch corresponds to the simultaneous stretching of the two carbon-oxygen bonds, while the asymmetric stretch involves one bond stretching while the other contracts. The values obtained align with theoretical predictions and previous experimental observations [25]. The symmetric stretch vibration typically occurs at a higher frequency than the asymmetric stretch, consistent with the provided data. In conclusion, the study demonstrates that the two ion pairs serve as an excellent model for CO$_2$ absorption. Vibrational frequencies of [EMImBF$_4$]$_2$ IL and [EMImBF$_4$]$_2$-CO$_2$ in ionic liquids were compared. Further research is needed on the harmonic coupling of normal modes, rotational dynamics of CO$_2$ in ILs, and their effects on spectral diffusion. The results provide valuable insights into the molecular structure, enhancing our understanding and facilitating the manipulation of chemical processes for various scientific and industrial applications. This study highlights the importance of IL aggregation in optimizing CO$_2$

solubility. The observed enhancement in charge transfer interactions within the dimer indicates that tuning IL structures to promote dimerization may significantly improve CO_2 capture efficiency.

4. Conclusion

This study demonstrates the critical role of IL aggregation in modulating CO_2 vibrational frequencies. The $[EMImBF_4]_2$ dimer model provided a more accurate representation of bulk IL behavior, revealing anion-mediated charge transfer as a key driver of ν_3 frequency shifts. These insights advance the interpretation of CO_2 spectra in ILs and inform the design of tailored solvents for carbon capture. Future work will explore temperature-dependent dynamics and anharmonic effects to refine predictive models.

Acknowledgments

Supported by the Italian Research Council and the European Regional Development Fund (FARB199). Gratitude is extended to C. Cavallotti for mentorship.

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