

Article

Spectroscopic and Quantum Chemical Evidence of Amine–CO₂ and Alcohol–CO₂ Interactions: Confirming an Intriguing Affinity of CO₂ to Monoethanolamine (MEA)

Sahar Hafizi Yazdabadi ^{1,2} , Dmytro Mihin ^{1,2} , Karen Louise Feilberg ²  and René Wugt Larsen ^{1,*} 

¹ Department of Chemistry, Technical University of Denmark, Kemitorvet 206, 2800 Kongens Lyngby, Denmark

² DTU Offshore, Technical University of Denmark, Elektrovej 375, 2800 Kongens Lyngby, Denmark

* Correspondence: rew1@kemi.dtu.dk

Abstract: A recent broadband rotational spectroscopic investigation of the cross-association mechanisms of CO₂ with monoethanolamine (MEA) in molecular beams [F. Xie et al., *Angew. Chem. Int. Ed.*, **2023**, 62, e202218539] revealed an intriguing affinity of CO₂ to the hydroxy group. These findings have triggered the present systematic vibrational spectroscopic exploration of weakly bound amine·CO₂ and alcohol·CO₂ van der Waals cluster molecules embedded in inert “quantum” matrices of neon at 4.2 K complemented by high-level quantum chemical conformational analyses. The non-covalent interactions formed between the amino and hydroxy groups and the electron-deficient carbon atom of CO₂ are demonstrated to lift the degeneracy of the doubly degenerate intramolecular CO₂-bending fundamental significantly with characteristic observed spectral splittings for the amine·CO₂ ($\approx 35\text{--}45\text{ cm}^{-1}$) and alcohol·CO₂ ($\approx 20\text{--}25\text{ cm}^{-1}$) interactions, respectively, despite the almost identically predicted total association energies ($\approx 12\text{--}14\text{ kJ}\cdot\text{mol}^{-1}$) for these van der Waals contacts, as revealed by benchmark Domain-based Local Pair Natural Orbital Coupled Cluster DLPNO-CCSD(T) theory. These high-level theoretical predictions reveal significantly higher “geometry preparation energies” for the amine·CO₂ systems leading to a more severe distortion of the CO₂ linearity upon complexation in agreement with the infrared spectroscopic findings. The systematic combined spectroscopic and quantum chemical evidences for cross-association between CO₂ and amines/alcohols in the present work unambiguously confirm an intriguing binding preference of CO₂ to the hydroxy group of the important carbon capture agent MEA, with an accurate vibrational zero-point energy corrected association energy (D_0) of $13.5\text{ kJ}\cdot\text{mol}^{-1}$ at the benchmark DLPNO-CCSD(T)/aug-cc-pV5Z level of theory.

Keywords: carbon capture; CO₂; monoethanolamine (MEA); amines; alcohols; vibrational spectroscopy; neon matrices; molecular association; non-covalent interactions; DLPNO-CCSD(T); local energy decomposition



Citation: Hafizi Yazdabadi, S.; Mihin, D.; Feilberg, K.L.; Wugt Larsen, R. Spectroscopic and Quantum Chemical Evidence of Amine–CO₂ and Alcohol–CO₂ Interactions: Confirming an Intriguing Affinity of CO₂ to Monoethanolamine (MEA). *Molecules* **2024**, *29*, 5521. <https://doi.org/10.3390/molecules29235521>

Academic Editors: Andrew Clayton and Feng Wang

Received: 30 October 2024

Revised: 14 November 2024

Accepted: 19 November 2024

Published: 22 November 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The concentration of CO₂ in the atmosphere, now exceeding 400 parts per million (ppm), poses a significant challenge as a potent greenhouse gas contributing to global warming and climate change [1]. This rise in CO₂ levels is primarily driven by human activities such as fossil fuel combustion, deforestation, and industrial processes. Despite global efforts to reduce CO₂ emissions through renewable energy adoption, energy efficiency improvements, and policy measures, it has become increasingly clear that mitigation strategies alone are insufficient to address this challenge. Consequently, carbon capture and storage technologies have emerged as an important complementary strategy in the efforts against climate change, aiming to directly remove CO₂ from the atmosphere or prevent its release directly from large-scale industrial sources.

The use of advanced solvents for carbon capture, including biphasic solvents and ionic liquids, has been reported extensively in the literature. Both classes of solvents pro-

vide unique advantages in terms of CO₂ absorption and regeneration efficiency. Biphasic solvents, in particular, are promising due to their phase separation properties at elevated temperatures, potentially lowering the energy demands of CO₂ regeneration compared to traditional aqueous amines [2,3]. Ionic liquids (ILs) have also emerged as promising candidates for CO₂ capture due to their high CO₂ solubility and unique properties, including negligible vapour pressure and recyclability, which qualify them as green solvents. ILs can be customised by modifying their anions or cations, allowing specific tuning of their CO₂ capture capabilities. Various IL types, such as conventional imidazolium-based ILs, task-specific ILs with amino groups, and amino acid-based ILs, have been explored for enhanced CO₂ absorption efficiency [4–10]. For post-combustion CO₂ capture, several non-amine compounds have so far been studied, such as potassium-based and calcium oxide-based sorbents, biochars, and metal–organic materials [11–15].

Despite these alternatives, CO₂ capture research predominantly focuses on amine-based technologies due to their ability to react reversibly and their cost-efficiency with CO₂ [11]. Although some amines such as piperazine have been studied as potential CO₂ absorbing compounds [16–18], the non-volatile alkanolamines containing both a hydroxy and an amino group such as monoethanolamine (MEA) and diethanolamine (DEA), are widely employed as absorbents in CO₂ capture processes [19–22]. A blend of different alkanolamines, such as a combination of a primary (MEA) or secondary (DEA) amine with a tertiary amine, e.g., *N*-methyldiethanolamine (MDEA) leverages the strengths of each. Tertiary amines provide relatively higher CO₂ absorption capacity, while primary and secondary amines offer faster CO₂ reaction rates. The blend improves both the CO₂ absorption efficiency and rate, as well as reducing the energy costs for solvent regeneration in the gas treatment [23,24].

Amine gas treating, also known as amine scrubbing, is a technology where the flue gas is passed through an aqueous amine solution, in which the amine absorbs CO₂ [11,25,26]. It is predicted that by 2030, this method will dominate CO₂ capture technology in coal-fired power plants [26]. Among the various agents employed for CO₂ capture in amine scrubbing and other technologies, monoethanolamine (MEA) stands out as the most widely utilised alkanolamine due to its high reactivity and efficiency in capturing CO₂ from industrial emissions [11,27].

The reaction mechanism of MEA with CO₂ has been a major topic of many investigations [28]. The formation of zwitterion as an intermediate in the carbamate-producing reaction between MEA and CO₂ in aqueous solutions has been investigated with quantum chemical and molecular dynamic simulation in several studies [29–31]. However, a ¹³C nuclear magnetic resonance study on analyzing the reaction intermediates has shown that the mechanisms of capturing CO₂ in MEA solutions vary with the CO₂ loading [32]. Moreover, the conformations of MEA and the zwitterion intermediate appear to play a crucial role in the reaction pathway. For instance, it has been shown that if the acidic hydrogen in the amino group of a zwitterion forms an intramolecular hydrogen bond with the oxygen in the hydroxy group, rather than interacting with nearby water molecules, CO₂ desorption is more favourable than the deprotonation process [33].

A recent broadband rotational spectroscopic work concerned with the vital cross-association mechanisms of CO₂ with MEA in molecular beams has investigated the initial stages of the gas-phase nucleation between CO₂ and MEA with the aid of extensive systematic theoretical conformational sampling [34]. The sub-nanometer-scale aggregation mechanisms involving the complexation of up to four CO₂ molecules with one MEA molecule under jet-cooled conditions were identified. The subtle competition between the strained directional intramolecular OH···N hydrogen bond within MEA and the intermolecular non-directional long-range van der Waals forces associated with the step-wise complexation of CO₂ was uncovered, revealing an intriguing affinity of the first CO₂ molecule to the hydroxy group instead of the amino group. These surprising findings are in contrast to the general understanding of the association between MEA and CO₂ in aqueous solutions [30–33,35,36] and have triggered the present systematic vibrational spectroscopic

exploration of prototypical binary 1:1 weakly bound amine $\cdots$ CO₂ and alcohol $\cdots$ CO₂ van der Waals complexes.

Although weak van der Waals forces usually solely give rise to minor complexation spectral shifts of intramolecular vibrational fundamentals, the aim has been to obtain spectroscopic evidence for the vibrational motion of the engaged functional groups aided by high-level quantum chemical modelling. The vibrational spectral signatures of weakly bound van der Waals complexes are normally only within reach experimentally under jet-cooled conditions in very specific and narrow spectral regions covered by sensitive laser spectroscopy approaches [37–40] but are still achievable with direct absorption in inert doped “quantum matrices” of neon with minor influence of the environment [41] by means of broadband Fourier transform infrared spectroscopy [42–45] at higher optical densities. The present work demonstrates that among the various potential infrared spectroscopic probes for the association between CO₂ and alcohols/amines, the lifting of the doubly degenerate bending transition of CO₂ upon complexation into two components with characteristic observed spectral splittings $\approx 20\text{--}45\text{ cm}^{-1}$ ($\approx 3\text{--}7\%$) is a very prominent specific signature for these complexation mechanisms.

2. Results and Discussion

2.1. Infrared Spectrum for the Weakly Bound Binary 1:1 MEA $\cdots$ CO₂ van der Waals Complex

Figure 1 shows the mid-infrared absorption spectra collected for an MEA/CO₂ mixture embedded in neon at 4.2 K in the relevant spectral regions together with a reference spectrum of pure MEA. The inspection of the complete spectral range has enabled the assignments of new emerging vibrational transitions in the spectral intervals revealing the IR-active fundamental transitions associated with the O–H stretching and large-amplitude OH torsional motion of MEA and the bending motion of CO₂. The strongly IR-active OH stretching fundamental, assigned to the binary 1:1 MEA $\cdots$ CO₂ van der Waals complex embedded in neon, is observed at 3538 cm^{-1} and is only slightly red-shifted by 16 cm^{-1} (0.4%) relative to the respective transition for the free MEA monomer reported at 3554 cm^{-1} [46]. A much more significant manifestation of the molecular association is observed for the large-amplitude OH torsional motion of MEA, where this fundamental for the MEA $\cdots$ CO₂ complex is assigned in the far-infrared part of the spectrum at 500 cm^{-1} . This OH torsional fundamental is thereby spectrally blue-shifted by 28 cm^{-1} (6%) relative to the fundamental transition of the free MEA monomer embedded in neon, reported at 472 cm^{-1} previously [46]. The collected spectra do not reveal any new vibrational bands in the vicinity of the previously reported IR-active transitions associated with the asymmetric N–H stretching (3439 cm^{-1}), NH₂ bending (1628 cm^{-1}), and NH₂ wagging (903 cm^{-1}) motions of MEA.

These experimental findings provide the first clue that the CO₂ subunit is not interacting strongly with the amino group, but rather with the hydroxy group of MEA in the cryogenic neon host, as will be supported further when considering the splitting of the doubly degenerate bending fundamental transition of the CO₂ molecule upon complexation. The double degeneracy of this strongly IR-active CO₂ bending fundamental is lifted significantly in the binary 1:1 MEA $\cdots$ CO₂ van der Waals complex resulting in a slightly blue-shifted (by 5 cm^{-1}) transition at 673 cm^{-1} associated with the out-of-plane motion and a more significantly red-shifted (by 18 cm^{-1}) transition at 650 cm^{-1} associated with in-plane motion with respect to the lone pair-donating atom of MEA. The observed splitting of the CO₂-bending fundamental in the order of 23 cm^{-1} (3.5%) relative to the fundamental at 668 cm^{-1} reported for free CO₂ molecules embedded in neon [45] turns out to be a specifically valuable and easily accessible spectroscopic probe for the cross-association mechanisms of CO₂ with amines and alcohols.

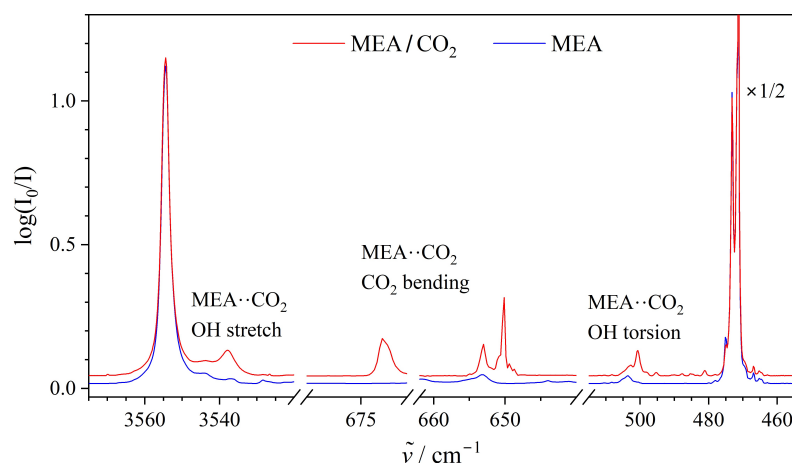


Figure 1. The mid- and far-infrared absorption spectra collected for a MEA/CO₂ mixture (red trace) and pure MEA (blue trace) embedded in neon at 4.2 K for selected spectral intervals with observed fundamental transitions associated with O-H stretching, CO₂ bending and large-amplitude OH torsional motion together with proposed vibrational assignments given for the binary 1:1 MEA·CO₂ van der Waals complex.

2.2. Infrared Spectra for Weakly Bound Binary 1:1 Amine·CO₂ and Alcohol·CO₂ van der Waals Complexes

Figure 2 shows the series of mid-infrared absorption spectra collected for selected amine/CO₂ and alcohol/CO₂ mixtures embedded in neon at 4.2 K in the relevant spectral region associated with the CO₂-bending fundamental transition together with the spectrum collected for the MEA/CO₂ mixture as a reference. The narrow spectral region of the strongly saturated absorption from the double degenerate bending transition of free monomeric CO₂ at 668 cm^{−1} and the weak absorptions of (CO₂)₂ at 670 and 665 cm^{−1} [45], respectively, have been omitted, whereas the absorption from the monomeric bending transition of natural abundant ¹³CO₂ at 649 cm^{−1} is observed in all the spectra.

It is evident from inspection of the entire series of spectra that the complexation of CO₂ with both amine and alcohol compounds systematically is manifested as a lifting of the doubly degenerate bending fundamental of the free monomer into two different bending transitions associated with the out-of-plane motion (the narrow 672–674 cm^{−1} spectral range) and in-plane motion (the more extended 632–651 cm^{−1} spectral range) with respect to the lone pair-donating atom of the complexation partner. The spectral signature observed for the weakly bound 1:1 binary ethylamine (EA)·CO₂ van der Waals complex is somewhat broad with a distinct sub-band structure assigned to at least three different conformations of the complex with zero-point corrected dissociation energies within 0.7 kJ·mol^{−1} based on the initial CREST conformational analysis, further RI-MP2 optimisations and single-point energies with the benchmark DLPNO-CCSD(T)/aug-cc-pV5Z methodology (Figure S1c–e in Supporting Information). Theoretical predictions employing the same step-wise procedure for the weakly bound 1:1 binary ethanol (EtOH)·CO₂ van der Waals complex also reveal spectral signatures for two different conformations where the ethanol subunit exists in either the *gauche* or the *trans* conformation (Figure S2b,c) with slightly different band origins for the in-plane CO₂ bending component (653 cm^{−1} and 654 cm^{−1}, respectively, Table 1). The overall trend observed for these spectral signatures of binary 1:1 complexes of CO₂ with the simplest alcohols methanol (MeOH) and ethanol (EtOH) and the simplest alkylated amines methylamine (MA) and ethylamine (EA) is, however, surprisingly convincing, although the CO₂-bending fundamentals only provide indirect information about the exact nature of the binding motifs. The out-of-plane CO₂ bending component turns out to be robustly spectrally blue-shifted by 6–8 cm^{−1} for the entire selection of investigated complexation partners, but interestingly the absolute spectral red-shift of the corresponding in-plane CO₂ bending component specifically appears to depend more delicately on the chemical nature of the complexation partner. The absolute

transition energies for these in-plane CO₂ bending components assigned for the simplest amine·CO₂ van der Waals complexes (640–641 cm^{−1}) are significantly lower than those observed for the corresponding prototypical alcohol·CO₂ van der Waals complexes with band origins in the 653–654 cm^{−1} spectral range. These spectroscopic findings provide empirical evidence that the affinity of the CO₂ molecule to the hydroxy group of MEA is also strongly favoured under inert neon embedding as the observed in-plane CO₂ bending transition for the MEA·CO₂ complex is assigned at 650 cm^{−1}, close to the findings for the simplest alcohol·CO₂ complexes.

Table 1. The observed ($\tilde{\nu}_{exp}$) and predicted harmonic ($\tilde{\omega}$) band origins (cm^{−1}) of the in-plane (ip) and out-of-plane (oop) components of the CO₂ bending transition, the observed ($\Delta\tilde{\nu}_{exp}$) and predicted ($\Delta\tilde{\omega}$) spectral splitting (cm^{−1}) of the doubly degenerate CO₂ bending transition, the “geometry preparation energy” $\Delta E_{geo}(\text{CO}_2)$ (kJ·mol^{−1}) together with the induced distortion angle ($\angle_{distort}$) away from linearity of the CO₂ molecule at equilibrium (180°–theoretically predicted O=C=O angle at equilibrium) upon complexation for the present series of binary 1:1 van der Waals complexes. The structural and harmonic vibrational predictions are computed employing the RI-MP2/aug-cc-pVQZ approach and the “geometry preparation energies” are computed employing the DLPNO-CCSD(T)/aug-cc-pV5Z level of theory.

System	$\tilde{\nu}_{ip}$	$\tilde{\nu}_{oop}$	$\Delta\tilde{\nu}_{exp}$	$\tilde{\omega}_{ip}$	$\tilde{\omega}_{oop}$	$\Delta\tilde{\omega}$	$\Delta E_{geo}(\text{CO}_2)$	$\angle_{distort}$
Methanol·CO ₂	654	672	18	651	668	17	0.31	2.10
Ethanol·CO ₂ (g)	653	672	19	643	669	26	0.35	2.16
Ethanol·CO ₂ (t)	653	672	19	648	667	19	0.25	1.95
Monoethanolamine·CO ₂	650	673	23	643	668	25	0.47	2.49
Methylamine·CO ₂	641	674	33 [47]	633	677	44	0.67	2.94
Ethylamine·CO ₂	640	673	33	632	675	43	0.71	2.98
Dimethylamine·CO ₂	634	673	39	626	669	43	0.93	3.42
Trimethylamine·CO ₂	627	673	46	612	670	58	1.27	3.99

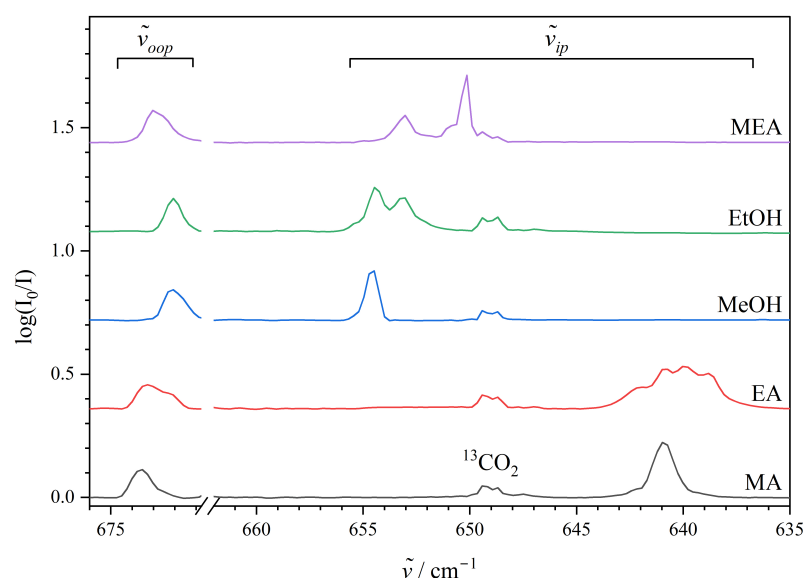


Figure 2. The infrared absorption spectra in the CO₂-bending region (635–680 cm^{−1}) collected for neon “quantum matrices” at 4.2 K doped with mixtures of CO₂ and methylamine, ethylamine, methanol, and ethanol, and monoethanolamine. The assignments of the red-shifted in-plane ($\tilde{\nu}_{ip}$) and blue-shifted out-of-plane ($\tilde{\nu}_{oop}$) components of the CO₂-bending transition for the binary weakly bound 1:1 van der Waals complexes are indicated together with the absorption from the monomeric bending transition of natural abundant ¹³CO₂ at 649 cm^{−1} [45]. The narrow region of the strongly saturated absorption from the bending transition of regular monomeric CO₂ at 668 cm^{−1} [45] has been omitted for clarity.

Before consulting the predictions from theoretical conformational analyses and refined high-level *ab initio* computations, the pronounced lifting of the degenerate CO₂-bending fundamental upon the association with amines has been explored further experimentally for an extended set including both ammonia and more alkylated amine compounds. Figure 3 shows the infrared absorption spectra collected for ammonia/CO₂, methylamine (MA)/CO₂, dimethylamine (DMA)/CO₂ and trimethylamine (TMA)/CO₂ mixtures embedded in neon at 4.2 K in the relevant spectral region associated with the CO₂-bending fundamental transition. This extended spectral series confirms that the slightly spectrally blue-shifted out-of-plane CO₂ bending component is basically unaffected by the specific amine complexation partner and is also observed at 673 cm^{−1} for both the binary 1:1 ammonia·CO₂ and trimethylamine (TMA)·CO₂ van der Waals complexes. The spectrally red-shifted in-plane CO₂ bending component of the latter (TMA)·CO₂ system involving a tertiary amine reveals some sub-band structures indicating multiple conformations of the complex although the dominating transition for the most favoured conformation is easily assigned at 627 cm^{−1}. This witnesses the largest splitting of 46 cm^{−1} (6.9%) observed for the degenerate CO₂ bending fundamental of the entire set of investigated complexation partners (Table 1). The complexation of CO₂ with the secondary amine, DMA, reveals a less spectrally red-shifted in-plane CO₂ bending component at 634 cm^{−1} for the most stable conformation, whereas the association with the simplest amine, ammonia, reveals the corresponding transition at 648 cm^{−1} and thereby almost in the vicinity of the observations for the set of alcohol·CO₂ van der Waals complexes. It is interesting to note that the observed spectral splitting of the degenerate CO₂-bending fundamental consequently increases almost linearly with the number of methyl groups replacing H atoms on the ammonia molecule in the series of primary, secondary, and tertiary amines as complexation partners (TMA·CO₂ > DMA·CO₂ > MA·CO₂ [47] > ammonia·CO₂). This observation perfectly correlates with the linear change in the gas-phase basicity of amines with the increase of alkyl substitution, which has been explained by the increase in the polarisability of the molecule [48,49]. These observations will be supported further by the present exploratory quantum chemical predictions.

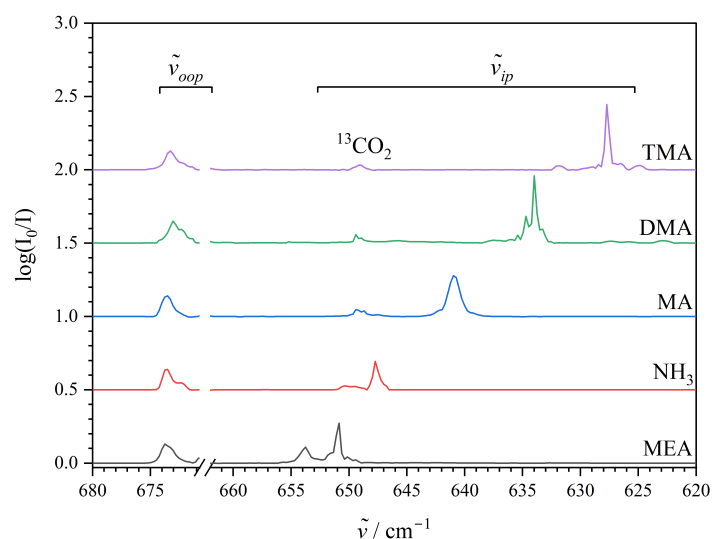


Figure 3. The infrared absorption spectra in the CO₂-bending region (620–680 cm^{−1}) collected for neon “quantum matrices” at 4.2 K doped with mixtures of CO₂ with monoethanolamine (MEA), ammonia, methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA). The assignments of the red-shifted in-plane ($\tilde{\nu}_{ip}$) and blue-shifted out-of-plane ($\tilde{\nu}_{oop}$) components of the CO₂ bending transition for the binary weakly bound 1:1 van der Waals complexes are indicated together with the absorption from the monomeric bending transition of natural abundant ¹³CO₂ at 649 cm^{−1} [45]. The narrow region of the strongly saturated absorption from the bending transition of regular monomeric CO₂ at 668 cm^{−1} [45] has been omitted for clarity.

2.3. Quantum Chemical Conformational Analysis of the Weakly Bound Binary 1:1 Amine·CO₂ and Alcohol·CO₂ van der Waals Complexes

The global potential energy minimum geometry of the weakly bound binary 1:1 MEA·CO₂ van der Waals complex identified via the CREST conformational space exploration tool by Schnell et al. [34], further optimised initially by the B3LYP-D4/aug-cc-pVQZ approach and subsequently employing the RI-MP2/aug-cc-pVQZ methodology, is visualised in Figure 4. In this global minimum structure the intramolecular O–H···N hydrogen bond of MEA persists and the C atom of the CO₂ subunit has established a van der Waals contact with the O atom on the hydrogen bond donating OH group. The refined DLPNO-CCSD(T)/aug-cc-pV5Z electronic energy corrections in combination with the RI-MP2/aug-cc-pVQZ harmonic vibrational zero-point energy corrections provides a dissociation energy D_0 13.5 kJ·mol^{−1}.

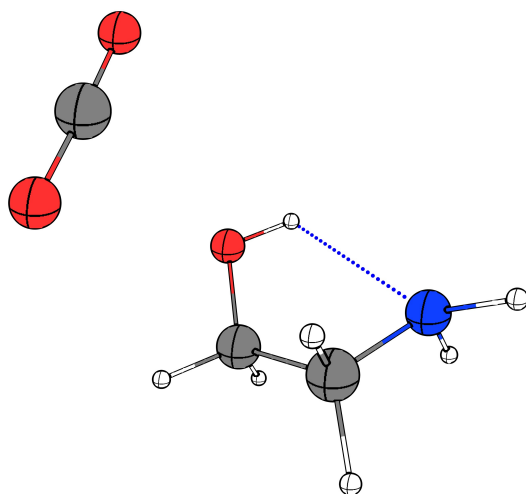


Figure 4. The most stable conformation for the binary MEA·CO₂ van der Waals complex as reported in Ref. [34] and re-optimised at the RI-MP2/aug-cc-pVQZ level of theory.

Table 2 shows the harmonically predicted complexation spectral shifts ($\Delta\omega = \omega_{\text{complex}} - \omega_{\text{monomer}}$) for the most IR-active O–H stretching, OH torsional, asymmetric NH₂ stretching, NH₂ bending and NH₂ wagging fundamentals together with the predicted splitting of the degenerate CO₂ bending fundamental for the MEA·CO₂ van der Waals complex. It is evident that the present observations are strongly supported even by these harmonic vibrational computations at the RI-MP2/aug-cc-pVQZ level of theory. This calculation predicts a harmonic spectral red-shift of 20 cm^{−1} owing to a minor predicted elongation of the O–H bond of 0.001 Å upon complexation (relative to the experimental spectral red-shift of 16 cm^{−1}) and accordingly the harmonic calculation predicts a spectral blue-shift of 24 cm^{−1} for the OH torsional fundamental (relative to the experimental spectral blue-shift of 28 cm^{−1}) resulting from a slightly stabilisation of the intramolecular O–H···N hydrogen bond within the MEA molecule upon complexation with CO₂ (shortening by 0.02 Å). The agreement between experiment and this harmonic prediction is surprisingly good considering the expected extent of anharmonic character for the latter large-amplitude torsional motion. The fact that the present experimental work does not allow any unambiguous assignments for the perturbed IR-active asymmetric NH₂ stretching, NH₂ bending and NH₂ wagging fundamentals of the binary MEA·CO₂ complex indirectly supports that the global potential energy minimum predicted and observed by Schnell et al. in molecular beams is also observed in the cryogenic neon “quantum matrix” environment. According to the harmonic vibrational predictions for this most stable conformation, all the spectral shifts of these fundamentals upon complexation should be less than 1 cm^{−1} and thus negligible. Interestingly, the experimentally observed splitting of the CO₂ bending fundamental of 23 cm^{−1} is also in excellent agreement with the harmonic prediction of 25 cm^{−1} and thereby significant less than observed for the investigated series of amine·CO₂ van der Waals com-

plexes. The animations of the two predicted (in-plane and out-of-plane) components of the motion associated with the CO₂ bending fundamental introduced with the complexation are visualised in Figure 5. The unexpected observed dependence of this spectral splitting on the exact intermolecular van der Waals binding motif is explored further by the exploratory theoretical predictions for the entire set of van der Waals complexes.

Table 2. Experimental ($\tilde{\nu}_{exp}$) and RI-MP2/aug-cc-pVQZ predicted harmonic ($\tilde{\omega}$) band origins (intensities given in parentheses, units of km·mol^{−1}) for vibrational fundamental transitions associated with the IR-active O-H stretching, OH torsional, asymmetric NH₂ stretching, NH₂ bending and NH₂ wagging fundamentals together with the two components of the CO₂ bending fundamental of the MEA·CO₂ van der Waals complex together with the observed complexation shifts $\Delta\tilde{\nu}_{exp}$ and the harmonically predicted complexation shifts $\Delta\tilde{\omega}$ (units of cm^{−1}).

Mode Description	System	$\tilde{\omega}$	$\Delta\tilde{\omega}$	$\tilde{\nu}_{exp}$	$\Delta\tilde{\nu}_{exp}$
OH str	MEA	3748 (76)		3554 [46]	
	MEA·CO ₂	3728 (88)	−20	3538	−16
NH ₂ asym str	MEA	3640 (10)		3439 [46]	
	MEA·CO ₂	3641 (11)	1	−	−
NH ₂ bend	MEA	1652 (30)		1628	
	MEA·CO ₂	1652 (30)	0	−	−
NH ₂ wag	MEA	932 (45)		903	
	MEA·CO ₂	931 (48)	−1	−	−
OH tors	MEA	557 (89)		472 [46]	
	MEA·CO ₂	581 (95)	24	500	28
CO ₂ bend	CO ₂	664 (23)		668 [45]	
	MEA·CO ₂ ip	643 (52)	−21	650	−18
	MEA·CO ₂ oop	668 (26)	4	673	5

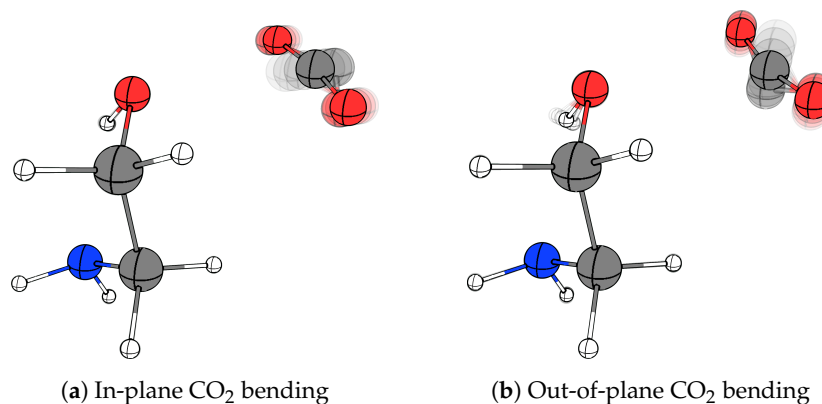


Figure 5. Visualisation of the two components of the CO₂-bending fundamental for the most stable conformation of the binary 1:1 MEA·CO₂ van der Waals complex. (a) in-line with the lone pair-donating atom (in-plane, red-shifted from CO₂ monomer) experimentally observed at 650 cm^{−1} (b) perpendicular (out-of-plane, blue-shifted from CO₂ monomer) experimentally observed at 673 cm^{−1}.

Table 1 shows the two harmonically predicted components of the CO₂-bending fundamental for the investigated series of weakly bound van der Waals complexes. In general, the predicted spectral splittings slightly overestimate the experimental values except for the methanol·CO₂ system, where the smallest observed splitting (18 cm^{−1}) is slightly larger than the theoretical (17 cm^{−1}) predictions. The theoretical predictions ($\Delta\tilde{\omega}$) strongly support the experimental findings ($\Delta\tilde{\nu}_{exp}$) that the splitting of the two different classes of alcohol·CO₂ and amine·CO₂ van der Waals complexes falls into two categories; $\Delta\tilde{\nu}_{exp} \approx 20$ cm^{−1} and $\Delta\tilde{\omega} \approx 20$ –25 cm^{−1} for the alcohol·CO₂ systems and $\Delta\tilde{\nu}_{exp} \approx 35$ –45 cm^{−1} and $\Delta\tilde{\omega} \approx 45$ –55 cm^{−1} for the amine·CO₂ systems. The splitting of the latter class of systems, however, seems to be more prone to the exact nature of the alkyl substituents.

This lifting of the doubly degeneracy of the CO₂-bending fundamental upon complexation is due to a distortion of the molecule's linear equilibrium structure as supported by the optimised “distortion angles” and the predicted “geometry preparation energies” for the investigated series of complexes given in Table 1. The distortion angle $\angle_{distort}$, defined as the difference between the predicted equilibrium O=C=O angle in a specific complex relative to the equilibrium O=C=O angle of 180° for the free non-bonded CO₂ molecule, is shown to increase significantly when CO₂ interacts with an amino group relative to the situation when a CO₂ interacts with a hydroxy group for molecules with the same alkyl substituents although the total predicted interaction energies D_0 are almost identical for the two different classes of 1:1 van der Waals complexes (Table 3). The O=C=O angle is distorted by 1.95–2.16° for the investigated alcohol·CO₂ systems upon complexation, whereas this angle is distorted by 2.94–3.99° for the amine·CO₂ systems. The distortion of the O=C=O angle in the most stable conformation of the MEA·CO₂ van der Waals complex is predicted to be 2.49°, which is only slightly more than for the corresponding alcohol·CO₂ series (but significantly less than for the amine·CO₂ series) owing to the additional polarisation of the hydroxy group engaging in the intramolecular O–H···N hydrogen bond with the amino group of MEA. The same trend is mirrored in the computed values of the “geometry preparation energy” for the CO₂ subunit, given for each of the investigated binary van der Waals complexes in Table 1, providing an estimate of the energy “cost” when the CO₂ subunit is distorted upon complexation. These computed geometry preparation energies show that the attractive stabilising forces in general are still slightly stronger for the van der Waals contacts between CO₂ and amino groups than between the CO₂ and hydroxy groups, although the total theoretical association energies are almost identical at the benchmark DLPNO-CCSD(T)/aug-cc-pV5Z level of theory. The geometry preparation energies are for example computed to 0.31 and 0.67 kJ·mol^{−1} for the methanol·CO₂ and the methylamine·CO₂ systems where the total zero-point corrected dissociation energies D_0 are calculated to 12.1 and 11.9 kJ·mol^{−1}, respectively. The same trend is observed for the pair of ethanol·CO₂ and ethylamine·CO₂ van der Waals complexes of similar size when considering both the computed geometry preparation energies and total zero-point corrected dissociation energies.

Table 3. Electronic energies D_e , harmonic vibrational zero-point energy factors ΔZPE and resulting corrected dissociation energies D_0 for the investigated binary alcohol·CO₂ and amine·CO₂ van der Waals complexes optimised at the B3LYP-D4/aug-cc-pVQZ and RI-MP2/aug-cc-pVQZ levels together with single-point electronic energies at the DLPNO-CCSD(T)/aug-cc-pV5Z level (units of kJ·mol^{−1}).

System	B3LYP-D4			RI-MP2			DLPNO-CCSD(T)	
	D_e	ΔZPE	D_0	D_e	ΔZPE	D_0	D_e ¹	D_0 ²
Methanol·CO ₂	14.3	2.7	11.5	15.1	2.8	12.3	14.9	12.1
Ethanol·CO ₂ (<i>t</i>)	14.0	2.2	11.8	15.2	2.2	13.0	14.9	12.7
Ethanol·CO ₂ (<i>g</i>)	14.3	2.5	11.8	15.1	2.4	12.7	14.8	12.5
Monoethanolamine·CO ₂	15.5	2.6	12.9	16.8	2.5	14.3	16.0	13.5
Methylamine·CO ₂	15.2	2.9	12.4	15.4	3.0	12.4	14.9	11.9
Ethylamine·CO ₂	16.0	2.8	13.2	16.8	3.0	13.8	15.9	12.9
DMA	16.8	2.7	14.1	18.1	2.7	15.4	16.6	14.0
TMA	18.0	2.6	15.4	20.1	2.2	17.9	17.9	15.7

¹ Electronic dissociation energies calculated at the DLPNO-CCSD(T)/aug-cc-pV5Z level based on optimised geometries at the RI-MP2/aug-cc-pVQZ level. ² Based on D_e -values at the DLPNO-CCSD(T)/aug-cc-pV5Z level in combination with ΔZPE -values at the RI-MP2/aug-cc-pVQZ level.

3. Materials and Methods

3.1. Experimental Details

The experimental facility consists of a Bruker Vertex 80V Fourier-transform spectrometer (Ettlingen, Germany) in combination with a customised 4 K closed-cycle cryo-cooler

(Model DE-204, Advanced Research Systems, Inc., Macungie, PA, USA). A direct transmission oxygen-free high-conductivity copper window holder attached with a wedged diamond sample window (Diamond Materials, GmbH, Freiburg im Breisgau, Germany) has been mounted onto the cold head of the cryo-cooler [50]. The cryostat is surrounded by a rotatable vacuum shroud equipped with two additional wedged diamond windows together with a gate valve allowing the insertion of the inlet copper tubes into the vacuum space of the cryostat [51]. The wedged diamond windows minimise spectral interference fringes from internal reflections in the windows. The optical arrangement of the spectrometer consists of an air-cooled Globar thermal radiation source, a Ge-coated KBr beam splitter together with a broad-band LN₂-cooled HgCdTe detector for the complete infrared spectral range (450–4500 cm^{−1}). A spectral resolution of 0.6 cm^{−1} has been applied throughout the measurements as the best compromise between the resulting signal-to-noise ratio and sufficient spectral resolution to resolve the observed vibrational sub-band structures.

The doped neon “quantum matrices” are obtained by the simultaneous deposition of neon gas (99.999%, Air Liquide Danmark A/S, Taastrup, Denmark) and co-deposition of specific samples through separate inlet tubes, which are brought to within 5 mm of the cold sample diamond window employing a motorised stage [52]. The neon gas is supplied from a mass flow controller (G-series, MKS Instruments, Inc., Andover, MA, USA) at a flow rate of 6–8 sccm depending on the desired mixing ratio and pre-cooled with a LN₂-cooled trap (77 K). Methanol (99.9%, Sigma Aldrich, Søborg, Denmark) and ethanol (99.9%, Sigma Aldrich, Søborg, Denmark) vapours were premixed with CO₂ (99.999%, AGA A/S, Ballerup, Denmark) beforehand, while the samples of the selected amines and CO₂ were co-deposited separately and flow regulated with fine metering valves. The samples of amines including ammonia (25 wt.%, AnalaR NORMAPUR, VWR Int., Søborg, Denmark), methylamine (40 wt.%, Sigma Aldrich, Søborg, Denmark), ethylamine (66.0–72.0 wt.%, Sigma Aldrich, Søborg, Denmark), dimethylamine (40 wt.%, Sigma Aldrich, Søborg, Denmark) and trimethylamine (25 wt.%, Sigma Aldrich, Søborg, Denmark) were all extracted from the aqueous solutions under vacuum. Pumped and pre-baked molecular sieves (4 Å) have been employed to reduce minor traces of H₂O in the non-volatile MEA sample (99%, Sigma Aldrich, Søborg, Denmark) while depositing MEA directly from a sublimation vessel thermostated to −7 °C [46]. The combined deposition procedures of neon host and the alcohol/CO₂ and amine/CO₂ sample mixtures onto the wedged diamond window were carried out simultaneously for a period of two hours.

Following the acquisition of the initial pre-annealing spectra, the neon “quantum matrices” were gently annealed by raising the temperature to 9.5 K for 60 min. The temperature is regulated by a combination of resistive heaters and silicon diode temperature sensors attached to the window holder and feedback electronics operated by a PID temperature controller (Model 335, LakeShore, Westerville, OH, USA). Subsequently, the heater was deactivated, allowing the sample temperature to relax back to 4–5 K before the collection of post-annealing spectra. The annealing softens the solid neon environment and usually circumvents rare residual matrix site splittings [53,54]. This procedure furthermore triggers the diffusion of molecules within the matrix accelerating the cross-association of CO₂ and the co-deposited alcohol/amine samples into weakly bound van der Waals cluster molecules. The background spectra were all collected of the fully evacuated cryostat at room temperature at the end of the experiments.

3.2. Computational Details

Quantum chemical calculations were performed using the Conformer-Rotamer Ensemble Sampling Tool CREST (version 2.12, Bonn, Germany) [55] and the ORCA quantum chemistry program package (version 5.0.4, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany) [56–58], both installed on the DTU High-Performance Computing (HPC) cluster [59]. The CREST tool with the NCI mode and the GFN2-xTB methodology [60] was employed to generate the most stable conformations of the investigated binary 1:1 alcohol–CO₂ and amine–CO₂ van der Waals complexes. For each

system, the first 10–15 conformations identified by the CREST utility were selected for further optimisations. These conformations underwent further geometry optimisation and harmonic vibrational frequency calculations using the dispersion-corrected B3LYP-D4 methodology [61–63], in combination with the aug-cc-pVQZ basis set and the RIJ-COSX approximation [64–66].

Following the B3LYP-D4 optimisation step, further geometry optimisations and harmonic vibrational frequency calculations were repeated using the RI-MP2 methodology [67–69], employing the same basis sets and approximations as for the B3LYP-D4 calculations. Finally, the optimised potential energy minima geometries obtained from the RI-MP2 calculations were employed for single-point energy calculations with Domain-based Local Pair Natural Orbital Coupled Cluster with Single, Double, and Perturbative Triple excitations (DLPNO-CCSD(T)) [70–74]. This step involved the aug-cc-pV5Z basis set, together with the RI-JK approximation [75] and tight PNO screening criteria [76] to provide the electronic dissociation energies (D_e) and vibrational zero-point energy corrected dissociation energies (D_0) ensuring highly accurate energy estimations. The geometric distortion of the linear CO₂ fragment caused by intermolecular interaction has been estimated via the “geometry preparation energy”, which is calculated as the electronic energy difference between the CO₂ subunit in the distorted geometry as found in the respective van der Waals complex, and the energy of the isolated CO₂ molecule employing the above-described combination of DLPNO-CCSD(T)/RI-MP2 electronic structure methodologies.

4. Conclusions

The present work reports a systematic infrared spectroscopic investigation of a series of weakly bound alcohol-CO₂ and amine-CO₂ van der Waals cluster molecules embedded in inert “quantum” matrices of neon at 4.2 K triggered by the recent broadband rotational spectroscopic investigation of the MEA-CO₂ van der Waals complex in molecular beams [34] revealing (indirectly) an intriguing affinity of CO₂ to the hydroxy group of MEA. The combined vibrational spectroscopic findings and harmonic RI-MP2/aug-cc-pVQZ quantum chemical predictions help to assign both the strongly IR-active vibrational fundamentals associated with the O-H stretching motion at 3538 cm^{−1} (slightly spectrally red-shifted by 16 cm^{−1} (0.4%) relative to the free MEA monomer) and large-amplitude OH torsional motion at 500 cm^{−1} (spectrally blue-shifted by 28 cm^{−1} (6%) relative to the free MEA monomer) of the MEA·CO₂ van der Waals complex. The collected spectra did not reveal any bands in the vicinity of the previously reported IR-active vibrational transitions associated with the asymmetric N-H stretching, NH₂ bending and NH₂ wagging fundamentals of MEA. The present findings reveal that the non-covalent complexation of CO₂ with MEA is manifested as a significant lifting of the doubly degenerate CO₂-bending fundamental of the free molecule into two different components associated with out-of-plane (slightly blue-shifted) and in-plane (significantly red-shifted) bending motion resulting in a spectral splitting of 23 cm^{−1} in accordance with the splitting of 25 cm^{−1} from the harmonic predictions. The out-of-plane CO₂ bending component turns out to be systematically spectrally blue-shifted by 6–8 cm^{−1} for the entire selection of investigated alcohol·CO₂ and amine·CO₂ van der Waals complexes, whereas the absolute spectral red-shift of the corresponding in-plane CO₂ bending component appears to be specifically dependent on the chemical nature of the complexation partner. Our present findings reveal characteristic spectral splittings for the amine·CO₂ (≈35–45 cm^{−1}) and alcohol·CO₂ (≈20–25 cm^{−1}) interactions, respectively, despite the almost identically predicted total association energies (≈12–14 kJ·mol^{−1}) for these van der Waals contacts as revealed by benchmark domain-based local pair natural orbital coupled cluster DLPNO-CCSD(T) theory. The spectroscopic findings provide unambiguous complementary empirical evidence that the affinity of the CO₂ molecule to the hydroxy group of MEA is also strongly favored in inert neon “quantum matrices”.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29235521/s1>, The material contains the optimized potential energy minima geometries of the studied alcohols, amines, and monoethanolamine van der Waals complex with CO₂ in XYZ format, the visualization of the respective structures and the predicted harmonic vibrational mode frequencies for the MEA/CO₂ complex.

Author Contributions: Conceptualization—R.W.L.; Methodology—D.M. and R.W.L.; Software—S.H.Y. and D.M.; Validation—S.H.Y., D.M. and R.W.L.; Formal analysis—S.H.Y., D.M. and R.W.L.; Investigation—S.H.Y., D.M. and R.W.L.; Resources—K.L.F. and R.W.L.; Data curation—S.H.Y. and R.W.L.; Writing—original draft preparation—S.H.Y. and R.W.L.; Writing—review and editing—S.H.Y., D.M., K.L.F. and R.W.L.; Visualization—S.H.Y.; Supervision—K.L.F. and R.W.L.; Project administration—K.L.F. and R.W.L.; Funding acquisition—K.L.F. and R.W.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Danish Offshore Technology Centre (DTU Offshore).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Acknowledgments: The authors acknowledge the DTU Computing Center for access to the high-performance computing services and the technical support provided. Finally, Alexandre Voute and the mechanical workshop at DTU Chemistry is acknowledged for help and advice in the design of the experimental facilities.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Hashimoto, K. Global Temperature and Atmospheric Carbon Dioxide Concentration. In *Global Carbon Dioxide Recycling*; Springer: Singapore, 2019; pp. 5–17. [\[CrossRef\]](#)
2. Zhang, G.; Qian, J.; Liu, J.; Yu, T.; Liu, Q. Insight and assessment of CO₂ capture using diethylenetriamine/2-(diethylamino)ethanol/n-propanol water-lean biphasic solvent: Experimental and quantum chemical calculation. *Chem. Eng. J.* **2024**, *500*, 156834. [\[CrossRef\]](#)
3. Jin, L.; Hou, X.; Zhan, L.; Hou, D.; Gu, L.; Zhang, D.; Shen, J.; Zheng, Z.; Lv, C.; Liu, S.; et al. Analysis of the changes in the absorption and regeneration performance of diethylenetriamine in carbon capture environments with functionalized alcohols and mixed amines. *Fuel* **2024**, *368*, 131375. [\[CrossRef\]](#)
4. Shaikh, A.R.; Ashraf, M.; AlMayef, T.; Chawla, M.; Poater, A.; Cavallo, L. Amino acid ionic liquids as potential candidates for CO₂ capture: Combined density functional theory and molecular dynamics simulations. *Chem. Phys. Lett.* **2020**, *745*, 137239. [\[CrossRef\]](#)
5. Earle, M.J.; Seddon, K.R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398. [\[CrossRef\]](#)
6. Brennecke, J.F.; Maginn, E.J. Ionic liquids: Innovative fluids for chemical processing. *AIChE J.* **2001**, *47*, 2384–2389. [\[CrossRef\]](#)
7. Shim, Y.; Jeong, D.; Manjari, S.; Choi, M.Y.; Kim, H.J. Solvation, Solute Rotation and Vibration Relaxation, and Electron-Transfer Reactions in Room-Temperature Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1130–1137. [\[CrossRef\]](#)
8. Cadena, C.; Anthony, J.L.; Shah, J.K.; Morrow, T.I.; Brennecke, J.F.; Maginn, E.J. Why Is CO₂ So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300–5308. [\[CrossRef\]](#)
9. Bates, E.D.; Mayton, R.D.; Ntai, I.; Davis, J.H. CO₂ Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927. [\[CrossRef\]](#)
10. Bao, W.; Wang, Z.; Li, Y. Synthesis of Chiral Ionic Liquids from Natural Amino Acids. *J. Org. Chem.* **2003**, *68*, 591–593. [\[CrossRef\]](#)
11. Dutcher, B.; Fan, M.; Russell, A.G. Amine-based CO₂ capture technology development from the beginning of 2013—A review. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2137–2148. [\[CrossRef\]](#)
12. Plaza, M.; González, A.; Pis, J.; Rubiera, F.; Pevida, C. Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO₂ capture. *Appl. Energy* **2014**, *114*, 551–562. [\[CrossRef\]](#)
13. Nugent, P.; Giannopoulou, E.G.; Burd, S.D.; Elemento, O.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; et al. Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* **2013**, *495*, 80–84. [\[CrossRef\]](#)
14. Lee, S.C.; Kwon, Y.M.; Jung, S.Y.; Lee, J.B.; Ryu, C.K.; Kim, J.C. Excellent thermal stability of potassium-based sorbent using ZrO₂ for post combustion CO₂ capture. *Fuel* **2014**, *115*, 97–100. [\[CrossRef\]](#)
15. Sedghkerdar, M.H.; Mahinpey, N.; Sun, Z.; Kaliaguine, S. Novel synthetic sol-gel CaO based pellets using porous mesostructured silica in cyclic CO₂ capture process. *Fuel* **2014**, *127*, 101–108. [\[CrossRef\]](#)

16. Rochelle, G.; Chen, E.; Freeman, S.; Van Wagener, D.; Xu, Q.; Voice, A. Aqueous piperazine as the new standard for CO₂ capture technology. *Chem. Eng. J.* **2011**, *171*, 725–733. [\[CrossRef\]](#)
17. Freeman, S.A.; Dugas, R.; Van Wagener, D.H.; Nguyen, T.; Rochelle, G.T. Carbon dioxide capture with concentrated, aqueous piperazine. *Int. J. Greenh. Gas Control* **2010**, *4*, 119–124. [\[CrossRef\]](#)
18. Chen, X.; Rochelle, G.T. Aqueous piperazine derivatives for CO₂ capture: Accurate screening by a wetted wall column. *Chem. Eng. Res. Des.* **2011**, *89*, 1693–1710. [\[CrossRef\]](#)
19. Yu, C.H.; Huang, C.H.; Tan, C.S. A review of CO₂ capture by absorption and adsorption. *Aerosol Air Qual. Res.* **2012**, *12*, 745–769. [\[CrossRef\]](#)
20. Kubota, Y.; Bučko, T. Carbon dioxide capture in 2,2'-iminodiethanol aqueous solution from ab initio molecular dynamics simulations. *J. Chem. Phys.* **2018**, *149*, 224103. [\[CrossRef\]](#)
21. Narku-Tetteh, J.; Muchan, P.; Idem, R. Effect of alkanol chain length of primary alkanolamines and alkyl chain length of secondary and tertiary alkanolamines on their CO₂ capture activities. *Sep. Purif. Technol.* **2017**, *187*, 453–467. [\[CrossRef\]](#)
22. Jackson, P.; Beste, A.; Attalla, M. Insights into amine-based CO₂ capture: An ab initio self-consistent reaction field investigation. *Struct. Chem.* **2011**, *22*, 537–549. [\[CrossRef\]](#)
23. Narimani, M.; Amjad-Iranagh, S.; Modarress, H. CO₂ absorption into aqueous solutions of monoethanolamine, piperazine and their blends: Quantum mechanics and molecular dynamics studies. *J. Mol. Liq.* **2017**, *233*, 173–183. [\[CrossRef\]](#)
24. Samanta, A.; Bandyopadhyay, S.S. Absorption of carbon dioxide into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chem. Eng. Sci.* **2009**, *64*, 1185–1194. [\[CrossRef\]](#)
25. Rochelle, G. 3—Conventional amine scrubbing for CO₂ capture. In *Absorption-Based Post-Combustion Capture of Carbon Dioxide*; Feron, P.H., Ed.; Woodhead Publishing: Cambridge, UK, 2016; pp. 35–67. [\[CrossRef\]](#)
26. Rochelle, G.T. Amine Scrubbing for CO₂ Capture. *Science* **2009**, *325*, 1652–1654. [\[CrossRef\]](#)
27. Yang, X.; Rees, R.J.; Conway, W.; Puxty, G.; Yang, Q.; Winkler, D.A. Computational Modeling and Simulation of CO₂ Capture by Aqueous Amines. *Chem. Rev.* **2017**, *117*, 9524–9593. [\[CrossRef\]](#)
28. Iida, K.; Sato, H. Proton transfer step in the carbon dioxide capture by monoethanol amine: A theoretical study at the molecular level. *J. Phys. Chem. B* **2012**, *116*, 2244–2248. [\[CrossRef\]](#)
29. Hwang, G.S.; Stowe, H.M.; Paek, E.; Manogaran, D. Reaction mechanisms of aqueous monoethanolamine with carbon dioxide: A combined quantum chemical and molecular dynamics study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 831–839. [\[CrossRef\]](#)
30. Kubota, Y.; Ohnuma, T.; Bučko, T. Carbon dioxide capture in 2-aminoethanol aqueous solution from ab initio molecular dynamics simulations. *J. Chem. Phys.* **2017**, *146*, 094303. [\[CrossRef\]](#)
31. Xie, H.; Wang, P.; He, N.; Yang, X.; Chen, J. Toward rational design of amines for CO₂ capture: Substituent effect on kinetic process for the reaction of monoethanolamine with CO₂. *J. Environ. Sci.* **2015**, *37*, 75–82. [\[CrossRef\]](#)
32. Lv, B.; Guo, B.; Zhou, Z.; Jing, G. Mechanisms of CO₂ Capture into Monoethanolamine Solution with Different CO₂ Loading during the Absorption/Desorption Processes. *Environ. Sci. Technol.* **2015**, *49*, 10728–10735. [\[CrossRef\]](#)
33. Xie, H.B.; Zhou, Y.; Zhang, Y.; Johnson, J.K. Reaction mechanism of monoethanolamine with CO₂ in aqueous solution from molecular modeling. *J. Phys. Chem. A* **2010**, *114*, 11844–11852. [\[CrossRef\]](#)
34. Xie, F.; Sun, W.; Pinacho, P.; Schnell, M. CO₂ Aggregation on Monoethanolamine: Observations from Rotational Spectroscopy. *Angew. Chem.-Int. Ed.* **2023**, *62*, e202218539. [\[CrossRef\]](#)
35. Han, B.; Zhou, C.; Wu, J.; Tempel, D.J.; Cheng, H. Understanding CO₂ Capture Mechanisms in Aqueous Monoethanolamine via First Principles Simulations. *J. Phys. Chem. Lett.* **2011**, *2*, 522–526. [\[CrossRef\]](#)
36. Davran-Candan, T. DFT Modeling of CO₂ Interaction with Various Aqueous Amine Structures. *J. Phys. Chem. A* **2014**, *118*, 4582–4590. [\[CrossRef\]](#)
37. Barclay, A.; McKellar, A.; Moazzen-Ahmadi, N. Infrared spectra of (CO₂)₂-Rg trimers, Rg = Ne, Ar, Kr, and Xe. *J. Mol. Spectrosc.* **2022**, *387*, 111673. [\[CrossRef\]](#)
38. Barclay, A.J.; McKellar, A.R.W.; Moazzen-Ahmadi, N. Spectra of CO₂-N₂ dimer in the 4.2 μm region: Symmetry breaking of the intramolecular CO₂ bend, the intermolecular bend, and higher K-Values Fundam. *J. Chem. Phys.* **2020**, *153*, 014303. [\[CrossRef\]](#)
39. Oliaee, J.N.; Dehghany, M.; Moazzen-Ahmadi, N.; McKellar, A.R.W. Spectroscopic identification of carbon dioxide clusters: (CO₂)₆ to (CO₂)₁₃. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1297–1300. [\[CrossRef\]](#)
40. Norooz Oliaee, J.; Dehghany, M.; McKellar, A.R.W.; Moazzen-Ahmadi, N. High resolution infrared spectroscopy of carbon dioxide clusters up to (CO₂)₁₃. *J. Chem. Phys.* **2011**, *135*, 044315. [\[CrossRef\]](#)
41. Bödecker, M.; Mihrin, D.; Suhm, M.A.; Wugt Larsen, R. Regularities and Anomalies in Neon Matrix Shifts of Hydrogen-Bonded O–H Stretching Fundamentals. *J. Phys. Chem. A* **2024**, *128*, 7124–7136. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Andersen, J.; Heimdal, J.; Mahler, D.W.; Nelander, B.; Wugt Larsen, R. Communication: THz absorption spectrum of the CO₂-H₂O complex: Observation and assignment of intermolecular van der Waals vibrations. *J. Chem. Phys.* **2014**, *140*, 091103. [\[CrossRef\]](#)
43. Andersen, J.; Voute, A.; Mihrin, D.; Heimdal, J.; Berg, R.W.; Torsson, M.; Wugt Larsen, R. Probing the global potential energy minimum of (CH₂O)₂: THz absorption spectrum of (CH₂O)₂ in solid neon and Para-Hydrog. *J. Chem. Phys.* **2017**, *146*, 244311. [\[CrossRef\]](#)
44. Andersen, J.; Heimdal, J.; Nelander, B.; Wugt Larsen, R. Competition between weak OH...π and CH...O hydrogen bonds: THz spectroscopy of the C₂H₂—H₂O and C₂H₄—H₂O complexes. *J. Chem. Phys.* **2017**, *146*, 194302. [\[CrossRef\]](#)

45. Soulard, P.; Tremblay, B. Vibrational investigations of CO₂-H₂O, CO₂-(H₂O)₂, and (CO₂)₂-H₂O complexes isolated in solid neon. *J. Chem. Phys.* **2015**, *143*, 224311. [\[CrossRef\]](#)
46. Yazdabadi, S.H.; Mihin, D.; Feilberg, K.L.; Wugt Larsen, R. Self-aggregation and microhydration mechanisms of monoethanolamine: Far-infrared identification of large-amplitude hydrogen bond libration. *J. Chem. Phys.* **2024**, *161*, 154301. [\[CrossRef\]](#)
47. Soulard, P.; Tremblay, B. Matrix infrared spectroscopic and ab initio investigations of methylamine-CO₂ and methylamine-CO₂-water complexes. *J. Mol. Struct.* **2023**, *1288*, 135777. [\[CrossRef\]](#)
48. Brauman, J.I.; Riveros, J.M.; Blair, L.K. Gas-phase basicities of amines. *J. Am. Chem. Soc.* **1971**, *93*, 3914–3916. [\[CrossRef\]](#)
49. Headley, A.D. Substituent effects on the basicity of dimethylamines. *J. Am. Chem. Soc.* **1987**, *109*, 2347–2348. [\[CrossRef\]](#)
50. Mihin, D.; Feilberg, K.L.; Wugt Larsen, R. Self-Association and Microhydration of Phenol: Identification of Large-Amplitude Hydrogen Bond Librational Modes. *Molecules* **2024**, *29*, 3012. [\[CrossRef\]](#)
51. Mihin, D.; Voute, A.; Jakobsen, P.W.; Feilberg, K.L.; Wugt Larsen, R. The effect of alkylation on the micro-solvation of ethers revealed by highly localized water librational motion. *J. Chem. Phys.* **2022**, *156*, 084305. [\[CrossRef\]](#)
52. Mihin, D.; Andersen, J.; Jakobsen, P.W.; Wugt Larsen, R. Highly localized H₂O librational motion as a far-infrared spectroscopic probe for microsolvation of organic molecules. *Phys. Chem. Chem. Phys.* **2019**, *21*, 1717–1723. [\[CrossRef\]](#)
53. Andersen, J.; Heimdal, J.; Wugt Larsen, R. The influence of large-amplitude librational motion on the hydrogen bond energy for alcohol–water complexes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23761–23769. [\[CrossRef\]](#)
54. Heger, M.; Andersen, J.; Suhm, M.A.; Wugt Larsen, R. The donor OH stretching–libration dynamics of hydrogen-bonded methanol dimers in cryogenic matrices. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3739–3745. [\[CrossRef\]](#)
55. Pracht, P.; Bohle, F.; Grimme, S. Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192. [\[CrossRef\]](#)
56. Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152*, 224108. [\[CrossRef\]](#)
57. Neese, F. Software update: The ORCA program system—Version 5.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, e1606. [\[CrossRef\]](#)
58. Neese, F. The SHARK integral generation and digestion system. *J. Comput. Chem.* **2022**, *44*, 381–396. [\[CrossRef\]](#)
59. DTU Computing Center. *DTU Computing Center Resources*; Technical University of Denmark: Kongens Lyngby, Denmark, 2024. [\[CrossRef\]](#)
60. Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671. [\[CrossRef\]](#)
61. Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627. [\[CrossRef\]](#)
62. Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A generally applicable atomic-charge dependent London dispersion correction. *J. Chem. Phys.* **2019**, *150*, 154122. [\[CrossRef\]](#)
63. Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D₃ dispersion coefficient model. *J. Chem. Phys.* **2017**, *147*, 034112. [\[CrossRef\]](#)
64. Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange. *Chem. Phys.* **2009**, *356*, 98–109. [\[CrossRef\]](#)
65. Helmich-Paris, B.; de Souza, B.; Neese, F.; Izsák, R. An improved chain of spheres for exchange algorithm. *J. Chem. Phys.* **2021**, *155*, 104109. [\[CrossRef\]](#)
66. Kossmann, S.; Neese, F. Efficient Structure Optimization with Second-Order Many-Body Perturbation Theory: The RIJCOSX-MP2 Method. *J. Chem. Theory Comput.* **2010**, *6*, 2325–2338. [\[CrossRef\]](#)
67. Bernholdt, D.E.; Harrison, R.J. Large-scale correlated electronic structure calculations: The RI-MP2 method on parallel computers. *Chem. Phys. Lett.* **1996**, *250*, 477–484. [\[CrossRef\]](#)
68. Kendall, R.A.; Dunning, T.H.; Harrison, R.J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806. [\[CrossRef\]](#)
69. Neese, F. An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. *J. Comput. Chem.* **2003**, *24*, 1740–1747. [\[CrossRef\]](#)
70. Neese, F.; Wennmohs, F.; Hansen, A. Efficient and accurate local approximations to coupled-electron pair approaches: An attempt to revive the pair natural orbital method. *J. Chem. Phys.* **2009**, *130*, 114108. [\[CrossRef\]](#)
71. Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **2013**, *139*, 134101. [\[CrossRef\]](#)
72. Neese, F.; Hansen, A.; Liakos, D.G. Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis. *J. Chem. Phys.* **2009**, *131*, 064103. [\[CrossRef\]](#)
73. Riplinger, C.; Neese, F. An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* **2013**, *138*, 034106. [\[CrossRef\]](#)

74. Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E.F.; Neese, F. Sparse maps—A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory. *J. Chem. Phys.* **2016**, *144*, 024109. [[CrossRef](#)] [[PubMed](#)]
75. Kossmann, S.; Neese, F. Comparison of two efficient approximate Hartee–Fock approaches. *Chem. Phys. Lett.* **2009**, *481*, 240–243. [[CrossRef](#)]
76. Liakos, D.G.; Sparta, M.; Kesharwani, M.K.; Martin, J.M.L.; Neese, F. Exploring the Accuracy Limits of Local Pair Natural Orbital Coupled-Cluster Theory. *J. Chem. Theory Comput.* **2015**, *11*, 1525–1539. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.