

An Experimental Investigation of Lewis Acid–Base Interactions of Liquid Carbon Dioxide Using Fourier Transform Infrared (FT-IR) Spectroscopy¹

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Presented here is an investigation into the solvent properties of liquid carbon dioxide by means of FT-IR spectroscopy. A high-pressure, circulation-type apparatus was designed and built specifically for this study. The spectra for the combination bands for carbon dioxide show that there are interactions between methanol and carbon dioxide. However, the spectra of the fundamental O–D vibration of deuterated methanol in liquid carbon dioxide indicate that there is no hydrogen bonding. Therefore, we conclude that the interactions between carbon dioxide and methanol are Lewis acid–base interactions rather than hydrogen bonding. This conclusion is supported by experiments where acetone is introduced into the CO₂/methanol-*d* binary system. FT-IR measurements show that acetone hydrogen bonds with deuterated methanol.

KEY WORDS: carbon dioxide; Fourier transform infrared spectroscopy; high pressures; hydrogen bonding; Lewis acid–base interactions.

1. INTRODUCTION

One approach to the study of molecular interactions is through the spectral behavior of probe molecules in different solvents. Systematic studies of the variations in spectra are particularly informative, since they reveal changes in the bond character caused by specific interactions and therefore are indicative of the strength of interactions between molecules. The use of Fourier transform infrared (FT-IR) spectroscopy has been shown to be

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useful for the characterization of molecular interactions. Application of infrared spectroscopy to systems of interest in supercritical fluid extraction processes has involved determining the concentration of a solute in a supercritical fluid [1-3] and investigating the behavior of entrainer cosolvents used in supercritical fluid extraction and, to a lesser degree, investigating the acid-base interactions of supercritical fluids [4-7].

The motivation for this work came from studies on the phase behavior of mixtures containing supercritical fluids [8,9]. An understanding of extracting chemicals with a high-pressure solvent requires phase equilibrium data. Further, since it has been shown [10-12] that the solubility of a chemical compound can be increased by addition of an "entrainer," additional data are required to study the effect of entrainer cosolvents on solubility. Recent applications of FT-IR spectroscopy have been used to describe quantitatively the entrainer effect, that is, the dramatic increase in the solvent power and selectivity of a supercritical fluid [13-17]. Walsh et al. [13] showed that the entrainer effect is due to chemical association between solute and cosolvent. Therefore, if one uses an entrainer to enhance the partitioning of a solute from one phase to another, data characterizing the extent of hydrogen bonding between the solute and the cosolvent would help determine the feasibility and effectiveness of the entrainer.

2. EVIDENCE OF CARBON DIOXIDE COMPLEXES

The purpose of this study is to gain insight into the behavior of high-pressure CO₂ solvent and to investigate the effectiveness of methanol as an entrainer cosolvent in CO₂-based systems using information about the chemical interactions between CO₂ and methanol molecules. The existence of specific interactions in CO₂-based systems can be inferred from a variety of studies in the literature.

Hemmaplardh and King [18] measured the solubilities of methanol in a variety of gases (N₂, Ar, CH₄, C₂H₄, N₂O, and CO₂) and calculated the second virial cross coefficient B_{12} for each methanol-gas pair from their data. (B_{12} is a measure of the deviation from ideality of a system.) Their results showed that the methanol-CO₂ system exhibited a more negative deviation than any other methanol-gas mixture. It was suggested that this increased nonideality of the methanol-CO₂ system may be due to chemical interactions.

The work of Hemmaplardh and King [18] was continued by Gupta et al. [19] and Massoudi and King [20]. Gupta et al. [19] measured the solubility of ethanol in He, H₂, Ar, CH₄, C₂H₄, C₂H₆, N₂O, and CO₂ and calculated the second virial cross coefficient for each ethanol-gas

system. These coefficients were then compared with propane-gas cross coefficients from the literature. The comparison showed that the ethanol-gas and propane-gas second virial cross coefficients differ (for a given gas) only when the gas is CO₂. This result also suggests chemical interactions between CO₂ and ethanol.

Massoudi and King [20] measured the solubility of 1-butanol, diethyl ether, and *n*-pentane in N₂, Ar, C₂H₄, C₂H₆, and CO₂ at room temperature and calculated each solute-solvent second virial cross coefficient. They found that the coefficient for a given gas was roughly constant for all three solutes with the exception of the solute-CO₂ systems. These systems showed a large decrease in B_{12} for diethyl ether and 1-butanol, compared with *n*-pentane. This nonideality suggests chemical interaction in the 1-butanol/CO₂ and diethyl ether/CO₂ systems that are not present in the *n*-pentane/CO₂ system.

Brunner et al. [21] measured the solubility of methanol in a variety of gases (CO₂, CO, CH₄, H₂). They found that methanol was 5–10 times more soluble in CO₂ at a given temperature than in methane. This suggests increased association, which can be explained by chemical interactions between CO₂ and methanol that are not present in the methane-methanol system.

Spectroscopic methods also have been used to investigate the properties of liquid and supercritical CO₂. Fulton et al. [6] used FT-IR spectroscopy to measure the degree of self-association of deuterated methanol solute molecules in supercritical CO₂, supercritical ethane, and liquid heptane. Their results show that CO₂ solvent shifts the self-association equilibrium of methanol-*d* toward the monomer form of the alcohol, whereas supercritical ethane and liquid heptane solvents favor the formation of methanol-*d* clusters. They attributed this behavior to a chemical complex between methanol-*d* and CO₂, which, according to their interpretation, favors the breakup of methanol-*d* clusters to methanol-*d* monomers.

Sigman et al. [22] investigated the acidity and basicity of liquid and supercritical CO₂ using UV spectroscopy. They used the solvatochromic method to quantify their results, and they calculated β , a parameter associated with the basicity of a molecule (molecules that exhibit a basic behavior have a large β value). The calculated value of β for CO₂ was small and negative, suggesting that there is very little basicity associated with carbon dioxide, or, in other words, CO₂ does not easily donate a pair of electrons. Sigman et al. [22] concluded that CO₂ does not easily form hydrogen bonds with the oxygen atom donating a pair of electrons.

Hyatt [4] also has used infrared spectroscopy to study liquid and supercritical carbon dioxide. He used acetone, cyclohexanone, and pyrrole as probes of the polarity of CO₂ by measuring its solvent effect on the shift

of the carbonyl and N-H stretches and comparing the frequency shift in CO₂ with the literature values of a few other organic solvents. The acidity probes (acetone, cyclohexanone) led to the conclusion that CO₂ is similar in acidity to the nonpolar hydrocarbons such as *n*-hexane and benzene. The basicity probe (pyrrole) led to a different conclusion: CO₂ is similar in basicity to diethyl ether and ethyl acetate. Since the diethyl ether-methanol system had been shown to hydrogen-bond, Walsh et al. [13] suggested that a CO₂-methanol system might hydrogen-bond.

To evaluate the ability of methanol to act as an entrainer-cosolvent in CO₂ solvent, information regarding the nature of the chemical complex between methanol and CO₂ is needed. If methanol does hydrogen-bond with CO₂, its effectiveness as an entrainer in CO₂-based systems will be limited. Presented here is an extension of Hyatt's [4] and Fulton and co-workers' [6] infrared studies on the acidity and basicity of liquid CO₂. In addition, we investigate the hydrogen bonding between a probe component and an entrainer-cosolvent in liquid CO₂. Our goal is to gain some insight into the nature of the specific interactions between CO₂ and methanol and, therefore, evaluate the ability of methanol to act as an entrainer-cosolvent in liquid CO₂ solvent.

3. EXPERIMENTS

3.1. Apparatus

All spectra were obtained on a Mattson FT-IR spectrometer (Polaris model). The spectrometer is a double-beam model with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter. Spectrometric-grade chemicals from Aldrich Chemical Company were used. Purity was checked by infrared spectroscopy. Carbon dioxide with a minimum purity of 99.99% was obtained from Potomac AirGas Inc.

The spectra obtained for a probe molecule in liquid CO₂ were measured using a flow-circulation apparatus as shown in Fig. 1, which provides a rapid and reproducible means of obtaining spectra at high pressures. The fluid of the system is circulated by a custom-made, piston-operated magnetic pump. The up-and-down motion of the permanent magnet was controlled with a Hurst motor (Model KN-2492-616) and an eccentric wheel. The fluid flow through the pump is about 10 cm³ · min⁻¹. The one-way check valve at the discharge side of the pump is from High Pressure Equipment Co. (Model 15.41AF1).

The heart of the apparatus is the high-pressure sample cell. The design of the cell is from the classical methods of preparing samples for infrared measurements. The sample is "sandwiched" between two sapphire plates

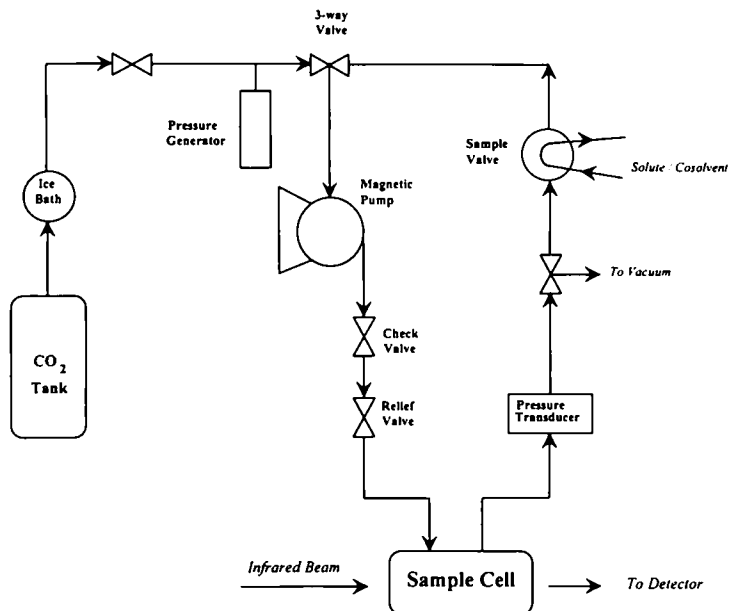


Fig. 1. High-pressure FT-IR spectroscopic apparatus.

and held together by a pair of stainless-steel plugs. For high pressure measurements the two most important issues are to eliminate leaks and to maintain high pressure without cell rupture due to mechanical failure. Shown in Fig. 2 is a schematic of the fixed-pathlength, high-pressure cell. The sample cell is made of 316 stainless steel and has an internal volume of 2.39 cm^3 . There are two external exit ports on the sample cell, forming a 90° angle with each other. The cell includes sapphire windows, spacers, o-rings, and stainless-steel plugs.

The crystal windows are sapphire material with a diameter of 2.5 cm and a thickness of 1.0 cm and were obtained from Harrick Scientific Inc. The sapphire windows are able to withstand the high pressures and transmit infrared light with frequencies higher than 1800 cm^{-1} . The spacers, made of Teflon, and the o-rings, made of Buna-n rubber, also were obtained from Harrick Scientific Inc. The plugs were made of stainless steel, with an opening to allow the infrared beam through the sample volume.

The pressure of the system was measured with a Dynisco pressure transducer (Model PT422A-5M-6118). The transducer has a full-scale range of 34.5 MPa (5000 psi) with an accuracy of 0.5% of the full-scale output. The pressure-transducer signal was processed and displayed with a Dynisco digital-pressure indicator (Model DR-482).

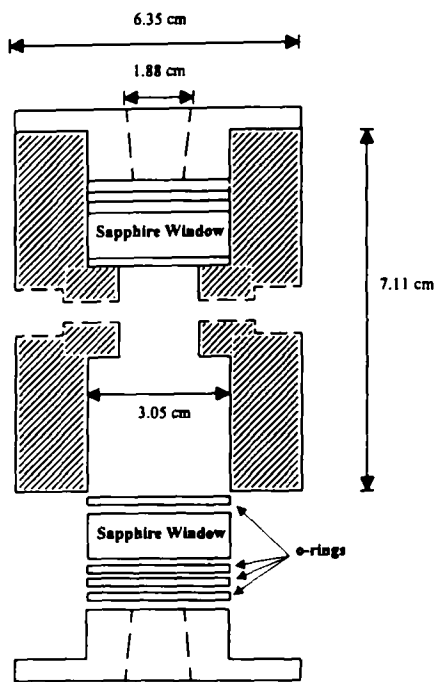


Fig. 2. High-pressure sample cell.

All connections were made with 0.15875 cm (1/16 in.)-outer diameter 316 stainless-steel tubing. Valves and fittings were obtained from High Pressure Equipment Inc. A Nupro relief valve (Model SS-4R3A1) was included in the circulation loop to prevent accidental overpressurization. The valve, which is spring loaded, is set to release for pressures in excess of 4000 psi (~ 275 bar).

The probe molecules were injected directly into the system using a six-port sampling valve, obtained from Rheodyne (Model 7413), located on line right after the three-way valve leading to the vacuum. This sampling valve has three internal loop with volumes of 0.5, 1.0, and 5.0 μl , and the 1.0- μl loop is in the active position.

3.2. Procedure

In general, the procedure involved evacuating the system to remove traces of impurities, pressurizing the system with CO_2 , and introducing the probe into the fluid.

The system was loaded with CO₂ directly from a tank containing CO₂ at room temperature and at a pressure of approximately 58 bar, its vapor pressure. Since pressures above 58 bar are of interest, the system was further pressurized using a pressure generator. The line from the regulator for CO₂ tank was coiled and immersed in an ice bath; this enables the system to be charged with liquid CO₂. The coiled line was connected to the high-pressure generator (obtained from High Pressure Equipment Co., Model 60-6-15), which was used to generate high pressures. For safety, the relief valve was set at 4000 psi (275 bar). Once the desired pressure was reached, the system was closed off from the pressure generator and the fluid was circulated using the magnetic pump. After several minutes of circulating the pure CO₂, the probe compound was injected using the sample valve. The use of the syringes and the sample valve allows fast and reproducible injections of the probe into the system. In addition, the advantage of this technique is that known amounts of the probe can be injected and that they can be added incrementally, so that a large range of concentrations can be studied during a single experiment.

To ensure complete mixing of the probe and the high-pressure fluid, the system was circulated for at least 0.5 h before any measurements were made. Then an FT-IR spectrum was taken. This was repeated until the infrared spectrum became constant.

To add a third component into the system, the syringes and the internal loop of the sample valve were cleaned with acetone, and then loaded with the third component. Then, the third component was incrementally injected into the system, and spectra were taken at various values of its concentration in the system.

4. RESULTS AND DISCUSSION

We have used methanol-*d* (rather than methanol) as a probe to investigate the hydrogen-bonding behavior of CO₂, since a pair of combination bands of CO₂ interfere with the O-H stretch of methanol at about 3650 cm⁻¹. The O-D stretch of methanol-*d* absorbs at much lower frequencies (due to the increased mass of the deuterated hydroxyl group), in a clean region of the mid-infrared.

Figure 3 shows the FT-IR peak of the O-D stretch of methanol-*d* in various liquid solvents. All liquid solvents were at room temperature and pressure [23] except CO₂, which was at room temperature and ~95-bar (~1400-psi) pressure. For the solvents CCl₄, chloroform, and toluene, with which methanol-*d* does not hydrogen-bond, the O-D peak of methanol-*d* occurs at about 2700 wavenumbers. However, in solvents with which methanol-*d* *does* hydrogen-bond (acetone, dimethyl sulfoxide, methyl ethyl

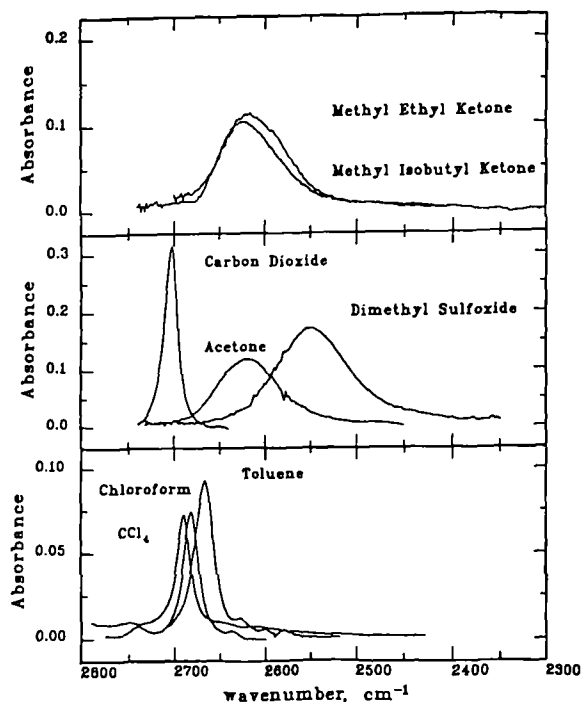


Fig. 3. O D stretch of methanol-*d* in various solvents.

ketone, and methyl isobutyl ketone), the peak due to the O-D stretch of methanol-*d* is shifted about 100 wavenumbers toward lower frequencies, and it becomes much broader. In the case of a high-pressure CO₂ solvent, the O-D stretch absorbs at about 2700 wavenumbers, as is the case with the non-hydrogen-bonding solvents. There is no shift in position or change in width and shape of the peak from solvents such as CCl₄. Therefore, by using a probe molecule such as methanol-*d*, which is very sensitive to the solvent environment and can potentially hydrogen-bond, we see no indication of hydrogen-bonding between methanol-*d* and CO₂ molecules.

This seems to be contradictory to the fact that methanol-*d* forms a chemical complex with CO₂. To probe this issue, we also examined the spectra of CO₂. This is shown in Fig. 4, where we plot part of the CO₂ infrared spectrum at a pressure of ~0.5 bar. The left-side band (~3720 cm⁻¹) corresponds to the combination of the symmetric and the asymmetric stretches of CO₂, and the right-side band (~3610 cm⁻¹) corresponds to the combination of the symmetric stretch and the overtone of the bend. (Both bands are split in two due to the rotational fine

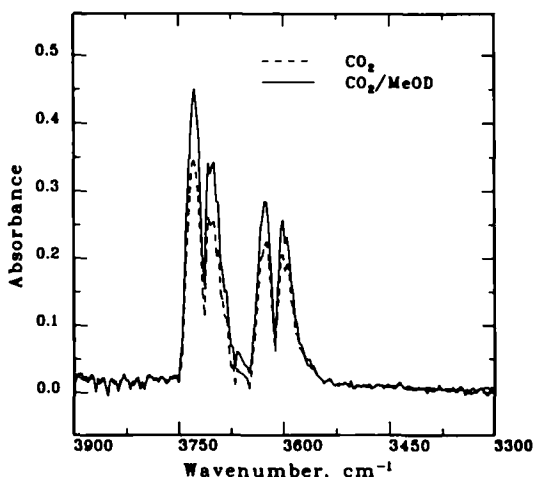
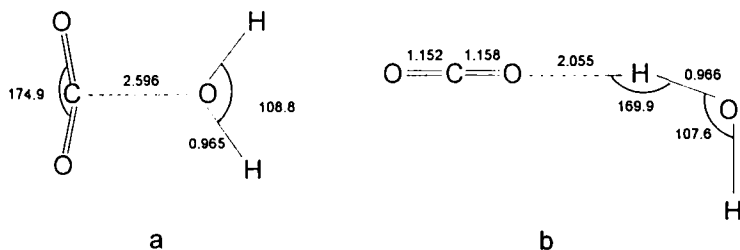


Fig. 4. CO_2 spectra at a pressure of ~ 0.5 bar: pure CO_2 (dashed line) and CO_2 methanol-*d* (solid line).

structure that is observed at low densities.) We see that the addition of trace amounts of methanol-*d* in pure CO_2 results in a significant increase in the intensity of both bands. This result suggest that the oxygen of methanol-*d* interacts with the carbon of CO_2 , and therefore it affects both the asymmetric stretch and the bend of the CO_2 molecule. (It should be noted that methanol-*d* does not affect the symmetric stretch of CO_2 . This is further evidence that there is no hydrogen bonding.)



This conclusion is consistent with molecular orbital calculations [24] which show that configuration a between a CO_2 and a water molecule, where the carbon atom interacts with the oxygen atom of water (a Lewis acid-base interaction), is more stable than configuration b, which involves hydrogen bonding. Damewood et al. [25] also investigated the 1:1 CO_2 -water potential surface using *ab initio* molecular orbital techniques. Their results showed that structure a, shown above, is the lowest-energy structure

for the 1:1 complex between CO_2 and water. Jönsson et al. [26] also performed molecular orbital calculations and found that configuration a is $3.25 \text{ kcal} \cdot \text{mol}^{-1}$ ($12.6 \text{ kJ} \cdot \text{mol}^{-1}$) stronger than the hydrogen-bonded structure b. (The energy of formation for complex a is $-25.7 \text{ kJ} \cdot \text{mol}^{-1}$, while the energy of formation for complex b is $-12.1 \text{ kJ} \cdot \text{mol}^{-1}$.) Jönsson et al. [26] also performed a simple analysis of electrostatic interactions using point charges at the atoms, obtained from a Mulliken population analysis of the free molecules; their results showed that the intermolecular electrostatic attraction is $4 \text{ kJ} \cdot \text{mol}^{-1}$ greater in complex a than in complex b. The CO_2 -water interactions also have been investigated spectroscopically. Fredin et al. [27] used IR spectroscopy and found a well-defined complex with the water oxygen bound to the carbon atom in CO_2 ; they also found no evidence of a hydrogen-bonded complex. Tso and Lee [28, 29] also studied the molecular complexes between water and carbon monoxide and carbon dioxide in solid oxygen using FT-IR spectroscopy. From their spectra they conclude that water and CO_2 form a van der Waals planar complex, with the hydrogens of the water molecule directed away from the CO_2 molecule. In addition, Peterson and Klemperer [30] measured the radiofrequency and microwave spectra of $\text{H}_2\text{O}-\text{CO}_2$, $\text{HDO}-\text{CO}_2$, and $\text{D}_2\text{O}-\text{CO}_2$ by molecular beam electric resonance spectroscopy. An extensive structural analysis of their data showed that the $\text{H}_2\text{O}-\text{CO}_2$ complex is planar, with the hydrogens pointed away from the

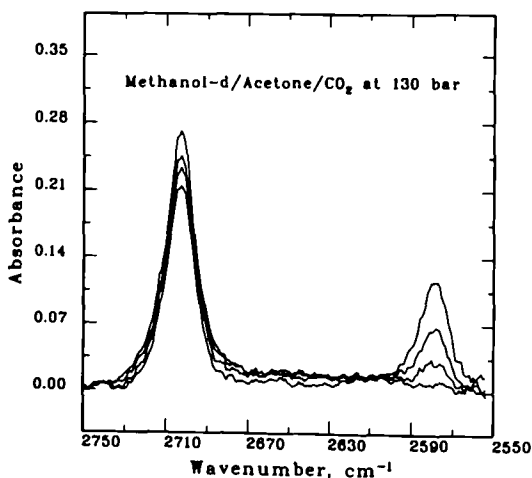


Fig. 5. FT-IR spectra of CO_2 methanol-*d* acetone at a pressure of 130 bar: methanol-*d* monomeric peak ($\sim 2700 \text{ cm}^{-1}$) and methanol-*d* acetone hydrogen-bonded peak ($\sim 2580 \text{ cm}^{-1}$) for various acetone concentrations.

CO₂ molecule. Therefore, the hydrogen atom should still be available to hydrogen-bond with an electron donor molecule.

To verify further this conclusion, we measured the FT-IR spectra of a CO₂/methanol-*d*/acetone ternary system at room temperature and at a pressure of 130 bar. The results are shown in Fig. 5. In the absence of acetone from the mixture, we obtain the peak due to the O-D stretch of methanol-*d* monomers at about 2700 cm⁻¹, and nothing at lower frequencies. When acetone is introduced into the fluid, the height and area of the monomeric peak decrease, and at the same time, an additional peak grows at about 120 wavenumbers away from the monomeric peak, toward lower frequencies. This peak increases with increasing concentration of acetone and is due to hydrogen-bonding between methanol-*d* and acetone [23]. Therefore, methanol-*d* is able to hydrogen-bond with a basic compound such as acetone even in the presence of liquid CO₂, and therefore, it should be a good entrainer cosolvent in liquid CO₂ systems.

In conclusion, we present a discussion of carbon dioxide complexes and an FT-IR spectroscopic investigation of the Lewis acid-base and hydrogen-bonding interactions of carbon dioxide at high pressures. For this purpose, we designed and built a high-pressure spectroscopic apparatus, which provides an accurate means of obtaining spectra at high pressures. FT-IR spectroscopic results of methanol-*d* in liquid CO₂ showed no indication of hydrogen-bonding between methanol-*d* and CO₂ molecules. We argue that the complex formed between methanol-*d* and CO₂ is a result of Lewis acid-base interaction between the carbon of the CO₂ and the oxygen of the methanol-*d*, rather than hydrogen-bonding interaction. Therefore, a CO₂ molecule is more likely to accept an electron pair than donate one. This was confirmed by the introduction of acetone in a CO₂/methanol-*d* system, where it was clearly observed that the methanol-*d* molecules are available to hydrogen-bond with the acetone molecules.

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