# Towards microsolvation of fluorocarbons by $CO_2$: Two isomers of Fluoroethylene-$(CO_2)_2$ observed using chirped-pulse Fourier-transform microwave spectroscopy

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**Abstract**

Understanding structural changes during microsolvation of a solute by increasing numbers of $CO_2$ molecules provides a path towards improved models of supercritical $CO_2$ solvent properties. Microwave spectroscopic observations of fluoroethylene (FE) microsolvation by $CO_2$ give two FE-$(CO_2)_2$ isomers, each with fragments similar to previously studied planar FE-$CO_2$ dimers. In each trimer, a second $CO_2$ is located above the FE plane, in a position not observed for FE-$CO_2$. Current work on FE/$CO_2$ mixtures focuses on deconvoluting interleaved spectra in the microwave scan, aiming to identify FE-$(CO_2)_3$ and other clusters, with patterns from at least five additional cluster spectra already identified.

**Keywords:** trimer, FTMW, *sc*-$CO_2$, microsolvation, weak hydrogen bonds

## I. Introduction

Supercritical $CO_2$ (*sc*-$CO_2$) is a versatile green solvent, with uses ranging from dry cleaning to extraction of essential oils and decaffeination, in addition to being used as a solvent in synthesis of polymers and other industrial processes. While nonpolar solutes tend to have good solubility in *sc*-$CO_2$, it is necessary to include a polar co-solvent to achieve solubility of many polar solutes. In addition, it has been found that fluorinated species typically have considerably higher solubility in *sc*-$CO_2$ than their hydrogen-containing analogs [1], leading to development of fluoropolymers and fluorinated surfactants with high *sc*-$CO_2$ solubilities (known as $CO_2$-philic compounds). Reasons for this increased solubility are not clearly understood, and it remains difficult to predict solvent properties of *sc*-$CO_2$ reliably for different chemical systems [2]. A summary of theoretical work on the subject is given in a recent review [3]. One difficulty with obtaining accurate models of *sc*-$CO_2$ behavior is the lack of experimental data on small systems that can be used to benchmark and compare with theoretical results. In the present letter, Fourier-transform microwave spectroscopy (FTMW), is combined with *ab initio* calculations to probe structures of small gas-phase clusters with two $CO_2$ molecules acting as solvent for a single fluoroethylene (FE) solute molecule. These FE-$(CO_2)_2$ trimers can be compared with previously studied FE-$CO_2$ dimers [4] to determine which solvation sites around FE are most favorable, and what changes to distances and orientation are likely as the number of $CO_2$ molecules continues to increase. The two binding sites occupied in the FE-containing dimers appear to be essentially equally favorable, making trimer studies of FE particularly interesting since there will also be a possibility of several favorable isomers for these larger clusters, and the choice of which binding sites will be occupied in the trimer will not necessarily be obvious. Both nearly isoenergetic isomers observed for FE-$CO_2$ are planar. A non-planar

structure with $CO_2$ above and nearly parallel to the FE plane was predicted to be the minimum energy configuration, both before and after zero-point energy (ZPE) and basis set superposition error (BSSE) corrections [4]; however, symmetry adapted perturbation theory (SAPT) interaction energies indicate that this nonplanar structure is slightly less stable than the two planar forms [5], consistent with the fact that it has not yet been identified experimentally. It will be interesting to observe whether FE-$(CO_2)_2$ has $CO_2$ molecules occupying the two in-plane sites already observed for the two FE-$CO_2$ isomers, or whether the non-planar $CO_2$ site will now play a role.

## II. Experimental Methods

The spectrum of a mixture containing 1% FE (Synquest Laboratories) and 1% $CO_2$ (Sigma Aldrich) diluted in about 2 atm of Ne buffer gas (Praxair) was scanned in the 2-8 GHz region using the chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer at the University of Virginia (UVa). The gas sample was expanded into the vacuum chamber through five 1 mm diameter nozzles, with a repetition rate of 3 Hz. Eight chirped pulses excited each gas pulse, giving an effective averaging rate of 24 free induction decays (FIDs) per second. A total of 1 million FIDs were averaged to give the final spectrum. A second scan was performed under similar conditions, but with a sample containing only FE, so that this could be used later for elimination of transitions not requiring both sample components.

*Ab initio* calculations were performed using Gaussian 09 at the MP2/6-311++G(2d,2p) level [6]. For all optimized structures, vibrational frequency calculations were performed using the CALCALL keyword, to confirm that structures were true minima on the potential energy surface and to obtain zero-point energy (ZPE) corrected relative energies.

## III. Results and Discussion

### A. Ab Initio Calculations

Structures of three predicted FE-$CO_2$ dimers (two of which have been observed

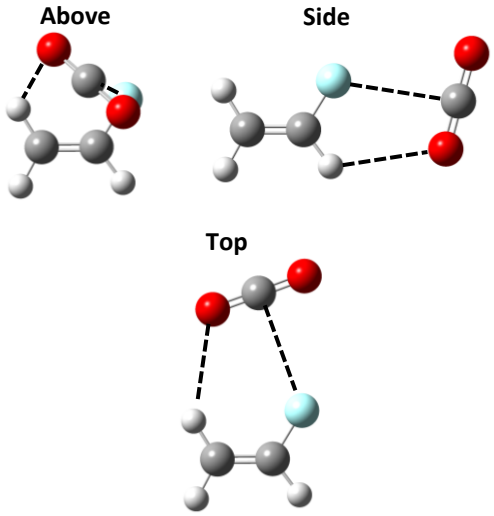


**Figure 1**. Three *ab initio* structures for FE-$CO_2$ [4]. The Top and Side structures are planar, while the Above structure has $CO_2$ located above the plane of FE. Only Top and Side structures have been observed experimentally.

experimentally) ([4], Figure 1) were used as a guide to predicting possible $CO_2$ positions within FE-$(CO_2)_2$ trimers. Ultimately, four optimized trimer configurations were obtained (Figure 2), with two of these lying significantly lower in energy than the others (Table 1). Harmonic

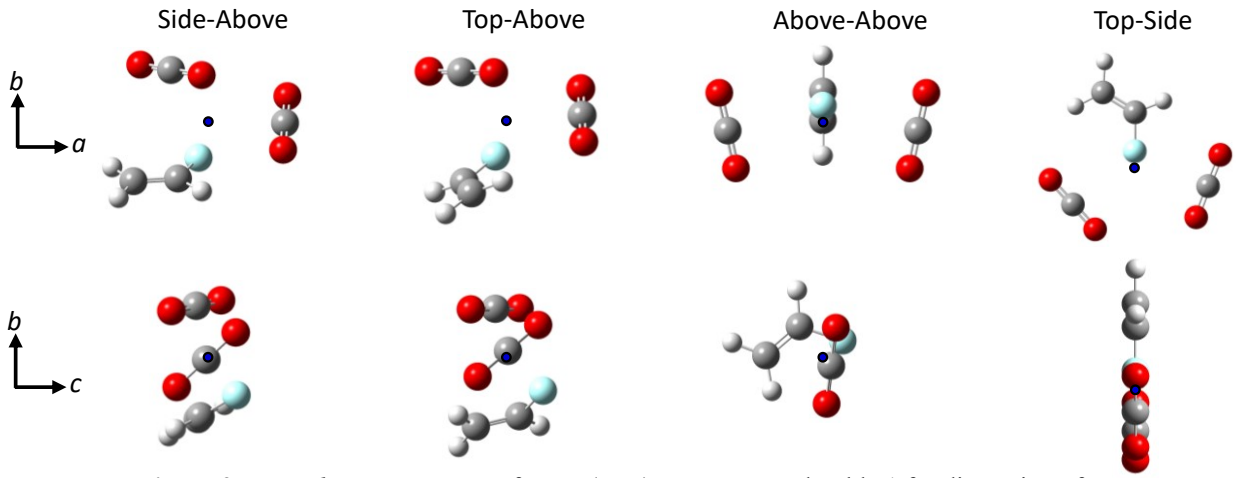


**Figure 2**. Four *ab initio* structures for FE-$(CO_2)_2$. See text and Table 1 for discussion of relative energies. Black circles mark the projection of the center of mass in the plane designated by the axes to the left of the figure.

frequency calculations confirmed that all four structures are minima on the potential energy surface, and ZPE corrections made little difference to relative energies. All four structures include combinations of $CO_2$ molecules placed in three orientations with respect to FE: on the side of and roughly perpendicular to the C=C bond (Side or S position), along the top of and roughly parallel to the C=C bond (Top or T position), or above the plane of FE lying roughly across the C–F bond (Above or A position). The two most stable trimer structures are similar to the two experimentally observed dimer configurations (Figure 2, $CO_2$ in Side or Top positions [4]), each with a second $CO_2$ molecule added in a position corresponding to the higher energy Above dimer; thus, experimental observation of these trimer structures would provide an indirect way to isolate the Above form of the dimer, even though that dimer orientation has not been observed on its own.

**B. Spectra**

Spectroscopic assignment was carried out with the help of Kisiel's AABS suite of programs [7], allowing removal of known transitions from the experimental spectrum, and facilitating visual interpretation of the dense spectra. In the present case, removing all transitions from the FE/$CO_2$ scan that were also present in the FE-only scan, eliminated, on average, more than one transition per megahertz from the 6 GHz wide spectrum. The remaining scan still had a density of nearly one line per 2 MHz (with S/N $\geq$ 2, with many additional clearly discernable transitions having lower S/N); however, enough transitions were removed to more readily identify patterns in remaining data. A survey of the spectrum focusing on transitions of ~1% – 10% of the intensity of assigned dimer lines led to identification, in the 6.7 – 7.3 GHz range, of

**Table 1.** Energies and rotational constants of four *ab initio* structures for FE-$(CO_2)_2$, along with fitted spectroscopic constants for the two experimentally observed isomers.

| | Side-Above | Top-Above | Above-Above | Top-Side | Isomer I (Side-Above) | Isomer II (Top-Above) |
|---|---|---|---|---|---|---|
| $A$ / MHz | 1734.3 | 1618.7 | 2933.3 | 1626.9 | 1660.35121(8) | 1552.10543(12) |
| $B$ / MHz | 1107.4 | 1174.0 | 643.5 | 922.8 | 1109.76469(6) | 1169.46004(11) |
| $C$ / MHz | 808.4 | 881.9 | 609.4 | 588.8 | 785.77728(6) | 847.25679(12) |
| $\Delta_J$ / kHz | | | | | 1.5373(10) | 2.143(4) |
| $\Delta_{JK}$ / kHz | | | | | -0.3410(18) | -4.0883(26) |
| $\Delta_K$ / kHz | | | | | 4.1842(17) | 7.577(3) |
| $\delta_J$ / kHz | | | | | 0.3739(3) | 0.6035(4) |
| $\delta_K$ / kHz | | | | | 1.4606(17) | 0.3219(18) |
| $P_{aa}$ / u Å$^2$ | 395.1 | 345.7 | 721.2 | 547.7 | 397.08512(4) | 351.51361(8) |
| $P_{bb}$ / u Å$^2$ | 230.1 | 227.4 | 108.1 | 310.7 | 246.07296(4) | 244.97498(8) |
| $P_{cc}$ / u Å$^2$ | 61.3 | 84.8 | 64.2 | 0.0 | 58.30782(4) | 80.63370(8) |
| $\mu_a$ / D | 0.84 | 1.16 | 0.00 | 0.03 | | |
| $\mu_b$ / D | 0.78 | 0.98 | 0.73 | 1.53 | | |
| $\mu_c$ / D | 1.08 | 0.68 | 1.37 | 0 | | |
| $N$ [a] | | | | | 136 | 83 |
| $RMS$ / kHz [b] | | | | | 1.4 | 1.5 |
| $\Delta E$ / cm$^{-1}$ [c] | 0.0 | 24 | 311 | 387 | | |
| $\Delta E_{ZPE}$ / cm$^{-1}$ [d] | 0.0 | 21 | 281 | 334 | | |

[a] $N$ = number of transitions in the fit.

[b] $RMS = \left(\frac{\sum(\nu_{obs}-\nu_{calc})^2}{N}\right)^{\frac{1}{2}}$.

[c] $\Delta E$ is the relative energy of each structure, compared to the minimum energy structure.

[d] $\Delta E_{ZPE}$ is the zero-point energy corrected relative energy.

two "constant difference" patterns, characteristic of closed loop energy differences between asymmetric top rotational energy levels. Predictions for the two lowest energy *ab initio* trimer structures suggested both species would have similar patterns in this frequency range, with the more narrowly spaced higher frequency pattern more closely matching predictions for the Top-Above (TA) structure (Figure 2). See Figure 3 for an example of the original and difference spectra, showing patterns assigned for both species. Many FE-only transitions are significantly

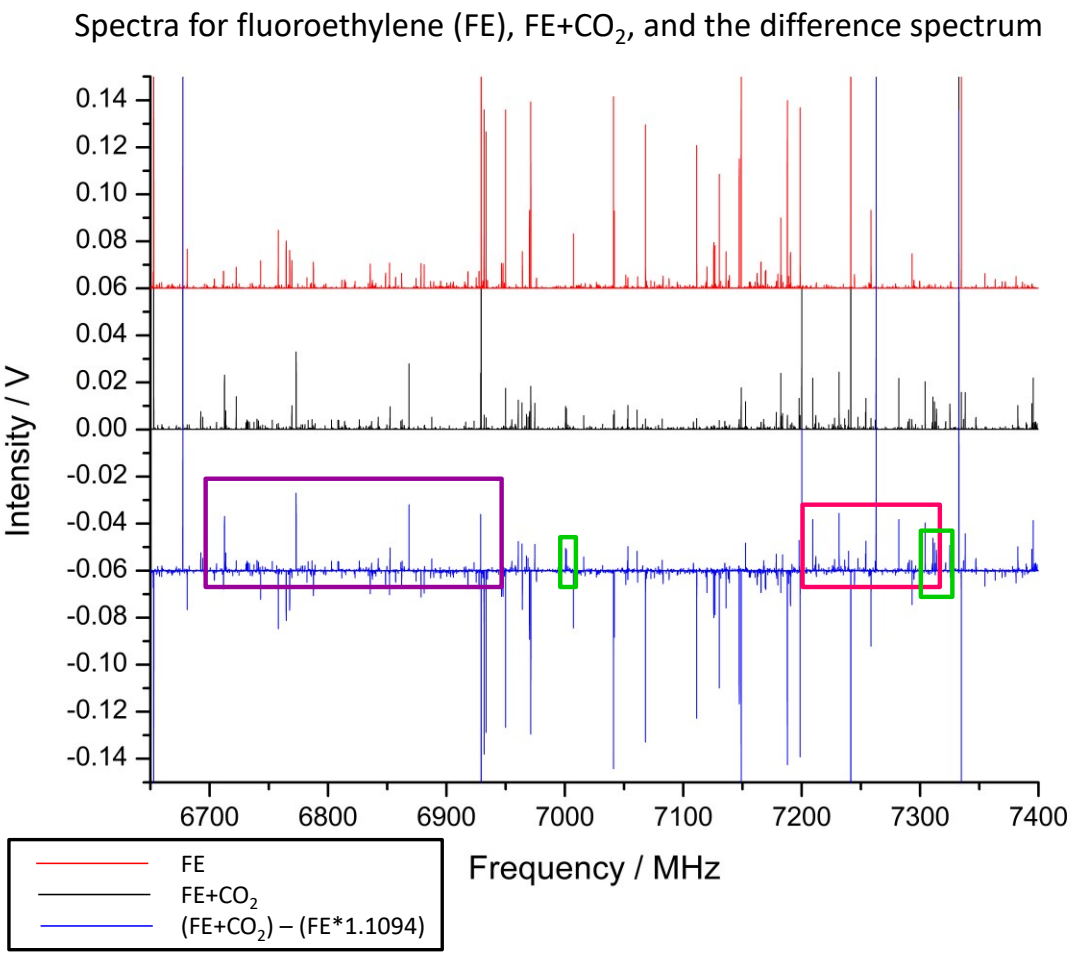


**Figure 3**. The 6650 MHz – 7400 MHz range of the FE-only scan (top), FE/$CO_2$ scan (middle), and the result of subtracting the FE scan from the FE/$CO_2$ scan (bottom). The FE-only scan intensities are scaled before subtraction to remove the strongest FE monomer transitions (scale factor = 1.1094). Purple and pink boxes outline closed loop patterns assigned for SA and TA structures, respectively (see text for structure descriptions). The two green boxes highlight additional narrowly spaced closed loop patterns that are assigned and fitted to two separate species, but for which the carriers of the spectra are not yet identified.

stronger in the scan that does not contain $CO_2$, indicating that a significant amount of FE is involved in complex formation when $CO_2$ is present.

Spectra were predicted and fitted to a Watson *A*-reduction Hamiltonian in the $I^r$ representation [8] using Pickett's SPFIT/SPCAT programs [9]. Resulting rotational constants were similar to those predicted for the two lowest energy *ab initio* structures, and assigned spectra will be referred to as Side-Above (SA) and Top-Above (TA). Ultimately, 136 and 83 transitions were fitted for SA and TA spectra, respectively. Fitted spectroscopic constants are included in Table 1, and frequencies of fitted transitions are provided as Electronic Supplementary Information.

Transitions for the TA structure are slightly weaker than those for the SA structure, despite predicted larger dipole moment components for the TA configuration. This might suggest a slightly lower abundance for TA, compared to SA, consistent with the slightly higher (~21 $cm^{-1}$) predicted energy of the TA structure (Table 1).

**C. Structural analysis and discussion**

The present data only allow for assignment of the most abundant isotopologue of each isomer of the trimer, thereby precluding detailed structural analysis at this time. Comparison of experimental with *ab initio* spectroscopic constants confirms the general arrangements of monomers within the two observed trimer forms. AA and TS structures can be eliminated, since both have at least one dipole component that is zero by symmetry, while both observed spectra display all three selection rules. Rotational constants and planar moments of the two observed spectra correspond much more closely to SA and TA *ab initio* constants, respectively, than to

constants of any of the other structures. Relative intensities of *a*-, *b*-, and *c*-type transitions are also consistent with predicted dipole moment components for the SA and TA configurations.

The predicted, but previously experimentally unobserved, Above dimer configuration (Figure 1, [4]) is a component of both experimental trimer structures, providing two snapshots of this nonplanar arrangement, despite the fact that it has so far eluded assignment as an isolated dimer. The planar TS structure (Figure 2), which would include fragments similar to both the experimentally observed Top and Side bonded dimers, is predicted to be the least stable optimized trimer configuration, lying over 300 $cm^{-1}$ higher in energy than the SA and TA structures (Table 1). Positioning $CO_2$ above the plane of FE in both observed isomers allows for interactions between the two $CO_2$ molecules within each observed trimer and for three-body interactions that would be impossible in the planar TS configuration. In comparing $(CO_2)_2$ fragments from the *ab initio* structures with the planar slipped parallel structure of isolated $CO_2$ dimer [10, 11], it is clear that there are relatively large perturbations. $CO_2$ dimer fragments within both trimers are skewed into an almost T-shaped nonplanar arrangement, where the O of one $CO_2$ is above the C of the other. The nearest neighbor O…C distances in both species are over 0.1 Å shorter than the experimental nearest neighbor distance in $CO_2$ dimer [10, 11], the C…C=O angles deviate by ~10-25° from $CO_2$ dimer values, and the O=C…C=O dihedral angles in both trimers are around 122° (vs 180° in the dimer). In comparison with *ab initio* calculations for $CO_2$ dimer, at the same level as presented here for the trimer, the distances still differ by 0.08-0.09 Å and angles by ~10-20°. The planarity of the FE-$CO_2$ fragments within each trimer is also lost. In each case, $CO_2$ lies slightly above the FE plane, and its axis is slightly twisted with respect to the plane, presumably in order to maximize favorable interactions with both FE and the second $CO_2$ molecule. In these fragments, *ab initio* C–H…O distances for the trimers are

0.04-0.06 Å shorter than in the equivalent *ab initio* isolated dimers, while F…C distances are about 0.08 Å shorter in both trimers. The planarity of the Top dimer fragment is quite perturbed in the TA trimer (O=C…H–C = 33°), while in the SA trimer, the deviation from planarity is only about 3°.

It appears that in building a $CO_2$ shell around an FE "solute" molecule, the first layer of solvating $CO_2$ molecules occupies locations surrounding the F atom. Dimers [4] and trimers show stable structures in which $CO_2$ occupies three binding sites (Top, Side, Above, Figures 1 and 2). Preliminary DFT level optimizations of the tetramer (FE-$(CO_2)_3$) give a structure in which all three sites are occupied; however, these initial ωB97XD/6-31+G(d,p) calculations indicate that this structure may not be the most stable configuration for the species with three $CO_2$ molecules. Other likely tetramer configurations can be described as $CO_2$-trimer-like clusters [10, 11, 12, 13, 14, 15], where FE interacts with the cyclic, propeller-like $(CO_2)_3$ moiety, rather than being surrounded by $CO_2$ molecules.

## IV. Conclusions

Chirped-pulse Fourier-transform microwave spectroscopy and *ab initio* optimizations have been used to study clusters containing two $CO_2$ molecules interacting with a single fluoroethylene molecule solute. In the present work, two structural isomers of FE-$(CO_2)_2$ were observed, each containing a fragment resembling one of the observed planar structures of FE-$CO_2$ [4], and each trapping a second $CO_2$ molecule above the plane of FE, in a position that has not yet been experimentally accessible for FE-$CO_2$. Further computational and experimental studies of FE-$(CO_2)_3$ and larger clusters are underway, with particular focus on finding ways to simplify identification and assignment of additional spectra within the rich dataset. At least five

additional spectra requiring both FE and $CO_2$ (and three requiring only FE) have been assigned and fitted (two examples are highlighted in green in Figure 3). One assigned FE/$CO_2$ spectrum appears to have rotational constants consistent with a near-planar $(CO_2)_3$ structure interacting with one FE molecule that is located near what would be the $C_3$ axis of isolated $(CO_2)_3$ [13]. At least two others may correspond to clusters containing more than one FE molecule.

We are currently developing a variety of approaches to identifying the plethora of spectra, and their carriers, that are present in deep-averaged CP-FTMW data. We are exploiting variation of intensities as a function of $CO_2$ concentration to reveal information on possible cluster size and/or composition, as well as making isotopic measurements to provide detailed structural determinations on the title complexes and to assist in determining cluster composition for other assigned spectra. One challenge is efficiently exploring the potential energy surfaces of larger clusters, and matching spectra with the correct predicted structures. As rotational constants of various conformers become similar for heavier species, correlating computational and experimental results is increasingly difficult.

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**Supplementary Materials**

Full information for reference [6] and fitted transition frequencies for both observed trimer spectra are available online as Electronic Supplementary Information.

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