Supporting Information

Experimental Determination of the Global Warming Potential of Carbonyl Fluoride (COF_2)

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This Supporting Information provides important data and detailed descriptions of certain experimental methods not included in the main text, which are crucial for the discussion in the study titled 'Experimental Determination of the Global Warming Potential of Carbonyl Fluoride (COF_2) via FTIR Spectroscopy and Atmospheric Lifetime Measurements'. It includes an investigation into the linear absorbance range of COF_2 in infrared spectroscopy (**Fig. S1**), as well as detailed information about the DFT methods applied to COF_2 and COH_2, along with the results of these calculations.

Furthermore, this section presents a comprehensive computational analysis of the molecular geometries and spectroscopic properties of COF_2 and COH_2, derived from Density Functional Theory (DFT) calculations. The optimized structures, bond lengths, and bond angles of COF_2 and COH_2 are provided, with particular attention to the molecular geometry of COH_2 (**Fig. S2**), including precise descriptions of bond lengths and angles. These data and methods complement the experimental results and provide further insights into the climate impact of carbonyl fluoride.

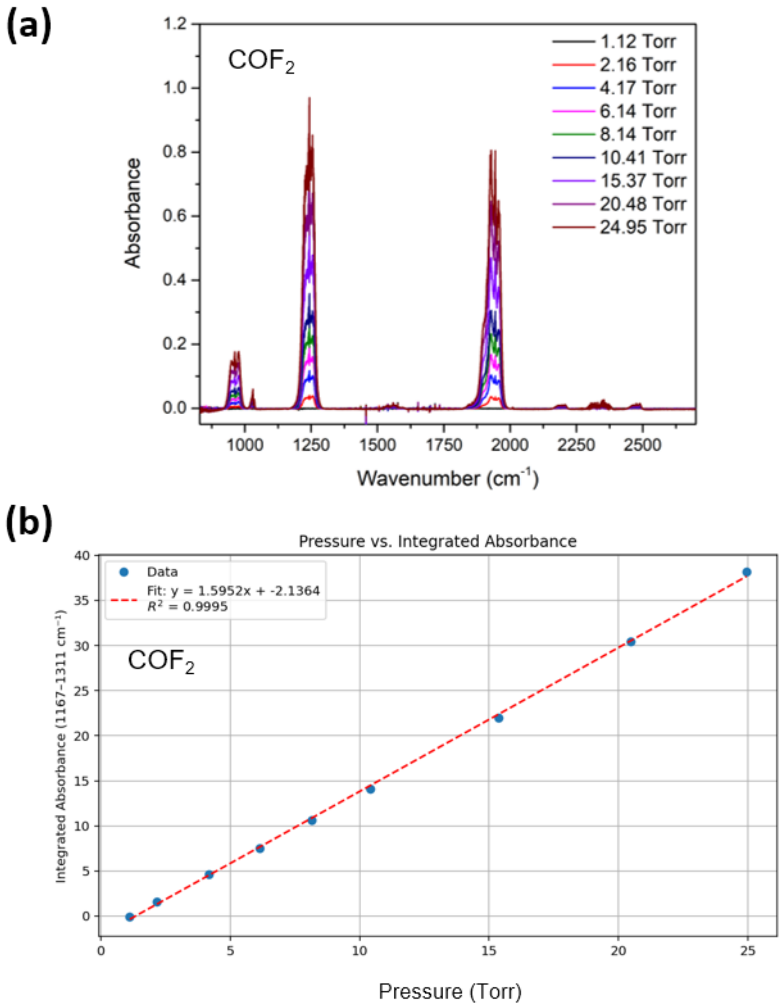


Figure S1. Linearity of COF_2 absorbance with pressure. (a) FTIR spectra of COF_2 at various pressures (from 1.12 to 24.95 Torr) showing the absorbance peaks across different wavenumbers. (b) Integrated absorbance values (1617-1311 cm^{-1}) plotted against pressure, demonstrating a strong linear relationship with a correlation coefficient (R^2) of 0.9995. The red dashed line represents the linear fit with the equation: $y = 1.5952x + 2.1364$.

Computational Properties of COF_2: Geometry and Spectroscopic Analysis

1. Computational Methods for COF_2

The geometry optimization and vibrational frequency calculation for COF_2 were performed using the following computational methods:

- Method: B3LYP (Hybrid Density Functional Theory)
- Basis Set: 6-31++G(d,p) (Double-zeta with polarization functions on heavy atoms)
- Job Types:
    - Geometry optimization (opt)

  - Frequency calculation (freq)
- Additional Options:
  - raman: Raman scattering activities calculation
  - nosymm: No symmetry applied
  - geom=connectivity: Atomic connectivity specified

These calculations were performed to determine the optimized molecular geometry and vibrational frequencies of COF_2.

2. Molecular Geometry of COF_2

Molecular Geometry (Z-Matrix Representation)

The optimized molecular geometry of COF_2 in Z-matrix format is provided below:

C	0.000000	0.145750	0.000000
F	-1.071041	-0.637527	0.000000
F	1.071122	-0.637374	0.000000
O	-0.000091	1.324951	0.000000

This structure represents the COF_2 molecule in its optimized geometry with the following key parameters:

- Carbon (C) at the origin, with two fluorine (F) atoms symmetrically positioned around it.
- The oxygen (O) atom is positioned along the y-axis.

3. Vibrational Frequencies and Infrared Intensities of COF_2

Vibrational Frequencies and IR Intensities

The following harmonic vibrational frequencies (in cm^{-1}) and their corresponding IR intensities are computed:

- 564.3403 cm^{-1}: IR intensity = 5.6377
- 604.2895 cm^{-1}: IR intensity = 7.1162
- 759.2987 cm^{-1}: IR intensity = 38.9245
- 957.8721 cm^{-1}: IR intensity = 61.8239
- 1224.8148 cm^{-1}: IR intensity = 458.8512
- 1973.4157 cm^{-1}: IR intensity = 487.6805

These frequencies correspond to various vibrational modes in the COF_2 molecule, with significant IR absorption intensities observed at higher frequencies, notably the C=O stretching mode around 1973.4157 cm^{-1}.

4. Raman Scattering Activities for COF_2

Raman Scattering Activities

The Raman activities (in arbitrary units) for the key vibrational modes are as follows:

- 564.3403 cm^{-1}: Raman activity = 1.2889
- 604.2895 cm^{-1}: Raman activity = 2.5761

- 759.2987 cm^{-1}: Raman activity = 0.7335

- 957.8721 cm^{-1}: Raman activity = 7.9966

- 1224.8148 cm^{-1}: Raman activity = 1.1309

- 1973.4157 cm^{-1}: Raman activity = 10.5506

These values provide insights into the molecular vibrations that are active in Raman spectroscopy.

● Computational Properties of COH_2: Geometry and Spectroscopic Analysis

1. Computational Methods for COH_2

The geometry optimization and vibrational frequency calculation for COH_2 were performed using the following computational methods:

- Method: B3LYP (Hybrid Density Functional Theory)
- Basis Set: 6-31++G(d,p) (Double-zeta with polarization functions on heavy atoms)
- Job Types:
  - Geometry optimization (opt)
  - Frequency calculation (freq)
- Additional Options:
  - raman: Raman scattering activities calculation
  - nosymm: No symmetry applied
  - geom=connectivity: Atomic connectivity specified

These calculations were performed to determine the optimized molecular geometry and vibrational frequencies of COH_2.

2. Molecular Geometry of COH_2

Molecular Geometry (Z-Matrix Representation)

The optimized molecular geometry of COH_2 in Z-matrix format is provided below:

C	0.000000	0.115053	0.000000
O	-0.000051	1.324660	0.000000
H	-0.941441	-0.470368	0.000000
H	0.941485	-0.470291	0.000000

This structure represents the COH_2 molecule with the following key parameters:

- Carbon (C) at the origin, with two hydrogen (H) atoms and one oxygen (O) atom.

3. Vibrational Frequencies and Infrared Intensities of COH_2

Vibrational Frequencies and IR Intensities

The following harmonic vibrational frequencies (in cm^{-1}) and their corresponding IR intensities are computed:

- 121.8725 cm^{-1}: IR intensity = 0.0
- 116.255 cm^{-1}: IR intensity = 0.0
- 121.8725 cm^{-1}: IR intensity = 0.0
- 180.0 cm^{-1}: IR intensity = 0.0

These frequencies correspond to various vibrational modes in the COH_2 molecule, with significant IR absorption intensities observed at higher frequencies.

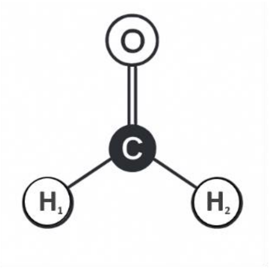
4. Raman Scattering Activities for COH_2

Raman Scattering Activities

The Raman activities (in arbitrary units) for the key vibrational modes are as follows:

- 121.8725 cm^{-1}: Raman activity = 0.0
- 116.255 cm^{-1}: Raman activity = 0.0
- 121.8725 cm^{-1}: Raman activity = 0.0
- 180.0 cm^{-1}: Raman activity = 0.0

These values reflect the molecular vibrations that are active in Raman spectroscopy.



Formaldehyde
(COH_2, MW = 30.03 g/mol)

• Bond lengths	• Bond angles
C=O: 1.2096 Å	∠H_1–C–O: 121.87°
C–H_1: 1.1086 Å	∠H_2–C–O: 121.87°
C–H_2: 1.1086 Å	∠H_1–C–H_2: 116.26°

Figure S2. Optimized structure of carbonyl fluoride (COH_2) obtained from DFT calculations. The molecular weight of COH_2 is 30.03 g/mol. The bond lengths are C=O: 1.2096 Å, and C–H_1 / C–H_2: 1.1086 Å. The bond angles are ∠$H_{1\text{ or }2}$–C–O = 121.87° and ∠H_1–C–H_2 = 116.26°.

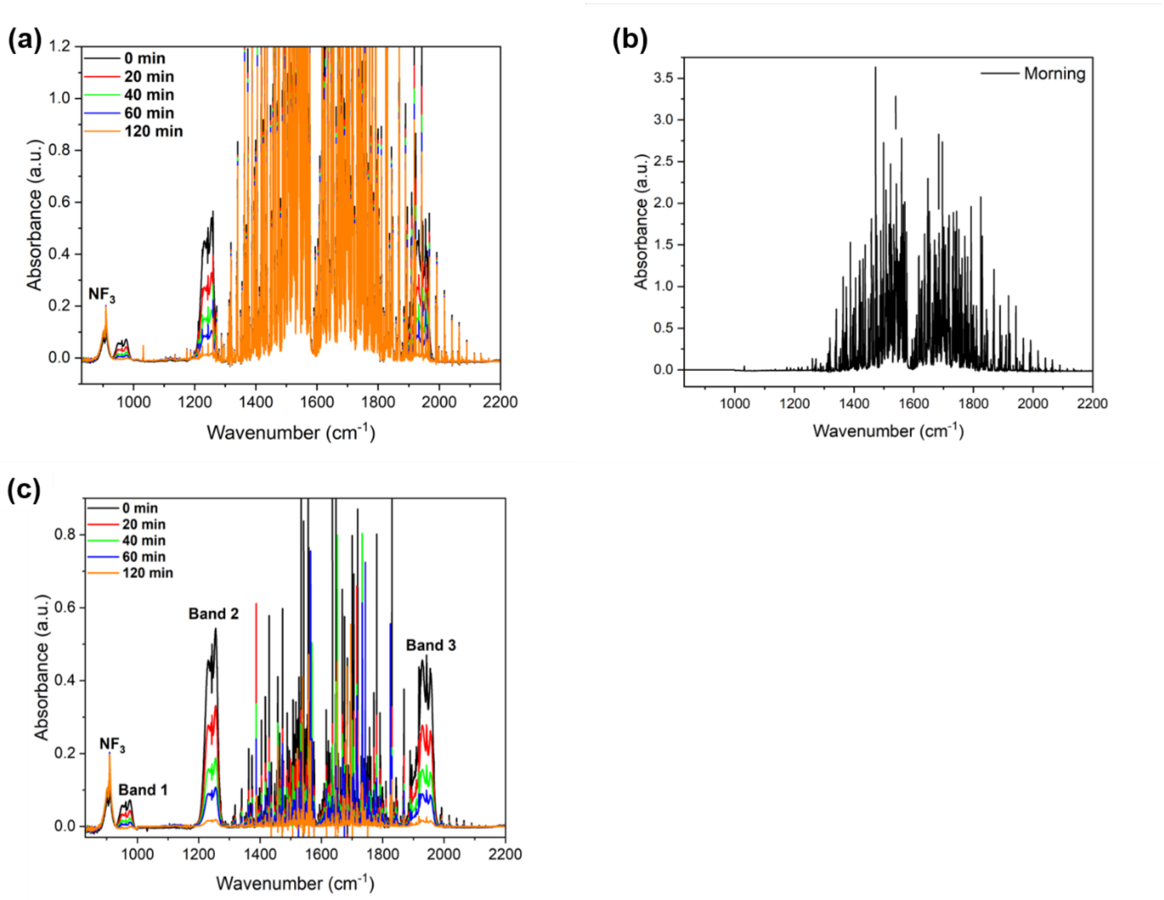


Figure S3. FTIR absorbance spectra obtained during the atmospheric chemical reactions under humid morning conditions. (a) Original spectra collected at different reaction times (0–120 min), showing the time evolution of absorption features. (b) Spectrum obtained after the end of reactions (180 min), which is consisted of atmospheric water vapor in the morning, shows of high humidity. (c) Spectra obtained after subtracting (b) from (a), clearly show NF_3 absorption and three characteristic COF_2 bands (Band 1–3) during the reaction.

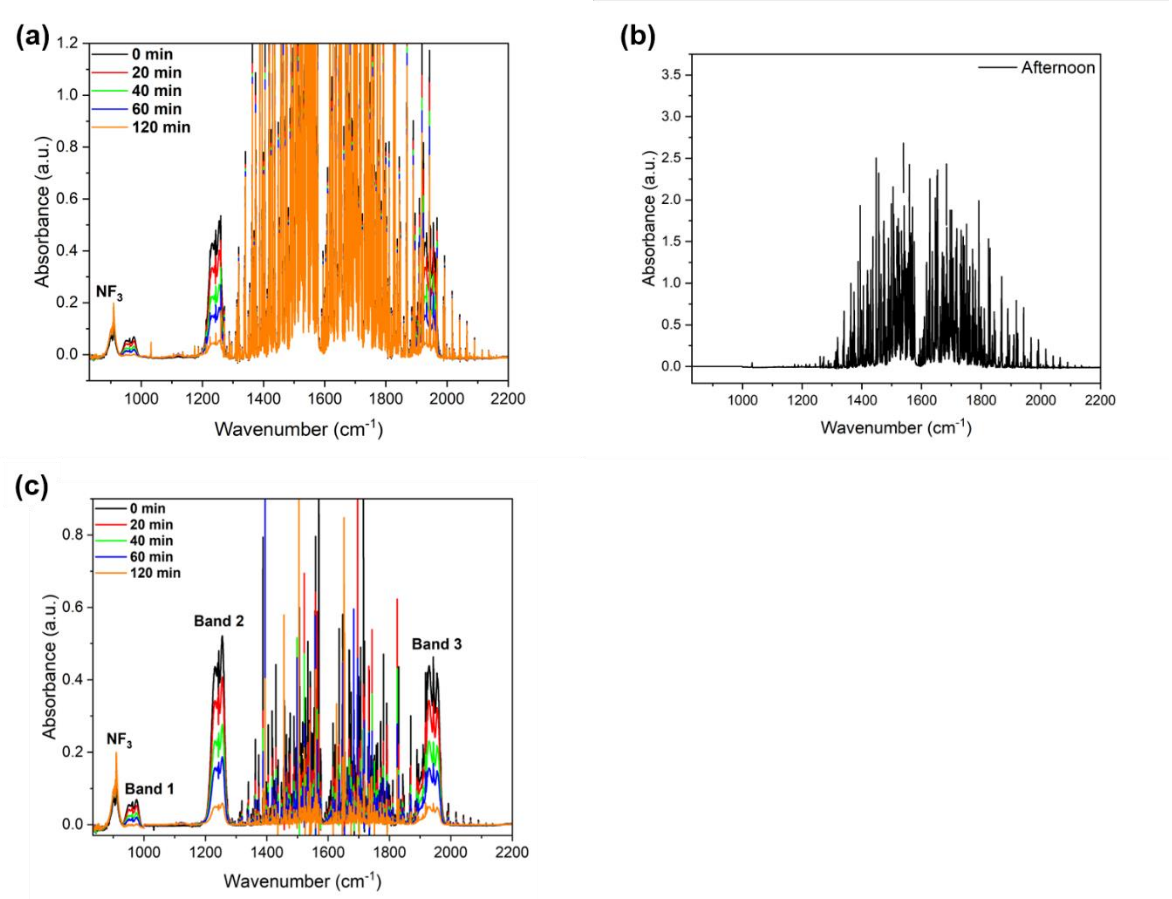


Figure S4. FTIR absorbance spectra obtained during the atmospheric chemical reactions at afternoon. (a) Original spectra collected at different reaction times (0–120 min), showing the time evolution of absorption features. (b) Spectrum obtained after the end of reactions (274 min), which is consisted of atmospheric water vapor of low humidity in the afternoon. (c) Spectra obtained by subtracting (b) from (a), clearly distinguishing the three absorption peaks of COF_2 (bands 1–3) and additionally NF_3 absorption during reaction.