membranes

Article

Performance and Enhanced Efficiency Induced by Cold Plasma on SAPO-34 Membranes for CO_2 and CH_4 Mixtures

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Membrane Continuity Testing

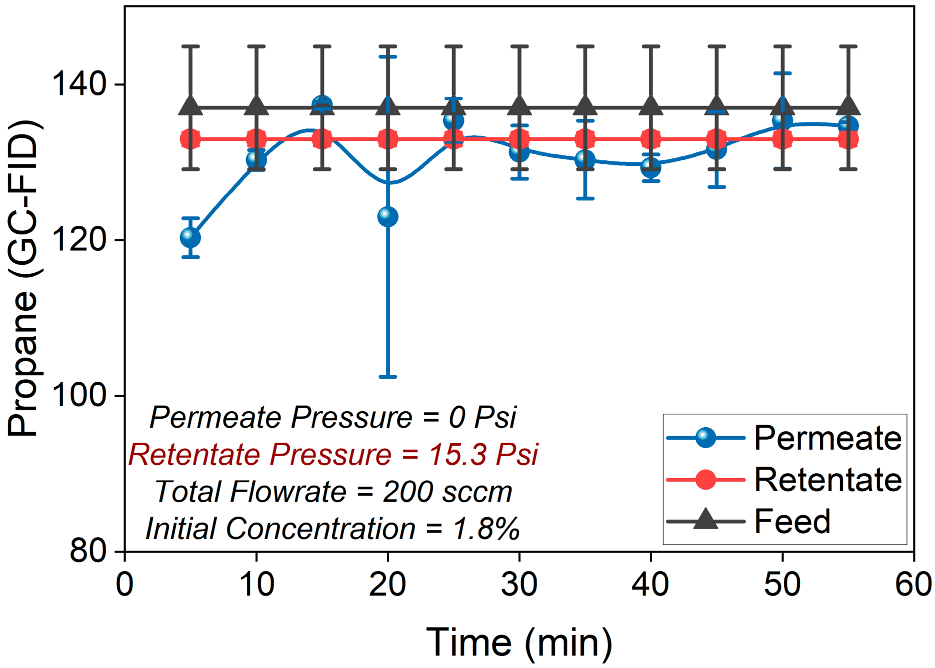

Figure S1. Membrane continuity testing with 1.8% Propane/Nitrogen mixtures.

XPS data

Table S1. BE values obtained from XPS analysis for SAPO-34 interaction with 92:8 (CH_4:CO_2) and 50:50 (CH_4:CO_2) feed composition.

		Feed Composition 92:8(CH_4:CO_2)		
	Al2p (eV)	**Si2p (eV)**	**P2p (eV)**	**O1s (eV)**
SAPO-34-Fresh	74.8	103.0, 100.1	133.9	532.2
SAPO-34-Pulsed Plasma	74.6	100.2	133.9	532.0
SAPO-34-Plasma	74.6	99.7	133.9	531.9
		Feed Composition 50:50 (CH_4:CO_2)		
	Al2p (eV)	**Si2p (eV)**	**P2p (eV)**	**O1s (eV)**
SAPO-34-Fresh	74.0	101.7	133.2	531.0
SAPO-34-Pulsed Plasma	72.7	100.7	132.7	530.2

		Feed Composition 92:8(CH_4:CO_2).		
92:8(CH_4:CO_2)	**Al (atm%)**	**Si (atm%)**	**P (atm%)**	**O (atm%)**
SAPO-34-Fresh	7.3	16.5	10.4	65.8
SAPO-34-Pulsed Plasma	8.9	17.8	9.3	64.0
SAPO-34-Plasma	9.5	18.1	10.5	62.0
		Feed Composition 50:50 (CH_4:CO_2)		
50:50 (CH_4:CO_2)	**Al (atm%)**	**Si (atm%)**	**P (atm%)**	**O (atm%)**
SAPO-34-Fresh	8.9	6.5	11.7	62.9
SAPO-34-Pulsed Plasma	7.4	4.7	10.1	49.5

Table S2. XPS-based elemental quantification without carbon.

	Al (atm%)	**Si (atm%)**	**P (atm%)**	**O (atm%)**
Fresh	7.3	16.5	10.4	65.8
Exposed 5 min	8.9	17.8	9.3	64.0
Exposed 10 minutes	9.5	18.1	10.5	62.0

Non-Thermal Plasma-Separation Unit

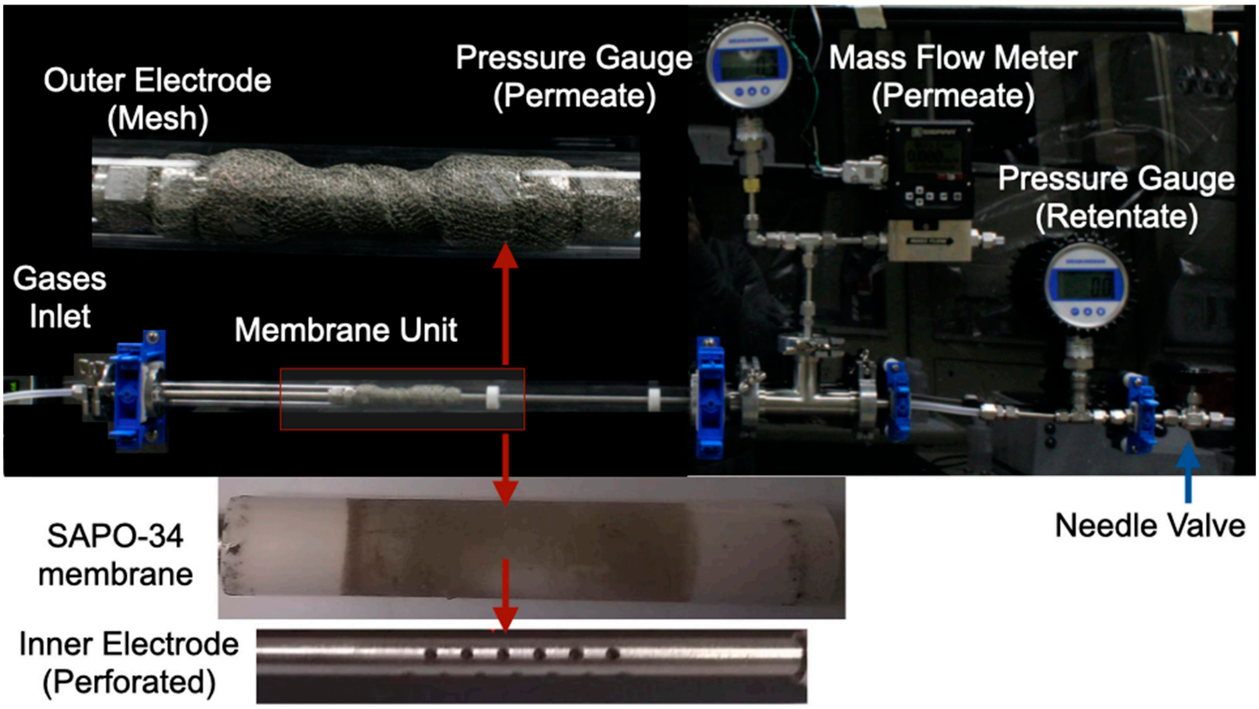

Figure S2. Non-Thermal Plasma Separation unit was employed in this study.

SEM image (Membrane and Porous Substrate interface)

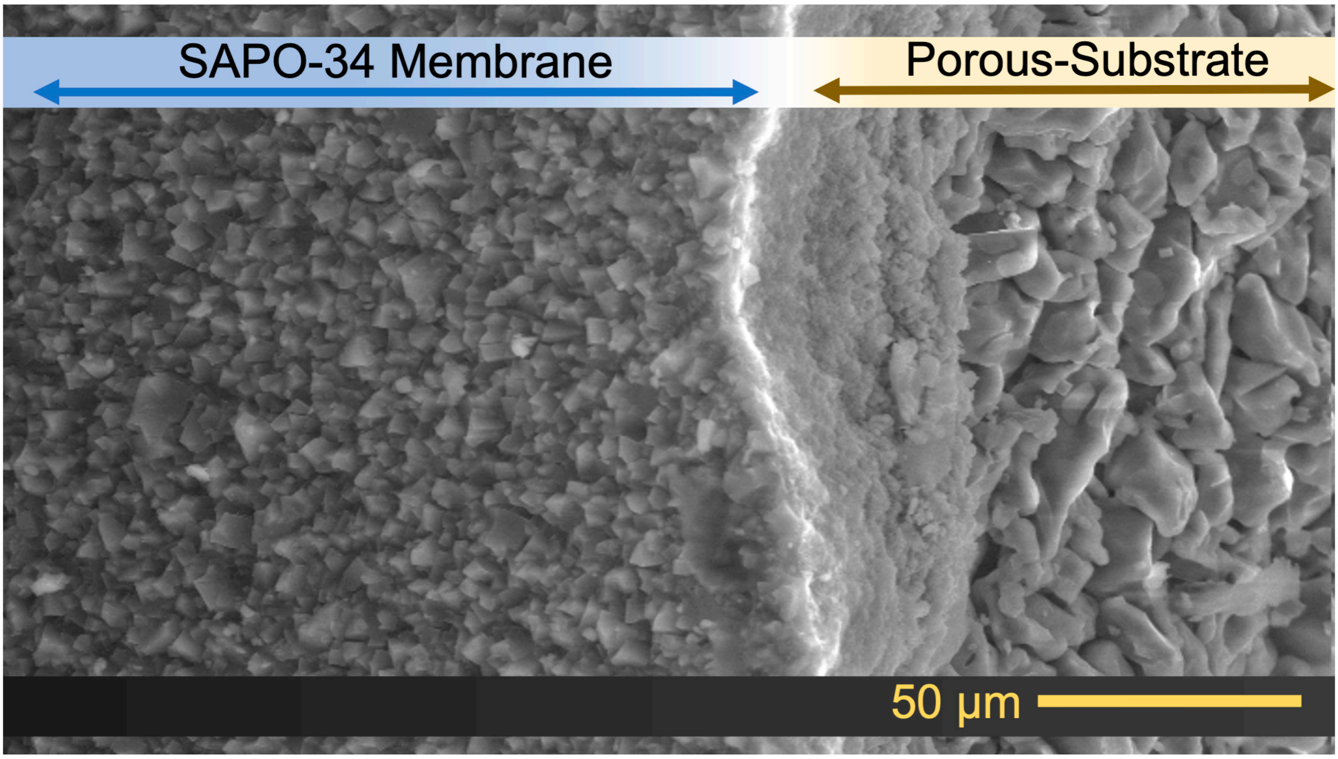

Figure S3. Scanning Electron Microscopy image of membrane and porous substrate interface.

CH_4/CO_2 Membrane Separation State of the Art

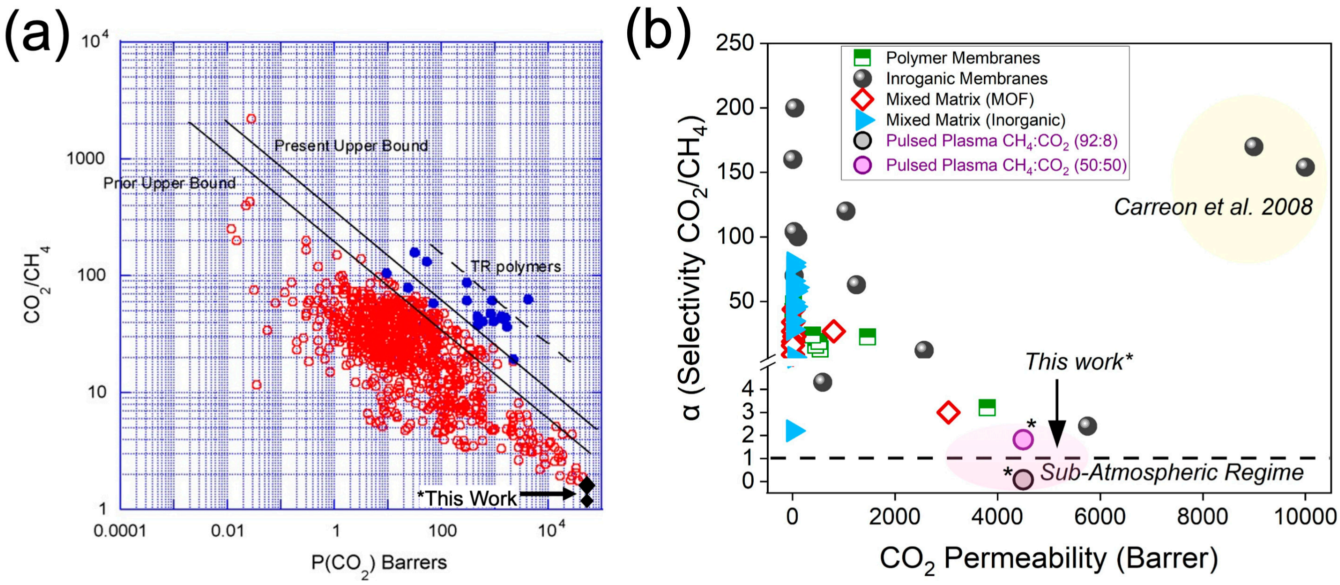

Figure S4. (**a**) Modified Robeson plot for CO_2/CH_4 separations representing the upper bound; (**b**) State-of-the-art figure displaying performance for various types of membranes in CO_2/CH_4 separations.

State-of-the-art table

Table S3. State-of-the-art CO_2/CH_4 Separation via membranes.

Membrane	Molar Feed Ratio	Temperature	CO_2 permeance	Selectivity	Separation Index (π)	Ref.
	(CO_2:CH_4)	°C	×10−8(mol/m²·s·Pa)	(CO_2/CH_4)	e×10⁻²(mol/m²·s)	
SAPO-34 A1	50:50	25	1×10^6	86	7.4	[1]
SAPO-34 A2	50:50	25	1×10^6	99	8.6	
SAPO-34 A3	50:50	25	1.2×10^6	131	13	
SAPO-34 A4	50:50	25	2×10^6	86	14	
SAPO-34 A5	50:50	25	1.8×10^6	171	25	
SAPO-34 nonfunctionalized	50:50	25	4.6×10^7	159	7.3	[2]
SAPO-34 0.15 mmol of ED	50:50	25	4.9×10^7	245	12	
SAPO-34 0.33 mmol of ED	50:50	25	4.4×10^7	233	10.3	
SAPO-34 1.66 mmol of ED	50:50	25	4.4×10^7	164	7.1	
SAPO-34 8.32 mmol of ED	50:50	25	5.3×10^7	92	4.8	
SAPO-34 0.15 mmol of HA	50:50	25	3.7×10^7	238	8.72	
SAPO-34 0.15 mmol of OA	50:50	25	1.9×10^7	229	4.31	
M1,2,3- 25 cm	50:50	25	6.6×10^7	142	7.8	[3]
M4,5,6- 25 cm	50:50	25	4.9×10^7	214	8.8	
M7,8,9- 5 cm	50:50	25	5.6×10^7	234	10.8	
M10,11,12- 25 cm	50:50	25	2.5×10^7	248	5.1	
M13-M18 - 5 cm	50:50	25	4.4×10^7	256	9.3	
M19,20 – 5 cm	50:50	25	4.5×10^7	254	9.6	
Notes:						

Breakthrough Curve

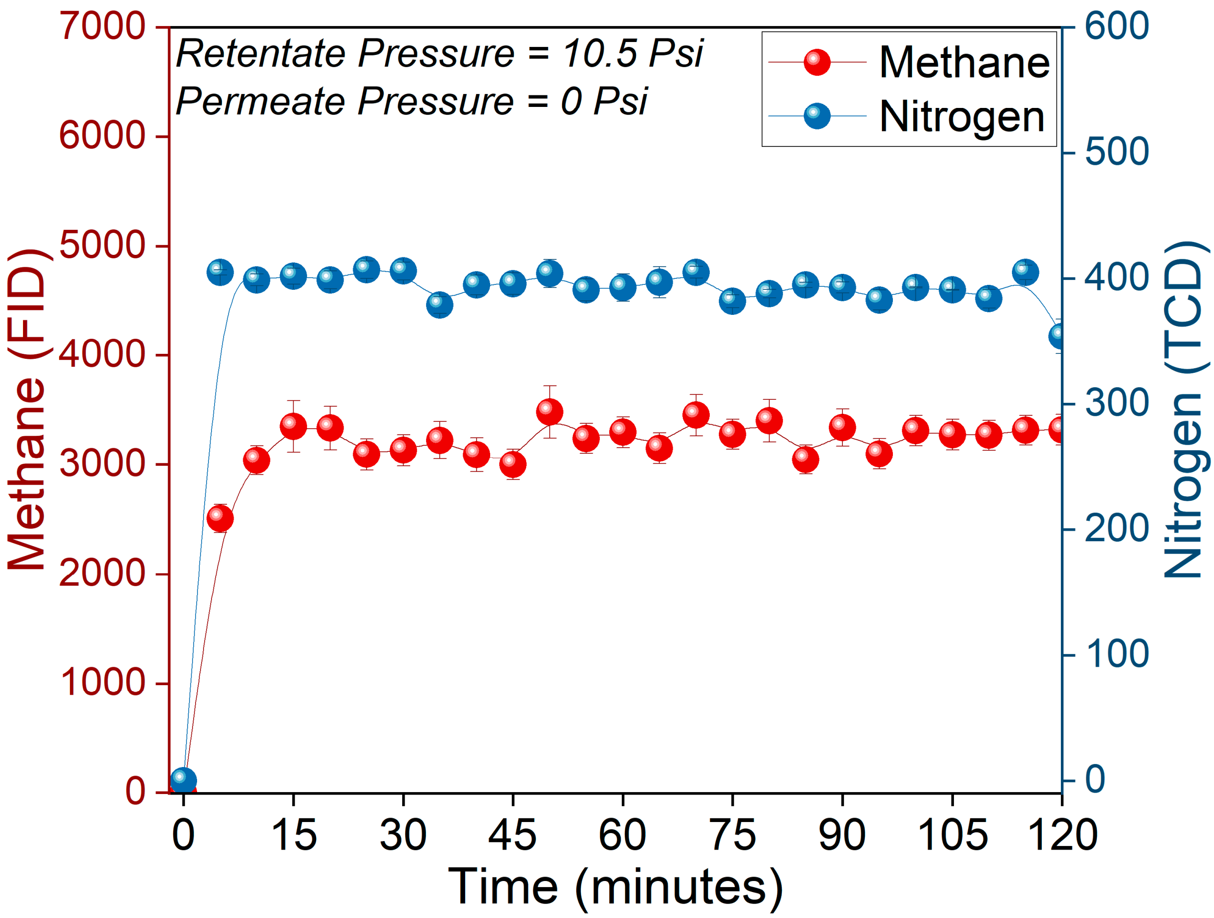

Figure S5. Breakthrough experiments with equimolar (50:50) mixtures of CH_4/N_2 gas over SAPO-34 membrane.

TEM-HAADF EDS Mapping

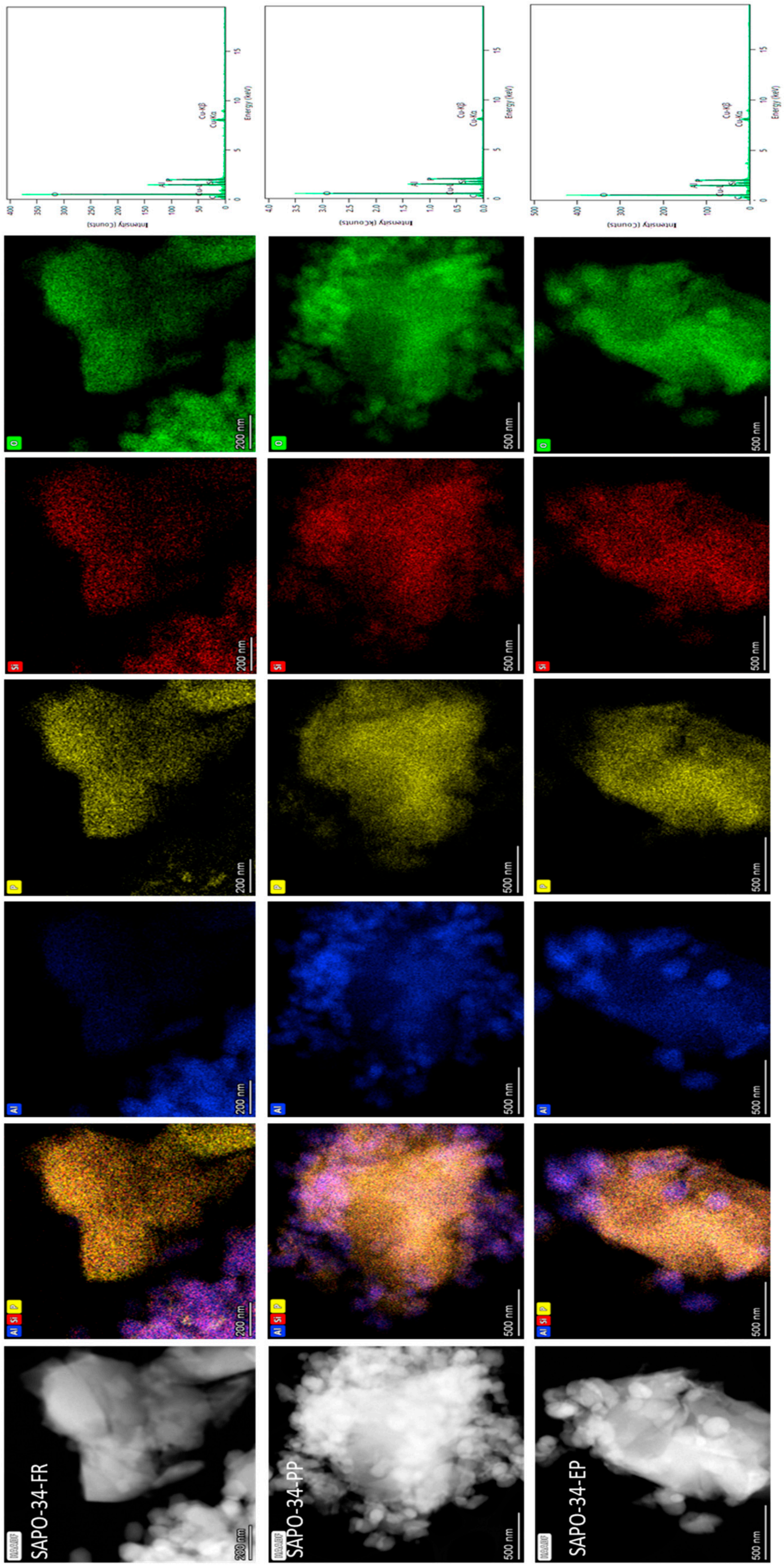

Figure S6. STEM-HAADF images (1st column), elemental maps (columns 2-6), and EDS spectra (column 7) of SAPO-34-FR (top), SAPO-34-PP (middle), and SAPO-34-EP (bottom) samples.

Table S4. Important Properties for presented Greenhouse Gases (GHGs) in this work.

Property		Units	Carbon Dioxide	Methane
Physical	Molecular Weight	g/mol	44.01	16.04
	Boiling Point	°C	-78.5	-161.5
	Melting Point	°C	-56.6	-182.5
	Freezing Point	°C	-78.5	-182.5
	Density (Gas, STP)	g/L	1.98	0.717
	Heat Capacity (Gas, STP)	J/mol·K	37.1	35.7
	Critical Temperature	°C	31.0	-82.6
	Critical Pressure	atm	73.8	45.8
	Density (Gas, STP)	g/L	1.98	0.717
Diffusivity	Kinetic Diameter	Å	3.30	3.80
	Collision Diameter	Å	3.70	3.80
	Diffusion Coefficient	cm^2/s	0.138	0.202
	Diffusivity in air	cm^2/s	0.16	0.21
	Schmidt Number	-	0.97	0.61
Thermodynamic	ΔH_{vap}	J/mol·K At STP	37.1	35.7
Electric Field	Dipole Moment	Debye	0.00 [4]	0.00 [4]
	Quadrupole Moment	Debye Å	4.30 [4]	0.02 [4]
	Polarizability	$Å^3$	2.9 [5]	2.5 [5]
	Dielectric Constant	-	1.000984	1.000918
	Refractive Index	-	1.00045	1.000444
	Ionization Energy	eV	13.77	12.61
	Bond Dissociation Energy	eV	5.5	4.7
	Electronic Affinity	eV	-0.51 [6]	+0.19 [6]
Environmental	GWP (Global Warming Potential)	20 year timescale	1	84
	Atmospheric Lifetime	years	50-200	12
	Radiative Efficiency	$W/m^2/ppb$	1.3 e-5	3.6 e-4
	Typical Atmospheric Concentration	ppm	419	1.9
	Atmospheric Concentration Growth Rate	%/year	0.6	2.5
	Carbon Cycle Impact	-	Acts as a critical component with long-term storage capabilities in oceans and the terrestrial biosphere.	Displays a short atmospheric lifetime, subsequently oxidizing to CO2, thereby further contributing to the greenhouse effect.

References

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