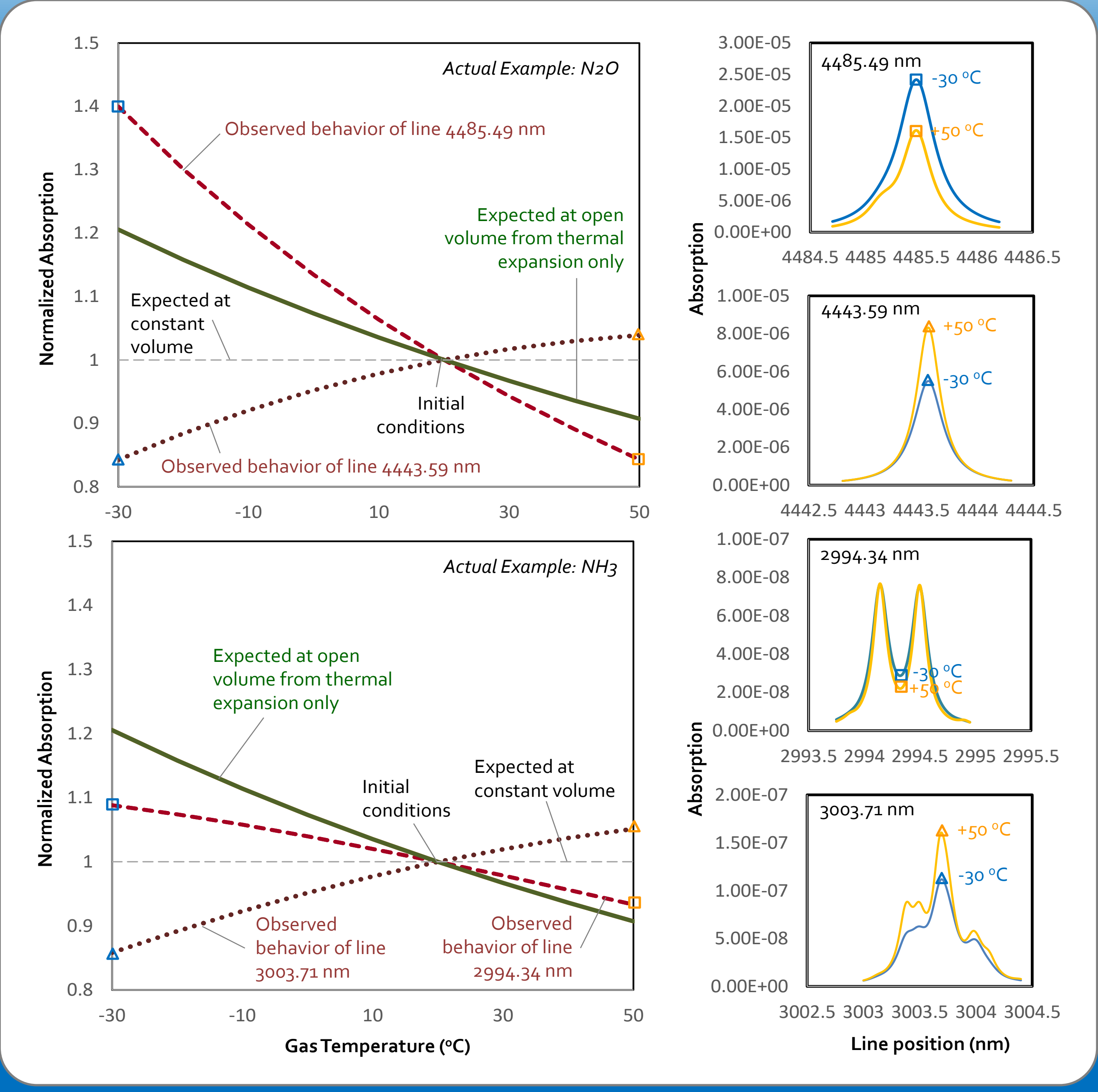
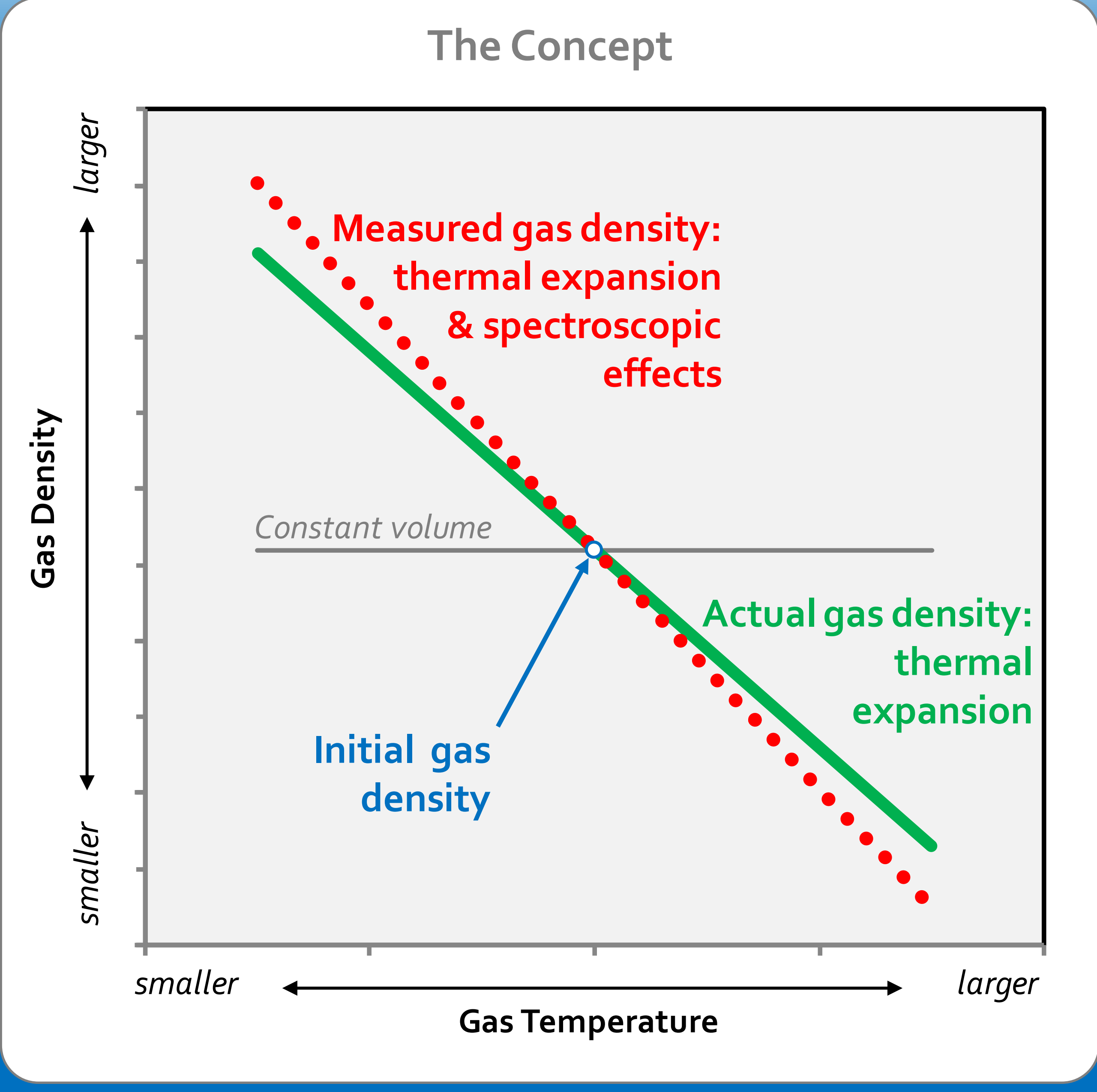
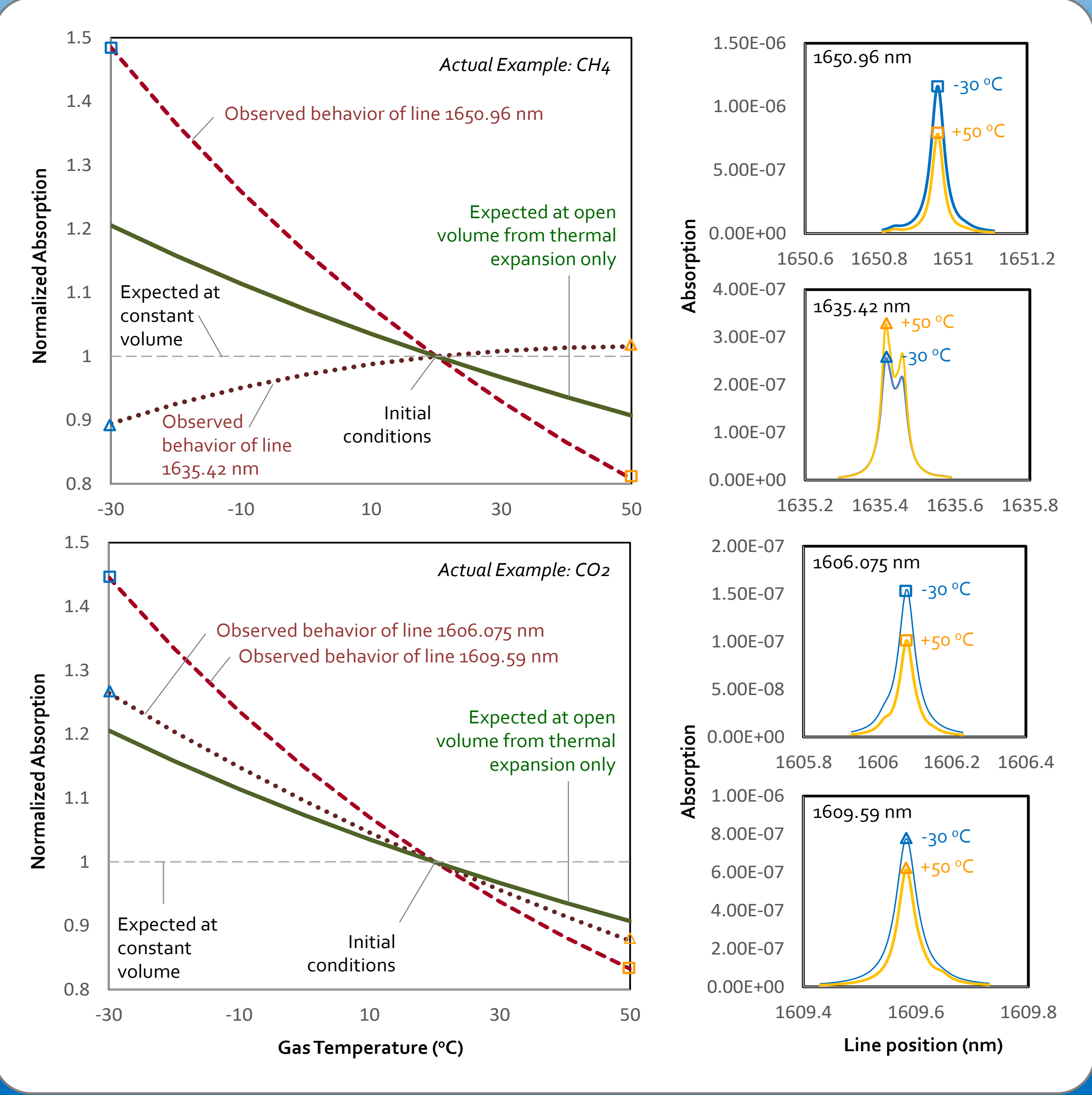


IMPORTANCE OF SPECTROSCOPIC EFFECTS IN LASER-BASED FLUX MEASUREMENTS

George Burba^{1,2}, Tyler Anderson³, and Anatoly Komissarov¹

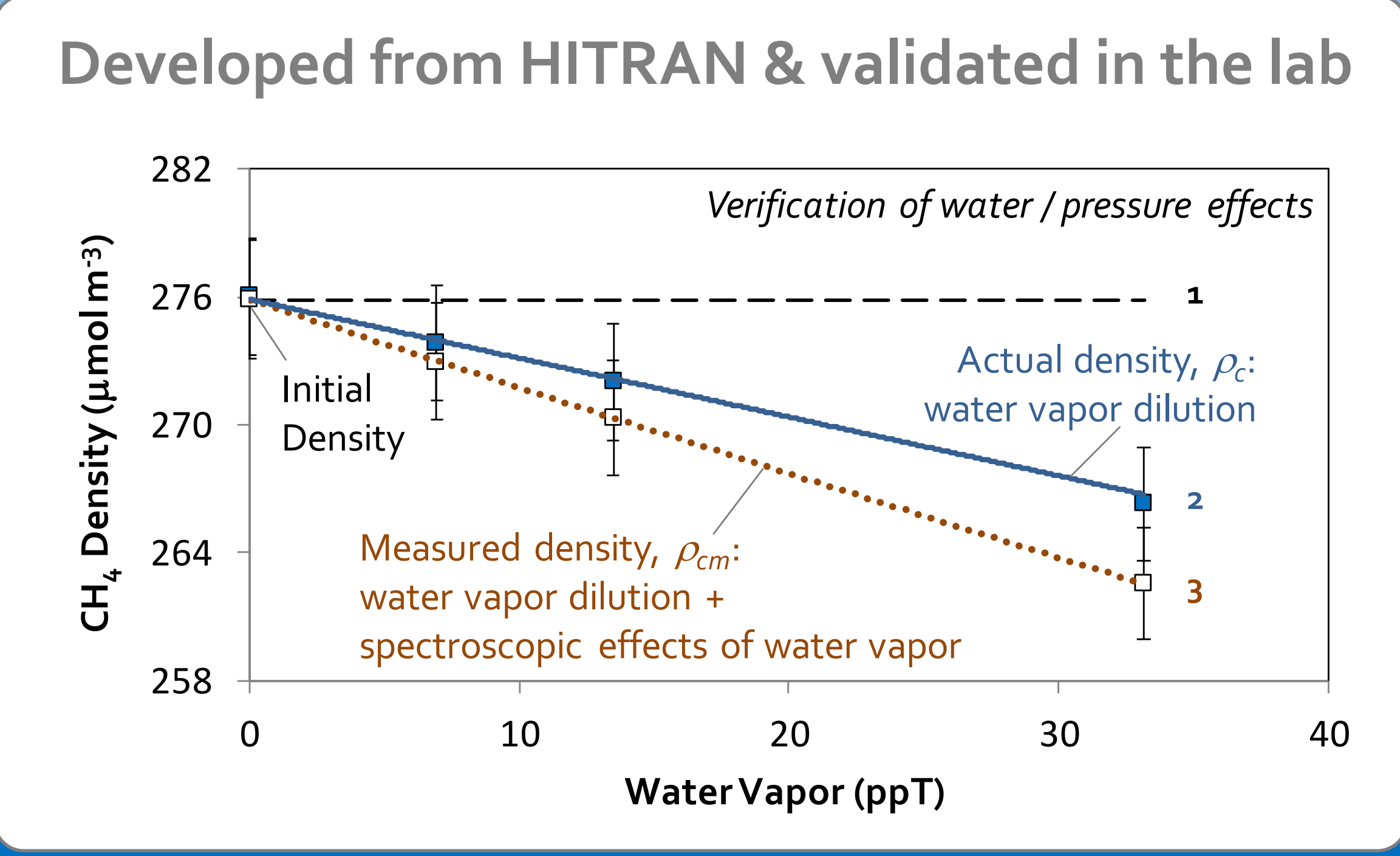
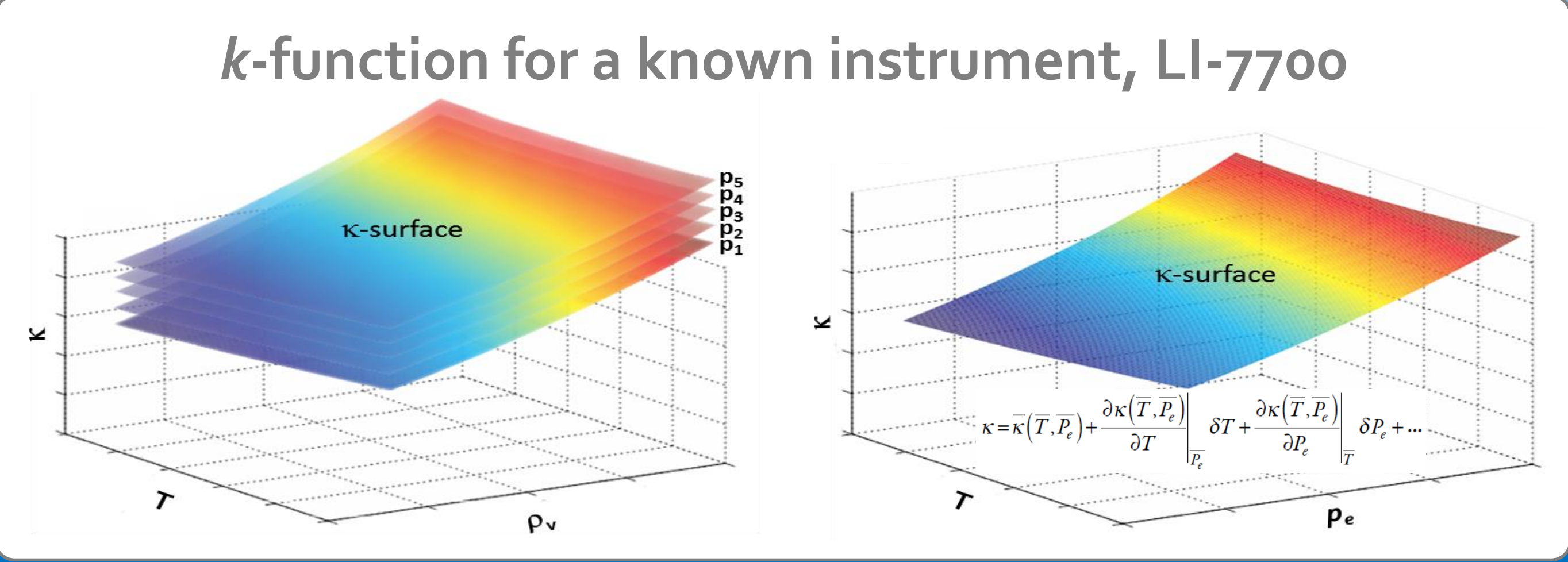
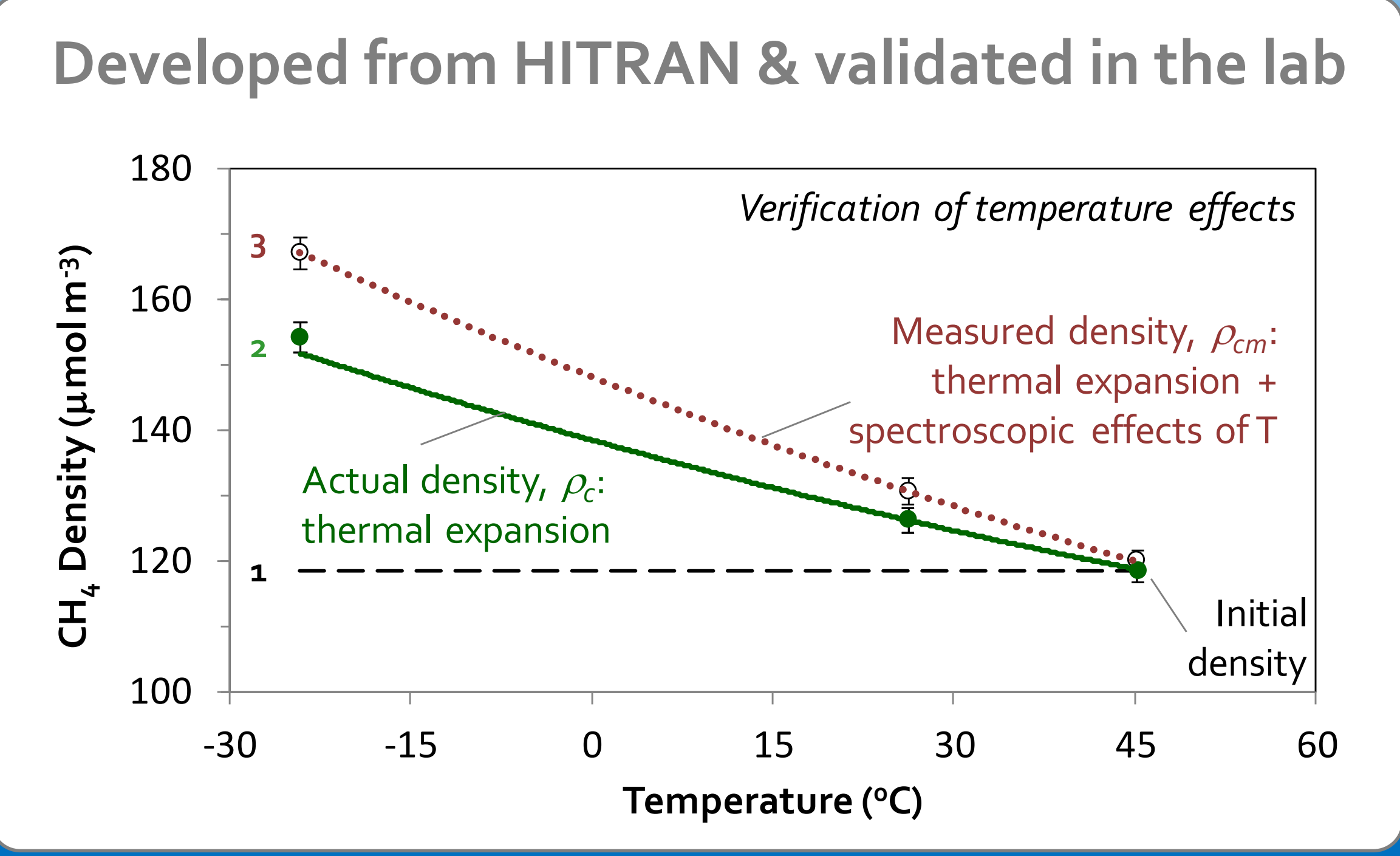
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LASER MEASUREMENTS IN UNCONTROLLED VOLUME: LOW-POWER, OPEN-PATH, ENCLOSED PATH, UNCONTROLLED CLOSED-PATH, etc.

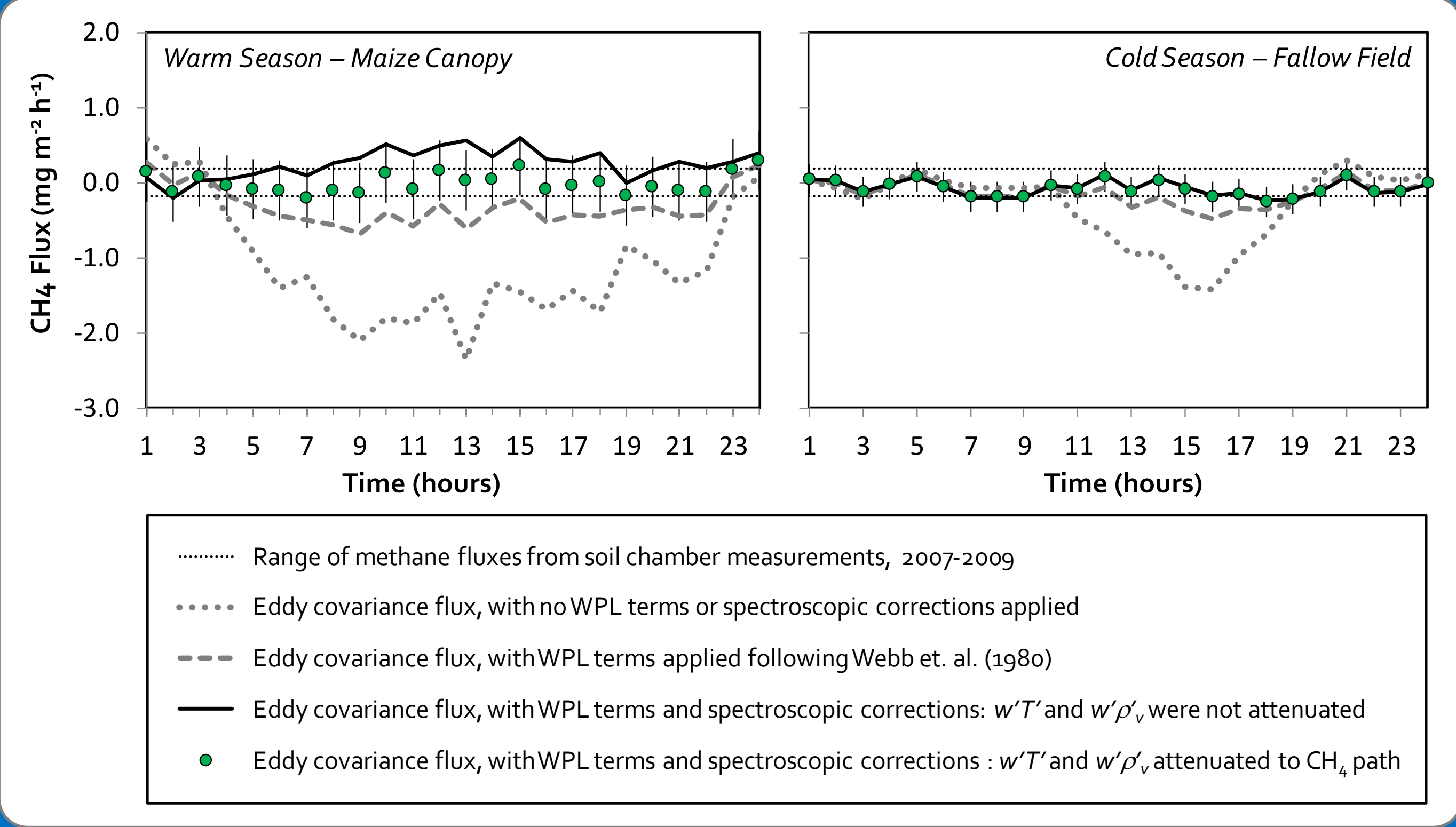


$$\rho_c = \rho_{cm} k \rightarrow F_c = \overline{w' \rho_c'} + \mu \frac{\overline{\rho_c}}{\overline{\rho_d}} \overline{w' \rho_v'} + \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_c}}{\overline{T}} \overline{w' T'} - \overline{\rho_c} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{w' p'}}{\overline{p}} \rightarrow F_c = \overline{k} \overline{w' \rho_{cm}'} + \overline{k} \mu \frac{\overline{\rho_{cm}}}{\overline{\rho_d}} \overline{w' \rho_v'} + \overline{k} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_{cm}}}{\overline{T}} \overline{w' T'} - \overline{k} \overline{\rho_{cm}} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{w' p'}}{\overline{p}} + \overline{w' k'} \overline{\rho_{cm}} + \overline{w' k' \rho_{cm}'}$$

LABORATORY & FIELD EXPERIMENTAL VALIDATIONS FOR AN INSTRUMENT WITH A KNOWN *k*-FUNCTION



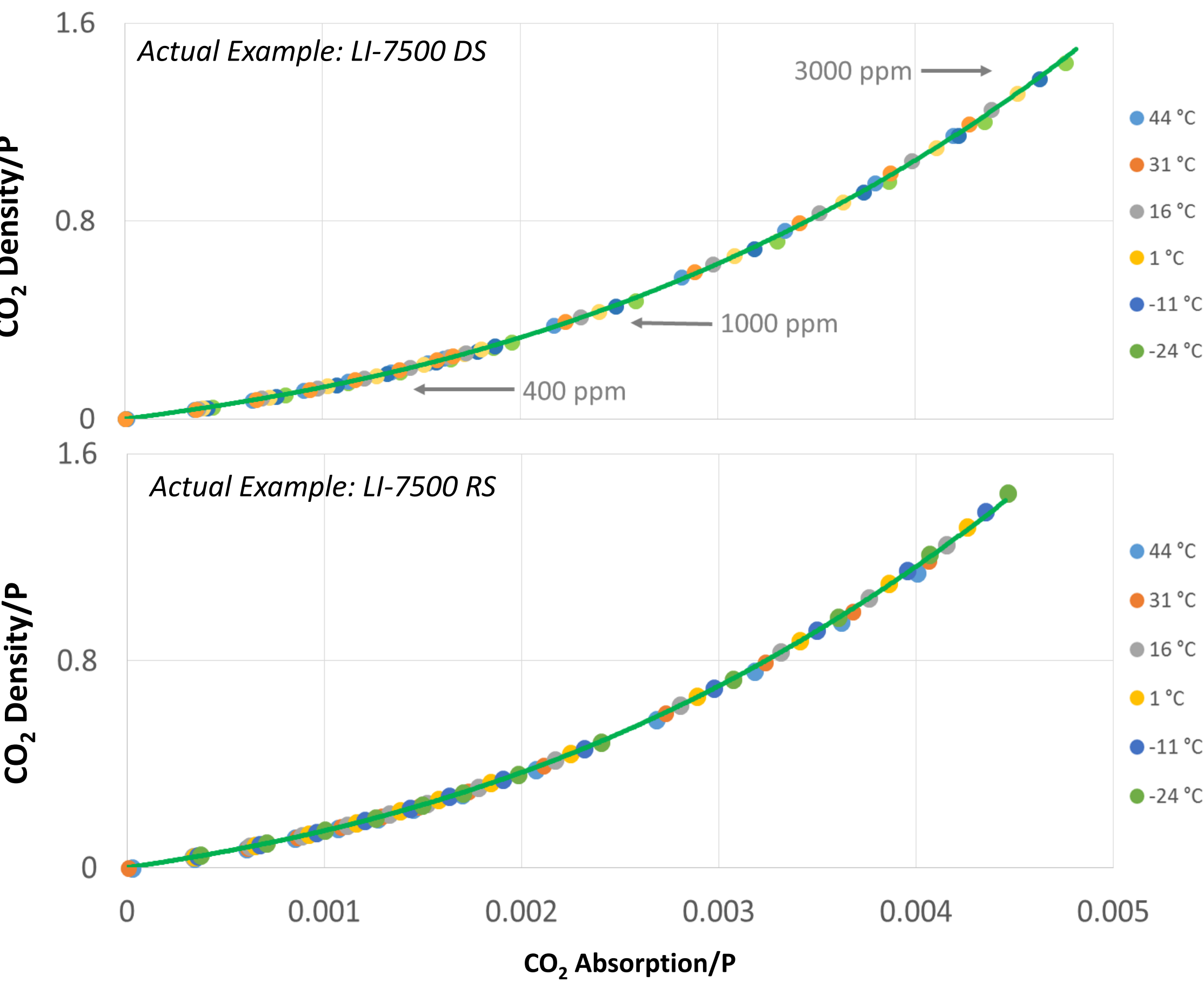
Implications for CH ₄									
H	LE	WPL Terms		Spectroscopic Effects					
W m ⁻²	W m ⁻²	WPLH mg m ⁻² h ⁻¹	WPLLE mg m ⁻² h ⁻¹	Temperature mg m ⁻² h ⁻¹	Water Vapor mg m ⁻² h ⁻¹	Contribution to final flux value			
				(=0.31xWPLH)	(=0.41xWPLLE)	μmol m ⁻² s ⁻¹	% of flux		
0	0	0.00	0.00	0.00	0.00	0.00	0.000	0	
50	50	0.61	0.13	0.19	0.05	0.34	0.004	8	
50	200	0.61	0.51	0.19	0.23	0.40	0.007	13	
50	400	0.61	1.03	0.19	0.42	0.61	0.011	20	
200	50	2.46	0.13	0.76	0.05	0.81	0.014	27	
200	200	2.46	0.51	0.76	0.21	0.97	0.017	32	
200	400	2.46	1.03	0.76	0.42	1.18	0.021	39	
400	50	4.92	0.13	1.52	0.05	1.58	0.027	53	
400	200	4.92	0.51	1.52	0.21	1.73	0.030	68	
400	400	4.92	1.03	1.52	0.42	1.94	0.034	65	



Implications for other gas species									
Specie	Line	Flux	Concentration	WPLH Term	Spectroscopic Effects of Temperature				
	nm	mg m ⁻² h ⁻¹	ppm	mg m ⁻² h ⁻¹	Fraction of WPLH	mg m ⁻² h ⁻¹	μmol m ⁻² s ⁻¹	% of final flux	
CH ₄	1650.96	3	1.81	2.46	0.44	1.08	0.019	36	
	1635.42				-2.47	-6.06	-0.105	-202	
CO ₂	1606.08	720	391	1434	0.49	698	4.407	97	
	1609.58				0.77	1105	6.978	154	
N ₂ O	4485.45	0.02	0.31	1.13	0.54	0.60	0.004	3021	
	4443.55				-1.54	-1.74	-0.011	-8684	
NH ₃	2994.35	0.00005	0.14	0.20	1.85	0.38	0.006	757915	
	3003.70				-1.54	-0.32	-0.005	-631596	

NOTE ON BROAD-BAND NDIR IRGAS

Properly designed IRGAs are different from laser



- The same fundamental spectroscopic effects have different impact on measurements by a properly designed broad-band instruments such as in NDIR IRGAS
- Examples above show typical calibration curves for two models, LI-7500RS and LI-7500DS, determined by using a full set of calibration gases at each specific temperature
- All the curves on each plot overlay each other well, showing that the calibration is consistent across the nearly 70 °C temperature range
- Such data are collected for each individual instrument as a part of routine factory calibration

SUMMARY OF EQUATIONS & CORRECTIONS FOR ANY INSTRUMENT OR GAS SPECIE

Application	Flux	Raw Covariance	Dilution by H ₂ O or any other dilutor	Thermal expansion & contraction	Pressure expansion & contraction	Spectr.	HOT
Any instrument No spectroscopic effects, WPL	$F_c =$	$\overline{w' \rho_c'}$	$\mu \frac{\overline{\rho_c}}{\overline{\rho_d}} \overline{w' \rho_v'}$	$\left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_c}}{\overline{T}} \overline{w' T'}$	$\overline{\rho_c} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{w' p'}}{\overline{p}}$	absent	absent
Any instrument Any spectroscopic effects	$F_c =$	$\overline{k} \overline{w' \rho_{cm}'}$	$\overline{k} \mu \frac{\overline{\rho_{cm}}}{\overline{\rho_d}} \overline{w' \rho_v'}$	$\overline{k} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_{cm}}}{\overline{T}} \overline{w' T'}$	$\overline{k} \overline{\rho_{cm}} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{w' p'}}{\overline{p}}$	$+\overline{w' k'} \overline{\rho_{cm}}$	$+\overline{w' k' \rho_{cm}'}$
Any instrument Spectroscopic effects of T, ρ_v, p	$F_c =$	$\overline{k} \overline{w' \rho_{cm}'}$	$\left(\overline{k} + \frac{\overline{\rho_d}}{\mu} k_{\rho_v}\right) \mu \frac{\overline{\rho_{cm}}}{\overline{\rho_d}} \overline{w' \rho_v'}$	$\left(\overline{k} + \frac{\overline{T}}{1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}} k_T\right) \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_{cm}}}{\overline{T}} \overline{w' T'}$	$\left(\overline{k} - \frac{\overline{p}}{1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}} k_p\right) \overline{\rho_{cm}} \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{w' p'}}{\overline{p}}$	unfolded into other terms	$+\overline{w' k' \rho_{cm}'}$
LI-7700 Spectroscopic effects of T, ρ_v, p	$F_c =$	$\overline{k_{7700}} \overline{w' \rho_{cm}'}$	$\left(\overline{k} + (1 - 1.46 \overline{x_v}) \alpha_v \overline{p_e} k_{7700 p_e}\right) \mu \frac{\overline{\rho_{cm}}}{\overline{\rho_d}} \overline{w' \rho_v'}$	$\left(\overline{k} + (1 - x_v) \overline{T} k_{7700 T} + \overline{x_v} (M_{v7700} - \overline{k})\right) \left(1 + \mu \frac{\overline{\rho_v}}{\overline{\rho_d}}\right) \frac{\overline{\rho_{cm}}}{\overline{T}} \overline{w' T'}$	neglected	unfolded into other terms	neglected