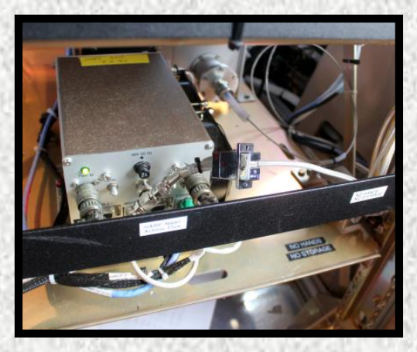
Cloud and aerosol influence on photolysis frequencies during CONTRAST



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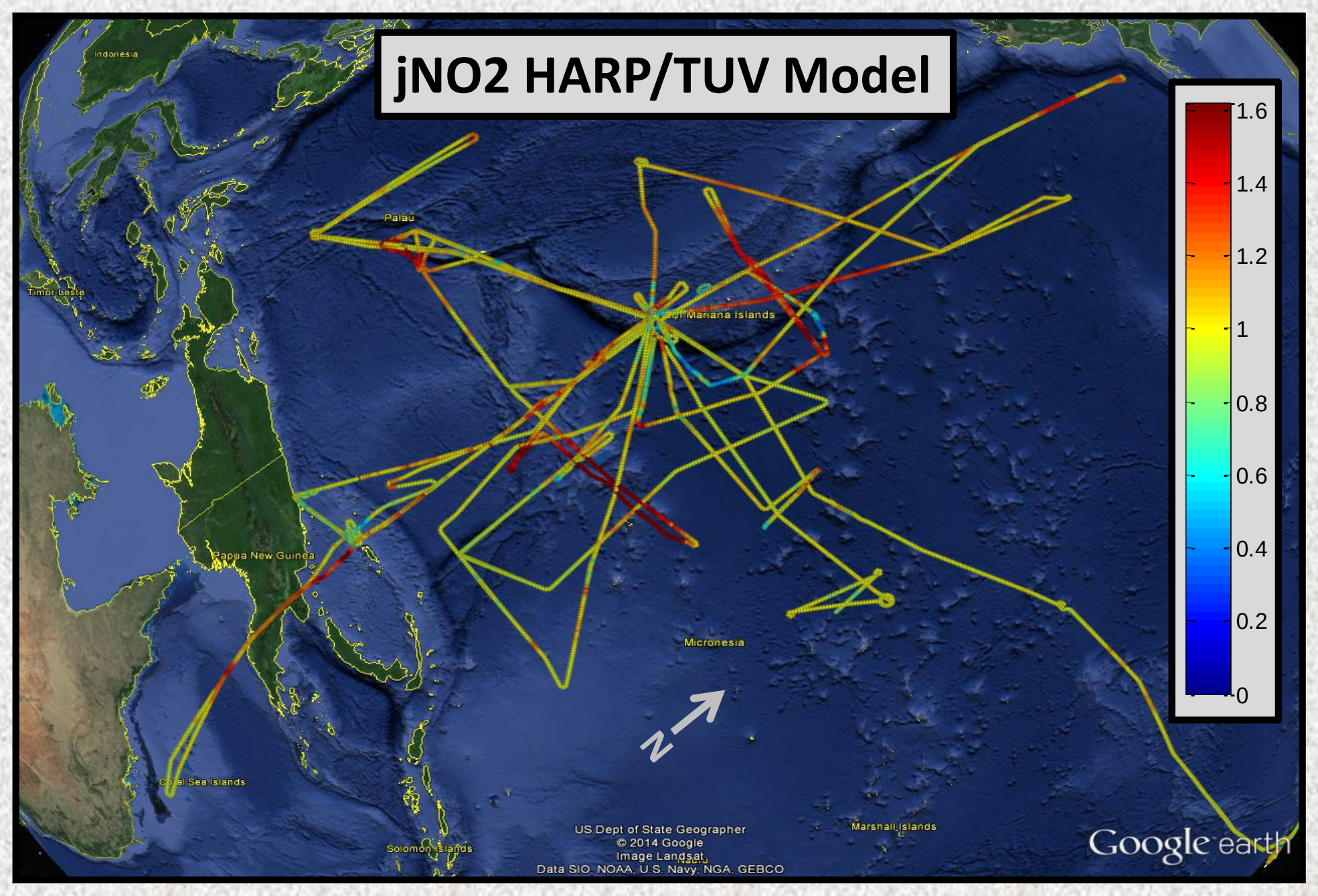
Summary

Clouds and aerosols influence the lifetime of photolytically active chemical species in the atmosphere through scattering and absorption. Below and within optically thick convective clouds, shading reduces the photochemistry thus permitting vertical motion within the cloud to transport short-lived species from the boundary layer to the free troposphere and episodically to the lower stratosphere. Conversely, near highly scattering cloud tops, photochemistry is greatly accelerated. In such rapidly evolving environments, accurate photolysis frequencies are required to study the chemical processes and evolution of distributed species. During the CONTRAST experiment, photolysis frequencies were calculated from measurements of spectrally resolved actinic flux by the HIAPER Airborne Radiation Package (HARP) on the NCAR G-V aircraft. Statistical correlations of the data reveal modal behavior that could help assess cloud fields in global and regional chemistry models.

CONTRAST
CONvective TRansport of
Active Species in the Tropics



Photolysis Frequencies

$j[O_3 \rightarrow O_2+O(^1D)]$

$j[NO_2 \rightarrow NO+O(^3P)]$

$j[H_2O_2 \rightarrow 2OH]$

$j[HNO_2 \rightarrow OH+NO]$

$j[HNO_3 \rightarrow OH+NO_2]$

$j[CH_2O \rightarrow H+HCO]$

$j[CH_2O \rightarrow H_2+CO]$

$j[CH_3CHO \rightarrow CH_3+HCO]$

$j[C_2H_5CHO \rightarrow C_2H_5+HCO]$

$j[CHOCHO \rightarrow H_2+2CO]$

$j[CHOCHO \rightarrow CH_2O+CO]$

$j[CHOCHO \rightarrow HCO+HCO]$

$j[CH3COCHO \rightarrow CH3CO+HCO]$

$j[CH_3COCH_3 \rightarrow CH_3CO+CH_3]$

$j[CH_3OOH \rightarrow CH_3O+OH]$

$j[CH_3ONO_2 \rightarrow CH_3O+NO_2]$

$j[CH_3COCH_2CH_3 \rightarrow CH_3CO+CH2CH_3]$

$j[CH_3CH_2CH_2CHO \rightarrow C_3H_7+HCO]$

$j[CH_3CH_2CH_2CHO \rightarrow C_2H_4+CH_2CHOH]$

$j[HO_2NO_2 \rightarrow HO_2+NO_2]$

$j[HO_2NO_2 \rightarrow OH+NO_3]$

$j[CH_3CH_2ONO_2 \rightarrow CH_3CH_2O+NO_2]$

$j[Br_2 \rightarrow Br+Br]$

$j[BrO \rightarrow Br+O]$

$j[Br_2O \rightarrow products]$

$j[BrCl \rightarrow Br+Cl]$

$j[HOBr \rightarrow HO+Br]$

$j[BrONO_2 \rightarrow Br+NO_3]$

$j[BrONO_2 \rightarrow BrO+NO_2]$

$j[Cl_2 \rightarrow Cl+Cl]$

$j[ClO \rightarrow Cl+O(^3P)]$

$j[ClONO_2 \rightarrow Cl+NO_3]$

$j[ClONO_2 \rightarrow ClO+NO_2]$

N E W R E A C T I O N S

$j[ClNO_2 \rightarrow Cl+NO_2]$

$j[ClONO \rightarrow Cl+NO_2]$

$j[BrNO \rightarrow Br+NO]$

$j[BrONO \rightarrow Br+NO_2]$

$j[BrONO \rightarrow BrO+NO]$

$j[BrNO_2 \rightarrow Br+NO_2]$

$j[CHBr_3 \rightarrow Products]$

$j[N_2O_5 \rightarrow NO_3+NO_2]$

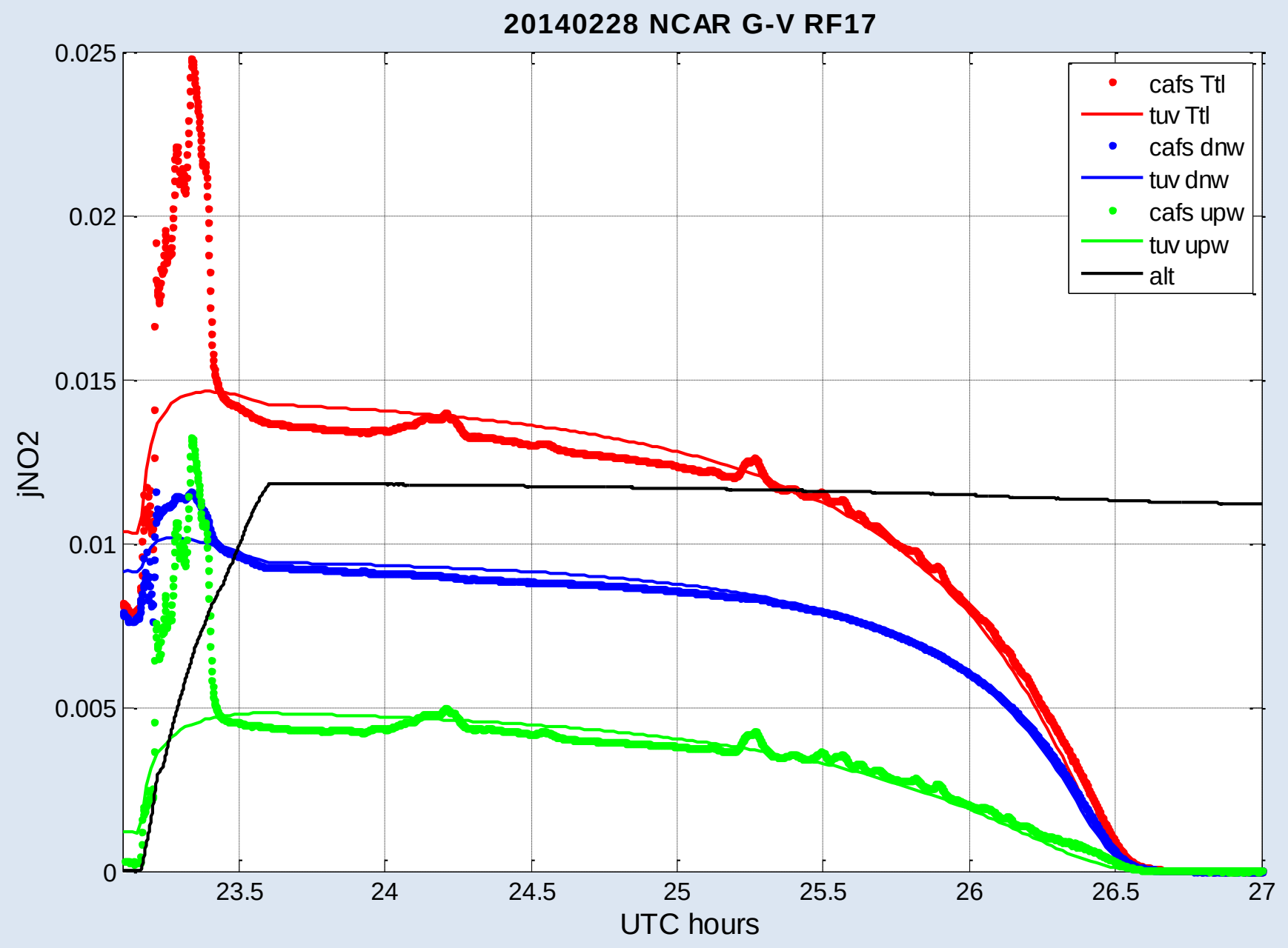
$j[CH_3CO(OONO_2) \rightarrow CH_3CO(OO)+NO_2]$

$j[CH_3CO(OONO_2) \rightarrow CH_3CO(O)+NO_3]$

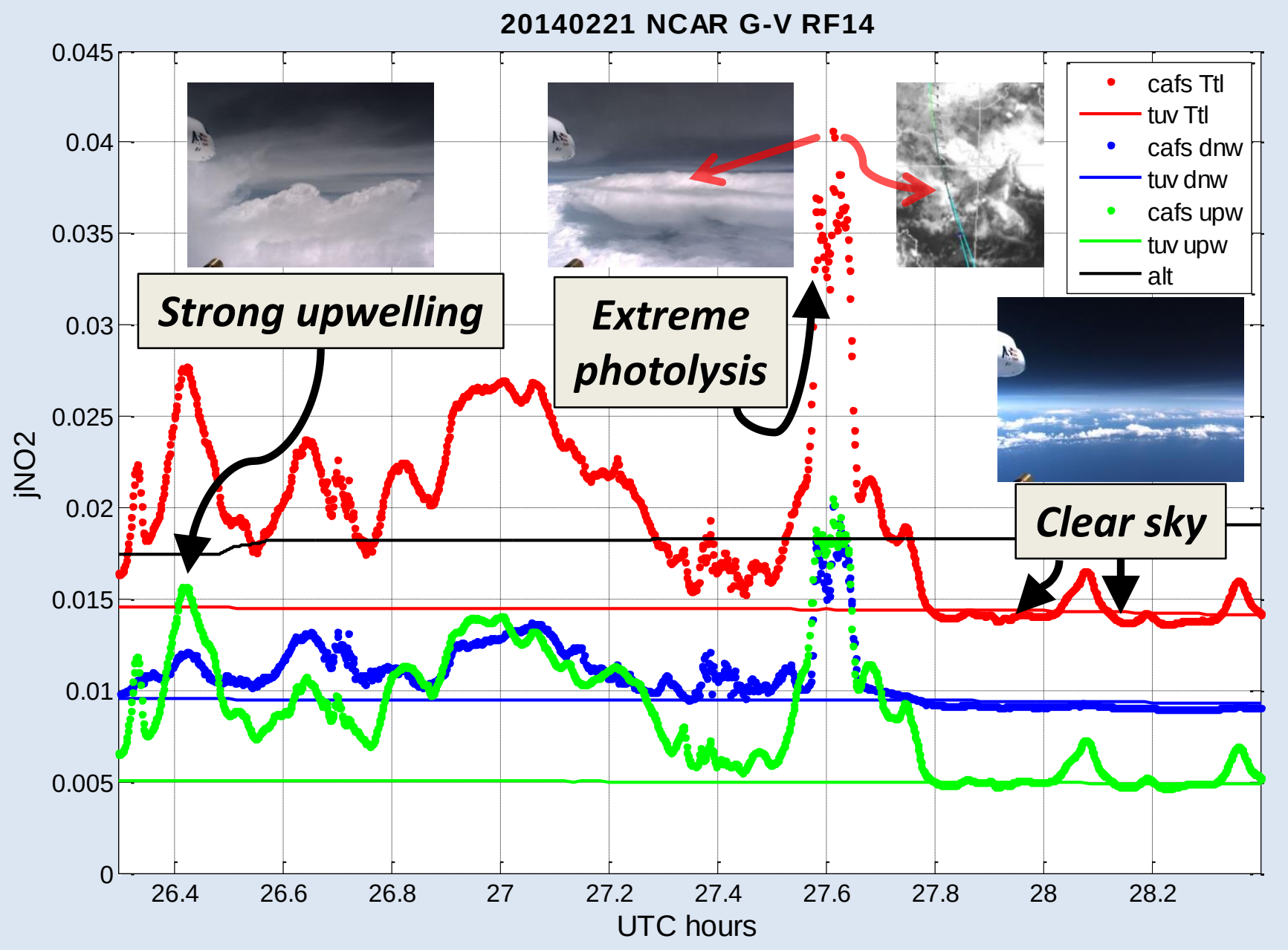
$j[CH_2{=}C(CH_3)CHO \rightarrow Products]$

$j[CH_3COCH{=}CH_2 \rightarrow Products]$

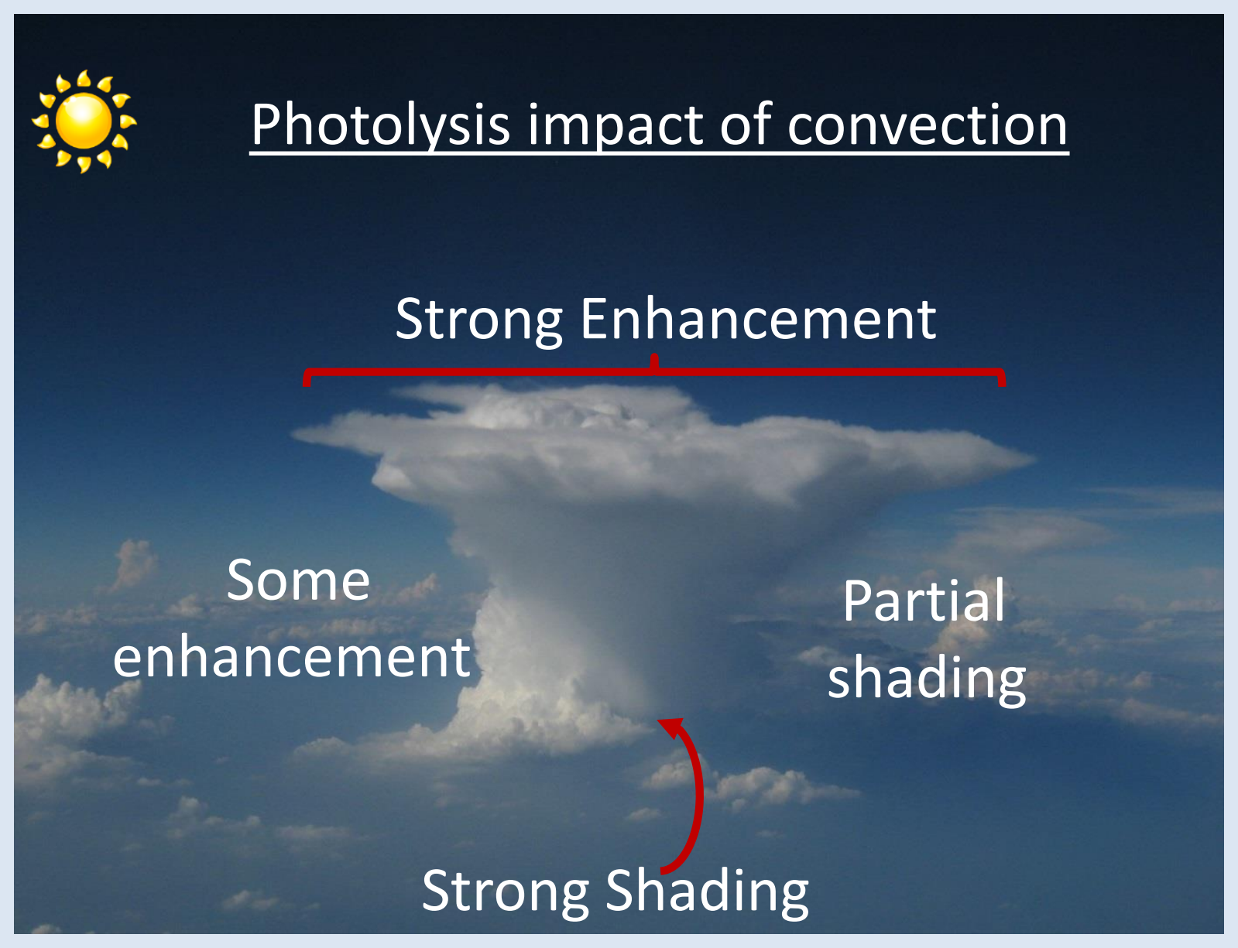
Comparisons to TUV clear sky model



Very clear sky over the Pacific ocean after ascending through a cloud on the return transit flight from Hawaii to Colorado.



Radiative Encounters: Strong upwelling with clouds below and to the side. Extreme photolysis values within a high cloud. Very clear sky outside of the cloud systems



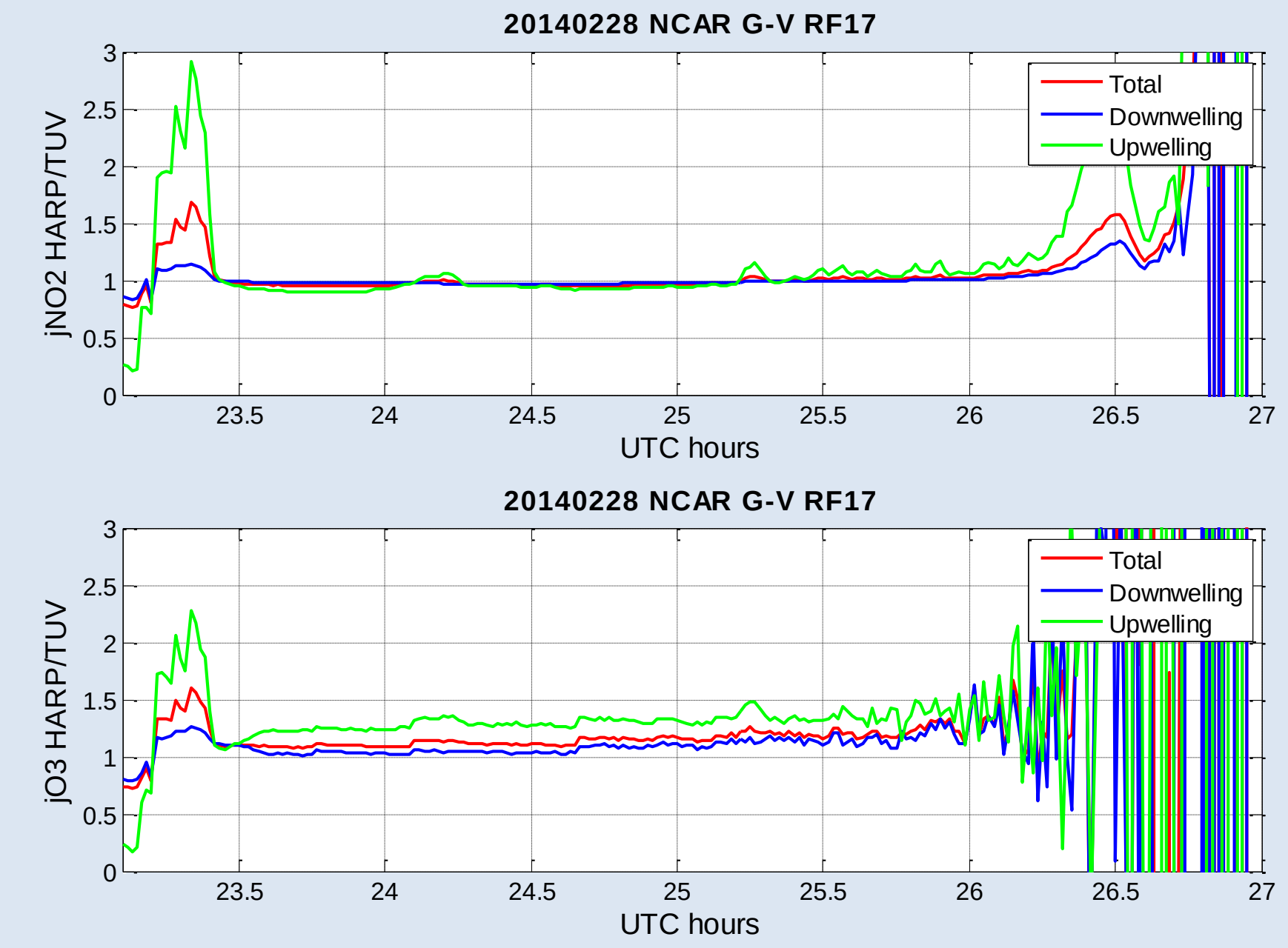
Photolysis impact of convection

Strong Enhancement

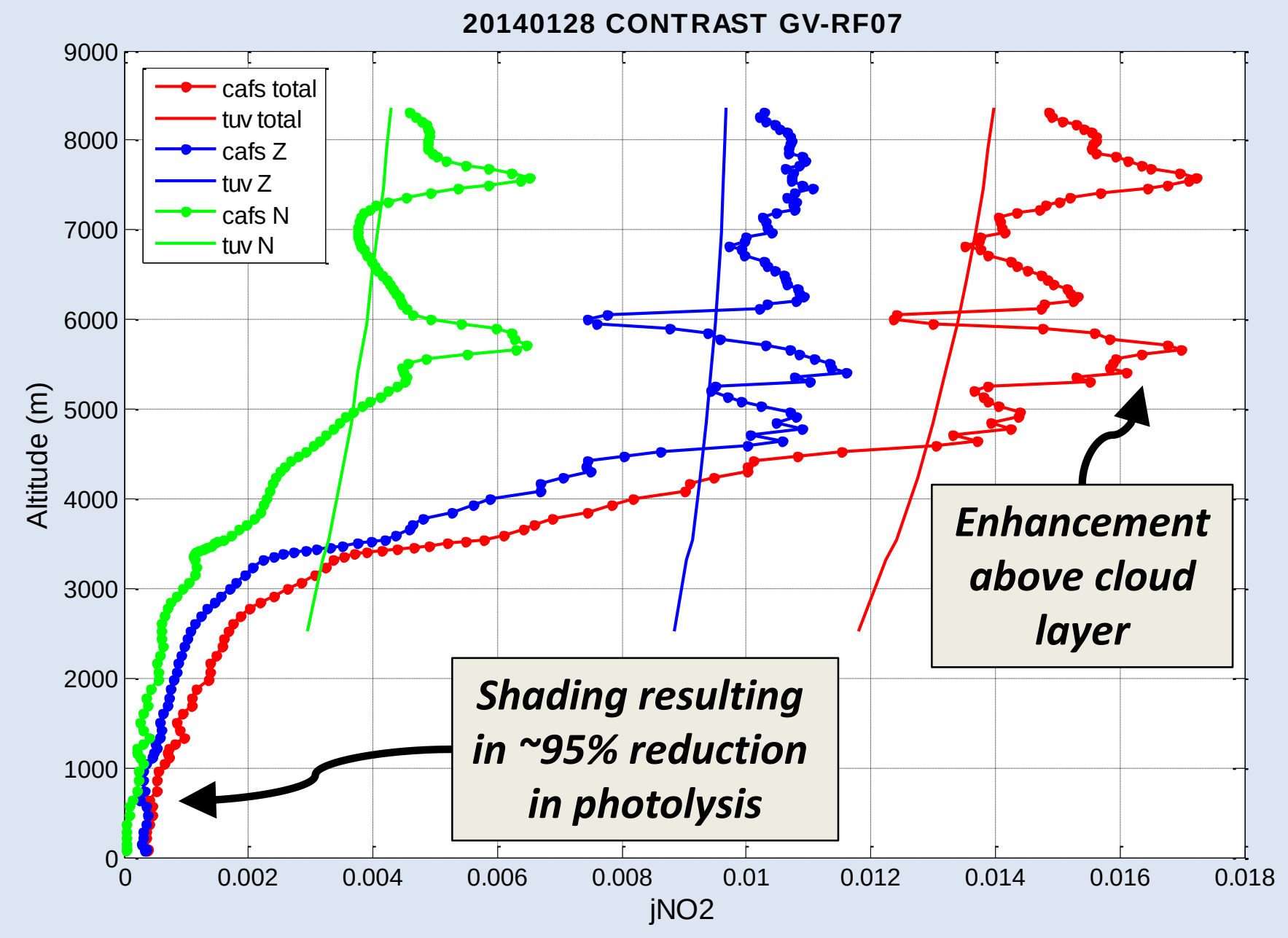
Some enhancement

Partial shading

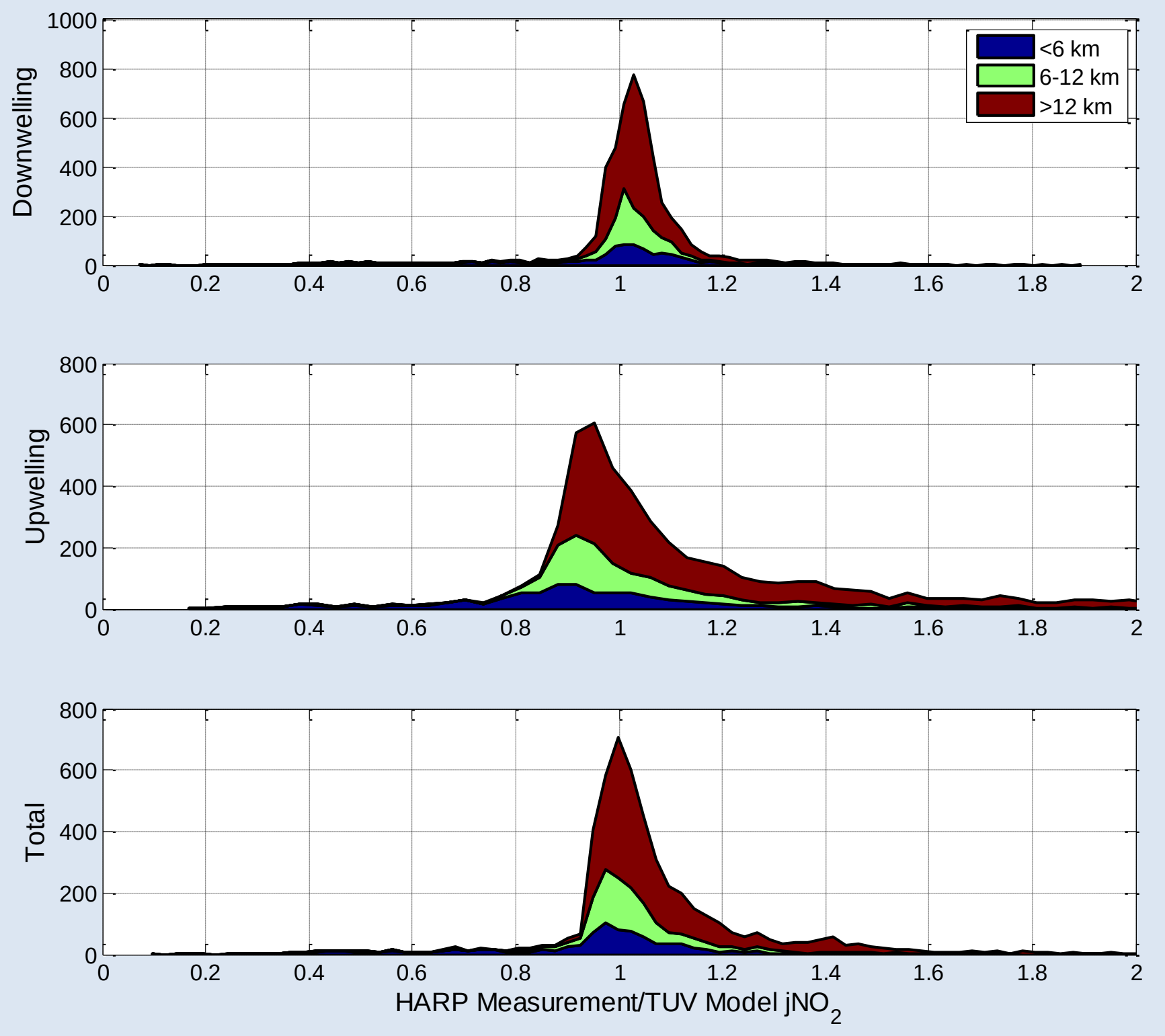
Strong Shading



Ratio of measurement/clear-sky TUV radiative transfer model showing excellent agreement with jNO2 and jO3 downwelling. jO3 upwelling differs by 30%.

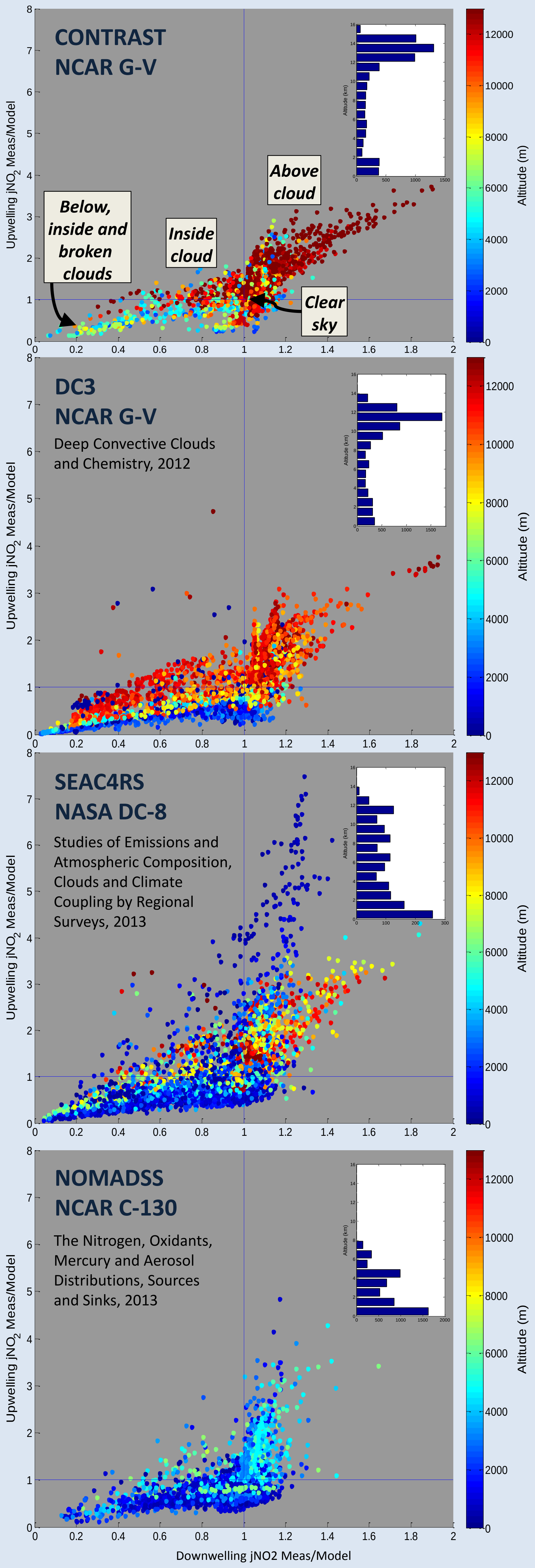


Profiles of jNO_2 measured and clear-sky modeled components as the G-V ascended through a thick cloud showing the transition from suppression to enhancement.



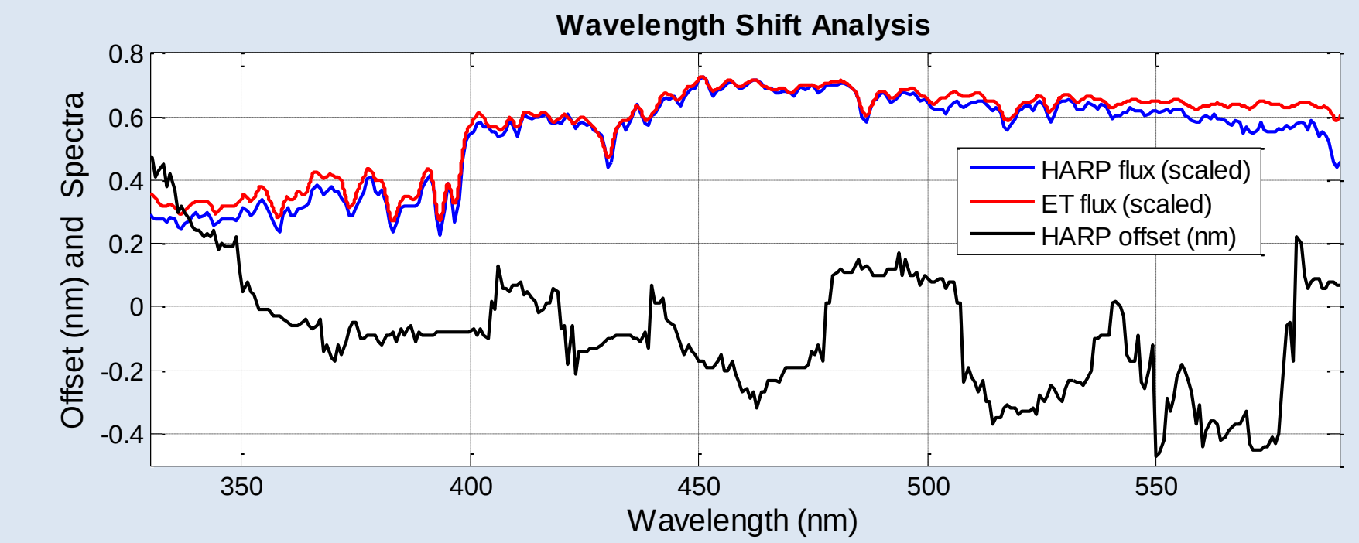
Histogram of all measured/clear-sky modeled components for the entire mission. Downwelling was slightly enhanced, upwelling was slightly suppressed.

Clear-sky Model Comparison

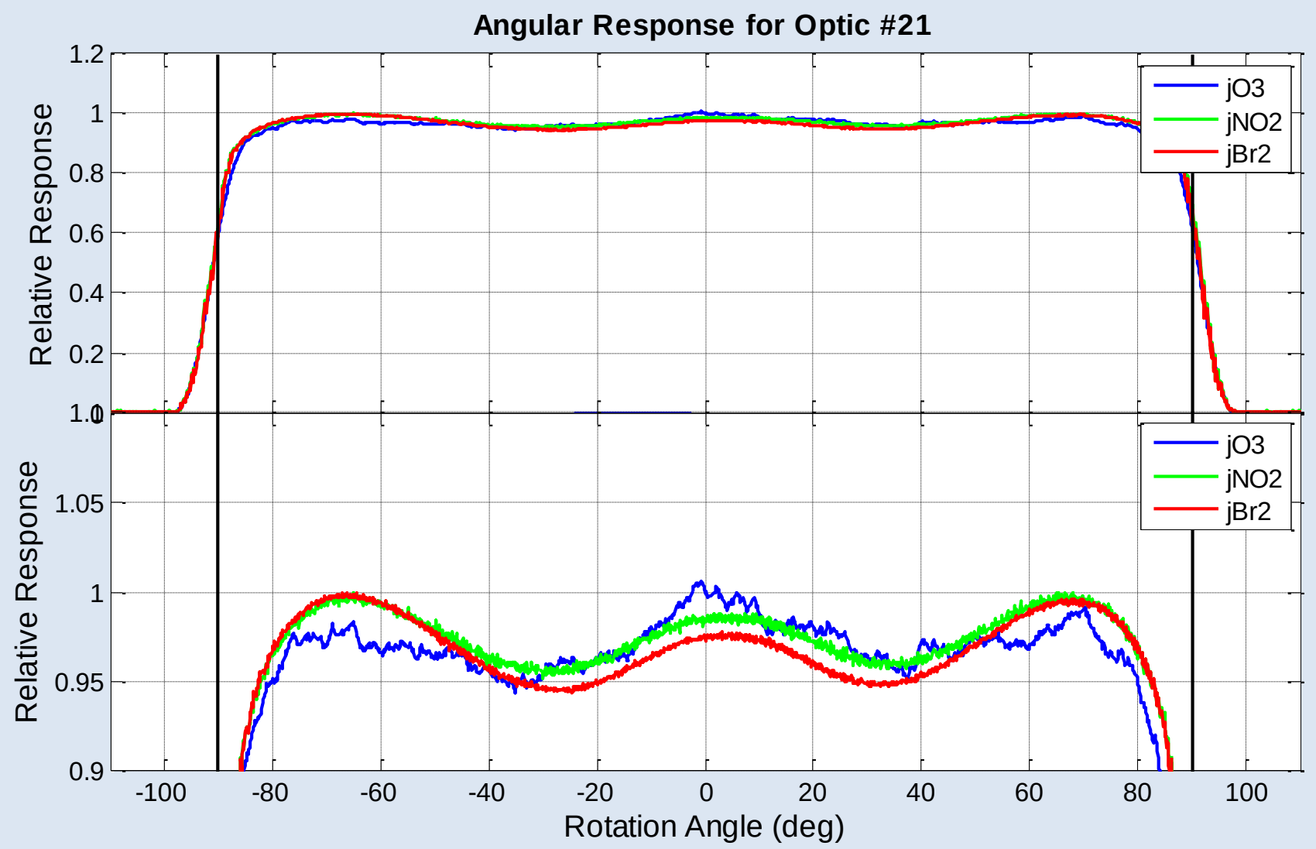


HARP/CAFS and TUV provide independent up and downwelling actinic flux components. The plots correlate measurement/model component ratios color coded by altitude. Cloud morphologies result in modal behaviors exhibiting enhancements and reductions (see Palancar et al., *ACP*, 2011) with some altitude dependence.

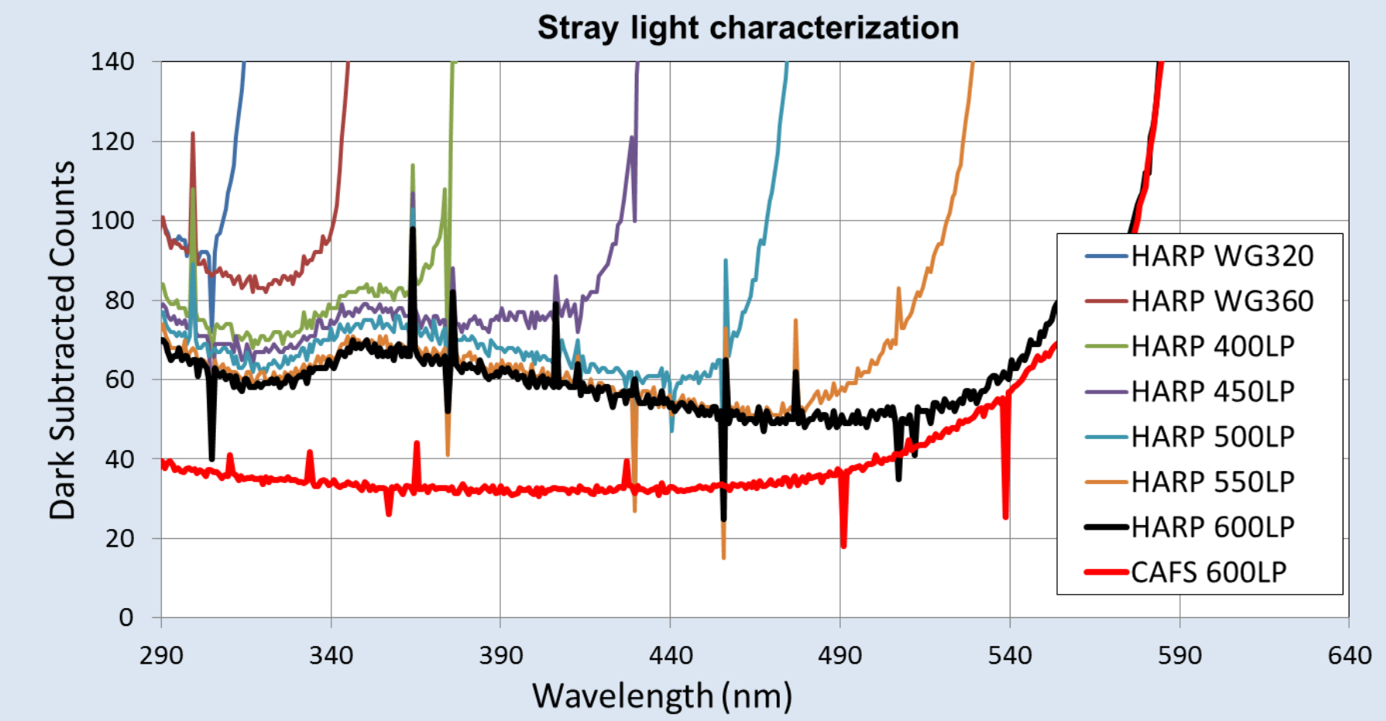
Instrument Characterization



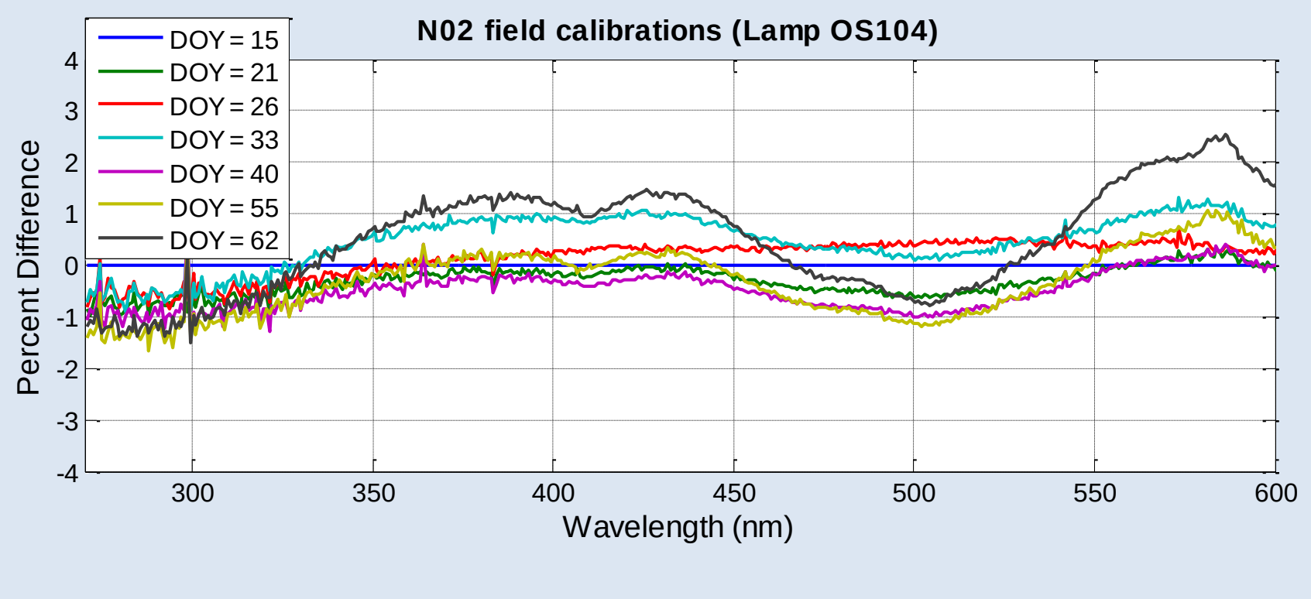
Determination of instrument wavelength offsets by comparison to features in the extraterrestrial solar flux spectrum (Slaper et al., *GRL* 22, 1995).



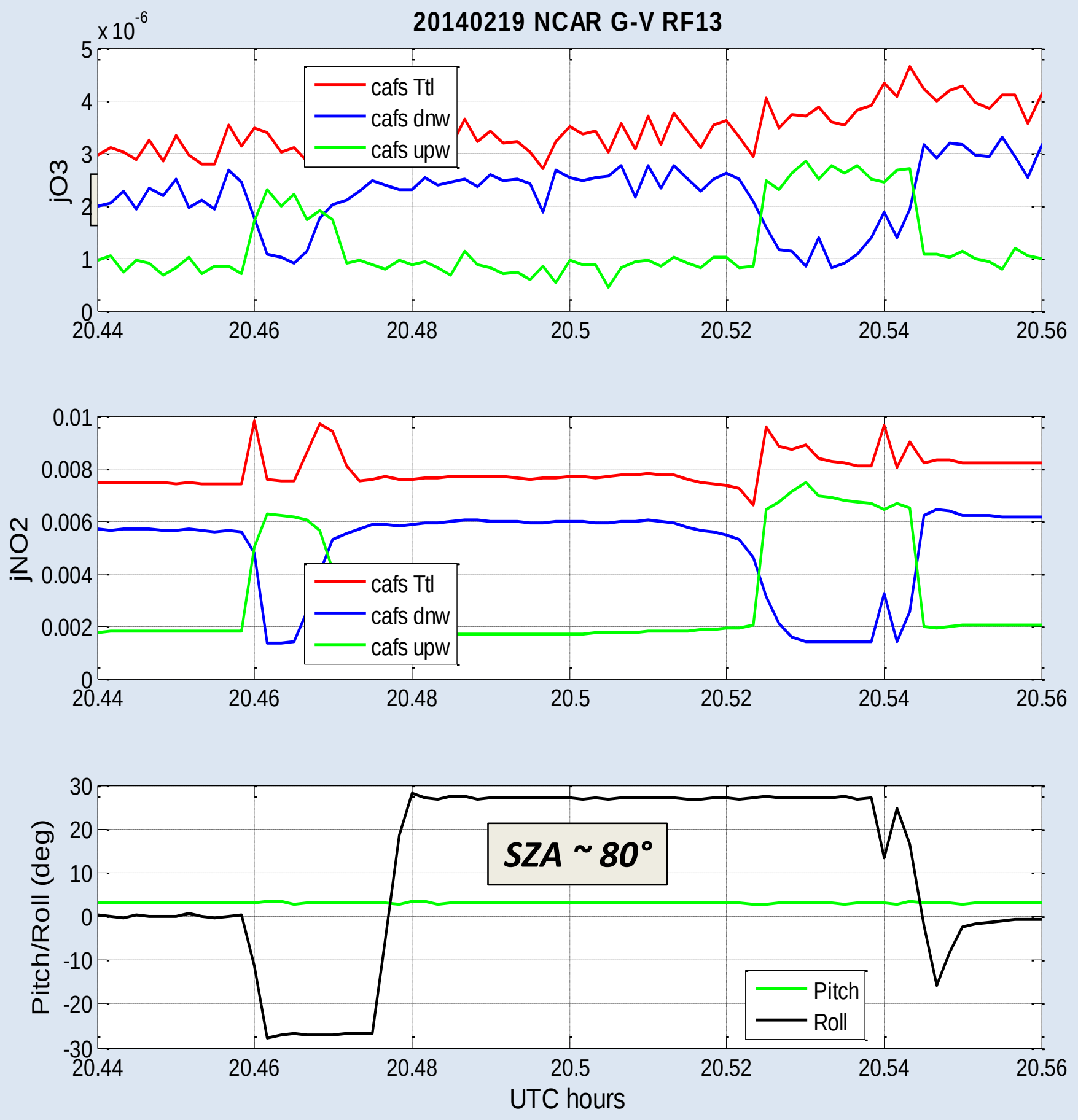
Angular response of the zenith optic optimized for a hemispherical response. Azimuthal response not shown.



Laboratory stray light characterization by long pass filter analysis used to assign spectral corrections. Note the structure in HARP that is not evident in the CAFS system.



HARP field calibration history indicating instrument stability throughout the campaign.



Demonstration of the angular response quality of the combined nadir and zenith optics at high solar zenith angle (low sun). Roll maneuvers have minimal effect on the total actinic flux, except when the sun approaches 90° relative to the optics. jO_3 is strongly impacted by scattering and thus the impact is muted relative to jNO_2.

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