

HARP photolysis frequencies

Samuel Hall Kirk Ullmann











HIAPER Airborne Radiation Package (HARP)

















HARP Zenith (downwelling)

-

1

National Science Joundation Where Discoveries Begin

HARP Nadir (upwelling)

T

HARP Actinic Flux Spectroradiometers

Measurement

CCD detection of spectrally resolved up and downwelling actinic flux

Calibrations

- NIST traceable absolute spectral sensitivity (primary lab, secondary field)
- Wavelength assignment (Hg and solar)
- Angular, azimuthal and effective plane
- Stray light characterization
- Radiative transfer model comparisons
- Chemical actinometer comparisons

Products

Photolysis frequencies calculated from cross-sections and quantum yields



Wavelengths	280-680 nm (unfiltered)
Resolution	~1.8 nm FWHM at 297 nm
Precision	1-2% wavelength dependent
Spectral Accuracy	5% (UV-B), 3% (UV-A/VIS) limited by NIST standards
Detection Limits	~0.04 mW/m2/nm at 300 nm
Data Rate	3-6 seconds



Aerosol Profile





$j [O_3 \rightarrow O_2 + O(^1D)]$ $j [NO_2 \rightarrow NO + O(^{3}P)]$ j [H₂O₂ \rightarrow 2OH] j [HNO₂ \rightarrow OH + NO] $j [HNO_3 \rightarrow OH + NO_2]$ j [CH₂O \rightarrow H + HCO] $j [CH_2O \rightarrow H_2 + CO]$ j [CH₃CHO \rightarrow CH₃ + HCO] $j [C_2 H_5 CHO \rightarrow C_2 H_5 + HCO]$ j [CHOCHO \rightarrow H₂ + 2CO] j [CHOCHO \rightarrow CH2O + CO] j [CHOCHO \rightarrow HCO + HCO] j [CH₃COCHO \rightarrow CH₃CO + HCO] j [CH₃COCH₃ \rightarrow CH₃CO + CH₃] j [CH₃OOH \rightarrow CH₃O + OH] $j [N_2O_5 \rightarrow NO_3 + NO_2]$ j [CH₃ONO₂ \rightarrow CH₃O + NO₂]

 $j [HO_2NO_2 \rightarrow HO_2 + NO_2]$ j [HO₂NO₂ \rightarrow OH + NO₃] j [CH₃CO(OONO₂) \rightarrow $CH_{3}CO(OO) + NO_{2}$ j [CH₃CO(OONO₂) \rightarrow $CH_3CO(O) + NO_3$] j [CH₃COCH₂CH₃ \rightarrow $CH_3CO + CH_2CH_3$] j [CH₃CH₂CH₂CH₂CHO \rightarrow $C_3H_7 + HCO]$ j [CH₃CH₂CH₂CH₂CHO \rightarrow $C_2H_4 + CH_2CHOH$] j [CH₃CH₂ONO₂ \rightarrow $CH_3CH_2O + NO_2$] j [Br₂ \rightarrow Br + Br] j [BrO \rightarrow Br + O] j [Br₂O \rightarrow products] j [HOBr \rightarrow HO + Br]

j [BrONO₂ \rightarrow Br + NO₃] j [BrONO₂ \rightarrow BrO + NO₂] j [BrCl \rightarrow Br + Cl] j [Cl₂ \rightarrow Cl + Cl] j [CIO \rightarrow CI + O(³P)] j [CIONO₂ \rightarrow CI + NO₃] j [CIONO₂ \rightarrow CIO + NO₂] Recent Additions j [CINO₂ \rightarrow CI + NO₂] j [CIONO \rightarrow CI + NO₂] j [BrNO \rightarrow Br + NO] j [BrONO \rightarrow Br + NO₂] j [BrONO \rightarrow BrO + NO] j [BrNO₂ \rightarrow Br + NO₂] j [CHBr₃ \rightarrow Products] j [CH₂=C(CH₃)CHO \rightarrow Products] j [CH₃COCH=CH₂ \rightarrow Products]

Photolysis frequencies calculated from HARP actinic flux

HARP Summary

- Measure spectrally resolved actinic flux density
- Calculate photolysis frequencies
- Photochemistry driver of daytime processes and evolution (ozone, NOx, halogens, HOx, VOCs, etc)
- Daytime/nightime transitions
- Aerosol and cloud impacts on photolysis
- Photolysis impacts on heterogeneous chemistry
- Excellent dark signal characterization