# The 2019 Ozone Cross-Section Consensus Value at 253.65 nm

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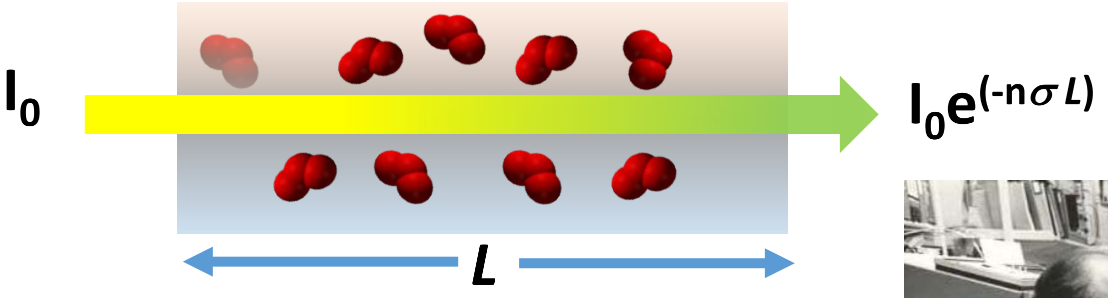


OPEN ACCESS
IOP Publishing
Metrologia
Metrologia 56 (2019) 034001 (12pp)
https://doi.org/10.1088/1681-7575/ab0bdd

## Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review

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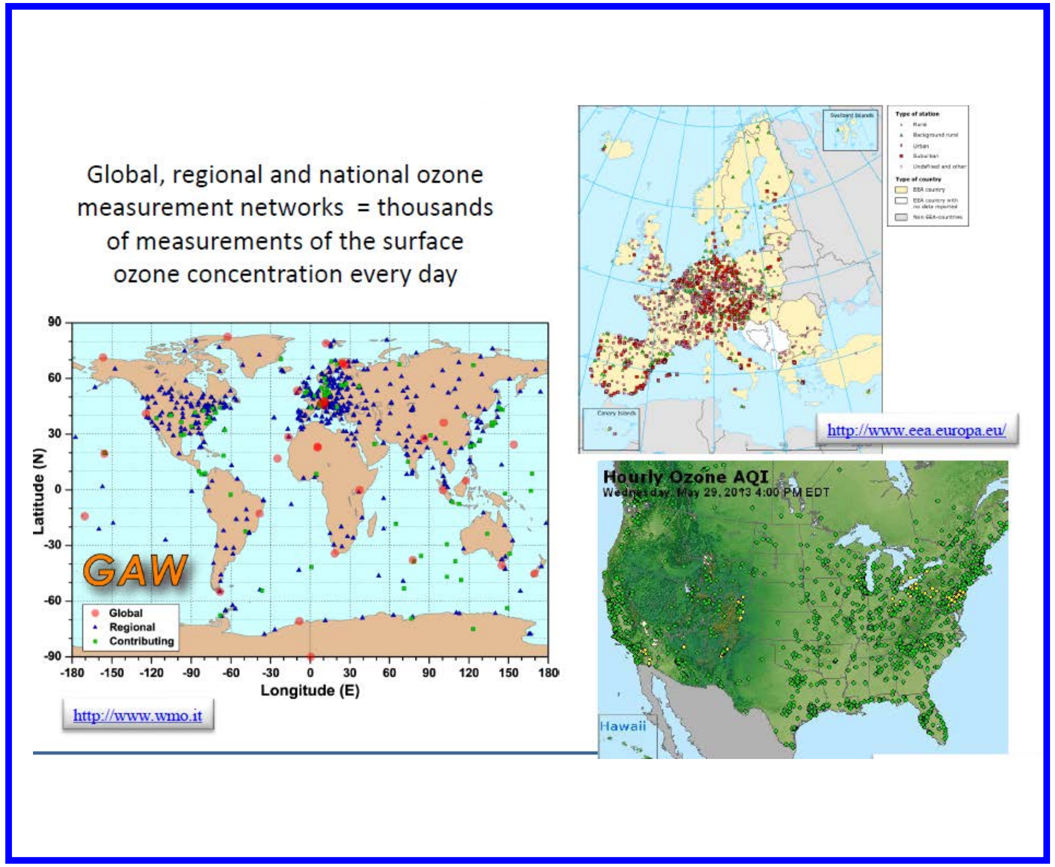
*Implementing a Globally Coordinated Change in Ozone Cross Section Value for Surface Ozone Monitoring Virtual Workshop*, (BIPM), October 5-9, 2020

# Standard Reference  Photometers (SRP) for Measurements of Ground-Level Ozone




$O_3$ measurements are linked to NIST-made SRPs maintained at NIST and BIPM

Over 60 SRPs are deployed world-wide

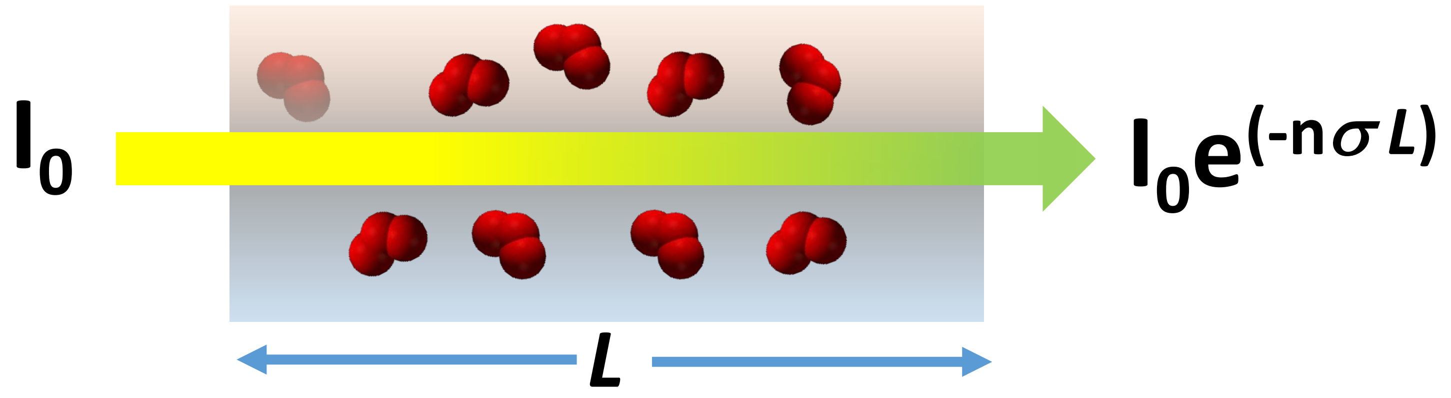
Basis for quantifying compliance with environmental regulations

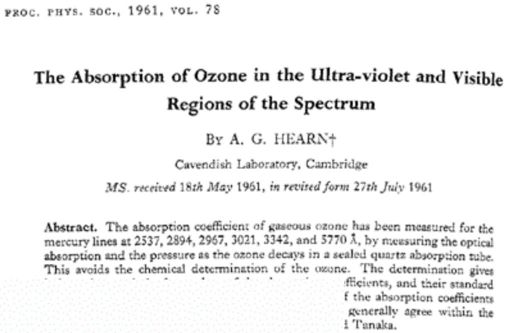
Range (1 – 1000 nmol/mol) in air

Cross section has an uncertainty of 1.9 %.

# Standard Reference Photometer Measurement Principle

SRP instruments are certified by comparison to primary SRPs for which the ozone mole fraction, $x_{O3}$, and its combined uncertainty, $u(x_{O3})$, are derived from the Beer-Lambert law and measured $T$, and $p$ of the sample; the Boltzmann constant, $k_B$; pathlength, $L$; and the 1961 Hearn value for the ozone absorption cross-section at 253.65 nm (air), $\sigma$.





PROC. PHYS. SOC., 1961, VOL. 78

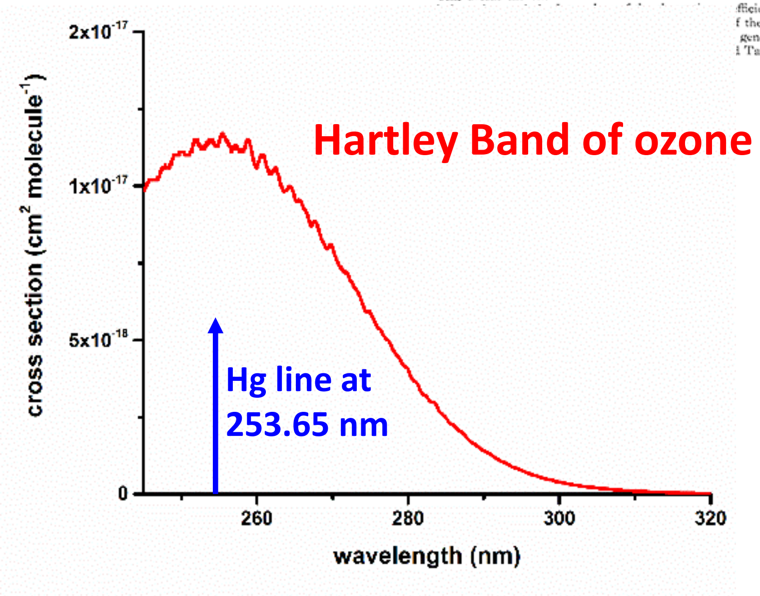
The Absorption of Ozone in the Ultra-violet and Visible Regions of the Spectrum

By A. G. HEARN†

Cavendish Laboratory, Cambridge

*MS. received 18th May 1961, in revised form 27th July 1961*

**Abstract.** The absorption coefficient of gaseous ozone has been measured for the mercury lines at 2537, 2894, 2967, 3021, 3342, and 5770 Å, by measuring the optical absorption and the pressure as the ozone decays in a sealed quartz absorption tube. This avoids the chemical determination of the ozone. The determination gives ... fficients, and their standard ... f the absorption coefficients ... generally agree within the ... Tanaka.



# Guidelines for Data Analysis & Review

- Identified a set of 14 independent, peer-reviewed 254-nm cross section measurements for $O_3$

  Selection Criteria

  Publication dates 1950 – 2016

  Room temperature (295 K ± 2.5 K) cross section data

  Cross-section explicitly indicated in publication or inferred via simple calculation

  For repeated measurements by a group, only the last published value will be used

- Data were not corrected.  Known bias was introduced via uncertainty; asymmetric components considered
- Uncertainties were evaluated according to GUM (1995).  In some cases, this required introducing additional uncertainty not specified in the original publication

# Studies Considered

**Table 1.** List of the fourteen independent publications selected to calculate the consensus value of the ozone absorption cross-section at 253.65 nm.

| Identification | Author(s) | Traceability | Sample purity |
|---|---|---|---|
| AFCRC-59 [35] | Inn and Tanaka | Ozone pressure | Assumed pure |
| Hearn-61 [3] | Hearn | Ozone pressure | Degradation to $O_2$ considered |
| JPL-64 [33] | De More and Raper | Oxygen pressure | Assumed full conversion of $O_3$ to $O_2$ |
| Griggs-68 [34] | Griggs | Ozone pressure | Assumed pure |
| JPL-86 [39] | Molina and Molina | Ozone pressure | Assumed pure |
| UniMin-87 [37] | Mauersberger *et al* | Ozone pressure | Assessed by mass spectrometry |
| HSCA-88 [41] | Yoshino *et al* | Ozone pressure | Assumed pure |
| UniReims-93 [32] | Daumont *et al* | Ozone pressure | Degradation to $O_2$ considered |
| UniBremen-99 [31] | Burrows *et al* | * $NO_2$ cross-section via GPT | NA air sample/SRP |
| UPMC-04[44] | Dufour *et al* | Ozone pressure | Assumed pure |
| NIES-06 [10] | Tanimoto *et al* | * $NO/N_2$ standards via GPT | NA air sample/SRP |
| UniBremen-14 [45] | Gorshelev *et al* | Ozone pressure | Degradation to $O_2$ considered |
| BIPM-15 [26] | Viallon *et al* | Ozone pressure | Assessed by residual pressure measurements |
| BIPM-16 [11] | Viallon *et al* | * $NO/N_2$ standards via GPT | NA air sample/SRP |

*GPT: Gas-phase titration of the $NO + O_3 \rightarrow NO_2 + O_2$ reaction

# Uncertainties

Common to all measurements:

Type A: repeatability

Type B : pressure, temperature, optical pathlength, absorbance

$u_{r,tot} = (u_{r,1}^2 + u_{r,2}^2 + \ldots)^{1/2}$

Experiment-specific:

sample purity. [(Mauersberger 1987, … Viallon 2015) ]

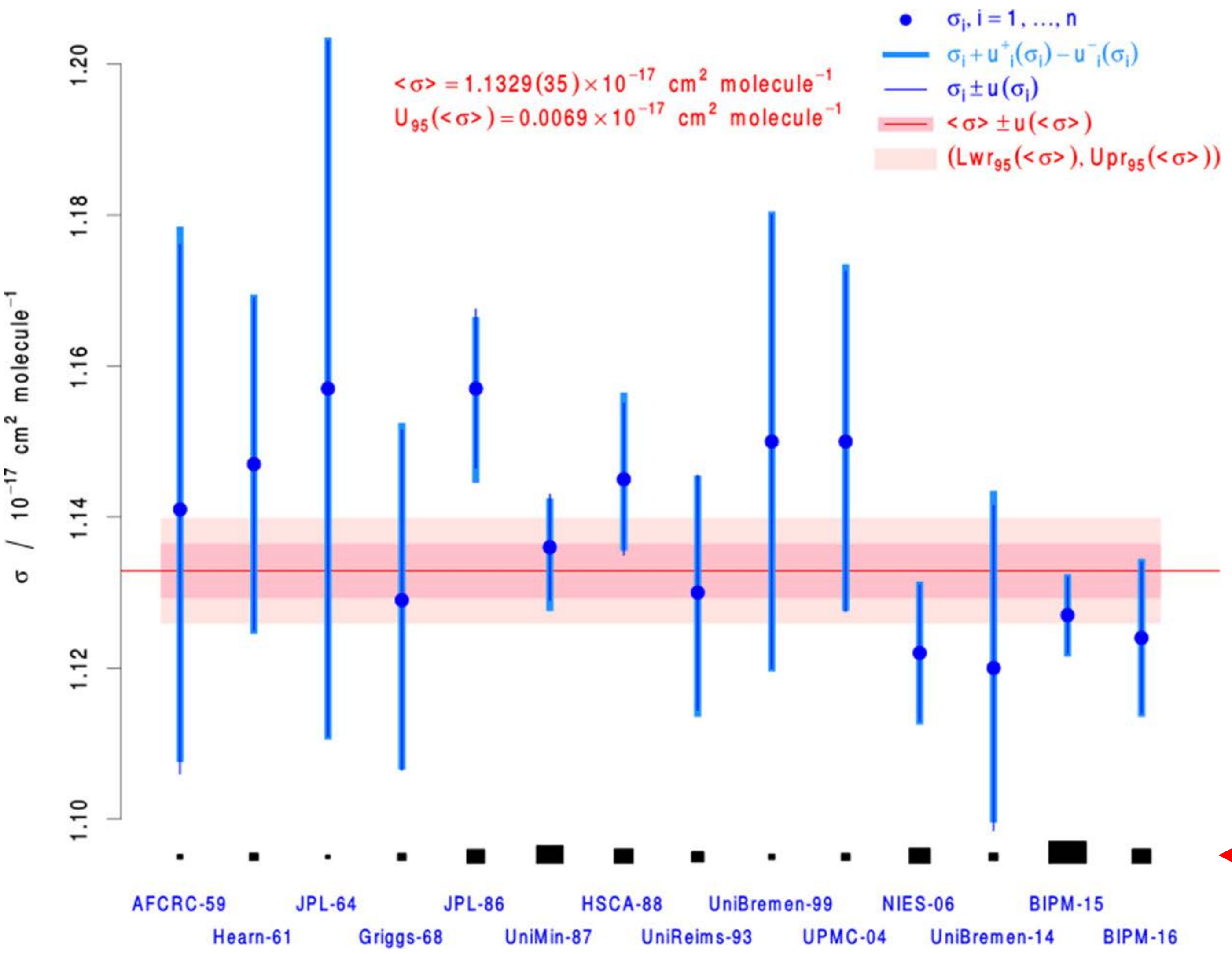
GPT with gas standards: [Tanimoto (2006), Viallon (2015)]

GPT with $NO_2$ absorption cross section: [Burrows (1999)

intensity of IR rovibrational transition of $O_3$: [Dufour (2004)]

effect of multiple reflections (Inn & Tanaka, Hearn, DeMore, Griggs, Molina Mauersberger, Yoshino, Brion, Gorshelev)

# Final Monte Carlo & DerSimonian Laird Statistical Analysis

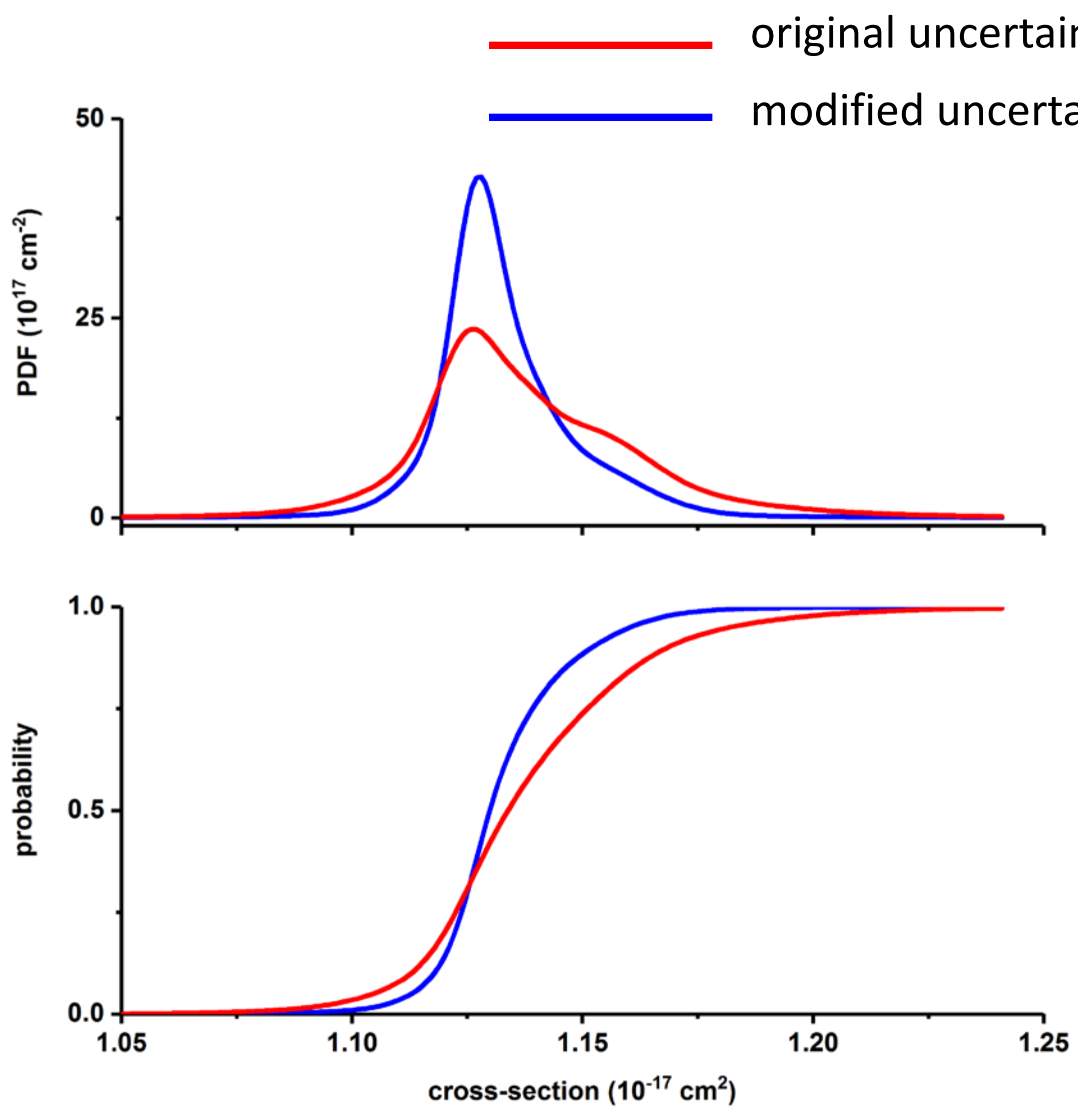



areas $\propto$ weighting factors

**Monte Carlo method with skew-normal distribution accounted for asymmetric uncertainties**

**(DL) DerSimonian-Laird analysis indicated that inter-laboratory heterogeneity was negligible**

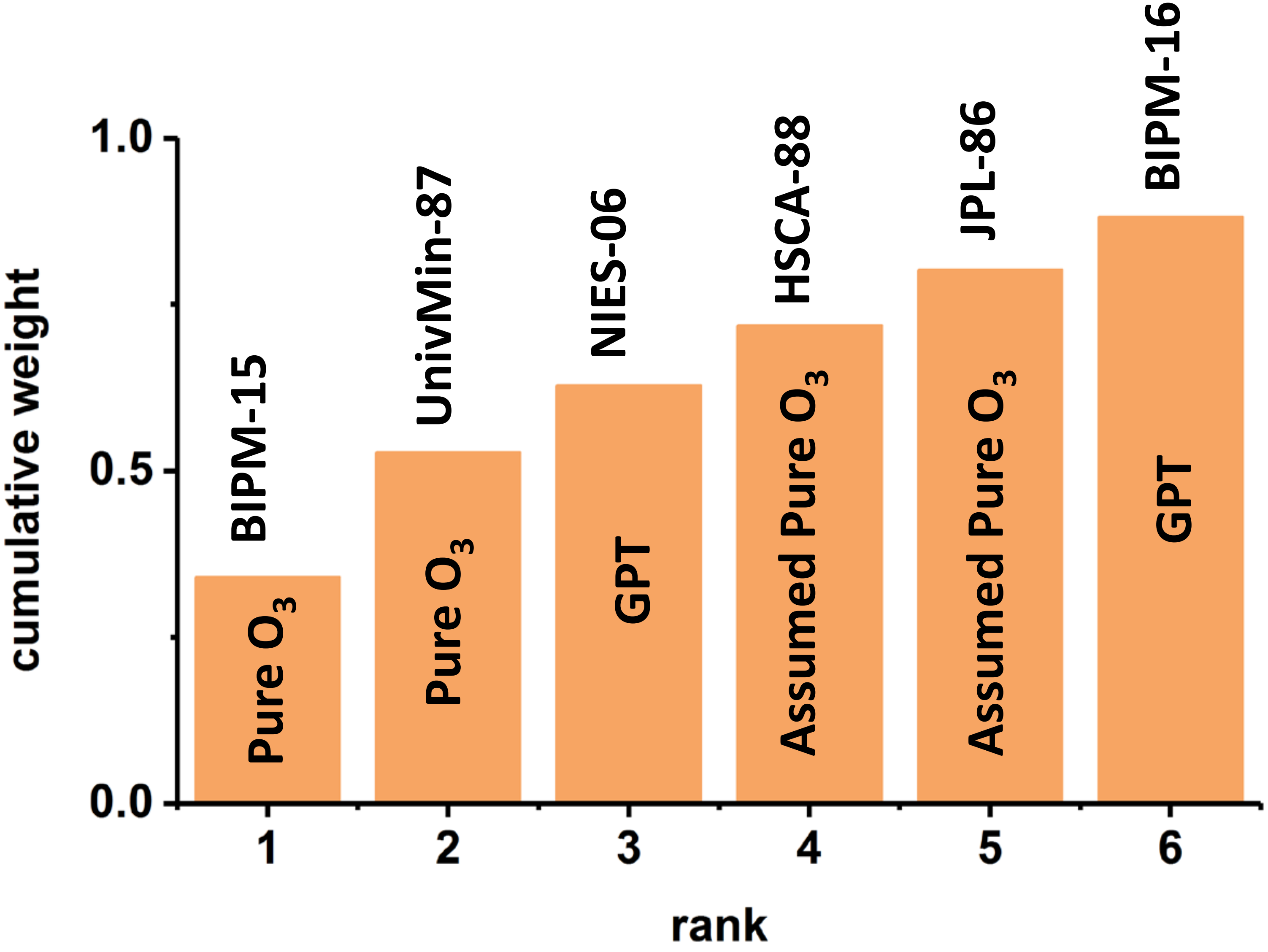
# Composite Distribution Function




Weighted analysis leads to narrower, more-symmetric distribution

Final pdf is still slightly skewed

# Studies Contributing to 90% of the Cumulative Weight



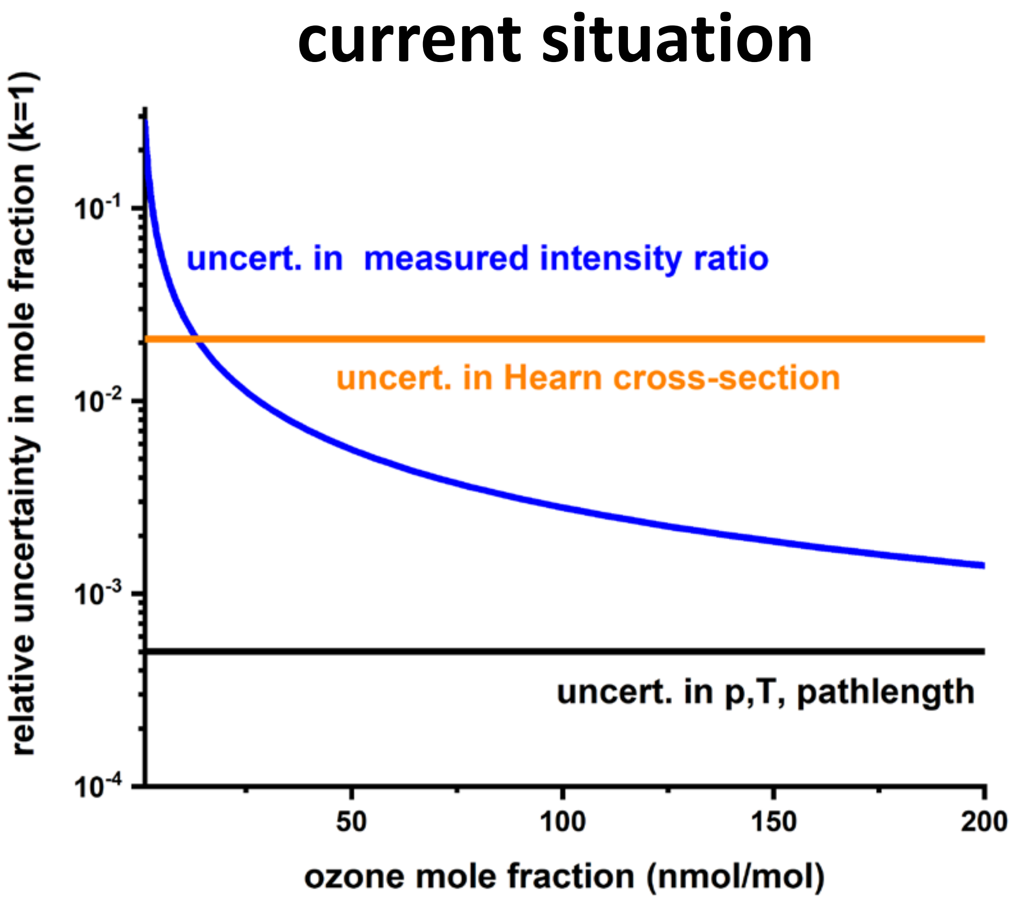
# Proposed Change in Ozone Cross-Section at 254 nm

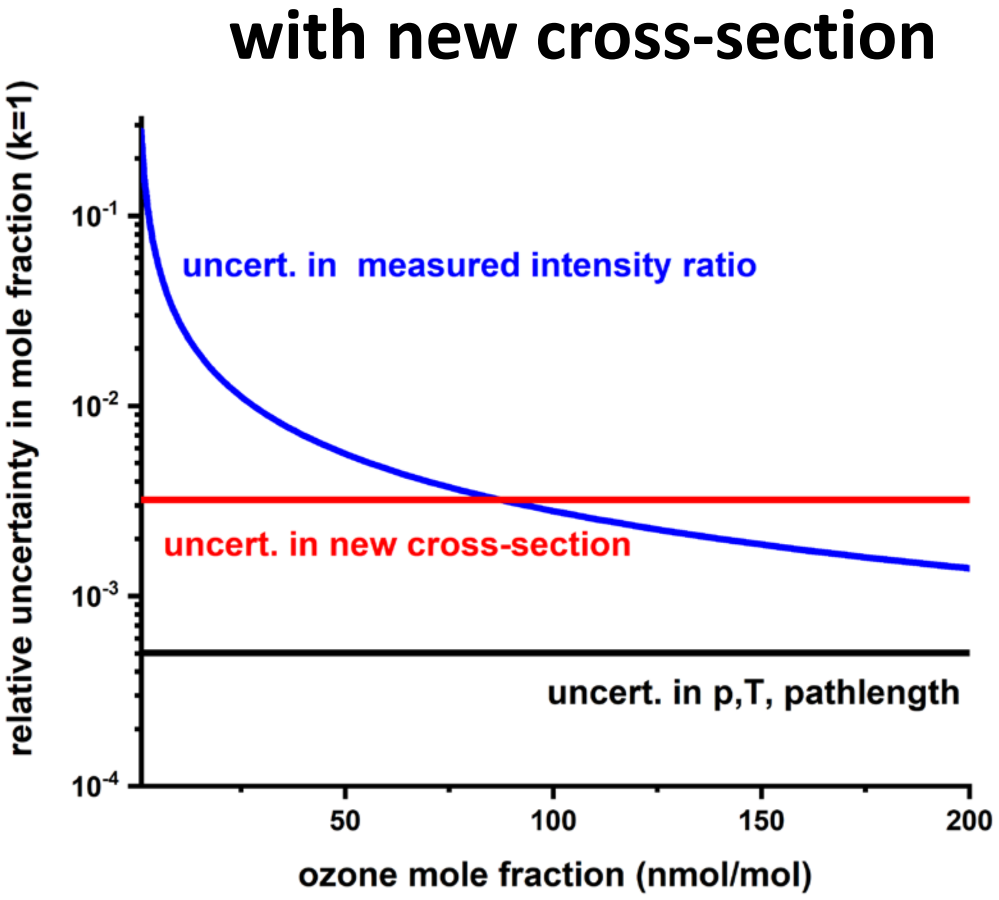
| Ref. | $\sigma$ ($10^{-17}$ $cm^2$/molecule ) | w.r.t. to Hearn | rel. std. unc. (%) |
|---|---|---|---|
| [1]Hearn-61 | 1.147 | | 1.9 |
| **Hodges/CCQM** | **1.1329** | **-1.23 %** | **0.31** |

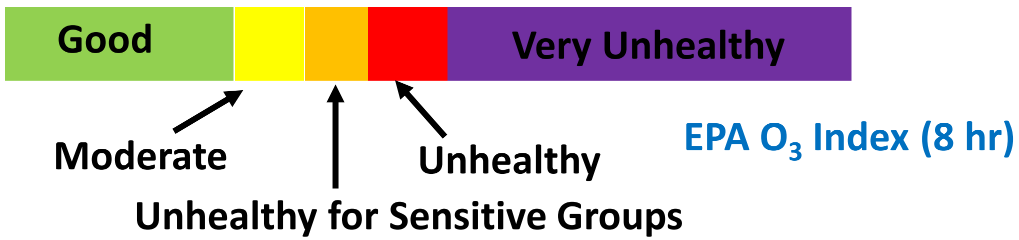
**This work reduces uncertainty in the ozone absorption cross-section by factors of 6.1 and 2.6, respectively compared to those of Hearn and ACSO.**


1. Hearn A. G., Proc. Phys. Soc. 78, 932-940 (1961)
2. WMO/GAW No. 218, Absorption Cross Sections of Ozone (ACSO) Status Report, (2015)

# Impact of New Cross Section on SRP uncertainty



# Impact of Consensus Cross-Section on Air-Quality Compliance

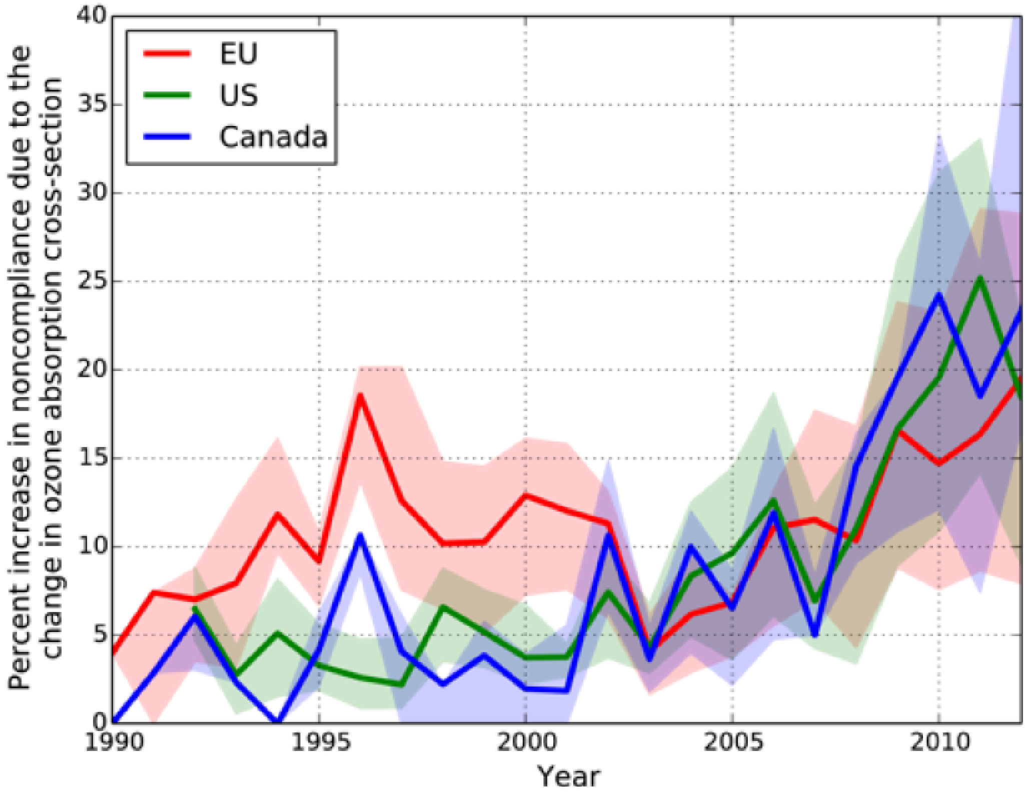



**Figure 3.** The percent increase in the number of sites that are out of compliance with air quality regulations due to the adjusted ozone abundances suggested by the new Viallon et al. (2015) cross section for the EU, the United States, and Canada between 1990 and 2012. Shaded regions indicate the uncertainty in the number of noncompliant sites associated with the 2 standard deviation uncertainty in the Viallon et al. cross section.

Atmos. Chem. Phys., 15, 13627–13632, 2015
www.atmos-chem-phys.net/15/13627/2015/
doi:10.5194/acp-15-13627-2015


Atmospheric Chemistry and Physics

**Updated ozone absorption cross section will reduce air quality compliance**

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[2]National Centre for Atmospheric Science, Department of Chemistry, University of York, York, YO10 5DD, UK
*Correspondence to:* E. D. Sofen (esofen@gmail.com)

$$x_{ozone} = -\frac{ln(A)}{\ell}\frac{k_B T}{p}\frac{1}{\sigma}$$

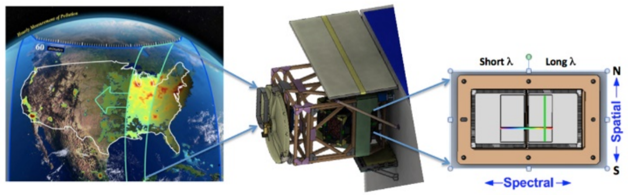
← cross-section

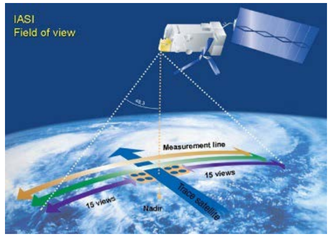
Based on BIPM-15, where
x-sec = 1.8 % less than the Hearn-61 value

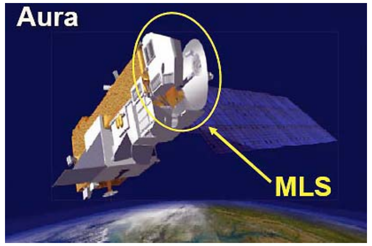
The new consensus value for the x-sec is
1.23 % less than the Hearn-61 value

Additional exceedances driven by reassignment of the x-sec will be ~ 2/3 that predicted by Sofen et al.

# Measurements of Atmospheric Ozone across the Electromagnetic Spectrum



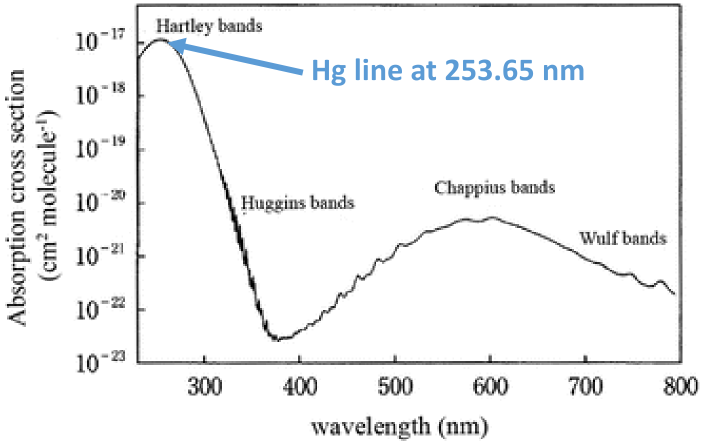



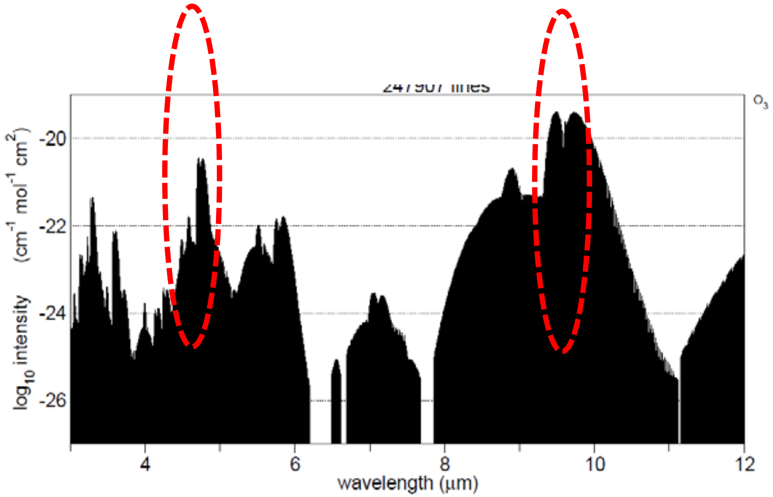



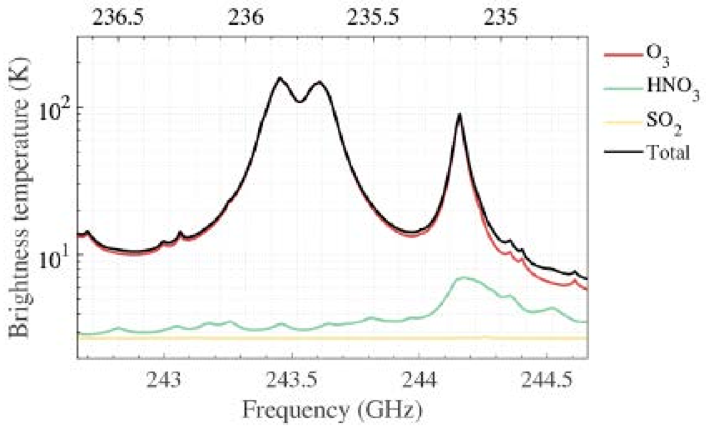

**Satellite:** OMI, TEMPO

OMI, ACE, IASI

MLS



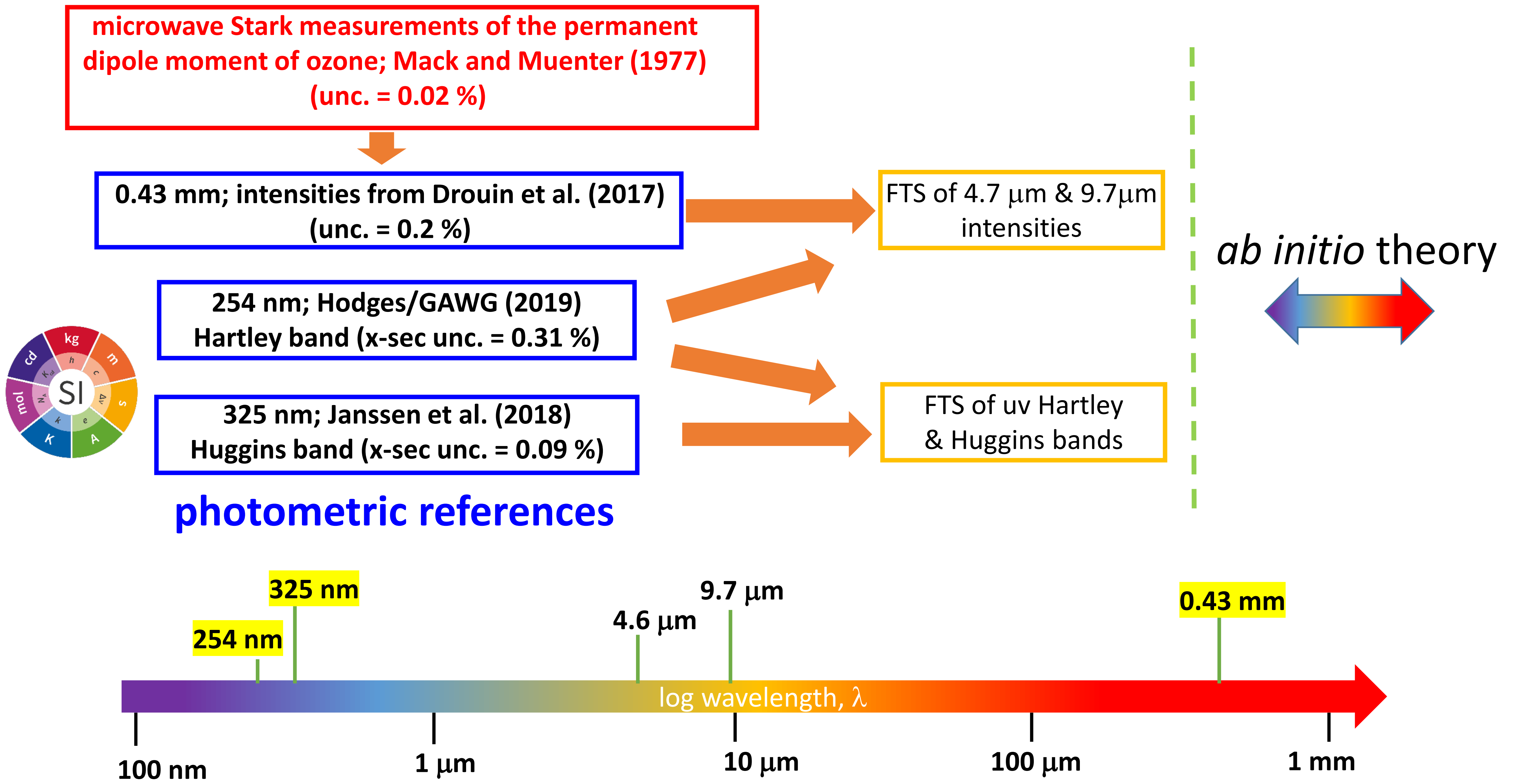

**Ground:** Brewer-Dobson instruments
LIDAR, direct absorption

ultraviolet- visible

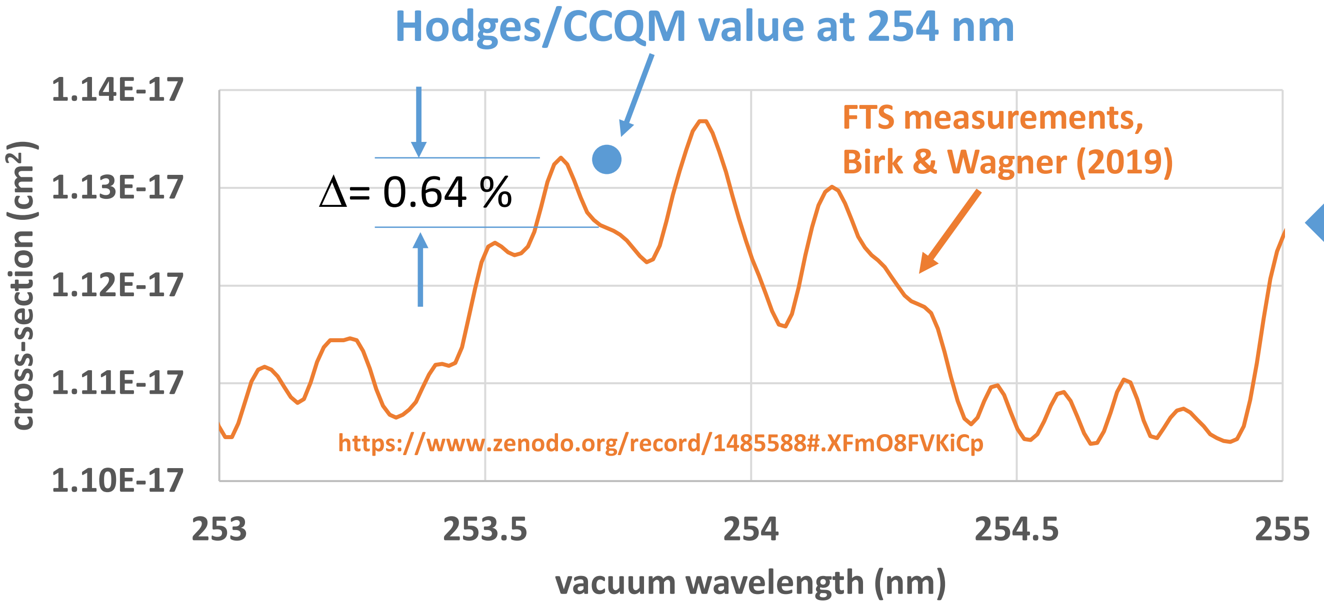
thermal infrared

microwave

# Unifying the Spectroscopic Properties of Ozone



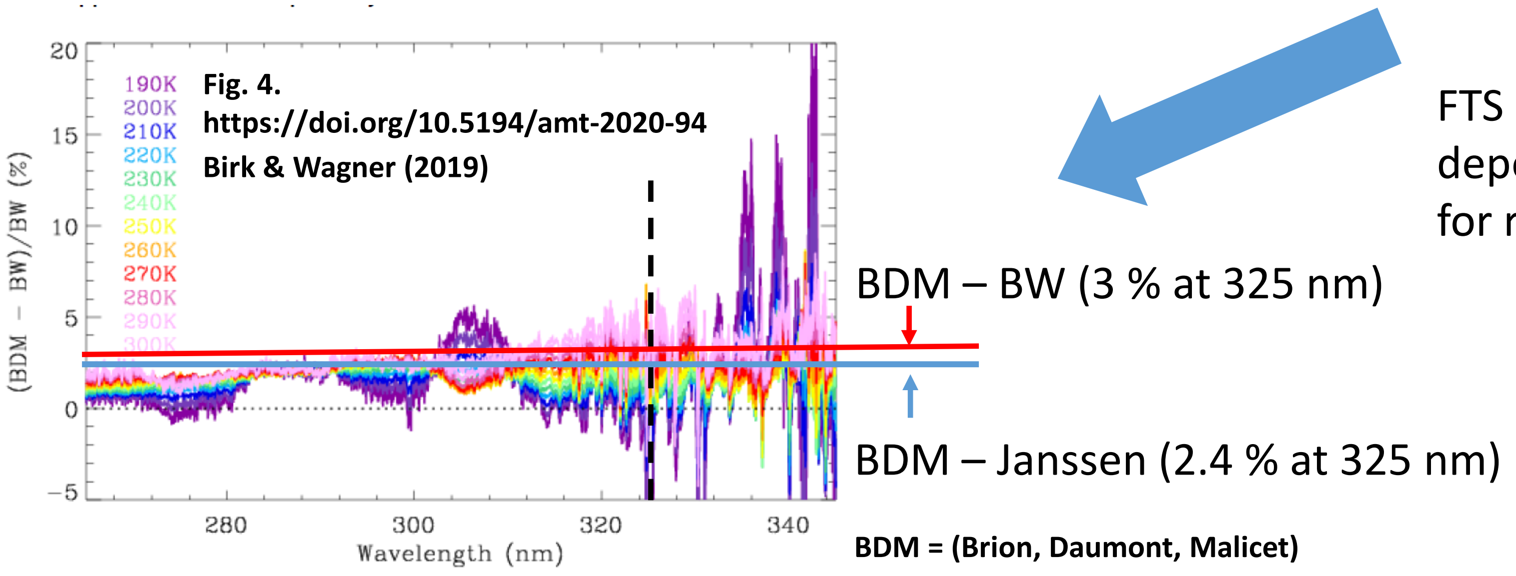
# Consistency of Cross Sections within the UV




New uv FTS measurements in agreement with Hodges/GAWG 254 x-sec to within 0.64 %

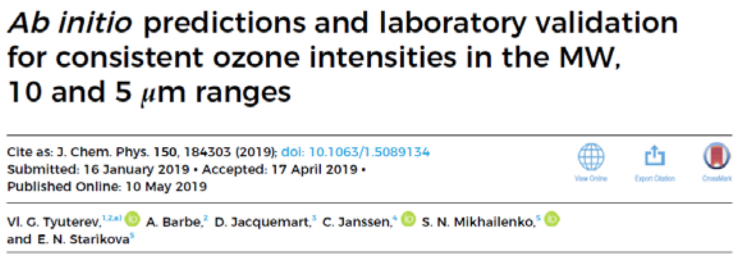
Consistency between 254 nm and 325 nm x-sec reference values demonstrated

FTS results provide improved temperature dependence over a wide spectral range for remote sensing applications




**BDM = (Brion, Daumont, Malicet)**

# Consistency between UV, IR and MW Measurements and with Theory


*Ab initio* predictions and laboratory validation for consistent ozone intensities in the MW, 10 and 5 $\mu$m ranges

Cite as: J. Chem. Phys. 150, 184303 (2019); doi: 10.1063/1.5089134
Submitted: 16 January 2019 • Accepted: 17 April 2019 •
Published Online: 10 May 2019

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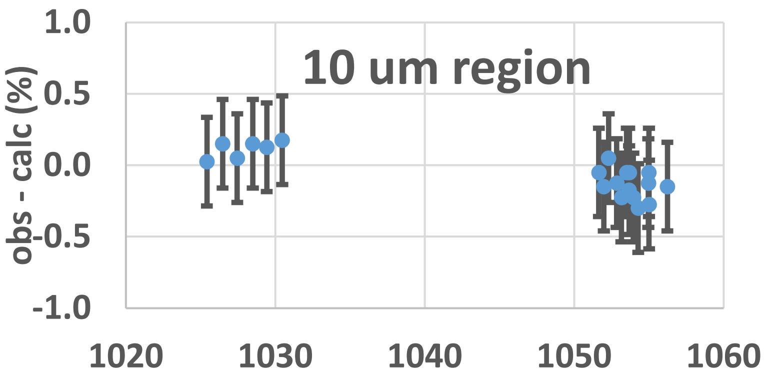
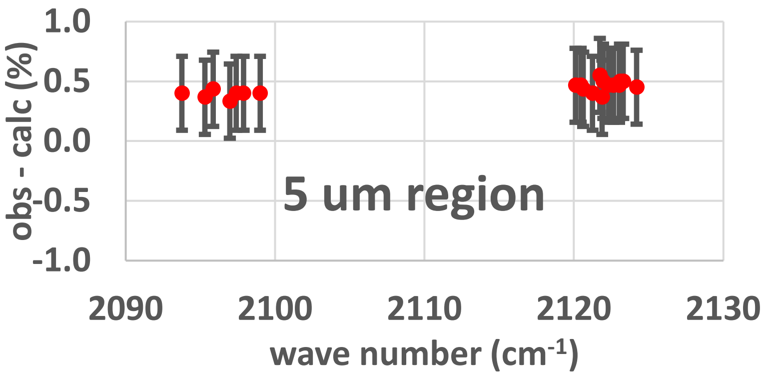
***ab initio*** **calculations of $O_3$ cross-sections were compared to UV and IR measurements that were scaled by CCQM/Hodges value at 254 nm**




Calculations agree with IR and MW measurements at 1 % level

Resolves 4 % level discrepancies in IR and UV measurements

Demonstrates consistency from UV to IR to MW regions

IR databases (e.g. HITRAN) to be updated accordingly

# Summary

**The Hodges/CCQM ozone absorption cross section at 254 nm is 1.23 % smaller than the current (Hearn) value, and therefore will increase field measurements of ozone mole fraction by 1.23 %**

**The uncertainty of this cross section has been reduced by a factor of 6 to ~0.3 %**

**This cross section is a key photometric reference point that contributes to SI traceability and a recently achieved percent-level consistency in laboratory ozone measurements and theory spanning the UV to MW regions of the electromagnetic spectrum.**

**Adoption of this cross section along with other reference values will help unify local and global measurements of atmospheric ozone.**

# Thanks !