EARTH SYSTEM RESEARCH LABORATORY

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Ozone Absorption Cross Sections Laboratory Measurements

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Earth System Research Laboratory
NOAA

Ozone Cross Section Workshop II
Geneva, March 2010

Outline and Objective

Stimulate Discussion of Laboratory Measurements

Is there a need for new studies?

Workshop Mandates

"New" measurement

Preliminary Work at NOAA

Implications for further studies

Mandates

(1) Review available database of spectral ozone measurements in the Huggins bands

(2) Evaluate their uncertainties (including temperature dependence)

(3) Initiate and coordinate new laboratory measurements

(4) Prepare written summary

Mandates (1) and (2): Evaluate database (Huggins) and Uncertainties

BP and DBM data posted on ACSO web page !

Avoids confusion (outsiders) over the BP data

No BP room temperature currently posted ?

Laboratory Measurements

Mandates (1) and (2): Evaluate database (Huggins) and Uncertainties

Orphal, J., "A critical review of the absorption cross-sections of O_3 and NO_2 in the 240-790 nm region", ESA Tech. Note MO-TN-ESA-GO-0302, 2002.
Orphal, J., "A critical review of the absorption cross-sections of O_3 and NO_2 in the ultraviolet and visible", J. Photochem. Photobio. A: Chemistry, 157, 185-209, 2003.

Key Issues Identified for Laboratory Measurements

Absolute Cross Sections	Resolution	Wavelength Calibration
Dynamic Range	Wavelength Range	
Temperature Dep. (200 K or lower)	Fitting (Extrap. or Inter.)	

Absolute Cross Sections: 1 – 2 %

(1) Absolute pressure measurements and chemical titration methods
(2) A number of measurements at specific wavelengths
(3) A number of spectrum measurements, some absolute and some scaled to recommended values

Resolution: Several Issues

(1) Comparing data sets with different resolutions (Molina and Molina report 1 nm data)
(2) Applications have different resolution requirements.
(3) Calibration with specific instruments preferred but not always possible.

Wavelength Calibration: Some discrepancies among data sets

Laboratory Measurements

Mandates (1) and (2): Evaluate database (Huggins) and Uncertainties

Key Issues Identified for Laboratory Measurements

Absolute Cross Sections	Resolution	Wavelength Calibration
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Dynamic Range: O_3 cross sections of interest cover 7 orders of magnitude !

(1) Lab instruments are not capable of accurate measurements over entire range simultaneously

(2) Measurements made at specific wavelengths or over narrower wavelength regions

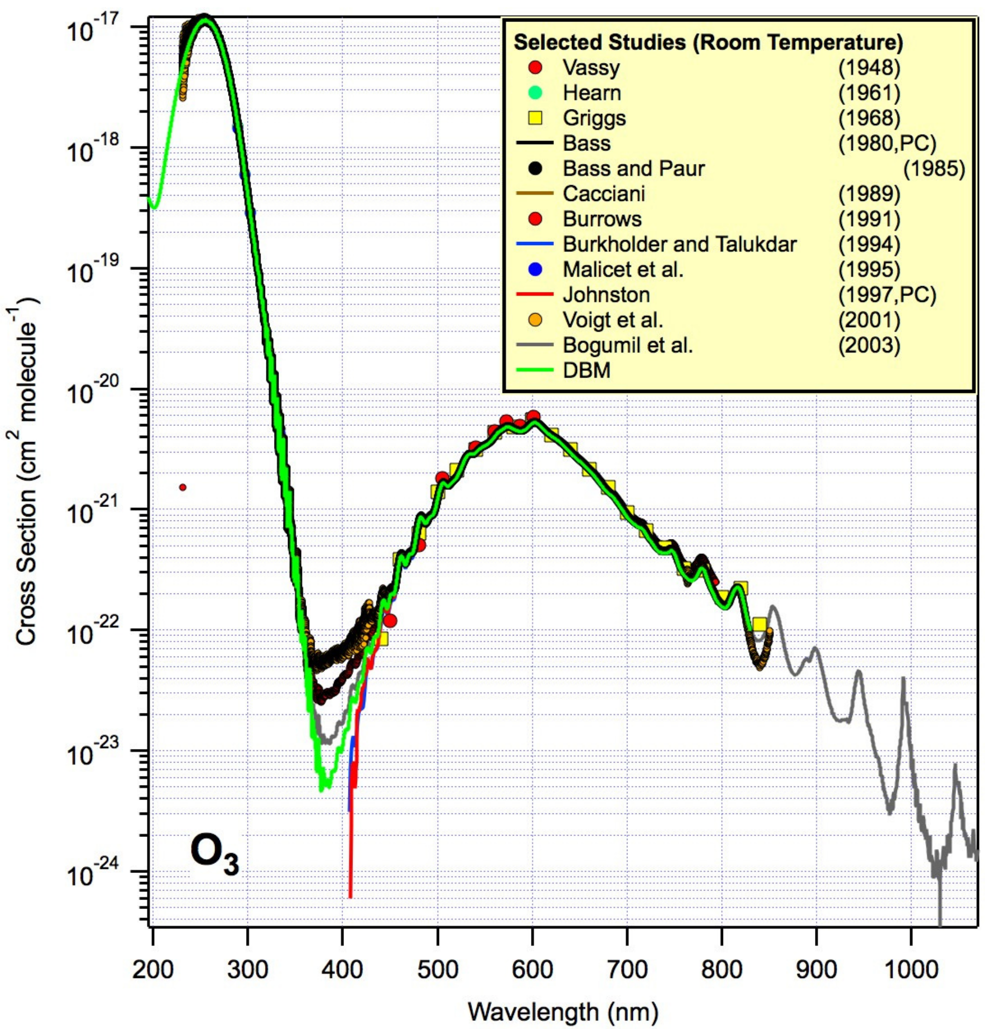
Temperature Dependence:

(1) Some T-dep observed at all wavelengths
(2) Large T-dep in valleys of Huggins bands
(3) Limited low-temperature data sets
    DBM, > 218 K
    BP and Bogumil et al., > 203 K
(4) Spread in T-dep cross sections significant, 5 – 10%

Fitting: Need to extrapolate or interpolate to full range of desired temperatures

(1) Laboratory measurements are typically limited to 4 or less specific temperatures (>203 K)
(2) O_3 cross sections are, usually, a smoothly varying function of temperature (Good News)
(3) What function works best? Should extrapolations be trusted?

Laboratory Measurements



Many laboratory studies available !

Some good, some better!

JPL and IUPAC evaluations are not focused on retrieval applications: *More directed towards modeling applications*

Data taken from Mainz database:
http://www.atmosphere.mpg.de/enid/2295

Laboratory Measurements

NEW CROSS SECTION MEASUREMENT

Mandate (1): Review available laboratory data

Environ. Sci. Technol. **2009,** *43,* 7831–7836

A Sensitive and Versatile Detector for Atmospheric NO_2 and NO_X Based on Blue Diode Laser Cavity Ring-Down Spectroscopy

HENDRIK FUCHS,[†,‡,§]
WILLIAM P. DUBÉ,[†,‡]
BRIAN M. LERNER,[†,‡]
NICHOLAS L. WAGNER,[†]
ERIC J. WILLIAMS,[†,‡] AND
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Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, and Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, CO

developed over the past decades. Nitric oxide (NO) is most commonly measured by its chemiluminescence (CLD) reaction in excess O_3 to produce electronically excited NO_2. The method is readily extended to NO_2 using a heated molybdenum surface or a photolytic converter to convert some fraction of NO_2 to NO (*2, 3*). While CLD methods are available as both commercial and custom built, research grade instruments, they require toxic excess reagents (e.g., NO, O_3) and vacuum systems. Furthermore, the indirect NO_2 detection may be subject to interference from conversion of compounds other than NO_2 to NO in commercial instruments (*4, 5*), is less precise than the NO detection due to the requirement for subtraction of two signals, and requires careful calibration of the NO_2 conversion fraction. Direct detection methods for NO_2 via, for example, mid infrared tunable diode laser spectroscopy (TDLS) (e.g., ref *6*) and laser induced fluorescence (LIF) (e.g., ref *7*) have addressed concerns related to interference in the NO_2 to NO conversion process. During the past decade, cavity ring-down spec-

T = 298 K

Cavity ring-down spectroscopy

Relative measurement: 404 nm vs 532 nm

Cross section at 532 nm well-established

No details/No data reported

Ozone measurements made as part of the instrument calibrations and tests

Laboratory Measurements

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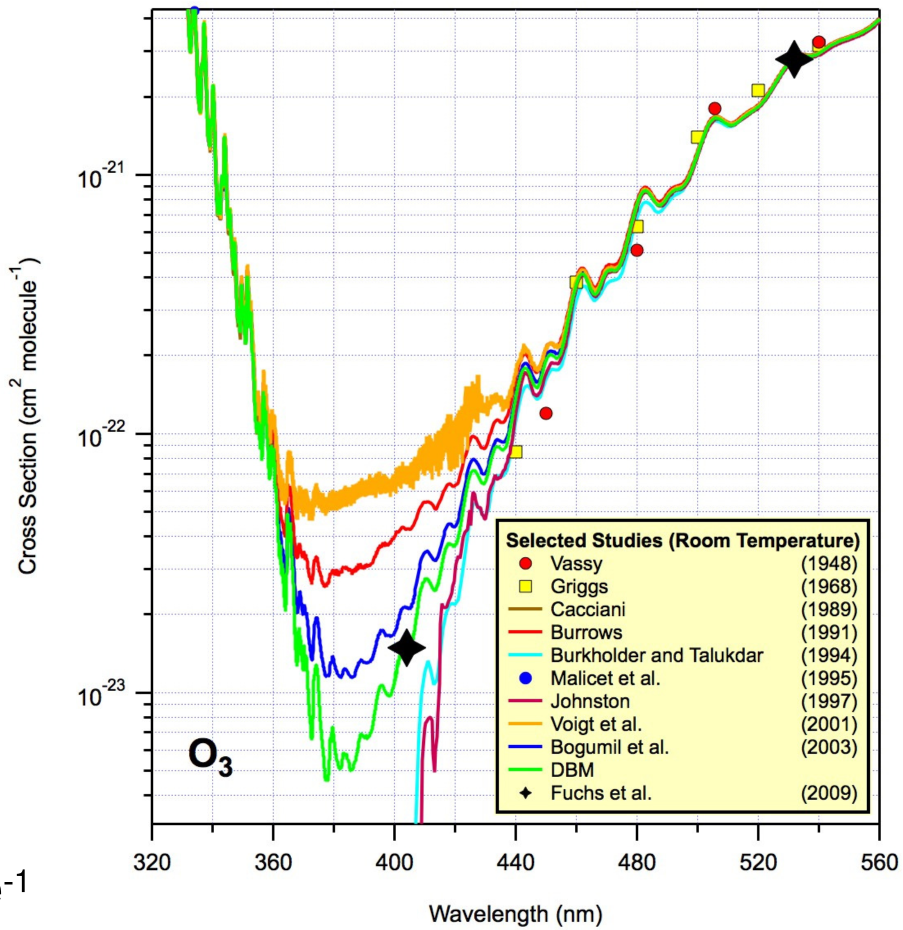

$$\sigma(404\text{ nm}) = 1.49\times10^{-22}\text{ cm}^2\text{ molecule}^{-1}$$

Laboratory Measurements

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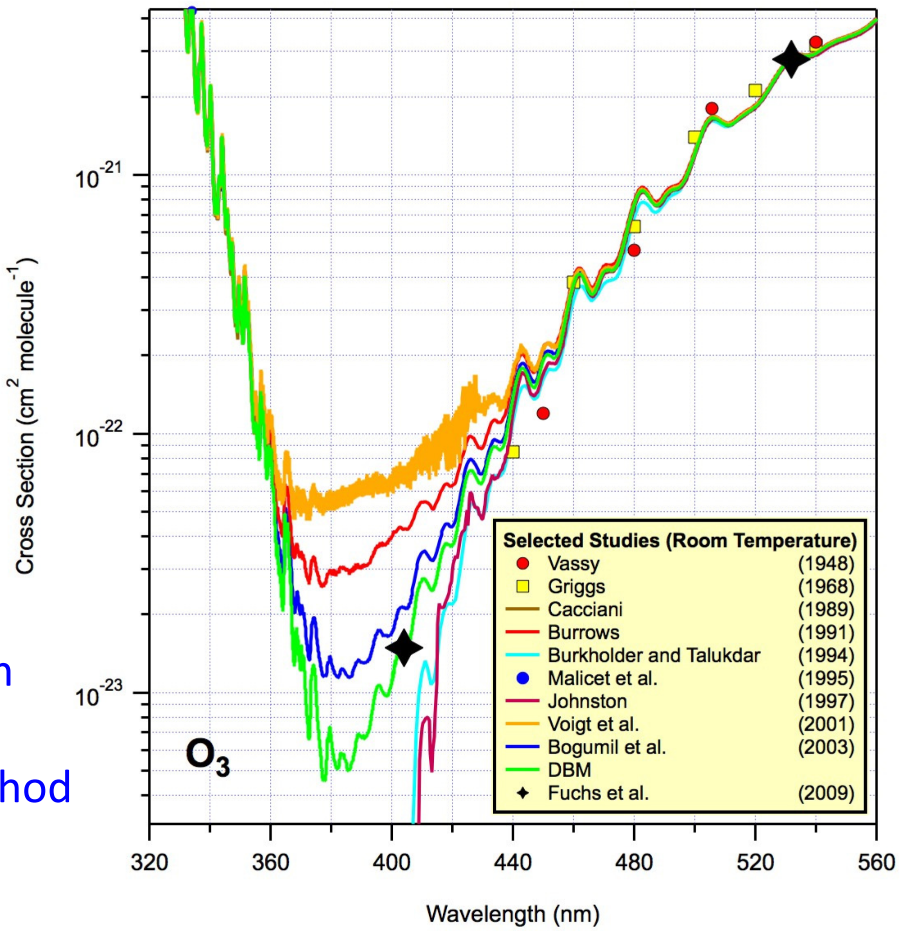


Excellent agreement with DBM at 404 nm

Illustrates capability of experimental method

- Stated precision better than <u>1%</u>
- Possible to extend to other wavelengths
- Possible to extend to other temperatures

Laboratory Measurements

Mandate (3): Initiate and coordinate new laboratory measurements

NOAA "Test" Experiments

We have **NOT** determined absolute absorption cross section values

Cavity ring-down spectroscopy (310 – 350 nm) relative to Hg line (253.65 nm)

- High spectral resolution (~0.1 cm^{-1}, ~0.001 nm)
- Accurate wavelength calibration
- Large dynamic range in Ozone cross sections
- Temperature range (200 – 298 K)

Initial focus:

Relative measurements (Wavelength and Temperature)

Evaluation and Validation (?) of existing data sets

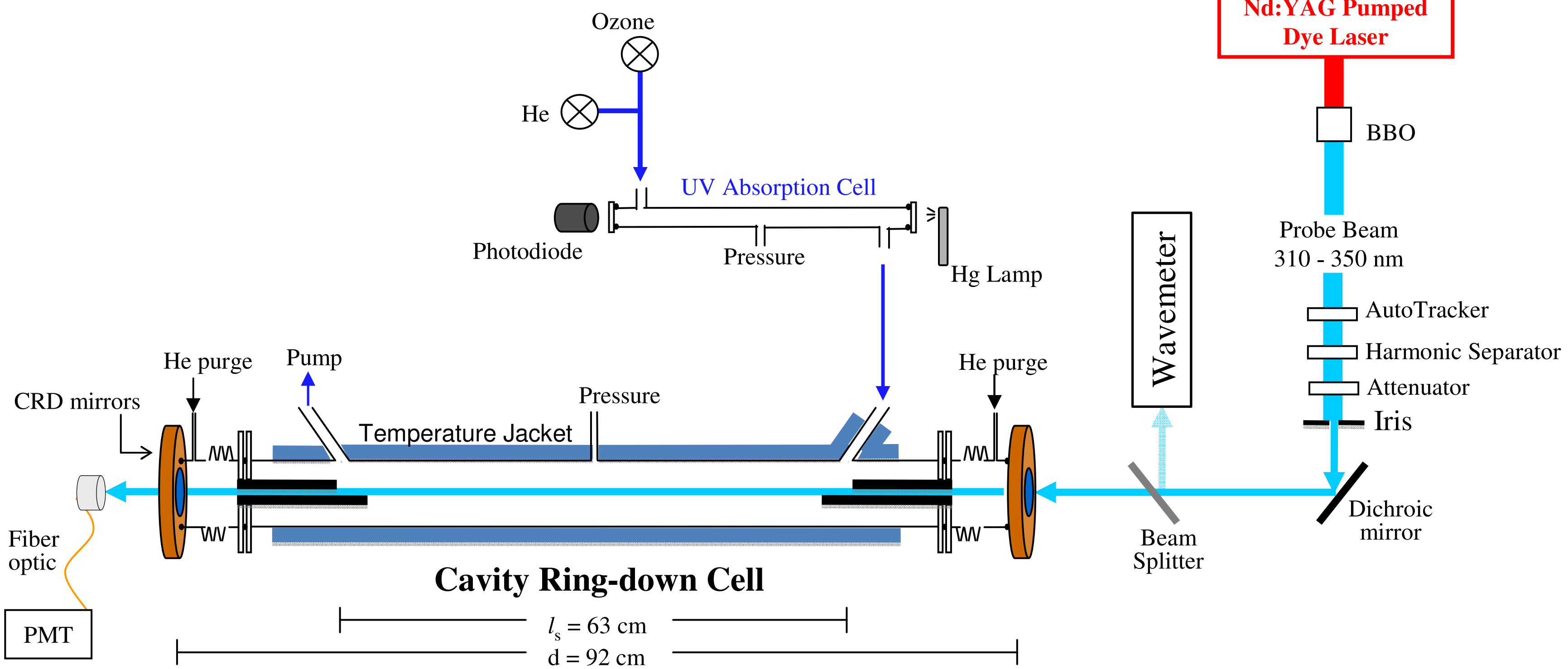
Laboratory Measurements

NOAA Experimental Apparatus

Mandate (3): Initiate and coordinate new laboratory measurements

Cavity Ring-down Spectroscopy – Hg Lamp

(310 – 350 nm) **(253.65 nm)**



- Relative cross section measurements
- Temperature dependence
- Single wavelength measurement
- Accurate wavelength calibration

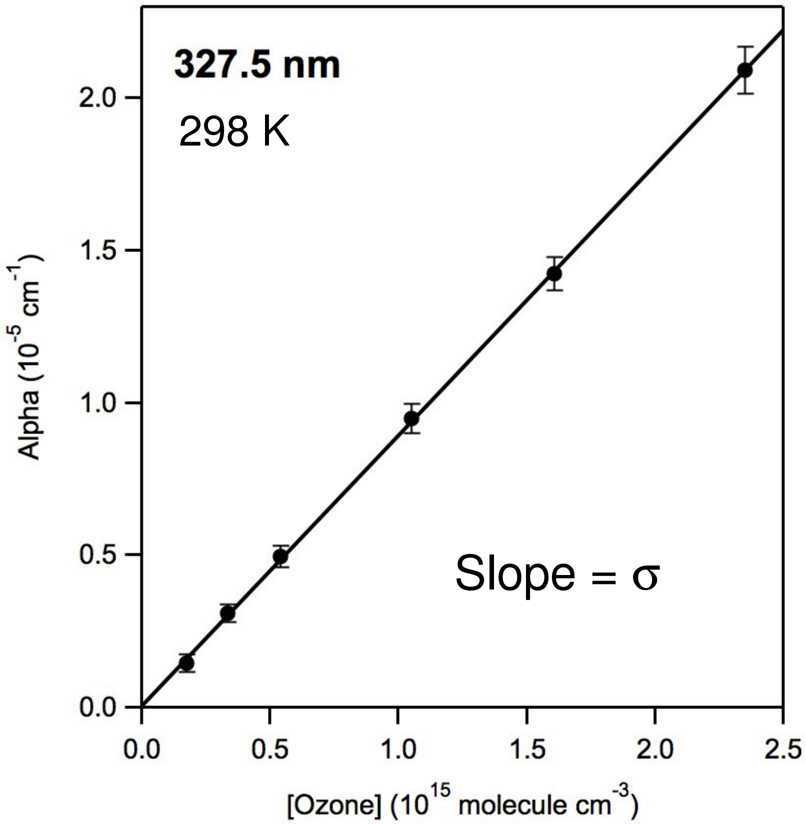
Laboratory Measurements

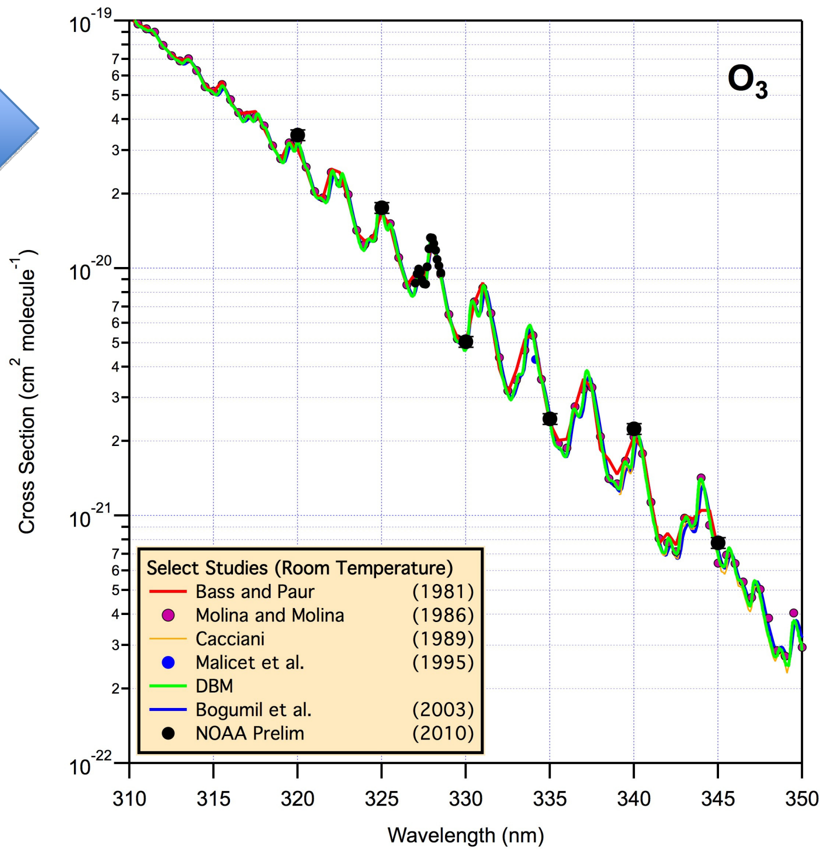
Preliminary NOAA Measurements

Mandate (3): Initiate and coordinate new laboratory measurements

- Measurements at 310, 320, 330, 335, 340, 345 nm
- 0.1 nm step scan between 327 and 328.5 nm
- Temperature dep. at 320 nm (210 – 298 K)

Beer-Lambert plot

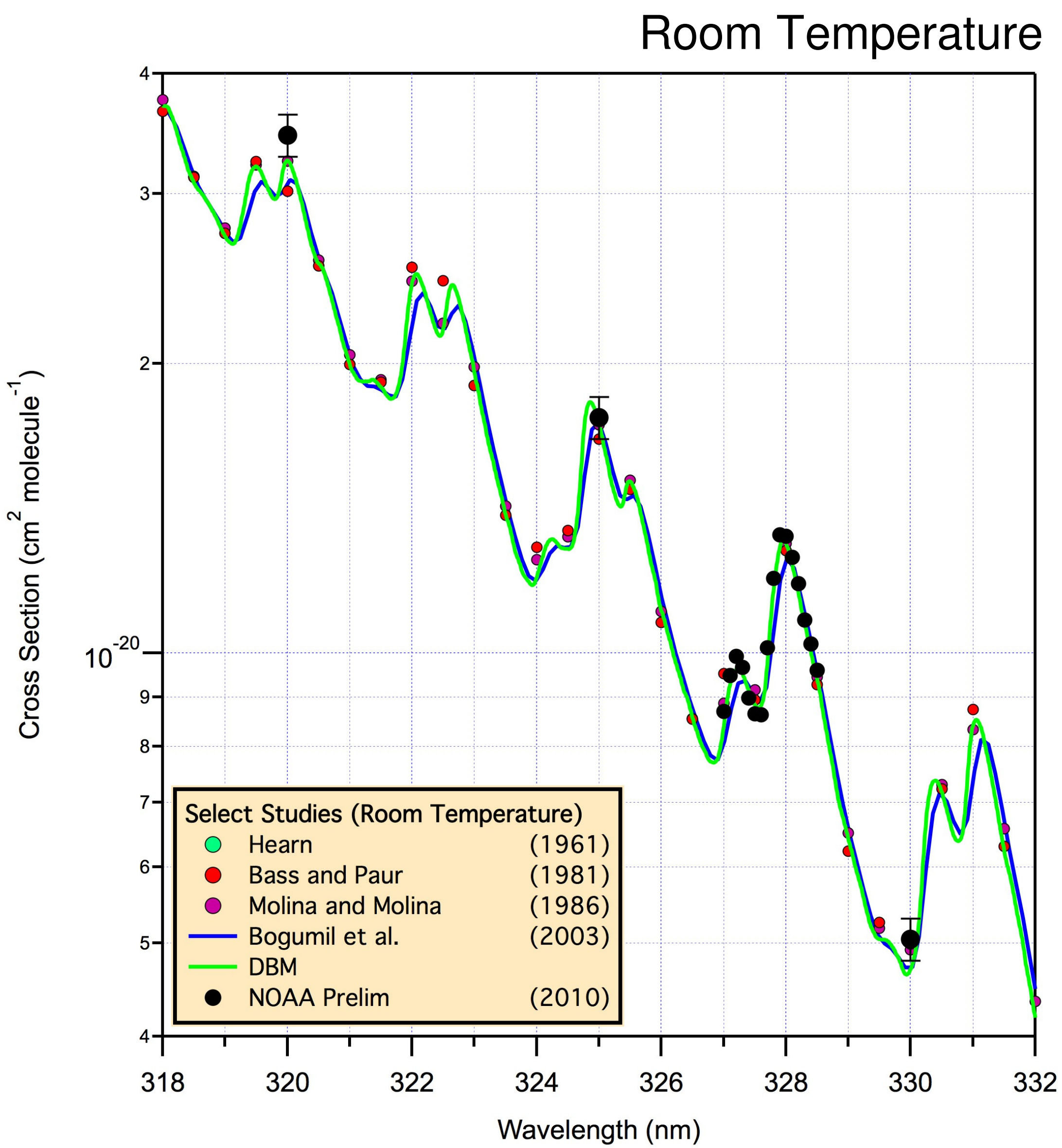




Laboratory Measurements

Preliminary NOAA Measurements

Mandate (3): Initiate and coordinate new laboratory measurements



Differences in wavelength calibration and differential structure apparent

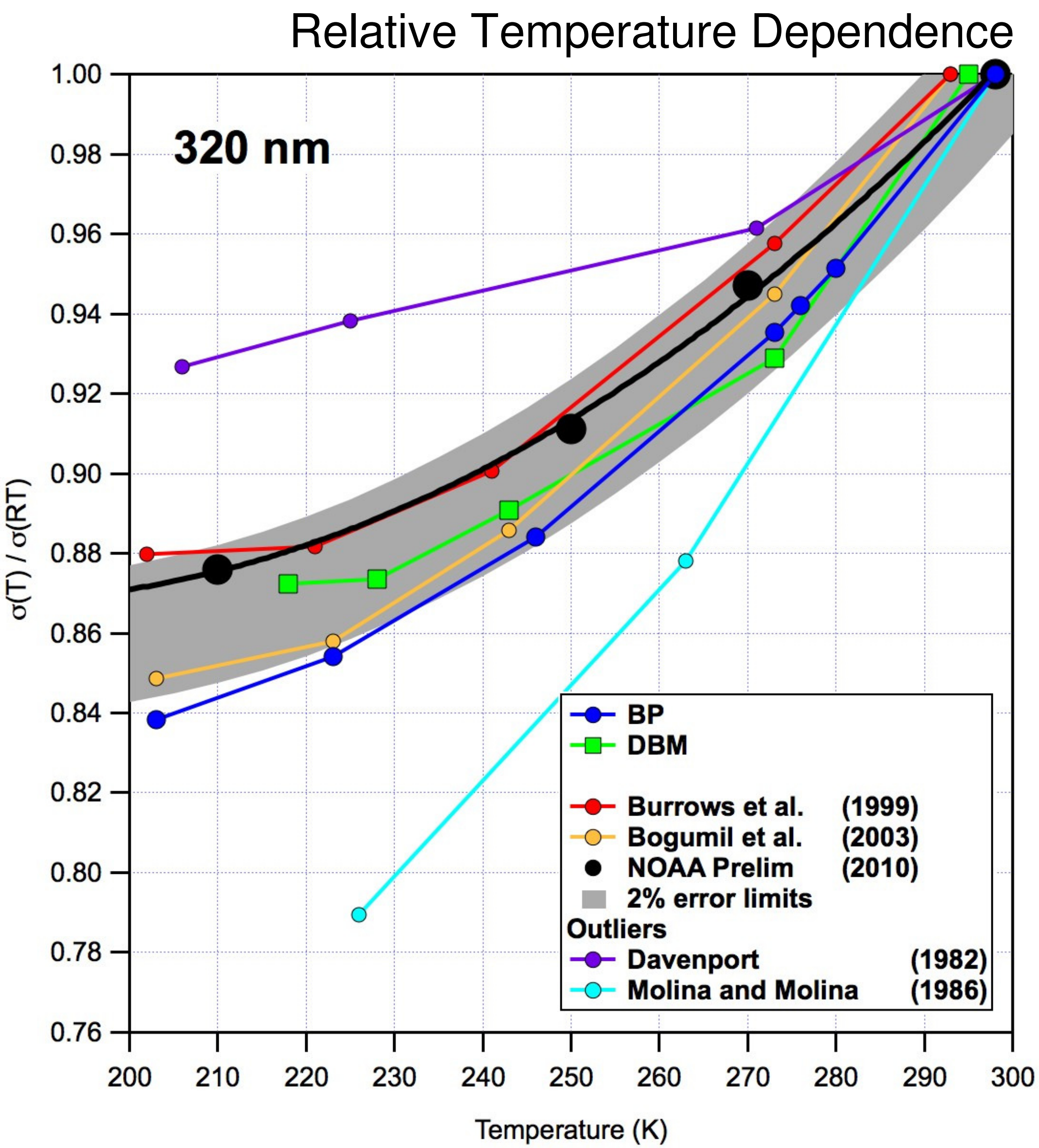
NOAA:
- Precision: ~2%
- Absolute accuracy: 2 – 4 %

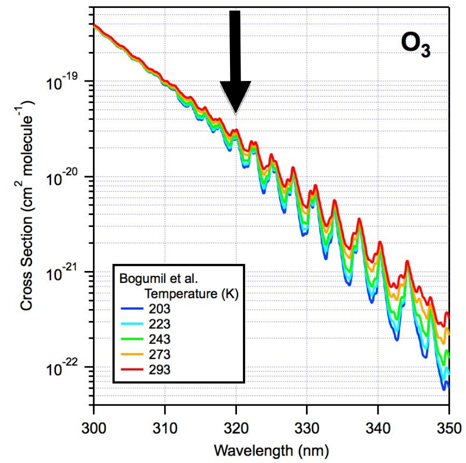
Agreement:
- DBM good
- BP also good

Structure: (*Resolution*)
- Bogumil et al. weaker
- NOAA slightly greater

Laboratory Measurements

Temperature Dependence Measurements





- Weak T-dep at 320 nm
- Good agreement among more reliable data sets

  Precision of the individual measurements ??

  NOAA: ~ 2-3%; limit ~ 1-2% (realistic)
- Largest spread at lowest T

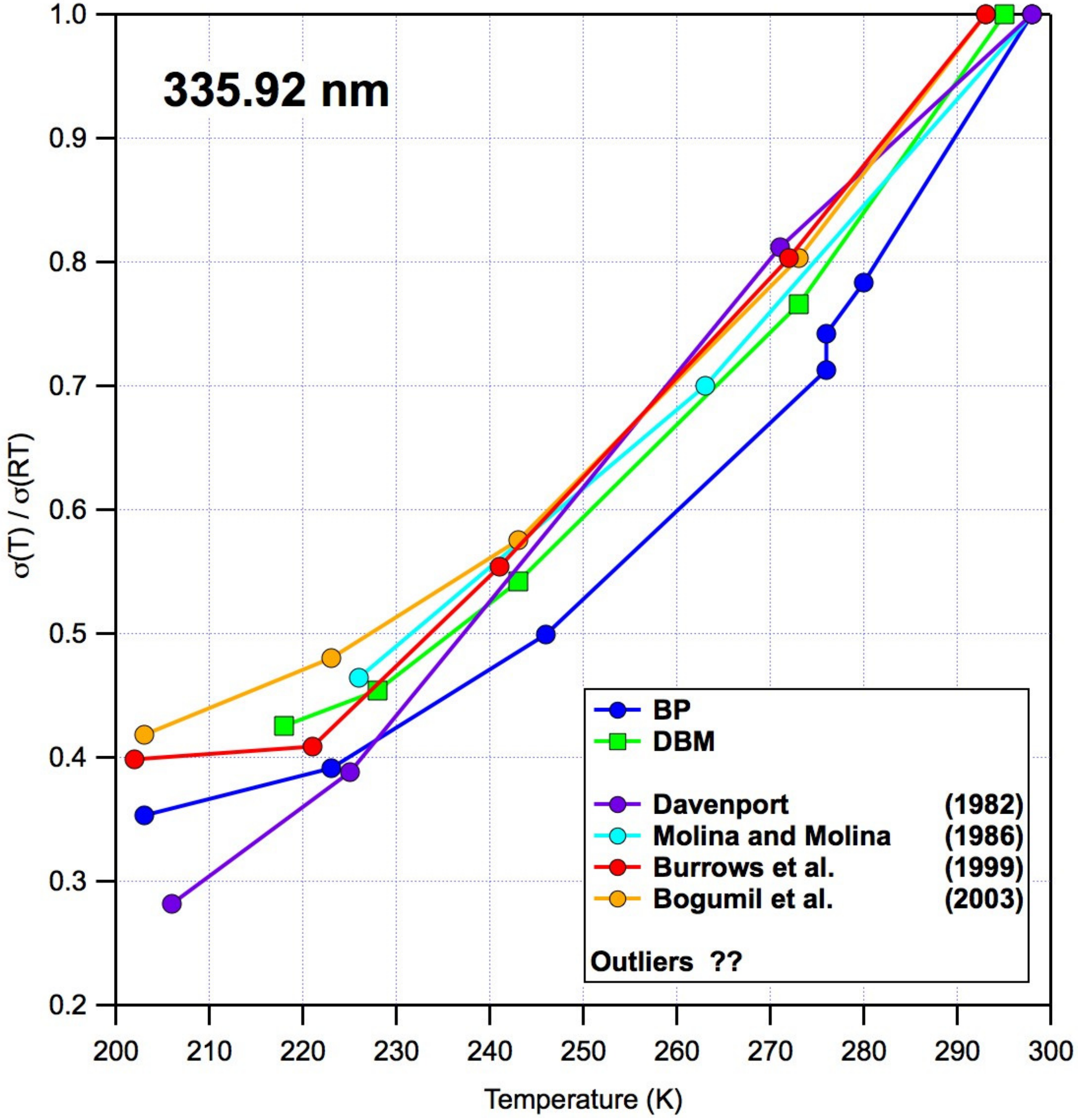
  Measurements show ~4% spread at lowest temperature

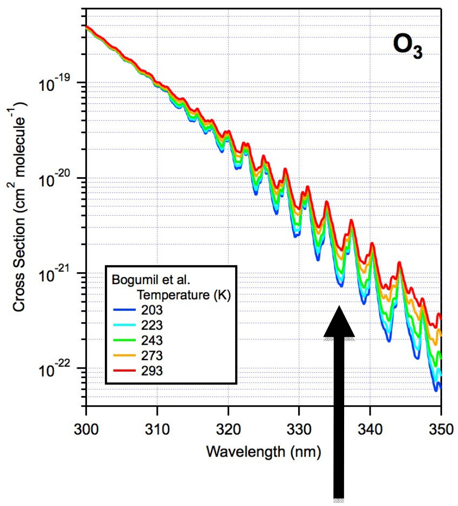
  BP: strongest temperature dependence

CRDS measurements could improve precision of temperature dependence !

Laboratory Measurements

What does it look like at another wavelength?





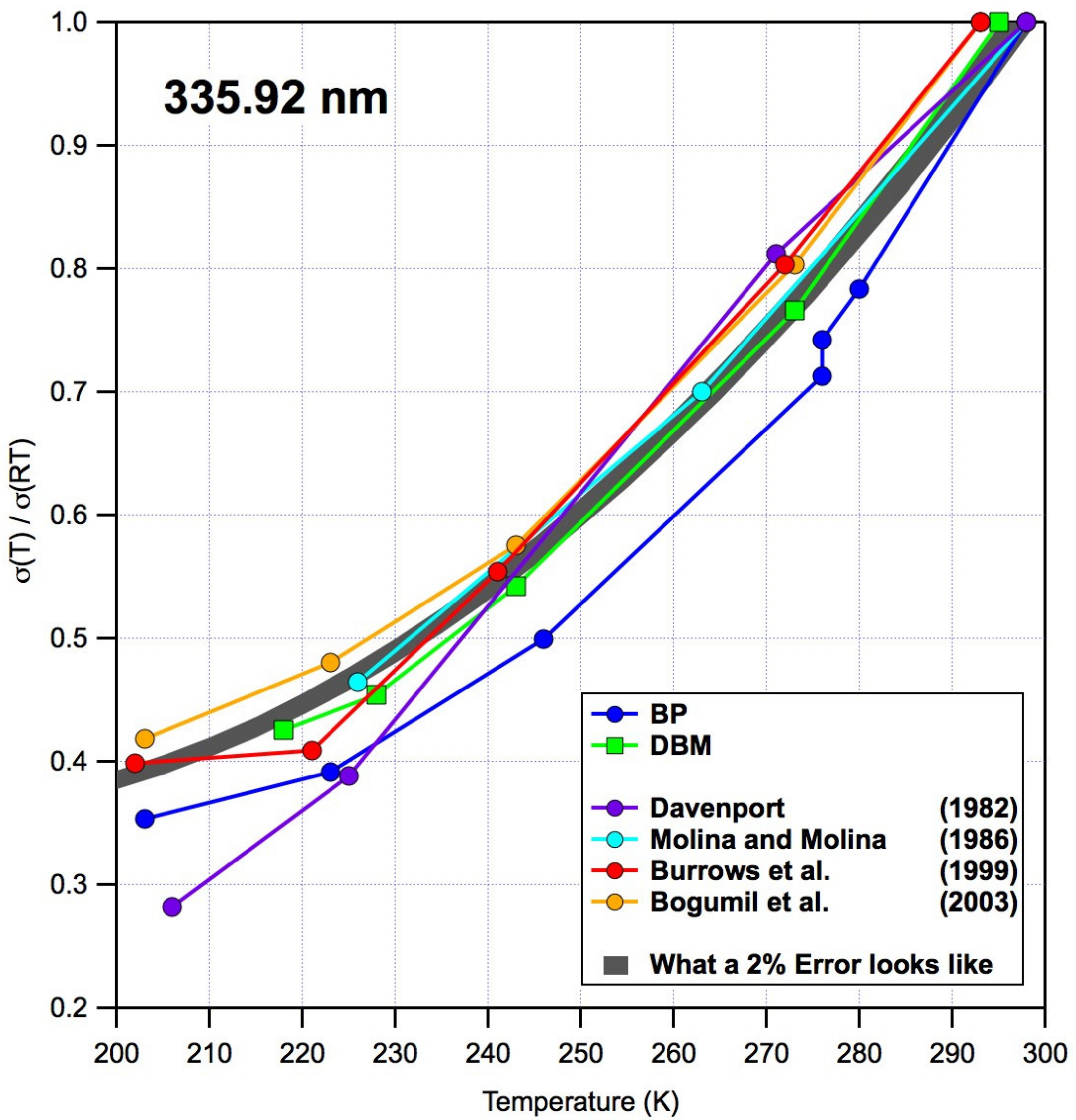
Stronger T-dep in longer wavelength valley

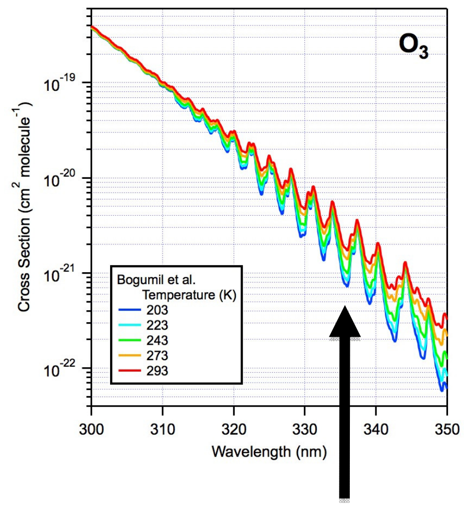
BP: Strongest T-dep

Others: <u>5% spread</u>

Laboratory Measurements

What does it look like at another wavelength?





Shaded Region:
2% Error bar

Precise CRDS laboratory measurements would reduce uncertainty in T-dep

Comments and Future Expert Team Activities

Mandate (3): Initiate and coordinate new laboratory measurements

New Laboratory Studies are on-going

Efforts at NOAA

Validation of existing data sets

Relative measurements

Target: Wavelength (310 – 420 nm) and Temperature (200 – 298 K)

Other Laboratories

Other wavelength regions

Mandate (4): Prepare written summary

Considerations

* Provisions for future refinements

  The perfect data set does not exist (?) and laboratory studies are on-going

* Clearly state NEEDS

  If we want new lab measurements we should say what is needed

* Provide recommended data sets

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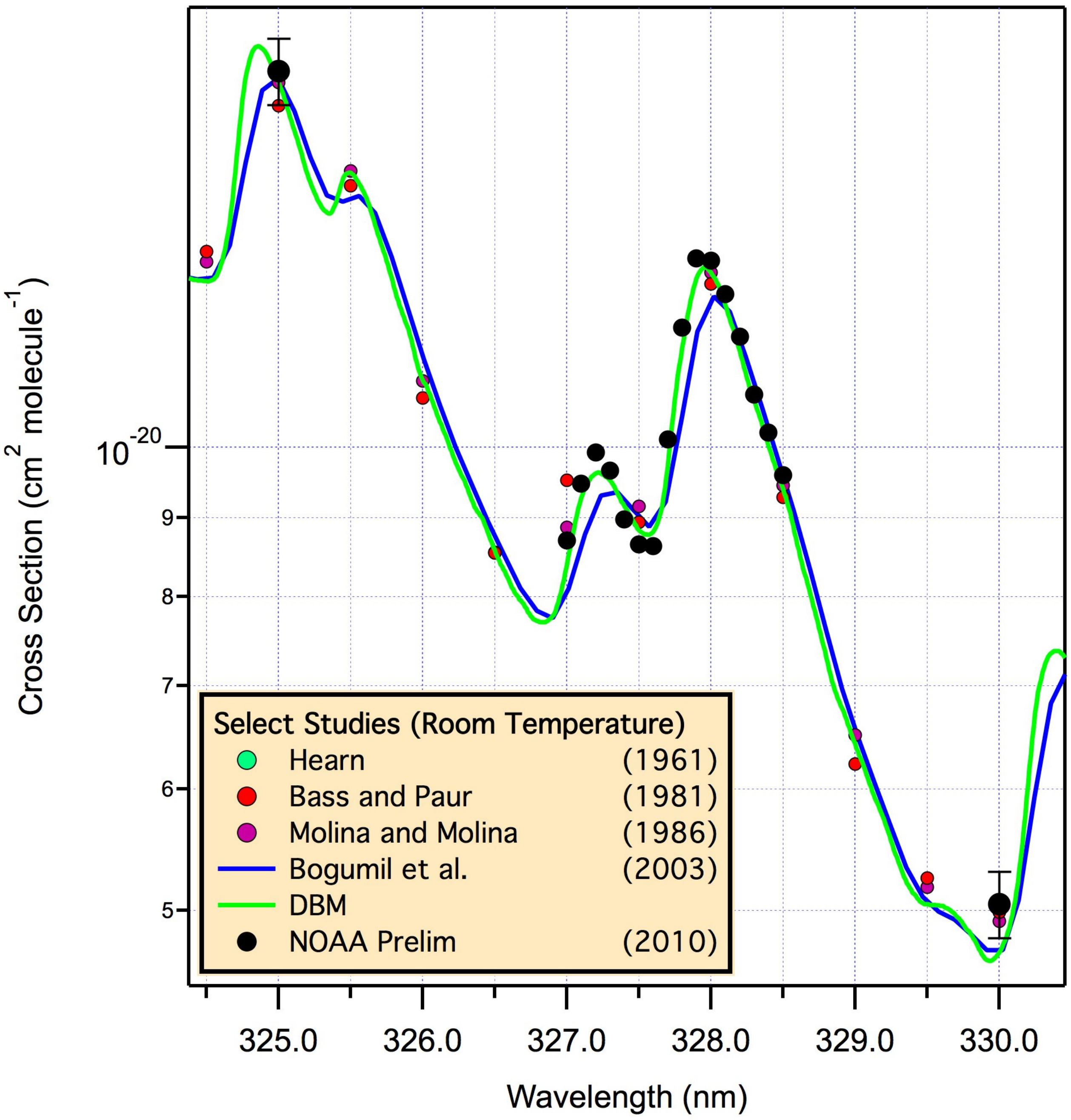
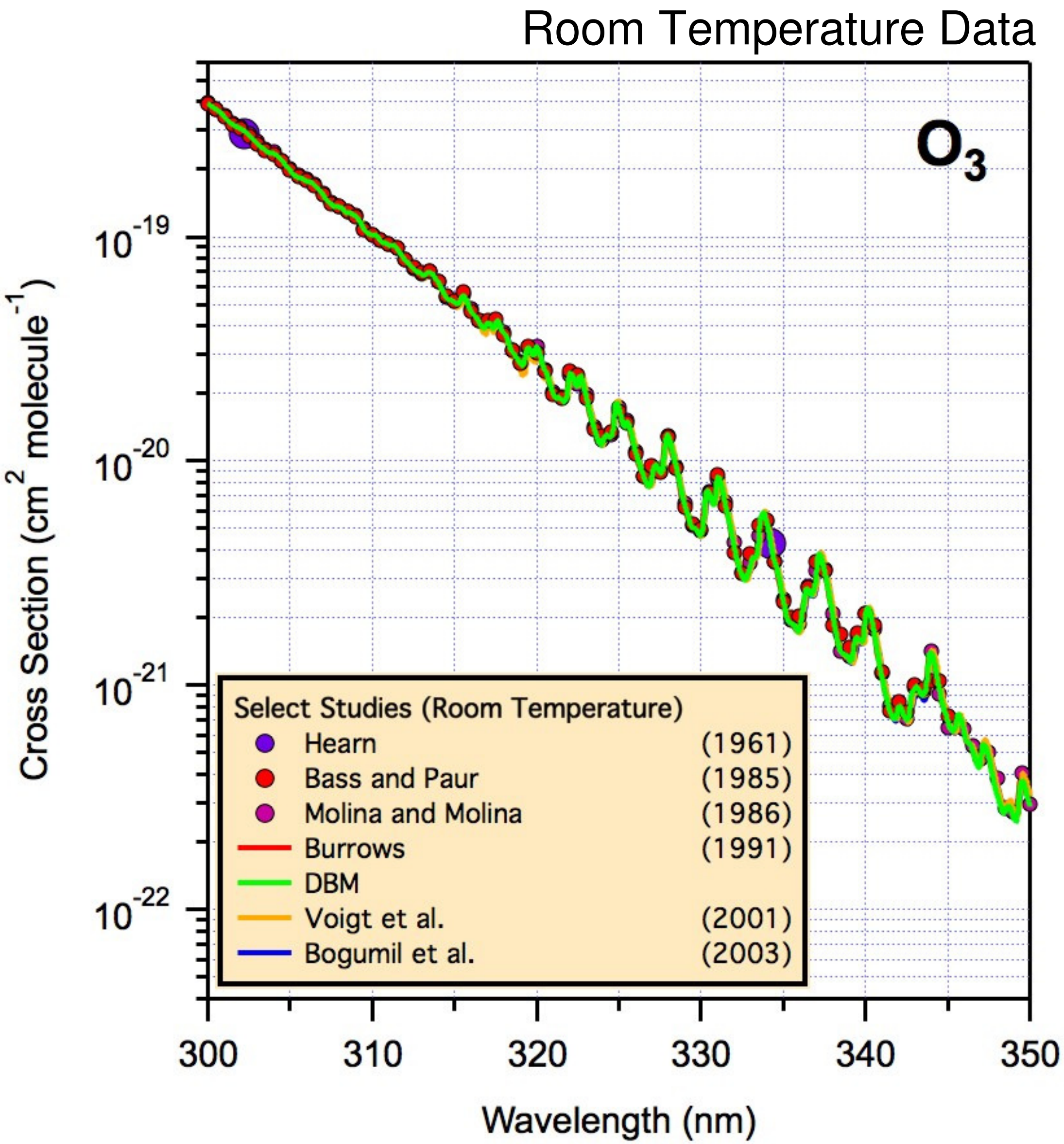


T = 296 K

Wavelength shifts ?

Good agreement with DBM

Laboratory Measurements



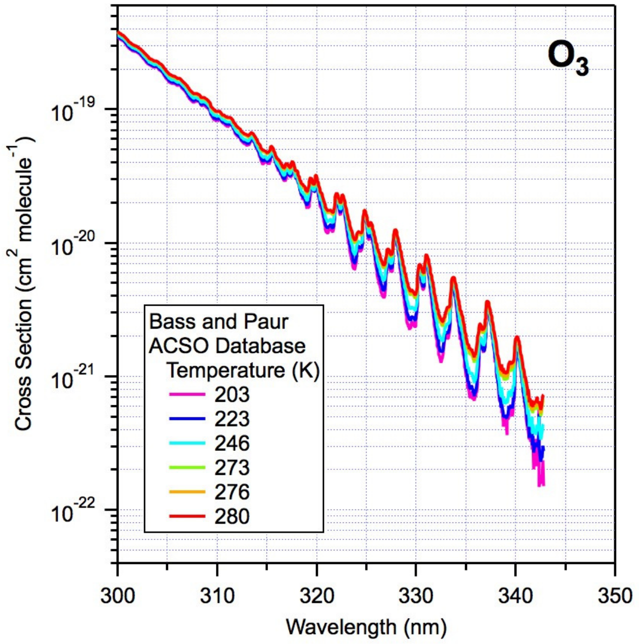
Reasonable agreement
(or is it ?)

Molina and Molina (1986):
1 nm data

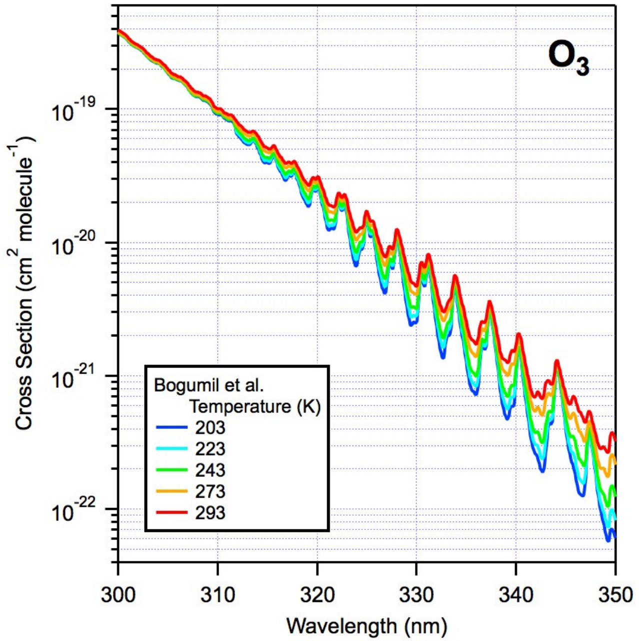
Similar measurements:
Burrows et al.
Voigt et al.
Bogumil et al.

Laboratory Measurements

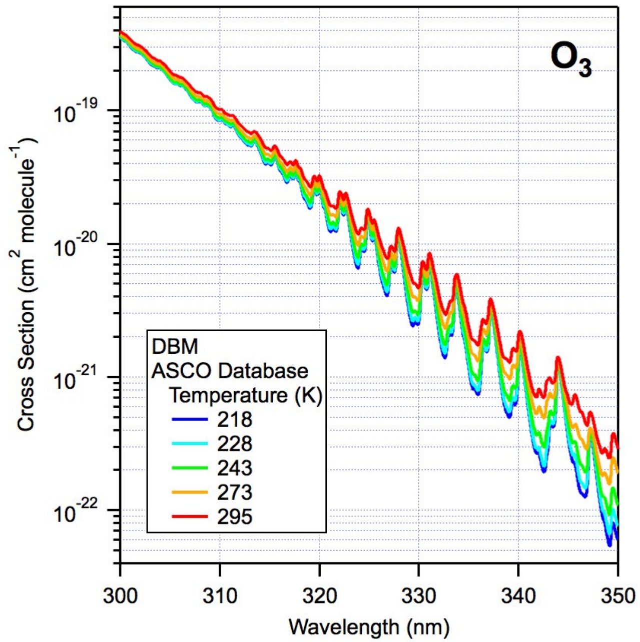
Bass and Paur



Bogumil et al.



DBM



- Temperatures similar but not identical
- Lowest DBM temperature is 218 K