Ozone Absorption Cross Sections
Laboratory Measurements

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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

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**Key Issues Identified for Laboratory Measurements**

<table>
<thead>
<tr>
<th>Absolute Cross Sections</th>
<th>Resolution</th>
<th>Wavelength Calibration</th>
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**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

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**Key Issues Identified for Laboratory Measurements**

**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

Mandate (1): Review available laboratory data


A Sensitive and Versatile Detector for Atmospheric NO₂ and NOₓ Based on Blue Diode Laser Cavity Ring-Down Spectroscopy

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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

NEW CROSS SECTION MEASUREMENT

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

developed over the past decades. Nitric oxide (NO) is most commonly measured by its chemiluminescence (CLD) reaction in excess O₂ to produce electronically excited NO₂. The method is readily extended to NO₂ using a heated molybdenum surface or a photolytic converter to convert some fraction of NO₂ 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, O₂) and vacuum systems. Furthermore, the indirect NO₂ detection may be subject to interference from conversion of compounds other than NO₂ 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 NO₂ conversion fraction. Direct detection methods for NO₂ 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 NO₂ to NO conversion process. During the past decade cavity ring-down spec-
A Sensitive and Versatile Detector for Atmospheric NO$_2$ and NO$_x$ Based on Blue Diode Laser Cavity Ring-Down Spectroscopy

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Relative measurement: 404 nm vs 532 nm
Cross section at 532 nm well-established
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\[ \sigma(404 \text{ nm}) = 1.49 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1} \]
Laboratory Measurements

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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

Excellent agreement with DBM at 404 nm

Illustrates capability of experimental method
Stated precision better than 1%
Possible to extend to other wavelengths
Possible to extend to other temperatures

Developed over the past decades, nitric oxide (NO) is most commonly measured by its chemiluminescence (CLD) reaction in excess O₂ to produce electronically excited NO₂. The method is readily extended to NO₂ using a heated moly-
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
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

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

\[ \text{Slope} = \sigma \]
**Laboratory Measurements**

**Mandate (3):** Initiate and coordinate new laboratory measurements

**Preliminary NOAA Measurements**

**Room Temperature**

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?

BP: Strongest T-dep
Others: 5% spread

Stronger T-dep in longer wavelength valley
Laboratory Measurements

What does it look like at another wavelength?

![Graph showing laboratory measurements at 335.92 nm.](image)

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
$T = 296 \, \text{K}$

Wavelength shifts?

Good agreement with DBM
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

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