Spectroscopy in Atmospheric Science

• Spectroscopy used for many atmospheric science analytical questions
  – Solar spectroscopy
    • Direct absorption or scattering in atmosphere (e.g. DOAS)
    • Remote sensing from space (e.g. UARS, GOME, etc.)
  – UV-vis-IR absorption spectroscopy
    • e.g. for ozone, H$_2$O, CO$_2$, CH$_4$, CO, etc.
  – Fluorescence spectroscopy
    • High specificity, sensitivity, and resolution; lab studies
    • Increasing amount of field-based instruments for important atmospheric species, such as HO$_x$, etc.

• Very specific and sensitive technique(s)!
Ways to measure ozone

• **UV absorption**
  – Modern analyzers (next slide)
  – Historically important: Dobson spectrophotometer
  – Remote sensing from space (back-scattering)

• **IR-absorption**
  – Highly resolving FT-IR of DOAS (rarely used)

• **Chemical methods**
  
  \[
  \text{I}^- + \text{O}_3 \rightarrow \text{IO}_3^- \quad \text{(iodate)}
  \]
  
  \[
  \text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \rightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O} \quad \text{(immediately)}
  \]
  
  \[
  \text{I}_2 + \text{starch} \rightarrow \text{intense blue color} \quad \text{(use colometry)}
  \]

  **Today**: “back”-electrolysis of I$_2$ to I$^-$ \(\text{precise current}\)
Ozone measurements via UV absorption

Figure 11.1. Instrument for measuring ozone concentration by ultraviolet absorption. This instrument has flown on a high-altitude aircraft to measure ozone in the lower stratosphere. The sample air is alternated in the two absorption tubes with air from which the ozone has been chemically removed. The difference in the transmission of the two cells in the two modes supplies the ozone absorption by a sample independently of the lamp intensity or cell transmission (after Proffitt and MacLaughlin, 1983).
**NO/NO\(_{x/y}\)** measurements

1. \[ \text{NO} + \text{O}_3 \rightarrow \{\text{NO}_2\}^* + \text{O}_2 \]

2. \[ \{\text{NO}_2\}^* \rightarrow \text{NO}_2 + \text{hv} \text{ (blue light)} \]

By reducing the pressure, the fraction of \{\text{NO}_2\}^* undergoing fluorescence is increased.

When carried out in a completely dark environment, measuring individual photons is possible!

\[ \Rightarrow \text{NO is measured very sensitively (~0.1 ppb)} \]

\(\text{NO}_x \) (\(\text{NO}_y\)) is measured after converting all \(\text{NO}_2\) (\(\text{NO}_y\)-NO) to NO by a catalyst (heated Au or MoO\(_3\) surface).

\(\text{NO}_x\) can be measured by converting \(\text{NO}_2\) photolytically:

3. \(\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}\(^{(3}\text{P})\)
Standard NO$_2$ fluorescence NO-instrument
CO$_2$/CO measurements

- **IR absorption**
  - \textit{CO$_2$ is a very strong IR absorber}
  - broadband light-source (filament) plus wavelength filter (on major absorption band)
  - highly sensitive and precise measurement (<0.1 ppm)
  - \textit{CO is poor IR absorber}
  - broadband light-source used with “gas-filter”
  - rather insensitive technique (± 30 ppb)

- **Chemical methods**
  - Gas chromatographic separation with selected detection, e.g.
    \[ \text{HgO} + \text{CO} + \text{heat} \rightarrow \text{CO}_2 + \text{Hg} \uparrow \] (UV absorption)
Standard Gas Filter Correlation (GFC) infrared absorption CO-instrument

*Model 48CTL - FLOW DIAGRAM*