

Introduction to Atmospheric Spectroscopy and Spectrum-Matching Technique

Bo-Cai Gao

June 2016
Remote Sensing Division,
Naval Research Laboratory, Washington, DC USA

OUTLINE

- Spectroscopy – Ultra-spectral, hyperspectral, multispectral, spectral resolution & sampling spacing, spectral smoothing
- Spectrum-matching techniques for wavelength and spectral resolution calibrations
- Solar spectral irradiance curve problems
- Finally, a brief summary

The Spectra Were Measured by Dr. John H. Shaw at Oxford University During World War II in 1940s. Unfortunately, Valley (1965) Handbook of Geophysics was cited the most.

68

ATMOSPHERIC RADIATION

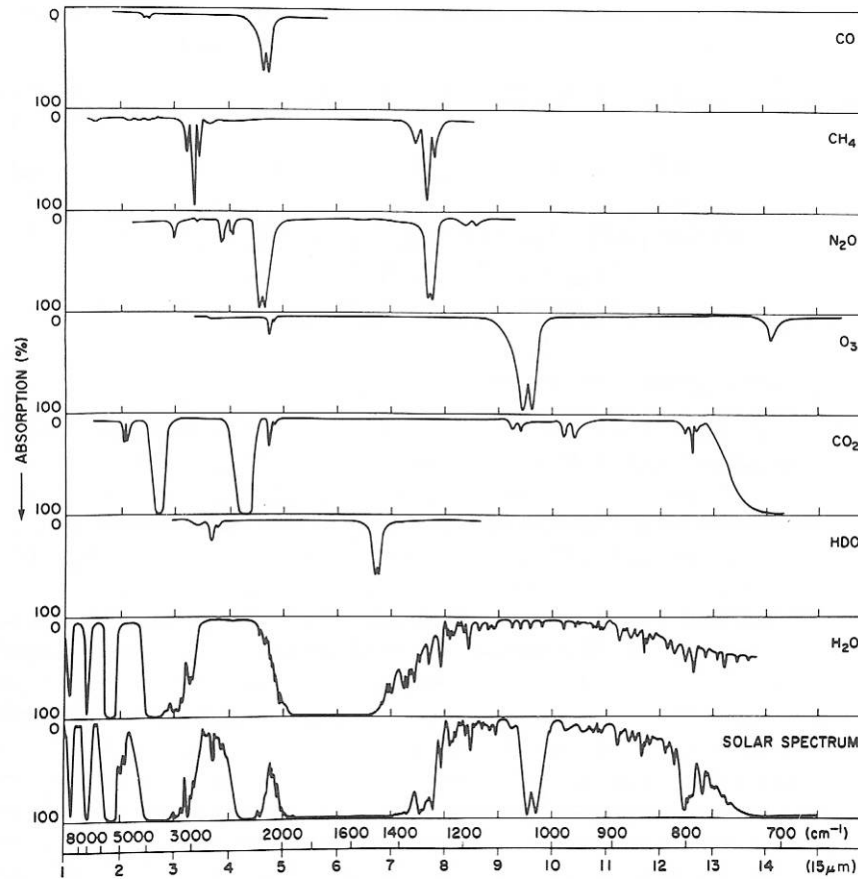


FIG. 3.1. Low-resolution absorption spectrum of the atmosphere. The top six panels are the absorption spectra of important atmospheric species. The bottom panel is a simulated absorption spectrum of the atmosphere. After Valley (1965).

Ultra-Spectrum – having sufficiently high spectral resolution to resolve individual vibration-rotational gas absorption lines.

70

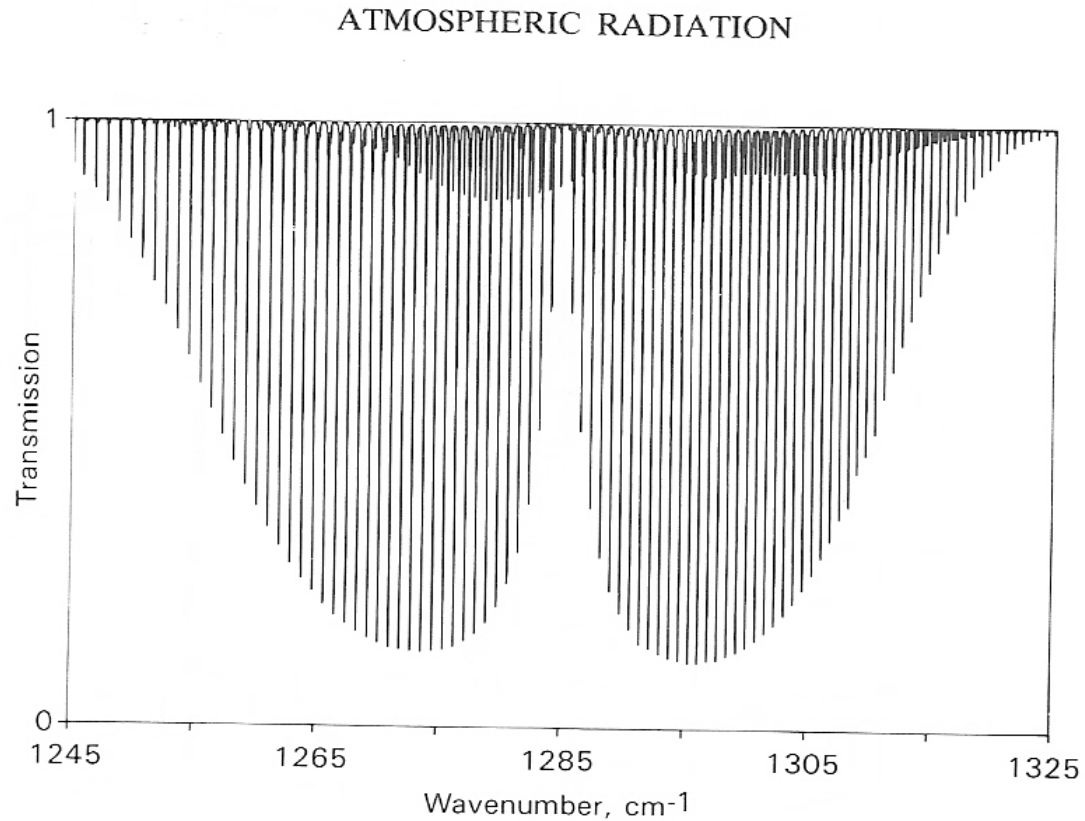
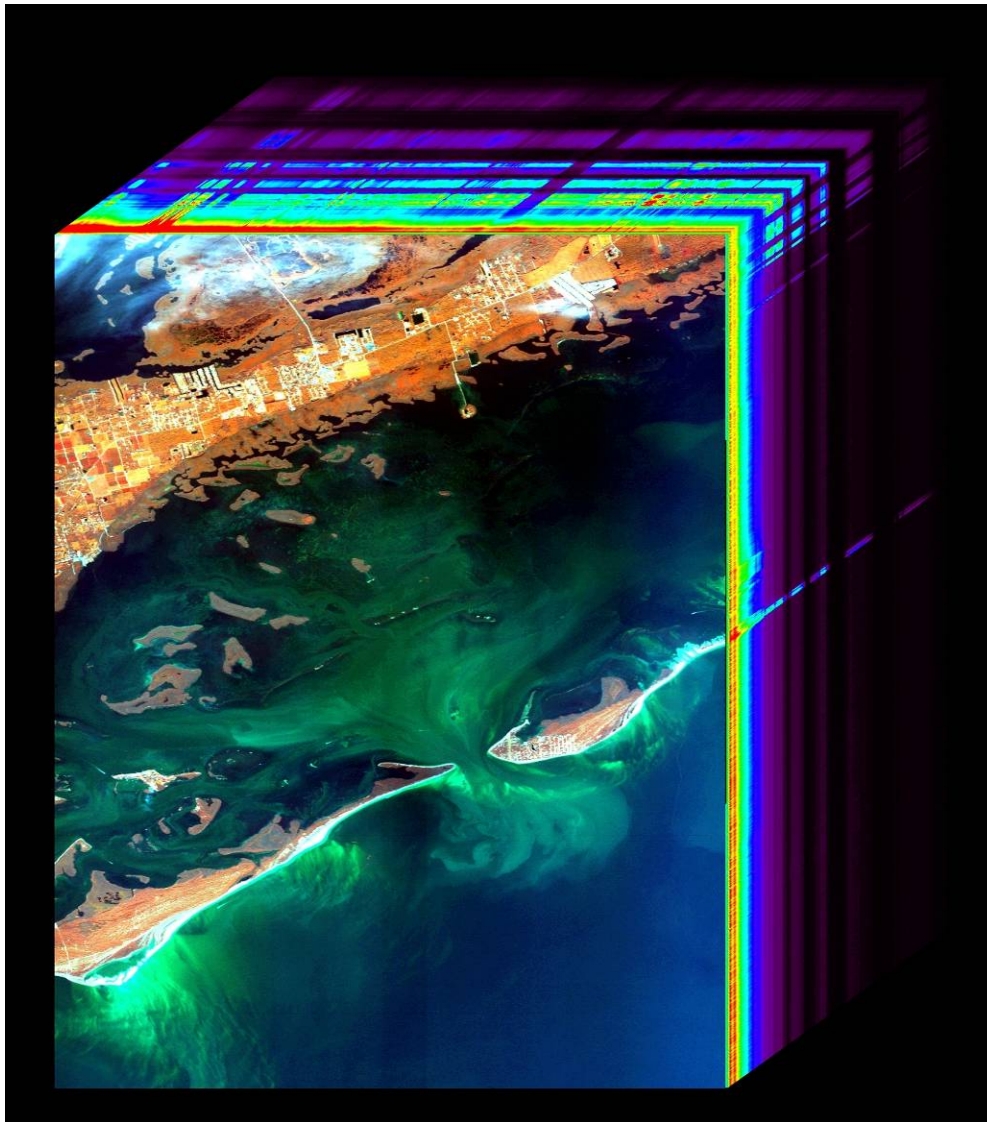


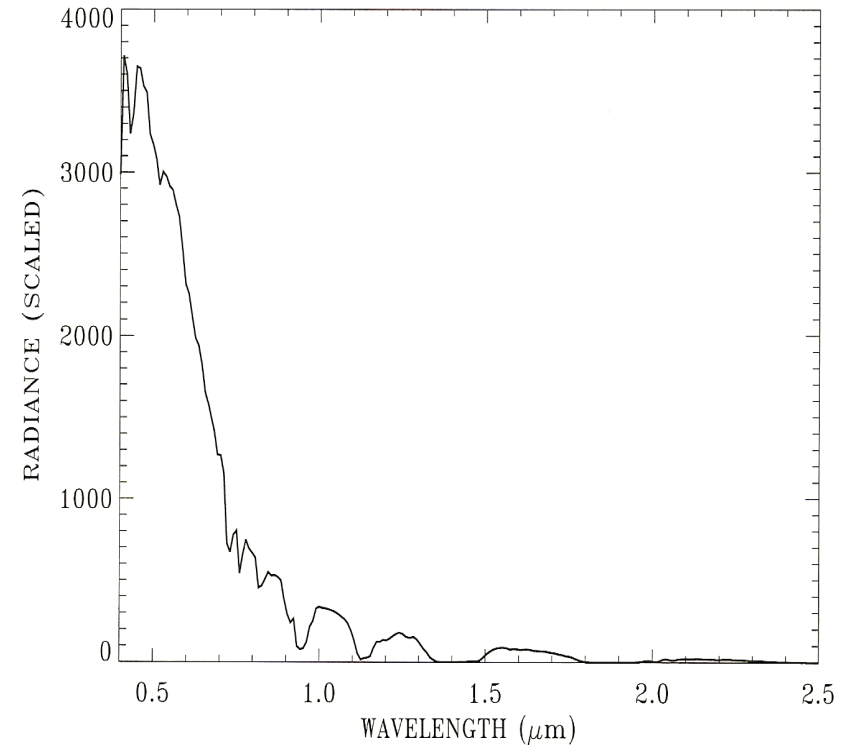
FIG. 3.3. Synthetic spectrum of N_2O near $7.78 \mu\text{m}$. Spectral range: $1245\text{--}1325 \text{ cm}^{-1}$. Altitude of observation: 15 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 1$.

Imaging Spectrometry Concept (Hyperspectrum)



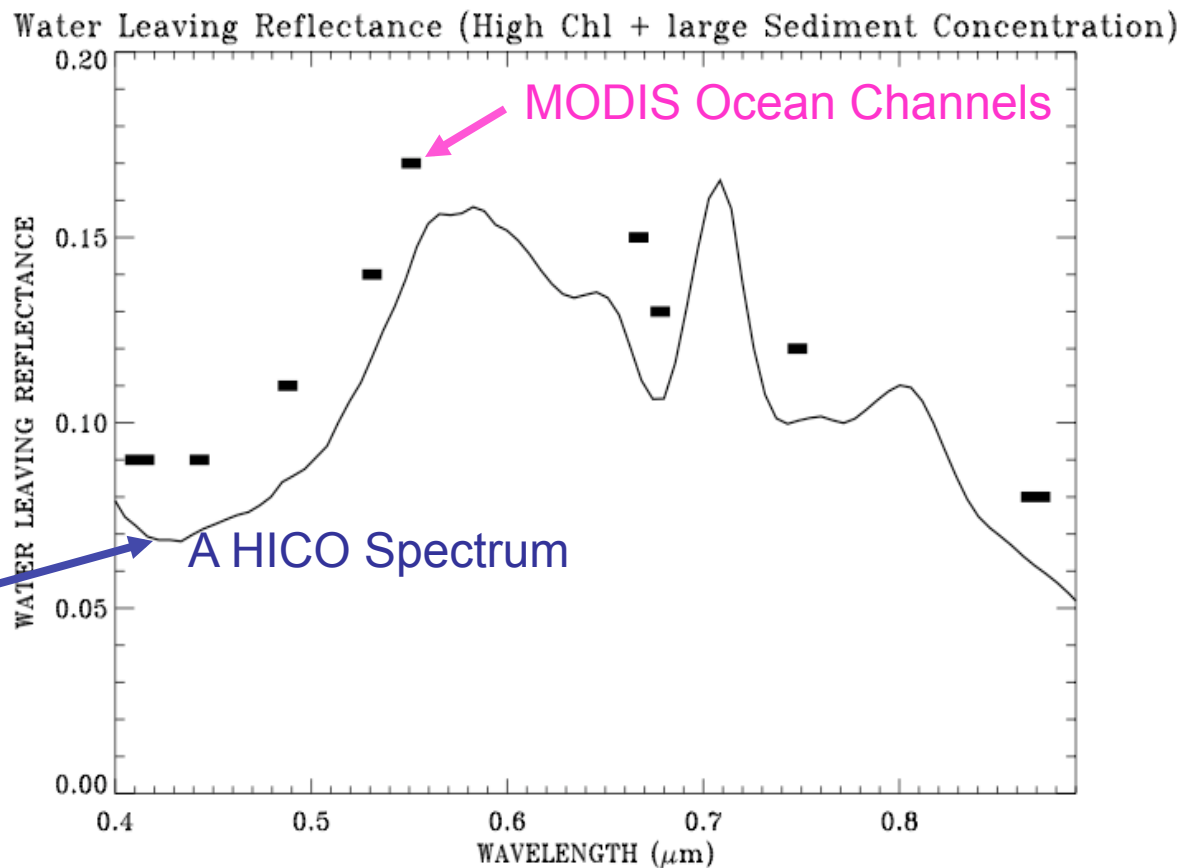
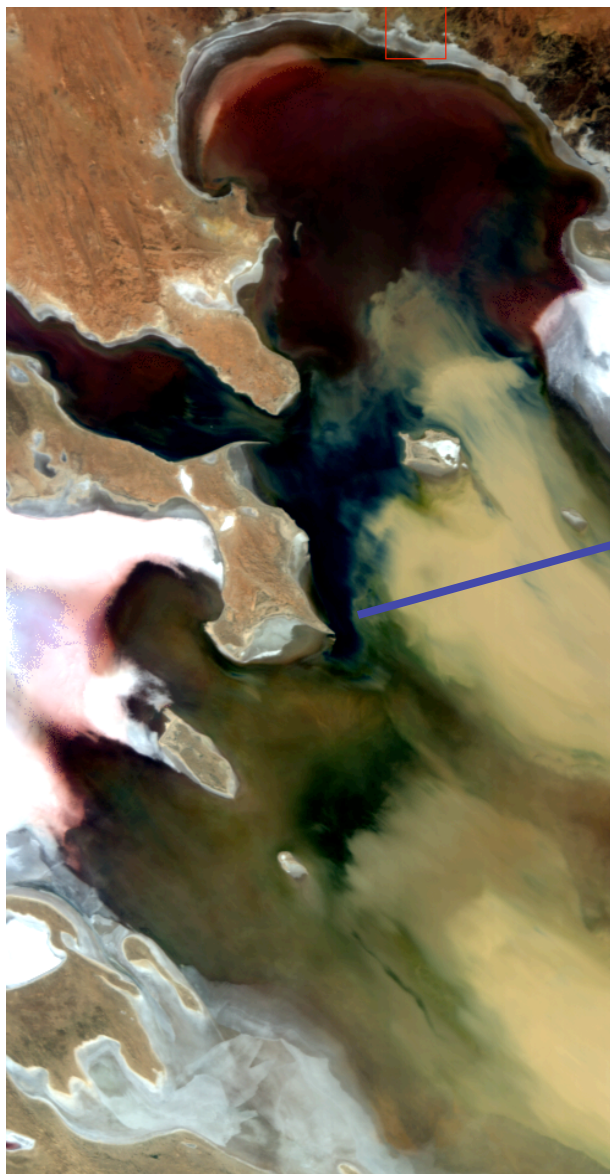
A Sample Spectrum

(Gas absorption bands are resolved, not the individual vibrational-rotational lines.)



Radiances above $1 \mu\text{m}$ are very small over water surfaces. Atmospheric absorption and scattering effects need to be removed in order to recover the water leaving reflectance spectra.

Illustration of Differences Between Hyperspectral & Multi-spectral Data Using HICO and the Multi-channel MODIS Bands



The discrete MODIS ocean channels missed several peaks in the HICO reflectance spectrum. Therefore, MODIS cannot fully characterize the shapes of the spectra acquired over the complex Case 2 waters.

Spectral Resolution & Sampling Interval

- Suppose that a narrow absorption feature needs to be resolved with a spectrometer at a resolution of R , the proper data sampling spacing, S , should satisfy the relationship (Nyquist Sampling):

$$S \leq \frac{1}{2} R$$

If $S > \frac{1}{2} R$, the absorption feature is not properly sampled, and we lose information about the narrow feature (“aliasing” in Fourier Transform Spectroscopy (FTS)).

- In the case of AVIRIS_Classic, 224 bands, spectral resolution = 10 nm, sampling spacing also = 10 nm, **under-sampled**. The new AVIRIS_NG is a properly sampled instrument having over 400 bands to cover the 0.38 – 2.5 micron spectral range.
- For the PACE OCI spectrometer, if the spectral resolution is 5 nm, the sampling spacing should, in principle, be 2.5 nm.

Under-Sampled Simulated Spectra at 5 nm spectral resolution and 5 nm sampling spacing near the 0.76 micron O₂ band region (Gao & Davis, SPIE, 1997)

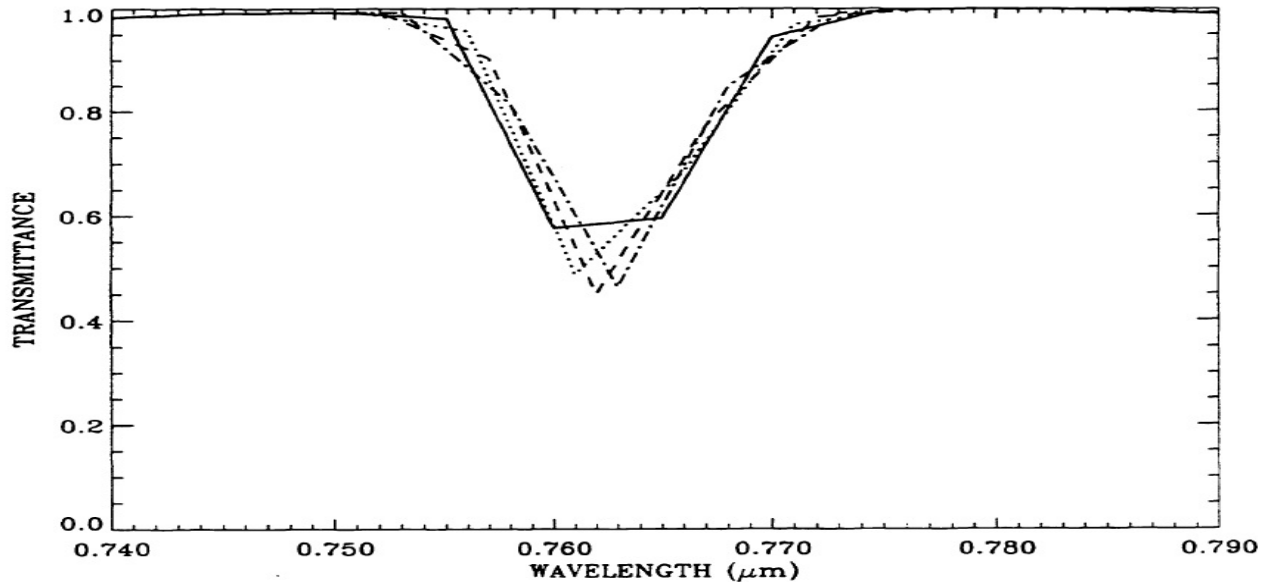


Fig. 7 Four simulated spectra covering the 0.76- μm oxygen band absorption region at the same resolution of 5 nm and the same sampling interval of 5 nm. The sampling grids for the dotted line, dashed line, and dot-dashed line are shifted relative to the solid line by 1, 2, and 3 nm, respectively. All the four spectra are under-sampled. The spectrum with one grid cannot be properly re-sampled to spectrum with another grid due to the under sampling problem.

If the spectra were originally sampled at 2.5 nm spacing, we can properly re-sample the data to any wavelength grids using a gaussian interpolation procedure.

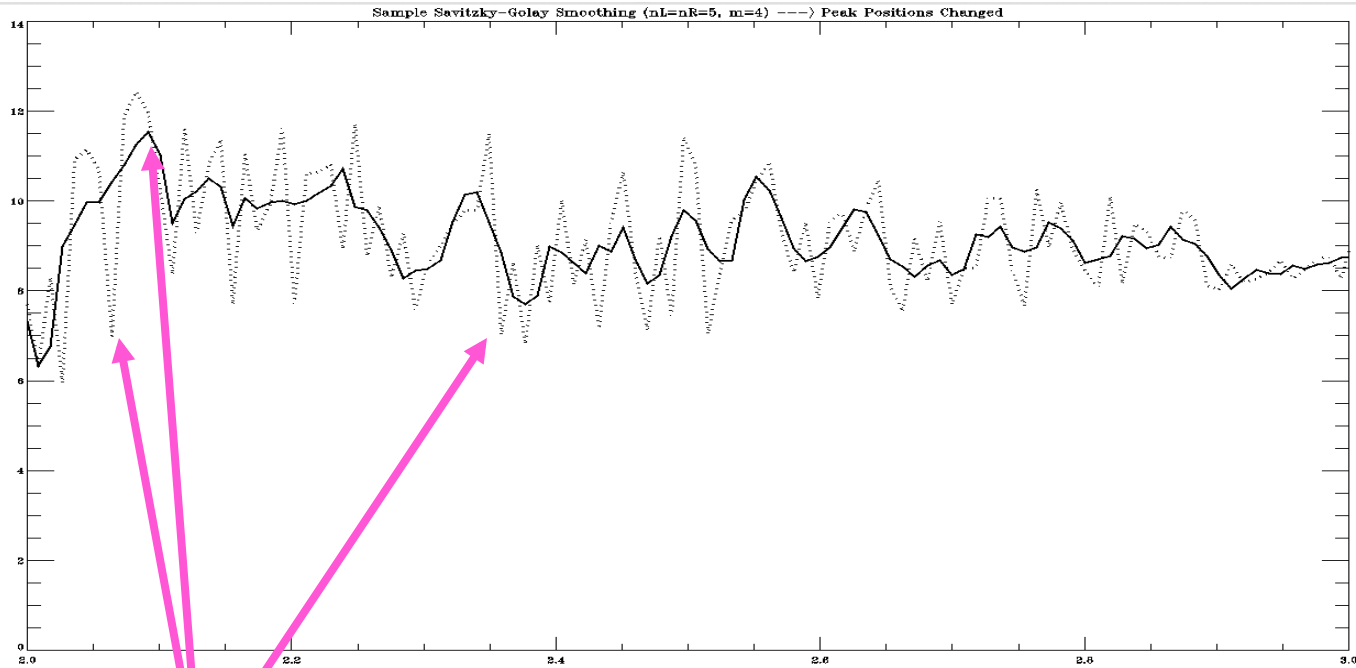
Spectral Smoothing (SG Smoothing)

Smoothing and differentiation of data by simplified least squares procedures.

A Savitzky, MJE Golay - Analytical chemistry, 1964 - ACS Publications

The Perkin-Elmer Corp., Norwalk, Conn. In attempting to analyze, on digital computers, data from basically continuous physical experiments, numerical methods of performing familiar operations must be developed. The operations of differentiation and filtering are ...

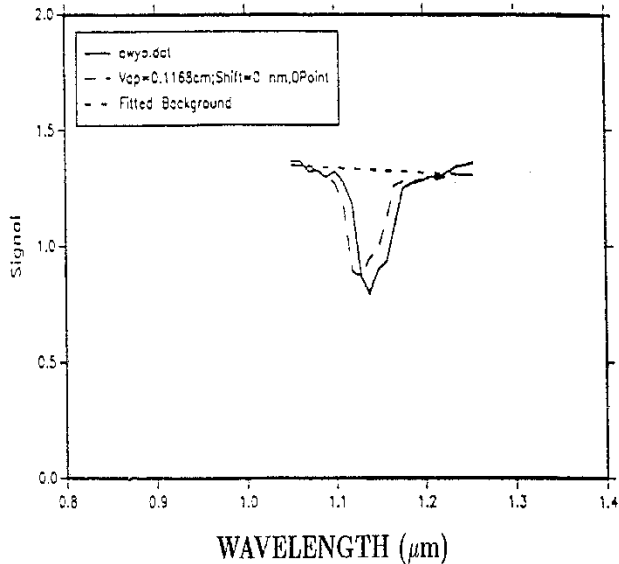
Cited by 10270 Related articles All 8 versions Cite Save More



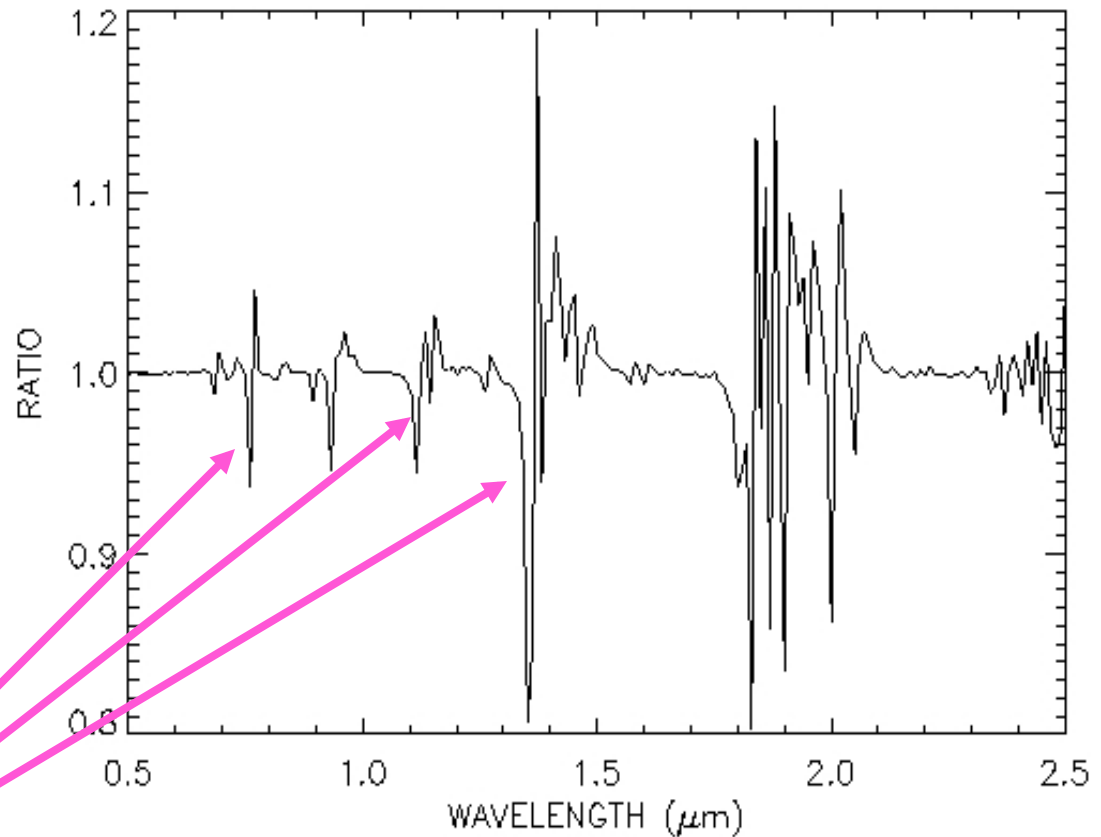
The well-known SG Smoothing does not preserve center positions and widths after smoothing. For grating spectrometer data, Gaussian smoothing filter is more appropriate to use because the instrument response function is very close to a Gaussian curve.

SPECTRUM-MATCHING TECHNIQUE

Sample Fitting of 1988
AVIRIS Spectra



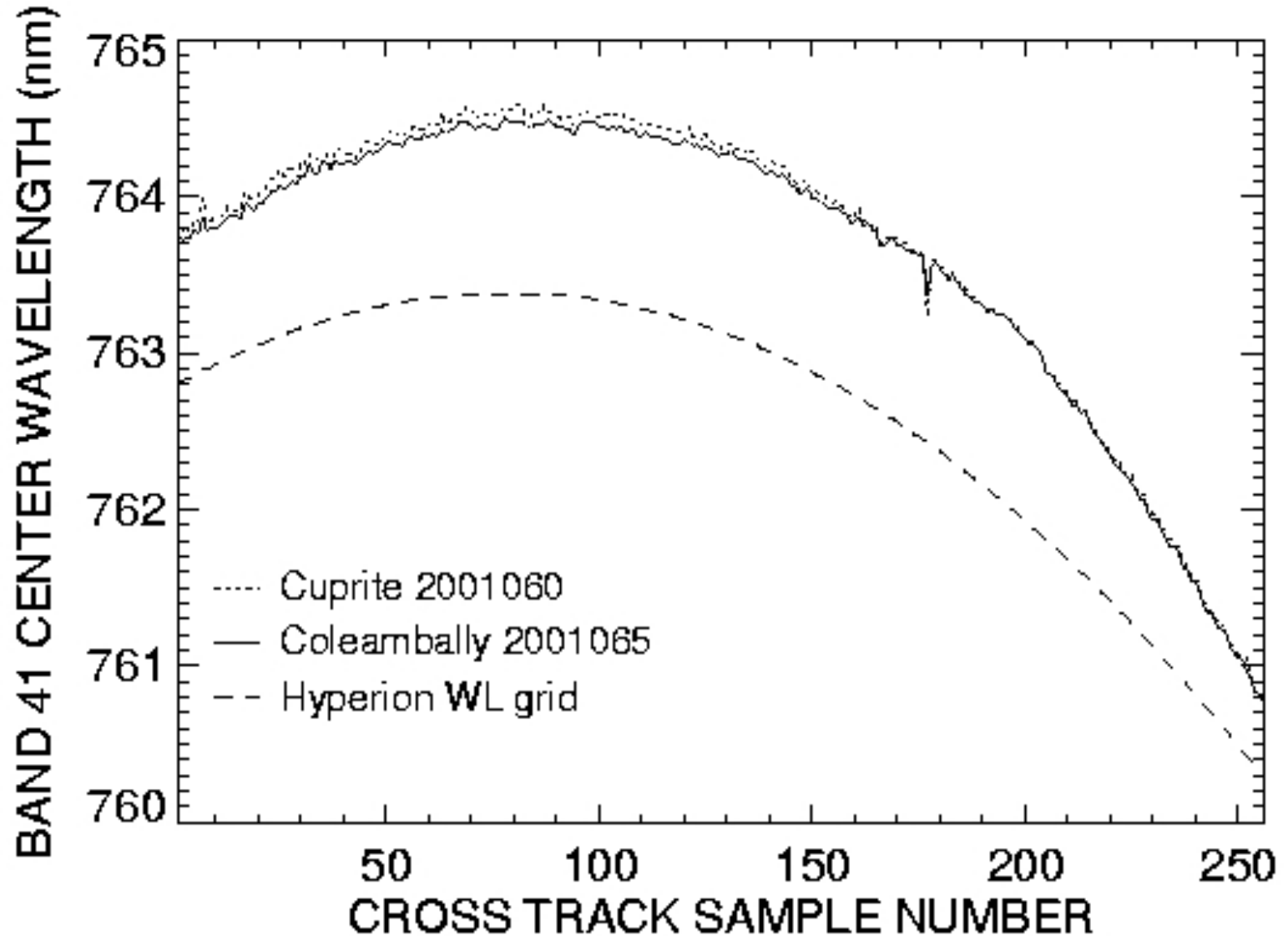
Ratio of Two Spectra with a Wavelength Shift



Spikes appear near the centers of atmospheric gas absorption bands

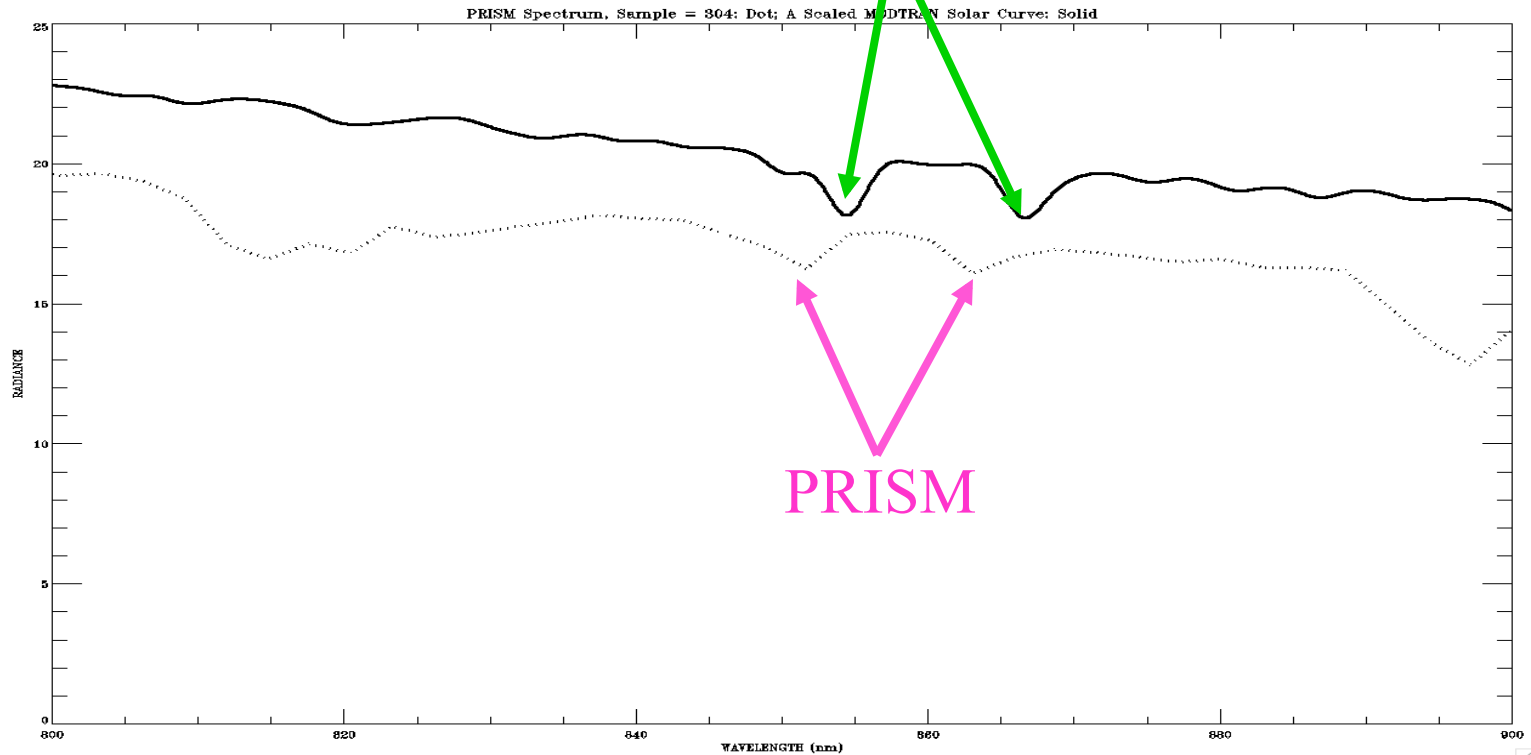
EO-1 Hyperion Wavelength Calibration

Fitting O₂ Band for the Estimation of **Hyperion** Band 41 Center Position in the cross track direction



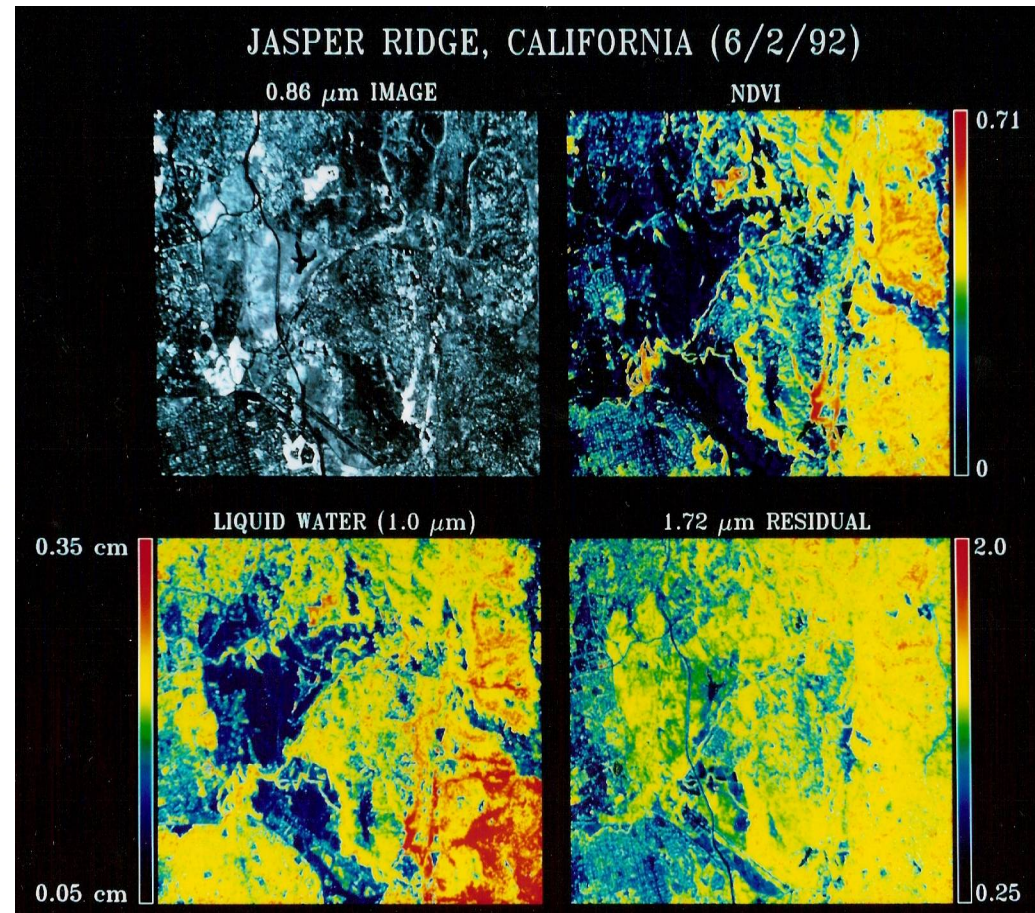
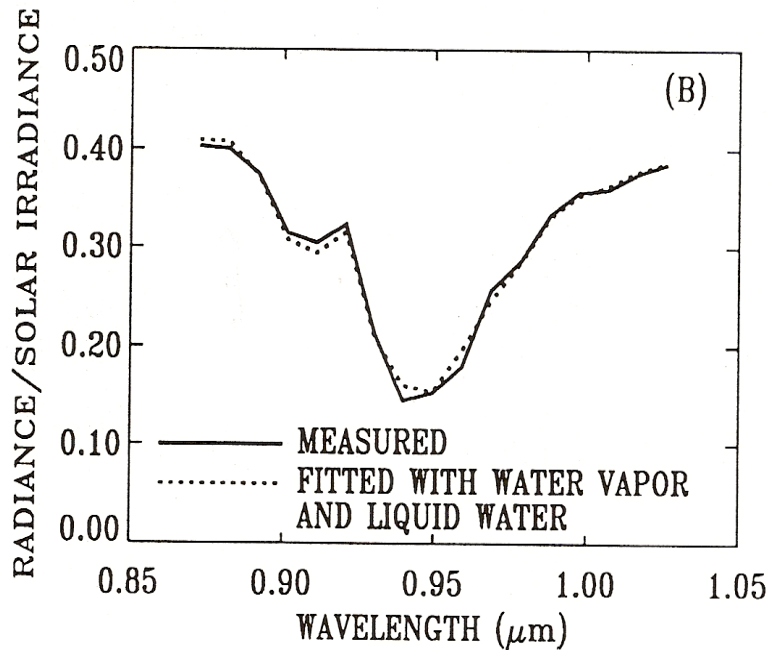
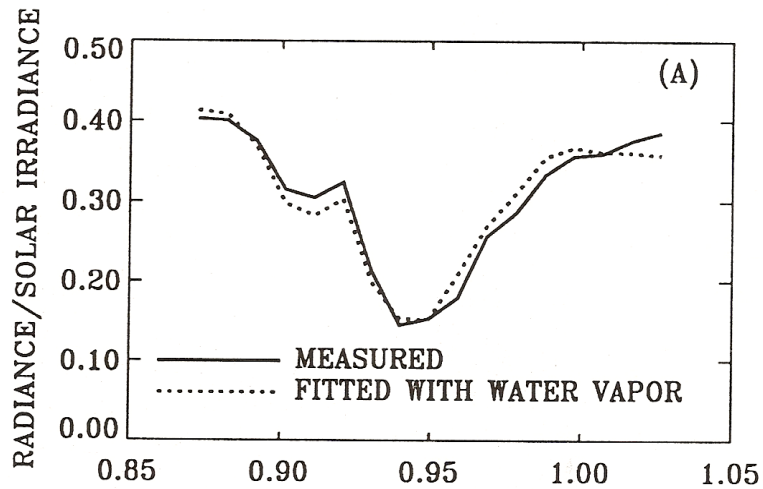
Solar lines useful for wavelength calibrations

Comparison between solar lines in an early **PRISM** data set and in a **MODTRAN** solar curve

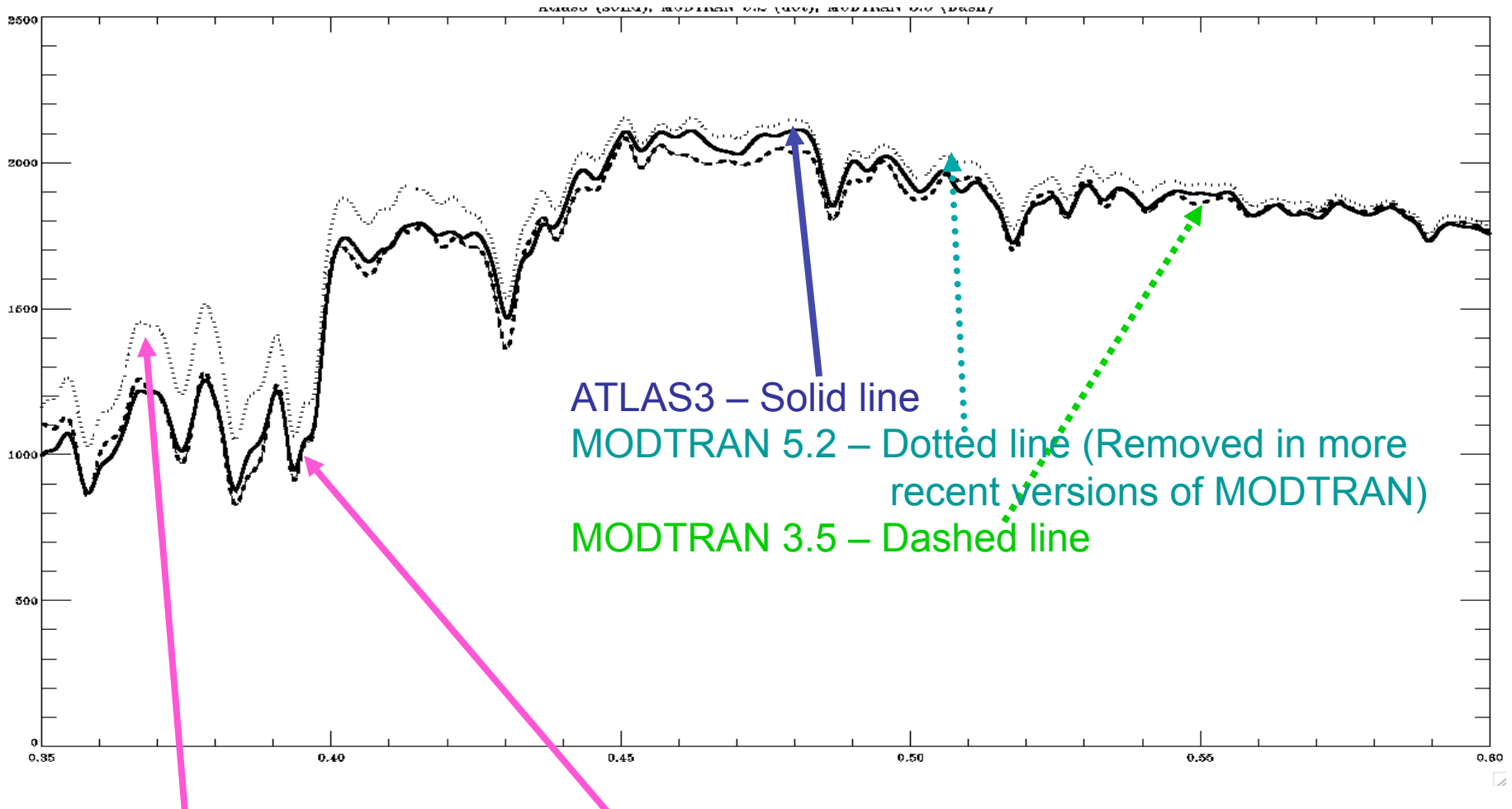


The PRISM wavelength file was soon refined to remove the wavelength shift problem.

Fitting spectrum over green vegetation area with and without including liquid water



Comparisons of three solar irradiance curves: Atlas3, MODTRAN 5.2,
& MODTRAN 3.5
(The data were smoothed to 3 nm spectral resolution for comparison)



The magnitudes and spectral shapes are very different for the 3 standard solar irradiance curves in the 350 – 600 nm wavelength range.

Summary

- In this presentation, I discussed various issues on spectroscopy, such as ultra-spectral, hyperspectral, multispectral, spectral resolution, sampling spacing, and spectral smoothing. I illustrated spectrum-matching techniques for wavelength and spectral resolution calibrations, and discussed problems with standard solar irradiance curves.
- Finally, thanks for your attention!

Introduction to Spectroscopy

- At present, the terms “ultra-spectral, hyperspectral, and multi-channel imager” are often used in the scientific community.
- Ultra-spectrum – sufficiently high spectral resolution to resolve individual vibration-rotational gas absorption lines. The spectrum-matching technique was invented in 1970s in the ultra-spectral research community, for developing the HITRAN line-by-line database.
- Hyperspectrum – medium resolution to resolve absorption bands of atmospheric gases and surface minerals. I first introduced the spectrum-matching technique to the hyperspectral research community in late 1980s for supporting the NASA HIRIS Project.
- Multi-channel imager – e.g., AVHRR, MODIS, VIIRS, discrete channels, no contiguous spectral coverage.
- PACE – Two components, an imaging spectrometer + a SWIR multi-channel imager

Spectrum-Matching Technique Developed in 1970s

A Nonlinear Least Squares Method of Determining Line Intensities and Half-widths

Y. S. CHANG and J. H. SHAW

Department of Physics, The Ohio State University, Columbus, Ohio 43210

A nonlinear least squares method of retrieving line intensities and half-widths from spectra degraded by a finite instrumental resolving power is discussed. Examples of the applications of this technique to obtain the parameters of a single isolated line and of an overlapping pair of lines are presented.

Index Headings: Computer, applications; Infrared; Methods, analytical; Techniques, spectroscopic.

INTRODUCTION

Rotation-vibration bands of gases occurring in the infrared region of the spectrum typically consist of many individual lines each characterized by a position, intensity, and shape. Near room temperature and at pressures greater than a few torr, the Lorentz expression is often used to represent the line shape,

$$k(\nu) = \frac{S\alpha}{\pi[(\nu - \nu_0)^2 + \alpha^2]} \quad (1)$$

where $k(\nu)$ = absorption coefficient at frequency ν , $S = \int_{-\infty}^{\infty} k(\nu) d\nu$, is the line intensity, 2α = separation between the frequencies at which the absorption coefficient is $k_{\max}/2$, and ν_0 = position of the line center.

This usually gives a good description of the line shape within a few half-widths of the line center, although deviations have been observed at greater distances.^{1,2}

There have been numerous determinations of line half-widths and intensities since these parameters are required in order to predict the absorbance by gases and they can be used to derive information concerning molecular structure and intermolecular forces.

The measurements typically consist of measuring the absorption spectrum of a known pathlength l of a gas sample containing a partial pressure P_a of the absorbing gas and a partial pressure P_b of a broadening gas. The total pressure $P = P_a + P_b$, and the amount of the

absorbing gas u (atm-cm at STP) = $l \frac{P_a K_0}{P_a K}$, where P_a and K_0 are standard pressure and temperature and K is the temperature of the sample.

A typical spectrum of an isolated line of a homogeneous gas sample obtained with a grating spectrometer and displayed by using a paper chart recorder, is shown in Fig. 1. The pen deflection is shown as a function of frequency. The observed "spectrum," $I(\nu)$, is shown as the middle curve, the top curve, $I_0(\nu)$, corresponds to the spectrum which would be obtained with no absorber present, and the bottom curve, $O(\nu)$, corresponds to the spectrum obtained if the absorber were completely opaque.

Auxiliary experiments, information, or guesses are usually required to estimate both $I_0(\nu)$ and $O(\nu)$. Once these have been obtained the spectral transmittance $T(\nu)$ and absorbance $A(\nu)$ are given by

$$A(\nu) = 1 - T(\nu) = 1 - \frac{I(\nu) - O(\nu)}{I_0(\nu) - O(\nu)}$$

where $[I_0(\nu) - O(\nu)]$ is proportional to the spectral radiant power incident on the sample and $[I(\nu) - O(\nu)]$ is proportional to the transmitted power. If the width of the spectral response function of the spectrometer is much less than the width of the spectral line so that there is no degradation of the line shape then

$$T'(\nu) = \frac{I(\nu) - O(\nu)}{I_0(\nu) - O(\nu)} = \exp[-k(\nu)u], \quad (2)$$

where $T'(\nu)$ represents the true monochromatic transmittance of the sample.

Until recently the widths of the spectral response functions of most spectrometers were greater than the widths of the lines being observed and the appearances of the spectra were modified by the instrument. Interferometers and tunable lasers can now produce spectra in which there is essentially no degradation in resolution and the line widths and intensities can be determined directly from the spectra provided the shapes of $I_0(\nu)$ and $O(\nu)$ are known.

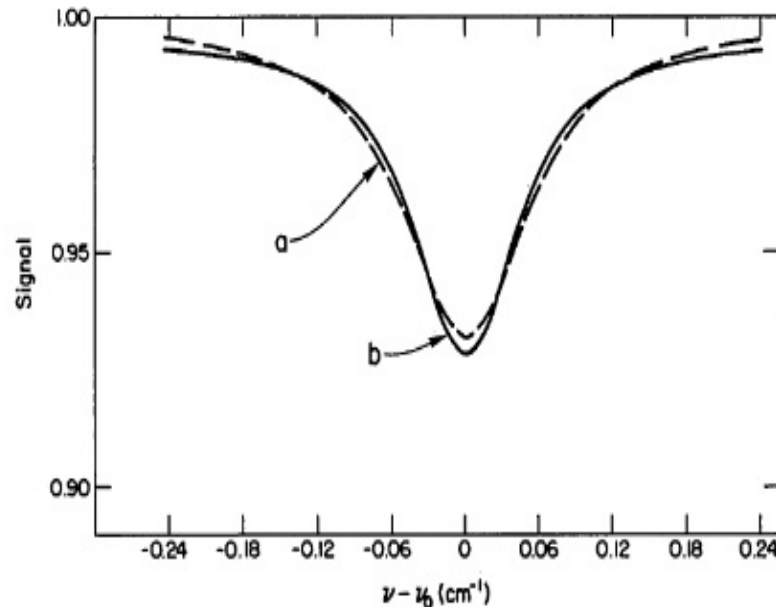


Fig. 2. Curve a, Lorentz-shaped line, width 0.06 atm⁻¹; curve b, best fit to the line in curve a obtained by retrieving the background and line intensity and assuming a width of 0.05 cm⁻¹.

Received 1 November 1976.

Volume 31, Number 3, 1977

APPLIED SPECTROSCOPY 213

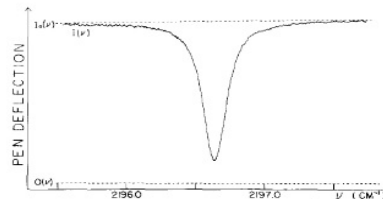


Fig. 1. Observed spectrum of the R14 line of ¹³C¹⁶O 1-0 band at 2196.666 cm⁻¹ obtained from a sample of 10.0 Torr CO and 740.0 Torr N₂ in a 7.6-cm cell. The estimated positions of $O(\nu)$ and the retrieved positions of $I_0(\nu)$ are shown ($\delta = 0.064$ cm⁻¹).

Gauss function is assumed. The results presented here were obtained by assuming

$$\sigma(\nu, \nu') = \exp \left[-4 \ln 2 \left(\frac{\nu - \nu'}{\delta} \right)^2 \right], \quad (4)$$

where δ is the full width of the Gauss function at half its maximum value. Then, since

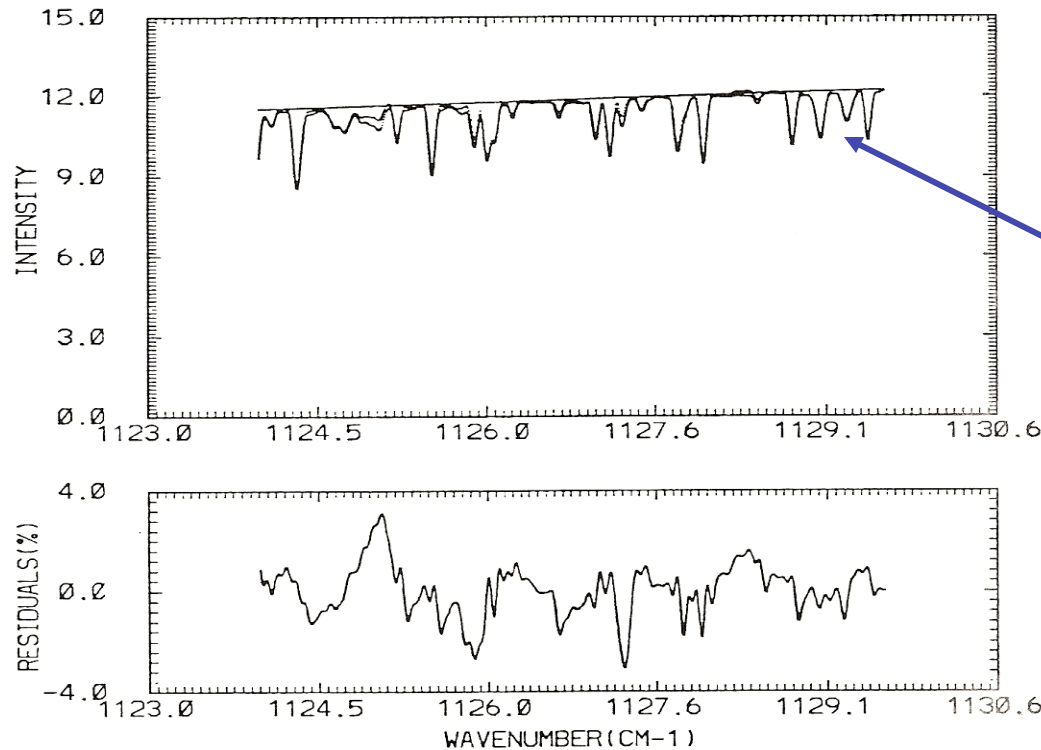
$$\int_{-\infty}^{\infty} \sigma(\nu, \nu') d\nu' = \int_{-\infty}^{\infty} \exp \left[-4 \ln 2 \left(\frac{\nu - \nu'}{\delta} \right)^2 \right] d\nu' = \left(\frac{\delta^2 \pi}{4 \ln 2} \right)^{1/2}, \quad (5)$$

Eq. (3) can be written

$$T(\nu) = \frac{I(\nu) - O(\nu)}{I_0(\nu) - O(\nu)} = \left(\frac{\delta^2 \pi}{4 \ln 2} \right)^{-1/2} \int_{-\infty}^{\infty} \exp$$

(6)

Development of a nonlinear least squares spectrum-matching technique to retrieve column atmospheric gas amounts



The matching technique allowed automated retrieval of minor and trace gas amounts using the NCAR Cray computer

Fig. 72: An example of curve fitting of O_3 absorption features in the 1125 cm^{-1} region. In the top plot, the solid curved line is the observed spectrum, the dotted curved line is the calculated spectrum and the solid straight line represents the estimated spectral background level. The bottom plot shows the percent differences between the observed and the calculated intensities.

Spectral Resolution Estimation

