Rotational Raman Scattering

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March 30, 2009

What is Raman scattering?

When light is scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering). The scattered photons have the same energy (frequency) or wavelength as the incident photons. However, a small fraction of the scattered light is scattered with the scattered photons having a frequency different from the frequency of the incident photons (lower frequency: Stokes lines; higher frequency: anti-Stokes lines). In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect.[1]
Rotational Raman scattering is important in the Earth's atmosphere and leads to filling in of line spectra (Ring effect).

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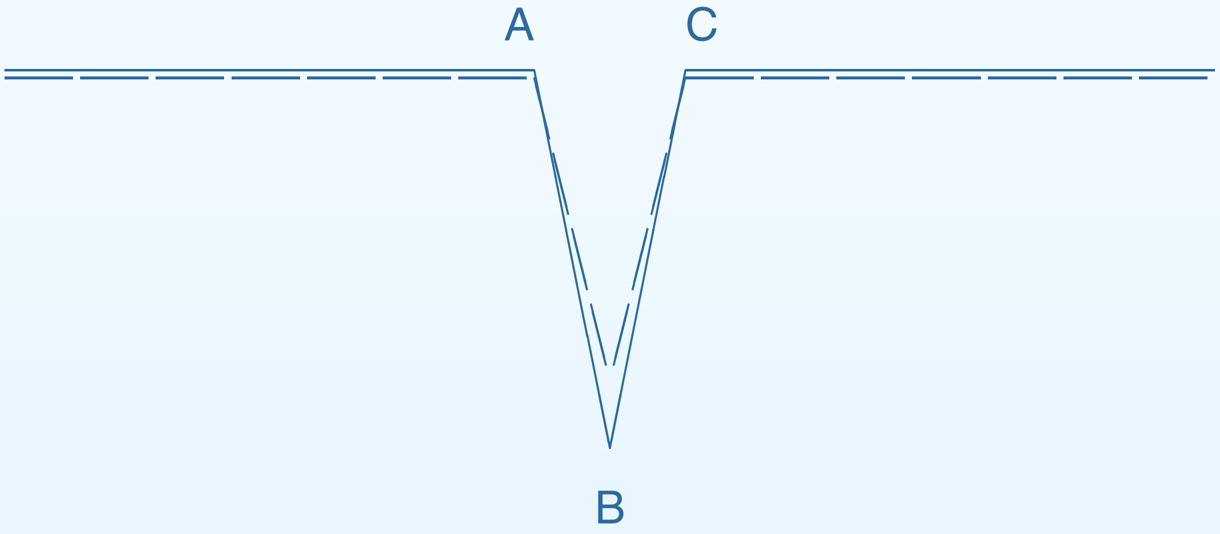
[1] Adopted from wikipedia.

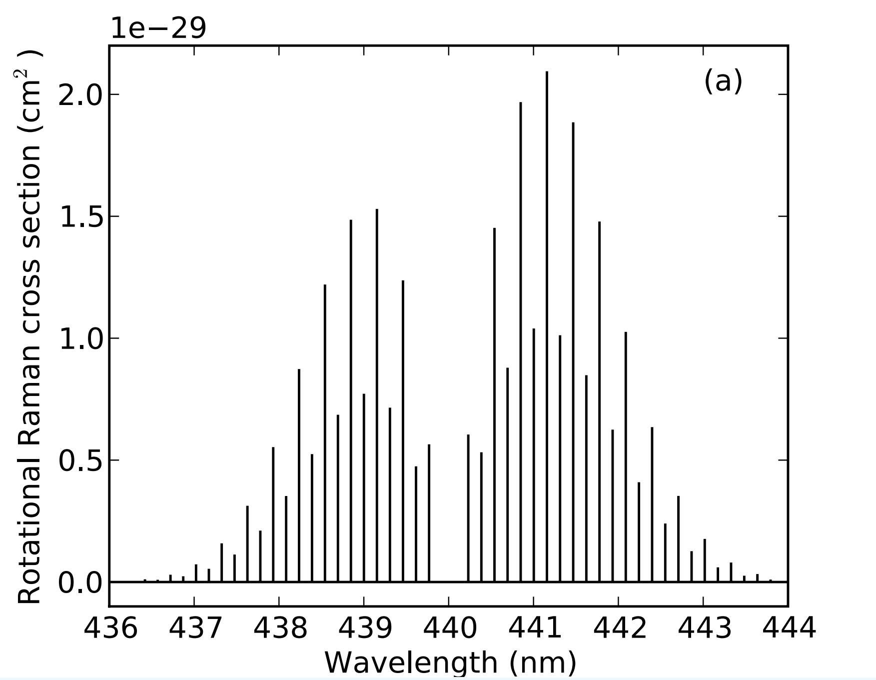
A naive example of filling in of line spectra

	A	B	C
Initial value	100	50	100
loss (scattered out of wavelength)	20	10	20
gain (scattered into from lower wavelength)	10	10	5
gain (scattered into from higher wavelength)	5	10	10
Total after scattering	95	60	95

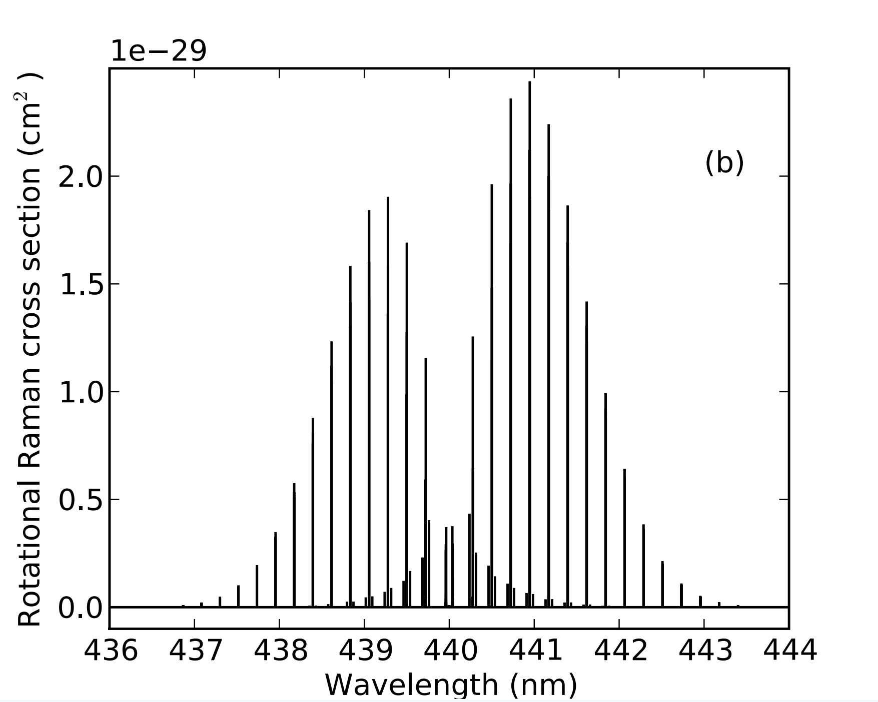


Raman scattering cross sections

N_2 $(S = 0, N = J)$



O_2 $(S = 1, N = J, J \pm 1)$



- Stokes scattering: molecule absorbs energy. The resulting photon of lower energy generates a Stokes line on the red side of the incident spectrum.
- anti-Stokes scattering: molecule loses energy. Incident photons are shifted to the blue side of the spectrum, thus generating an anti-Stokes line.

The Radiative Transfer Equation

The monochromatic RTE may be written as

$$\begin{aligned}\mu\frac{\mathrm{d}I(z,\Omega,\lambda_k)}{\mathrm{d}z} &= -\beta_{ext}(z,\lambda_k)I(z,\Omega,\lambda_k)\\ &\quad+\frac{\beta_{sca}(z,\lambda_k)}{4\pi}\int P_{sca}(z,\lambda_k,\Omega,\Omega')I(z,\Omega',\lambda_k)\mathrm{d}\Omega'.\end{aligned}$$

The first term on the right side is due to extinction and the second term describes multiple scattering. Including Raman scattering implies including one gain term Q_G for radiation scattered into λ_k and a loss term Q_L for radiation scattered out of the wavelength λ_k :

$$\begin{aligned}Q_G &= \sum_{i=1}^{L}\frac{r(z,\lambda_i,\lambda_k)}{4\pi}\int P_{rrs}(\Omega,\Omega')I(z,\Omega',\lambda_i)\mathrm{d}\Omega'\\ Q_L &= -\sum_{i=1}^{L}\frac{r(z,\lambda_k,\lambda_i)}{4\pi}\int P_{rrs}(\Omega,\Omega')I(z,\Omega',\lambda_k)\mathrm{d}\Omega'\end{aligned}$$

The Radiative Transfer Equation cont'd

The RTE with Raman scattering may thus be written as

$$\mathcal{R} I(z,\Omega,\lambda_k) = \varepsilon_{rss}(z,\Omega,\lambda_k)$$

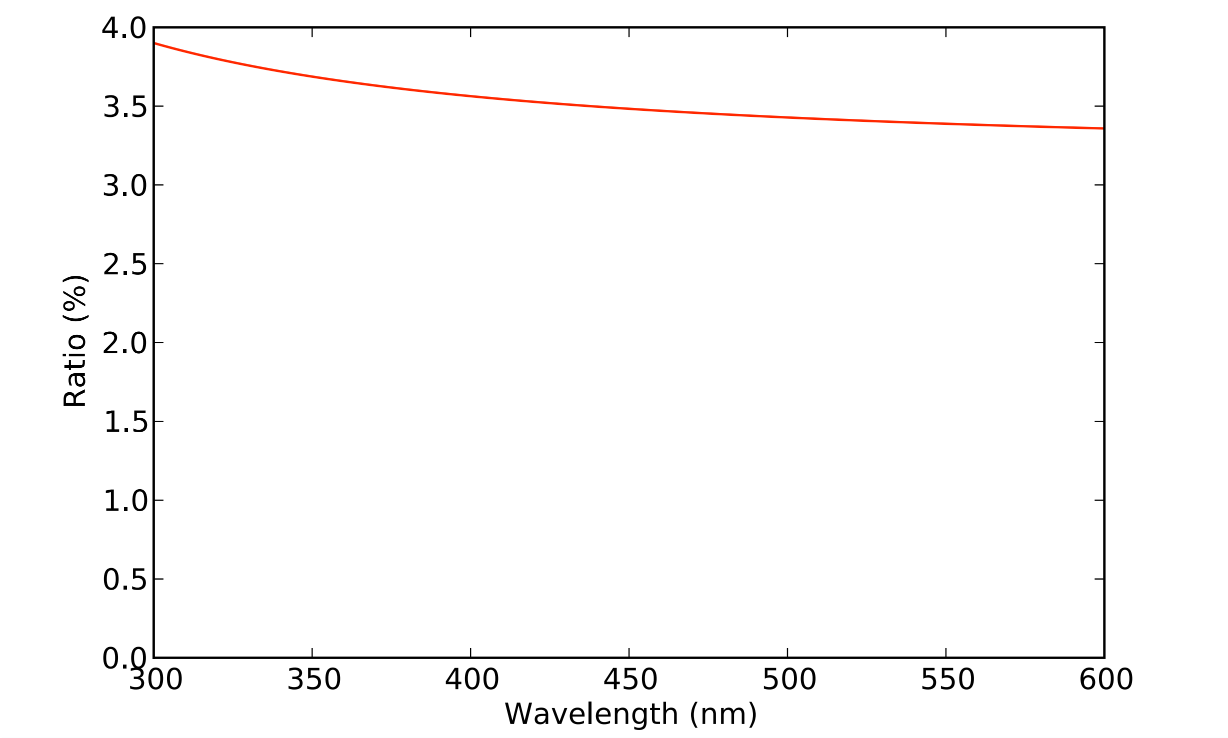
where the operator $\mathcal{R}$

$$\mathcal{R} \equiv \mu \frac{\mathrm{d}}{\mathrm{d}z} + \beta_{ext}(z,\lambda_k) - \frac{\beta_{sca}(z,\lambda_k)}{4\pi} \int P_{ray}(z,\lambda_k,\Omega,\Omega')\mathrm{d}\Omega'$$

and

$$\begin{aligned} \varepsilon_{rss}(z,\Omega,\lambda_k) &= \sum_{i=1}^{L} \frac{r(z,\lambda_i,\lambda_k)}{4\pi} \int P_{rrs}(\Omega,\Omega') I(z,\Omega',\lambda_i)\mathrm{d}\Omega' \\ &\quad - \sum_{i=1}^{L} \frac{r(z,\lambda_k,\lambda_i)}{4\pi} \int P_{rrs}(\Omega,\Omega') I(z,\Omega',\lambda_k)\mathrm{d}\Omega' \end{aligned}$$

Raman versus Rayleigh scattering



Raman scattering is weaker than Rayleigh scattering. The figure shows the ratio of the summed Raman cross section and the Rayleigh cross section.

Iterative solution

Formal solution:

$$I(z,\Omega,\lambda_k) = \mathcal{R}^{-1}[Q_{el}(z,\Omega,\lambda_k) + \varepsilon_{rss}(z,\Omega,\lambda_k)]$$

Iterative solution, set $\varepsilon_{rss} = 0$ for first step:

$$I^{(0)}(z,\Omega,\lambda_k) \quad = \quad I_{el}(z,\Omega,\lambda_k)$$

First order solution with single Raman scattering

$$I^{(1)}(z,\Omega,\lambda_k) \quad = \quad I^{(0)}(z,\Omega,\lambda_k) + \mathcal{R}^{-1}\varepsilon^{(0)}_{rss}(z,\Omega,\lambda_k)$$

Multiple inelastic scattering contributes less than 0.6% (van Deelen et al., 2005)[2].

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[2] van Deelen et al,, Multiple elastic and inelastic light scattering in the Earth's atmosphere: a doubling-adding method to include rotational Raman scattering by air, *J. Quant. Spectrosc. Radiat. Transfer*, **95**, 309-330, 2005.

Implementation of Raman scattering in uvspec

uvspec monochromatic: for each wavelength

- calculate Raman N_2 and O_2 scattering cross sections
- calculate elastic scattering for Raman shifted wavelengths, 233 calls to qdisort
- calculate Raman scattering loss and gain source
- solve RTE for the Raman source
- add elastic and inelastic contributions

The *qdisort* solver is used to solve the RTE. It is based on *sdisort* and may solve the RTE for arbitrary user supplied source functions. *sdisort* is a pseudo-spherical double precision version of the standard *DISORT* solver by Stamnes et al. (1988)[3].

Simple for the user. Just add **raman** in the input file.

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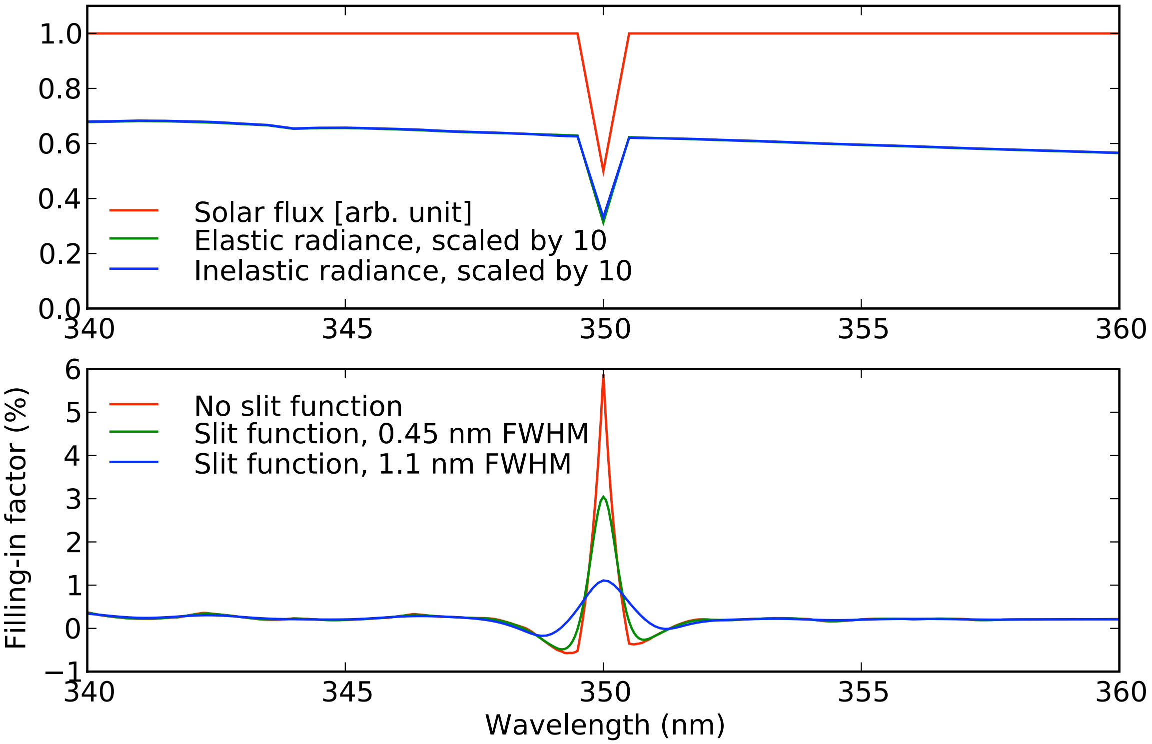
[3] Stamnes et al,, Numerically stable algorithm for discrete-ordinate-method radiative transfer in multiple scattering and emitting layered media, *Appl. Opt.*, **39**, 415-419, 1988.

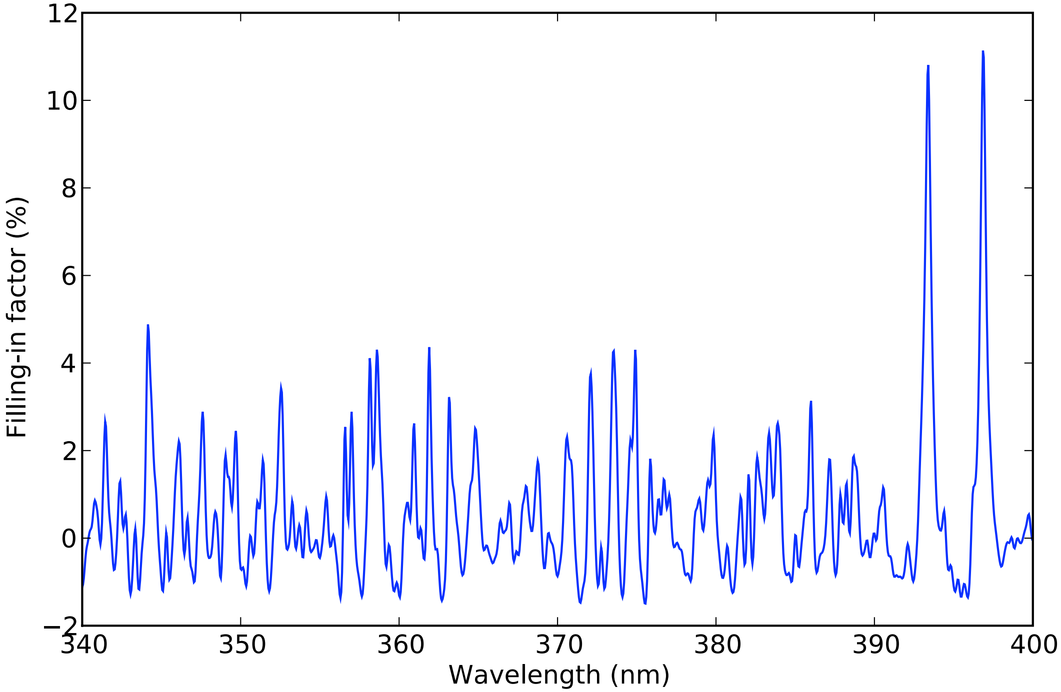
Example: Single absorption line

```
data_files_path /Users/arve//libRadtran/data/
atmosphere_file /Users/arve/projects/raman/afglus.dat
ozone_column 300
solar_file /Users/arve//projects/raman/single_absline_sun
wavelength 335.0 365.0
sza 21
albedo 0
zout toa
umu 1
phi 0
rte_solver qdisort
nstr 16
raman
quiet
```



$$FI(\lambda) = \frac{I_{\text{inelastic}} - I_{\text{elastic}}}{I_{\text{elastic}}}$$

Atmospheric Raman filling-in



The spectral dependence of the filling-in at GOME resolution (0.17 nm) for top-of-the-atmosphere nadir view. The surface albedo is 0.1 and the solar zenith angle 45°. The plot is similar to Fig. 6 in Joiner et al. (2004)[a].

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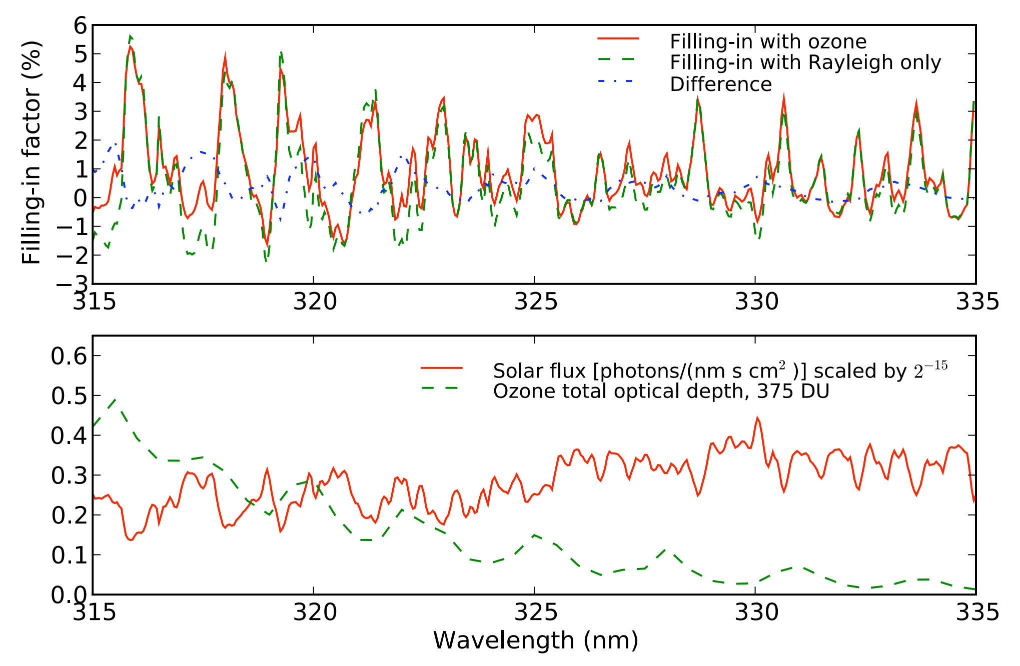
[a] Joiner et al,, Retrieval of cloud pressure and oceanic chlorophyll content using Raman scattering in GOME ultraviolet spectra, *J. Geophys. Res.*, **109**, doi:10.1029/2003JD003698, 2004.

Huggins band-ozone effect



The wavelength dependent structures of the ozone cross section affect Rotational Raman scattering filling-in. This has impact on the accuracy of backscatter-UV ozone prifile and column retrievals. The figure shows a uvspec simulation similar to the one reported by Spurr et al. (2009)[a].

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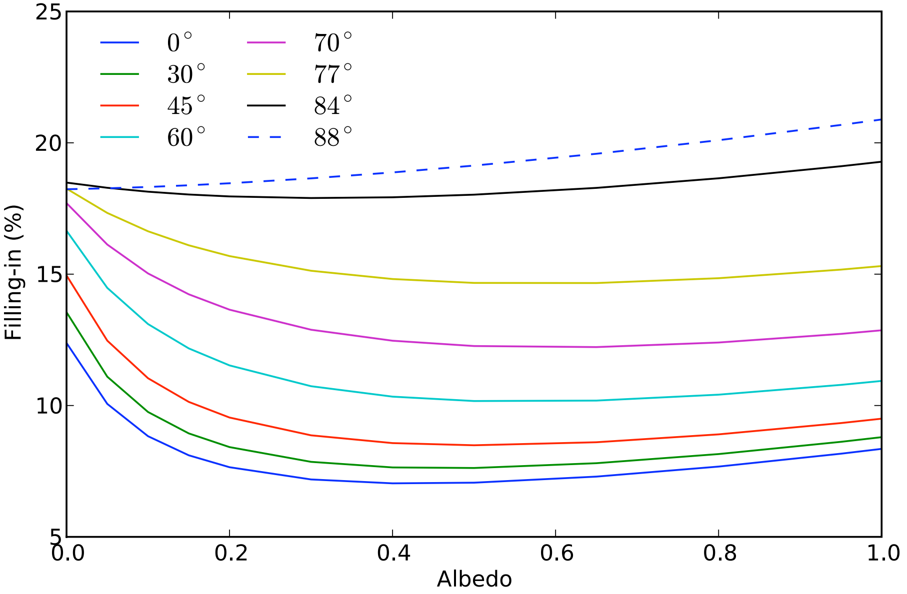
[a] Spurr et al,, Discrete ordinate radiative transfer in a stratified medium with first order rotational Raman scattering, *J. Quant. Spectrosc. Radiat. Transfer*, **109**, 404-425, 2009.

Albedo effect



The Lambert-equivalent reflectivity (LER) concept may be used to derive cloud pressures using Rotational Raman scattering. The figure is a uvspec simulation of filling-in at the Ca K line for a surface at 700 hPa similar to Fig. 2 in Joiner et al.(2004)[4].

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[4] Joiner et al,, Retrieval of cloud pressure and oceanic chlorophyll content using Raman scattering in GOME ultraviolet spectra, *J. Geophys. Res.*, **109**, doi:10.1029/2003JD003698, 2004.

Future work

- Current implementation is computationally expensive. Look into methods for reducing the number of wavelength calculations. Also calculation time increases linearly with the number of layers.
- Perform more tests.
- Model intercomparison.
- Comparison with measurements.