## 8. Atmospheric Scattering

Extinction $(\varepsilon)$ = absorption $(k)$ + scattering $(m)$:

$$\varepsilon_\sigma = k_\sigma + m_\sigma,$$

$$\frac{m_\sigma}{\varepsilon_\sigma} = \frac{m_\sigma}{k_\sigma + m_\sigma} = \text{ single scattering albedo (SSA).}$$

As before, except for polarization (which is quite important, although we largely neglect it), extinction, SSA, and the scattering phase function $\Phi$ completely describe a scattering event. For *single scattering* problems it is all that is needed.

For scattering in general, there is an electric interaction (complex, with the dielectric and optical properties of the scatterer) involving electromagnetic induction and re-radiation.

Rayleigh scattering $(\lambda \gg r_{scatterer})$ for a spherical molecule (*i.e.*, an atom)
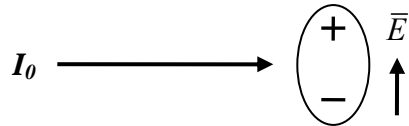


$$\Phi = \frac{3}{4}(1 + \cos^2\theta)$$

The induced dipole moment re-radiates. Consider the polarization of the input and scattered light (*N.B.*, solar radiation is unpolarized to a very high degree of accuracy):



$V$ = vertical, $H$ = horizontal, $S$ = scattered
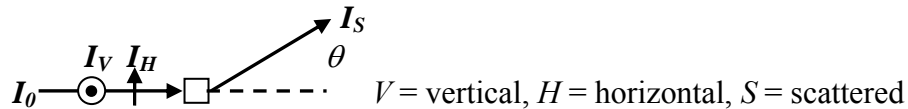
For $I_V$, $\Phi$ = constant (isotropic in the plane), vertically polarized
For $I_H$, $\Phi = \cos^2\theta$, null at $\pi/2$, horizontally polarized, or:

$$\Phi = \frac{3}{4}(1 + \cos^2\theta) \qquad \text{Perpendicular to the plane of the paper, the opposite holds.}$$

In general, the output intensities for scattering in the plane are proportional to:

| | $V$ in | $H$ in | Unpolarized in |
|---|---|---|---|
| $V$ out | 1 | 0 | 1 |
| $H$ out | 0 | $\cos^2\theta$ | $\cos^2\theta$ |
| Total out | 1 | $\cos^2\theta$ | $1 + \cos^2\theta$ |

As before, $Q_R \times 10^{28} = \dfrac{1.0455996 - 341.29061\lambda^{-2} - 0.9023085\lambda^{2}}{1 + 0.0027059889\lambda^{-2} - 85.968563\lambda^{2}}$, where $\lambda$ is the wavelength in $\mu$m, and $Q$ is in cm$^2$.

The analytic form is $Q_R = \dfrac{128\pi^5\alpha^2}{3\lambda^4}$, where the polarizability $\alpha$ is (usually) quite weakly dependent on wavelength, except at wavelengths where electronic states of the atom or molecule are being excited (*e.g.*, below 242 nm for $O_2$).

In cgs units, the *permittivity of vacuum* $\varepsilon_0 = 1/4\pi$. The cross section above is thus the same as **Bernath**, eq. 8.70: $Q_R = \dfrac{P}{I} = \dfrac{8\pi^3\alpha^2}{3\varepsilon_0^2\lambda^4}$. The permittivity of vacuum (AKA permittivity of free space) from *Wikipedia* is a physical quantity that describes how an electric field affects and is affected by a dielectric medium, and is determined by the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. Thus, permittivity relates to a material's ability to transmit (or "permit") an electric field. **Permittivity** is directly related to electric susceptibility. For example, in a capacitor, an increased permittivity allows the same charge to be stored with a smaller electric field (and thus a smaller voltage), leading to an increased capacitance.

**Bernath** derives the Rayleigh cross section in eqs. 8.65-8.69 by taking the power emitted by a classical oscillating dipole moment and dividing by the power driving it: $\vec{\mu} = \mu_0 \cos\omega t = \alpha\vec{E} = \alpha E_0 \cos\omega t$. The power emitted is $P = \dfrac{16\pi^4 c|\mu_0|^2}{3\lambda^4}$. The incident intensity is $I = \dfrac{E_0^2 c}{8\pi}$, and thus $Q_R = \dfrac{P}{I}$, as given. Bernath notes that the equation for radiated power was discussed in his Chapter 1, but you won't actually find it there specifically. However, it agrees, by implication, with the derivation in **Goody & Yung**:

**Goody & Yung** (Sections 7.1 through 7.3) actually does a complete derivation *except* that the most critical part is presented rather than developed. This is that for scattering by small particles $(r \ll \lambda)$ for propagation to "longer" distances $(d \gg \lambda)$, the electric field components are given by $E^{l,r} = (2\pi/\lambda_0)^2 \dfrac{\mu^{l,r}}{d}\sin\gamma^{l,r}$, where $\mu = \alpha E_0$ and $\gamma^{l,r}$ is the angle between $\mu$ and the direction of observation (see **Figure 7.2**).

Then, employ the *Poynting vector*, $\vec{S}$ which measures the energy flux carried by an electromagnetic wave (in cgs units, $\vec{S} = \dfrac{c}{4\pi}\vec{E}\times\vec{H}$ (erg s$^{-1}$ cm$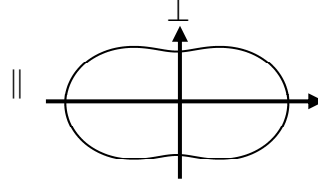^{-2}$)) to determine radiated power versus direction, integrate over a sphere, and get total power emitted, as above, and the cross section (eq. 7.30).

## 9. Rayleigh scattering with depolarization

In general, the polarizability is not isotropic. For diatomics such as $N_2$ and $O_2$ (*i.e.*, "air")

$\alpha_\parallel \neq \alpha_\perp$

$\bar{\alpha} = 1/3 \left[ \alpha_\parallel + 2\alpha_\perp \right].$

$\varepsilon$ (a measure of the effect of anisotropy on the spectrum) is defined as
$\varepsilon = (\gamma / \bar{\alpha})^2, \gamma = \alpha_\parallel - \alpha_\perp.$

The corresponding *depolarization factor* or *ratio*, defined as the ratio of the horizontally polarized component to the vertically polarized component of the scattered light for

unpolarized input at $90^\circ$ scattering angle in the horizontal plane, is given by $\delta = \dfrac{6\varepsilon}{45 + 7\varepsilon}.$

The induced dipole moment allows rotational *Raman* transitions – Raman scattering is simple the *inelastic* part of Rayleigh scattering.

The rotational Raman transitions usually have selection rules $\Delta J = \pm 2$ (as opposed to the usual $\Delta J = \pm 1$ for electric dipole transitions).
$\Delta J = +2 \equiv$ *Stokes* transitions; $I_0$ loses energy to molecule.
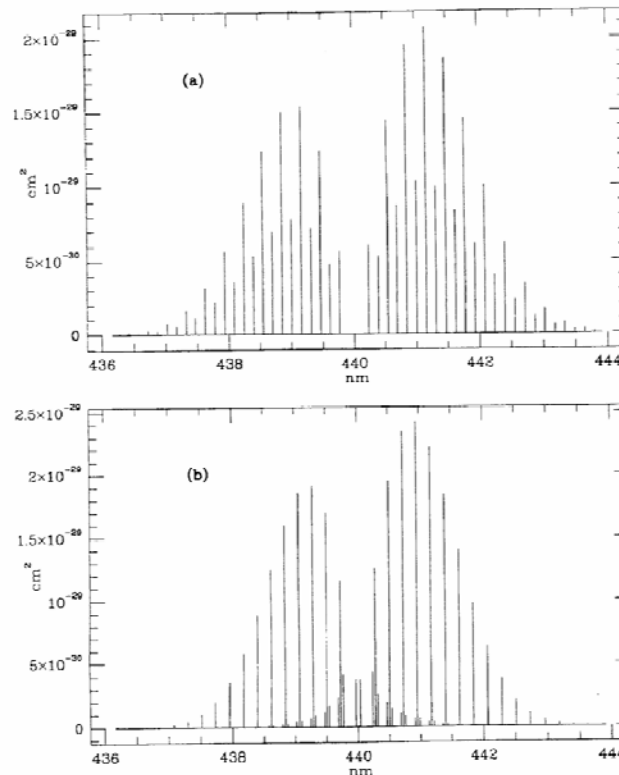$\Delta J = -2 \equiv$ *anti-Stokes* transitions; $I_0$ gains energy from molecule.



Fig. 1. Rotational Raman cross sections for (a) $N_2$ and (b) $O_2$ calculated for a temperature of 250 K and an excitation wavelength of 440 nm, appropriate to investigations of the effect of the Ring effect on retrievals of atmospheric $NO_2$ concentrations. The cross sections in this figure do not include the relative abundances of $N_2$ and $O_2$ in air.

(polyatomics are naturally more complicated)

Because molecules rotate before re-emitting, the scattered radiation is less polarized (but not completely unpolarized).

Complete intensities, $\gamma_{N_2}, \gamma_{O_2}, Q_R(\lambda), \hat{n}(\lambda)$ (the last two pre-Bodhaine) and polarized scattering phase functions are described in *Chance and Spurr*, 1997 (http://cfa-www.harvard.edu/atmosphere/) and given in ringdata.txt. Also, see table, below.

Vibrational Raman scattering is in general much weaker and less important in atmospheric scattering, but it is not entirely absent. Here, the transitions are almost entirely Stokes. (*See why?*)

Also, liquid water (*i.e.*, in the oceans) can be important, for ocean color sensing. Here it is mostly due to *librational* Raman (intermolecular transitions). Raman scattering from sea ice may prove useful in the future.

For air, at wavelengths 300 nm $\leq \lambda \leq$ 500 nm, 3.8% of Rayleigh scattering is inelastic (Raman) scattering. Since the Raman scattering is a component of Rayleigh scattering, it also has the $\lambda^{-4}$ wavelength dependence.

The occurrence of Raman scattering in atmospheric spectra is called the *Ring Effect* (after Grainger and Ring, 1962), who noticed Fraunhofer lines shapes changing with air mass (becoming broader and less deep with increasing air mass) during zenith sky measurements at various solar zenith angles.

**Relative Rayleigh and Raman Scattering Intensities[†]**

| *V* Polarization in | *H* Polarization in | Sum (Natural Light in) |
|---|---|---|
| Rayleigh-Brillouin | | |
| $^V C_V = 180 + 4\varepsilon$ | $^H C_V = 3\varepsilon$ | $^0 C_V = 180 + 7\varepsilon$ |
| $^V C_H = 3\varepsilon$ | $^H C_H = 3\varepsilon + (180 + \varepsilon)\cos^2\theta$ | $^0 C_H = 6\varepsilon + (180 + \varepsilon)\cos^2\theta$ |
| $^V C_0 = 180 + 7\varepsilon$ | $^H C_0 = 6\varepsilon + (180 + \varepsilon)\cos^2\theta$ | $^0 C_0 = (180 + 13\varepsilon) + (180 + \varepsilon)\cos^2\theta$ |
| | | $\rho_0{}^C = 6\varepsilon / (180 + 7\varepsilon)$ |
| Raman | | |
| $^V W_V = 12\varepsilon$ | $^H W_V = 9\varepsilon$ | $^0 W_V = 21\varepsilon$ |
| $^V W_H = 9\varepsilon$ | $^H W_H = 9\varepsilon + 3\varepsilon\cos^2\theta$ | $^0 W_H = 18\varepsilon + 3\varepsilon\cos^2\theta$ |
| $^V W_0 = 21\varepsilon$ | $^H W_0 = 18\varepsilon + 3\varepsilon\cos^2\theta$ | $^0 W_0 = 39\varepsilon + 3\varepsilon\cos^2\theta$ |
| | | $\rho_0{}^W = 6 / 7$ |
| Sum | | |
| $^V T_V = 180 + 16\varepsilon$ | $^H T_V = 12\varepsilon$ | $^0 T_V = 180 + 28\varepsilon$ |
| $^V T_H = 12\varepsilon$ | $^H T_H = 12\varepsilon + (180 + 4\varepsilon)\cos^2\theta$ | $^0 T_H = 24\varepsilon + (180 + 4\varepsilon)\cos^2\theta$ |
| $^V T_0 = 180 + 28\varepsilon$ | $^H T_0 = 24\varepsilon + (180 + 4\varepsilon)\cos^2\theta$ | $^0 T_0 = (180 + 52\varepsilon) + (180 + 4\varepsilon)\cos^2\theta$ |
| | | $\rho_0{}^T = 6\varepsilon / (45 + 7\varepsilon)$ |

The complications to UV (especially) and visible atmospheric measurements are several:

**1.** $I \div I_0$ only to 96% (for the single-scattering Rayleigh part of the source), while we are generally trying to fit absorptions to much better than 1%. Accurate Ring effect corrections must be made. Here is an example of fitting for BrO in a GOME spectrum showing that we can fit very precisely for BrO (to better than $3 \times 10^{-4}$ RMS in this case) even in the presence of Ring effect structure that is about 10 times as large as the BrO absorption.



Fitting of GOME spectrum (nm)
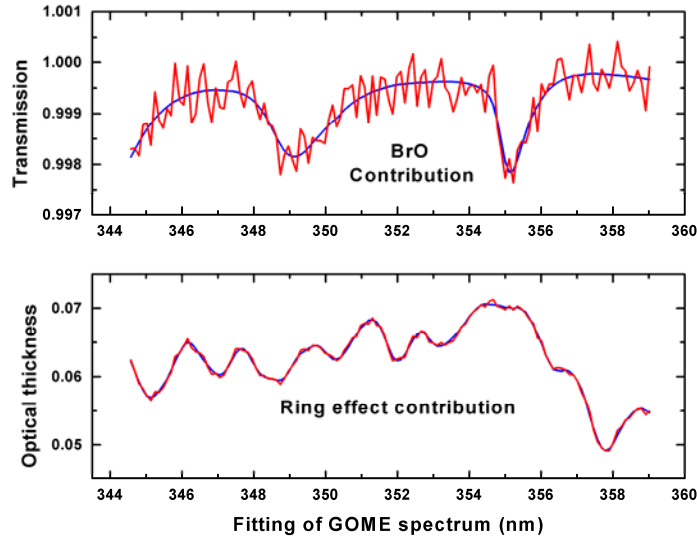
**2.** The amount of Ring effect is proportional to the number of air molecules encountered: It can be used to help determine cloud amount (*cf.* J. Joiner and P. K. Bhartia, The determination of cloud pressures from rotational Raman scattering in satellite backscatter ultraviolet measurements, *J. Geophys. Res.* **100**, 23,019– 23,026, 1995).

The effect on Fraunhofer shapes is often referred to as *filling-in* since it makes the Fraunhofer lines broader and less deep. There are *filling-in factors* and *filling-in spectra*, as examples (often with varying definitions). Filling-in is an instrument-dependent quantity and a departure from the basic physics. I prefer not to use it unless more basic descriptions fail – which I have never seen happen.

The simplest way to take the Ring effect into account when fitting an atmospheric spectrum is to calculate a Ring single-scattering corrections as $I_0 \otimes Q_{RR}$, where $I_0$ is the Fraunhofer spectrum and the $Q_{RR}$ are the rotational Raman cross sections.

Higher-order corrections may be obtained to account for interference from strong atmospheric absorption (*e.g.*, by $O_3$ in the UV Huggins bands) as
$$I_0 \to I_0 e^{-\tau} \simeq I_0(1 - \tau + \tau^2/2 - \cdots),$$
and forming an orthogonal set of correction spectra using a *Gram-Schmidt* orthogonalization process.

For GOME, this technique has been tested against Ring corrections using radiative transfer modeling calculations; it consistently gives the best results. It is used operationally in GOME, SCIAMACHY, and for some gases in OMI.

For ground-based measurements, an experimental Ring correction spectrum may be derived by making measurements at two polarizations, measuring at two significantly different angles with respect to the Sun (usually, but not necessarily, perpendicular and parallel to the direction to the Sun [Solomon *et al.*, 1987]) and using an algebra derived from Table 1 of *Chance and Spurr*, 1997 or Table I of Kattawar *et al.*, 1981 (which supplied most of the *Chance and Spurr* table) to derive the Raman scattered component.