When a monochromatic laser beam at an optical frequency (angular frequency), \( \nu(\omega = 2\pi\nu) \), illuminates a neutral atom or molecule, the electrons oscillate relative to the nucleus at the optical frequency, which induces multipole electric and magnetic moments on the atom or molecule. Since the speed of electrons is much less than that of light, the electric dipole interaction energy is by far the largest, so we only need to consider its effect on light scattering. Therefore, we can conceptually picture an induced electric dipole moment, \( \vec{p}(t) = 0.5(\vec{p}e^{-i\omega t} + \vec{p}^*e^{i\omega t}) = 0.5|p|(\vec{e}e^{-i\omega t} + \vec{e}^*e^{i\omega t}) \), oscillating at the same (angular) frequency \( \omega \) on the atom or molecule, resulting from this dominating interaction. The induced oscillating electric dipole moment in turn radiates electromagnetic waves. The intensity of the radiation at a point \( \vec{r} \) from this electric dipole moment is given by the Poynting vector, \( \vec{S} \), along its wave-propagating direction \( \hat{k} = \hat{r} \). Classical electromagnetic theory – in chapter 9 of Griffiths [2.1], or in chapter 2 of Corney [2.2] – shows that the cycle-averaged Poynting vector \( \langle \vec{S} \rangle \) is the radiated power per unit area, giving rise to radiated power per unit solid angle, \( dP/d\Omega = r^2[\hat{r} \cdot \langle \vec{S} \rangle] \). Since only the transverse dipole component radiates, it is convenient to project the dipole moment onto the scattering coordinates \( (\hat{e}_a', \hat{e}_b', \hat{r}) \); see Fig. B.1, as \( \vec{p} = p_\perp + p_\parallel \hat{r} = pa\hat{e}_a' + pb\hat{e}_b' + p\parallel \hat{r} \). The directions of the radiation electric and magnetic fields are then, respectively, parallel to \( (\hat{r} \times \vec{p}) \times \hat{r} = pa\hat{e}_a' + pb\hat{e}_b' \) and to \( (\hat{r} \times \vec{p}) \). The resulting \( \langle \vec{S} \rangle \) and \( dP/d\Omega \) can then be derived in terms of the absolute square of the transverse components of the induced dipole moments as \( |pa|^2 + |pb|^2 \), yielding respectively,

\[
\langle \vec{S} \rangle = \frac{\omega^4}{32\pi^2\epsilon_0c^3r^2} |p_\perp|^2 \hat{r}; \quad \text{with} \quad |p_\perp|^2 = |pa|^2 + |pb|^2 \quad \text{and} \quad |pa,\hat{b}|^2 = |\vec{p} \cdot \hat{e}_{a,b}|^2, \quad \\
\frac{dP}{d\Omega} = r^2[\hat{r} \cdot \langle \vec{S} \rangle] = \frac{\omega^4}{32\pi^2\epsilon_0c^3} |p_\perp|^2 = \frac{\omega^4|p|^2}{32\pi^2\epsilon_0c^3} \left[ (\hat{e} \cdot \hat{e}_a')^2 + (\hat{e} \cdot \hat{e}_b')^2 \right].
\]
where \( \omega, e_0, \) and \( c \) are, respectively, angular frequency, vacuum permittivity, and the speed of light. We note that the last expression of (2.1.b) is identical to (2) of [2.3], where the unit vector \( \hat{e}^' \) represents the polarization of the scattering radiation, which lies on the \( \hat{e}_a^' - \hat{e}_b^' \) plane.

The dipole moment in question is induced by the incident laser with electric field, \( \vec{E}(t) = \frac{1}{2}(\vec{e} e^{-i\omega t} + \vec{e}^{*} e^{i\omega t}) \) and intensity \( I = \frac{e_0 c}{2} |\vec{e}|^2 \). For light scattering from an isotropic medium like atmospheric atoms, the polarizability is a scalar \( \alpha(\omega) \), leading to \( \alpha(\omega)\vec{e} = \vec{p} = |p|\hat{e} = \alpha(\omega)\hat{e} \), where \( |p| \) and \( \hat{e} \) are, respectively, the magnitudes of the induced dipole moment and its polarization direction. Thus, the absolute square of the transverse components of the induced dipole moment and light scattering differential cross section summed over both scattering polarizations may be written as

\[
|p_a|^2 = |\alpha(\omega)|^2 (\hat{e} \cdot \hat{e}_a)^2; \quad \text{and} \quad |p_b|^2 = |\alpha(\omega)|^2 (\hat{e} \cdot \hat{e}_b)^2,
\]

and

\[
\frac{d\sigma}{d\Omega} = \frac{d\mathcal{P}}{d\Omega}/I = \frac{\omega^4}{32\pi^2 e_0 c^3} \left( |p_a|^2 + |p_b|^2 \right) / \left( \frac{e_0 c}{2} |\vec{e}|^2 \right) = \frac{\omega^4 |\alpha(\omega)|^2}{16\pi^2 e_0^2 c^4} (\hat{e} \cdot \hat{e}^')^2,
\]

where \( (\hat{e} \cdot \hat{e}^')^2 = (\hat{e} \cdot \hat{e}_a)^2 + (\hat{e} \cdot \hat{e}_b)^2 \) is the sum of received scattered light from the two independent polarizations. We note that (2.2.b) is identical to Eq. (3) of She et al. [2.3].

In general, the induced dipole moment is related to the second rank polarizability tensor \( \hat{\alpha} \) of the atom or molecule in question as \( \vec{p} = \hat{\alpha} \cdot \vec{e} \) – see, for example, chapter 3 of Long [2.4] – or in the Cartesian components as \( p_i = \alpha_{ij}(\omega)\epsilon_j \), with \( i, j = (1, 2, 3) \) representing \( (x, y, z) \) axes. For scattering from an isotropic medium, which we assume for the treatments in Chapters 2 and 3 of this book, the directions of \( \vec{p}, \vec{e} \), and \( \hat{e} \) are parallel to one another. This assumption will not be valid for a medium with linear molecules, where the polarizabilities parallel and perpendicular to the molecular axis are different, necessitating the use of tensor polarizability, \( \hat{\alpha} \); this situation will be treated in Chapter 4.

### 2.1 A Simple Model of Atomic Polarizability and Differential Scattering Cross Section

To reveal the frequency structure of \( \alpha(\omega) \) and \( |\alpha(\omega)|^2 \), we need a physical model for the atom, thus its polarizability. A simple (weakly) damped harmonic electron oscillator with one resonance frequency \( \omega_0 \) is a suitable model in which a dipole moment \( p(t) = -ex(t) \) may be induced under the illumination by an optical field, with a linear equation of motion for electronic displacement \( x \) as
\[
\frac{d^2 x(t)}{dt^2} + \gamma \frac{dx(t)}{dt} + \omega_0^2 x(t) = -\frac{e}{m_e} E(t), \tag{2.3.a}
\]

where \(m_e\), \(\gamma\), \(\omega_0\), and \(e\) are respectively the mass, damping rate, resonance frequency, and charge of the electron oscillator, which may be thought of as driving the superposition of external, restoring, and damping forces, as given in (2.3.a); see chapter 2 of [2.5]. Without an externally applied force (i.e., setting \(E(t)\) to zero), a perturbation in displacement \(x(0)\) initiated at \(t = 0\) will oscillate at the frequency \(\omega_0'\) and decay at its amplitude rate of \((\gamma/2)\), resulting in the following solution to (2.3.a):

\[
x(t) = 0.5x(0)e^{-(\gamma/2)t}[e^{-i\omega_0't} + e^{i\omega_0't}]; \\
\omega_0' = \sqrt{\omega_0^2 - (\gamma/2)^2} \approx \omega_0, \text{ since } \gamma \ll \omega_0. \tag{2.3.b}
\]

The decay rate of the individual dipole energy will then be \(\gamma\). With this model, we can relate the induced dipole moment \(p(t) = 0.5(pe^{-i\omega't} + p^*e^{i\omega't})\) and the applied electric field \(E(t) = 0.5(e^{-i\omega't} + e^{i\omega't})\), and easily determine the associated frequency-dependent complex polarizability, \(\alpha(\omega)\), as, for example, in Chapter 8 of Griffiths [2.1]:

\[
(-\omega^2 - i\gamma + \omega_0^2)x = -\frac{e}{m_e} E \rightarrow p = -ex \\
= \frac{e^2/m_e}{\omega_0^2 - \omega^2 - i\omega\gamma} E \rightarrow \alpha(\omega) = \frac{e^2/m_e}{\omega_0^2 - \omega^2 - i\omega\gamma}. \tag{2.3.c}
\]

Because the damping rate \(\gamma \ll \omega, \omega_0\), we can decompose the polarizability into two contributions, corresponding to the rotating and counterrotating wave terms as

\[
\alpha(\omega) = \frac{e^2/m_e}{\omega_0^2 - \omega^2 - i\omega\gamma} \approx \frac{e^2}{2\omega_0 m_e} \left[ -\frac{1}{(\omega - \omega_0) + i(\gamma/2)} + \frac{1}{(\omega + \omega_0) + i(\gamma/2)} \right]. \tag{2.3.d}
\]

Notice that when \(\omega \approx \omega_0\), the first term is much larger; we only need to keep it. This is the case for resonant scattering. We can then make the rotating-wave approximation leading to resonant polarizability, \(\alpha^R(\omega)\). When \(\omega, \gamma \ll \omega_0\), we need to keep both (rotating and counterrotating) terms, and they may be combined to yield the nonresonant polarizability, \(\alpha^{NR}(\omega)\). These are explicitly given in (2.3.e):
\[ \alpha^R(\omega) = -\frac{e^2/2m_e\omega_0}{(\omega - \omega_0) + i(\gamma/2)}; \quad \alpha^{NR}(\omega) = \frac{e^2}{m_e\omega_0} = \left(\frac{e^2}{4\pi\epsilon_0 m_e c^2}\right) \frac{4\pi\epsilon_0 c^2}{\omega_0^2} = r_e^2 \frac{4\pi\epsilon_0 c^2}{\omega_0^2}, \]

(2.3.e)

where \( r_e = e^2/4\pi\epsilon_0 m_e c^2 = 2.82 \times 10^{-15} \text{m} \) is the classical electron radius. Since both rotating and counterrotating terms make equal contributions to \( \alpha^{NR}(\omega) \), it is a factor of two larger than \( \alpha^R(\omega) \) in the limit of \( \omega, \gamma \ll \omega_0 \). Substituting (2.3.e) into (2.2.b), we obtain

\[ \frac{d\sigma^\text{RS}}{d\Omega} = r_e^2 \pi \omega_0^2 g(\omega - \omega_0)(\hat{e} \cdot \hat{e}')^2; \quad \text{with } g(\omega - \omega_0) = \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2}, \text{ and} \]

(2.3.f)

\[ \frac{d\sigma^{NR}}{d\Omega} = r_e^2 \left(\frac{\omega}{\omega_0}\right)^4 (\hat{e} \cdot \hat{e}')^2 = \sigma^C_\pi (\hat{e} \cdot \hat{e}')^2; \quad \text{with } r_e = \frac{e^2}{4\pi\epsilon_0 m_e c^2}. \]

(2.3.g)

Here, \( g(\omega - \omega_0) \) is the Lorentzian lineshape function with full width at half maximum of \( \Delta\omega_L = \gamma = 1/\tau \), where \( \gamma \) and \( \tau \) are, respectively, the energy damping rate and the radiative lifetime of an electron oscillator.

The quantity \( \sigma^C_\pi \) is known as the differential Cabannes scattering (CS) cross section; for scattering from air molecules at 532 nm, \( \sigma^C_\pi = 5.96 \times 10^{-32} \text{m}^2/\text{sr} \) (see Table 1, She [2.6]). This leads to an estimate of the ratio of resonant wavelength \( \lambda_0 \) to the laser wavelength \( \lambda \) by equating \( (\omega/\omega_0)^4 = (\lambda_0/\lambda)^4 \) to \( \sigma^C_\pi/r_e^2 = 5.96 \times 10^{-32}/(2.82 \times 10^{-15})^2 \approx 7.5 \times 10^{-3} \), resulting in \( \lambda_0 \approx 157 \text{ nm} \), or about 7.9 eV, which represents the effective dipole-allowed excited states of atmospheric molecules. This value is interesting, as the ionization potentials (wavelengths) of \( \text{O}_2 \) and \( \text{N}_2 \) are, respectively, 12.2 (101.6) and 15.6 eV (79.5 nm); see Table 37, Herzberg [2.7].

Of practical interest is to compare the resonant differential cross section at 589 nm from a Na atom to the nonresonant cross section from an air molecule at 532 nm, because these are the wavelengths of a Na lidar and a Cabannes (often termed a Rayleigh) lidar. Using (2.3.e), we see that the peak backward resonant differential cross section is

\[ d\sigma^\text{RS}/d\Omega = r_e^2 (\omega_0/\gamma)^2. \]

If we substitute \( (\hat{e} \cdot \hat{e}')^2 = 1 \) and \( \omega_0/2\Gamma \approx 1/(2 \times 10^{-8}) \) into (2.3.e), we obtain

\[ d\sigma^\text{RS}/d\Omega = 2 \times 10^{-14} \text{m}^2/\text{sr}, \text{ roughly } 3 \times 10^{17} \text{ larger than } \sigma^C_\pi \text{ and in reasonable agreement with quantum mechanical results to be discussed at the end of Section 3.2.} \]
2.2 Resonant and Nonresonant Scattering from the Atmosphere

To apply the above treatment to a system of atmospheric metal atoms and air molecules, we must account for their motion due to the background wind as well as random motions relative to one another with a speed variation dependent on background or ambient temperature. At thermal equilibrium (ignoring the effects of pressure for simplicity), the probability of finding an air molecule with line of sight (LOS) thermal velocity $u$ is given by the well-known Maxwellian distribution:

$$G(u, T) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left[\frac{-mu^2}{2k_B T}\right] \equiv \frac{1}{\sqrt{2\pi\sigma_u^2}} \exp\left[\frac{-u^2}{2\sigma_u^2}\right].$$

Here, the variance of this velocity distribution is $\sigma_u^2 = k_B T/m$, with $k_B$, $m$, and $T$ being, respectively, Boltzmann constant, mass of the molecule (or metal atom), and temperature. As we pointed out in Chapter 1, for atmospheric molecules above 30 km altitude, their correlated motions (Brillouin scattering) are negligible; we need only consider the Doppler broadening due to their random motion and Doppler shift due to background wind. For air molecules moving (in dynamic equilibrium) with the background LOS wind, $V$, the instantaneous LOS velocity is the sum of thermal velocity and background LOS wind (i.e., $\nu = u + V$).

For nonresonant scattering (or Cabannes scattering) from a single atom or molecule (ignoring correlated motion for simplicity here), the differential cross section has a mild 4th-power frequency dependence, as can be seen in (2.3.g); $\sigma_\pi^C$ is nearly constant. The Doppler-shifted frequency of a particle moving with the LOS (thermal) velocity, $u$, in the background LOS wind $V$ becomes $\nu_s = \nu - 2(u + V)/\lambda$, where $\lambda$ is the wavelength of the incident light. For an ensemble of atmospheric atoms or molecules, the velocity distribution, $G(u, T)$, transformed into the frequency domain becomes the normalized Gaussian spectrum for CS, $G^{CS}(\nu - \nu_s - 2V/\lambda, T)$; it is obtained from (2.4) by substituting $0.5(\nu - \nu_s - 2V/\lambda)$ for $u/\lambda$, and $\lambda d\nu/2$ for $du$. The spectral differential resonant backscattering cross section is then simply the product of $d\sigma_\pi^{CS}/d\Omega$ and the backward-scattering spectrum, $G^{CS}(\nu - \nu_s - 2V/\lambda, T)$, where the backscattering Doppler shift of $-2V/\lambda$ from the incident frequency, $\nu = c/\lambda$, is well known, and it will be further treated in Chapter 3. Thus, with $G^{CS}(\nu - \nu_s - 2V/\lambda, T)$, the spectral backscattering differential cross section is peaked at $\nu_s = \nu - 2V/\lambda$ as
\[
\frac{d\sigma_{CS}}{d\Omega} = \sigma_{\pi}(v) \rightarrow \frac{d^2\sigma_{CS}(v-v_s, T, V)}{dv_s d\Omega} = \sigma_{\pi}^{CS}(v-v_s - 2V/\lambda, T), \text{ where}
\]
\[
G^{CS}(v-v_s - 2V/\lambda, T) = \frac{\lambda}{2} \frac{1}{\sqrt{2\pi}\sigma_u} \exp \left[ -\frac{u^2}{2\sigma_u^2} \right]
\]
\[
= \frac{1}{\sqrt{2\pi}\sigma_{v}^{CS}} \exp \left[ -\frac{(v-v_s - 2V/\lambda)^2}{2(\sigma_{v}^{CS})^2} \right].
\]

When integrating over the entire scattering spectrum, we retrieve \( d\sigma_{CS}(v)/d\Omega = \sigma_{\pi}^{CS} \). Here, \( \sigma_{v}^{CS} = (2/\lambda)\sqrt{k_B T/M} \) is the standard deviation (RMS variation) of the CS frequency spectrum; its corresponding full width at half maximum (FWHM) is then
\[
\Delta v_{D}^{CS} = 2\sqrt{2\ln 2} \sigma_{v}^{CS} = \frac{1}{\lambda} \sqrt{\frac{32(\ln 2)k_B T}{m}} \rightarrow \Delta v_{D}^{CS}(GHz) = \frac{1}{\lambda(nm)} \sqrt{\frac{1.84 \times 10^{5}T(K)}{M(amu)}},
\]

(2.5a)

where \( k_B \) is the Boltzmann constant, and \( m \) and \( M \) are the mass of air molecule in kg and amu. For air molecules \( (M = 28.97 \text{ amu}) \) at 300 K, the FWHM Doppler width from (2.5.a), \( \Delta v_{D}^{CS} \) is 2.59 GHz at 532 nm. Similarly, it is 2.15 GHz and 1.26 GHz, respectively, for Na \((M = 22.99 \text{ amu}) \) at 589 nm and for K \((M = 39.1 \text{ amu}) \) at 770 nm, both at 200 K.

For absorption and resonant backscattering (or laser induced fluorescence, LIF), we note that a metal atom can absorb a photon only when the incident laser frequency in its rest frame \( (i.e., v - \nu/\lambda) \) falls within the natural linewidth, \( \Delta \nu \), of an atomic transition, where \( \nu \) is the LOS velocity of the atom in question. Thus, the peak absorption occurs when \( v - \nu/\lambda = v_0 \). In the presence of background LOS wind, \( V \), the LOS individual velocity is \( \nu = u + V \). Thus, the frequency in the resonant differential scattering cross section (2.3.f) should be its Doppler-shifted frequency \( (i.e., v - (u + V)/\lambda) \) and

\[
\frac{d\sigma_{RS}}{d\Omega} = \frac{\pi^2 A r_e^2}{\nu_0^2 \Delta \nu} (\hat{e} \cdot \hat{e}')^2 g \left( v - \frac{u + V}{\lambda} - v_0 \right), \text{ with}
\]

ug \left( \frac{v - u + V}{\lambda} - v_0 \right) = \frac{\Delta \nu}{2\pi \left( \left( v - \frac{u + V}{\lambda} - v_0 \right)^2 + \left( \Delta \nu/2 \right)^2 \right)}; \Delta \nu = \frac{1}{2\pi} = \frac{\nu}{2\pi} = \frac{\Delta \omega_L}{2\pi}.
\]

(2.6.b)

Since frequency is the quantity that is measured, it is often desirable to express the differential cross section as a function of frequency, as given above. In (2.6.a), we
have related the natural lineshape function \( g(\omega - \omega_0) \) in angular frequency, (2.3.f), to that in frequency, \( g(v - v_0) \), with \( v_0 = \omega_0 / 2\pi \). Here, \( \Delta v = \gamma / 2\pi \) is the full width at half maximum (FWHM) linewidth due to lifetime (natural) broadening, and \( \gamma = 1/\tau = \Delta \omega_L \) is the energy damping rate of the oscillator, or the inverse of lifetime.

For an ensemble of atoms in thermal equilibrium at temperature \( T \), (2.6.a) should be integrated over its thermal distribution \( g(u, T) \) in the frequency domain. This is a Gaussian function \( G_{RS}(v / \nu_0, T) \), which may be obtained from (2.4) by substituting \( \nu / \nu_0 = \lambda / \nu_0 \) for \( u = \lambda \), and \( \lambda dv \) for \( du \), leading to the resonant differential scattering cross section:

\[
\frac{d\sigma_{RS}}{d\Omega} = \frac{\pi^2 v^2 e^2}{v_0^2 \Delta v} (\hat{\epsilon} \cdot \hat{\epsilon}')^2 G[(v - \lambda - v_0), T], \quad \text{with} \quad (2.7.a)
\]

\[
G[(v - \lambda - v_0), T] = \int_{-\infty}^{\infty} g\left(v - \frac{u + V}{\lambda} - v_0\right) g(u, T) du , \quad \text{and}
\]

\[
\frac{v' = \lambda'}{v'} G[(v - \lambda - v_0), T] = \int_{-\infty}^{\infty} g\left(v - \frac{V}{\lambda} - v' - v_0\right) G_{RS}(v', T) dv'. \quad (2.7.b)
\]

The spread of Gaussian function, \( G_{RS}(v - \lambda - v_0, T) \), results from absorption rather than backward scattering; thus, its standard deviation (RMS variation) is a factor of 2 smaller (i.e., \( \sigma_{RS}^v = \sigma_{CS}^v / 2 = (1/\lambda) \sqrt{k_B T / M} \); the same for the full width at half maximum (FWHM),

\[
\Delta \nu_{D}^{RS} = 2 \sqrt{2 \ln 2} 2 \sigma_{RS}^v = \frac{1}{\lambda} \sqrt{\frac{8(\ln 2) k_B T}{M}} \rightarrow \Delta \nu_{D}^{RS} (\text{GHz}) = \frac{1}{\lambda (\text{nm})} \sqrt{\frac{4.61 \times 10^4 T(\text{K})}{M(\text{amu})}}. \quad (2.7.c)
\]

For Na (\( M = 22.99 \text{ amu} \)) at 589 nm and K (\( M = 39.1 \text{ amu} \)) at 770 nm, the Doppler-broadened widths at 200 K are 1.08 GHz and 0.63 GHz, respectively. Since typically, \( \Delta \nu \approx 10 \text{ MHz} \) and \( \Delta \nu_{D}^{RS} \approx 1,000 \text{ MHz} \) at 200 K, the Voigt function, \( G[(v - v_0), T] \) in (2.7.b) may generally be approximated by the Gaussian function \( G_{RS}[(v - v_0), T] \).

Equation (2.7.a) represents the magnitude of the resonant backscattering scattering cross section, which is dictated by the absorption process in LIF; it does not reveal the fluorescence emission frequency or spectrum. The fluorescence frequency is determined by the Doppler effect to be further analyzed in Chapter 3; it turns out to be \( \nu_e = 2v_0 - v \), within the natural linewidth of the respective
spontaneous emission. This can be briefly understood by considering resonant scattering as a combination of absorption followed by emission. As noted, the peak absorption occurs when \( \nu - \nu/\lambda = \nu_0 \), that is, the resonant frequency and the incident laser frequency select atoms with correct LOS velocity \( \nu \), and these are excited by absorbing the incident photon. Once excited (coherently, say by a laser), the atom could emit a photon at its transition frequency \( \nu_0 \) in its rest frame. Since the moving atom carries much higher momentum than that of the emitted photon, its velocity will remain essentially the same to satisfy linear momentum conservation. The emitted frequency in the laboratory frame (or to a detector on ground) will be Doppler shifted again by the same amount i.e., \( \nu_e = \nu_s = \nu_0 - \nu/\lambda = \nu_0 - (\nu - \nu_0) = 2\nu_0 - \nu \), leading to an emission (or resonantly backscattered) frequency depending only on the laser and atomic transition frequencies (i.e., independent of atom’s motion), in other words the background conditions (temperature or LOS wind). Therefore, the spectral differential resonant backscattering cross section, or simply, LIF spectrum of atmospheric metal atoms, is the product of \( d\sigma_{RS} / d\Omega \) and the natural-broadened emission lineshape function centered at \( \nu_e \):

\[
\frac{d^2\sigma_{RS}}{dv_s d\Omega} = \frac{2\pi^3 v^4 r_e^2}{v_0^2 \gamma} (\hat{e} \cdot \hat{e'})^2 G[(\nu - V/\lambda - \nu_0), T] g(\nu_s - 2\nu_0 + \nu).
\]  

(2.8)

Thus, the spectral backward resonant scattering cross section is a Lorentzian line centered at \( \nu_s = 2\nu_0 - \nu \) with magnitude dependent on the resonant cross-section weighted by the propagation factor, \( (\hat{e} \cdot \hat{e'})^2 \), and the thermal distribution as a function of resonance frequency and background LOS wind, \( G[(\nu - V/\lambda - \nu_0), T] \), via the absorption process.

### 2.3 Physical Causes of Broadened Light Scattering Spectra

We have introduced the Doppler-broadened Lorentzian-scattered light spectra for an atmosphere free of collisions. Doppler shift is the frequency difference between scattered and incident light, \( \Delta \omega = \omega_S - \omega_L = -(\nu/c) \omega_L \), when a monochromatic light beam at frequency \( \omega_L \) impinges on and is scattered by a particle moving away with the LOS speed \( \nu \). For atmosphere in thermal equilibrium at temperature \( T \), the Maxwellian speed distribution of the molecular population divides molecules into different speed groups, leading to a Gaussian-shaped, inhomogeneous Doppler-broadened frequency spectrum. Lorentzian broadening, on the other hand, is due to the decay of individual dipole moments at a rate of \( \gamma \), which corresponds to the Einstein A coefficient of spontaneous emission from an excited atom/molecule. Therefore, both broadening mechanisms could be associated with
individual molecules without collisions with other molecules during the scattering event. In nonresonant scattering, the individual dipole moment is not supposed to decay, and the resulting CS scattering spectrum is purely Doppler-broadened, as given in (2.5). On the other hand, in resonant scattering, not only does the individual dipole decay via spontaneous emission, the effect of the Maxwellian distribution also broadens the spectrum, leading to a LIF spectrum as the convolution of Doppler-broadened and Lorentzian lineshapes, or the Voigt function as given in (2.7).

As molecular density in gas increases, since the impact duration is much shorter than the time between collisions, the collisional perturbation causes a sudden and random change in the phase of the scattered light. Like the decay of individual dipoles, the effect of dephasing collisions also leads to a Lorentzian lineshape; an excellent discussion of this mechanism is given in Chapter 2 of Siegman [2.5]. Briefly, suppose the external electric field initially (at \( t = 0 \)) induces a macroscopic dipole moment of \( N(0) \) molecules per unit volume (each with dipole moment \( p \)), with all individual dipoles oscillating in phase. As time passes, some dipoles suffer dephasing collisions, and the density of dipoles that continue to oscillate in phase is reduced to \( N(t) = N(0)e^{-t/T_2} \), where \( T_2 \) is the mean time of dephasing collisions, giving a dipole energy decay rate of \( 2/T_2 \). This leads to a Lorentzian distribution with FWHM of \( 2/T_2 \). The lineshape resulting from dephasing collisions was attributed to Lorentz’s 1906 paper, and the dephasing time \( T_2 \) is the inverse of the collision frequency \( \lambda_c \), with \( \lambda_c = N\sigma\overline{v} \) [2.8]. Here, \( \sigma \) and \( \overline{v} \) are, respectively, the collision cross section and average molecular speed. Since the dephasing collision could occur with or without internal energy transfer, we include the dephasing broadening in both nonresonant scattering and resonant scattering spectra in the form of a Voigt function, that is, the convolution between the respective Doppler-broadened function \( G^{CS}(\nu, T) \) or \( G^{RS}(\nu, T) \) and the Lorentzian function as

\[
g(\nu) = \frac{\Delta\nu}{2\pi \left\{ (\nu)^2 + (\Delta\nu/2)^2 \right\} } \quad \text{with} \quad \Delta\nu = \frac{1}{\pi T_2} \quad \text{for} \quad CS, \quad \Delta\nu = \frac{\gamma}{2\pi} + \frac{1}{\pi T_2} \quad \text{for} \quad RS.
\]

The time between collisions gets shorter as gas density increases, leading to a change in the velocities of the scattering molecules. In this case, the gas can no longer be unambiguously divided into different speed groups during a scattering event. The Maxwellian speed distribution then collapses and the collisions become diffusive, and substantial narrowing of the Doppler-broadened line occurs, as was first considered by Dicke [2.9]. The simple Voigt-type folding can no longer describe the resulting lineshape function. Galatry [2.10] has proposed a spectral
lineshape model to account for simultaneous Doppler broadening and both collisional effects (dephasing and Dicke narrowing). Though the Galatry model has been used to successfully fit the lineshape of the Q-branch vibrational-rotational Raman spectrum in nitrogen [2.11], given in Section 4.3.4, it is inadequate for describing the Cabannes scattering spectrum. In fact, the dynamics of the two-body collisions become much more complex as the gas density increases, since in addition to Doppler and pressure-induced broadening and narrowing effects, gas density perturbations associated with the translational degrees of freedom can also propagate in a gas. The shape of the Cabannes scattering spectrum for pressures larger than 5 kPa requires solving the kinetic equations and figuring out the density–density correlation functions for molecular gas, an area of intensive research in the 1960s and 1970s. The shape and dependence of the Cabannes spectrum will be discussed in some detail in Section 4.4.

References