Notes on Temperature-Dependent Lidar Equations

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ABSTRACT

The temperature dependence of molecular backscatter coefficients must be taken into account when narrowband interference filters are used in lidar measurements. Thus, the spectral backscatter differential cross section of the molecules involved in the backscattering of the radiation has to be calculated or measured and the interference filter transmission efficiency must be known. The present paper is intended to describe in an easily reproducible manner the procedure involved in calculating the temperature-dependent functions introduced in the lidar equations, including the computation of the differential cross sections for air, nitrogen, and water vapor. The temperature-dependent functions are computed for the Howard University Raman lidar (HURL). The interference filter efficiencies are given by the manufacturer. Error estimates in water vapor mixing ratio and aerosol backscatter ratio involved when temperature-dependent functions are omitted are given for measurements taken with HURL. For the data analyzed, it is found that errors in estimating the water vapor mixing ratio are up to ~6% while in estimating the aerosol backscattering ratio the errors are up to ~1.3% in the planetary boundary layer and ~2.2% in cirrus clouds. Theoretical computations are performed to determine temperature-dependent functions for nitrogen, water vapor, and their ratio, using simulated Gaussian-shaped filters. The goal is to find the optimum combination of different filters that will determine the ratio profiles of the temperature-dependent functions that are either the closest to unity or the least variable. The analyses reveal that quite constant profiles can be obtained for several combinations of the filters.

1. Introduction

While the total cross sections in Raman spectra are expected to be temperature independent, the individual rotational line strengths are temperature dependent and this must be taken into consideration when narrowband interference filters used for signal detection allow the transmission of only a portion of the pure rotational (PR) or vibrational rotational (VR) Raman signals. Not considering this dependence may lead to significant errors in retrieving water vapor mixing ratios and aerosol backscatter/extinction coefficients for lidar systems when narrowband interference filters are used [full width half maximum (FWHM) of a few nanometers or less]. Narrowband detection is employed to reduce the background skylight along with the use of a narrow field-of-view (FOV) telescope, without substantially reducing the Raman signals (Bisson et al. 1999). Moreover, along with a high-power laser and combined analog-to-digital and photon counting data acquisition, it can be used to optimize the performance (increased signal-to-noise ratio, SNR) of a daytime Raman water vapor lidar (Whiteman et al. 2006a).

In the literature, the Rayleigh scattering is sometimes defined as the molecular scattering due to the elastic scattering [Cabannes lines; e.g., Inaba (1976)] while sometimes it is defined as the molecular scattering due to both elastic and PR Raman (inelastic) scattering (e.g., She 2001). In this paper, we use the second approach. Whiteman et al. (1993) discuss the temperature sensitivity of the Raman return signals of nitrogen (N₂), oxygen (O₂), and water vapor for an XeF excimer laser. Whitman et al. suggest that the use of ideal (wide) square-edge bandpass filters will eliminate the temperature dependence on the VR lines of the N₂, O₂, and water vapor (suggested bandpasses of 8.5, 9.2, and 17.7 nm for N₂, O₂, and water vapor, respectively). Sherlock et al. (1999) describes a methodology for absolute calibration of the water vapor mixing ratio (WVMR), where the temperature dependence of the water vapor spectrum is

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taken into account. However, the anisotropic part of the water vapor spectrum was not considered in their scattering model. More details and comments regarding the temperature dependence of Rayleigh–Mie, \( N_2 \), and water vapor channels are found in Whiteman (2003a,b), who justify the introduction of a temperature-dependent function. Here, the water vapor scattering is considered using the theoretical work of Avila et al. (1999).

The present paper combines all the elements needed for each step in the calculation of the temperature-dependent functions, in a straightforward and easily reproducible manner. The paper is structured as follows. Section 2 presents the lidar equations and expressions of WVMR and aerosol backscatter ratio (ABR), which incorporate the temperature-dependence functions. In section 3, the temperature-dependent functions are described along with the calculations of the backscatter cross sections for the Rayleigh and \( N_2 \) VR Raman spectra. We consider the molecules to be nonrigid rotators. For the water vapor Raman shift, computed backscatter cross sections are used, following Avila et al. (2004). Explicit temperature-dependent expressions for WVMR and ABR are given and illustrated with the incorporation of the interference filter for the HURL system. Section 4 shows the errors involved with the omission of temperature-dependent functions for experimental data acquired by HURL. Section 5 presents some theoretical considerations about filter choices in the case of WVMR. The last section will cover the concluding remarks.

2. Lidar equations, water vapor mixing ratio, and aerosol backscatter ratio equations

a. Lidar equations

The lidar equation for the Raleigh–Mie channel can be written as (Adam and Venable 2007 and very similar with Whiteman 2003a)

\[
P(\lambda_L, r) = \frac{P_0 c t}{2} O_L(r) A \kappa(\lambda_L) \xi(\lambda_L) \left[ \frac{F_L(T) N(r)}{r^2} \frac{d\sigma(\lambda_L, \pi)}{d\Omega} + \beta_{\text{aer}}(r) \right] \exp \left[ -2 \int_0^r [a(\lambda_L, r') + \alpha(\lambda_L, r')] dr' \right],
\]

where \( P(\lambda_L) \) is the backscatter power (W), \( P_0 \) is the outgoing laser power (W), \( c \) is the speed of light (m s\(^{-1}\)), \( t \) is the pulse duration (s), \( O_L(r) \) is the overlap function (dimensionless), \( A/r^2 \) is the solid angle (sr) defined by the telescope area \( A \) (m\(^2\)) and the distance \( r \) (m) from the lidar to backscatter, \( \beta_{\text{aer}} \) is the aerosol backscatter coefficient (m\(^{-1}\) sr\(^{-1}\)), and \( d\sigma(\lambda_L, \pi)/d\Omega \) is the total molecular differential backscatter cross section (m\(^2\) sr\(^{-1}\)). The exponential term represents the round-trip transmission from the lidar to the backscatter. The total extinction coefficient, \( \alpha(\lambda_L, r) \) (in m\(^{-1}\)), is the sum of the molecular and aerosol components at the laser wavelength \( \lambda_L \) (in nm). We define the total system efficiency given in Eq. (1) as a product of the interference filter transmission efficiency, \( \xi(\lambda_X) \), and \( \kappa(\lambda_X) \), which represents all other system efficiencies (such as telescope reflectivity, transmission through the conditioning optics, the quantum efficiency of the detector, and other filters transmission). Here, \( \xi(\lambda_X) \) is wavelength dependent while \( \kappa(\lambda_X) \) is considered to be constant within the range of the interference filter bandwidth \( \Delta \lambda_X \). Here, \( X \) stands for either the laser-emitting wavelength (\( L \)) or the Raman-shifted wavelength (\( H \) for water vapor or \( N \) for nitrogen). In the case of a Raman signal, the lidar equation is [Adam and Venable (2007) and very similar to Whiteman (2003a)]

\[
P(\lambda_X, r) = \frac{P_0 c t}{2} O_X(r) A \kappa(\lambda_X) N_X(r) F_X(T) \frac{d\sigma(\lambda_X, \pi)}{d\Omega} \xi(\lambda_X) \exp \left\{ - \int_0^r [\alpha(\lambda_X, r') + \alpha(\lambda_X, r')] dr' \right\},
\]

where \( N_X \) is the number of molecules of the \( X \) species (\( N_2 \) or water vapor), \( \alpha(\lambda_X, r) \) is the total extinction coefficient at Raman-shifted wavelength \( \lambda_X \) (386.7 and 407.5 nm for \( N_2 \) and the water vapor, respectively), and \( O_X(r) \) is the overlap function at wavelength \( \lambda_X \). The

\[
\text{temperature dependence factor } F_X(T) \text{ (dimensionless)}
\]

at wavelength \( \lambda_X \) is defined by Whiteman (2003a) in its integral form for water vapor. In practice, the computation for water vapor as well as \( N_2 \) is performed using the sum
The index $i$ implies summation over all spectral lines within the interference filter’s bandpass. The air is assumed to be composed mainly of N$_2$ and O$_2$ (e.g., Vaughan et al. 1993; She 2001; Behrendt and Nakamura 2002); thus,

$$F_X(T) = \sum_i \frac{d\sigma(\lambda_{X,i}, T, \pi)}{d\Omega} \xi(\lambda_{X,i}).$$

The eventual departure from unity of the overlap ratio must be corrected. The ratio of $\kappa(\lambda_N)$ to $\kappa(\lambda_H)$ is the system calibration factor, $\kappa(\lambda_N, \lambda_H)$. Equation (5) simply becomes (Adam and Venable 2007)

$$\text{WVMR} = C_1 \kappa(\lambda_N, \lambda_H) \frac{P(\lambda_H, r)}{P(\lambda_N, r)} \frac{F_N(T)}{F_H(T)} \frac{d\sigma(\lambda_N, \pi)}{d\Omega} \xi(\lambda_N) \Delta \tau(\lambda_N, \lambda_H, r).$$

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$$F_X(T) = \sum_i \frac{d\sigma(\lambda_{X,i}, T, \pi)}{d\Omega} \xi(\lambda_{X,i}).$$

where $\eta_n$ represents the atmospheric abundances for N$_2$ and O$_2$. Here, $d\sigma(\lambda, \pi)/d\Omega$ is temperature insensitive (Measures 1984; Sherlock et al. 1999; Whiteman 2003a) and it represents the sum of all cross sections over the Q, S, and O branches (Rayleigh or VR lines).

b. Water vapor mixing ratio

Recall that the WVMR is defined as the ratio of mass of water vapor to the mass of dry air, where the number of molecules of dry air is approximately 1/0.78 of the number of N$_2$ molecules. The WVMR equation becomes

$$\text{WVMR} = C_1 \kappa(\lambda_N, \lambda_H) \frac{P(\lambda_H, r)}{P(\lambda_N, r)} \frac{F_N(T)}{F_H(T)} \frac{d\sigma(\lambda_N, \pi)}{d\Omega} \xi(\lambda_N) \Delta \tau(\lambda_N, \lambda_H, r).$$

The eventual departure from unity of the overlap ratio must be corrected. The ratio of $\kappa(\lambda_N)$ to $\kappa(\lambda_H)$ is the system calibration factor, $\kappa(\lambda_N, \lambda_H)$. Equation (5) simply becomes (Adam and Venable 2007)

$$\text{WVMR} = C_1 \kappa(\lambda_N, \lambda_H) \frac{P(\lambda_H, r)}{P(\lambda_N, r)} \frac{F_N(T)}{F_H(T)} \frac{d\sigma(\lambda_N, \pi)}{d\Omega} \xi(\lambda_N) \Delta \tau(\lambda_N, \lambda_H, r).$$

where $C_2 \approx 0.78$. Values for $F_N(T)$ and $F_L(T)$ are computed using Eqs. (3) and (4), and the differential transmission term is determined in the same manner as for WVMR (Adam et al. 2007). Here, $\kappa(\lambda_N, \lambda_L)$ is the calibration factor and it is the ratio of $\kappa(\lambda_N)$ to $\kappa(\lambda_L)$. It is determined using clear-air normalization, that is, from a region where $\text{ABR} = 1$ (e.g., Whiteman 2003b).

c. Aerosol backscattering ratio

The ABR is defined as the ratio between the total volume backscatter coefficient and the molecular volume backscatter coefficient. Assuming that the ratio of the overlaps is unity, ABR can be written as (Adam and Venable 2007)

$$\text{ABR} = 1 - F_L(T) + C_2 \kappa(\lambda_N, \lambda_L) F_N(T) \frac{d\sigma(\lambda_N, \pi)}{d\Omega} \xi(\lambda_N) \Delta \tau(\lambda_N, \lambda_L, r).$$

3. Calculation of the temperature-dependent function

The calculation of $F_X(T)$ requires the computation of the differential backscatter cross section within the spectral range of a given interference filter transmission efficiency. The main exercise that remains is the computation of the cross sections. Below, we describe the
computation of the backscatter cross sections in this order: Rayleigh, N₂ VR, and water vapor VR.

a. Rayleigh backscatter differential cross section

Explicit formulas for PR backscatter cross sections are given by Behrendt (2005), where PR cross sections are used to determine atmospheric temperature profiles. However, one has to pay attention because the energy and Raman shifts consider the molecules to be rigid rotors while the partition function does not. The individual spectral lines for the Q, S, and O branches can be written as

\[
Q : \frac{\partial \sigma}{\partial \Omega} = \frac{112\pi^4}{45} (\nu_0)^4 g_{nJ}(2J + 1) \exp\left(-\frac{E_{rot,J}}{K_BT}\right) \frac{[454a^2 + \frac{7(2J + 1)}{(2J - 1)(2J + 2)}\gamma^2]}{J = 0, 1, 2, \ldots}
\]

\[
S : \frac{\partial \sigma}{\partial \Omega} = \frac{112\pi^4}{45} (\nu_0 - \Delta \nu)^4 g_{nJ}(2J + 1) \exp\left(-\frac{E_{rot,J}}{K_BT}\right) \frac{3(J + 1)(J + 2)}{2(2J + 2)(2J + 3)}\gamma^2, \quad J = 0, 1, 2, \ldots,
\]

\[
O : \frac{\partial \sigma}{\partial \Omega} = \frac{112\pi^4}{45} (\nu_0 - \Delta \nu)^4 g_{nJ}(2J + 1) \exp\left(-\frac{E_{rot,J}}{K_BT}\right) \frac{3(J - 1)}{2(2J + 1)(2J - 1)}\gamma^2, \quad J = 2, 3, 4, \ldots \tag{9-11}
\]

The derivation is shown in appendix A. Here, \(Q_{rot}\) represents the rotational partition function; \(g_{nJ}\) is the statistical weight, which depends on nuclear spin; \(E_{rot,J}\) is the state energy of the molecule, considered to be a nonrigid rotator; \(J\) represents the rotational quantum number; \(\Delta \nu\) is the Raman shift, and \(\nu_0\) stands for the wavenumber corresponding to the excitation wavelength (354.7 nm). Here, \(a\) and \(\gamma\) are the isotropic and anisotropic polarizabilities, respectively, while \(K_B\) and \(T\) represent the Boltzmann constant and the temperature in kelvins.

The total cross section for \(Q\) and \(S + O\) branches can be computed either by summing the above expression over all \(J\) or using the following expressions, which are obtained from the expressions above for \(J \rightarrow \infty\) (classical limit) (e.g., Inaba 1976; Wandinger 2005). According to She (2001), the classical limit is obtained for \(J > 30\). Inaba (1976) uses 26–28 lines for PR and VR for N₂. We have chosen the number of N₂ spectral lines (30) such that the change in the total cross section, if we further increase \(J\), is less than 0.01%. The number of O₂ lines was chosen such that the spectral region covered is the same as that covered by the N₂ lines. However, a smaller number can be used for O₂ since the contribution of the large \(J\) is very small. The total backscatter cross sections over \(Q, S + O\), and \(Q + S + O\) (total Rayleigh backscatter cross section) are

\[
Q : \frac{\partial \sigma}{\partial \Omega} = (2\pi)^4(\nu_0)^4\left(a^2 + \frac{7}{180}\gamma^2\right), \tag{12}
\]

\[
S + O : \frac{\partial \sigma}{\partial \Omega} = (2\pi)^4(\nu_0)^4\left(\frac{7}{60}\gamma^2\right), \quad \text{and} \tag{13}
\]

\[
Q + S + O : \frac{\partial \sigma}{\partial \Omega} = (2\pi)^4(\nu_0)^4\left(a^2 + \frac{7}{45}\gamma^2\right). \tag{14}
\]

We assume that the air is approximately 79% N₂ and 21% O₂ (e.g., She 2001; Behrendt and Nakamura 2002), such that the total backscatter cross section for air is 0.79 times the N₂ total backscatter cross section plus 0.21 times the O₂ total backscatter cross section. Figure 1 shows the PR lines for the \(S\) and \(O\) branches for O₂ and N₂ molecules at \(T = 300\) K as well as the Rayleigh cross section due to Cabannes lines (Q branch). Also shown is the interference filter transmission efficiency, \(\xi\). The maximum efficiency (0.364) occurs at \(\lambda = 354.69\) nm. Figure 2 shows the filter transmission efficiency and the Rayleigh spectral lines (\(T = 300\) K) as a function of wavelength (panel a) and wavenumber shift (panel b).

b. Nitrogen VR backscatter differential cross section

Explicit formulas are also obtainable in the case of VR spectra. Wandinger (2005) formulates a general expression for both PR and VR backscatter cross sections. Note that the rotational partition function is given as an approximate formula, while the exact formulation should be used in computations. The formulations given by Wandinger assume the molecules to be rigid rotors.

The individual spectral lines for the Q, S, and O branches can be written as
\[ Q:\left(\frac{\partial \sigma}{\partial \Omega}\right)_f = \frac{112 \pi^4}{45} (\nu_0 - \nu_{\text{vib}} + \Delta \nu)^4 g_{n,J}(2J + 1) \exp\left(\frac{-E_{\text{rot},J}}{K_BT}\right) \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \]
\times \left[\frac{45}{7} a'^2 + \frac{J(J + 1)}{(2J - 1)(2J + 3)} \gamma'^2\right], \quad J = 0, 1, 2, \ldots. \quad (15)\]
\[ S:\left(\frac{\partial \sigma}{\partial \Omega}\right)_f = \frac{112 \pi^4}{45} (\nu_0 - \nu_{\text{vib}} + \Delta \nu)^4 g_{n,J}(2J + 1) \exp\left(\frac{-E_{\text{rot},J}}{K_BT}\right) \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \]
\times \frac{3(J + 1)(J + 2)}{2(2J + 1)(2J + 3)} \gamma'^2, \quad J = 0, 1, 2, \ldots. \quad (16)\]
\[ O:\left(\frac{\partial \sigma}{\partial \Omega}\right)_f = \frac{112 \pi^4}{45} (\nu_0 - \nu_{\text{vib}} + \Delta \nu)^4 g_{n,J}(2J + 1) \exp\left(\frac{-E_{\text{rot},J}}{K_BT}\right) \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \]
\times \frac{3J(J - 1)}{2(2J + 1)(2J - 1)} \gamma'^2, \quad J = 2, 3, 4, \ldots. \quad (17)\]

where \(\nu_{\text{vib}}\) is the vibrational Raman shift [2331 cm\(^{-1}\) for \(\text{N}_2\); Herzberg (1950)], and \(a'\) and \(\gamma'\) are the derivatives of the isotropic and anisotropic polarizabilities, respectively. The derivation is shown in appendix B. The total backscatter cross section for \(Q, S + O, \) and \(Q + S + O\) can be computed by either summing over all \(J\) in Eqs. (15)–(17) or using the expressions obtained from the above equation for \(J \to \infty\) (e.g., Inaba 1976; Wandinger 2005) as follows:

\[ Q:\left(\frac{\partial \sigma}{\partial \Omega}\right) = (2\pi)^4 (\nu_0 - \nu_{\text{vib}})^4 \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \left(a'^2 + \frac{7}{180} \gamma'^2\right), \quad (18)\]
\[ S + O:\left(\frac{\partial \sigma}{\partial \Omega}\right) = (2\pi)^4 (\nu_0 - \nu_{\text{vib}})^4 \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \left(\frac{7}{60} \gamma'^2\right), \quad \text{and} \quad (19)\]
\[ Q + S + O:\left(\frac{\partial \sigma}{\partial \Omega}\right) = (2\pi)^4 (\nu_0 - \nu_{\text{vib}})^4 \frac{h}{8\pi^2 c \nu_{\text{vib}}} \frac{1}{1 - \exp\left(-\frac{h c \nu_{\text{vib}}}{K_BT}\right)} \left(a'^2 + \frac{7}{45} \gamma'^2\right). \quad (20)\]

Figure 3 shows the \(\text{N}_2\) VR spectral lines and the interference filter transmission efficiency as a function of wavelength for a narrow (~0.25 nm FWHM) and a wide (~5 nm FWHM) filter. Figure 4 shows the filter transmission efficiency and the spectral lines as a function of wavelength (panels a and b) and wavenumber shift (panels c and d) over the spectral range significant for each filter. The narrow filter efficiency values are given by the manufacturer while the wide filter efficiency values are measured in the laboratory. The maximum efficiency for the narrow filter (0.578) occurs at \(\lambda = 386.68\) nm, while the maximum efficiency for the wide filter (0.275) occurs at \(\lambda = 384.92\) nm.

c. Water vapor backscatter differential cross section

The differential cross section for water vapor, following Avila et al. (2004), is

\[ \left(\frac{\partial \sigma}{\partial \Omega}\right)_f = (\nu_0 - \nu_{\text{vib}} + \Delta \nu)^4 \frac{e^{K_{\text{rot}}}}{Q(T)} (A^{XX} + A^{XY}), \quad (21)\]

Figure 3 shows the \(\text{N}_2\) VR spectral lines and the interference filter transmission efficiency as a function of wavelength for a narrow (~0.25 nm FWHM) and a wide (~5 nm FWHM) filter. Figure 4 shows the filter transmission efficiency and the spectral lines as a function of wavelength (panels a and b) and wavenumber shift (panels c and d) over the spectral range significant for each filter. The narrow filter efficiency values are given by the manufacturer while the wide filter efficiency values are measured in the laboratory. The maximum efficiency for the narrow filter (0.578) occurs at \(\lambda = 386.68\) nm, while the maximum efficiency for the wide filter (0.275) occurs at \(\lambda = 384.92\) nm.
where $\nu_0$ is the wavenumber (cm$^{-1}$) of the exciting wavelength (354.7 nm), $\nu_{\text{vib}}$ is the vibrational Raman shift [3654 cm$^{-1}$ for water vapor; e.g., Penney and Lapp (1976)], $\Delta \nu$ is the rotational shift, and $A_{XX}$ and $A_{XY}$ are the parallel and perpendicular polarizability coefficients. In addition, $Q(T)$ is the partition function. The product of the exponential term, $2J+1$, and the reciprocal of the partition function represents the rotational Maxwell–Boltzmann distribution function. Here, $E_i$ is the ground state energy. Avila et al. (2004) provide tables for $E_i$, $A_{XX}$, $A_{XY}$, and $Q(T)$. The authors reported the accuracy to be within 8% as compared with the measurements of Penney and Lapp (1976) for the computed $Q$ branch cross section.

Figure 5 shows the filter transmission efficiency at 407.5 nm and the spectral lines of the OH stretching region for the shift of 3654 cm$^{-1}$ for $T=300$ K ($Q$ branch of $n_1$ water vapor, wavenumber range of 3630–3660 cm$^{-1}$) as a function of wavelength (panels a and b) and wavenumber shift (panels c and d). The narrow filter efficiency values are given by the manufacturer while the wide filter efficiency values are measured in the laboratory. The maximum efficiency for the narrow filter (0.487) occurs at $\lambda = 407.49$ nm, while the maximum efficiency for the wide filter (0.357) occurs at $\lambda = 400.4$ nm.
d. Temperature-dependent function

The total cross sections as given by the asymptotical formulas [Eqs. (14) and (20)] are found to be the following: $3.119 \times 10^{-31}$ m$^2$ sr$^{-1}$ and $2.745 \times 10^{-34}$ m$^2$ sr$^{-1}$ for Rayleigh and N$_2$ VR, respectively. When using the summation over all $J$, we observe very small temperature dependence in the total backscatter cross section. The relative difference between the case of using the sum and the case using an asymptotic formula (temperature independent) ranges between 0.035% ($T = 320$ K) and 0.038% ($T = 200$ K) for the Rayleigh case and it is almost constant (0.005%) for the VR case. Small temperature dependence in the total backscatter cross section.

![Fig. 4](image_url)  
**FIG. 4.** Filter transmission efficiency curve (where the dots are interpolated values at the spectral lines position) and the VR spectral lines corresponding to the N$_2$ Raman shift of 2331 cm$^{-1}$ as a function of (a),(b) wavelength and (c),(d) wavenumber shift. The spectrum is calculated for $T = 300$ K. (a),(c) The case of the narrow filter (FWHM $\sim 0.25$ nm) and (b),(d) the case of a wide filter (FWHM $\sim 5$ nm).

![Fig. 5](image_url)  
**FIG. 5.** Filter transmission efficiency curve and spectral lines of water vapor at the Raman shift of 3654 cm$^{-1}$ as a function of (a),(b) wavelength and (c),(d) wavenumber shift. Spectral lines are calculated at $T = 300$ K. Plots corresponding to the (a),(c) narrow filter (FWHM $\sim 0.25$ nm) and (b),(d) wide filter (FWHM $\sim 20$ nm).
section is observed as well for water vapor. The total cross section at $T = 200$ K differs from the one at $T = 320$ K by 0.5%. However, we can consider these variations to be negligible and thus the total cross section temperature to be independent. Whiteman (2003a,b) uses a total cross section of $6.34 \times 10^{-34}$ m$^2$ sr$^{-1}$ for water vapor as derived from Measures (1984), while we calculated a mean total backscatter cross section of $6.95 \times 10^{-34}$ m$^2$ sr$^{-1}$. The theoretical calculations of the total backscatter cross section for N$_2$ PR and O$_2$ PR as well as for N$_2$ VR when using an excitation wavelength of 337.1 nm agree well with those given by Inaba (1976). Small differences exist that come from the use of slightly different values for the polarization invariants. For example, our theoretical computation for the N$_2$ VR Q branch for 337.1 nm and $T = 300$ K gives us $2.91 \times 10^{-34}$ m$^2$ sr$^{-1}$ while Inaba’s calculations give $2.9 \times 10^{-34}$ m$^2$ sr$^{-1}$. The mean experimental backscatter cross section for the Q branch (as computed using Inaba’s references, where we have excluded two references, namely, Stansbury et al. and Fenner et al.) gives $2.87 \pm 0.08 \times 10^{-34}$ m$^2$ sr$^{-1}$ (using a weighted average as a function of the standard deviation). Thus, our result is also within the measurement error range. If we convert this cross section to our excitation wavelength (354.7 nm), we obtain a mean experimental value of $2.34 \pm 0.07 \times 10^{-34}$ m$^2$ sr$^{-1}$. Our computation gives us $2.33 \times 10^{-34}$ m$^2$ sr$^{-1}$.

Corresponding functions $F_X(T)$ for HURL are shown in Figs. 6–8. For the N$_2$ and water vapor cases, where wide filters were also available, the corresponding temperature-dependent functions are given as well (see the b panels in Figs. 6–8). Whiteman’s (2003a) functions are also shown. Note that Whiteman’s functions are obtained for a narrowband filter with FWHM of 0.3 nm and a wide filter with 2-nm FWHM using theoretical Gaussian-shaped filters. The HURL results are obtained for the actual filters used in the system with an FWHM of 0.25 nm (narrow) for Rayleigh, N$_2$, and water vapor and with FWHM of ~5 and ~20 nm (wide) for N$_2$ and water vapor, respectively (recall Figs. 1–5). As FWHM increases and the efficiency becomes constant over the spectral range of interest, $F_X(T)$ will be closer to unity (see Fig. 8b).

Note that if we consider the N$_2$ and O$_2$ molecules to be rigid rotators [no distortion constant $D_0$ in Eqs. (A4) and (A5)], the errors in $F_X(T)$ that arise from this assumption (as compared with the nonrigid rotator case) are 0.29% for the Rayleigh case and between 0.28% ($T = 320$ K) and 0.48% ($T = 200$ K) for the N$_2$ VR case (both filters). The differences can be considered to be negligible and one can assume the molecules to be rigid rotators.

Besides Whiteman (2003a,b), Sakai et al. (2007) used temperature correction functions in a slightly different approach when computing WVMR. The authors determine an empirical relation between the correction factor at 298.15 K and the actual temperatures.

![Fig. 6. The $F_L(T)$ for Rayleigh at 354.7 nm for the HURL system (this work) and as reported by Whiteman (2003a). Note that we used a narrow filter of FWHM of ~0.25 nm while Whiteman used a theoretical (Gaussian shaped) filter of 0.3 nm. Moreover, Whiteman’s $F_L(T)$ is considered constant (0.97) over the temperature range.](image)

![Fig. 7. The $F_N(T)$ for N$_2$ VR at 386.7 nm for the HURL system (this work) and as reported by Whiteman (2003a). (a) The case of the ~0.25-nm FWHM filter and (b) the case of the ~5-nm FWHM filter for the HURL system. Note that Whiteman used theoretical filters with FWHM of (a) 0.3 and (b) 2 nm.](image)
4. Errors in estimating water vapor mixing ratio and aerosol backscatter ratio when omitting $F_X(T)$

We have determined the correction for the ratio of the overlap functions by comparing the lidar WVMR with that measured by radiosondes (e.g., Whiteman et al. 2006a,b; Adam et al. 2007). Equation (7) contains the ratio of the N$_2$ to water vapor temperature-dependent functions, $F_N(T)/F_H(T)$. This ratio, as obtained for the HURL interference filters, is shown in Fig. 9 for both filters. There is a change of about 13.2% between the $F_N(T)/F_H(T)$ ratio at 320 and 200 K for the 0.25-nm filter. For the 20-nm filter, there is a change of about 0.7%. When calibration is performed with respect to a radiosonde (RS), then the error due to the omission of $F_X(T)$ is proportional with the $F_N(T)/F_H(T)$ ratio. If for example the calibration is done somewhere where $T = 300$ K, then it will be a maximum error of 10.7% at $T = 200$ K for the 0.25-nm filter. Thus, the errors depend on the height ($T$) where the calibration is performed. When calibration is performed with respect to a microwave radiometer (MWR) [by comparing the total precipitable water; e.g., Turner et al. (2002); Ferrare et al. (2004); Whiteman et al. (2006a); Adam et al. (2007)], the errors due to the omission of $F_X(T)$ might be slightly different from the case of RS calibration. We show two examples of the relative errors with respect to the case of $F_X(T)$ incorporation, using HURL measurements (information online at http://meiyu.atmphys.howard.edu/~adam/HRL_WAVES.html) during the 2006 Water Vapor Validation Experiment (WAVES) campaign (MWR calibration). The first example is from 25 July (0048–0759 UTC) and the second is from 12 August (0007–0742 UTC). Four averaged profiles (over ~50 min each) of the WVMR are shown in Fig. 10 for both datasets [with $F_X(T)$ applied]. The spatial resolution is 30 m. However, the error analysis is performed over the entire dataset, at the original temporal resolution of 1 min. No smoothing was applied. The four averages corresponding to $T$, $F_N/F_H$, and the WVMR relative error for the two datasets are shown in Fig. 11. Note that for 25 July, three radiosondes were launched during the lidar measurement period, whereas for 12 August only one radiosonde was launched. Thus, for the first case the four averages are slightly different, while for 12 August the averages are the same (the same $T$ implies the same $F_N/F_H$ and further the same WVMR relative error). The radiosondes $T$ were interpolated at the times and heights of the lidar stamps. For the first case, the WVMR relative error ranges from ~$-2.87$% at the surface to ~$-6.11$% at the highest altitude (15 km), while for the second case, the error ranges from ~$-3.27$% at the surface to ~$-5.36$ at 15 km. We have also performed an RS calibration at 4.5 km ($T \approx 275$ K) and we obtained a similar range for the errors. Whiteman (2003a,b) reports relative differences up to 5% between $T = 300$ K and $T = 200$ K through the theoretical calculations, using theoretical Gaussian-shaped filters and the $T$ profile given by the U.S. Standard Atmosphere, 1976 model.

Now, recall the equation for the ABR [Eq. (8)]. For this calculation, we consider the ratio of the overlap...
functions to be unity. However, this might not be true in
the region of the incomplete overlap so that special at-
tention over the ABR retrievals in this region is re-
quired. Using clear-air normalization, when one does
not consider $F_X(T)$, the calibration factor will be dif-
ferent from the case of using $F_X(T)$ and it can also
incorporate the ratio of the total cross sections and ef-
ficiencies (considered to be constants). Below, we show
two examples of the ABR relative error for the same
dates as for WVMR. Figure 12 shows the four averages
for both datasets. Note that a strong artificial increase
in the first 400 m in the ABR occurred (caused by the
reflection in the receiving window on the roof of the
building, placed 2 m above the telescope, and possibly
other effects such as fluorescence of the window and
saturation of the 354.7-nm detector). Thus, we did not
consider the first 400 m for ABR. The ABR relative
errors with respect to the case where we apply $F_X(T)$ are
shown in Fig. 13 for the two datasets. For the first case
(Fig. 13a), the errors occurring within the PBL are up to
~1.5% while those in the clouds region are up to
~2.4%. Otherwise, the ABR relative error is in average
within ~0.5% to 0.5%. In the second case (Fig. 13b), the
ABR has smaller values in the PBL (up to ~1%) and
similar errors in the clouds region (~2.4%). Note that
above the clouds region (smaller SNR), the relative
ers increases (~ ~5% in the first case and ~ ~2% in
the second case). We can conclude that the influence of
the temperature-dependent function is less critical when
estimating the ABR as compared with WVMR esti-
ation. Note that no multiple-scattering correction was
applied and we consider that this missing correction
does not significantly affect the relative error comu-
tation we are interested in.

Fig. 10. WVMR-averaged profiles for (a) 25 Jul and (b) 12 Aug 2006. Each averaged profile corresponds
to a ~50-min average. Profiles used for each average are specified in the legend.

Fig. 11. Four series of averaged variables: (a) $T$, (b) $F_X(T)/F_H(T)$, and (c) WVMR relative error for 25 Jul and 12 Aug 2006. The WVMR
relative error is determined w.r.t. the case where $F_X(T)$ is applied.
5. Theoretical consideration for WVMR case

Slightly different positioning of the interference filters with respect to the wavelength corresponding to the vibrational shift (386.67 and 407.517 nm) involves slightly different $F_X(T)$ for both the $N_2$ and water vapor channels, as well as for their ratio. The wavelength displacement (blue shift) is performed by tilting (e.g., Behrendt and Reichardt 2000; Whiteman et al. 2006a) and is computed as (Born and Wolf 1987)

$$\lambda(\theta) = \lambda \sqrt{1 - \frac{\sin^2(\theta)}{n^2}},$$

where $\lambda$ is the wavelength at the normal incidence of light, $n$ is the index of refraction of the filter, and $\theta$ is the tilting angle. In the present simulations, $n = 1.5$.

The main purpose of the tilting was to find the smallest variation of the temperature-dependent function $F_X(T)$ for a particular channel or for the $F_N(T)/F_H(T)$ ratio. However, here we focus on two aspects. First, we focus on finding the filters tilting such that the mean $F_N(T)/F_H(T)$ ratio is the closest to unity. Second, we focus on finding the filters tilting such that the standard deviation (STD) of the mean $F_N(T)/F_H(T)$ ratio is small (the smallest variation). The numerical quantification for the two goals is provided by the root-mean-square (RMS) error and the relative error (RE), defined as

$$\text{RMS}(\%) = 100 \sqrt{\frac{1}{n} \sum_{i=1}^{n} (F_i - 1)^2},$$

$$\text{RE}(\%) = 100 \frac{\sigma(F)}{\overline{F}}.$$  \hspace{1cm} (23)

For RMS, $F_i$ can be either $F_X(T)$ for any of the channels or the $F_N(T)/F_H(T)$ ratio at a specific temperature $T_i$. For RE, $\overline{F}$ and $\sigma(F)$ can be the mean and STD over the temperature range of either one $F_X(T)$ or the $F_N(T)/F_H(T)$ ratio.

In the case of VR, the total cross section for the $Q$ branch is $\sim$100 times larger than the individual cross sections for the $S$ and $O$ branches. Thus, we want the maximum filter efficiency to be centered at the corresponding wavelength for the $Q$ branch (386.67 nm). Consequently, for the WVMR case, we tilt only the filter

![Fig. 12. ABR-averaged profiles for (a) 25 Jul and (b) 12 Aug 2006. Each averaged profile corresponds to a $\sim$50-min average. Profiles used for each average are specified in the legend. Note that in the clouds, the maximum ABRs are $\sim$52 and $\sim$12 for 25 Jul and 12 Aug 2006, respectively.](image)

![Fig. 13. ABR relative error (averaged profiles) for (a) 25 Jul and (b) 12 Aug 2006.](image)
for the water vapor channel. The interference filters used in the simulations are Gaussian shaped, and characterized by the maximum efficiency of 60% and various FWHMs. Our simulations imply in the first stage the computation of $F_X(\theta)$ for the N$_2$ and water vapor channels for the following conditions: $T$ varies from 200 to 320 K in 1-K steps, FWHM varies from 0.05 to 0.5 nm in steps of 0.05 nm, and the water vapor filter is tilted from 0° to 3° in steps of 0.1°. The results represent two matrices of dimensions $1 \times 10 \times 121$ and $31 \times 10 \times 121$ for N$_2$ and water vapor, respectively. Various analyses can be performed as a function of specific goals. Here, we focus on a few examples. Note that at the normal incidence of light (no tilting) the N$_2$ and water vapor filters are centered at $\lambda = 386.67$ nm and $\lambda = 407.517$ nm.

In the first example, the N$_2$ and water vapor filters are identical and there is no tilting for water vapor. Figure 14 shows the variation of $F_X(T)$ for N$_2$, water vapor, and their ratio over the temperature and FWHM ranges specified above. As expected, $F_X(T)$ tends to unity (RMS is small) with increasing FWHM (see Figs. 14a–d). On the other hand, as seen in Figs. 14b and 14d, $F_X(T)$ tends to be constant (small RE) over the temperature range for small FWHM in the case of N$_2$ and for large FWHM in the case of water vapor. The $F_N(T)/F_H(T)$ ratio tends to be constant for large FWHM (Figs. 14e and 14f). For the $F_N(T)/F_H(T)$ ratio, the smallest RMS (3.67%) occurs for FWHM = 0.3 nm while the smallest RE (1.6%) occurs at FWHM = 0.5 nm. The maximum absolute deviation (MAD) for RMS [the maximum absolute difference between unity and the $F_N(T)/F_H(T)$ profile] is 6.88% while MAD for RE [the maximum absolute difference between the mean $F_N(T)/F_H(T)$ ratio and the $F_N(T)/F_H(T)$ profile] is 2.91%. The filters chosen for the RMS and RE cases are shown in Fig. 15 along with the cross sections for N$_2$ and water vapor.

In the second example, we also consider identical filters for the two channels but we tilt the water vapor filter. RMS and RE as functions of FWHM and $\theta_H$ are shown in Fig. 16. In the case of RMS, for $\theta_H$ greater than 1.6°, RMS decreases as FWHM increases. However, for smaller tilting angles, smaller RMS occurs for FWHMs smaller than 0.3 nm. In general, RE decreases as FWHM increases. Usually, we are interested in estimating the RMS or RE for a specific FWHM. The minimum RMS and RE for each FWHM are shown in Fig. 17. Also shown are the tilting angles for which these minima occur. The minimum of RMS$_{\text{min}}$ (2.82%) occurs at $\theta_H = 1.1°$ (filter centered at $\lambda = 407.484$ nm) and FWHM = 0.2 nm while the minimum of RE$_{\text{min}}$ (0.147%) occurs at $\theta_H = 1.7°$ (filter centered at $\lambda = 407.438$ nm) and FWHM = 0.5 nm. The filters chosen for this case are shown in Fig. 15 as well. As one may still be interested in using smaller filters (e.g., smaller than 0.3 nm), the next question that arises is which combination of FWHM and $\theta_H$ can still provide an acceptable RE (within a few percentage points error). Thus, the next investigation concerns finding the local minima (i.e., other minima besides

![Fig. 14](image-url). Shown are (a),(b) $F_N(T)$, (c),(d) $F_H(T)$, and (e),(f) $F_N(T)/F_H(T)$ as functions of temperature and FWHM ($\theta_H = 0°$). The temperature and FWHM range are specified in the text.
that at FWHM = 0.5 nm). Figure 18 shows the local minima for RE for all the possible tilting angles (ranging from 0.8° to 1.6°). As seen in Fig. 18a, most of the local minima occur at the smallest FWHM (0.05 nm). If we plot the local minima as a function of tilting angle (Fig. 18b), the minimum of the local minima (0.39%) occurs at θ_H = 1.6° (filter centered at λ = 407.446 nm). The corresponding FWHM is 0.25 nm. Thus, if one is interested in using smaller filters with RE within 1% error, subsequently there are three options (according to Fig. 20):

1) RE = 0.95% for FWHM = 0.15 nm and θ_H = 1.4° (filter centered at λ = 407.463 nm),
2) RE = 0.66% for FWHM = 0.2 nm and θ_H = 1.5° (filter centered at λ = 407.455 nm), and
3) RE = 0.39% for FWHM = 0.25 nm and θ_H = 1.6° (filter centered at λ = 407.446 nm).

The third type of analysis involves the use of different combinations of filters for the two channels. Note that the smallest RMS or RE for each channel does not imply the smallest RMS or RE for the F_N(T)/F_H(T) ratio. The smallest RMS and RE for the F_N(T)/F_H(T) ratio, as well as the specific RMS and RE for each channel, are shown in Figs. 19 and 20. As seen in Fig. 19, the smallest RMS (2.82%) occurs for a N_2 filter with FWHM = 0.2 nm and for a water vapor filter with FWHM = 0.2 nm and a tilting angle of θ_H = 1.1° (as revealed within the previous analysis). Thus, if we consider this combination of filters to be the one that gives the value closest to unity, we will encounter an MAD of 5% at T = 320 K. Errors larger than 2% (with respect to unity) occur for T > 290 K and T < 242 K. For the RE case, as seen in Fig. 20, the smallest RE (0.139%) occurs for a N_2 filter with FWHM = 0.4 nm and for a water vapor filter of FWHM = 0.5 nm and tilted to θ_H = 1.7°. Thus, if we consider the mean of the F_N(T)/F_H(T) ratio (0.8614) in our analyses, we encounter an MAD -0.3% at T = 320 K and T = 200 K. Errors larger than 0.2% occur for T > 303 K and T < 214 K. The filters chosen for this case are also shown in Fig. 15. Within this case of using different filters, we can search the minimum RE or RMS when we specifically want to use certain filters. For example, if one desires to use a filter for N_2 with an FWHM = 0.3 nm and a filter for water vapor with FWHM = 0.25 nm, then the

---

**Fig. 15.** (a) Nitrogen and (b) water vapor filters used in the theoretical analyses.

**Fig. 16.** (a) RMS and (b) RE for the F_N(T)/F_H(T) ratio as a function of FWHM and θ_H. The ranges of T, FWHM, and θ_H are given in the text.
optimum tilting for the water vapor filter to obtain the minimum RMS (3.26%) is $\theta_H = 0.8^\circ$ (filter centered at $\lambda = 407.499$ nm). Thus, if we consider the $F_X(T)/F_H(T)$ ratio to be unity, we encounter errors larger than 2% for $T > 290$ K and $T < 247$ K, while MAD (5.6%) occurs at the lowest temperature (an absolute deviation of 5.2% is found at the highest $T$). For RE (0.389%), the optimum tilting is $\theta_H = 1.6^\circ$. Within this configuration, if we consider the mean $F_X(T)/F_H(T)$ ratio to be constant, errors larger than 0.5% occur for $T > 307$ K and $T < 204$ K with an MAD of 0.92% at $T = 320$ K. Whitman et al. (2006a) describe the tilting of the water vapor filter necessary to obtain an almost constant profile for the $F_X(T)/F_H(T)$ ratio. The tilting was such that the filter was centered at 407.45 nm. The N$_2$ and water vapor channels used 0.3- and 0.25-nm FWHM filters. As mentioned above, our theoretical computations suggest a tilting angle of 1.6$^\circ$, which corresponds to the center wavelength displacement to 407.446 nm. All the results are synthesized in Table 1.

6. Summary

A methodology able to compute the temperature-dependent function in the lidar equations was envisaged in this research. The main goal was to present an easily reproducible procedure that describes the computation of the backscatter cross section for both pure rotational Raman and vibrational–rotational Raman cases and the temperature-dependent function, used to correct the temperature dependence of the molecular backscatter cross sections. We have considered the total system efficiency to be composed of two terms. While one term represents the interference filter transmission efficiency (wavelength dependent), the other represents all the remaining system efficiencies (assumed constant over the interference filter bandpass). The molecules are considered to be nonrigid rotators. The errors occurring within the $F_X(T)$ terms, if we omit the centrifugal term, are 0.28%–0.48% for the N$_2$ case and 0.29% for the Rayleigh case and thus they can be considered negligible if we consider the molecules to be rigid rotators. The interference filter efficiencies were given by the manufacturer. The $F_X(T)$ functions are given for all three channels of the HURL system. Examples of the errors introduced by the omission of the temperature-dependent functions are given using two sets of HURL data. For these particular sets of data, the errors in evaluating the WVMR were up to 6%. For the ABR, the errors were up to 1.3% within the PBL and up to 2.2% within cirrus clouds regions. As previously mentioned, we can conclude that the influence of the $F_X(T)$ correction on ABR is small and, thus, the correction may be ignored. The systematic errors in WVMR and ABR due to the omission of the $F_X(T)$ correction, as well as other factors (calibration, gluing, incomplete overlap correction), are
discussed in a forthcoming paper (Adam and Venable 2008, manuscript submitted to J. Appl. Remote Sens.), where the dataset from 25 July 2006 is discussed. In general, the error due to the $F_X(T)$ omission is smaller compared with the other error contributions. The methodology and the preliminary results can be found in Adam and Venable (2007).

Theoretical computations are performed to determine $F_X(T)$ for N$_2$ and water vapor, as well as for their ratio (used in WVMR calculation), for simulated Gaussian-shaped filters. The goal is to find the optimum combination of different filters such that we obtain either the $F_N(T)/F_H(T)$ ratio profile closest to unity (smallest RMS) or the least variable profile of the $F_X(T)/F_H(T)$ ratio (smallest RE). The analyses reveal that even for the best combination of the filters, as well as the optimum tilting for water vapor filter, the RMS shows $\sim$3% error and a maximum absolute deviation of $\sim$7%, which is not suitable when computing the water vapor mixing ratio. However, for small RE (profile almost constant), we found several combinations of the filters such that RE is smaller than 1% (minimum RE is found as 0.139% while the maximum absolute deviation is 0.3%). As in general, the cases analyzed here are not representative of the multitude of available filters, our recommendation is to compute $F_X(T)$ for each experimental data point. Our belief is that the procedure detailed here allows an easy implementation of these correction functions.

Acknowledgments. This research was carried out with the help of a grant from NASA under the Aura validation program.
TABLE 1. RMS and RE of the ratio of the nitrogen to water vapor temperature-dependent functions $F_N(T)/F_W(T)$ for the three cases analyzed.

<table>
<thead>
<tr>
<th>Case</th>
<th>Min RMS for $F_N(T)/F_W(T)$</th>
<th>Min RE for $F_N(T)/F_W(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1; same filters, $\theta_H = 0^\circ$</td>
<td>3.67% MAD at 6.88% at 0.5 nm</td>
<td>1.6% MAD at 2.91% at 0.5 nm</td>
</tr>
<tr>
<td>2; same filters, variable $\theta_H$</td>
<td>2.82% MAD at 5% at 0.5 nm</td>
<td>0.147% MAD at 0.4% at 0.5 nm and $\theta_H = 1.7^\circ$</td>
</tr>
<tr>
<td>3; different filters, variable $\theta_H$</td>
<td>2.82% MAD at 5% at 0.5 nm</td>
<td>0.139% MAD at 0.3% at 0.5 nm and $\theta_H = 1.7^\circ$</td>
</tr>
</tbody>
</table>

APPENDIX A

Rayleigh Backscatter Differential Cross Section

The rotational differential cross section can be written in a concise form as

$$
\left( \frac{\partial \sigma}{\partial Q} \right)_j = (2\pi)^4 (\nu_0 + \Delta \nu)^4 F_{\text{MB},j} \Phi_j, \quad (A1)
$$

where $\nu_0$ is the wavenumber (cm$^{-1}$) corresponding to the excitation wavelength and $\Delta \nu$ is the PR Raman frequency shift (cm$^{-1}$). Here, $\Phi_j$ is a function containing the Placzek–Teller factors and molecular polarizability (described below), and $F_{\text{MB}}$ is the Maxwell–Boltzmann distribution function, which in the rotational case (e.g., Herzberg 1950; Long 2002) is

$$
F_{\text{MB},j} = \frac{g_{n,j}(2J + 1) \exp \left(-\frac{E_{\text{rot},j}}{K_B T}\right)}{Q_{\text{rot}}}, \quad (A2)
$$

where $J$ is the rotational quantum number, $K_B$ is the Boltzmann constant (J K$^{-1}$), and $T$ is temperature (K). Here, $Q_{\text{rot}}$ is the partition function given by (e.g., Herzberg 1950; Long 2002)

$$
Q_{\text{rot}} = \sum_j g_{n,j}(2J + 1) \exp \left(-\frac{E_{\text{rot},j}}{K_B T}\right), \quad (A3)
$$

where $E_{\text{rot},j}$ is the ground-state energy considering the molecule to be a nonrigid rotator that can be expressed as (e.g., Herzberg 1950; Long 2002)

$$
E_{\text{rot},j} = \hbar c \left[ J(J + 1)B_0 - J^2(J + 1)^2 D_0 \right]. \quad (A4)
$$

where $h$ is the Planck constant (J s$^{-1}$), and $B_0$ and $D_0$ are the rotational and centrifugal distortion constants (cm$^{-1}$), respectively. We define $B_0$ as (Herzberg 1950)

$$
B_0 = \frac{h}{8\pi^2 c I_b},
$$

where $I_b$ is the moment of inertia of the molecule about an axis through its center of gravity and perpendicular to the internuclear axis. In Eq. (A2), $g_{n,j}$ is the statistical weight factor, which depends on the nuclear spin, I (nuclear spin degeneracy; Table A1), and $2J + 1$ is the rotational degeneracy (see Herzberg 1950; Long 2002; Rokni and Flusberg 1986).

The Raman shift is computed for the $Q$, $S$, and $O$ branches as (e.g., Behrendt 2005)

$$
Q : \Delta \nu = 0,
$$

$$
S : \Delta \nu_{\text{Stokes}}(J) = -B_0(2J + 3) + D_0[3(2J + 3)^2 + (2J + 3)^3], \quad J = 0, 1, 2, \ldots,
$$

$$
O : \Delta \nu_{\text{Anti-Stokes}}(J) = B_0(2J - 1) - D_0[3(2J - 1)^2 + (2J - 1)^3], \quad J = 2, 3, 4, \ldots. \quad (A5)
$$

TABLE A1. The statistical weight (nuclear degeneracy) $g_{n,j}$, the rotational constants (adapted from Behrendt 2005), and polarizability tensor (adapted from Long 2002) for the O$_2$ and N$_2$ molecules.

<table>
<thead>
<tr>
<th>Gas</th>
<th>I</th>
<th>$T_J = 2I, 2I-1, \ldots, 0$</th>
<th>$g_{n,j} = \Sigma(2T_J + 1)$</th>
<th>Even J</th>
<th>Odd J</th>
<th>$B_0$ (cm$^{-1}$)</th>
<th>$a^2$ (m$^2$)</th>
<th>$\gamma^2$ (m$^2$)</th>
<th>$a^2$ (m$^4$ kg$^{-1}$)</th>
<th>$\gamma^2$ (m$^4$ kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1</td>
<td>2, 1, 0</td>
<td>6</td>
<td>3</td>
<td>1.98957</td>
<td>5.76</td>
<td>3.17</td>
<td>0.52</td>
<td>2.62</td>
<td>4.23</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.43768</td>
<td>4.85</td>
<td>2.66</td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Here I, nuclear spin; $T_J$, total nuclear spin; $g_{n,j}$, statistical weight factor.
The $\Phi_J$ terms for the $Q$, $S$, and $O$ branches are

\begin{align*}
Q: \Phi_J &= a^2 + \frac{7}{45} \frac{J(J+1)}{(2J-1)(2J+3)} \gamma^2, \quad J = 0, 1, 2, \ldots, \\
S: \Phi_J &= \frac{7}{45} \frac{3(J+1)(J+2)}{(2J+1)(2J+3)} \gamma^2, \quad J = 0, 1, 2, \ldots, \\
O: \Phi_J &= \frac{7}{45} \frac{3(J-1)}{2J-1)(2J+1)} \gamma^2, \quad J = 2, 3, 4, \ldots,
\end{align*}

(A6)

where $a$ and $\gamma$ are invariants of the polarizability tensor (Table A1) denoting the isotropic and anisotropic polarizabilities; the fraction terms containing $J$ (without the 7/45 term) are called Placzek–Teller coefficients, as given in Herzberg, also contain the 2$J + 1$ term. One should pay close attention since many authors cite these terms in various ways [e.g., as given in Eq. (A6), multiplied with 2$J + 1$, without the 3/2 factor, etc.]. Taking into account Eq. (2), Eq. (A1) can be rewritten as

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_J = (2\pi)^4 (v_0 + \Delta \nu)^4 \frac{g_{n,J}(2J+1) \exp \left( -\frac{2E_{\text{rot},J}}{K_B T} \right)}{Q_{\text{rot}}} \Phi_J,
\]

(A7)

Note that in the case of a rigid rotator ($D_0 = 0$), the rotational partition function can be determined analytically, having the expression $Q_{\text{rot}} = (2J + 1)^2 K_B T (2hcB_0)$. The individual spectral lines for branches $Q$, $S$, and $O$ become

\[
Q: \left( \frac{\partial \sigma}{\partial \Omega} \right)_J = \frac{112\pi^4}{45} (v_0)^4 \frac{g_{n,J}(2J+1) \exp \left( -\frac{2E_{\text{rot},J}}{K_B T} \right)}{Q_{\text{rot}}} \left( \frac{45}{7} a^2 + \frac{J(J+1)}{(2J-1)(2J+3)} \gamma^2 \right), \quad J = 0, 1, 2, \ldots,
\]

\[
S: \left( \frac{\partial \sigma}{\partial \Omega} \right)_J = \frac{112\pi^4}{45} (v_0 - \Delta \nu)^4 \frac{g_{n,J}(2J+1) \exp \left( -\frac{2E_{\text{rot},J}}{K_B T} \right)}{Q_{\text{rot}}} \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \gamma^2, \quad J = 0, 1, 2, \ldots,
\]

\[
O: \left( \frac{\partial \sigma}{\partial \Omega} \right)_J = \frac{112\pi^4}{45} (v_0 - \Delta \nu)^4 \frac{g_{n,J}(2J+1) \exp \left( -\frac{2E_{\text{rot},J}}{K_B T} \right)}{Q_{\text{rot}}} \frac{3(J-1)}{2(2J+1)(2J-1)} \gamma^2, \quad J = 2, 3, 4, \ldots
\]

(A8)–(A10)

APPENDIX B

Nitrogen VR Backscatter Differential Cross Section

In the case of the Stokes VR, the frequency shift will be $-\nu_{\text{vib}} + \Delta \nu$. Then, Eq. (A1) becomes the VR differential cross section:

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_J = (2\pi)^4 (v_0 - \nu_{\text{vib}} + \Delta \nu)^4 F_{\text{MB}} \Phi_J,
\]

(B1)

where $\nu_{\text{vib}}$ is the vibrational Raman shift [2331 cm$^{-1}$ for N$_2$; Herzberg (1950)]. The Maxwell–Boltzmann distribution function depends on both rotational and vibrational transitions. The vibrational distribution function is (e.g., Herzberg 1950; Long 2002)

\[
F_{\text{MB},v} = \frac{\exp \left( -\frac{E_{\text{vib},v}}{K_B T} \right)}{Q_{\text{vib}}(T)},
\]

(B2)

where $E_{\text{vib},v}$ is the vibrational energy, in a simple harmonic approximation (e.g., Long 2002):

\[
E_{\text{vib},v} = h \nu_{\text{vib}} \left( v + \frac{1}{2} \right),
\]

(B3)

where $\nu$ is the vibrational quantum number and $Q_{\text{vib}}$ is the partition function for vibrational states and is given by (e.g., Herzberg 1950; Long 2002)

\[
Q_{\text{vib}}(T) = \sum_v \exp \left[ -\frac{hc\nu_{\text{vib}}}{K_B T} \left( v + \frac{1}{2} \right) \right]
= \exp \left( \frac{hc\nu_{\text{vib}}}{2K_B T} \right) \frac{1}{1 - \exp \left( -\frac{hc\nu_{\text{vib}}}{K_B T} \right)}.
\]

(B4)

The factors $\Phi_J$ are expressed as a function of the derivative of the polarizability tensor invariants, $a'$ and $\gamma'$.
The total Stokes scattered intensity involves summing $N(v + 1)F_{MB,v}$ over all $v$ for a given mode (Long 2002, p. 119), where $N$ is the total number of molecules. Thus, Eq. (B2) involves the sum over $(v + 1)F_{MB,v}$:

$$\sum_v (v + 1)F_{MB,v} = \frac{1}{1 - \exp(-hcv_{vib}/K_BT)}.$$  \hspace{1cm} (B5)

Equation (B1) becomes

$$\frac{(\partial \sigma)}{(\partial \Omega)}_J = (2\pi)^4 (v_0 - \nu_{vib} + \Delta \nu)^4 \frac{g_{n,J}(2J + 1) \exp\left(-\frac{E_{vib,J}}{K_BT}\right)}{Q_{rot}} \frac{h}{8\pi^2cv_{vib}} \frac{1}{1 - \exp(-hcv_{vib}/K_BT)} \Phi_J,$$  \hspace{1cm} (B6)

where $b_J^2 = h/8\pi^2cv_{vib}$ (Long 2002) is called the amplitude of the zero-point vibrational energy. The individual spectral lines for the $Q$, $S$, and $O$ branches are then given by

$$Q:\frac{(\partial \sigma)}{(\partial \Omega)}_J = \frac{112\pi^4}{45} (v_0 - \nu_{vib} + \Delta \nu)^4 \frac{g_{n,J}(2J + 1) \exp\left(-\frac{E_{vib,J}}{K_BT}\right)}{Q_{rot}} \frac{h}{8\pi^2cv_{vib}} \frac{1}{1 - \exp(-hcv_{vib}/K_BT)} \times \left(\frac{45}{7} a^2 + \frac{J(J + 1)}{(2J - 1)(2J + 3)} \gamma^2\right), \quad J = 0, 1, 2, \ldots,$$  \hspace{1cm} (B7)

$$S:\frac{(\partial \sigma)}{(\partial \Omega)}_J = \frac{112\pi^4}{45} (v_0 - \nu_{vib} + \Delta \nu)^4 \frac{g_{n,J}(2J + 1) \exp\left(-\frac{E_{vib,J}}{K_BT}\right)}{Q_{rot}} \frac{h}{8\pi^2cv_{vib}} \frac{1}{1 - \exp(-hcv_{vib}/K_BT)} \times \frac{3(J + 1)(J + 2)}{2(2J + 1)(2J + 3)} \gamma^2, \quad J = 0, 1, 2, \ldots, \text{ and}$$  \hspace{1cm} (B8)

$$O:\frac{(\partial \sigma)}{(\partial \Omega)}_J = \frac{112\pi^4}{45} (v_0 - \nu_{vib} + \Delta \nu)^4 \frac{g_{n,J}(2J + 1) \exp\left(-\frac{E_{vib,J}}{K_BT}\right)}{Q_{rot}} \frac{h}{8\pi^2cv_{vib}} \frac{1}{1 - \exp(-hcv_{vib}/K_BT)} \times \frac{3(J - 1)(J + 1)}{2(2J + 1)(2J - 1)} \gamma^2, \quad J = 2, 3, 4, \ldots.$$  \hspace{1cm} (B9)

REFERENCES


