

# Temperature sensitivity of an atmospheric Raman lidar system based on a XeF excimer laser

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The temperature sensitivity of Raman backscattering from atmospheric nitrogen, oxygen, and water vapor is considered over the range of temperatures expected in the troposphere. These results are applied to the Raman spectrum induced by a XeF excimer laser, which produces three line groups centered at approximately 349, 351, and 353 nm. Bandpass filter characteristics are determined for this case.

Atmospheric measurements using the Raman lidar technique have been made since the late 1960's, when early measurements of nitrogen and water vapor were performed.<sup>1,2</sup> Within the last decade, the Raman technique has been used to observe and analyze the passage of warm and cold frontal systems, gravity waves, and the variation of moisture over crop fields.<sup>3-6</sup> However, little attention has been given to whether the temperature sensitivity of the spectrum of Raman backscattering might affect atmospheric measurements. We consider here the temperature sensitivity of Raman backscattering from nitrogen, oxygen, and water vapor over a range of temperatures that might be expected in tropospheric measurements. The initial calculations are performed assuming a single-line laser source. These results are then applied to the case of a Raman lidar based on a XeF excimer laser exhibiting three line groups in its output spectrum.

We first consider the spectral characteristics for the three major species contributing to the Raman return signals for our system: N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O. The pure rotational spectra are superposed, close to the excitation frequency, and the resulting signal is difficult to analyze. This case is not considered further here.

In a fluid sample, if the excitation frequency is far from resonance with electronic levels, Raman scattering can be described in terms of the two rotational invariants of the polarizability tensor, the trace and anisotropy.<sup>7</sup> Allowed transitions for trace scattering must obey more limited selection rules than those for anisotropy scattering. For diatomic molecules, trace scattering for the fundamental vi-

brational transition consists only of the rotational Q branch, with rotational selection rule  $\Delta J = 0$ . However, the anisotropy scattering includes not only the Q branch but O and S branches ( $\Delta J = \pm 2$ ) as well; these transitions consist of nearly equally spaced lines on either side of the Q branch, with spacing determined by the rotational spectroscopic constant of the molecule.<sup>8</sup>

The cross sections and depolarization ratios for the fundamental vibrational bands of nitrogen and oxygen have been measured<sup>9</sup>; with the estimate that one quarter of the anisotropy cross section occurs in the Q branch,<sup>7</sup> we find that less than 17% of the total cross section for N<sub>2</sub> is made up of anisotropy scattering, whereas for O<sub>2</sub> it makes up 32% of the total cross section. While these results are for excitation at 514 nm, we assume that the low dispersion in the depolarization ratio of Rayleigh scattering<sup>10</sup> carries over to Raman scattering and that these predictions are valid for the XeF laser excitation conditions considered here as well.

In general, the individual lines within the O, Q, and S branches are temperature sensitive. However, for atmospheric temperatures, essentially all molecules are in the ground vibrational state, and the integrated total cross section for the Raman backscatter is independent of temperature.<sup>11</sup> On the other hand, the distribution of energy within the rotational branches is temperature dependent, and if some of the rotational structure is excluded by the detection system, the temperature dependence of the detected signal can be significant.

The temperature sensitivity is considered here for Raman backscatter when it is excited by a monochro-

matic source and detected with ideal, square-edge bandpass filters—ones that transmit uniformly at their center and block completely outside of this region. For nitrogen and oxygen, we have calculated the spectral range that must be included in order that the temperature variation due to the excluded signal be negligible. We have assumed that the vibrational and rotational states are decoupled, so that relations for pure rotational Raman scattering may be used in this case.<sup>11</sup> The number of transitions in the *O* and *S* branches that must be included in order to produce no more than 0.5% change in the total Raman backscatter intensity was calculated for the temperature range 220–300 K, the range of temperatures one might expect for tropospheric measurements of water vapor. For nitrogen, *O* and *S* transitions from states up to  $J = 16$  ( $\pm 139$  cm<sup>-1</sup> with respect to the *Q* branch) must be included, and for oxygen, states up to  $J = 21$  ( $\pm 129$  cm<sup>-1</sup>).

In considering the temperature sensitivity of the Raman spectrum of water vapor, one notes that the OH stretching region is complicated by three factors: (1) The water molecule is an asymmetric top, so that the rotational structure is much more complicated than in the diatomic molecule case. (2) There are two vibrational modes, the symmetric and asymmetric stretching modes,  $\nu_1$  and  $\nu_3$ , that contribute to this region. (3) The rotational levels of the two vibrational modes are perturbed by each other and by the nearby overtone of the bending mode<sup>12</sup>; any simulation should take this into account.

The polarizability components for the water stretching vibrations have been estimated<sup>13</sup>; these may be used to predict the various contributions to the total Raman spectrum. Trace scattering is allowed for only the *Q* branch of the totally symmetric stretching mode,  $\nu_1$ , and, owing to the vibrational dependence of the rotational constants, this extends from the band origin at 3657 to  $\sim 3625$  cm<sup>-1</sup>. The room-temperature anisotropy spectrum extends from 3200 to 4300 cm<sup>-1</sup> and contributes 20% of the total cross section, with the  $\nu_3$  contribution being two thirds of this amount.

Because of the complexity of the anisotropy scattering spectrum in this region, the analysis of the temperature dependence must be accomplished through consideration of the simulated spectra. Spectra were calculated for the two temperatures used in the N<sub>2</sub> and O<sub>2</sub> analysis, 220 and 300 K, by use of the routine for calculation of asymmetric top Raman rotational contours,<sup>14</sup> as modified for the case of  $\nu_1$ - $\nu_3$  interactions in H<sub>2</sub>X.<sup>15</sup> Running integrals of the two contours were determined, and their difference was obtained. The extreme points in the spectrum where the difference becomes 0.25% of the total cross section are 3420 and 4140 cm<sup>-1</sup>, which give a total error of 0.5% of the total Raman backscatter signal. For these limits, over 99% of the total backscatter is detected.

The difference of the running integrals can be used to test other proposed bandpass limits. A preliminary proposal of a 210-cm<sup>-1</sup> bandwidth filter centered at the  $\nu_1$  maximum (3549–3759 cm<sup>-1</sup>) gives an error

of 0.23% while detecting 86% of the total intensity. A bandpass from 3481 to 3751 cm<sup>-1</sup> gives a negligible error for these two temperatures while detecting 87% of the total intensity. The worst case for these temperatures is a bandpass from 3589 to 3971 cm<sup>-1</sup>, having an error of 1.5% while detecting 94% of the total intensity. The characteristics of the scattering spectra discussed above are now considered for the case of a XeF excimer laser that exhibits multiple line groups.

The output of the XeF laser is attractive for use as the transmitter in a lidar system because output powers of several tens of watts can easily be achieved in commercially available units. In addition, various manufacturers have advertised that all the output energy is available in a single line group centered at 351 nm. However, the fluorescence energy spectrum for XeF under electron-beam excitation<sup>16</sup> reveals the presence of several regions that support laser action. In addition to the 351-nm region that is due to *B* → *X* electronic transitions, where as many as three line groups have been reported,<sup>17–20</sup> there is the 450–550-nm region that is due to *C* → *X* transitions, where tunability has been demonstrated.<sup>21</sup>

Measurements of the output spectrum of the Lambda Physik LPX 240 iCC confirm the presence of three line groups that are due to *B* → *X* transitions (Fig. 1). These line groups are centered at  $348.77 \pm 0.05$  nm,  $351.10 \pm 0.05$  nm, and  $353.18 \pm 0.05$  nm. The measurements were made using an Instruments S.A. HR-640 spectrometer with a 2400-line/mm grating. Slit widths were 10  $\mu$ m, which provided an instrument resolution of 0.006 nm. A neon lamp was used for calibration. With the 351-nm line group as reference, the relative intensities of the other groups were 0.18 and 0.78 for 349 and 353 nm, respectively. The laser manufacturer's suggested gas pressures were used for these measurements; the discharge voltage was 21 kV. It has been shown<sup>19</sup> that the relative energy distribution of the output lines of XeF is a function of the temperature, pressure, and concentrations of the gases used, but we did not investigate these dependencies.

The presence of three line groups in the output of the laser has significant consequences for the Raman measurements of the water-vapor mixing ratio. With the newly developed NASA Goddard Space Flight Center Raman water-vapor lidar system, we

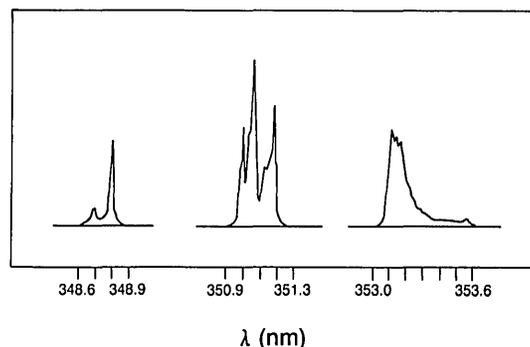


Fig. 1. Spectral measurement of the output of a Lambda Physik LPX 240 iCC laser using a XeF gas mixture.

**Table 1. Conversion of Frequency Shifts to Absolute Wavelengths**

Band Positions and Passband Limits (cm <sup>-1</sup> )		Laser Wavelength (nm)		
		348.8	351.1	353.2
O <sub>2</sub> : -limit	1437	367.2	369.8	372.1
O <sub>2</sub> : Q branch	1555	368.8	371.4	373.7
O <sub>2</sub> : +limit	1673	370.4	373.0	375.8
N <sub>2</sub> : -limit	2174	377.4	380.1	382.6
N <sub>2</sub> : Q branch	2329	379.6	382.4	384.9
N <sub>2</sub> : +limit	2484	381.9	384.6	387.2
H <sub>2</sub> O: -limit	3420	396.0	399.0	401.7
H <sub>2</sub> O: Q branch	3654	399.7	402.8	405.5
H <sub>2</sub> O: +limit	4140	407.7	410.8	413.7

measured the Raman returns (Stokes shift, Q-branch maxima) from oxygen (1555 cm<sup>-1</sup>), nitrogen (2329 cm<sup>-1</sup>), and water vapor (3654 cm<sup>-1</sup>). Each of the transmitted line groups from the laser stimulated a Raman shifted return from the three molecules mentioned and complicated the interpretation of the observation. The use of a single-line laser would simplify this situation.

By using an intracavity étalon<sup>22</sup> or a grazing-incidence grating,<sup>23</sup> a nearly single-line energy distribution can be achieved in a XeF laser. However, if one injects the output of a single-line XeF laser into a single-pass XeF amplifier, the other line groups tend to be excited in the amplification process owing to the fact that there are electronic transitions in both the 351- and 353-nm line groups, which share the same upper state.<sup>20</sup> Since we may incorporate a single-pass amplifier into the system in the future, we have designed the detection system of the lidar to handle the presence of three line groups for each molecule.

The results of considering the temperature sensitivity of the Raman backscatter for each of the three line groups present in the XeF spectrum are presented in Table 1, which gives the transformation of the frequency shift data to wavelengths. Since there is no overlap between species' ranges of scattering from each of the three source wavelengths, bandpass filters could be specified to pass the extreme limits for all three exciting lines for each species: O<sub>2</sub>, 367.0–375.5 nm; N<sub>2</sub>, 377.7–386.9 nm; H<sub>2</sub>O, 396.0–413.7 nm. This assumes monochromatic excitation at each of the XeF wavelengths, and, as stated above, ideal, square-edge bandpass filters. Since we have the facility to simulate each of the spectra, we have the capability to investigate other approaches in order to take into account nonmonochromatic laser outputs, nonideal filter characteristics, and optimization of the measurement in the presence

of background signal. These details are beyond the scope of this Letter.

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