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MODTRAN® and the GrossDoppler Line-shape Function

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ABSTRACT

MODTRAN models the molecular absorption for the entire 0 to 50,000 cm^{-1} spectral range. Typically, radiative transfer models define distinct line-shape functions depending on the spectral region. This can produce spectral anomalies at the transitions. A 3-parameter GrossDoppler line-shape function is defined that provides a spectrally-universal model for computing molecular absorption.

Key Words: Voigt line-shape, Weiskopf line-shape, Gross line-shape, MODTRAN, molecular absorption

1. INTRODUCTION

The MODTRAN6 radiative transfer model enjoys widespread use within the remote sensing, data analysis, scene simulation and climate forecasting communities. Much of MODTRAN's appeal derives from its statistical band model algorithm, which enables the radiative transfer equations to be rapidly solved over narrow spectral channels without requiring finely gridded monochromatic calculations.

Recently, a line-by-line (LBL) algorithm was developed for MODTRAN6[1]. At first, it may seem as if adding this capability is counter to the fundamental MODTRAN philosophy of providing rapid in-band radiative transfer. However, statistical algorithms, by their very nature, require methods or metrics for evaluating their accuracy. The MODTRAN LBL method was introduced to provide users of the model the ability to evaluate the statistical uncertainties of MODTRAN results for their specific applications.

Molecular absorption in the MODTRAN LBL algorithm is modeled using the Van-Vleck Huber (VVH) line-shape function[1]. This three parameter line-shape function defines the contribution of molecular absorption for frequencies extending 25 cm^{-1} from line center; the parameters are the transition frequency, ν_{ij}, the collision-broadened half-width at half-maximum (HWHM), γ_c, and the Doppler half-width at $1/e$ of maximum line-shape value, γ_d. Temperature and pressure dependent continua coefficients are used to model the more distant molecular line contributions. The VVH spectral form provides a smooth transition from the Voigt line-shape function in the infrared to the Van-Vleck Weiskopf, or simply Weiskopf, line-shape function in the microwave. However, MODTRAN models the absorption arising from the full suite of HITRAN molecular transitions[2] thus, its spectral range extends to even longer radio waves, where the VVH line-shape is not applicable. In this paper, an effort is initiated to define a spectrally-universal, 3-parameter line-shape function.

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2. BACKGROUND

The normalized Voigt line-shape function,

$$f_\nu^V\left(\gamma_c,\gamma_d;\nu_{if}\right)=\int_{-\infty}^{\infty}\frac{\gamma_c\,\exp\left(-t^2\right)}{\gamma_c^2+\left(\nu-\nu_{if}-\gamma_d t\right)^2}\frac{dt}{\pi^{3/2}}\quad , \tag{1}$$

is commonly used to model the spectral dependence of molecular absorption in the infrared, visible and ultraviolet spectral regions. The Voigt line-shape is a function of the spectral displacement from line center, the difference between the measurement frequency, ν, and the transition frequency. The Voigt form arises from the spectral convolution of the normalized Lorentz and Doppler line-shape functions:

$$f_\nu^L\left(\gamma_c;\nu_{if}\right)=\frac{\gamma_c/\pi}{\left(\nu-\nu_{if}\right)^2+\gamma_c^2}\quad and\quad f_\nu^D\left(\gamma_d;\nu_{if}\right)=\frac{\exp\left[-\left(\nu-\nu_{if}\right)^2/\gamma_d^2\right]}{\gamma_d\sqrt{\pi}}\quad . \tag{2}$$

It is well known that the Voigt lineshape does not accurately capture the spectral dependence of molecular absorption in the microwave, where the line-shape begins to exhibit asymmetric absorption about the line center. In this region, contributions from Doppler shifting are small and the Weiskopf line-shape function is most commonly used:

$$f_\nu^W\left(\gamma_c;\nu_{if}\right)\equiv\left(\nu/\nu_{if}\right)^2\left[\frac{\gamma_c/\pi}{\left(\nu-\nu_{if}\right)^2+\gamma_c^2}+\frac{\gamma_c/\pi}{\left(\nu+\nu_{if}\right)^2+\gamma_c^2}\right]\quad . \tag{3}$$

This form is somewhat deceptive in that the maximum of the line-shape function does not occur exactly at the transition frequency, ν_{if}, and the HWHM is not exactly equal to γ_c. However, the discrepancies between these paired values is proportional to the square of the ratio of the half-width to the transition frequency, i.e. $\Delta\nu_{if}\propto(\gamma_c/\nu_{if})^2$ and $\Delta\gamma_c\propto(\gamma_c/\nu_{if})^2$. For a 30 GHz (1 cm) line, this ratio at 1 atm pressure is typically small: $(\gamma_c/\nu_{if})^2\approx(0.06)^2\approx 0.004$. Thus, the Weiskopf line-shape can be evaluated at the measured transition frequency and HWHM in the microwave spectral region.

Optimally, one would create a smooth transition from the microwave to the infrared by spectrally convolving the Weiskopf and Doppler line-shape functions. This is not possible because the Weiskopf form is not integrable (normalizable). Instead, line-by-line models often transition smoothly between the microwave and infrared spectral regions by simply replacing the Lorentzian contributions with their Voigt counterpart:

$$f_\nu^W\left(\gamma_c,\gamma_d;\nu_{if}\right)\equiv\frac{\nu^2}{\nu_{if}^2}\left[f_\nu^V\left(\gamma_c,\gamma_d;\nu_{if}\right)+f_\nu^V\left(\gamma_c,\gamma_d;-\nu_{if}\right)\right]\quad . \tag{4}$$

Note that this form for the Weiskopf line-shape includes dependence on the Doppler half-width. As the transition frequency increases from the microwave into the infrared, the coefficient of the bracketed term approaches one near line center ($|\nu-\nu_{if}|\le 25$ cm^{-1}) and the negative resonance term (dependent on $-\nu_{if}$) becomes small. Thus, the Eq. (4) line-shape approaches the Voigt form of Eq. (1).

As one transitions in the opposite direction, to even longer radio waves, the accuracy of the Weiskopf form deteriorates. At these wavelengths, an alternate line-shape function, attributed to Gross, is commonly used:

$$f_\nu^G\left(\gamma_c;\nu_{if}\right)\equiv\frac{4\nu^2\gamma_c/\pi}{\left(\nu^2-\nu_{if}^2\right)^2+4\nu^2\gamma_c^2}\quad . \tag{5}$$

This form has a number of appealing features. It approaches zero at zero frequency; it is integrable since it falls off as $1/\nu^2$ for large ν; it is normalized; and it does not become exceedingly large when ν_{if} is small ($<<1$ cm^{-1}) and $\nu>\nu_{if}$.

Furthermore, the maximum of f_ν^{Gross} occurs at $\nu = \nu_{if}$, and although the line-shape is asymmetrical, the half-width at half-maximum (HWHM) is equal to γ_c. Finally, the value of the Gross line-shape at line center, $1/(\pi\,\gamma_c)$ equals the Lorentz line-shape transition frequency value.

It is natural to ask what the relationship is between the Gross line-shape function and the microwave line-shape functions. To make this comparison, the Gross line-shape function for $\nu_{if} \geq \gamma_c$, a condition applicable in the microwave, can be rewritten as follows:

$$f_\nu^G\left(\gamma_c;\nu_{if}\right) = \frac{\gamma_c \nu^2}{\pi \nu_{if}^2}\left[\frac{2-\nu\Big/\sqrt{\nu_{if}^2-\gamma_c^2}}{\left(\nu-\nu_{if}\right)^2+\gamma_c^2\dfrac{2\nu}{\sqrt{\nu_{if}^2-\gamma_c^2}+\nu_{if}}}+\frac{2+\nu\Big/\sqrt{\nu_{if}^2-\gamma_c^2}}{\left(\nu+\nu_{if}\right)^2-\gamma_c^2\dfrac{2\nu}{\sqrt{\nu_{if}^2-\gamma_c^2}+\nu_{if}}}\right] \quad , \quad \nu_{if} \geq \gamma_c$$

$$\approx \frac{\nu^2}{\nu_{if}^2}\left[\frac{\gamma_c/\pi}{\left(\nu-\nu_{if}\right)^2+\gamma_c^2}+\frac{3\gamma_c/\pi}{\left(\nu+\nu_{if}\right)^2-\gamma_c^2}\right] \quad for \quad \nu \approx \nu_{if} >> \gamma_c \quad . \tag{6}$$

When $\nu \approx \nu_{if} >> \gamma_c$, the term on the left approaches the term on the left in the Weiskopf line-shape expression, Eq. (3). The primary difference between the Gross and Weiskopf line-shape functions arises from the contributions to the significantly smaller negative resonance terms; the numerator of the right-hand side term in Eq. (6) approaches 3 [not 1]. Also, the γ_c^2 term in the denominator is subtracted, not added, but this term is small compared to $(\nu - \nu_{if})^2$.

3. A SPECTRALLY UNIVERSAL LINE-SHAPE FUNCTION

Since the Gross line-shape function is normalized and it approaches the Lorentz line-shape in the infrared, it can be convolved with the Doppler line-shape to produce a single, normalized GrossDoppler (GD) line-shape function applicable for all radio wave through UV wavelengths. For $\nu_{if} < \gamma_c$, Doppler contributions will always be extremely small and the Gross form, Eq. (5), can be used directly. When the transition frequency exceeds the Lorentz half-width, the spectral convolution can be shown to be given by the following expression:

$$f_\Delta^{GD}\left(\gamma_c,\gamma_d;\nu_{if}\right) = \int_{-\infty}^{\infty} f_t^D\left(\gamma_d;\nu_{if}\right) f_{\Delta-t}^G\left(\gamma_c;\nu_{if}\right) dt$$

$$= \frac{1}{\gamma_d\sqrt{\pi}}\left[\begin{array}{l} K\left(x+\dfrac{y\,\gamma_c}{\nu_{if}+\sqrt{\nu_{if}^2-\gamma_c^2}},y\right)+\dfrac{\gamma_c}{\sqrt{\nu_{if}^2-\gamma_c^2}}L\left(x+\dfrac{y\,\gamma_c}{\nu_{if}+\sqrt{\nu_{if}^2-\gamma_c^2}},y\right) \\ +K\left(x+\dfrac{\nu_{if}+\sqrt{\nu_{if}^2-\gamma_c^2}}{\gamma_d},y\right)-\dfrac{\gamma_c}{\sqrt{\nu_{if}^2-\gamma_c^2}}L\left(x+\dfrac{\nu_{if}+\sqrt{\nu_{if}^2-\gamma_c^2}}{\gamma_d},y\right) \end{array}\right] \quad , \quad \nu_{if} \geq \gamma_c \tag{7}$$

where

$$x \equiv \frac{\Delta}{\gamma_d} \quad , \quad y \equiv \frac{\gamma_c}{\gamma_d} \quad , \quad K\left(X,Y\right) = \frac{Y}{\pi}\int_{-\infty}^{\infty}\frac{\exp\left(-\tau^2\right)d\tau}{Y^2+\left(X-\tau\right)^2} \quad and \quad L\left(X,Y\right) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\left(X-\tau\right)\exp\left(-\tau^2\right)}{Y^2+\left(X-\tau\right)^2}d\tau \quad . \tag{8}$$

The functions $K(X, Y)$ and $L(X, Y)$ are the real and imaginary parts of the complex probability function (CPF), respectively.

Only the first term in Eq. (7) is significant in the infrared (IR), visible (VIS) and ultraviolet (UV), and this term essentially equals to the Voigt line-shape function

$$f_{\Delta}^{Voigt}\left(\gamma_c,\gamma_d;\nu_{if}\right)=\frac{1}{\gamma_d\sqrt{\pi}}K\left(x,y\right)\approx\frac{1}{\gamma_d\sqrt{\pi}}K\left(x+\frac{y\,\gamma_c}{\nu_{if}+\sqrt{\nu_{if}^{2}-\gamma_c^{2}}},y\right)\quad\left|\begin{array}{l}\nu_{if}>400\ cm^{-1}\quad and\\ \left|\nu-\nu_{if}\right|<25\ cm^{-1}\end{array}\right.\quad . \tag{9}$$

Here, the frequency offset, $x_1^{off} \approx ½\ \gamma_c\ (\gamma_c / \nu_{if})$, is a small fraction of the Lorentz half-width, and the Voigt line-shape does not vary appreciably on this scale.

3.1 Examples of the GrossDoppler Line-Shape Function

The Gross Doppler line-shape function is examined in this section for three molecular transitions: one in the thermal infrared, one in the microwave and a radio wave transition long of the microwave. HITRAN 2016 parameters[2] define the chosen transitions, which were all selected to be relative strong within their spectral sub-region. Table I lists the HITRAN data. The line-shapes were all computed at 296 K.

Table 1. HITRAN2016 Data for Examined Molecular Transitions

CH_4: 61 1327.074020 9.694E-20 2.322E+00.05820.075 62.87820.76-.001700 0 0 0 1 1F2 0 0 0 0 1A1 4A1 1 3A2 1 336654574736 6 5 6 45.0 35.0
NH_3: 111 0.796222 6.607E-23 2.558E-07.10720.600 85.06820.730.000000 0000 00 0 A2" 0000 00 0 A1' 3 3 a A1"A2' 3 3 s A2"A2" 546650 8 8 4 2 2 0 84.0 84.0
OH: 131 0.002967 1.077E-31 8.525E-18.04000.000 608.19630.660.000000 X1/2 0 X1/2 0 4.0 QQ 4.5ef 5.0603010 4 4 2 0 1 0 9.0 11.0

3.2 Thermal Infrared CH4 Molecular Transition

The first molecular transition examined was a CH_4 line at 1327.074020 cm^{-1}, 7.535 μm. Since this line is in the IR, the GrossDoppler line-shape function is expected to equal the Voigt line-shape. The pressure was set to 0.1 atm so that the Lorentz (γ_c = 0.00582 cm^{-1}) and Doppler (γ_d = 0.00245 cm^{-1}) contributions to the line-shape would be comparable. With pressure shifting, the transition frequency is 1327.073850 cm^{-1}. The GrossDoppler, the Voigt and the Gross line-shape are all plotted on the left in Figure 1.

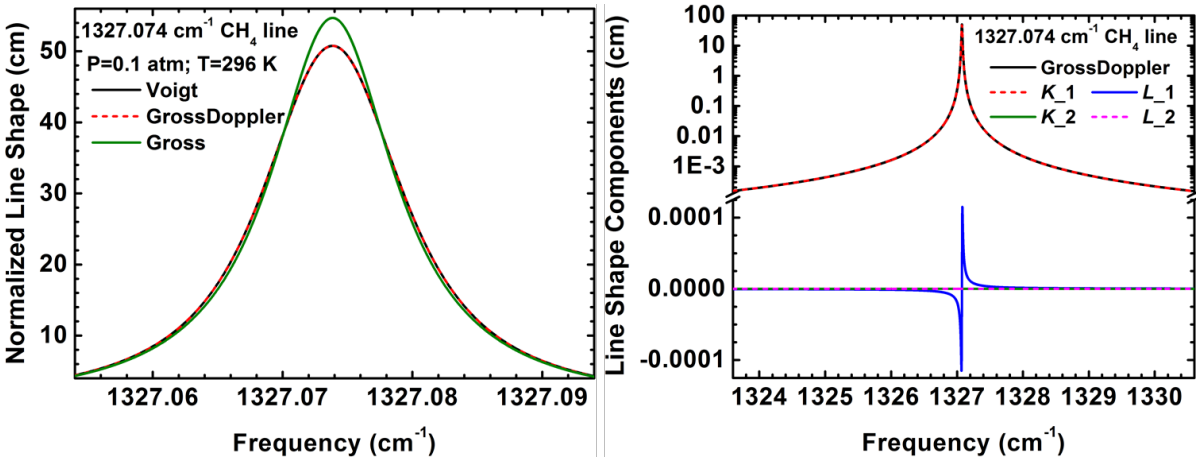

Figure 1. (left) The Voigt, GrossDoppler and Gross line-shape functions for a thermal infrared CH_4 molecular transition. (right) The relative contribution of the CPF terms in the GrossDoppler line-shape.

The difference between the Gross and GrossDoppler line-shapes in Figure 1 attest to the importance of the Doppler contribution. The Voigt and GrossDoppler line-shape functions are essentially identical. The relative contributions of the four CPF components to the GrossDoppler line-shape are plotted on the right in Figure 1. The first term in Eq. (7), which is denoted as K_1, completely dominates. The second term, L_1, is the primary source of the residual between the Voigt and GrossDoppler line-shape functions. The K_2 and L_2 terms have a negative sum and the magnitude of their contributions is exceedingly small at infrared and shorter wavelengths.

Voigt, GrossDoppler, Weiskopf and Gross line shape functions are plotted on the left in Figure 2 for an OH molecular transition centered near 89 MHz (0.002967 cm^{-1}) at a pressure of 0.07 atm and at 296 K. For this line at this pressure, the half-width (0.0028 cm^{-1}) is not much smaller than the transition frequency. This is evident in Figure 1, since the symmetric Voigt line shape function does not drop to much more than half the peak value at 0 cm^{-1}. Since the line-shape should drop to 0 cm at 0 cm^{-1}, the Voigt form clearly does not provide a good representation of the spectral dependence. The absurdity of using the Weiskopf form, Eq. (3), parameterized with the measured transition frequency and collision half-width, in this spectral region is also demonstrated. Not only are the peak frequency and value too large by more than a factor of 2, the half-width is infinite. That is, the short wavelength side of the line-shape never decreases to one-half of the peak value.

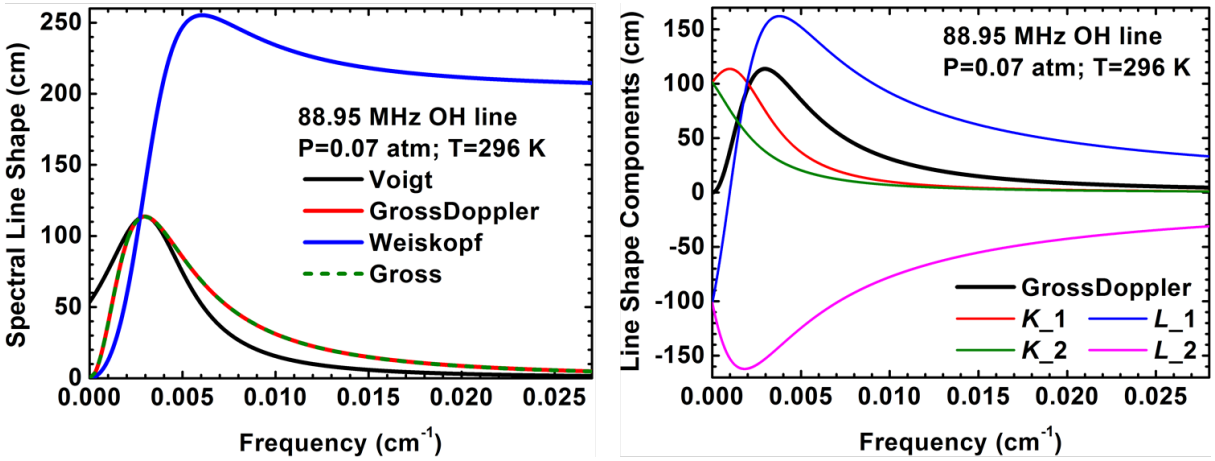

Figure 2. (left) The Voigt, GrossDoppler, Weiskopf and Gross line-shape functions for an 89 MHz OH molecular transition. (right) The relative contribution of the CPF terms in the GrossDoppler line-shape.

Since Doppler contributions are essentially zero in this region, and Gross and GrossDoppler line-shapes overlap. Certainly the Gross line-shape function, Eq. (5), is much simpler to compute than the GrossDoppler, Eq. (7). But it is interesting to observe on the right in Figure 2 that all four CPF values contribute significantly to the total line-shape value.

3.3 Microwave NH3 Molecular Transition

An NH_3 molecular transition centered at 0.796222 cm^{-1}, 23.863 GHz, was used to compare line-shapes in the microwave. Figure 3 contains plots of the Voigt, GrossDoppler, Weiskopf and Gross line-shape functions for this molecular transition with both a log and linear based vertical scale. The pressure was set to 0.5 atm, producing a Lorentz half-width of γ_c = 0.0536 cm^{-1}. The Doppler contribution is negligible in this region, so the GrossDoppler and Gross line-shape functions are essentially identical. The Voigt line-shape does not decrease to zero at 0 cm^{-1}, as is evident on the left in Figure 3. On the other hand, Weiskopf form does not fall off proportional to one over frequency squared for $\nu >> \nu_{if}$ and produces too much absorption at large displacement frequencies (not shown). The Gross and GrossDoppler line-shape functions have neither of these problems. However, previous comparisons to measurements illustrate that the Weiskopf form is most accurate near line center. The Voigt line-shape is symmetric about the line center. The linear scale plot on the right in Figure 2 illustrates that the Weiskopf line-shape asymmetry about line center is more pronounced than that observed for the Gross line-shape. The inset illustrates the fact that the Weiskopf form displaces the transition frequency and intensity, but these effects are small in this region.

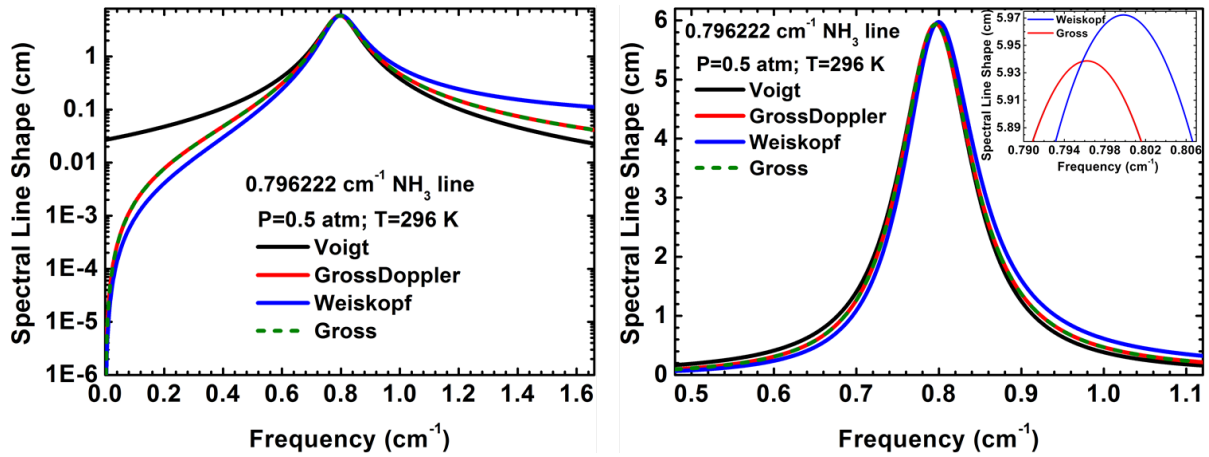

Figure 3. The Voigt, Gross Doppler, Van Vleck – Weiskopf and Gross line-shape functions for a microwave NH_3 molecular transition. Log scale is shown on left, and a linear scale on the right.

Line-shape residuals relative to GrossDoppler are plotted on the left in Figure 4. Even with this expanded scale, there is no appreciable difference between the Gross and Gross Doppler line-shape functions for this microwave line. The Voigt and Weiskopf line-shape residuals have a dominant anti-symmetric component about the transition frequency. However, the magnitudes of the Weiskopf line-shape residual peaks differ substantially with values of – 0.296 cm at 0.758 cm^{-1} and + 0.335 cm at 0.839 cm^{-1}. The question arises as to whether the deviation from a true anti-symmetric shape is primarily an artifact of the Weiskopf slow drop off with increasing frequency? Can an anti-symmetric correction to the Gross line-shape be defined that eliminates the predominant Weiskopf residual?

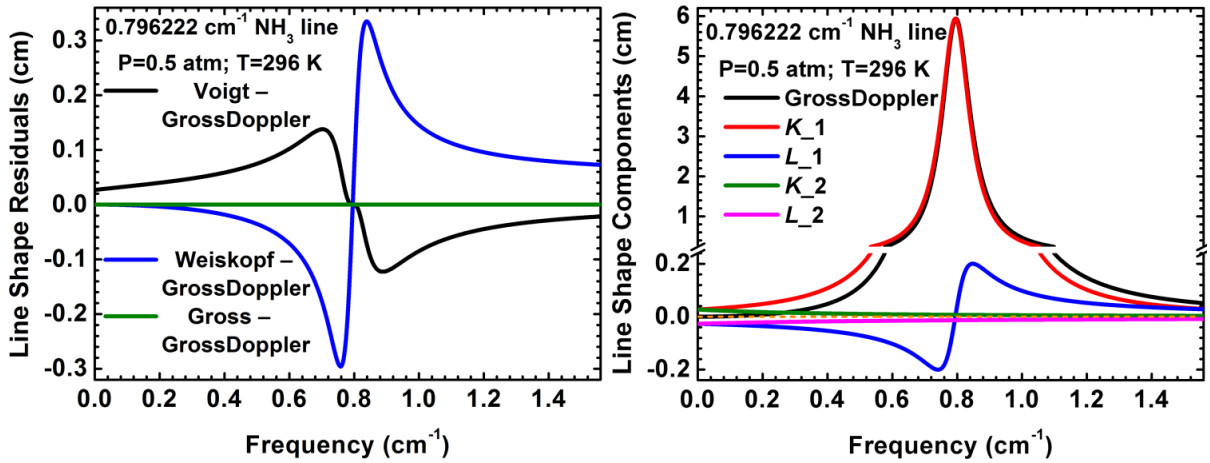

Figure 4. (left) The Voigt (**black**), Van Vleck – Weiskopf (**blue**) and Gross (**green**) line-shape function residuals for a microwave NH_3 molecular transition. (right) The total relative contribution of the CPF terms from Eq. (8). Notice the break in the vertical scale at 0.24 cm, and the zero residual line is plotted as a dashed orange line.

The relative contributions CPF terms to the Gross Doppler line-shape are plotted on the right in Figure 4. A break in the vertical scale at 0.22 cm is introduced to expand the plot for the smaller terms. This expanded vertical scale enables one to observe the deviation of both the K_2 and L_2 functions from zero. The K_1 function continues to be dominant, but the contribution of L_1 is significant – approximately 4% of the total near line center. Furthermore, the shape of the L_1 function resembles the shape of the Weiskopf to GrossDoppler line-shape residual (both curves are blue), although the magnitude of the residual is ~70% larger than that of the L_1 function. This suggests that a correction to the GrossDoppler form, appropriate for the microwave, could be made by introducing a half-width, γ_c, and transition frequency, ν_{if}, dependent coefficient to the L_1 term. For ν_{if} near γ_c, the coefficient should approach 1 (no correction). In the microwave, where γ_c is much less than ν_{if}, the coefficient would be defined to match the near line center Weiskopf line-shape. At shorter wavelengths, the L_1 term drops off precipitately, so that a converged microwave value for the coefficient would not contribute significantly to the IR through UV lineshape.

4. CONCLUSION AND FUTURE WORK

The presence of spectral branch points in radiative transfer modeling is problematic. In particular, system studies can be adversely affected by spectral discontinuities in the modeling of molecular absorption. In this paper, a spectrally universal 3-parameter GrossDoppler line-shape function is introduced. In its most general form, the calculation of this lineshape requires approximately twice the effort required to compute the Voigt lineshape. However, the spectral regions where this generality is needed are quite limited. In the IR through UV, the GrossDoppler and Voigt forms converge. At long wavelengths, Doppler contributions become negligible and the Gross line-shape is appropriate. In the transition between these regions, GrossDoppler provides a smooth transition.

This issue remains that the GrossDoppler and Gross line-shape functions are not as accurate as the Weiskopf form in the microwave. Work is underway to define a modified GrossDoppler line-shape function that matches Weiskopf near the center of microwave lines. This work is expected to be completed in the next few months.

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