

Importance of Combined Lorentz–Doppler Broadening in High-Temperature Radiative Heat Transfer Applications

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Abstract

The importance of combined Lorentz–Doppler (or Voigt) broadening of spectral lines in high-temperature radiative heat transfer applications is investigated. Employing narrow-band transmissivities as the criterion, the critical total pressure below which, and the critical temperature above which Doppler broadening has a significant effect on the absorption coefficient is established for gaseous H_2O and CO_2 .

Keywords: thermal radiation; absorption coefficient; line broadening

Introduction

The absorption coefficient of a gaseous medium governs the radiative heat transfer rates through it. While the highly oscillating nature of the absorption coefficient along the spectrum makes it computationally expensive to evaluate radiative transfer rates from absorption coefficient data directly by the so-called line-by-line (LBL) approach, modern absorption models, such as narrow-band k -distributions [1, 2], spectral line based weighted-sum-of-gray-gases (SLW) [3, 4], absorption distribution functions (ADF) [5, 6] and full-spectrum k -distributions (FSK) [7–13], were developed based on detailed absorption coefficient data. The LBL approach has been recognized as the most accurate approach to date and has been utilized as a benchmark in radiation calculations.

The absorption coefficient at a specific spectral location is a result of the overlap of nearby spectral lines which are broadened to overlap with each other due to natural line broadening, collision broadening and Doppler broadening [14]. The effect of natural line broadening is fairly small compared to collision broadening, but its shape is identical to that of a collision-broadened line. Generally, natural line broadening and collision broadening are combined, and the combined

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effect is known as Lorentz broadening. The importance of Lorentz broadening is directly proportional to total pressure, and inversely proportional to the square-root of temperature. Doppler broadening, on the other hand, is independent of pressure and increases with the square-root of temperature. Therefore, Lorentz broadening tends to be dominant at modest-to-high pressures and low-to-moderate temperatures. It follows that, in most engineering applications, such as industrial boilers and combustors as well as gas turbines, Lorentz broadening is the most important broadening mechanism and, therefore, Doppler broadening is usually neglected. On the other hand, in the atmospheric sciences, dealing with extremely low pressures in the upper atmosphere, Doppler broadening becomes important and may even be dominant. Modern high-temperature applications, such as rocket nozzles and closed-cycle gas turbines, combine both relatively low pressures and high temperatures, such that the importance of Doppler broadening needs to be investigated. The combined effect of Lorentz broadening and Doppler broadening leads to the Voigt line broadening profile. Employing the Voigt profile is much more CPU-time intensive than that of the Lorentz profile, but several fast algorithms for Voigt profile calculations have been developed [15, 16].

The purpose of the present note is to investigate under what conditions (i.e., what pressures and temperatures) the Voigt profile should be employed in the absorption coefficient evaluation rather than the Lorentz profile, and to determine the error if the Lorentz profile is used. Currently, water vapor and carbon dioxide, the two major products of hydrocarbon-air combustion, have been studied. The spectral line parameters for the evaluation of the absorption coefficients were obtained from spectroscopic databases: HITEMP 2000 [17] was employed for water vapor, while for carbon dioxide CDSD-1000 [18] was used, which is considered more reliable than HITEMP for temperatures higher than 1000 K [19, 20].

Absorption Coefficient Calculation

Evaluation of the absorption coefficient at a specific wavenumber location η consists of collecting the contributions of all spectral lines that contribute to that wavenumber location, i.e.,

$$\kappa_\eta = \sum_i \kappa_i(\eta, \underline{\phi}_i), \quad (1)$$

where κ_η is the absorption coefficient at the wavenumber location η , κ_i is the contribution of the spectral line i , and $\underline{\phi}_i$ is its line parameter vector containing the line intensity S , the line center wavenumber η_o , the Lorentz broadening half-width b_L , and the Doppler broadening half-width b_D , which are obtained or calculated from the spectroscopic databases. The line shape can be the Lorentz profile [14]

$$\kappa_L = \frac{S}{\pi} \frac{b_L}{(\eta - \eta_o)^2 + b_L^2}, \quad (2)$$

or the Voigt profile [14]

$$\kappa_V = \frac{S b_L}{\pi^{3/2}} \int_{-\infty}^{+\infty} \frac{e^{-x^2} dx}{(\eta - \eta_o - x b_D / \sqrt{\ln 2})^2 + b_L^2}. \quad (3)$$

Unlike the Lorentz profile, the Voigt profile cannot be stated in closed form. In the current work, the Humlíček algorithm [16] was employed to evaluate the Voigt profile.

Table 1. Narrow band division

Spectral range (cm ⁻¹)	Interval (cm ⁻¹)	Number
200 – 300	10	10
300 – 4000	25	148
4000 – 5000	50	20
5000 – 10000	100	50
10000 – 15000	250	20
		total: 248

In order to describe the irregularity of the absorption coefficient across the spectrum, κ_η must be evaluated from spectroscopic databases at close enough spectral intervals. Since the Lorentz profile always causes weaker overlap between lines and the resulting absorption coefficient is much more oscillating than the Voigt profile with its additional broadening due to Doppler effects, a fine enough wavenumber resolution for the Lorentz profile is also always sufficient for the Voigt profile. As stated earlier, Lorentz broadening (or b_L) is proportional to total pressure. Therefore, lower pressures need fine wavenumber resolution than higher pressures. Similarly, since b_L is inversely proportional to the square-root of temperature, higher temperatures cause weaker broadening and less overlap. However, as temperature rises, “hot” lines become more important, which induce more overlap between spectral lines. The combined effect leads to a need for higher resolution at high temperatures. In our work, a constant spacing across the entire spectrum was used; the resolution was considered sufficient if, when doubling the resolution, the error of narrow-band mean absorption coefficients stayed below 0.5 percent in major absorption bands of the entire spectrum, with the Lorentz profile employed. With this criterion, the wavenumber resolution was determined, using the Lorentz profile, for the evaluation of the pressure-based absorption coefficients. Then the same wavenumber resolution was utilized to evaluate the pressure-based absorption coefficients using the Voigt profile.

Narrow-Band Transmissivity

In our work, the effect of line-broadening mechanism on the narrow-band transmissivity has been investigated. A narrow band is a narrow spectral interval in which the blackbody radiation intensity can be regarded as constant, leading to the definition of narrow-band transmissivity:

$$\bar{\tau}_\eta(X) = \frac{\int_{\Delta\eta} I_{b\eta} e^{-\kappa_\eta X} d\eta}{\int_{\Delta\eta} I_{b\eta} d\eta} = \frac{1}{\Delta\eta} \int_{\Delta\eta} e^{-\kappa_\eta X} d\eta, \quad (4)$$

where X is the optical path-length, $\Delta\eta$ is the narrow-band width, and $I_{b\eta}$ is the blackbody intensity (or Planck function).

The entire spectrum was divided into 248 narrow bands as shown in Table 1 [21]. The narrow-band widths were chosen based on the variation of the Planck function and the importance of narrow bands.

Results and Discussion

When comparing the effects of Lorentz and Voigt profiles based on the narrow-band transmissivity, the same optical path-length should be used in both calculations, and the transmissivities should be adjusted to a moderate value to make the comparison meaningful.

Therefore, for each narrow band an optimal path-length X_o was chosen, such that the narrow-band transmissivity was 0.5 when the Voigt profile was employed in the absorption coefficient evaluation. For some narrow bands with near-negligible absorption coefficient, the necessary path-length to achieve a transmissivity of 0.5 is extremely large ($X_o > 100$ cm-bar), which is unlikely to occur in engineering applications. In such narrow bands, the optimal path-length was set to $X_o = 100$ cm-bar. Using the optimal path-length, the transmissivity evaluated from the absorption coefficient of the Lorentz profile was compared to that of the Voigt profile, and the relative error was defined as

$$\epsilon = \frac{\left(\bar{\tau}_\eta(X_o)\right)_{\text{Lorentz}} - \left(\bar{\tau}_\eta(X_o)\right)_{\text{Voigt}}}{\left(\bar{\tau}_\eta(X_o)\right)_{\text{Voigt}}} \times 100\%, \quad (5)$$

where $\left(\bar{\tau}_\eta(X_o)\right)_{\text{Lorentz}}$ is the narrow-band transmissivity evaluated from the pressure-based absorption coefficient employing the Lorentz profile, and $\left(\bar{\tau}_\eta(X_o)\right)_{\text{Voigt}}$ is that of the Voigt profile.

Since the mole fraction (x) of the absorbing gas affects the pressure-based absorption coefficient only slightly through its molecular size in collision broadening, the effects of varying the mole fraction are minor. All results presented in this note are for a mole fraction of $x = 1.0$. At other mole fractions, the differences between the Lorentz and the Voigt profiles are slightly smaller.

Figure 1 shows the narrow-band transmissivity of H_2O evaluated at the optimal path-length X_o for a total pressure of 1.0 bar and a temperature of 2500 K. Results of both the Lorentz and Voigt profiles and their differences are presented. Figure 2 shows the same results for CO_2 for the same total pressure and temperature. The narrow bands with transmissivity larger than 0.5 are unimportant narrow bands, since their absorption coefficients are so small that, even at $X = 100$ cm-bar, the gas is optically thin. In both figures, the maximum difference between the results for Lorentz and Voigt profiles is approximately 1%, which implies that it is safe to employ the Lorentz profile at 1.0 bar or higher total pressures and any temperature below 2500 K, since the higher the total pressure and the lower the temperature, the more dominant Lorentz broadening becomes. On the other hand, at low pressures the Lorentz profile may cause large errors, as shown in Figures 3 and 4 which were calculated for $p = 0.1$ bar and $T = 1500$ K. Large errors always occur at important narrow bands, i.e., where the transmissivity is 0.5. Therefore, the Voigt profile should be employed in the evaluation of absorption coefficients at such pressures and temperatures.

For H_2O and CO_2 Tables 2 and 3 list some low-pressure (p, T) combinations at which the maximum error of the Lorentz profile is approximately 1.0% in terms of the narrow-band transmissivity. These two tables supply a guideline to determine whether the Lorentz profile can be safely employed at low pressures. For example, for H_2O at $p = 0.1$ bar, the Lorentz profile causes errors of narrow band transmissivity less than 1% if the temperature is lower than 800 K. At temperatures higher than 800 K, Doppler broadening becomes more important, leading to larger errors if neglected.

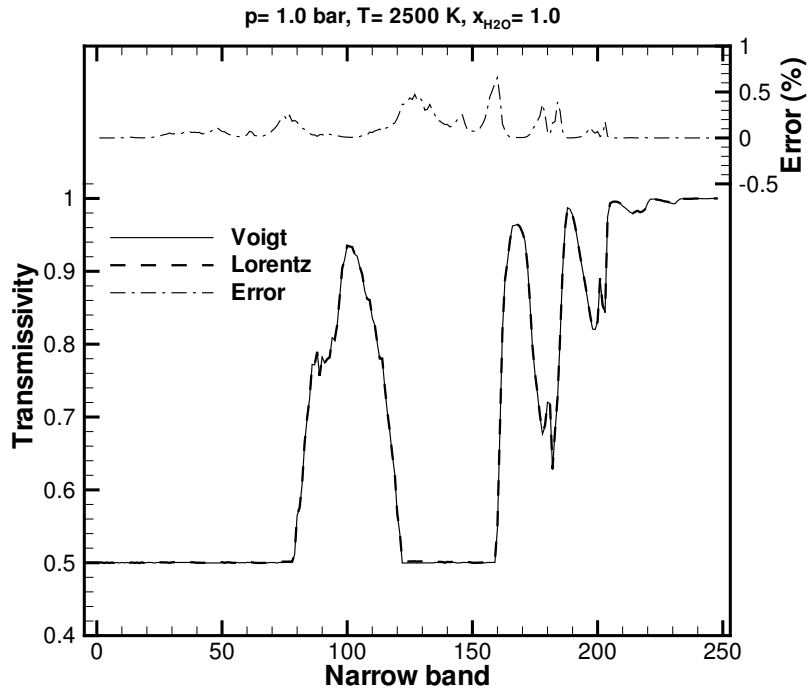


Figure 1. Narrow-band transmissivity of H_2O at $p = 1.0\text{bar}$, $T = 2500\text{K}$ and $x = 1.0$.

Table 2. Maximum error of narrow-band transmissivity for H_2O .

p (bar)	0.1	0.2	0.3	0.4	0.5	0.7	1.0
T (K)	800	1100	1400	1700	1900	2400	2500
ϵ_{max} (%)	1.04	0.92	1.00	1.06	0.99	1.01	0.65

Table 3. Maximum error of narrow-band transmissivity for CO_2 .

p (bar)	0.1	0.2	0.4	0.5	0.7	1.0
T (K)	500	700	1000	1200	1500	2500
ϵ_{max} (%)	1.01	1.07	1.03	1.11	0.95	1.06

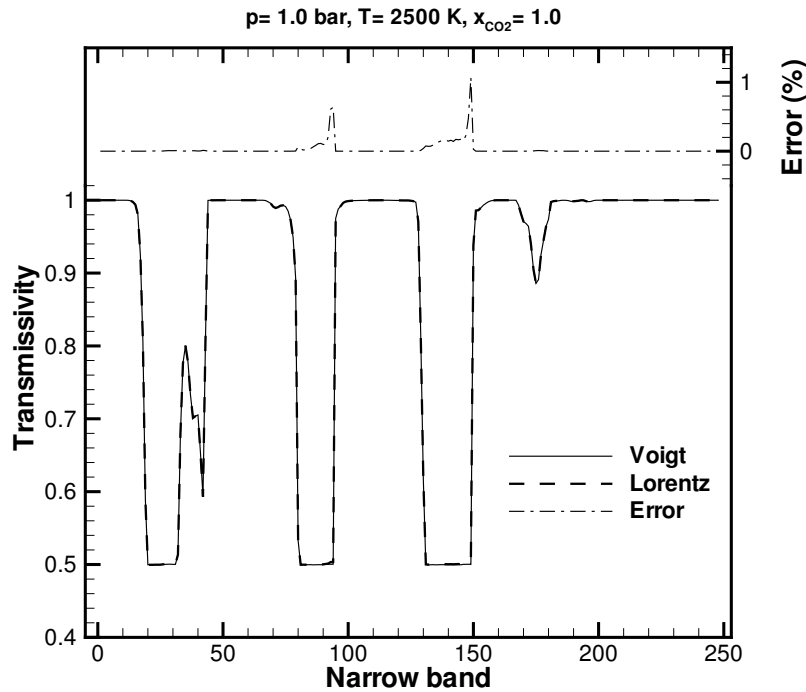


Figure 2. Narrow-band transmissivity of CO_2 at $p = 1.0\text{bar}$, $T = 2500\text{K}$ and $x = 1.0$.

Summary

At low pressures and high temperatures, Doppler broadening tends to become an important spectral line broadening mechanism. The ranges of pressure and temperature, for which the effect of combined Lorentz–Doppler (or Voigt) broadening on the absorption coefficient must be accounted for, has been investigated in this note. Care was taken to evaluate the spectral absorption coefficient with high accuracy from spectroscopic databases. For H_2O and CO_2 , based on an optimized optical path-length, the narrow-band transmissivity was evaluated from the absorption coefficients, employing the line shape of either the Lorentz profile (for pure Lorentz broadening) or the Voigt profile (for combined Lorentz–Doppler broadening). The transmissivities from these two broadening mechanism were compared at various total pressures and temperatures. It was shown that at total pressure of 1.0 bar or higher, Doppler broadening is negligible for all temperatures below 2500 K. For low pressures (less than 1.0 bar), Doppler broadening may become important at high temperatures. The critical temperature above which combined broadening should be employed has been established as a function of pressure for H_2O and CO_2 .

References

- [1] Lacis, A. A. and Oinas, V., 1991, “A Description of the Correlated- k Distribution Method for Modeling Nongray Gaseous Absorption, Thermal Emission, and Multiple Scattering in Ver-

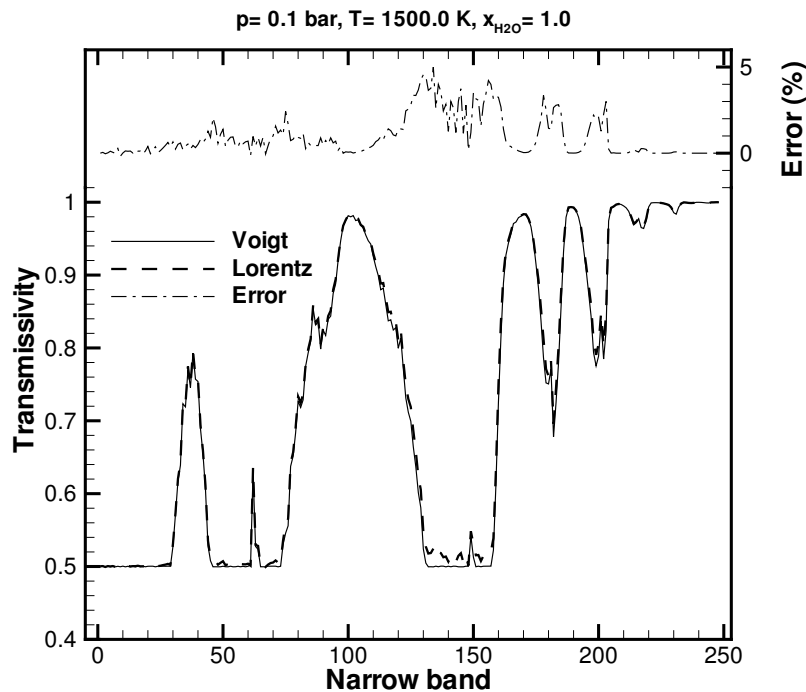


Figure 3. Narrow-band transmissivity of H_2O at $p = 0.1\text{bar}$, $T = 1500\text{K}$ and $x = 1.0$.

- tically Inhomogeneous Atmospheres”, *Journal of Geophysical Research*, **96**(D5), pp. 9027–9063.
- [2] Goody, R. M. and Yung, Y. L., 1989, *Atmospheric Radiation – Theoretical Basis*, Oxford University Press, New York, 2nd ed.
- [3] Hottel, H. C. and Sarofim, A. F., 1967, *Radiative Transfer*, McGraw-Hill, New York.
- [4] Modest, M. F., 1991, “The Weighted-Sum-of-Gray-Gases Model for Arbitrary Solution Methods in Radiative Transfer”, *ASME Journal of Heat Transfer*, **113**(3), pp. 650–656.
- [5] Rivière, Ph., Soufiani, A., Perrin, M. Y., Riad, H., and Gleizes, A., 1996, “Air Mixture Radiative Property Modelling in the Temperature Range 10000–40000 K”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **56**, pp. 29–45.
- [6] Pierrot, L., Rivière, Ph., Soufiani, A., and Taine, J., 1999, “A Fictitious-gas-based Absorption Distribution Function Global Model for Radiative Transfer in Hot Gases”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **62**, pp. 609–624.
- [7] Modest, M. F. and Zhang, H., 2000, “The Full-Spectrum Correlated- k Distribution and its Relationship to the Weighted-Sum-of-Gray-Gases Method”, In *Proceedings of the 2000 IMECE*, **HTD-366-1**, Orlando, FL, ASME, pp. 75–84.
- [8] Modest, M. F., 2003, “Narrow-band and full-spectrum k -distributions for radiative heat transfer—correlated- k vs. scaling approximation”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **76**(1), pp. 69–83.

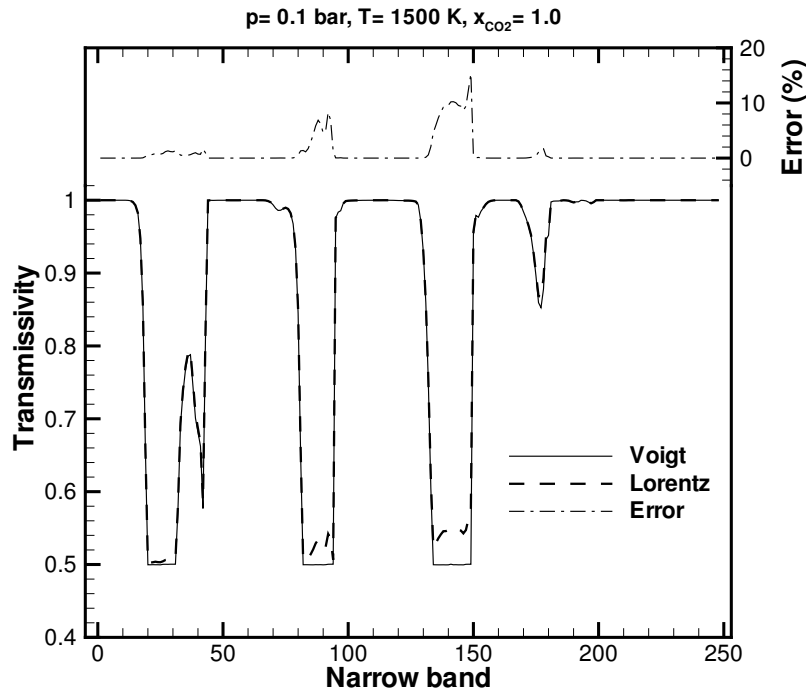


Figure 4. Narrow-band transmissivity of CO_2 at $p = 0.1\text{bar}$, $T = 1500\text{K}$ and $x = 1.0$.

- [9] Modest, M. F. and Zhang, H., 2002, “The Full-Spectrum Correlated- k Distribution For Thermal Radiation from Molecular Gas-Particulate Mixtures”, *ASME Journal of Heat Transfer*, **124**(1), pp. 30–38.
- [10] Zhang, H. and Modest, M. F., 2002, “A Multi-Level Full-Spectrum Correlated- k Distribution For Radiative Heat Transfer in Inhomogeneous Gas Mixtures”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **73**(2–5), pp. 349–360.
- [11] Zhang, H. and Modest, M. F., 2003, “Full-Spectrum k -Distribution Correlations for Carbon Dioxide Mixtures”, *Journal of Thermophysics and Heat Transfer*, **17**(2), pp. 259–263.
- [12] Zhang, H. and Modest, M. F., 2003, “Scalable Multi-Group Full-Spectrum Correlated- k Distributions For Radiative Heat Transfer”, *ASME Journal of Heat Transfer*, **125**(3), pp. 454–461.
- [13] Zhang, H. and Modest, M. F., 2003, “Multi-Group Full-Spectrum k -Distribution Database For Water Vapor Mixtures in Radiative Transfer Calculations”, *International Journal of Heat and Mass Transfer*, **46**(19), pp. 3593–3603.
- [14] Modest, M. F., 2003, *Radiative Heat Transfer*, Academic Press, New York, 2nd ed.
- [15] Hui, A. K., Armstrong, B. H., and Wray, A. A., 1978, “Rapid computation of the Voigt and complex error functions”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **19**, p. 509.

- [16] Humlíček, J., 1982, “Optimized computation of the Voigt and complex probability functions”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **27**, p. 437.
- [17] Rothman, L. S., Camy-Peyret, C., Flaud, J.-M., Gamache, R. R., Goldman, A., Goorvitch, D., Hawkins, R. L., Schroeder, J., Selby, J. E. A., and Wattson, R. B., 2000, “HITEMP, the High-Temperature Molecular Spectroscopic Database”, available through <http://www.hitran.com>.
- [18] Tashkun, S. A., Perevalov, V. I., Bykov, A. D., Lavrentieva, N. N., and Teffo, J.-L., 2002, “Carbon Dioxide Spectroscopic databank (CDSD)”, available from <ftp://ftp.iao.ru/pub/CDSD-1000>.
- [19] Tashkun, S. A., Perevalov, V. I., Teffo, J.-L., Bykov, A. D., and Lavrentieva, N. N., 2003, “CDSD-1000, the high-temperature carbon dioxide spectroscopic databank”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **82**(1–4), pp. 165–196.
- [20] Modest, M. F. and Bharadwaj, S. P., 2002, “High-Resolution, High-Temperature Transmissivity Measurements and Correlations for Carbon Dioxide–Nitrogen Mixtures”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **73**(2–5), pp. 329–338.
- [21] Wang, A. and Modest, M. F., 2004, “High-accuracy, compact database of narrow-band k -distributions for water vapor and carbon dioxide”, *Journal of Quantitative Spectroscopy and Radiative Transfer*, in print.