Doppler Shift Effects on Infrared Band Models

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Band-model calculations typically are employed in the analysis of low-spectral-resolution radiometer, photometer, and spectrometer measurements of hot-gas emission and absorption. Although they are not used to compute the profiles of individual lines directly, nevertheless, band models are sensitive to line shape. This line-shape sensitivity causes the net band-model emission and absorption to be sensitive to Doppler shift effects. This paper reviews the treatment of Doppler shifts on a Voigt profile spectral line, and then generalizes this result to the curve of growth, i.e., equivalent width, for both single-line and infrared band models. Finally, a synthetic spectrum for the CO_2 4.3-μ band is computed with and without Doppler shifts to illustrate the magnitude of the effect. It is found that band-model computations are unaffected by Doppler shift in the limiting cases of small and large absorber amounts. In the case of intermediate absorber amounts, significant effects are predicted for hypersonic flows.

Nomenclature

A	= total band-model absorbance, dimensionless
c	= speed of light
d	= line spacing, cm^{-1}
k	= absorption coefficient, $cm^{-1} \cdot atm^{-1}$
$P(S)$	= line strength distribution function for band model
S	= line strength, $cm^{-2} \cdot atm^{-1}$
u	= gas absorber amount, cm · atm
v	= flow velocity, cm/s
W	= line equivalent width, cm^{-1}
x	= spatial coordinate along line of sight, cm
θ	= flow angle
Υ_l	= Lorentz linewidth
Υ_d	= thermal Doppler linewidth
ω	= frequency of radiation, cm^{-1}

Introduction

THE objective of this work is to assess the impact of Doppler shift effects on infrared band-model calculations. The importance of Doppler shift effects on high-resolution laser measurements of hypersonic flowfields has been demonstrated previously by Penner and Chen,[1,2] and in fact, is the basis for spatially resolved velocity mapping by laser-induced fluorescence.[3,4] Doppler shift effects on spectral line shapes are also well known in astrophysics.[5] There has been no corresponding investigation for infrared band models. Broadband infrared band-model measurements of gas emission and absorption (e.g., H_2O and CO_2) are used widely for combustion gas and flowfield diagnostics because they are robust and have high signal levels. These measurements typically are performed with low-spectral-resolution (0.01–0.1 μ) spectrometers and radiometers. In contrast to high-spectral-resolution devices, these instruments measure only the net aggregate effect of dozens or even hundreds of individual molecular lines that fall within the instrument's bandpass. The Doppler shift is far too small to be measured directly with this type of instrumentation, even for a highly supersonic flow. For this reason, it is not immediately obvious that slight Doppler shifts can produce an observable effect. The major point of this paper is to note that the importance of Doppler shift effects is determined not by the instrument's resolution, but rather by the size of the shift relative to the spectral linewidth of the molecular lines. These can be very narrow indeed, especially in cool, low-density hypersonic flows.

When there is a single uniform relative velocity between the observer and the emitting gas, the Doppler shift results in a simple net translation of the entire spectrum. Since flowfields have significant velocity gradients, a more complicated situation arises. This is the situation addressed in this paper. Figure 1 shows one such example, which consists of a detector placed broadside to an expanding hypersonic flow. Radiation emitted from the far side of the flow will be red-shifted, whereas that emitted from the near side of the flow will be blue-shifted. The resulting lack of correlation between molecular line center positions on opposite sides of the flow is the physical basis of the Doppler shift band-model effect. This effect is highly geometry- and flowfield-dependent. Following Refs. 1 and 2, a simple one-dimensional conical source flowfield is used for the sake of illustration, with velocity and density functions of axial distance only. However, the techniques employed are general and have been applied to inhomogeneous flows computed using the NASA two-dimensional kinetic (TDK) nozzle code.[6] The baseline conditions of Table 1 have been used. Essentially these involve determination of the ν_3 CO_2 band absorption near 2350 cm^{-1} (4.3 μ) in a highly expanded (5 Torr), fast (Mach 7) supersonic flow. These values were not chosen to maximize the Doppler shift effect; they are representative hypersonic flow conditions.

The importance of the Doppler shift can be assessed by comparing it with the spectral width of the molecular lines. From Table 1, the longitudinal Doppler shift $\omega[v/c \sin(\theta)]$ for a velocity v of 3.3×10^5 cm/s and a divergence angle θ of 15 deg is roughly 0.006 cm^{-1}. At atmospheric pressure, where spectral linewidths are on the order of 0.1 cm^{-1} wide, this is hardly noticeable. At low pressure, however, the situation is different. The Voigt linewidth in the present example is approximately 0.003 cm^{-1}. The Doppler shift from one side of the flowfield to the other is, therefore, approximately twice the linewidth, and significant changes in the gas radiative transfer process can be expected.

In the following text, the case of a single Voigt profile spectral line with Doppler shift[1] is first reviewed and then extended to infrared band models. Since the literature on both single-line spectral profiles and band models is extensive, reference to this material is kept to an absolute minimum. All formulas and definitions used can be found in any of Refs. 7–10. Only homogeneous paths are considered.

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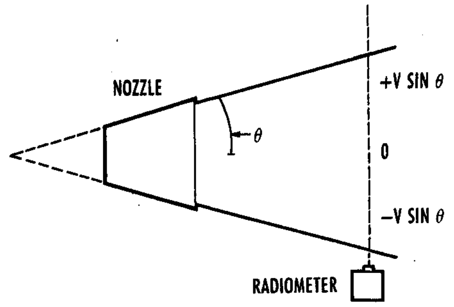

Fig. 1 Geometry of directed-velocity Doppler shift.

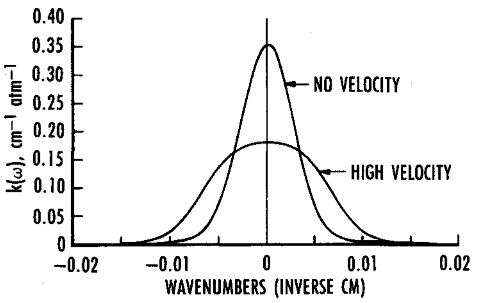

Fig. 2 Directed-velocity effects on line shape of CO_2 Voigt line at 5 Torr, 600 K, 2300 cm^{-1}.

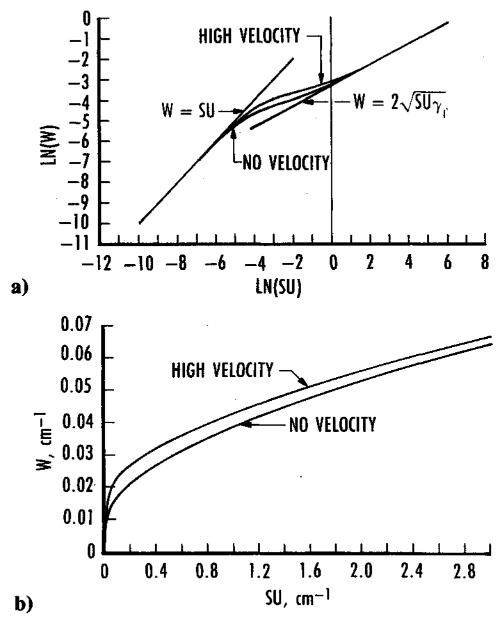

Fig. 3 Curves of growth of CO_2 Voigt lines with and without directed-velocity effects, Su and W in cm^{-1} units: a) logarithmic scale; b) linear scale.

Single-Line Study

The Voigt profile for a single spectral line is the convolution of a Lorentzian pressure-broadened profile with a Maxwellian velocity distribution:

$$k(\omega) = \frac{Sa}{\pi \Upsilon_d}\frac{\ell n 2}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-y^2)}{a^2 + (\epsilon - y)^2}\,\mathrm{d}y \qquad (1)$$

$$a = (\ell n 2)^{1/2}\Upsilon_l/\Upsilon_d \qquad \epsilon = (\ell n 2)^{1/2}(\omega - \omega_0)/\Upsilon_d$$

k is the absorption coefficient, ω the wave number, Υ_d the Lorentz linewidth (half width-half maximum), Υ_l the thermal Doppler width, and S the line strength. The Doppler and Lorentz half-widths were taken to be constant for all lines in the CO_2 band. They were based on the flow conditions of Table 1 and the Lorentz broadening parameters of the Air Force Cambridge Research Laboratories line atlas compilation.[11] The frequency of the line center is ω_0. The Doppler shift merely shifts ω_0 to a new value, i.e., substitute ω_0^* for ω

$$\omega_0^* = \omega_0(1 + v \sin \theta/c) \qquad (2)$$

A number of computationally fast approximation techniques have been developed to evaluate Voigt line profiles without direct numerical integration of Eq. (1).[12,13] The polynomial approximation of Ref. 12 was used in this work to generate the line profiles, i.e., $k(\omega)$, shown in Fig. 2. Although the line strength is variable from transition to transition, all lines in the CO_2 band will have essentially the same spectral profile. Thus, Fig. 2 is applicable to the entire band. When the Doppler shift term for the example flowfield is taken into account, the absorption coefficient at the line center is halved and the linewidth is roughly doubled.

The total amount of energy absorbed by a spectral line is determined by the frequency integral over the absorption line. This integral has wave-number units (cm^{-1}) and is termed the "equivalent width." It is a fundamental quantity in the theory of infrared band models and is related to the absorption coefficient k, Eq. (1) and Fig. 2, by a double integration over both path (dx) and frequency (dω):

$$W(S,u) = \int_{-\infty}^{\infty}\left\{1 - \exp\left[-\int_0^x k(\omega,x)\,\mathrm{d}x\right]\right\}\mathrm{d}\omega \qquad (3)$$

The variation of equivalent width W vs absorber amount u, commonly expressed in centimeter · atmospheres, is termed the "curve of growth." It is used to infer absorber amount from the observed equivalent width. An analytic solution to Eq. (3) is known only for Lorentzian lines in a homogeneous gas (the Ladenburg-Reiche function). Numerical results and series expansions are available for homogeneous gases with either thermal Doppler- or Voigt-shaped lines.[13] Crosbie and Viskanta[14] have evaluated $W(S,u)$ for rectangular, triangular, and exponential line profiles, and compared these to the results for Lorentzian and thermal Doppler-broadened lines. The spectral line shape in a nonuniform flowfield with Doppler shifts, however, depends on the flowfield and will vary from case to case. The solution is straightforward, but of necessity is numerical. For consistency, comparative curves of growth with and without Doppler shift effects were evaluated using the numerical integration of Eq. (3). These are shown in Fig. 3.

It is seen that the calculation for the Doppler shift case converges to the correct asymptotic limits for low and high absorber amounts. In the limit of low absorber amount, there is no self-absorption and the curve of growth is insensitive to line shape. In the limit of large absorber amount, the line centers are completely saturated, the incremental absorption is due solely to the Lorentzian pressure-broadened line wings, and the curve converges to the Lorentzian square-root limit. Figure 3b shows the region of intermediate absorber amounts, where maximum sensitivity to the line profile occurs. As expected, on the basis of the relative line shapes (Fig. 2), the effective line broadening caused by the Doppler shift leads to slower saturation in the curve of growth. In this respect, the role of the Doppler shift is quite similar to pressure broadening. The worst-case error in this specific example is a 28%

Table 1 Flowfield conditions

CO_2 partial pressure, Torr	5
Temperature, K	600
Exit velocity, cm/s	3.3×10^5
Spectral line center, cm^{-1}	2300
Maximum divergence angles, deg	15

error in W, which corresponds to a factor of 3 error in absorber amount.

Band-Model Study

The extension of the single-line curve-of-growth result (Fig. 3) to infrared band models with Doppler shifts was done numerically using the same classic procedure as employed in Refs. 7–9. Classical band models assume one of three specific spectral line profiles—Lorentz, thermal Doppler, or Voigt—because these are the common and naturally occurring cases. There is nothing, however, that prevents development of a band model for other spectral line shapes. This section simply develops the appropriate band model for the Doppler shift distorted line shape studied in the previous section.

The two fundamental relations of a random band model are Eq. (4) for the mean equivalent width and Eq. (5) for the net band absorbance. The average equivalent linewidth in a molecular band depends on the probability distribution function for line strengths $P(S)$

$$\bar{W}(u) = \int_0^\infty W(S,u)P(S)\,\mathrm{d}S \tag{4}$$

The band absorbance A, in turn, is related to the average equivalent width and the mean line spacing $1/d$ by

$$A = 1 - \exp[-\bar{W}(u)/d] \tag{5}$$

By Kirchoff's law, emissivity equals absorbance A. Note that neither Eq. (4) nor Eq. (5) places any restrictions or requirements on the spectral line shape. The band model is defined completely by the curve of growth $W(u)$, the distribution function $P(S)$, and the line density (inverse spacing) $1/d$.

Numerical evaluation of the band-model curve of growth [Eq. (5)] was done using the single-line curve-of-growth calculations shown in Fig. 3. The exponential tailed $1/S$ distribution function of Ref. 15 was recommended for CO_2. Use of an alternate distribution function $P(S)$ would not have changed the overall conclusions of this investigation. The band-model curves of growth with and without Doppler shift are shown in Fig. 4. The dimensionless quantity (W/d) is the band absorbance A [Eq. (5)], and Su/d, also dimensionless, is the customary band-model optical depth parameter. The same phenomena seen in Fig. 3 for the single line are repeated. The principal difference is the slight decrease of the Doppler shift

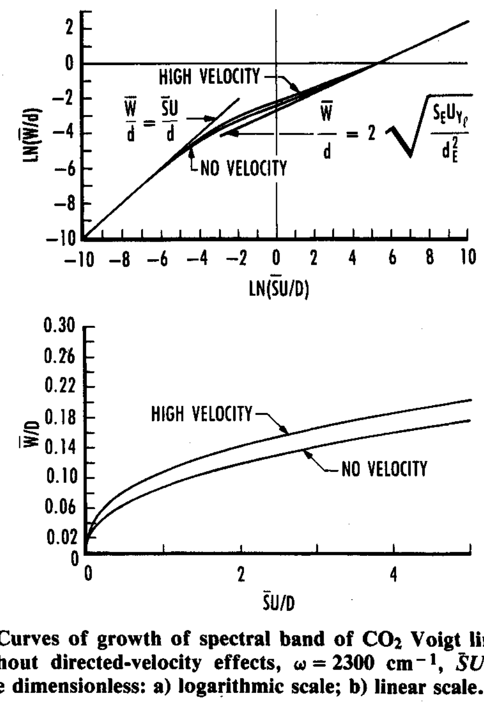

Fig. 4 Curves of growth of spectral band of CO_2 Voigt lines with and without directed-velocity effects, $\omega = 2300$ cm^{-1}, $\bar{S}U/D$ and $\bar{W}/D$ are dimensionless: a) logarithmic scale; b) linear scale.

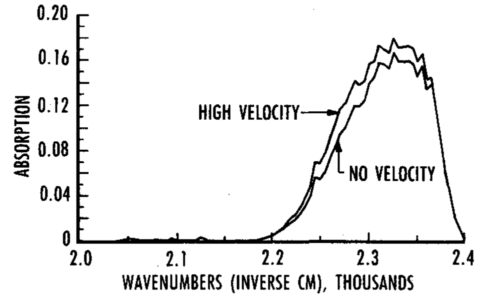

Fig. 5 Absorption spectra of CO_2 4.3-μ band with and without directed-velocity effects using SIRRM parameters with a 5-cm^{-1} spectral interval.

effect attributable to the averaging process. The worst-case error in Fig. 4 is approximately a 20% increase in absorbance, corresponding to a factor of 1.7 overestimate of absorber amount.

As an additional example of the impact of Doppler shift effects on infrared band models, 2000–2400 cm^{-1} CO_2 absorption spectra are shown in Fig. 5. Band-model parameters, S/d and $1/d$, were taken from the JANNAF Standardized Infrared Radiation Model (SIRRM code)[16] at 5-cm^{-1} intervals. Optical depth, Su/d, at each frequency was determined from the absorber amount (Table 1) and the tabulated band-model parameters. The single-line group model was used. The band absorbance corresponding to the computed optical depth was then derived from the Fig. 4 curve of growth using a table lookup–interpolation routine. The spectra indicate a 5–10% effect near the band center and larger errors, up to 20% near 2250 cm^{-1}, in the wings.

Conclusions

Doppler shifts are predicted to be important for infrared band-model computations of hypersonic flows. The driving parameter is not the ratio of Doppler shift to instrument resolution, but rather the ratio of Doppler shift to spectral linewidth. Since the Doppler shift effect basically is determined by the flowfield, no general solution is possible. A numerical solution was provided for a simple homogeneous flowfield. The results exhibited the correct asymptotic limits for small and large absorber amounts and, for intermediate amounts, indicated a deviation consistent with that expected from well-established studies on pressure broadening effects. If one simply is interested in the net band-model emission or absorption, then the effects for representative hypersonic flows do not appear to be large. However, if one is interested in using the band-model calculations for diagnostics (e.g., species concentrations, as in Ref. 9), then Doppler shift effects can become significant.

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References

[1]Penner, S. S., and Chen, H. K., "Velocity Effects on Pollutant Diagnostics with Tunable Lasers for Doppler-Broadened Lines," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 13, 1973, pp. 1315–1324.

[2]Chen, H. K., and Penner, S. S., "Velocity Distortions of Spectral Lines with Combined Doppler and Collision Broadening," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 14, 1974, pp.

239-241.

[3]Zimmerman, M., and Miles, R. B., "Hypersonic Helium Flowfield Measurements with the Resonant Doppler Velocimeter," *Applied Physics Letters,* Vol. 37, No. 10, 1980, pp. 885-887.

[4]McDaniel, J. C., Beganoff, D. and Byer, R. L., "Density Measurements in Compressible Flows Using Off Resonant Laser Induced Fluorescence," *Physics of Fluids,* Vol. 25, 1982, pp. 1105-1109.

[5]Sobolev, V. V., "A Course in Theoretical Astrophysics," NASA TT F-531, Dec. 1969.

[6]Nickerson, G. R., Coates, D. E., and Bartz, J. L., "Engineering and Programming Manual: Two-Dimensional Kinetic (TDK) Computer Program," NASA CR-152999, Dec. 1973.

[7]Penner. S. S., *Quantitative Molecular Spectroscopy,* Addison-Wesley, Reading, MA, 1958.

[8]Ludwig, C. B., Malkmus, W., Reardon, J. E., and Thomson, J. A. L., *Handbook of Infrared Radiation from Combustion Gases,* NASA SP-3080, 1973.

[9]Limbaugh, C. C., "The Infrared Emission-Absorption Method for Temperature and Species Partial Pressure Determination in Flames and Plumes," *Infrared Methods for Gaseous Measurements,* edited by J. Wormhoudt, Marcel Dekker, New York, 1985, pp. 197-245.

[10]Plass, G. N., "Models for Spectral Band Absorption," *Journal of the Optical Society of America,* Vol. 48, No. 10, 1958, pp. 690-703.

[11]Whiting, E. E., "An Empirical Approximation to the Voigt Profile," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 8, 1968, pp. 1379-1384.

[12]Olivero, J. J., and Longbothum, R. L., "Empirical Fits to the Voigt Line Width: A Brief Review," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 17, 1977, pp. 233-235.

[13]Rodgers, C. D., and Williams, A. P., "Integrated Absorption of a Spectral Line with Voigt Profile," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 14, 1974, pp. 319-323.

[14]Crosbie, A. L., and Viskanta, R., "Effect of Band or Line Shape on the Radiative Transfer in a Nongray Planar Medium," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 10, 1970, pp. 487-509.

[15]Malkmus, W., "Random Lorentz Band Model with Exponential-Tailed S-1 Line Intensity Distribution Function," *Journal of the Optical Society of America,* Vol. 57, No. 1, 1967, pp. 323-329.

[16]Bernstein, L. S., Robersun, D. C., and Conant, J. A., "Band Model Parameters for the 4.3 μm CO_2 Band from 200 to 3000 K," *Journal of Quantitative Spectroscopy and Radiative Transfer,* Vol. 23, 1980, pp. 169-185.