

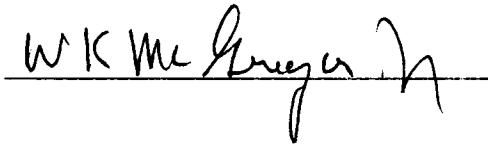
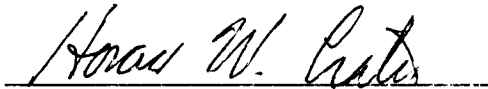
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DIRECTED MOTION DOPPLER SHIFT EFFECTS ON INFRARED
BAND MODELS OF EMISSION AND ABSORPTION
IN A HYPERSONIC CONICAL FLOW

A Thesis
Presented for the
Master of Science
Degree
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James A. Drakes

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ABSTRACT

S. S. Penner, et al (Journal of Quantitative Spectroscopy and Radiative Transfer, Vol. 13, p. 1314, 1973) investigated the importance of directed-motion Doppler-shift effects in the measurement of hypersonic gaseous flowfields using tunable laser-absorption spectroscopy. They concluded that the distortion of spectral-line shapes due to Doppler effects would prevent useful laser measurements at many conditions of interest. This work extends the foregoing analysis to lower spectral resolution, infrared band models, which are employed in conventional radiometer and spectrometer measurements. Although these instruments do not directly observe the profiles of individual spectral lines, they are sensitive to the Doppler-induced distortion of the line shapes.

This study begins with a comparative treatment of a Voigt profile spectral line with and without flowfield Doppler shifts. It first reproduces the earlier results of Penner, et al, and then generalizes this result to treat the curves of growth of a single line and the curves of growth for an infrared band model. The final step was to generate predicted CO₂ 4.3 micron-band spectra based on the obtained curves of growth to illustrate the significance of the directed-motion Doppler-shift effects.

For the particular conditions of this study, listed in Table 1 on page 48, it was shown that the inclusion of directed-motion Doppler shifts could increase the single-line curve of growth by up to 30 percent over that which was based on the neglect of this effect. The curve

of growth for an infrared band model with this effect exhibited a maximum discrepancy of 26 percent over the curve of growth without this effect. Finally, comparison of the predicted band spectra showed the enhancement of the band-center absorption by 7 to 10 percent with the inclusion of directed-motion Doppler-shift effects.

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CHAPTER I

THE NATURE OF DIRECTED-VELOCITY EFFECTS

Background

Directed velocity effects on emitted molecular radiation are changes in the appearance of a spectral line caused by the relative motion of the sources of the spectral line. This relative motion produces a Doppler shift which alters the line-center frequency of the absorption coefficient. Depending upon the system under consideration, this alteration may or may not have a significant effect upon the amount of energy that the system is capable of emitting or absorbing.

In one form or another these effects have been the subject of curiosity for quite some time. Astronomers are very familiar with the broadening of spectral lines due to the relative motion of the sources of the radiation [1,2]. This is not the same as the usual Doppler shift which is caused by the motion of the source relative to the detector. For example, an analysis of the radiation emitted by a celestial body having finite angular dimensions, which are in relative motion, can yield information on the body's angular size and velocity. Another common use of directed velocity effects is for laser-induced fluorescence experiments on high-velocity flowfields [3]. This technique utilizes the fact that directed velocities maximize the fluorescence of nearly monochromatic radiation at particular spatial points corresponding to different velocities. Hence, the result is the ability to create a velocity map of the flowfield by measuring the amount of absorption or emission at various points.

This study will be concerned with the directed-velocity effect as it pertains to conical flows in a low density environment. The sources of radiation will be the gas molecules in the flow. The relative motion of the molecules is caused by the geometry of the expanding flow. Under the proper conditions, this configuration introduces a Doppler shift of significant proportions when compared to the spectral lines being measured. The purpose of this study is to examine this effect and determine its impact on low-resolution radiometric measurements under flowfield conditions that will be of practical interest.

To understand the origin of the problem of this study, begin by assuming that there exists a conical flowfield similar to the one shown in Figure 1. Suppose that a radiation detector is positioned such that its line of sight extends normal to the cone axis. Notice that the exit velocity of the gas can be broken into components which are parallel and normal to the axis of the cone. Obviously, there will be gas-velocity components both parallel and antiparallel to the line of sight, as is shown in Figure 1. The detector will see gas molecules at the axis with zero radial velocity and also molecules with high velocities in opposite directions relative to each other. This motion will produce a line centered at the natural line center but with a Doppler shift to both lower and higher wavelengths which will alter the spectral-line shape.

The essentials of the directed-velocity effect can be illustrated by a two-body model. Suppose that an observer is viewing in a direction normal to a surface of a box of gas, labeled A. Now place an identical box of gas, labeled B, behind box A such that as the observer looks through the two boxes, they appear to be just one long box.

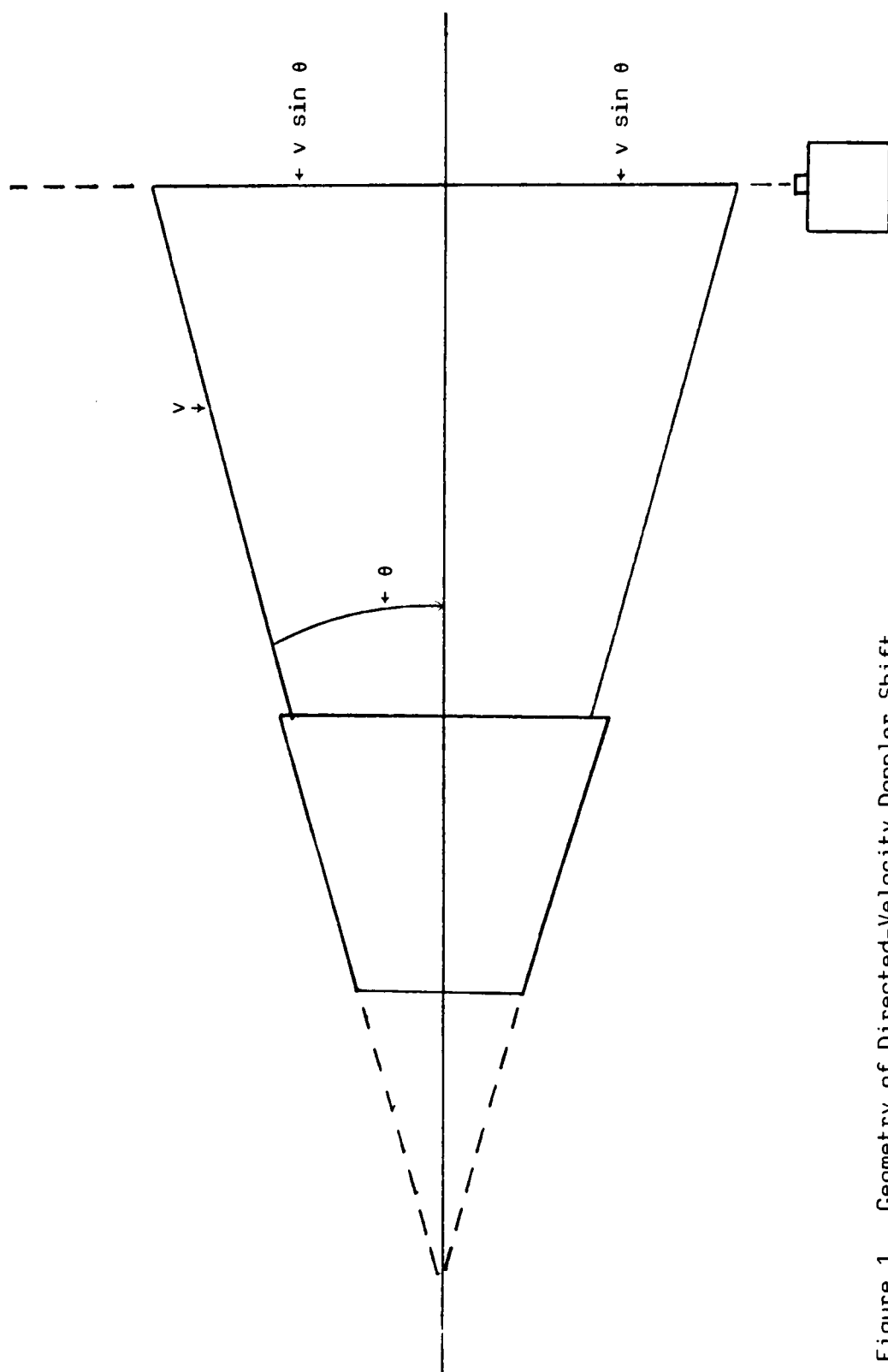


Figure 1. Geometry of Directed-Velocity Doppler Shift.

Further suppose that the gas in the boxes is emitting or absorbing radiation which is governed by some spectral-line structure. While the boxes are stationary, the emitted or absorbed radiation is described by a spectral-line centered about the particular frequency of interest. By allowing the boxes to move in opposite directions along the line of sight of the observer, such that box A moves towards the observer and box B moves away from the observer, any radiation that is emitted or absorbed by the boxes is subject to Doppler's Law. As the boxes move, the radiation which is emitted from box A will be blue-shifted and that which is emitted from box B will be red-shifted relative to the stationary observer. Thus the one spectral line splits into two distinct lines.

This Doppler shifting is depicted in Figure 2 with a Voigt spectral line [4] for a pressure of 5 Torr and a temperature of 600 Kelvin. The magnitude of the relative velocity of the boxes to each other was 1500 m/sec. In this figure, the center line is that which the observer would see when the boxes are stationary. A feel for the size of this shift can be obtained by the ratio of the directed-velocity-induced Doppler shift, given by $|\bar{v}_1 - \bar{v}_2| \frac{v}{c}$, to the half width of the line at half maximum, δv . As this ratio approaches unity, the directed-velocity effect will become increasingly evident and some interesting behavior should be seen.

Figure 2 illustrates the extent that directed-velocity effects can have on the spectral-line profile. Since this alteration of the profile can be significant, directed velocities must be considered in the use of high-resolution diagnostic measurements such as laser-induced

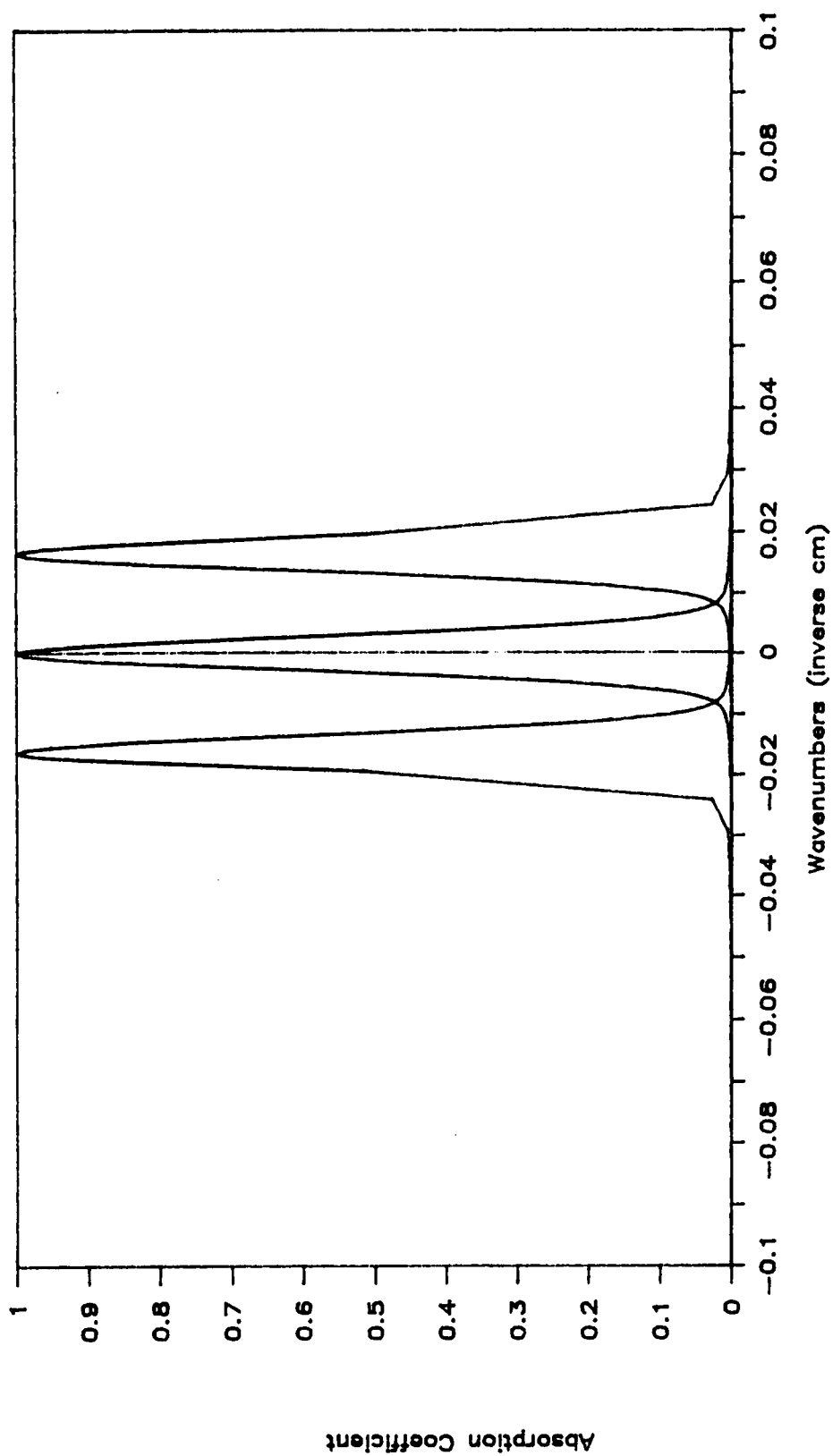


Figure 2. Doppler Shift of a Voigt Profile CO₂ Line at ± 1500 m/sec
(Pressure = 5 Torr; Temperature = 600 Kelvin).

fluorescence and spectral emission and absorption techniques. This study will view the directed-velocity effect not just as an alteration in the spectral-line profile, but as an alteration of the energy absorption capability of the gas. One of the most important questions to be resolved is how the distortion of the spectral line will affect the absorption as a function of the concentration of absorbing molecules, or optical depth.

The optical depth describes the ease or difficulty with which radiation travels through, or escapes from, a medium. This will be discussed further in Chapter II, but for now it is important to utilize the optical depth to realize the role which the spectral shifting plays in radiation absorption. For the two-box model, it will suffice to say that the system is optically thin if there are relatively few gas molecules in the boxes. This implies that if radiation were to pass through a box, the intensity would only be attenuated to a small degree. An optically thick path is one in which there exists a high concentration of absorbers, thus resulting in a high degree of intensity loss.

For certain optical depths, the spectral splitting shown in Figure 2 will reduce, at one spatial location, the absorption of radiation which is emitted at some other spatial location. This is referred to as a reduction of self-absorption. Note that in the above two-box model, while the boxes are stationary, radiation emitted due to a certain gas-state transition in box B has to pass through box A to be detected. Since it is at the frequency of the same gas-state transition in Box A, it is absorbed to an extent.

However, if the boxes are in relative motion, the spectral line corresponding to this state transition shifts into two parts, one blue-

shifted and one red-shifted. An emitted photon from box B can be red-shifted far enough that it no longer corresponds to the frequency of the same state transition occurring in box A, which at the same time, appears to the photon to have been blue-shifted. Hence the photon proceeds on its way without being absorbed. For low optical depths, this makes little difference to the net energy transfer, since the photon from box B would have likely made it through box A. However, when the optical depth becomes larger, the appearance of this extra photon is highly unexpected. It should have been absorbed by the time it made it to the detector. Hence, the spectral shifting due to the directed velocities causes a reduction of the self-absorption.

Although the self-absorption of the moving boxes has been reduced, the energy absorbing capability, or absorption, of the boxes has been increased. It will be shown in Chapter II that the attenuation of incident monochromatic radiation is determined by the spectral absorptance, α_λ . The absorption is just the integral of the profile of α_λ over all wavelengths. From Beer's Law, α_λ is related to the absorption coefficient, k_λ , such that when k_λ is modified by the directed motion Doppler effect as in Figure 2, the profile of α_λ is also modified in a manner resembling Figure 2. This increases the area under the α_λ profile and results in an increase in the absorption. Physically the reduction of self-absorption allows a larger fraction of the molecules to be exposed to, and thus absorb, the incident radiation.

From the basic physics and geometry of the conical flowfield, it is evident that directed-velocity effects exist. The real problem is determining their significance. It may appear that even for hypersonic

flows the frequency shifting will be negligibly small, since the Doppler shift is small. However, if the lines are sufficiently narrow, then a slight shift will become important. If the lines are wide, the directed-velocity effect still exists, but it is imperceptible.

Therefore, the conditions where directed-velocity effects might be important must imply narrow spectral lines and/or a large frequency shift. Primarily there exist two phenomena that broaden spectral lines [4]. One is the random molecular collisions of the radiating gas. These collisions disrupt the normal radiative-transfer process and lead to a direct proportionality between the gas concentration and the spectral-line width. The second phenomena responsible for line width is the thermal agitation of the gas molecules. If the gas molecules possess large amounts of kinetic energy, then the spread of molecular speeds will be greater than that due to lower kinetic energies. In turn this leads to a Doppler shift which increases the width of a spectral line since the molecules are traveling at random velocities and directions. Hence, higher temperatures will also tend to broaden the spectral line. Note that the thermal agitation of the molecules is not to be confused with the directed-velocity effect. Although they both involve Doppler shifting, the directed-velocity effect results from the en masse motion of the molecules as opposed to the random motion of the thermal broadening. Unless it is readily apparent, the spectral-line shape associated with the thermal agitation of the molecules will be termed a thermal Doppler line.

It can be shown that the width of a Lorentzian spectral line varies directly with the pressure and directly with the square root of the

temperature [4]. Thus the line width is more sensitive to the pressure. The magnitude of the frequency shift is dependent on the exit velocity of the gas and the divergence angle of the cone. Therefore, to observe directed-velocity effects, one must have fairly low to moderate temperatures and low pressures along with a suitable combination of the exit velocity and the divergence angle.

This requirement is displayed in Figures 2 and 3. In both Figures 2 and 3 the temperature was 600 Kelvin. However, the pressure in Figure 2 was 5 Torr, while that of Figure 3 was 760 Torr. In Figure 2 the spectral lines are narrow enough for the spectral shifting to introduce a severe change in the overall profile of the absorption coefficient. By contrast, the spectral lines in Figure 3 are much too wide to exhibit the same radical change in the absorption coefficient. It may have a slightly different value at a given wavenumber, but the overall form of the spectral line has changed little. This makes the Doppler shift in Figure 3 relatively undetectable by other than high-resolution measurements. Hence, at atmospheric pressures the directed-velocity effect is unimportant to broad-band measurements. Although, at the low pressures of interest to this study, the exact same Doppler shift produced extreme deformation of the spectral profile.

It is possible to generalize the results of the two-box model to describe the expected results in a conical flowfield. The computation of the spectral profile will involve an integration over the contributions from all the possible spatial positions. Instead of a constant velocity to determine the Doppler shift, the velocity component will vary along the line of sight as $v \sin \theta$, where v is the exit velocity

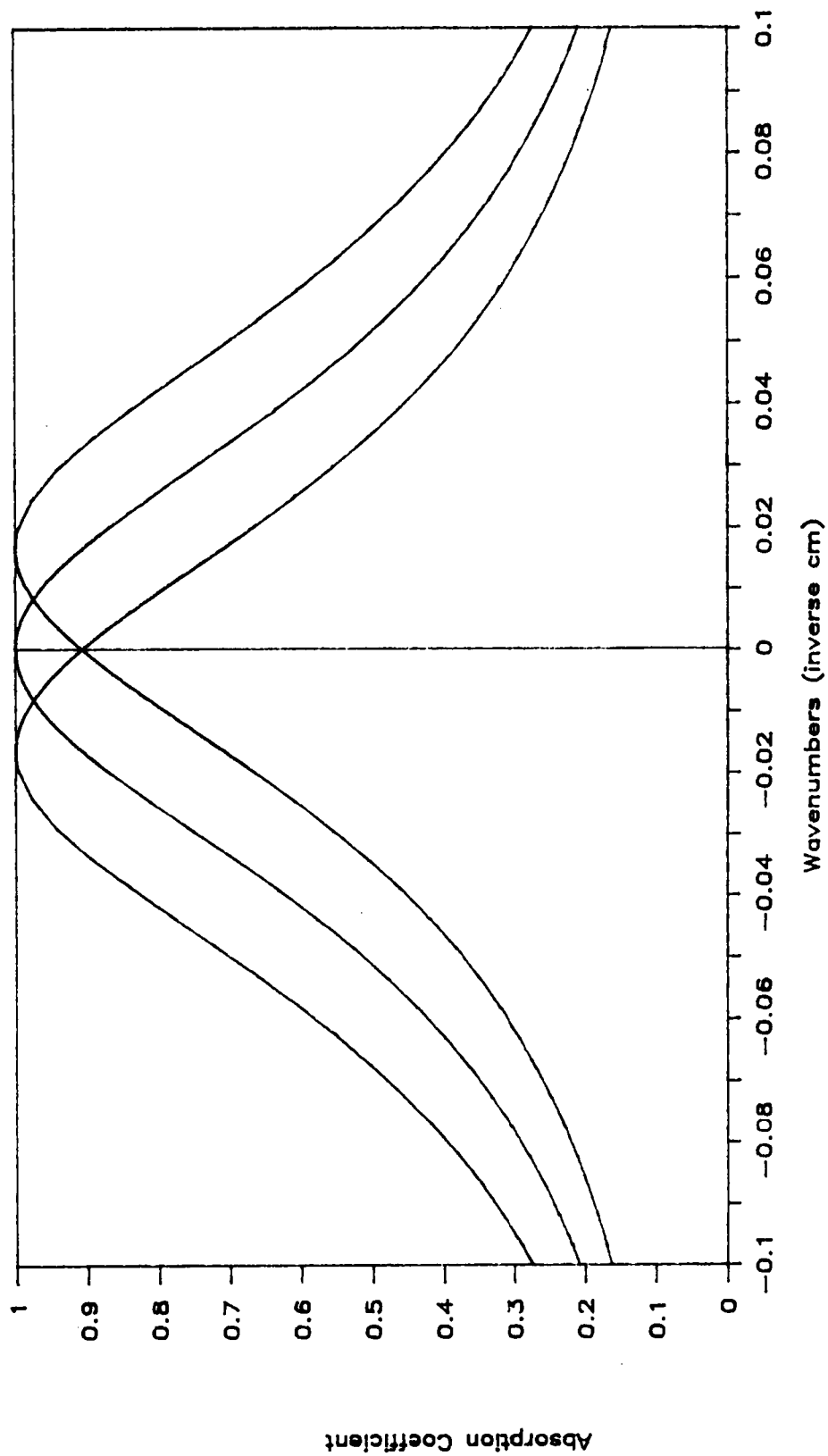


Figure 3. Doppler Shift of a Voigt Profile CO₂ Line at ± 1500 m/sec
(Pressure = 760 Torr; Temperature = 600 Kelvin).

and θ is the angle from the cone axis. Rather than the spectral line splitting into two parts, one blue-shifted and one red-shifted, it now will meld into one broad, distorted spectral line caused by the velocity gradient along the line of sight.

Motivation

As early as 1973, preliminary work on directed-velocity effects was being done by S. S. Penner et al. [5,6]. Their research examined the distortion of the spectral-line profile caused by directed velocities of a conical flowfield. The motivation for this was to determine the applicability of high-resolution laser measurements to problems involving high-altitude conical flowfields. They reached the conclusion that the distortion of these lines would render laser measurements useless at many conditions of interest to modern aerospace systems.

Although Penner's investigation limited itself to high-resolution measurements, it provided a clear indication that the ramifications of directed-velocity effects could be felt in low-resolution, broad-band applications. Until now, however, this topic has received little attention, even though this type of measurement is widely used and is very effective for determining information about the radiative processes occurring in a hot, gaseous flow. Based on the classical models of spectral-band absorption, it is apparent that this type of measurement is sensitive to the spectral-line shape, Lorentzian, Voigt, thermal Doppler, etc. [7]. It follows that band-model measurements should be sensitive to other mechanisms that alter the spectral-line profile, viz. the directed-velocity effect.

The lack of attention given to this effect has been primarily based upon the lack of practical importance. To date, few flowfields have had the prescribed conditions. Thus any spectral-line shifting that would occur would resemble the lines of Figure 3. Since the alteration was so slight, it was completely ignored. However, the advent of the high-expansion-ratio motors indicates that the directed-velocity effect may have more than just a slight affect on the line profile. The possibility of observing significant directed-velocity effects in broad-band measurements is the motivation for a more extensive study than that of Penner's.

As will be seen in Chapter 4, broad-band radiometry can measure the average absorption and/or emission over a given spectral region. This is one technique employed in diagnostics associated with the development of modern rocket engines. At the present time, there exist some discrepancies between the predicted results and the measurements. Several possible causes are currently under investigation. One is the nonaxisymmetric spatial structure in combustion flows. This assumption is made for most radiative calculations. Likewise, it is plausible to assert that there exists a freezing of molecular states implying that the expected radiative transitions are altered. This will tend to enhance the emitted radiation from the flowfield.

The intention of this work is to determine the feasibility of directed-velocity effects contributing to the measurement differences. This will be done by first reproducing the previous work done on this problem by Penner. Once firmly established, this study will size up

the influence of this effect on band models. The prime objective of this study is to discover and to evaluate all aspects of the directed-velocity effect in terms of broad-band parameters.

CHAPTER II

SINGLE-LINE STUDY

Radiative Transfer Basics

It would seem appropriate to present the basic principles of radiative transfer. One of the most fundamental basics is the well-known Beer's Law. This law quantizes the passage of monochromatic radiation through a homogeneous media. It is also known as Lambert's Law, Bouguet's Law, or any combination of the three.

Suppose nearly monochromatic radiation of intensity, I_λ , is traversing through a homogeneous medium. By Beer's Law, the change in intensity of the radiation is proportional to the distance traveled. If $d\ell$ is an infinitesimal length, then the change in intensity at wavelength, λ , due to absorption of the radiation is given by [7]

$$dI_\lambda = - k_\lambda \rho I_\lambda d\ell \quad (1)$$

where ρ is the local density and the constant of proportionality, k_λ , is called the absorption coefficient. The units of k_λ are in terms of an inverse length-density.

From Beer's Law we can define the optical depth, denoted in this study by ϕ , of a homogeneous or nonhomogeneous media as the integral of $k_\lambda \rho$ over the path length. For an incremental length, $d\ell$, we can write $d\phi$ as

$$d\phi = k_\lambda \rho d\ell \quad (2)$$

where k_λ and ρ are functions of the path. In a gaseous medium, ρ can be rewritten such that

$$d\phi = k_\lambda \times p \, d\ell \quad (3)$$

where X is the mole fraction of the absorbing gas and p is the static pressure.

When k_λ is not a function of position, it can be taken outside the integral. The integral of $X p$ is called the optical path, u , [8]

$$u = \int X p \, d\ell \quad (4)$$

In a homogeneous gas with path length, L , u is merely $X p L$. Notice that this defines the units of u as length-pressure and thus the units of k_λ as length-pressure⁻¹. Often k_λ is tabulated with reference to standard temperature and pressure (STP), 273 Kelvin and 760 Torr, respectively, with the units of cm-amagat⁻¹. Usually the optical path will also be referenced to STP and will take the form

$$u = L \frac{P}{760} \frac{273}{T} \quad (5)$$

where P represents the partial pressure in Torrs and the units of u are termed cm-amagat. This assumes a uniform, homogeneous gaseous medium.

The emission of monochromatic radiation is treated in a similar fashion as absorption. The spectral radiant power emitted by a volume element of the medium with thickness $d\ell$ and unit area can be written as

$$dI_{\lambda} = \frac{1}{4\pi} j_{\lambda} \rho d\ell \quad (6)$$

where j_{λ} is the emission coefficient with the units of inverse length-density.

For the purpose of this study, we assume that all absorption and emission effects are independent and that scattering can be neglected. It is possible to write the net radiative transfer as a combination of the absorption and the emission. Hence, the net change of intensity is given by

$$dI_{\lambda} = dI_{\lambda} \text{ (absorption)} + dI_{\lambda} \text{ (emission)} \quad (7)$$

$$dI_{\lambda} = I_{\lambda} (p, \ell) d\phi + S_{\lambda} (p, \ell) d\phi$$

where the source function $S_{\lambda} (p, \ell)$ is defined by $S_{\lambda} (p, \ell) = \frac{1}{4\pi} \frac{j_{\lambda}}{k_{\lambda}}$.

This is the fundamental equation of radiative transfer.

Other basic radiative transfer quantities that need to be defined are the spectral transmittance, τ_{λ} , and the spectral absorptance, α_{λ} . If we assume that a homogeneous, uniform density gas is absorbing radiation, then we can obtain directly from Beer's Law, Equations (4) and (5), a formulation for the ratio of emergent to incident radiation intensity. Clearly, the solution of Beer's Law for these conditions is that I_{λ} be

$$I_{\lambda} = I_0 \exp (-k_{\lambda} u) \quad (8)$$

where $\exp (-k_{\lambda} u)$ is the spectral transmittance, τ_{λ} .

For the purpose of this study, there is no reflection of radiation so that whatever is not transmitted must be absorbed. The spectral

absorptance of the media then follows as

$$\alpha_{\lambda} = 1 - \tau_{\lambda} = 1 - \exp(-k_{\lambda}u). \quad (9)$$

This quantity will be used when we explore the variation of absorption with absorber amount.

Quantum Theory of Radiative Transfer

Up to this point, all has been done while considering a monochromatic source of radiation. It is more important to understand the behavior of absorption as a function of frequency since this dependence can be verified experimentally. It will suffice to examine the dependence of the absorption coefficient upon the frequency of the observed radiation [9].

The quantum mechanical description of radiative transfer processes begins with the assumption of a state transition between two discrete, bound states of an atomic or molecular system. For example, this state could represent a particular electronic configuration, a rotational mode, a vibrational mode, or any combination of these. The absorption or emission of electromagnetic radiation will result in a change of the internal energy eigenstate which is defined as an eigenvalue of the Hamiltonian operator of the system.

To understand the processes involved with radiative transfer, one solves the time-dependent Schrödinger Equation for a system of charged particles in an electromagnetic field. The general solution is a wave function that is a linear combination of the set of basis energy eigenfunctions. The elements of the linear combination will have time-dependent coefficients, denoted as $c_n(t)$. The square

of the modulus of $c_n(t)$ yields the probability of finding the system in the n th eigenstate at time t .

Using first order perturbation theory on the interaction Hamiltonian operator to solve for the coefficients, one finds that three independent processes can occur. They are the absorption, spontaneous emission, and stimulated emission of radiation. Suppose that the system is initially in a state, n , with energy E_n . Absorption is the process whereby the system absorbs the proper frequency of incident radiation, a photon, for the $n - n'$ transition. This raises the system to a final state, n' , with energy $E_{n'}$, such that $E_{n'} > E_n$. The reverse of absorption is emission of a photon. Spontaneous emission is the unforced transition from an initial higher energy state, n' , to a lower energy state, n , with the release of the energy differential in the form of radiation. Stimulated emission is the process where the incident radiation will force the system from the higher energy state, n' , to the lower energy state, n , with the release of energy as radiation.

Radiative transitions between any two arbitrary states are not always allowed. The probability that the system will have a transition is given by the final-state coefficient, $c_{n'}(t)$. The solution for $c_{n'}(t)$ involves the evaluation of matrix elements defined by [9]

$$M(n, n') = \int \psi_n^*(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) \vec{\epsilon} \cdot \vec{\nabla} \psi_{n'}(\vec{r}) d\vec{r} \quad (10)$$

where ψ refers to the eigenfunction of the initial and final states, $\vec{k}$ is the wavevector of the incident radiation, and $\vec{\epsilon}$ is the direction of polarization of the radiation. This matrix has nonzero elements

only for certain $n - n'$ transitions which satisfy the state selection rules. These selection rules arise from the quantization of the angular momentum of the initial and final states. Quite often the exponential term is approximated as unity. This is known as the electric dipole approximation.

From the time-dependent coefficients, one can determine a transition rate which will describe the rate at which a given atomic or molecular system will change states. The transition rates can be used to determine the rate of absorption or emission of radiation of a particular frequency for a macroscopic system of many atoms or molecules. In the case of absorption, the number of atoms making a transition per unit time from state n to state n' is directly proportional to the total number of atoms available and to the energy density of the states. The constant of proportionality is called the Einstein coefficient for absorption $B(n,n')$. Similar definitions exist for the Einstein coefficients of spontaneous emission $A(n',n)$, and stimulated emission $B(n',n)$.

To this point, we have been working under the assumption that the probability of finding the wave function in the initial state at the time of the state transition is unity, such that $c_n(t) = 1$ for all t . This was an easy way to decouple the equations of motion of the coefficients, but it does not accurately reflect the behavior of an actual energy state. In reality, all states except for the ground state will decay in a finite lifetime, meaning that $c_n(t)$ is not a constant. A better approximation is that the probability of finding the system in the initial state prior to the radiative transition decays exponentially. This can be written as $c_n(t) = 1$ for $t < 0$ and

$c_n(t) = \exp(-\frac{t}{2\tau})$ for $t \geq 0$ where τ is a characteristic decay time.

The repercussions of a finite lifetime are dictated by the Heisenberg Uncertainty Principle. This principle states that one cannot know the exact energy of the state with unlimited precision, but that the energy will be uncertain by an amount $\frac{h}{2\pi\tau} \equiv \Gamma$. Thus, there exists a probability of a state transition occurring in response to radiation that has energy in an interval centered about the energy differential $E_{n'} - E_n$, having a width of $\Gamma_{n'} + \Gamma_n$. The important thing to note is that instead of absorption occurring at infinitely thin spectral positions like a delta function, absorption now occurs over a small spectral region.

The dependence of the absorption on the frequency can be obtained by solving the coupled equations of motion of the probability amplitudes. To do this, one must first resolve the vector potential of the radiation, $\bar{A}(\bar{x}, t)$, into its Fourier components in frequency space. The equation for the final state probability amplitude c_n , in the case of emission will have the form [9]

$$\dot{c}_n(\nu, t) = -\frac{e}{m} A_0(\nu) M(n', n) \exp \left[i2\pi t(\nu - \frac{1}{h}(E_{n'} - E_n)) \right] c_n(t) \quad (11)$$

where $A_0(\nu)$ is the amplitude of the vector potential and e/m is the charge to mass ratio. Substituting the exponential decay term in for $c_n(t)$ allows one to carry out the time integration leaving

$$c_n(\nu, t) = -\frac{e}{m} A_0(\nu) M(n', n) \frac{\exp \left[i2\pi t(\nu - \nu_0) - \frac{t}{2\tau} \right] - 1}{i2\pi(\nu - \nu_0) - \frac{1}{2\tau}} \quad (12)$$

where $\nu_0 \equiv \frac{1}{h}(E_{n'} - E_n)$

For t large compared to τ , the probability that a photon has been emitted is given by the modulus of $c_n(v,t)$. The intensity of emitted or absorbed radiation is proportional to this probability and can be described by the absorption coefficient for natural broadening [4]

$$k = \frac{S}{\pi} \frac{\gamma_N}{(v-v_0)^2 + \gamma_N^2} \quad (13)$$

where S is a constant line strength and $\gamma_N = \frac{1}{4\pi\tau}$. This type of broadening represents a lower limit on the width of spectral lines since it follows directly from the Uncertainty Principle. However, it is not the only type of spectral-line broadening that occurs.

Spectral Lines

A spectral line can be defined by both its strength and shape. The strength of a spectral line is the total amount of energy emitted or absorbed due to one isolated radiator/absorber if all the emitted/absorbed photons from that line are detected. The line strength, S , is merely the integral of the absorption coefficient over all frequencies [8],

$$S = \int_0^{\infty} k_v dv. \quad (14)$$

It is found that a spectral line originates in the quantum mechanics of radiative state transitions of atoms and molecules. The solution to that problem leads to the process of natural broadening. The complete expression for the absorption coefficient of a spectral line due to natural broadening is given by Equation 13.

This result for natural broadening assumes a macroscopic system of noninteracting atoms/molecules. In a gas, the atoms and molecules will emit and absorb radiation, with the process of natural broadening taking place. They will also undergo physical collisions with other gas atoms/molecules. These collisions will serve to alter the decay lifetime of a given state through the transfer of kinetic energy from one particle to another. These radiationless transitions shorten the decay lifetime of the absorbing or emitting state. This leads to a larger uncertainty in the energy of the state, which can be described by $\Gamma_{\ell} = \frac{h}{2\pi\tau} + W_c$ where W_c is some empirical transition rate due to molecular collisions [9]. Thus collision phenomena will not alter the Lorentzian line shape of natural broadening, but will only further broaden the line profile. This width is often measured at the half maximum value point in terms of the half width of the line (HWHM), or the full width of the line (FWHM). For the conditions of this study, collision broadening is orders of magnitude larger than natural broadening and will be the dominating factor. The effects of collision broadening are defined by the absorption coefficient of the Lorentzian line. (For convenience, the spectral line, which is due to the combination of natural and collision broadening phenomena, will be termed a Lorentzian line.)

$$k(\omega) = \frac{S}{\pi\gamma_{\ell}} \frac{1}{1 + \left[\frac{\omega - \omega_0}{\gamma_{\ell}} \right]^2} \quad (15)$$

where ω_0 corresponds to the natural frequency, S is the line strength, and γ_{ℓ} is the spectral-line HWHM such that $\gamma_{\ell} = (\gamma_N + W_c)/c$. Notice

that the frequency units have been changed. Rather than writing the frequency in Hertz, it can be written in terms of reciprocal wavelengths called wavenumbers, denoted by ω . Explicitly, ω has the form $\omega = \frac{1}{\lambda}$ where λ represents wavelength. Common units for ω are cm^{-1} , inverse centimeters. Thus, ω differs from ν by a factor of c . One should be aware of what type of frequency variable is actually being used. In this study, ω will be used except where explicitly stated otherwise.

There exists another influence on radiation absorption which is pertinent to this research which is independent of natural and collision broadening. In a gas, the particles are moving at a high rate of speed (nonrelativistic) with respect to each other. This speed is high enough to warrant consideration of the Doppler effect. The Doppler effect describes the appearance of a wave when the source and the receiver are in relative motion. Suppose that an atom is moving in the x direction with velocity $\bar{v}(x)$ and emits radiation at a wavenumber ω_0 in its own reference frame. The wavenumber of that radiation in the lab frame, ω , is related to the natural wavenumber ω_0 by [9]

$$\omega = \frac{\omega_0}{1 \pm \frac{\bar{v}(x)}{c}} \approx \omega_0 \left(1 \mp \frac{\bar{v}(x)}{c}\right) \quad (16)$$

where $\pm \bar{v}(x)$ is the velocity and c is the speed of wave propagation. The upper sign corresponds to the particle receding from the observer (a red shift).

If the atoms are in random motion, Maxwell's one-dimensional Gaussian speed distribution indicates the number of atoms having a

speed between v and $v + dv$ [10]. Hence it is possible to determine the number of atoms emitting in a wavenumber range ω to $\omega + d\omega$. Since the intensity of the emitted radiation in a wavenumber range ω to $\omega + d\omega$ is directly proportional to the number of atoms emitting in that wavenumber range, the intensity distribution will have a Gaussian distribution also. Expressing this distribution in terms of the absorption coefficient yields [11]

$$k(\omega) = \frac{S}{\gamma_d} \sqrt{\frac{\ln 2}{\pi}} \exp \left[-\ln 2 \left(\frac{\omega - \omega_0}{\gamma_d} \right)^2 \right] \quad (17)$$

$$\text{where } \gamma_d = \omega_0 \sqrt{\frac{2kT \ln 2}{Mc^2}}$$

is the spectral line HWHM associated with Doppler broadening, ω_0 is the natural wavenumber, S is the line strength, k is Boltzmann's constant, T is the temperature, and M is the mass of the atom.

These three mechanisms--1) natural broadening, 2) collision broadening, and 3) Doppler broadening--are the fundamental phenomena that determine spectral-line structure. Natural broadening is orders of magnitude smaller than the other two; and, in most applications, it is usually neglected. Pressure broadening and natural broadening are both described by a Lorentzian profile while Doppler broadening evolves into a Gaussian shape. Important differences exist in these two curves. The Doppler curve falls rather quickly to very small values; but the Lorentzian curve, while possibly not as wide, demonstrates very significant wings. Far from the line center, the Doppler curve could be negligible even though the Lorentzian curve could still be significant. For example, at two full widths from the line center, the

Lorentzian curve has dropped to 6 percent of the line center intensity. However, at the same distance, the Doppler curve has dropped to 0.2 percent of the line center intensity. This fundamental difference is of utmost importance in understanding the behavior of absorption at increasing optical depths.

To analyze the results of an experiment, quite often a decision is made to use either a Lorentzian line profile or a Gaussian line profile based on the existing conditions. In cases of high pressure, for example, collision broadening might make Doppler broadening negligible. At other times, it might occur that high temperatures and extreme low pressures will make the Doppler profile more appropriate.

However, there is a regime where neither thermal motion nor collision broadening can be neglected. In this instance, there is a need for a combination of the two effects. The Voigt profile was developed to blend both thermal and collision broadening together in proportionate amounts to provide a better description of the physical reality of the situation.

Since thermal motion and collision broadening are independent phenomena, one can consider the convolution of them in two ways. First one can think of a pure Doppler curve in which every infinitesimal frequency range is collision broadened. Contrary to that, one can assume a pure Lorentzian curve in which every infinitesimal frequency range is Doppler broadened [12].

Choosing the latter, assume there exists a Lorentzian curve which will be Doppler broadened in the sense that one must sum over all the possible line of sight molecular speeds, weighted by Maxwell's speed

distribution. The line center of the Lorentzian will be shifted by $\omega_0^* = \omega_0(1 + \frac{v}{c})$, yielding the resultant Voigt absorption coefficient [7]

$$k(\omega) = S \int_{-\infty}^{+\infty} dv \left[\frac{\gamma_L/\pi}{(\omega - \omega_0 - \omega_0 \frac{v}{c})^2 + \gamma_L^2} \right] \left[\sqrt{\frac{M}{2\pi kT}} \exp \left(-\frac{Mv^2}{2kT} \right) \right] \quad (18)$$

Substituting the Doppler half width into the exponential and performing a change of variables to $y = \sqrt{\ln 2} \omega_0 v / \gamma_D c$ it follows that the Voigt profile is

$$k(\omega) = \frac{Sa}{\pi \gamma_D} \sqrt{\frac{\ln 2}{\pi}} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{a^2 + (\epsilon - y)^2} dy \quad (19)$$

where

$$a = \sqrt{\ln 2} \frac{\gamma_L}{\gamma_D}$$

and

$$\epsilon = \sqrt{\ln 2} \frac{\omega - \omega_0}{\gamma_D}.$$

The limiting forms of the Voigt line can be seen by looking at the pieces of Equation 18. When there is very little Doppler broadening, the Gaussian term becomes sharply peaked compared with the Lorentzian term. In the limit of no Doppler broadening, this acts as a delta function and yields the ordinary collision broadened form, Equation 15. On the other hand, when γ_L is very small the Lorentzian term acts like a delta function in the limit of no collision broadening. The

limiting case will replace v with $(\omega - \omega_0) \frac{c}{\omega_0}$ in the exponential, which is exactly the Doppler broadening result, Equation 17. Equation 19 demonstrates the need for a simple approximation to circumvent the difficulties of computing a large integral at every spectral location. It is precisely for that reason that the Voigt function was the subject of much approximation study before the advent of modern, powerful computers. As a result of those studies, many very accurate techniques were produced. These techniques prove invaluable in saving computer time that would ordinarily be wasted by computing the integral term over and over again.

Since the Voigt profile is a convolution of Doppler and Lorentzian profiles, it will have characteristics of both. The relative importance of the contributing terms is measured by the ratio of the half widths, which is the parameter, "a". The part near the line center will tend to have the sharper Gaussian shape, while the Lorentzian wings will be present farther away. The Voigt half width is a vaguely defined quantity because solving for it analytically involves inverting the above integral. Hence, the Voigt half width is usually determined by empirical approximations or direct measurements.

Familiarization with the features of each spectral-line type allows one to understand the behavior of observables such as absorption upon the form of the absorption coefficient. This is very important since the absorption coefficient is governed by the existing system conditions, which is often the desired resultant quantities. The next step is to determine this functional dependence of observables, like absorption and emission, upon spectral-line structure.

Measurables

The discussion of spectral-line structure implied the existence of absorption at locations other than the line center, i.e., natural frequency or wavenumber. Because absorption is not monochromatic, there are various quantities of interest based upon the dependence of absorption on frequency.

The total absorptance, which is also referred to as the absorption, differs from the line strength in that it takes into account the absorbing/emitting properties of the entire medium. Recall that the spectral absorptance, $\alpha(\omega)$, was defined as $1 - \tau(\omega)$ in Equation (9). To find the total absorptance due to a spectral line, one needs to integrate the spectral absorptance over all frequencies. Hence, the total absorptance, W , of the line is just [11]

$$W = \int_0^{\infty} \left[1 - \exp \left(- \int_{x_1}^{x_2} \rho k(\omega) dx \right) \right] d\omega. \quad (20)$$

The total absorptance is commonly cited as the equivalent width. It represents the amount of absorption due to a perfectly absorbing, or "black," line of that particular width. On a plot of absorptance versus wavenumber, a perfectly black absorption line would have the shape of a rectangle. The height of the black line would, of course, have the value of unity. The line would have a particular width depending on the amount of energy it could absorb from the radiation. By defining an equivalent width for all spectral lines, one eliminates line-shape factors and is able to compare the energy absorbed by a particular line with that of any other line. It is worthwhile to emphasize

that the line strength depends solely upon the absorption coefficient; but the equivalent width depends upon the optical depth, which is defined as the product of the absorption coefficient and the optical path, $k(\omega)u$.

Implicit in this definition is the distinction between a spectral line and an absorption line. Although they are similar in shape, spectral lines and absorption lines are distinct quantities. The profile of a spectral line is given by the dependence of the absorption coefficient on wavenumber. The integral of the absorption coefficient over all wavenumbers is the line strength, Equation 14, and is proportional to the number of emitters or absorbers. The profile of an absorption line is defined by the unitless spectral absorptance, Equation 9.

The integrated spectral absorptance is the equivalent width, a measurable quantity. The absorption line is related to the spectral line through Beer's Law, Equation 8. For a homogeneous gaseous medium, it is possible to expand the exponential. When $k(\omega)u$ is small enough to neglect second-order terms, one can write $\alpha(\omega)$ as

$$\alpha(\omega) = k(\omega)u. \quad (21)$$

Thus the absorption profile is proportional to the spectral profile only when $k(\omega)u$ is small; i.e. only for optically thin systems.

The dependence of the equivalent width upon the optical depth is very important to gaseous emission and absorption. Quite often this relation is plotted on log-log scales. These plots are referred to as curves of growth since they show explicitly the effect of increasing optical depth on absorption. Their importance is due to the fact that the absorption is an observable. Suppose that a particular

measurement finds a given value of the absorption.' Then a value for the gas concentration may be backed out of that measurement through the curve of growth.

The curve of growth is so vital to absorbing/emitting systems that it merits further discussion. It consists of a plot of equivalent width, W , versus the product of the line strength and the path length, Su . To see this, one needs only to expand the exponential in the definition of W . Then W becomes

$$W = \int_0^{+\infty} \left[1 - 1 + \int_{x_1}^{x_2} \rho k(\omega) d\ell + O(2) \right] d\omega. \quad (22)$$

For homogeneous systems, $k(\omega)$ can be pulled outside the integral of $d\ell$ leaving the integral of $X \rho d\ell$. This is just the optical path, u . If $k(\omega)u$ is small enough to neglect high-order terms in the series expansion, then we are left with

$$W = \int_0^{\infty} k(\omega)u d\omega. \quad (23)$$

Since u is not frequency dependent, it may be pulled outside the integral and the integration will be recognized as the line strength. So, for small optical depths, W is linear with Su .

$$W = Su \text{ (small } k(\omega)u \text{ limit)}. \quad (24)$$

Physically, this means that the absorption of a system varies linearly with the optical depth. For example, doubling the gas concentration will result in twice the absorption. An additional doubling

of the gas concentration will result in four times the initial absorption. This process does not proceed ad infinitum, however. There is a point at which the absorption line center will be absorbing 100 percent of the radiation. It will not be able to absorb any more radiation since it is impossible to become blacker than black. This point is called saturation. This is not to say that the spectral line is unable to continue to increase the amount of total absorption. Since the absorption line has some sort of bell-shaped profile, increases in optical depth will continue to increase the total absorption. However, they will no longer be linearly related. Further increases of absorption will depend upon the wings of the spectral line. It is the behavior of the absorption after saturation that can uniquely distinguish between the types of spectral lines.

One of the features of the Lorentzian spectral line is that it has rather large wings compared to the Doppler line. After saturation is reached, these wings cause the two line shapes to absorb distinctively. A Lorentzian line will absorb according to a square-root relation. This can be seen rather easily by first noting that the solution to the equivalent width of the Lorentzian line is given by [11]

$$W = 2\pi\gamma_{\ell} f(x) \quad (25)$$

where $x = \frac{Su}{2\pi\gamma_{\ell}}$ and $f(x)$ is the Ladenburg-Reiche function defined by

$$f(x) = x \exp(-x) \left[I_0(x) + I_1(x) \right]. \quad (26)$$

$I_0(x)$ and $I_1(x)$ are the modified Bessel functions of order zero and one. The Bessel functions have asymptotic expansions when x is much larger than the order of the function [13], such that for $x \gg n$

$$I_n(x) \rightarrow \frac{1}{\sqrt{2\pi x}} \exp(x) \left[1 + O\left(\frac{1}{x}\right) \right]. \quad (27)$$

By retaining only the first term of the expansion and inserting it into Equation (25), the equivalent width becomes

$$W = 2\pi\gamma_\ell \left[x \exp(-x) \frac{2 \exp(x)}{\sqrt{2\pi x}} \right]. \quad (28)$$

This can be reduced to obtain

$$W = 2 (S\gamma_\ell)^{1/2} \quad (\text{Lorentz large } ku \text{ limit}). \quad (29)$$

A similar approach is taken to determine the large ku limit of Doppler lines. Due to their lack of significantly absorbing wings, it is found that they will absorb according to a power series of logarithms [14]

$$W = \frac{2\gamma_d}{\sqrt{\ell n 2}} \left[(\ell n y)^{1/2} + 0.2886 (\ell n y)^{-1/2} - 0.2473 (\ell n y)^{-3/2} + \dots \right] \quad (30)$$

where

$$y = \frac{\sqrt{\ell n 2}}{\pi} \frac{S u}{\gamma_d}.$$

Even though Voigt lines are a combination of Lorentzian and Doppler features, their limiting forms have the characteristics of a Lorentzian line. Eventually, it is the Lorentzian wings that will

become the dominant form and the "square-root region" will become apparent after saturation is reached.

In summary, the relation of absorption to the optical depth is called the curve of growth. A curve can be broken into three regions, determined by the slope of the curve. There exists an optically thin region extending linearly from zero optical depth. This is common to all spectral lines regardless of line profile. This is followed by a region where the spectral line begins to saturate and particular line features start to become noticeable. Then there is the optically thick region where absorption occurs only in the wings of the line. In this region, there is a significant distinction between Doppler and Lorentzian lines, and Voigt lines will follow the Lorentzian curve.

CHAPTER III

SINGLE-LINE COMPUTATIONS

Voigt Profile Approximation

Since the Voigt profile cannot be solved analytically, it has been the subject of much analysis and approximation. One empirical approximation was devised by E. E. Whiting [15]. It consists of an easily handled quadratic polynomial for the absorption coefficient given by

$$\frac{k_{\lambda}}{k_{\lambda_0}} = \left(1 - \frac{w_L}{w_V}\right) \exp \left[-2.772 \left(\frac{\lambda - \lambda_0}{w_V} \right)^2 \right] + \left(\frac{w_L}{w_V} \right) \frac{1}{1 + 4 \left(\frac{\lambda - \lambda_0}{w_V} \right)^2} \quad (31)$$

$$+ 0.016 \left(1 - \frac{w_L}{w_V} \right) \left(\frac{w_L}{w_V} \right) \left[\exp \left(-0.4 \left(\frac{\lambda - \lambda_0}{w_V} \right)^{2.25} \right) - \frac{10}{10 + \left(\frac{\lambda - \lambda_0}{w_V} \right)^{2.25}} \right]$$

where k_{λ} is the absorption coefficient, λ is the wavelength, λ_0 is the line center wavelength corresponding to the natural frequency, w_L is the Lorentz FWHM in wavelength units, and w_V is the Voigt FWHM in wavelength units.

The accuracy of this algorithm varies as a function of distance from the line center. The worst values of error for the set of conditions of this study are -4.5 percent located at 1.5 full widths from line center, and +1.0 percent located at 0.8 full widths from line

center. This level of accuracy is more than sufficient since the purpose of this study is comparative in nature.

Notice that the polynomial approximation given in Equation (31) is in terms of wavelength units. This means that the half widths which are usually given in terms of wavenumber units must be converted into wavelength units. Also note that the approximation uses the FWHM rather than the HWHM. The Lorentz FWHM is obtained by determining the half width in frequency units and solving for the full width in wavelength units. The half width, in cm^{-1} units, is found by computing a sum of experimentally based collision-broadening parameters. These parameters account for aspects of the molecular collisions such as collisions of a species with itself as well as other species, species concentrations, pressure, and temperature. The full width can then be solved from the half width with a little algebra.

Unfortunately, calculating the Voigt FWHM is not so straightforward. The algebra is the same, but there is no convenient expression for the Voigt half width. Olivero and Longbothum devised an empirical fit to the Voigt half width [16]. Their analysis adopted the parameters R and d which are defined in terms of the Lorentz HWHM γ_L , the Doppler HWHM γ_D , and the Voigt HWHM γ_V , by the equations

$$R = \frac{\gamma_V}{\gamma_L + \gamma_D} \quad (32)$$

and

$$d = \frac{\gamma_L - \gamma_D}{\gamma_L + \gamma_D} \quad (33)$$

By using curve-fitting techniques, they discovered a function for $R(d)$ given by

$$R(d) = 1 - a(1 - d^2) - b(d) \sin(\pi d) \quad (34)$$

where $a = 0.18121$. The parameter b is given by another function in terms of d ,

$$b(d) = 0.023665 \exp(0.6d) + 0.00418 \exp(-1.9d) \quad (35)$$

From these two expressions, one can back out the Voigt HWHM and then determine the Voigt FWHM. An investigation of the accuracy of the $R(d)$ function performed by Olivero and Longbothum determined that the correct Voigt HWHM can be computed to within 0.01 percent.

Computational Methods

In the previous section, an approximation to the Voigt profile was exhibited. However, as it stands, it does not incorporate any directed velocity effects. The spectral line center, λ_0 , that appears in the quadratic polynomial approximation is the quantity that must be modified to account for velocity effects.

In the physical situation of this study, the spectral line center undergoes a Doppler shift due to the macroscopic motion or the flow of the gas. The correct amount of spectral shift is given by Doppler's Law [19],

$$\lambda_0^* = \lambda_0 \left(1 \pm \frac{v}{c} \sin \theta\right) \quad (36)$$

or

$$\omega_0^* = \frac{\omega_0}{(1 \pm \frac{v}{c} \sin \theta)} \approx \omega_0 (1 \pm v \sin \theta) \quad (37)$$

where ω_0 is the natural wavenumber of the state transition responsible for the radiation, ω_0^* is the shifted line center, and $v \sin \theta$ is the velocity component along the line of sight of the observer (Figure 1). Hence, inclusion of directed-velocity effects is obtained by substituting Equation 36 into the polynomial Voigt approximation Equation 31 for λ_0 .

This now gives the absorption coefficient a dependence upon velocity which can be interpreted as a dependence upon position, thus $k = k(\omega, x)$. If velocity components do not exist along the line of sight, meaning that $\theta = 0$, Equation (37) reduces to $\omega_0^* = \omega_0$, $k(\omega)$ is not a function of position, and we have the usual Voigt profile.

It will be necessary to define our nomenclature to avoid confusing the results of the comparison calculations. A 'no-velocity spectral line' or 'no-velocity line' will refer to a spectral line originating from a flowfield with a high-flow velocity, but with $\theta = 0$, thus lacking any velocity components along the line of sight of the observer. A "high-velocity spectral line" or "high-velocity line" will refer to a spectral line originating from a flowfield with the same high-flow velocity, but with a nonzero θ .

The dependence of $k(\omega)$ on position is important when considering integrals of the type introduced in Chapter II. No longer can $k(\omega)$ given by Equation 31 automatically be brought through spatial integrals such as the path-integrated absorption coefficient

$$\phi(\omega) = \int p k(\omega, x) dx \neq k(\omega, x) \int p dx \quad (38)$$

where p represents the partial pressure of the absorbing gas, even though the flowfield is assumed to be homogeneous.

This integral was performed to obtain ϕ as a function of wave-number, $\phi = \phi(\omega)$. For no-velocity spectral lines where $k = k(\omega)$, this is just the absorption coefficient times the pressure-path length, $k(\omega)u$. Hence, $\phi(\omega)$ is directly proportional to the Voigt profile. For the high-velocity cases, the profile will not be proportional to the Voigt profile near the spectral-line center. Far away from the line center, though, one would expect the high-velocity profile to merge with the no-velocity profile. This arises as the velocity term becomes less important.

$$(\omega - \omega_0) \sim \left[\omega - \omega_0 \pm \left(\frac{v}{c} \sin \theta \right) \omega_0 \right] \quad (39)$$

for large values of ω .

The integration in Equation (38) was done by evaluating $\phi(\omega)$ at 300 wavenumber increments ranging to $\pm 0.50 \text{ cm}^{-1}$ from the line center. At each of these wavenumbers a path integral across the flowfield was done using Simpson's Rule with 50 spatial points, where $k(\omega, x)$ was evaluated by the polynomial approximation given in Equation (31) and summed appropriately. It was found that better accuracy was obtained in subsequent calculations involving $\phi(\omega)$ if the wavenumber points were more densely packed near the line center. One hundred points were evenly spaced between -0.50 cm^{-1} and -0.02 cm^{-1} , relative to line center. One hundred more points were evenly spaced between -0.02 and $+0.02 \text{ cm}^{-1}$. The final 100 points were then placed evenly between 0.02 and 0.50 cm^{-1} . For the sake of comparison, an average half width at

half maximum of spectral lines in this study is on the order of 0.003 cm^{-1} , indicating that all pertinent spectral information should be observed within the range of the calculations.

With the calculation of $\phi(\omega)$, one can compute the curve of growth of the line profile. Recall that the curve of growth is the functional dependence of the total absorption upon the optical depth. This dependence was already derived to be

$$W = \int_0^{+\infty} \left[1 - \exp \left[- \int_{x_1}^{x_2} k(\omega, x) p \, dx \right] \right] d\omega, \quad (40)$$

which can be written as

$$W = \int_0^{+\infty} \left[1 - \exp \left[- \phi(\omega) \right] \right] d\omega. \quad (41)$$

The trapezoid rule was used for the numerical integration since the data points of $\phi(\omega)$ were unevenly spaced over the spectral interval. The integral was done from -0.50 cm^{-1} to $+0.50 \text{ cm}^{-1}$ relative to line center, and involved 300 points. This was sufficient to approximate negative infinity to positive infinity. Values of the integrand at the end points of -0.50 and $+0.50 \text{ cm}^{-1}$ were on the order of 10^{-300} .

The numerical computations were carried out in double precision on an IBM PC-AT utilizing the IBM Professional Fortran Software package.

Spatial Variations on Absorption Coefficient

The spatial dependence of $k(\omega)$ along a line of sight across the cone axis, as in Figure 1, for various velocities, angles, and

pressures is demonstrated in Figures 4, 5, and 6. All three plots are an evaluation of the Voigt profile at the spectral-line center at spatial positions in the flowfield. The y-axis is the magnitude of the high-velocity line absorption coefficient relative to the no-velocity line absorption coefficient. The x-axis is the normalized spatial position along a line of sight which is normal to the cone axis, see Figure 1.

One point to note on all three spatial plots is that the relative value of the absorption coefficient always returns to unity at the cone axis of symmetry. Since the exit velocity at the cone axis is normal to the line of sight, $\theta = 0$ and there is no shifting of the spectral-line center.

Away from the cone axis the absorption coefficient is reduced in all three graphs because the conditions present at a particular spatial location create a Doppler shift of the spectral line. The shift of the spectral line means that the line center will no longer occur at ω_0 . Since the line center is the maximum of the profile, $k(\omega_0)$ is less than $k(\omega')$ where ω' is the new spectral position of the line center.

Another way to view this is that the original spectral-line center has moved spatially. Suppose one passed a laser of certain wavenumber across the flowfield as in Figure 1.

Assuming that the laser is operating at some wavenumber ω' , the maximum absorption of the laser beam will occur when the incident beam becomes shifted far enough in the atoms frame to coincide with the natural wavenumber of a spectral line of the gas, ω_0 . Conversely,

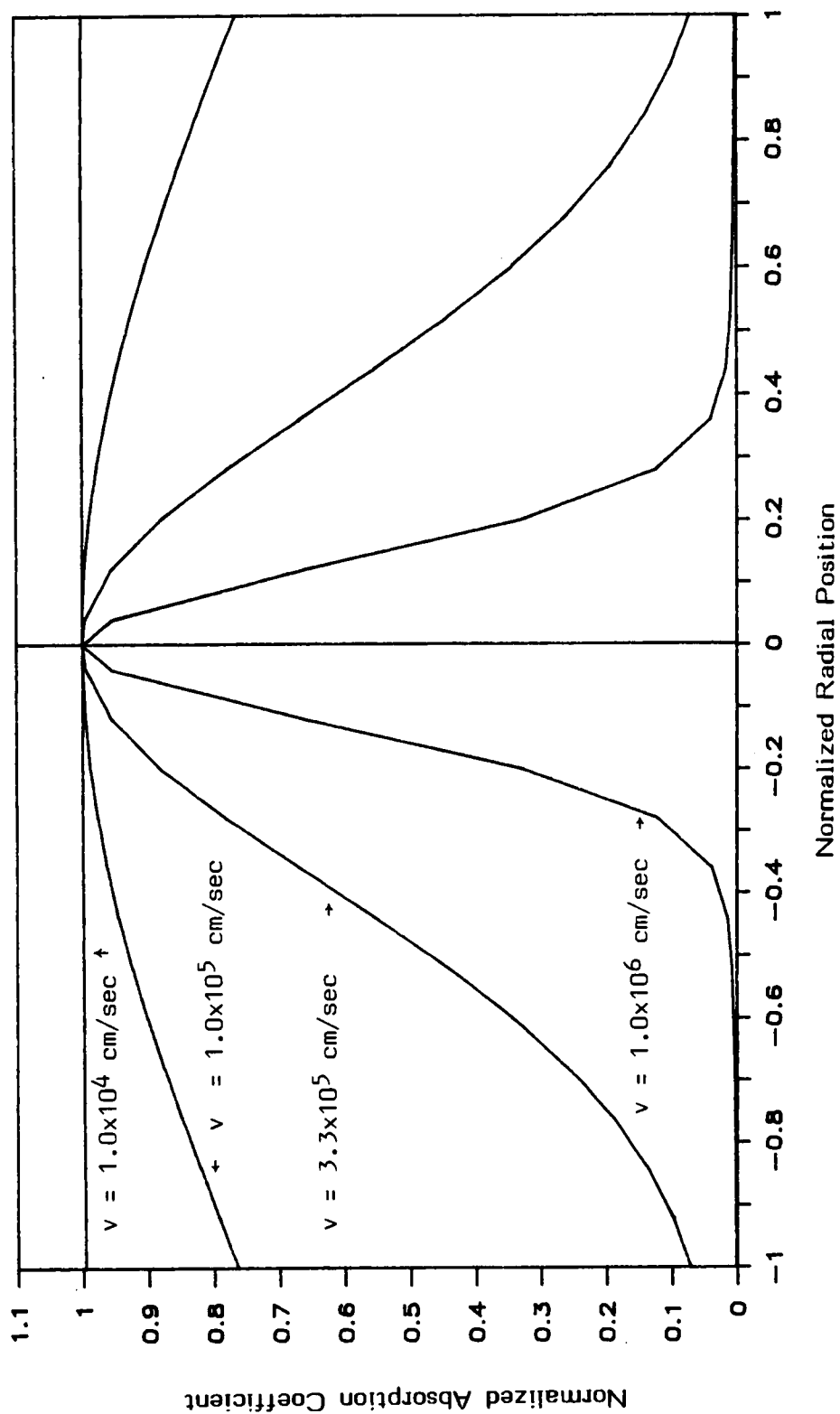


Figure 4. Spatial Dependence of the Line-Center Absorption Coefficient for Various Flow Exit Velocities.

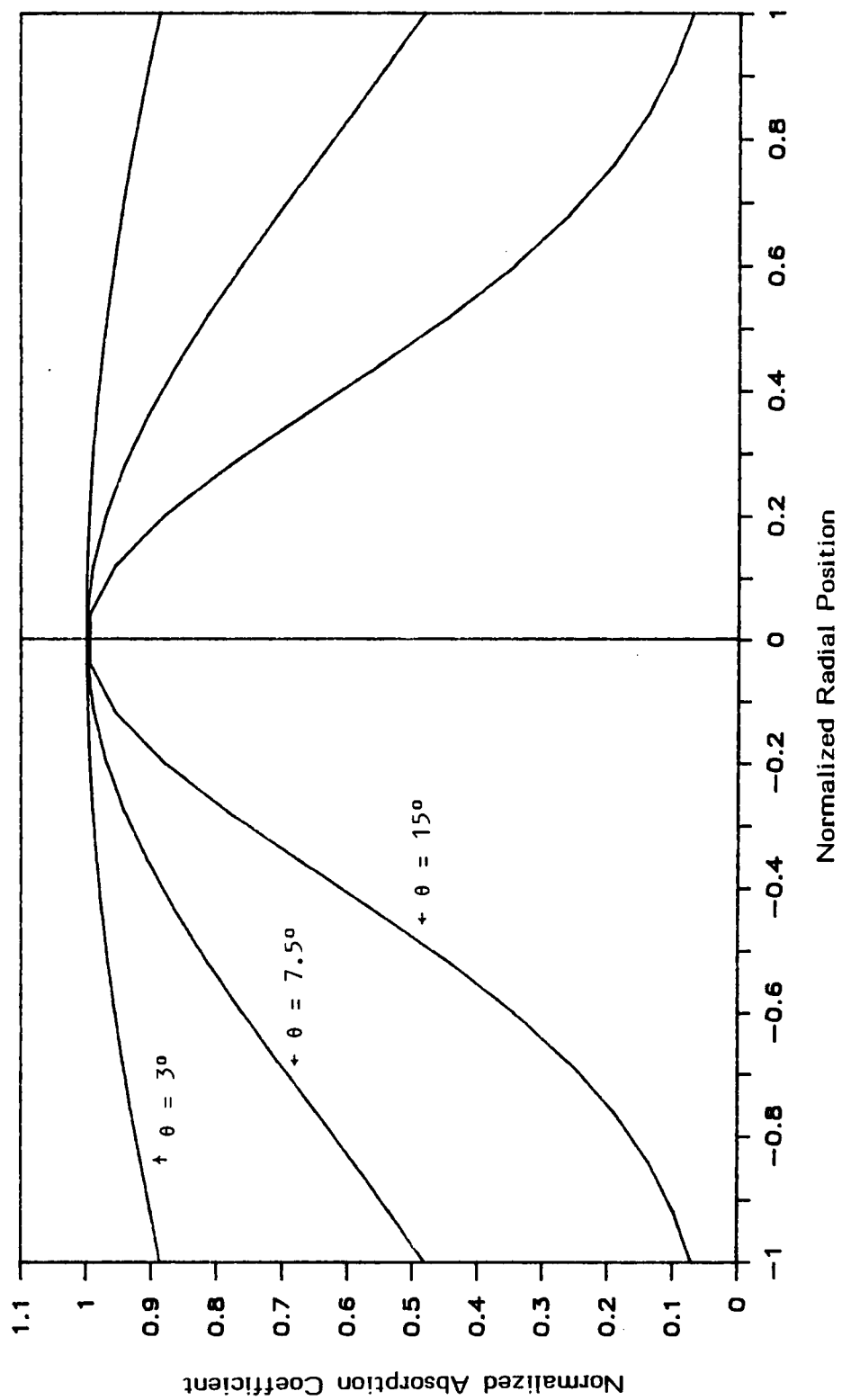


Figure 5. Spatial Dependence of the Line-Center Absorption Coefficient for Various Maximum Divergence Angles.

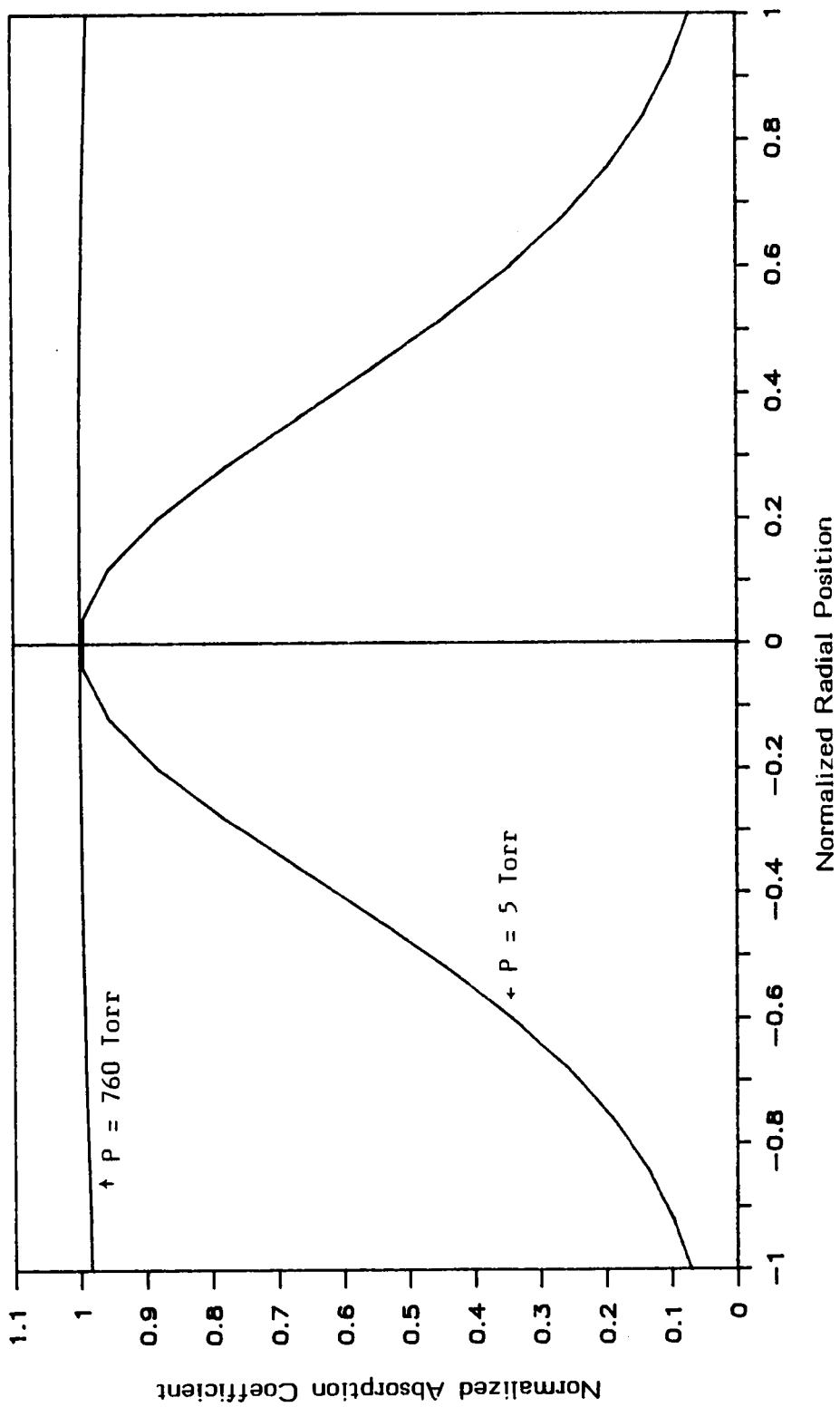


Figure 6. Spatial Dependence of the Line-Center Absorption Coefficient for Various Pressures.

maximum absorption will occur when ω_0 has been shifted in the lab frame to coincide with ω' . Since the shifting has a spatial dependence, so will be absorption. Thus, it is possible to say the spectral line can move spatially, depending on the value of ω' . This idea can be applied to map out the velocity of flowfields [3].

Figure 4 illustrates a comparison of the effects of increasing the exit velocity, v , while holding the pressure at 5 Torr and the cone divergence angle at 15° . This indicates that the line center absorption coefficient can be dramatically reduced at the outer edges of the cone. For example, an exit velocity of 3.3×10^5 cm/sec lowers the absorption coefficient to ≈ 6 percent of its no-velocity value at the outer edges of the flow.

The effect of cone-divergence angle on the line-center absorption coefficient is shown in Figure 5. In this figure, the velocity was fixed at 3.3×10^5 cm/sec and the pressure was 5 Torr. The importance of flow geometry is displayed as the larger cone angles show significant reduction of the line-center absorption coefficient. For a 15° cone, this effect is very prominent everywhere except close to the cone axis.

Figure 6 is a plot of pressure effects on the center-line absorption coefficient, holding the exit velocity at 3.3×10^5 cm/sec and $\theta = 15^\circ$. As stated in Chapter I, very broad spectral lines are not sensitive to the directed-velocity phenomena because the line-center shift is very small compared to the line width. Note that at atmospheric pressures, the line-center absorption coefficient has dropped only 2.5 percent at the outer edge of the flowfield, compared with the 94-percent drop due to the conditions of this study.

Line Shape--Comparison of Results

It is evident from the above section that directed velocities do have an observable effect on the absorption coefficient. That was illustrated by the determination of the absorption coefficient as a function of spatial position. The results provide the incentive for this study, but more important to our goal is the directed-velocity effects on the absorption coefficient as a function of wavenumber.

For a no-velocity line, the path-integrated absorption coefficient $\phi(\omega)$ follows from the absorption coefficient and the optical path,

$$\phi(\omega) = u k(\omega). \quad (42)$$

Since the optical path, u , is known, Equation (42) can be solved for $\phi(\omega)$ by simply evaluating the Voigt profile approximation and multiplying by u . This eliminates much unnecessary computer integration across the flowfield

However, when directed velocities do exist, it becomes nonsensical to speak of the "spectral-line profile" since the Voigt profile does not exist at the same spectral location for all spatial locations. The only quantity that can be utilized in comparisons is the path-integrated absorption coefficient because it merges all the individual spectral profiles. In one sense, $\phi(\omega)$ becomes an effective spectral profile. Consequently, a comparison of spectral information with and without directed velocities must be a comparison of $\phi(\omega)$ with and without directed velocities. The next step is to determine such a spectral comparison.

A spectral line or an effective spectral line, such as $\phi(\omega)$, can be well described by three parameters: 1) the line-center maximum; 2) the half width; and 3) the limiting form far from line center. These areas will be the focal points to determine any spectral deviations caused by directed velocities.

In Figure 4, we have seen that the spectral-line center of a high-velocity line changes as the spatial position varies, thus causing a lowering of the absorption coefficient. Since path integration has an averaging effect on the spectral lines, one would expect that the high-velocity path-integrated absorption coefficient will also be lowered at the line center relative to the no-velocity case.

This implies that in order to maintain a constant line strength, the line must broaden to compensate for the lowered center of the line profile. Intuitively, one would anticipate this behavior since the high-velocity line is being shifted from the original line center into areas where the no-velocity line has negligible values. The requirement that the line strength be a constant is simply a statement that the number of emitting/absorbing molecules is the same for both calculations. The number of available photons must be a constant; but if and where they become absorbed is controlled by the nature of the gas flow.

It was remarked earlier that far from the line center, actual spectral lines will exhibit Lorentzian wings. This is due to the dying out of the thermal motion Doppler profile after a few line widths. To carry this principle over to directed velocities one would also expect to find Lorentzian wings on the high-velocity line. More

specifically, beyond the region of spectral shifting, it will be necessary to find the exact same wings on the high-velocity line as on the no-velocity line because they have been generated by the same pressure and temperature conditions. It is evident from Equation (14) that the limiting form of a Lorentzian line will go as ω^{-2} .

A computation of $\phi(\omega)$ was carried out for the no-velocity line and the high-velocity line using the conditions shown in Table 1. The resulting comparisons are shown in Figures 7 and 8. Figure 7 agrees with similar results obtained by S. S. Penner and H. K. Chen [5,6].

Figure 7 illustrates two of the above-mentioned characteristics. It is a plot of path-integrated absorption coefficient, $\phi(\omega)$, versus the wavenumber relative to line center, $\omega - \omega_0$. The high-velocity line center has been lowered dramatically due to the directed velocities, by approximately 50 percent for this set of conditions. At the same time, the line has broadened immensely, exhibiting an increase of line width of approximately 90 percent. A check calculation of the area under each profile indicated that the total line strength remained the same for both.

The asymptotic behavior of $\phi(\omega)$ for the no-velocity and the high-velocity lines can be observed in Figure 8. This plot is the same information of Figure 7, but plotted on a logarithmic scale. Again one can see the line-center structure differences between the two cases. Clearly shown in this plot, however, is the reconciliation of the line profiles far from the line center. Notice that the slope of the curve for values of $\ln(\omega - \omega_0) > -4$ has the value of -2. This indicates that the Voigt calculation is correct and that most of the important

Table 1. Baseline Flowfield Conditions.

	No-Velocity Case	High-Velocity Case ¹
CO ₂ Partial Pressure (Torr)	5	5
Temperature (Kelvin)	600	600
Exit Velocity (cm/sec)	3.3×10^5	3.3×10^5
Spectral-Line Center (cm ⁻¹)	2300	2300
Maximum Divergence Angle	0°	15°

¹The high-velocity case gives a directed velocity along the line of sight which leads to a Doppler-shifted spectral-line profile. The no-velocity case does not.

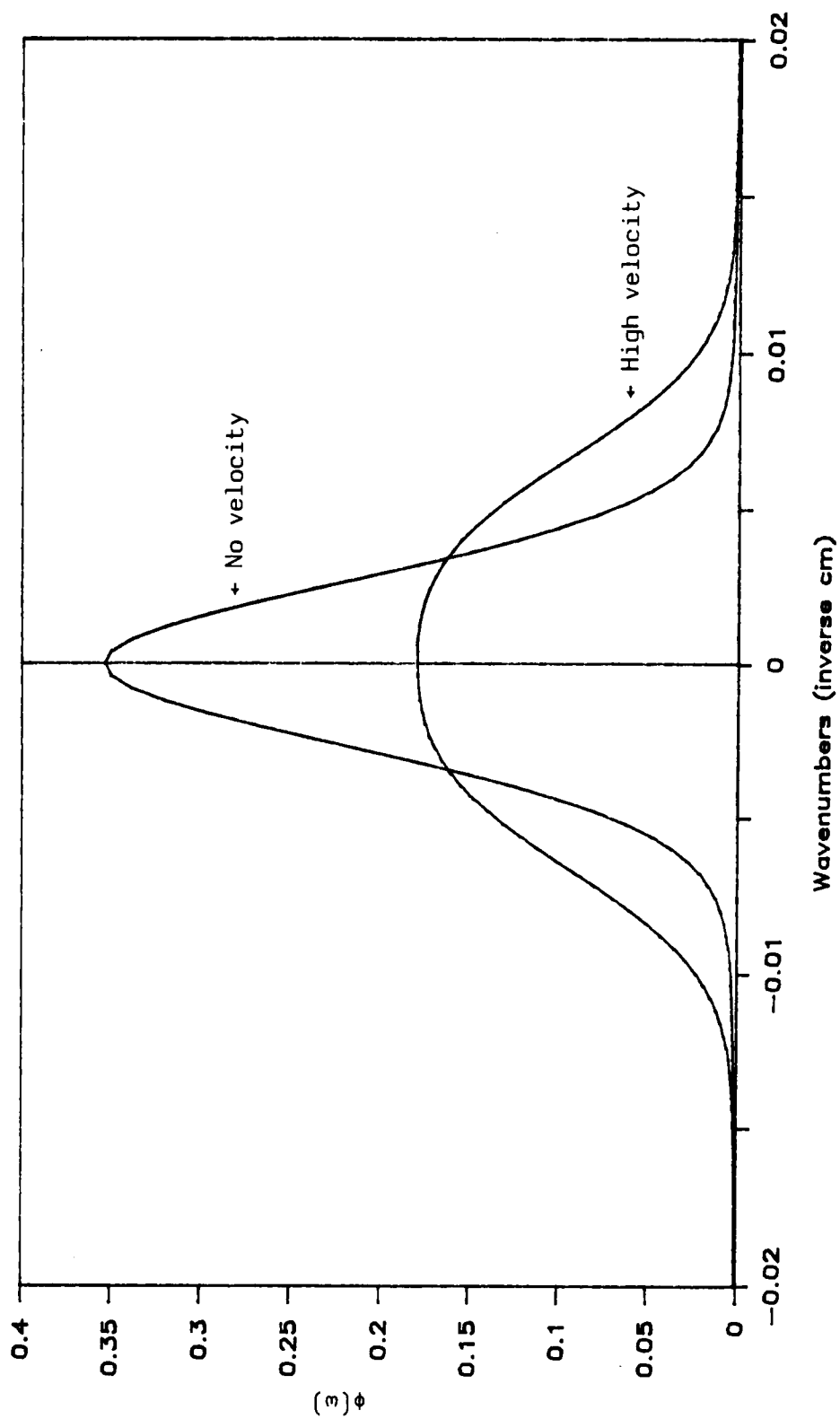


Figure 7. Directed-Velocity Effects on Line Shape of CO_2 Voigt Line at 5 Torr, 600 Kelvin, 2300 cm^{-1} .

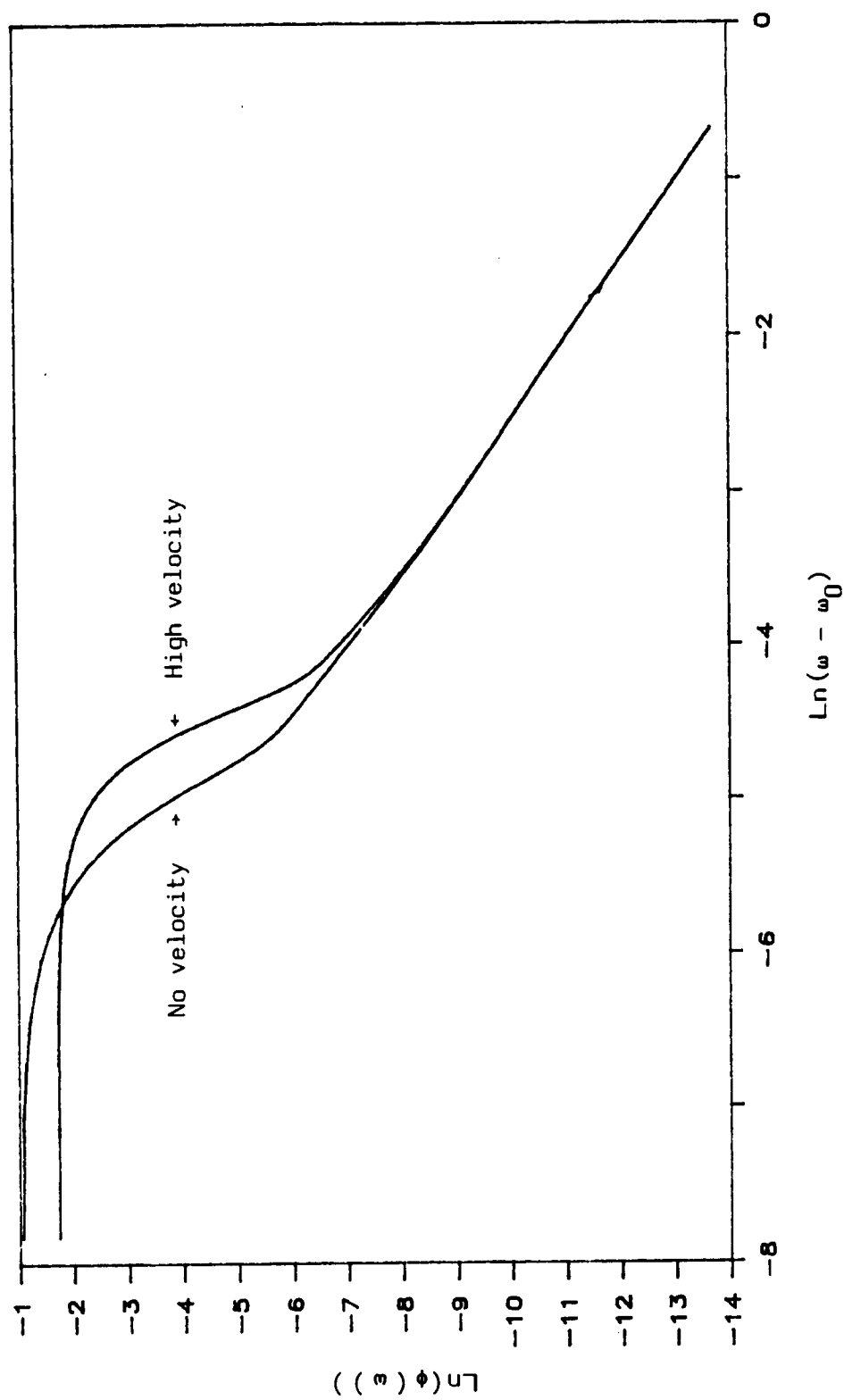


Figure 8. Asymptotic Behavior of Directed-Velocity Effects on Line Shape of CO₂ Voigt Line at 5 Torr, 600 Kelvin, 2300 cm⁻¹.

spectral information occurs within 0.019 cm^{-1} of the line center. At $\ln(\omega - \omega_0) = -4$, $\phi(\omega)$ has decreased to ≈ 0.3 percent and 0.6 percent of the line-center value of the no-velocity and high-velocity cases, respectively.

The large amount of distortion of the path-integrated absorption coefficient raises the question as to the effect of directed velocities on observables such as spectral absorption. While Figures 7 and 8 are themselves a demonstration of some interesting phenomena, the importance of directed-velocity effects on measurements can be evaluated through a discussion of the curves of growth of each spectral profile.

Curves of Growth--Comparison of Results

At the heart of emission/absorption measurements lies the curve of growth. As mentioned in Chapter II, given a measured amount of the absorption of a particular spectral line, one is able to interpret the pressure and temperature of the medium. The mechanism by which this is done is the curve of growth. Different spectral lines define different absorption lines. In turn, different absorption lines have unique variances of total absorption, i.e., equivalent width, as a function of optical depth. In fact, whether an observed spectral line is a Lorentzian, thermal Doppler, or Voigt line can be determined by its behavior on a curve of growth. Since the spectral profile of the no-velocity and high-velocity lines are so radically different, it follows that their curves of growth will be different. This implies that an important reconsideration of predicted gas properties may be necessary to account for the use of an incorrect curve of growth

obtained from the no-velocity line. It will be expedient to determine where to anticipate deviations between the two curves of growth.

For an optically thin system, the absorption due to the high-velocity line will not differ from that caused by the no-velocity line for the reason given above; i.e., the curve of growth is linear for all spectral-line shapes in this region, regardless of their shape. Thus, there should be no difference in the curves of growth of the no-velocity and the high-velocity lines in this regime.

Increasing the optical depth implies that S_u , the product of the line strength and the optical path, increases. Physically this can be done by extending the path length or increasing the pressure. The corresponding increase in absorption should be linear up to the saturation point. One should expect the no-velocity absorption line to reach this point before the high-velocity absorption line since it has a larger line-center value. The high-velocity absorption line will saturate at some point later, depending on the degree of velocity-induced distortion of the line.

If one continues to increase the optical depth beyond the saturation point, recall that a Lorentzian spectral line will follow a square-root asymptote. This is due to absorption that occurs in the wings of the Lorentzian profile after the line-center area has been completely blacked out. As illustrated in Figure 8, the no-velocity Voigt wings are actually Lorentzian wings; and, thus, will follow a square-root asymptote. Also apparent in that plot is that the wings of the no-velocity and high-velocity lines eventually blend together. Because the spectral-line profiles recombine, the curves of growth

should recombine at some point after saturation and remain identical for all larger optical depths.

An actual computation of the curves of growth for the no-velocity and high-velocity spectral lines, defined above, yielded Figure 9, where the expected results are clearly shown. The ordinate is the natural logarithm of the equivalent width and the abscissa is the natural logarithm of the line-strength optical-path product. Both curves of growth are shown; the lower one belonging to the no-velocity absorption line. We can examine the effects of directed velocities by breaking this plot into the three regions described above.

For small optical depths, both the no-velocity and high-velocity lines display identical curves of growth. Furthermore, the curve is defined by the line $W = Su$, as the imposed asymptote shows. This is exactly what one would expect based on Equation (24).

In the large optical depth regime, the expected convergence of the two curves is evident. Both the no-velocity and high-velocity lines display the same asymptotic behavior in this area since they have the same spectral profile far from line center. Notice that the asymptote the curves follow is defined by the Lorentzian large optical depth limit expressed in Equation (29), $W = 2 \sqrt{Su\gamma_L}$, indicated by a straight line with slope of $+\frac{1}{2}$.

The most important part of Figure 9 is the section between the linear and square-root regions. This is the area that displays the most prominent characteristics of directed-velocity effects. The curves of growth of the no-velocity and high-velocity lines deviate significantly with the lower curve being the no-velocity case. This

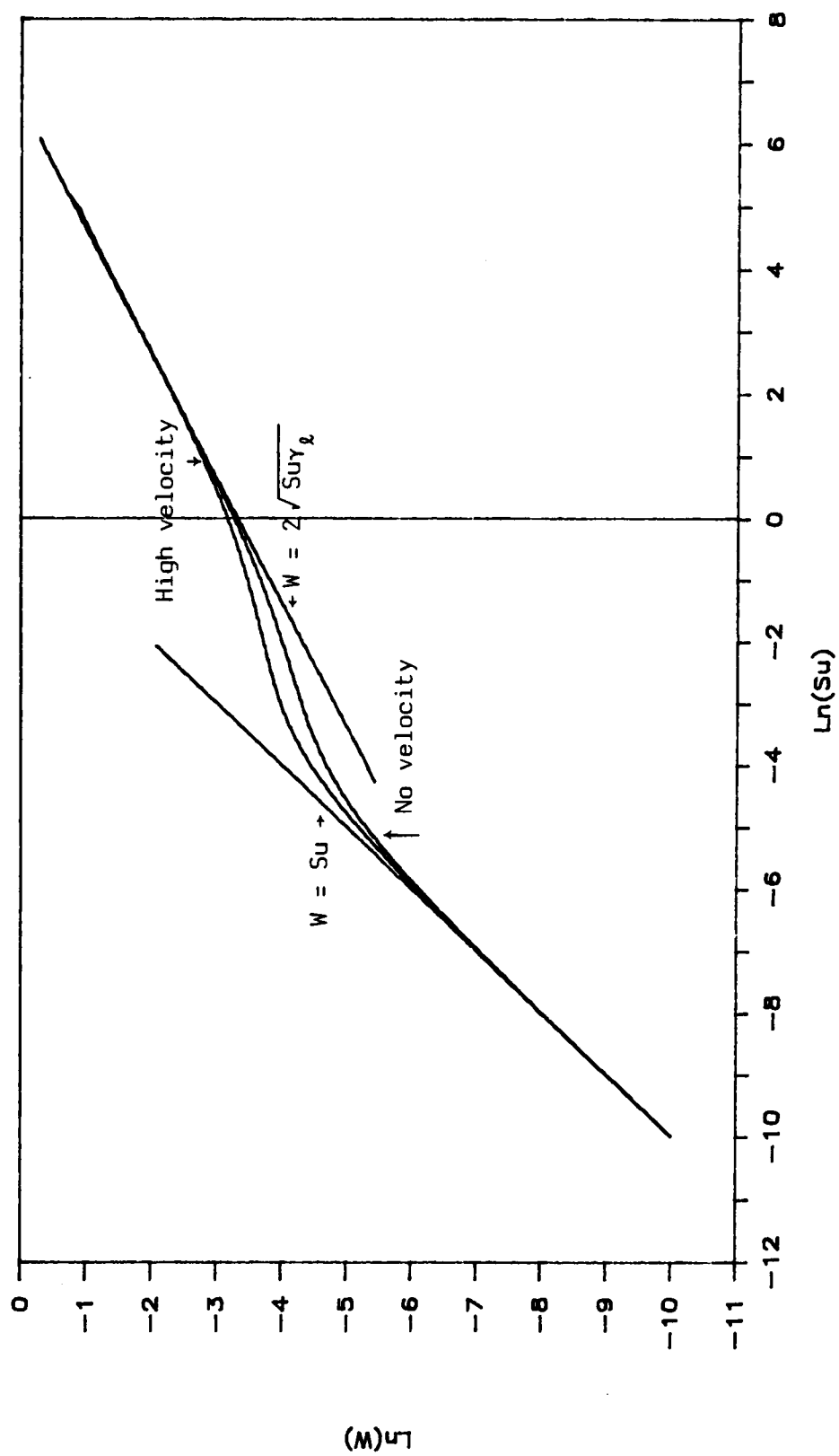


Figure 9. Curves of Growth of CO_2 Voigt Lines With and Without Directed-Velocity Effects.

demonstrates that the no-velocity line saturates first since it has a higher line-center value. The high-velocity line will continue to absorb in a linear fashion due to its compressed shape.

The amount of departure in the saturation region can be best determined from looking at a linear plot of the curves of growth. Figure 10 is the same information as on Figure 9 but on linear scales to eliminate the logarithmic distortion. The square-root region is far off the scale to the right side and the linear region is compressed into a narrow area on the left side, but the saturation region is clearly shown. The higher of the two curves is due to the high-velocity line. The deviation between the equivalent widths of the no-velocity and high-velocity curves has a maximum of ≈ 30 percent at $S_u = 0.1 \text{ cm}^{-1}$, although the difference is very significant over the entire region. For example, at $S_u = 2.0 \text{ cm}^{-1}$, the difference is still over 6 percent.

The importance of these discrepancies can be realized by recalling that gas properties are determined from these curves. Performing a sample calculation, suppose that a hypothetical measurement of the absorption of a particular spectral line obtained a value of the equivalent width of 0.04 cm^{-1} . One then looks at the curve of growth to find the S_u responsible for that measured value. Using the no-velocity curve of growth, one would determine a value for S_u of 1.11 cm^{-1} . However, using the high-velocity curve of growth, that same equivalent width corresponds to a S_u value of 0.84 cm^{-1} , representing a difference of -24 percent.

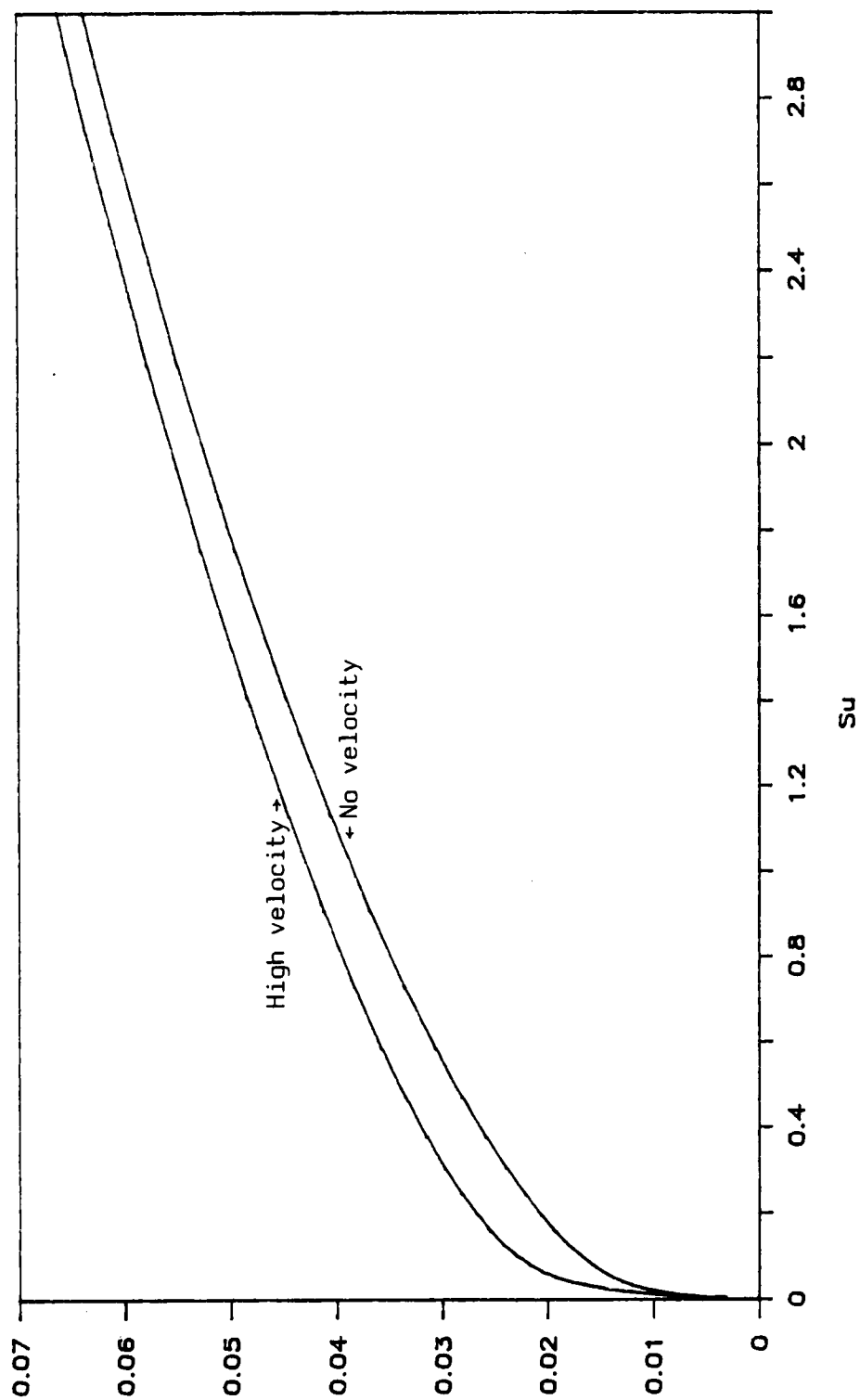


Figure 10. Linear Curves of Growth of CO₂ Voigt Lines With and Without Directed-Velocity Effects.

It should be emphasized that the high-velocity spectral line is not a fictitious line. It is, in fact, a more complete description of the basic physics of a homogeneous conical flowfield. Although this type of flow may be an idealization of actual systems, the results of Figures 7, 8, 9, and 10 indicate reason for concern of the accuracy of actual measurements. The degree of concern should be commensurate with the appropriateness of a homogeneous conical flow approximation.

CHAPTER IV

BAND-MODEL THEORY

Spectral Bands

In Chapter II, the problem of radiative transitions in atomic and molecular systems between two states was considered. The solution resulted in the emission or absorption of radiation that corresponded to an energy eigenvalue of the Hamiltonian operator. In a typical system, there exists a large number of energy eigenstates of the Hamilton operator. Radiative transitions can take place among the eigenstates which satisfy the proper selection rules. The result will be a large number of frequencies where emission and absorption can occur, each frequency corresponding to an energy eigenvalue. For many atoms or molecules, the absorption or emission appears as spectral lines at the frequency positions. This results in a large number of observable spectral lines, the collection of which is called a spectral band.

An observer's perception of the band is dependent upon the resolution of the apparatus used to measure band characteristics. This study is concerned with the realm of broad-band or low-resolution spectroscopy. In this case, the intensity of a spectral band can be distinguished as a function of frequency. However, the details of the individual spectral lines are undiscernable as they all seem to meld together to produce the band contour. Broad-band spectroscopy is concerned with the manner in which the band, acting as a single unit, will absorb or emit radiation. Nevertheless, the absorption or emission of radiation is not due to the perception of the band contour,

but rather it is governed by the physics of the individual spectral lines that make up the band. It is the purpose of band-model theory to find some isomorphism between the collective result of the many spectral lines and the absorptive behavior of a single line.

One example of a spectral band is the antisymmetrical vibrational mode of the CO_2 molecule. Carbon dioxide is a linear symmetric molecule with the carbon atom at the center. Antisymmetrical vibration arises when the two oxygen atoms are oscillating completely out of phase with each other. The band produced by this motion is centered at 2349 cm^{-1} (4.3 microns) and ranges from about 2200 to 2400 cm^{-1} . In this band region there exist approximately 14,000 spectral lines resulting from the combination of this band and the overlap of other nearby bands. At one time, a calculation of the overall effect of the band using a line-by-line method would have been overwhelming. Even with the supercomputers available today, it is still a nontrivial and expensive task. Therein lies the motivation for analytic mathematical formulations and solutions to the problem of the cumulative effects of the numerous spectral lines, viz., band models.

The general nature of band models will be to produce some type of average or effective quantity that can be used to perform simplified calculations of absorption and emission. Since a low-resolution absorption measurement would measure the average absorption of a given spectral line over the spectral interval where the line is significant, it is important to know what the average absorption of that line is.

One starting point is supposing that a given spectral line in the band does not in any way affect any other spectral line. This

is the assumption of nonoverlapping lines. Nonoverlapping lines are spaced far enough apart that the effect of one line to any other is negligible. Recall that the total absorption, or equivalent width, of an isolated spectral line was defined in Chapter II by Equation (20). The integral in that equation was taken from zero to infinity. By referencing the zero of the wavenumber to the line center, the integral equivalently runs from negative infinity to positive infinity. However, it was just stated that beyond the spacing between the lines in the group, there is no significant contribution to the absorption profile of any one line by another line. Thus, the average absorption, $\bar{A}$, of a single line can be defined as the total absorption, W , divided by the mean-line spacing, δ , [7]

$$\bar{A} = \frac{1}{\delta} \int_{-\infty}^{+\infty} \left[1 - \exp(-uk(\omega)) \right] d\omega. \quad (43)$$

The average transmittance of a single line then follows as

$$\bar{T} = 1 - \bar{A}. \quad (44)$$

This is often called the single-line model of a band. It does not account for any spectral line overlapping. Unfortunately, the results of measurements have indicated that spectral line overlap is important. It will be shown that Equation (43) is the lowest order approximation for the exact solution of the overlapping line average absorption.

Line overlap can be taken into account by examining the absorption coefficient. One result obtained from experimental measurements is

that the resultant transmittance of two overlapping spectral lines at a particular wavenumber is the product of the transmittance of each line at that wavenumber. Using the monochromatic transmittance of a single line from Equation (8), the resultant transmittance of the two lines at a given wavenumber is [7]

$$\begin{aligned} T_{\omega}(1,2) &= \exp(-uk_{\omega}(1)) \exp(-uk_{\omega}(2)) \\ &= \exp(-u(k_{\omega}(1) + k_{\omega}(2))). \end{aligned} \tag{45}$$

For a large number, N , of such lines, the transmittance at a given wavenumber is simply

$$T_{\omega} = \prod_{i=1}^N \exp(-uk_{\omega}(i)) \tag{46}$$

The purpose of a band model is to determine the average transmittance and absorption over a spectral interval containing a large number of lines. This amounts to summing the transmittance or absorption at each frequency and dividing by the length of the interval, while allowing for irregular line placement and varying line strength.

Models

One of the underlying assumptions of a band model is that the real band to be modeled has a fairly constant contour. This allows one to define the average absorption or transmittance of the band as a number which will hold true over the entire spectral range of the band. Of course, a real band, such as the CO_2 4.3 micron band described above, will have great fluctuations in the contour. These variations

of the band contour can be handled by breaking the band into suitably small sections of flat contours. This method becomes evident in the use of band model parameters to be discussed in Chapter V.

Two different approaches were taken in trying to develop a model. One way assumed that the spectral lines were placed at regular spectral intervals and is called the regular band model. At first glance, this may seem rather unphysical; but regular bands can describe the spectra of many linear molecules, including sections of the CO₂ spectrum. The first useful regular model was developed by W. M. Elsasser and bears his name. It considers an infinite number of identical spectral lines all equally spaced from each other. The Elsasser model is solved for the Lorentzian line shape and yields an integral form for the average absorption. The solution to this closed form requires numerical integration.

An alternative to the regular band model is the statistical or random model. The principle is that the structure of a band can be created using an infinite array of randomly placed spectral lines having random line strengths. Thus, the position, as well as the intensity, of the individual spectral lines are determined by probability functions. From these probability functions it is possible to obtain an expression for the average absorption of the band over a given spectral interval which includes any possible overlapping of any and all other lines in the band. The derivation of this expression can be done in several ways. The most straightforward is perhaps that given by Plass [17]. Notice that the frequency, ν , is used rather than the wavenumber.

First, suppose that a band of width D is centered about a zero frequency and composed of n spectral lines, possibly overlapping. Further, assume that all the lines are described by the same type of broadening mechanism. Let $N(v_1, \dots, v_n) dv_1 \dots dv_n$ be the probability that the center of the first line is in the frequency interval dv_1 when the center of the second line is in dv_2 and so forth. Also, let $P(S_i) dS_i$ be the normalized probability of the i th line having a line strength in the range dS_i . To take into account the varying line strengths, define the relation

$$k_{v_i} = S_i b(v_i) \quad (47)$$

where S_i is the strength of the i th line and $b(v_i)$ is a line-shape factor. In this way it is possible to write the transmittance of the i th line when its center is at v_i as $\exp(-u S_i b(v_i))$.

The average absorption over the entire interval follows as $1 - \bar{T}$ and can be written

$$\bar{A} = 1 - \frac{\int_{-D/2}^{D/2} \dots \int_{-D/2}^{D/2} N(v_1 \dots v_n) dv_1 \dots dv_n \int_0^{\infty} \dots \int_0^{\infty} \prod_i P(S_i) \exp\left[-u S_i b(v_i)\right] dS_i}{\int_{-D/2}^{D/2} \dots \int_{-D/2}^{D/2} N(v_1 \dots v_n) dv_1 \dots dv_n \int_0^{\infty} \dots \int_0^{\infty} \prod_i P(S_i) dS_i} \quad (48)$$

The probability that each line has its center at a given frequency in the interval D , regardless of the position of the other lines, can be assumed a constant. Then $N(v_1, \dots, v_n)$ is a constant which can be

pulled out of the integrals. The denominator then reduces to D^n because the total probability is normalized to unity.

Since all the lines in the band have the same spectral shape, the integral over each line is identical to the integral over any other line. Thus, the absorption may be written

$$\bar{A} = 1 - \left[\frac{1}{D} \int_{-D/2}^{D/2} dv \int_0^{\infty} P(S) \exp(-uSb(v)) dS \right]^n. \quad (49)$$

Extracting unity from the integral,

$$\bar{A} = 1 - \left[1 - \frac{1}{D} \int_{-D/2}^{D/2} dv \int_0^{\infty} P(S) \left(1 - \exp(-uSb(v)) \right) dS \right]^n. \quad (50)$$

Interchanging order of integration,

$$\bar{A} = 1 - \left[1 - \frac{1}{D} \int_0^{\infty} P(S) dS \int_{-D/2}^{D/2} (1 - \exp(-uSb(v))) dv \right]^n. \quad (51)$$

Defining the second integral as $W(S,u,D)$

$$\bar{A} = 1 - \left[1 - \frac{1}{D} \int_0^{\infty} P(S) W(S,u,D) dS \right]^n. \quad (52)$$

Notice that $W(S,u,D)$ is similar to the equivalent width of a single spectral line except that it is evaluated over the interval D . Now define a mean line spacing d such that $nd = D$. Further, define the average equivalent width of a spectral line as

$$\bar{W}(\bar{S},u) = \int_0^{\infty} W(S,u,D) P(S) dS. \quad (53)$$

If the number of lines approaches infinity, while at the same time the mean-line spacing remains a constant, the frequency interval, D , will tend toward infinity. The limiting form of $W(S,u,D)$ will be the equivalent width of a single line as given in Equation (20). Thus, Equation (53) may be written

$$\bar{W}(\bar{S},u) = \int_0^{\infty} W(S,u) P(S) dS. \quad (54)$$

Then by using the definition of the exponential, the final expression for the average absorption of the band, regardless of spectral line shape, is

$$\bar{A} = 1 - \exp \left(\frac{-\bar{W}(\bar{S},u)}{d} \right). \quad (55)$$

The significance of this form is that by simply knowing the average absorption of a single line in the band, the average absorption over the entire band can be computed. In most cases, the average absorption of a single line can be easily computed which allows for quick solutions to the absorption over the entire band. This is the power of a band model.

The accuracy of a random band model is thus dependent upon the line strength probability distribution used to calculate $\bar{W}(\bar{S},u)$. Four distributions have been primarily used [11]. They are a delta function, an exponential function, an inverse-power function, and an exponentially-tailed inverse-power function. The only criterion for choosing a particular distribution is the desire for accuracy of the predicted results when compared to that of the experimental data.

The delta function distribution is

$$P(S) = \delta(S - S_0), \quad (56)$$

which says that all lines in the band have the same line strength, although their position is entirely random. This is the simplest and easiest distribution to use.

More realistic, and hence accurate, is the exponential distribution of line strengths given by

$$P(S) = \frac{1}{S_0} \exp \left(-\frac{S}{S_0} \right) \quad (57)$$

where S_0 represents the average line strength. Although it is a better description than the delta function, it tends to underestimate the number of low-intensity lines in the band. The ease of computation is the primary motivation for its use.

The inverse power distribution is given by

$$P(S) = \begin{cases} \frac{1}{2nR} \frac{1}{S} \frac{S_M}{R} & \frac{S_M}{R} < S < S_M \\ 0 & S < \frac{S_M}{R} \text{ and } S > S_M \end{cases} \quad (58)$$

where R is the ratio of a maximum line strength, S_M , to the minimum line strength. This distribution can be justified by a hand-waving type of argument. Returning to the quantum mechanics of the absorber, assume that the energy levels are spaced equally apart. This implies that the number density of energy levels, dn/dE , is nearly a constant. The line strength, S , can be shown to be proportional to $\exp(-E/kT)$,

where k is Boltzmann's constant [18]. Thus, d_E/d_S is proportional to $1/S$. Using the fact that $P(S)$ is proportional to $dn/dS = (dn/dE)(dE/dS)$, it is apparent that $P(S)$ is proportional to $1/S$.

The main problem with the $1/S$ distribution is that it cannot be used over the range from zero to infinity. For that purpose, the exponentially tailed inverse distribution was developed by Malkmus [19].

The normalized function is

$$P(S) = \frac{1}{\ln R} \frac{1}{S} \left[\exp \left(-\frac{S}{S_M} \right) - \exp \left(-\frac{RS}{S_M} \right) \right]. \quad (59)$$

It is this distribution that will be used in further calculations of this study. By defining an average line strength with

$$\bar{S} = \int_0^{\infty} S P(S) dS, \quad (60)$$

we can eliminate the S_M term in the distribution. The result is

$$P(S) = \frac{1}{\ln R} \frac{1}{S} \left[\exp \left(-\frac{R-1}{R \ln R} \frac{S}{\bar{S}} \right) - \exp \left(-\frac{R-1}{\ln R} \frac{S}{\bar{S}} \right) \right]. \quad (61)$$

The average equivalent width is computed by placing Equation (61) into Equation (54) along with the expression for the equivalent width of a single line that was obtained in Chapter II. The equivalent width of a Voigt line has no analytic solution, which makes Equation (54) analytically impossible. However, the Lorentzian line shape does have an analytic solution to its equivalent width, namely the Ladenburg-Reiche function. In Chapter II, it was stated that asymptotically the Voigt line behaved as a Lorentzian line. Since the asymptotic solutions to the average equivalent width of a band of Lorentzian lines can be found analytically, the asymptotic behavior of the average

equivalent width for a band of Voigt lines can be checked. Thus, it will be important to determine the solution of Equation (54) for a band of Lorentzian lines.

Malkmus found that the average equivalent width for a band of Lorentzian lines was

$$\frac{\bar{W}}{d} = \frac{2\pi\gamma_\ell}{d \ln R} \left[\left(1 + \frac{R \ln R \bar{S}u}{(R-1)\pi\gamma_\ell} \right)^{1/2} - \left(1 + \frac{\ln R \bar{S}u}{(R-1)\pi\gamma_\ell} \right)^{1/2} \right]. \quad (62)$$

In the small u limit, $\frac{\bar{W}}{d}$ approaches $\frac{\bar{S}u}{d}$ as expected. In the limit of large u

$$\frac{\bar{W}}{d} \rightarrow 2 \sqrt{\pi\gamma_\ell} \frac{(\bar{S}u)^{1/2}}{d} \frac{1}{(\ln R)^{1/2}} \frac{R^{1/2} - 1}{(R - 1)^{1/2}}. \quad (63)$$

At this point, two parameters, S_E and d_E are introduced. They are merely an effective line strength and an effective mean-line spacing that allow the asymptotic limits of the average equivalent width to follow the same asymptotic limits of the single line equivalent width. They are defined by the limits

$$\lim_{u \rightarrow 0} \left(\frac{\left(\frac{\bar{W}}{d} \right)}{u} \right) = \frac{S_E}{d_E} \quad (64)$$

$$\lim_{u \rightarrow \infty} \left(\frac{\left(\frac{\bar{W}}{d} \right)}{u^{1/2}} \right) = 2 \frac{(S_E \gamma_\ell)^{1/2}}{d_E}. \quad (65)$$

Comparing Equations (64) and (65) with the limiting forms of Equation (62), it is evident that

$$S_E = \bar{S} \frac{\ln R}{\pi} \frac{R^{1/2} + 1}{R^{1/2} - 1} \quad (66)$$

and

$$d_E = d \frac{\ln R}{\pi} \frac{R^{1/2} + 1}{R^{1/2} - 1} \quad (67)$$

Their use is prevalent and they should not be confused with the average line strength, $\bar{S}$, or mean-line spacing, d , of the band, even though S_E/d_E is equal to $\bar{S}/d$. The significance of the quantity S_E/d_E is that it does represent an average value of S/d . It also follows from Equations (63) and (65) that $S_E^{1/2}/d_E$ represents the mean value of $S^{1/2}/d$.

The importance of band models to low-resolution spectroscopy can clearly be seen. From the knowledge of the equivalent width of one line in the band, it is possible to predict the average absorption over the entire spectral band. Since the average absorption is the measured observable, predictions of radiative transfer of certain processes can be made.

CHAPTER V

BAND-MODEL COMPUTATIONS

Computational Methods

Having discovered significant differences in the single-line curves of growth for the no-velocity and high-velocity cases reported in Chapter III, it was decided to ascertain the extent of detectability of the directed-velocity effect upon broad-band radiometric measurements. The first step was to obtain the curves of growth for bands made of no-velocity and high-velocity spectral lines. This was done with the results of the band-model theory developed in Chapter IV. Then it was possible to produce the absorption spectra for both cases by using band-model parameters.

A desired result from a band-model calculation is to determine the dependence of the average absorption upon the optical depth, i.e., the curve of growth. After some calculation, one can extract information about gas concentrations and temperatures from the optical depth defined by a measured absorption value. Hence, there is good reason to solve the integral equation which determines the average equivalent as a function of Su . This equation was given by Equation (54) of Chapter IV and is repeated here for convenience,

$$\frac{\bar{W}}{d} = \frac{1}{d} \int_0^{\infty} W(S,u) P(S) dS.$$

Since band-model theory was developed about 30 years ago, this expression has been the subject of much investigation. Most of this work

has been in the form of faster numerical solutions for various spectral-line shapes and probability distributions. The result was the determination of polynomial functions which approximate the average equivalent width for a given line shape and probability distribution. The difficulty with these approximations is that they are solutions of Equation (54) for a specific line shape, i.e., Lorentzian, Doppler, or Voigt. Even though the spectral lines of this study are Voigt lines, the velocity-induced distortion has changed their shape to the point that the approximations are no longer valid. Hence, the computation of the curve of growth of the band in this study begins with Equation (54).

Given the proper knowledge, this computation is a fairly straightforward problem of numerical integration. The input required for Equation (54) is information about the equivalent width for the particular type of spectral line that makes up the band. Also required is a normalized line-strength probability distribution. The output is the average equivalent width of the band as a function of the optical path, u , and the average line strength, $\bar{S}$.

This study deals with the exponentially-tailed, inverse-power, line-strength probability distribution because it is recommended for CO_2 , meaning that this distribution yields results that closely match the experimental results [20]. Recall that $P(S)$ was given in Equation (61) as

$$P(S) = \frac{1}{\bar{S}} \frac{1}{\ln R} \left\{ \exp \left[-\frac{R-1}{R} \frac{S}{\bar{S}} \right] - \exp \left[-\frac{R-1}{\ln R} \frac{S}{\bar{S}} \right] \right\}.$$

For our calculations, the ratio of the maximum line strength to the minimum line strength, R , is assumed to be 10^6 . In the analytic formulation of the average equivalent width, the limit as R approaches infinity is taken after $\bar{W}$ is computed [19]. Physically, this states that all possible line strengths are considered. After performing some numerical investigation into the effect of the behavior of R on $\bar{W}$, it became clear that $R = 10^6$ produced results sufficiently close to the asymptotic limit for the requirements of this study.

The average line spacing, d , is another parameter required for the solution of Equation (61). The band-model tables suggest that near the band center the number of spectral lines per cm^{-1} varies from about 13 to 17. Hence, the average line spacing used in the calculations is $d = 0.0667 \text{ cm}^{-1}$, representing 15 spectral lines per cm^{-1} .

The equivalent width for the no-velocity and high-velocity single lines was obtained from their respective curves of growth developed in Chapter III. This information was structured as a data file of S_u versus $W(S,u)$. After a change of variable from S to S_u , the integral of Equation (54) could be done numerically by evaluating the integrand at S_u points that coincided with the S_u points used to find the single-line equivalent width. Then all that was needed was to sum the terms appropriately.

The integration was performed by the trapezoid rule. Simpson's Rule could not be used because the single-line equivalent widths had been computed at unevenly spaced S_u points. The choice of the exponentially-tailed, inverse-power probability distribution lent itself to an asymptotic solution in the limit of small optical depths. Since

the equivalent width at small optical depths is linear with Su , $W(S,u)$ can be replaced with Su in this region. This canceled the factor of Su in the denominator which originated from the probability distribution, thus allowing for an exact solution. This was used to compute the integral from $Su = 0$ to the first Su point of the above data set. It should be noted that the linear behavior of $W(S,u)$ extended well beyond this first Su point; hence, the replacement of $W(S,u)$ with Su over this region should not introduce appreciable errors.

The rest of the integration range was carried out numerically, starting from the first Su point and proceeding to the last Su point which had a value of $Su = 1.60 \times 10^5 \text{ cm}^{-1}$. Since a ballpark figure for a black line is approximately $Su = 5 \text{ cm}^{-1}$, this was quite sufficient to ensure accuracy. Convergence of the integral can be seen from the limiting forms of the terms of the integrand. From Chapter II, the asymptotic solution to the equivalent width of a single Voigt line for large Su is identical to the asymptotic solution for a Lorentzian line given by Equation (29).

$$W(S,u) = 2 \sqrt{Su\gamma_g}.$$

Thus, for the integral to converge, the probability distribution must decrease faster than $\sqrt{Su}$. From Equation (61), it can be seen that

$$\lim_{Su \rightarrow \infty} P(Su) \sim \frac{1}{Su} \left[\exp(-\alpha Su) - \exp(-\beta Su) \right] \quad (68)$$

where α and β are constants involving R , $\bar{S}$, and u . Thus, the probability distribution decreases much faster than the equivalent width such that the integral converges.

Using the results of Equation (54), an absorption spectrum could be produced. An absorption spectrum is merely the functional dependence of the average absorption upon wavenumber. Recall that a band model can be used to develop the average absorption of the band, but only when the band contour is fairly constant. In the case of the CO₂ 4.3 micron band, the contour is very irregular. To apply band models, one breaks the entire band into small sections where each of the individual contours is relatively flat. It will be shown that the average absorption, $\bar{A}$, can then be uniquely determined for a given spectral section by specifying two parameters: 1) the effective line strength and 2) the effective line spacing.

Since the average absorption is obtained from the average equivalent width, the spectral dependence of the average equivalent width must be determined. This enters through the probability distribution. Physically, this says that it is more likely to have certain line strengths at a given spectral position than at some other. For example, it is more likely to have large line strengths near the band center than far removed from it. Thus, Equation (54) can be rewritten as

$$\frac{\bar{W}}{d} \big|_{\Delta\omega_i} = \frac{1}{d} \int_0^{\infty} P(S, \Delta\omega_i) W(S, u) dS. \quad (69)$$

The problem reduces to determining the probability distribution of the line strengths for a particular wavenumber.

The band-model parameters satisfy this task. These parameters are an experimentally-based set of S_E and d_E that are determined for each of the spectral intervals. Recall from Chapter IV that the ratio

(S_E/d_E) is equal to $(\bar{S}/d)$. Thus, the value of $\bar{S}$, and in turn $P(S)$, is defined for each spectral interval in the spectrum. This leads to a computation of the average equivalent width, $\bar{W}$, for a particular spectral interval. Finally, a unique value of the average absorption, $\bar{A}$, over the spectral interval is computed from $\bar{W}$ using Equation (55).

The calculations of this study use the Standard InfraRed Radiation Model (SIRRM) band-model parameter set [21]. The values of S_E and d_E were given at 5 cm^{-1} intervals over the range of 2000 to 2400 cm^{-1} . From Equations (66) and (67), the values of $\bar{S}$ and d for each wavenumber interval could be computed using $R = 10^6$.

The next step determines $\bar{W}$ as a function of wavenumber. The same algorithm that computes the curve of growth is used, except that this program is modified to input specified values of the average line strength and line spacing for a particular wavenumber. This results in a set of average equivalent widths which vary according to wavenumber. Finally, Equation (55) for $\bar{A}$ determines the absorption as a function of wavenumber, yielding the absorption spectrum.

Average Curve of Growth--Comparison of Results

Since the average equivalent width, $\bar{W}(\bar{S}, u)$ is a convolution of two functions, $W(S, u)$ and $P(S)$, it is difficult to estimate a quantitative result. Intuitively, though, $\bar{W}$ for an infrared band model should follow the same general form as $W(S, u)$ for a single line, but with features which are less pronounced.

One would expect to find a linearity of the average equivalent width with small $\bar{S}u$. Physically, one could imagine a large number of

small spectral lines where the overlap would be rather limited.

Increasing the optical depth will increase the average equivalent width in the same manner that it did in Chapter II for the single-line equivalent width. To see this, begin by explicitly writing $W(S,u)$ in Equation (54).

$$\frac{\bar{W}}{d} = \frac{1}{d} \int_0^{\infty} dS P(S) \int_0^{\infty} \left[1 - \exp(-uk(\omega)) \right] d\omega. \quad (70)$$

Expanding the exponential yields,

$$\frac{\bar{W}}{d} = \frac{1}{d} \int_0^{\infty} dS P(S) \int_0^{\infty} \left[uk(\omega) - (uk(\omega))^2 + O(3) \right] d\omega. \quad (71)$$

When $k(\omega)u$ is small enough to neglect second-order terms, the wavenumber integration can be performed and $\frac{\bar{W}}{d}$ can be written as

$$\frac{\bar{W}}{d} = \frac{1}{d} \int_0^{\infty} dS P(S) Su. \quad (72)$$

Since u can be pulled out of the integral, this leaves the definition of the average line strength, $\bar{S}$, such that

$$\frac{W}{d} = \frac{\bar{S}u}{d} \quad (73)$$

in the small $\bar{S}u$ limit.

The large $\bar{S}u$ limit can be found in a similar fashion. It is again possible to use the asymptotic solution to the Lorentzian band to determine the solution of the Voigt band for large $\bar{S}u$. The equivalent width of a single Lorentzian line was given in Equation (25). The asymptotic

solution for large optical depths was given by Equation (29). To find $\bar{W}$, one merely places Equation (29) into Equation (54) with the result that

$$\frac{\bar{W}}{d} = \left(\frac{1}{d}\right) 2 \int_0^{\infty} dS P(S) S^{1/2} (u\gamma_L)^{1/2}. \quad (74)$$

It is now possible to use the effective line strength and the effective average line spacing. It was stated that from their definitions, $S_E^{1/2}/d_E$ represented the average of $S^{1/2}/d$. Thus, by moving $(u\gamma_L)^{1/2}$ outside the integral in Equation (74), the average equivalent width of Lorentzian band in the large $\bar{S}u$ limit becomes

$$\frac{\bar{W}}{d} = 2 \sqrt{\frac{S_E u \gamma_L}{d_E^2}}. \quad (75)$$

This is the limit which the average equivalent width for a band of Voigt lines will take when $\bar{S}u$ is large.

For the region between small $\bar{S}u$ and large $\bar{S}u$, one can expect to find a similar behavior as that of the single-line equivalent width. However, since there is an averaging procedure occurring, the severity of the results should be lessened.

A computation of the average equivalent width was done for both the no-velocity and high-velocity cases and the results are displayed in Figure 11. The ordinate is the natural logarithm of the average equivalent width, $\bar{W}$, divided by the mean-line spacing, d . The abscissa is the natural logarithm of $\bar{S}u/d$, where $\bar{S}$ is the average line strength and u is the optical path.

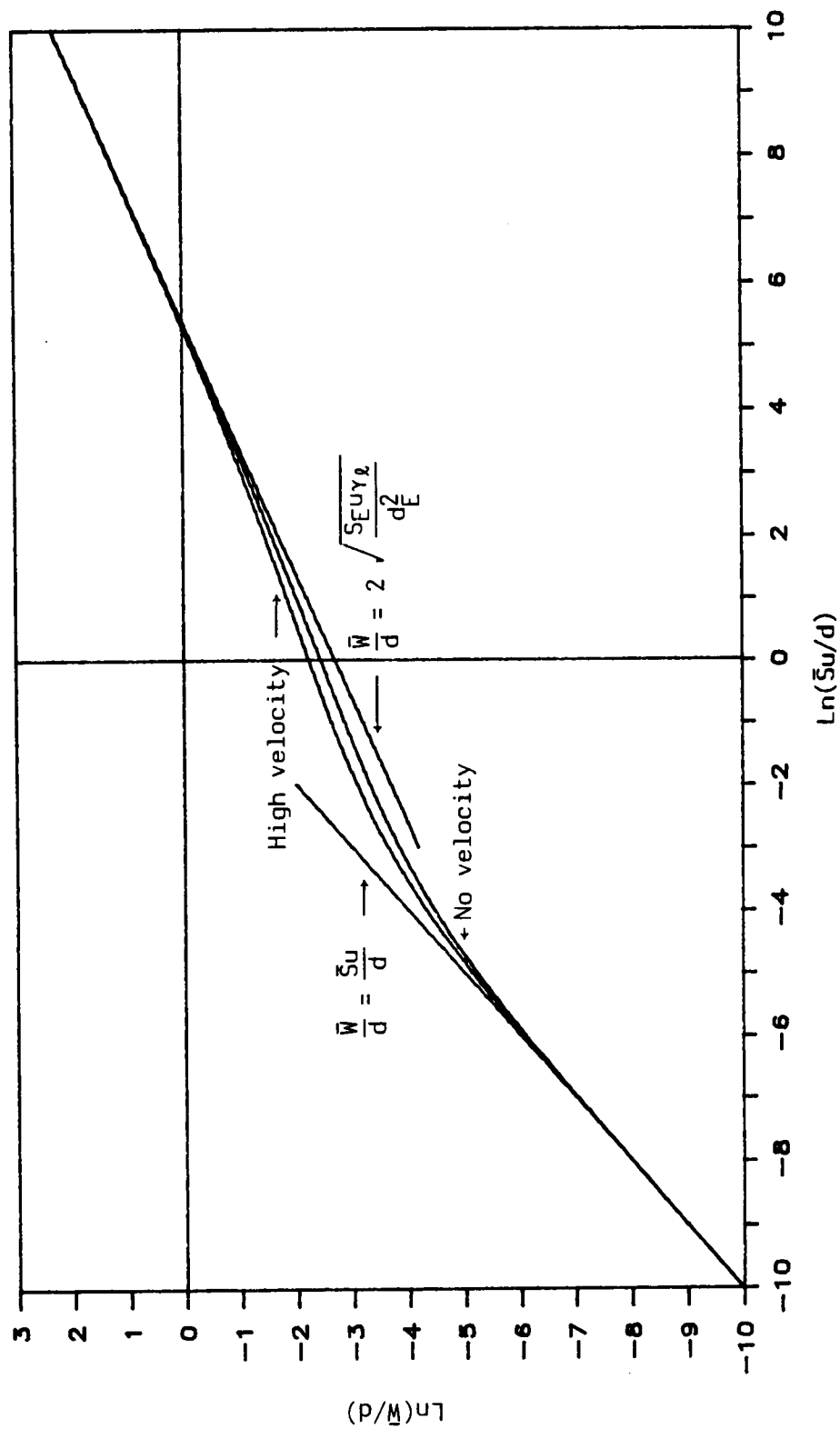


Figure 11. Curves of Growth of Spectral Band of CO₂ Voigt Lines With and Without Directed-Velocity Effects, $\bar{\nu} = 2300 \text{ cm}^{-1}$.

The limiting forms of $\bar{W}/d$ are clearly evident. In the region of small $\bar{S}u/d$, the average equivalent width definitely converges to the line given by $\bar{W}/d = \bar{S}u/d$ for both the no-velocity and high-velocity cases. In the realm of large $\bar{S}u/d$, both curves again converge to a common limit defined by Equation (75). The convergence of the no-velocity curve to this limit shows the applicability of Lorentzian asymptotes to Voigt lines.

As it was for the single-line curve of growth, the main area of interest is the saturation region. The same basic behavior is shown in Figure 11 as was earlier in Figure 9, but the deviation between the no-velocity and high-velocity cases has been lessened. Again, the high-velocity curve of growth is the upper curve. The same physics is responsible for this behavior as it was for the prior results. The no-velocity spectral lines will saturate first, while the shorter, broader high-velocity lines will continue to absorb in a linear fashion. The difference between this graph and that of Figure 9 is that this portrays the spectral average due to a large number of lines. The discrepancies due to directed velocities still appear; however, the process of taking a spectral average has diminished the severity of the observable error.

Changing from a logarithmic scaling in Figure 11 to a linear scaling in Figure 12, we can better observe the disagreement in the saturation region. The deviation has a maximum of just under 27 percent at $\bar{S}u/d = 0.25$, and it slowly tapers off from that point. At $\bar{S}u/d = 2$, the error is about 20 percent while at $\bar{S}u/d = 5$, the error has only diminished to 15.5 percent.

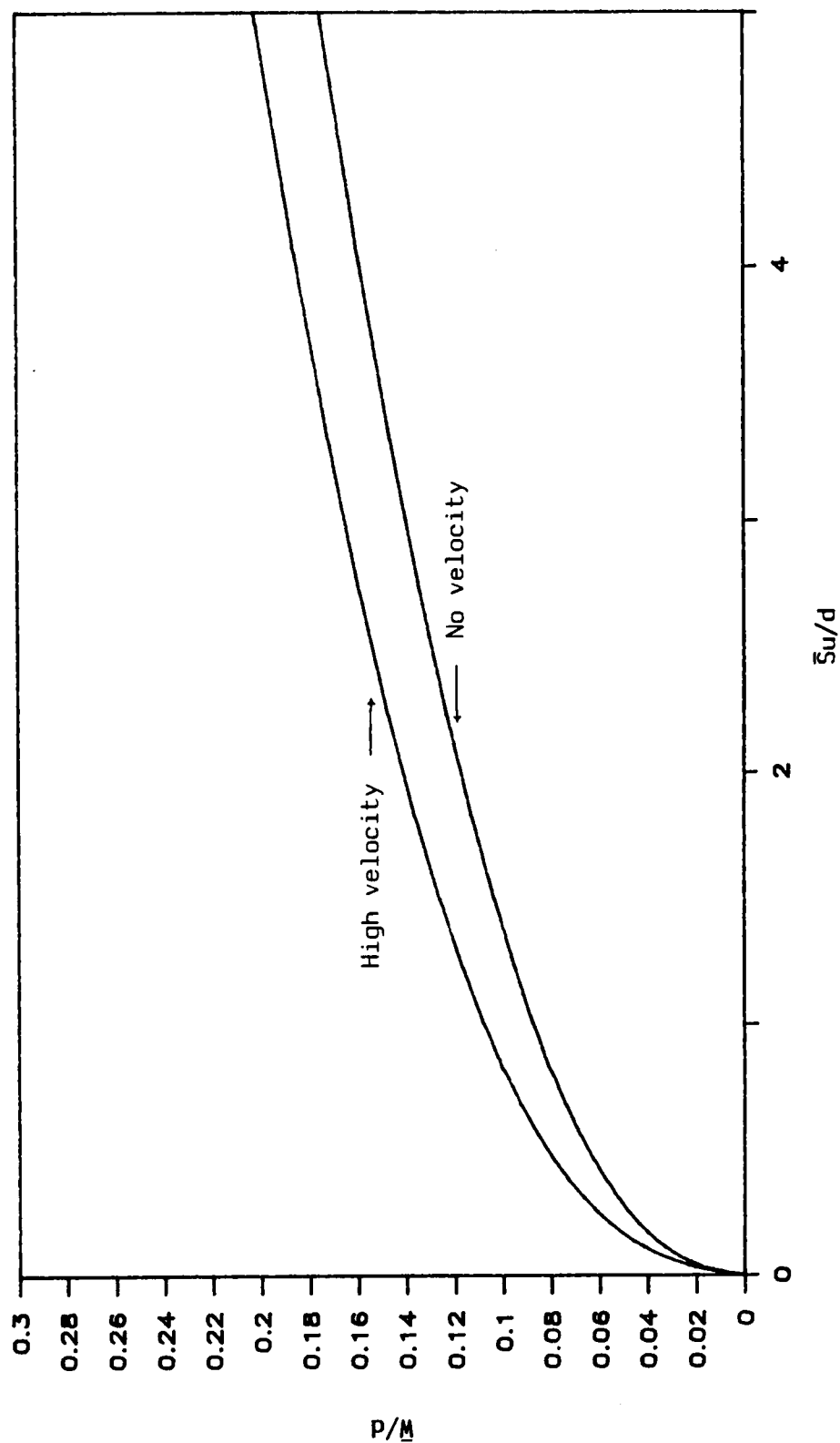


Figure 12. Linear Curves of Growth of Spectral Band of CO_2 Voigt Lines With and Without Directed-Velocity Effects, $\bar{\nu} = 2300 \text{ cm}^{-1}$.

It had not been shown prior to this study that directed-motion Doppler shifts could have a significant impact on the procedure for interpreting broad-band measurements. Yet, from the curves of growth of the average equivalent width for the no-velocity and high-velocity cases, one finds large deviations from the expected results. Since the average equivalent width comes directly from the measured average absorption, errors of over 20 percent will be readily apparent. Conversely, systems that are designed to produce a specific value of the average absorption will have measurements indicating absorptions which are too high. This amount of increase in the average absorption is easily detected by broad-band radiometers and demonstrates the importance of accounting for directed-velocity effects.

Figures 11 and 12 show that although it is possible to smooth out the spectral lines into an average quantity, the absorption of the apparent band contour is quite dependent upon the nature of the lines. It has been stated that the high-velocity spectral line offers a more accurate description of the real physics of the spectral line than does a purely Voigt line. Thus, to ignore the high-velocity profile could be an invitation for trouble. The curves of growth show that under the conditions of this study, the neglect of directed-velocity distortions could result in significant errors in subsequent calculations based on the interpretation of the measured absorption.

Spectra--Comparison of Results

Inspired by the existing differences in the curves of growth of the no-velocity and high-velocity cases, an absorption spectrum for

the CO₂ 4.3 micron band was computed. It was plainly apparent that directed velocities would cause discrepancies for sufficiently large optical depths. The purpose of computing a spectrum was to ascertain whether or not the optical depth would reach those values under practical flowfield conditions. Recall that to compute this spectrum, the SRRM band-model parameters would provide a value of the average line strength for a given wavenumber interval. This is equivalent to sliding up and down the x-axis on the curve of growth. Then, at each $\bar{S}u/d$ point, the value of the average equivalent width is obtained and turned into an average absorption via Equation (55). Thus, when the optical depth reaches into the saturation region, deviations should be noticed. Since the high-velocity case has a greater average equivalent width than the no-velocity case in the saturation region, its absorption spectrum should always have equal or greater value.

The resultant spectra for the no-velocity and high-velocity cases are shown in Figure 13. This figure depicts the baseline flowfield conditions of Table 1. As expected, the high-velocity case has an equal or higher absorption value than does the no-velocity case. The maximum deviation occurs at 2250 cm^{-1} , where the high-velocity spectrum is 25.7 percent higher than the no-velocity spectrum. At that point, the no-velocity absorption is 0.054, corresponding to an average equivalent width of 0.055. Referring to Figure 11, this value of $\bar{W}/d$ occurs around $\bar{S}u/d = 0.30$. As expected, this location is close to the point of maximum discrepancy in the two curves of growth. It follows that the maximum relative error between the two spectra will always occur for $\bar{S}u/d = 0.30$, thus always having a magnitude of approximately 25.7 percent.

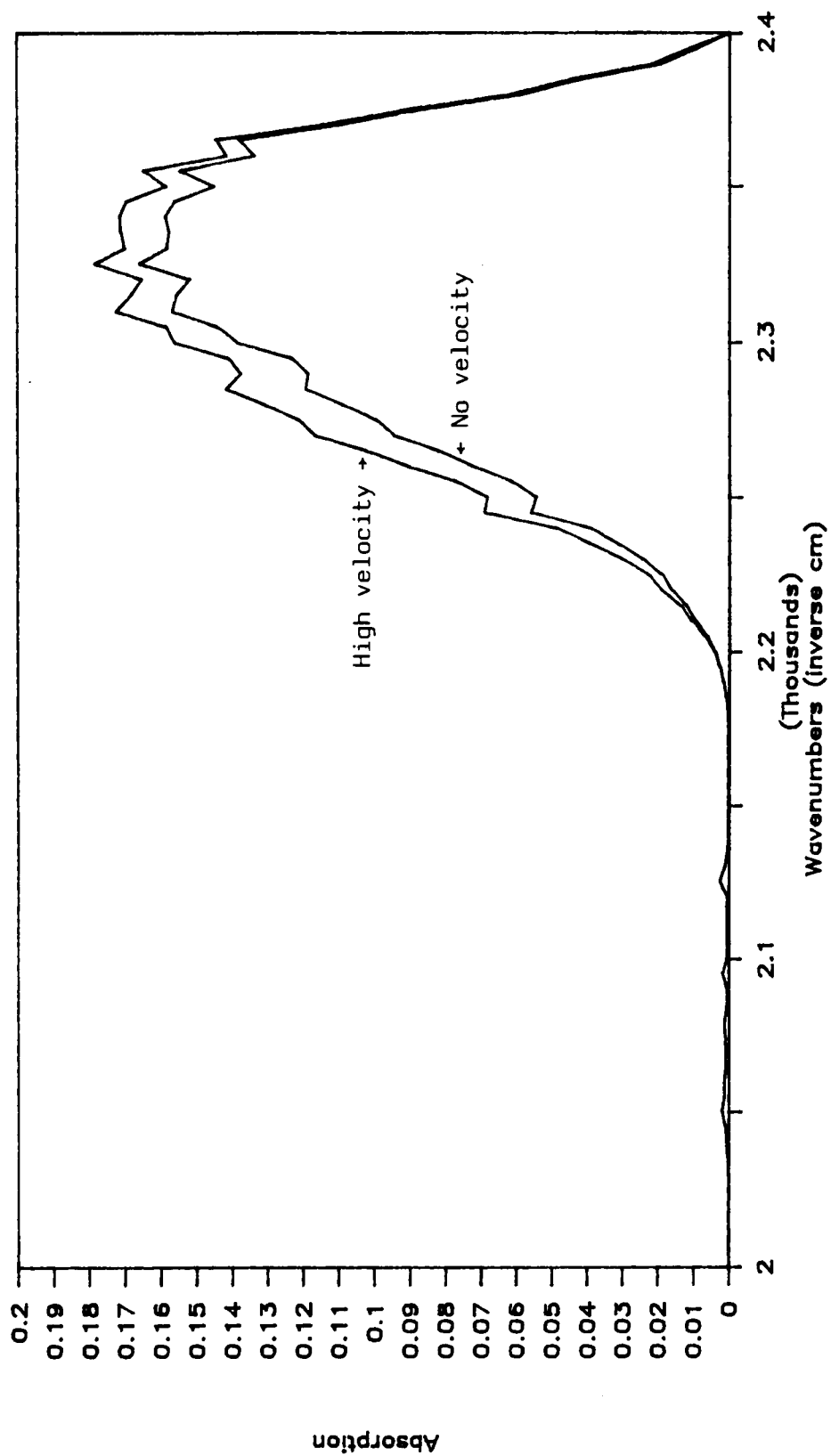


Figure 13. Absorption Spectra of CO₂ 4.3 Micron Band With and Without Directed-Velocity Effects Using SIRM Parameters With a 5 cm⁻¹ Spectral Interval.

Also apparent is that when the no-velocity spectrum reaches absorption values greater than that at 2250 cm^{-1} , the optical depth is well into the saturation region. For wavenumbers greater than 2250 cm^{-1} , the absorption spectrum continues to climb, where it peaks at 2325 cm^{-1} . The deviation between the two spectra is now at 7.5 percent. The error remains in the 7- to 10-percent range for most of the peak region.

Often in a radiometric measurement, the band pass of the instrument is selected to coincide with the band center to obtain maximum signal intensity. For the conditions in Figure 13, it was shown that there exists an error in the predicted spectra in the band-center region of over 7 percent. Since the high-velocity spectrum is based on a more complete physical picture, measurements should be closer to the predicted high-velocity spectrum than to the predicted no-velocity spectrum. If directed-velocity effects are neglected and the no-velocity spectral lines are assumed, it would appear that the measured data are too high by about 7 percent; whereas, the predicted result is too low because it lacks a complete description of fundamental physics.

Since the absorption spectra shown in Figure 13 are so important, it was decided to generate spectra for several optical depths. The optical depth was varied by increasing the partial pressure of CO_2 . This brings up some important implications that should alter the results. An increase in the optical depth means that the magnitude of the absorption becomes larger in the peak region of the spectrum, which is roughly from 2250 to 2380 cm^{-1} . This will push the optical depth past the point of maximum discrepancy on the curve of growth and toward the square-root region where the high-velocity and no-velocity curves are

in closer agreement. Secondly, narrow spectral lines are vital to the observance of the directed-velocity effect. As was shown in Chapter I, when the lines become pressure-broadened, directed-velocity effects become less important. From this combination of occurrences, it would seem that, due to directed motion, the errors in the absorption near the band center should decrease as the optical depth increases.

The absorption spectra for CO_2 pressures at 5, 50, 100, and 250 Torr were computed. Figure 14 is merely the same information as Figure 13, except that the scaling has been changed for comparison purposes.

The result of increasing the partial pressure to 50 Torr is shown in Figure 15. In the peak region, the reduction of the absolute deviation by about 25 percent is evident. Also notice that the spectral location of the maximum relative error, 26 percent, has moved away from the band center to 2220 cm^{-1} . For comparison with Figure 14, the relative error at 2340 cm^{-1} has been reduced to 2.4 percent.

Figure 16 displays the same trends except that the CO_2 partial pressure is now 100 Torr. The location of the maximum relative error, 25.7 percent, has moved even further away from the peak region to 2210 cm^{-1} . The relative error at 2340 cm^{-1} has decreased to 1.5 percent.

Figure 17 shows spectra when CO_2 pressure is 250 Torr. This figure reinforces the trends shown in Figures 15 and 16. The spectral location of maximum relative error, 26 percent, has moved out even further to 2195 cm^{-1} ; while at 2340 cm^{-1} , the relative error is reduced to 0.8 percent.

These four figures clearly describe the anticipated behavior. As the optical depth increases, the deviations between the high-velocity

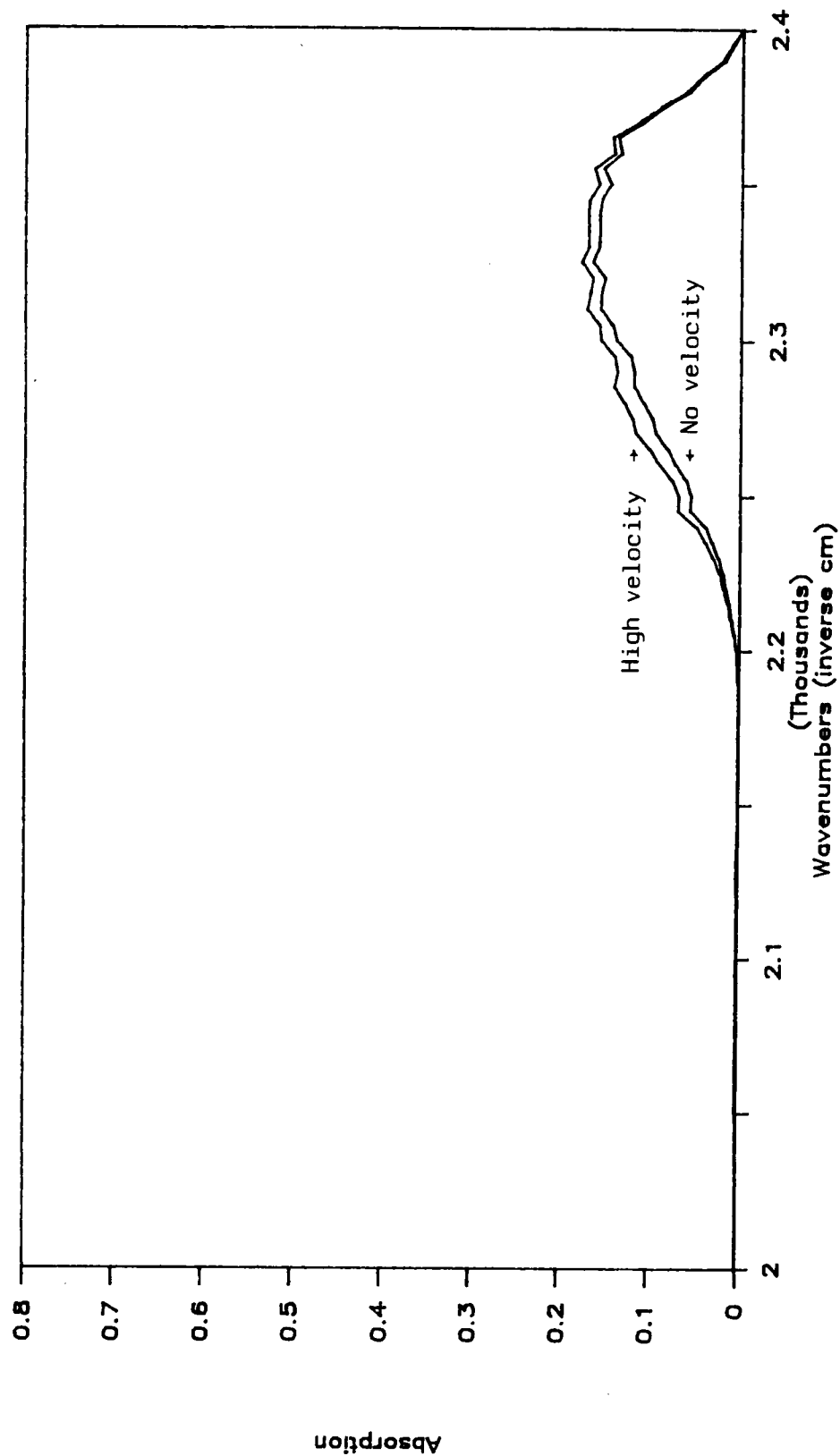


Figure 14. Absorption Spectra of CO_2 4.3 Micron Band Using SIRR Parameters With a 5 cm^{-1} Spectral Interval (Pressure = 5 Torr; Temperature = 600 Kelvin).

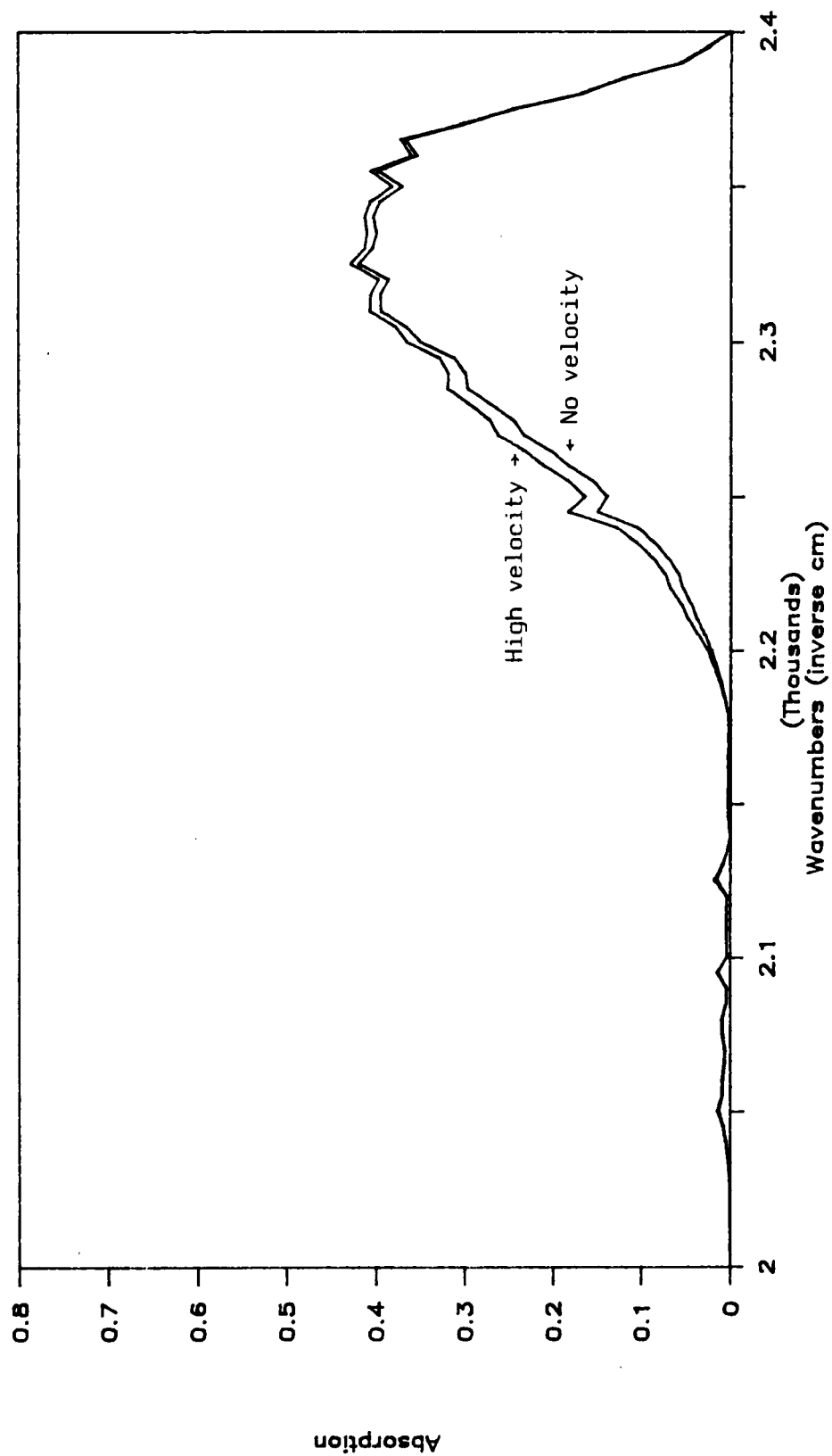


Figure 15. Absorption Spectra of CO₂ 4.3 Micron Band Using SIRR Parameters With a 5 cm⁻¹ Spectral Interval (Pressure = 50 Torr; Temperature = 600 Kelvin).

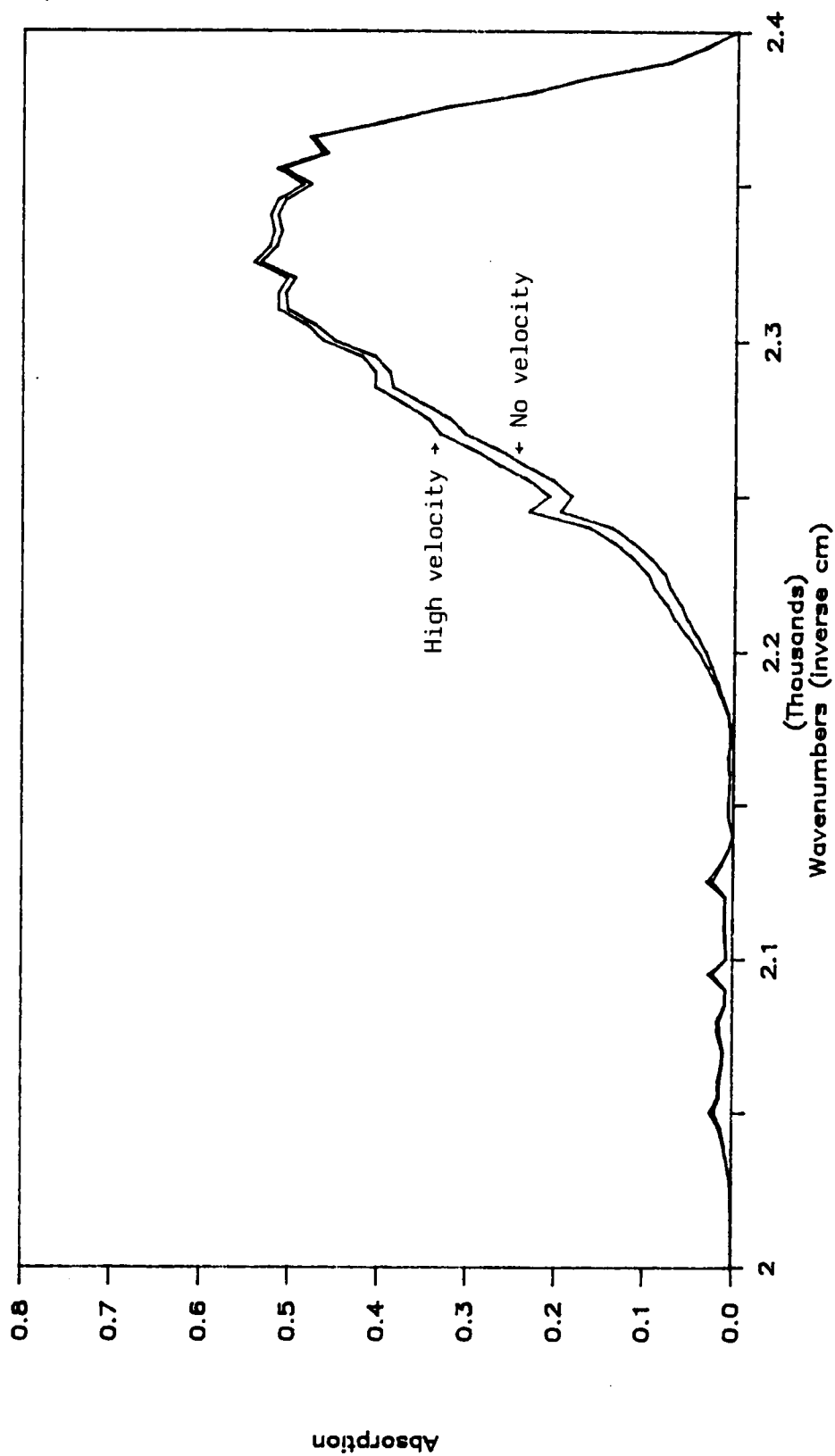


Figure 16. Absorption Spectra of CO₂ 4.3 Micron Band Using SIRM Parameters With a 5 cm⁻¹ Spectral Interval (Pressure = 100 Torr; Temperature = 600 Kelvin).

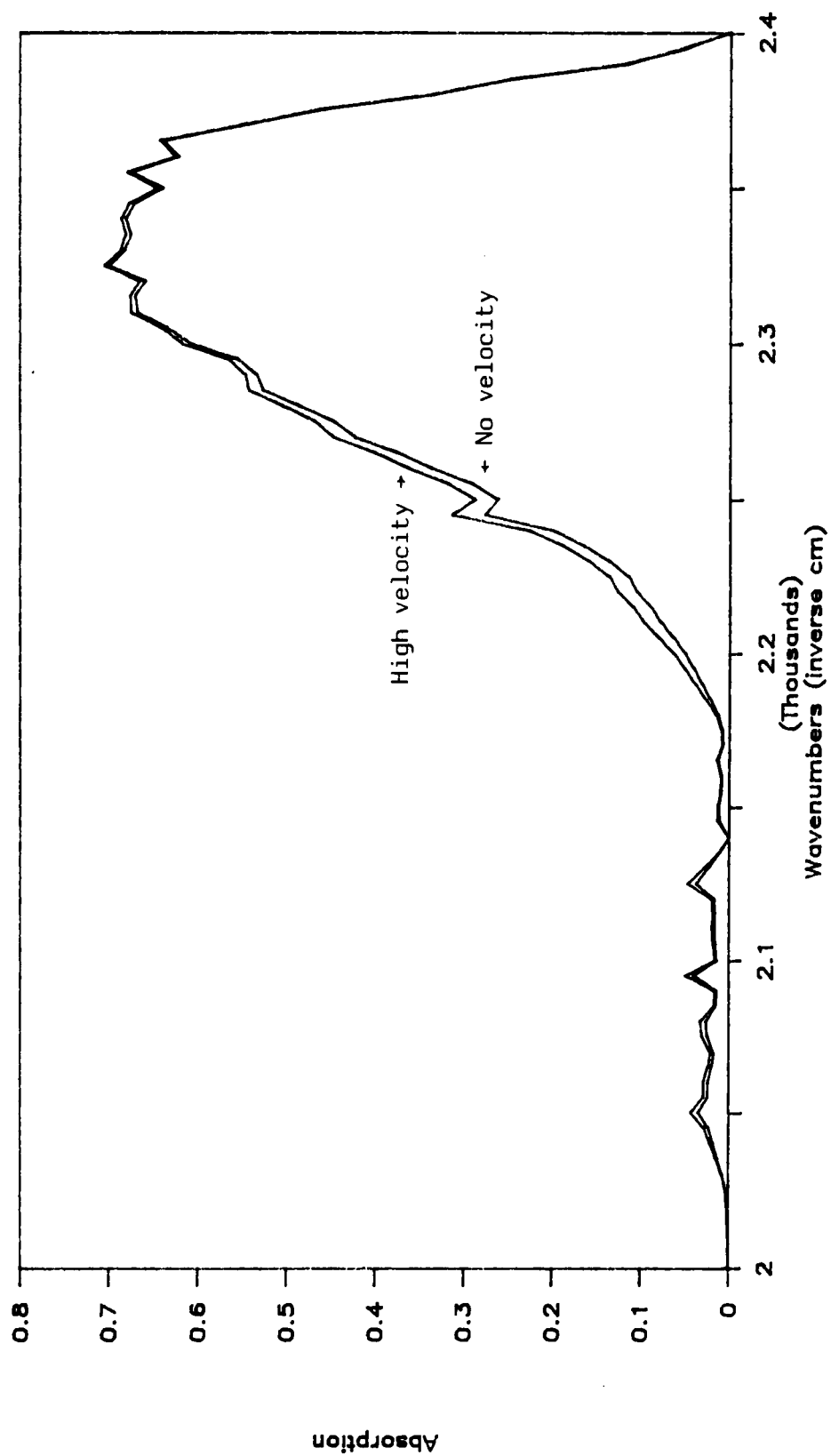


Figure 17. Absorption Spectra of CO₂ 4.3 Micron Band Using SIRR Parameters With a 5 cm⁻¹ Spectral Interval (Pressure = 250 Torr; Temperature = 600 Kelvin).

and no-velocity cases are lessened near the band center. The discrepancy in absorption still exists, but it has moved outward from the band center. Since broad-band measurements are usually done near the band center, the error that will be introduced by neglect of directed-velocity effects will be lessened for increasing optical depth.

However, the conditions of interest to this study predict spectra that yield significantly different absorption within the spectral region of prime interest. Errors of 7 to 10 percent were discovered near the band center. This would seem to indicate that the manner in which measured spectra are interpreted is not quite in order. Therefore, it is important to include directed-velocity effects when the flowfield conditions are at least similar to those of this study. Perhaps, at the very least, it would be possible to perform a computation of the curve of growth for both the no-velocity and high-velocity cases of interest to the particular flowfield in question. This will suffice to determine the impact of directed effects and will provide evidence to support a decision to include or neglect them in further analysis.

One curious artifact displayed in all four spectra is the lack of discrepancy between the no-velocity and high-velocity spectra on the high-frequency side of band center. The cause of this is unknown and should provide a source for future study.

CHAPTER VI

DISCUSSION

Summary of Results

It has been demonstrated that directed-velocity effects on infrared spectroscopy can provide some very interesting results under certain conditions. The absorption behavior of spectral lines and spectral bands can be significantly altered by the inclusion of a Doppler shift characteristic of conical flowfields.

The concept of directed velocities and their subsequent Doppler shifts originated in the area of astrophysics [1,2]. Applying it to the conical flowfields of interest in this study, it was determined that the absorption in the flowfield could be described by a spatially dependent absorption coefficient. This was shown in Figures 4, 5, and 6, as an extreme decrease of the spectral-line center absorption coefficient as the directed velocity increased. These figures suggested that under the proper conditions, directed-velocity effects could produce an observable deviation in the amount of absorption measured.

The spatial dependence of a single spectral line was then translated into a spectral distortion of the path-integrated absorption coefficient. This can be thought of as an effective spectral line and is used for comparison between the no-velocity and the high-velocity cases, as shown in Figures 7 and 8. For the conditions of Table 1, there was a 50-percent decrease in the line-center magnitude and a 90-percent increase in the line half width at half maximum. The broadening of

the line is caused from the combination of the Doppler shifted line profiles from every spatial position along the line of sight. Since the line widens, the magnitude of the line center must decrease to conserve the line strength. This is based on the conservation of the number of absorbers in the flowfield. These results support those obtained by Penner [5,6].

It was also seen that far from line center, the distorted, high-velocity line profile converged to the undistorted, no-velocity line profile. In this instance, the Doppler shift term in the line profile which is due to the directed velocity becomes very small in comparison to the distance from the line center. This term can then be dropped from the expression. This removal means that the absorption coefficient of the high-velocity line is identical to that of the no-velocity line. Thus, the no-velocity and high-velocity lines must converge. This feature is very important in further discussions of the absorption due to these lines.

The curve of growth is the forum to discuss absorption as a function of optical depth. Figure 9 displays curves for absorption lines due to both the no-velocity and high-velocity spectral lines. As expected for optically thin systems, the absorption varies linearly with the optical depth, regardless of the line shape. Recall that in this instance it is possible to drop second-order terms in the expression of the equivalent width, as in Equation (22). The result is that the total absorption depends directly on the line strength and the optical path, which is the same for all line shapes.

In the limit of large optical depths, convergence of the high-velocity and no-velocity absorption is based upon the wings of a spectral line. In this region, the absorption due to the spectral-line center has reached its maximum, it is blacked out, and it no longer contributes. Any further absorption must originate in the wings of the spectral line. Since the high-velocity and no-velocity lines converge in the wings, the absorption must also converge.

More importantly, though, is the behavior of the two curves near the onset of saturation. The absorption line due to the high-velocity spectral line does not saturate simultaneously with the no-velocity absorption line. For the conditions of this study, the high-velocity line will have a maximum of 30 percent greater absorption because of its shorter, broader shape. This occurs at $S_u = 0.1 \text{ cm}^{-1}$ but the difference between the curves of growth is significant over a large range of optical depths.

Since the absorption is a measurable quantity, the meaning of this difference must be appreciated. Through the curve of growth, one can extract information about gas concentrations and temperatures for a given value of the absorption. If the curve of growth of the high-velocity line is greater than that for the no-velocity line, the interpretation of a measured amount of absorption can be misconstrued. The sample calculation given in Chapter 3 shows that for a certain absorption value, it is possible to overestimate the line strength optical-path product by 24 percent. Although the spectral-line results are very revealing, the primary objective of this study is to determine the impact of this spectral-line distortion on infrared band model measurements.

Even though broad-band measurements are sensitive to the particular type of spectral line in the band, they are blind to each individual spectral-line profile and can only detect the result of the combination of all the lines. Hence, it is not apparent that a 24-percent deviation in the absorption of a single line will correlate into a significant deviation of the average absorption of many thousands of lines.

Based upon the computation of the single-line equivalent widths for the no-velocity and high-velocity spectral lines, the average equivalent widths for spectral bands of both such lines are computed. The curve of growth of the band shows that it is possible to find significant differences of the absorptive behavior in the saturation region of the two types of bands. Since the average absorption of a band comes directly from the absorption characteristics of one of the lines in the band, one can expect to find similar curves of growth between the spectral lines and the bands, although any differences due to directed velocities should be lessened by the averaging.

For the curves of growth of the two bands, the limit of low-optical depths yield a linear relationship between the absorption and optical depth for both the no-velocity and high-velocity bands. For large optical depths, Figure 11 shows a convergence of the absorption of the high-velocity and no-velocity bands to the square root limit. The appearance of the correct anticipated asymptotic behavior is a useful double-check to assure that the computations are being performed correctly.

The saturation region is again the area of much interest. The discrepancy between the no-velocity and high-velocity band absorption is clearly evident, with a 26-percent maximum deviation. However, the

significant differences are not sharply peaked at a particular optical depth but extend over the entire saturation region and into the square-root region. The band of high-velocity lines have a greater absorption for the same reasons that the high-velocity single line has greater absorption. The individual high-velocity lines saturate at a higher optical depth than the no-velocity lines. Figure 11 shows that even though it may not be possible for a detector to perceive the details of the absorption process, the effects of a change in that process may be apparent.

The importance of this result cannot be understated. In the past, the directed-velocity effect on spectral absorption was usually dismissed as negligible. However, Figure 11 suggests that directed-motion Doppler shifts may need to be included to increase predictive accuracy. This figure shows that under the conditions of Table 1, which are representative of the expected next generation of motors, the measured absorption of a flowfield can be significantly different than that which is intended.

As examples of the difference in the measured absorption between the no-velocity band and the high-velocity band, absorption spectra are computed for both cases. These spectra compare the difference in the expected amount of absorption from the CO_2 4.3 micron band when directed-velocity effects are taken in account to when they are neglected. The spectra, Figures 13 through 17, show a significant deviation in the predicted absorption from the two cases. The band which considers only no-velocity lines largely underestimates the expected absorption. The extent and spectral location of this difference is dependent

upon the optical depth. As the optical depth decreases, the error near the band center increases.

Since most broad-band measurements are taken near the band center to maximize the input signal, the trend of the increasing error should alert those working in this area. At the conditions of Table 1, there exists a 7-percent difference between the expected absorption from the no-velocity and high-velocity bands. Since the high-velocity line is a more complete description of the physics of the radiative transfer process, one should anticipate the no-velocity absorption results to be 7 percent lower than the measured absorption.

Conclusions

This study of the directed-motion Doppler-shift effect was broken into two parts, the first dealt with the high-resolution measurements of spectral-line absorption, and the second extended the single-line results to determine the effects on low-resolution measurements of broad-band absorption.

The results of the single-line study clearly had a negative impact on the feasibility of high-resolution measurements for conical flowfield diagnostics. It was shown that for the conditions of Table 1, the ability of a Voigt line to absorb incident radiation was greatly increased by the flowfield Doppler shift. Without considering this phenomena, the analysis of absorption measurements would predict substantially higher concentrations of the absorbing specie. These results substantiated those achieved earlier by Penner, et al. This discrepancy existed only over the saturation region of the optical depth. In the

areas of either low or very large optical depths, the absorptive behavior of the two cases was identical. Thus, it may be possible to utilize high-resolution measurements, but only for those flowfields operating in the proper optical depth ranges.

The extension of the comparison cases of Table 1 to infrared band models was done by way of the average curves of growth. The results showed the same phenomena. Because of the lowering of the absorption saturation point, the band of lines which were distorted by the directed-motion Doppler shift was able to enhance absorption by up to 26 percent. Again, the incorporation of this effect did not produce any discrepancies in either the linear or square-root regions of the curve of growth. The implication of this is that it is again possible to considerably overestimate the number of absorbers or emitters in the flowfield based upon an analysis of an absorption measurement when the optical depth is in the saturation region.

As a further example of the directed-motion Doppler-shift effect on broad-band measurements, predicted CO₂ absorption band spectra were computed based upon the band curves of growth computed from the data of Table 1. For these conditions it was shown that the inclusion of these effects enhanced the band center absorption by 7 to 10 percent. The band center is often used in absorption measurements to maximize the signal-to-noise ratio of the detector. It was shown that for conditions of increasing optical depths, the error near the band center decreased, since the optical depth moved into the square-root region of the curve of growth. Therefore, one should be concerned with the interpretation of low-resolution absorption measurements when there

exist optical depths which are in the saturation region of the curve of growth.

Two final remarks are in order. The first is to emphasize the fact that the inclusion of directed-motion Doppler-shift effects yields a more complete description of the manner in which energy is absorbed. It will always provide more accurate flowfield calculations for an actual flow. However, this study has been founded upon the idealized example of a homogeneous conical flow. Therefore, the suitability of its results are only as good as the suitability of the conical approximation to an actual flow.

Secondly, the extent of the directed-motion Doppler shift is dependent upon the geometry of each individual flowfield. To justify neglect of this effect, a calculation should be done similar to that of this thesis for every flowfield being studied. All conical flows, along with flows which are only approximately conical, will have directed-motion Doppler shifting. The important point to know is when it is necessary to include them to protect the integrity of the absorption calculations.

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LIST OF REFERENCES

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APPENDIX

APPENDIX

PROGRAMS USED TO COMPUTE LINE PROFILES, CURVES OF GROWTH, AND SPECTRA

```

c      NUMSP.FOR  Program to determine the line shape in
c                  frequency space for various constraints
c                  Ref: E.E. Whiting, Olivero and Longbothum
c
c      Define constants:
c
c      k .....Absorption Coefficient (no vel)
c      ku .....Path integrated abs coef
c      kzero ...Absorption Coefficient @ line center
c                  Defined = 1.0 1/cm
c      l .....Path length (cm)
c      T .....Static Temp
c      M .....CO2 Molecular mass (amu)
c      VE .....Exit velocity (cgs)
c      RZ .....planar coordinate
c      Z .....axial coordinate
c      Lamcl ...Center line wavelength
c      Numcl ...Center line wavenumber
c      Px .....Static pressure (torr)
c      W .....Degree of weight function
c      Theta ...Angle of cone
c      c .....Light speed (cm/sec)
c      r .....Radius of plume at z (cm)
c
c      implicit real*8 (a-h,o-z)
c      real*8 num,lamcl,k4,m,numcl,init,delt,theta
c      real*8 k,ku,kzero,l,temp
c      integer h,h1,j,trash1,trash2,trash3,trash4
c      integer trash5
c      character yl*64,outfnm*64
c      dimension P(151),x(151)
c      dimension num(1001),ku(1001),k(1001)
c      dimension duma(1001),dumb(1001)
c      data numcl/2300.0d0/, m/44.0d0/, rz/0.0d0/
c      data z/100.0d0/, theta/15.0d0/, j/50/
c      data c/3.0d10/, pi/3.141592d0/
c      data px/5.0d0/, t/600.0d0/, dist/5.0d-1/, h1/300/
c      data kzero/1.0d0/
c
c      exp(yx)=dexp(yx)
c      sin(yx)=dsin(yx)
c      sqrt(yx)=dsqrt(yx)
c      tan(yx)=dtan(yx)
c      r=z*tan(theta/57.1)
c      lamcl = 1./numcl
c
c      write(*,*)' Input pressure ..... '
c      read(*,*)px
c      write(*,*)' Input temperature ..... '
c      read(*,*)t
c      write(*,*)' Input velocity ..... '
c      read(*,*)ve
c      write(*,*)' Input distance from line center.. '
c      read(*,*)dist

```

```

c      write(*,*)' Input # of iterations..... '
c      read(*,*)h1
c
c      gl=(Px/760.0d0)*(.01*(273.0d0/T)+.0691*sqrt(273.0d0/t))
c      gd=3.581d-7*numcl*sqrt(t/m)
c      gamd=.71561996d-6*lamcl*sqrt(T/M)
c      gaml=abs(1/(numcl-gl)-1/(numcl+gl))
c      Q2= SQRt(R**2-rz**2)
c      Q1=-SQRt(R**2-rz**2)
c      l=q2-q1
c
c      write(*,*)'
c      write(*,*)' Which line shape do you want? '
c      write(*,*)'          1 for Voigt '
c      write(*,*)'          2 for Lorentz '
c      write(*,*)'          3 for Doppler '
c      write(*,*)'
c      read(*,*)trash5
c
c      Lorentz line
c      if(trash5 .ne. 2)goto 1178
c      gamv=gaml
c      gd=0.d0
c      gamd=0.d0
c      al=1.d0
c      goto 1200
c
c      Doppler line
c      1178 if(trash5 .ne. 3)goto 1179
c      gamv=gamd
c      gl=0.d0
c      gaml=0.d0
c      al=0.d0
c      goto 1200
c
c      Voigt line
c      From Olivero and Longbothum
c      1179 D1=(GAML-GAMD)/(GAML+GAMD)
c      BETA=.023865d0*dEXP(.6d0*D1)+.00418*dEXP(-1.9d0*D1)
c      GAMV=(GAML+GAMD)*(1-.18121*(1-D1**2)-BETA*dSIN(PI*D1))
c      Damp is the 'a' parameter
c      damp=gl/gd*sqrt(.893d0)
c      A1=GAML/GAMV
c      Compute gv in 1/cm
c      1200 gv= .5*abs(1/(lamcl-.5*gamv)-1/(lamcl+.5*gamv))
c
c
c
c      write(*,*)'The parameters are:'
c      write(*,*)'pressure ..... ',px
c      write(*,*)'temperature..... ',t
c      write(*,*)'velocity ..... ',ve
c      write(*,*)'Line widths'
c      write(*,*)'Halfwidth, 1/cm          Fullwidth, cm'
c      write(*,*)'Collision '

```

```

write(*,*)gl,gaml
write(*,*)'Doppler '
write(*,*)gd,gamd
write(*,*)'Voigt '
write(*,*)gv,gamv
write(*,*)'Damping parameter. ',damp
write(*,*)' '
write(*,*)' Do you want abs or path int abs?'
write(*,*)'          0 for abs coef'
write(*,*)'          1 for path int abs coef'
write(*,*)'
read(*,*)trash3
c
c      Use Polynomial to evaluate Absorption Coef at all freq
c
      init=numcl-dist
      delt1=(dist-.02)/h1*3
      delt2=0.04/h1*3
      num(0)=init-delt1
c
      do 590 h=0,h1
      if(h.ge.2*h1/3)goto 75
      if(h.le.h1/3)goto 75
      num(h+1)=num(h)+delt2
      goto 80
75      num(h+1)=num(h)+delt1
c
80      if(ve .ne. 0.d0)goto 5000
      call polly(num,lamcl,vsin,gamv,k4,h+1,i+1,a1)
      if(trash3 .eq. 1)goto 4990
      k(h+1)=k4
      goto 590
c      Optical path, u, is just X p L for no velocity line
4990      ku(h+1)=k4*kzero*(px/760.d0)*l
      goto 590
c
c      Simpson's rule integration over x for high velocity line
c
5000      do 500 i=0,j
      x(i+1)=ql+i*l/j
      vsin = ve/c*x(i+1)/sqrt(x(i+1)**2 + z**2 + rz**2)
c
      call polly(num,lamcl,vsin,gamv,k4,h+1,i+1,a1)
      P(I+1)=K4
      IF( I.ne. 0) goto 430
      SUM= P(1)
      GOTO 500
430      IF (I .ne. J) goto 460
      SUM= SUM+ P(J+1)
      GOTO 500
460      IF (I/2. .eq. float(I/2)) goto 490
      SUM = SUM + 4.*P(I+1)
      GOTO 500
490      SUM = SUM + 2.*P(I+1)
500      continue

```

```

c      ku is the      path integrated absorption coefficient
      ku(h+1) = SUM *(Q2-Q1)/(3.*float(J))*kzero*(px/760)
590      continue
c
c      Output of calculations
c
6000      write(*,*)' What is the output file name?'
      read (*,'(a64)')outfnm
c
      write(*,*)' Do you want the wavenumber values?'
      write(*,*)'          (0 or 1)      '
      read(*,*)key
      if (key .eq. 0)goto 2400
c
      write(*,*)' Do you want the wavenumbers '
      write(*,*)' normalized to the Voigt HW?'
      write(*,*)'          (0 or 1)      '
      read(*,*)trash1
      if (trash1 .eq. 0)goto 701
      write(*,*)'Normalizing wavenumbers'
      do 2100 i=0,h1
      duma(i+1)=(num(i+1)-numcl)/gv
2100      continue
      goto 2400
701      do 2101 i=0,h1
      duma(i+1)=(num(i+1)-numcl)
2101      continue
c
2400      write(*,*)' '
      write(*,*)' Do you want a semi ln file?'
      write(*,*)'          (0 or 1)      '
      read(*,*)trash2
      if (trash2 .eq. 0)goto 2300
      write(*,*)' '
      write(*,*)'Computing ln values'
      do 2250 i=0,h1
      if(trash3 .eq. 1)goto 2251
      dumb(i+1)=dlog(k(i+1))
      goto 2250
2251      dumb(i+1)=dlog(ku(i+1))
2250      continue
      write(*,*)' '
      write(*,*)'Outputting values'
      call output(outfnm,duma,dumb,h1,key)
      goto 2000
c
2300      write(*,*)' '
      write(*,*)'Outputting values'
      if (trash3 .eq. 1)goto 2305
      call output(outfnm,duma,k,h1,key)
      goto 2000
2305      call output(outfnm,duma,ku,h1,key)
c
c
1100      CLOSE (1)

```

```

2000  write(*,*)' '
      write(*,*)' Do you want to output again? '
      write(*,*)'          (0 or 1) '
      read(*,*)trash
      if (trash .eq. 1)goto 6000
      write(*,*)'Finished.'
      stop
      END
c
c  Subroutine to evaluate phi bar as a fn of wavenumber
c
      subroutine polly(num,lamcl,vsin,gamv,k4,h,i,a1)
      implicit real*8 (a-z)
      integer h,i
      dimension num(1001)
      exp(yx)=dexp(yx)
      sqrt(yx)=dsqrt(yx)
      K1=0
      K2=0
      K3=0
      A3=0
      K4=0
      A3=(1/NUM(H)-LAMCL*(1+vsin))/gamv
c
      arg1=2.772d0*(a3**2)
      arg2=.4*((a3**2)**1.125)
      if (arg1 .lt. 700)goto 5000
      K1=0.d0
      goto 5010
5000  K1=(1-A1)*EXP(-2.772*A3**2)
5010  if (arg2 .lt.700)goto 5015
      k3=0.d0
      goto 5020
5015  K3=.016*(1-A1)*A1*(EXP(-.4*(A3**2)**1.125)-10/(10+(A3**2)**
* 1.125))
5020  K2=A1*(1/(1+4*A3**2))
c
      K4=K1+K2+K3
1000  RETURN
      END
c
c  Subroutine to output data
c
      Subroutine output(outfnm,numa,numb,h1,key)
      dimension numa(1001),numb(1001)
      real*8 numa,numb,mark
      integer i,h1,key
      character*64 outfnm
      data mark/-999.d0/
c
      open(1,status='new',file=outfnm)
      if(key .eq. 0)goto 3100
c
      do 3000 i=0,h1
      write(1,'(e30.12)')numa(i+1)

```

```

3000      continue
          write(1,'(e30.12)')mark
c
3100      do 3001 i=0,h1
          write(1,'(e30.12)')numb(i+1)
3001      continue
          close (1)
          return
          end

```

```

c   COG.FOR ... Curve of growth program to evaluate Doppler effects
c
c   Parameters:
c       ku ...functional values generated by NUMSP.FOR
c           These numbers are the absorption coefficient
c           integrated over a homogeneous path.
c
c       lnw ...Logarithmic Values of equivalent width
c
c       dimension lnw(1001),ku(1001),ta(1001),xd(1001)
c       dimension num(1001)
c       implicit real*8 (a-g,o-z)
c       real*8 dimf,lnw,ku,sum,ta,dum,sk,num
c       integer j,y,ymin,ymax,q,h,len
c       character*64 infnm,outfnm
c       data px/5.d0/,t/800.d0/
c
c       gl=px/760.d0*(.01*273.d0/t+.0691*dsqrt(273.d0/t))
c       len=0
c       sk=0.d0
c
c       write(*,*)' What is input file name? '
c       read(*, '(a64)') infnm
c       write(*,*) infnm
c       write(*,*)' '
c       open (1,file=infnm)
c       do 8 i=1,5002
c       read (1, '(e30.12)') num(i)
c       if (num(i) .eq. -999.d0) goto 9
c       len=len+1
c       continue
c       write(*,*)' Lorentz halfwidth.. ',gl
c       write(*,*)' Number of points... ',len
c       do 11 i = 1,len
c       read (1, '(e30.12)') ku(i)
c       continue
c       close (1)
c
c
c       write(*,*)' Ln(Su) starting value      '
c       read(*,*) rinit
c       write(*,*)' Ln(Su) ending value        '
c       read(*,*) rend
c       if(rinit .ge. rend ) goto 15
c       delta = (rend - rinit)/100
c
c       Integrate (ku)dw over freq range
c       do 500 i= 2,len
c       sk= sk+(ku(i-1)+ku(i))/2.d0
c       & *abs(num(i)-num(i-1))
c       continue
c       write(*,*)' Su =      ',sk
c

```

```

c      do 10 h= 1,101
          sum=0.d0
          xd(h) = rinit +(h-1)*delta
c      Compute small optical depth asymptotic solution
          if(xd(h).le. 5.d0)goto 120
          lnw(h)=dlog(2.d0*dsqrt(dexp(xd(h))*gl))
          goto 10
120      dimf = dexp(xd(h))/sk
c
c      Integrate [ 1-exp(-ku*y) ]dw using trapezoidal rule
c
          val=ku(1)*dimf
          if(val.ge. 709.d0 )goto 140
          ta(1)= 1.-1.d0/dexp(val)
140      do 150 q=2,len
          val=ku(q)*dimf
c
          if(val .ge. 709.d0)goto 155
          ta(q) = 1.d0-1.d0/dexp(val)
          goto 160
c
155      if(val/50 .ge. 709.d0)goto 149
          ta(q) = 1.d0-(1.d0/dexp(val/50))*50
          goto 160
c
149      ta(q)=1.d0
c
160      sum=sum+(ta(q-1)+ta(q))/2.d0*
& abs(num(q)-num(q-1))
150      continue
          lnw(h) = dlog(sum)
10      continue
c
c      Output data to .prn file
          write(*,*)' What is the output file name? '
          read(*,'(a64)')outfnm
          open(1,file=outfnm,status='new')
c
          write(*,*)' Do you want the x-axis (0 or 1)? '
          write(*,*)' Note: It is needed for the '
          write(*,*)' band model calculation. '
          read(*,*)h2
          if(h2 .eq. 0)goto 302
c
          do 205 y = 1,101
          write(1,'(e30.12)')xd(y)
205      continue
c
302      do 201 y = 1,101
          write(1,'(e30.12)')lnw(y)
201      continue
c
          close(1)
1000      write(*,*)'All done.'

```

```

c      BNDCOG.FOR ... This will calculate the equivalent width
c      of a line using band model theory. The particular
c      distribution in use is the exp inverse tailed.
c      Requirements:
c      Single line equivalent widths generated by COG.FOR
c
c
c
c      Nomenclature:
c      lnsu      Nat log of Su, ave line strength * optical path
c      lnw       Nat log of W, ave equivalent width
c      lnsud     Nat log of Su/d
c      lnwd      Nat log of W/d computed for band cog
c      check     % area of last integration box
c      wb        ave equivalent width
c      sub       ave line strength * optical path
c
c      dimension lnsud(102),lnwd(102)
c      dimension grand(505),check(102)
c      dimension w(505),su(505),lnw(505),lnsu(505)
c      implicit real*8 (a-g,o-z)
c      real*8 lnsud,lnwd,lnsu,lnw
c      integer i,j,h,key
c      character infnm1*15,infnm2*15,outfnm*15
c      data pi/3.14159d0/,od/15.d0/
c      data rend/10.d0/,rinit/-10.d0/
c      data R/1.0d6/
c      R1=(R-1)/R/dlog(R)
c      write(*,*)' What is 1/d ?
c      read(*,*)od
c      d=1./od
c
c
c      write(*,*)' What is the fnm for the Ln(Su) '
c      write(*,*)' and Ln(W) data?
c      read(*,1000)infnm1
c      write(*,*)infnm1
c      open(1,file=infnm1)
c      do 50 i=1,101
c      read(1,'(e30.12)')lnsu(i)
c      su(i)=dexp(lnsu(i))
50      continue
c      do 51 i=1,101
c      read(1,'(e30.12)')lnw(i)
c      w(i)=dexp(lnw(i))
51      continue
c      close (1)
c
c      write(*,*)'      Ln(Su)                Ln(W) '
c      write(*,*)lnsu(1),lnw(1)
c      write(*,*)lnsu(101),lnw(101)
c      write(*,*)'
c      write(*,*)'
c      write(*,*)'      Ln(Su/d ave)          Ln(W/d ave)'
c

```

```

c      write(*,*)' Ln(Su/d) starting value?      '
c      read(*,*)rinit
c      write(*,*)' Ln(Su/d) ending value?      '
c      read(*,*)rend
c      delta=(rend-rinit)/100
c
c      do 100 i=1,101
c          lnsud(i)=rinit+(i-1)*delta
c          sub=d*dexp(lnsud(i))
c          wb=0
c      Integrate via Trapezoid
c
c          do 200 j=1,101
c              val1=su(j)*R1/sub
c              val2=su(j)*R*R1/sub
c              if(val1 .ge. 709)goto 201
c              t1=dexp(-val1)
c              goto 202
201          t1=0.d0
202          if(val2 .ge. 709)goto 203
c              t2=dexp(-val2)
c              goto 204
203          t2=0.d0
c
204          grand(j)=w(j)/su(j)*(t1-t2)
c
c              if(j .ne. 1)goto 205
c      Since j=1 find the asymptotic beginning
c              wb=sub/R1*(-t1+t2/R+1.d0-1.d0/R)
c              goto 200
c
c      205          oldwb=wb
c              wb=wb+((grand(j)+grand(j-1))/2*(su(j)-su(j-1)))
c
c
c      200          continue
c
c              lnwd(i)=dlog(wb/d/dlog(R))
c              write(*,*)lnsud(i),lnwd(i)
c              check(i)=(wb-oldwb)/wb*100.0
100          continue
c
c      Output of numbers
c          write(*,*)' '
c          write(*,*)' The input file was ..... ',infnm1
c          write(*,*)' '
c          write(*,*)' Do you want Ln(Su/d) values? (0 or 1) '
c          read(*,*)key
410          call output(lnsud,lnwd,key)
c
c          write(*,*)' Do you want the check #s ? (0 or 1) '
c          read(*,*)trash
c          if(trash .eq. 0)goto 600
c          write(*,*)' Do you want the x axis ? (0 or 1) '

```

```

c      read(*,*)key
c      call output(linsud,check,key)
600    write(*,*)' Terminate execution.'
      stop
1000   format(a15)
999   end
c
      Subroutine output(numa,numb,key)
      dimension numa(105),numb(105)
      character outfnm*15
      real*8 numa,numb
      integer key,i,trash
      write(*,*)' What is the output file name      '
      read(*,'(a15)')outfnm
      write(*,*)'          ',outfnm
      open(1,status='new',file=outfnm)
c      Output one or two files
      if (key .eq. 0)goto 560
      do 550 i=1,101
        write(1,'(e30.12)')numa(i)
550    continue
c
560    do 551 i=1,101
        write(1,'(e30.12)')numb(i)
551    continue
c
9000   close (1)
      return
      end

```

```

c   SPECTRA.FOR ...
c   This will calculate the spectra using band model
c   theory. The particular distribution in use is
c   the exp inverse tailed.
c   Requirements:
c       SIRR band model params in a file containing
c       frequency(arbitrary units), Sbar(1/atm-cm^2),
c       1/d(1/cm).
c
c   Nomenclature:
c       lnsu    Nat log of Su
c       lnw     Nat log of W
c       check   % area of last integration box
c
c       dimension tau(1000),sub(1000),freq(1000)
c       dimension grand(505),check(102),od(1000)
c       dimension w(505),su(505),lnw(505),lnsu(505)
c       implicit real*8 (a-g,o-z)
c       real*8 lnsu,lnw
c       integer i,j,h,key
c       character infnm1*15,infnm2*15,outfnm*15
c       data pi/3.14159d0/
c       data rend/10.d0/,rinit/-10.d0/
c       data R/1.0d6/
c       R1=(R-1)/R/dlog(R)
c   Input optical path data
c   Optical Path will be in cm-atm
c       write(*,*) ' Assume Startech conditions? '
c       write(*,*) ' (0 or 1) '
c       read(*,*)n1
c       if( n1 .eq. 0)goto 10
c   Compute optical path assuming 5 torr & 15 degree
c   nozzle at 100 cm downstream
c       u=2*100*tan(15*pi/180)*5/760
c       goto 11
10  write(*,*) ' Input physical path length '
c       write(*,*) ' (in cm)..... '
c       read(*,*)z1
c       write(*,*) ' Input partial pressure of gas '
c       write(*,*) ' (in torrs)..... '
c       read(*,*)px
c       u=px/760.d0*z1
c
c   11  write(*,*) ' What is the fnm for the Ln(Su) '
c       write(*,*) ' and Ln(W) data? '
c       read(*,1000)infnm1
c       write(*,*)infnm1
c       open(1,file=infnm1)
c       do 50 i=1,101
c       read(1,'(e30.12)')lnsu(i)
c       su(i)=dexp(lnsu(i))

```

```

50      continue
      do 51 i=1,101
      read(1,'(e30.12)')lnw(i)
      w(i)=dexp(lnw(i))
51      continue
      close (1)
c
      write(*,*)'      Ln(Su)                Ln(W)  '
      write(*,*)lnsu(1),lnw(1)
      write(*,*)lnsu(101),lnw(101)
c
      write(*,*)' '
      write(*,*)' Are the band model parameters in '
      write(*,*)' CO2PARM.PRN ?                (0 or 1) '
      read(*,*)h
      if(h .eq. 1) goto 29
      write(*,*)' What is the fnm for the band model'
      write(*,*)' parameters?
      read(*,1000)infnm2
      goto 30
29      infnm2='co2parm.prn'
30      write(*,*)' '
      write(*,*)infnm2
      open(1,file=infnm2)
      do 60 k=1,1000
      read(1,'(e30.12)')freq(k)
      if(freq(k).eq.-999.0d0)goto 61
      continue
60      write(*,*)' Starting Frequency.. ',freq(1)
61      write(*,*)' Ending Frequency.... ',freq(k-1)
      do 62 i=1,k-1
      read(1,'(e30.12)')sub(i)
      sub(i)=u*sub(i)
62      continue
      do 63 i=1,k-1
      read(1,'(e30.12)')od(i)
63      continue
c
c
      do 100 i=1,k-1
      wb=0
c      Integrate via Trapezoid
c
      do 200 j=1,101
      val1=su(j)*R1/sub(i)
      val2=su(j)*R*R1/sub(i)
      if(val1 .ge. 709)goto 201
      t1=dexp(-val1)
      goto 202
201      t1=0.d0
202      if(val2 .ge. 709)goto 203
      t2=dexp(-val2)
      goto 204
203      t2=0.d0
c

```

```

204      grand(j)=w(j)/su(j)*(t1-t2)
c
      if(j .ne. 1)goto 205
c   Since j=1 find the asymptotic beginning
      wb=sub(i)/R1*(-t1+t2/R+1.d0-1.d0/R)
      goto 200
c
205      oldwb=wb
      wb=wb+((grand(j)+grand(j-1))/2*(su(j)-su(j-1)))
c
c
200      continue
c
      tau(i)=dexp(-wb*od(i)/dlog(R))
c      check(i)=(wb-oldwb)/wb*100.0
100      continue
c
c   Output of numbers
      write(*,*)' Do you want frequency values? (0 or 1) '
      read(*,*)key
410      call output(freq,tau,key,k-1)
c
c      write(*,*)' Do you want the check #s      ? (0 or 1) '
c      read(*,*)trash
c      if(trash .eq. 0)goto 600
c      write(*,*)' Do you want the x axis      ? (0 or 1) '
c      read(*,*)key
c      call output(lnsud,check,key)
600      write(*,*)' Terminate execution.'
      stop
1000     format(a15)
999     end
c
      Subroutine output(numa,numb,key,h)
      dimension numa(105),numb(105)
      character outfnm*15
      real*8 numa,numb
      integer key,i,h,trash
      write(*,*)' What is the output file name      '
      read(*, '(a15)')outfnm
      write(*,*)'      ',outfnm
      open(1,status='new',file=outfnm)
c   Output one or two files
      if (key .eq. 0)goto 560
      do 550 i=1,h
          write(1,'(e30.12)')numa(i)
550      continue
c
560      do 551 i=1,h
          write(1,'(e30.12)')numb(i)
551      continue
c
9000     close (1)
          return
          end

```

```

c MACH.FOR
c Computes dependence of spectral shift on Mach #
c
c
c
c      implicit real*8 (a-h,o-z)
c      real*8 m,lamcl
c      integer i
c      character outfnm*64
c      dimension m(30),p(30),t(30),ratio(30)
c      data c/3.0d10/, k/1.38d-16/, pi/3.141592d0/
c
c
c
c Define constants:
c      write(*,*) Available Data
c      write(*,*) 'N2O4/MMH', 'O2-H2'
c      write(*,*)
c      write(*,*) 'Chmbr Press Torr', 7000, 51700
c      write(*,*) 'Chmbr Temp K', 2000, 3000
c      write(*,*) 'Sp Ht Rat', 1.24, 1.204
c      write(*,*) 'Gas Cnst', 449, 665
c      write(*,*) 'Mole Fractions'
c      write(*,*) 'H', .03
c      write(*,*) 'H2', .30
c      write(*,*) 'H2O', .35
c      write(*,*) 'CO', .20
c      write(*,*) 'CO2', .10
c      write(*,*) 'N2', .30
c      write(*,*)
c      write(*,*) 'Enter 0 for O2-H2 or 1 for N2O4/MMH'
c      write(*,*) 0, 1
c      read(*,*)trash
c      if(trash.eq. 0)goto 10
c      if(trash.eq. 1)goto 9
c      goto 8
c
c n2o4/mmh
c 9      pc=7000.0d0
c      tc=2000.d0
c      gam=1.24d0
c      r=449.0d0
c      goto 15
c
c o2-h2
c 10     pc=57100.0d0
c      tc=3000
c      gam=1.204d0
c      r=665.0d0
c
c
c      m(0)=0
c 15     do 100 i=1,25
c      m(i)=m(i-1)+.4
c      p(i)=pc/((1+(gam-1)/2*m(i)**2)**(gam/(gam-1)))
c      t(i)=tc/((pc/p(i))**((gam-1)/gam))
c

```

```

c      Compute Voigt Halfwidth
c      Reference 'Astrophysics' and CPIA
c      if(trash .eq. 0)goto 200
c
c      n2o4/mmh 2300 1/cm CO2
c      lamcl=4.347828d-4
c      gl=(P(1)/760.0d0)*(.01*.10*273.0d0/t(1) + (.08*.35 +.07*.20
$      +.06*.05 +.09*.1 +.07*.30)*dsqrt(273./t(1)) )
c      wd=.71561996d-6*lamcl*sqrt(t(1)/44.0)
c      goto 150
c
c      o2-h2 3100 1/cm H2O
200    lamcl=3.2258d-4
c      gl=(p(1)/760.)*(.44*.67*273./t(1) +(.05*.03 +.05*.30
$      +.09*.67)*dsqrt(273./t(1)) )
c      wd=.71561996d-6*lamcl*sqrt(t(1)/18.0)
c
c      150    wl=2.0d0*LAMCL**2*gl/(1.0d0+LAMCL*GL)
c      From review of Whiting's paper
c      D1=(wl-wd)/(wl+wd)
c      BETA=.023665d0*dEXP(.6d0*D1)+.00418*dEXP(-1.9d0*D1)
c      wv = (wl+wd)*(1-.18121*(1-D1**2)-BETA*dSIN(PI*D1))
c      Compute gv in 1/cm
c      gv= wv/(2*lamcl**2-wv*lamcl)
c
c      Compute Ratio of vsin / gv
c      vsin will be in m/sec*100=cm/sec
c      vsin=m(1)*dsqrt(gam*r*t(1))*dsin(.2617994d0)*100.0
c      ratio(1)=(1./lamcl)*vsin/c/gv
c
c      100    continue
c
c      Output
c      write(*,*)' Enter new output filename '
c      read(*, '(a64)')outfnm
c      write(*,*)' ',outfnm
c      open(1,status='new',file=outfnm)
c      write(*,*)' '
c      write(*,*)' Do you need the Mach #s ? (0 or 1) '
c      read(*,*)trash1
c      if(trash1 .eq. 0)goto 905
c      do 900 i=1,25
c      write(1,'(e30.12)')m(i)
900    continue
c      do 901 i=1,25
c      write(1,'(e30.12)')ratio(i)
901    continue
c      close (1)
c
c      write(*,*)' Output completed '
9000   end

```

VITA

James A. Drakes was born on November 23, 1963. He was raised in a small farm town named North East, Pennsylvania, located along the shores of Lake Erie. In June 1981, he graduated from North East High School. That fall, he enrolled at The University of Dayton, Dayton, Ohio. While attending, he was an active member and officer of both the Society of Physics Students and Chi Sigma Alpha, a social fraternity. The author was also elected a member of Sigma Pi Sigma. On April 28, 1985, the author graduated from The University of Dayton with a Bachelor of Science degree, with a major in Physics.

In September 1985, he entered the graduate physics program at The University of Tennessee Space Institute. He was awarded a graduate research assistantship which was performed in conjunction with Sverdrup Technology, Arnold Air Force Station, Tennessee. In June 1987, the author received his Master of Science degree with a major in Physics.

He plans to continue his graduate education in the field of Condensed Matter Physics at Pennsylvania State University, where he was awarded the David P. Duncan Fellowship.

The author's interests include running, hiking, backpacking, racquetball, and fishing. He was married on July 20, 1985, to the former Nancy Susan Ollinger, also of North East, Pennsylvania.