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Hyunsoo Chang

Louisiana State University and Agricultural & Mechanical College

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Determination of the wavelength dependence of the optical properties of soot from \textit{in-situ} measurements

Chang, Hyunsoo, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1989
Determination of the Wavelength Dependence of the Optical Properties of Soot from In-Situ Measurements

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Mechanical Engineering

by

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A  Kramers-Kronig function (complex), defined in eqns (4.4)-(4.5)

$a_n$  electric multipole coefficient of the scattered light

$B$  value of the autocorrelation function at large time, defined in eqn. (2.18)

$b$  experimental constant in autocorrelation function, defined in eqn. (2.18)

$b_n$  magnetic multipole coefficient of the scattered light

$C_s$  Cunningham correction factor, defined in eqn. (2.24)

$C_t$  intensity autocorrelation function, defined in eqn. (2.18)

$C_{pp}$  particle scattering cross-section, defined in eqn. (2.4)

$\overline{C}_{pp}$  mean scattering cross-section, defined in eqn. (2.3)

$\overline{C}_{ext}$  mean particle extinction cross-section, defined in eqn. (2.11)

$c_o$  speed of light in vacuum

$D$  particle diffusion coefficient, defined in eqn. (2.23)

$d$  soot particle diameter

$e$  electric charge

$eV$  electron volt, 1.602E-19 joule

$g_f$  damping constant of free electrons
$g_b$ damping constant of bound electrons

$H$ height above the burner surface

$h$ Planck's constant

$I_o$ incident energy flux, defined in eqn. (2.1)

$i_{pp}$ Mie scattering functions, defined in eqn. (2.5)-(2.6)

$i$ $\sqrt{-1}$

$K_e$ particle extinction coefficient, defined in eqn. (2.10)

$K_B$ Boltzmann's constant

$\bar{K_e}$ mean extinction coefficient

$k$ index of absorption, imaginary part of the complex refractive index

$L$ pathlength of the flame

$\ell$ mean free path of the gas molecule

$M$ total number of correlator channels

$m$ complex refractive index of soot particles, $\bar{m} = n - ik$

$m_e$ electron mass

$N$ number density of particles

$n$ index of refraction, real part of $\bar{m}$

$n_f$ number density of free electrons

$n_{bi}$ number density of bound electrons

$n_m$ refractive index of the medium (real)

$P$ Cauchy Principle value of the integral
$P(r)$  particle size distribution function, defined in eqn. (2.7)
$q''$  radiative flux
$Q_{\text{ext}}$  extinction efficiency
$Q_s$  scattering efficiency
$q$  scattering wavevector, defined in eqn. (2.21)
$R$  ratio of the electrical permittivity
$r$  soot particle radius
$r_o$  most probable radius
$S_{pp}$  scattered light intensity
$S_o$  Mie scattering amplitude function in the forward direction
$T$  temperature
$t$  time
$V$  gas flow velocity
$V_f$  volume fraction
$x$  size parameter
$\Gamma$  line width of diffusional broadening, defined in eqn. (2.25)
$\bar{\Gamma}$  average line width
$\Delta t$  sampling time
$\Delta \Omega$  solid angle
$\eta$  viscosity of the combustion gas
$\eta_o$  efficiency of the optical elements
\( \epsilon \)  \hspace{1em} \text{complex dielectric function} \\
\( \epsilon' \)  \hspace{1em} \text{real part of the complex dielectric function} \\
\( \epsilon'' \)  \hspace{1em} \text{imaginary part of the complex dielectric function} \\
\( \varepsilon_\lambda \)  \hspace{1em} \text{spectral emissivity} \\
\( \theta \)  \hspace{1em} \text{scattering angle} \\
\( \lambda \)  \hspace{1em} \text{wavelength of the incident radiation} \\
\( \sigma \)  \hspace{1em} \text{geometric width of particle size distribution} \\
\( \sigma_{VV} \)  \hspace{1em} \text{scattering coefficient for the vertical polarization orientation} \\
\( \sigma_{HH} \)  \hspace{1em} \text{scattering coefficient for the horizontal polarization orientation} \\
\( \sigma \)  \hspace{1em} \text{variance of the size distribution, defined in eqn. (2.26)} \\
\( \tau_\lambda \)  \hspace{1em} \text{transmittance} \\
\( \phi \)  \hspace{1em} \text{fuel equivalence ratio, defined in eqn. (3.1)} \\
\( \omega \)  \hspace{1em} \text{angular frequency} \\
\( \omega_{bi} \)  \hspace{1em} \text{natural frequency of bound electrons}
Abstract

The index of refraction of soot particles is of considerable importance in many areas of research and engineering applications such as combustion diagnostics and radiative transfer from combustion systems. The present study aims toward the analysis of compositional effect on the refractive index and the spectral variation of the indices of soot particles by combining classical and dynamic light scattering measurements with the Kramers-Kronig relations in hydrocarbon flames. The particle size distribution is determined from photon correlation measurements. The number densities, volume fractions and refractive indices are then determined as a function of the height above the burner and fuel equivalence ratio for premixed propane/oxygen and methane/oxygen flames. This information is then combined with the spectral extinction measurements in the wavelength range 0.2 to 7 μm to determine the spectral variation of the refractive indices of soot. Premixed propane/oxygen and methane/oxygen flames with various fuel equivalence ratios were considered. It was found that the soot effective refractive indices change not only with the position within a given flame but they also change significantly with the fuel equivalence ratio. On the other hand, an absorption resonance exists
between 0.25 μm and 0.28 μm, depending on the height above the burner surface.

It was demonstrated that the Kramers-Kronig method of analysis can yield the refractive indices over the whole spectrum with the least number of assumptions as compared with the Drude-Lorentz dispersion model that has been used so far.
Chapter 1

Introduction

The index of refraction of soot particles is of considerable importance in many areas of research and engineering applications such as combustion diagnostics, radiative transfer from combustion systems, climate, visibility and the carbon black industry. Despite the wide range of refractive index data reported in the visible and infrared wavelengths by Erickson et al. [1], Foster and Howarth [2], Dalzell and Sarofim [3], Chippet and Gray [4], Janzen [5], Bockhorn et al. [6], Lee and Tien [7], Charalamopoulos [8], Tomaselli et al. [9], Felske et al. [10], Powell and Zinn [11], and Habib and Vervisch [12] one is always confronted with the dilemma as to which value to use in a particular application. For example, radiative flux calculations can differ by a factor of two when a spectral variation of 20 percent in the optical properties is considered [7]. On the other hand, in the case of laser diagnostics, Harris and Weiner [13], among others, have pointed out that mass growth rates of soot may differ by 100 percent or more when different refractive indices are employed in the data analysis.
The techniques that have been used for determining the spectral variation of the index of refraction may be divided into two categories—those which have employed *in-situ* measurements and those which have performed measurements on soot particles extracted from flames (= *ex situ*). *In situ* techniques have been employed by Chippet and Gray [4], Lee and Tien [7] and Habib and Vervisch [12], who used spectral transmittance measurements, and by Erickson *et al.* [1], Bockhorn *et al.* [6] and Powell and Zinn [11], who determined the optical properties from scattering measurements at various angles in both planes of polarization.

*Ex situ* studies have utilized two methods. In one method, used by Dalzell and Sarofim [3], Tomaseli *et al.* [9] and Felske *et al.* [10], the soot particles were collected with sampling probes or water cooled plates and then compressed into smooth surfaced pellets. The reflection coefficients are then measured in both planes of polarization as a function of the angle and wavelength and the optical properties are determined by matching the reflection data to the Fresnel equations. The problem associated with the reflection measurement is that the pellet is a two phase mixture of particle and void, and the inferred properties are not of the particles but rather of the mixture. However, it was demonstrated that at infrared wavelengths, these problems can be overcome [10]. In the other method, utilized by Janzen [5] the particles are dispersed in a medium of known refractive index and then the spectral transmittance of the mixture is measured. A fundamental problem that arises with respect to all *ex situ* techniques is that the particle morphology and
temperature is not representative of the soot particles under flame conditions.

The *in situ* method employing only transmittance measurements requires the introduction of a theory for the dispersion of the optical properties with wavelength in order to reduce the data. Chippet and Gray [4] assumed no dispersion at all which is the least accurate assumption to make. Lee and Tien [7] on the other hand, employed the multivariable Drude-Lorentz dispersion model. However, there are inherent limitations to this approach both in terms of the applicability of the Drude-Lorentz dispersion model, and as it has been pointed out by Latimer [14] and Janzen [5,15] in terms of the unknown parameters that can be extracted from spectral transmittance measurements.

The *in situ* techniques which employ angular scattering measurements will allow the determination of the refractive index and particle size when the particles are large enough spheres to yield angular distribution of scattered light that has a unique dependence on the combination of refractive index and size [16]. However, as it has been demonstrated by Wersborg *et al.* [17] and by Prado and Lahaye [18] unagglomerated soot particles in the flames are always of Rayleigh size, and, hence this technique cannot be used to determine the refractive index. On the other hand, as it has been shown by Erickson *et al.* [1], Dalzell *et al.* [19], and by Bockhorn *et al.* [6] the angular distribution of scattered light from agglomerated soot particles does depend on the refractive index. Nevertheless, interpretation of the measured angular distribution requires knowledge of the precise morphological
features of the agglomerate and this has yet to be established.

Recently, Charalampopoulos and Felske [20] demonstrated that by using dynamic light scattering to obtain the particle size distribution and by measuring the extinction and scattering coefficient at the same position in a premixed flame, the soot number densities, and the refractive index, can be determined by introducing a relation between the real and imaginary part of the complex electrical permittivity.

The present study aims in the spectral determination of the complex index of refraction of soot from measurements of scattering and extinction coefficients in hydrocarbon flames. In chapter 2, the classical and dynamic light scattering theories are presented briefly. Then in chapter 3, the optical properties of soot particles in the visible wavelength are presented. The particle size distribution is determined from the photon correlation measurement. The number densities, volume fractions and refractive indices are then determined as a function of the height above the burner and fuel equivalence ratio for premixed propane/oxygen and methane/oxygen flames. Chapter 4 deals with the Kramers-Kronig theory and calculations using simulated data to test the theory and to analyze the effects of extrapolation, polydispersity as well as uncertainties in the measurements. Then in chapter 5, the experimental methods and data analysis that yields for the first time the complex index of refraction of soot particles over all wavelengths are presented. This is accomplished using spectral extinction measurements, number densities, and particle size distribution obtained from the same point in the flame. A summary
of the results along with some recommendations for future work are presented in Chapter 6.
Chapter 2

Light Scattering Theory

2.1 Classical Light Scattering

When a particle is illuminated by an electromagnetic wave, electric charges in the particle are set into oscillatory motion by the electric field of the incident wave. These oscillating electric charges radiate electromagnetic energy in all directions, that energy is called scattered light. In addition to reradiating electromagnetic energy, the excited electric charge transforms part of the incident energy into other forms, a process called absorption.

Consider a cloud of spherical soot particles that is illuminated by a beam of light [Figure 2.1]. The plane containing the incident light beam and the line of sight to the detector define a plane called the scattering plane. In the Figure 2.1 this is the \( x - y \) plane and in the present experiments this plane is horizontal. The measured scattered light \( S \) is related to the properties of the particles and the parameters of the optical system [21,28] by the expression

\[
S_{pp} = I_o \Delta \Omega \Delta V \sigma_{pp} \eta_o \tau_\lambda, \quad (2.1)
\]
Figure 2.1: Typical light extinction schematic
where $I_o$ is the incident energy flux, $\Delta \Omega$ is the solid angle aperture of the collection optics, $\Delta V$ is the scattering volume, $\eta_o$ accounts for the efficiency of the optical and electronic components, the subscript $p$ denotes the polarization state (vertical or horizontal), and the double subscript indicates the states of polarization of the incident and scattered beams. The parameter $\sigma_{pp} \, (cm^{-1} \, str^{-1})$ denotes a differential scattering coefficient and is defined as the energy scattered per unit time and per unit volume into a unit solid angle about a direction $\theta$.

Since the scattering intensity is attenuated as the light travels between the scattering volume and the detector the factor, $\tau_\lambda$, was introduced to account for this attenuation. It is noted that the attenuation of the scattering intensity beyond the flame boundaries will be insignificant. This is due both to the low absorption coefficient of air at the laser wavelength (0.488 $\mu$m) and to the relatively short pathlength ($\sim 0.47$ m). Thus, the factor $\tau_\lambda$ can be taken as being equal to the transmission through the flame.

The differential scattering coefficient for a size distribution of particles is given by

$$\sigma_{pp} = N \overline{C}_{pp}, \quad (2.2)$$

where $N \, (cm^{-3})$ is the particle number density and $\overline{C}_{pp} \, (cm^2 \, str^{-1})$ is the mean differential scattering cross-section for all spheres in the scattering volume given by

$$\overline{C}_{pp} = \int_{r=0}^{\infty} C_{pp} P(r) dr. \quad (2.3)$$

The differential scattering cross-section for a single spherical particle of radius $r$ is
given by the expression

\[ C_{pp} = \frac{\lambda^2}{4\pi^2} i_{pp}, \]  

(2.4)

where \( i_{pp} \) are the Mie scattering amplitude functions [22].

\[ ivv = \left| \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n + 1)} (a_n \pi_n + b_n \tau_n) \right|^2, \]

\[ i_{HH} = \left| \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n + 1)} (a_n \tau_n + b_n \pi_n) \right|^2. \]

(2.5)

(2.6)

The functions \( a_n \) and \( b_n \) are the electric and magnetic multipole coefficients of the scattered light expressed in terms of the size parameter \( x = 2\pi r/\lambda \) and complex refractive index \( \bar{n} = n - ik \). The functions \( \pi_n \) and \( \tau_n \) are expressed in terms of the associated Legendre polynomials and depend only on the scattering angle \( \theta \). The function \( P(r) \) represents the size distribution of the particles and in this study is taken to be the zeroth order lognormal distribution function (ZOLD) [16]. For a distribution of sizes with average particle radius \( r_o \) and geometric width \( \sigma \), \( P(r) \) may be expressed as

\[ P(r) = \frac{\exp(-ln^2\sigma/2)}{\sqrt{2\pi r_o ln\sigma}} \exp \left[ -\frac{ln^2 r/r_o}{2ln^2\sigma} \right]. \]

(2.7)

Since a flat flame configuration is used in the present study, the geometric path length transversed by the laser beam may be considered as homogeneous. Furthermore, the multiple scattering is negligible since in the present study the particles are considered as a dilute suspension in the flame (the soot volume fraction is of
the order $10^{-6}$). Thus the transmittance, $\tau_\lambda$, of the flame is given by

$$\tau_\lambda = \frac{I(L)}{I_0}$$  \hspace{1cm} (2.8)

$$= \exp(-K_{ext}L),$$  \hspace{1cm} (2.9)

where $L$ is the path length through the flame and $K_{ext}$ (cm$^{-1}$) is the extinction coefficient, which for polydisperse spheres may be written as

$$K_{ext} = N\overline{C}_{ext},$$  \hspace{1cm} (2.10)

where $\overline{C}_{ext}$ (cm$^2$) is the mean extinction cross-section defined as

$$\overline{C}_{ext} = \int_{r=0}^{\infty} C_{ext}P(r)dr.$$  \hspace{1cm} (2.11)

The term $C_{ext}$ represents the extinction cross-section of a single spherical particle and is given by the Mie theory [45] as

$$C_{ext} = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n+1)Re(a_n + b_n),$$  \hspace{1cm} (2.12)

where $Re(a_n + b_n)$ denotes the real part of $(a_n + b_n)$.

The above results for scattering and extinction are valid for spherical particles of arbitrary size. However, during the initial stages of soot formation in the flame, the particle diameters are much smaller than the wavelength ($\lambda = 0.488 \mu m$) of the incident laser beam. Thus, their scattering and absorption cross sections can be approximated by the Rayleigh limit of the Mie theory. In this limit, the differential
scattering cross-section of a single particle [16,22,23] in the vertical polarization orientation reduces to

\[ C_{VV} = \left( \frac{2\pi}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 r^6, \quad (2.13) \]

and in the horizontal polarization orientation is given by

\[ C_{HH} = C_{VV} \cos^2 \theta. \quad (2.14) \]

On the other hand, the extinction cross-section of the particle is expressed as

\[ C_{ext} = -\frac{8\pi^2}{\lambda} \text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) r^3, \quad (2.15) \]

in which \( \text{Im} \) denotes the imaginary part of the complex quantities.

Combining equations (2.3), (2.13) and (2.7) and substituting into equation (2.2) yields a relation for the differential scattering coefficient for Rayleigh size polydisperse particles given by

\[ \sigma_{VV} = N \left( \frac{2\pi}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 r^6 \exp(24\ln^2 \sigma). \quad (2.16) \]

Similarly, the extinction coefficient of Rayleigh size polydisperse particles may be obtained by combining equations (2.11), (2.15) and (2.7) and substituting into equation (2.10). Thus \( K_{ext} \) may be expressed as

\[ K_{ext} = -N \frac{8\pi^2}{\lambda} \text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) r^3 \exp(7.5\ln^2 \sigma). \quad (2.17) \]

It should be noted that the most probable particle radius, \( r_0 \), and the geometric width of the size distribution, \( \sigma \), are determined from photon correlation measure-
ments. The principles of the photon correlation technique and the method for determining the parameters \( r_0 \) and \( \sigma \) are presented in the next section.

### 2.2 Dynamic Light Scattering

The soot particles in the flame exhibit a continuously random motion due to temperature. As a result, both the phase and amplitude of the scattered field are continuously modulated and hence the intensity of the field possesses a random fluctuation in time about a mean value. The mean value is defined as the classical light scattering intensity. In dynamic light scattering the fluctuations are analyzed. From this data, the diffusional diameter can be inferred without knowing the refractive index of the particles [24-26]. In the homodyne mode, when the scattered light is temporally Gaussian, the time autocorrelation function \( C(t) \) [24] may be written as

\[
C(t) \propto B \left\{ 1 + b \left[ \exp \left( -\frac{V^2 t^2}{4 \sigma_o^2} \right) \exp(-t/\tau) \right]^2 \right\},
\]

(2.18)

in which \( B \) is the value of the autocorrelation function at large time, \( b \) is an experimental constant, \( V \) is the bulk flow velocity, \( \sigma_o \) is the width of the Gaussian profile of the incident laser beam, and \( \tau \) is the characteristic diffusional time scale of the particles. It is noted that the first exponential term accounts for the nonuniform illumination of the sensing volume and for low flow velocities (typically in the order
of 2 cm/sec for the present study) \( \exp(-V^2t^2/4\sigma^2) \approx 1 \) across the decay time of \( \exp(-t/\tau) \). Hence, to a good approximation, equation (2.18) may be written as

\[
C(t) = B \left\{ 1 + b[\exp(-\Gamma t)]^2 \right\}, \quad (2.19)
\]

where

\[
\Gamma = \frac{1}{\tau} = |q|^2 D, \quad (2.20)
\]

in which \( D \) is the diffusion coefficient of the particles and \( q \) is the scattering wave vector with its magnitude given by

\[
|q| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. \quad (2.21)
\]

In sooting flames a distribution of particles is present, and hence there is a corresponding distribution of linewidths \( \Gamma \). In this case, the measured autocorrelation function takes the form

\[
\frac{C(t)}{B} = b \left[ \int_0^\infty G(\Gamma) \exp(-\Gamma t) d\Gamma \right]^2 \quad (2.22)
\]

where \( G(\Gamma) \) is the normalized distribution of linewidths \( \Gamma \), characterized by two parameters-its mean \( \bar{\Gamma} \) and its variance \( \epsilon \). The diffusion coefficient can therefore be inferred from the decay rate of the measured \( C(t) \). The particle radius can then be determined since, for a spherical particle, the radius \( r \) is related to the diffusion coefficient \( D \) by the expression

\[
D = \frac{K_B T}{6\pi \mu r} C_s, \quad (2.23)
\]
where \( K_B \) is the Boltzmann constant, \( \mu \) is the viscosity and \( T \) is the temperature of the host medium. \( C_s \) is the Cunningham correction factor, which accounts for the increased mobility of the particle due to noncontinuum effects. This semiempirical factor is given by [27,47]

\[
C_s = 1.0 + [1.257 + 0.4\exp(-1.1r/l)]l/r, \tag{2.24}
\]

where \( l \) is the mean free path of the gas molecules. To determine the most probable radius, \( r_o \), and the geometric width of the distribution, \( \sigma \), it is first noted, that for the Rayleigh size polydisperse spheres the average decay rate, \( \bar{\Gamma} \), may be expressed as

\[
\bar{\Gamma} = \frac{\int_0^\infty r^6 \Gamma(r)P(r)dr}{\int_0^\infty r^6 P(r)dr}, \tag{2.25}
\]

whereas the variance of the distribution, \( \epsilon \), is related to the linewidth, \( \Gamma(r) \), and to the measured average decay rate, \( \bar{\Gamma} \), by the relation

\[
\epsilon = \frac{\int_0^\infty [\Gamma(r) - \bar{\Gamma}]^2 P(r)dr}{\bar{\Gamma}^2 \int_0^\infty r^6 P(r)dr}. \tag{2.26}
\]

The average decay rate, \( \bar{\Gamma} \), and the variance, \( \epsilon \), (polydispersity index) are obtained from the measured autocorrelation function, \( C(t) \), whereas the parameters, \( r_o \) and \( \sigma \), are determined by solving equations (2.25) and (2.26) simultaneously. A detailed presentation of the dynamic light scattering theory may be found in the references [48-51]. More details about the actual photon correlation measurements and the method of data analysis will be presented in the next chapter.
Chapter 3

In-Situ Optical Properties of Soot Particles in the Visible Wavelengths

3.1 Experimental Facility

The experimental facility for light scattering and extinction measurements consists of light sources, optics for focusing the incident light beam, burner system for premixed flame, optics for collecting the scattered light, detectors, and signal processing system. Figure 3.1 shows the planar view of the light scattering system. The facility allows both the classical and dynamic light scattering measurements to be made on the same scattering volume in the flame. This is accomplished by using the same detector/detection optics for each measurement and processing the signal in two different ways. The signal for the dynamic light scattering measurements is processed in a digital mode (using photon counting) and is analyzed by a digital autocorrelator. For the classical light scattering measurements the light beam is chopped and the detected signal is processed in an analog mode so that
the lock-in detection system can separate the scattered signal from the background flame emission.

A vertically polarized, 5W, model 164 Spectra Physics argon-ion laser is used. When performing the classical scattering and extinction measurements the beam is chopped by a mechanical chopper [model 196 of Princeton Applied Research (PAR)]. The spatial resolution and the signal to noise ratio are simultaneously improved by focusing the laser beam by lens L1 (see Figure 3.1) down to a spot size of 0.103 mm. The scattering volume is focused on the diaphragm D4 by lens L2. The distance of the lens L2 from the central axis of the flame is selected to be twice the focal length \( f = 125 \text{ mm} \) of the lens as is the distance of the diaphragm D4 from the lens. As a result, an image of the sampling volume is formed at the center of the diaphragm D4 with magnification of unity.

The premixed propane/oxygen and methane/oxygen flames are supported on a water-cooled porous plug burner. The burner consists of 60-mm-diameter central region surrounded by a 4-mm-wide annular region which allows for a shroud of nitrogen to be employed (see Figure 3.2). The flame is stabilized by a Corning honeycomb made of cordierie with 31 cells per square centimeter, 144 mm in diameter and 76 mm long. The stabilizer is supported firmly on the burner so that its position with respect to the burner surface is fixed when the burner is moving with respect to the light beams and the focusing and detection optics.

The detection optics are mounted on an electronically driven arm that allows
Figure 3.1: Plan view of the light scattering system
Figure 3.2: Premixed flat flame burner
scattering measurements in the range of ± 160° with respect to the forward direction. The performance of the mechanical, optical and electronic components is tested by performing angular scattering measurements from nitrogen molecules in both planes of polarization [56].

3.2 Experimental Measurements

The quantities that were measured in this part of the present study are: (1) autocorrelation for propane/oxygen and methane/oxygen flames at a scattering angle 7.5° and wavelength 0.488 μm, (b) scattering and extinction coefficients at the wavelengths 0.4577, 0.4729, 0.488, 0.5017 and 0.5145 μm for propane/oxygen flame with φ = 1.8, (3) scattering and extinction coefficients for propane/oxygen and methane/oxygen flames with various fuel equivalence ratios at 0.488 μm, and (4) extinction coefficients in the wavelength range 0.34 μm to 0.6 μm for propane/oxygen flame with fuel equivalence ratio φ = 1.8. Various fuel to oxidizer ratios were considered in order to assess their effect on the refractive index of flame soot. The fuel equivalence ratio is defined as

$$\phi = \frac{[\text{mass fuel/mass oxidizer}]_{\text{actual}}}{[\text{mass fuel/mass oxidizer}]_{\text{stoichiometric}}}.$$  (3.1)

Measurements were performed in a premixed propane/oxygen flame with fuel equivalence ratio φ = 1.8, 2.1, and 2.4 and flow rate of the gas mixture 178 liters per hour corresponding to a unburned gas velocity 1.75 cm/sec as well as methane/oxygen
flames with $\phi = 2.2, 2.4, \text{ and } 2.6 \text{ and flow rate of 229 liters per hour corresponding to a unburned gas velocity } 2.2 \text{ cm/sec, under identical flame stabilization conditions. Such low unburned gas velocity, as it may be seen from equation (2.18), results in reduction of the nonuniform illumination effects on the photocorrelation measurements. The flame was surrounded by a shroud of nitrogen gas with a velocity of } 5.6 \text{ cm/sec.}

3.2.1 Photon Correlation Measurements

The photon pulses generated by the photomultiplier tube (EMI, 9863B/350) were amplified and discriminated by an amplifier discriminator (model 1182, PAR) with a threshold level adjustable from 150 mV to 500 mV. The standarized pulses were autocorrelated at each position above the burner surface by a Langly Ford correlator (Model 1096) and were analyzed by the method of cummulants introduced by Pusey et al. [52]. The mean decay rate, $\bar{\Gamma}$, and the variance, $\epsilon$, of the distribution is determined by performing a weighted least squares fit of a quadratic equation to the natural log of the measured autocorrelation function after the baseline has been subtracted. Assuming that the particle polydispersity is not too large from equation (2.22) it follows that

$$\ln[C(m\Delta t) - B] = \ln\alpha - 2\bar{\Gamma}(m\Delta t) + \epsilon\bar{\Gamma}^2(\Delta t)^2, \quad (3.2)$$
where $m$ is the correlator channel number and $\Delta t$ is the sampling time. Data analysis will therefore yield the parameters $\alpha$, $\bar{r}$ and $\epsilon$. The geometric width $\sigma$ and the most probable radius $r_\sigma$ is obtained by combining the measured $\bar{r}$ and $\epsilon$ with equations (2.25) - (2.26).

The gas temperatures were measured by a Pt-Pt/13% Rd thermocouple. The mean free path and gas viscosities were computed from standard correlations [53] using the measured temperature and estimated gas compositions. The result of the analysis is presented in Table 3.1 (the results for the propane flames with $\phi = 2.1, 2.4$ and methane flames are listed in pages 46 - 52). It is noted that in all cases the geometric width $\sigma$ has the tendency to decrease with position above the burner surface. The same trends were observed in a previous study [29]. A possible explanation for such trends may be that for this type of rich flames the agglomeration process starts at the early stages of soot formation. As a result, the photon correlation technique, due to its high sensitivity for small particle sizes and sampling times, yields at lower heights a more realistic representation of the size distribution characterized by a larger $\sigma$. At positions beyond the reaction zone, the agglomerates possess larger effective diffusional diameters, and thus the photon correlation technique being less sensitive to larger sampling times and larger sizes yields an average distribution with narrower geometric width. Figures 3.3 and 3.4 compare the measured autocorrelations at heights 8 and 12 mm for the propane/oxygen flames $\phi = 1.8$ with the predictions of equation (3.2). The com-
Table 3.1: Photon correlation results for the propane/oxygen flame with $\phi = 1.8$.

<table>
<thead>
<tr>
<th>H (mm)</th>
<th>T (K)</th>
<th>$\Gamma \times 10^{-4}$ (rad/s)</th>
<th>$\varepsilon$</th>
<th>$r_0$ (nm)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1330</td>
<td>13.5</td>
<td>.232</td>
<td>16.8</td>
<td>1.258</td>
</tr>
<tr>
<td>7</td>
<td>1285</td>
<td>4.31</td>
<td>.221</td>
<td>20.2</td>
<td>1.256</td>
</tr>
<tr>
<td>8</td>
<td>1250</td>
<td>2.38</td>
<td>.198</td>
<td>23.8</td>
<td>1.247</td>
</tr>
<tr>
<td>9</td>
<td>1225</td>
<td>1.89</td>
<td>.201</td>
<td>26.9</td>
<td>1.248</td>
</tr>
<tr>
<td>10</td>
<td>1195</td>
<td>1.68</td>
<td>.196</td>
<td>27.0</td>
<td>1.244</td>
</tr>
<tr>
<td>11</td>
<td>1170</td>
<td>1.52</td>
<td>.188</td>
<td>30.0</td>
<td>1.239</td>
</tr>
<tr>
<td>12</td>
<td>1150</td>
<td>1.36</td>
<td>.173</td>
<td>31.5</td>
<td>1.229</td>
</tr>
<tr>
<td>13</td>
<td>1145</td>
<td>1.20</td>
<td>.176</td>
<td>33.7</td>
<td>1.230</td>
</tr>
<tr>
<td>14</td>
<td>1130</td>
<td>1.09</td>
<td>.173</td>
<td>35.2</td>
<td>1.229</td>
</tr>
<tr>
<td>16</td>
<td>1100</td>
<td>0.97</td>
<td>.180</td>
<td>36.5</td>
<td>1.231</td>
</tr>
</tbody>
</table>
puted autocorrelations were based on particle sizes inferred from the ratio of the scattering and extinction coefficients $[\sigma_{VV}(90)/K_{est}]$ using the refractive indices proposed by Dalzell and Sarofim [3] and Lee and Tien [7]. It is clear, that at the height of 8 mm above the burner surface, one of the predicted autocorrelations is in good agreement with the data. However, the differences are amplified by assigning the same refractive index throughout the flame. The method for determining the scattering/extinction coefficients is presented in the following section.

### 3.2.2 Scattering and Extinction Measurements

The differential scattering coefficient of soot particles at 90° are inferred through an internal calibration procedure [54]. Using this procedure the scattering coefficient of the soot particles, at a wavelength, $\lambda$, are obtained from the relation

$$\sigma_{VV}(90), \text{soot}|_\lambda = \sigma_{VV}(90), CH_4|_\lambda \frac{S_{VV}(90), \text{soot}|_\lambda \tau_g}{S_{VV}(90), CH_4|_\lambda \tau_\lambda},$$

(3.3)

where $S_{VV}$ are the scattered fluxes for soot and methane molecules, and $\sigma_{VV}(90)$, $CH_4|_\lambda$ is the differential scattering coefficient of methane molecules at standard temperature and pressure conditions. The factor $(\tau_g/\tau_\lambda)$ was introduced to account for the attenuation of the laser beam before the scattering volume and the attenuation of the scattered flux between the scattering volume and detector. Specifically, $\tau_g$ represents the attenuation through the stream of the methane molecules and $\tau_\lambda$ represents the attenuation through the flame.
Figure 3.3: Measured and predicted intensity autocorrelation functions at a height 8 mm above the burner surface. Points are the data; dotted lines are the predictions with refractive indices $\bar{m} = 1.57 - 0.56i$ and $\bar{m} = 1.90 - 0.55i$; solid line is the prediction of Eq.(3.2).
Figure 3.4: Measured and predicted intensity autocorrelation functions at a height 12 mm above the burner surface. Points are the data; dotted lines are the predic­tions with refractive indices $\bar{m} = 1.57 - 0.56i$ and $\bar{m} = 1.90 - 0.55i$; solid line is the prediction of Eq.(3.2).
It is to be emphasized that the measurement of the molecular scattered fluxes required prolonged experimentation periods due to the low level light signal. For example, at a height of 6 mm above the burner surface the scattered flux from the soot particles was approximately 200 times larger than the flux from the methane molecules. To ensure repeatability of the measured differential scattering coefficient of soot the ratio of the scattered fluxes from pure methane and oxygen molecules was determined prior to each measurement. Furthermore, the light chopper was set at a high frequency (2360 Hz) in order to maximize the reduction of the noise associated with the preamplifier of the lock-in detection system and therefore improve signal stability. The measured ratio of methane to oxygen scattered fluxes was in the range 2.3 to 2.5 whereas the reported literature value of the ratio is 2.6. The determination of the extinction coefficients, on the other hand, requires no calibration since they are obtained from the transmission which is a relative measurement. The extinction coefficients that yielded the second independent piece of information were measured with a power meter (model 404, Spectra Physics).

A tunable argon-ion laser was used for the measurements of the scattering and extinction coefficients for propane/oxygen flame with $\phi = 1.8$ at the wavelengths presented in Table 3.2. Although laser emission was observed at 0.4658 $\mu$m and 0.4965 $\mu$m scattering measurements were not possible due to the poor stability of the laser output. Measurements of the scattering and extinction coefficients for propane/oxygen and methane/oxygen flames with various fuel equivalence ratios
Table 3.2: Measured scattering [$\sigma_{VV}(90^\circ)$] and extinction coefficients ($K_{ext}$) for the propane/oxygen flame with $\phi = 1.8$.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$H$ (mm)</th>
<th>$\sigma_{VV}$ (cm$^{-1}$str$^{-1}$)</th>
<th>$K_{ext}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>457.9</td>
<td>6</td>
<td>$1.50 \times 10^{-4}$</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$5.30 \times 10^{-4}$</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$1.08 \times 10^{-3}$</td>
<td>0.106</td>
</tr>
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<td></td>
<td>12</td>
<td>$1.70 \times 10^{-3}$</td>
<td>0.127</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>$2.14 \times 10^{-3}$</td>
<td>0.141</td>
</tr>
<tr>
<td>472.9</td>
<td>6</td>
<td>$1.40 \times 10^{-4}$</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$4.70 \times 10^{-4}$</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$9.60 \times 10^{-4}$</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$1.45 \times 10^{-3}$</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>$1.84 \times 10^{-3}$</td>
<td>0.135</td>
</tr>
<tr>
<td>488.0</td>
<td>5</td>
<td>$0.60 \times 10^{-4}$</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$1.50 \times 10^{-4}$</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>$2.70 \times 10^{-4}$</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$4.20 \times 10^{-4}$</td>
<td>0.070</td>
</tr>
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<td>9</td>
<td>$5.90 \times 10^{-4}$</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$7.40 \times 10^{-4}$</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>$8.80 \times 10^{-4}$</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$1.06 \times 10^{-3}$</td>
<td>0.103</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>$1.18 \times 10^{-3}$</td>
<td>0.110</td>
</tr>
<tr>
<td>501.7</td>
<td>6</td>
<td>$1.20 \times 10^{-4}$</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$1.30 \times 10^{-4}$</td>
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<td>0.085</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$1.14 \times 10^{-3}$</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>$1.49 \times 10^{-3}$</td>
<td>0.113</td>
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<td>0.039</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
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<td>$6.50 \times 10^{-4}$</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$1.00 \times 10^{-3}$</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>$1.29 \times 10^{-3}$</td>
<td>0.103</td>
</tr>
</tbody>
</table>
were also carried out. The results are shown in Tables 3.11 - 3.13 (see page 53) as function of height above the burner surface. Additional spectral transmission measurements were carried out by focusing the light beam emerging from a 150 Watt Xenon lamp onto the central axis of the burner by the set of lenses L3-L5 shown in Figure 3.1. The transmitted light beam was analyzed by an ORIEL monochromator (model 77250) and the transmitted intensity was measured by an RCA 1P28 photomultiplier tube. More details about the spectral transmission measurements will be presented in Chapter 5.

3.3 Data Analysis and Discussion

3.3.1 Sensitivity of Optical Measurements to the Refractive Indices

As it was pointed out in Chapter 1 the radiative flux calculations and mass growth rate of soot can vary considerably when different refractive indices are employed. This is also true for particle size and volume fraction calculations. Various investigators have determined soot particle sizes in flames by reducing the scattering/extinction data using a constant refractive index (see, for example, Prado et al. [18]). It is noted that the particle size can differ by 29%, the number density by 28%, and the volume fraction by 58% when two different refractive indices, \( \bar{m} = 2.0 - 0.95i \) [57] and \( 1.46 - 0.27i \) [12] are employed in the data analysis. In this section, the sensitivity of the particle size, volume fraction, spectral emissivity and
of the radiative flux to the values of the reported range of the refractive indices is presented.

The sensitivity of particle size to the refractive index is assessed by considering the ratio of equations (2.2) and (2.10) in conjunction with the Rayleigh limit equations (2.13) and (2.15) and using the measured values of $K_{ext} = 0.047 \ cm^{-1}$ and $\sigma = 1.5 \times 10^{-4} \ cm^{-1} \ sr^{-1}$ at the wavelength $\lambda = 0.488 \ \mu m$. The particle radius is computed by varying $n$ from 1.3 to 2.0 and $k$ from 0.3 to 1.0 as shown in Figure 3.5. It is noted that the particle radius changes by approximately 76 percent when $n$ decrease from 2.0 to 1.3 and is relatively insensitive to $k$. The volume fraction, $V_f$, is calculated from the relation $V_f = 4\pi r^3 N / S$ and as shown in Figure 3.6 it changes by a factor of two for the same range of values of the real part $n$. The effect of change in the imaginary part is more pronounced in the changes of the volume fraction. As it may be seen from Figure 3.6 when $k$ varies in the range $0.3 < k < 1$, $V_f$ may change by a factor 3.

For homogeneous pathlengths the spectral emissivity of the flame, $\epsilon_\lambda$, can be obtained from the relation

$$\epsilon_\lambda = 1 - \exp(-K_{ext} L),$$

(3.4)

where the extinction coefficient, $K_{ext}$ [see equation (2.10)], is computed from the Mie equations with the values of $N = 10^{10} \ cm^{-3}$ and $L = 5 \ cm$ at the wavelength of $0.63 \ \mu m$. Figure 3.7 shows a strong dependence ($\sim$ a factor of two) of the spectral emissivity on the imaginary part of the index. On the other hand, the dependence
Figure 3.5: Sensitivity of the particle size with respect to the refractive index
Figure 3.6: Sensitivity of the volume fraction with respect to the refractive index
Figure 3.7: Sensitivity of the spectral emissivity with respect to the refractive index
of radiative flux per unit area, \( q'' \), on the refractive index can be estimated from the expression

\[
q'' = \int_0^\infty \epsilon_\lambda e_{\lambda \lambda} d\lambda,
\]

where \( e_{\lambda \lambda} \) is Planck's spectral distribution of emissive power and \( \epsilon_\lambda \) is computed using the Drude-Lorentz relations with the dispersion constants shown in Table 3.17. The effect of using the dispersion constants proposed by various investigators were assessed by varying simultaneously both the real and imaginary part of the index by the same amount. Figure 3.8 displays a linear variation of \( q'' \) in the range of -40 to +40 percent change in the index. The effect of the individual variations of \( n \) and \( k \) in \( q'' \) is shown in Figure 3.9.

### 3.3.2 Data Analysis

1. **Visible Wavelengths - Constant Fuel Equivalence Ratio (\( \phi = 1.8 \))**

Equations (2.2) and (2.10) provide two independent pieces of information for the determination of the three unknowns \( n \), \( k \) and \( N \) for polydisperse particles. An additional, independent relationship is obtained by introducing the ratio between the real and imaginary part of the complex electrical permittivity [20] expressed as

\[
\frac{n^2 - k^2 - 1}{2nk} = R_\lambda,
\]

where \( R_\lambda \) may be evaluated from the data for graphite [55]. For the argon-ion laser used in this study the values of \( R_\lambda \) are 0.531, 0.528, 0.517, 0.514 and 0.508 at the
Figure 3.8: Sensitivity of radiative flux with respect to the refractive index
Figure 3.9: Sensitivity of radiative flux with respect to the refractive index
wavelengths 0.4579, 0.4729, 0.488, 0.5017 and 0.5145 μm, respectively. Therefore, the real and imaginary part of the index at the laser wavelength λ and the number density \( N \) are determined by solving equations (2.2), (2.10) and (3.6) using the measured values of \( \sigma_{VV}(90), K_{ext}, \tau_o \) and \( \sigma \). Since the size parameter increases with height above the burner surface beyond the Rayleigh limit, the complete Mie solution was utilized to infer \( n, k \) and \( N \). A comparison between the Rayleigh limit and the Mie solution results showed that the Rayleigh solution yields number densities higher by 19 percent over all heights whereas \( n \) and \( k \) are underpredicted by 4.3 and 9.3 percent respectively for the propane/oxygen flame \( \phi = 1.8 \).

For monodisperse particles, equations (2.2) and (2.10) are solved from the ratio of the scattering and extinction coefficients \( [\sigma_{VV}/K_{ext}] \):

\[
\frac{\sigma_{VV}}{K_{ext}} = \frac{i_{VV}}{\pi x^2 Q_{ext}},
\]

(3.7)

where \( Q_{ext} \) is the extinction efficiency defined as

\[
Q_{ext} = C_{ext}/\pi r^2.
\]

(3.8)

The ratio \( \sigma_{VV}/K_{ext} \) is determined from experiment whereas the right hand side can be calculated from the Mie theory [46] by iteration until equations (3.7) and (3.6) are simultaneously satisfied. The number density, \( N \), is then determined from equation (2.2) or (2.10) with the known values of \( n \) and \( k \).

For polydisperse particles, the ratio \( [\sigma_{VV}/K_{ext}] \) is expressed as

\[
\frac{\sigma_{VV}}{K_{ext}} = \frac{\lambda^2}{4\pi^3} \int_0^\infty \frac{i_{VV} P(r) dr}{Q_{ext} r^2 P(r) dr}
\]

(3.9)
The procedure for determining \( n \), \( k \) and \( N \) in the polydisperse case is similar to that for the monodisperse.

The inferred \( n \) and \( k \) at wavelengths 0.4579, 0.4729, 0.488, 0.5017 and 0.5145 \( \mu \text{m} \) are shown in Figure 3.10. For a given position in the flame (12 mm) the indices of glassy carbon are in good agreement with the measured real and imaginary parts of the index. The indices of soot particles for the other positions in the flame are seen to be different from the properties of graphite [55]. These differences may be attributed to the fact that the existing soot dispersion models do not account for changes in the electron number densities as the soot matures in the flame.

The volume fractions of soot determined with constant refractive indices (\( \bar{m} = 1.57 - 0.56i \) [3] and \( \bar{m} = 1.90 - 0.55i \) [7]) through the flame differ by 13.5 percent and 36.5 percent respectively when compared with the results determined with variable refractive indices for the propane/oxygen flame with \( \phi = 1.8 \). Significant variations in the mass growth rates are also noted with respect to the residence time when a single refractive index is used throughout the flame (see Figure 3.11).

The sensitivity of the quantities, \( n \), \( k \) and \( N \), to each of the parameters, \( \sigma \), \( r \lambda \), \( r \) and \( R \lambda \), was assessed assuming \( \pm 5\% \) random errors in \( \sigma_V V \), \( r \), \( \lambda \), \( r \lambda \) and \( R \lambda \). This result is shown in Table 3.3. It is noted that the present scheme of data inversion depends strongly on the particle diameter and is not as sensitive to the scattering coefficient \( \sigma_V V \). For example, a 5 percent uncertainty in the scattering coefficient causes only a 0.9 percent uncertainty in \( N \), 1.6 percent in \( n \), and 3.4 in \( k \) over
Figure 3.10: Comparison of the measured optical constants for propane/oxygen flame with $\phi = 1.8$ at various heights above the burner surface with those of other investigators.
Figure 3.11: Comparison of volume fractions of soot determined with the refractive indices of the present study and with refractive indices $\bar{m} = 1.57 - 0.56i$ and $\bar{m} = 1.90 - 0.55i$. Propane/oxygen flame $\phi = 1.8$. 
all heights. The uncertainty in $N$, $n$, and $k$ based on the uncertainties in the measured quantities $\sigma_{VV}(90)$, $K_{ext}$ and the size was estimated from the expression

$$\Delta E = \pm \left\{ \left[ \frac{\partial E}{\partial \sigma_{VV}} (\Delta \sigma_{VV}) \right]^2 + \left[ \frac{\partial E}{\partial \tau_\lambda} (\Delta \tau_\lambda) \right]^2 + \left[ \frac{\partial E}{\partial r} (\Delta r) \right]^2 \right\}^{1/2},$$

where $E = (n, k, N)$ and the uncertainty in $\sigma_{VV}$ is computed according to equation (3.3). The values are presented in Table 3.4.

2. Agglomeration Effects

Apart from the uncertainty in the inferred quantities associated with the experimental measurements, several other factors may contribute to the level of accuracy of the optical properties and number density determined by the present method. Such factors include the degree of agglomeration of the primary particles into specific or arbitrary structures and the changes in carbon to hydrogen ratio of the particles due to their heterogeneous chemical activity with the gaseous species. The effect of agglomeration in the refractive index is assessed in the section that follows.

Soot particles, at the stage of their inception from morphological viewpoint, are nearly spherical units [58]. Beyond the stage of formation, agglomerated structures such as chains and clusters dominate. Jones [59] has demonstrated that when the overall agglomerate size, $l''$, is such that the size parameter ($\alpha'' = \pi l''/\lambda$) is small, the extinction and scattering cross-section may be approximated in terms of the scattering functions for spherical particles. For the purpose of the present analysis
Table 3.3: Percent uncertainties in $N$, $n$, and $k$ resulting from $\pm 5\%$ random errors in $\sigma_Y$, $\tau_\lambda$, $r$, and $R_\lambda$.

<table>
<thead>
<tr>
<th></th>
<th>$N$</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$</td>
<td>12.0</td>
<td>4.9</td>
<td>10.2</td>
</tr>
<tr>
<td>$\sigma_Y$</td>
<td>0.9</td>
<td>1.6</td>
<td>3.4</td>
</tr>
<tr>
<td>$\tau_\lambda$</td>
<td>10.2</td>
<td>1.7</td>
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</tr>
<tr>
<td>$R_\lambda$</td>
<td>3.1</td>
<td>0.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Combined (rms)</td>
<td>16.1</td>
<td>5.4</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Table 3.4: Percent uncertainties in the inferred $N$, $n$ and $k$

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$N$</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
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<td>10</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
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<td>7</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>
a 3-particle straight chain, a cluster, and a random agglomerate are considered. For all three structures the extinction and scattering cross-sections may be expressed as

\[ C_{\text{ext}, A} = C_1 N_p C_{\text{ext}, S}(\alpha_p, \bar{m}_p), \quad (3.11) \]

\[ C_{s, VV, A} = C_2 N_p^a C_{s, VV, S}(\alpha_p, \bar{m}_p), \theta = 90^\circ, \quad (3.12) \]

in which the subscript, \( A \), refers to the agglomerate, \( p \) represents the primary particle, whereas \( \text{ext} \) and \( s \) correspond to extinction and scattering respectively. \( N_p \) is the number of primary particles of the agglomerate, \( \alpha_p \) is the primary particle size parameter \((\pi d_p/\lambda)\) and \( S \) indicates that the function for a spherical particle is to be used. The constants \( C_1 \) and \( C_2 \) depend on the type of agglomerate, the number of primary particles and the primary particle size. For all three morphologies [60] the exponent \( a \) may be estimated from the expression

\[ a = 2 - 0.0573\alpha_p - 0.00115\alpha_p^2. \quad (3.13) \]

Solving simultaneously equations (3.11), (3.12) and (3.13) with \( \alpha_p = 0.1 \), at a wavelength of 488 nm, the refractive index of the primary particle of the agglomerate was estimated. Table 3.5 shows the results for the primary particle refractive index \( \bar{m}_p \) and the parameters characterizing the agglomerate. It is seen that for all three morphologies the refractive indices of the primary particles are slightly larger than that of the agglomerated particle \((\bar{m} = 1.57 - 0.65i)\). This result possesses the correct physical trend in the sense that the primary particle is expected to have a higher refractive index. Also, it is reasonable to expect that for higher positions
Table 3.5: Primary particle refractive indices and values of the parameters of the agglomerated structures.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$n_p$</th>
<th>$k_p$</th>
<th>$N_p$</th>
<th>$l'$ (nm)</th>
<th>$\alpha_r$</th>
<th>$\alpha_p$</th>
<th>$d_p$ (nm)</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-particle straight chain, $C_1 = 0.948$, $C_2 = 0.985$</td>
<td>5</td>
<td>1.587</td>
<td>0.660</td>
<td>27</td>
<td>143</td>
<td>0.92</td>
<td>0.1</td>
<td>15.5</td>
</tr>
<tr>
<td>Cluster, $C_1 = 0.943$, $C_2 = 0.870$</td>
<td>5</td>
<td>1.600</td>
<td>0.671</td>
<td>27</td>
<td>60</td>
<td>0.39</td>
<td>0.1</td>
<td>15.5</td>
</tr>
<tr>
<td>Random agglomerate, $C_1 = 0.948$, $C_2 = 0.937$</td>
<td>5</td>
<td>1.596</td>
<td>0.667</td>
<td>27</td>
<td>180</td>
<td>1.1</td>
<td>0.1</td>
<td>15.5</td>
</tr>
</tbody>
</table>

in the flame, larger differences are to be encountered because of the larger void associated with the agglomerated structures. However, a precise analysis of this effect for all positions in the flame requires expressions valid for agglomerates with larger number of primary particles.

3. Variable Fuel Equivalence Ratio

In an attempt to better understand the effects of the type of fuel and fuel equivalence ratio on the soot indices, measurements were carried out as a function of the fuel equivalence ratio for two different flames, methane/oxygen and propane/oxygen. The results are shown in Tables 3.6 - 3.13 and Figures 3.12 - 3.13.

The inferred number densities $N$ and the real and imaginary part of the index for various fuel equivalence ratios are shown in Tables 3.14 and Figures 3.14 - 3.15.

The number densities are consistent with those reported in the literature [58]. The
indices can be seen to vary substantially not only with respect to the position in the flame but also with the fuel equivalence ratio both for propane and methane flames. For example, as it may be seen from Figure 3.14 and Table 3.15 for the propane/oxygen flame when the fuel equivalence ratio increases from 1.8 to 2.4 the real part of the index may change up to 22% whereas the imaginary part by 39% for the same position in the flame.

It is not clear at the present time whether the changes in the soot refractive indices with respect to height and fuel equivalence ratio can be decoupled from the actual degree of agglomeration that prevails under flame conditions. It is also noted that the present results indicate that both the real and imaginary part of the indices increase with height at lower positions in the flame. Furthermore, it can be seen that the refractive indices for the methane/oxygen flame with $\phi = 2.6$ and for the propane/oxygen flame with $\phi = 2.4$ are much lower than those corresponding to smaller $\phi$'s and increase sharply with height. This is probably due to the lower carbon content in the soot or higher hydrogen to carbon ratio (H/C). Lower scattering and extinction coefficients (see Tables 3.11 - 3.13) and higher concentrations (see Table 3.14) than those corresponding to smaller $\phi$'s at lower positions indicate that the reaction zones could have been moved upward, further away from the burner surface. The decrease in the indices at higher positions in the flame may be attributed to the variable degree of agglomeration. Thus, it is reasonable to suggest that the compositional effects (particularly at lower heights) and the
agglomeration (particularly at higher positions) should play a more important role in the soot refractive indices.

The volume fractions for propane and methane flames are also shown in Figure 3.16 as a function of time and position above the burner surface. It is noted that the volume fractions increase by a factor of two or more when the fuel equivalence ratio increases.

Clearly, the assumption of constant refractive index throughout the flame and for different flames can be called into question. Since at the present time reliable quantitative inference for the absolute value of the soot refractive indices cannot be made due to the multiple possible effects addressed in the previous sections the present refractive indices can be considered only as "effective" and not actual material properties. For the lower positions in the flame where the sphericity assumption is reasonable due to low degree of agglomeration, it was felt that it is appropriate to utilize the spectral extinction coefficients in the visible wavelengths and determine the soot dispersion constants for comparison purposes. The details for the inference of these constants is presented in the next section.
Table 3.6: Photon correlation results for the propane/oxygen flame with $\phi = 2.1$.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$T$ (K)</th>
<th>$\Gamma \times 10^{-4}$ (rad/s)</th>
<th>$\epsilon$</th>
<th>$r_o$ (nm)</th>
<th>$\sigma$</th>
</tr>
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<tbody>
<tr>
<td>7</td>
<td>1280</td>
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</tr>
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<td>8</td>
<td>1245</td>
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</tr>
<tr>
<td>9</td>
<td>1220</td>
<td>1.61</td>
<td>.187</td>
<td>29.5</td>
<td>1.233</td>
</tr>
<tr>
<td>10</td>
<td>1285</td>
<td>1.37</td>
<td>.186</td>
<td>31.6</td>
<td>1.233</td>
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<td>11</td>
<td>1160</td>
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<tr>
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<tr>
<td>14</td>
<td>1100</td>
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<td>.191</td>
<td>37.8</td>
<td>1.237</td>
</tr>
<tr>
<td>16</td>
<td>1070</td>
<td>0.84</td>
<td>.193</td>
<td>38.6</td>
<td>1.239</td>
</tr>
</tbody>
</table>
Table 3.7: Photon correlation results for the propane/oxygen flame with $\phi = 2.4$.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$T$ (K)</th>
<th>$\Gamma \times 10^{-4}$ (rad/s)</th>
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<th>$r_o$</th>
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<td>16</td>
<td>1045</td>
<td>0.76</td>
<td>.196</td>
<td>38.0</td>
<td>1.246</td>
</tr>
</tbody>
</table>
Figure 3.12: Flame temperatures of propane/oxygen and methane/oxygen flames
Figure 3.13: Geometric widths ($\sigma$) of propane/oxygen and methane/oxygen flames
Table 3.8: Photon correlation results for the methane/oxygen flame with $\phi = 2.2$.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$T$ (K)</th>
<th>$\Gamma \times 10^{-4}$ (rad/s)</th>
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<th>$\tau_0$ (nm)</th>
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</table>
Table 3.9: Photon correlation results for the methane/oxygen flame with $\phi = 2.4$.

<table>
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<th>$r_\sigma$ (nm)</th>
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<td>1.55</td>
<td>.188</td>
<td>29.3</td>
<td>1.237</td>
</tr>
<tr>
<td>14</td>
<td>1160</td>
<td>1.32</td>
<td>.179</td>
<td>31.3</td>
<td>1.233</td>
</tr>
<tr>
<td>16</td>
<td>1130</td>
<td>1.25</td>
<td>.192</td>
<td>32.8</td>
<td>1.240</td>
</tr>
</tbody>
</table>
Table 3.10: Photon correlation results for the methane/oxygen flame with $\phi = 2.6$.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$T$ (K)</th>
<th>$\Gamma \times 10^{-4}$ (rad/s)</th>
<th>$\epsilon$</th>
<th>$r_\circ$ (nm)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1300</td>
<td>3.24</td>
<td>.202</td>
<td>19.7</td>
<td>1.244</td>
</tr>
<tr>
<td>10</td>
<td>1245</td>
<td>2.30</td>
<td>.181</td>
<td>23.7</td>
<td>1.234</td>
</tr>
<tr>
<td>11</td>
<td>1225</td>
<td>1.82</td>
<td>.181</td>
<td>26.3</td>
<td>1.234</td>
</tr>
<tr>
<td>12</td>
<td>1200</td>
<td>1.53</td>
<td>.190</td>
<td>28.7</td>
<td>1.239</td>
</tr>
<tr>
<td>13</td>
<td>1175</td>
<td>1.39</td>
<td>.194</td>
<td>30.2</td>
<td>1.241</td>
</tr>
<tr>
<td>14</td>
<td>1150</td>
<td>1.27</td>
<td>.192</td>
<td>32.3</td>
<td>1.240</td>
</tr>
<tr>
<td>16</td>
<td>1100</td>
<td>1.09</td>
<td>.195</td>
<td>34.2</td>
<td>1.241</td>
</tr>
</tbody>
</table>
Table 3.11: Measured scattering coefficients $\sigma_{VV}$ ($cm^{-1}sr^{-1}$) for the propane/oxygen flames.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>Propane/oxygen flames.</th>
<th>(\phi = 1.8)</th>
<th>(\phi = 2.1)</th>
<th>(\phi = 2.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.50x10^{-4}</td>
<td>1.61x10^{-5}</td>
<td>3.19x10^{-6}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.70x10^{-4}</td>
<td>4.09x10^{-4}</td>
<td>5.03x10^{-5}</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4.20x10^{-4}</td>
<td>8.25x10^{-4}</td>
<td>2.87x10^{-4}</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5.90x10^{-4}</td>
<td>1.24x10^{-3}</td>
<td>7.48x10^{-4}</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.40x10^{-4}</td>
<td>1.66x10^{-3}</td>
<td>1.35x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>8.80x10^{-4}</td>
<td>2.07x10^{-3}</td>
<td>1.96x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.06x10^{-3}</td>
<td>2.34x10^{-3}</td>
<td>2.54x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.18x10^{-3}</td>
<td>2.79x10^{-3}</td>
<td>3.12x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.39x10^{-3}</td>
<td>2.93x10^{-3}</td>
<td>3.56x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.60x10^{-3}</td>
<td>3.32x10^{-3}</td>
<td>4.09x10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.12: Measured scattering coefficients $\sigma_{vv}$ ($cm^{-1}sr^{-1}$) for the methane/oxygen flames.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>Methane/oxygen flames</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi = 2.2$</td>
<td>$\phi = 2.4$</td>
<td>$\phi = 2.6$</td>
</tr>
<tr>
<td>7</td>
<td>$1.27 \times 10^{-6}$</td>
<td>$1.20 \times 10^{-5}$</td>
<td>$1.19 \times 10^{-6}$</td>
</tr>
<tr>
<td>8</td>
<td>$4.33 \times 10^{-5}$</td>
<td>$5.32 \times 10^{-5}$</td>
<td>$2.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>9</td>
<td>$1.04 \times 10^{-4}$</td>
<td>$1.40 \times 10^{-4}$</td>
<td>$5.52 \times 10^{-5}$</td>
</tr>
<tr>
<td>10</td>
<td>$1.70 \times 10^{-4}$</td>
<td>$2.82 \times 10^{-4}$</td>
<td>$1.73 \times 10^{-4}$</td>
</tr>
<tr>
<td>11</td>
<td>$2.80 \times 10^{-4}$</td>
<td>$4.60 \times 10^{-4}$</td>
<td>$3.34 \times 10^{-4}$</td>
</tr>
<tr>
<td>12</td>
<td>$4.06 \times 10^{-4}$</td>
<td>$6.52 \times 10^{-4}$</td>
<td>$5.56 \times 10^{-4}$</td>
</tr>
<tr>
<td>13</td>
<td>$5.35 \times 10^{-4}$</td>
<td>$8.63 \times 10^{-4}$</td>
<td>$7.98 \times 10^{-4}$</td>
</tr>
<tr>
<td>14</td>
<td>$6.66 \times 10^{-4}$</td>
<td>$1.09 \times 10^{-3}$</td>
<td>$1.10 \times 10^{-3}$</td>
</tr>
<tr>
<td>16</td>
<td>$8.96 \times 10^{-4}$</td>
<td>$1.46 \times 10^{-3}$</td>
<td>$1.57 \times 10^{-3}$</td>
</tr>
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</table>
Table 3.13: Measured extinction coefficients $K_{ext}$ ($cm^{-1}$).

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>Propane/oxygen</th>
<th>Methane/oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi = 1.8$</td>
<td>$\phi = 2.1$</td>
</tr>
<tr>
<td>6</td>
<td>.047</td>
<td>.099</td>
</tr>
<tr>
<td>7</td>
<td>.059</td>
<td>.136</td>
</tr>
<tr>
<td>8</td>
<td>.070</td>
<td>.166</td>
</tr>
<tr>
<td>9</td>
<td>.079</td>
<td>.188</td>
</tr>
<tr>
<td>10</td>
<td>.088</td>
<td>.209</td>
</tr>
<tr>
<td>11</td>
<td>.096</td>
<td>.230</td>
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<td>12</td>
<td>.103</td>
<td>.246</td>
</tr>
<tr>
<td>13</td>
<td>.110</td>
<td>.259</td>
</tr>
<tr>
<td>14</td>
<td>.127</td>
<td>.272</td>
</tr>
<tr>
<td>15</td>
<td>.134</td>
<td>.285</td>
</tr>
</tbody>
</table>
Table 3.14: Number densities as a function of position above the burner surface and fuel equivalence ratio for the propane/oxygen and methane/oxygen flames.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>Propane/oxygen, N×10^{-9}(cm^{-9})</th>
<th>Methane/oxygen, N×10^{-9}(cm^{-9})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi = 1.8$</td>
<td>$\phi = 2.1$</td>
</tr>
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<td>7</td>
<td>10.3</td>
<td>18.4</td>
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<tr>
<td>8</td>
<td>7.4</td>
<td>12.1</td>
</tr>
<tr>
<td>9</td>
<td>5.7</td>
<td>9.3</td>
</tr>
<tr>
<td>10</td>
<td>5.2</td>
<td>8.1</td>
</tr>
<tr>
<td>11</td>
<td>4.6</td>
<td>7.5</td>
</tr>
<tr>
<td>12</td>
<td>4.3</td>
<td>6.7</td>
</tr>
<tr>
<td>13</td>
<td>3.7</td>
<td>6.2</td>
</tr>
<tr>
<td>14</td>
<td>3.4</td>
<td>6.0</td>
</tr>
<tr>
<td>16</td>
<td>3.1</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Figure 3.14: Real and imaginary part of the index as a function of the fuel equivalence ratio and height above the burner surface for the propane/oxygen flame.
Figure 3.15: Real and imaginary part of the index as a function of the fuel equivalence ratio and height above the burner surface for the methane/oxygen flame.
Table 3.15: Real and imaginary part of the index as a function of the fuel equivalence ratio and height above the burner surface for the propane/oxygen flame.

<table>
<thead>
<tr>
<th>H (mm)</th>
<th>( \phi = 1.8 )</th>
<th>( \phi = 2.1 )</th>
<th>( \phi = 2.4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n ) ( k )</td>
<td>( n ) ( k )</td>
<td>( n ) ( k )</td>
</tr>
<tr>
<td>5</td>
<td>1.57 0.65</td>
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</tr>
<tr>
<td>6</td>
<td>1.61 0.68</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1.70 0.76</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1.71 0.76 1.59 0.66</td>
<td>1.41 0.51</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.72 0.77 1.59 0.67</td>
<td>1.46 0.55</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.74 0.78 1.60 0.67</td>
<td>1.52 0.61</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.78 0.77 1.59 0.66</td>
<td>1.52 0.61</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.72 0.77 1.59 0.66</td>
<td>1.53 0.61</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.68 0.74 1.55 0.63</td>
<td>1.52 0.61</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.65 0.71 1.52 0.61</td>
<td>1.51 0.60</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.64 0.70 1.54 0.62</td>
<td>1.51 0.60</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.16: Real and imaginary part of the index as a function of the fuel equivalence ratio and height above the burner surface for the methane/oxygen flame.

<table>
<thead>
<tr>
<th>$H$ (mm)</th>
<th>$\phi = 2.2$</th>
<th></th>
<th>$\phi = 2.4$</th>
<th></th>
<th>$\phi = 2.6$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
<td>$k$</td>
</tr>
<tr>
<td>8</td>
<td>1.63</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.81</td>
<td>0.84</td>
<td>1.54</td>
<td>0.62</td>
<td>1.24</td>
<td>0.33</td>
</tr>
<tr>
<td>10</td>
<td>1.83</td>
<td>0.86</td>
<td>1.66</td>
<td>0.72</td>
<td>1.38</td>
<td>0.48</td>
</tr>
<tr>
<td>11</td>
<td>1.85</td>
<td>0.87</td>
<td>1.74</td>
<td>0.78</td>
<td>1.47</td>
<td>0.56</td>
</tr>
<tr>
<td>12</td>
<td>1.84</td>
<td>0.86</td>
<td>1.72</td>
<td>0.77</td>
<td>1.52</td>
<td>0.60</td>
</tr>
<tr>
<td>13</td>
<td>1.83</td>
<td>0.85</td>
<td>1.69</td>
<td>0.75</td>
<td>1.58</td>
<td>0.66</td>
</tr>
<tr>
<td>14</td>
<td>1.83</td>
<td>0.85</td>
<td>1.69</td>
<td>0.75</td>
<td>1.64</td>
<td>0.71</td>
</tr>
<tr>
<td>16</td>
<td>1.82</td>
<td>0.84</td>
<td>1.71</td>
<td>0.76</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.16: Volume fractions as a function of the fuel equivalence ratio and height above the burner surface for the propane/oxygen and methane/oxygen flames
3.3.3 Drude-Lorentz Dispersion Constants

Previous studies of the refractive indices of soot have utilized the Drude-Lorentz dispersion model to predict the variation of the soot optical properties with respect to the wavelength and temperature [2,3,7,56]. Using the measured spectral transmission data for propane/oxygen flame $\phi = 1.8$ at the height of 6 mm above the burner and in the range 340 - 600 nm a new set of dispersion constants was sought. A nonlinear optimization routine (IMSL, “ZXMWD”) was used with the function to be optimized defined as

$$F = \sum_{j=1}^{NP} (K_{ext} - K_{ext,c})^2,$$

(3.14)

where $NP$ is the number of wavelengths that transmission measurements were performed and $K_{ext,c}$ is the extinction coefficient to be computed from the Mie solution in conjunction with the Drude-Lorentz relations. The real and imaginary part of the index $(n,k)$ may be expressed in terms of the number densities of the bound and free electrons $(n_b, n_f)$, the natural frequencies of the bound electrons $(\omega_b)$, and the damping constants of the bound and free electrons $(g_b, g_f)$ through the dispersion equations [7]

$$n^2 - k^2 = 1 + \frac{e^2}{m \epsilon_p} \sum_{i=1}^{2} \frac{n_{bi}(\omega_{bi}^2 - \omega^2)}{\omega_{bi}^2 + \omega^2 g_{bi}^2} - \frac{e^2}{m \epsilon_p} \frac{n_{f}}{\omega^2 + g_{f}^2},$$

(3.15)

$$2nk = \frac{e^2}{m \epsilon_p} \sum_{i=1}^{2} \frac{n_{bi}\omega g_{bi}}{\omega_{bi}^2 + \omega^2 g_{bi}^2} + \frac{e^2}{m \epsilon_p \omega} \frac{n_{fgf}}{\omega^2 + g_{f}^2}.$$  

(3.16)
The parameters \( m \) and \( m_e \) represent the masses of the bound and free electrons respectively, \( \omega \) is the frequency of the incident radiation, and \( \varepsilon_p \) is the permittivity constant. In the present analysis four variables were treated as unknown: the number density of the free electrons, \( n_f \), the number density of the first bound electron, \( n_{b1} \), and the damping constant for the first and second bound electron, \( g_{b1} \) and \( g_{b2} \). The damping constant for free electrons was estimated at 1378°K. The inferred electron number densities and damping constants are presented in Table 3.17 along with the values proposed by previous investigators.

Although the present dispersion constants were obtained using limited experimental data in the visible wavelengths the differences in the electron number densities and damping constants with those determined by previous investigators [3,7] may be attributed to several reasons. In the first case the dispersion constants were determined from the optical properties of soot particles collected and compressed into smooth pellet surfaces. However, such properties are only effective properties and not the actual material properties, unless they are corrected for the void fraction associated with the participating layers in the reflection process and for the non specular character of the surface.

In the second case, transmission data in the visible and infrared from polysterene and plexiglass flames were employed to determine the dispersion constants. The lower hydrogen to carbon ratio (\( H/C = 1/1 \)) for polysterene and \( H/C = 1/0.63 \) for plexiglass) as compared with the propane flame soot studied in the present exper-
iments (H/C = 1/0.38) probably contribute to the differences in the free electron number densities. The spectral variation of $n$ and $k$ in the visible wavelength is shown in Figure 3.17 along with the predictions of previous models.
Figure 3.17: Optical properties of soot ($n$, $k$) predicted by the models of previous investigators and by the use of dispersion constants determined from the present study.
Table 3.17: Dispersion constants

<table>
<thead>
<tr>
<th>Type of electron</th>
<th>Electron number density ((m^{-3}))</th>
<th>Frequency ((sec^{-1}))</th>
<th>Damping constant ((sec^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dalzell and Sarofim (1969)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>free: (n_f)</td>
<td>(4.06 \times 10^{27})</td>
<td>-</td>
<td>(6.0 \times 10^{15})</td>
</tr>
<tr>
<td>bound 1: (n_1)</td>
<td>(2.69 \times 10^{27})</td>
<td>(1.25 \times 10^{15})</td>
<td>(6.0 \times 10^{15})</td>
</tr>
<tr>
<td>bound 2: (n_2)</td>
<td>(2.86 \times 10^{28})</td>
<td>(7.25 \times 10^{15})</td>
<td>(7.25 \times 10^{15})</td>
</tr>
<tr>
<td>Lee and Tien (1981), 1450 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>free: (n_f)</td>
<td>(4.00 \times 10^{25})</td>
<td>-</td>
<td>(1.2 \times 10^{15})</td>
</tr>
<tr>
<td>bound 1: (n_1)</td>
<td>(4.07 \times 10^{27})</td>
<td>(1.25 \times 10^{15})</td>
<td>(5.9 \times 10^{15})</td>
</tr>
<tr>
<td>bound 2: (n_2)</td>
<td>(4.47 \times 10^{28})</td>
<td>(7.25 \times 10^{15})</td>
<td>(5.6 \times 10^{15})</td>
</tr>
<tr>
<td>Present</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>free: (n_f)</td>
<td>(4.82 \times 10^{26})</td>
<td>-</td>
<td>(1.2 \times 10^{15})</td>
</tr>
<tr>
<td>bound 1: (n_1)</td>
<td>(3.88 \times 10^{27})</td>
<td>(1.25 \times 10^{15})</td>
<td>(6.1 \times 10^{15})</td>
</tr>
<tr>
<td>bound 2: (n_2)</td>
<td>(4.26 \times 10^{28})</td>
<td>(7.25 \times 10^{15})</td>
<td>(9.8 \times 10^{15})</td>
</tr>
</tbody>
</table>
Chapter 4

Kramers-Kronig Analysis to Obtain Spectral Refractive Index

4.1 Introduction

The concept of dispersion relations was originally introduced with the work of Kronig [30] and Kramers [31]. The term 'dispersion' comes from optical dispersion, a consequence of the dependence of the index of refraction on wavelength or angular frequency. Kronig and Kramers showed that the real part of refractive index can be expressed as an integral of the imaginary part and the imaginary part as an integral of its real part [31]. The dispersion relation is well known in the theory of dispersion of light in a dielectric, where the complex refractive index is expressed as an integral of the absorption coefficient over all frequencies. Other applications include studies of the scattering of nuclear particles as well as electric networks (relation between the input voltage and output current). Thus, the dispersion relations are of wide generality and usefulness [32], and they may be considered as a consequence of causality. As a result, they must be satisfied by any causal model.
of a dispersive medium [33].

The Kramers-Kronig dispersion relations (KK) are most commonly employed in the analysis of reflectance data by many investigators (see, for example, Taft and Philip [34], Andermann et al. [35], Roessler [36], and Bachrach and Brown [37]. In such studies, the reflection coefficient is obtained from the measured reflectivity and then the phase is determined through the KK relations. Hence, the refractive indices, \( n \) and \( k \), are obtained from Fresnel's relations. Recently, Goodwin and Mitchner [38] applied the KK relations to the reflectance measurements of coal ash in the wavelength range from 1 \( \mu \)m to 12 \( \mu \)m.

Ahrenkiel [39] derived a subtractive Kramers-Kronig relation (SKK), which offers greater convergence than the conventional expression when reflectance data are available over a limited range. Milham et al. [40] employed the SKK relations to determine the optical constants of an o-phosphoric-acid aerosols from extinction data in the wavelength range 7 \( \mu \)m to 14 \( \mu \)m. However, their approach requires knowledge of the real part of the refractive index of the particle at some wavelength within the spectral range of the data, which is generally not known for flame soot.

Hulthen [41] derived generalized Kramers-Kronig relations, from which the real and imaginary parts may be calculated for all frequencies from knowledge of these parts for at least partly overlapping frequency intervals. However, such information cannot be obtained directly from the experimental data and it was demonstrated that the experimental errors in certain frequencies yield unreliable real and imagi-
nary parts [41]. Recently, Ku and Felske [42] developed Kramers-Kronig relations for semi-conducting particles, from which the refractive index spectra may be determined from spectral extinction data without requiring the value of the index to be known at any frequency a priori. However, their approach has not been applied to soot particles in flames and in addition requires experimental measurements obtained with minimum uncertainties.

The advantage of using the KK technique is that it employs only transmittance measurements and may yield accurate optical constants of particulates over a broad spectral range provided that the particle size distribution and number density of the particulates are known. The drawback of this technique is that in reality, experimental data can only be obtained over finite frequency interval whereas the Kramers-Kronig relations require data over all frequencies. The basic theoretical concepts pertinent to the Kramers-Kronig relations and the means for reliable extrapolation beyond the range of experimental data will be presented in the following section.

4.2 Theory

Kramers [31] and Kronig [30] developed a set of mathematical relations which follows from the principle of causality. The general meaning of causality is that the effect cannot precede the cause or no signal can propagate with velocity greater than the speed of light. The Kramers-Kronig relations apply to bounded, analytic functions
which in essence represent linear, causal relationship between the input and output of a passive physical system \([32,33,43,44]\). Let such a system be represented by the complex function

\[
A(\omega) = A_r(\omega) - iA_i(\omega),
\]

which vanishes at large frequency, namely:

\[
\lim_{\omega \to \infty} A(\omega) = 0,
\]

and in addition satisfies the crossing condition

\[
A(-\omega) = A(\omega).
\]

Then the two real integral relations may be expressed as

\[
A_r(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' A_i(\omega')}{\omega'^2 - \omega^2} d\omega',
\]

and

\[
A_i(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\omega A_r(\omega')}{\omega'^2 - \omega^2} d\omega',
\]

where \(P\) signifies the Cauchy principle value of the integral and \(\omega\) is the angular frequency. Equations (4.4) and (4.5) are called Kramers-Kronig or dispersion relations. Their implication is that the real and imaginary part of \(A(\omega)\) are not independent but connected by integral relations. Moreover, if \(A_r\) is known over a sufficiently large range of frequencies around \(\omega\), \(A_i(\omega)\) can be obtained by integration, and vice versa.
It has been shown [42,44] that for a homogeneous spherical particle of radius \( r \), the scattering amplitude function, \( S_0 \), in the forward direction satisfies the KK relations:

\[
A(\omega) = A_r(\omega) - iA_i(\omega),
\]

\[
= -iS_0(\omega)/x^3.
\]

The function, \( S_0 \), is given by the Mie scattering theory [45] and depends on the particle refractive index and size parameter:

\[
S_0 = \frac{1}{2} \sum_{j=1}^{\infty} (2j + 1)(a_j + b_j),
\]

where

\[
a_j = \frac{\overline{m}\psi(\overline{m}x)\psi'_n(x) - \psi(x)\psi'_n(\overline{m}x)}{\overline{m}\psi(\overline{m}x)\xi'_n(x) - \xi(x)\psi'(\overline{m}x)},
\]

and

\[
b_j = \frac{\psi(\overline{m}x)\psi'_n(x) - \overline{m}\psi(x)\psi'_n(\overline{m}x)}{\psi(\overline{m}x)\xi'_n(x) - \overline{m}\xi(x)\psi'(\overline{m}x)},
\]

in which \( \psi \) and \( \xi \) are functions of the Riccati-Bessel functions. Furthermore, from the optical theorem [22] the extinction cross-section \( C_{ext} \) is related to the scattering function \( S_0 \) and consequently the imaginary part of \( A(\omega) \) may be expressed in terms of \( C_{ext} \) by the relation

\[
C_{ext} = 4\pi r^2 \text{Re}(S_0)/x^2
\]

\[
= 4\pi A_i(\omega).
\]
For monodisperse particles $C_{\text{ext}}$ is related to the measured transmittance, $\tau_\lambda$, by

$$\tau_\lambda = \exp(-NC_{\text{ext}}L), \quad (4.13)$$

where $L$ is the pathlength of the flame. Therefore, the function, $A_i$, is determined from the measured transmittance, $\tau_\lambda$, by the relation:

$$A_i(\omega) = -\ln\tau_\lambda/4\pi r^2 xNL. \quad (4.14)$$

Thus, by measuring the transmittance $\tau_\lambda$ over a sufficiently broad wavelength range, the refractive index of the particle can be determined by solving the equations for $A_i(\omega)$ and $A_r(\omega)$ simultaneously at each wavelength for the unknown refractive indices $n$ and $k$ provided that the particle number density $N$, and the radius, $r$, are known from independent measurements.

Although $A_r(\omega)$ may be evaluated using equation (4.4) a more useful expression is obtained by employing the subtractive Kramers-Kronig (SKK) technique which offers greater convergence than the KK relations and is less sensitive to the extrapolations when experimental data are available over a limited range. The SKK relation for $A_r(\omega)$ is obtained by first evaluating equation (4.4) at $\omega = 0$ and then subtracting the result from equation (4.4). Thus, the function $A_r(\omega)$ may be expressed as

$$A_r(\omega) = 1 + \frac{2\omega^2}{\pi} P \int_0^\infty \frac{A_i(\omega')}{\omega'(\omega'^2 - \omega^2)} d\omega'. \quad (4.15)$$

Noting that $S_0$ is a complex function and equating the real and imaginary parts of equations (4.6) and (4.7) we obtain two equations that can be solved for $n$ and $k$.
at the corresponding wavelength, namely:

\[ \frac{1}{x^3} \text{Re}(S_o) = A_i(\omega), \]  

(4.16)

and

\[ -\frac{1}{x^3} \text{Im}(S_o) = A_r(\omega). \]  

(4.17)

As it was pointed out in section 4.2 a successful application of the KK relations to infer refractive index spectra requires integration over the whole range of frequencies \((0 \rightarrow \infty)\), see equation (4.15). In addition, the particle number density and particle radius must be independently determined. With these constraints in mind a sensitivity analysis was carried out in order to: a) assess the effect of the limited range of available spectral extinction data; and b) to establish a priori a realistic lower and upper limit of wavelengths where extinction measurements can be carried out reliably in a flame environment. These aspects along with the sensitivity of the functions \(A_i\) and \(A_r\) and of the inferred refractive indices with respect to particle size and number density are presented in the next sections.

4.3 Calculations from Simulated Data

In order to test the KK method of analysis computations were carried out in the wavelength range 0.04 to 248 \(\mu m\) \((0.005 \leq \omega \leq 30\ eV)\). Since no experimental data are available over a broad wavelength range, equation (4.14) cannot be used to determine experimentally the function \(A_i\). Instead, \(A_i\) was calculated from known
refractive indices using equation (4.12). The required indices to compute \( A_i \) were generated from measurements in a propane/oxygen flame with fuel equivalence ratio \( \phi = 1.8 \) at the height of 6 mm. The indices are obtained by fitting the extinction data in the visible to the Drude-Lorentz model (see section 3.3.3). The reason the indices from Drude-Lorentz model are used in these calculations is that, for soot, only the results from Drude-Lorentz model give the refractive index for wavelengths ranging from the ultraviolet to infrared. The dispersion constants used in these calculations are shown in Table 3.17.

The function \( A_i(\omega) \) was then calculated from equation (4.12) using the MIE program [46] in the range \( 0.2 \leq \lambda \leq 27 \, \mu \text{m} \) \((0.045 \leq \omega \leq 6.2 \, \text{eV})\) and with particle diameters typical of flame soot \( 0.02 \leq d \leq 0.2 \, \mu \text{m} \). The function \( A_r(\omega) \) was then computed from equation (4.15) by extrapolation in the range \( 0.04 \leq \lambda \leq 0.2 \, \mu \text{m} \) and \( 27 \leq \lambda \leq 248 \, \mu \text{m} \). The results for \( A_i(\omega) \) and \( A_r(\omega) \) are shown in Figure 4.1. The sensitivities of the \( A_i(\omega) \) and \( A_r(\omega) \) function with respect to particle size are also explored. It is seen that as the particle size increases from 0.02 to 0.2 \( \mu \text{m} \) the function \( A_i \) varies by a factor of two in the visible. The refractive indices are then reproduced within 2.5% in the range \( 0.25 \leq \lambda \leq 25 \, \mu \text{m} \). The calculations have demonstrated that the inferred indices are insensitive to the extrapolations of \( A_i \) in the region of long wavelengths.

Comparisons of the assumed exact refractive indices predicted from the Drude-Lorentz equations with those inferred from KK analysis are shown in Figure 4.2. In
Figure 4.1: Variation of the functions $A_i$ and $A_r$ with respect to the wavelength for particle diameters in the range 0.02 to 0.2 μm.
Figure 4.2: Comparison of the deduced index spectra with their exact value. The particle diameter used was 0.06 μm.
addition, the values of exact and inferred indices as well as their percent differences are shown in Table 4.1. The calculations also show that the refractive indices can be inferred with the same uncertainty when the limit of extrapolation in the higher wavelength range was set equal to 7 \( \mu m \). This result suggests that transmission measurements in the range \( 0.2 \leq \lambda \leq 6.7 \mu m \) should be sufficient in order to infer reliable indices. The required number density \((N)\) and radius \((r)\) are determined from the scattering/extinction and photon correlation data at the wavelength of 0.488 \( \mu m \).

The integrations defined by equation (4.15) were carried out using the Simpson’s rule with step size of \( \Delta \omega = 0.005 eV \). An inspection of equation (4.8) reveals that the scattering amplitude function \( S_o \) is non-linear with respect to complex refractive index \( \overline{m} \). Thus, data reduction using equations (4.16) - (4.17) in conjunction with \( A_i \) and \( A_r \) can result in multiple sets of \( n \) and \( k \). In order to circumvent the multiplicity and to obtain unique values for \( n \) and \( k \) at each wavelength it is necessary to introduce independent relation between the complex function \( A \) and the indices \( n \) and \( k \). To accomplish this it is noted that for sufficiently small frequencies (i.e. large wavelengths) the function, \( S_o \), is given by [23]

\[
S_o = i x^3 \frac{\epsilon - 1}{\epsilon + 2},
\]

where \( \epsilon = \epsilon' - i \epsilon'' = \overline{m}^2 \) is the complex dielectric function defined as the permittivity of the particle relative to that of free space. Therefore, the complex function, \( A \)
Table 4.1: Comparison of the deduced index spectra with their exact values.

<table>
<thead>
<tr>
<th>$\lambda$ ($\mu$m)</th>
<th>Exact</th>
<th>KK analysis</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
</tr>
<tr>
<td>.25</td>
<td>1.19</td>
<td>.81</td>
<td>1.16</td>
</tr>
<tr>
<td>.30</td>
<td>1.37</td>
<td>.82</td>
<td>1.36</td>
</tr>
<tr>
<td>.40</td>
<td>1.59</td>
<td>.74</td>
<td>1.58</td>
</tr>
<tr>
<td>.51</td>
<td>1.69</td>
<td>.66</td>
<td>1.69</td>
</tr>
<tr>
<td>.62</td>
<td>1.73</td>
<td>.62</td>
<td>1.73</td>
</tr>
<tr>
<td>.80</td>
<td>1.75</td>
<td>.62</td>
<td>1.76</td>
</tr>
<tr>
<td>1.03</td>
<td>1.76</td>
<td>.67</td>
<td>1.76</td>
</tr>
<tr>
<td>1.98</td>
<td>1.93</td>
<td>1.07</td>
<td>1.94</td>
</tr>
<tr>
<td>4.00</td>
<td>2.49</td>
<td>1.63</td>
<td>2.49</td>
</tr>
<tr>
<td>6.20</td>
<td>2.96</td>
<td>1.95</td>
<td>2.97</td>
</tr>
<tr>
<td>8.26</td>
<td>3.28</td>
<td>2.16</td>
<td>3.29</td>
</tr>
<tr>
<td>13.05</td>
<td>3.79</td>
<td>2.59</td>
<td>3.79</td>
</tr>
<tr>
<td>16.53</td>
<td>4.07</td>
<td>2.95</td>
<td>4.07</td>
</tr>
<tr>
<td>20.66</td>
<td>4.37</td>
<td>3.24</td>
<td>4.36</td>
</tr>
<tr>
<td>24.80</td>
<td>4.65</td>
<td>3.57</td>
<td>4.64</td>
</tr>
<tr>
<td>27.55</td>
<td>4.82</td>
<td>3.78</td>
<td>4.82</td>
</tr>
</tbody>
</table>
[see equation (4.7)], may be expressed as

\[ A = \frac{\varepsilon - 1}{\varepsilon + 2}. \]  \hspace{1cm} (4.19)

Since \( \varepsilon \) and \( \overline{\varepsilon} \) are related by the expressions

\[ \varepsilon' = n^2 - k^2, \]  \hspace{1cm} (4.20)

and

\[ \varepsilon'' = 2nk, \]  \hspace{1cm} (4.21)

by combining equations (4.19) - (4.21) it follows that

\[ n = \sqrt{\frac{\varepsilon' + \varepsilon'' + \varepsilon'}{2}}, \]  \hspace{1cm} (4.22)

and

\[ k = \sqrt{\frac{\varepsilon' + \varepsilon'' - \varepsilon'}{2}}. \]  \hspace{1cm} (4.23)

It is noted that the functions \( \varepsilon' \) and \( \varepsilon'' \) are related to the real and imaginary part of the complex function \( A \) through the expressions

\[ \varepsilon' = \frac{3(1 - A_r)}{(1 - A_r)^2 + A_i^2} - 2, \]  \hspace{1cm} (4.24)

and

\[ \varepsilon'' = \frac{3A_i}{(1 - A_r)^2 + A_i^2}. \]  \hspace{1cm} (4.25)

Equations (4.22) and (4.23) when solved provide an initial guess in solving equations (4.16) and (4.17) for larger wavelength (27.5 \( \mu \text{m} \) in the present analysis). For
smaller wavelengths unique values can be obtained using the previous values of \( n \) and \( k \) as initial guesses. Comparisons of the solutions from equations (4.16)- (4.17) with those from equations (4.22)- (4.23) are shown in Table 4.2. It is seen that the percent differences increase as the wavelength decrease.

At this point it should be mentioned that equation (4.15) has a singularity at \( \omega = \omega' \). Therefore a special integration technique is required when \( A_r(\omega) \) is computed from \( A_i(\omega) \). For this purpose equation (4.15) can be rewritten as

\[
A_r(\omega) = 1 + \frac{2\omega^2}{\pi} \left[ \lim_{\delta \to 0} \int_0^{\omega - \delta} \frac{A_i(\omega')}{\omega'(\omega^2 - \omega'^2)} d\omega' + \lim_{\delta \to 0} \int_{\omega + \delta}^{\infty} \frac{A_i(\omega')}{\omega'(\omega^2 - \omega'^2)} d\omega' \right] \tag{4.26}
\]

Calculations were performed by decreasing \( \delta \) from \( 10^{-4} \) to \( 10^{-7} \) as shown in Table 4.2. The values of \( A_i(\omega - \delta) \) and \( A_i(\omega + \delta) \) were computed by linear interpolation between the points \( A_i(\omega - \Delta \omega) \) and \( A_i(\omega + \Delta \omega) \). It is seen that the differences in the values of the first and second integrand in equation (4.26) decrease as \( \delta \) takes lower values. This is because \( A_i(\omega - \delta) \cong A_i(\omega + \delta) \) for small values of \( \delta \). Hence their contributions to the overall integration is cancelled and the effect of the Cauchy Principal value of the integral is indeed negligible.

### 4.3.1 Effect of Uncertainties in the Measurements

The effect of uncertainties in the inferred spectra of \( n \) and \( k \) was assessed by assuming a \( \pm 5\% \) variation in the inferred number density and the soot particle diameter.
Table 4.2: Comparisons of solutions from equations (4.22)-(4.23) with those from equations (4.16)-(4.17).

<table>
<thead>
<tr>
<th>$\lambda$ ($\mu$m)</th>
<th>Real part, $n$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eqn. (4.22)-(4.23)</td>
<td>Eqn. (4.16)-(4.17)</td>
</tr>
<tr>
<td>27.5</td>
<td>4.817</td>
<td>4.818</td>
</tr>
<tr>
<td>22.5</td>
<td>4.488</td>
<td>4.490</td>
</tr>
<tr>
<td>16.5</td>
<td>4.064</td>
<td>4.066</td>
</tr>
<tr>
<td>12.4</td>
<td>3.728</td>
<td>3.730</td>
</tr>
<tr>
<td>8.8</td>
<td>3.359</td>
<td>3.361</td>
</tr>
<tr>
<td>4.0</td>
<td>2.489</td>
<td>2.492</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda$ ($\mu$m)</th>
<th>Imaginary part, $k$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eqn. (4.22)-(4.23)</td>
<td>Eqn. (4.16)-(4.17)</td>
</tr>
<tr>
<td>27.5</td>
<td>3.787</td>
<td>3.787</td>
</tr>
<tr>
<td>22.5</td>
<td>3.426</td>
<td>3.425</td>
</tr>
<tr>
<td>16.5</td>
<td>2.946</td>
<td>2.945</td>
</tr>
<tr>
<td>12.4</td>
<td>2.586</td>
<td>2.584</td>
</tr>
<tr>
<td>8.8</td>
<td>2.258</td>
<td>2.255</td>
</tr>
<tr>
<td>4.0</td>
<td>1.657</td>
<td>1.652</td>
</tr>
</tbody>
</table>
Table 4.3: Values of the integrands in equation (4.26)

<table>
<thead>
<tr>
<th>$d\omega$ (eV)</th>
<th>$\omega = 0.1$ eV ($\lambda = 12.4$ $\mu$m)</th>
<th>$\omega' = \omega + d\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega'$</td>
<td>$\omega - d\omega$</td>
<td>$\omega' = \omega + d\omega$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>$-4.03856 \times 10^{3}$</td>
<td>$+4.03999 \times 10^{3}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>$-4.03514 \times 10^{4}$</td>
<td>$+4.03439 \times 10^{4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>$-4.03481 \times 10^{5}$</td>
<td>$+4.03475 \times 10^{5}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>$-4.03477 \times 10^{6}$</td>
<td>$+4.03477 \times 10^{6}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d\omega$ (eV)</th>
<th>$\omega = 0.6$ eV ($\lambda = 2.07$ $\mu$m)</th>
<th>$\omega' = \omega + d\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega'$</td>
<td>$\omega - d\omega$</td>
<td>$\omega' = \omega + d\omega$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>$-1.05169 \times 10^{4}$</td>
<td>$+1.05118 \times 10^{4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>$-1.05146 \times 10^{5}$</td>
<td>$+1.05141 \times 10^{5}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>$-1.05144 \times 10^{6}$</td>
<td>$+1.05143 \times 10^{6}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>$-1.05143 \times 10^{7}$</td>
<td>$+1.05143 \times 10^{7}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d\omega$ (eV)</th>
<th>$\omega = 2.0$ eV ($\lambda = 0.62$ $\mu$m)</th>
<th>$\omega' = \omega + d\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega'$</td>
<td>$\omega - d\omega$</td>
<td>$\omega' = \omega + d\omega$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>$-8.75445 \times 10^{3}$</td>
<td>$+8.75353 \times 10^{3}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>$-8.75402 \times 10^{4}$</td>
<td>$+8.75396 \times 10^{4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>$-8.75399 \times 10^{5}$</td>
<td>$+8.75399 \times 10^{5}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>$-8.75398 \times 10^{6}$</td>
<td>$+8.75398 \times 10^{6}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d\omega$ (eV)</th>
<th>$\omega = 6.0$ eV ($\lambda = 0.21$ $\mu$m)</th>
<th>$\omega' = \omega + d\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega'$</td>
<td>$\omega - d\omega$</td>
<td>$\omega' = \omega + d\omega$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>$-1.59486 \times 10^{4}$</td>
<td>$+1.59480 \times 10^{4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>$-1.59483 \times 10^{5}$</td>
<td>$+1.59483 \times 10^{5}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>$-1.59483 \times 10^{6}$</td>
<td>$+1.59483 \times 10^{6}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>$-1.59483 \times 10^{7}$</td>
<td>$+1.59483 \times 10^{7}$</td>
</tr>
</tbody>
</table>
It was found that the uncertainty in the measurements have a stronger effect on the real part $n$ than the imaginary part $k$. Figure 4.3 shows that the percent differences between the exact and inferred values of $n$ resulting from 5% positive error in number density are less than 4.2% over the wavelength range 0.3 $\mu$m to 25 $\mu$m whereas the percent differences in $k$ are less than 3.6%. As it may be seen from Figure 4.4 the uncertainty in diameter has stronger effect on the inferred indices. Tables 4.4 and 4.5 show the values of exact and inferred indices and percent errors assuming ± 5% errors in number density and particle size, respectively. Specifically, the percent difference for $n$ varies from 5 - 9% and from 0 - 6% for $k$ in the range from 0.3 $\mu$m to 25 $\mu$m. On the other hand, a 5% negative error in the measurements results in similar percent differences as shown in Tables 4.4 and 4.5.

4.3.2 Extrapolation Effects

In section 4.3, it was mentioned that the extrapolation was carried out in the range $0.04 \leq \lambda \leq 0.2 \mu$m and $27 \leq \lambda \leq 248 \mu$m. The effect of extrapolation in the inferred indices $n$ and $k$ is assessed by varying the limit of extrapolation in this section. First, the upper wavelength limit was decreased from 248 $\mu$m (0.005 eV) to 124, 82, and 50 $\mu$m (0.025 eV). The results are shown in Figures 4.5 and 4.6. It is noted that the percent error increases as the extrapolation limit decreases with the errors in $k$ being much higher than the corresponding errors $n$. Moreover, the resulting $k$ is unreliable by more than 50% in the range 2 - 10 $\mu$m, when the upper
Figure 4.3: Percent errors in the inferred indices assuming a 5% error in particle number density

Figure 4.4: Percent errors in the inferred indices assuming a 5% error in particle diameter
Table 4.4: Sensitivity of the real\( (n) \) and imaginary \( (k) \) part of the index with respect to ± 5% variation in particle number density.

<table>
<thead>
<tr>
<th>( \lambda ) (( \mu m ))</th>
<th>Real part, ( n )</th>
<th>Imaginary part, ( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exact</td>
<td>+5% N</td>
</tr>
<tr>
<td>0.30</td>
<td>1.37</td>
<td>1.43(3.7)</td>
</tr>
<tr>
<td>0.40</td>
<td>1.59</td>
<td>1.62(3.6)</td>
</tr>
<tr>
<td>0.50</td>
<td>1.68</td>
<td>1.74(3.7)</td>
</tr>
<tr>
<td>0.62</td>
<td>1.73</td>
<td>1.79(3.9)</td>
</tr>
<tr>
<td>0.80</td>
<td>1.75</td>
<td>1.82(4.1)</td>
</tr>
<tr>
<td>1.03</td>
<td>1.76</td>
<td>1.84(4.2)</td>
</tr>
<tr>
<td>1.98</td>
<td>1.93</td>
<td>2.00(2.5)</td>
</tr>
<tr>
<td>4.00</td>
<td>2.49</td>
<td>2.56(3.1)</td>
</tr>
<tr>
<td>6.20</td>
<td>2.96</td>
<td>3.05(2.9)</td>
</tr>
<tr>
<td>8.26</td>
<td>3.28</td>
<td>3.37(2.8)</td>
</tr>
<tr>
<td>10.78</td>
<td>3.58</td>
<td>3.67(2.7)</td>
</tr>
<tr>
<td>13.05</td>
<td>3.79</td>
<td>3.89(2.7)</td>
</tr>
<tr>
<td>16.53</td>
<td>4.07</td>
<td>4.19(2.9)</td>
</tr>
<tr>
<td>20.66</td>
<td>4.37</td>
<td>4.50(2.9)</td>
</tr>
<tr>
<td>24.80</td>
<td>4.65</td>
<td>4.79(3.1)</td>
</tr>
</tbody>
</table>

Numbers in parentheses represent percent errors in the inferred quantities.
Table 4.5: Sensitivity of the real($n$) and imaginary ($k$) part of the index with respect to ± 5% variation in particle diameter.

<table>
<thead>
<tr>
<th>$\lambda$ (\mu m)</th>
<th>Real part, $n$</th>
<th></th>
<th>Imaginary part, $k$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exact</td>
<td>+5% d</td>
<td>-5% d</td>
<td>exact</td>
</tr>
<tr>
<td>0.30</td>
<td>1.37</td>
<td>1.51(9.6)</td>
<td>1.22(-11.2)</td>
<td>.82</td>
</tr>
<tr>
<td>0.40</td>
<td>1.59</td>
<td>1.72(8.0)</td>
<td>1.45(-8.5)</td>
<td>.74</td>
</tr>
<tr>
<td>0.62</td>
<td>1.73</td>
<td>1.85(7.7)</td>
<td>1.60(-7.2)</td>
<td>.62</td>
</tr>
<tr>
<td>0.80</td>
<td>1.75</td>
<td>1.88(7.7)</td>
<td>1.63(-7.2)</td>
<td>.62</td>
</tr>
<tr>
<td>1.00</td>
<td>1.76</td>
<td>1.90(8.0)</td>
<td>1.64(-6.9)</td>
<td>.66</td>
</tr>
<tr>
<td>2.00</td>
<td>1.93</td>
<td>2.07(7.4)</td>
<td>1.80(-6.3)</td>
<td>1.07</td>
</tr>
<tr>
<td>4.00</td>
<td>2.49</td>
<td>2.64(6.2)</td>
<td>2.34(-5.7)</td>
<td>1.63</td>
</tr>
<tr>
<td>6.20</td>
<td>2.96</td>
<td>3.13(5.8)</td>
<td>2.80(-5.5)</td>
<td>1.95</td>
</tr>
<tr>
<td>8.27</td>
<td>3.28</td>
<td>3.47(5.7)</td>
<td>3.11(-5.3)</td>
<td>2.16</td>
</tr>
<tr>
<td>10.78</td>
<td>3.58</td>
<td>3.77(5.5)</td>
<td>3.39(-5.3)</td>
<td>2.38</td>
</tr>
<tr>
<td>13.05</td>
<td>3.79</td>
<td>4.00(5.5)</td>
<td>3.60(-5.1)</td>
<td>2.59</td>
</tr>
<tr>
<td>16.53</td>
<td>4.07</td>
<td>4.30(5.6)</td>
<td>3.87(-4.9)</td>
<td>2.89</td>
</tr>
<tr>
<td>20.66</td>
<td>4.37</td>
<td>4.62(5.7)</td>
<td>4.17(-4.7)</td>
<td>3.23</td>
</tr>
<tr>
<td>24.80</td>
<td>4.65</td>
<td>4.91(5.8)</td>
<td>4.43(-4.6)</td>
<td>3.57</td>
</tr>
</tbody>
</table>

Numbers in parentheses represent percent errors in the inferred quantities.
limit of integration is reduced to 50 μm (see Figure 4.6).

When the initial wavelength for extrapolation varies from 27 μm to 6.7 μm and follows the same step as above the refractive indices can be inferred with the same uncertainty as shown in Figures 4.7 and 4.8. On the other hand, when the limit 248 μm is fixed and the limit 6.7 μm is decreased to 5.9 and 4.3 μm the results are shown in Figures 4.9 and 4.10. It is seen that the errors both for n and k increase when the extrapolation limit decreases. However, the effect of decreasing the limit is less severe for the visible and near infrared wavelengths. Specifically, the error is less than 2% for the real part n and less than 6% for the imaginary part k for wavelengths less than about 2.0 μm.

### 4.3.3 Polydispersity Effects

As it was mentioned earlier soot particles in flames possess a distribution of sizes due to agglomeration and surface growth. Thus, it is reasonable to assess the effects of polydispersity level on the inferred index spectra. In this section a sensitivity analysis is presented for the effects of different size distribution parameters, \( r_o \), \( \sigma \), on the functions, \( A_i \), \( A_s \), and subsequently on the inferred indices \( n \) and \( k \). For a polydispersion of spherical particles, the expression for the light transmittance through a homogeneous pathlength \( L \) reduces to

\[
\tau_\lambda = \exp[- \int_0^\infty C_{ext} NLP(r) dr],
\]  

(4.27)
Figure 4.5: Percent errors in deduced $n$ for extrapolation range from 27 $\mu$m to 248, 124, 82, and 50 $\mu$m.
Figure 4.6: Percent errors in deduced $k$ for extrapolation range from 27 $\mu$m to 248, 124, 82, and 50 $\mu$m.
Figure 4.7: Percent errors in deduced $n$ for extrapolation range from 6.7 $\mu$m to 248, 124, 82, and 50 $\mu$m.
Figure 4.8: Percent errors in deduced $k$ for extrapolation range from 6.7 $\mu$m to 248, 124, 82, and 50 $\mu$m.
Figure 4.9: Percent errors in deduced $n$ for extrapolation range from 6.7, 5.9, and 4.3 $\mu$m to 248 $\mu$m.
Figure 4.10: Percent errors in deduced $k$ for extrapolation range from 6.7, 5.9, and 4.3 $\mu$m to 248 $\mu$m.
where \( P(r) \) is the normalized particle size distribution. Using equation (4.12) and expressing \( P(r) \) as a zeroth order lognormal distribution [see equation (2.7)] equation (4.27) yields:

\[
\tau_\lambda = \exp[-8\pi r_0^2 \exp(7.5 \ln^2 \sigma) N L \overline{A}_i(\omega)/\lambda].
\] (4.28)

Then the function, \( A_i \), for polydisperse particles may be written as

\[
\overline{A}_i(\omega) = \exp(-7.5 \ln^2 \sigma) \int_0^\infty (r/r_o)^3 A_i(\omega) P(r) dr,
\] (4.29)

whereas the function, \( A_r \), is of the same form as in the monodisperse case, namely:

\[
\overline{A}_r(\omega) = 1 + \frac{2\omega^2}{\pi} P \int_0^\infty \frac{\overline{A}_i(\omega')}{\omega'(\omega'^2 - \omega^2)} d\omega'.
\] (4.30)

The procedure for determining \( n \) and \( k \) for polydisperse particles is similar to that for monodisperse. However, the computational burden is substantially larger because of the required integrations over the size distribution. For example, for a particle size distribution with average radius 60 nm, the integration range must be at least from 10 nm to 140 nm, and requires more than sixty times the computing time needed for the monodispersion. Assuming that data are obtainable at intervals of 0.05 eV, equivalent to 124 data points over the range 0.05 - 6.2 eV (0.2 \( \leq \lambda \leq 25 \mu m \)) and corresponding to a spectral resolution of 0.01 \( \mu m \) at the wavelength 0.5 \( \mu m \), the program requires approximately 20 minutes of execution time (CPU) on the LSU IBM main computer.
The function, $\bar{A}_i(\omega)$, is obtained from equation (4.28) and $\bar{A}_r(\omega)$ from equation (4.30). Then, the following equations expressed in terms of $\bar{A}_i(\omega)$, $\bar{A}_r(\omega)$, and $\bar{S}_o$ (polydisperse analog of $S_o$) are to be solved for $n$ and $k$ at each wavelength:

$$\int_0^\infty \frac{1}{x^3} Re(\bar{S}_o)dx = \bar{A}_i(\omega), \quad (4.31)$$

and

$$-\int_0^\infty \frac{1}{x^3} Im(\bar{S}_o)dx = \bar{A}_r(\omega). \quad (4.32)$$

Computations were performed using the same refractive index which was used to calculate the function, $A_i$, for monodisperse particles. The functions, $\bar{A}_i$ and $\bar{A}_r$, were computed from equation (4.29) and (4.30) for the most probable diameter, $d_o = 0.06 \mu m$. Figure 4.11 shows the sensitivities of the $\bar{A}_i$ and $\bar{A}_r$ with respect to geometric width, $\sigma$. It is seen that both $\bar{A}_i$ and $\bar{A}_r$ vary strongly with $\sigma$ in the near ultraviolet and visible. This result is consistent with that of monodisperse analysis (section 4.3) since higher $\sigma$ implies broader distribution of particle sizes. Comparisons of the assumed exact refractive indices predicted from the Drude-Lorentz equations (see section 4.3) with those inferred from the KK analysis are shown in Figures 4.11 - 4.15 with the geometric width $\sigma$ varying from 1.0 to 1.3. It is noted that typical values of $\sigma$ range from 1.14 to 1.25 for the propane/oxygen and methane/oxygen flames investigated in the present study. The percent differences for particle diameter, $d_o$, equal to 0.02 $\mu m$ are less than 2.5% in the range 0.3 $\mu m$ to 27 $\mu m$. 
On the other hand, for a particle diameter equal to 0.06 μm the corresponding percent differences range from zero to 9% with the lower wavelength displaying larger uncertainties. This observation is consistent with the behavior of the functions $A_i$ and $A_r$ noted earlier both in terms of the monodisperse particle diameter and the wavelength, see section 4.3 and Figure 4.1. This trend suggests that the uncertainties in inferred indices increase in the near ultraviolet as the geometric width $\sigma$ increases.
Figure 4.11: Variation of the functions $\bar{A}_i$ and $\bar{A}_r$ with respect to geometric width and wavelength, $d_o = 0.06 \, \mu m$. 
Figure 4.12: Percent errors in deduced $n$ of polydisperse particles, $d_o = 0.02 \mu m$.

Figure 4.13: Percent errors in deduced $k$ of polydisperse particles, $d_o = 0.02 \mu m$. 
Figure 4.14: Percent errors in deduced $n$ of polydisperse particles, $d_o = 0.06 \mu m$.

Figure 4.15: Percent errors in deduced $k$ of polydisperse particles, $d_o = 0.06 \mu m$. 
Chapter 5

Spectral Extinction Measurements

5.1 Setup of Optical System

The Kramers-Kronig dispersion relations presented in Chapter 5 require knowledge of the particle size, number density of particles as well as of the spectral transmittance in order to invert the data for the spectral refractive index. The particle size is determined from the analysis of the measured autocorrelation and the number density from scattering/extinction measurements described in Chapter 3. In this Chapter, the transmission measurements from 0.2 to 7 microns and the data analysis using the Kramers-Kronig relations are presented. Since the experimental set-up for the scattering/extinction measurements was described in Chapter 3 only the detailed description of the equipment and the procedure for the spectral transmission measurements will be addressed in this section.

The experimental set-up consists of ultraviolet-visible and infrared light sources, grating monochromator, order-sorting long-pass filters, and detectors as shown in Figure 5.1. An ideal optical arrangement for transmission measurements would be
one with dual-beam paths of equal intensity so that the effects of source intensity fluctuations and atmospheric absorption will be minimized. However, such arrangement was not possible because of difficulties associated with system alignment and more importantly because of weak source intensity especially at the infrared wavelengths. The light source housing (ORIEL, model 7340) used is a universal type monochromator illuminator capable of producing radiation from 0.19 \mu m in the far ultraviolet (UV) to beyond 20 microns in the infrared. The two sources can be easily aligned and then switch selected. Separate screw adjustments focus the images of the source and position it horizontally and vertically. The Xenon Arc lamp (ORIEL, model 6253) has a continuous spectrum from 190 to 750 nm at 600 K. The infrared element (ORIEL, model 6363) is cylindrical in shape with 6.2 mm diameter and length of 100 mm long. The active area of the rod has dimensions $6.2 \times 20$ mm and when operated at 11 volts the peak temperature is about 1000 K. A regulated DC power supply (ORIEL, model 68735) is used for the infrared source. A 10 percent line voltage change produces only a 0.4 percent change in light output. After 30 minutes warm up the fluctuation of the output was less than 1 percent over one hour period. The lenses used to focus the two beams onto the center of the burner are made of calcium fluoride ($CaF_2$), which is usable from 0.15 \mu m to 9 microns. Details about the lenses and their locations are shown in Figure 5.1.

A compact high resolution monochromator (ORIEL, model 77250) was used to
Figure 5.1: Experimental set-up for spectral transmission measurements.
disperse the beam. The monochromator is useable in the spectral range 190 nm to 24 microns with interchangeable gratings and scan rate of 100 nm/min. The entrance and exit slits of the monochromator are adjustable from 0 to 3.2 mm. The bandwidth (resolution) of the monochromator range from 0.5 nm to 20 nm using 1200 lines/mm gratings. Order-sorting long-pass filters with cut-on wavelength shown in Table 5.1 were mounted at the exit slit of the monochromator to block the higher order harmonics. The signals are detected by an RCA 1P28 photomultiplier tube in the ultraviolet and visible wavelengths. Indium Antimonide (InSb) and Mercury Cadmium Telluride (HgCdTe) detectors were used for the infrared wavelengths. Table 5.1 summarizes the wavelength ranges for separate transmission measurements to be carried out with appropriate combinations of the monochromator gratings and filters. This indicates that at least seven different steps of experiments are required in order to cover the wavelength range of 0.2 to 7 microns.

5.2 Alignment and Calibration

In any experiment involving spatial and spectral resolutions as in the present study alignment of the optical system and calibration of its components are of critical importance. Alignment is achieved using the Argon-ion laser, visible and infrared light sources and a mirror placed vertically on top of the burner. The mirror is placed in such a way that its reflecting surface coincides with the central axis of
Table 5.1: Wavelength range for monochromator grating and long-pass filter combinations.

<table>
<thead>
<tr>
<th>Light source</th>
<th>UV - Visible</th>
<th>Near infrared - Infrared</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xenon</td>
<td>Silicon Carbide glowbar</td>
</tr>
<tr>
<td>Wavelength range (μm)</td>
<td>0.2 - 0.3</td>
<td>0.6 - 1.1</td>
</tr>
<tr>
<td>Gratings:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength region (μm)</td>
<td>0.18 - 0.7</td>
<td>0.6 - 2</td>
</tr>
<tr>
<td>Groove spacing (lines/mm)</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>Part No. (ORIEL)</td>
<td>77296</td>
<td>77299</td>
</tr>
<tr>
<td>Filters:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% cut-on wavelength (μm)</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Part No. (Corion)</td>
<td>-</td>
<td>51250</td>
</tr>
<tr>
<td>Detector</td>
<td>1P28</td>
<td>1P28</td>
</tr>
</tbody>
</table>
the burner. The light beams emerging from the Xenon lamp and glowbar were focused onto the mirror by the set of lenses as shown in Figure 5.1. Caution was exercised so that the beams from the laser, and the visible and infrared sources were propagating on the same plane and intersecting precisely at the same point on the central axis above the burner surface. For the infrared wavelengths the point of intersection was determined by using an infrared sensitive plate (model Q-42-A1, Quantex).

After the alignment is complete, the spectral performance of the system is checked by detecting the emission lines of a mercury arc lamp for the ultraviolet and visible wavelengths, the absorption lines of liquid chloroform from 1 µm to 2.2 µm as well as the absorption spectrum of polysterene film from 2.5 µm to 9 µm. The liquid chloroform was placed in a 1 cm diameter cell, whereas the polysterene film (Perkin-Elmer, model 186-2082) used has a thickness of 0.05 mm. Figure 5.2 shows the emission lines of a mercury arc lamp (San Gabriel, model SCT1) whereas Table 5.2 shows the comparison of the emission lines from the calibration with those provided by ORIEL [61]. The data were taken with entrance and exit slits openings of 10 nm. A comparison of the detected and reported emission lines shows only a 0.4 nm difference, which is considered to be quite satisfactory. The calibration curves for liquid chloroform and the polysterene film are shown in Figures 5.3 - 5.5. Comparisons with published data [62] show excellent agreements. These results suggest that the present optical system works properly for transmission measure-
Figure 5.2: Calibration emission lines for mercury arc lamp.
Figure 5.3: Spectrum of liquid chloroform in the wavelength range 0.96 to 1.89 μm.
Figure 5.4: Spectrum of liquid chloroform in the wavelength range 1.7 to 2.92 µm.
Figure 5.5: Spectrum of polystyrene film
Table 5.2: Comparison of the emission lines for mercury arc lamp.

<table>
<thead>
<tr>
<th>Present (μm)</th>
<th>ORIEL (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2533</td>
<td>.2537</td>
</tr>
<tr>
<td>.2966</td>
<td>-</td>
</tr>
<tr>
<td>.3132</td>
<td>-</td>
</tr>
<tr>
<td>.3649</td>
<td>.3650</td>
</tr>
<tr>
<td>.4044</td>
<td>.3650</td>
</tr>
<tr>
<td>.4357</td>
<td>.4358</td>
</tr>
<tr>
<td>.5462</td>
<td>.5461</td>
</tr>
<tr>
<td>.5769</td>
<td>.5770</td>
</tr>
<tr>
<td>.5792</td>
<td>.5791</td>
</tr>
</tbody>
</table>

A typical intensity spectrum obtained from the Xenon lamp and the Silicon Carbide glowbar light sources is shown in Figures 5.6 - 5.7. It is noted that the absorption bands of water vapor (~1.8 and ~2.8 μm) and carbon dioxide (~4.3 μm) were evident in these experiments.

5.3 Measured Extinction Spectra of Propane and Methane Flames

Transmission measurements from 0.2 μm to 7 μm for propane/oxygen and methane/oxygen flames with various fuel equivalence ratios were performed. The transmitt-
Figure 5.6: Typical intensity spectrum of Xenon lamp.
Figure 5.7: Typical intensity spectrum of Silicon Carbide glowbar.
tance is determined as the ratio of the signal level with the flame on to that without flame. The reference intensities (without flame) are measured before and after each measurement for a given wavelength range to ensure that light intensity remains steady throughout the measurement. Four separate measurements were carried out in the visible wavelengths instead of two steps as shown in Table 5.1. This is due to the sharp increase in the intensity of the Xenon lamp in the range 0.2 to 0.25 μm. Thus, the actual wavelength ranges are 200 - 250, 250 - 300, 300 - 350 and 350 - 600 μm. In addition, the monochromator scan rate 100 nm/min. was too fast to obtain reliable data in this wavelength region. Therefore the monochromator was driven using an external driving unit providing scan rates in the range 20 nm to 50 nm/min.

The results of transmission measurements for the propane/oxygen and methane/oxygen flames with various fuel equivalence ratios are presented in Figures 5.8 - 5.14. The extinction coefficient is computed using equation (2.9). In all cases, a marked maximum of extinction coefficient is observed in the ultraviolet region of 0.25 - 0.28 μm. The maxima are shifted progressively toward longer wavelengths as the fuel equivalence ratio increases. The maxima also moved toward longer wavelengths as the height above the burner surface increases. This phenomenon is in agreement with the results reported in previous work [63]. Table 5.3 compares the wavelengths where the maximum extinction occurs for each flame. It has been shown by electron microscope that the typical soot particles are formed by graphitic layer of about
Table 5.3: Resonance wavelength of absorption in the ultraviolet region.

<table>
<thead>
<tr>
<th></th>
<th>Propane/oxygen</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\phi)</td>
<td>1.8</td>
<td>2.1</td>
<td>2.4</td>
</tr>
<tr>
<td>H (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu m)</td>
<td>0.253</td>
<td>0.266</td>
<td>0.265</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.266</td>
<td>0.265</td>
<td>0.278</td>
</tr>
<tr>
<td></td>
<td>Mathane/oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\phi)</td>
<td>2.2</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>H (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu m)</td>
<td>0.251</td>
<td>0.260</td>
<td>0.255</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.259</td>
<td>0.268</td>
<td></td>
</tr>
</tbody>
</table>

20 Å in size [64]. Since the optical transitions of graphite involving the \(\pi\) bands are in the near ultraviolet and infrared (0.26 \(\mu m\) and 1.5 \(\mu m\)) [55, 65] it may be argued that the absorption peak of soot in the ultraviolet is due to the \(\pi\) electron excitation as in the case of graphite. However, a precise physical interpretation of this phenomenon is not warranted at this time.

It is also seen that the extinction coefficients in all cases decrease strongly with wavelength in the visible and infrared spectrum covered. Moreover, the extinction coefficients of the propane flames are higher than those of methane flame (see Figures 5.9 - 5.14). This is due to higher volume fractions of propane soot as compared with the methane flame. For the propane flame, the extinction coefficient in the ultraviolet increase by a factor of three when the fuel equivalence ratio increase from 1.8 to 2.4 whereas the methane flames display a smaller increase,
Figure 5.8: Measured spectral transmittance for the propane/oxygen flame with $\phi = 1.8$. 
Figure 5.9: Measured spectral extinction coefficient for the propane/oxygen flame with $\phi = 1.8$. 
Figure 5.10: Measured spectral extinction coefficient for the propane/oxygen flame with $\phi = 2.1$. 
Figure 5.11: Measured spectral extinction coefficient for the propane/oxygen flame with $\phi = 2.4$. 
Figure 5.12: Measured spectral extinction coefficient for the methane/oxygen flame with $\phi = 2.2$. 

METHANE/OXYGEN, $\phi = 2.2$

$H (\text{MM})$

6
8
16

WAVELENGTH (MICRON)

EXTINCTION COEFFICIENT (cm$^{-1}$)
Figure 5.13: Measured spectral extinction coefficient for the methane/oxygen flame with $\phi = 2.4$. 

METHANE/OXYGEN, $\phi=2.4$

$H$ (mm)

- 6
- 8
- 16
Figure 5.14: Measured spectral extinction coefficient for the methane/oxygen flame with $\phi = 2.6$. 

METHANE/OXYGEN, $\phi = 2.6$

WAVELENGTH (MICRON)

EXTINCTION COEFFICIENT (cm$^{-1}$)
about a factor of two when the fuel equivalence ratio increases from 2.2 to 2.6.

5.4 Data Analysis and Discussion

5.4.1 Data Analysis

The extinction coefficients for propane/oxygen flame with $\phi = 1.8$ at the height of 6 mm were used for analysis. The refractive indices determined from Kramers-Kronig analysis are shown in Figure 5.15 and Table 5.4. The present results were compared with the indices of Dalzell and Sarofim [3] and Lee and Tien [7] as well as with indices determined by fitting the extinction data to the Drude-Lorentz equations. The results show fair agreement with the results of existing method in the infrared. However, in the top ultraviolet and infrared some discrepancies are noted.

It should be pointed out that the present results are only for a particular flame at one height. As mentioned in Chapter 3, the indices change with fuel equivalence ratio as well as the height above the burner. Therefore it is expected that further analysis will show how the indices for other $\phi$'s and at different heights change with wavelength.

5.4.2 Discussion

Apart from the error introduced because of the extrapolation inherent in the KK method of analysis several other factors may contribute to the uncertainties as-
associated with the refractive index of the primary particle as it exists under flame conditions. Specifically, the particle diameter inferred from the autocorrelation possesses an uncertainty because of the sensitivity of the measured decay rate at low sampling times ($\sim 10^{-6}$ sec) [21]. This results in uncertainty in the number density since $N$ is proportional to $r^3$. It should also be pointed out that reliable data analysis is only possible for positions in the flame where the "diffusional" diameter can be considered to be the same with the "optical" diameter as required by the Mie equations. This limits the region in the flame where data analysis can yield the soot indices with the minimum possible error. In addition, even for the low position in the flame the single primary particle assumption can be called into question. Thus, the inferred refractive indices can only be considered as "effective" and not "absolute". However, it should be pointed out that the present method can yield the "effective" refractive indices over the whole spectrum with the least number of assumptions as compared with the Drude-Lorentz dispersion model that has been used so far. The main drawbacks of the approach are: 1) infrared transmission measurements under flame conditions are difficult to obtain and 2) the experimental uncertainty, over the whole range of measurements and especially in the infrared upper limit, must be as low as possible.
Figure 5.15: Experimentally determined real ($n$) and imaginary ($k$) part of the refractive index using the KK analysis.
Table 5.4: Optical properties of soot determined from the present study and predicted by the models of previous investigators.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
<td>n</td>
</tr>
<tr>
<td>0.258</td>
<td>0.89</td>
<td>0.87</td>
<td>1.18</td>
</tr>
<tr>
<td>0.354</td>
<td>1.34</td>
<td>0.81</td>
<td>1.49</td>
</tr>
<tr>
<td>0.539</td>
<td>1.63</td>
<td>0.54</td>
<td>1.58</td>
</tr>
<tr>
<td>0.751</td>
<td>1.59</td>
<td>0.57</td>
<td>1.61</td>
</tr>
<tr>
<td>1.033</td>
<td>1.63</td>
<td>0.61</td>
<td>1.66</td>
</tr>
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Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The results of the present study may be summarized as follows:

1. The sensitivity of optical measurements to the reported range of the refractive indices showed that the particle size changes up to 76 percent when the real part \(n\) decreases from 2.0 to 1.3 and is relatively insensitive to \(k\). The volume fraction changes by a factor of two for the same range of values of the real part \(n\) and changes by factor 3 when the imaginary \(k\) varies from 0.3 to 1. Also, the spectral emissivity and radiative flux show a strong dependence on the refractive index. This implies that reliable optical properties are important in the area of the combustion diagnostics, radiative transfer and other applications.

2. Classical and dynamic light scattering measurements were performed for premixed propane/oxygen flame with fuel equivalence ratio \(\phi = 1.8\) as function of height above the burner surface. The particle size distributions were determined
from autocorrelation measurement. A tunable argon-ion laser was used for the measurements of the scattering and extinction coefficients in the visible wavelengths. For a given positions in the flame (12 mm) the indices of glassy carbon are in good agreement with the measured real and imaginary parts of the index. The volume fractions of soot determined with constant indices (\( \overline{m} = 1.57 - 0.56i \) and \( \overline{m} = 1.90 - 0.55i \)) throughout the flame differ by 13.5 and 36.5 percent respectively when compared with the results determined with variable indices. The analysis of agglomeration effect showed that the refractive indices of the primary particles are slightly higher than that of the agglomerated particle. A set of dispersion constants was obtained using the extinction data in the range 340 - 600 nm.

3. The effects of the type of fuel and fuel equivalence ratio on the soot indices were analyzed for two different flames, propane/oxygen and methane/oxygen. Both the number densities and volume fractions increases when the fuel equivalence ratio increases. It was found that the indices varied substantially not only with respect to the position in the flame but also with the fuel equivalence ratio both for propane and methane flames. It was suggested that the compositional effects (particularly at lower heights) and the agglomeration (particularly at higher positions) should play an important role in the soot indices.

4. The Kramers-Kronig dispersion theory to obtain the spectral refractive index of soot over the whole wavelengths was presented along with the analysis of the effects of experimental error and the extrapolation on the data reduction. Spec-
tral transmission measurements were carried out in the wavelength range 0.2 to 7 microns for propane and methane flames with various fuel equivalence ratios. In all cases, the extinction spectra showed a similar trend: a marked maximum in the range of wavelengths 0.25 to 0.27 μm, depending on the height above the burner surface, and then a strong decrease with wavelength. The refractive index from Kramers-Kronig analysis for a propane/oxygen flame with $\phi = 1.8$ at the height 6 mm was compared with the results of existing techniques. It was demonstrated that the present method could yield the refractive indices of soot particles over the whole spectrum with the least number of assumptions as compared with methods that have been used.

### 6.2 Recommendations

The following recommendations are made for future work:

1. The present method utilizes the relation between the real and imaginary part of the complex electrical permittivity to determine the number density and refractive index at the laser wavelength in conjunction with the scattering and extinction data. Obtaining the particle number density from exact relation or other experimental data may reduce the error in the Kramers-Kronig analysis.

2. The soot particles at their early stage of formation are small pseudo-spherical units. However, they grow into agglomerated structures such as chain and cluster. Thus, the agglomeration effects need to be considered in the data analysis, especially for higher positions in the flame. In addition, higher flow rates are desirable to
reduce the degree of agglomeration in further measurements.

3. Further analysis of extinction data is needed. This will provide a better insight into the spectral variation of soot refractive index.
Bibliography


Appendix A

Experimental Conditions in Autocorrelation Measurements

The experimental conditions for photon correlation measurements for the propane and methane flames are presented in this section. The sample time ($\Delta t$), voltage of the power supply, laser ampare, prescale of correlator, and run time at each height are summarized. The sample times used are approximately 10 times longer than the optimum sample time which is expressed as

$$ (\Delta t)_{opt} = \frac{2}{|q|^2DM}. \quad (A.1) $$

It is noted that the sample time becomes short whereas the voltage, laser power and run time increase when the height above the burner surface decreases (usually the measurement starts from higher positions). This is due to the higher temperature and smaller size of the soot at lower positions.
Table A.1: Experimental conditions in autocorrelation measurements for propane/oxygen flame with $\phi = 1.8$.

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Table A.2: Experimental condition in autocorrelation measurement for the propane/oxygen flame with $\phi = 2.1$.

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Table A.3: Experimental condition in autocorrelation measurement for the propane/oxygen flame with $\phi = 2.4$.

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Table A.4: Experimental condition in autocorrelation measurement for the methane/oxygen flame with $\phi = 2.2$.

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Table A.5: Experimental condition in autocorrelation measurement for the methane/oxygen flame with $\phi = 2.4$.

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Appendix B

Computer Programs for Data Reduction

The investigation of the optical properties of soot particles using in situ light scattering technique not only requires extensive experimental work but also a considerable amount of computational effort. Several computer programs have been developed during the course of this work. They include the programs for autocorrelation data analysis, for scattering and extinction data analysis for Rayleigh and Mie regimes (monodisperse and polydisperse), for extinction efficiency of cylindrical particles, and for Kramers-Kronig analysis. Among them, four programs are listed here: scattering/extinction data analysis for Mie regime; Kramers-Kronig analysis of extinction data; and determination of mean radius and variance of size distribution from autocorrelation data.
C THIS PROGRAM COMPUTES THE NUMBER DENSITY AND COMPLEX REFRACTIVE
C INDEX FROM SCATTERING/EXTINCTION DATA AND PARTICLE SIZE.
C MIE MONODISPERSE SOLUTION.

C-----------------------------------------------------------------
1 REAL ND, KL, KH
2 PI = 3.141593
3 PRINT 60
4 WL = .488
5 DI = .05849
6 QV = .1194E-3
7 TAU = .71
8 PL = 6.
9 ANG = 90.
10 CLAM = .5165
11 KL = .58
12 KH = .62
13 QVV = QV * .985 / TAU
14 RK1 = KL * 100.
15 RK2 = KH * 100.
16 LK1 = RK1
17 LK2 = RK2
18 DO 10 LK = LK1, LK2
19 RF1 = FLOAT(LK) * .01
20 RFR = CLAM ** 2 * SQRT(CLAM ** 2 * RF1 ** 2 + RF1 ** 2 + 1.)
21 SCA = ANG + 1.
22 CALL FUNC(DI, R2, RFR, RF1, ND, EXPT, QE, WL, QV, TAU, PL, SCA)
23 10 PRINT 55, RFR, RF1, ND, R2
24 FORMAT(/ 2X,2F10.3,E12.3,2F13.6)
25 55 FORMAT(1', 9X,'N',9X,'K', 9X,'DEN.',9X,'RES')
26 STOP
27 END

SUBROUTINE FUNC(DI, R2, RFR, RF1, ND, EXPT, QE, WL, QV, TAU, PL, SCA)

REAL*8 THETD(100), ELMX(4, 91, 2), QEXT, QSCAT
REAL*8 PI = 3.141593
X = PI * DI / WL
EXPT = -QV / (ALOG(TAU) / PL)
THETD(1) = 0.
JX = 91
AF = 1.
DO 2 J = 1, JX
2 THETD(J) = (J-1) * AF + THETD(1)
CALL DBMIE(X, RFR, RF1, THETD, JX, QEXT, ELMX)
PIQE = PI * X ** 2 * QEXT
RATIO = ELMX(2, SCA, 1) / PIQE
R2 = EXPT - RATIO
ND = -4. * ALOG(TAU) / (PL * PI * QEXT * (DI + 1.E-4) ** 2)
RETURN
END

SUBROUTINE DBMIE(X, RFR, RF1, THETD, JX, QEXT, ELMX)
REAL*8 THETD(100), ELMX(4, 91, 2)
REAL*8 QEXT, QSCAT, CTBRQS
DIMENSION T(5), TA(4), TB(2), TC(2), TD(2), TE(2)
DIMENSION PI(3, 91), TAU(3, 91), CSTHT(91)
DIMENSION SIZHT(91), WFN(2), ACAP(500)
COMPLEX RF, RRF, RRFX, WH1, FNA, FNB, TC1, TC2, WFN, ACAP
5 FORMAT(T10,' THE VALUE OF THE SCATTERING ANGLE IS GREATER THAN
   . 90.0 DEGREES. IT IS ',E15.4)
6 FORMAT(//T10,' PLEASE READ COMMENTS.'//)
7 FORMAT(//T10,' THE VALUE OF THE ARGUMENT JX IS GREATER THAN 100')
8 FORMAT(//T10,' THE UPPER LIMIT FOR ACAPT IS NOT ENOUGH. SUGGEST GET
   . DETAILED OUTPUT AND MODIFY SUBROUTINE'//)

EQUIVALENCE (WFN(1),TA(1)),(FNA,TB(1)),(FNB,TC(1))
EQUIVALENCE(FNAP,TD(1)),(FNBP,TE(1))

IF ( JX .LE. 100 ) GO TO 20
WRITE(6,7)
WRITE(6,6)
CALL EXIT

20 RF = CMPLX(RFR,-RFI)
   RRF=1./RF
   RX=1./X
   RRFX = RRF * RX
   T(1) = (X**2)*((RFR**2 + RFI**2)
   T(1)= SQRT(T(1))
   NMX1=1.1*T(1)
   IF(NMX1.LE.2399) GO TO 21
   IX=1
   CALL EXIT

21 NMX2 = T(1)
   IF ( NMX1 .GT. 150 ) GO TO 22
   NMX1 = 150
   NMX2 = 135
   ACAP(NMX1+1)=(0.,0.)
   DO 23 N = 1,NMX1
      NN = NMX1 - N + 1
      ACAP(NN) = (NN+1) * RRFX - 1.0 /((NN+1)*RRFX + ACAP(NN+1))
   CONTINUE

23 CONTINUE
   DO 30 J = 1,JX
      IF ( THETD(J) .LT. 0.0 ) THETD(J) = ABS(THETD(J))
      IF ( THETD(J) .GT. 0.0 ) GO TO 24
      CSTHT(J) = 1.0
      SI2THT(J) = 0.0
      GO TO 30
   24 IF ( THETD(J) .GE. 90.0 ) GO TO 25
      T(1) = (.3141593E1*THETD(J))/180.
      CSTHT(J) = COS(T(1))
      SI2THT(J) = 1.0 - CSTHT(J)**2
      GO TO 30
   25 IF ( THETD(J) .GT. 90.0 ) GO TO 28
      CSTHT(J) = 0.0
      SI2THT(J) = 1.0
      GO TO 30
   28 WRITE(6,5) THETD(J)
      WRITE(6,6)
      CALL EXIT

30 CONTINUE
   DO 35 J = 1,JX
      PI(1,J) = 0.0
      PI(2,J) = 1.0
      TAU(1,J) = 0.0
      TAU(2,J) = CSTHT(J)
   CONTINUE

35 CONTINUE
   T(1) = COS(X)
   T(2) = SIN(X)
WM1 = CMPLX( T(1),-T(2))
WFN(1) = CMPLX(T(2), T(1))
WFN(2) = RX * WFN(1) - WM1
TC1 = ACAP(1) * RRF + RX
TC2 = ACAP(1) * RF + RX
FNA = (TC1*TA(3) - TA(1))/(TC1*WFN(2) - WFN(1))
FNB = (TC2*TA(3) - TA(1))/(TC2 * WFN(2) - WFN(1))
N=1
FNAP = FNA
FNBP = FNB
T(1)=1.5
TB(1) = T(1) * TB(1)
TB(2) = T(1) * TB(2)
TC(1) = T(1) * TC(1)
TC(2) = T(1) * TC(2)
DO 60 J = 1,JX

ELTRMX(1,J,1) = TB(1) * PI(2,J) + TC(1) * TAU(2,J)
ELTRMX(2,J,1) = TB(2) * PI(2,J) + TC(2) * TAU(2,J)
ELTRMX(3,J,1) = TC(1) * PI(2,J) + TB(1) * TAU(2,J)
ELTRMX(4,J,1) = TC(2) * PI(2,J) + TB(2) * TAU(2,J)
ELTRMX(1,J,2) = TB(1) * PI(2,J) - TC(1) * TAU(2,J)
ELTRMX(2,J,2) = TB(2) * PI(2,J) - TC(2) * TAU(2,J)
ELTRMX(3,J,2) = TC(1) * PI(2,J) - TB(1) * TAU(2,J)
ELTRMX(4,J,2) = TC(2) * PI(2,J) - TB(2) * TAU(2,J)

60 CONTINUE
QEXT=2.*(TB(1)+TC(1))
QSCAT = (TB(1)**2 + TB(2)**2 + TC(1)**2 + TC(2)**2 )/ .75
CTBRS = 0.
N = 2
65 T(1) = 2*N - 1
T(2) = N - 1
T(3) = 2 * N + 1
DO 70 J = 1,JX
PI(3,J) = (T(1)*PI(2,J)*CSTHT(J)-N*PI(1,J))/T(2)
TAU(3,J) = CSTHT(J)*(PI(3,J)-PI(1,J))-T(1)*SI2THT(J)*PI(2,J)+
+ TAU(1,J)
70 CONTINUE

WM1 = WFN(1)
WFN(1) = WFN(2)
WFN(2) = T(1)*RX*WFN(1) - WM1
TC1 = ACAP(N)*RRF + N*RX
TC2 = ACAP(N)*RF + N*RX
FNA = (TC1*TA(3)-TA(1))/(TC1*WFN(2) - WFN(1))
FNB = (TC2*TA(3)-TA(1))/(TC2 * WFN(2) - WFN(1))
T(5) = N
T(4) = T(1)/(T(5)*T(2))
T(2) = (T(2)*T(5) + 1.0 )/T(5)
CTBRS = CTBRS + T(2)*TD(1)*TB(1) + TD(2)*TB(2) + TE(1)*TC(1) +
+ TE(2)*TC(2) + T(4)*(TD(1)*TE(1) + TD(2)*TE(2))
QEXT = QEXT + T(3)*(TB(1)+TC(1))
QSCAT = QSCAT + T(3) *T(4)
T(2) = N*(N+1)
T(1) = T(3)/T(2)
K = (N/2)**2
DO 80 J = 1,JX
ELTRMX(1,J,1) = ELTRMX(1,J,1)+T(1)*(TB(1)*PI(3,J)+TC(1)*TAU(3,J))
ELTRMX(2,J,1) = ELTRMX(2,J,1)+T(1)*(TB(2)*PI(3,J)+TC(2)*TAU(3,J))
ELTRMX(3,J,1) = ELTRMX(3,J,1)+T(1)*(TC(1)*PI(3,J)+TB(1)*TAU(3,J))
ELTRMX(4,J,1) = ELTRMX(4,J,1)+T(1)*(TC(2)*PI(3,J)+TB(2)*TAU(3,J))
169   IF ( K .EQ. N ) GO TO 75
170   ELTRMX(1, J, 2) = ELTRMX(1, J, 2) + T(1) * (TB(1) * PI(3, J) - TC(1) * TAU(3, J))
171   ELTRMX(2, J, 2) = ELTRMX(2, J, 2) + T(1) * (TB(2) * PI(3, J) - TC(2) * TAU(3, J))
172   ELTRMX(3, J, 2) = ELTRMX(3, J, 2) + T(1) * (TC(1) * PI(3, J) - TB(1) * TAU(3, J))
173   ELTRMX(4, J, 2) = ELTRMX(4, J, 2) + T(1) * (TC(2) * PI(3, J) - TB(2) * TAU(3, J))
174   GO TO 80
175   75   ELTRMX(1, J, 2) = ELTRMX(1, J, 2) + T(1) * (-TB(1) * PI(3, J) + TC(1) * TAU(3, J))
176   ELTRMX(2, J, 2) = ELTRMX(2, J, 2) + T(1) * (-TB(2) * PI(3, J) + TC(2) * TAU(3, J))
177   ELTRMX(3, J, 2) = ELTRMX(3, J, 2) + T(1) * (-TC(1) * PI(3, J) + TB(1) * TAU(3, J))
178   ELTRMX(4, J, 2) = ELTRMX(4, J, 2) + T(1) * (-TC(2) * PI(3, J) + TB(2) * TAU(3, J))
179   80  CONTINUE
180   IF ( T(4) .LT. 1.0E-11 ) GO TO 100
181   N = N + 1
182   DO 90 J = 1, JX
183      PI(1, J) = PI(2, J)
184      PI(2, J) = PI(3, J)
185      TAU(1, J) = TAU(2, J)
186      TAU(2, J) = TAU(3, J)
187   90  CONTINUE
188   FNAP = FNA
189   FNBP = FNB
190   IF ( N .LE. NMX2 ) GO TO 65
191   WRITE(6, 8)
192      CALL EXIT
193   100 DO 120 J = 1, JX
194      DO 120 K = 1, 2
195      DO 115 I = 1, 4
196      T(I) = ELTRMX(I, J, K)
197   115 CONTINUE
198      ELTRMX(2, J, K) = T(1) ** 2 + T(2) ** 2
199      ELTRMX(1, J, K) = T(3) ** 2 + T(4) ** 2
200      ELTRMX(3, J, K) = T(1) * T(3) + T(2) * T(4)
201      ELTRMX(4, J, K) = T(2) * T(3) - T(4) * T(1)
202   120 CONTINUE
203      T(1) = 2. * RX ** 2.
204      QEXT = QEXT * T(1)
205      QSCAT = QSCAT * T(1)
206      CTBRQS = 2. * CTBRQS * T(1)
207      RETURN
208 END

$ENTRY
C THIS PROGRAM COMPUTES THE PARTICLE NUMBER DENSITY AND
C REFRACTIVE INDEX FROM SCATTERING/EXTINCTION DATA, MEAN
C PARTICLE RADIUS AND GEOMETRIC WIDTH. MIE POLYDISPERSE
C SUBROUTINES: FCN, NORM, ZOLD AND DBMIE

1  WL= .488
2  DIA= .0526
3  SIGMA= 1.155
4  QVV= .1502E-3
5  TAU= .67
6  PL= 5.5
7  CLAM= .5165
8  ANG= 90.
9  KL= .59
10  KH= .62
11  PRINT 460
12  PI=3.141593
13  RO= DIA* .5
14  DELR= 2.E-3
15  RK1= KL*100.
16  RK2= KH*100.
17  LK1= RK1
18  LK2= RK2
19  QVV=QVV*.985/TAU
20  EXPT= - QVV/(ALOG(TAU) /PL)
21  SCA= ANG+1.
22  CHK= DIA*.5E3
23  IF(CHK.LT.34) IRDB= 8
24  IF(CHK.GE.34) IRDB= 16
25  IF(CHK.GE.45) IRDB= 20
26  DO 10 LL= LK1.LK2
27    RFI= FLOAT(LL)*.01
28    RFR= CLAM*RFI + SQRT(CLAM**2 * RFI**2 + RFI**2 +1.)
29   S1= 0.
30   S2= 0.
31   D2= 0.
32   S3= 0.
33  ALSIG= ALOG(SIGMA)
34  CALL NORM(ALSIG,RO,IRDB,IE)
35  DO 5 I= IRDB,IE,2
36    RAD= FLOAT(I)* 1.E-3
37    X= 2.*RAD *PI/WL
38  CALL FUNC(RO,R2,RF,RFI,X,RAD,DELR,ALSIG,PN1,PN2,DN2,SCA)
39    S1= S1 + PN1
40    S2= S2 + PN2
41  5  D2= D2 + DN2
42    S1= S1 *(WL*1.E-4)**2
43    S2= S2 *4. *PI**3
44    RAT= S1/S2
45  R2= EXPT -RAT
46  DN= -.4.*ALOG(TAU) / (PL* D2* PI)
47  10 PRINT 455, RFR,RF,RFI, X,RAD,DELR,ALSIG,PN1,PN2,DN2,SCA
48  455 FORMAT( / 7X,2F10.3,E12.3,F12.5)
49  460 FORMAT( '1',14X,'N',9X, 'K', 6X, 'NO.DEN',8X,'RES')
50  STOP
51  END

SUBROUTINE FUNC(RO,R2,RF,RFI,X,RAD,DELR,ALSIG,PN1,PN2,DN2,SCA)
REAL*8 THETD(100),ELTRMX(4,91,2),QEXT,QSCAT
THETD(1) = 0.
JX = 91
AF = 1.
DO 2 J = 1,JX
  2 THETD(J) = (J-1) * AF + THETD(1)
CALL DBMIE(X,RFR,RFI,THETD,JX,QEXT,QSCAT,ELTRMX)
CALL ZOLD(ALSIG,RO,PA,RAD)
PN1 = PA * ELTRMX(2,SCA,1) * DELR
DN2 = PA * QEXT * DELR * (RAD*2.E-4)**2
PN2 = PA * QEXT * DELR * (RAD*1.E-4)**2
RETURN
END

SUBROUTINE ZOLD(ALSIG,RO,PA,RAD)
PI = .3141593E1
EXP1 = EXP(-.5* ALSIG**2)
EXP2 = EXP(- ALOG(RAD/RO)**2/ (2.* ALSIG**2))
PA = EXP1 * EXP2/ (SQRT(2.*PI) * RO * ALSIG)
RETURN
END

SUBROUTINE NORM(ALSIG,RO,IRDB,IRW)
REAL SM(300),NR
IDR = 2
DR = FLOAT(IDR)*1.E-3
PI = 3.141593
J = 1
IR = IRDB
SUM = 0.
5 R = FLOAT(IR)
RAD = R*1.E-3
CALL ZOLD(ALSIG,RO, NR, RAD)
SM(J) = NR * DR
SUM = SUM + SM(J)
IF(SUM.GT..9995) GO TO 20
IR = IR + IDR
J = J + 1
GO TO 5
20 XSUM = 0.
IRW = IR
RETURN
END

$ENTRY
$JOB
TIME=20

C-----------------------------------
C THIS PROGRAM COMPUTES THE COMPLEX REFRACTIVE INDEX FROM
C SPECTRAL TRANSMISSION DATA USING KRAMERS-KRONIG DISPERSION
C RELATIONS.
C SUBROUTINES: FCN, GAUSS, LOF, ZSCNT(IMSL), DISP, BHM
C-----------------------------------
REAL W(2500), WSQ(2500), Y(2500), H(2500), PERN(2500), PV(2500)
REAL PV1(500), PV2(500), H(2500), WL(2500), DELW(2500)
REAL RR(2500), RI(2500), S1Z(2500), HV(500), WAV(500)
REAL PERK(2500), WW(500), TAU(2500)
REAL*8 AI(2500), AR(2500), SH11, SM12, SM22, QE(2500)
REAL WK(42), X(2), PAR(5), FNORM, NR(2500), NI(2500), FREQ(200)
REAL ERN(500), ERK(500), DELR(2500)
REAL DIA(3), SENS(2), WAVR(2500)
REAL WAVL(2500), RET(2500), AIPT(2500), WPT1(2500)
REAL KEKT(2500), TAUT(2500), AIPL(2500)
COMPLEX REFREL, S1(200)

DATA XLEN/10./, YLEN/6.5/, PI/3.141593/, NTS/111/

EXTERNAL FCN
CALL IDENT
CALL PLOT(2., 2., -3)
DIA(1)= .04798
AIZERO = 0.
MX1 = 1200
MX2 = 1220
IST= 37
MAX = MX1 + MX2
NPTS= MAX
MM2 = MAX - 2
MPRT = MX1 - 20
HB = 6.5822E-16
N = 2
NSIG = 4
ITMAX = 100
PL= 4.7
DEN= 6.500E9
DO 8 J = 1, MX1
HF(J) = EV
HW(J) = EV
8 DELW(J) = .005 / HB
DO 9 J = 1, MX2
EV = FLOAT(J) *.005
HW(J+ MX1) = EV
9 DELW(J+ MX1) = .02 / HB
DO 10 J = 1, MAX
W(J) = HW(J) / HB
10 WSQ(J) = W(J)**2

C READ DATA
DO 11 J = 1, NTS
11 READ(10, 12) WAVL(J), TAU(J)
12 FORMAT(/F10.5, F8.4)
13 DELR(J) = WAVL(J+1) - WAVL(J)
14 J= MX1
241 I= 1
242 RMIN= WAVL(I) - WL(J)
243 IF(RMIN.EQ.0.) GO TO 243
53 IF(RMIN.GT.0.) GO TO 244
54 I= I + 1
55 GO TO 242
56 243 RET(J)= TAU(I)
57 KEXT(J)= -ALOG(RET(J))/PL
58 GO TO 245
59 244 TAU=D TAU(I) - TAU(I-1)
60 RET(J)= TAU(I-1) + TAU *(W(L(J)-WAVL(I-1))/DELR(I-1)
61 KEXT(J)= -ALOG(RET(J))/PL
62 245 IF(J.EQ. IST) GO TO 259
63 J= J - 1
64 GO TO 241
65 259 ID= 1
66 PAR(5) = 1.
67 DO 18 J = 9, MX1
68 XX= DIA(ID) * PI / WL(J)
69 SIZ(J) = XX
70 CALL DISP(WL,RR,RI,J)
71 RFR = RR(J)
72 RFI = RI(J)
73 18 REFREL = CMPLX(RFR,RFI)
74 DO 19 J = 1, ISTM1
75 QE(J) = -ALOG(RET(J))/ (PL*PI* (DIA(1)*.5E-4)**2 *DEN)
76 XX= DIA(ID) * PI / WL(J)
77 19 AI(J) = QE(J) / (4. * XX)
78 CALL LOF(W,AL,IST)
79 ISTM1= IST - 1
80 DO 262 J= 1, ISTM1
81 XX= DIA(1) * PI /WL(J)
82 SIZ(J)= XX
83 PRN= PI *(DIA(1)*.5E-4)**2 * DEN * 4. * SIZ(J) * AI(J)
84 RET(J)= EXP(-PRN * PL)
85 262 KEXT(J)= PRN
86 RHS = 2.09 /SIZ(MX1) +3.94 /SIZ(MX1)**2 - 8.3 /SIZ(MX1)**3
87 . + 6.53 /SIZ(MX1)**4
88 CB= AI(MX1) /RHS
89 MXM1= MX1 - 1
90 S39 = SIZ(MXM1)
91 RHS1= 2.09 / S39 +3.94 / S39**2 - 8.3 / S39 **3
92 . + 6.52 / S39**4
93 CB1 = AI(MXM1)/ (CB * RHS1)
94 R = - ALOG(CB1) /ALOG(W(MXM1)/W(MX1))
95 MXP1= MX1 + 1
96 DO 21 J = MXP1, MAX
97 XX= DIA(ID) * PI / WL(J)
98 SIZ(J)= XX
99 AI(J) = CB * ( 2.09/XX + 3.94/XX**2 - 8.3/XX**3 + 6.53/XX**4)
100 . / (W(J)/W(MX1))**R
101 PRN= PI *(DIA(1)*.5E-4)**2 * DEN * 4. * SIZ(J) * AI(J)
102 RET(J)= EXP(-PRN * PL)
103 21 KEXT(J)= PRN
104 PRINT 275, AI(9), AI(8), AI(6), AI(5), AI(4), AI(3), AI(2), AI(1)
105 275 FORMAT(/4X,9F9.4)
106 SI = 1.E-7 / HB
107 SIQ = SI**2
108 PRINT 107
109 I = 9
110 IPL = 1
111 IX = 0
112 IX1 = 0
110  IX2 = 0
111  IX3 = 0
112  PAR(3) = DIA(ID)
113  GO TO 23
114  22  IF(I.LE. 29) GO TO 1
115  IF(I.GE.30.AND.I.LE. 69) GO TO 2
116  IF(I.GE.70.AND.I.LE.395) GO TO 3
117  IF(I.GE.400.AND.I.LE.MPR) GO TO 4
118  1  I= I + 1
119  GO TO 23
120  2  I= I + 2
121  GO TO 23
122  3  I= I + 5
123  GO TO 23
124  4  I= I + 20
125  23  DLSQ = DELW(I)**2
126  PIDL = PI * DELW(I)
127  XP = 2. * WSQ(I) / PI
128  NM1 = I - 1
129  DO 25 J = 1, NM1
130  25  Y(J) = AL(J) / (W(J) * (WSQ(J) - WSQ(I)))
131  SM11 = 0.
132  NM3 = I - 3
133  DO 27 J = 1,NM3,2
135  CHK = FLOAT(I)/2. - 1/2
136  IF(CHK.GT.0.) GO TO 28
137  SUM1 = SM11 * DELW(I) * XP
138  GO TO 44
139  28  SUM1 = (SM11 + .5*(Y(1) + Y(2))) * DELW(I) * XP
140  44  NE = MAX - 2
141  IP1 = I + 1
142  DO 45 J = IP1, MAX
143  45  Y(J) = AL(J) / (W(J) * (WSQ(J) - WSQ(I)))
144  SM21 = 0.
145  MX1M2= MX1- 2
146  DO 46 J = IP1, MX1M2,2
147  46  SM21 = SM21 + (Y(J) + 4.*Y(J+1) + Y(J+2))/ 3.
148  SM21 = SM21 * XP * DELW(I)
149  IF(CHK.EQ.0.) GO TO 50
150  GO TO 51
151  50  SM21 = SM21 + .5*(Y(MX1-1) + Y(MX1)) * XP * DELW(I)
152  51  SM22 = 0.
153  DO 53 J = MX1 , MM2,2
154  53  SM22 = SM22 + ( Y(J) + 4.*Y(J+1) + Y(J+2))/ 3.
155  SUM2 = SM21 + SM22 * DELW(1250) * XP
156  TW = 2. * W(I)
157  TWS = TW * SI
158  TWDL = TW * DELW(I)
159  WSI = W(I) - SI
160  T1 = -2. * AL(I) * (ALOG( WSI /TWDL) ) - ALLOG((W(I) -DELW(I))
        . / (TWDL- DLSQ)) /PI
161  IF( I.GE.2 ) GO TO 57
162  T2 = 2. * W(I) * (AI(I) - AIZERO) * (ALOG((TW-SI) / WSI)
        . - ALLOG((TW - DELW(I)) / (W(I) - DELW(I)) )) / PIDL
163  GO TO 58
164  57  T2 = 2. * W(I) * (AI(I) - AI(I-1)) * (ALOG((TW-SI) / WSI)
        . - ALLOG((TW - DELW(I)) / (W(I) - DELW(I)))) / PIDL
165  58  T3 = -2.*AI(I)*(ALOG((W(I)+DELW(I))/ (TWDL+DLSQ)) -ALLOG((W(I)+SI)
        ./(TWS +SIQ))) / PI
T4 = TW * (AI(I+1) - AI(I)) * ( ALOG((TW+DELW(I))/ (W(I)+DELW(I)))
    - ALOG((TW + SI) / (W(I) + SI))) / PIDL
TSUM = T1 + T2 + T3 + T4
AR(I) = 1. + SUM1 + SUM2 + TSUM
PAR(1) = AR(I)
PAR(2) = AI(I)
PAR(4) = WL(I)
PAR(5) = 2.
ISTP1= IST + 1
IF(I.GE.ISTP1) GO TO 59
DRR= 3. / (1.-AR(I )**2 + AI(I )**2)
ESR= -2. + DRR * (1-AR(I ))
ESI= DRR * AI(I )
ESRISQ= SQRT(ESR**2 + ESI**2)
X(1) = SQRT(.5 * (ESR + ESRISQ))
X(2) = SQRT(.5 * (-ESR + ESRISQ))
GO TO 61
59 X(1)= NR(IPL )
X(2)= NI(IPL )
61 CALL ZSCNT(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
NR(IPL+1)= X(1)
NI(IPL+1)= X(2)
IF(I.EQ.9) NR(I)= X(1)
IF(I.EQ.9) NI(I)= X(2)
PERN(I) = 100. *(NR(IPL+1)-RR(I))/ RR(I)
PERK(I) = 100. *(NI(IPL+1)-RI(I))/ RI(I)
67 IF( I.LE. 30) GO TO 79
IF( I.GE.31.AND.I.LE. 70 ) GO TO 71
IF( I.GE. 71.AND.I.LE.200 ) GO TO 73
IF( I.GE.201.AND.I.LE.400 ) GO TO 75
IF( I.GE.401.AND.I.LE.MPRT ) GO TO 77
71 I30 = ( I - 30 - IX * 2 ) / 2
IF( I30.EQ.0 ) GO TO 22
IPL = IPL + I30
IX = IX + 1
AIPL(IPL)= AI(I)
IF(IPL.EQ.29) PRINT 107
GO TO 80
73 I70 = ( I - 70 - IX1 * 5 ) /5
IF (I70.EQ.0) GO TO 22.
IPL = IPL + I70
IX1 = IX1 + 1
AIPL(IPL)= AI(I)
IF(IPL.EQ.57) PRINT 107
GO TO 80
75 I200= ( I-200 -IX2 *10 ) /10
IF (I200.EQ.0) GO TO 22
IPL = IPL + I200
IX2 = IX2 + 1
AIPL(IPL)= AI(I)
IF(IPL.EQ.85) PRINT 107
GO TO 80
77 I400= ( I-400 -IX3 *20 ) /20
IF (I400.EQ.0) GO TO 22
IPL = IPL + I400
IX3 = IX3 + 1
AIPL(IPL)= AI(I)
IF(IPL.EQ.111) PRINT 107
GO TO 80
79 IPL = I - 8
**WARNING** BECAUSE OF PARAMETER 1, THIS DO-LOOP WILL TERMINATE AFTER THE FIRST TIME THROU

IF(J.EQ.1) GO TO 170

DO 171 I = 1, NPTS

PV(I) = AIP1(I)
PV(NPTS+1) = 0.
PV(NPTS+2) = .1

CALL VTHICK(2)

CALL SCALOG(WPT1,XLEN,NPTS,1)

CALL GRID(0.,0.,0.,XLEN,WPT1(NPTS+2),2,YLEN,2.)

CALL LGAXIS(0.,0.,' MICRON ',-15,XLEN,0.,WPT1(NPTS+1),WPT1(NPTS+2))

CALL AXIS(0.,0.,' AI ',19,YLEN,90.,0.,1)

CALL LGLINE(WPT1,PV,NPTS,1,0,0,-1)

GO TO 176

CALL PLOT(0.,0.,-3)

CONTINUE

END

SUBROUTINE FCN(X,F,N,PAR)

REAL X(2),F(2),PAR(5),WL(2500),XX

COMPLEX S1(200),REFREL

REFREL = CMPLX(X(1),X(2))

CALL BHM(XX,REFREL,NANG,QEXT,PAR,S1)

F(1) = -AIMAG(S1(1))/XX**3 - PAR(1)

F(2) = REAL(S1(1))/XX**3 - PAR(2)

RETURN

END
SUBROUTINE LOF( W, AI, IST)
REAL*8 AI(2500)
DIMENSION W(2500), D(4), X(4)
D(1) = AI(IST)
D(2) = AI(IST+1)
D(3) = AI(IST+2)
D(4) = AI(IST+3)
CALL GAU(X,D, W, IST)
ISTM1 = IST - 1
DO 3 L = 1, ISTM1
3 AI(L) = X(4)* W(L) + X(3)* W(L)**2 + X(2)* W(L)**3 + X(1)* W(L)**4
RETURN
END

SUBROUTINE DISP(WL, N, K, I)
DIMENSION WB(2), C5(2), WL(2500)
DIMENSION GB(2), C2(2), T(2)
COMPLEX RH, RIM, EPS
REAL M, NB(2), MO, N(2500), K(2500), LAMD(2500), LAM(2500), NF
PI = .3141593E1
E = 1.6019E-19
M = 9.1E-31
PE = 1.0
PM = PE * 8.854E-12
NB(1) = 3.88E27
NB(2) = 4.26E28
NF = 4.82E25
T(1) = 1378.
GB(1) = 6.15E15
GB(2) = 1.03E16
GF = 1.20E15
WB(1) = 1.25E15
WB(2) = 7.25E15
LAM(1) = WL(1) * 1.E-6
LAMD(I) = LAM(1) * 1.E6
MO = M/18.
TREF = 1450.
W = 2.*PI * 2.998E8/ LAM(1)
GF = GF * SQRT(T(1)) / SQRT(TREF)
GB(1) = GB(1) * SQRT(T(1)) / SQRT(TREF)
GB(2) = GB(2) * SQRT(T(1)) / SQRT(TREF)
C1 = E**2 / (M * PM)
DO 30 J = 1, 2
30 C2(J) = NB(J) * (WB(J)**2 - W**2) / ((WB(J)**2 - W**2)**2 + W**2 * GB(J)**2)
C3 = E**2 / (MO * PM)
C4 = NF / (W**2 + GF**2)
DO 35 J = 1, 2
35 C5(J) = NB(J) * W * GB(J) / ((WB(J)**2 - W**2)**2 + W**2 * GB(J)**2)
C6 = NF * GF / (W**2 + GF**2))
P1 = 1. + C1 * (C2(1) + C2(2)) - C3 * C4
P2 = C1 * (C5(1) + C5(2)) + C3 * C6
N(I) = SQRT( .5 * P1 + .5 * (SQRT (P1**2 + P2**2)) )
K(I) = P2 / (2. * N(I))
RETURN
END

SUBROUTINE BHM (XX, REFREL, NANG, QEXT, PAR, S1)
DIMENSION AMU(100), THETA(100), PI(100), TAU(100), PIO(100), PI1(100)
DIMENSION WL(2500), PAR(5)

COMPLEX D(NMNX), Y, REFREL, XI, XI0, XI1, AN, BN, S1(200), S2(200)

REAL *8 PSI0, PSI1, PSI, DN, DX

NANG = 11

IF(PAR(5).EQ.1.) GO TO 1

XX = 3.141593 * PAR(3)/ PAR(4)

1

DX = XX

Y = XX * REFREL

XSTOP = XX + 4. * XX**0.3333 + 2.

NSTOP = XSTOP

YMOD = CABS(Y)

DANG = 1.5707963 / FLOAT(NANG-1)

DO 555 J = 1, NANG

555

THETA(J) = (FLOAT(J)-1.) * DANG

AMU(J) = COS(THETA(J))

D(NMX) = CMPLX(0., 0.)

NN = NMX - 1

DO 120 N = 1, NN

RN = NN - N + 1

120

D(NMX-N) = RN / Y - ( 1. / (D(NMX-N+1) + RN / Y))

DO 666 J = 1, NANG

666

PIO(J) = 0.

PI1(J) = 1.

S1(J) = CMPLX(0., 0.)

S2(J) = CMPLX(0., 0.)

PSIO = DCOS(DX)

PSI1 = DSIN(DX)

CHI0 = - SIN(XX)

CHI1 = COS(XX)

APSIO = PSIO

APSI1 = PSI1

XI0 = CMPLX(APSIO, -CHI0)

XI1 = CMPLX(APS11, -CHI1)

QSCA = 0.

N = 1

DO 200 N = N

200

FN = (2. * RN + 1.) / (RN * (RN + 1.))

PSI = (2. * DN - 1.) * PSI1 / DX - PSI0

APSI = PSI

CHI = (2. * RN - 1.) * CHI1 / XX - CHI0

XI = CMPLX(APSI, -CHI)

AN = (D(N) / REFREL + RN / XX) * APSI - APSI1

AN = AN / ((D(N) / REFREL + RN / XX) * XI - XI1)

BN = (REFREL * D(N) + RN / XX) * APSI - APSI1

BN = BN / ((REFREL * D(N) + RN / XX) * XI - XI1)

QSCA = QSCA + (2.* RN + 1.) * (CABS(AN) * CABS(AN) + CABS(BN) * CABS(BN))

DO 789 J = 1, NANG

789

JJ = 2 * NANG - J

PI(J) = PI1(J)

TAU(J) = RN * AMU(J) * PI(J) - (RN + 1.) * PI0(J)

P = (-1.)**(N-1)

S1(J) = S1(J) + FN * (AN * PI(J) + BN * TAU(J))

T = (-1.)**N

S2(J) = S2(J) + FN * (AN * TAU(J) + BN * PI(J))

IF(J.EQ.JJ) GO TO 789

S1(JJ) = S1(JJ) + FN * (AN * PI(J) * P + BN * TAU(J) * T)
S2(JJ) = S2(JJ) + FN* (AN*T(J) + BN*PI(J) *P)

CONTINUE

PSI0 = PSI1
PSI1 = PSI
APSI1 = PSI1
CHI0 = CHI1
CHI1 = CHI
X11 = CHMPLX(APS11, -CHI1)
N = N+1
RN = N
DO 999 J = 1, NANG
PI1(J) = ((2. *RN - 1) / (RN-1.)) * AMU(J) * PI(J)
PI1(J) = PI1(J) -RN*PIO(J) /(RN-1.)
999 PIO(J) = PI(J)
IF(N-1-NSTOP) 200, 300, 300
300 QSCA = (2./((XX*XX))) * QSCA
QEXT = (4./((XX*XX))) *REAL(S1(1))
QBACK = (4./((XX*XX))) * CABS(S1(2*NANG-1)) * CABS(S1(2*NANG-1))
RETURN
END

SUBROUTINE GAU(X,D,W,IST)
REAL A(4,4),B(4),X(4),CCF(10),ZN(6),ZK(6),C(4),D(4),W(2500)
MAINDM=4
N=4
C1 = W(IST )
C2 = W(IST+1)
C3 = W(IST+2)
C4 = W(IST+3)
A(1,1) = C1**4
A(1,2) = C1**3
A(1,3) = C1**2
A(1,4) = C1
A(2,1) = C2**4
A(2,2) = C2**3
A(2,3) = C2**2
A(2,4) = C2
A(3,1) = C3**4
A(3,2) = C3**3
A(3,3) = C3**2
A(3,4) = C3
A(4,1) = C4**4
A(4,2) = C4**3
A(4,3) = C4**2
A(4,4) = C4
B(1) = D(1)
B(2) = D(2)
B(3) = D(3)
B(4) = D(4)
CALL GAUSS(A,B,X,N,MAINDM,IERRO,RNORM)
C(1) = X1*C1**4 + X(2)*C1**3 + X(3)*C1**2 + X(4)*C1
C(2) = X1*C2**4 + X(2)*C2**3 + X(3)*C2**2 + X(4)*C2
C(3) = X1*C3**4 + X(2)*C3**3 + X(3)*C3**2 + X(4)*C3
C(4) = X1*C4**4 + X(2)*C4**3 + X(3)*C4**2 + X(4)*C4
RETURN
END

SUBROUTINE GAUSS(A,B,X,N,MAINDM,IERRO,RNORM)
DIMENSION A(MAINDM,MAINDM),B(MAINDM),X(MAINDM)
DIMENSION AUG(10,11)
NM1=N-1
NP1=N+1
DO 2 I=1,N
  DO 1 J=1,N
  AUG(I,J)=A(I,J)
1  CONTINUE
2  CONTINUE
DO 8 I=1,NM1
PIVOT=0.
DO 3 J=I,N
  TEMP=ABS(AUG(J,I))
  IF(PIVOT.GE_TEMP) GO TO 3
3  PIVOT=TEMP
  IPIVOT=J
4  CONTINUE
5 IF(PIVOT.EQ.0.) GO TO 13
6 IF(IPIVOT.EQ.I) GO TO 5
DO 4 K=I,NP1
  TEMP=AUG(K,I)
4  AUG(K,I)=AUG(IPIVOT,K)
5  AUG(IPIVOT,K) = TEMP
6  CONTINUE
7 IP1=I+1
DO 7 K=IP1,N
  Q=-AUG(K,I)/AUG(I,I)
  AUG(K,I)=0.
7  DO 6 J=IP1,NP1
6  AUG(K,J)=Q*AUG(I,J)+AUG(K,J)
8  CONTINUE
9 X(N)=AUG(N,NP1)/AUG(N,N)
10 DO 12 K=1,NM1
11 Q=0.
12 DO 9 J=1,K
  Q=Q+AUG(N-K,NP1-J)*X(NP1-J)
9  CONTINUE
10  X(N-K)=(AUG(N-K,NP1)-Q)/AUG(N-K,N-K)
11 RSQ=0.
12 DO 14 I=1,N
13 Q=0.
14 DO 11 J=1,N
  Q=Q+A(I,J)*X(J)
11  CONTINUE
RESI=B(I)-Q
RMAG=ABS(RESI)
RSQ=RSQ+RMAG**2
12 CONTINUE
RNORM=SQRT(RSQ)
IERROR=1
RETURN
13 IERROR=2
RETURN
END
ENTRY
This program computes the most probable radius and geometric width of ZOLOD size distribution from average line width and polydispersity index.

```
$JOB
TIME=5

REAL MEAN,LAMD,INT,MUGAM,MIDPT,RES2(50)
DIMENSION LDO(50)
LAMD=.488
THETA=9.
T=1067.
GAMAV=2.0911E4
MUGAM=.111
IRDI=28
IRDF=43
PHI=3.141593
PRINT 130
PRINT 105,GAMAV,T,LAMD,THETA,MUGAM
ISTP=1
20 J=1
LDO(J)=IRDI
25 IF(ISTP.EQ.1) CMUF=1.
IF(ISTP.EQ.2) CMUF=.1
IF(ISTP.EQ.3) CMUF=.01
RO=FLOAT(LDO(J))*.1E-9*CMUF
CHK=RO*1.E9
MEAN=1.E-9*(-.251697E-7*T**3-.137185E-3*T**2+
+.739804*T-.30689E3)
BOL=1.3806E-23
THET=THETA*.5*PHI/180.
ETA=1.E-5*(.416091E-8*T**3-.190684E-4*T**2+
+.0321383*T-13.829)
DIFF=BOL*T/(6.*PHI*ETA)
QS=(4.*PHI*SIN(THET)/LAMD*1.E-6)**2
C1=DIFF*QS
IF(CHK.LT.34.) IRDB=5
IF(CHK.GE.34.) IRDB=8
IF(CHK.GE.45.) IRDB=12
IF(CHK.GE.55.) IRDB=16
IF(CHK.GE.65.) IRDB=25
A=1.5
B=1.13
Y=1.
CALL GAMMA(C1,A,B,RO,MIDPT,Y,GAMAV,MEAN,RES1,RIGT,IRDB)
FA=RES1
1 MIDPT=(A+B)/2.
Y=2
CALL GAMMA(C1,A,B,RO,MIDPT,Y,GAMAV,MEAN,RES1,RIGT,IRDB)
FM=RES1
IF(FA*FM.LE.0.) GO TO 2
A=MIDPT
FA=FM
GO TO 3
B=MIDPT
3 IF(ABS(RES1).LE.1.) GO TO 4
GO TO 1
4 SIGMA=(A+B)/2.
CALL PI(C1,RO,MUGAM,MEAN,RIGT2,SIGMA,GAMAV,IRDB)
POLIN=RIGT2/(GAMAV**2)-1.
```
RES2(J) = MUGAM - POLIN
DIA = 2.* CHK
PRINT 120, CHK, DIA, SIGMA, RIGT, POLIN, RES2(J)
IF (J.EQ.1) GO TO 6
CHRES = RES2(J-1)*RES2(J)
IF (CHRES.LT.0.) GO TO 10
J = J+1
LDO(J) = LDO(J-1)+1
GO TO 25
ISTP = ISTP+1
IF (ISTP.GE.4) GO TO 200
IRDI = LDO(J-1)*10
GO TO 20
120 format(/ / 8.2, F 10.2, F 11.4, E 16.5, F 10.4, F 12.5)
130 format('/ 1', 12X, 'ZEROTH ORDER LOG-NORMAL SIZE DISTRIBUTION')
STOP
END

SUBROUTINE GAMMA(C1, A, B, RO, MIDPT, Y, GAMMAV, MEAN, RES1, RIGT, IRDB)
REAL MEAN, MIDPT, SM(1500), INT(1500)
PHI = 3.141593
X = A
IF(Y.EQ.1.) GO TO 1
X = MIDPT
ALSIG = ALOG(X)
SIGMS = ALSIG**2
CC = EXP(-24.5*SIGMS)/(RO**7)
C2 = CC/(SQRT(2.*PHI) * ALSIG)
J = 1
CALL NORM(ALSIG, RO, IRDB, IF)
SUM = 0.
DO 10 LR = IRDB, IF
CALL INTEGRAL(MEAN, RO, SIGMS, LR, RAD, X1, X2)
EPN = EXP(X1+X2)
INT(LR) = RAD**4 * EPN
SM(J) = INT(LR)
10 J = J+1
IRFN = J-3
DO 30 I = 1, IRFN, 2
SUM = SUM + (SM(I) + 4.*SM(I+1) + SM(I+2))/3.
SUH = SUM*2.9*MEAN*C1*C2 * 1.E-9
P1 = EXP(-6.5*SIGMS)*C1/RO
P2 = .864*C1*MEAN*EXP(-12.*SIGMS)/RO**2
RIGT = P1 + P2 + SUM
RES1 = GAMMAV - RIGT
RETURN
END

SUBROUTINE PI(C1, RO, MUGAM, MEAN, RIGT2, SIGMA, GAMMAV, IRDB)
REAL MEAN, INT(1500), MUGAM, MIDPT, INT1(1500), INT2(1500)
REAL SM(1500), SM1(1500), SM2(1500)
PHI = 3.141593
ALSIG = ALOG(SIGMA)
SIGMS = ALSIG**2
CC = EXP(-24.5*SIGMS)/(RO**7)
C2 = CC/(SQRT(2.*PHI) * ALSIG)
P1 = C1**2 * EXP(-SIGMS**12.)/(RO**2)

P2 = 1.728*C1**2*MEAN* EXP(-SIGMS*16.5)/(RO**3)

P3 = .746496*C1**2*MEAN**2*EXP(-20.*SIGMS)/(RO**4)

SUM = 0.

SUM1 = 0.

SUM2 = 0.

J = 1

CALL NORM(ALSIG, RO, IRDB, IF)

DO 15 LR = IRDB, IF

CALL INTEG(MEAN, RO, SIGMS, LR, RAD, X1, X2)

EPN = EXP(X1 + X2)

INT(LR) = RAD**3 * EPN

INT1(LR) = RAD**2 * EPN

X3 = X1**2.

EPN2 = EXP(X3 + X2)

INT2(LR) = RAD**2 * EPN2

SM(J) = INT(LR)

SM1(J) = INT1(LR)

SM2(J) = INT2(LR)

J = J + 1

IRFN = J - 3

DO 30 I = 1, IRFN, 2

SUM = SUM + (SM(I) + 4.*SM(I+1) + SM(I+2))/3.

SUM = SUM + (SM(I) + 4.*SM(I+1) + SM(I+2))/3.

SUM = SUM + (SM(I) + 4.*SM(I+1) + SM(I+2))/3.

SUM = SUM + (SM(I) + 4.*SM(I+1) + SM(I+2))/3.

SUM1 = SUM1 + .50112*MEAN**2 * C1**2 * C2 * 1.E-9

SUM2 = SUM2 + .0841*MEAN**2 * C1**2 * C2 * 1.E-9

RIGT2 = P1 + P2 + P3 + SUM + SUM1 + SUM2

RETURN

SUBROUTINE INTEG(MEAN, RO, SIGMS, LR, RAD, X1, X2)

REAL MEAN

R = FLOAT(LR)

RAD = R*1.E-9

X1 = -1.25*RAD/MEAN

X2 = -(ALOG(RAD/RO)**2/ (2.*SIGMS)

RETURN

END

SUBROUTINE NORM(ALSIG, RO, IRDB, IRW)

REAL SM(1500), NR

IDR = 2

DR = FLOAT(IDR)*1.E-9

PI = 3.141593

J = 1

IR = IRDB

SUM = 0.

R = FLOAT(IR)

RAD = R*1.E-9

EX1 = EXP(-ALSIG**2/2.)

EX2 = EXP(-(ALOG(RAD/RO)**2/ (2.*ALSIG**2)

NR = EX1*EX2/ (SQRT(2.*PI)* RO * ALSIG)

SM(J) = NR * DR

SUM = SUM + SM(J)

IF(SUM.GT. .9995) GO TO 20

IF = IR + IDR

J = J + 1

GO TO 5
20 XSUM = 0.
IRW = IR
RETURN
END
$ENTRY
Vita

Hyunsoo Chang was born on May 17, 1951 in Kunsan, S. Korea. After graduating from Hanyang High School, Seoul, Korea, he entered Ulsan Institute Technology, Ulsan, Korea in 1971. After obtaining his Bachelor of Engineering in Mechanical Engineering in 1975, he worked several years at the Agency for Defence Development in Korea. He started graduate study in Mechanical Engineering at the University of Minnesota in 1982 and obtained a Master of Science degree in 1984. He entered the Ph.D. program in Mechanical Engineering at Louisiana State University in January, 1985.
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Major Field: Mechanical Engineering

Title of Dissertation: Determination of the wavelength dependence of the optical properties of soot from in-situ measurements

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