RADIATIVE PROPERTIES OF PARTICLES IN FLAMES

M. P. MENGÜÇ and S. MANICKAVASAGAM

DEPARTMENT OF MECHANICAL ENGINEERING
UNIVERSITY OF KENTUCKY
LEXINGTON, KY 40506

FINAL TECHNICAL REPORT

DECEMBER, 1996

No: DOE/PC/92533-F

(GRANT #DE-FG22-92PC92533)

submitted to

DEPARTMENT OF ENERGY,
PITTSBURGH ENERGY TECHNOLOGY CENTER,
PITTSBURGH, PENNSYLVANIA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CLEARED BY
PATENT COUNSEL

MASTER

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

PREFACE

This is the Final Technical Report for the project originally titled "Radiative Properties of Char, Fly-Ash, Soot Particles in Coal Flames". This project has been funded by the Department of Energy, Pittsburgh Energy Technology Center through a grant #DE-FG22-92PC92533. It started on September 15, 1992, and was expected to be completed in two-years. Towards the end of the project, a one-year, no-cost extension was granted. This extension was needed as the first Ph.D. student who started on the project abruptly left the academic life, and a substitute student had to be found. Mr. Ramaswamy Govindan joined the project and was expected to receive his Master of Science Degree by September 1995. Unforeseen experimental difficulties adversely affected his work, and he was re-scheduled to complete his degree by December 1995. Unfortunately, Rama has lost his life in a tragic traffic accident on November 5, 1995.

Rama's thesis was almost ready, and the final touches on it were made by the authors of this report. However, this was not easy, neither technically nor emotionally. These corrections took more than five months to incorporate. Meanwhile, the University of Kentucky has agreed to grant a MSME Degree to Rama posthumously.

Dr. Sivakumar Manickavasagam served as a Research Associate on the project and was responsible from modeling particulate optical and radiative properties, operating the Nd:YAG-laser system, burner, and fluidized bed. He has completed his Ph.D. Dissertation at the University of Kentucky. Another Research Associate, Dr. Sarbajit Ghosal has joined us in November 1993 from Stanford University. His responsibility was setting up the Nd:YAG laser diagnostic system. During the Summer of 1993, an undergraduate student, Mr. Stig Alstedt helped us to visualize the shape and structures of soot agglomerates using the I-DEAS computer software package. Two other Ph.D. students, Ms. Deepti Bhanti (Chemical Engineering) and Mr. Zeljko Ivezic (Physics and Astronomy) have also contributed to the project and the published papers with us.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SUMMARY

During the course of this project, we completed a total of eight publications. In this report, we include these studies as Appendices. A short summary of these papers and how they are interrelated are given here.

The overall objective of the project was to develop a methodology to identify different type of particles in flames using light diagnostic techniques. Our studies have shown us that if polarized light is employed and the scattering matrix elements of a particle cloud are measured, we can have clear signatures of different type of particles. In other words, a careful set of experiments, followed by a detailed rigorous data analysis would yield particle types and volume fractions of soot agglomerates, and fly-ash, char, and coal particles in flames. This capability is very important for understanding the combustion of fossil fuels, and soot agglomeration, coagulation, and oxidation processes.

For the analytical studies, we developed two new codes to calculate the scattering characteristics of different particles. The first algorithm (called, AGGLOME) was to determine the scattering signals of soot agglomerates. The second one was for multi-layer spheres. In the experimental part of the project, we designed an extensive Nd:YAG laser diagnostic system.

In **Appendix A**, we present the overall objective of our numerical studies in detail. This paper, which was presented at the *Chandrasekhar Memorial Symposium* in October 1996, will appear in a special issue of the *Journal of Engineering Sciences* in 1997. *preprint removed.*

An earlier version of this paper, which was presented at Berkeley, California in November 1995, in a Symposium to honor UC-Berkeley Chancellor Chang-Lin Tien is given in **Appendix B**. *reprint removed.*

The idea behind our AGGLOME code, and how it can be used to identify the fractal characteristics of soot agglomerates are outlined in the paper included in **Appendix C**. This paper, which gives an extensive review of literature, will appear in the *Applied Optics* in February 1997. *preprint removed.*

Appendix D includes a paper we published in the *Journal of Quantitative Spectroscopy and Radiative Transfer*. Here, we outlined the effects of radial inhomogeneity in spherical particles on the scattering characteristics of coal-soot or droplet-soot systems. *reprint removed.*

In order to identify the effect of dependent scattering on the scattering characteristics of coagulating soot particles, we used another computer code called DDSCAT, developed by B.

Draine of Princeton University. The results of this study were reported in a paper published in the *International Journal of Heat and Mass Transfer*, and included in **Appendix E**. The extension of this work was focused on identification of soot agglomeration process. A paper written based on this study was submitted to the *Journal of Quantitative Spectroscopy and Radiative Transfer*, a copy of which is included in **Appendix F**. *reprint removed.* *preprint removed.*

The details behind the experimental design was given in a paper presented at the First International Symposium on Radiation Transfer, which was held in Kuşadası, Turkey in August 1995. This paper, which appeared in the Symposium proceedings, is included in *reprint removed,* **Appendix G**. Note that this work was based on Mr. Ramaswamy Govindan's M.S. thesis, which is included in **Appendix H**. We expect to publish at least one additional paper from this work soon.

We believe that the work we carried out during the course of this project was innovative new and has a potential of being used in the monitoring of furnaces and flames in the future. Even though several unexpected events hampered our progress, the overall outcome is still comprehensive and significant.

When we look back, we see important contributions made by Rama to this work, particularly to the experimental set-up. It is only natural for us to devote this report to *Rama's Memory*, as every time we use our experimental facility, we remember him.

APPENDICES

- Appendix A:** M.P. Mengüç and S. Manickavasagam, "Characterization of Size and Structure of Agglomerates and Particles via Polarized Light," presented at the "S. Chandrasekhar Memorial Symposium", which was held in Tempe, AZ, in October 1996; to appear in a special issue of *Journal of Engineering Sciences*, 1997 (in press).
- Appendix B:** M.P. Mengüç, S. Manickavasagam, and R. Govindan, "Diagnostics of Particulate Size and Structure Using Polarized Light and Scattering Matrix Concept," presented at "The Symposium on Thermal Science and Engineering" in Honor of Chancellor Chang-Lin Tien, November 14, 1995, University of California, Berkeley.
- Appendix C:** S. Manickavasagam and M.P. Mengüç, "Scattering Matrix Elements of Fractal-like Soot Agglomerates", *Applied Optics*, 1997 (in press).
- Appendix D:** D. Bhanti, S. Manickavasagam, and M.P. Mengüç, "Identification of Non-Homogeneous Spherical Particles from their Scattering Matrix Elements," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 56, No. 4, pp. 591-608, 1996.
- Appendix E:** Z. Ivezic and M.P. Mengüç, "An Investigation of Dependent/Independent Scattering Regimes for Soot Particles Using Discrete Dipole Approximation," *International Journal of Heat and Mass Transfer*, Vol. 39, No. 7, pp. 811-822, 1996.
- Appendix F:** Z. Ivezic, M.P. Mengüç, and T.G. Knauer, "A Procedure to Determine the Onset of Soot Agglomeration from Multiwavelength Experiments," *Journal of Quantitative Spectroscopy and Radiative Transfer*, 1996 (under review).
- Appendix G:** R. Govindan, S. Manickavasagam, and M.P. Mengüç, "On Measuring the Mueller Matrix Elements of Soot Agglomerates", in *Radiative Transfer - 1*, Proceedings of the International Symposium on Radiative Heat Transfer, Editor: M. P. Mengüç; presented at Kuşadasi, Turkey, August 1995.
- Appendix H:** R. Govindan, *Measurement of the Mueller Matrix Elements for Identification of the Structure of Soot Agglomerates in Flames*, Master Thesis, Department of Mechanical Engineering, University of Kentucky, Lexington, KY, 1996.

APPENDIX H

R. Govindan, *Measurement of the Mueller Matrix Elements for Identification of the Structure of Soot Agglomerates in Flames*, Master Thesis, Department of Mechanical Engineering, University of Kentucky, Lexington, KY, 1996.

MEASUREMENT OF THE MUELLER MATRIX ELEMENTS
FOR IDENTIFICATION OF
THE STRUCTURE OF SOOT AGGLOMERATES IN FLAMES

THESIS

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science
in Mechanical Engineering
at the University of Kentucky

By
Ramaswamy Govindan
Lexington, Kentucky
Director: Dr. M.P. Mengüç
Professor, Department of Mechanical Engineering
University of Kentucky
Lexington, Kentucky

1996

ABSTRACT OF THESIS

MEASUREMENT OF THE MUELLER MATRIX ELEMENTS FOR IDENTIFICATION OF THE STRUCTURE OF SOOT AGGLOMERATES IN FLAMES

In this study, a methodology is discussed to identify the Mueller (scattering) matrix elements of soot agglomerates in diffusion flames. For this purpose, an experimental system based on Nd:YAG laser and Optical Parametric Oscillator is designed and built. The technique is first tested numerically for different size soot agglomerates and very good agreements were observed. After that, elliptically polarized laser light is directed on an ethylene diffusion flame. Scattered light from the flame is passed through a polarizer/retarder pair before being measured. By repeating this procedure for a six different conditions, six important elements of the scattering matrix are measured. The comparison of the trends of experimental and numerical data shows that this method is very promising for flame studies.

(Author's Name)

(Date)

Contents

ABSTRACT	
Acknowledgements	iii
List of Figures	vi
List of Tables	viii
Nomenclature	ix
1 INTRODUCTION	1
1.1 Background	1
1.2 Research Objectives	2
1.3 Literature Survey	2
1.4 Outline of Thesis	4
2 THEORETICAL BACKGROUND	6
2.1 Stokes Vector	6
2.2 Mueller Matrix	6
2.3 Derivation of the Mueller Matrix for Scatterers	7
2.3.1 General Formulation	7
2.3.2 The Amplitude Scattering Matrix (Jones Matrix)	9
2.3.3 Mueller Matrix	11
2.4 Symmetry in Mueller Matrices for scattering in an arbitrary direction . . .	14
2.5 Symmetry in Mueller Matrices for Particles in Flames	18
3 PROPOSED EXPERIMENTAL SYSTEM	19
3.1 Proposed Experimental System	19
3.2 Mathematical Analysis	19
4 NUMERICAL ANALYSIS TO OBTAIN OPTIMUM POLARIZER AND RETARDER ANGLES	23
4.1 Numerical Procedure	23
4.2 Results and Discussion	24
4.2.1 Effect of Condition Number on Recovered Mueller Matrix Elements	24
4.2.2 Recovered Mueller Matrix Elements for Optimal Set-Up	27

5	DESCRIPTION OF THE EXPERIMENTAL SYSTEM	35
5.1	Layout of Experimental System	35
5.2	Light Source	35
5.2.1	OPO Theory of Operation	35
5.2.2	Pumping Laser	36
5.3	Directing Optics	36
5.4	Burner	37
5.5	Light Collection System	37
5.6	Data Acquisition System	38
6	RESULTS AND DISCUSSIONS	41
6.1	Numerical Results	41
6.1.1	S_{11}	41
6.1.2	S_{12}	42
6.1.3	S_{33}	42
6.1.4	S_{34}	42
6.1.5	Other S_{ij} Elements	43
6.2	Experimental Results and Discussions	43
7	CONCLUSIONS	54
	REFERENCES	55
	APPENDIX I	58
	APPENDIX II	63

List of Figures

1	Effect of incident field ($\vec{E}_i, \vec{H}_i$) on an arbitrary particle.	8
2	Scattering by an arbitrary particle: definition of basis vectors along the forward and scattering directions, and the scattering plane.	10
3	Detector to collect the scattered light from the particle	13
4	Definitions of the directions of incidence and scattering, scattering plane and the bisectrix plane (from Bohren and Huffman, 1983).	16
5	Two positions of an arbitrary particle and the positions that result from mirroring these with respect to the bisectrix plane (from Bohren and Huffman, 1983).	17
6	Schematic of the Experimental Setup; POL: Polarizer, HWP: Half wave plate, QWP: Quarter wave plate, F: Flame.	20
7	Soot agglomerate model: 25 spheres.	25
8	Soot agglomerate model: 75 spheres.	25
9	Soot agglomerate model: 125 spheres.	26
10	Relative error ϵ on recovered S_{11} and S_{12} elements at various scattering angles between 0° and 180° for various values of the condition number CN	29
11	Relative error ϵ on recovered S_{34} and S_{44} elements at various scattering angles between 0° and 180° for various values of the condition number CN	30
12	Input and recovered S_{11} elements for the optimal setup conditions given in Tables 1 and 2.	31
13	Input and recovered S_{12} elements for the optimal setup conditions given in Tables 1 and 2.	32
14	Input and recovered S_{34} elements for the optimal setup conditions given in Tables 1 and 2.	33
15	Input and recovered S_{44} elements for the optimal setup conditions given in Tables 1 and 2.	34
16	Layout of the Experimental System	39
17	Principle of Operation of the BBO	40
18	Schematic of the light collection system	40
19	Effect of N and d_p on the angular profile of S_{11} elements; $\lambda = 532 \text{ nm}$; $m = 1.85 - 0.50i$	44

20	Effect of N and d_p on the angular profile of S_{12} elements; $\lambda = 532 \text{ nm}$; $m = 1.85 - 0.50i$	45
21	Effect of N and d_p on the angular profile of S_{33} elements; $\lambda = 532 \text{ nm}$; $m = 1.85 - 0.50i$	46
22	Ratio of total forward scattered light to that of backward scattered light (asymmetry ratio) based on S_{33} at $\lambda = 532$ and 1000 nm	47
23	Effect of N and d_p on the angular profile of S_{34} elements; $\lambda = 532 \text{ nm}$; $m = 1.85 - 0.50i$	48
24	Angular variation of S_{11} measured from experiments.	49
25	Angular variation of S_{12} measured from experiments.	50
26	Angular variation of S_{33} measured from experiments.	51
27	Angular variation of S_{34} measured from experiments.	52
28	Angular variation of S_{44} measured from experiments.	53

List of Tables

1	Set of optical component angles (in degrees) which yields $CN < 10$ ($CN=9.58$).	27
2	Coefficient matrix C for optical component angles given in Table 1.	27

NOMENCLATURE

$\vec{A}$	Amplitude vector, see Eq. (15)
B	intensity vector obtained from experiments, see Eq. (57)
C	coefficient matrix, see Eq. (57)
CN	condition number, see Eq. (59)
D	area [m^2]
d_p	diameter of primary spheres [nm]
$\vec{E}$	electric field amplitude
$\vec{H}$	magnetic field amplitude
I	Stokes parameter; see Eq. (1)
k	imaginary part of refractive index
k	wavenumber, $2\pi/\lambda$
K	Stokes vector, see Eq. (5)
$\tilde{m}$	complex index of refraction, $n + ik$
N	number of primary soot particles in agglomerates
n	real part of refractive index
$\vec{P}$	Poynting vector; see Eq. (19)
P	Mueller matrix for polarizers, see Eq. (53)
Q	Stokes parameter; see Eq. (2)
R	Mueller matrix for retarders, see Eq. (54)
$S(\theta)$	Mueller (scattering) matrix for particles, see Eqs. (27) and (55)
S_j	amplitude scattering matrix elements; see Eq. (18)
S_{ij}	Mueller (scattering) matrix elements; see Eqs. (27) - (43)
U	Stokes parameter; see Eq. (3)
V	Stokes parameter; see Eq. (4)
x	size parameter
Z	Mueller matrix elements determined from experiments, see Eq. (58)

Greek Letters

β	extinction coefficient ($= \sigma + \kappa$), [m^{-1}]
β	angle between the parallel axis of the retarder and the horizontal
Δ	fractional quantity
δ	retardance of the retarder
ε	dielectric constant
θ	zenith angle component of the scattering angle
κ	absorption coefficient, [m^{-1}]
λ	wavelength, [nm]
μ	magnetic permeability
σ	scattering coefficient, [m^{-1}]
Φ	scattering phase function
ϕ	azimuthal angle
ψ	orientational angle of scattering plane; see Fig. 2
Ω	solid angle [sr]
ω	angular frequency
ξ	angle between the transmission axis of the polarizer and the parallel axis of the incident beam

Subscripts/Superscripts

<i>abs</i>	absorption
<i>i</i>	incident
<i>o</i>	outgoing
<i>s</i>	scattered
$\parallel$	parallel component
$\perp$	perpendicular component
*	complex conjugate

1 INTRODUCTION

1.1 Background

Expenditures on fossil fuels such as natural gas, oil and coal account for a significant fraction of any country's resources. Improved understanding of combustion systems which use fossil fuels may result in improved energy efficiency, which in turn could make a significant impact on both the local and global economy. An important goal in this effort is to develop theoretical as well as experimental models which could be used for the design and optimization of combustion systems.

Some of the most important engineering applications of thermal radiation are in the areas of combustion of gaseous, liquid (usually in droplet form) or solid (often pulverized) fuels. Since thermal radiation contributes strongly to the heat transfer mechanism of combustion, any understanding and modeling of the process must include knowledge of the radiative properties of the combustion gases as well as any particulates that are present. Nearly all flames are luminous, i.e. visible to the human eye and emit radiation at wavelengths where there are no vibration-rotation bands for any combustion gases. This luminous emission comes mostly from carbonaceous matter known as *soot*, which is generated during the combustion process. On the other hand, the combustion of pulverized coal yields larger-size coal and fly ash particles which also contribute to flame emission.

When an electromagnetic wave or a photon interacts with a medium containing small particles, the radiative intensity may be changed by absorption and/or scattering. How much and into which direction a particle scatters an electromagnetic wave passing through its vicinity depends on:

1. the shape of the particle,
2. the material of the particle (i.e. the complex index of refraction, $m = n - ik$),
3. the relative size of the particle with respect to wavelength of incident radiation, and
4. the clearance between particles.

The information about the scattered energy can be used to determine the physical properties of particles if the signals collected can be interpreted carefully. In this work we are specifically focused on light scattering measurements in flames to obtain more information about the shape and volume fraction distribution of the particles.

When light in some arbitrary polarization state is incident on a medium, the polarization state of the scattered or transmitted light can be related to the polarization state of the incident light by a 4×4 matrix. This matrix, which is called the *Mueller* or *Scattering Matrix*, is a characteristic of the medium. This will be discussed in detail later. It depends on the wavelength of incident light and, in the case of light scattering, is a function of the scattering angle. It yields invaluable information about the physical properties of the scattering particulates. It is a necessary and major part of the complete optical description of a medium.

1.2 Research Objectives

The specific objective of this work is to develop a methodology to measure the significant elements of the Mueller matrix for a diffusion flame in order to identify the structure of particles in such flames. For this purpose, a diagnostic system is designed and built, and scattered intensity measurements are performed using different combinations of polarizers and retarders. The results are compared against available theoretical data for fractal-like soot agglomerates.

1.3 Literature Survey

Most of the previous work similar in nature to the present study have been performed in the field of atmospheric optics measurements. The earliest known work was carried out by Pritchard and Elliott (1960). They designed a polar nephelometer to measure six elements of the Mueller matrix for fog and clear air. They used six independent combinations of polarizers and analyzers to make scattered intensity measurements and then used subtractive techniques to recover the Mueller matrix elements. This technique is very time consuming because the polarizer and analyzer have to be replaced for each combination. Also because of the large time involved, the accuracy of these measurements is questionable. Beardsley (1968) measured the Mueller matrices of sea water using several independent combinations of polarizers and analyzers. Because each of the sixteen elements requires a different combination of settings, this technique also takes a significant amount of time and results in less accuracy.

Holland and Gagne (1970) used a polar nephelometer similar to the one developed by Pritchard and Elliott to measure all the elements of the Mueller matrix for polydisperse systems of irregular, randomly-oriented particles. These results were compared to

the matrix elements that were calculated for assemblies of spherical particles that fit the same particle size distribution function and have the same refractive index. For this they recorded intensity information for eighteen combinations of filters and subsequently took differences between the recorded values to obtain the matrix elements. The disadvantage of this technique is that the values needed to obtain the elements appear as small differences between relatively large quantities. Hence small errors introduced by drift and instabilities are magnified.

Kemp (1969) developed a piezo-optical birefringence modulator. This instrument is based on the piezo-optic or photoelastic effect (stress-induced birefringence). An acoustic vibration is set up in a block of isotropic transparent material, such as glass or fused silica; this vibration is sustained by a transducer. The resulting birefringence can be used to produce a beam of alternately left and right circularly polarized light for circular dichroism measurements.

Hunt and Huffman (1973) used the piezo-optical birefringence modulator developed by Kemp (1969) to construct a polarization-modulated light scattering instrument. This instrument consists of a polarizer and a modulator before the scattering cell and an analyzer after the scattering cell. They used two combinations of the modulator and polarizer angles with respect to the scattering plane to obtain six elements of the Mueller matrix. Experimental results were reported for polystyrene latex spheres dispersed in water and sulfur sols and compared with the Lorenz-Mie theory calculations. Since this instrument uses only one modulator, it could measure only the combinations of matrix elements. Later, Perry, Hunt and Huffman (1978) made measurements to determine all sixteen elements of the Mueller scattering matrix for two types of non-spherical particles.

Thompson (1978) designed a sophisticated instrument to measure all sixteen elements of the Mueller matrix. He used a four modulator photo-polarimeter which makes use of four electro-optic modulators and two polarizers. Boyer, Lamouroux and Prade (1979) designed a system which measures the Stokes parameters of light automatically over a wide range of wavelengths. This system uses two piezo-optic modulators.

Recently, Kuik, Stammes and Hovenier (1991) designed an experimental setup to measure six independent elements of the Mueller matrix. By using a single electro-optic Pockels cell modulator along with two polarizers and a quarter wave plate, they were able to obtain the desired elements from four separate measurements. They reported results for irregularly shaped particles.

On the theoretical side, much of the work in this area has been focussed on developing relations between the Mueller matrix elements for a single particle and modifying them for an arbitrary particle and a collection of such particles. Abhyankar and Fymat (1969) derived nine relations between the sixteen elements of the Mueller matrix for the three most commonly used representations of the intensity vector, viz. Wolf's coherency matrix formalism, Chandrasekhar's (1950) and Stokes' (1852) representations. These relations were derived for a single particle or a collection of identical particles. They also demonstrated the invariance of these relations under the action of any system of optical components characterized by their Jones representation. Fry and Kattawar (1981) showed that when Stokes matrices from an ensemble of particles differing in size, orientation, morphology, or optical properties are added, six of the nine equalities become one-way inequalities which are quadratic in nature. From this they concluded that the use of them may provide a good test for observing small differences between the Mueller matrix elements of slightly dissimilar objects. Hovenier, van de Hulst and van der Mee (1986) derived the nine independent relations between the sixteen Mueller matrix elements for scattering by one particle of arbitrary size, shape and composition. They also derived the inequalities for the elements of the Mueller matrix for an assembly of particles.

The literature survey indicated that no attempts have been made to measure the Mueller (scattering) matrix for particles in flames. The major reason for this is that soot particles in flames are dynamic in nature and hence diagnostics becomes difficult. Also measurement over a wide range of wavelengths is necessary to get meaningful results.

In this work, we use an instrument similar to the one used by Kuik, Stammes and Hovenier (1991) and consider the fact that for randomly oriented particles, the Mueller matrix has only six elements. Even though our method uses subtractive techniques to obtain the six elements, the accuracy is not affected because the elements to be recovered appear as significant differences between large quantities. Initially measurements are made using a MOPO laser at 532 nm. In future measurements will be made over a range of wavelengths to get the spectral variation of these quantities.

1.4 Outline of Thesis

In the next chapter the necessary theoretical background for the present work is described. The derivations for the amplitude scattering matrix and the Mueller scattering matrix are given. The symmetry in Mueller matrices for particles in flames is also described. In

Chapter 3, the system proposed is outlined and a mathematical analysis is performed to derive the proportion of the various matrix elements in the intensities measured. Chapter 4 describes the numerical analysis performed to derive the optimum combination of the orientation angles of the various optical components so that the desired Mueller matrix elements are recovered accurately. Experimental setup is discussed in Chapter 5, and the experiments performed are outlined in Chapter 6. Finally, the conclusions drawn are presented in Chapter 7.

2 THEORETICAL BACKGROUND

2.1 Stokes Vector

We may represent a beam of arbitrary polarization, including partially polarized light by a column vector called the Stokes Vector; as expected the four elements of which are the Stokes parameters. The Stokes parameters may be expressed equivalently in terms of quadratic functions of the electric fields as

$$I = \langle E_{\parallel} E_{\parallel}^* + E_{\perp} E_{\perp}^* \rangle \quad (1)$$

$$Q = \langle E_{\parallel} E_{\parallel}^* - E_{\perp} E_{\perp}^* \rangle \quad (2)$$

$$U = \langle E_{\parallel} E_{\perp}^* + E_{\perp} E_{\parallel}^* \rangle \quad (3)$$

$$V = i \langle E_{\parallel} E_{\perp}^* - E_{\perp} E_{\parallel}^* \rangle \quad (4)$$

The subscripts refer to the components of the electric field parallel ($\parallel$), and perpendicular ($\perp$) to the scattering plane which is defined by the direction of the incoming and scattered waves. The angular brackets refer to time averages and the asterisks (*) denote the complex conjugates.

Here, I represents the total intensity, Q the difference between the horizontal and vertically polarized intensities, U the difference between the $+45^\circ$ and -45° polarized intensities, and V the difference between the right-handed and left-handed circularly polarized intensities.

2.2 Mueller Matrix

In general, the state of polarization of a beam is changed on interaction with an optical element (for example, a polarizer, retarder, reflector or scatterer). Thus it is possible to represent such optical elements by a 4×4 matrix, which describes the relation between "incident" and "transmitted" Stokes vectors; "incident" refers to the beam before the interaction with the optical element, and "transmitted" is after that. Then, we can write

$$K_o = SK_i \quad (5)$$

where K_i and K_o represent the incident and transmitted (outgoing) Stokes vectors, respectively, and S is the so called *Mueller Matrix* (Mueller, 1948).

2.3 Derivation of the Mueller Matrix for Scatterers

The following discussion for the derivation of the Mueller matrix of scattering particles is taken directly from Bohren and Huffman (1983) for the sake of completeness of the analysis presented here.

2.3.1 General Formulation

Given a particle of specified size, shape and optical properties that is illuminated by an arbitrarily polarized monochromatic wave, we are interested in determining the electromagnetic field at all points in the particle and at all points of the homogeneous medium in which the particle is embedded.

The field inside the particle is denoted by $(\vec{E}_1, \vec{H}_1)$; the field $(\vec{E}_2, \vec{H}_2)$ in the medium surrounding the particle is the superposition of the incident field $(\vec{E}_i, \vec{H}_i)$ and the scattered field $(\vec{E}_s, \vec{H}_s)$ (Fig. 1):

$$\begin{aligned}\vec{E}_2 &= \vec{E}_i + \vec{E}_s, \\ \vec{H}_2 &= \vec{H}_i + \vec{H}_s\end{aligned}\quad (6)$$

where

$$\begin{aligned}\vec{E}_i &= \vec{E}_0 \exp[i(kx - \omega t)], \\ \vec{H}_i &= \vec{H}_0 \exp[i(kx - \omega t)]\end{aligned}\quad (7)$$

Here $k = 2\pi/\lambda$ is the wave vector in the surrounding medium and ω is the angular frequency. The fields must satisfy the *Maxwell Equations*:

$$\nabla \cdot \vec{E} = 0, \quad (8)$$

$$\nabla \cdot \vec{H} = 0, \quad (9)$$

$$\nabla \times \vec{E} = i\omega\mu\vec{H}, \quad (10)$$

$$\nabla \times \vec{H} = -i\omega\varepsilon\vec{E}, \quad (11)$$

at all points where ε , the dielectric constant and μ , the magnetic permeability are continuous.

However, on crossing the boundary between particle and medium, there is a sudden change in ε and μ . Therefore, there is a discontinuity at the boundary. To overcome this

Figure 1: Effect of incident field $(\vec{E}_i, \vec{H}_i)$ on an arbitrary particle.

difficulty, the following conditions are imposed on the fields:

$$[\vec{E}_2(x) - \vec{E}_1(x)] \times \hat{n} = 0, \quad (12)$$

$$[\vec{H}_2(x) - \vec{H}_1(x)] \times \hat{n} = 0, \quad (13)$$

Here, x on D , where $\hat{n}$ is the outward directed normal to the surface D of the particle (see Fig. 1).

The formulation given here is for scattering of plane monochromatic waves. We use the fact that an arbitrarily polarized wave can be expressed as the superposition of two orthogonal polarization states. Hence, we need to solve each scattering problem twice to determine the scattering of an arbitrarily polarized plane wave. Of course, the spectral nature of light should be accounted for by solving the problem for different wavelengths.

2.3.2 The Amplitude Scattering Matrix (Jones Matrix)

Let us consider an arbitrary particle that is illuminated by a plane harmonic wave (Fig. 2). A rectangular Cartesian coordinate system, (x, y, z) is chosen with the origin O . Orthonormal basis vectors $\hat{e}_x, \hat{e}_y$ and $\hat{e}_z$ are chosen in the directions of the positive x, y and z axes. A scattering plane is defined by the scattering direction $\hat{e}_r$ and the forward direction $\hat{e}_z$ with an azimuthal angle of ϕ from the positive x -axis. The incident electric field $\vec{E}_i$ in the xy plane is resolved as follows:

$$\begin{aligned} \vec{E}_i &= (E_{o\parallel} \hat{e}_{\parallel i} + E_{o\perp} \hat{e}_{\perp i}) \exp[i(kz - \omega t)] \\ &= E_{\parallel i} \hat{e}_{\parallel i} + E_{\perp i} \hat{e}_{\perp i} \end{aligned} \quad (14)$$

where $k = 2\pi/\lambda$ is the wave number in the medium surrounding the particle, and λ is the wavelength of the incident light within the medium.

At sufficiently large distances from the origin ($kr \gg 1$), in the far-field region, the scattered electric field $\vec{E}_s$ is approximately *transverse* ($\hat{e}_r \cdot \vec{E}_s \simeq 0$) and has been shown by Jackson (1975) to have the asymptotic form

$$\vec{E}_s \sim \frac{e^{ikr}}{-ikr} \vec{A}, \quad kr \gg 1 \quad (15)$$

where $\hat{e}_r \cdot \vec{A} = 0$, $\vec{A}$ being the amplitude vector. Hence the scattered field in the far-field region may be written as

$$\vec{E}_s = E_{\parallel s} \hat{e}_{\parallel s} + E_{\perp s} \hat{e}_{\perp s} \quad (16)$$

Figure 2: Scattering by an arbitrary particle: definition of basis vectors along the forward and scattering directions, and the scattering plane.

$$\begin{aligned}
\hat{e}_{\parallel s} &= \hat{e}_\theta, \\
\hat{e}_{\perp s} &= -\hat{e}_\phi, \\
\hat{e}_{\perp s} \times \hat{e}_{\parallel s} &= \hat{e}_r
\end{aligned} \tag{17}$$

Because of the linearity of the boundary conditions, the amplitude of the field scattered by an arbitrary particle is a linear function of the amplitude of the incident field. The relation between incident and scattered fields is conveniently written in matrix form as

$$\begin{pmatrix} E_{\parallel s} \\ E_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix} \tag{18}$$

where the elements S_j ($j = 1, 2, 3, 4$) constitute the *amplitude scattering matrix* (or *Jones Matrix*). and depend, in general, on the zenith angle θ and the azimuthal angle ϕ .

Each of the four amplitude scattering matrix elements has real and imaginary parts which have to be measured for all values of θ and ϕ . To do so we have to measure the amplitude and phase of the light scattered in all directions for two incident orthogonal polarization states. In general, measurement of the phase of the scattered light is difficult and few such experiments have been performed. Because of this, the scattering matrix elements are not measured directly. These are related to quantities whose measurement poses fewer experimental problems than phases. These quantities are explored in the following sections.

2.3.3 Mueller Matrix

Once the distribution of the electromagnetic fields inside and scattered by the particle are obtained, the time averaged Poynting vector $\vec{P}$ can be determined at any point in the medium surrounding the particle as

$$\begin{aligned}
\vec{P} &= \frac{1}{2} \text{Re}\{\vec{E}_2 \times \vec{H}_2^*\} = \vec{P}_i + \vec{P}_s + \vec{P}_{ext} \\
\vec{P}_i &= \frac{1}{2} \text{Re}\{\vec{E}_i \times \vec{H}_i^*\} \\
\vec{P}_s &= \frac{1}{2} \text{Re}\{\vec{E}_s \times \vec{H}_s^*\} \\
\vec{P}_{ext} &= \frac{1}{2} \text{Re}\{\vec{E}_i \times \vec{H}_s^* + \vec{E}_s \times \vec{H}_i^*\}
\end{aligned} \tag{19}$$

Here $\vec{P}_i$ is the Poynting vector associated with the incident wave, $\vec{P}_s$ is that for the scattered field, and $\vec{P}_{ext}$ is the term that arises because of the interaction between the incident and scattered waves.

Let us consider a detector placed at a distance r from a particle in the far-field region, with its surface ΔD aligned normal to $\hat{e}_r$ (Fig. 3). The detector will record a signal proportional to $\vec{P}_s \cdot \hat{e}_r \cdot \Delta D$. The detector "sees" only the scattered light provided that it does not "look at" the source of incident light. From Eqns. (15) and (19) it follows that

$$\vec{P}_s \cdot \hat{e}_r \cdot \Delta D = \frac{k}{2\omega\mu} \frac{|\vec{A}|^2}{k^2} \Delta\Omega \quad (20)$$

$$k = \frac{2\pi}{\lambda} \quad (21)$$

$$\omega = 2\pi\nu \quad (22)$$

where $\Delta\Omega = \Delta D/r^2$ is the solid angle subtended by the detector. Thus we obtain $|\vec{A}|^2$ as a function of the direction by recording the detector response at various locations on a hemisphere surrounding the particle.

By interposing various polarizers between particle and detector and recording the resulting irradiances, we obtain the Stokes parameters of the light scattered by a particle:

$$I_s = \langle E_{\parallel s} E_{\parallel s}^* + E_{\perp s} E_{\perp s}^* \rangle \quad (23)$$

$$Q_s = \langle E_{\parallel s} E_{\parallel s}^* - E_{\perp s} E_{\perp s}^* \rangle \quad (24)$$

$$U_s = \langle E_{\parallel s} E_{\perp s}^* + E_{\perp s} E_{\parallel s}^* \rangle \quad (25)$$

$$V_s = i \langle E_{\parallel s} E_{\perp s}^* - E_{\perp s} E_{\parallel s}^* \rangle \quad (26)$$

Here, the multiplicative factor $k/2\omega\mu$ is not written explicitly. The relation between incident and scattered Stokes parameters is obtained from the amplitude scattering matrix Eq.(18) as

$$\begin{pmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{pmatrix} = \frac{1}{k^2 r^2} \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix} \quad (27)$$

$$S_{11} = \frac{1}{2}(|S_1|^2 + |S_2|^2 + |S_3|^2 + |S_4|^2) \quad (28)$$

$$S_{12} = \frac{1}{2}(|S_2|^2 - |S_1|^2 + |S_4|^2 - |S_3|^2) \quad (29)$$

$$S_{13} = \text{Re}\{S_2 S_3^* + S_1 S_4^*\} \quad (30)$$

$$S_{14} = \text{Im}\{S_2 S_3^* - S_1 S_4^*\} \quad (31)$$

$$S_{21} = \frac{1}{2}(|S_2|^2 - |S_1|^2 - |S_4|^2 + |S_3|^2) \quad (32)$$

Figure 3: Detector to collect the scattered light from the particle

$$S_{22} = \frac{1}{2}(|S_2|^2 + |S_1|^2 - |S_4|^2 - |S_3|^2) \quad (33)$$

$$S_{23} = \text{Re}\{S_2 S_3^* - S_1 S_4^*\} \quad (34)$$

$$S_{24} = \text{Im}\{S_2 S_3^* + S_1 S_4^*\} \quad (35)$$

$$S_{31} = \text{Re}\{S_2 S_4^* + S_1 S_3^*\} \quad (36)$$

$$S_{32} = \text{Re}\{S_2 S_4^* - S_1 S_3^*\} \quad (37)$$

$$S_{33} = \text{Re}\{S_1 S_2^* + S_3 S_4^*\} \quad (38)$$

$$S_{34} = \text{Im}\{S_2 S_1^* + S_4 S_3^*\} \quad (39)$$

$$S_{41} = \text{Im}\{S_2^* S_4 + S_3^* S_1\} \quad (40)$$

$$S_{42} = \text{Im}\{S_2^* S_4 - S_3^* S_1\} \quad (41)$$

$$S_{43} = \text{Im}\{S_1 S_2^* - S_3 S_4^*\} \quad (42)$$

$$S_{44} = \text{Re}\{S_1 S_2^* - S_3 S_4^*\} \quad (43)$$

As pointed out before, the 4×4 S matrix in Eq. (27) is the *Scattering Matrix* or the *Mueller Matrix* for scattering by a single particle. Not all the 16 elements of the scattering matrix are independent; only seven of them are, corresponding to the four moduli $|S_j|$ ($j = 1, 2, 3, 4$) and the three differences in phase between the S_j . Thus, there must be nine independent relations among the S_{ij} ; as outlined by Abhyankar and Fymat (1969).

If unpolarized light of irradiance I_i is incident on one or more particles, the Stokes parameters of the scattered light are

$$\frac{I_s}{I_i} = S_{11}, \quad \frac{Q_s}{I_i} = S_{21}, \quad \frac{U_s}{I_i} = S_{31}, \quad \frac{V_s}{I_i} = S_{41} \quad (44)$$

where, $k^2 r^2$ product is accounted for in the normalization implicitly. Therefore S_{11} specifies the angular distribution of the scattered light given unpolarized incident light. The degree of polarization of the scattered light is given by

$$\sqrt{(S_{21}^2 + S_{31}^2 + S_{41}^2)/S_{11}^2} \quad (45)$$

The Stokes parameters of the light scattered by a collection of randomly oriented particles are the sum of the Stokes parameters of the light scattered by the individual particles. Therefore, the scattering matrix for such a collection is merely the sum of the individual particle scattering matrices.

2.4 Symmetry in Mueller Matrices for scattering in an arbitrary direction

A cloud, or medium, of scattering particles contains many identical particles with different orientations in space. In this section we will discuss the simplifications of the scattering matrix that will result if we make certain assumptions about the distribution of particle orientations.

If the scattering matrix of a particle in a particular position and for a particular direction is known, the scattering matrix of the same particle, or its mirror image, in certain symmetrical positions is also known. When different particles or differently oriented particles are present together in the same medium, the elements of the individual scattering matrices have to be added to obtain the scattering matrix of the medium. The addition causes certain non-diagonal elements of the final matrix to vanish and others to become equal, depending on the exact assumptions made.

Let us consider a direction for which the scattering angle is not 0° or 180° . The directions of incidence and scattering define the *scattering plane*. This is taken as the plane of reference (plane ZOY in Fig. 4). The line in the scattering plane that bisects the angle between the incident and scattered beam is called the *bisectrix*. The plane through the bisectrix and perpendicular to the plane of scattering is called the *bisectrix plane*.

A given position of the particle is taken as the initial position (a) (Fig. 5). Three other positions for which the scattering matrix may be expressed in terms of the same coefficients as in position (a) are also shown in Fig. 5. Rotation of 180° about the bisectrix plane puts the particle (a) in the position (b). (b) is called the *reciprocal position* of (a). Mirroring with respect to the plane of scattering gives a position (c). Mirroring with respect to the bisectrix plane gives another position (d). The corresponding amplitude matrices are given as (van de Hulst, 1957)

$$\begin{pmatrix} (a) \\ S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} (b) \\ S_2 & -S_4 \\ -S_3 & S_1 \end{pmatrix} \begin{pmatrix} (c) \\ S_2 & -S_3 \\ -S_4 & S_1 \end{pmatrix} \begin{pmatrix} (d) \\ S_2 & S_4 \\ S_3 & S_1 \end{pmatrix} \quad (46)$$

We shall now introduce certain assumptions about the distribution of particles among these positions. The various cases are shown below:

1. The cloud contains one kind of particles. For each particle in one position a particle in the reciprocal position is found. Adding the scattering matrices of (a) and (b) we get the following matrix

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{12} & S_{22} & S_{23} & S_{24} \\ -S_{13} & -S_{23} & S_{33} & S_{34} \\ S_{14} & S_{24} & -S_{34} & S_{44} \end{pmatrix} \quad 10 \text{ parameters} \quad (47)$$

2. The cloud contains particles and their corresponding mirror image particles with respect to the plane of scattering. For any particle in position (a) a mirror particle in position (c) is found. In this case the resulting matrix is

$$\begin{pmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{22} & 0 & 0 \\ 0 & 0 & S_{33} & S_{34} \\ 0 & 0 & S_{43} & S_{44} \end{pmatrix} \quad 8 \text{ parameters} \quad (48)$$

Figure 4: Definitions of the directions of incidence and scattering, scattering plane and the bisectrix plane (from Bohren and Huffman, 1983).

Figure 5: Two positions of an arbitrary particle and the positions that result from mirroring these with respect to the bisectrix plane (from Bohren and Huffman, 1983).

3. The cloud contains particles and their mirror image particles with respect to the bisectrix plane. For any particle in position (a) a mirror particle in position (d) is found. In this case the resulting matrix is

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{12} & S_{22} & S_{23} & S_{24} \\ S_{13} & S_{23} & S_{33} & S_{34} \\ -S_{14} & -S_{24} & -S_{34} & S_{44} \end{pmatrix} \quad 10 \text{ parameters} \quad (49)$$

4. The cloud contains particles and their mirror particles, while any two of the preceding assumptions are made. The third one follows automatically so that there are equal numbers of particles in positions (a), (b), (c), and (d). The resulting matrix has the form

$$\begin{pmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{22} & 0 & 0 \\ 0 & 0 & S_{33} & S_{34} \\ 0 & 0 & -S_{34} & S_{44} \end{pmatrix} \quad 6 \text{ parameters} \quad (50)$$

5. The cloud contains one kind of asymmetric particles with random orientation. The assumptions of Case 1 are then fulfilled and the scattering matrix has 10 parameters.
6. The cloud contains particles that have a plane of symmetry and are randomly oriented.

In this case the assumptions of Case 4 are satisfied and the scattering matrix has 6 parameters.

2.5 Symmetry in Mueller Matrices for Particles in Flames

Flames contain a large number of soot particles. These particles are randomly oriented and it may be possible to find a plane of symmetry for them. Hence the assumptions of Case 6 in the previous section are fulfilled and the Mueller matrix in this case consists of six independent parameters.

3 PROPOSED EXPERIMENTAL SYSTEM

In this chapter, the experimental system proposed is outlined and a mathematical analysis is performed to derive the proportion of the various matrix elements in the intensities measured.

3.1 Proposed Experimental System

As discussed before, the interaction of an optical device with a beam of light can be described as a transformation of an incident Stokes vector K_i into an emerging Stokes vector K_o .

$$K_o = S \cdot K_i \quad (51)$$

where S is the 4×4 Mueller matrix. The transformation of an incident Stokes vector by a sequence of optical devices is given by the matrix that is the sequential product of the matrices representing each optical device.

The schematic diagram of the optical setup proposed to measure the Mueller matrix elements for particles in flames is shown in Fig. 6. For this setup, the transformation from the incident Stokes vector to the emergent Stokes vector can be written as

$$K_o = \{[P_2] \cdot [R_3] \cdot S(\theta) \cdot [R_2] \cdot [R_1] \cdot [P_1]\} \cdot K_i \quad (52)$$

3.2 Mathematical Analysis

The Mueller matrices for an ideal linear polarizer P and a retarder R are given as (Bohren and Huffman, 1983)

$$P = \frac{1}{2} \begin{pmatrix} 1 & \cos 2\xi & \sin 2\xi & 0 \\ \cos 2\xi & \cos^2 2\xi & \cos 2\xi \sin 2\xi & 0 \\ \sin 2\xi & \sin 2\xi \cos 2\xi & \sin^2 2\xi & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (53)$$

$$R = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & C^2 + D^2 \cos \delta & CD(1 - \cos \delta) & -D \sin \delta \\ 0 & CD(1 - \cos \delta) & D^2 + C^2 \cos \delta & C \sin \delta \\ 0 & D \sin \delta & -C \sin \delta & \cos \delta \end{pmatrix} \quad (54)$$

Figure 6: Schematic of the Experimental Setup; POL: Polarizer, HWP: Half wave plate, QWP: Quarter wave plate, F: Flame.

where $C = \cos 2\beta$, $D = \sin 2\beta$. Here ξ is the angle between the transmission axis of the polarizer and the parallel axis of the incident beam, β is the angle between the parallel axis of the retarder and the horizontal, and δ is the retardance of the retarder.

For a cloud of scattering particles, the corresponding Mueller matrix is called *Scattering Matrix*, and is given in the general form as (Bohren and Huffman, 1983)

$$S(\theta) = \frac{1}{k^2 r^2} \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix} \quad (55)$$

where θ is the scattering angle, k is the wave number and r is the distance from the center of the flame to the detector. Note that each of the matrix elements is a function of the scattering angle θ . The scattering matrix for a cloud of particles is the sum of the individual scattering matrices for each of the particles.

For a cloud of particles that have a plane of symmetry and are randomly oriented, the

scattering matrix reduces to (see Eq. (50))

$$S(\theta) = \frac{1}{k^2 r^2} \begin{pmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{22} & 0 & 0 \\ 0 & 0 & S_{33} & S_{34} \\ 0 & 0 & -S_{34} & S_{44} \end{pmatrix} \quad (56)$$

Given that soot particles/agglomerates in flames are randomly oriented, they can have a plane of symmetry. Hence the scattering matrix for particles in flames consists of six independent parameters.

The Mueller matrices corresponding to the polarizers and retarders (as given by Eqns. 53 and 54) and the cloud of soot particles in the flame (as given by Eqn. 56) are substituted in Eqn. 52 to obtain the output Stokes vector. The detector measures only the intensity of the scattered light; therefore, we consider only the first element of the emergent Stokes vector K_o , which is the output intensity I_o . The expression for I_o contains a combination of various terms involving sines and cosines of the orientation angles ξ_1 , ξ_2 , β_1 , β_2 and β_3 of the retarders and polarizers and the Mueller matrix elements of the particle cloud (from Eqn. 56).

The *FORTTRAN* program used to calculate the coefficients of the various Mueller matrix elements given the various orientation angles is presented in Appendix 1. This was obtained by multiplying the Mueller matrices of the individual optical components (see Eqn. 52) and separating the coefficients of the Mueller matrix elements of the particle cloud (see Eqn. 56). Since we are interested in identifying six Mueller matrix elements, we have to have six independent equations, which can be obtained by using six different sets of the orientation angles ξ_1 , ξ_2 , β_1 , β_2 and β_3 . The system of equations obtained can be written in matrix form as

$$CZ = B \quad (57)$$

$$Z = \begin{pmatrix} S_{11} \\ S_{12} \\ S_{22} \\ S_{33} \\ S_{34} \\ S_{44} \end{pmatrix} \quad (58)$$

Here $\mathbf{C}$ is the coefficient matrix consisting of the coefficients of the Mueller matrix elements obtained and the elements of $\mathbf{B}$ correspond to the intensities obtained from measurements with six different orientation angles of polarizers and retarders.

The multiplicative constant in the expression for the intensity is $(I_i + U_i)/(k^2 r^2)$. Since we do not know k , I_i and U_i , we have to normalize this intensity with the intensity measured using particles of known size and refractive index. Another alternative is to normalize all elements of the Mueller matrix with respect to S_{11} and use the same normalization while generating the theoretical results.

4 NUMERICAL ANALYSIS TO OBTAIN OPTIMUM POLARIZER AND RETARDER ANGLES

Here, a numerical analysis is presented to derive the optimum combination of the orientation angles of the various optical components so that the desired Mueller matrix elements are recovered accurately. For this, the theoretical results obtained for the scattering matrix elements of soot agglomerates from the *AGGLOME* algorithm, which was developed by Manickavasagam and Mengüç (1996), are used.

4.1 Numerical Procedure

In this section, we outline the procedure followed to arrive at an optimum combination of ξ_1 , ξ_2 , β_1 , β_2 , and β_3 angles of polarizers and retarders, which will enable us to measure the scattering matrix elements of the particles accurately. The procedure followed is as follows:

- Soot agglomerates with fractal dimension of 1.8 are generated numerically with primary sphere diameters (d_p) of either 20 nm or 60 nm. The number of primary spheres (N) in each agglomerate is taken as 25, 75, or 125. These agglomerate structures are shown in Figs. 7, 8 and 9, respectively. The Mueller matrix elements S_{11} , S_{12} , S_{22} , S_{33} , S_{34} , and S_{44} , which are the elements of $\mathbf{Z}$ (see Eqn. 58) are calculated for each agglomerate using the *AGGLOME* algorithm for scattering angles between 0° and 180° .
- The coefficient matrix $\mathbf{C}$ is generated by using 6 sets of input values for the orientation angles of the polarizers and retarders. Note that the $\mathbf{C}$ matrix has a dimension of 6×6 .
- The product of $\mathbf{C}$ and $\mathbf{Z}$ is evaluated to obtain the $\mathbf{B}$ vector. Note that in reality, $\mathbf{B}$ contains measured values of the scattered light and hence its elements are expected to have some experimental errors.
- Using *ESSL* and *IMSL* routines, a set of random numbers is generated and used to perturb the elements of the $\mathbf{B}$ vector, which will eventually be considered as the experimental data in the inverse analysis. Two different error ranges $\pm 3.0\%$ and $\pm 7.5\%$ are chosen to represent the experimental uncertainty in $\mathbf{B}$. Another case with no error is also considered.

- Using these new values of perturbed $\mathbf{B}$ (or $\mathbf{B}_1$), the system of equations $\mathbf{C}\mathbf{Z}_1 = \mathbf{B}_1$ is solved to obtain $\mathbf{Z}_1$ vector elements, which are called "recovered Mueller matrix elements". These elements are employed to identify the structure of agglomerates in a given experimental system.
- The procedure given above is repeated for 50 sets of random numbers and thus we obtain 50 sets of $\mathbf{Z}_1$ for a given set of polarizer and retarder angles. The arithmetic average of these sets of $\mathbf{Z}_1$ is taken and stored as recovered $\mathbf{Z}$ (or $\mathbf{Z}_1^{ave}$).
- The entire procedure is repeated for several different scattering angles between 0° and 180° .
- The relative error between $\mathbf{Z}$ and $\mathbf{Z}_1^{ave}$ is evaluated for each scattering angle.

4.2 Results and Discussion

The numerical procedure discussed above was performed for different sets of retarder and polarizer angles. It is found that the relative error between input ($\mathbf{Z}$) and recovered ($\mathbf{Z}_1^{ave}$) Mueller matrix elements depends on the orientation of the retarders and polarizers. Since the elements of the coefficient matrix $\mathbf{C}$ depend on these orientations, first the properties of $\mathbf{C}$ are investigated. After that, the S_{ij} matrix elements recovered using perturbed $\mathbf{B}$ vector elements are discussed. The results are presented for three different agglomerate structures shown in Figs. 7, 8 and 9.

4.2.1 Effect of Condition Number on Recovered Mueller Matrix Elements

For a given system of linear equations (as in Eqn. 57), the effect of error in $\mathbf{B}$ on the solution vector $\mathbf{Z}$ is a function of the condition number of the coefficient matrix $\mathbf{C}$ (Conte and de Boor, 1981). The condition number for a matrix $\mathbf{C}$ is defined as

$$CN = \|\mathbf{C}\| \|\mathbf{C}^{-1}\| \quad (59)$$

where $\|\mathbf{C}\|$ refers to the norm of $\mathbf{C}$. CN provides a measure of how the relative residual $\|\mathbf{B} - \mathbf{B}_1\| / \|\mathbf{B}\|$ relates to the relative error $\epsilon = \|\mathbf{Z}_1 - \mathbf{Z}\| / \|\mathbf{Z}\|$ of the perturbed system of linear equations. If CN is small, then the relative residual and relative error are proportional.

In order to arrive at an optimum set of retarder and polarizer angles, we study the effect of CN on the recovered Mueller matrix elements ($\mathbf{Z}_1^{ave}$). Various random sets of retarder

Figure 7: Soot agglomerate model: 25 spheres.

Figure 8: Soot agglomerate model: 75 spheres.

Figure 9: Soot agglomerate model: 125 spheres.

and polarizer angles are chosen to form several different $\mathbf{C}$ matrices and the relative error in $\mathbf{Z}$ is evaluated for each case. The results obtained are discussed below.

Figure 10 shows the magnitude of ϵ on recovered S_{11} and S_{12} elements respectively, at various scattering angles between 0° and 180° . The input Mueller matrix elements ($\mathbf{Z}$) are generated in this case by assuming $d_p = 60 \text{ nm}$ and $N = 25$. $\mathbf{B}$ is perturbed by random errors in the range of $\pm 3.0\%$. It is seen that for a condition number of 10 the maximum ϵ on S_{11} is about 0.1%, yet increases to almost 50% if $\text{CN} = 10000$. The relative error on recovered S_{12} , on the other hand, is more sensitive to CN , which depends on the retarder and polarizer angles chosen. For $\text{CN} = 10$, the maximum ϵ is about 10%, and for all the other cases, it is more than 100%.

Figure 11 depicts the relative error ϵ on recovered S_{34} and S_{44} as a function of condition number at various scattering angles. The maximum ϵ on S_{44} for $\text{CN} = 10$ is about 8% and is more than 100% for $\text{CN} = 10000$. It is also observed that for all CN values, ϵ on recovered S_{34} is more than 100%. Hence, it seems that that S_{34} cannot be obtained from experimental measurements with reasonable accuracy for any given set of retarder and polarizer angles.

Since for $\text{CN} = 10$, the maximum relative error on recovered Mueller matrix elements is less than 10%, the corresponding set of retarder and polarizer angles were chosen to be

the optimum set-up conditions for experimental measurements. This set of optimum angles and the corresponding elements of the coefficient matrix $\mathbf{C}$ are given in Tables 1 and 2. It is to be noted this choice is not unique: many other optimum conditions can be found such that the condition number of $\mathbf{C}$ is less than 10.

Table 1: Set of optical component angles (in degrees) which yields $CN < 10$ ($CN=9.58$).

ξ_1	ξ_2	β_1	β_2	β_3
45	80	70	60	80
45	20	30	20	10
45	30	0	30	40
45	70	50	10	10
45	0	70	30	0
45	50	60	80	60

Table 2: Coefficient matrix $\mathbf{C}$ for optical component angles given in Table 1.

$$\mathbf{C} = \begin{pmatrix} 1.000000 & -1.110702 & 0.160697 & 0.101307 & -0.321395 & 0.000000 \\ 1.000000 & 1.637427 & 0.666157 & 0.203449 & -0.160696 & 0.059392 \\ 1.000000 & -0.269836 & -0.070658 & -0.694061 & 0.206194 & -0.171010 \\ 1.000000 & -0.469842 & -0.000001 & 0.000000 & 0.171008 & -0.866026 \\ 1.000000 & 0.678607 & -0.321393 & 0.000000 & 0.000000 & 0.000000 \\ 1.000000 & -1.395259 & 0.434801 & 0.274109 & 0.256517 & -0.059392 \end{pmatrix}$$

4.2.2 Recovered Mueller Matrix Elements for Optimal Set-Up

Figures 12, 13, 14 and 15 depict the input and recovered Mueller matrix elements for the optimal setup conditions given in Table 1. In the two cases considered, the $\mathbf{B}$ matrix is perturbed to have random error within the range of either $\pm 3.0\%$ or $\pm 7.5\%$. The computer generated agglomerates used have N values of 25, 75 or 125, with monomer diameters of either $d_p = 20 \text{ nm}$ or 60 nm (see Figs. 7, 8 and 9). In Figs. 12, 13, 14 and 15, four Mueller matrix elements S_{11} , S_{12} , S_{34} and S_{44} are plotted. Each figure displays the input and recovered S_{ij} elements. Practically there is no difference between the input and recovered values even if the random error on $\mathbf{B}$ elements is in the range of $\pm 7.5\%$. This means that the recommended optical setup can be used to recover these S_{ij} elements. Note that the

recovered S_{34} deviates from actual S_{34} significantly (see Fig. 14). This indicates that S_{34} cannot be measured from experiments accurately with the proposed set-up. Note that if there is no error in **B** elements, the S_{ij} elements recovered are identical to those used as input.

Examination of Figs. 12 and 13 shows that there are significant differences between S_{11} and S_{12} elements of different size agglomerates. Also variation in monomer size (d_p) affects the values of the Mueller matrix elements. Since the S_{ij} elements can be recovered quite accurately from the analysis presented, it will be possible to identify agglomerate size and structure (N, d_p) after performing carefully planned experiments.

Figure 10: Relative error ϵ on recovered S_{11} and S_{12} elements at various scattering angles between 0° and 180° for various values of the condition number CN .

Figure 11: Relative error ϵ on recovered S_{34} and S_{44} elements at various scattering angles between 0° and 180° for various values of the condition number CN .

Figure 12: Input and recovered S_{11} elements for the optimal setup conditions given in Tables 1 and 2.

Figure 13: Input and recovered S_{12} elements for the optimal setup conditions given in Tables 1 and 2.

Figure 14: Input and recovered S_{34} elements for the optimal setup conditions given in Tables 1 and 2.

Figure 15: Input and recovered S_{44} elements for the optimal setup conditions given in Tables 1 and 2.

5 DESCRIPTION OF THE EXPERIMENTAL SYSTEM

5.1 Layout of Experimental System

The experimental system to be used to measure the Mueller matrix elements of soot agglomerates in flames consists of a light source (a Nd:YAG laser/Optical Parametric Oscillator system) and various directing optics to direct the laser beam to the flame and the collecting optics to collect the scattered light. The layout of this system is shown in Fig. 16.

5.2 Light Source

The light source used in the experiments was an Optical Parametric Oscillator (OPO) (Spectra Physics/Quanta Ray MOPO-710) pumped by a single-frequency injection seeding Nd:YAG laser (Spectra Physics/Quanta Ray GCR 170, 30 Hz). A brief description of the theory of OPO as well as the pumping YAG laser is given below.

5.2.1 OPO Theory of Operation

The Optical Parametric Oscillator (OPO) is based on a different principle of operation from that of a conventional laser system. The conventional laser is based on the process of *stimulated emission*. When an incident photon of resonant energy $E_1 - E_0$ passes by an atom in excited state E_1 , it "stimulates" the atom to drop to the lower states, E_0 . In the process, the atom releases a photon of the *same* energy, direction, phase, and polarization as that of the photon passing by. The net effect is two identical photons in the place of one, or an increase in the intensity of the incident beam. This process of stimulated emission makes possible the amplification of light in lasers. On the other hand, the OPO's gain is derived from a nonlinear frequency conversion process arising from the nonlinear interaction between an intense optical wave and a crystal having a large nonlinear polarizability coefficient. The most commonly used nonlinear crystal is BBO.

When a pump photon at frequency ω_p is incident on a nonlinear crystal such as BBO, its energy is transferred to two other photons ω_s (the signal wave) and ω_i (the idler wave) so as to satisfy the energy conversion law:

$$\omega_p = \omega_s + \omega_i \quad (60)$$

Or, in terms of wavelength:

$$\frac{1}{\lambda_p} = \frac{1}{\lambda_s} + \frac{1}{\lambda_i} \quad (61)$$

By placing the nonlinear BBO crystal in a resonant cavity, oscillation at the signal and/or idler wavelength can be obtained. By varying the angle of the BBO with respect to the pump beam, one can obtain a signal beam of varying wavelength and hence an idler beam also of varying wavelength so as to satisfy the energy conversion law.

The OPO makes use of the third harmonic from the Nd:YAG laser at 355 nm as the pump beam. In theory, an infinite number of signal and idler wavelengths exist to satisfy the energy conversion law. In practice, we obtain a signal beam of wavelength ranging from 410 to 690 nm and an idler beam of wavelength 730 to 2000 nm as shown in Fig. 17. Hence the OPO can tune continuously from 410 nm to 2000 nm. In contrast, a versatile Ti:sapphire laser can tune over 200 nm wavelength range only. Dye lasers can tune over a wider range but they require several dye compounds to cover the visible wavelength range. It is the wide tunable range of OPOs that make them attractive for research applications requiring measurements over a range of wavelengths.

5.2.2 Pumping Laser

The pumping laser used is a Nd:YAG laser (Quanta Ray GCR-170, 30 Hz) This gives an output beam at 355 nm which is sent to the OPO for the nonlinear frequency conversion process. The pumping laser is equipped with an *injection seeding system*. Injection seeding refers to the process of injecting radiation from a very narrow linewidth, continuous-wave "seed" laser into the pulsed "host" laser cavity during the time the Q-switch opens. This process produces single longitudinal mode output pulses of smooth temporal profile and extremely narrow linewidth which can substantially improve the performance of the BBO.

5.3 Directing Optics

Three light beams emerge out from the OPO unit. The first one is the 1064 nm beam from the Nd:YAG pumping laser, which passes through the OPO unchanged and is finally trapped by a beam trap. The other two beams are the visible beam, called the *signal*, of wavelength 410 to 690 nm, and the infra-red beam, called the *idler*, of wavelength 730 to 2000 nm. The idler beam is also trapped by a beam trap. Due to limitations in the range of optics used in the setup, we work with a signal beam of wavelength 532 nm. This beam is horizontally polarized at the exit from the OPO.

The signal beam is split into two components using a beam splitter. One component passes through a series of neutral density filters and is collected by a photomultiplier tube.

This serves as the reference signal for the experiments. The filters used are absorptive type, neutral density filters (CVI Laser) with internal transmittances 0.0040 (specified as NG10), 0.2700 (NG4) and 0.0001 (NG1). Four such filters are used in the sequence NG10, NG1, NG1 and NG4 resulting in a transmittance of 1.08×10^{-11} . Such a reduction in the reference signal is necessary not to saturate the photomultiplier tube (PMT). The PMT used in the experiments is Hamamatsu R446 with a spectral response range of 185 to 870 nm, a peak wavelength of 330 nm and a maximum anode to cathode voltage of 1250 V DC.

The other component of the signal beam is directed to the flame by two prisms as indicated in Fig. 16. After this redirection, the optical components necessary to change the polarization characteristics of the incident light, namely a polarizer, half wave plate and quarter wave plate, are imposed in the path of the incident beam. The polarizer used is a sheet metal polarizer (DPM-0.5-HN38S, Meadowlark Optics). The quarter and half wave plates used are PQM-1.0-0532 and PHM-1.0-0532 (both Meadowlark).

Following the quarter wave plate is a lens of focal length 1000 mm. The collimated beam is brought to a focus using this lens. A 0.5 mm spatial filter is used to clean the beam of any outer fringes. The cleaned beam is then collimated again using another lens of focal length 62.9 mm before passing through the flame.

5.4 Burner

The burner used in the experiments was a coflow diffusion burner. The burner consists of a central fuel tube surrounded by a co-annular oxidizer tube. The fuel used was ethylene and the oxidizer was air from the building compressor through an air line. Details of this burner were given by Mahadeviah (1991).

5.5 Light Collection System

The schematic of the light collection system for the scattered signal is shown in Fig. 18. Scattered light from a small control volume in the flame is collected using a set of two lenses, one of focal length 50.2 mm and the other of focal length 25.4 mm. The solid angle seen is limited by a variable aperture at the inlet of the light collection system. A quarter wave plate (PQM-1.0-532, Meadowlark) and a polarizer (DPM-1.0-532, also Meadowlark) are placed after the 50.2 mm lens. The light collected from the flame in this manner is made incident on the photomultiplier tube detector (Burle 4840). A narrow bandpass filter is attached to the PMT surface to allow only the scattered light onto the detector. The

collection system is mounted on a rotary table which can be rotated by a two-axis controller system (Newport, PMC200).

5.6 Data Acquisition System

The reference as well as the scattered signal is sent to a gated integrator and boxcar averager module (SRS 250) which is a versatile, high speed instrument for recovering fast, low duty cycle, analog signal from relatively noisy backgrounds. The gate generator, which can be triggered externally by the Nd:YAG laser's Q-switch output signal, provides an adjustable delay in the range of $\approx 1 \text{ ns} - 10 \text{ ms}$, and generates a gate of continuously variable width in the range $2 \text{ ns} - 15 \mu\text{s}$. Only that part of the signal overlapping with the gate is recorded. A dual channel 400 *MHz* oscilloscope (HP 54502A) is used to adjust the delay so that the gate is positioned over the signal. The fast-gated integrator integrates the input signal, its output being normalized by the gate width to produce a voltage proportional to the average input signal during the sampling gate.

The Computer Interface Module (SRS 245) is used to transfer the averaged signal data to a PC where a commercial data acquisition software (LabTech) receives, plots and records the data. Two gated integrators are used to record both the scattered and the reference signal simultaneously.

Figure 16: Layout of the Experimental System

Figure 17: Principle of Operation of the BBO

Figure 18: Schematic of the light collection system

6 RESULTS AND DISCUSSIONS

In this chapter, the scattering matrix elements obtained for soot agglomerates from experiments are presented and the trends are discussed. A series of numerically obtained results are presented first to establish a basis for the qualitative comparison against the experimental data.

6.1 Numerical Results

The section is divided into different subsections to highlight how each of the scattering matrix elements may change with respect to changes in size of an agglomerate.

S_{11} is the differential scattering cross section of the scatterer and its magnitude changes with the scattering angle. If normalized by the area under the $S_{11} - \theta$ curve, S_{11} becomes the phase function of the scatterers (which is essential in estimating the distribution of radiation intensity in a medium containing scatterers). S_{12} is the measure of linearly polarized scattered light for an incident unpolarized light. In general, the angular pattern of S_{12} shows how much the agglomerate deviates from Rayleigh scattering regime. For example, for Rayleigh particles, S_{12} shows a dip at 90° . S_{34} indicates how much of an obliquely polarized light (45°) is transformed to circularly polarized light because of the scatterer, and S_{44} has the similar angular pattern as S_{33} .

In all figures presented, N is the total number of primary spheres in an agglomerate, d_p is the diameter of the primary sphere, λ is the wavelength of incident radiation and m is complex index of refraction of the agglomerate.

6.1.1 S_{11}

Figure 19 depicts the angular variation of S_{11} as a function of N and d_p at the Nd:YAG laser wavelength of 532 nm . The value of S_{11} near the forward directions increases an order of magnitude as d_p goes up from 20 to 40 and to 60 nm . This sensitivity may suggest that an experimental technique may be developed for obtaining the values of N , d_p . However, with the current set-up, we cannot make measurements at angles smaller than 30 degrees.

It may also be possible to determine the fractal dimension of soot agglomerates by measuring angular variation of S_{11} . However, there is a possibility of non-uniqueness in the predictions. For example, a soot agglomerate comprised of 25 primary spheres of diameter 60 nm will scatter the incident radiation similar to that of a 75 or 100 sphere agglomerate

with $d_p = 40 \text{ nm}$. Even if we compare the total scattered energy for these agglomerates (area under S_{11}), which will be their scattering coefficients, the difference will not be large enough to accurately determine N or d_p .

6.1.2 S_{12}

The angular variation of S_{12} for various N and d_p values are shown in Figure 20. The maxima of S_{12} gradually shifts from near 60° to forward angles as N is increased. The same behavior is observed for increasing d_p values. This suggests possible diagnosis of N , if we know the primary sphere diameter (d_p) *a priori*, which can be obtained from SEM pictures.

6.1.3 S_{33}

Figure 21 depicts the angular behavior of S_{33} (or, S_{44}) at 532 nm , as a function of N and d_p values. As N is increased, the S_{33} peaks towards the forward angles. In other words, if we take the area under a typical S_{33} curve, the ratio of area in the forward direction to that in the backward angles (greater than 90°) becomes a strong function of d_p and N .

Figure 22 shows the asymmetry ratio for S_{33} at wavelengths of 532 and 1000 nm , respectively. The asymmetry ratio is calculated as the ratio of total forward scattered light to that of backward scattered light (greater than 90°). This ratio increases as d_p and N are increased at both the wavelengths. Note that there is a non-unique combination of N and d_p which yields the same value of the asymmetry ratio if these wavelengths are considered. However, if we take into account the spectral variation of asymmetry ratio then it provides a unique combination of N and d_p .

6.1.4 S_{34}

The angular pattern of S_{34} as a function of N is displayed in Figure 23. S_{34} has some unique features which were not observed for other elements. For a given wavelength and a primary sphere diameter a minimum can be noted for various N at about the same scattering angle. In other words, the angle at which this minima occurs is a strong function of d_p but not N . Thus the non-uniqueness which we discussed in the earlier section can be removed if we can measure angular variation of S_{34} accurately.

6.1.5 Other S_{ij} Elements

The discussion of the behavior of other elements of the Mueller matrix, i.e. S_{22} and S_{44} is not needed as their behaviors are comparable to those of S_{11} and S_{33} , respectively. In the calculations, the ratio of S_{22} to S_{11} varied between 1 and 0.97, indicating non-spherical behavior.

6.2 Experimental Results and Discussions

Experiments were performed on a diffusion flame with ethylene as fuel and air as the oxidizer. The flame was about 30 cm high and 1.2 cm in diameter. Measurements were made at heights of 1 cm, 3 cm, and 5 cm on the flame at several different angles between 30 and 150 degrees. The sensitivity of box-car averager was kept constant at 50 mV and the number of samples averaged at the box-car was 100. The results obtained for scattering matrix elements, after following the rigorous procedure described earlier, are presented in Figures 24 to 28. Since the experimental data were not calibrated, the results are presented in terms of normalized volts for all the scattering elements.

Figure 24 depicts the angular variation of S_{11} obtained from experiments at three different heights. Note that the magnitude of S_{11} increases with height. It indicates that the soot volume fraction has increased significantly in the flame. It is also noted that the symmetry of the profiles which is obvious at 1 cm height is lost and not seen at 5 cm. This indicates that the soot particles have agglomerated at this height and they no longer behave as Rayleigh spheres.

Figure 25 shows the angular variation of S_{12} at three heights. As expected, the magnitude has increased with change in increasing height. Still, however, this information is not sufficient to predict the soot growth in the flame.

Figure 26 depicts the variation of S_{33} as a function of scattering angle. S_{33} profile has a more pronounced forward peak at a height of 5 cm than at a height of 1 cm. Also the magnitude of S_{33} at backward angles is less than the magnitude at forward angles at 5 cm, whereas, at 1 cm, the profile is more or less symmetric. This indicates that the likelihood of soot agglomerates at 5 cm height in the flame.

Figures 27 and 28 show the angular variation of S_{34} , and S_{44} . It is clear that the experimental data have the expected angular variation. The error involved in obtaining S_{34} is large and hence it does not serve as any useful tool in characterizing the agglomerates.

Figure 19: Effect of N and d_p on the angular profile of S_{11} elements; $\lambda = 532$ nm; $m = 1.85 - 0.50i$.

Figure 20: Effect of N and d_p on the angular profile of S_{12} elements; $\lambda = 532$ nm; $m = 1.85 - 0.50i$.

Figure 21: Effect of N and d_p on the angular profile of S_{33} elements; $\lambda = 532$ nm; $m = 1.85 - 0.50i$.

Figure 22: Ratio of total forward scattered light to that of backward scattered light (asymmetry ratio) based on S_{33} at $\lambda = 532$ and 1000 nm .

Figure 23: Effect of N and d_p on the angular profile of S_{34} elements; $\lambda = 532$ nm; $m = 1.85 - 0.50i$.

Figure 24: Angular variation of S_{11} measured from experiments.

Figure 25: Angular variation of S_{12} measured from experiments.

Figure 26: Angular variation of S_{33} measured from experiments.

Figure 27: Angular variation of S_{34} measured from experiments.

Figure 28: Angular variation of S_{44} measured from experiments.

7 CONCLUSIONS

In this study, an experimental system is designed and built to measure the scattering matrix elements of soot agglomerates in diffusion flames. Preliminary numerical results based on fractal-like agglomerate structures used as a guideline to determine optimum sets of polarizer/retarder angles. These sets yield a matrix with a small condition number; this matrix is then used in an inverse analysis to determine the Mueller matrix elements of agglomerates.

The experiments performed show that if the primary sphere diameter is known *a priori*, for example from SEM pictures, one can identify the structure and size of the soot agglomerates. Even though S_{11} element plays a significant role for this identification, the angular behaviors of other elements indicate the subtle differences between possible agglomerate sizes and structures. In other words, the predictions based on this present methodology are, overall, more convincing than those based on scattered intensity experiments.

This work can readily be extended to multiwavelength studies, provided that proper sets of polarizers and retarders are used. This extension can also help identifying different type of particles in flames.

REFERENCES

- Abhyankar, K.D., Fymat, A.L., (1969), "Relations between the elements of the phase matrix for scattering", *Journal of Mathematical Physics*, Vol. 10, No. 10, pp. 1935-1938.
- Beardsley Jr., G.F., (1968), "Mueller scattering matrix of sea water", *Journal of the Optical Society of America*, Vol. 58, No. 1, pp. 52-57.
- Bell, B.W., (1989), "Mueller matrix: an experimental and analytical tool for magneto-optics", *Optical Engineering*, Vol. 28, No. 2, pp. 114-119.
- Bohren, C.F., Huffman, D.R., (1983), *Absorption and Scattering of Light by Small Particles*, John Wiley, New York.
- Boyer, G.R., Lamouroux, B.F., Prade, B.S., (1979), "Automatic measurement of the Stokes vector of light", *Applied Optics*, Vol. 18, No. 8, pp. 1217-1219.
- Chandrasekhar, S., (1950), *Radiative Transfer*, Oxford Press; Dover Publications, New York (1960).
- Clarke, D., Grainger, J.F., (1971), *Polarized Light and Optical Measurement*, Pergamon Press.
- Conte, S.D., de Boor, C., (1981), *Elementary Numerical Analysis: An Algorithmic Approach*, McGraw Hill, New York.
- Fry, E.S., Kattawar, G.W., (1981), "Relationships between elements of the Stokes matrix", *Applied Optics*, Vol. 20, No. 16, pp. 2811-2814.
- Goldstein, D.H., (1992), "Mueller matrix dual-rotating retarder polarimeter", *Applied Optics*, Vol. 31, No. 31, pp. 6676-6683.
- Govindan, R., Manickavasagam, S., Mengüç, M.P., (1995), "On measuring the Mueller matrix elements of soot agglomerates", *Proceedings of the International Symposium on Radiative Heat Transfer*, Begell House, New York (submitted for publication).
- Hage, J.I., Greenberg, M.J., Wang, R.T., (1991), "Scattering from arbitrarily shaped particles: theory and experiment", *Applied Optics*, Vol. 30, No. 9, pp. 1141-1152.

- Hofer, M., Glatter, O., (1989), "Mueller matrix calculations for randomly oriented rotationally symmetric objects with low contrast", *Applied Optics*, Vol. 28, No. 12, pp. 2389-2400.
- Holland, A.C., Gagne, G., (1970), "The scattering of polarized light by polydisperse systems of irregular particles", *Applied Optics*, Vol. 9, No. 5, pp. 1113-1121.
- Hovenier, J.W., van de Hulst, H.C., van der Mee, C.V.M., (1986), "Conditions for the elements of the scattering matrix", *Astronomy and Astrophysics*, Vol. 157, pp. 301-310.
- Hunt, A.J., Huffman, D.R., (1973), "A new polarization-modulated light scattering instrument", *Review of Scientific Instrumentation*, Vol. 44, No. 12, pp. 1753-1762.
- Jackson, J.D., (1975), *Classical Electrodynamics*, Wiley, New York.
- Kemp, J.C., (1969), "Piezo-optical birefringence modulators: new use for a long-known effect", *Journal of the Optical Society of America*, Vol. 59, No. 8, pp. 950-954.
- Kerker, M., (1969), *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York.
- Kuik, F., Stammes, P., Hovenier, J.W., (1991), "Experimental determination of scattering matrices of water droplets and quartz particles", *Applied Optics*, Vol. 30, No. 33, pp. 4872-4881.
- Mahadeviah, A., (1991), *Study of Morphology of Soot Particles in a Diffusion Flame Using the Discrete Dipole Approximation*, M.S. Thesis, Department of Mechanical Engineering, University of Kentucky, Lexington, KY.
- Manickavasagam, S., Mengüç, M.P., (1996), "Mueller matrix elements of fractal-like soot agglomerates", *Applied Optics* (submitted for publication).
- Mengüç, M.P., Manickavasagam, S., Govindan, R., (1995), "Diagnostics of particulate size and structure using polarized light and scattering matrix concept", *Proceedings of the Symposium on Thermal Science and Engineering in honor of Chancellor Chang-Lin Tien*.
- Mueller, H., (1948), "The foundation of optics", *Journal of the Optical Society of America*, Vol 38, p. 661.
- Pedrotti, F.L., Pedrotti, L.S., (1993), *Introduction to Optics*, Prentice Hall, New Jersey.
- Perry, R.J., Hunt, A.J., Huffman, D.R., (1978), "Experimental determinations of Mueller

scattering matrices for nonspherical particles", *Applied Optics*, Vol. 17, No. 17, pp. 2700-2710.

Pritchard, B.S., Elliott, W.G., (1960), "Two instruments for atmospheric optics measurements", *Journal of the Optical Society of America*, Vol. 50, No. 3, pp. 191-202.

Stokes, G.G., (1852), "On the composition and resolution of streams of polarized light from different sources", *Transactions of the Cambridge Philosophical Society*, Vol. 9, pp. 399. (Reprinted in *Mathematical and Physical Papers*, Vol. 3, pp. 233, Cambridge. University Press, London (1901))

Thompson, R.C., Bottiger, J.C., Fry, E.S., (1980), "Measurement of polarized light interactions via the Mueller matrix", *Applied Optics*, Vol. 19, No. 8, pp. 1323-1332.

van de Hulst, H.C., (1957), *Light Scattering by Small Particles*, Dover Publications, New York.

Wiscombe, W.J., Mugnai, A., (1986), "Single scattering from nonspherical Chebyshev particles: a compendium of calculations". NASA Reference Publication 1157, January 1986.

APPENDIX I

FORTRAN program for calculating the coefficients of the various Mueller matrix elements for input values of the retarder and polarizer angles

The Mueller matrices of the individual optical components (see Eqn. 52) were multiplied using the symbolic manipulation software *REDUCE*. The resulting expression was converted into a *FORTRAN* expression from which the coefficients of the individual Mueller matrix elements were separated. The program is given below:

```

      program mueler
C      *****
C      This program calculates the various Mueller Matrix element
C      coefficients for various values of the retarder and polarizer
C      angles.
C
C      The inputs to this program are: (all in degrees)
C      eta1 = Orientation angle of polarizer 1 (assumed as 45 deg always)
C      beta1 = Orientation angle of retarder 1 (HWP)
C      beta2 = Orientation angle of retarder 2 (QWP)
C      beta3 = Orientation angle of retarder 3 (QWP)
C      eta2 = Orientation angle of polarizer 2
C
C      The output of this program is the coefficients of the
C      various Mueller Matrix elements in the output intensity, i.e
C      cf11, cf12, cf22, cf33, cf34, cf44
C
C      Written: 15th February 1994 by Ramaswamy Govindan
C      Last modified: 15th February 1994 by Ramaswamy Govindan
C      *****
      implicit real(a-h,o-z)
      pi=4.d0*datan(1.d0)

      open (unit=11, file='/coeff out')

      do 10 i=1,6

      read(5,*) eta2, beta1, beta2, beta3

      b1=beta1/180.0*pi

```

```

b2=beta2/180.0*pi
b3=beta3/180.0*pi
e2=eta2/180.0*pi

```

```

C   cf11:-

```

```

C   ----

```

```

cf11=1.0

```

```

C   cf12:-

```

```

C   ----

```

```

cf12=SIN(2.*B2)*SIN(2.
. *B1)**2*COS(2.*B2)
.
. -SIN(2.*B2)*COS(
. 2.*B2)*COS(2.*B1)**2
.
. +2.*SIN(2.*B1
. )*COS(2.*B2)**2*COS(2.*B1)
.
. +COS(2.*E2)*COS(2.*B3)
. **2
.
. +SIN(2.*E2)*SIN(2.*B3)*COS(2.*
. B3)

```

```

C   cf22:-

```

```

C   ----

```

```

cf22=SIN(2.*B2)*SIN(2.*B1)**2*COS(
. 2.*E2)*COS(2.*B3)**2*COS(2.*B2)
. -
. SIN(2.*B2)*COS(2.*E2)*COS(2.*
. B3)**2*COS(2.*B2)*COS(2.*B1)**2
. +
. 2.*SIN(2.*B1)*COS(2.*E2)*COS
. (2.*B3)**2*COS(2.*B2)**2*COS(2.*B1)
. +
. SIN(2.*E2)*SIN(2.*B3)*SIN(2.*B2)*SIN(2.*B1)
. **2*COS(2.*B3)*COS(2.*B2)
. -
. SIN(2.*E2)*SIN(2.*B3)*
. SIN(2.*B2)*COS(2.*B3)*COS(2.*B2)*COS(2.*B1)**2

```

```

. +
. 2.*SIN(2.*E2)*SIN(2.*B3)*SIN(2.*B1)*COS(2.*B3)*COS(2.
. *B2)**2*COS(2.*B1)

C      cf33:-
C      ----

      cf33=SIN(2.*B3)*SIN(2.*
. B2)**2*SIN(2.*B1)**2*COS(2.*E2)*COS(2.*B3)
. -
. SIN
. (2.*B3)*SIN(2.*B2)**2*COS(2.*E2)*COS(2.*B3)*COS(2.*
. B1)**2
. +
. 2.*SIN(2.*B3)*SIN(2.*B2)*SIN(2.*B1)*COS
. (2.*E2)*COS(2.*B3)*COS(2.*B2)*COS(2.*B1)
. +
. SIN(2.*E2)*SIN(2.*B3)**2*SIN(2.*B2)**2*SIN(
. 2.*B1)**2
. -
. SIN(2.*E2)*SIN(2.*B3)**2*SIN(2.*B2)**2*
. COS(2.*B1)**2
. +
. 2.*SIN(2.*E2)*SIN(2.*B3)**2*SIN(2.
. *B2)*SIN(2.*B1)*COS(2.*B2)*COS(2.*B1)

C      cf34:-
C      ----

      cf34=-SIN(2.*B3)*SIN(2.*B1)**2*COS(2.*E2)*COS(2.*B3)*
. COS(2.*B2)
.
. +SIN(2.*B3)*COS(2.*E2)*COS(2.*B3)*COS(
. 2.*B2)*COS(2.*B1)**2
.
. -2.*SIN(2.*E2)*SIN(2.*B2)*SIN(2.*B1)*COS(2.*B3)*
. COS(2.*B2)*COS(2.*B1)
.
. +SIN(
. 2.*B3)*SIN(2.*B2)**2*SIN(2.*B1)**2*COS(2.*E2)
.
. -SIN(2.*B3)*SIN(2.*B2)**2*COS(2.*E2)*COS(
. 2.*B1)**2

```



```

. +2.*SIN(
. 2.*B3)*SIN(2.*B2)*SIN(2.*B1)*COS(2.*E2)*COS(2.*B3)*
. COS(2.*B1)
.
. +2.*SIN(2.*B3)*SIN(2.*B2)*SIN(2.*B1)*
. COS(2.*E2)*COS(2.*B2)*COS(2.*B1)
.
. +2.*SIN(2.*
. E2)*SIN(2.*B3)**2*SIN(2.*B2)*SIN(2.*B1)*COS(2.*B1)
.
. -SIN(2.*E2)*SIN(2.*B3)**2*SIN(2.*B1)**2*COS(2.*B2)
.
. +SIN(2.*E2)*SIN(2.*B3)**2*COS(2.*B2)*COS(2.*B1)
. **2
.
. -SIN(2.*E2)*SIN(2.*B2)**2*SIN(2.*B1)**2*COS(
. 2.*B3)
.
. +SIN(2.*E2)*SIN(2.*B2)**2*COS(2.*B3)*COS(2.
. *B1)**2

```

C cf44:-

C ----

```

cf44=SIN(2.*B3)*SIN(2.*B1)**2*COS(2.*E2)*
. COS(2.*B2)
.
. -SIN(2.*B3)*COS(2.*E2)*COS(2.
. *B2)*COS(2.*B1)**2
.
. +2.*SIN(2.*E2)*SIN(2.*B2)*
. SIN(2.*B1)*COS(2.*B3)*COS(2.*B1)
.
. -SIN(2.*E2)*SIN(
. 2.*B1)**2*COS(2.*B3)*COS(2.*B2)
.
. +SIN(2.*E2)*COS(2.
. *B3)*COS(2.*B2)*COS(2.*B1)**2
.
. -2.*SIN(2.*B3)*
. SIN(2.*B2)*SIN(2.*B1)*COS(2.*E2)*COS(2.*B1)

```

```
        write (11,5) eta2,beta1,beta2,beta3,cf11,cf12,cf22,cf33,cf34,  
        . cf44  
5      format (4(1x,f4.1),6(1x,f8.4))  
  
10     continue  
  
      end
```

APPENDIX II

Calibration of Detectors

The photomultiplier tubes in the experimental setup record the scattered as well as reference signal in mV . In order to interpret these readings, it is necessary to calibrate the detectors of the system. This involves the determination of the conversion factor whereby the output of the detector (in mV) can be expressed in terms of the intensity of radiation incident on the detector. For this purpose scattering experiments can be performed without the polarizers and retarders in the setup using ethylene gas as the fuel. Even though no calibration is performed, we present below how one can go about calibrating the experiments.

The effective radii of ethylene molecules are very small when compared to the wavelength of the incident radiation, i.e. the size parameter $x \ll 1$. Hence in this case Rayleigh scattering can be used to study the radiative properties of the molecules. The phase function for Rayleigh scattering from small spheres is given by

$$\Phi(\Theta) = \frac{3}{4}[1 + \cos^2(\Theta)] \quad (62)$$

where Θ is the scattering angle. Here the two terms are contributions from the two perpendicular polarizations of the incident beam. In our experimental setup, the laser beam is horizontally polarized with respect to the plane of the paper. Therefore, the phase function becomes:

$$\Phi(\Theta) = \frac{3}{4}[\cos^2(\Theta)] \quad (63)$$

Let us assume that the detector sees a solid angle of $d\Omega$ and is at a scattering angle of θ . Let the scattering control volume be dV with a cross sectional area of dD and a length of ds . As the scattering angle changes, the control volume length changes as $ds/\sin\theta$.

The total radiative heat flux impinging on dD from within the solid angle $d\Omega_i$ is given by

$$I(\hat{s}_i) \cdot dD(\hat{s}_i \cdot \hat{s}) \cdot d\Omega_i \quad (64)$$

The total amount of energy scattered away from $\hat{s}_i$ is

$$\sigma I(\hat{s}_i) \cdot dD \cdot d\Omega_i \cdot ds \quad (65)$$

Of this amount, the fraction $\Phi(\hat{s}_i, \hat{s})d\Omega/4\pi$ is scattered into the cone $d\Omega$ around the direction $\hat{s}$. Hence the amount of energy flux scattered into the cone $d\Omega$ is

$$\sigma I(\hat{s}_i) \cdot dD \cdot d\Omega_i \cdot \frac{ds}{\sin\theta} \cdot \frac{\Phi(\hat{s}_i, \hat{s})d\Omega}{4\pi} \quad (66)$$

Here the term $1/\sin\theta$ is included to account for variation in the control volume length ds as the scattering angle θ changes.

If we normalize this with respect to the intensity at 30° , then we are left with a normalized energy flux on the detector as

$$\frac{\Phi(\hat{s}_i, \hat{s})/\sin(\theta)}{\Phi(\hat{s}_i, \hat{s})/\sin(30)} = \frac{4 \cos^2\theta}{3 \sin\theta} \quad (67)$$

Integrating this to account for the small angle range covered in each measurement, we can obtain the normalized intensity detected.