TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS …….....iv

LIST OF TABLES…….……vii

LIST OF FIGURES…….....vii

LIST OF SYMBOLS……..…….....xiii

Chapter

I. INTRODUCTION……...1

1.1 Motivation and Goals……1
1.2 Previous Raman Work…….. 6
1.3 Present Raman Work…… 8
1.4 Organization……..9

II. ULTRAVIOLET RAMAN SCATTERING THEORY……...11

2.1 Raman Frequencies and Transition Strengths…….11
2.2 Spectral Linewidths and Lineshapes……...31

III. EXPERIMENTAL SYSTEM……..37

3.1 Introduction…….37
3.2 Laser Source……... 37
3.3 UV Raman Light Collection System…….. 41
3.4 Detector Response…….. 46
3.5 Burners…… 48
3.6 Marshall Space Flight Center Tests…… 51

IV. NUMERICAL METHODOLOGY FOR CONTOUR-FIT TEMPERATURE MEASUREMENTS AND STATISTICAL ANALYSIS……..... 57

4.1 Theoretical Spectra Generation…….....57
4.2 Contour Fitting Procedure and Parameter Estimation…… 62
4.3 Statistical Analysis Methods..…… 67

V. TEMPERATURE MEASUREMENTS AND DISCUSSION OF RESULTS…… 73

5.1 Laboratory Results……..73
5.2 MCTA Test Results……..... 101

VI. CONCLUSIONS……..... 114

6.1 Summary……...114
6.1.1 Raman Model…….114
6.1.2 Laboratory Results…….115
6.1.3 MCTA Test Results……... 117
6.2 Conclusions……...118

REFERENCES……..... 119

LIST OF TABLES

Table		Page
2-1	Rayleigh and Raman scattering nomenclature …….....18	
2-2	OH Collisional lineshift parameter values for H_2-H_2, N_2, H_2O collision partners (data taken from Sinclair et al. 1996 and Hussong 2002). ……..20	
2-3	Example showing the evaluation of P_J using a linearly polarized incident radiation source with observation/collection at 90° to the direction of propagation (using scattering geometry configurations and tables in Long 1977).……26	
2-4	Single resonance intermediate state frequencies and electronic energy states……..28	
2-5	Collisional linebroadening parameter values for H_2-H_2, N_2, H_2O collision partners (data taken from Hussong 2002 and Clauss et al. 2002……...34	
3-1	OH absorption and resulting fluorescence lines excited by the KrF laser from Diecke and Crosswhite (1962)……..43	
3-2	Flow-rates for the laboratory Raman measurements in the H_2/N_2 mixtures and H_2-air flames……...50	
3-3	MCTA hot-fire test conditions…….. 55	
5-1	Comparison of statistical results from the average spectral fit and Monte Carlo simulation for T = 295K…….83	
5-2	Uncertainty estimates for the fitted Raman spectra……...99	

LIST OF FIGURES

Figure Page

2-1 Raman and Rayleigh light scattering processes with respect to the electronic states if the scattering molecule. The energy of the incident photon is depicted as the virtual energy state..……...…….....13

2-2 Typical experimental Raman scattering system configuration……..26

2-3 Near resonant enhancement showing proximity of excited vibrational levels with the intermediate state……...29

2-4 "Stick" diagrams of the H_2 Stokes vibrational *Q*-branch Raman bandshape: a) normal H_2 heated to 700 K; b) cooled equilibrium H_2 at 77K heated to 700K; and c) normal H_2 heated to 3400K……..30

2-5 Theoretical calculation of the first two rotational lines of the H_2 Stokes vibrational *Q*-branch spectrum at 300 K including natural linewidths for three pressures. Assumes dilute H_2 in N_2……..35

3-1 Theoretical calculation of the first two rotational lines of the H_2 Stokes vibrational *Q*-branch spectrum at 300 K including natural linewidths for three pressures. Assumes dilute H_2 in N_2……..39

3-2 Rayleigh spectrum of the narrowband KrF excimer laser compared to narrowband 80%Gaussian/20%Lorentzian and a superposition of the narrowband 80%Gaussian/20%Lorentzian and broadband 80%Gaussian/20%Lorentzian profiles scaled by the locking efficiency (η = 90%). The narrowband laser bandwidth, $\Delta\nu_L = 0.8\text{cm}^{-1}$, is determined using the convolution method described in Chapter 4 which includes the spectrometer linewidth and slit function……40

3-3 OH excitation spectrum showing the (3←0) band of the $A^2\Sigma$ - $X^2\Pi$ transition. The spectrograph is set to 36297.6cm^{-1}. The arrow indicates the optimum operating frequency of the laser for the Raman flame spectra, ν_L = 40257.487cm^{-1} 248.401nm)……... 42

3-4 Schematic of experimental UV Raman system……45

3-5 A 40 pixel region of a typical (3→1) OH fluorescence spectrum used for calibration of the spectrograph/CCD. The OH fluorescence line illustrated is *$Q_2(15)$* at 36377.3cm^{-1} resulting from laser excitation of R2(14) at 40314.98cm^{-1}. The frequency scale is ~2cm^{-1} per pixel……....47

3-6 Measurement of the instrumental linewidth of the spectrograph/CCD using the $Q_2(16)$ $3\rightarrow1$ OH fluorescence line resulting from excitation of the $R_2(15)$ $3\leftarrow0$ OH absorption line. The spectrograph instrumental linewidth, $\Delta\nu_{spect}$, is 6.75cm^{-1} after de-convolution of the slit function and laser bandwidth……... 49

3-7 Cross-section schematic of the modular combustion test article (MCTA) in various test configurations. The top schematic shows the MCTA with the thermocouple rack installed for spatial temperature measurements, the middle schematic shows the calorimeter installed for combustion efficiency measurements, and the bottom schematic shows the windowed section installed for shadowgraphy and Raman measurements.....53

3-8 View of the 7 element co-axial injector looking through the exhaust nozzle down the combustion chamber. The injector is composed of two annular flows, the inner injector post supplies LO_X, while the outer shroud supplies LH_2……...54

3-9 Hot-fire test of the MCTA. Windowed section is installed just aft of the injector to provide shadowgraphy measurements during injection……... 56

4-1 Wavelength dependent absorbance scan of the dielectric thin-film notch filter. The figure shows how the filter blocks the Rayleigh/laser line and due to the dielectric film has a wave-like response. Transmission across the H_2 Raman signal varies as much as ~4%.....60

4-2 Spectral synthesis showing the convolution method used to generate the total H_2 Raman spectrum and match the spectral response of the CCD. The spectral parameters are T = 293K, ρ = 0.933amagats, $\Delta\nu_{spect}$ = 6.75cm^{-1}, $\Delta\nu_{slit}$ = 2.1cm^{-1}, ν_L = 40257.65cm^{-1}, $\Delta\nu_L$ = 0.8cm^{-1}, ν_B = 40249.55cm^{-1}, $\Delta\nu_B$ = 50cm^{-1}, and η = 0.85. The narrowband spectrum is convoluted with the broadband spectrum according to η. At T = 293K only $Q_0(1)$ through $Q_0(4)$ transitions are visible……... 61

4-3 Monte Carlo simulated H_2 Stokes Raman spectrum for T = 295K…….....72

5-1 Sample of best-fit spectrally matched H_2 Stokes Q-branch Raman averaged spectrum (400 pulses) from a 2%H_2/98%N_2 mixture at $T_{thermocouple}$ = 294K ±2K, T_{Raman} = 294.8K ±6.9K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ (68%CI) = ±3.0K)…… 74

5-2 Change in residuals of the least squares fit for the H_2 Raman temperature measurement in a 2%H_2/98%N_2 mixture with $T_{thermocouple}$ = 294K±2K and T_{Raman} = 294.8 (295)K±6.9K……...…78

5-3 Temperature pdf for 100 single-pulse H_2 Raman spectra from a 2%H_2/98%N_2 mixture at $T_{thermocouple}$ = 294K ±2K and P = 1atm. The smooth curve fitted to the distribution is a Gaussian with σ = ±6K ……79

5-4 Histogram showing the Monte Carlo results for N = 1000 H_2 Stokes Raman spectra with a reference spectrum of T = 295K, peak S/N = 67:1, and background of 2000 counts with 2% fluctuations. The smooth curve is a Gaussian with σ = ±13.9K fitted to the distribution. The average confidence intervals for the Monte Carlo fits are: 95% = ±8.9K and 68% (standard σ) = ±3.91K.……..…….....82

5-5 Sample of best-fit spectrally matched single-pulse H_2 Stokes Q-branch Raman spectrum from a 2%H_2/98%N_2 mixture at $T_{thermocouple}$ = 294K ±2K, T_{Raman} = 290K ±8.6K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ (68%) = ±3.8K. From propagation of errors the total uncertainty in the measurement is σ = ±14.9K (~5%)…….. 85

5-6 Best-fit spectrally matched H_2 Stokes Q-branch Raman averaged (400 pulses) spectrum from a 2%H_2/98%N_2 mixture at $T_{thermocouple}$ = 709K ±6K, T_{Raman} = 713.3K ±0.19K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ = ±0.09K)……....86

5-7 Temperature pdf for 100 single-pulse H_2 Raman spectra from a 2%H_2/98%N_2 mixture at $T_{thermocouple}$ = 709K ±6K and P = 1atm. The smooth curve fitted to the distribution is a Gaussian with σ = ±12.24K……...88

5-8 Histogram showing the Monte Carlo results for N = 1000 H_2 Stokes Raman spectra with a reference spectrum of T = 713K, peak S/N = 48:1, and background of 2000 counts with 2% fluctuations. The smooth curve is a Gaussian with σ = ±19.97K fitted to the distribution. The average confidence intervals for the Monte Carlo fits are: 95% = ±12.0K and 68% (standard σ) = ±5.6K…….....89

5-9 Best-fit spectrally matched H_2 Stokes *Q*-branch Raman averaged (400 pulses) spectrum from an H_2-air flame in a 12.5mm diameter Hencken burner at $T_{adiabatic}$ = 1448K±20K, $T_{thermocouple}$ = 1422K±33K, T_{Raman} = 1432.1K±7.5K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ = ±3.8K). Mass flow-rates in the burner are H_2 = 12.5 L/min and air = 6.0 L/min…..... 90

5-10 Temperature pdf for 100 single-pulse H_2 Raman spectra from an H_2-air flame in a 12.5mm diameter Hencken burner at $T_{adiabatic}$ = 1448K±20K, $T_{thermocouple}$ = 1422K±33K, T_{Raman} = 1432.1K±7.5K and P = 1atm. The smooth curve fitted to the distribution is a Gaussian with σ = ±12.24K….....92

5-11 Histogram showing the Monte Carlo results for N = 2000 H_2 Stokes Raman spectra with a reference spectrum of T = 1432K, peak S/N = 29:1, and background of 2000 counts with 2% fluctuations. The smooth curve is a Gaussian with σ = ±38.5K fitted to the distribution. The average confidence intervals for the Monte Carlo fits are: 95% = ±29.5K and 68% (standard σ) = ±13.7K…….....93

5-12 Best-fit spectrally matched H_2 Stokes *Q*-branch Raman averaged (400 pulses) spectrum from an H_2-air flame in a 12.5mm diameter Hencken burner at $T_{adiabatic}$ = 2209K ±31K, $T_{thermocouple}$ = 2193K ±137K, T_{Raman} = 2187.4K ±11.5K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ = ±5.75K). Mass flow-rates in the burner are H_2 = 8.35 L/min and air = 12.94 L/min…… 94

5-13 Sample of best-fit spectrally matched single-pulse H_2 Stokes *Q*-branch Raman spectrum from an H_2-air flame in a 12.5mm diameter Hencken burner at $T_{adiabatic}$ = 2209K ±31K, $T_{thermocouple}$ = 2193K ±137K, T_{Raman} = 2237.6K ±148K and P = 1atm. The signal-to-noise weighted residual (experimental minus fit) is plotted under the spectrum. Uncertainty in T_{Raman} is determined from the 95% confidence interval for the parameter estimates and the χ^2 goodness-of-fit (σ (68%) = ±69K. The arrows indicate OH LIF interferences. Mass flow-rates in the burner are H_2 = 8.35 L/min and air = 12.94 L/min……..96

5-14 Histogram showing the Monte Carlo results for $N = 2000$ H_2 Stokes Raman spectra with a reference spectrum of $T = 2187$K, peak S/N = 7:1, and background of 2000 counts with 2% fluctuations. The smooth curve is a Gaussian with $\sigma = \pm 156.2$K fitted to the distribution. The average confidence intervals for the Monte Carlo fits are: 95% = ±166.4K and 68% (standard σ) = ±77.1K……....97

5-15 Absolute uncertainty (standard deviates) in the H_2 Raman measured temperatures as a function of ΔT and the % of the measured T versus the derived Raman T……100

5-16 Typical MCTA hot-fire test pressure trace……..102

5-17 Typical MCTA hot-fire test temperature trace. The T's are averaged measurements from 32 thermocouples at various axial and radial positions and at depths from 1.25-5cm……103

5-18 Single-pulse H_2 Raman Q-branch spectrum obtained in the exhaust plume of the MCTA during a hot-fire test at $t = 3$s. Note: the spectral resolution of the Raman system is degraded by the 100micron slit width, which is used to capture more light and overcome beam-steering problems. Despite these attempts the peak S/N is still only 4:1…….....105

5-19 Single-pulse H_2 Raman Q-branch spectrum obtained in the exhaust plume of the MCTA during a hot-fire test at $t = 5.75$s. The LH_2 is injected at $T = 40$K and the chamber temperature $T_c = 85$K……...107

5-20 P_c and T_c traces of MCTA hot-fire tests for in-chamber Raman measurements. The T_c's are measured at ~20, 22.5, and 25 cm downstream of the injector faceplate with the main combustion zone occurring at ~17-25cm……109

5-21 Comparison of line-integrated N_2 Raman signal strengths at $P_c = 14.7$ and 1000psi. The CCD is binned into 192 strips or 2 pixels/strip. For the $P_c = 1000$psi N_2 Raman spectrum the signal intensity is ~24,000 counts/strip or ~12,000 counts/pixel. The A/D saturation limit is ~66,000 counts/pixel…….....111

5-22 Normalized comparison of the line-integrated N_2 Raman spectra for $P_c = 14.7$ and 1000psi……112

LIST OF SYMBOLS

a	excited electronic state
A	excited electronic state
$\mathbf{b}$	estimated parameters of β
$b_{J,J}$	Placzek-Teller rotational scattering coefficients
B	rotational term value, excited electronic state
B_e	rotational constant for an electronic state
B_v	rotational term value for a vibrational state
c	speed of light
C	species concentration
cm	centimeters
cm^{-1}	wavenumber units
D	1^{st} order centrifugal stretch correction factor
D_e	1^{st} order centrifugal stretch correction constant for an electronic state
D_o	optical diffusion coefficient
D_v	1^{st} order centrifugal stretch correction factor for a vibrational state
e	electron charge
e^-	photoelectrons
E	energy
E_e	electronic energy
E_J	rotational energy
E_o	peak energy of a transition or state
E_t	translational energy
E_v	vibrational energy
$E_{(v,J)}$	energy of the specified vibrational and rotational state
f	focal length, f number
g_i	rotational-nuclear spin coupling degeneracy
g_n	nuclear degeneracy
h	Planck's constant
$\hbar$	Planck's constant divided by 2π
i	unit imaginary number
Δh	Box-Kanemasu parameter interpolation scalar value
H	2^{nd} order centrifugal stretch correction factor, Hamiltonian
H_e	2^{nd} order centrifugal stretch correction constant for an electronic state
H_v	2^{nd} order centrifugal stretch correction factor for a vibrational state
Hz	frequency in Hertz
J	rotational quantum number
I_{nm}	intensity for a transition from state m to n
I_o	peak intensity of a transition
$I_{(v)}$	transition strength
$I_{(v,J)}$	intensity of Raman scattering for transition with initial state (v,J)
k	Boltzmann's constant
K	degrees Kelvin
L	3^{rd} order centrifugal stretch correction factor

L_e	3rd order centrifugal stretch correction constant for an electronic state
L_v	3rd order centrifugal stretch correction factor for a vibrational state
m	meter
m	molecular mass
m_e	electron mass
mJ	energy in milliJoules
mm	millimeter
m_n	nuclear spin quantum number
mrad	laser divergence in milliradians
M	transition dipole moment matrix
MR	oxidizer to fuel mass ratio
n	number, nuclear quantum number, number of laser pulses, number of data
n_D	species number density
nm	nanometer
N	number of samples in Monte Carlo calculations
N_n	population of the initial level
N_{ortho}	number of molecules in the ortho state
N_{para}	number of molecules in the para state
$O_v(J)$	Raman transition with $\Delta\nu = \pm 1$ and $\Delta J = -2$
p	number of parameters
P	pressure, parameter estimation matrix
P_c	chamber pressure
P_J	rotational dependent Placzek-Teller coefficient
P_{nm}	probability matrix for transition form state m to n
$P_v(J)$	electronic transition with $\Delta\nu = \pm 1$ and $\Delta J = +1$
q_N	nuclear charge
Q	partition function
$Q_v(J)$	Raman or electronic transition with $\Delta\nu = \pm 1$ and $\Delta J = 0$
$Q_{ro\text{-}nuc}$	rotational-nuclear partition function
$Q_{ro\text{-}vib\text{-}nuc}$	rotational-vibrational-nuclear partition function
r	intermediate state level
r_e	internuclear separation
$R_v(J)$	electronic transition with $\Delta\nu = \pm 1$ and $\Delta J = -1$
s	seconds
s	parameter estimate variance
S	sum of the squares
$S_v(J)$	Raman transition with $\Delta\nu = \pm 1$ and $\Delta J = +2$
t	time
$t_{1-\alpha/2}$	confidence interval for parameter estiamtes
T	temperature
T_c	chamber temperature
T_r	characteristic rotational temperature
$T_{adiabatic}$	adiabatic flame temperature
T_{Raman}	Raman measured temperature
$T_{thermocouple}$	Thermocouple measured temperature
v	velocity

w	weights for measurement points
$\boldsymbol{W}$	weight matrix
$\boldsymbol{X}$	independent variable matrix
$\mathbf{X}$	sensitivity matrix
y	measured values
$\mathbf{Y}$	measured values vector
$[i]$	concentration/number density of species i
α	polarizability, isotropic polarizability
α_e	rotational constant for an electronic state
α_o	derived isotropic polarizability
$\boldsymbol{\beta}$	dependent variables vector
β_e	2nd order centrifugal stretch correction constant for an electronic state
χ^2	chi-squared
δ	collisional energy shift coefficient, residuals (measured-predicted)
δ_o	collisional energy shift term
$\bar{\delta}$	collisional energy shift term
δ	parameter estimation convergence criteria
δ_x	evaluation constant for parameter estimation convergence criteria
γ	radiation damping constant, anisotropic polarizability
γ_e	2nd order centrifugal stretch correction constant for an electronic state
γ_J^o	collision broadening coefficient
γ_o	collision broadening term, derived anisotropic polarizability
$\bar{\gamma}$	collision broadening term
X	ground electronic energy state, normal coordinate tensor
δ_e	2nd order centrifugal stretch correction constant for an electronic state
ε	random error vector
ε_o	permittivity of free space
Δ	change
η	locking efficiency
$\boldsymbol{\eta}$	predicted values vector
η_e	3rd order centrifugal stretch correction constant for an electronic state
Γ	linewidth
$\Gamma_{Coll,Broad}$	collisionally broadened linewidth
Γ_{Dicke}	Dicke narrowed linewidth
Γ_{Dopp}	Doppler broadened linewidth
μm	micrometer
ν	frequency, vibrational frequency, vibrational quantum number, and degrees of freedom
ν_{AS}	anti-Stokes Raman transition frequency
ν_B	broadband laser frequency
ν_i	intermediate state frequency
ν_L	narrowband laser frequency
ν_{nm}	frequency difference from state m to n
ν_o	incident photon frequency

ν_r	transition frequency center
ν_S	Stokes Raman transition frequency
ν_{slit}	spectrograph slit width
ν_{spect}	spectrometer frequency
ϕ	equivalence ratio
λ_{slit}	spectrograph dispersion
μ	reduced mass
ρ_e	rotational constant for an electronic state
Σ	summation
π	pi
π_e	rotational constant for an electronic state
Π	first excited electronic energy state
Ψ	wave function
Ψ_e	electronic wavefunction
Ψ_J	rotational wavefunction
Ψ_n	nuclear wavefunction
Ψ_t	translational wavefunction
Ψ_v	vibrational wavefunction
ρ	density
σ	Raman scattering cross-section, standard deviation
σ^2	variance
ΣR^2	least squares residuals
Σ	electronic energy state
θ	collection angle
ω_e	fundamental vibration frequency
$\omega_e x_e$	1st anharmonic correction factor
$\omega_e y_e$	2nd anharmonic correction factor
$\omega_e z_e$	3rd anharmonic correction factor

Subscripts

e	constant for a given electronic state
i	indexer, intermediate state
j,k	indexers
J	rotational quantum number or constant for a given rotational state
t	translation quantum number or constant for a given translation state
v	vibrational quantum number or constant for a given vibrational state
n	molecular state *n*, nuclear state
nm	transition from state *m* to *n*
r	virtual state
rm	transition from state *m* to virtual state *r*
rn	transition from state *n* to virtual state *r*
S	Stokes transition
AS	anti-Stokes transition
L	narrowband laser source

B	broadband laser source

Superscripts

T	transpose
k	iteration
0	initial value
$'$	final state
$''$	initial state

Symbols

∂	partial derivative
[]	mole fraction