CARS TEMPERATURE MEASUREMENTS IN THE FUEL PREBURNER OF THE SPACE SHUTTLE MAIN ENGINE: A FEASIBILITY STUDY

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I. Introduction
A. Scope

This report discusses the feasibility of making temperature profile measurements in the fuel preburner of the main engine of the space shuttle (SSME) using coherent anti-Stokes Raman spectroscopy (CARS). The principal thrust of the work is to identify problems associated with making CARS measurements in high temperature gas phase hydrogen at very high pressures (~400 atmospheres). To this end a theoretical study was made of the characteristics of the CAR spectra of H₂ as a function of temperature and pressure and the accuracy with which temperatures can be extracted from this spectra. In addition the experimental problems associated with carrying out these measurements on a SSME at NSTL were identified. A conceptual design of a CARS system suitable for this work is included.

Many of the results of the calculations made in this report are plotted as a function of temperature. In the course of presenting these results, it was necessary to decide whether the number density or the pressure should be treated as a fixed parameter. During a test firing, the SSME is throttled and the fuel preburner acts neither as a constant density nor a constant pressure environment. Since most physical quantities scale with number density rather than pressure (linewidth, optical dispersion, CARS signal strength, etc.) it was decided to present results holding density constant. The unit of density used throughout this report is the amagat (1 amagat density equals the density of a gas at 1 atmosphere pressure at 0° C). Conversion from density to pressure is accomplished via the equation of state. For convenience Appendix A presents isotherms for hydrogen gas for the pressures, densities and temperatures of interest in this study.

B. Characteristics of the Fuel Preburner

The following values were stated as design criteria for the temperature profiling system in RFP No. 8-1-2-EC-25732 and are taken as the characteristics of the preburner where measurements are required.

1. Temperature of gas:
   a. Steady state 2100 R° (1167 K)
   b. Transient maximum 3000 R° (1667 K)
   c. Normal minimum 1500 R° (833 K)
d. Transient minimum 200 R° (111 K)

2. Gas composition from H₂ to Steam + H₂ + O₂.
3. Gas velocity: ~ 200 fps (61 m/sec) maximum.
4. Chamber pressure: 5500 psi (374 atmospheres).
5. Combustion chamber material: Haynes 188 + Zirconium Oxide Coating.
6. Coating (wall) temperature: 2100 R° (1167 K)
7. Measurement accuracy: 10 R° (5.6 K)
8. Measurement resolution:
   a. Thermal - 10 R° (5.6 K)
   b. Spatial - from 0.25 to 0.50 inch square (1.6 to 3.2 cm²)
9. Time Response: 10 milliseconds

Hydrogen and oxygen are fed into the fuel preburner in equal amounts by weight and hence lead to the reaction 16 H₂ + O₂ + 2H₂O + 14 H₂. Presumably this reaction takes place near the injector head and is completed by the time the gas mixture reaches the ends of the baffle plates and ports (see Figures 20a and 21b). Because little oxygen is expected to be present in the line of sight of the ports, it was decided at the initial contractor's meeting that there would be little point in studying O₂ as a probe species. In accordance with discussions held at Marshall Space Center and NSTL, the gas streamlines in the preburner are assumed to be steady except at the center. The maximum duration of a test firing is 500 seconds. Information on the fuel preburner, the SSME test stand, instrument accessibility to the preburner, physical environment adjacent to the preburner during a test run, etc. can be found in Section VII.

C. Background

CARS is a relatively new combustion diagnostic tool that is undergoing rapid development [1,2,3]. It is an example of four-wave mixing in which three photons, usually two at a pump frequency ω₁ and one at a Stokes frequency ω₂ mix through the third order susceptibility of a medium to produce a fourth or anti-Stokes photon at frequency ω₃. The intensity of the anti-Stokes beam I₃ can be written

\[ I_3 = \left( \frac{4\pi^2\omega_3}{c^2} \right)^2 I_1^2 I_2 |x|^2 z^2 \]

where I₁ and I₂ are the pump and Stokes laser beam intensities, z is the
length in which these beams coherently interact and $\chi$ is the third order susceptibility of the medium which consists of a frequency dependent resonant part, $\chi' + i\chi''$, and a nonresonant part, $\chi_{nr}$. When the frequency difference $\omega_1 - \omega_2$ approaches the frequency of a Raman active energy resonance of a major species in the bulk media, the resonant susceptibility becomes large compared to the non-resonant susceptibility. Because the intensity depends on the absolute value squared of the total susceptibility, the spectra appears as a resonant modulation on a non-resonant background.

The resonant susceptibility is a function of the number density and the population difference between the levels involved in the transitions. This latter dependence means that the spectrum of a ro-vibration band of a molecule will be temperature sensitive since the population distribution of the rotational energy levels is governed by the Boltzman factor. Hence the temperature, number density, and bulk non-resonant susceptibility of the medium must be known in addition to the molecular parameters in order to theoretically model the CAR spectra of a molecular species in a multi-component gas medium. The bulk non-resonant susceptibility is obtained from a knowledge of the individual susceptibilities of the component gases and their approximate relative concentrations. The temperature can be obtained by examining the CAR spectrum of a major species. Comparison of the experimental spectra to calculated spectra has been the most reliable method of extracting accurate temperature information. Several excellent reviews of the theory and applications of CARS which discuss these considerations are available in the literature [4,5].

The accuracy with which temperature measurements can be made using CARS depends to a large extent on how well the CAR spectra of the chemical species under study can be theoretically modeled. The molecules present in the preburners are $\text{H}_2$, $\text{O}_2$, and $\text{H}_2\text{O}$, all of which have been successfully modeled for atmospheric pressure CARS combustion studies [6,7,8]. However, the complexity of the water spectra with its many closely spaced rotational lines invites one to consider this species for thermometry only as a last alternative. Since hydrogen will be the major species in the fuel preburner, it is the species of choice for temperature measurements. Oxygen is a trace species after combustion occurs and in accordance
with the above discussion will not be considered in this study.

In many respects, $H_2$ is an ideal molecule for CARS thermometry. It has widely spaced rotational levels ($B_e = 60.85 \text{ cm}^{-1}$) reducing the number of rotational energy levels populated at elevated temperatures and hence reducing the number of Q-branch spectral lines. In addition it has a large vibration-rotation interaction constant ($\alpha_e = 3.06 \text{ cm}^{-1}$) leading to widely spaced rotational lines. These properties mean that the individual intensities of the few and widely spaced rotational lines can be studied which greatly simplifies analysis. Furthermore, the energy difference between the lowest and first excited vibrational levels is so great ($\approx 4400 \text{ cm}^{-1}$) that no significant population of this excited level is expected even at the maximum expected temperatures. The small linewidth pressure broadening coefficient ($0.0015 \text{ cm}^{-1} / \text{amagat}$) and the large spacing between rotational lines ($\approx 20 \text{ cm}^{-1}$) indicates that spectral lines will not overlap even at the high densities present in the preburner.

Thermometry using the broadband CAR spectra of $H_2$ has been performed in an atmospheric pressure $H_2$-air diffusion flame [6,7]. The relative intensity peaks of individual rotational lines were used to extract the temperatures in a range of 900 K to 2100 K. Standard deviations of 2% - 8% were obtained with the poor precision due to the low signal-to-noise ratios that are characteristic of low number density environments.
II. **Calculated H₂ CAR Spectra**

There are several methods that can be used to extract temperature measurements from CAR spectra. Three are considered in this report. Two are simply variants of measuring intensity of individual ro-vibrational lines or groups of lines and these are discussed in Sections VI and VII. The third is to record all the rotational lines in a given spectral interval (i.e. 100 cm⁻¹) and to compare this data with a library of computed spectra calculated for the expected experimental conditions and temperatures. This method is perhaps the surest and most accurate method of extracting temperature from the spectra since many lines are observed and anomalies can be easily detected. However, it is more difficult and expensive to implement than the other methods.

Calculation of non-linear spectra, such as CARS, of a multiline molecular species is considerably more complex than the prediction of linear absorption or emission spectra. Much of this complexity is caused by the interference that takes place among the transitions and the interaction of these transitions with the nonresonant background. A synopsis of the theory used to calculate CAR spectra is presented here. Various details can be found in the appendices. An effort has been made to point out some of the approximations used and limits of this theory.

In general, the dipole moment per unit volume $\hat{P}$ induced in a medium by electric fields $\hat{E}(r,i)$ can be written

$$
\hat{P}(r,i) = \sum_{n=1}^{\infty} \hat{P}^+(n)(r,i)
$$

where $r$ is the space coordinate, $i$ represents the polarization of the field, $\omega$ is the angular frequency and $\chi(n)$ is the susceptibility tensor of rank $n + 1$. If one considers only isotropic or centrosymmetric media, all even-numbered terms in this sum are zero because of inversion symmetry. Then, truncating the series at $n = 3$, Eq. (1) can be written as

$$
P_{\alpha}(r,i) = \chi^{(1)}_{\alpha\beta}(\omega_1)E_{\beta}(\omega_1) + \chi^{(3)}_{\alpha\beta\gamma\delta}(\omega_1,\omega_2,\omega_3) E_{\beta}(r,1)E_{\gamma}(r,2)E_{\delta}(r,3)
$$

where the summation over repeated indices convention is used.
In general, $\chi^{(3)}$ has 81 elements. However, for isotropic media only 21 are nonzero, of which only 3 are independent \[9\]

$$
\begin{align*}
\chi_{1111} &= \chi_{xxxx} = \chi_{yyyy} = \chi_{zzzz} \\
\chi_{1122} &= \chi_{xxyy} = \chi_{yyxx} = \chi_{xxxx} = \chi_{zzxx} = \chi_{yyzz} = \chi_{zzyy} \\
\chi_{1212} &= \chi_{xyxy} = \chi_{xxyy} = \chi_{xxzx} = \chi_{xzxx} = \chi_{yzyz} = \chi_{zyzy} \\
\chi_{1221} &= \chi_{xxyx} = \chi_{xyxx} = \chi_{xxzz} = \chi_{xzzz} = \chi_{zzyy} = \chi_{zyzy}
\end{align*}
$$

with $\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221}$

Most practical applications of CARS use the same frequencies for two of the E fields (three-color CARS) making $\chi_{1122} = \chi_{1212}'$ since $\chi^{(3)}$ is invariant to the six permutations of the pairs $(\beta, \omega_1), (\gamma, \omega_2), (\delta, \omega_3)$. Hence, for this case there are only two independent elements (i.e. $\chi^{(3)}_{1111}, \chi^{(3)}_{1221}$).

If the summation of the $\chi^{(3)}$ of Eq. (2) is performed for these conditions, the third order polarization vector becomes \[10\]

$$
\begin{align*}
\mathbf{p}^{(3)} &= \left[ 6 \chi_{1122}^{(3)}(\omega_1, \omega_1, -\omega_2) \mathbf{e}_1(\hat{\mathbf{e}}_1 \cdot \mathbf{e}_2) \\
&+ 3 \chi_{1221}^{(3)}(\omega_1, \omega_1, -\omega_2) \mathbf{e}_2 \right] \mathbf{E}(1)^2 \mathbf{E}(2)^* \\
&\times \exp \left[ i(2\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r} \right] \\
&= \chi_{\text{CARS}} \hat{\mathbf{e}}_{\text{CARS}} \mathbf{E}(1)^2 \mathbf{E}(2)^* \exp[i(2\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}]
\end{align*}
$$

where the input fields $\mathbf{E}(1)$ and $\mathbf{E}(2)$ are assumed to be plane waves with polarization vectors $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ and wave vectors in the medium of $\mathbf{k}_1$ and $\mathbf{k}_2$ ($k = n\omega/c$, $n = \sqrt{1 + 4\pi\chi^{(1)}}$). If the Stokes and pump fields are parallel ($\hat{\mathbf{e}}_2 = \hat{\mathbf{e}}_1$), $\hat{\mathbf{e}}_{\text{CARS}} = \hat{\mathbf{e}}_1$ (the three fields have the same polarization) and

$$
\chi_{\text{CARS}} = 6\chi_{1122}^{(3)} + 3\chi_{1221}^{(3)}(\omega_1, \omega_1, -\omega_2) = 3\chi_{1111}^{(3)}(\omega_1, \omega_1, -\omega_2) \tag{5}
$$

If the polarizations of the Stokes and pump fields are perpendicular ($\hat{\mathbf{e}}_1 \perp \hat{\mathbf{e}}_2$), the anti-Stokes polarization is parallel to the Stokes field ($\hat{\mathbf{e}}_{\text{CARS}} = \hat{\mathbf{e}}_1$) with

$$
\chi_{\text{CARS}} = 3\chi_{1221}^{(3)}(\omega_1, \omega_1, -\omega_2). \tag{6}
$$

In this latter configuration, the CARS susceptibility is less than in the first configuration by the term $6\chi_{1122}^{(3)}$. \[6\]
Substitution of the linear polarization \( p^{(1)} \) into Maxwell's equations leads to the usual plane wave solution with frequency and polarization vector unchanged but with wave vector \( k = \frac{n\omega}{c} \) where \( n = \sqrt{1 + 4\pi x^{(1)}} \). Similarly, one can obtain an expression for the intensity of the CARS wave with Maxwell's equations using Eq. (4) for \( \rho^{(3)} \). If, in addition to the above restrictions, it is assumed that

1. all input fields are plane monochromatic waves,
2. the polarization vector is written as an expansion of plane wave frequencies,
3. the CARS wave is a plane wave whose amplitude can be a function of longitudinal position, and
4. \( \Delta k \equiv 2k_1 - k_2 - k_3 \ll 2k_3 \),

then the time-averaged intensity of the anti-Stokes wave created in a length \( \ell \) is given by [10]

\[
I_3 = \frac{16\pi^4 \omega_2^2}{n_1 n_2 n_3 c^4} |x_{\text{CARS}}|^2 I_1^2 I_2 \ell^2 \left[ \frac{\sin(\Delta k \ell/2)}{\Delta k \ell/2} \right]^2.
\]  
(7)

For exact phase matching \( \Delta k = 0 \) and

\[
I_3 = \frac{16\pi^4 \omega_2^2}{n_1 n_2 n_3 c^4} |x_{\text{CARS}}|^2 I_1^2 I_2 \ell^2
\]  
(8)

The frequency dependence of \( x_{\text{CARS}} \) is obtained from a quantum mechanical calculation of the microscopic molecular dipole moment arising from the third power of the microscopic fields. Averaging this over all molecular orientations and multiplying the result by the specie number density yields the bulk dipole moment \( \rho^{(3)} \). \( x^{(3)} \) is obtained as the coefficient of the various third order products. Using diagrammatic perturbation theory one obtains 24, four-fold sums over all molecular states [11]. If

1. all terms containing no Raman resonant terms in the denominator are lumped into a nonresonant term, \( x_{\text{NR}} \),
2. there are no one- or two-photon resonances, and
3. the Stokes and pump fields have parallel polarizations
   \( \hat{e}_1 = \hat{e}_2 \),

then \( x_{\text{CARS}} \) can be written in terms of the differential cross section for
spontaneous Raman scattering, \( \frac{d\sigma}{d\Omega} \), for two stationary states (k and n) of the molecule, viz \([10]\]

\[
\chi_{\text{CARS}} = \chi_{\text{NR}} + \frac{(N_n - N_k)h c}{\hbar n_2 \omega_2^2} \left( \frac{d\sigma}{d\Omega} \right) \frac{1}{\Omega_{kn} - \omega_1 + \omega_2 - i\gamma_{kn}}
\]  

(9)

where \( N_i \) is the number density in the \( i \)th state, \( \Omega_{kn} \) is the energy difference between states \( k \) and \( n \), and \( \gamma_{kn} \) is the homogeneous line half width (HWHM). (Equations (7) and (8) differ by a factor of 1/16 and Eq. (9) differs by a factor of 2 from those given by Ref. [10].)

As noted above, the equations were derived under the assumption that the input radiation is monochromatic. However, all real light sources have finite line widths, and in particular, CARS employed for thermometry on practical combustion systems uses a broadband Stokes field in order to simultaneously view many transitions of molecular species. Yuratich [12] has considered the problem of finite line widths of the incident fields in detail. If the input waves are approximated as stationary stochastic processes, he finds that the anti-Stokes spectral intensity \( I_3 \) is given by the double convolution

\[
I_3 = \int L_1(\omega_1) \left[ \int \left| \chi_{\text{CARS}}(\omega_2 - \omega_1) \right|^2 L_1(\omega_3 + \omega_2 - \omega_1) L_2(\omega_2) \ d\omega_2 \right] d\omega_1
\]

(10)

where \( L_1(\omega_1) \) is the normalized lineshape of the pump intensity (using a single pump laser). \( L_2(\omega_2) \) is the normalized lineshape of the Stokes intensity.

Equation (9) is the expression for the susceptibility for a single resonance. A molecule has many closely spaced resonances and the CARS susceptibility will be the sum over all such resonances, i.e.

\[
\chi_{\text{CARS}} = \chi_{\text{NR}} + \frac{N_n c h}{\hbar n_2 \omega_2^2} \sum_j \frac{\Delta_j}{\Omega_j - (\omega_1 - \omega_2) - i\gamma_j} \left( \frac{d\sigma}{d\Omega} \right)_j
\]

(11)

where \( N \) is the number density of the Raman active molecule and \( \Delta_j \) is the population difference between upper and lower vibration-rotation states. Substituting Eq. (11) into Eq. (10) and performing the integrations over frequency intervals where the molecular resonances occur will yield a CAR spectrum for realistic physical situations.
If the line width of the Stokes radiation is assumed to be much greater than the pump laser line width, $\Delta \omega_2 \gg \Delta \omega_1$, then the narrow $d\omega_1$ integration can be performed and

$$I_3(\omega_3) \sim \int |\chi_{\text{CARS}}(\omega_2-\omega_1)|^2 L_1(\omega_3+\omega_2-\omega_1^0) L_2(\omega_2) d\omega_2$$

(12)

where $\omega_1^0$ is the center frequency of $L_1(\omega_1)$. Using Gaussian lineshapes for the laser spectral profiles, this integral can be numerically performed to obtain a CAR spectrum. This is the approach used successfully by Hall [14] to generate synthetic CAR spectra of $N_2$ and CO.

It is possible to integrate Eq. (10) using Lorentzian or Gaussian lineshapes and obtain an analytical solution in terms of the complex error function without resorting to the broad line width approximation. These solutions were obtained for several combinations of Gaussian and Lorentzian lineshapes by Yuratich [12].

Spectra presented in this report were calculated using a computer program based on the analytical solution of Yuratich. Comparisons of CAR spectra of molecular nitrogen using the two methods yield similar results [13].

Evaluation of Eq. (10) begins with the calculation of $\chi_{\text{CARS}}$. Rewriting Eq. (11) results in

$$\chi_{\text{CARS}} = \chi_{\text{NR}} + \sum_j \frac{a_j}{\Omega_j+\omega_2-\omega_1-i\gamma_j}$$

(13)

where

$$a_j = \frac{Nn_1c^4}{\hbar n_2 \omega_2^2} \Delta_j \frac{d\sigma}{d\Omega} \bigg|_j$$

The rotational selection rules for CARS are the same as those for Raman scattering [10], i.e. $\Delta J = 0, \pm 2$. For forward scattering, the spontaneous Raman cross section can be expressed in terms of the components of the derived polarizability tensor. For the $Q$ branch [14]

$$\left. \frac{d\sigma}{d\Omega} \right|_Q = \left( \frac{\omega_2}{c} \right)^4 \frac{M}{2\omega_o} \left[ \frac{a^2}{M} + \frac{7}{45} \frac{\gamma^2}{M} b^j \right] (v + 1)$$

(14)

where $M$ and $\omega_o$ are the reduced mass and molecular oscillator frequency respectively; $b^j$ is the Placzek-Teller coefficient [5]; $\alpha$ and $\gamma$ are the derivatives with respect to internuclear coordinate of the mean molecular
polarizability and anisotropy; \( v \) is the vibrational quantum number of the initial level. Evaluation of Eq. (14) for the case of \( \text{H}_2 \) is delineated in Appendix B. The calculation of the population difference \( \Delta_j \) of Eq. (13) is outlined in Appendix C and the formulae for the energy differences \( \Omega_j \) are presented in Appendix D. The homogeneous line half widths, \( \gamma_j \), are functions of temperature and pressure and a discussion of these quantities is presented in Section III. \( \chi_{\text{NR}} \) is a measured constant that must be scaled with number density. The value for the nonresonant susceptibility for deuterium was used in this study [17].

The lineshapes \( L(x) \) in Eqs. (10) and (12) may be of any profile. Laser line widths may be Lorentzian

\[
L_L(x) = \frac{\gamma_L}{\pi(x^2 + \gamma_L^2)} ; \quad \int L_L(x) dx = 1
\]

or Gaussian

\[
L_G(x) = \frac{\exp(-x^2/\gamma_G^2)}{\gamma_G \sqrt{\pi}} ; \quad \int L_G(x) dx = 1
\]

where \( \gamma_G = \gamma_L / \sqrt{2n^2} \) and \( \gamma \) are HWHM. For multimode laser fields, the output is more closely approximated by a Gaussian profile. Substitution of Eq. (16) into Eq. (12) for the Stokes and pump laser fields and integrating yields broadband CAR spectra. This calculation using the analytical expression of Yuratich is detailed in Appendix E.

\( \text{H}_2 \) CAR spectra were calculated for a range of temperatures, densities, and Stokes beam widths. Figures (1) and (2) show computed, normalized spectra for two temperatures \((800, 1600 \ \text{K})\) that span the operating range. The four spectra in each figure show the effects of the variation of number density from 1 amagat (upper row) to 100 amagat (lower row) and the variation of Stokes beam width from 100 cm\(^{-1}\) (left column) to 250 cm\(^{-1}\) (right column). For all spectra, a Stokes beam center of 14679 cm\(^{-1}\) was used, so that the resultant anti-Stokes beam is centered between the Q(0) and Q(5) lines. Appendix F contains a series of such spectra for \( 800 \leq T \leq 1800 \ \text{K} \), at 100 K steps.

The prominent features of the spectra in these figures are the line broadening with increasing temperature and density, and the relative peak intensity rescaling with Stokes beam narrowing. Since the spectral
Figure 1. Calculated CAR spectra of H$_2$ for a temperature of 800 K. Spectra were computed for densities of 1 and 100 amagat and Stokes beams with spectral widths of 100 and 250 cm$^{-1}$. Each spectrum is normalized to the maximum peak intensity for that spectrum.
Figure 2. Calculated CAR spectra of H₂ for a temperature of 1600 K. Other details same as those in Figure 1.
extent, Q(0) to Q(5), is about 100 cm$^{-1}$, the relative peak heights (Q(3)/Q(1), Q(5)/Q(3)) for the 100 cm$^{-1}$ Stokes width compared to the 250 cm$^{-1}$ width differs by a factor of 1.37 and 0.65; i.e. the Q(1) and Q(5) lines are reduced in intensity by factors of 1.37 and 1.53 for 100 cm$^{-1}$ width, thus the ratios differ by the factors 1.37 and 1/1.53.
III. $H_2$ Linewidth

The calculation of the Raman linewidth of $H_2$ is extremely important since the power of the CARS signal is inversely proportional to its square or for broadband CARS it is inversely proportional to the linewidth. Furthermore, to extract temperature measurements from the ratio of the signal strengths of the individual rotational lines, it is necessary to know the variation of the linewidth with rotational quantum number $J$. Unfortunately, the behavior of the $H_2$ linewidth is complex and its variation with $J$ and with temperature at high densities is not well known.

The variation of hydrogen's linewidth with density can be divided into three regimes. At low density ($\lesssim 0.1$ amagat) line broadening is due principally to the Doppler effect. For Raman scattering this line has a Gaussian profile whose width (FWHM) can be written [18]

$$\Delta\nu_D = \frac{2}{c} \left(2\ln2 \frac{kT}{m}\right)^{1/2} \left[4\left(\nu_0^2 + \nu_R^2\right) \sin^2\left(\frac{\theta}{2}\right) + \nu_R^2\right]^{1/2} \quad (17)$$

where $\nu_0$ is the exciting frequency, $\nu_R$ is the frequency of the Raman resonance, $\theta$ is the scattering angle and the other symbols have their usual meaning. For CARS, only scattering in the forward direction is considered ($\theta = 0$) and

$$\Delta\nu_D = \frac{2\nu_R}{c} \left(2\ln2 \frac{kT}{m}\right)^{1/2} \quad (18)$$

In this range, the linewidth is independent of density and varies as the square root of temperature.

When the mean free path for elastic collisions is comparable to the wavelength of the scattered light, but is less than the mean free path for collisional line broadening, the linewidth can become less than that due to Doppler broadening. This phenomena, known as Dicke narrowing [19], is important in reducing the linewidth of molecular hydrogen in the density regime between $\sim 0.5$ amagat and $\sim 25$ amagat [20]. Above this density, the lineshape becomes Lorentzian and its width increases linearly with the density (homogeneous or pressure broadening regime). Theoretically this linear variation with density is a consequence of assuming that only binary collisions take place. If the time between collisions is long
compared to the collision time, this criterion is met. Hunt et al. [21] have estimated for \( \text{H}_2 \) that the time between collisions is approximately three times the collision time for pressures of \( \sim 100 \) atmospheres for a hard sphere collision model. This would seem to indicate that linear pressure broadening would be suspect above this value. However, Allin et al. [22] have found linear variation holds between 30 and 600 atmospheres of pressure, presumably at room temperature. Since the collision frequency scales \( n \sqrt{T} \) and the pressure as \( nT \), where \( n \) is the number density and \( T \) the absolute temperature, the collision frequency will decrease with increasing temperature for a given pressure indicating that the line will broaden linearly in this range at elevated temperatures.

The effects of Doppler and pressure broadening can be accounted for simultaneously using an expression for the resonant part of the third order susceptibility developed by Henesian and Byer [23]

\[
\chi^{(3)} = \frac{Nn_1c}{\pi n_2\omega_0^2\Delta \omega_D} \sum_j \frac{\Delta_j \delta \sigma_j}{\Delta \Omega_j} w^*(\delta_j + iE_j) \tag{19}
\]

where \( w(z) = \text{complex error function (see Appendix E)} \)

\( \delta_j = [\Omega_j - (\omega_1 - \omega_2)]/\Delta \omega_D \)

\( E_j = \frac{r_j}{4\pi \Delta \nu_j} \)

\( \Delta \omega_D (= 2\pi \Delta \nu_D) \) is defined by Eq. (18), \( r_j \) is the linewidth (FWHM), and the other quantities are defined as in Eq. (11). Dicke narrowing can be included in a simple way introduced by Galatry [24]. This requires that \( r_j \) be replaced by

\[
r_j \rightarrow D_0(T)k^2 + A_j(T)\rho \tag{20}
\]

where \( D_0 \) is the diffusion coefficient for the scattering molecule, \( \rho \) is the density, \( A_j \) is the pressure broadening coefficient, and \( k \) is an effective wave vector for Raman scattering i.e. [20]

\[
k = [2k_1k_2(1-\cos \theta)^2 + (k_1-k_2)^2]^{\frac{1}{2}} \tag{21}
\]

which for the case of CARS (\( \theta = 0 \)) becomes the difference between the wave
vectors of the incident and emitted photons. (This means that the line-
width will be a minimum in the forward direction and a maximum in the
backward direction. See, for example Lallemand et al. [25].) It should
be noted that at high pressures ($E_j \gg 1$)

$$w(z) + \frac{1}{i\sqrt{\pi} z}$$

and Eq. (19) reduces to Eq. (11), the usual expression for the suscepti-
bility.

The diffusion coefficient $D$ is usually written as $D_0/\rho$ and has a
temperature dependence that varies at $T^\alpha$ where $\alpha$ varies between 1.5
(rigid elastic spheres model) and 2 (Maxwellian models) [26]. The more
conservative value of 1.5 is adopted here which, after the temperature
dependence of $\rho$ is removed, implies that $D_0 \propto T^2$. Several spectroscopic
determinations of $D_0$ have been made ([20], [27]) but the measurement of
the diffusion of parahydrogen through normal hydrogen made by Harteck and
Schmidt [28] is the most accurate to date. Their value of $1.396 \pm
0.0025$ cm$^2$ sec$^{-1}$ at 785 torr and 20° C is used in these calculations.

There is little data on the temperature dependence of the broadening
coefficient at elevated temperatures. The half width of the Raman lines
is given by $\nu \sigma'$ where $\nu$ is the average velocity of the colliding pair
and $\sigma'$ is the real part of the optical cross section [29]. If $\sigma'$ is
assumed temperature independent, the linewidth would have a $\sqrt{T}$ dependence.
This is consistent with the data of Lallemand and Simova [30] who mea-
ured the temperature dependence of the broadening coefficient of the Q(1) line of H$_2$ between room temperature and 150° C. (These measurements were
made using a backward wave Raman amplifier and hence their linewidth is
larger than that of the forward wave.) Lallemand and Simova found their
results in disagreement with the theory of Ref. [29]. For simplicity,
the $\sqrt{T}$ dependence of $A_j$ will be used in our estimates of linewidth.

There have been a variety of measurements made of the pressure
broadening coefficients of forward direction Raman scattering of hydrogen
at room temperature for the lowest values of $J(0-4)$. Table 1 compares
these and also lists some theoretical values. Columns 1 and 2 show the
broadening coefficients measured by spontaneous Raman scattering over a
TABLE 1

H₂ Pressure Broadening Coefficients (10⁻³ cm⁻¹/amagat)

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Q(0)</td>
<td>2.32 ± 0.04</td>
<td>2.2 ± 0.15</td>
<td></td>
<td>2.78 ± 0.10</td>
<td></td>
<td>2.2</td>
<td>2.59</td>
</tr>
<tr>
<td>Q(1)</td>
<td>1.40 ± 0.03</td>
<td>1.5 ± 0.1</td>
<td>1.77</td>
<td>1.83 ± 0.10</td>
<td>1.71 ± 0.02</td>
<td>0.6</td>
<td>.72</td>
</tr>
<tr>
<td>Q(2)</td>
<td>2.53 ± 0.03</td>
<td>2.6 ± 0.2</td>
<td></td>
<td>3.05 ± 0.10</td>
<td></td>
<td>2.6</td>
<td>2.87</td>
</tr>
<tr>
<td>Q(3)</td>
<td>3.66 ± 0.04</td>
<td>5.5 ± 1</td>
<td></td>
<td>4.60 ± 0.10</td>
<td></td>
<td>3.6</td>
<td>3.87</td>
</tr>
<tr>
<td>Q(4)</td>
<td></td>
<td></td>
<td></td>
<td>3.26 ± 0.10</td>
<td></td>
<td>3.0</td>
<td>3.86</td>
</tr>
</tbody>
</table>

a. Spontaneous Raman scattering, 300-600 amagat.
b. Spontaneous Raman scattering, 5-100 amagat.
d. Electric-field-induced measurements, 4.4-35 amagat.
e. High resolution CW stimulated Raman spectroscopy, 0.26-14 amagat.
f. Theory, isotropic scattering due to quadrupolar interaction.
g. Calculation using theory of Van Kranendonk with revised molecular constants.
very wide range of densities (5-600 amagat). These show good agreement except for the Q(3) lines. As noted above, Ref. [22] found the broadening to be linear to 600 amagat. Columns three and four display the linewidths measured by electric field induced dipole transitions over a more restricted density range. Brannon et al. [31] has shown that the theory of Raman line broadening may be applied without modification to electric field induced lines. These values tend to be somewhat higher than those measured by Raman scattering. Column 5 lists a measurement using the high resolution technique of CW stimulated Raman spectroscopy. Columns 6 and 7 give theoretical values obtained using the theory of Van Kranendonk [29]. Hunt et al. [21] has used this theory to recalculate the linewidths utilizing pressure modified effective rotational constants. The disagreement between theory and experiment for the Q(1) line is discussed in Ref. [22].

The pressure broadening coefficients of Allin et al. are adopted for the Q(0) - Q(3) lines in this study. The measured value of Hunt et al. is used for the Q(4) line. Finally it is useful to have a value of $A_J$ for the Q(5) line to obtain temperatures from the ratio of its strengths at higher temperatures. Unfortunately, there is no measured value. Using parameters calculated from Hunt et al., based on Van Kranendonk's theory, a calculated value of $1.08 \times 10^{-3}$ cm$^{-1}$/amagat @ 300 K was obtained. This is a particularly risky procedure, however, as the agreement of the modified calculated linewidth with the experimental values becomes poor with higher J numbers [21].

Figure 3 shows a log-log plot of the Q(1) linewidth of $H_2$ for room temperature and two temperatures that bracket the minimum and maximum temperatures that could be encountered in the SSME preburner. The density range is between 35 amagat (3000 psi, 1700 K) and 150 amagat (6000 psi, 850 K) and the line broadening is well within the pressure broadening regime.

As a final remark, it should be noted that St. Peters [32] has found that when high power lasers are used, the appropriate linewidth for CARS may be larger than the Raman linewidth due to the laser mode structure.
Figure 3. Variation of Hydrogen Q (1) linewidth as a function of density for several temperatures.
According to Eq. (7) the input laser beams should be phasematched in order to generate appreciable signal levels. The phasematching condition

$$\Delta \vec{k} = 2\vec{k}_1 - \vec{k}_2 - \vec{k}_3$$  \hspace{1cm} (22)

where \( |\vec{k}| = \frac{n_0}{c} \) is a vector relationship that must be simultaneously satisfied with the energy conservation condition

$$2\omega_1 - \omega_2 - \omega_3 = 0.$$  \hspace{1cm} (23)

If the medium has little dispersion \((n_1 \approx n_2 \approx n_3)\) as is the case with gases at moderate pressures, these conditions can be met with all beams parallel to one another (See Figure (4a)). In this geometry the intensity of the CARS signal varies as the sine squared i.e.

$$I \propto \left[ \frac{1}{\Delta k} \sin \left( \frac{\Delta k L}{2} \right) \right]^2$$

and reaches a maximum in a coherence length \( L_c \) where \( L_c = \pi/\Delta k \). This length can be calculated by expanding the refractive index of the medium with respect to frequency [35]

$$L_c = \frac{\pi c}{\omega_v} \left[ 2 \frac{\partial n}{\partial \omega} + n_1 \frac{\partial^2 n}{\partial \omega^2} \right]^{-1}.$$  \hspace{1cm} (24)

For gases at atmospheric pressure this distance can be tens of centimeters while for liquids it can be fractions of millimeters. Since the CARS intensity is proportional to the square of \( L_c \), the signal levels will be unacceptably small if one works with parallel beams when the medium has appreciable dispersion. Hence, in these media, phasematching is usually achieved by crossing the input beams at a small angle (see Figure 4b). The interaction length in this situation is then limited by beam walkoff.

It is possible to estimate the coherence length of a gas as a function of density by calculating the frequency derivatives of the dispersion equation. The variation of the index of refraction with density can be represented with a high degree of accuracy using the Lorenz-Lorentz relation [36,37]

$$\frac{n^2 - 1}{n^2 + 2} = R(\lambda) \rho$$  \hspace{1cm} (25)
Figure 4. Wavevector diagrams illustrating different phasematching configurations. (a) Collinear phasematching. (b) Crossed beam phasematching necessary for media with appreciable dispersion. (c) Relationship between wavevectors and $\Delta k$ for phase mismatched beams.
where \( n \) is the index of refraction and \( R(\lambda) \) is the specific refraction that depends on the polarizability of the species. The dispersion equation for \( \text{H}_2 \) at a density of one amagat is [38]

\[
2n^2 - 1 = a + \frac{b}{\lambda^2 - \lambda_0^2} \tag{26}
\]

where the empirical constants, \( a, b \) and \( \lambda_0 \) have been measured by Koch [39]. Solving Eq. (25)

\[
n^2 - 1 = \frac{3R_\rho}{1-R_\rho}. \tag{25}
\]

Putting \( \rho = 1 \) in this equation and equating it to the right hand side of Eq. (26) one finds \( R = A/(A+3) \) and

\[
n^2 - 1 = \frac{3\rho A(\lambda)}{3-(\rho-1)A(\lambda)} \tag{27}
\]

where

\[
A(\lambda) \equiv (a + \frac{b}{\lambda^2 - \lambda_0^2}).
\]

Equation (27) is the density dependent dispersion equation. This equation can be simplified by noting that even at high densities \((\rho-1)A(\lambda) << 3\) (at 200 amagat \( \rho A = 0.056 \) at \( \lambda = 532 \text{ nm} \)) and

\[
n^2 - 1 \approx \rho A(\lambda) \tag{28}
\]

Table 2 delineates the calculation of \( L_c \) for the \( \text{H}_2 \) Q(1) line assuming a pump laser at 532 nm. This analysis indicates that the dispersion of \( \text{H}_2 \) scales linearly with density and not with the square root of pressure as stated by Wilke and Schmidt [40] and except for extremely high densities the coherence length varies inversely with density. Figure 5 shows the coherence length as a function of density. At \( \rho = 100 \) amagat, \( L_c \approx 2 \text{ mm} \).
TABLE 2

\[ L_c = \frac{\pi c}{\omega_v} \left[ 2n' + \omega_1 n'' \right] \]

where

\[ n = [A_0 + 1]^{1/2} \]

\[ n' = \frac{dn}{d\omega} = \frac{A'}{2n} \rho \]

\[ n'' = \frac{1}{n} \left[ \frac{A''}{2} \rho - \left( \frac{A' \rho}{2n} \right)^2 \right] \]

\[ A(\omega) = a + b[\rho/\omega^2 - \lambda_0^2]^{-1} \]

\[ A' = \frac{2bd}{\omega^3} \left[ \frac{4d}{\omega^2} \right] \]

\[ A'' = \frac{2bd}{\omega^4} \left\{ \frac{4d}{\omega^2} \left[ \frac{3}{2} - \frac{3}{2} \right] \right\} \]

\[ \left[ \right] \equiv d \omega^{-2} - \lambda_0^2 \]

\[ d = (2\pi c)^2 \]

For the Q(1) line of hydrogen at \( \lambda = 0.532 \, \mu m \)

\[ a = 2.716 \times 10^{-4} \]

\[ b = 2.112 \times 10^{-6} \]

\[ \lambda_0^2 = 7.760 \times 10^{-3} \] for \( \lambda \) in \( \mu m \) [Ref. 39]

and

\[ L_c = \frac{1.54}{6.92(10^{-2}) \rho + 1.75(10^{-7}) \rho^2} \] (cm)

\[ = \frac{22.2}{\rho} \] cm \( \rho \) in amagat
Figure 5. Hydrogen Q(1) coherence length for beams in collinear phasematching geometry as a function of density.
To predict the behavior of the CARS signal in the medium, this value of coherence length should be compared to the distance, b, near the beam waist over which a focused beam remains essentially parallel. If a beam of divergence half angle \( \delta_{1/2} \) is focused by a lens of focal length \( f \), this distance is approximately given by \( 2\pi f^2 \delta_{1/2}^2 / \lambda \). Even for a conservative divergence of \( \delta_{1/2} = 0.1 \text{ mrad} \), \( b \approx 12 \text{ cm} \) when a beam passes through a 1 m focal length lens. Hence, at a density of 100 amagat, the CARS signal would have a squared sinusoidal variation with a period of \( \sim 4 \text{ mm} \) in this region. (It is interesting to note that when \( b \ll L_c \), collinearly phase-matched beams generate only 75% of the CARS signal in a length of \( \sim 7.5b \) [35].)

It is clear, at the high densities expected in the preburner, the pump and Stokes laser beams must be crossed at a small angle. Using the linear momentum conservation equations implied by Figure 4b and the energy conservation relationship Eq. (23), an expression for crossing angle \( \theta \) can be found:

\[
\cos \theta = \frac{4\omega_1 \omega_2 n_3^2 - 4\omega_1^2 (n_3^2 - n_2^2) - \omega_2^2 (n_3^2 - n_2^2)}{4\omega_1 \omega_2 n_1 n_2}.
\]

This crossing angle was calculated for the hydrogen Q(1) line and a pump laser wavelength of 532 nm. The result, shown as a function of density, is given in Figure 6. At a density of 100 amagat the phasematching angle is \( \sim 0.78^\circ \).

It is interesting to calculate the sensitivity of the CARS intensity to a small phase mismatch due to a non-optimum matching angle \( \theta \). From Eq. (7) the intensity varies as \( \text{sinc}(x) = \sin(x)/x \), where \( x = \frac{\Delta k \ell}{2} \), \( \Delta k \) is the magnitude of the wave vector mismatch (see Figure 4c), and \( \ell \) is the interaction length. Holding \( \phi \) constant at the phasematched value, the CARS intensity was calculated as a function of \( \theta \) for the Q(1), Q(3), and Q(5) lines of H\(_2\). The results are shown in Figure 7 for \( \rho = 1 \) and \( \rho = 100 \) amagat density and \( \ell = 1 \text{ cm} \). The FWHM's of the sinc functions are \( \sim 0.01 \text{ mrad} \) (\( \sim 7 \times 10^{-4} \text{ degrees} \)) and the intensities for the Q lines overlap for the low density case. However, at 100 amagat the increased dispersion separates the lines in \( \theta \)-space. This would indicate that separate angles are required for the individual lines. In practice, however, the beam divergence of the laser beam are greater than the
Figure 6. Crossing angle required for Q(1) line phasematched beams as a function of hydrogen density.
Figure 7. CARS normalized intensity variation for the first three strong Q branch lines of hydrogen as a function of crossing angle. (a) 1 amagat density. (b) 100 amagat density.
angular separation between the Q(1) and Q(5) lines and signal can be pro-
duced for these lines simultaneously - albeit at considerably lower in-
tensities than those calculated for the ideal case of exact phasematching.

The details of the intensity of various lines will depend on the in-
tensity distribution as a function of angle of the laser. By its nature
this variation cannot be folded into the signal and error calculations of
Section VI. Indeed, ratios of the intensities of the Q lines may depend
on the exact angle of crossing and could differ for identical conditions
of temperature and pressure. This is an area where experimental investi-
gation is warranted before attempting a measurement.
V. Laser Intensity Limitations

There are several effects that will place upper limits on the intensity of the pump beam in the medium. These in turn will limit the CARS signal strength and hence, the accuracy with which temperature measurements can be made. Although these effects generally are not important when performing diagnostics in flames at atmospheric pressure they can become important considerations at higher pressure.

Two of these effects were first discussed by Reginer et al. [41]. The first is most important when using a collinear phasematching geometry and results in an augmentation of the Stokes intensity through the process of stimulated Raman gain. A high intensity laser beam with angular frequency $\omega_1$ travelling through a Raman active medium can induce coherent radiation to propagate parallel to it at frequency $\omega_2$ and intensity $I_2$. Assuming negligible depletion of the pump beam intensity $I_1$

$$I_2(\ell) = I_2(0) e^{g\ell I_1} \quad [30]$$

where $\ell$ is the length that $I_1$ interacts with the medium, $I_2(0)$ is the Stokes field originally present and $g$ is the Raman gain of the medium given by [see for example, Ref. 42]

$$g = \frac{(4\pi c)^2 N_0 \Delta \omega_j}{n_2 \omega_2^2 \mu_\omega_1 F_j} \left( \frac{d\sigma}{d\Omega} \right)_j \quad [31]$$

where $N_0$ is the number density at 1 amagat ($2.69 \times 10^{-19} \text{cm}^{-3}$) and all other symbols in this expression have been previously defined. Where the linewidth decreases or remains constant as the density increases, the gain increases (Dicke narrowing regime). In the pressure broadening regime, the gain is independent of density. For the Q(1) line at 1200 K and 100 amagat, $g \sim 6 \times 10^{-10} \text{cm/watt}$. If $I_1^{\text{max}}$, the highest allowable pump beam intensity is considered to be that which will induce a 10% growth in the Stokes field ($I^*_S/I^*_S(0) = 1.1$) then $I_1^{\text{max}} \sim 1.7 \times 10^8 \text{watts cm}^{-2}/\ell$. For an interaction length approximately equal to the Rayleigh length ($> 10 \text{cm}$), this maximum value is quite low and presents a severe constraint that must be avoided if reasonable signal levels are to be attained. This points out another difficulty with performing the measurement using the more geometrically simple collinear phasematching. If the pump and Stokes beams
are crossed, this hazard can be avoided.

It should be noted that the pump beam alone can generate a co-propagating Stokes wave with an appreciable intensity. This could yield spurious temperature measurements even when the pump and Stokes beams are crossed if the CARS signal produced parallel to the pump beam were not separated from the crossed beam CARS signal. In this case, Eqs. (30) and (31) are again used to calculate the power of the stimulated Stokes wave, but in the absence of an external Stokes beam the initial Stokes power is taken as the initial spontaneous Raman noise level, i.e. \( P_s(0) = h\omega_2 \Gamma_j \) [42]. For the Q(1) line at 100 amagat density, this is \( \sim 2 \times 10^{-3} \) watt. Therefore, for a pump intensity of \( 10^9 \) watts/cm\(^2\), a distance of \( \sim 46 \) cm would be required to generate the same spectral power density as that available from the Stokes beam (assuming a 1 megawatt pulse and a 100 cm\(^{-1}\) spectral width). Since the preburner diameter is \( \sim 25 \) cm, the stimulated Stokes power is less than \( 10^{-5} \) of this value and no special precautions need be considered.

In reality, both of these calculations will overestimate the power generated by stimulated Raman scattering since it has been found experimentally that saturation of the Stokes intensity in H\(_2\) begins near a density of 10 amagat (at room temperature) and even suffers decreases in intensity [43,44]. This diminution is attributed to a decrease in the gain at higher densities and the fact that the increased optical dispersion at these densities makes the four wave mixing process more difficult.

A second phenomena that can cause measurement inaccuracies if \( I_1 \) and \( I_2 \) are too intense is a population perturbation between the lower and upper rotational levels. Stimulated Raman coupling between these two levels can affect \( \Delta_j \) (see Eq. (11)) such that

\[
\Delta_j(t) = \Delta_j(0) \exp(-t/\tau_{\Delta})
\]

where, on resonance, the time constant for this perturbation is given by [41]

\[
\tau_{\Delta}^{-1} = 2g_j \left( \frac{4\pi c}{\hbar\omega_2} \right)^2 \left( \frac{d\sigma}{dn} \right)_j I_1 I_2 \Gamma_j
\]

where \( g_j = 2v_j + 1 \) and \( I_2 \) is the Stokes intensity within the Raman linewidth. In the density region where the Raman linewidth is homogeneously

30
(pressure) broadened, this time constant varies linearly with density. However for broadband CARS $I_2 = I_2^{\text{tot}} \left( \frac{\Gamma}{\Delta \omega_2} \right)$ where $\Delta \omega_2$ is the spectral width of the Stokes beam the time constant is independent of density. For the Q(1) of H$_2$ with $\Delta \omega_2 = 2\pi c (100 \text{ cm}^{-1})$, $	au_\Delta^{-1} = (2 \times 10^{-28}) I_1 I_2^{\text{tot}}$. If $I_1^{\text{max}}$, the maximum allowable intensity, is defined as that which causes a 10% population perturbation, it is assumed $I_2 = 0.5 I_1$, and the time of the perturbation is taken to be the laser pulse width ($10^{-8}$ sec) then $I_1^{\text{max}} = 10^{10}$ watt cm$^{-2}$. This value should not be exceeded.

The third effect that may limit the CARS signal strength is the maximum pump beam power than can be focused into the H$_2$ without causing an ionization breakdown. The breakdown threshold intensity for most gases exhibits a minimum in the pressure range of 100 - 1000 atm [45]. The variation with pressure of the threshold minima is slower for molecular gases than for atomic gases [46]. Measurements of the breakdown threshold intensity have been taken for various gases (He, N$_2$, Ar) over a large enough pressure range to determine the minima [47]. However, data for H$_2$, in the range $0.5 \leq P \leq 100$ atm [48], do not cover sufficiently high pressures to show the breakdown minimum nor to cover the pressure region of interest to this study. The pressure at which the breakdown minimum occurs can be calculated from the classical impact ionization description of breakdown [45]. An approximation to the calculated minimum should give a reasonable approximation for pressures near 400 atmospheres. The electron energy change is a maximum when the momentum-transfer collision frequency $\nu_m$ is equal to the incident field frequency. In terms of the reduced pressure (torr), collision probability $P_c$, and mean energy (eV), the collision frequency is expressed as

$$\nu_m = 5.93 (10^7) P_c \sqrt{e} p_0, \quad (p_0 \text{ in torr, } e \text{ in eV}).$$

From tabulations [49] of $P_c$ vs $\sqrt{e}$, the mean value of $P_c \sqrt{e}$ for H$_2$ can be estimated to be approximately 80. It has been noted [45] that for hydrogen the collision frequency is very weakly dependent on electron energy, so

$$\nu_m = 5.9 (10^9) p_0 \quad (p_0 \text{ in Torr}).$$

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With these two relations a bound can be placed on the pressure of the minimum for the data presented in Ref. 48. Figure 8a shows the ruby laser H₂ breakdown data (converted to power density using a beam focal diameter of $1.2 \times 10^{-3}$ cm) as a function of pressure for a wavelength of 594.3 nm ($\omega = 2.71 \times 10^{15}$ sec$^{-1}$). The curve is an approximate fit extrapolated to the calculated minimum: $600 \leq p_0 \leq 750$ atmospheres.

For this data to be applicable to this study it must be scaled to the expected experimental conditions. The effect of the differences in temperature, beam focal volume, and beam frequency are the most significant. Since the minimum breakdown threshold scales with density (reduced pressure), the data from Fig. 8a should be shown as a function of density (assuming the data was taken at or near room temperature). The dependence of the breakdown field strength on beam focal volume has been shown [45] to vary as $E = \Lambda^{-3/4}$ (or $S = \Lambda^{-3/2}$ for power density), where $\Lambda$ is the characteristic diffusion length of the focal volume. For a cylindrical focal volume with diameter $d$, length $L$,

$$\Lambda^{-2} = \left(\frac{(2.4)}{(d/2)}\right)^2 + \left(\frac{\pi}{L}\right)^2 \right)^{-1}\right.$$  

For most beam geometries $d<<L$ so $\Lambda = d/4.8$. As the focal spot size increases, the breakdown threshold decreases. For the data of Ref. 48: $f = 2$ cm, $d = 1.2 \times 10^{-3}$ cm; so $\Lambda = 2.3 \times 10^{-4}$ cm. Possible values for this study include:

$$f = 100 \text{ cm}, \ 0.01 \leq d \leq 0.05 \text{ cm}; \text{ thus } 2.08(10^{-3}) \leq \Lambda \leq 1.04(10^{-2}) \text{ cm}.$$  

The power density focal spot scaling factor, $(\Lambda/\Lambda_0)^{-3/2}$, should be in the range $3.43(10^{-3}) \leq (\Lambda/\Lambda_0)^{-3/2} \leq 3.73(10^{-2})$. The beam frequency dependence of the threshold power density should be $S = \omega^2$, since the rate of increase of the electron energy is inversely proportional to the square of the incident field frequency. This naive view is consistent with the behavior of threshold in the frequency range of a ruby laser (used in Ref. 48) and a frequency-doubled Nd:YAG laser (present study) [45] i.e. $2.71(10^{15}) \leq \omega \leq 3.54(10^{15})$ sec$^{-1}$. The frequency scaling factor should increase the breakdown threshold by the factor $(\omega/\omega_0)^2 = 1.7$.

Figure 8b shows the possible range of the power density breakdown threshold for the experimental conditions of this study as a function of
Figure 8. H₂ breakdown threshold power density as a function of pressure and density (a) Data from reference [48]. Curve is approximate fit extrapolated to predicted minimum at ~ 675 atmospheres. (b) Expected range of breakdown power density scaled to parameters of interest in this study for a range of focal spot diameters. Calculated from data given in (a).
gas density. For the expected number density of 100 amagat, the limiting power density will be $8.5 \times 10^8 \leq S \leq 9.5 \times 10^9$ watt/cm$^2$, for the range of focal spot sizes $0.05 \geq d \geq 0.01$ cm. Note that similar predictions of the minimum threshold for single mode lasers have been within a factor of 2 in the power density and pressure [45,47]. If the laser is significantly multi-mode, the threshold will be lower than that calculated [50].
VI. **Signal Strength and Expected Error**

An estimate of the expected signal strength can be made using Eq. (8) which assumes the condition of exact phasematching ($\Delta k = 0$),

$$P_3 = \left( \frac{4\pi^2 \omega_3}{c^2} \right)^2 |\chi_{\text{CARS}}|^2 I_1^2 P_2 \ell^2$$

where $\ell$ is the interaction length, it has been noted that $n_1 = n_2 = n_3 = 1$ and powers have been substituted for intensities $I_2$ and $I_3$ by assuming that the CARS signal is generated with the same cross-sectional area as the Stokes beam. The CARS susceptibility is given by Eq. (11) which on resonance is

$$\chi_{\text{CARS}} = \frac{2\Delta J Nc^6}{\hbar \omega_2^2} \left( \frac{d\sigma}{d\Omega} \right)_j \frac{1}{\Gamma_j}$$

where the full width $\Gamma_j$ has replaced the half width $\gamma_j$ and it is taken that $\chi_{NR} = 0$. Combining these expressions one may calculate the number of photons generated per laser pulse $\hat{N}_j$ for a given resonance $j$ in terms of the energy of the Stokes beam $E_2$,

$$\hat{N}_j(T, \rho) = \left[ \left( \frac{8\pi^2 c^2}{\hbar} \right) N_o \left( \frac{\omega_3}{\omega_2} \right)^{\Delta_j} \left( \frac{d\sigma}{d\Omega} \right)_j I_1 \ell \right]^2 \frac{E_2}{\hbar \omega_3}$$

(32)

where $N_o$ is the number density of 1 amagat ($2.69 \times 10^{19}$ cm$^{-3}$), $\rho$ is the density in amagat, $\Delta_j$ is the fractional population difference between upper and lower states (see Appendix C), and $(\frac{d\sigma}{d\Omega})_j$ is the Raman cross section (see Appendix B). $E_2$ is the Stokes energy within the Raman linewidth which for a broadband beam of spectral width $\Delta \omega_2$ is

$$E_2 = E_{\text{total}} \left( \frac{\Gamma_j}{\Delta \omega_2} \right)$$

Hence for broadband CARS, the signal strength is inversely proportional to $\Gamma_j$ and in the pressure broadened region increases linearly with density. The signal strength varies quadratically with pump laser intensity, an attractive parameter to use to increase measurement accuracy. However, the upper limits to the intensity set by population perturbations, stimulated Raman gain, and laser induced gas breakdown as described in Section V must be observed.
For the purposes of this calculation, a pump beam intensity of $10^9$ watts cm$^{-2}$ and a Stokes beam energy of 10 mJ in a spectral width of 100 cm$^{-1}$ will be considered. Modern Nd:YAG lasers are capable of producing nearly 100 times this intensity at a wavelength of 532 nm when focused by a 1 m lens. An interaction length of 1 cm is used in accordance with the discussion in Section VII. Figure 9 shows the expected CARS signal strength (photons per laser pulse) calculated from Eq. (32) as a function of temperature for the case of a constant number density of 100 amagat for the first six Q lines of hydrogen. As is evident from these curves, the expected signals are quite large. The odd valued Q lines have greater signal strengths due to the statistical weight factor and hence the analysis will concentrate on these lines.

As discussed in Section VII, there are several methods that can be used to recover and analyse the CARS signal. Two are considered here. The first is to ratio the signals obtained from the individual lines and the second is to ratio the signals obtained from two interference filters. Figure 10a shows calculated ratios of the odd (strong) lines using Eq. (32) as a function of temperature for a constant density of 100 amagat. Figure 10b shows the expected ratios if the CAR spectra is convoluted by 1.0 nm (FWHM) interference filters with triangular spectral profiles (characteristic of two period filters). The filters are centered at 438, 437, and 436 nm respectively (see Figure 19). Note that these two figures have different ordinates.

The $Q_5/Q_1$ ratio has the greatest slope of the Q ratios and varies more than an order of magnitude for the range of temperatures of interest (800-1600 K). The $F_2/F_3$ ratio has the greatest ratio among the F ratios, but the slope is considerably less than that of the $Q_5/Q_1$, its value varying less than a factor of 4 in this same temperature interval.

**Error Analysis**

It is useful to consider the accuracy with which the temperature can be extracted from these ratios. This can be done in terms of simple error propagation theory [51]. The variance $\sigma_X^2$ of a quantity x in terms of the variances of variables u and v is approximately

$$\sigma_X^2 = \sigma_u^2 \left( \frac{\partial x}{\partial u} \right)^2 + \sigma_v^2 \left( \frac{\partial x}{\partial v} \right)^2 + 2\sigma_{uv} \left( \frac{\partial x}{\partial u} \right) \left( \frac{\partial x}{\partial v} \right)$$
Figure 9. Calculated CARS signal strength for Q branch lines of H$_2$ at 100 amagat density.
Figure 10. (a) Calculated CARS Q line signal ratios for 100 amagat density. (b) Calculated ratios from CARS H$_2$ Q line signals taken through the three interference filters displayed in Figure 19.
where the covariance $\sigma_{uv}^2$ is zero if the fluctuations in $u$ and $v$ are uncorrelated. The error in temperature due to error in the ratio of counts $R$ is simply

$$\sigma_T^2 = \sigma_R^2 \left(\frac{\partial T}{\partial R}\right)^2$$

where $R = N_1/N_2$. The uncertainty in the ratio will consist of the experimental uncertainty with which the ratio can be measured $\sigma_{MR}^2$ (due to gated integration electronics, ratiometers, A/D etc.) and that due to uncertainty in the number of counts $\sigma_{NR}^2$ so

$$\sigma_R^2 = \sigma_{MR}^2 + \sigma_{NR}^2$$

and

$$\sigma_{NR}^2 = \sigma_{N_1}^2 \left(\frac{\partial N_1}{\partial T}\right)^2 + \sigma_{N_2}^2 \left(\frac{\partial N_2}{\partial T}\right)^2$$

The uncertainty in the number of counts can be ascribed to purely statistical causes $\sigma_{stat}$ and to the dependence of this number on the linewidth, which itself has appreciable uncertainty. If the measurements are taken using the interference filter configuration, the counts will depend on contributions from several lines so

$$\sigma_N^2 = \sigma_{stat}^2 + \sum_i \sigma_{\Gamma_i}^2 \left(\frac{\partial N_i}{\partial \Gamma_i}\right)^2$$

Then, noting $\left|\frac{\partial R}{\partial N_1}\right| = \frac{R}{N}$ and letting $\sigma_{stat} = \sqrt{N}$ the variance in temperature due to these uncertainties can be written

$$\sigma_T^2 = \left[\sigma_{MR}^2 + \left(\frac{\partial N_1}{\partial T}\right)^2 \left(\frac{R}{N_1}\right)^2 + \sum_{\Gamma_i} \sigma_{\Gamma_i}^2 \left(\frac{\partial N_i}{\partial \Gamma_i}\right)^2 \left(\frac{R}{N_i}\right)^2 \left(\frac{\partial T}{\partial \Gamma_i}\right)^2 \right] \left(\frac{\partial T}{\partial R}\right)^2$$

(33)

Figures 11 through 16 show the calculated error $\sigma_T$ for the same conditions used for the signal strength plot (Figure 9). Figures 11 and 12 consider uncertainty in temperature due to statistics, ratio measurement and linewidth uncertainty (two cases) individually. These calculations assume that only 5% of the photons are recovered and impinge on a photomultiplier with a quantum efficiency of 0.2. For these conditions, Figure 11a shows that the projected error in temperature due to statistical uncertainty alone is quite small. Figure 11b displays the uncertainty in $T$ expected

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Figure 11. Calculated temperature standard deviation for Q line ratios. (a) $\sigma_T$ due to signal statistics only. (b) $\sigma_T$ due to 0.5% projected error in measured signal ratio.
due to measurement error in the ratio. These curves were calculated assuming a 0.5% relative accuracy ($\sigma_{MR/R} = 0.005$), a reasonable value for matched detectors when the variation of $R$ is less than two orders of magnitude.

The uncertainty in the linewidth broadening coefficient can lead to appreciable error in the temperature at high densities. Figure 12 displays the error for two cases. If the listed uncertainties of Allin et al. [22] are used for lines $Q(0) - Q(3)$ (column 1 Table 1) and $0.1 \times 10^{-3}$ cm$^{-1}$/amagat is the assumed error for lines $Q(4)$ and $Q(5)$, the resulting error in $T$ due to this linewidth uncertainty alone is shown in Figure 12a. However, the spread among the broadening coefficient values listed in Table 1 is considerably greater than this error. Figure 12b displays $\sigma_T$ due to the uncertainty in $r_i$ above if the various broadening coefficients are assumed to have constant uncertainty of $0.25 \times 10^{-3}$ cm$^{-1}$/amagat. Clearly, this uncertainty in the linewidths will contribute substantially to the uncertainty in the temperature if the published values in the linewidth are used in the analysis of the data. Using Eq. (31) the total calculated uncertainty in the temperature can be computed. The results, using the above parameters and the smaller uncertainties in the line broadening coefficients, are shown in Figure 13.

It is interesting to note that the ratio that yields the least uncertainty differs for each of the plots. Under the assumptions of Figure 13 the preferred ratio is the $Q_3/Q_1$ in accordance with the linewidth uncertainties used in Figure 12a. This would not be the case for the more liberal uncertainties assumed for Figure 12b which indicates the $Q_5/Q_1$ ratio is the preferred quantity. Near the operating temperature of the preburner ($\sim 1200$ K), these calculations indicate a temperature uncertainty of $\sim 10-40$ K (depending on the linewidth uncertainty assumed) or an accuracy of 1-3%.

It is possible to extract temperature from the measurements of the ratios without using the linewidth data by precalibrating the instrument using a variable temperature high pressure cell. The uncertainty would then approach that given by Figure 11b. That is, it would be due to the experimental uncertainty in the ratio. In this case, the $Q_5/Q_1$ ratio would be the preferred value to use for temperature extraction consistent
Figure 12. Calculated temperature standard deviation for Q line ratios. (a) $\sigma_T$ due to linewidth uncertainties of Ref [22]. (b) $\sigma_T$ due to a constant linewidth uncertainty of $2.5 \times 10^{-4}$ cm$^{-1}$/amagat.
Figure 13. Calculated temperature standard deviation for Q line ratios when the effects of statistics, the linewidth uncertainties of Ref [22], and ratio measurement uncertainty are included.
with the fact it has the steepest slope. Then the temperature uncertainty would be $\sim 1.5 \text{ (K)}$ at 1200 K corresponding to a 0.1% accuracy.

Figures 14, 15 and 16 show the corresponding error calculations for the filter ratios. Here, the calculation assumes that 40% of the signal is recovered and is divided by a 50% beam splitter, passes through an interference filter with 50% peak transmission and is focused onto a PMT with 0.2 quantum efficiency. The results are similar to those of the Q ratios. Again the uncertainty due to statistics is negligible and somewhat less than those of the Q ratio due to the higher signal throughput and the fact that the filters accept contributions from several lines. The linewidth uncertainties yield somewhat higher temperature uncertainties for the filters because the uncertainties from several lines contribute to the signal from each filter. Using the $F_2/F_3$ ratio, Figure 16 projects a total uncertainty of $\sim 25 \text{ K}$, about 2.5 times greater than that for the Q ratio. Considering the case of a calibrated instrument and using the uncertainty implied by the measured ratio accuracy of Figure 14b, the $R_1/R_3$ ratio projects only a slightly greater uncertainty in temperature (1.75 K) than the $Q_5/Q_1$ ratio.

It should be noted that there is another source of error that could not be included in these calculations. A variation of density in the pre-burner due to temperature and/or pressure variations can change the phase-matching angle. Not only will this have the effect of reducing the signal strength, but could also change the relative intensity of the spectral lines in a random fashion as discussed in Section IV. Furthermore, the CARS signal strength used in these error calculations consider the case of perfect phasematching. This cannot be the accomplished for all the Q lines simultaneously and the signal levels obtained here are surely overestimates. This would imply greater statistical errors than those shown in Figures 11a and 14a.
Figure 14. Calculated temperature standard deviations for filter ratios. (a) $\sigma_T$ due to statistics only. (b) $\sigma_T$ due to a 0.5% projected error in measured signal ratio.
Figure 15. Calculated temperature standard deviation for filter ratios. (a) $\sigma_T$ due to linewidth uncertainties of Ref [22]. (b) $\sigma_T$ due to constant linewidth uncertainty of $2.5 \times 10^{-4}$ cm$^{-1}$/amagat.
Figure 16. Calculated temperature standard deviation for filter ratios when the effects of statistics, linewidth uncertainties of Ref [22], and ratio measurement uncertainty are included.
VII. Instrument and Facility Considerations

In this section, the experimental layout of a CARS system is briefly discussed. This system would be capable of producing laser beams and CARS signals with the characteristics discussed in previous sections.

Generally, a CARS system can be divided into three parts: a source of high intensity radiation, beam transfer and focusing optics, and signal recovery and processing assembly. The beam transfer optics are necessarily dependent on the physical design of the test facility and will be discussed last. Due to signal strength considerations the choice of laser for the pump radiation $\omega_2$ is limited to high intensity pulsed lasers for most practical purposes. Of those that are readily available, ruby and Nd:YAG lasers offer the highest intensity. The latter is the first choice since its doubled output can pump visible dyes useful for creating the Stokes laser radiation and has the advantage of offering higher pulse rates resulting in a higher data acquisition rate.

Figure 17 displays the optical design of the front end of a CARS system built around a Nd:YAG laser which is suitable for $\text{H}_2$ temperature measurements. A portion of the second harmonic of the Nd:YAG laser serves to pump a broadband dye laser oscillator-amplifier system. After passing through telescopes that modify the beam diameters and divergences, the pump and Stokes radiation are rendered parallel and relayed to the measurement point. The characteristics of this and similar systems have been discussed previously [52, 53]. Shirley et al. [7] have done single pulsed CARS thermometry of $\text{H}_2$ in laboratory burners using a similar set-up. They find a dye mixture of cresyl violet perchlorate and oxazine 725 satisfactory to efficiently produce the Stokes radiation at 681.5 nm with an acceptable bandwidth when pumped by the second harmonic of a Nd:YAG laser (2xNd). This set-up is sensitive to misalignment and must be placed in a mechanically and thermally stable environment.

There are several methods to process the recovered CARS signal. The three considered in this study are shown schematically in Figure 18 in order of decreasing complexity. The first two require monochrometers while the last needs only narrow band interference filters. The first method will yield the greatest information. Here all the lines of a CAR
Figure 17. A suitable design for the front end, or laser sources, of a CARS system. Code: P, prism; 2X, KDP doubler; M, mirror; D, dichroic, BD, beam dump; IRF, infrared filter; DC, dye cell; L, lens; BS, beamsplitter; OF, optical flat.
Figure 18. Three variations of detecting and processing H₂ CAR spectra. (a) Viewing complete spectra using optical multichannel detector (OMD). (b) Viewing individual odd numbered Q branch lines. (c) Viewing portion of spectra through interference filters.
spectrum within an interval defined by the spectral width of the broadband Stokes laser are viewed using an optical multichannel detector (OMD). This is the most common arrangement used for N₂ CARS thermometry. However, the OMD is expensive and very sensitive to mechanical vibration.

The second technique eliminates the OMD and collects the signals from individual Q branch lines using fiber optics and transfers these to photomultiplier tubes. A one meter spectrograph using a 2400 λ/mm grating can produce a dispersion of ~0.3 mm/Å at the anti-Stokes wavelength. This results in a spatial separation of ~1.8 mm between Q(1) and Q(3) lines and ~3.3 mm between Q(3) and Q(5) lines - a sufficient distance to allow the placement of optical fibers. The electronic signals are then processed and ratioed.

The last method considered eliminates the spectrograph and uses two interference filters. Interference filters with bandpasses of 10 Å are commercially available. Figure 19 shows the spectral position of filters with triangular passbands (somewhat characteristic of two period filters) used in the calculations of Section VI with the positions of several of the Q branch lines indicated. As noted in that section, this technique is somewhat less sensitive to temperature changes than taking ratios of the signals from individual lines. However, due to its simplicity, mechanical stability and insensitivity to signal beam position, it is experimentally the method of choice. This technique is only marginally less accurate than system (b) of Figure 18 when using a ratio calibrated CARS system.

The Fuel Preburner and Test Facility at NSTL

Figure 20 shows vertical and horizontal cross sections of the SSME fuel preburner. A photograph of the interior of the fuel preburner is shown in Figure 21a. The interior diameter of the main wall is 10.89 inches and surrounds a thin (0.05") liner with a 10.43" interior diameter. On some versions, there are two ports of ~0.4" diameter located ~60° and +165 from the 0° degree line pointed toward the preburner vertical axis (see Figure 21b). These ports may or may not have access to the interior gas flow through the liner. Three vertical baffle plates extend down from the injector head to the centerline of ports at 120° intervals.
Figure 19. Bandpasses of filters used in calculations of Section VI. Position of Q branch lines are indicated.
Figure 20. Two views of the SSME fuel preburner. (a) Three baffles extend from injector head to center line of ports. (b) Cross-section showing dimensions and positions of ports and liner.
Figure 21. Two views of SSME fuel preburner. (a) Interior view looking towards injector head. (b) Exterior view of ~1.0 cm diameter port.
At NSTL the preburner is located on the 4th floor of the test stand building. During assembly the SSME is surrounded by temporary metal flooring which allows access to the engine components. During a test, these grates are removed and the remaining flooring is ~15 feet from the SSME. This permanent deck, mounted on a ~2½ feet thick concrete wall, is one level below a room that houses the electronics for processing the data received from the sensors placed on the test engine. This amplifier room is a vibration-free, thermally stable environment.

A possible physical configuration for the location of the laser system and beam transfer optics is shown in Figure 22. The CARS system shown in Figure 17 could be placed in the amplifier room near the concrete wall. The parallel pump and Stokes beams would pass through the floor of this room, be rendered horizontal by a prism secured to the concrete wall, pass through the wall and be transferred to a mirror mounted directly to the preburner by another mirror mounted directly to the other side of the concrete wall. Because of the severe vibration, no optics could be mounted on any other surrounding structures.

Figure 23 shows a mechanism that could accept the transferred beams. Here a lens that rides on a travelling nut of a lead screw assembly serves to focus and cross the incoming beams. The crossing point of the beams defines the region where the measurement is taken and this point is transferred across the preburner by the movement of the lens. The CARS signal thus created passes through a spectral filter and is focused by a short focal length lens onto an optical fiber. This fiber transfers the signal back to the amplifier room for processing. The focal length of this lens and the diameter of the fiber are chosen such that maximum diameter of the focused signal beam does not extend beyond the diameter of the fiber optic. The ports are shown in the same position as those that currently exist on the fuel preburner. The 12" to 14" clearance necessary for the travelling lens assembly is available in the current setup. Only ~3 inches of clearance is available outside the other port and hence the need for a compact recovery arm. With ports placed at these positions, a temperature profile would be taken across a chord instead of the diameter of the preburner. This is a desirable situation from an experimental point of view as the gas streamlines are expected to be static in this region while the
Figure 22. Fifth floor plan of test stand facility at NSTL. The possible location of a CARS system is shown in the amplifier room which is one level above the fuel preburner. Positions of mirror mounts attached to the concrete wall are indicated.
Figure 23. Hypothetical beam receiving arm attached to fuel preburner. All optics and beam paths are hermetically sealed.
center is believed to be subject to turbulence. The windows of the ports could be made of crystalline sapphire as it has excellent mechanical strength, high temperature stability, chemical inertness, and good optical transmission (its melting point is above 2300 K and a 0.5 inch diameter, 0.2 inch thick window has a hydrostatic burst point of 9600 psi with a built-in safety factor of 3 [54]). Because of the cryogenic fuel flowing through the rocket system, all fixtures attached to the preburner must be purged to avoid frozen condensate. Furthermore, all beams must be transferred in hermetically sealed tubes as the air adjacent to the SSME becomes clouded during tests.

It is useful to consider a few numbers in light of the geometry of the fuel preburner and test facility. As discussed in Section IV, hydrogen has considerable optical dispersion at high densities requiring a simple two beam phasematching geometry. At a density of 100 amagat the crossing angle $\theta$ is $\sim 0.8^\circ$. Using simple geometry, two beams of width $d$ can overlap over a length of no more than $l = d/\sin(\theta/2)$. The diameter of a laser beam with a Gaussian intensity profile focused by a lens of focal length $f$ is $\sim 2f\delta_{1/2}$ where $\delta_{1/2}$ is the half angle divergence of beam. As indicated in Figure 23 a lens with a 36 cm focal length would allow measurements to be made across a chord of the preburner. Taking $\delta_{1/2} = 0.25$ mrad (factory specification of a Quanta Ray Nd:YAG laser) one finds $l \sim 2$ cm. This crossing angle and lens also result in a pump and Stokes beam separation of $\sim 0.5$ cm at the lens. If both beams have a 0.5 cm diameter, then the ports in the preburner should have approximately 1 cm diameter (or somewhat larger to facilitate alignment). In accordance with the discussion in Section IV, the angle between the Stokes and pump beams must be maintained to an accuracy better than the individual beam divergences. This indicates that beam separation tolerance of less than $8.75 \times 10^{-3}$ cm over the path length of the relay system ($\sim 25$ meters). Our experience is that this can be achieved if single optical components are used to relay both beams. However, these components must not be stressed and the vibration of these pieces must be less that required to cause the focused CARS signal to wander from the end of the fiber optic ($\sim 1$ mm for a macrofiber). Furthermore, it is likely that once set up the system will require an initial alignment under operating density to maximize the
signal.

In order for this design to be implemented, the following conditions must be met. Two facing ports with at least 1 cm diameters and an unobstructed line of sight view of each other must be available in the preburner. In current preburners, the ports have marginally adequate diameters, but do not face each other and offer no through-beam access. Furthermore, half the area of the current ports are obstructed by the baffles extending from the injector head. Line of sight access must exist from the main concrete wall to the preburner, through the concrete wall, and from the outside of the concrete wall to the amplifier room. It is believed that this access could be made available, albeit with some modifications to the test facility. Mirror mounts and housings must be anchored directly to the concrete wall and not to surrounding structures.
VIII. Conclusions and Recommendations

The theoretical analysis in this report indicates that temperature measurements can be made using CAR spectra of hydrogen with the spatial and temperature precision indicated in NASA RFP No. 8-1-2-EC-25732 (0.25 to 0.5 in² and 10 °R). The temperature resolution for a calibrated instrument will be limited by the precision with which the ratio of signals from individual rotational lines can be measured. Spatial resolution can approach ~2 cm in the longitudinal direction (with respect to beam direction) and ~0.01 cm in a transverse direction. The time resolution would be limited by the pulse width of the laser (~10⁻⁸ sec) with a data acquisition rate limited by the pulse rate available from high power Nd:YAG lasers (currently ~30 Hz).

A study of the physical environment of the test facility and access to the currently configured fuel preburner does not present such a sanguine picture. As presently configured, there is no acceptable optical access to the preburner. CARS requires two line of sight optical ports with clear access diameters of ~0.5 in. and modifications to the preburner would have to be made. Furthermore, the area adjacent to the SSME is subject to extreme vibration during a test and is unsuitable for the placement of spectroscopic equipment. This requires a system of relay optics over which critical alignment must be maintained.

Because there are unknowns in the physical environment during a test firing, several on site tests are recommended before proceeding with a CARS temperature measurement. The amount of physical motion experienced by optical mounts anchored to the main concrete support wall and an arm attached to the preburner port must be measured. The observation of beam wander over the projected light path during a test firing measured using a HeNe laser and a reticon detector would be a simple and useful test. In addition, the amount of deviation experienced by a laser beam passing through the preburner during a firing also should be measured. Significant deviations caused by turbulence-induced index of refraction gradients could cause significant dephasing of the pump and Stokes beams.

Since there are several untested aspects of the CARS technique in this environment it is also advisable to undertake a number of
laboratory measurements using a variable temperature high pressure cell. CARS generated in high pressure hydrogen would allow a system to be calibrated taking note of the sensitivity of the variation of line intensities as a function of the phasematching angle. These studies could also be used to eliminate many of the uncertainties associated with the linewidth pressure broadening coefficients considering the paucity of data available on their variation as a function of temperature. In addition, this work could set experimental limits on the effects of stimulated Raman gain and laser induced gas breakdown for hydrogen. Finally, more realistic limits on the absolute signal strength could be obtained since the theoretical limits are seldom realized even under the most ideal experimental conditions.
Appendix A
Density to Pressure Conversion

The conversion from pressure to density for a given temperature is readily accomplished using the equation of state. Using Van der Waal's equation for H₂ [55]

\[(P + \frac{n^2a}{V^2}) (V - nb) = nRT\]

where
- \(n\) = number of moles of gas
- \(R = 0.08206\) liter atm mole\(^{-1}\) K\(^{-1}\)
- \(P\) = pressure in atmospheres
- \(V\) = volume in liters

and for H₂
- \(a = 0.2444\) (liters\(^2\)) atm/mole
- \(b = 0.02661\) liters/mole

If \(n = n/V\) (molar number density), then the above equation can be written

\[abn^3 - an^2 + (bP + RT)n = P\]

and \(n/n_o\) is the density in amagat where \(n_o\) is the molar number density at \(T = 273.15\) K and \(P = 1\) atm. Figures A1 and A2 show pressure verses density for the temperatures, pressures and densities important to this study.
Figure A1. H₂ pressure-density curves, 300 ≤ T ≤ 1000 K.
Figure A2. H₂ pressure-density curves, 1000 ≤ T ≤ 1000 K.
Appendix B
Raman Cross Section

The Raman cross section for forward scattering as a function of rotational quantum number is [14]

$$\frac{d\sigma}{d\Omega} \bigg|_Q = \left(\frac{\omega_e}{c}\right)^4 \frac{\hbar}{2\omega_o} \left[ \alpha^2 + \frac{7}{45} \left(\frac{\gamma^2}{M}\right) b_J \right] (v + 1)$$  \hspace{1cm} (B1)

$$\frac{d\sigma}{d\Omega} \bigg|_{0,S} = \left(\frac{\omega_e}{c}\right)^4 \frac{\hbar}{2\omega_o} \frac{7}{45} \left(\frac{\gamma^2}{M}\right) b_{J \pm \frac{1}{2}} (v + 1)$$

It is often useful to be able to calculate $\alpha$ and $\gamma$ from the Raman scattering cross section $\sigma_{zz}$ (the cross section for scattering an incident beam travelling along the x-axis with polarization in the z-direction into the x-y plane with polarization in the z-direction) and the depolarization $\rho$ (the ratio of light intensity scattered in the y-direction polarized in the x-direction to that polarized in the z-direction for an incident beam travelling in the x-direction polarized in the z-direction). Taking $\rho = 0, 1$.

$$\alpha^2 = \frac{2\omega_o}{3\hbar g_v} \left(\frac{\omega_2}{\omega_o}\right)^4 \left(1 - \frac{4\rho}{\gamma^2}\right) \sigma_{zz} ; \quad \gamma^2 = \frac{30\omega_o}{\hbar g_v} \left(\frac{\omega_2}{\omega_o}\right)^4 \frac{\rho}{1 + \rho} \sigma_{zz}$$

Taken from

$$\rho = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2} ; \quad \sigma_{zz} = \frac{\hbar}{90\omega_o} \left(\frac{\omega_2}{\omega_o}\right)^4 g_v (45\alpha^2 + 7\gamma^2)$$

See Ref. (56, 57, 58).

The Placzek-Teller coefficients are available from several references (59, 60, 61). For a diatomic molecule

$$b_J = \frac{J(J + 1)}{(2J-1)(2J+3)}$$

$$b_{J+2} = \frac{3 (J+1)(J+2)}{2 (2J+1)(2J+3)}$$

$$b_{J-2} = \frac{3 (J-1)}{2 (2J+1)(2J-1)}$$

$g_v = v + 1$ is contributed by the vibrational matrix element.
Application to Hydrogen

\[
\omega_2 = 2.714 \times 10^{15} \text{ rad/sec (14396 cm}^{-1})
\]

\[
\omega_0 = 7.832 \times 10^{14} \text{ rad/sec (4155 cm}^{-1})
\]

\[
p = 0.07
\]

\[
\frac{\alpha}{M} = 1.8 \times 10^{-8} \text{ cm}^4 \text{ gm}^{-1}
\]

\[
\frac{\gamma}{M} = 1.08 \times 10^{-8} \text{ cm}^4 \text{ gm}^{-1}
\]

Ref [10]

and

\[
\chi_{NR} = 9.75 \times 10^{-18} \text{ cm}^3 \text{ erg}^{-1} [17]
\]

Analysis shows [62] that for very light molecules the Q branch matrix element is subject to a J-dependent correction factor i.e. Eq.(B1) must be multiplied by (see [63])

\[
\left[ 1 + \frac{3}{4} \left( \frac{2B}{\omega_e} \right)^2 |a_1| - 1 \right] J(J + 1)
\]

where \(a_1\) is the first Dunham anharmonic coefficient [64]. Using Eq.(19) of Ref [65] \(a_1\) can be written

\[
a_1 = \frac{He\omega_e^4}{16B_5 e} - 3
\]

\[-1.62293 \text{ cm}^{-1}\]

where the remaining constants are defined in Appendix D.
Appendix C
Population Difference Between Initial and Final States $\Delta_j$

The fractional population difference between upper and lower rotational-vibrational energy levels is

$$\Delta_j = f_{v', J'} - f_{vJ}$$

where $f_{vJ}$ is the fraction of molecules in the energy level designated by $v$ and $J$.

In thermal equilibrium, the fraction of molecules in a quantum mechanically allowed eigenstate is equal to the Boltzmann factor divided by the partition function $Q$ [66]

$$f_i = \frac{\exp(-E_i/kT)}{Q}$$

If there are degenerate states, the fraction of molecules in a given energy level is weighted by the degree of degeneracy or the statistical weight $g_k$

$$f_k = \frac{g_k \exp(-E_k/kT)}{Q}$$

where the partition function is given by

$$Q = \sum_{\text{all states}} \exp(-E_i/kT) = \sum_{\text{all levels}} g_k \exp(-E_k/kT)$$

Considering all degrees of freedom (electronic motion and spin, nuclear motion and spin) but considering $\Lambda$-doubling to be zero and all electron and nuclear spin levels to be degenerate, $f_{vJ}$ can be written as

$$f_{vJ} = \frac{(2 - \delta_{ov})(2S + 1)(2J + 1)[\Sigma(2T + 1)]}{Q} \exp(-E_{vJ}/kT)$$

where $(2 - \delta_{ov})$ accounts for $\Lambda$-doubling

$(2S + 1)$ is the electronic spin statistical weight

$(2J + 1)$ is the statistical weight of a given rotational level excluding nuclear spin

$\Sigma(2T + 1)$ is the sum over all allowed nuclear levels weighted by the number of their magnetic sublevels.
The values of $T$ are taken from the individual nuclear spins of the atoms $(I_1, I_2)$, i.e.

$$T = |I_1 + I_2|, |I_1 + I_2 - 1|, \ldots |I_1 - I_2|$$

However, for homonuclear molecules, the symmetry of the total wavefunction is preserved by allowing only even values of $T$ for symmetric wavefunctions and only odd values of $T$ for antisymmetric wavefunctions.

If the various degrees of freedom are considered to be completely decoupled (which is not always the case, as indicated below) then the partition function can be approximated by

$$Q = Q_{el} Q_{v} Q_{rot} Q_{es} Q_{ns}$$

For all temperatures important to combustion, only the ground electronic state will contribute appreciably to the sum (ignoring $\Lambda$-doubling).

$$E_{el} = 0 \quad \text{so} \quad Q_{el} = 1.$$ 

The vibrational term energy can be written

$$G(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \ldots$$

Defining the zero point energy ($\frac{\omega_e}{2}$) to be at $E = 0$

$$\tilde{G}(v) = v(\omega_e - \omega_x x_e v + \omega_y y_e v^2 + \omega_z z_e v^3 + \ldots)$$

$$v = 0, 1, 2, \ldots$$

$$Q_v = 1 + \exp(-\hbar \omega_e /kT) + \exp(-2\hbar \omega_e /kT) + \ldots$$

The rotational energy can be approximated by

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

$$J = 0, 1, 2, \ldots$$

$$Q_{rot} = \sum_{\text{all states}} \exp(-E_J/kT) = \sum_{\text{all levels}} (2J+1)\exp(-F(J)/kT)$$

$$= (1 + 3 \exp(-2\hbar \omega_e /kT) + 5\exp(-6\hbar \omega_e /kT) + \ldots)$$

For sufficiently large $T$ or small $B$ (see Ref. 67):
\[ Q_{\text{rot}} = \int_0^{\infty} (2J+1) \exp\left[-\frac{\hbar cBJ(J+1)}{kT}\right] dJ = \frac{kT}{\hbar cB} \]

\[ Q_{\text{es}} = \sum_{\text{all states}} \exp\left(-\frac{E_{\text{es}}}{kT}\right) = (2S + 1) \text{ for degenerate electron spin states.} \]

\[ Q_{\text{ns}} = \sum_{\text{all states}} \exp\left(-\frac{E_{\text{ns}}}{kT}\right) = \sum_{\text{all levels}} (2T + 1) \exp\left(-\frac{E_{\text{ns}}}{kT}\right) = \sum_{T} (2T + 1) \text{ for degenerate states.} \]

The Boltzmann factor is given by

\[ f_{\text{BOLTZ}} = \exp\left[-\frac{E_{\text{TOTAL}}}{kT}\right] \]

\[ E_{\text{TOTAL}} = \hbar c \left( T_e + \bar{G}(v) + F(J) \right) \]

\[ T_e = 0 \text{ for ground electronic state (cm}^{-1}\text{)} \]

\[ \bar{G}(v) = G(v) - G(0) \]

\[ = G(v) - \frac{1}{2} \left( \omega_e - \frac{\omega_e^2}{2} + \frac{\omega_e^3}{4} + \frac{\omega_e^4}{8} \right) \text{ (cm}^{-1}\text{)} \]

\[ (= 0 \text{ for lowest vibrational level}) \]

\[ F(J) = BJ(J+1) - DJ^2(J+1)^2 \]

Application to Molecular Hydrogen

Consider the ground state of \( \text{H}_2 \)

\[ \chi^1_{\Sigma^+} \]

\[ s = 0 \]

\[ \Lambda = 0 \]

\[ I = \frac{1}{2} \rightarrow T = 1, 0 \]

even \( J \rightarrow +, s \) (symmetric under electron and nuclear coordinate inversion)

odd \( J \rightarrow -, a \)

Then

\[ Q = (1) \left[ 1 + \exp\left(-\frac{\hbar c \omega_e}{kT}\right) \right](2s + 1) Q_{\text{RN}} \]

where the rotational-vibrational part of the homonuclear molecule cannot
be decoupled because of symmetry considerations, i.e.

\[ Q_{RN} = \sum_{\text{all allowed states}} \exp(-E/kT) = \sum_{\text{allowed } T,J} (2T + 1)(2J + 1) \exp(-E_j/kT) \]

\[ = \sum_{\text{even } J} (2J + 1) \exp(-hcFJ/kT) + 3 \sum_{\text{odd } J} (2J + 1) \exp(-hcFJ/kT) \]

\[ = \sum_{J} (2J + 1) \exp(-hcFJ/kT) + 2 \sum_{\text{even } J} (2J + 1) \exp(-hcFJ/kT) \]

since only even T values are allowed for even J states. The above series can be truncated when the exponentials become sufficiently small. Then

\[ Q(T) = \left[ 1 + \exp\left(\frac{-6331}{T}\right) \right] Q_{RN}(T) \]

and

\[ f_{vJ} = \frac{g_I(2J + 1)}{Q(T)} \exp\left[\frac{-hc}{kT} (T_e + \bar{G}(v) + F(J))\right] \]

\[ = \frac{g_I(2J + 1)}{Q(T)} \exp\left[\frac{2170 - G(v) - F(J)}{.695T}\right] \]

where

\[ g_I = 1 \text{ for even } J \]
\[ = 3 \text{ for odd } J \]
Appendix D
Energy Differences $\Omega_{vJ}$ and Line Positions

The difference in energy between upper and lower energy levels participating in transitions $\Omega_{vJ}$ is

$$\Omega_{vJ} = E_{v',J'} - E_{v''J''}$$

where

$$E_{vJ} = h\epsilon(T_e + G(v) + F_s(J))$$

$T_e$ = electronic energy (cm$^{-1}$)

= 0 for ground state

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_x e (v + \frac{1}{2})^2 + \omega_y e (v + \frac{1}{2})^3 + \omega_z e (v + \frac{1}{2})^4 + \ldots$$

$$F_s(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2$$

$$D_v = D_e + \beta_e(v + \frac{1}{2})$$

The subscript $s$ differentiates electron spin components. For multiplet states there is an expression for each spin component characterized by a spin splitting constant. The form of the expression depends upon the angular momentum coupling employed.

For H$_2$ (all values in cm$^{-1}$, Ref 34)

$\omega_e = 4401.213^*$

$\omega_x e = 121.336^*$

$\omega_y e = 0.8129^*$

$\omega_z e = 0.0$

$B_e = 60.8530$

$\alpha_e = 3.0622 + 0.0577 (v + \frac{1}{2}) + 0.0051 (v + \frac{1}{2})^2$

$D_v = 0.0471 - 0.00274 (v + \frac{1}{2}) + 0.00040 (v + \frac{1}{2})^2$

$H_v = [4.9 - 0.5 (v + \frac{1}{2})]10^{-5}$

* accurate for $v = 0, 1, 2, 3$.

In addition, each of the line positions is pressure shifted. To good approximation this shift can be written for the Q branch lines as

$$Q(J) = a_J \rho + b_J \rho^2$$
where $p$ is the density and $b_J$ is small and will be taken to be zero here. $a_J$ is related to the relative population of the initial $j$th level $n_j/n$ [68]

$$a_J = a_o + a_c \frac{n_j}{n}.$$ 

For $H_2$, $a_o = -(2.0 \pm 0.2) \times 10^{-3}$, $a_c = -(1.7 \pm 0.4) \times 10^{-3}$ cm$^{-1}$/amagat at 300 K.
Appendix E

Analytical Form of Anti-Stokes Spectrum

The formula for the general case of a broadband Stokes laser of Gaussian profile and narrow, but finite band pump laser beams is given by Eq. (55) of Yuratich [12]:

\[
S_{as}(\omega_{as}) = \left[\exp(-\delta_{as}/\gamma_{2d}^2)/(\pi \gamma_{2d})\right]
\]

\[
\times \left\{ \chi_{NR}^2 - \frac{2}{\gamma_{2d}} \sum_j \chi_{NR} \ a_j \text{Im}(\tilde{w}_j) - \frac{\sqrt{\pi} \gamma_{2d}}{\gamma_{2d} \gamma_d} \sum_{j,k} a_j a_k \text{Im} \left( \frac{\tilde{w}_j + \tilde{w}_k^*}{\Delta_{kj} + i(\gamma_j + \gamma_k)} \right) \right\}
\]

where \( \tilde{w}_j = w \left( \frac{n_{2d}\delta_{as} - \Delta_j + i\gamma_j}{\gamma_{2d}/\gamma_d} \right) \)

and \( w(z) \) is the complex error function given by

\[
w(z) = \exp(-z^2) \left[ 1 + \frac{2i}{\sqrt{\pi}} \int_0^z \exp(t^2) dt \right]
\]

\[
= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{z-t} dt, \quad \text{Im}z > 0.
\]

\[
a_j = \frac{N_n c^4}{\hbar n_2 \omega_2^2} \Delta_j \frac{d\sigma}{dn} \bigg|_j
\]

\[
\delta_{as} = \omega_{as} - \omega_{as}^o ; \quad \gamma_d = (\gamma_1^2 + \gamma_2^2)^{1/2}
\]

\[
\gamma_{2d} = (\gamma_2^2 + \gamma_d^2)^{1/2} ; \quad n_{2d} = (1 + \gamma_2^2/\gamma_d^2)^{-1} = (\gamma_d/\gamma_{2d})^2
\]

\[
\Delta_{kj} = \tilde{\Delta}_k - \tilde{\Delta}_j ; \quad \tilde{\Delta}_j = \Omega_j - (\omega_{s}^o - \omega_{s}^o)
\]

\[
\gamma = \gamma/\sqrt{\ln2}
\]

\( \omega_{as}^o, \omega_{s}^o, \omega_1^o \) = the anti-Stokes, Stokes, and pump center angular frequencies, respectively.

\( \gamma_1, \gamma_2, \gamma_s, \gamma_j \) = the pump #1, pump #2, Stokes, and Raman linewidths (HWHM), respectively

\( \Omega_j \) = Raman resonance angular frequency (calculated in Appendix D).
Appendix F
Computed H₂ CAR Spectra

The following figures show calculated H₂ CAR spectra for a range of temperatures: 800 ≤ T ≤ 1800 K, ΔT = 100 K. Each figure consists of four spectra at the same temperature but computed with differing number density and Stokes beam width: ρ = 1 and 100 amagat; Γ_s = 100 and 250 cm⁻¹. The other fixed parameters assumed for the computation are:

- Stokes beam center: 14679 cm⁻¹ (5812 Å)
- Pump beam center: 18797 cm⁻¹ (5320 Å)
- Pump beam width (FWHM): .8 cm⁻¹

Each spectrum is normalized to the maximum peak intensity of that spectrum. Instrument profile convolution is not included.
F. 1. Computed H₂ CAR Spectra at T = 800 K.
F. 2. Computed H₂ CAR Spectra at T = 900 K.
F. 3. Computed H₂ CAR Spectra at T = 1000 K.
F. 4. Computed $\text{H}_2$ CAR Spectra at $T = 1100$ K.
F. 5. Computed $H_2$ CAR Spectra at $T = 1200$ K.
F. 6. Computed H$_2$ CAR Spectra at T = 1300 K.
F. 7. Computed H₂ CAR Spectra at T = 1400 K.
F. 8. Computed $\text{H}_2$ CAR Spectra at $T = 1500$ K.
F. 9. Computed H₂ CAR Spectra at T = 1600 K.
F. 10. Computed H₂ CAR Spectra at T = 1700 K.
F. 11. Computed H₂ CAR Spectra at T = 1800 K.
References

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