COHERENT ANTI-STOKES RAMAN SCATTERING OF GASES

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1. INTRODUCTION

The first measurements involving Coherent Anti-Stokes Raman Scattering (CARS) in gases were by Rado (1967) [1], who determined the nonresonant susceptibilities of a number of gases by using a ruby laser and a $\text{H}_2$ Stokes beam stimulated in a high pressure hydrogen cell. By employing pressure tuning of the Stokes beam, DeMartini (1972) [2] used CARS to scan the $\text{H}_2 \, \text{Q}_1$ line and measure the linewidth andDicke narrowing as a function of pressure. However, the major impetus for development of the technique came from the pioneering experiments of Taran and coworkers (1973) [3] in which the important potential application of CARS to concentration measurements in combustion systems was demonstrated.

With the subsequent development of tunable dye lasers of high power and narrow linewidth, the CARS experiment has become much more convenient and much progress has been made in its application. Its success in the study of flames and practical combustors such as automobile and jet engines has been quite impressive and will be discussed in other lectures. The use of CARS in studies of electric discharges and plasmas has been demonstrated [4] and it has also been utilized to measure rotational temperatures and relaxation rates in free jet expansions [5-8]. With picosecond sources, CARS has been applied to the study of gas phase reaction dynamics [9] and relaxation mechanisms [10].

The above applications are based on intensity measurements.
of CARS signals for molecules with known vibrational resonances. One can also take advantage of the high resolution capabilities of CARS to make accurate determination of Raman frequencies and linewidths. With pulsed lasers, high resolution (~0.01 cm⁻¹) vibrational [11,12] and rotational [13] CARS spectra have been reported and even higher resolution (~0.001 cm⁻¹) has been achieved using CW sources [14-17]. A more detailed discussion of many of these results is presented in a later section of this paper and in review articles [18-21].

2. THEORETICAL ASPECTS IMPORTANT FOR GASES

As discussed in earlier talks, the intensity (I) generated at the anti-Stokes frequency (ω₃) by plane wave pump (ω₁) and Stokes (ω₂) beams is given by [20-22].

\[
I_3 = \frac{16\pi^4 \omega_3^2}{n_1^2 n_2 n_3 c} |3\chi^{(3)}| I_1^2 I_2^2 L^2 \left[ \sin(\Delta kL/2) \right]^2
\]

where \( n_i \) is the index of refraction of the medium at \( \omega_i \), \(|3\chi^{(3)}|\) is the third order susceptibility, \( L \) is the length of interaction in the medium and \( \Delta k = 2k_1-k_2-k_3 \) is the momentum mismatch of the beams. The term in brackets is a maximum for \( \Delta k = 0 \), a condition achieved for liquids and solids by crossing the \( \omega_1 \) and \( \omega_2 \) beams at a small angle (<5°). For gases at low pressure, the dispersion is so small that collinear beams can be used and the term in brackets is unity for lengths of many centimeters.

Because of the \( I_1^2 I_2^2 \) power density dependence, large signal gains are obtained by focusing the beams. One treatment [22] of the effect of focusing assumes the focal region to be a cylinder of plane waves of diameter \( W_0 = 4\lambda f/\pi W \) and length equal to the confocal parameter \( b = \pi W_0^2/2\lambda_1 \). Here \( f \) is the lens focal length and \( W \) is the beam diameter at which the intensity has dropped to 1/e² of the peak value. Taking \( L = b \), \( \Delta k = 0 \), \( n_1 = 1 \) and \( P_3 = I_3 = \pi(W_0/2)^2 \), eq. (1) becomes

\[
P_3 = \left( \frac{2}{\lambda_1} \right)^2 \left( \frac{4\pi^2}{c^2} \right)^2 |3\chi^{(3)}|^2 P_1^2 P_2
\]

We note the fortuitous cancellation of beam diameter and lens focal length in this expression. More exact numerical calculations [23] show about a three fold increase in signal as \( f \) goes from 50 cm to 3 cm, a variation in accord with experimental observations [20]. The same calculations show that about 75% of the signal is generated within a length of 6b, implying that good