

CARS DIAGNOSTICS IN REACTING MIXTURES

James J. Valentini

Department of Chemistry
University of California
Irvine, CA 92717

INTRODUCTION

Coherent anti-Stokes Raman scattering (CARS) is a coherent optical variant of the inelastic light scattering process known as the Raman effect. CARS spectroscopy possesses the universality of Raman spectroscopy but with greatly enhanced sensitivity. It is insensitive to background luminescence, can be configured to allow remote measurements, has excellent temporal and spatial resolution, and can provide detailed information on both the chemical composition and physical state of gas, liquid, and solid samples. Because of these desirable attributes CARS has become an important optical diagnostic method, in particular for characterizing combustion media, plasmas, and chemically reacting mixtures. This article provides a brief introduction and overview of such applications of CARS, with a particular emphasis on the last of these.

PHENOMENOLOGY

CARS is non-linear optical process, a four-wave mixing process, in which optical radiation at three incident frequencies, $\omega_1, \omega_2, \omega_3$, interacts with a sample to generate optical radiation at a fourth frequency, ω_0 :

$$\omega_0 = \omega_1 - \omega_2 + \omega_3. \quad (1)$$

It is not necessary to have three distinct incident frequencies, and in fact CARS is most generally carried out with $\omega_1 = \omega_3$. It is conventional then to describe ω_1 as the "pump" or "laser" frequency, and designate it ω_L , and to call ω_2 the Stokes frequency, and write it as ω_S , so that Eq. 1 becomes

$$\omega_{AS} = \omega_L - \omega_S + \omega_L = 2\omega_L - \omega_S, \quad (2)$$

with ω_0 replaced by ω_{AS} , the so-called anti-Stokes frequency. Both ω_L and ω_S are provided by high intensity laser beams, and the signal at ω_{AS} is laser-like also, in that it too is coherent. The four-wave mixing process of CARS generates a signal at ω_{AS} under all conditions for all media. However, the magnitude of the signal is greatly enhanced when the frequency difference $\omega_L - \omega_S$ is resonant with the frequency, ω_R , of a Raman-allowed transition in the sample in which the four-wave mixing is taking place,

$$\omega_S = \omega_L - \omega_R \quad (3)$$

for which

$$\omega_{AS} = \omega_L + \omega_R \quad (4)$$

Although the Raman transition may be between different electronic states of a molecule or atom, it is most commonly a transition between different vibrational or rotational states of a molecule.

An energy level schematic for CARS illustrating the relation between ω_L , ω_S , and ω_{AS} is shown in Fig. 1. The molecular rovibrational states connected by the Raman transition are labeled r and g. The states labeled o and p are the lowest excited electronic states of the molecule, and those labeled v are virtual electronic states. Since only the frequency difference $\omega_L - \omega_S$ matters, the frequencies can be chosen arbitrarily, and only one of these frequencies need be tunable. To take advantage of efficient fixed-frequency and tunable pulsed lasers these frequencies are usually chosen to be in the visible region of the spectrum. A very common choice is a Nd:YAG/dye laser system, in which the second harmonic of the Nd:YAG laser at 532 nm serves both as ω_L and as the pump source for the dye laser, which generates ω_S .

Figure 2 shows a block diagram of the essential elements of a CARS spectroscopy apparatus. Note that the ω_L and ω_S beams are crossed at some angle θ , and that the angle between the ω_L and ω_{AS} beams is ϕ . The angle θ is chosen to satisfy the phase-matching requirement,

$$\underline{k}_L + \underline{k}_L = \underline{k}_S + \underline{k}_{AS} \quad (5)$$

where k_α is the wave-vector for the optical beam at frequency α . The magnitude of the wave-vector is given by

$$k_\alpha = \omega_\alpha n_\alpha / c, \quad (6)$$

with n_α the index of refraction at frequency α . For gases at pressures less than about 1 atmosphere, the medium is essentially dispersionless, that is $n_\alpha = 1$ for all α . For such dispersionless media $\theta = \phi = 0$ and all the beams are collinear.

APPLICATIONS

As a light scattering technique CARS has very high intrinsic temporal resolution, determined solely by the temporal widths of the laser pulses used to generate the signal. This makes CARS a very attractive technique for the investigation of rapidly time-varying phenomena, such as chemical reactions and photochemistry. This has been the principal application of CARS in our laboratory. The high temporal resolution is complemented by the universality of Raman scattering, making CARS suitable for monitoring chemical species not easily detected by other spectroscopic

techniques. Figure 3 shows an example of such an application. This is the vibrational Q-branch spectrum of $O_2(^3\Sigma_g^-)$ formed in the photolysis of ozone. The spectrum is recorded 2 nanoseconds after photolysis, and characterizes the nascent rotational and vibrational distribution of this O_2 photofragment, without any collisional relaxation. The peaks at $1550 - 1560\text{ cm}^{-1}$ are due to the 300K thermal distribution of O_2 impurity in the O_3 sample. Note that the photofragments are produced in high rotational and vibrational states that are not appreciably populated under 300K thermal equilibrium conditions. Figure 4 shows portions of a Q-branch CARS spectrum of H_2 formed in the $H + HI$ reaction. The H atoms were generated by pulsed-laser photolysis of HI, and the H_2 detected only 3.5 ns later, a time delay which allowed at most one H atom collision. Very high rotational and vibrational states are observed, with internal energies as great as $17,750\text{ cm}^{-1}$, equivalent to kT at 25,000 K. The spectrum indicates a population inversion between $v = 1$ and $v = 0$.

Transient species can also be detected under the non-thermal-equilibrium conditions of an electric discharge. Figure 5 shows a CARS spectrum taken in a pure oxygen microwave discharge. Q-branch and O-branch transitions of the ground and first excited vibrational states of $O_2(^3\Sigma_g^-)$, which is the ground electronic state, are evident. Also in the spectrum are transitions due to $O_2(^1\Delta_g)$, the first excited electronic state of molecular oxygen. Under the conditions of the discharge only a few percent of the 5-Torr sample is in the $^1\Delta_g$ state.

Figures 6 and 7 exemplify further the generality of CARS, showing detection of two important radical species, OH and CH_3 . The former was produced by laser photolysis of hydrogen peroxide, the latter by laser photolysis of methyl iodide. In each case the sample pressure was a few hundred millitorr, at which a spectrum with very good signal-to-noise ratio could be obtained in a scan of a few minutes duration.

ACKNOWLEDGMENTS

Financial support for this work was provided by the National Science Foundation and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U. S. Department of Energy.

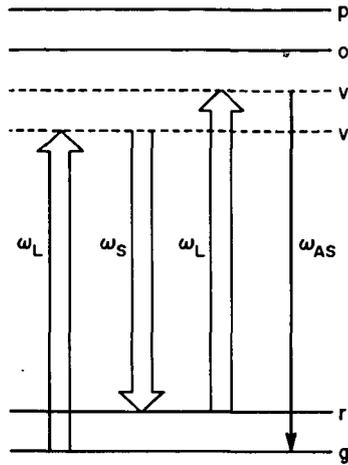


Figure 1. Energy level schematic for CARS.

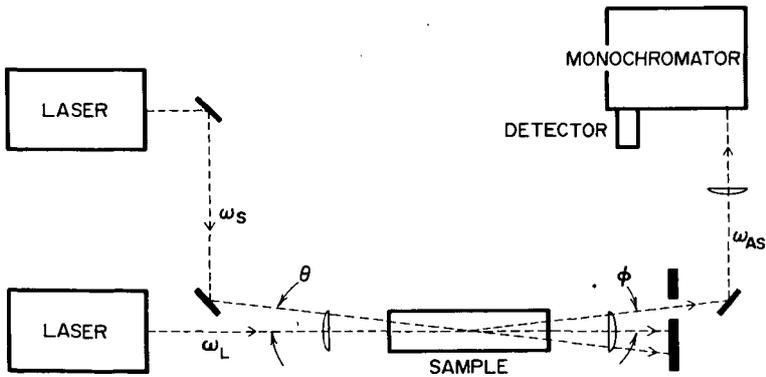


Figure 2. Block diagram of a CARS apparatus.

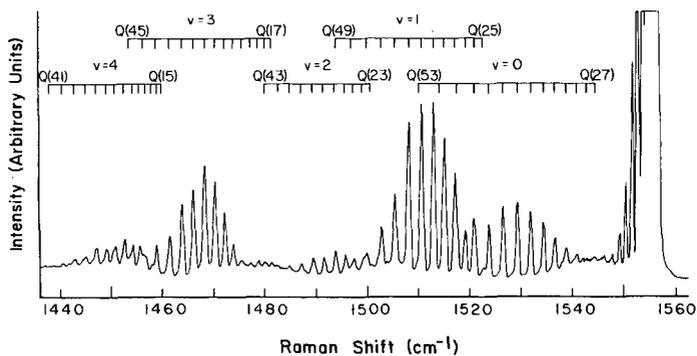


Figure 3. Vibrational Q-branch CARS spectrum of $O_2(3\Sigma_g)$ photofragment from the photolysis of O_3 .

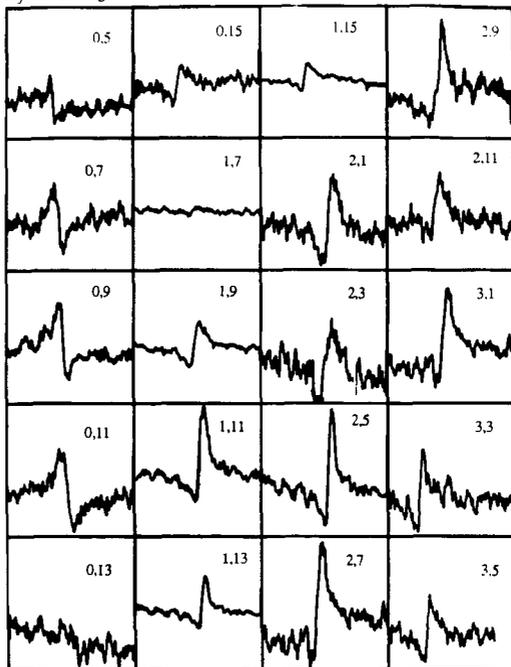


Figure 4. Vibrational Q-branch CARS spectrum of H_2 from the $H + HI \rightarrow H_2 + I$ reaction at 1.6 eV collision energy. The peaks are labeled as v, J .

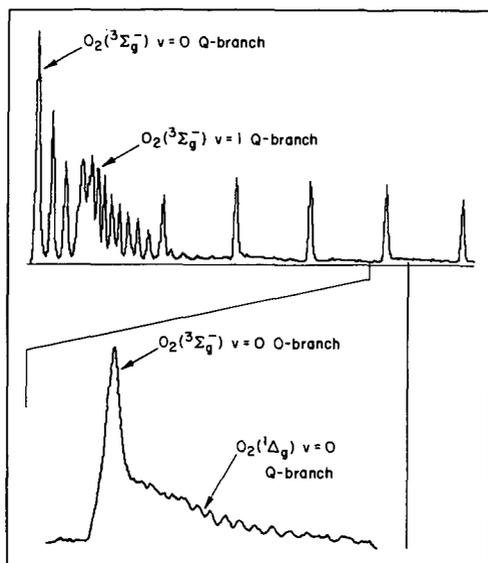


Figure 5. CARS spectrum of an O_2 microwave discharge.

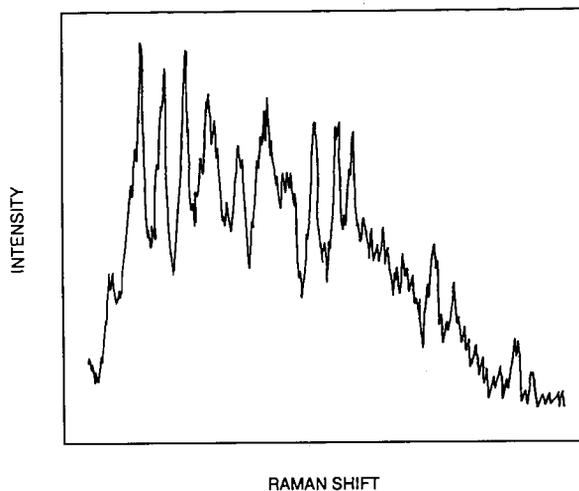


Figure 6. Vibrational Q-branch CARS spectrum of the CH_3 ν_1 vibration at 3000 cm^{-1} . The methyl radicals were formed by photolysis of methyl iodide.

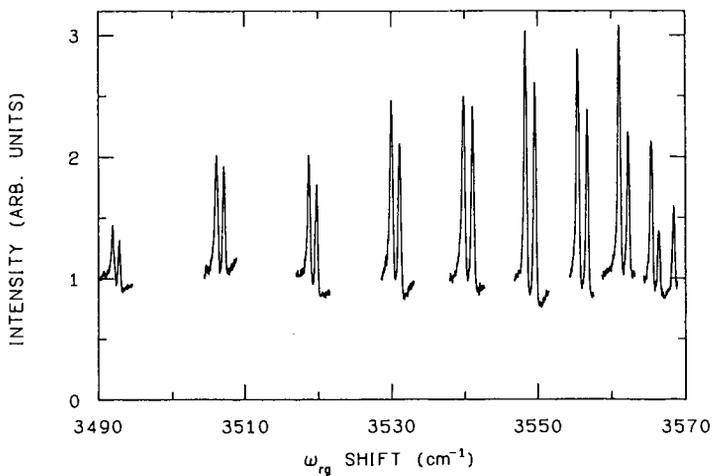


Figure 7. Vibrational Q-branch CARS spectrum of OH radicals from the photolysis of hydrogen peroxide.