Non-equilibrium thermometry in gases and plasmas using hybrid CARS

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Coherent Anti-Stokes Raman Scattering (CARS) has been proven to be a very useful spectroscopic tool for measuring Raman rotational and vibrational spectra [1]. Our fs/ps hybrid CARS diagnostic allows for single shot in-situ coherent Raman spectroscopy [2]. The molecular excitation is achieved using a combination of broadband femtosecond laser pulses, which coherently stimulate the transitions in the fingerprint spectral region. A time delay between the excitation pulses and the probe pulse ensures a drastic reduction of the non-resonant background, otherwise a limiting factor in CARS. This allows for real-time identification of molecular species based on their chemical fingerprint, with applications in the standoff detection and identification of chemical [3], biological [4], and explosive traces [5], with high specificity and sensitivity. For a half of century, CARS has been successfully used to measure the temperature in gases in plasmas by identifying the Maxwell-Boltzmann distribution of the vibrational and rotational modes of the constituent molecules (Eq. (1)).

$$N(v,J) \propto exp\left(-\frac{E_{vib}\,(v)}{kT_{vib}}\right) exp\left(-\frac{E_{rot}(J)}{kT_{rot}}\right) \tag{1}$$

The hybrid fs/ps CARS allows for measuring the distributions expressed in Eq. (1), and, hence, determine the vibrational and rotational temperatures in a single laser shot. This capability offers not only the identification of the state of thermodynamic non-equilibrium of the system, but it also provides the temporal dynamics of the vibrational and rotational temperatures. The talk will present rotational and vibrational temperature results obtained in conditions of thermodynamic equilibrium such as in steady-state flows, combustion, and plasmas, and also in non-equilibrium conditions such as in hypersonic flows and nanosecond discharge plasmas. Fig. 1 shows the case of a methane:air flame where the rotational and vibrational modes are thermodynamically in equilibrium, hence the vibrational and rotational temperature are identical. In the case of nanosecond plasma discharges we obtain thermal non-equilibrium during and immediately after the discharge, and we monitor the evolution towards equilibrium by recording the time delayed CARS spectra. During highly non-equilibrium conditions such as hypersonic flows, over-population of the higher vibrational levels occurs, such that the non-equilibrium is not only between the rotational (and hence translational) and the vibrational modes, but also between the vibrational modes which no longer follow a Maxwell-Boltzmann distribution. In this case the definition of temperature given by Eq. (1) fails completely, and we

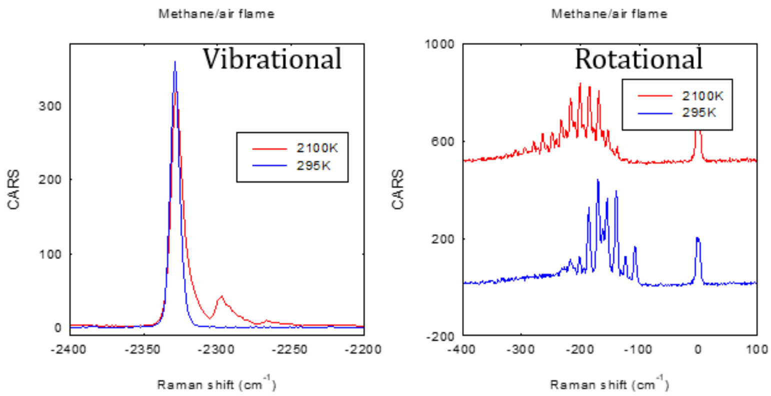

Fig. 1: Vibrational (left) and rotational (right) spectra indicating thermodynamical equilibrium in a methan:air flame.

can no longer measure a gas temperature. As an example, Fig. 2 shows the CARS spectra measured behind a normal shock in a Mach 6 hypersonic flow. During the high enthalpy flow (left in Fig. 2), the CARS spectra cannot be uniquely fitted using a Boltzmann distribution. The distribution of the first vibrational peaks indicate a temperature slightly higher than 3000K, while the higher vibrational levels are populated according to a distribution closer to 5000K. In this case the non-equilibrium is defined by the population distribution rather than a temperature. The right CARS spectrum in Fig. 2 shows that a vibrational temperature can be used to thermodynamically characterize the gas 1ms after the hypersonic interaction, while the gas there is still significant non-equilibrium between the vibrational and rotational energetic levels.

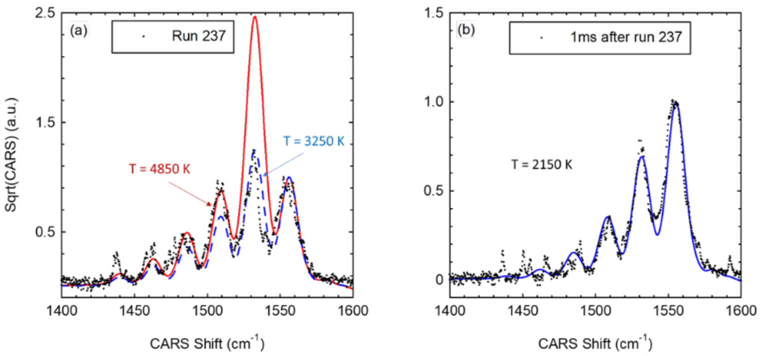

Fig. 2: CARS spectra during a highly vibrational non-equilibrium hypersonic flow (left), and in vibrational equilibrium 1ms after the Mach 6 flow (right).

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