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Stimulated Raman spectroscopy as the essential tool for studying collisional effects: application to combustion

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The main purposes of this paper are to give an overview of coherent Raman techniques with a particular emphasis on Stimulated Raman Spectroscopy (SRS) because this process can be considered as an essential tool for investigating collisional processes.

Coherent Raman techniques result from non linear processes described by the third order nonlinear susceptibility. Two processes play an important role in optical diagnostic methods : Stimulated Raman Spectroscopy (SRS) and Coherent anti-Stokes Raman Spectroscopy (CARS).

In CARS, the signal is generated at the frequency $2\omega_1 - \omega_2$, that is to say at a frequency different from those of interacting waves. In SRS, a non linear polarization appears at frequency ω_1 or ω_2 and modifies the two interacting waves. So, we can measure a gain at frequency ω_2 or losses at frequency ω_1 .

It is to notice that this SRS technique must not be confused with the auto stimulated Raman effect, where the ω_2 wave is generated by spontaneous Raman effect.

Laser systems for Coherent Raman Spectroscopy

Pulsed lasers play an important role in investigations of non linear processes. Indeed to increase the signal to noise ratio, it is most of the time easier to increase the signal than to reduce the noise.

In SRS, the best compromise to have a high signal to noise ratio consists in associating a high power pulsed laser as pump beam with a CW laser as probe beam. Argon or krypton lasers are generally used as probe laser because of their remarkable stability.

The tunable pulsed source is obtained by amplifying a very stable dye laser in a 3-stage amplifier system, which is pumped by a single mode Nd-YAG laser. That provides pulses in the MW range (Fig.1).

The great flexibility of our device at the Dijon University to pass from the SRS technique to CARS technique can be noticed : one only needs to mix a part of the single mode Nd-YAG laser with the tunable source ω_2 used in SRS. However, the frequency of such a single mode

Figure 1 :Experimental set-up at the Dijon University

commercial system Nd-YAG-laser can vary within a few GHz which is too much for high resolution spectroscopy. We have stabilized the laser frequency on an external Fabry-Perot interferometer which is controlled by a polarization stabilized He-Ne laser. The fringe patterns are imaged on to a diode array and three rings are detected. A computer program calculates the ring diameters and determines the wavelength. The stabilization is realized by slowly modifying the temperature control of the mini-continuous Nd-YAG laser.

A crucial point for spectroscopy is frequency measurement. In our device, since the pulsed tunable source is obtained by amplification of a CW dye laser, we have the possibility during the scan to achieve an absolute calibration of the dye frequency by using a travelling Michelson wavemeter. In the wavemeter at the Dijon University, a corner cube moves vertically in an evacuated cylinder over a distance of about one meter. The frequency reference is given by a stabilized He-Ne laser. The accuracy of the wavemeter is about 3 MHz (0.0001 cm^{-1}).

High resolution Raman data are now available with an accuracy similar to infrared data obtained by Fourier transform spectroscopy. That changes the role of Raman spectroscopy in molecular studies. Raman spectra are now recorded at a few Torr of pressure and are Doppler limited.

Optical diagnostics in combustion media

The main applications of coherent Raman techniques are the study of collisional processes via lineshape investigations leading to temperature and concentration measurements. The temperature is determined from the spectral shape of the Raman Q-branch, which is a strong

function of pressure, temperature and of foreign perturbers. In fact CARS and SRS play a complementary role in diagnostic methods :

- broad band CARS technique is used for direct measurements in a turbulent medium,
- but for obtaining precise information on the linebroadening, as lineshifting coefficients, SRS is chosen over CARS because the SRS signal is linear in the imaginary part of the susceptibility, and so there is no distortion in the lineshape as opposed to CARS .

That is why high resolution stimulated Raman spectroscopy has been used for the study of the Q-branch profile of major species present in combustions with the goal to model the different collisional processes.

The rotational energy transfer is an important process affecting the spectroscopy in the gas phase. The effects of collisional relaxation in nitrogen have been studied in 1992 by B. Lavorel et al. [1] ; the study is made in an extremely large range of pressure from 100 bar up to near 7000 bar. In this range of density the linewidth corresponds to the sum of two contributions :

- the rotational relaxation leading to a narrowing of the linewidth. The higher the density, the higher the narrowing.
- the vibrational dephasing which linearly increases with density.

This results in the observation of a minimum of the linewidth at 670 amagat. Concerning the lineshift, we observe an inversion of the shift at 522.3 amagat. This behavior is due to the competition between attractive and repulsive intermolecular forces.

Raman spectroscopy has a great advantage over IR techniques because of the possibility to work at high pressure and because it brings an important contribution to the determination of the relaxation matrix. Indeed, the diagonal elements W_{JJ} are related to the linebroadening and lineshifting coefficients :

$$W_{JJ} = \gamma_J - i\delta_J$$

The non diagonal elements are related to the collision induced transition rates :

$$W_{JJ'} = -K_{JJ'} \leftarrow J$$

If the determination of linebroadening coefficients is relatively easy in Infrared and Raman spectroscopy, more difficult is the determination of lineshifting coefficients which are often one order of magnitude weaker than the linebroadening. In Raman spectroscopy working at high pressure and using an accurate wavemeter, such measurements are possible.

Informations on non-diagonal elements of the relaxation matrix can be obtained :

- either from high density spectra. In this case, it is necessary to model the non diagonal elements by using fitting laws and, afterwards to adjust the parameter of these fitting laws by inversion of linebroadening coefficients through this relation $\gamma_J = - \sum_{J' \neq J} \text{Re } W_{JJ'}$

connecting diagonal to non-diagonal elements. Coherent Raman spectra are extremely important to

test the degree of accuracy in the modelling of relaxation rates.

- Or by direct state to state measurements. Stimulated Raman pumping plays an important role in this double resonance process. This is achieved in our device by mixing the single mode Nd-YAG laser with the pulsed dye laser previously described. Because of the high monochromaticity of lasers, Raman saturation is obtained in the Torr range of pressure. After an appropriate time interval, the rotational levels of the excited state are populated by energy transfers and could be probed by different techniques :

- by using the REMPI process (Resonance Enhanced Multiphoton-Ionization) Farrow and Sitz [2] have studied N_2 .

- by infrared spectroscopy, G. Millot and Cl.Roche [3] have recently measured the energy transfer rates in CO_2 .

In most applications for motors or reactors, N_2 is used as probe molecule. A particular interest has been focused in our laboratory on the following collisional systems : N_2 , O_2 , CO_2 , H_2O and also the mixtures N_2-O_2 , N_2-CO_2 , N_2-H_2O .

H_2 , H_2-H_2O , O_2 , O_2-H_2O are now studied at the Dijon University for the diagnostic of combustion of H_2 . The mixture H_2-H_2O is of importance, because H_2 is usually in excess in a rocket. These data will be used by the ONERA in France in the MASCOTTE program for the diagnostics of combustion in rocket engines.

Concluding remarks

Stimulated Raman Spectroscopy is a powerful tool to study collisional processes :

- it provides accurate linebroadening and lineshifting coefficients which are the basis for the determination of temperatures and concentrations.

- Raman spectra at high density allow a critical test of relaxation rate models.

- stimulated Raman pumping allows direct measurement of state to state rotational energy transfers for any molecule.

A detailed survey of the key developments in high-resolution Coherent Raman Spectroscopy as well as of its application are given in Refs [4,5].

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