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COHERENT RAMAN SPECTROSCOPY IN GASES

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ABSTRACT

The instrumental resolution in nonlinear coherent Raman spectroscopy is determined by the convoluted linewidths of the lasers used for excitation. This is of special importance for the investigation of high resolution rotation-vibrational spectra of gases. It is now possible not only to determine line positions with accuracies better than 10^{-3} cm^{-1} , but also to study linewidths as a function of pressure. Methods and results of coherent anti-Stokes Raman scattering are treated here.

INTRODUCTION

The applicability of the techniques of Raman spectroscopy to the investigation of gases has been greatly improved by the development of the different methods of coherent or nonlinear Raman scattering. When two laser beams, one of which has a tunable frequency, are brought to a common focus in a sample, a stimulated Raman process occurs as soon as the frequency difference between the two lasers is equal to a Raman active rovibrational or rotational transition frequency of the sample and the corresponding state is populated above equilibrium. This enhanced population can be detected in different ways : by coherent anti-Stokes Raman scattering (CARS) /1/ or the corresponding Stokes process (CSRS) /2/, by a gain in one of the beams (stimulated Raman gain spectroscopy, SRGS) /3/ or a loss in the other one (inverse Raman spectroscopy, IRS) /4/, or even by detection of a photoacoustic signal (photoacoustic Raman spectroscopy, PARS) /5/. The selective ionisation of the excited molecules by a third ultraviolet laser pulse (ionisation detected stimulated Raman scattering, IDSRS) /6/ has considerably increased the sensitivity in special cases by about a factor of 1000 over the other techniques. Here we want to report on CARS experiments carried out in our laboratories in Munich and in Dijon.

CARS SPECTROSCOPY IN THE CAVITY OF AN ARGON ION RING LASER

The possibility to excite CARS spectra with c.w. lasers has been demonstrated by Barrett and Begley /7/ and further developments of the technique are due to Hirth and Voilrath /8/ and Fabelinsky et al. /9/.

In Munich a CARS spectrometer has been constructed consisting of a single mode c.w. argon ion ring laser with an intracavity power of over 100 W, a c.w. tunable dye ring laser with a power of 100 to 200 mW, and an intracavity sample cell with focusing spherical mirrors /10/. The CARS signals are detected after appropriate filtering by a photomultiplier connected to a photon-counting system and a dedicated computer for data acquisition. The instrumental resolution is determined by the combined linewidths of the two lasers which amounted to $\sim 10^{-3} \text{ cm}^{-1}$.

The CARS spectra of the Q-branches of nitrogen /10/ and the ν_1 bands of methane /11/, hydrogen sulfide /12/ and ammonia /13/ have been resolved at pressures between 1.3 and 2 kPa, assigned and evaluated. The Q-branch of the ν_3 band of methane has also been studied /14/. In the case of the Q-branches of the ν_1 band of benzene /14/ the rotational structure could not be resolved.

CARS SPECTROSCOPY WITH FLASHLAMP PUMPED DYE LASER AMPLIFIERS

As an alternative to the c.w. intracavity operation described above high power and narrow linewidth can be obtained by combining the power of pulsed lasers with the spectral qualities of c.w. lasers by injection-locking. If single mode radiation is injected into a pulsed laser cavity the length of which is adjusted to a multiple of the injected wavelength, one can force the pulsed laser to deliver its power on a single longitudinal mode at the same wavelength. The CARS spectrometer in Dijon consists of two flashlamp pumped dye laser amplifiers which are injection-locked to the frequency of stabilized single mode c.w. dye lasers or a krypton and a dye laser /15/. The amplifiers are operated in a 3m long ring cavity with four mirrors. Mode matching is achieved by adjusting the cavity length through piezoelectric translation of one mirror with an automatic electronic servo-loop. The amplifiers deliver pulses of about 300 ns duration with peak powers up to 12 kW and a repetition rate of 10 Hz, resulting in a line width of $2 \cdot 10^{-4} \text{ cm}^{-1}$. The two pulsed beams are sent on a beam splitter which mixes the two beams and sends the resulting two equivalent combinations on separate paths to be focused in two cells of 40 cm length, one sample cell and one reference cell filled with an inert gas which is non-resonant at the excitation frequencies. After appropriate

optical filtering the CARS signals are monitored by two photomultipliers and the ratio is stored in a data acquisition system and averaged over 8 or 16 successive shots. Wavelength calibration is achieved with an iodine absorption cell, a wavemeter /16/ measuring the wavenumber at the start and at the end of each scan, and a confocal Fabry-Perot-interferometer for interpolation.

With this spectrometer the CARS spectra of the Q-branches of oxygen /17/ and of the ν_1 band of carbon dioxide have been investigated /18/. O_2 spectra have been recorded at pressures between 1.3 and 130 kPa and by adjustment of the line profiles collisional line broadening coefficients have been determined for the lines with rotational quantum numbers $N = 1$ to $N = 17$, the values varying monotonically from 52 to $38 \cdot 10^{-3} \text{ cm}^{-1}/\text{atm}$.

For the first time it has been possible to resolve the rotational structure of the Q-branch of the ν_1 band about 1285.5 cm^{-1} at a pressure of 5 kPa and to assign the lines for angular momentum quantum numbers $J = 8$ to $J = 38$. The line positions are in excellent agreement with those calculated from molecular constants given in the literature /19,20/. The collisional linewidths have been obtained by a least-squares fitting procedure taking Doppler broadening into account. Fig.1 shows the good agreement between the experimental and the adjusted line profiles.

Fig. 1
CARS spectrum of the Q-branch
of the ν_1 band of carbon dioxide
at room temperature and a pres-
sure of 5 kPa.

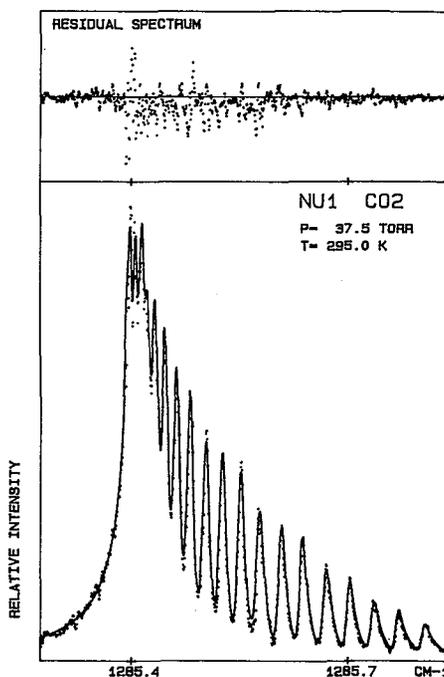
Lower traces :

... experimental profile,

— adjusted profile,

upper part :

.... residual spectrum.



CONCLUSION

The investigation of high-resolution CARS spectra discussed here and the results of the other techniques of coherent Raman spectroscopy are not only important for the determination of molecular structure, but form also a basis for the application of CARS to the measurement of temperatures and concentrations in hot gases, especially combustion processes. These applications and other aspects of nonlinear Raman spectroscopy, included a more detailed account of our work, are being published elsewhere /21/.

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