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Author's Review

High-Resolution Nonlinear Raman Spectroscopy in Gases

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The applicability of Raman spectroscopy to the investigation of gases has been greatly improved by the development of the different methods of 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. The Raman resonance can be detected in different ways: by coherent anti-Stokes Raman scattering (CARS) or the corresponding Stokes process (CSRS), by a gain in one of the beams (stimulated Raman gain spectroscopy, SRGS) or a loss in the other one (inverse Raman spectroscopy, IRS), or even by detection of a photoacoustic signal (photoacoustic Raman spectroscopy, PARS). The selective ionisation of the excited molecules by a third ultraviolet laser pulse (ionisation detected stimulated Raman scattering, IDSRS) has considerably increased the sensitivity in special cases.

The instrumental resolution of these techniques 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.

INTRODUCTION

As long as no lasers with variable frequency were available, only the Raman lines with the highest peak intensity could be observed with the stimulated Raman effect^{1,2} because these alone were sufficiently amplified. The observation of the inverse Raman effect³ required a strong continuum source simultaneously with the narrow-band pulsed laser. For the first demonstration of coherent anti-Stokes Raman scattering⁴ the second frequency was generated by stimulated Raman scattering in different liquids.

The development of tunable dye lasers (see ⁵) made the different techniques of nonlinear or coherent Raman scattering applicable as a powerful

tool of molecular spectroscopy. In this article we restrict our attention to those techniques which have been used to record high-resolution spectra of molecules in the gas phase.

All these coherent Raman processes are generated when two laser beams, one of which has a tunable frequency, are brought to a common focus in the sample (see Figure 1). As soon as the frequency difference $\omega_1 - \omega_2$ of the two

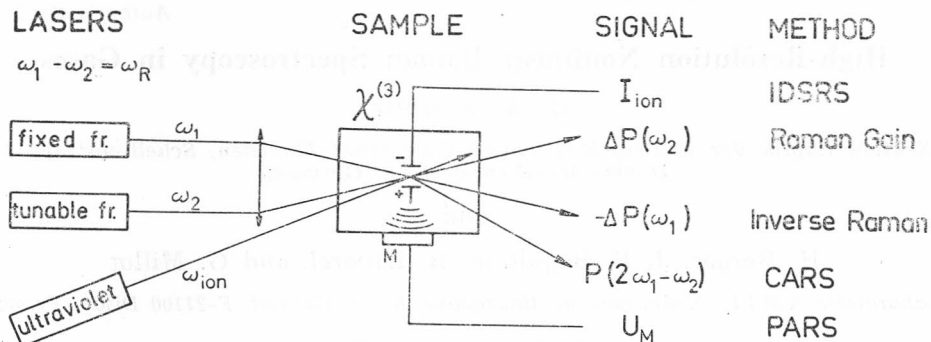


Figure 1. Various nonlinear Raman scattering processes (M sensitive microphone, ω_{ion} ionizing laser frequency).

lasers corresponds to the frequency ω_R of a Raman allowed rovibrational transition, a nonlinear interaction with the molecules occurs via the third order nonlinear susceptibility χ^3 (see references 6–11) and the corresponding state is coherently excited. This interaction can be monitored by one of the methods mentioned in the abstract (and summarized in Figure 1) and the spectrum is obtained by scanning the tunable laser.

In this article we want to describe briefly these different techniques of nonlinear Raman spectroscopy and give some examples of their application. More detailed information can be found in previously published books^{9,12,13} and review articles^{7,11,14,15}.

STIMULATED RAMAN GAIN SPECTROSCOPY (SRGS) AND INVERSE RAMAN SPECTROSCOPY (IRS)

Stimulated Raman amplification with tunable lasers has at first been demonstrated in liquids^{16–18}. With the help of a multipass optical cell high enough sensitivity was achieved by Owyong *et al.*¹⁹ for nearly Doppler-limited resolution in the spectrum of the ν_1 band of methane at a pressure of 4.6 kPa by the c. w. SRGS technique. This work marked a breakthrough of nonlinear Raman spectroscopy to the resolution of the Q-branches of rotation-vibrational bands of polyatomic molecules and their detailed analysis.

The mechanical or electrooptical modulation of c. w. lasers was soon superseded by the use of injection locked pulse amplified pump lasers in combination with quasi- c. w. probe lasers^{14,20}. When the probe laser has a higher frequency than the pump laser, one obtains a Raman loss or inverse Raman spectrum, when the probe laser has the lower frequency, a Raman gain spectrum is observed by tuning one of the two lasers. Through the pulse amplification of the pump laser its linewidth is increased over that of a c. w. laser to between 60 and 100 MHz (0.002 to 0.003 cm^{-1}). Nevertheless, the resolution in

these experiments is largely determined by Doppler and residual pressure broadening.

Figure 2 shows the experimental setup for high-resolution inverse Raman spectroscopy at the Université de Bourgogne. The probe laser is a single mode argon ion laser stabilized to a hyperfine component of $^{127}\text{I}_2$ by saturated absorption spectroscopy. The pump source is a very narrow bandwidth c.w. dye laser amplified by a fourstage dye amplifier pumped by a frequency-doubled Nd:YAG laser and delivers pulses of about 1 MW at a repetition rate of 10 Hz. A Michelson wavemeter operating in vacuum provides measurements of the absolute dye laser frequency with an accuracy of about 2 MHz²¹.

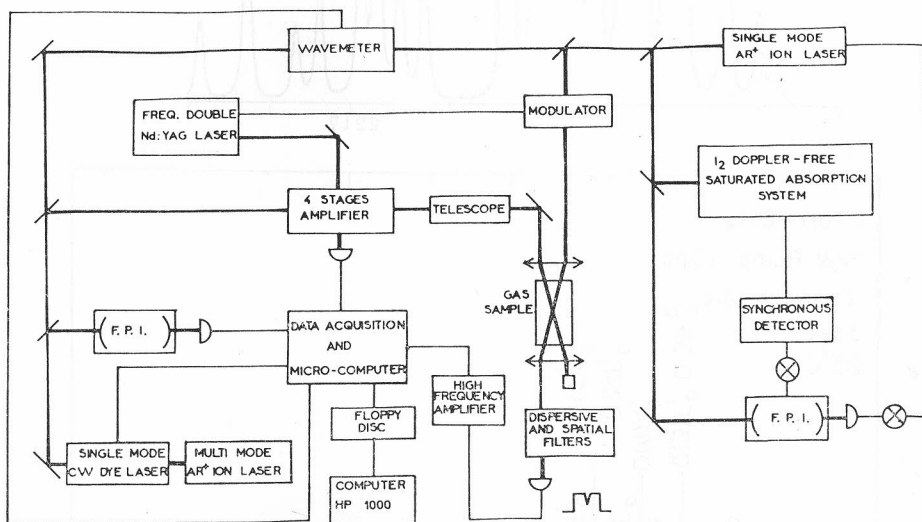


Figure 2. Experimental setup for high resolution inverse Raman spectroscopy (from Millot *et al.*, Ref. 25).

Using the techniques of SRGS or IRS the Q-branches of the ν_1 bands of the spherical top molecules $^{12}\text{CH}_4$ ^{19,20}, $^{13}\text{CH}_4$ ²², $^{12}\text{CD}_4$ ^{23,24}, $^{13}\text{CD}_4$ ²⁵, SiH_4 ^{26,27}, GeH_4 ^{15,28,29}, CF_4 ³⁰ and SF_6 ³¹ have been resolved and analysed. As example we show in Figure 3 a part of the ν_1 band of methane $^{12}\text{CH}_4$ ²⁰. The simulated spectrum in the upper part of the figure was calculated by using the energy levels obtained in the course of analysis of the CARS spectrum of the same band³², which will be discussed below. A more recent example is the inverse Raman spectrum of the ν_1 band of the rarest methane isotope $^{13}\text{CD}_4$ ²⁵ which has been analyzed together with the infrared spectra of this molecule. Figure 4 shows a section of the extended spectrum, in which also contributions from the $2\nu_4$, $\nu_2 + \nu_4$, and $2\nu_2$ bands were recorded, and demonstrates the excellent agreement between the experimental (upper) and calculated (lower) spectrum.

The Q-branches of the CH-vibrations of the symmetric top molecules ethane C_2H_6 ¹⁴ and cyclopropane C_3H_6 ³³ yielded very complicated structures under high resolution. In such cases it is useful to reduce the complexity of the spectra by cooling or by supersonic expansion molecular jets in which the temperature and thus the number of populated rovibrational levels is

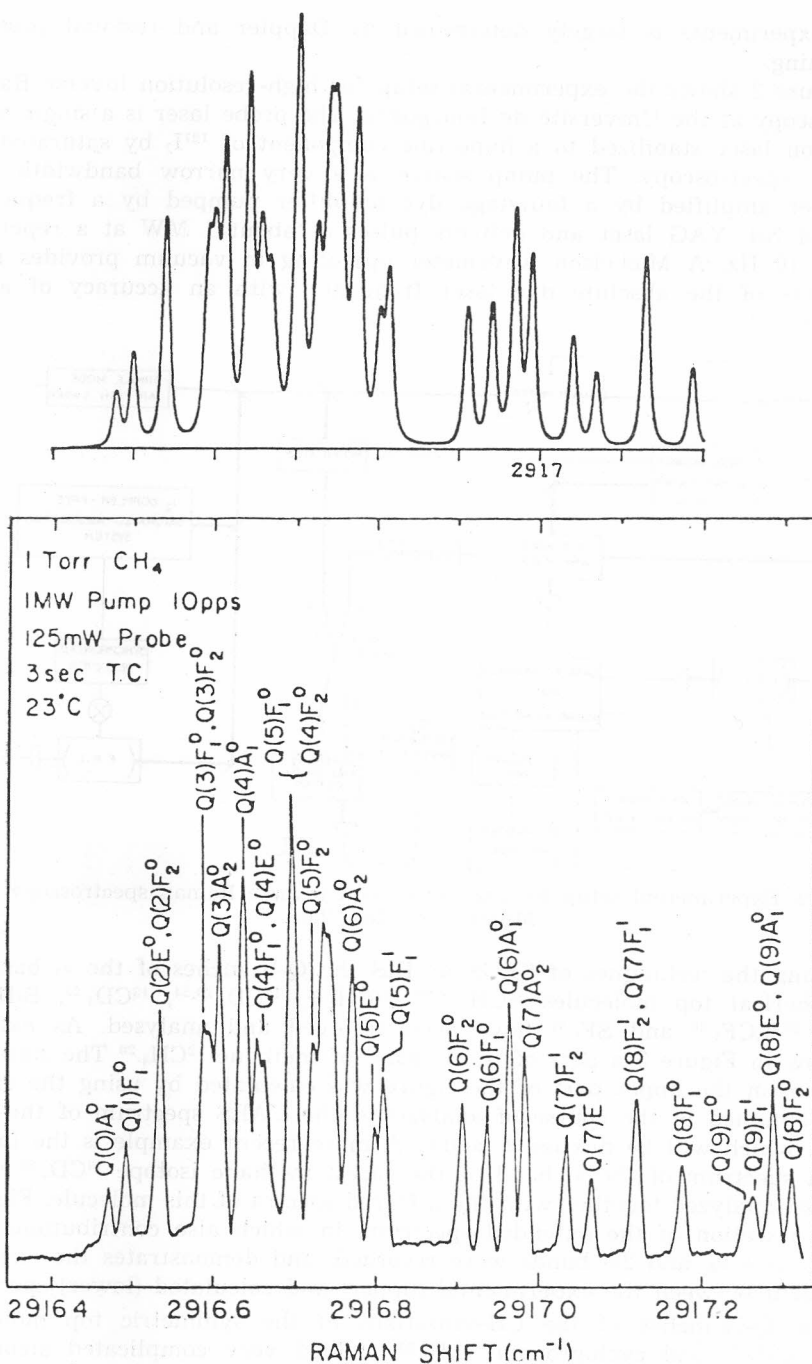


Figure 3. Inverse Raman spectrum of the ν_1 band of methane $^{12}\text{CH}_4$ at a pressure of 130 Pa. Top: calculated spectrum, Bottom: experimental spectrum (from Owyong, Ref. 20).

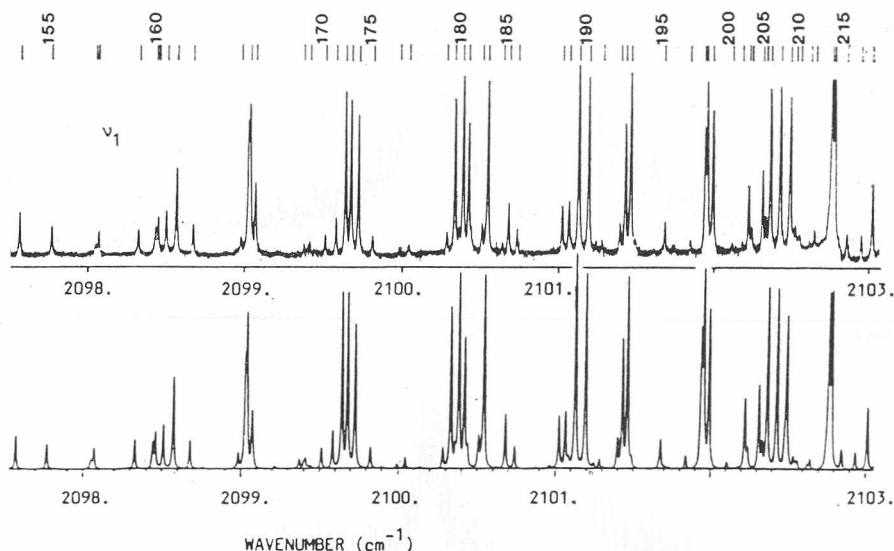


Figure 4. Inverse Raman spectrum of the ν_1 band of methane $^{13}\text{CD}_4$ at a pressure of 4 kPa. a) Experimental and b) calculated spectrum. Part of the complete pentad spectrum ($2\nu_4$, $\nu_2 + \nu_4$, ν_1 , ν_3 , $2\nu_2$) from Millot *et al.*, Ref. 25).

drastically reduced, as had been demonstrated already for methane³⁴. Whereas for the prolate top C_2H_6 the Raman spectrum was considerably simplified¹⁴, the effect is less pronounced for the oblate tops because of the many low lying rotational levels due to K-splitting.

Figure 5 shows inverse Raman spectra of the Q-branch of the ν_1 band of cyclopropane under different conditions. Reduction of pressure and temperature greatly improves the resolution, however, also in a molecular beam experiment at an effective temperature of 50 K the spectrum remained complicated³³. In addition to the ν_1 Q-branch, other bands appear in this spectral range at 3016 cm^{-1} , 3018 cm^{-1} , 3020 cm^{-1} , and 3036 cm^{-1} , respectively. Vibrational assignments are not easy except for $2\nu_2$ at 3016 cm^{-1} because many bands fall in this region and can interact with ν_1 through Fermi or Coriolis interactions. As a consequence the ν_1 band is strongly perturbed and rotational assignments are not possible in the scheme of an isolated band. Starting from a deconvoluted spectrum, Pliva³⁵ has arrived at an assignment using an effective Hamiltonian with seven interacting states.

Another interesting application of nonlinear Raman techniques is the measurement of pressure broadening coefficients. Many investigations have concentrated on nitrogen N_2 because of its importance for temperature and pressure determination by the CARS technique³⁶. The temperature dependence of collisional broadening in N_2 had been measured by two groups independently^{37,38} and agrees so well, that a joint evaluation was possible³⁹. The unified data were used to determine the characteristic parameters of fitting laws for rotational transfer rates which are needed to calculate line profiles at high pressure. Both a polynomial energy gap law (P.E.G.L.)⁴⁰ and an exponential energy gap law (E.G.L.)⁴¹ have been used to fit measurements

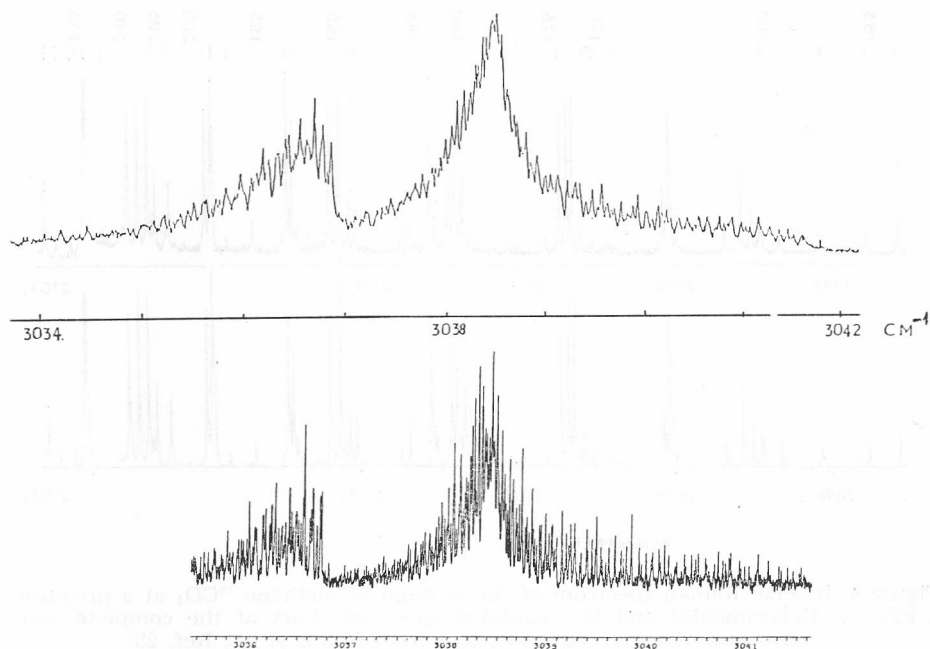


Figure 5. Inverse Raman spectrum of the ν_1 band of cyclopropane C_3H_6 .
 a) pressure 10 kPa, $T = 295$ K,
 b) pressure 2 kPa, $T = 220$ K (From Terki-Hassaine, Ref. 33).

up to pressures of 3.5 MPa. The results are compared in Figure 6. When the recently and accurately measured pressure shift of the rovibrational frequencies of N_2 ⁴² is taken into account, the fit with the E.G.L. model is significantly better at room temperature.

COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS)

The narrowest linewidths and the best resolution can be obtained with continuous lasers. The possibility to excite CARS spectra with c.w. lasers has been demonstrated by Barrett and Begley⁴³ and further developments of the technique are due to Hirth and Vollrath⁴⁴, and Fabelinsky *et al.*⁴⁵.

In order to make the best possible use of the power of a c.w. laser, we have constructed in Munich a CARS spectrometer 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, see Figure 7⁴⁶. 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 $\approx 10^{-3}$ cm^{-1} .

With this spectrometer the CARS spectra of the Q-branches of nitrogen⁴⁶ and the ν_1 bands of methane³², hydrogen sulfide⁴⁷ and ammonia⁴⁸ 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 studied⁴⁹. As an example

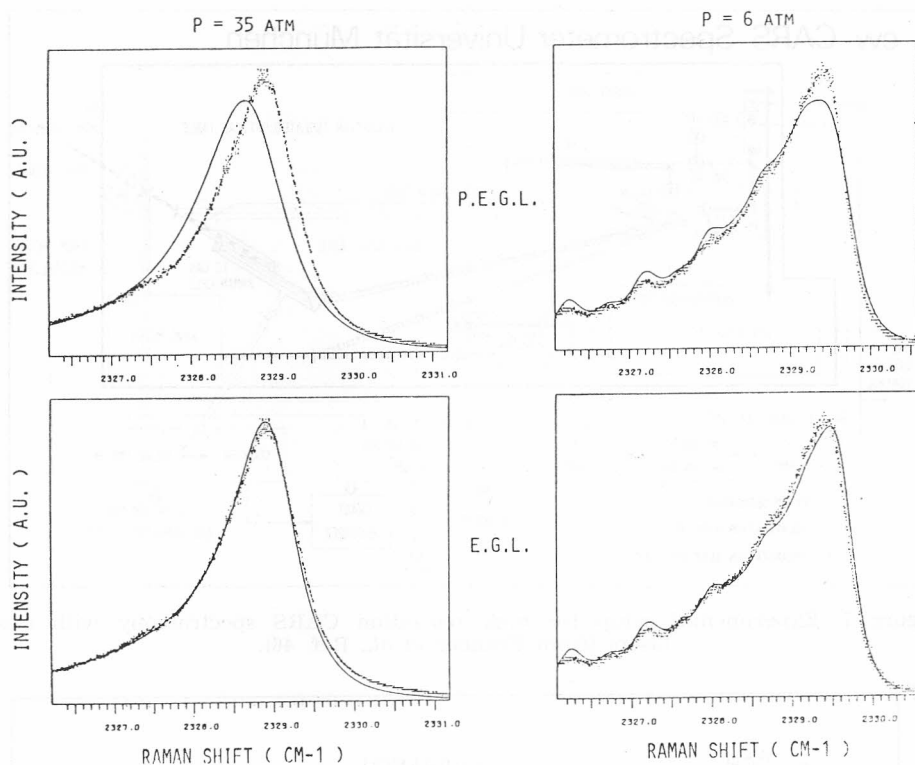


Figure 6. Inverse Raman spectra of the Q-branch of nitrogen N_2 at pressures of 3.5 MPa (left) and 0.6 MPa (right). The experimental points are fitted with profiles calculated from the P.E.G.L. (above) and E.G.L. (below) models (from Lavorel *et al.*, Ref. 39).

we show in Figure 8 the CARS spectrum of the ν_1 band of methane $^{12}CH_4$ which can be compared with the inverse Raman spectrum of Figure 3. In the course of the analysis of this spectrum it was found³² that about 10 energy levels with angular momentum quantum numbers from $J = 6$ to $J = 10$ had to be adjusted in an empirical fit in order to reproduce the band profile by computer simulation. Later this was confirmed by Lolck⁵⁰. The wavenumber and linestrength data of the empirical fit have also been used to calculate the upper spectrum in Figure 3.

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.⁵¹ The amplifiers are operated in a 3 m long ring cavity with four mirrors. Mode matching is achie-

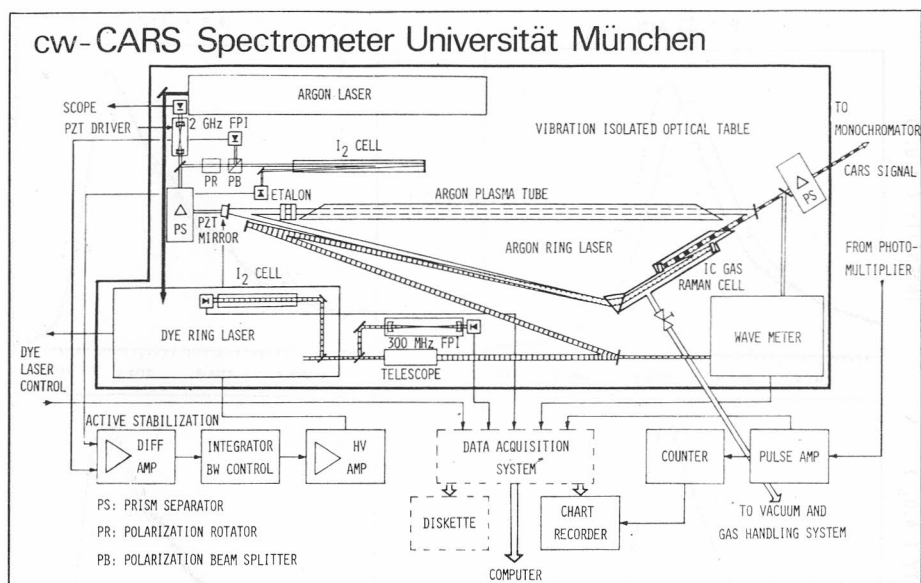


Figure 7. Experimental setup for high resolution CARS spectroscopy with c.w. lasers (from Frunder *et al.*, Ref. 46).

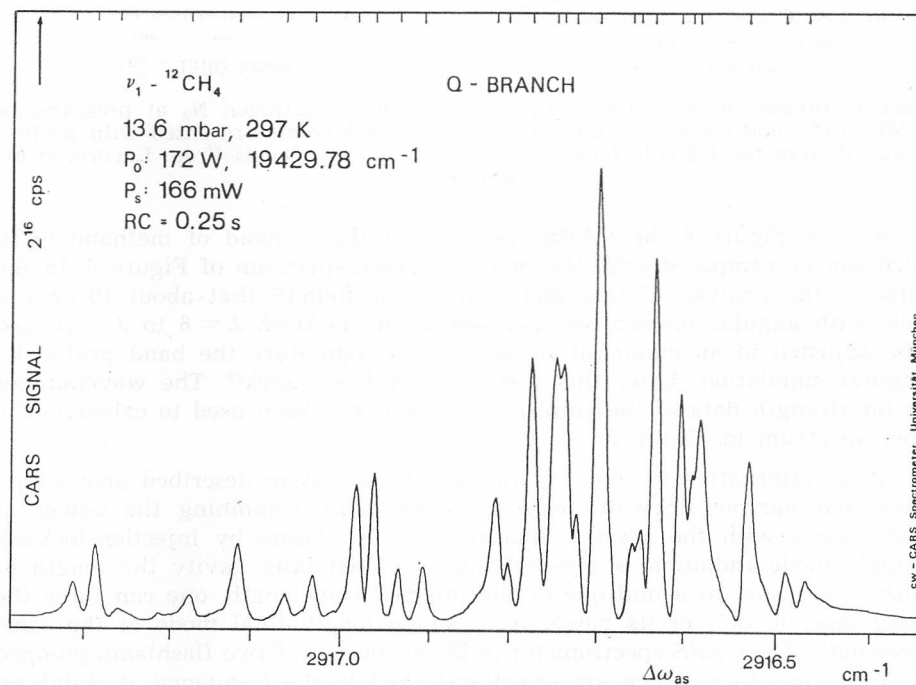


Figure 8. CARS spectrum of the ν_1 band of ${}^{12}\text{CH}_4$ at a pressure of 1.36 kPa (from Frunder *et al.*, Ref. 32).

ved by adjusting the cavity length through piezoelectric translation of one mirror with an automatic electronic servo-loop, see Figure 9. 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 $2.10^{-4} \text{ cm}^{-1}$. 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 wavemeter²¹ measuring the wavenumber at the start and at the end of each scan, and a confocal Fabry-Perot-interferometer for interpolation.

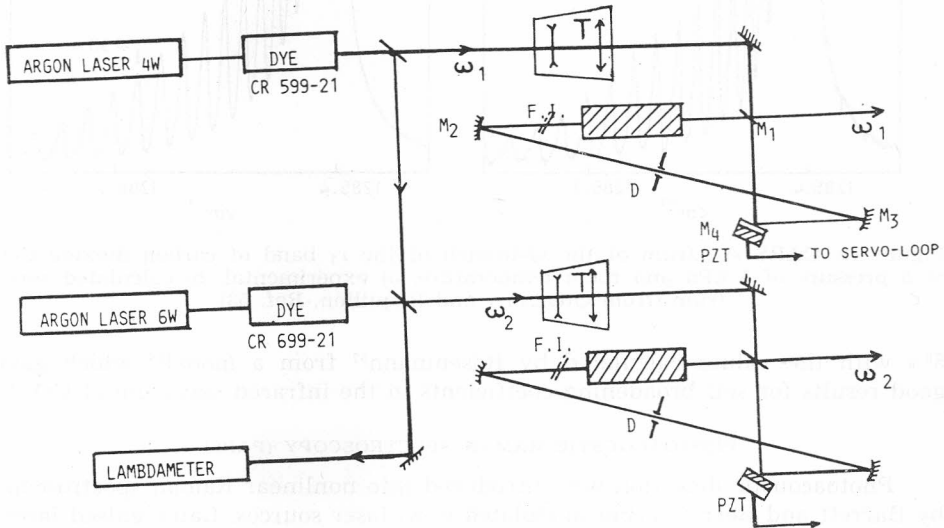


Figure 9. Laser configuration for high resolution CARS spectroscopy with injection-locked flashlamp-pumped dye laser amplifiers. (M mirrors, T magnifying telescopes, PZT piezo-translators, D diaphragms; from Boquillon *et al.*, Ref. 51).

With this spectrometer the CARS spectra of the Q-branches of oxygen⁵² and of the ν_1 band of carbon dioxide have been investigated^{53,54}. Oxygen 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 decreasing monotonically from 52 to $38.10^{-3} \text{ cm}^{-1}/\text{atm}$.

For the first time it has been possible to resolve the rotational structure of the Q-branch of the ν_1 band of CO_2 at about 1285.5 cm^{-1} at a pressure of 5 kPa and to assign the lines for angular momentum quantum numbers $J = 8$ to $J = 38$ as shown in Figure 10. The line positions are in excellent agreement with those calculated from molecular constants given in the literature^{55,56}. The collision linewidths have been obtained by a least-squares fitting procedure taking Doppler broadening into account and were found to agree within

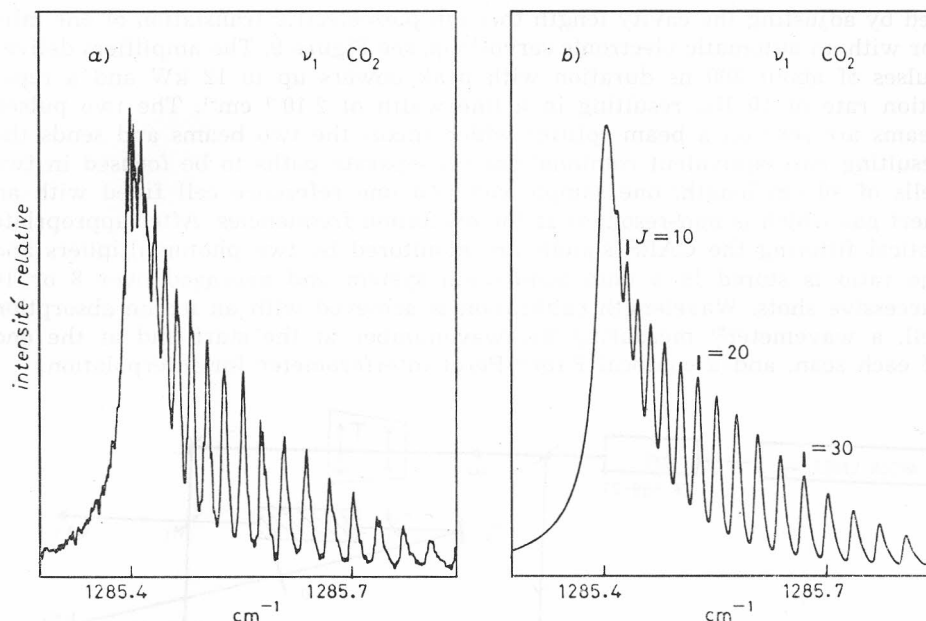


Figure 10. CARS spectrum of the Q-branch of the ν_1 band of carbon dioxide CO_2 at a pressure of 5 kPa and room temperature. a) experimental, b) calculated spectrum (from Ouazzany and Boquillon, Ref. 53).

50% with the values calculated by Rosenmann⁵⁷ from a model⁵⁸ which gave good results for self broadening coefficients in the infrared spectrum of CO_2 .^{59,*}

PHOTOACOUSTIC RAMAN SPECTROSCOPY (PARS)

Photoacoustic detection was introduced into nonlinear Raman spectroscopy by Barrett and Berry⁶⁰ using modulated c. w. laser sources. Later pulsed lasers were applied for the excitation of rotational and rovibrational PARS spectra⁶¹. In this technique the energy deposited in the sample by excitation of e. g. a vibration by the stimulated Raman process leads to a temperature and pressure increase through relaxation to translational energy and can therefore be detected by a sensitive microphone. Figure 11 shows a setup for PARS which uses a frequency-doubled Nd:YAG laser for the pump beam and a dye laser with amplifier pumped by the third harmonic of the Nd:YAG for the Stokes beam⁶¹. This makes the recording of pure rotational PARS spectra possible, a medium resolution spectrum of carbon dioxide is shown in Figure 12. There is no signal at the usual position of the Rayleigh line, because no energy is deposited in the sample. Although it was demonstrated⁶¹ that the sensitivity of the technique is sufficient to observe Q-branches at pressures below 1 kPa, to our knowledge no high resolution PARS spectra have been published so far.

* Note added in proof: In the meantime the same Q-branch has been resolved even better by the technique of SRGS at a pressure of 200 Pa employing a multiple reflection cell with 50 passes.⁶⁶

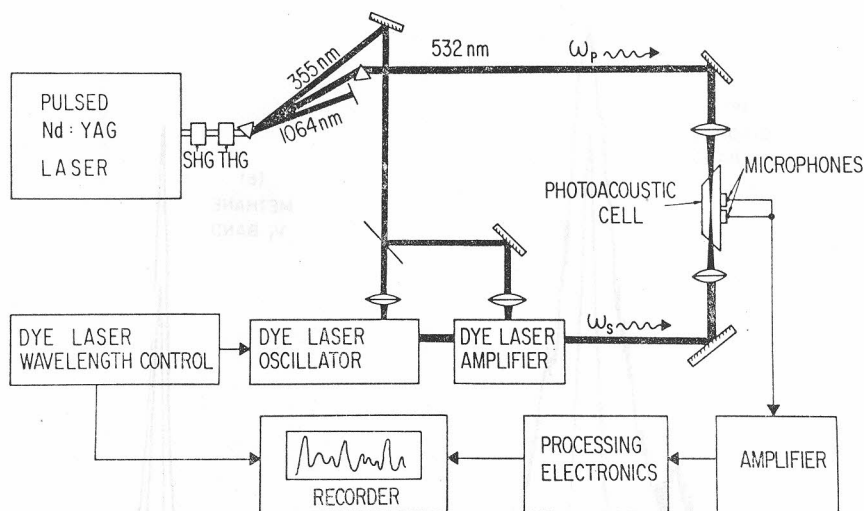


Figure 11. Experimental setup for PARS spectroscopy (from Barrett, Ref. 61).

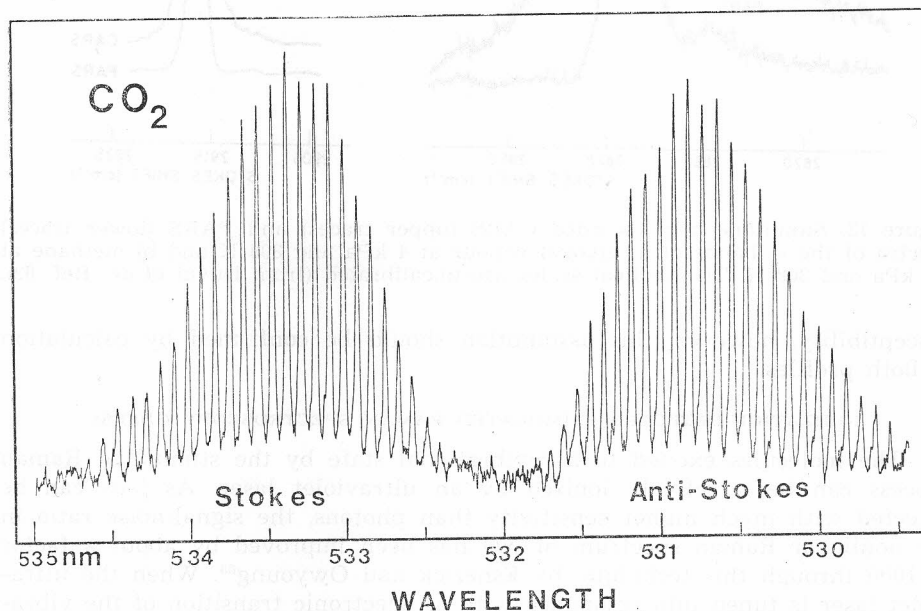


Figure 12. Rotational PARS spectrum of carbon dioxide at a pressure of 80 kPa (from Barrett, Ref. 61).

In another medium resolution experiment a direct comparison between PARS and CARS spectra excited under similar conditions has been made⁶². Figure 13 shows the spectra of the ν_1 bands of glyoxal and of methane at pressures of 4 kPa and 6.7 kPa, respectively. The broader appearance of the CARS profiles may be due to the contribution of the real part of the nonlinear

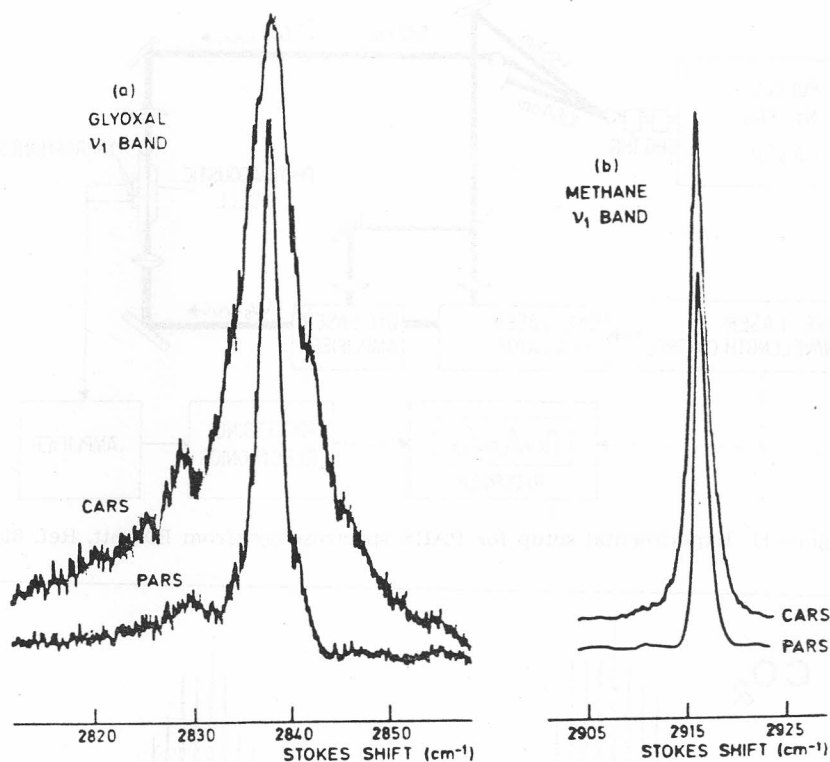


Figure 13. Simultaneously recorded CARS (upper traces) and PARS (lower traces) spectra of the ν_1 bands of a) glyoxal vapour at 4 kPa and 308 K and b) methane at 6.7 kPa and 308 K. The vertical scales are uncalibrated (from Duval *et al.*, Ref. 62).

susceptibility, however, this assumption should be confirmed by calculation of both profiles.

IONIZATION-DETECTED STIMULATED RAMAN SPECTROSCOPY (IDSRS)

The molecules excited to a rovibrational state by the stimulated Raman process can be selectively ionized by an ultraviolet laser. As ions can be detected with much higher sensitivity than photons, the signal/noise ratio in the nonlinear Raman spectrum of NO has been improved by about a factor of 1000 through this technique by Esherick and Owyong⁶³. When the ultraviolet laser is tuned into resonance with an electronic transition of the vibrationally excited molecule, the ionization occurs in a two-photon resonant absorption process.

Figure 14 shows the experimental arrangement that has been used to resolve the degenerate Fermi doublet ν_{16} and $\nu_2 + \nu_{18}$ of benzene C_6H_6 in a molecular beam experiment⁶⁴. The two Fermi sub-bands could be recorded separately by selectively tuning the UV laser into resonance with electronic transitions from one of the two states as shown in Figure 15. When the Stokes laser is tuned, the rovibrational structure of only one Raman transition is

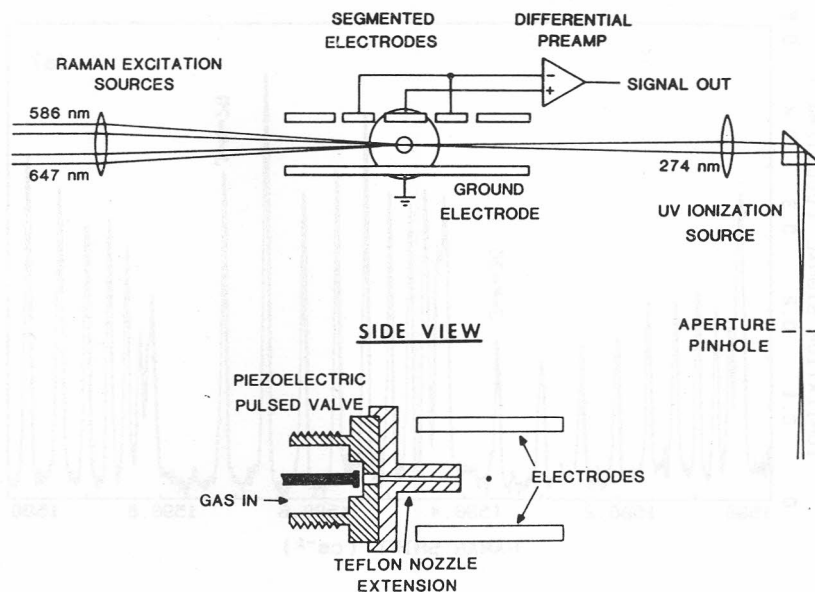


Figure 14. Experimental setup for ionization detected stimulated Raman spectroscopy in a pulsed molecular jet (from Esherick *et al.*, Ref. 64).

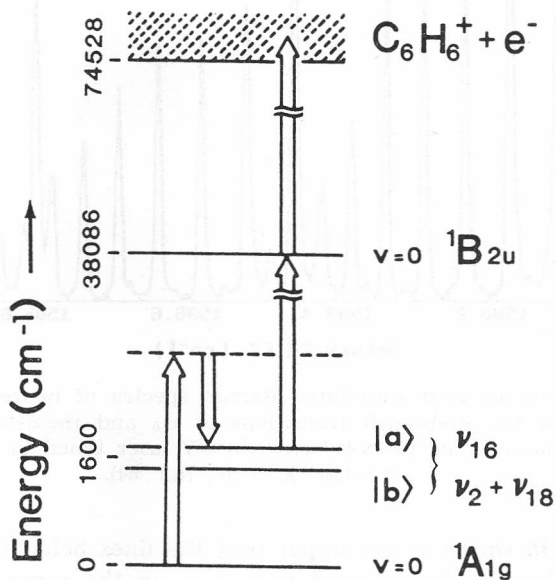


Figure 15. Energy level diagram illustrating the excitation scheme used by IDSRS (from Esherick *et al.*, Ref. 64).

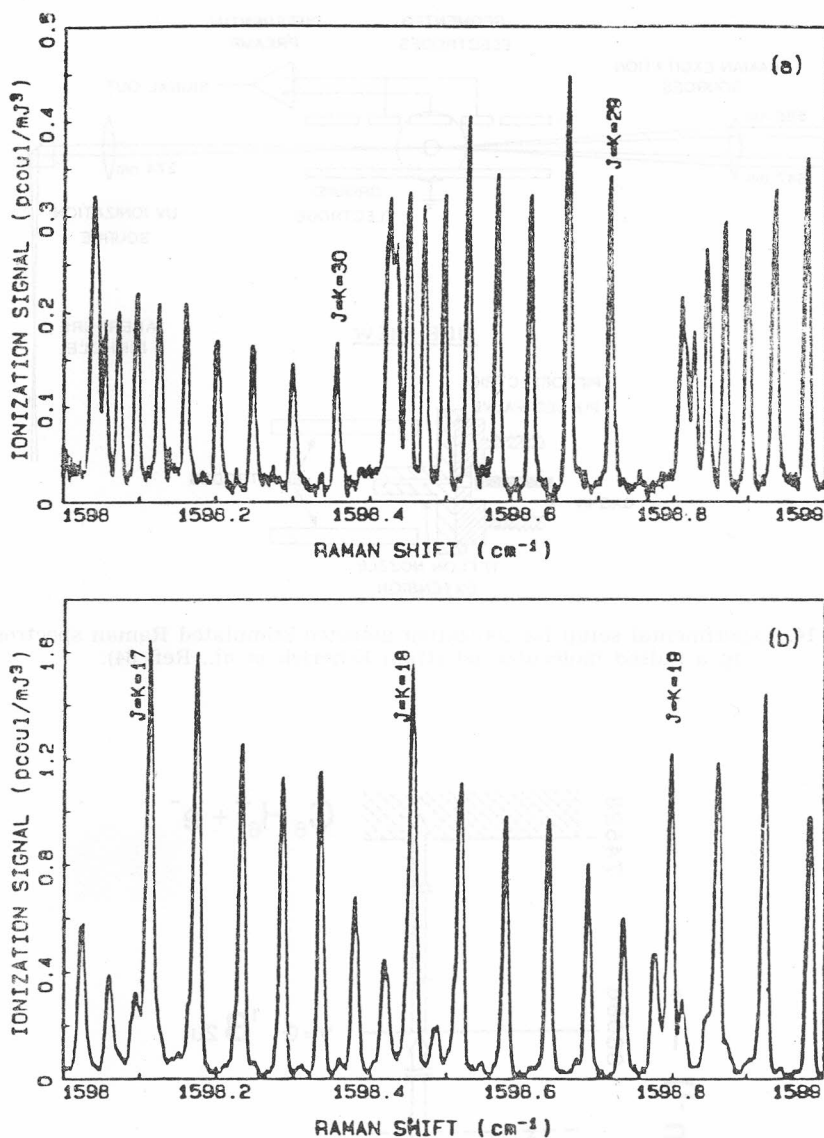


Figure 16. Ionization detected stimulated Raman spectra of benzene in the region of overlap between the $^{\circ}$ O-branch transitions of ν_{16} and the $^{\circ}$ S-branch transitions of $\nu_2 + \nu_{18}$. a) UV laser tuned to 36 467 cm^{-1} , b) UV laser tuned to 36 496 cm^{-1} (from Esherick *et al.*, Ref. 64).

recorded. Figure 16 shows in the upper part the lines belonging to ν_{16} and in the lower part those to be assigned to $\nu_2 + \nu_{18}$ in the same spectral region. An extensive analysis of the deconvoluted spectra⁶⁵ yielded deperturbed spectroscopic constants for the interacting states which reproduce the line positions

with a standard deviation of 0.0013 cm^{-1} , which is comparable in accuracy with the results of modern infrared spectroscopic investigations.

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SAŽETAK

Nelinearna Ramanova spektroskopija visokog razlučivanja u plinovima

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Primjenljivost Ramanove spektroskopije na istraživanje plinova uvelike je poboljšana razvojem različitih metoda nelinearnog Ramanova raspršenja. Kada se dva laserska snopa, od kojih je jedan promjenljive frekvencije fokusiraju na uzorku, dolazi do stimuliranog Ramanova procesa čim je razlika frekvencija dvaju lasera jednaka Raman-aktivnoj rovibracijskoj ili rotacijskoj frekvenciji prijelaza u uzorku, a odgovarajuće stanje je napučeno iznad prosjeka. Ramanova rezonancija može se detektirati na različite načine: koherentnim anti-Stokesovim Ramanovim raspršenjem (CARS), pojačanjem u jednom od snopova (stimulirana Ramanova spektroskopija pojačanja, SRGS) ili slabljenjem u drugom (inverzna Ramanova spektroskopija, IRS), ili čak detekcijom fotoakustičkog signala (fotoakustička Ramanova spektroskopija, PARS). Selektivna ionizacija pobuđenih molekula trećim, ultraljubičastim laserskim pulsom (ionizacijski detektirano stimulirano Ramanovo raspršenje, IDSRS) znatno pojačava osjetljivost u posebnim slučajevima.

Instrumentalno razlučivanje tih tehnika određeno je konvolviranim širinama linija lasera upotrebljenih za pobudu. To je posebno važno za istraživanje rotacijsko-vibracijskih spektara visokog razlučivanja u plinovima.