

## High-resolution nonlinear rotation-vibrational Raman spectroscopy of gases

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**Abstract** - Recent results on high-resolution nonlinear rotation-vibrational Raman spectra of gases are described.

### INTRODUCTION

In the last 10 years the resolution in rotation-vibrational Raman spectroscopy of gases has been increased by about two orders of magnitude through the application of the nonlinear techniques which are based on the excitation with two lasers, one of which is tunable (ref. 1). Whereas Q-branches of rotation-vibrational Raman bands of polyatomic molecules could generally not be resolved by linear Raman techniques (ref. 2), it has now become possible to study their rotational structure in some detail. Early examples are the Coherent Anti-Stokes Raman Scattering (CARS) spectra of the Q-branches of the  $\nu_1$  and  $\nu_2$  bands of acetylene  $C_2H_2$  which have first been resolved by Nitsch and Kiefer (ref. 3) and Fabelinsky et al. (ref. 4). The rotational structure of the O- and S-branches of these bands had previously been studied by Kostyk and Welsh (ref. 5) and Wang and Weber (ref. 6) by photographic recording of the linear Raman spectrum.

Other nonlinear Raman techniques that have been used to resolve rotation-vibrational bands are Stimulated Raman Gain Spectroscopy (SRGS) (ref. 7), Inverse Raman Spectroscopy (IRS) (ref. 8,9), Raman Induced Kerr Effect (RIKE) (ref. 10), Photo-Acoustic Raman Spectroscopy (PARS) (ref. 11) and more recently Ionization-Detected Stimulated Raman Spectroscopy (IDSRS) (ref. 12-14) and Fourier Transform Raman Spectroscopy (FTRS) (ref. 15,16). Here we report on some of the results obtained in our laboratories in Munich (ref. 17) and Dijon (ref. 18-20). A more detailed account of our work is published elsewhere (ref. 21).

### COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS)

Because the instrumental resolution depends on the convoluted linewidth of the two lasers and the narrowest linewidths can be obtained with stabilized single mode continuous lasers, we have constructed a CARS spectrometer for c.w. intracavity excitation in Munich (ref. 22). It consists of an argon ion ring laser with an etalon, a prism, and a gas cell containing two spherical mirrors in the cavity and a dye ring laser, the beam of which is coupled into the gas cell at the prism for collinear excitation.

The CARS spectrum of the Q-branch of the rotation-vibrational band of nitrogen  $N_2$  has been recorded at pressures of 2 kPa and 14.5 kPa (ref. 22, 23) and the difference of the rotational constants in the ground and first vibrational states has been determined as  $\Delta B = -(0.17385 \pm 0.0000035) \text{ cm}^{-1}$ , in close agreement with the values obtained by Bendtsen (ref. 24) from the linear Raman spectrum and by Reuter et al. (ref. 25) from the infrared quadrupole absorption spectrum.

The structure of the  $\nu_3$  Raman band of methane  $CH_4$  has been studied by many authors, from Stoicheff et al. (ref. 26) to Berger et al. (ref. 27). Now it has also been possible to resolve the Q-branch of this band by Coherent Stokes Raman Scattering (CSRS) (ref. 28) and CARS (ref. 29) techniques. Figure 1 shows the CARS spectrum in the region of the Q branch recorded at a pressure of 13.6 kPa. Starting from the energy levels derived from an analysis of the infrared spectrum in the region of the CH - vibrations (ref. 30) the CARS spectrum has been calculated and found to be in good agreement with the experimental one, as shown in Fig. 2, where the contributions of the real and imaginary parts of the nonlinear susceptibility  $\chi^{(3)}$  are plotted separately.

On the other hand, the analysis of the intensity profile of the CARS spectrum of the  $\nu_1$  band of methane recorded at a pressure of 1.4 kPa (ref. 23,31) on the basis of available assignments (ref. 7,30,32) led at first to discrepancies which could be removed by an empirical reassignment of transitions with  $J = 7$  to  $J = 10$  (ref. 31). Later Lolck (ref. 33) has shown that the empirically found line positions (ref. 31) can also be derived from theoretical calculations.

The pressure dependence of the CARS spectrum of the  $\nu_1$  band has also been investigated (ref. 29) between 1.4 kPa and 40 kPa and is shown in Fig. 3. The lowest pressure in our static cell at which a satisfactory signal/noise ratio has been obtained for a single scan was 0.3 kPa (ref. 34).

The analysis of the CARS spectrum of the  $\nu_1$  band of hydrogen sulfide  $\text{H}_2\text{S}$  recorded at a pressure of 1.3 kPa led to excellent agreement with a spectrum calculated from energy levels and wave functions derived from a study of the infrared spectrum (ref. 35).

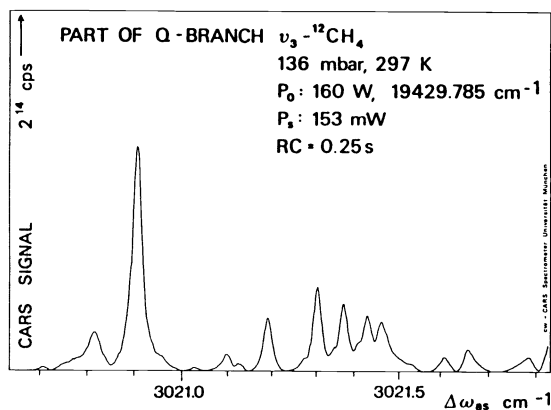


Fig. 1. Experimental CARS spectrum of the  $Q^+$ -branch of the  $\nu_3$  band of methane at a pressure of 13.6 kPa.

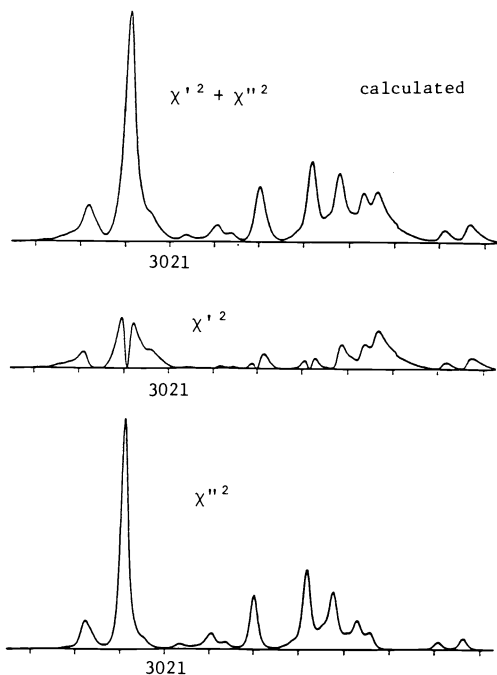


Fig. 2. Calculated CARS spectrum of the  $Q^+$ -branch of the  $\nu_3$  band of methane. Upper trace: total spectrum. Middle trace: contribution of real part of the nonlinear susceptibility. Lower trace: contribution of imaginary part of the nonlinear susceptibility.

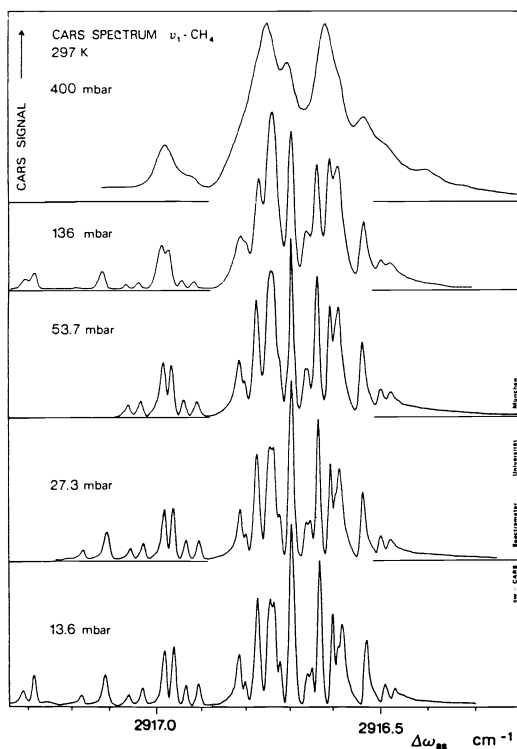


Fig. 3. Experimental CARS spectrum of the  $\nu_1$  band of methane at pressures of 1.36 kPa, 2.73 kPa, 5.37 kPa, 13.6 kPa and 40 kPa. CARS signal in arbitrary units.

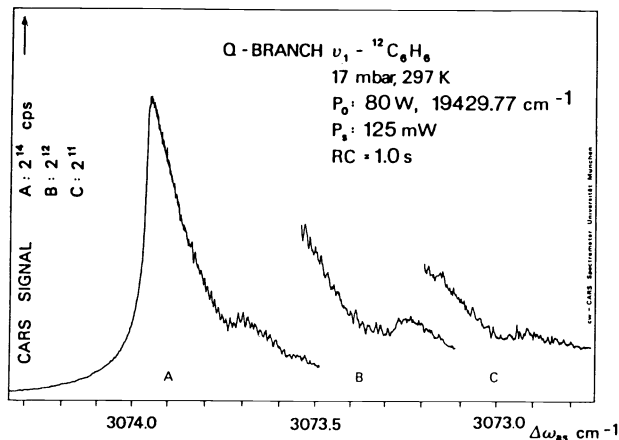


Fig. 4. Experimental CARS spectrum of the  $Q$ -branch of the  $\nu_1$  band of benzene at a pressure of 1.7 kPa.

The CARS spectrum of the Q-branch of the  $\nu_1$  band of benzene  $C_6H_6$  recorded at a pressure of 1.7 kPa is shown in Fig. 4. Although the rotational structure could not be resolved, the positions of the hot band  $\nu_1 + \nu_{20} - \nu_{20}$  and of the  $\nu_1$  band of the isotopomer  $^{12}C_5^{13}CH_6$  have been determined (ref. 29).

The structure of the CARS spectrum of the  $\nu_1$  band of allene  $C_3H_4$  has been found to be rather complicated (ref. 34).

In the case of the CARS spectrum of the Q-branch of the  $\nu_1$  band of ammonia  $NH_3$  at a pressure of 1.5 kPa (ref. 36) the recorded and calculated spectra could only be brought into agreement by the introduction of a pressure broadened linewidth (FWHM) depending on the quantum numbers J and K of the symmetric top molecule. The empirical formula

$$\Gamma_{JK} = 0.004 \text{ cm}^{-1} + (0.012 \text{ cm}^{-1}) [K^2/J(J+1)]^{\frac{1}{2}}, \quad (1)$$

led to a satisfactory fit. The line broadening effect has also been observed in the infrared spectrum of the Q-branch of the  $\nu_1$  band recorded with the technique of difference frequency laser spectroscopy by Pine (ref. 37) and is being investigated theoretically by Buffa (ref. 38) on the basis of a theory that has been successfully applied to the  $\nu_2$  and  $2\nu_2$  bands of ammonia (ref. 39,40).

In Dijon a CARS spectrometer with flashlamp pumped dye laser amplifiers (ref. 41) injection locked to the frequency of stabilized single mode c.w. krypton or dye lasers has been constructed by Boquillon et al. (ref. 20). The amplifiers deliver pulses of about 400 ns with peak powers up to 10 kW and a repetition rate of 10 Hz, leading to an instrumental resolution of about 10 MHz. With this spectrometer CARS spectra of the Q-branch of the rotation-vibrational band of oxygen  $O_2$  at pressures between 1.3 kPa and 130 kPa have been recorded and collisional line broadening parameters have been determined for the lines with  $N = 1$  to  $N = 17$ .

## INVERSE RAMAN SPECTROSCOPY

Also in Dijon an Inverse Raman Spectrometer (ref. 42) has been developed which uses a c.w. argon ion probe laser and a high power pulsed pump laser (Fig. 5). The pump laser is obtained by amplifying a tunable single mode dye laser in a four stage amplifier pumped by a Nd-YAG laser. In our recent investigations, the probe laser was actively stabilized with a Fabry-Pérot interferometer and its frequency was locked to a Doppler-free saturated absorption line of  $I_2$ . This laser is used as the reference source for the travelling corner cube wavemeter which measures the dye laser frequency at the beginning and at the end of each  $1 \text{ cm}^{-1}$  scan. The induced absorption signal is detected on the probe laser, is amplified and then averaged and stored in a data acquisition system.

The Raman spectrum of  $^{13}CD_4$  has been investigated for the first time and recorded in the region corresponding to the pentad ( $\nu_1, \nu_3, 2\nu_2, \nu_2 + \nu_4, 2\nu_4$ ) (ref. 19). The observed spectrum covers a  $50 \text{ cm}^{-1}$  spectral range and the frequencies of about 300 Raman transitions

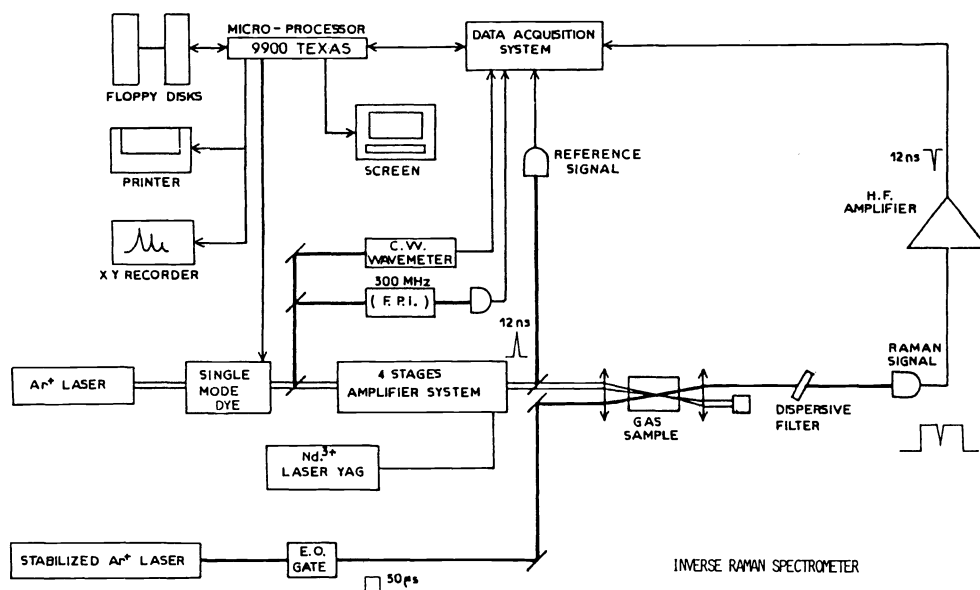


Fig. 5. Inverse Raman Spectrometer, Université de Dijon.

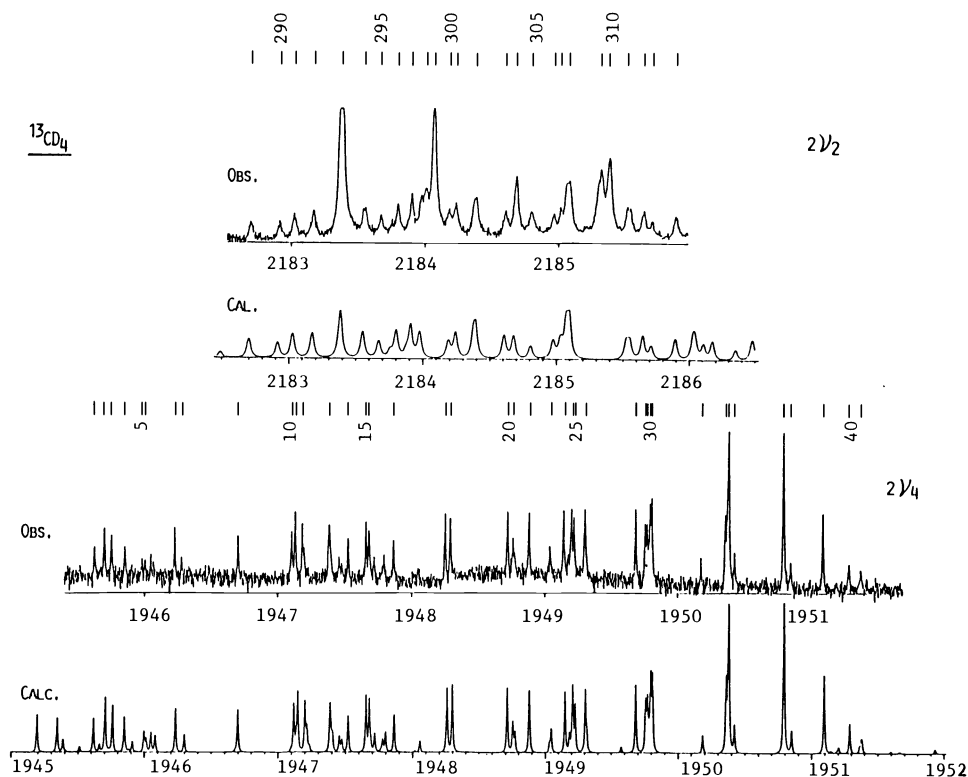


Fig. 6. Observed and calculated inverse Raman spectra of the  $2\nu_2$  (pressure 20 kPa) and  $2\nu_4$  (pressure 4 kPa) bands of  $^{13}\text{CD}_4$ .

have been measured. Fig. 6 shows high resolution spectra of the harmonic bands  $2\nu_2$  and  $2\nu_4$ . The observed Raman frequencies have been combined with the infrared data recorded by Henry and Valentin in Paris (ref. 43,44) in a simultaneous analysis of the pentad. Moreover, the collisional linewidth of Q(4) lines of the  $\nu_1$  band has been extracted by fitting a Raman profile to the experimental spectra.

The symmetric top molecule  $\text{C}_3\text{H}_6$  has been also investigated to get high resolution Raman spectra of the C-H stretching region ( $3000$  to  $3040\text{ cm}^{-1}$ ). Many lines appear in this region and lead to a complicated structure not yet fully assigned. Nevertheless, the  $2\nu_2$  Q-branch exhibits a band head which allows us to estimate some molecular constants.

In addition to molecular structure investigations, we have studied collisional effects on the lineshape of the Q-branch of nitrogen. Two phenomena occur as the density increases: at low density, the Doppler contribution is reduced through the Dicke narrowing (ref. 45), and for high density, the spectrum is narrowed by vanishing of the rotational inelastic contribution (ref. 46). The Dicke narrowing has been demonstrated in a backward scattering configuration on the Q(18) line of  $\text{N}_2$  (ref. 47) by using a Galatry profile in the fit (ref. 48). An error of 10% is made in the broadening coefficient if the phenomenon is neglected in this configuration.

With a view to apply IRS data to laser Raman diagnostic techniques such as CARS, we have studied the temperature dependence of the collisional linewidths in the Q-branch of  $\text{N}_2$ , from room temperature up to 1310 K (ref. 49). This study is an extension of previous investigations in this domain (ref. 50,51). The collisional linewidths have been extracted by least squares fitting procedures using Voigt or Rosenkranz profiles. The latter was useful when the lines overlapped. Indeed, the Rosenkranz profile well describes the non-additivity of the lines resulting from line mixing in the case of small overlap (ref. 52). The measured broadening coefficients are plotted in Fig. 7 against J for different temperatures. The solid lines correspond to semi-classical calculations performed by Robert and Bonamy (ref. 53). These calculations, which are very consistent with the measured coefficients, have been extended to higher J values and to higher temperatures (up to 2500 K).

This set of measurements and the recent investigations of Rahn and Palmer (ref. 54) are in very good concordance.

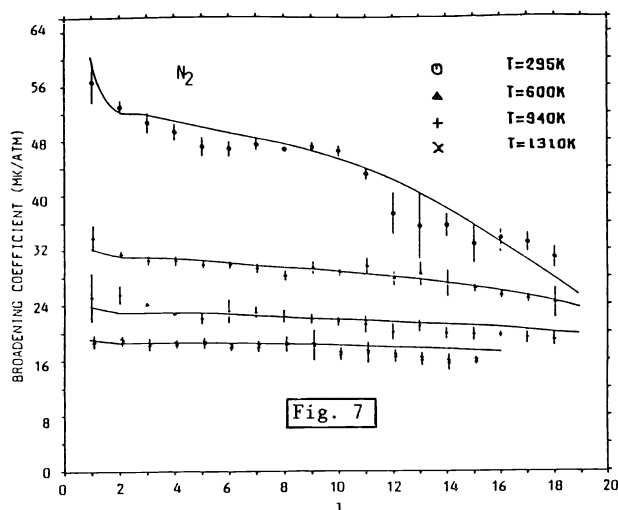


Fig. 7. Experimental (points) and calculated (—) line broadening coefficients for the Q-branch of nitrogen as function of the rotational quantum number  $J$  for various temperatures.  $1 \text{ MK/ATM} = 10^{-3} \text{ cm}^{-1} \text{ bar}^{-1} = 10^{-8} \text{ cm}^{-1} \text{ Pa}$ .

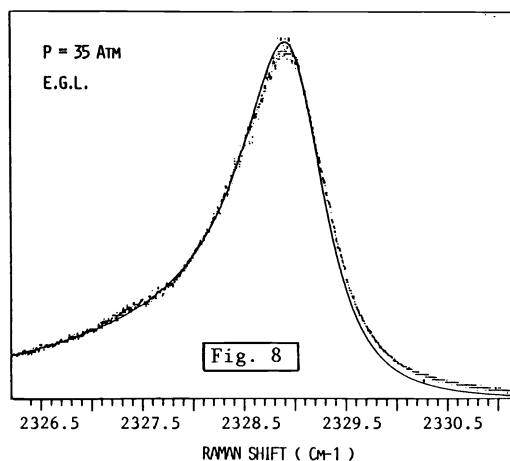


Fig. 8. Profile of the Q-branch of nitrogen at a pressure of 35 bar = 3.5 MPa. Comparison of experimental points with calculated curve according to the EGL model.

The description of the collisional narrowing, which begins at moderate pressures (100 kPa at room temperature) in the  $\text{N}_2$  Q-branch, involves the knowledge of all the elements of the relaxation matrix  $W$ . Simple models use energy based fitting laws (ref. 55) for predicting off-diagonal elements  $W_{J',J}$  from measured or calculated linewidths. Among them, we have adopted the model of Greenhalgh and coworkers (ref. 56) which assumed a polynomial inverse energy gap law for  $W_{J',J}$ . The parameters of the model have been adjusted by fit to the two sets of broadening coefficients of ref. 49 and 54. Then it was possible to predict high temperature linewidths, as well as collisionally narrowed spectra of  $\text{N}_2$  for high pressures. A comparison with experimental spectra has led to good agreement (ref. 57).

Another model for the  $W$ -matrix has been developed by Sala and coworkers (ref. 57). This model uses the strong collisions approximation and satisfies both detailed balance and unitarity of the  $S$ -matrix, in contrast with previous approaches (ref. 58,59). The agreement with the experiment is good.

To improve the test of  $W$ -models, we have measured the pressure induced frequency shift of some  $Q(J)$  lines and found a mean value of  $150 \text{ MHz amagat}^{-1}$  (ref. 60). By taking this shift into account, we have found that the EGL model proposed by Koszykowski and coworkers (ref. 61) describes the collisional narrowing in  $\text{N}_2$  very well (ref. 62), as shown in Fig. 8.

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### REFERENCES

1. W. Kiefer and D. A. Long, Eds., *Non-Linear Raman Spectroscopy and Its Chemical Applications*, Reidel, Dordrecht, 1982.
2. S. Brodersen, in: *Raman Spectroscopy of Gases and Liquids* (A. Weber, Ed.) *Topics in Current Physics*, Vol. 11, Springer Verlag, Berlin 1979, p. 7.
3. W. Nitsch and W. Kiefer, *Opt. Commun.*, 23, 240 (1977).
4. V. I. Fabelinsky, B. B. Krynetsky, L. A. Kulevsky, V. A. Mishin, A. M. Prokhorov, A. D. Savel'ev, and V.V. Smirnov, *Opt. Commun.*, 20, 389 (1977).
5. E. Kostyk and H. L. Welsh, *Can. J. Phys.*, 58, 534 (1980).
6. I-Yan Wang and A. Weber, *Indian J. Pure Appl. Phys.*, 16, 358 (1978).
7. A. Owyong, C. W. Patterson and R. S. McDowell, *Chem. Phys. Letters*, 59, 156 (1978).
8. A. Owyong, in: *Laser Spectroscopy IV* (H. Walther and K. W. Rothe, Eds.), *Springer Ser. in Opt. Sci.*, Vol. 21, Springer, Berlin 1979, p. 175.
9. P. Esherick and A. Owyong, in: *Advances in Infrared and Raman Spectroscopy* (R. J. H. Clark and R. E. Hester, Eds.), Vol. 9, Heyden, London 1982, p. 130.
10. S. Q. Mao, R. Saint-Loup, A. Aboumajd, P. Lepage, H. Berger and A. G. Robiette, *J. Raman Spectrosc.*, 13, 257 (1982).
11. J. J. Barrett, in: *Chemical Applications of Nonlinear Raman Spectroscopy* (A. B. Harvey, Ed.), Academic Press, New York, 1981, p. 89.

12. P. Esherick and A. Owyong, *Chem. Phys. Lett.*, **103**, 235 (1983).
13. P. Esherick, A. Owyong and J. Pliva, *J. Chem. Phys.*, **83**, 3311 (1985).
14. P. Esherick and A. Owyong, in: *Proc. Xth Int. Conf. Raman Spectrosc.* (W. L. Peticolas and B. Hudson, Eds.), Univ. of Oregon, Eugene 1986, p. 15-4.
15. H. Graener and A. Laubereau, *Opt. Commun.*, **54**, 141 (1985).
16. A. Laubereau, in: *Proc. Xth Int. Conf. Raman Spectrosc.*, (W. L. Peticolas and B. Hudson, Eds.) Univ. of Oregon, Eugene, p. 19-1, 1986.
17. H. W. Schrötter, in: *Proc. Xth Int. Conf. Raman Spectrosc.*, (W. L. Peticolas and B. Hudson, Eds.), Univ. of Oregon, Eugene, p. 15-19, 1986.
18. B. Lavorel, in: *Proc. Xth Int. Conf. Raman Spectrosc.*, (W. L. Peticolas and B. Hudson, Eds.), Univ. of Oregon, Eugene, p. 15-16, 1986.
19. G. Millot, B. Lavorel, R. Chaux, R. Saint-Loup, G. Pierre and H. Berger, in: *Proc. Xth Int. Conf. Raman Spectrosc.*, (W. L. Peticolas and B. Hudson, Eds.), Univ. of Oregon, Eugene, p. 15-18, 1986.
20. J. P. Boquillon, Y. Ouazzany and R. Chaux, in: *Proc. Xth Int. Conf. Raman Spectrosc.*, (W. L. Peticolas and B. Hudson, Eds.), Univ. of Oregon, Eugene, p. 15-35, 1986.
21. H. W. Schrötter, H. Frunder, H. Berger, J. P. Boquillon, B. Lavorel and G. Millot, in: *Advances in Infrared and Raman Spectroscopy* (R. J. H. Clark and R. E. Hester, Eds.), Vol. 16, Wiley, Chichester (in press).
22. H. Frunder, L. Matziol, H. Finsterhölzl, A. Beckmann, and H. W. Schrötter, *J. Raman Spectrosc.*, **17**, 143 (1986).
23. H. Frunder, D. Illig, H. Finsterhölzl, A. Beckmann, H. W. Schrötter, B. Lavorel and G. Roussel, in: *Laser Spectroscopy VI*, (H. P. Weber and W. Lüthy, Eds.), Springer Ser. Opt. Sci., **40**, 334 (1983).
24. J. Bendtsen, *J. Raman Spectrosc.*, **2**, 133 (1974).
25. D. Reuter, D. E. Jennings and J. W. Brault, *J. Mol. Spectrosc.*, **115**, 294 (1986).
26. B. P. Stoicheff, C. Cumming, G. E. St. John, and H. L. Welsh, *J. Chem. Phys.*, **20**, 498 (1952).
27. H. Berger, M. Faivre, J. P. Champion, and J. Moret-Bailly, *J. Mol. Spectrosc.*, **45**, 298 (1973).
28. J. P. Boquillon and R. Bregier, *Appl. Phys.*, **18**, 195 (1979).
29. H. Frunder, Dissertation LMU München, 1983.
30. G. Poussigue, E. Pascaud, J. P. Champion and G. Pierre, *J. Mol. Spectrosc.*, **93**, 351 (1982).
31. H. Frunder, D. Illig, H. Finsterhölzl, H. W. Schrötter, B. Lavorel, G. Roussel, J. C. Hilico, J. P. Champion, G. Pierre, G. Poussigue and E. Pascaud, *Chem. Phys. Letters*, **100**, 110 (1983).
32. J. E. Lolck and A. G. Robiette, *Chem. Phys. Letters*, **64**, 195 (1979).
33. J. E. Lolck, *Chem. Phys. Letters*, **106**, 143 (1984).
34. D. Illig, unpublished.
35. H. Frunder, R. Angstl, D. Illig, H. W. Schrötter, L. Lechuga-Fossat, J. M. Flaud, C. Camy-Peyret, and W. F. Murphy, *Can. J. Phys.*, **63**, 1189 (1985).
36. R. Angstl, H. Finsterhölzl, H. Frunder, D. Illig, D. Papousek, P. Pracna, K. Narahari Rao, H. W. Schrötter, and S. Urban, *J. Mol. Spectrosc.*, **114**, 454 (1985).
37. A. S. Pine, unpublished.
38. G. Buffa, unpublished.
39. G. Baldacchini, S. Marchetti, V. Montelatici, G. Buffa and O. Tarrini, *J. Chem. Phys.*, **76**, 5271 (1982).
40. G. Baldacchini, S. Marchetti, V. Montelatici, V. Sorge, G. Buffa and O. Tarrini, *J. Chem. Phys.*, **78**, 665 (1983).
41. J. P. Boquillon and O. Bazemlal, *Revue Phys. Appl.*, **16**, 365 (1981).
42. B. Lavorel, R. Saint-Loup, G. Pierre and H. Berger, *J. Physique Lett.*, **45**, 295 (1984).
43. G. Millot, B. Foy, J. I. Steinfeld, G. Pierre, A. Valentin and L. Henry, *IXth Int. Conf. on High Resolution Infrared Spectroscopy*, Liblice (Prague) 1986.
44. G. Millot, B. Lavorel, R. Chaux, R. Saint-Loup, G. Pierre, H. Berger and J. I. Steinfeld, paper in preparation.
45. R. H. Dicke, *Phys. Rev.*, **89**, 472 (1953).
46. A. D. May, J. C. Stryland and G. Varghese, *Can. J. Phys.*, **48**, 2331 (1970).
47. G. Millot, B. Lavorel, R. Saint-Loup and H. Berger, *J. Physique*, **46**, 1925 (1985).
48. L. Galatry, *Phys. Rev.*, **122**, 1218 (1961).
49. B. Lavorel, G. Millot, R. Saint-Loup, C. Wenger, H. Berger, J. P. Sala, J. Bonamy and D. Robert, *J. Physique*, **47**, 417 (1986).
50. L. A. Rahn, A. Owyong, M. E. Coltrin and M. L. Koszykowski, in: *Proc. 7th Int. Conf. on Raman Spectrosc.*, (W. F. Murphy, Ed.), North Holland, Amsterdam, p. 694, 1980.
51. G. J. Rosasco, W. Lempert, W. S. Hurst, in: *Proc. 6th Int. Conf. on Spectral Line Shape*, **2**, Boulder, CO., USA (1982).
52. P. W. Rosenkranz, *IEEE Trans. Antennas Propag.*, **23**, 498 (1975).
53. D. Robert and J. Bonamy, *J. Physique*, **40**, 923 (1979).
54. L. A. Rahn and R. E. Palmer, *J. Opt. Soc. Am. B*, **3**, 1164 (1986).
55. T. A. Brunner and D. Pritchard, *Advan. Chem. Phys.*, **50**, 589 (1982).
56. D. A. Greenhalgh, F. M. Porter and S. A. Barton, *J. Quant. Spectrosc. Radiat. Transfer*, **34**, 95 (1985).
57. J. P. Sala, J. Bonamy, D. Robert, B. Lavorel, G. Millot and H. Berger, *Chem. Phys.*, **106**, 427 (1986).
58. S. R. J. Brueck, *Chem. Phys. Letters*, **50**, 516 (1977).
59. R. J. Hall and D. A. Greenhalgh, *Opt. Commun.*, **40**, 417 (1982).
60. B. Lavorel, R. Saint-Loup and H. Berger, paper in preparation.
61. M. L. Koszykowski, L. A. Rahn and R. E. Palmer, submitted to *J. Phys. Chem.*
62. B. Lavorel, G. Millot, J. Bonamy and D. Robert, paper in preparation.