J. Phys. Chem. A **1998,** *102,* 7273−7276

CHF_2Cl and CH_3CF_2Cl Detection by Coherent Anti-Stokes Raman Scattering and Photoacoustic Raman Spectroscopy

A. Melchior, I. Bar,*,† and S. Rosenwaks

Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

Received: May 19, 1998

The coherent anti-Stokes Raman scattering (CARS) and photoacoustic Raman spectroscopy (PARS) spectra of gaseous CHF_2Cl and CH_3CF_2Cl in the 3000 cm^{-1} region are reported for the first time. Several vibrational bands are observed related to C−H stretch fundamentals of CHF_2Cl isotopomers, and to CH_3 stretches and the first overtone of CH_3 deformation of CH_3CF_2Cl. The simultaneous detection of CARS/PARS signals aids the assignment of the isotopomer bands. Both methods are appropriate for detection of these compounds and can be applied in chemical dynamics studies.

Introduction

Hydrochlorofluorocarbons (HCFC’s) have been suggested as interim replacements for the ozone destroying chlorofluorocarbons (CFC's) and halons.[1−3] The HCFC’s, containing at least one C−H bond, have been pursued as substitutes since they have shorter atmospheric lifetimes than the CFC’s. Substantial usage of HCFC’s leads to high emissions, which are assumed to grow at 3% per year until 2020 with reductions to zero emissions by 2040.[2] Because of the direct environmental relevance, the interest in these compounds is increasing and so is the number of their studies. Recent research is directed toward kinetics and dynamics measurements of their reactions with O(^{1}D)[4,5] OH,[6−9] and Cl,[10] to photodissociation dynamics studies,[11−13] and to detailed theoretical and spectroscopic studies to obtain a basis for their environmental monitoring.[14−22]

Extensive measurements of microwave and infrared spectra revealed spectroscopic constants for the ground state and different vibrational levels of HCFC compounds.[14−21] In the past, the Raman spectra of several HCFC’s have been recorded by a three-prism glass spectrograph[23] and by mercury arc excitation.[24,25] Recently, the high-pressure Raman scattering of liquid and crystalline CHF_2Cl has been studied.[21] These studies characterized the position of the bands, at low resolution, and the absolute intensities and depolarization ratios. Nowadays, sensitive nonlinear optical spectroscopies as coherent anti-Stokes Raman scattering (CARS)[26,27] and photoacoustic Raman spectroscopy (PARS)[28] may be applied to obtain rovibrational spectra of molecules.

CARS and PARS have been shown to be sensitive and powerful methods for different applications. CARS has been used for temperature and density measurements in flames, internal combustion and jet engines, plasmas, chemically reacting mixtures, and explosions.[26,27,29−32] It has been also employed[33] and suggested to be employed[34] in chemical dynamics experiments to monitor the photofragments and reaction products. Moreover, in other chemical dynamics experiments it has been used to monitor the efficacy of vibrational excitation by stimulated Raman excitation (SRE).[33,35−37] The PARS method has been utilized in spectroscopic[28] and molecular dynamics studies[38] of a variety of molecular species, and to trace analysis of gaseous mixtures.[28]

We employed both methods simultaneously and report, to the best of our knowledge, the first observed CARS/PARS spectra of gaseous HCFC methane and ethane derivatives, i.e., chlorodifluoromethane, CHF_2Cl (HCFC-22), and 1-chloro-1,1-difluoroethane, CH_3CF_2Cl (HCFC-142b). Both molecules, having only one plane of symmetry, belong to the C_s point group. CHF_2Cl has nine fundamental vibrations of $A'(\nu_1-\nu_6)$ and $A''(\nu_7-\nu_9)$ symmetry species[16] and CH_3CF_2Cl has 18 vibrational modes belonging to symmetries $A'(\nu_1-\nu_{11})$ and A'' $(\nu_{12}-\nu_{18})$.[17] Our measured CARS/PARS spectra of CHF_2Cl, in the 3000 cm^{-1} region, are characterized by an intense Q branch of the C−H fundamental of $CHF_2{}^{35}Cl$ and by a red-shifted small peak corresponding to the same band of the $CHF_2{}^{37}Cl$ isotopomer. The CH_3CF_2Cl spectra exhibit CH_3 stretch vibrational bands and the first overtone of CH_3 deformation. The ratios of the integrated intensities of the CHF_2Cl and CH_3CF_2Cl bands to that of methane, CH_4, are obtained. The results show that CARS and PARS are sensitive enough to detect CHF_2Cl and CH_3CF_2Cl in dynamics studies.

Experiment

In CARS, a four-wave mixing process,[26,27] three waves at frequencies ω_p, ω_S, and ω_p are mixed in a sample to generate a new coherent wave at frequency $\omega_{AS} = \omega_p - \omega_S + \omega_p$ (ω_p, ω_S, and ω_{AS} are the pump, Stokes, and anti-Stokes beams, respectively). When $\omega_p - \omega_S = \Omega$, where Ω is the frequency of a Raman active transition, the nonlinear mixing is greatly enhanced. By varying ω_S while ω_p is kept constant, it is possible to go across a vibrational band and generate a CARS spectrum. In PARS,[28] stimulated Raman scattering is obtained when $\omega_p - \omega_S = \Omega$. The nonlinear process results in the amplification of the ω_S beam and attenuation of the ω_p beam. For each generated Stokes photon a molecule is transferred to the rovibrationally excited level, producing excess population in it. The PARS signal monitors the sound wave generated by vibrational relaxation as the Stokes laser is tuned through rovibrational transitions.

Our CARS/PARS apparatus consists a Nd:YAG pumped tunable dye laser (DCM dye) to generate ω_S in the range 626−

[†] Also with The Institutes for Applied Research.

S1089-5639(98)02311-1 CCC: $15.00

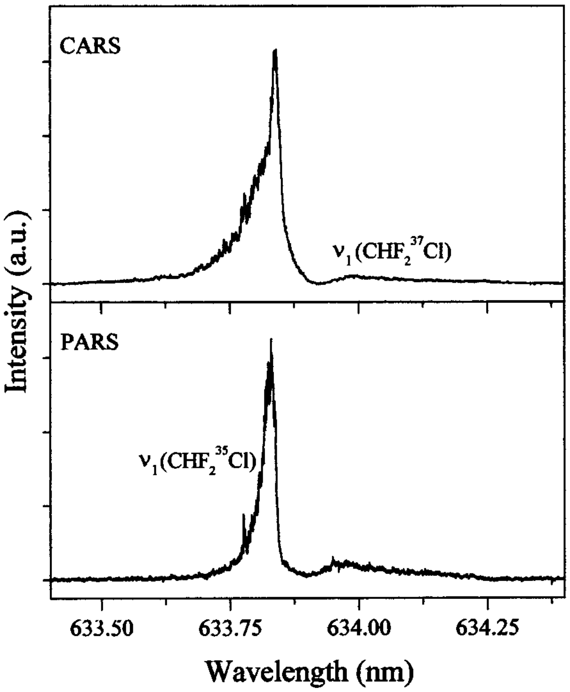

Figure 1. Rovibrational CARS/PARS spectra of $CHF_2{}^{35}Cl$ and CHF_2-^{37}Cl ν_1 bands at 10 Torr and room temperature.

636 nm. The residual of the Nd:YAG first harmonic is doubled and provides the ω_p beam at the fixed wavelength, 532 nm. The ω_p and ω_S have line widths of 0.2 and 0.07 cm^{-1}, respectively. The energies of the beams are controlled by changing the Q-switch delay of the Nd:YAG and are typically ~16 mJ for ω_p and ~1.5 mJ for ω_S. Both beams are vertically polarized. Wavelength calibration is achieved by monitoring CARS/PARS spectra of the ν_1 (2916.8 cm^{-1}) and ν_3 (3020 cm^{-1}) levels of methane.[27]

The beams are collinearly combined by a dichroic mirror and focused with a 12 in. focal length (fl) lens into the reaction cell. The beams are spatially and temporally overlapped, the latter being achieved by optical delay of the ω_p beam. At the cell exit ω_p, ω_S, and ω_{AS} are recollimated by a 12 in. fl lens; then ω_{AS} is spatially and spectrally separated from the input beams by a Pellin-Broca prism and by color glass filters. The ω_{AS} is attenuated by neutral-density filters and then monitored by a photodiode. The PARS signal is simultaneously detected by a microphone mounted in the cell. The experiments are performed in a gas cell, at room temperature, with a static or flowing sample of the compound's vapor. The gaseous CHF_2Cl (99.5%), CH_3CF_2Cl (>99.85%) and CH_4 (99.5%) are used without further purification. The CARS signal and the amplified PARS signal are captured by two different channels of a boxcar averager. Thirty pulses are averaged for each point in the spectrum. Both signals are passed to a personal computer for data reduction.

Results and Discussion

CHF_2Cl. The CARS/PARS spectra of CHF_2Cl are shown in Figure 1. The spectra exhibit two peaks: a relatively large one at 633.84 nm (3020 cm^{-1}) and a small one at 633.98 nm (3023.5 cm^{-1}). Only Q-branches are observed, and the moderate bandwidth of our system (0.3 and 0.21 cm^{-1} for the CARS and PARS, respectively) is too low to resolve individual rotational lines. The intensity ratio of the peaks in the CARS spectrum is smaller than that observed in the PARS. The large peak is assigned as the ν_1 fundamental (C−H stretch) of the $CHF_2{}^{35}Cl$ isotopomer and the small one as the ν_1 fundamental of $CHF_2{}^{37}Cl$. The identification is based on the relative intensities of the peaks in the CARS/PARS spectra.

The CARS signal intensity[26,27] depends on the square of the third-order nonlinear susceptibility, $|\chi^{(3)}|^2$, and therefore on ΔN^2, where ΔN is the number density difference in population

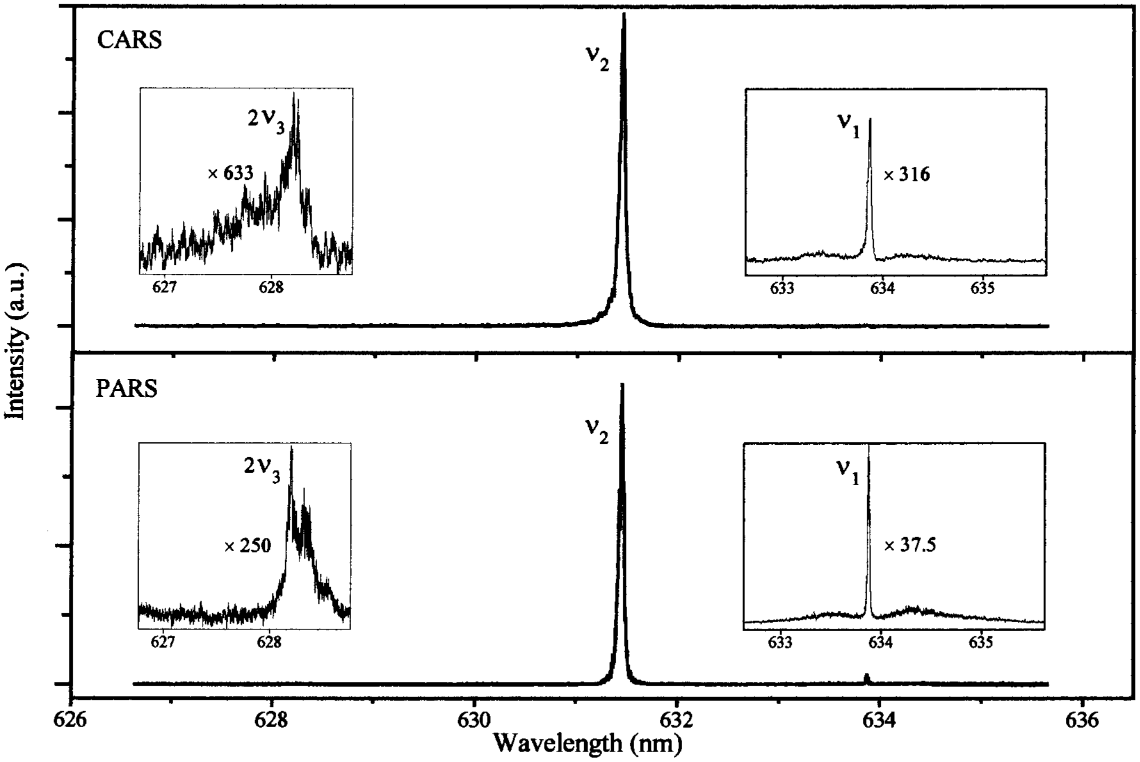

Figure 2. Rovibrational CARS/PARS spectra of CH_3CF_2Cl ν_1, ν_2, and $2\nu_3$ bands at 100 Torr and room temperature. The insets show portions of the spectral region under different experimental conditions (an increased microphone amplifier gain in the PARS and fewer neutral-density filters in the CARS). The intensity scale of the insets in each panel is similar to that of ν_2.

between the two Raman coupled states accessed in the spectrum. The PARS signal is proportional to $\chi^{(3)}$, and therefore to ΔN.[28] Since, the natural abundance of ^{35}Cl:^{37}Cl is 0.76:0.24, the CHF_2Cl consists of a mixture of $CHF_2{}^{35}Cl$ (76%) and $CHF_2{}^{37}Cl$ (24%), and therefore the CARS intensity should scale as 10:1 and the PARS as 3.17:1. From the average of 10 scans we obtain that the integrated intensity of the large peak is 9.3 ± 2.3 and 3.2 ± 0.6 times larger than the small peak for the CARS and PARS, respectively, and thus unambiguously identify the peaks.

The ν_1 band of $CHF_2{}^{35}Cl$ has been observed previously[16,39] in the infrared at 3021.27 and 3020.5 cm^{-1} and in Raman at 3024 cm^{-1}.[24] The ν_1 band of $CHF_2{}^{37}Cl$ has not previously been observed, but from force field calculations[16] it was predicted to be at 3034 cm^{-1} compared to 3032.8 cm^{-1} for the $CHF_2{}^{35}Cl$ isotopomer. Our measured Raman frequency for the ν_1 fundamental of $CHF_2{}^{35}Cl$ is 3020 cm^{-1}, quite close to the previously measured values. The calculated shift between the ν_1 bands of the isotopomers[16] is 1.2 cm^{-1}, compared to our measured shift of 3.5 cm^{-1}.

We also measured the integrated CARS intensities of the ν_1 band of $CHF_2{}^{35}Cl$ relative to that of ν_3 of CH_4 under the same conditions. The signal for the former band is 7.2 ± 2.3 times higher than for the latter, suggesting that the Raman cross section, $d\sigma/d\Omega$, for the particular bands is higher for $CHF_2{}^{35}Cl$ by a factor of 2.7, since CARS signal intensity scales as $(d\sigma/d\Omega)^2$. The observed ratio does not agree with the values of the absolute Raman scattering cross sections given in ref 25, where ν_3 of CH_4 has about twice higher cross section than ν_1 of CHF_2Cl. It is noteworthy that the absolute normalized differential Raman scattering cross sections have been measured long ago using mercury arc excitation at much higher pressures (0.7−2 atm).

Reducing the CHF_2Cl pressure enabled us to detect the CARS signals resulting from 1 Torr with a signal-to-noise (S/N) ratio of 10. 2 Torr was needed for PARS detection; however, improvements in the gas cell design and in the amplification system are expected to lead to higher sensitivities. Both the CARS and PARS methods can be used to directly monitor the conditions of the SRE excitation and also to detect the CHF_2Cl in molecular dynamics experiments.

CH_3CFCl_2. Figure 2 shows representative CARS/PARS spectra of CH_3CFCl_2. The ν_1 Q-branch with 3020 cm^{-1} (ω_S = 633.85 nm) Raman shift, the ν_2 Q-branch with 2960 cm^{-1} (ω_S = 631.45 nm), and the $2\nu_3$ Q-branch with a 2878 cm^{-1} (ω_S = 628.2 nm) shift are the prominent features of the spectra. Our measured Raman shifts agree with recent high-resolution FTIR measurements[17] which located ν_1 at 3021.5 cm^{-1}, ν_2 at 2960.8 cm^{-1}, and ν_3 at 1448 cm^{-1}. A relatively high pressure is used to monitor the CARS and PARS spectra to enable the observation of the $2\nu_3$ overtone. The sharp Q-branch of ν_1 is also accompanied by P- and R-branches. From the general appearance of this band it seems that it corresponds to an A-type band. The ν_1 and ν_2 bands have been assigned to the CH_3 antisymmetric and symmetric stretches, respectively, while the ν_3 to the antisymmetric CH_3 deformation.[17,19,22]

The CH_3CF_2Cl spectra do not show any shifted peaks that can be attributed to the $CH_3CF_2{}^{37}Cl$ isotopomer. This behavior differs from that of CHF_2Cl, but agrees very well with very recent predicted vibrational frequencies,[17] calculated by ab initio at the MP2/6-311G** level. McNoughton and Evans[17] predicted that no shift will be observed for the CH_3 stretches and CH_3 deformation bands, but large shifts are expected for other bands. For example, 2.00 and 6.59 cm^{-1} shifts are expected for the C−Cl stretch and for the CF_2 wagging, respectively.

The integrated intensity of the ν_2 band of CH_3CF_2Cl is higher than that of the ν_1 band of CHF_2Cl. The ratio between the CARS integrated intensities of the two bands is 6.4 ± 1.6, i.e., a ratio of 2.5 between the Raman cross sections. The PARS integrated intensities give a ratio of 2.8 ± 0.3, agreeing well with the CARS value, but again differing from that given in ref 25, namely 1.7. The calculated ratios between the integrated intensities of the ν_1 and ν_2 bands of CH_3CF_2Cl in the CARS and PARS are 410 ± 140 and 124 ± 38, respectively. The ratios of the Raman cross sections obtained by the two methods, ∼20 and 120, are quite different. This is probably due to the large difference in the intensities of the two bands necessitating very different experimental conditions (filters, amplification). Anyhow, both our values are much larger than the ratio 2.9 calculated from ref 25.

The intensities obtained for CH_3CF_2Cl show that the sensitivity of its detection via the ν_2 band is even higher than that of CHF_2Cl and reducing its pressure to 1 Torr still allows its CARS detection with a S/N of 20. Under the same conditions the PARS S/N was 3. These sensitivities offer the possibility to apply CARS and PARS in dynamics studies of CH_3CF_2Cl.

Conclusions

Using the CARS/PARS methods we monitored the vibrational bands of two HCFC compounds. The bands were identified and attributed to the C−H stretches of CHF_2Cl isotopomers and to CH_3 stretches and CH_3 deformation overtone of CH_3CF_2Cl. The assignment was greatly aided by the employment of both methods because of the different dependencies of the CARS/PARS signals on ΔN. The application of both methods may be of importance in other isotopic systems as well.

The large signals obtained show that detection of these molecules can be accomplished by CARS/PARS methods. Moreover, they suggest that large number densities of vibrationally excited molecules may be obtained in different vibrational states and even in the CH_3 deformation overtone, allowing study of bimolecular and unimolecular reactions of vibrationally excited HCFC's.

Acknowledgment. We thank Prof. P. J. Dagdigian for useful discussions. This research was supported by grant No. 96-00140 from the United States−Israel Binational Foundation (BSF) and by the James Franck Binational German−Israeli Program in Laser-Matter Interaction. A.M. thanks the Israeli Ministry of Science for a Levy Eshkol scholarship.

References and Notes

(1) Rowland, F. S. *Environ. Sci. Techol.* **1991**, *25*, 622.

(2) McFarland, M.; Kaye, J. *Photochem. and Photobiol.* **1992**, *55*, 911.

(3) *Scientific Assessment of Ozone Depletion: 1991*; World Meteorological Organization Global Research and Monitoring Project Report No. 25; World Meteorological Organization: Geneva, Switzerland, 1992.

(4) Laurent, T.; Lillich, H.; Volpp, H.-R.; Wolfrum, J.; Bar, I.; Melchior A.; Rosenwaks, S. *Chem. Phys. Lett.* **1995**, *247*, 321.

(5) Warren, R.; Gierezak, T.; Ravishankara, A. R. *Chem. Phys. Lett.* **1991**, *183*, 403.

(6) Zhang, Z.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **1992**, *96*, 1533. Liu, R.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **1990**, *94*, 3247.

(7) DeMore, W. B. *J. Phys. Chem.* **1996**, *100*, 5813.

(8) Fang, T. D.; Taylor, P. H.; Dellinger, B. *J. Phys. Chem.* **1996**, *100*, 4048.

(9) Gierczak, T.; Talukdar, R.; Vaghjiani, G. L.; Lovejoy, E. R.; Ravishankara. A. R. *J. Geophys. Res.* **1991**, *96*, 5001.

(10) Sawerysyn, J. P.; Talhaoui, A. Meriaux, B.; Devolder, P. *Chem. Phys. Lett.* **1992**, *198*, 197.

(11) Yang, X.; Felder, P.; Huber, J. R. *Chem. Phys.* **1994**, *189*, 129.

(12) Melchior, A.; Knupfer, P.; Bar, I.; Rosenwaks, S.; Laurent, T.; Volpp, H.-R., Wolfrum, J. *J. Phys. Chem.* **1996**, *100*, 13375. Melchior A.; Bar, I.; Rosenwaks, S. *J. Chem. Phys.* **1997**, *107*, 8476. Melchior, A.; Lambert, H. M.; Dagdigian, P. J.; Bar, I.; Rosenwaks, S. *Isr. J. Chem.* **1997**, *37*, 455.

(13) Brownsword, R. A.; Hillenkamp. M.; Laurent, T.; Volpp, H.-R., Wolfrum, J.; Vatsa, R. K.; Yoo, H.-S. *J. Chem. Phys.* **1997**, *107*, 779. Brownsword, R. A.; Hillenkamp. M.; Laurent, T.; Vatsa, R. K.; Volpp, H.-R.; Wolfrum, J. *J. Phys. Chem. A* **1997**, *101*, 5222; *J. Chem. Phys.* **1997**, *106*, 1359; *J. Phys. Chem. A* **1997**, *101*, 995.

(14) Palmieri, P.; Tarroni, R.; Huhn, M. M.; Handy, N. C.; Willetts, A. *Chem. Phys.* **1995**, *190*, 327.

(15) Kisiel, Z.; Alonso, J. L.; Blanco, S.; Cazzoli, G.; Colmont, J. M.; Cotti, G.; Graner, G.; Lopez, J. C.; Merke, I.; Pszxzolkowski, L. *J. Mol. Spectrosc.* **1997**, *184*, 150.

(16) Cramb, D. T.; Bos, Y.; Jemson, H. M.; Gerry, M. C. L.; Marsden, C. J. *J. Mol. Struct.* **1988**, *190*, 387.

(17) McNaughton, D.; Evans, C. *J. Mol. Spectrosc.* **1997**, *182*, 342.

(18) Cazzoli, G.; Cotti, G.; Esposti, C. D. *J. Mol. Spectrosc.* **1993**, *159*, 127.

(19) Newnham, D.; Ballard, J. *J. Quant. Spectrosc. Radiat. Transfer* **1995**, *53*, 471.

(20) Fraser, G. T.; Domenech, J.; Junttila, M.-L.; Pine, S. *J. Mol. Spectrosc.* **1992**, *152*, 307.

(21) Wu, Y. H.; Onomichi, M.; Sasaki, S.; Shimizu, H. *J. Raman Spectrosc.* **1993**, *24*, 845.

(22) Paddison, S. J.; Chen, Y.; Tschuikow-Roux, E. *Can. J. Chem.* **1994**, *72*, 561.

(23) Smith, D. C.; Brown, G. E. *J. Chem. Phys*. **1952**, *20*, 473.

(24) Holzer, W. *J. Mol. Spectrosc.* **1968**, *25*, 123. Murphy, W. F.; Holzer, W.; Bernstein, H. J. *Appl. Spectrosc.* **1969**, *23*, 211.

(25) Schrotter, H. W.; Klockner, H. W. in *Raman Spectroscopy of Gases and Liquids*; Topics in Applied Physics, Vol. 11; Weber, A., Ed.; Springer: Berlin, 1979; p 123.

(26) Valentini, J. J. in *Laser Spectroscopy and its Applications*; Opt. Eng. Vol. 11; Radziemsky, L. J., Solarz, R. W., Paisner, J. A., Eds.; Marcel Dekker: New York, 1987; p 507. Valentini, J. J. *Spectrometric Techniques*; Vanasse, G. A. Ed.; Academic Press: New York, 1985; Vol. 4, p 1.

(27) Nibler, J. W.; Knighten, G. V. in *Raman Spectroscopy of Gases and Liquids*, Topics in Applied Physics, Vol. 11. Weber, A. Ed.; Springer, Berlin/Heidelberg/New York, 1979; p 253.

(28) West, G. A.; Barrett, J. J.; Siebert, D. R.; Reddy, K. V. *Rev. Sci. Instrum.* **1983**, *54*, 797.

(29) Woyde, M.; Stricker, W. *Appl. Phys. B* **1990**, *50*, 519. Bouche, T.; Dreier, T.; Lange, B.; Wolfrum, J.; Franck, E. U.; Schilling, W. *Appl. Phys. B* **1990**, *50*, 527. Attal-Tretout, B.; Bouchardy, P.; Magre, P.; Pealat, M.; Taran, J. P. *Appl. Phys. B* **1990**, *51*, 17. Kroll, S.; Bengtsson, P.-E.; Alden, M.; Nilsson, D. *Appl. Phys. B* **1990**, *51*, 25. Porter, F. M.; Greenhalgh, D. A.; Stopford, P. J.; William, D. R.; Baker, C. A. *Appl. Phys. B* **1990**, *51*, 31. Marowsky, G.; Lupke, G. *Appl. Phys. B* **1990**, *51*, 49. Lange, B.; Wolfrum, J. *Appl. Phys. B* **1990**, *51*, 53. Bombach, R.; Gerber, T.; Hemmerling, B.; Hubschmid, W. *Appl. Phys. B* **1990**, *51*, 59. Wenzel, N.; Lange, B.; Marowsky, G. *Appl. Phys. B* **1990**, *51*, 61. Cottereau, M. J.; Grisch, F.; Marie, J. J. *Appl. Phys. B* **1990**, *51*, 63.

(30) Druet, S. A.; Taran, J. P. *Prog. Quantum. Electron.* **1981**, *7*, 1.

(31) Baxter, G. W.; Johnson, M. J.; Haub, J. G., Orr, B. J. *Chem. Phys. Lett.* **1996**, *251*, 211.

(32) Grisch, F.; Pealat, M.; Collin, G.; Taran, J. P.; Bar. I.; Heflinger, D.; Rosenwaks, S. *Appl. Phys. Lett.* **1991**, *59*, 3516.

(33) Lanzisera, D. V.; Valentini, J. J *J. Phys. Chem. A* **1997**, *101*, 6496; *J. Chem. Phys*. **1995**, *103*, 607. Anda, A. A.; Phillips, D. L.; Valentini, J. J. *J. Chem. Phys.* **1986**, *85*, 1719.

(34) Zhang, J.-X.; Aker, P. M. *J. Phys. Chem*. **1994**, *98*, 765.

(35) Bar, I.; Cohen, Y.; David, D.; Arusi-Parpar, T.; Rosenwaks, S.; Valentini, J. J. *J. Chem. Phys*. **1991**, *95*, 3341. Bar, I.; Cohen, Y.; David, D.; Rosenwaks, S.; Valentini, J. J. *J. Chem. Phys*. **1990**, *93*, 2146.

(36) Ravichandran, S.; Yorgancioglu, M.; Fletcher, T. R. *J. Chem. Phys*. **1994**, *101*, 3406.

(37) Chadwick, B. L.; Milce, A. P.; Orr, B. J. *Can. J. Phys.* **1994**, *72*, 939. Chadwick, B. L.; Orr, B. J. *J. Chem. Phys.* **1992**, *97*, 3007.

(38) Brown, S. S.; Berghout, H. L.; Crim, F. F. *J. Chem. Phys*. **1997**, *106*, 5805.

(39) Brown, A.; McKean, D. C.; Duncan, J. L. *Spectrochim. Acta* **1988**, *44A*, 553.