

# Precise measurement of the depolarization ratio from photoacoustic Raman spectroscopy

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Received 9 February 2007; Accepted 21 March 2007

**A new method for the accurate determination of the Raman depolarization ratio is reported with an improved setup for photoacoustic Raman spectroscopy (PARS). The precise measurement is achieved by measuring the dependence of the acoustic signal intensity on the cross-angle between the polarizations of two incident laser beams. We demonstrate this sensitive and simple method with several gaseous molecules, such as CH<sub>4</sub> and H<sub>2</sub>. The measured results of depolarization ratios agree well with the theoretical values with an upper error limit of  $\pm 0.005$ , which is comparable to that with polarization-resolved CARS spectroscopy. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** depolarization ratio; precise measurement; PARS; counterpropagating laser beams; global fitting

## INTRODUCTION

The depolarization ratio  $\rho$  is a fundamental physical parameter in the studies of Raman spectroscopy and molecular dynamics since it characterizes the symmetry of a Raman-active vibrational mode of molecules in gaseous and liquid phases and is helpful in the assignment of the Raman spectrum.<sup>1</sup> The precise measurement of the depolarization ratio is also of great importance in the sense that it distinguishes different vibrational bands with close  $\rho$  values, and helps in the detection of small distortions of molecular structures in liquids and solutions caused by different chemical environments in a quantitative manner.<sup>2–4</sup> In recent years, accurate determination of the depolarization ratio has become essentially important in the spectroscopic and dynamic studies of molecules at the vapor/liquid interface using the sum frequency generation (SFG) technique.<sup>5–7</sup>

Traditionally, the depolarization ratio is obtained from the conventional spontaneous Raman spectroscopy, and is measured as the ratio of scattered light intensities  $I_{\perp}$  to  $I_{\parallel}$ ,  $\rho = I_{\perp} / I_{\parallel}$ , where  $I_{\perp}$  and  $I_{\parallel}$  are intensities of the scattered light with polarizations perpendicular and parallel to the polarization plane of the incident laser beam, respectively. However, the precision of the depolarization ratio measured in this way is generally low.<sup>1,8–11</sup> First, in the case of measuring small  $\rho$ , the intensity  $I_{\perp}$  is quite weak compared to the intensity  $I_{\parallel}$ , and the measurement of  $I_{\perp}$  usually has

a large uncertainty, and consequently it is impossible to obtain the  $\rho$  value with high precision. Second, unlike a plane wave with a well-defined direction of polarization, the scattered light collected with a lens in a finite solid angle is a spherical wave, and its polarization is relatively complicated. Polarization measurements made in this way would bring some errors to the depolarization ratio and need to be corrected.<sup>8</sup> Third, the reflection efficiency of the dispersing monochromator varies with the polarization of the scattered light, although this can be theoretically obviated using a polarization scrambler.

Recently, Saito *et al.*<sup>12</sup> reported a new method to measure the depolarization ratio, called polarization-resolved coherent anti-Stokes Raman scattering (CARS). With this method, the depolarization ratio could be determined with an unprecedented accuracy of  $\pm 0.002$ . However, unlike in the spontaneous Raman spectrum, a nonresonant background usually exists in the CARS spectrum, since the third-order nonlinear susceptibility tensor  $\chi^{(3)}$  consists of a resonant part, and a nonresonant part which varies slowly with the Raman shift. In CARS spectroscopy, the depolarization ratio at the Raman resonant position is defined as<sup>12–14</sup>

$$\rho = \chi_{2112}^R / \chi_{1111}^R \quad (1)$$

where  $\chi_{2112}^R$  and  $\chi_{1111}^R$  are the resonant parts of the third-order nonlinear susceptibility tensor elements of  $\chi_{2112}^{(3)}$  and  $\chi_{1111}^{(3)}$ , respectively. Saito *et al.*<sup>12</sup> deduced that the depolarization ratio in polarization-controlled CARS spectroscopy could be obtained from

$$\rho = \tan \phi_R / \tan \theta \quad (2)$$

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where  $\theta$  is the cross-angle between polarizations of the two incident laser beams, i.e. the pump laser and the Stokes laser, and  $\phi_R$  is the cross-angle between polarizations of the pump beam and the resonant part of the CARS signal. For a certain Raman band and a prefixed angle  $\theta$ , the angle  $\phi_R$  was measured with a polarization analyzer, and the depolarization ratio could be determined from Eqn (2). The key step of this method is to eliminate the interference from the nonresonant background in the CARS spectrum. By simulating the CARS spectra at different angles of the polarization analyzer, the dependence of the Raman resonance signal intensity on the analyzer angle was obtained, and the angle  $\phi_R$  corresponding to the analyzer angle at which the Raman resonance signal vanished was precisely determined. The accuracy of the depolarization ratio thus measured was much higher than that with spontaneous Raman spectroscopy. Depolarization ratios of several molecules have been precisely measured with this method.<sup>12,15</sup>

In this paper, we introduce another nonlinear spectroscopic method to measure the depolarization ratio, called polarized photoacoustic Raman spectroscopy (PARS). The accuracy with this method is comparable to that with the polarization-resolved CARS spectroscopy. In addition, the operation procedure of this method is simple and straightforward, and the spectral sensitivity is relatively high.

### DEPOLARIZATION RATIO FROM POLARIZED PARS

In PARS spectroscopy, the photoacoustic signal originates from a stimulated Raman scattering process by the pump and Stokes laser beams. When the frequency difference between the two spatially overlapped laser beams is in resonance with a Raman-active vibrational transition, a stimulated Raman scattering process occurs, and the molecules are populated from the ground vibrational level to an excited vibrational level. The molecular population at this excited level will be reduced by the subsequent collision-induced vibrational relaxation. Consequently, the translational temperature is increased in the local interaction area, and an excess pressure wave is generated and then detected by a sensitive microphone or a piezoelectric transducer as the photoacoustic signal. The PARS spectrum is obtained by monitoring the photoacoustic signal intensity with the variation of the frequency difference between the pump and Stokes laser beams. The sensitivity of the PARS technique is greatly increased in contrast to the direct measurement of spontaneous Raman scattering photons. This technique was invented originally by Barrett and Berry to measure the Raman spectrum of gaseous methane.<sup>16</sup> Almost simultaneously, Patel and Tam developed and successfully applied this method to experiments in liquid and solid phases using a piezoelectric transducer as the acoustic detector instead of a microphone used in the gaseous phase.<sup>17,18</sup> From then on,

PARS has been widely applied to gaseous trace component analysis and molecular dynamic processes.<sup>19–23</sup>

The basic theory of PARS has already been described elsewhere.<sup>20,21</sup> Here, only a brief description of PARS is introduced, and the relation of PARS intensity with polarization cross-angle of the two laser beams will be shown. For parallel polarized pump and Stokes laser beams (both linearly polarized plane waves), the PARS signal intensity can be expressed as

$$I \propto NL\sigma_{//}I_P I_S \tag{3}$$

where  $N$  is the molecular number density,  $I_P$  and  $I_S$  are the intensities of pump and Stokes laser beams, respectively,  $\sigma_{//}$  is the Raman cross section for parallel polarization of the two laser beams and  $L$  is the effective interaction length between sample and two laser beams. Similarly, when the polarizations of two laser beams are orthogonal to each other, the PARS signal intensity can be written as

$$I \propto NL\sigma_{\perp}I_P I_S \tag{4}$$

where  $\sigma_{\perp}$  is the Raman cross section for orthogonal polarization of the two laser beams.

Since the intrinsic property of stimulated Raman scattering is the same as that of spontaneous Raman scattering, the ratio between cross-sections  $\sigma_{\perp}$  and  $\sigma_{//}$  is also the depolarization ratio, i.e.  $\rho = \sigma_{\perp}/\sigma_{//}$ . When the polarizations of two laser beams cross with a certain angle  $\theta$ , the contributions of parallel and orthogonal polarization configurations give the total PARS signal intensity,

$$\begin{aligned} I &\propto NL(\sigma_{//}I_P I_S + \sigma_{\perp}I_P I_S) \\ &= NL(\sigma_{//}I_P I_S \cos^2 \theta + \sigma_{\perp}I_P I_S \sin^2 \theta) \end{aligned} \tag{5}$$

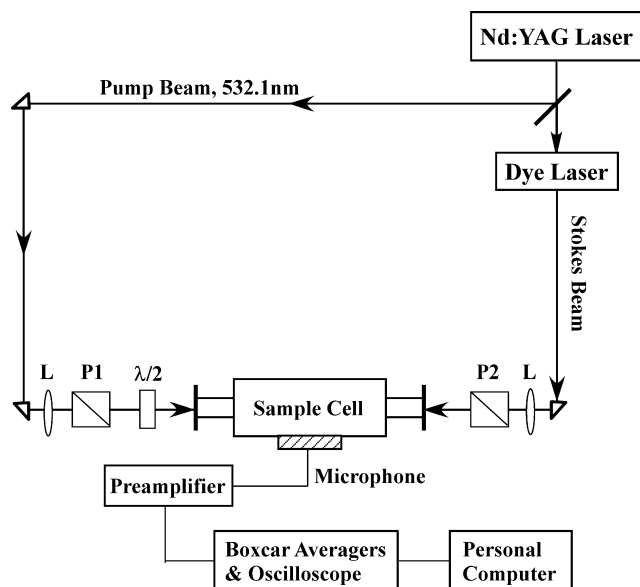
It can also be written in an alternative form,

$$I \propto NL\sigma_{//}I_P I_S (\cos^2 \theta + \rho \sin^2 \theta) \tag{6}$$

where the relation  $\rho = \sigma_{\perp}/\sigma_{//}$  is used. It is evident that the PARS signal intensity is periodically dependent on the cross-angle  $\theta$  between the polarizations of two laser beams. By measuring the  $I-\theta$  curve, the depolarization ratio  $\rho$  can be obtained from a global fitting with Eqn (6). As will be seen in the following section, the depolarization ratio can be measured precisely with this method.

### IMPROVED EXPERIMENTAL SETUP OF PARS

The experimental setup is shown schematically in Fig. 1, which is similar to that described previously,<sup>24</sup> but a few modifications were made for the purpose of the depolarization ratio measurement. The second-harmonic output from a pulsed Nd:YAG laser (Spectra Physics, Pro-190-10, 532.1nm, linewidth 1.0 cm<sup>-1</sup>, pulse width 10 ns) is

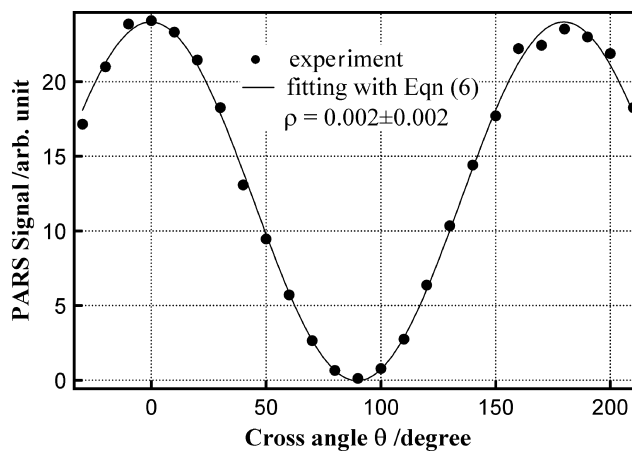


**Figure 1.** The experimental setup for polarized PARS. L: quartz lens, P1 and P2: Glan-Taylor prism,  $\lambda/2$ : half-wave plate.

split into two beams by a quartz plate. About 90% of the 532.1 nm laser energy is used to pump a dye laser system (Continuum, ND6000, linewidth  $0.05 \text{ cm}^{-1}$ ) to generate a tunable Stokes laser beam, and the residual 10% of the 532.1 nm laser output is used as a pump beam in PARS experiments. The pump and Stokes laser beams are focused by two lenses with  $f = 45 \text{ cm}$ , and counterpropagate into a homemade photoacoustic cell, where both laser beams are temporally and spatially overlapped with each other. The energies of the pump and Stokes beams are typically  $10 \text{ mJ/pulse}$  and  $3 \text{ mJ/pulse}$ , respectively.

The generated photoacoustic signal is detected by a microphone, subsequently preamplified and monitored by an oscilloscope. The peak height of the oscillatory photoacoustic signal is measured as the PARS signal intensity, or is averaged by a Boxcar integrator and sent to a PC to obtain the PARS spectrum. Since the spectral resolution of PARS is determined by the convolution of the linewidths of two laser beams, the final spectral resolution in the present experiment is expected to be  $\sim 1.0 \text{ cm}^{-1}$ . Pure sample gases were used during the experiment, and the pressure in the cell was adjusted in the range 5.0–100 Torr according to the PARS signal intensity.

In order to measure the depolarization ratio precisely, the pump and Stokes laser beams must be highly polarized, which was achieved by two Glan-Taylor prisms, P<sub>1</sub> and P<sub>2</sub> in Fig. 1 (extinction ratio  $< 10^{-6}$ ). To minimize the polarization distortion of two laser beams by all optics, the two focusing lenses were placed ahead of the Glan-Taylor prisms, and the quartz plate windows of the acoustic cell were carefully selected and mounted. During the experiment, the polarization of the Stokes beam was fixed in the vertical direction, and that of pump beam was rotated by a  $\lambda/2$  wave



**Figure 2.** A typical global fitting of the  $I-\theta$  curve with Eqn (6) to determine the depolarization ratio. The example here is obtained at the Q-branch of the  $\nu_1$  band of  $\text{CH}_4$ . The theoretical depolarization ratio is 0, and the experimentally determined value is 0.002 within an error of  $\pm 0.002$ .

plate mounted on a mirror holder, which could rotate with the smallest angle setting of  $0.5^\circ$ . In this way, the polarization cross-angle  $\theta$  between the two laser beams was controlled. The angle  $\theta$  was calibrated at  $\theta = 90^\circ$  where the pump beam could not pass through the P<sub>2</sub> prism in Fig. 1. A typical photoacoustic Raman signal intensity *vs* the polarization cross-angle  $\theta$  is shown in Fig. 2 along with the global fitting with Eqn (6).

## MERITS OF PRESENT PARS EXPERIMENT

### Comparison with spontaneous Raman experiment

In contrast with the spontaneous Raman experiment, the depolarization ratio obtained with present polarized PARS method is more accurate. First, the depolarization ratio determined from a global fitting of the  $I-\theta$  curve will reduce the uncertainty of the ratio between only two intensities  $I_\perp$  and  $I_\parallel$  in the spontaneous Raman experiment, especially for the measurement of small  $\rho$ , where the scattered intensity  $I_\perp$  is too weak to be measured accurately. Second, the polarization dependence of PARS signal is the result of a precise matching between the polarizations of two laser beams. This is different from the spontaneous Raman experiment, where the Raman scattered light is a spherical wave and is collected in a finite solid angle with relatively complex polarizations. Third, since the PARS signal originates from a stimulated Raman scattering process by two laser beams, the spectral sensitivity is very high compared to the spontaneous Raman experiment, which is especially suitable to measure the Raman spectra of molecules in the gaseous phase.

### Comparison with conventional PARS experiment

The optical arrangement of our experiment is different from that of a conventional PARS experiment. In the

present experiment, the pump and Stokes laser beams counterpropagate in the photoacoustic cell where both laser beams are temporally and spatially overlapped with each other, while in a conventional PARS experiment the two laser beams are overlapped collinearly (using a 45° setting dichroic mirror as the beam combiner) and copropagate in the photoacoustic cell.<sup>16–23</sup> It can be seen that the optical alignment of our counterpropagating arrangement is simple and can be easily achieved in the experiment. In addition, when using a dichroic mirror as the beam combiner in conventional PARS experiment, the spectrum with small Raman shift cannot be measured, since there exists a certain wavelength interval between the reflected and transmitted laser beams for a dichroic mirror. Without the use of the dichroic mirror, this limitation was removed in the present experiment. Moreover, when using a 45° setting dichroic mirror in conventional PARS experiment and rotating the polarization of pump laser or Stokes laser to measure the depolarization ratio, the actual intensity of the pump laser or Stokes laser in the photoacoustic cell will not remain constant, since the reflection and transmission efficiencies of the dichroic mirror vary with the laser polarization direction. This makes the measurement of depolarization ratio in a conventional PARS experiment unfavorable. Finally, with two counterpropagating laser beams in the present method, Doppler effect can be effectively suppressed when recording high-resolution spectra in the gaseous phase. Therefore, it is an appropriate choice to measure the depolarization ratio using two counterpropagating laser beams as in present PARS experiment.

### Comparison with polarization-resolved CARS experiment

As reported by Saito *et al.*,<sup>12</sup> the Raman depolarization ratio can be accurately determined with the polarization-resolved CARS method. However, in contrast with the polarization-resolved CARS spectrum, the PARS spectrum is free from the interference from the nonresonant background, which distorts the spectral band shape, since the PARS spectrum is essentially the same as the spontaneous Raman spectrum. Therefore, the procedure of spectral simulation in the CARS experiment to derive the contribution of resonant Raman scattering is not needed in the present experiment. Furthermore, as seen from above, the experimental setup and the operation procedure with our method are relatively simple, while in the CARS experiment the pump and Stokes laser beams must be carefully aligned to meet the phase-matching condition, and the polarization direction of CARS signal has to be analyzed with respect to that of the pump or Stokes beam in order to obtain the depolarization ratio from Eqn (2). On the other hand, for experiments in the region of electronic Raman resonance, the CARS method has special advantages in the measurement of the depolarization ratios. In this case, both the pump and Stokes lasers excite molecules to the electronically excited state, the excited molecules will

decay to the ground state and the subsequent vibrational relaxation at the ground state will generate a strong acoustic wave. Therefore, when measuring the depolarization ratios in the region of electronic Raman resonance, the PARS experiment is an unfavorable choice due to the strong background acoustic signal.

It should be stated that the present method could also be applied to experiments in liquid and solid phases. Patel and Tam<sup>17,18</sup> measured the PARS spectra of molecules in liquid and solid phases using a piezoelectric transducer as the acoustical detector. Substituting the microphone in present experiment with a piezoelectric transducer, depolarization ratios of molecules in liquid and solid phases can also be accurately determined with present method.

## RESULTS DEMONSTRATED WITH RAMAN BANDS OF KNOWN DEPOLARIZATION RATIOS

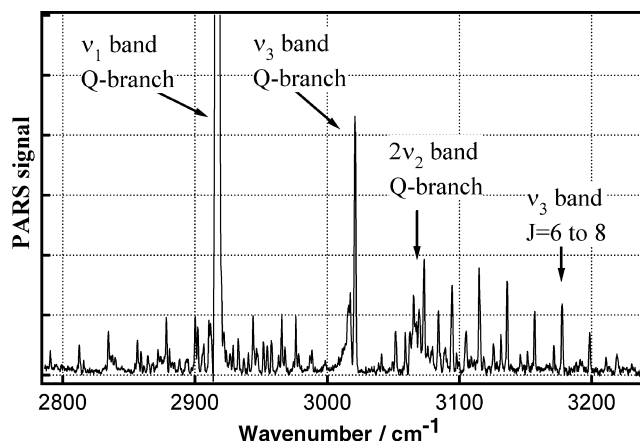
The reliability and accuracy of depolarization ratio measurement with the present polarized PARS method were tested with the gaseous molecules CH<sub>4</sub> and H<sub>2</sub>, since their theoretical depolarization ratios of some ro-vibrational Raman bands are known from the literature. The depolarization ratios were determined with an error limit of ±0.005 in the present experiment.

### CH<sub>4</sub>

Methane is a spherically symmetric molecule, and is usually taken as a calibration medium for the depolarization ratio measurement in the gaseous phase.<sup>25,26</sup> The symmetries of vibrational modes  $\nu_1$  (2916.7 cm<sup>-1</sup>) and  $\nu_3$  (3018.9 cm<sup>-1</sup>) are A<sub>1</sub> and T<sub>2</sub> in the T<sub>d</sub> point group, respectively. For linearly polarized pump laser and under electronically off-resonant conditions, their theoretical values of the depolarization ratio are 0 and 3/4, respectively. For the rotational lines in the vibration-rotation Raman spectrum, depolarization ratio is expected to be dependent on the rotational transition (see Chapter 6 in Ref. 1). For transitions  $\Delta J = -2, -1, 1$  and 2 (O-, P-, R- and S-branches), depolarization ratio  $\rho$  is 3/4, while for transition  $\Delta J = 0$  (Q-branch), the  $\rho$  value is between 0 and 3/4, depending on the symmetry of vibrational mode.

The PARS spectrum of CH<sub>4</sub> in the range 2780–3200 cm<sup>-1</sup> is shown in Fig. 3, which consists of ro-vibrational transitions of the  $\nu_1, 2\nu_2$  and  $\nu_3$  bands. The spectrum is essentially similar to those in the literature and the assignments were adopted from those made originally by Herranz and Stoicheff.<sup>27</sup> Since the spectral resolution in the present experiment was ~1.0 cm<sup>-1</sup>, rotational lines in the spectrum were not completely resolved, except for several lines such as the  $J = 6 \rightarrow J = 8$  transition in the S-branch of  $\nu_3$  band.

Following the approaches described above, depolarization ratios of the Q-branches of  $\nu_1$  and  $\nu_3$  bands, as well



**Figure 3.** The PARS spectrum of CH<sub>4</sub> in the range 2780–3200 cm<sup>-1</sup>. The pressure of gas sample was kept at 100.0 Torr and the energies of pump and Stokes laser beams were 10 mJ/pulse and 3 mJ/pulse, respectively. The spectral resolution was ~1 cm<sup>-1</sup>.

as the  $J = 6 \rightarrow J = 8$  rotational line of  $\nu_3$  band, were measured. Figure 4 shows the change of the PARS signal with the polarization cross-angle of the two laser beams, measured respectively at the Q-branches of the  $\nu_1$  and  $\nu_3$  bands. For each Raman transition, four independent measurements were performed. As can be seen from Fig. 4, these four measurements gave almost indistinguishable results, showing the stability of the present measuring system. The four experimental curves were averaged and fitted to the theoretical curve of Eqn (6) with the depolarization ratio as a parameter to be determined. The obtained values of depolarization ratios are listed in Table 1. For comparison, the theoretically predicted values<sup>1</sup> and the results measured by a spontaneous Raman experiment<sup>26</sup> are also listed in the table.

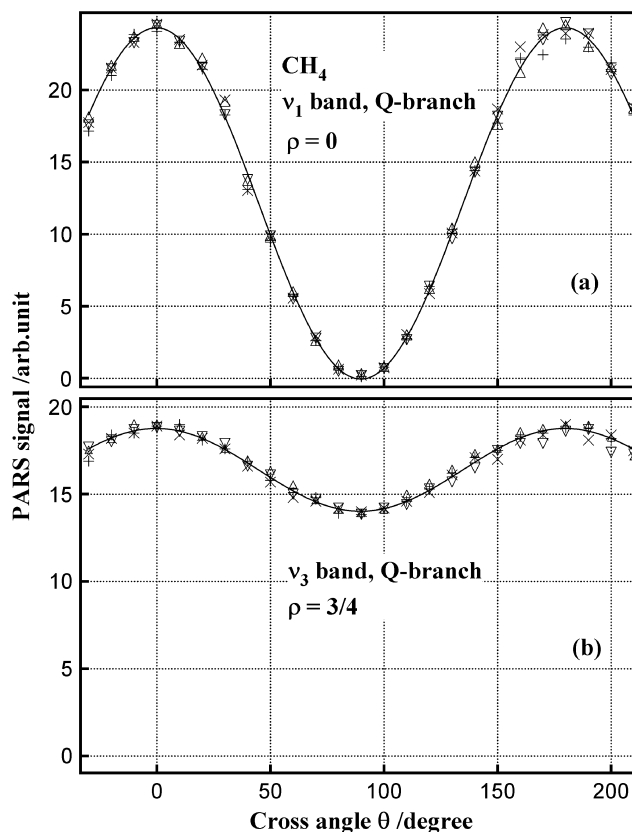
It can be seen from Table 1 that the precision of our determined depolarization ratio is quite high, within an error limit of  $\pm 0.005$ . The measured values are slightly larger than the theoretical values. This might have resulted from the polarization degradation of the two laser beams by optical components, such as the quartz windows of photoacoustic cell and the half-wave plate.

**Table 1.** Depolarization ratios of the Q-branches of the  $\nu_1$  and  $\nu_3$  bands and the  $J = 6 \rightarrow J = 8$  rotational line of  $\nu_3$  band of methane, determined from the global fittings of the measured  $I - \theta$  curves

Transition	Position/cm <sup>-1</sup>	Depolarization ratio		
		Theoretical <sup>a</sup>	Ref. 26	This work
$\nu_1$ band, Q-branch	2916.7	0	$0.025 \pm 0.005$	$0.002 \pm 0.002$
$\nu_3$ band, Q-branch	3018.9	3/4	$0.76 \pm 0.02$	$0.752 \pm 0.003$
$\nu_3$ band, $J = 6 \rightarrow J = 8$	3177.0	3/4	–	$0.752 \pm 0.005$

<sup>a</sup> Ref. 1

Reference 26: Spontaneous Raman experiment.



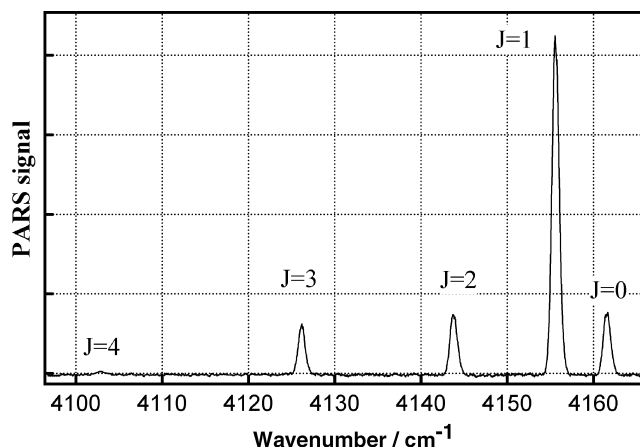
**Figure 4.** The  $I - \theta$  curves of the Q-branches of  $\nu_1$  and  $\nu_3$  bands of CH<sub>4</sub>. For each Raman transition, four independent measurements were performed, averaged and fitted globally with Eqn (6) to determine the depolarization ratio.

## H<sub>2</sub>

The rotational constant of H<sub>2</sub> is the largest among all molecules, and the maximum populated rotational level at room temperature is  $J = 1$ . The Q-branch of the vibrational Raman band could be easily resolved in our experiment as shown in Fig. 5. Holzer *et al.*<sup>28</sup> studied theoretically the rotational dependence of the depolarization ratio, and calculated the depolarization ratios of the rotational components of the Q-branch of the vibrational Raman band of H<sub>2</sub>. The depolarization ratios of the transitions  $J = 0 - 4$

**Table 2.** Depolarization ratios of rotational components of the Q-branch of vibrational Raman band of H<sub>2</sub>

J	Position/cm <sup>-1</sup>	Depolarization ratio	
		Calculated <sup>a</sup>	This work
0	4161	0.0000	0.002 ± 0.002
1	4155	0.0195	0.021 ± 0.002
2	4143	0.0140	0.015 ± 0.002
3	4126	0.0131	0.014 ± 0.002
4	4103	0.0128	0.013 ± 0.005
∞	–	0.0123	–

<sup>a</sup> Ref. 28.**Figure 5.** The Q-branch of vibrational Raman band of H<sub>2</sub> in the range 4100–4165cm<sup>-1</sup>. The spectrum was recorded under the same experimental conditions as in Fig. 3.

of the Q-branch of H<sub>2</sub> were measured with the method described above, and the results are summarized in Table 2. It can be seen from Table 2 that our experimental results agree well with the theoretical values.<sup>28</sup> The error limit of our determined depolarization ratio is estimated to be ±0.005.

## CONCLUSIONS

We have reported the experimental construction and procedure to precisely measure the Raman depolarization ratios, based on a modified PARS measuring system. The reliability and accuracy of the depolarization ratio measurement have been demonstrated with some ro-vibrational Raman bands of gaseous CH<sub>4</sub> and H<sub>2</sub> molecules, whose depolarization ratios are theoretically known. The measured results of the depolarization ratios agree well with the theoretical values with

the maximum experimental uncertainty of ±0.005, which is comparable to that obtained with polarization-resolved CARS spectroscopy. The present method has been proved to provide accurate determination of Raman depolarization ratios in gaseous and condensed phases. Compared to the method of CARS spectroscopy, the experimental operation with this method is simple, and the procedure to determine the depolarization ratio is straightforward.

## Acknowledgments

The present work was supported financially by the Natural Science Foundation of China (NSFC, No. 20533070, No. 20573100, No. 20373066).

## REFERENCES

- Long DA. *The Raman effect: A Unified Treatment of the Theory of Raman Scattering by Molecules*. John Wiley & Sons: New York, 2002.
- Ebata T, Hamakado M, Moriyama S, Morioka Y, Ito M. *Chem. Phys. Lett.* 1992; **199**: 33.
- Holzer W, Duff YL. *Phys. Rev. Lett.* 1974; **32**: 205.
- Duff YL. *Phys. Rev. A* 1983; **28**: 2714.
- Zhang D, Gotow J, Eisenthal KB. *J. Phys. Chem.* 1994; **98**: 13729.
- Zhuang X, Miranda PB, Kim D, Shen YR. *Phys. Rev. B* 1999; **59**: 12632.
- Lu R, Gan W, Wu BH, Chen H, Wang HF. *J. Phys. Chem. B* 2004; **108**: 7297.
- Dawson P. *Spectrochim. Acta* 1972; **28A**: 715.
- Deb SK, Bansal ML, Roy AP. *Appl. Spectrosc.* 1984; **38**: 500.
- Teboul V, Godet JL, Duff YL. *Appl. Spectrosc.* 1992; **46**: 476.
- Spinner E. *Spectrochim. Acta, Part A* 2003; **59**: 1441.
- Saito Y, Ishibashi T, Hamaguchi H. *J. Raman. Spectrosc.* 2000; **31**: 725.
- Yuratich MA, Hanna DC. *Mol. Phys.* 1977; **33**: 671.
- Eesley GL. *Coherent Raman Spectroscopy*. Pergamon Press: Oxford, 1981.
- Saito Y, Hamaguchi H. *Chem. Phys. Lett.* 2001; **339**: 351.
- Barrett JJ, Berry MJ. *Appl. Phys. Lett.* 1979; **34**: 144.
- Patel CKN, Tam AC. *Appl. Phys. Lett.* 1979; **34**: 760.
- Patel CKN, Tam AC. *Rev. Mod. Phys.* 1981; **53**: 517.
- West GA, Barrett JJ. *Opt. Lett.* 1979; **4**: 395.
- West GA, Siebert DR, Barrett JJ. *J. Appl. Phys.* 1980; **51**: 2823.
- West GA, Barrett JJ, Siebert DR, Reddy KV. *Rev. Sci. Instrum.* 1983; **54**: 797.
- Schrötter HW, Berger H, Boquillon JP, Lavorel B, Millot G. *J. Raman. Spectrosc.* 1990; **21**: 781.
- Brown SS, Berghout HL, Crim FF. *J. Chem. Phys.* 1997; **106**: 5805.
- Yu YQ, Wang H, Shi Y, Li QF, Dai JH, Liu SL, Ma XX. *Chin. J. Chem. Phys.* 2004; **17**: 385.
- Ziegler LD, Chung YC, Wang P, Zhang YP. *J. Chem. Phys.* 1989; **90**: 4125.
- Wang PG, Ziegler LG. *J. Phys. Chem.* 1993; **97**: 3139.
- Herranz J, Stoicheff BP. *J. Mol. Spectrosc.* 1963; **10**: 448.
- Holzer W, Duff YL, Altmann K. *J. Chem. Phys.* 1973; **58**: 642.