

ARTICLE

Accurate Measurement of Raman Depolarization Ratio in Gaseous CO₂Yu-juan Jin^a, Yuan-qin Yu^{a*}, Yu-xi Wang^b, Ke Lin^b, Xiao-guo Zhou^b, Shi-lin Liu^b*a. School of Physics and Material Science, Anhui University, Hefei 230039, China**b. Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China*

(Dated: Received on September 17, 2014; Accepted on October 23, 2014)

The Raman depolarization ratios of gaseous CO₂ in the spectral range of 1240–1430 cm⁻¹ are determined with a sensitive photoacoustic Raman spectroscopy, and more accurate data compared to the literature results are presented. The precision of the obtained depolarization ratio is achieved by measuring and fitting the dependence of the PARS signal intensity on the cross angle between the polarizations of two incident laser beams.

Key words: Depolarization ratio, Accurate measurement, Photoacoustic Raman spectroscopy, Global fitting

I. INTRODUCTION

Raman spectroscopy is a valuable tool to study the molecular structures and molecular interaction. In Raman measurement, the depolarization ratio is a fundamental physical quantity that indicates the symmetry of a Raman-active vibrational mode of molecules, and defined as the intensity ratio of scattered light I_{\perp} to I_{\parallel} ($\rho = I_{\perp}/I_{\parallel}$), where I_{\perp} and I_{\parallel} are the intensities of scattered photons with polarizations perpendicular and parallel to the polarization plane of the incident beam, respectively [1]. Generally, the higher the symmetry of a vibrational mode is, the smaller of its depolarization ratio. Therefore, the accurate determination of the depolarization ratio not only can assign the observed Raman band but also help us to better detect small distortion of molecular structures induced by different environments, such as in pure states, in the mixtures or on the interface [2–8]. On the other hand, the accurate measurement of the depolarization ratio has also become necessary in the validation of the associated theories on the calculation of molecular polarizabilities and intensities of Raman bands since the accurate prediction of these parameters are still a challenge work in quantum chemistry at present [9].

In the past decades, experimental and theoretical methods have been developed to accurately determine the Raman depolarization ratio based on linear or non-linear spectral technique [2, 4, 10–13]. Very recently, James *et al.* precisely measured the Raman depolarization ratios for individual $Q(J)$ branch lines of all diatomic hydrogen isotopologues—H₂, HD, D₂, HT, DT, and T₂ with an uncertainty of 5% relative to the theo-

retical values, using a set of complex experimental arrangements and corrected data processing [13]. In this work, we measured the depolarization ratio for gaseous carbon dioxide in the spectral range of 1240–1430 cm⁻¹ using a sensitive photoacoustic Raman spectroscopy (PARS).

Carbon dioxide is a simple and important molecule since it is significantly involved in combustion media (flame, engine) and is major atmospheric component of a number of planets such as Venus and has a dominant contribution to the greenhouse effect in earth's atmosphere. Also, carbon dioxide can be used as an excellent supercritical solvent, which makes the compound receive a lasting concern from scientists in the field of weakly bound intermolecular complexes. In order to better understand the role of CO₂ in the terrestrial atmosphere combustion and supercritical processes, the vibrational spectral properties of CO₂ have been extensively studied in gaseous and liquid phase as well as solid states [9, 14–18].

Carbon dioxide is a highly symmetric linear triatomic molecule and has $3N-5=4$ ($N=3$) fundamental vibrational modes. They can be described as follows: $\nu_1(\Sigma_g^+)$, the symmetry stretching mode; $\nu_2(\Sigma_u)$, the doubly degenerate bending mode; and $\nu_3(\Sigma_u)$, the antisymmetry stretching mode. Among three fundamental modes, only ν_1 mode is Raman active while ν_2 and ν_3 modes are both infrared active. Since the frequency of bending overtone $2\nu_2(02^00, \Sigma_g^+)$ is very close to symmetric stretching fundamental $\nu_1(000)$ and both has the same symmetry category, a Fermi resonance occurs. The Fermi resonance is so strong that there is still a controversy for Fermi doublet which is the fundamental band or the overtone [19]. Many analyses were theoretically and experimentally conducted to the dependence of the Fermi resonance coupling on the temperature, pressure, and concentration to obtain the information on molecule interactions, such as the colli-

* Author to whom correspondence should be addressed. E-mail: yyq@ahu.edu.cn, FAX: +86-551-63861257

sional effects in gaseous combustion process, where the CO₂ molecule is significantly involved [20–22].

Recently, the attention has been paid to the intermolecular interaction between CO₂ and organic liquids (ethanol, acetone and benzene) and complex fluids such as ionic liquids using Raman spectroscopy, motivated not only from the fundamental point of view but also mainly under the impetuous motivation of the interactions of CO₂ in the field of environmental studies [23–28]. It is known that the Raman depolarization ratios can provide a highly sensitive probe on intermolecular interactions between CO₂ and complexes in different environments. The depolarization ratios of CO₂ obtained by conventional spontaneous Raman spectroscopy from different groups were not consistent [9, 14, 15, 27]. Here, we measured the Raman depolarization ratio of CO₂ by a newly developed I - θ curve (photoacoustic Raman signal intensity *vs.* the polarization cross-angle θ) method based on a polarized PARS technique, and more accurate data were presented.

The basic theory of PARS has been fully described in Refs.[29–32]. Here, only a short review is given. When the frequency difference between two laser beams (called as pump and Stokes beams) is resonant with a Raman-active vibrational transition, the molecules are transferred to the vibrationally excited state by a stimulated Raman scattering process. Then collisions cause the excitation energy to be converted into local heating. This creates a sound wave that is detected by a microphone. The spectral sensitivity of PARS is greatly increased compared to the direct measurement of weak spontaneous Raman scattering photons. The PARS intensity, I , can be expressed as

$$I \propto \cos^2 \theta + \rho \sin^2 \theta \quad (1)$$

where ρ is Raman depolarization ratio, θ is the cross angle between the polarizations of two laser beams. It can be seen that the PARS intensity is periodically dependent on the cross angle θ . By measuring the I - θ curve, the depolarization ratio can be determined by a global fitting with Eq.(1), as shown in Fig.1.

II. EXPERIMENTAL SETUP

The experimental setup has been reported previously in detail [4, 30–32]. The second-harmonic output of 532.1 nm from a pulsed Nd:YAG laser (line width 1.0 cm⁻¹, pulse width 10 ns) was split into two beams by a quartz wedge. About 90% of the 532.1 nm laser energy directly entered into the dye laser system (line width 0.05 cm⁻¹) for generating a tunable Stokes beam (570–580 nm), and the remainder was used as a pump beam for PARS. The pump and Stokes beams were focused in the center of the photoacoustic cell with counter-propagating configuration. The generated photoacoustic signal was detected by a sensitive microphone and monitored by an oscilloscope or averaged by a Boxcar

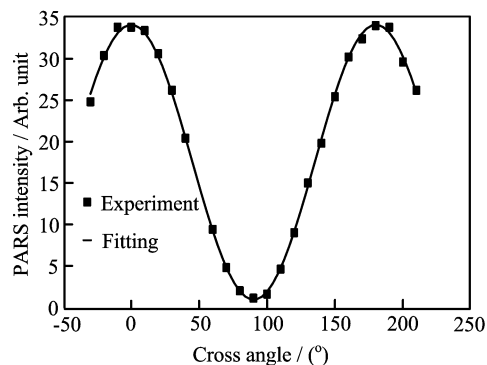


FIG. 1 A typical I - θ curve of gaseous CO₂ along with a global fitting with Eq.(1).

integrator. The energies of pump and Stokes beams were typically 7 and 4 mJ/pulse, respectively, and the sample pressure of CO₂ was kept at 25 Torr.

In order to assure the precision of the measurements of depolarization ratio, the pump and Stokes beams were highly linearly polarized, which were achieved by two Glan-Taylor prisms with an extinction ratio of 10⁻⁶. Additionally, the whole passage of the laser beams including the two polarizers and lens as well as quartz window of photoacoustic cell were carefully arranged and adjusted to minimize the polarization distortions from optical components. During the experiment, the polarization of Stokes beam was fixed in the vertical direction while that of pump beam was rotated by a $\lambda/2$ wave plate. In this way, the polarization cross-angle between the two laser beams was precisely controlled. A typical I - θ curve is shown in Fig.1 along with a global fitting with Eq.(1). The precision of the obtained depolarization ratio was checked by measuring the depolarization ratio of the totally symmetric stretching mode of CH₄ at 2917 cm⁻¹ and antisymmetric stretching mode at 3020 cm⁻¹, achieving a value of 0.002±0.002 and 0.75±0.005, respectively (the theoretical depolarization ratios of those two modes are 0 and 0.75, respectively).

III. RESULTS AND DISCUSSION

The polarized and depolarized Raman spectra of gaseous CO₂ under a low pressure of 25 Torr in the spectral range of 1240–1430 cm⁻¹ are presented in Fig.2. It can be seen that there are two intense and sharp peaks at 1387.2 and 1284.3 cm⁻¹ with an interval of 102.9 cm⁻¹ and an intensity ratio of 1.75, which can be assigned to the Fermi doublet from symmetric stretching fundamental $\nu_1(100)$ and bending overtone $2\nu_2(02^00)$, respectively, as mentioned above. Although the wavefunctions of the Fermi doublet are severely mixed, we still label them as $\nu_1(100)$ and $2\nu_2(02^00)$, as shown in Fig.2. There are also three weak satellite bands situated at 1408.4, 1368.9, and 1264.0 cm⁻¹. According to

TABLE I The measured depolarization ratios ρ of the gaseous $C^{12}O_2$ and $C^{13}O_2$ in the spectral range of 1240–1340 cm^{-1} .

Species transition	Frequency/ cm^{-1}	ρ				
		Ref.[15]	Ref.[9]	Ref.[14]	Ref.[27]	This work
(000) \rightarrow (02 ⁰ 0) $C^{12}O_2$	1284.3		0.0438	0.042(4)	0.07	0.042(2)
(000) \rightarrow (100) $C^{12}O_2$	1387.2	0.027	0.0277	0.029(3)	0.07	0.027(2)
(010) \rightarrow (03 ¹ 0) $C^{12}O_2$	1264.0		0.143	0.050(5)		0.043(2)
(010) \rightarrow (110) $C^{12}O_2$	1408.4		0.081	0.024(3)		0.054(4)
(000) \rightarrow (100) $C^{13}O_2$	1368.9					0.067(5)

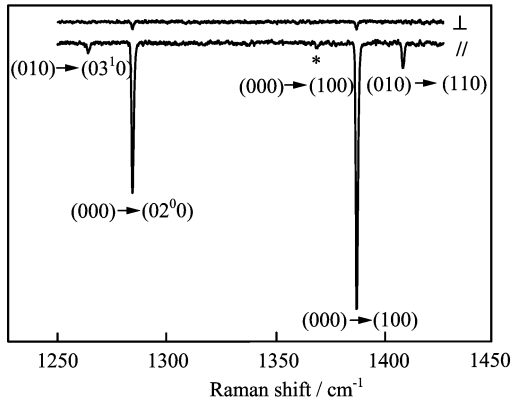


FIG. 2 The polarized (//) and depolarized (\perp) PARS spectra of gaseous CO_2 in the spectral range of 1240–1430 cm^{-1} measured under parallel and perpendicular laser polarization configurations, respectively. The peak labeled with star is from $C^{13}O_2$ and the others are from $C^{12}O_2$.

Montero reports [9], the first one and the last one can be assigned to another Fermi doublet of CO_2 from the hot bands corresponding to the transitions (010) \rightarrow (110) and (010) \rightarrow (03¹0), respectively, and the second one corresponds to the symmetric stretching fundamental $\nu_1(100)$ of isotope $C^{13}O_2$, which has a natural abundance of about 1.1% in pure CO_2 molecule. It should be mentioned that the hot band at 1264.0 cm^{-1} also contains the weak contribution from the bending overtone $2\nu_2(02^00)$ of $C^{13}O_2$ molecule, which is in Fermi resonance with the symmetric stretching fundamental [9]. However, the peak intensity of $C^{13}O_2$ is so weak that the contribution from overtone $2\nu_2(02^00)$ of $C^{13}O_2$ can be neglected.

The Raman depolarization ratios of gaseous CO_2 measured by I - θ curve method are summarized in Table I along with the available values from Refs.[9, 14, 15, 27]. For a pair of strong Fermi bands at 1284.3 and 1387.2 cm^{-1} , the depolarization ratios determined in the present work are 0.042 and 0.027, respectively. These values are in good agreement with those from other reports except [27], in which the values are 0.07 for both Fermi bands. However, for weak hot bands at 1264.0 and 1408.4 cm^{-1} , the depolarization ratios from different literatures are different from each other. For the transition (010) \rightarrow (110) at 1408.4 cm^{-1} , our mea-

sured depolarization ratio is 0.054 whereas that from Ref.[14] and Ref.[9] were 0.081 and 0.024, respectively. For the transition (010) \rightarrow (03¹0) at 1264.0 cm^{-1} , our result is 0.043 whereas that from Ref.[14] and Ref.[9] were 0.143 and 0.050, respectively.

The depolarization ratios determined in the present work are accurate and reliable. First, in the present work, the depolarization ratio determined from a global fitting of the I - θ curve significantly reduces the uncertainty of the ratio between only two intensities I_{\perp} and $I_{//}$ in the spontaneous Raman experiment, where the scattered intensity I_{\perp} is too weak to be measured accurately in many cases, especially for the small depolarization ratio of polarized bands. Secondly, the PARS signal originates from a precise matching of the polarizations between two laser beams. This is different from the conventional Raman experiment, in which the Raman scattered photos are collected in a finite solid angle with relatively complex polarizations and the depolarization ratio must be corrected to be accurate. Thirdly, PARS is a very sensitive spectral technique, and especially suitable to detect weak Raman signal. Therefore, for weak hot bands, we can still obtain the accurate depolarization ratio.

In addition to $C^{12}O_2$ molecule, we also determined the depolarization ratios for symmetric stretching fundamental $\nu_1(000)$ of $C^{13}O_2$ isotope, which had never been measured previously due to the low natural abundance of $C^{13}O_2$ isotope in pure CO_2 . Although $C^{13}O_2$ and $C^{12}O_2$ molecules only differ by a neutron, their depolarization ratios are different. One is 0.067 and the other is 0.027, as shown in Table I. This indicates that the molecular polarizability of $C^{13}O_2$ is different from that of $C^{12}O_2$. The differences brought by neutron in isotopes are reflected not only on the depolarization ratio but also on other aspects. For example, many investigations indicate that the formation of hydrogen-bonding in liquid D_2O are much stronger than that in normal H_2O [33]. Further theoretical investigations are needed to interpret these subtle differences.

IV. CONCLUSION

We reported the accurate depolarization ratio measurement of gaseous $C^{12}O_2$ and $C^{13}O_2$ molecules by a

newly developed I - θ curve method based on the polarized PARS technique, and the maximum experimental uncertainty is ± 0.005 . As the molecular system of CO_2 is often used as a model case for comparative studies between theory and experiment and for investigations on the molecular interaction, the accurate depolarization ratio provided here are helpful to quantitatively assess the calculations of the molecular polarizabilities and Raman intensities in *ab initio* method in the future and to better understand the role of CO_2 in different environment such as in gaseous, liquid phase, as well as solid state.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20903002, No.21273211, No.91127042, and No.21373194) and the Anhui Provincial Natural Science Foundation (No.1408085MA18), and the National Key Basic Research Special Foundation (No.2013CB834602 and No.2010CB923300).

- [1] D. Long, *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules*, New York: John Wiley & Sons, (2002).
- [2] Y. Saito, T. Ishibashi, and H. Hamaguchi, *J. Raman Spectrosc.* **31**, 725 (2000).
- [3] R. Lu, W. G., B. H. Wu, H. Chen, and H. F. Wang, *J. Phys. Chem. B* **108**, 7297 (2004).
- [4] Y. Q. Yu, K. Lin, X. G. Zhou, H. Wang, S. L. Liu, and X. X. Ma, *J. Raman Spectrosc.* **38**, 1206 (2007).
- [5] K. Lin, N. Y. Hu, X. G. Zhou, S. L. Liu, and Y. Luo, *J. Raman Spectrosc.* **43**, 82 (2012).
- [6] K. Lin, N. Y. Hu, X. G. Zhou, S. L. Liu, and Y. Luo, *Chin. J. Chem. Phys.* **26**, 127 (2013).
- [7] K. Lin, X. G. Zhou, S. L. Liu, and Y. Luo, *Chin. J. Chem. Phys.* **26**, 121 (2013).
- [8] K. Lin, X. G. Zhou, S. L. Liu, and Y. Luo, *J. Phys. Chem. B* **114**, 3567 (2010).
- [9] S. Montero, *J. Chem. Phys.* **79**, 4091 (1983).
- [10] E. W. Blanch, R. L. Keir, and G. L. D. Ritchie, *J. Phys. Chem. A* **106**, 4257 (2002).
- [11] F. Munhoz, S. Brustlein, R. Hostein, P. Berto, S. Bras-selet, and H. Rigneault, *J. Raman Spectrosc.* **43**, 419 (2012).
- [12] A. Bray, R. Chapman, and T. Plakhotnik, *Appl. Opt.* **52**, 2503 (2013).
- [13] T. M. James, M. Schlosser, S. Fischer, M. Sturm, B. Bornschein, R. J. Lewis, and H. H. Telle, *J. Raman Spectrosc.* **44**, 857 (2013).
- [14] W. F. Murphy, W. Holzer, and H. Bernstei, *Appl. Spectrosc.* **23**, 211 (1969).
- [15] C. M. Penney, L. M. Goldman, and M. Lapp, *Nature Phys. Sci.* **235**, 110(1972).
- [16] J. F. Bertran, *Spectrochimica Acta A* **39**, 119 (1983).
- [17] L. Wan, L. Wu, A. W. Liu, and S. M. Hu, *J. Mol. Spectrosc.* **257**, 217 (2009).
- [18] C. F. Windisch, V. A. Glezakou, P. F. Martin, B. P. McGrail, and H. T. Schaef, *Phys. Chem. Chem. Phys.* **14**, 2560 (2012).
- [19] O. Sode, M. Keçeli, K. Yagi, and S. Hirata, *J. Chem. Phys.* **138**, 074501 (2013).
- [20] B. Lavorel, G. Millot, R. Saintloup, H. Berger, L. Bonamy, J. Bonamy, and D. Robert, *J. Chem. Phys.* **93**, 2176 (1990).
- [21] G. Fanjoux, B. Lavorel, and G. Millot, *J. Raman Spectrosc.* **29**, 391 (1998).
- [22] S. Roy, P. J. Wrzesinski, D. Pestov, M. Dantus, and J. R. Gord, *J. Raman Spectrosc.* **41**, 1194 (2010).
- [23] P. Van Ginderen, W. A. Herrebout, and B. J. van der Veken, *J. Phys. Chem. A* **107**, 5391 (2003).
- [24] M. Besnard, M. I. Cabaco, S. Longelin, T. Tassaing, and Y. Danten, *J. Phys. Chem. A* **111**, 13371 (2007).
- [25] M. Besnard, M. I. Cabaco, D. Talaga, and Y. Danten, *J. Chem. Phys.* **129**, 224511 (2008).
- [26] J. J. Schuster, S. Will, A. Leipertz, and A. Braeuer, *J. Raman Spectrosc.* **45**, 246(2014).
- [27] M. I. Cabacião, S. Longelin, Y. Danten, and M. Besnard, *J. Phys. Chem. A* **111**, 12966 (2007).
- [28] M. Besnard, M. I. Cabaco, S. Longelin, T. Tassaing, and Y. Danten, *J. Phys. Chem. A* **111**, 13371(2007).
- [29] J. J. Barrett and M. J. Berry, *App. Phys. Lett.* **34**, 144 (1979).
- [30] Y. Q. Yu, H. Wang, Y. Shi, Q. F. Li, J. H. Dai, S. L. Liu, and X. X. Ma, *Chin. J. Chem. Phys.* **17**, 385 (2004).
- [31] Y. Q. Yu, Y. X. Wang, N. Y. Hu, K. Lin, X. G. Zhou, and S. L. Liu, *J. Raman Spectrosc.* **45**, 259 (2014).
- [32] Y. Q. Yu, Y. X. Wang, K. Lin, N. Y. Hu, X. G. Zhou, and S. L. Liu, *J. Phys. Chem. A* **117**, 4377 (2013).
- [33] A. D. Buckingham, *J. Mol. Struct.* **250**, 111 (1991).