

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/253801648>

Identification of overlapping features in the sum frequency generation vibrational spectra of air/ethanol interface

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JUNE 2006

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2006.03.084

CITATIONS

27

READS

62

4 AUTHORS, INCLUDING:



[Wei Gan](#)

Chinese Academy of Sciences

31 PUBLICATIONS 1,220 CITATIONS

SEE PROFILE



[Zhen Zhang](#)

Max Planck Institute for Polymer Research

20 PUBLICATIONS 626 CITATIONS

SEE PROFILE



[Hong-fei Wang](#)

Pacific Northwest National Laboratory

56 PUBLICATIONS 1,708 CITATIONS

SEE PROFILE

Identification of overlapping features in the sum frequency generation vibrational spectra of air/ethanol interface

Wei Gan¹, Zhen Zhang¹, Ran-ran Feng¹, Hong-fei Wang^{*}

State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R.China

Received 2 March 2006; in final form 25 March 2006

Available online 5 April 2006

Abstract

The stretching vibrations of the $-\text{CH}_3$ and $-\text{CH}_2-$ groups not only overlap but also interfere with each other in the Sum-Frequency Generation (SFG) vibrational spectra of the air/ethanol interface. Using deuterated ethanol samples, i.e., $\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$, the C–H stretching vibrational modes are clearly assigned for the SFG vibrational spectra of their air/liquid interfaces according to the polarization selection rules. It is found that the CH_3 -ss and CH_2 -ss modes overlap in the $\sim 2875\text{ cm}^{-1}$ peak, the CH_3 -as and CH_2 -ss-Fermi modes overlap in the $\sim 2970\text{ cm}^{-1}$ peak, and the $\sim 2930\text{ cm}^{-1}$ peak belongs to the CH_3 -ss-Fermi mode, respectively.

© 2006 Elsevier B.V. All rights reserved.

1. Introduction

Spectra assignments are of great importance in both spectroscopic and dynamical studies. Assignments are the starting step for understanding of molecular interactions, energy transfer mechanisms and pathways in chemical reactions and other transient phenomena. Generally speaking, the vibrational spectra of simple molecules are relatively easily studied, and their assignments have been well documented [1,2]. Raman and Infrared spectroscopy have been used in determination of vibrational modes, and in investigations of chemical, physical or biophysical processes, as well as in material or environmental science studies [2–5]. Through interpretation of the vibrational spectra, one can obtain information on molecular structure, conformation, dynamics, molecular interactions, etc. [6,7].

The vibrational spectra of complex molecules or molecules in complex systems, such as biological molecules, liquids, polymers, and glasses can be highly congested, and their microscopic information is usually averaged and buried under broad and featureless spectral profiles. Recent

developments in ultrafast coherent multidimensional spectroscopy seek to use spatial correlations between different molecular groups to determine detailed microscopic structure as well as interactions of molecules in solution [8–11]. As an example, Hochstrasser et al. presented a polarization control method in two-dimensional infrared spectroscopy to eliminate the diagonal elements and to get detailed correlations of the vibrational modes in determination of peptide structure and conformation in solution [12]. However, such analysis can be very difficult without full prior knowledge of the different vibrational modes from different molecular groups overlapped in the vibrational spectra.

The region of C–H vibrational stretching between 2800 cm^{-1} and 3100 cm^{-1} is one of the most intensively studied regions because C–H containing structures exist widely in organic and bio-molecules. Experimental and theoretical investigations of vibrational spectra of $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ groups was performed as early as 1938 by Fox et al. [13]. However, in IR and Raman studies it is well known that assignment of the C–H vibrational stretching spectra is difficult because of the congestion of many modes of these different groups, including the symmetric stretch, the asymmetric stretch, the Fermi resonance modes, and other combination modes. The latter two are especially complex since they are quite sensitive to the specific cou-

^{*} Corresponding author. Fax: +86 10 62563167.

E-mail address: hongfei@mrclab.icas.ac.cn (H.-f. Wang).

¹ Also at the Graduate School of the Chinese Academy of Sciences.

plings of conformational and environmental factors [14,15]. For molecules with groups containing more than one kind of C–H group, isotope substitution has been generally used in assignment of vibrational spectra of different groups in the same molecule. However, as we have pointed out previously, some of the assignments for the C–H vibrational modes were ambiguous or incorrect even for very simple molecules [16–18]. This applies to very common molecules such as methanol and ethanol.

Ethanol is one of the most important alcohols because it has been generally used in drink, as a disinfectant for medical treatment, and as an important solvent in industry. It is also an ideal model molecule for investigations of the structure, molecular interaction and dynamics in bulk liquids or at liquid surfaces/interfaces [6,19–25]. Unfortunately, even though there were comprehensive studies of the IR and Raman spectra with 12 kinds of deuterated ethanol molecules [19,26,27], we have recently noticed that the assignment of the C–H vibrational spectra of ethanol is still troublesome [17,18], leading to erroneous applications in interpretation of vibrational energy transfer mechanisms [6]. Moreover, interpretation of the molecular orientation at the air/ethanol-aqueous solution interface based on such assignment may also need to be carefully re-examined [24]. Therefore, explicit assignment of the ethanol SFG spectra is not only important for interface studies, but it is also useful for understanding its spectroscopy and dynamics in the gas, as well as in the condensed phase.

SFG-VS is a unique surface specific technique for obtaining vibrational spectra of molecular interfaces [18,28,29]. Our recent works have revealed that using the polarization selection rules in SFG-VS, vibrational modes for –CH, –CH₂, and –CH₃ groups in SFG-VS can be distinguished and explicitly assigned according to their different polarization dependence [16–18]. Polarization analysis of SFG vibrational spectra in different experimental configurations can further help discern the spectral details, as well as interference effects between different vibrational modes of different molecular groups [18,30].

Here, we present a SFG-VS study of spectral assignments at the air/ethanol and air/deuterated ethanol interfaces. It is found that the CH₃-ss and CH₂-ss modes overlap in the $\sim 2875\text{ cm}^{-1}$ peak, the CH₃-as and CH₂-ss-Fermi modes overlap in the $\sim 2970\text{ cm}^{-1}$ peak, and the $\sim 2930\text{ cm}^{-1}$ peak belongs to the CH₃-ss-Fermi mode, respectively. These findings clarify confusion and misinterpretation in previous literature on spectral assignments and dynamics studies related to the ethanol C–H vibrational modes. This work further demonstrates that SFG-VS, as an intrinsically coherent polarization spectroscopic technique, is not only a powerful surface probe, but also a powerful spectroscopic method.

2. Experimental

Details of the SFG-VS experiment have been reported previously [16,17,30,31]. Briefly, the 10 Hz and 23 picosec-

ond SFG spectrometer laser system with co-propagating configuration is from EKSPLA. The efficiency of the detection system has been improved [30]. A high-gain low-noise photomultiplier (Hamamatsu, PMT-R585) and a dual channel Boxcar averager system (Stanford Research Systems) are integrated. The voltage of R585 was typically set at 1100 V in the measurement. The visible wavelength is fixed at 532 nm and the full range of the IR tunability is $1000\text{--}4300\text{ cm}^{-1}$. The incident angle for our co-propagating geometry is $62^\circ \pm 1^\circ$ (β_1) for the visible beam and $55^\circ \pm 1^\circ$ (β_2) for the IR beam. Each scan was with a 2 cm^{-1} increment and was averaged over 100 laser pulses per point if not specified. The spectral intensity is normalized to the intensities of the corresponding visible and IR beams. All measurements were carried out at controlled room temperature ($22.0 \pm 0.5^\circ\text{C}$). Pure ethanol (CH₃CH₂OH) is obtained from Fluka (>99.8%, GC grade), and Pure CD₃CH₂OH (>98%) and CH₃CD₂OH (>98%) are from Cambridge Isotope Laboratory. These samples were used as received.

3. Methodology for spectra assignment

Here, we briefly describe the framework for spectral assignment of SFG vibrational spectra [16–18].

As is well known, isotope substitution in vibrational spectra measurement can help identify specific vibrational peaks. However, sometimes, even with isotope substitution, assignment of specific peaks to specific vibrational modes is not straightforward, and can end up with confusion [19,26,26]. We have recently demonstrated that knowledge of relative SFG peak intensity in different polarization combinations is key for determination of the symmetry properties of the observed spectral peaks. In order to simplify the problem, we deduced a set of polarization selection rules for identifying the symmetry classification of the vibrational modes for methyl, methylene, and methane groups in SFG-VS [16–18]. We have shown that these selection rules are robust against the orientational distribution width of the molecular groups for molecular interfaces, and are generally valid for a broad range of parameters which can influence the SFG spectral intensity [18]. Here, we shall use those selection rules for the methyl and methylene groups in the ethanol molecule.

The major polarization selection rules of SFG-VS in a reflective geometry from a molecular interface without a metal or semiconductor substrate are listed below [18].

For methylene group [16,18]

- The ssp intensity for the ss peak is always many times of that in ppp.
- For the as peak, the ppp intensity is always several times that in ssp. That is to say, if there is any peak which is stronger in the ssp than ppp spectra, it can not be from the as mode.

For methyl group [17,18]

- (c) For the ss mode, the ssp intensity is always many times that in ppp, as well as for in sps and pss.
- (d) For the as mode, the ppp intensity is always many times that in ssp, and both of them are largest when $\theta = 54.7^\circ$. Here θ is the tilt angle between the main axis of the molecular group and the interface normal.

4. Results and discussion

The SFG spectra of the air/CH₃CH₂OH interface, air/CH₃CD₂OH interface, and air/CD₃CH₂OH interface in the C–H vibrational stretching range are plotted in Fig. 1. It is obvious that the peak at $\sim 2875\text{ cm}^{-1}$ contains a contribution from both methyl and methylene groups since the spectra from the air/CD₃CH₂OH interface and the air/CH₃CD₂OH interfaces both give SFG intensity near this position. The intensity of this peak in the SFG spectrum of the air/CH₃CH₂OH interface is stronger than those in the air/CH₃CD₂OH spectra and the air/CD₃CH₂OH spectra. This explicitly indicates that the contributions from methyl and methylene groups are constructively interfering with each other. Detailed analysis of the interference effects will be further reported elsewhere. The spectra in Fig. 1 also indicate that the peak at $\sim 2930\text{ cm}^{-1}$ contains a contribution from the methyl group only, while both methyl and methylene groups have SFG intensity at $\sim 2970\text{ cm}^{-1}$, although they contribute to different polarization combinations.

With the contribution from methyl and methylene groups distinguished, we can determine the symmetry category of these vibrational modes with the polarization selection rules in SFG-VS. For methyl groups, according to selection rules c and d, the peak at $\sim 2875\text{ cm}^{-1}$ and $\sim 2930\text{ cm}^{-1}$ in the ssp spectra of the air/CH₃CD₂OH interface belongs to a symmetric category since the SFG intensity in the ssp spectra are much stronger than those in their ppp spectra. The peak at $\sim 2970\text{ cm}^{-1}$ in the ppp spectra of the air/CH₃CD₂OH interface should be an asymmetric stretching mode since its ppp intensity is much stronger than that in the ssp spectra. For methylene groups, according to selection rules a and b, both the peaks at $\sim 2886\text{ cm}^{-1}$ and $\sim 2974\text{ cm}^{-1}$ in the ssp spectra of air/CD₃CH₂OH interface should belong to the symmetric category.

From the above analysis, some of the debate on the assignment of the vibrational spectra of ethanol molecules can be settled. Recent SFG studies on vibrational spectra of ethanol [24,25] followed the assignment of previous Raman investigation [19]. The peak at $\sim 2875\text{ cm}^{-1}$ was assigned to the symmetric stretching mode of methylene groups (CH₂-ss). The peak at $\sim 2970\text{ cm}^{-1}$ was assigned to the asymmetric vibrational stretching mode of methyl and/or methylene groups (CH₃-as/CH₂-as). However, the IR and Raman study with deuterated ethanol suggested that the peak at $\sim 2870\text{ cm}^{-1}$ is a methyl group combination mode [26,27]. This confusion has not been clearly resolved before. Our SFG spectra of both CD₃CH₂OH and CH₃CD₂OH interfaces presents clear spectral features

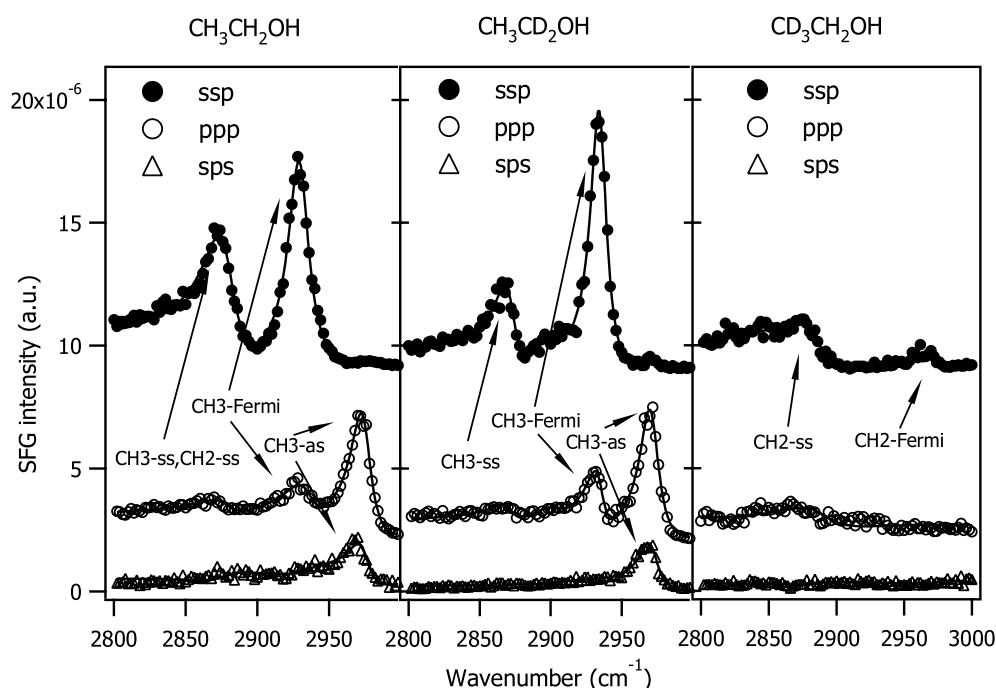


Fig. 1. SFG-VS spectra of the air/CH₃CH₂OH, air/CH₃CD₂OH and air/CD₃CH₂OH interfaces. The spectra of ssp and ppp polarization are offset for clarity. The pss spectra are not shown because they are essentially the same as the sps spectra, as they must be. Solid lines are fitting curves with Lorentzian lineshapes.

above the noise level at the $\sim 2875\text{ cm}^{-1}$ peak position. This proves that the peak around 2875 cm^{-1} in the SFG spectra of air/ $\text{CH}_3\text{CH}_2\text{OH}$ interface contains contributions from both methyl and methylene groups, and they both belong to symmetric stretching modes ($\text{CH}_3\text{-ss}$ and $\text{CH}_2\text{-ss}$). This conclusion can be directly used to aid the assignment of the IR and Raman spectra of ethanol molecule since SFG activity exist only when the vibrational mode has both IR activity and Raman activity [28,29].

The peak at about 2930 cm^{-1} for air/ $\text{CH}_3\text{CH}_2\text{OH}$ and air/ $\text{CH}_3\text{CD}_2\text{OH}$ interfaces, which also belong to the symmetric category, should be assigned to the Fermi resonance of the $\text{CH}_3\text{-ss}$ mode.

Polarization analysis of the SFG spectra also shed new light on assignment of the $\sim 2970\text{ cm}^{-1}$ peak in the ethanol spectra. As generally accepted in the literatures [2,4,5], this peak belongs to an asymmetric stretching mode. However, the SFG spectra of the air/ $\text{CD}_3\text{CH}_2\text{OH}$ interface, shows that the peak at about 2970 cm^{-1} belongs to a symmetric category. This is to say, it has to be a Fermi resonance with the $\text{CH}_2\text{-ss}$ mode, rather than the $\text{CH}_2\text{-as}$ mode. Otherwise, according to the selection rule b, if the weak signal in the ssp spectra were assigned to the $\text{CH}_2\text{-as}$ mode, there should be a much stronger SFG intensity in the ppp spectra at the same position. However, this is obviously not the case. So the peak at $\sim 2970\text{ cm}^{-1}$ in the ethanol spectra is the result of interference between the $\text{CH}_3\text{-as}$ mode and the Fermi resonance of the $\text{CH}_2\text{-ss}$ mode. To our knowledge, this is a novel feature for the $\text{CH}_2\text{-ss}$ Fermi resonance mode for the methylene group at this position.

It should be noted that there is a small peak at about 2900 cm^{-1} in the spectra of air/ $\text{CH}_3\text{CD}_2\text{OH}$ interface. This peak has been detected by Perchard and Josien and assigned to a combination mode of the methyl group [26,27]. Polarization analysis indicates that this peak belongs to a symmetric category. With all the evidence, this peak may be another resonance mode between one of the possible combinational modes and the symmetric stretching mode of the methyl group. Multiple resonance are commonly found in spectra of methylene groups [14]. For methyl groups, such a feature has also been found in the SFG spectra of the air/methanol interface [17,32]. When CD_2 groups are replaced with CH_2 groups, the strong peak at about 2930 cm^{-1} broadens and the small peak at about 2900 cm^{-1} becomes less obvious. Further theoretical investigations are still needed to interpret subtle changes of these spectra features.

The overlapping features around the 2875 cm^{-1} and 2970 cm^{-1} regions of the $-\text{CH}_3$ and $-\text{CH}_2$ modes have not been clearly discussed in the literatures. The assignments from the ethanol molecule can shed new light on understanding the vibrational spectra of other long-chain alcohols, which also contain both $-\text{CH}_3$ and $-\text{CH}_2$ groups. The spectral overlap and interference between these spectral features can be complicated and also useful for understanding details of the molecular structures, interactions, and dynamics. Recently, due to our suggestion, such spectra overlaps in the ethanol molecule have been identified

with photoacoustic stimulated Raman spectroscopy of ethanol, $\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$ molecules in the gaseous phase (to be reported separately by Professor Shilin Liu at USTC).

It is worth mentioning that the study of simple molecules such as methanol and ethanol is very important because they are often used as molecular probes for surface/interface investigations or model molecules in the investigations of the mechanism of vibrational energy transfer process [6,11]. Assignment of the spectra features is the stepstone for these investigations. For example, vibrational energy relaxation from the excited OH bonds at 3300 cm^{-1} to the CH vibrational stretching modes at about 2875 cm^{-1} has been used to probe energy transfer from the OH bond to the CH_2 bond in the ethanol molecule. Since the SFG spectra proved that the symmetric stretching vibrational modes of both CH_3 group and CH_2 group significantly contribute to the $\sim 2875\text{ cm}^{-1}$ peak, the mechanism of such energy transfer process should be carefully checked according to the spectral assignment in this study.

5. Conclusion

With investigations of the SFG spectra of the air/ethanol, air/ $\text{CH}_3\text{CD}_2\text{OH}$ and air/ $\text{CD}_3\text{CH}_2\text{OH}$ interfaces, we discuss the assignment of the vibrational spectrum of the ethanol molecule, which was misassigned in previous literature. In this work, explicit assignment to the vibrational modes of methyl and methylene groups was obtained with polarization analysis of the SFG spectra in different polarization combinations. The $\sim 2875\text{ cm}^{-1}$ peak, $\sim 2930\text{ cm}^{-1}$ and $\sim 2970\text{ cm}^{-1}$ peak in ethanol spectra are assigned to the overlapping $\text{CH}_3\text{-ss}$ and $\text{CH}_2\text{-ss}$ modes; Fermi resonance of $\text{CH}_3\text{-ss}$ mode; and the overlapping ($\text{CH}_3\text{-as}$ and the Fermi resonance of $\text{CH}_2\text{-ss}$) modes, respectively. The overlapping features of the $-\text{CH}_3$ and $-\text{CH}_2$ modes around the 2875 cm^{-1} and 2970 cm^{-1} regions are novel and important findings in understanding the vibrational spectroscopy of alcohols and other related molecules.

Since the spectral features in the SFG-VS spectra are generally narrower than those in the condensed phase, more spectral features can be identified in the SFG-VS spectra [16–18]. Because SFG-VS is an intrinsic polarization spectroscopy on the generally ordered molecular interfaces, it is ideal for identification of symmetry properties of the observed spectral features. With this work we show that SFG-VS is not only an effective technique for probing molecular interfaces in situ, but also an effective tool for interpretation of molecular spectra in general.

Acknowledgements

H.F.Wang thanks support from the Natural Science Foundation of China (NSFC No. 20425309, No. 20533070) and the Chinese Ministry of Science and Technology (MOST No. G1999075305).

References

- [1] NIST Chemistry Webbook Database at <http://webbook.nist.gov>.
- [2] L.J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Chapman & Hall Ltd., London, 1975.
- [3] G. Herzberg, *Molecular Spectra and Molecular Structure*, D Van Nostrand Co. Inc., New York, 1945.
- [4] J.M. Chalmers, P.R. Griffiths, *Handbook of Vibrational Spectroscopy*, John Wiley and Sons Ltd., New York, 2002.
- [5] D.I. Bower, W.F. Maddams, *The Vibrational Spectroscopy of Polymers*, Cambridge University Press, New York, 1992.
- [6] Z.H. Wang, A. Pakoulev, D.D. Dlott, *Science* 296 (2002) 2201.
- [7] J.X. Cheng, S. Pautot, D.A. Weitz, X.S. Xie, *PNAS* 100 (2003) 9826.
- [8] Y. Tanimura, S. Mukamel, *J. Chem. Phys.* 99 (1993) 9496.
- [9] I. Noda, *Vib. Spectrosc.* 36 (2004) 143.
- [10] S. Mukamel, A. Piryatinski, V. Chernyak, *Acc. Chem. Res.* 32 (1999) 145.
- [11] D.D. Dlott, *Chem. Phys.* 266 (2001) 149.
- [12] M.T. Zanni, N.H. Ge, Y.S. Kim, R.M. Hochstrasser, *PNAS* 98 (2001) 11265.
- [13] J.J. Fox, A.E. Martin, *Proc. R. Soc. A* 167 (1938) 257.
- [14] R.G. Snyder, J.R. Scherer, *J. Chem. Phys.* 71 (1979) 3221.
- [15] R.G. Snyder, S.L. Hsu, S. Krimm, *Spectrochim. Acta A* 34 (1978) 395.
- [16] R. Lu, W. Gan, B.H. Wu, H. Chen, H.F. Wang, *J. Phys. Chem. B* 108 (2004) 7297.
- [17] R. Lu, W. Gan, B.H. Wu, Z. Zhang, Y. Guo, H.F. Wang, *J. Phys. Chem. B* 109 (2005) 14118.
- [18] H.F. Wang, W. Gan, R. Lu, Y. Rao, B.H. Wu, *Int. Rev. Phys. Chem.* 24 (2005) 191.
- [19] K. Kamogawa, S. Kaminaka, T. Kitagawa, *J. Phys. Chem.* 91 (1987) 222.
- [20] M.J. Colles, J.E. Griffiths, *J. Chem. Phys.* 56 (1972) 3384.
- [21] S.S. Ju, T.D. Wu, Y.L. Yeh, T.H. Wei, J.Y. Huang, S.H. Lin, *J. Chin. Chem. Soc.* 48 (2001) 625.
- [22] R. Laenen, C. Rauscher, *Chem. Phys. Lett.* 274 (1997) 63.
- [23] K. Mizuno, Y. Miyashita, Y. Shindo, H. Ogawa, *J. Phys. Chem.* 99 (1995) 3225.
- [24] J. Sung, K. Park, D. Kim, *J. Phys. Chem. B* 109 (2005) 18507.
- [25] C.D. Stanners, Q. Du, R.P. Chin, P. Cremer, G.A. Somorjai, Y.R. Shen, *Chem. Phys. Lett.* 232 (1995) 407.
- [26] J.P. Perchard, M.L. Josien, *J. Chim. Phys.* 65 (1968) 1834.
- [27] J.P. Perchard, M.L. Josien, *J. Chim. Phys.* 65 (1968) 1856.
- [28] K.B. Eisenthal, *Chem. Rev.* 96 (1996) 1343.
- [29] X.W. Zhuang, P.B. Miranda, D. Kim, Y.R. Shen, *Phys. Rev. B* 59 (1999) 12632.
- [30] W. Gan, D. Wu, Z. Zhang, R.R. Feng, H.F. Wang, *J. Chem. Phys.* 124 (2006) 114705.
- [31] W. Gan, D. Wu, Z. Zhang, R.R. Feng, H.F. Wang, *Chin. J. Chem. Phys.* 19 (2006) 20.
- [32] R. Superfine, J.Y. Huang, Y.R. Shen, *Phys. Rev. Lett.* 66 (1991) 1066.