

LETTER

Quantitative Interpretation of Polarization SFG Vibrational Spectra of Air/Methanol Interface

Hui Wu^a, Wen-kai Zhang^b, Wei Gan^b, Zhi-feng Cui^{a*}, Hong-fei Wang^{a,b*}*a.* Department of Physics, Anhui Normal University, Wuhu 241000, China; *b.* State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

(Dated: Received on May 20, 2006; Accepted on May 30, 2006)

Even though in IR and Raman spectra of liquid methanol there is always an apparent feature for the asymmetric stretching mode of the CH₃ group around 2970 cm⁻¹, this feature has not been observed in the Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) in any polarizations from the air/methanol interface. Here we present a treatment based on a corrected bond additivity model to quantitatively interpret the SFG-VS of the air/methanol interface from the IR and Raman spectra of liquid methanol.

Key words: Sum frequency generation, Bond additivity model, Raman polarizability

Because of its unique interface selectivity and sensitivity, SFG-VS has been widely used to investigate vibrational spectroscopy of various molecular interfaces, including vapor/liquid, liquid/liquid, air(vacuum gas)/solid, and liquid/solid interfaces [1-3]. The air/methanol interface was the first liquid interface studied with SFG-VS [4], and many subsequent SFG-VS studies on this system followed [5-13]. One observation in all these works is that the asymmetric stretching (AS) mode of the CH₃ group around 2970 cm⁻¹ is always absent from the SFG-VS spectra, even though this feature clearly presents in the IR and Raman spectra of liquid methanol. In most of the works, the SFG vibrational spectrum of the air/methanol interface was obtained only with one set of experimental polarization configuration (generally for the ssp polarization). Therefore, the absence of the AS mode peak in one particular polarization configuration may be easily attributed to the molecular orientational effect at the interface. However, recent works reported the spectra in different polarizations, and the AS mode peak is generally absent [9-13]. This fact excludes the possibility of the orientational effect and it becomes peculiar to us because the second order polarizability tensor of a particular molecular vibrational mode ($\beta_{i'j'k'}^q$, here q represents the q th vibrational mode) is the product of the corresponding Raman polarizability derivative tensor ($\partial\alpha_{i'j'}/\partial Q_q$, usually denoted as $\alpha'_{i'j'}$) and dipole moment derivative tensor ($\partial\mu_{k'}/\partial Q_q$, usually denoted

as $\mu'_{k'}$), of this mode [14]. This is given by,

$$\beta_{i'j'k'}^q = -\frac{1}{2\epsilon_0\omega_q} \frac{\partial\alpha_{i'j'}}{\partial Q_q} \frac{\partial\mu_{k'}}{\partial Q_q} \quad (1)$$

Here ($i'j'k'$) represents the molecular coordinates system, ω_q and Q_q are the vibrational frequency and the normal mode coordinate of the q th vibrational mode, respectively. Therefore, a closer look on this problem for the SFG vibrational spectra of the air/methanol interface is certainly needed.

It is known that the key for quantitative interpretation of polarization SFG vibrational spectra lies on the ability to obtain or estimate the ratios between different microscopic polarizability $\beta_{i'j'k'}$ tensor elements of a chemical group in a molecule [15-17]. According to Eq.(1), if the proper ratios between different $\alpha'_{i'j'}$ terms and the ratios between different $\mu'_{k'}$ terms are known, the ratios of $\beta_{i'j'k'}^q$ elements can be readily obtained. In order to calculate the $\beta_{i'j'k'}^q$ ratios, the bond additivity model (BAM) was first formulated by Hirose *et al.* in the early 1990s [18,19].

Recent quantitative calculation using the BAM can successfully treat the SFG-VS polarization dependence of the CH₃ symmetric stretching (SS) mode, and can accurately obtain the orientation angle of the CH₃ group at the air/methanol interface [10-13,15]. However, the same calculation also predicts that the AS mode of methanol molecule is observable in some polarizations of the SFG spectra. This calculation is based on $\beta_{ccc}/\beta_{aca}=1.1$ for the CH₃ group in the methanol molecule as calculated with the BAM following Eq.(6) below [11,15]. Here, β_{ccc} and β_{aca} are the symmetric and asymmetric tensor elements responsible to the SS and AS mode SFG-VS intensity [15].

The BAM uses the Raman bond polarizability derivative tensors $\alpha'_{i'j'}$ and the bond moment derivative ten-

*Author to whom correspondence should be addressed. E-mail: zfcui@mail.ahnu.edu.cn, hongfei@iccas.ac.cn; Tel: 86-10-62555347, Fax: 86-10-62563167

sors $\mu'_{k'}$, to calculate $\beta_{i'j'k'}$ tensors according to Eq.(1) [15,19]. In Raman and IR spectroscopy studies, the bond polarizability theory and the bond moment theory have been used to interpret the IR and Raman spectral intensity [20]. As we have known, even though the Raman bond polarizability derivative model has worked well with the intensities of the SS modes, it has not been very effective on the relative intensity between the SS and AS modes of the same molecular group [20,21]. Furthermore, the bond moment hypothesis, also called the zero-order bond moment theory, as used in the bond additivity model in SFG-VS, has not been successful in interpretation of IR intensities in general [20,22-25]. This is because the simple bond moment theory essentially neglects all coupling effect between the single bonds even within the same molecular group. Therefore, modified bond moment theory which includes such and other coupling effects has been proposed [20], but such modified theory becomes complicated by introducing many unknown parameters in order to address the coupling terms. In short, these facts certainly limit the effectiveness of the Hirose's BAM in SFG-VS, which was based on the zeroth order bond polarizability and bond moment theory, for quantitative interpretation of the SFG-VS spectra.

The limitation of the BAM is illustrated in Fig.1. Figure 1 presents the SFG-VS spectra and the calculated polarization dependence in the ssp, ppp, and sps polarizations against the CH_3 group orientational angle θ from the interface normal. The detail procedures of the calculation using the BAM were presented elsewhere [11,15]. Here ssp, ppp and sps denote three different experimental polarization configurations. For example, ssp denotes that the SF signal, visible and IR electric field polarizations are perpendicular, perpendicular, and parallel to the laser incident plane in the SFG experiment, respectively [10,15]. It is clear from the calculation in Fig.1 that the sps intensity of the AS mode at 2970 cm^{-1} is about 1/3 of the ssp intensity of the SS mode at 2830 cm^{-1} when the orientational angle of the CH_3 group is $\theta=0^\circ$ [10,13]. This is certainly not in agreement with the experiment observations in Fig.1, and with the known orientation of the CH_3 - group [10,12,13]. Therefore, the bond additivity model in SFG-VS needs to be reexamined and corrected.

In order to avoid getting into the trouble to deal with all the coupling effects in the complex bond moment and polarizability theory, here a complete empirical approach is employed to determine all the necessary $\alpha'_{i'j'}$ and $\mu'_{k'}$ ratios towards the calculation of the $\beta_{i'j'k'}$ ratios. From Eq.(1), one has,

$$\frac{\beta_{ccc}}{\beta_{aca}} = \frac{\omega_{AS}}{\omega_{SS}} \frac{\alpha'_{cc}}{\alpha'_{ac}} \frac{\mu'_c}{\mu'_a} \quad (2)$$

Therefore, with the frequencies of the symmetric and

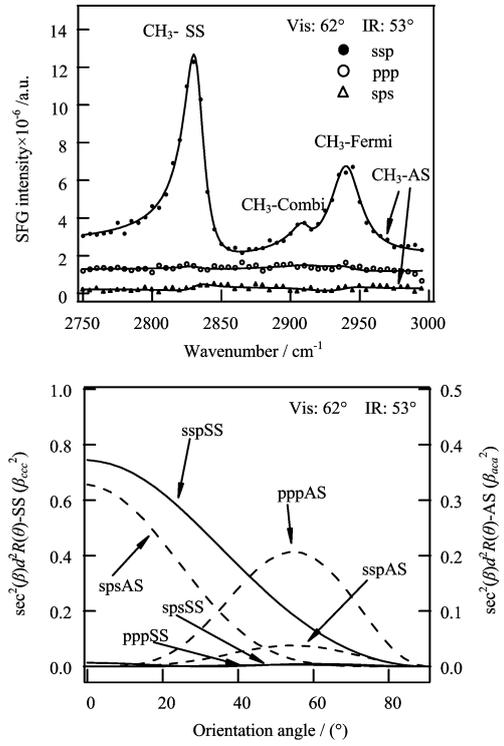


FIG. 1 SFG spectra of the air/methanol interface in different polarizations with incident angles as: visible= 62° and IR= 53° . The SFG-VS intensity is proportional to $\sec^2(\beta)d^2R(\theta)$, where β in $\sec^2(\beta)$ is the angle between the SFG signal beam and the surface normal. In the calculation, please note that unit for the SS mode is β_{ccc}^2 , while the unit for the AS mode is β_{aca}^2 . The solid lines in the left figure are fittings with Lorentzian lineshapes.

asymmetric modes (ω_{SS} and ω_{AS} , respectively) known, only the Raman tensor ratio $\alpha'_{cc}/\alpha'_{ac}$ and the IR tensor ratio μ'_c/μ'_a need to be known for calculation of β_{ccc}/β_{aca} . In the corrected BAM, the following relationships are used to obtain $\alpha'_{cc}/\alpha'_{ac}$ and μ'_c/μ'_a ratios from IR and Raman experimental measurements. The detail of the derivation of these relationships are reported elsewhere [26].

$$\rho_{SS}^{\text{Raman}} = \frac{0.75}{1 + 11.25[(1 + 2r)/(1 - r)]^2} \quad (3)$$

$$\frac{I_{SS}^{\text{Raman}}}{I_{AS}^{\text{Raman}}} = \frac{45(1 + 2r)^2 + 4(1 - r)^2}{8(1 + 8r)^2} \left(\frac{\alpha'_{cc}}{\alpha'_{ac}} \right)^2 \quad (4)$$

$$\frac{I_{SS}^{\text{IR}}}{I_{AS}^{\text{IR}}} = \frac{\mu'_c{}^2}{\mu'_a{}^2 + \mu'_b{}^2} = \frac{\mu'_c{}^2}{2\mu'_a{}^2} \quad (5)$$

In contrast, in the BAM [26], one has

$$\frac{\beta_{ccc}}{\beta_{aca}} = \frac{\omega_{AS}}{\omega_{SS}} \frac{1 + 8r}{4(1 - r)} \frac{37}{40} \quad (6)$$

It is easy to see that in the BAM, the only experimentally determined parameter is r from the Raman de-

polarization ratiion measurement. However, in the corrected bond additivity model the values of r , $\alpha'_{cc}/\alpha'_{ac}$ and μ'_c/μ'_a ratios are all obtained from IR and Raman spectra experimental measurements according to Eqs.(3), (4) and (5), respectively.

In the IR and Raman literatures, Raman depolarization measurement data, IR and Raman spectra data are generally available for simple molecules in liquids. $\rho_{SS}^{\text{Raman}}=0.014$ for the SS mode of the CH₃ group of liquid methanol was obtained from Raman depolarization measurement [27]. $I_{SS}^{\text{Raman}}/I_{AS}^{\text{Raman}}=5.0$ is obtained by fitting the Raman spectra at 298 K obtained by Griffiths *et al.* [27]. $I_{SS}^{\text{IR}}/I_{AS}^{\text{IR}}=0.86$ was obtained from the IR spectra measurement and fitting by Bertie *et al.* [28].

Therefore, it is ready to have the following corrected values for CH₃OH from Eqs.(3), (4) and (5). With $\omega_{SS}=2836\text{ cm}^{-1}$ and $\omega_{AS}=2987\text{ cm}^{-1}$ [27,28], one has,

$$r = 0.28 ; \quad \frac{\alpha'_{cc}}{\alpha'_{ac}} = 1.9 ; \quad \frac{\mu'_c}{\mu'_a} = 1.3 ; \quad \frac{\beta_{ccc}}{\beta_{aca}} = 2.7$$

Thus, the corrected value of β_{ccc}/β_{aca} is 2.7, and it is very different from the value of 1.1 calculated from the BAM. Now, with the corrected value $\beta_{ccc}/\beta_{aca}=2.7$, the SFG-VS intensity ratio $I_{\text{CH}_3\text{-AS}}^{\text{sps}}/I_{\text{CH}_3\text{-SS}}^{\text{ssp}}$ must be $(2.7/1.1)^2=6.0$ times smaller. Calculation with BAM gives $I_{\text{CH}_3\text{-AS}}^{\text{sps}}/I_{\text{CH}_3\text{-SS}}^{\text{ssp}}\approx 1/3$ when $\theta=0^\circ$. Now this ratio is $I_{\text{CH}_3\text{-AS}}^{\text{sps}}/I_{\text{CH}_3\text{-SS}}^{\text{ssp}}\approx 1/18$. This predicts a much smaller signal for the AS mode in sps spectrum, and such a small signal has to be below the noise level in the SFG-VS experiment presented in Fig.1. Further examination demonstrates that with the corrected β_{ccc}/β_{aca} value, the calculation in Fig.1 is fully consistent with the experimental data.

There have been few attempts to use Raman and IR spectra in the condensed phase to quantitatively interpret SFG-VS spectra from molecular interfaces in detail. It has been demonstrated that the bond additivity model has been successful in quantitative interpretation of SFG-VS of the CH₃- and CH₂-, as well as H₂O groups for their SS modes [15], but it has not been as successful with the AS mode of these molecules or molecular groups. Here we show that the empirical correction for the β_{ccc}/β_{aca} ratio is quite significant (2.7 *vs.* 1.1) from the BAM. This indicates strong coupling between CH₃ group and the OH group within the methanol molecule. The BAM is meant to fail for such case. The BAM based on the zeroth order approximation of the bond polarizability and bond moment theory certainly has its limitations in quantitative interpretation of SFG spectra.

In summary, we successfully demonstrated that a complete empirical approach can make correction to the BAM, and such correction can successfully interpret the polarization SFG spectra of the air/methanol interface. The complete empirical approach presented here

can provide new understandings of the effectiveness and limitations of the BAM, and it also provided a practical way to extend and correct the BAM for quantitative SFG-VS studies on the molecular interfaces. Detailed derivations and discussions on the corrected BAM is to be reported elsewhere [26].

- [1] Y. R. Shen, *Nature* **337**, 519 (1989).
- [2] K. B. Eisenthal, *Chem. Rev.* **96**, 1343 (1996).
- [3] P. B. Miranda and Y. R. Shen, *J. Phys. Chem. B* **103**, 3292 (1999).
- [4] R. Superfine, J. Y. Huang and Y. R. Shen, *Phys. Rev. Letts.* **66**, 1066 (1991).
- [5] K. Wolfrum, H. Graener and A. Laubereau, *Chem. Phys. Lett.* **213**, 41 (1993).
- [6] J. Y. Huang and M. H. Wu, *Phys. Rev. E* **50**, 3737 (1994).
- [7] C. D. Stanners, Q. Du, R. P. Chin, P. Cremer, G. A. Somorjai and Y. R. Shen, *Chem. Phys. Letts.* **232**, 407 (1995).
- [8] G. Ma and H. C. Allen, *J. Phys. Chem. B* **107**, 6343 (2003).
- [9] J. Sung, K. Park and D. Kim, *J. Phys. Chem. B* **109**, 18507 (2005).
- [10] (a) R. Lu, W. Gan and H. F. Wang, *Chin. Sci. Bull.* **48**, 2183 (2003); (b) *Chin. Sci. Bull.* **49**, 899 (2004).
- [11] R. Lu, W. Gan, B. H. Wu, Z. Zhang, Y. Guo and H. F. Wang, *J. Phys. Chem. B* **109**, 14118 (2005).
- [12] H. Chen, W. Gan, R. Lu, Y. Guo and H. F. Wang, *J. Phys. Chem. B* **109**, 8064 (2005).
- [13] W. Gan, B. H. Wu, H. Chen, Y. Guo and H. F. Wang, *Chem. Phys. Lett.* **406**, 467 (2005).
- [14] Y. R. Shen, *The Principles of Nonlinear Optics*; New York: John Wiley & Sons, 1984.
- [15] H. F. Wang, W. Gan, R. Lu, Y. Rao and B. H. Wu, *Int. Rev. Phys. Chem.* **24**, 191 (2005).
- [16] X. Zhuang, P. B. Miranda, D. Kim and Y. R. Shen, *Phys. Rev. B* **59**, 12632 (1999).
- [17] D. K. Hore, D. K. Beaman, D. H. Park and G. L. Richmond, *J. Phys. Chem. B* **109**, 16846 (2005).
- [18] C. Hirose, N. Akamatsu and K. Domen, *J. Chem. Phys.* **96**, 997 (1992).
- [19] C. Hirose, H. Yamamoto, N. Akamatsu and K. Domen, *J. Phys. Chem.* **97**, 10064 (1993).
- [20] L. Dixit, P. Kumar, R. B. Gupta and P. L. Gupta, *Appl. Spectro. Rev.* **18**, 373 (1982).
- [21] T. Yoshino and H. J. Bernstein, *J. Mol. Spec.* **2**, 213 (1958).
- [22] D. Steele, *Quat. Rev.* **18**, 21 (1964).
- [23] I. C. Hisatsune, *J. Chem. Phys.* **23**, 487 (1955).
- [24] D. F. Eggers, I. C. Hisatsune and L. V. Alten, *J. Phys. Chem.* **59**, 1124 (1955).
- [25] D. F. Hornig and D. C. Mckean, *J. Phys. Chem.* **59**, 1133 (1955).
- [26] H. Wu, W. K. Zhang, W. Gan, Z. F. Cui and H. F. Wang, Submitted to *J. Chem. Phys.*
- [27] M. J. Colles and J. E. Griffiths, *J. Chem. Phys.* **56**, 3384 (1972).
- [28] J. E. Bertie and S. L. Zhang, *J. Mol. Structure* **413-414**, 333 (1997).