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Populations of Ethanol Conformers in Liquid CCl$_4$ and CS$_2$ by Raman Spectra in OH Stretching Region

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Combining Raman spectroscopy with density functional theory, the populations of the *trans*- and *gauche*- ethanol conformers are investigated in carbon tetrachloride (CCl$_4$) and carbon disulfide (CS$_2$). The spectral contributions of two ethanol conformers are identified in OH stretching region. The energy difference between both conformers is estimated with the aid of the calculated Raman cross sections. It can be seen that the *trans*- ethanol is more stable in CCl$_4$ and CS$_2$ solutions. The spectra are also obtained at different temperatures, and it is found the van't Hoff analysis is invalid in these solutions. By taking accounts of the Boltzmann distribution and theoretical Raman cross section, the energy difference is found to be increased with temperature, which shows the weak intermolecular interactions can enhance the population of *trans*- ethanol.

Key words: Raman spectroscopy, Ethanol, Conformer, Energy difference

I. INTRODUCTION

It is well-known that conformers extensively exist in an organic and biological molecule [1]. Conformers play a very significant role in the related chemical or biologic processes, *e.g.* the transformation between the proline conformers can cause some diseases, such as the dialysis-related amyloidosis [2]. The isomerization between conformers with a small energy interval is difficult to study. Ethanol has two conformers of *trans*- conformer and *gauche*- conformer, in which the dihedral angles of the hydroxyl and C−C bond are 180° and 60° respectively. As the energy difference between *trans*- and *gauche*- ethanol is very small, a few arguments still exist about the populations of the two conformers in solutions.

Both conformers were identified by plenty of spectroscopies, such as IR, Raman, microwave, electron momentum spectroscopy and so on. All these spectroscopies suggested that the *trans*- conformer was more stable than the *gauche*- one in gaseous ethanol, and the energy difference between the two conformers ($\Delta E = E_{gauche} - E_{trans}$) varied within a wide range of 0.11−0.82 kcal/mol [3−9]. These experimental values roughly agreed well with the theoretical calculations based on SCF, HF, B3LYP, MP2, CCSD(T) [5,

8, 10−16]. In gaseous phase, all the methods with high level basis set also predicted that the *trans*- ethanol was more stable, and the value of ΔE was determined as 0.13−0.23 kcal/mol. Both the experiment and theoretical calculations showed that the energy differences ΔE were all very small. Because of the small ΔE, the populations of the two conformers are sensitive to ambient environment [17]. Furthermore, the relationship between the population and the environment of the conformers might help us understand the intermolecular interactions.

In ethanol solutions, the populations of conformers become more difficult to predict due to the interference of the complicated intermolecular interactions. In the solution of ethanol diluted in carbon tetrachloride (CCl$_4$), the *trans*- conformer was still more stable than the *gauche*- ethanol [10, 18]. The energy interval of ΔE was determined as 0.24 kcal/mol in the ^{1}H NMR [10]. However this ΔE was questioned by Fourier transform infrared spectroscopy (FTIR), the ΔE was recorded as 0.62 kcal/mol using the OH stretching vibration band [18]. Interestingly, recent Raman spectroscopy and quantum chemistry calculations [19] questioned the spectral assignments of OH stretching bands in FTIR [18]. As shown in the theoretical calculations, the spectral split of OH stretching vibrational band could be caused by the different types of intermolecular interactions between ethanol and CCl$_4$, as well as two conformers of ethanol.

In this work, the populations of ethanol conformers in various organic solutions have been investigated by

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employing Raman spectroscopy and theoretical calculations. Through measuring the spontaneous Raman spectra of methanol in organic solutions, we clearly observe the influence of intermolecular interactions on spectral shape of the OH stretching band. Then the mixed solutions of ethanol in CCl_4 and CS_2 have been selected as the benchmark to identify spectral contributions of the two ethanol conformers in the OH stretching region. The temperature dependences of ΔE and the populations of the two conformers are obtained in these solutions.

II. EXPERIMENTAL AND COMPUTATIONAL

Methanol, ethanol, carbon tetrachloride (CCl_4), carbon disulfide (CS_2), cyclohexane (C_6H_{12}), chloroform ($CHCl_3$), *o*-xylene, *m*-xylene and *p*-xylene were purchased from Sinopharm chemical Reagent Co., with the purities of more than 99.5%. All these solvents were used without further purification. The concentrations of all solutions were 0.1% (mole fraction). The temperature of solutions was controlled by a heating bath with the precision of 0.1 K.

Details of the Raman spectrometer have been introduced previously [20−23], thus we describe it briefly here. The excitation light was a 532 nm continuous laser (Coherent, Verdi-V5) with a power of 4 W. A Glan-prism was used to purify the linear polarization of incident light. The Raman scattering light were dispersed by a triple monochromator (Acton Research, Triplepro) and recorded by a liquid nitrogen cooled-CCD (Princeton Instruments, Spec10:100B). The measured Raman shift was calibrated with the standard lines of mercury lamp, and the typical spectral resolution is $\sim$1 cm^{-1}. The Raman spectra were recorded in the OH stretching vibrational region (3500−3700 cm^{-1}) for ethanol and methanol in solutions.

The Raman shifts and relative intensities of the *trans*- and *gauche*- ethanol were calculated with the density functional theory (DFT) of B3LYP/6-311+G(d,p). The polarizable continuum model (PCM) was used to simulate solvent effects for ethanol in solutions. The calculated vibrational frequencies were scaled by a factor of 0.9593. All the calculations were carried out by using the Gaussian 09 program package [24].

III. RESULTS AND DISCUSSION

A. Raman spectra in the OH stretching vibration region of methanol in organic solvents

The vibrational spectra of ethanol conformers can be resolved in the OH stretching region. In the gas phase, the frequency of the OH stretching vibration of *trans*-ethanol is larger than that of the *gauche*- one [4, 5, 9−11, 18, 25−30]. Hence the overlap of the OH stretch-
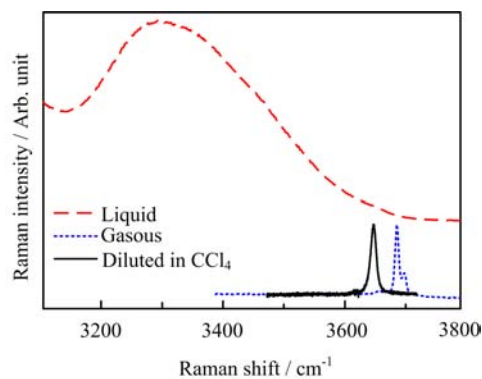

FIG. 1 Raman spectra in the OH stretching region of liquid methanol, gaseous methanol, and methanol diluted in CCl_4 at 25.0 °C.

ing bands of the two conformers induced the asymmetric shape in the FTIR of ethanol/CCl_4 solution [18]. However a quantum chemistry calculation provided a different interpretation to the asymmetric shape [19]. Besides the conformer assignments, various kinds of intermolecular interactions between ethanol and solvents induced the asymmetric profile. Different intermolecular interactions produce different OH stretching vibration frequencies, and they would overlap with each other to produce an asymmetric profile. Take ethanol in benzene for an example, there are the interactions between hydroxyl and hydrogen atom of benzene, and the interactions between hydroxyl and π electrons of benzene [19]. In one word, both the conformers and the different intermolecular interactions may induce the asymmetric band. Therefore it is necessary to find a solvent in which there is only one kind of intermolecular interaction between solvent and ethanol.

The structure of ethanol is similar to methanol, and both ethanol and methanol molecules mainly interact with solvents with hydroxyl groups. Consequently, the molecular interactions in ethanol solutions are similar to those in methanol solutions. Furthermore because methanol has no conformer, we record the Raman spectra of methanol in various organic solutions to select these solvents. The OH stretching vibrational band is sensitive to the intermolecular interactions between methanol and solvents. The OH Raman band of methanol in liquid is very broad, and the position of this band is $\sim$3300 cm^{-1}, which is much different from the spectrum of gaseous methanol. The Raman bands for gaseous methanol are very sharp, which are located at $\sim$3685 and $\sim$3698 cm^{-1} (Fig.1). The doublet for gasous methanol was also observed previously [31], which is due to the tunneling splitting. The difference between gaseous and liquid methanol is due to the strong hydrogen bonds between methanol molecules in the forms of various methanol clusters in liquid methanol [20]. In methanol/CCl_4 diluted solution with the concentration 0.1% (mole fraction), the sharp Raman band

TABLE I Experimental and calculated vibrational frequencies (in cm^{-1}) of the OH stretching mode of ethanol in gas and solutions.

Gas/solution	*Gauche*		*Trans*		$\Delta\nu$	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
Gas	3654	3673	3671	3687	17	14
C$_6$H$_{12}$	3633	3585	3642	3590	9	5
CCl$_4$	3631	3573	3638	3578	7	5
CS$_2$	3618		3626		8	

(Fig.1) demonstrates that CCl$_4$ molecules completely break the hydrogen bonds between methanol molecules. The frequency $\sim$3647 cm^{-1} of OH stretching vibration in methanol/CCl$_4$ solution is a little lower than that $\sim$3681 cm^{-1} in gaseous methanol, which suggests the weak intermolecular interaction between methanol and CCl$_4$. Importantly, this band is symmetric, which demonstrates there is only one kind of interaction in this methanol/CCl$_4$ solution.

The spectra of methanol in diluted C$_6$H$_{12}$ and CS$_2$ are similar to that in CCl$_4$ solutions, as shown in Fig.2. A very sharp and symmetric peak locates at high frequency region above 3600 cm^{-1}. The frequency and the width of the band can reflect qualitatively the intermolecular interaction [32]. The frequencies of the symmetrical bands of methanol in these solutions are lower than that in gaseous methanol, and its width is obviously broadened as well. This implies there is only one kind of weak methanol-solvent interaction in these solutions. Figure 2 shows the frequency differences ($\Delta\nu$) between the band in these solvents and that in gas, and also the full width at half maximum (ω). Both values increase with the sequence of C$_6$H$_{12}$, CCl$_4$ and CS$_2$, thus the weak interactions between methanol and the solvents are enhanced in the same order.

Different from the above solutions, in CHCl$_3$, *o*-xylene, *m*-xylene and *p*-xylene, the OH stretching band of methanol is asymmetric as shown in Fig.3. Hence there are at least two kinds of intermolecular interactions between methanol and these solvents [19]. Taking methanol in CHCl$_3$ for an example, there might be the intermolecular interactions between hydroxyl of methanol with chlorine and hydrogen atom of CHCl$_3$ respectively. The methanol/CHCl$_3$ is an equilibrium system with both kinds of interactions. Therefore, the solvent CHCl$_3$, *o*-xylene, *m*-xylene and *p*-xylene cannot be used to investigate the ethanol conformers. In this work we employ the solvent C$_6$H$_{12}$, CCl$_4$ and CS$_2$ to study ethanol conformers, since there is only one type of intermolecular interaction between ethanol and these solvents.

B. Raman spectra in the OH stretching vibration region of ethanol in C$_6$H$_{12}$, CCl$_4$, and CS$_2$

The experimental and calculated Raman spectra in the OH stretching vibration region of gaseous
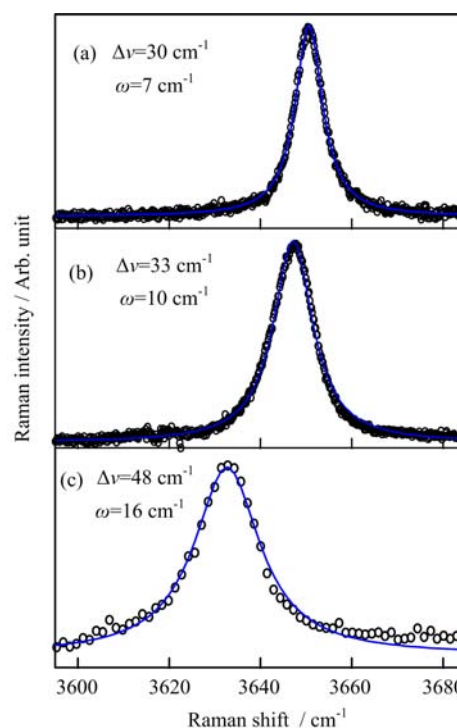

FIG. 2 Experimental (symbol) and fitted (solid line) Raman spectra of methanol in solvents of (a) C$_6$H$_{12}$, (b) CCl$_4$, and (c) CS$_2$, where a Lorentz band is used in the fitting process. The Raman shift difference ($\Delta\nu$) against gaseous methanol and FWHM (ω) of the band in these solutions are shown as well.

ethanol are presented in Fig.4(a). The *trans*- and *gauche*- conformers contribute the doublet at $\sim$3671 and $\sim$3654 cm^{-1} respectively [4, 5, 9−11, 27, 29, 30]. The Raman spectra of ethanol in C$_6$H$_{12}$, CCl$_4$ and CS$_2$ are shown in Fig.4 (b), (c), and (d), respectively. All the bands are asymmetric, and they can be fitted well with two Lorentz bands.

Only one kind of intermolecular interaction exists in the diluted solutions of ethanol with C$_6$H$_{12}$, CCl$_4$ and CS$_2$, so the ethanol conformers induce the asymmetric band in Fig.4. We used two Lorentz bands to fit these bands. Table I summarizes the fitting results, and the theoretical OH stretching vibrational frequencies of the *trans*- and *gauche*- ethanol in these solutions. The fitting errors of these frequencies are $\sim$0.2 cm^{-1}.
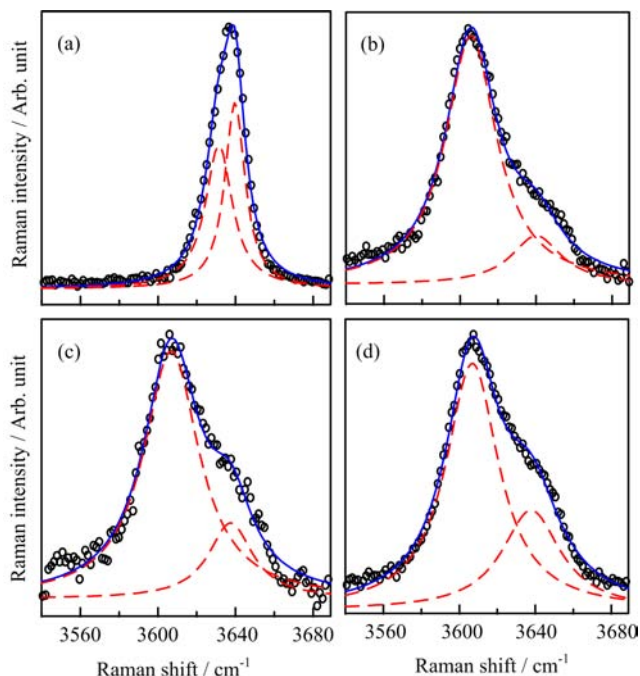
FIG. 3 Raman spectra in the OH stretching region of methanol in (a) CHCl₃, (b) *o*-xylene, (c) *m*-xylene, and (d) *p*-xylene. The asymmetrical spectra were fitted with two Lorentz bands.

FIG. 4 Raman spectra in the OH stretching region of ethanol in (a) gas, (b) C_6H_{12}, (c) CCl_4 and (d) CS_2. The calculated spectra of *trans*- and *gauche*- ethanol in gas are shown in (a) as well. The spectra in (b, c, d) were fitted with two Lorentz bands.

As suggested by the present theoretical frequency, the *trans*- and *gauche*- conformers contribute the band with higher and lower frequency respectively. This assignment is consistent with the previous FTIR experiment [18]. According to both our experiment and theory results, the frequencies of the OH stretching vibration are red-shifted from gaseous ethanol to solutions due to the weak molecular interactions. The red shift for ethanol in C_6H_{12} is the smallest, thus the molecular interaction between the ethanol and C_6H_{12} is the weakest. Consequently, the Raman bands of ethanol in C_6H_{12} are hardly widened by the weak interaction, thus the doublet of the *trans*- and *gauche*- conformers are much more obvious for the solution C_6H_{12} (Fig.4).

C. Temperature dependence of populations of ethanol conformers in CCl_4 and CS_2

According to the above identified spectral contributions of the *trans*- and *gauche*- ethanol, we can estimate the populations of both conformers in solutions. The Raman spectra of ethanol/CCl_4 solution in the OH stretching vibration region were measured from -6.9 °C to 73.8 °C with an interval of ~5 °C. Figure 5(a) presents only two spectra at 4.6 and 73.8 °C for clarity. As shown in Fig.5(a), the intensity of the Raman component at the higher frequency is enhanced with temperature, indicating that the population of *trans*-ethanol is increased. The conclusion seems contrary
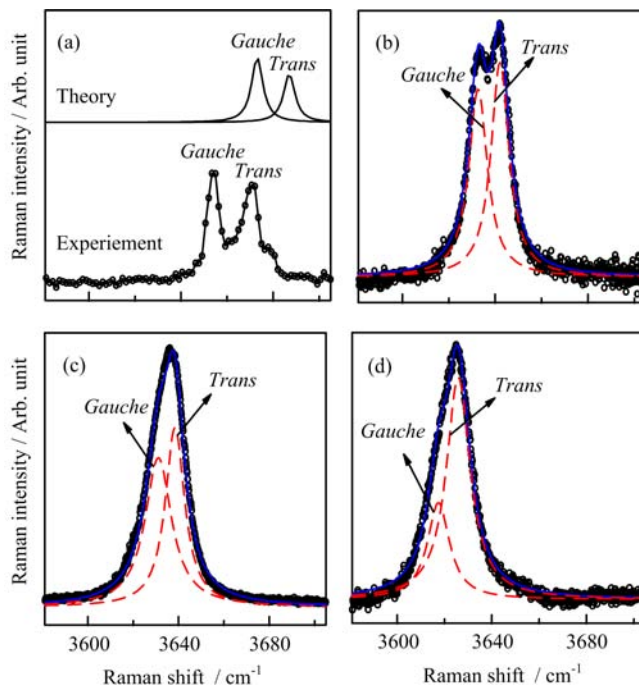
to that of the previous molecular dynamics (MD) simulation in pure liquid ethanol, where the percentage of *trans*- ethanol was decreased at high temperature [33−37]. It may be because of the different intermolecular interactions in liquid ethanol and ethanol/CCl_4 solution. The weak molecular interaction between hydroxyl of ethanol and chloride atom of CCl_4 is dominant in the diluted solution, while the main interactions in liquid ethanol are the strong hydrogen bonds between ethanol molecules. The hydrogen bonds would broaden the OH stretching band in liquid ethanol, so the conformers cannot be identified in this band.

We fitted all the spectra with two Lorentz bands to estimate the OH stretching frequencies and the spectral contributions of the two conformers, as shown in Fig.5(a). The molecular thermal motion would weaken the molecular interactions between ethanol and CCl_4 at high temperature, thus the OH stretching frequency becomes larger at higher temperature. Take the OH stretching frequency of *gauche*- ethanol for an example, it blue-shifts from ~3628.6 cm⁻¹ to ~3632.5 cm⁻¹ with a nearly linear rate of ~0.05 cm⁻¹·K⁻¹ from -6.9 °C to 73.8 °C, as shown in Fig.5(b). The trend of the blue shift for ethanol in CCl_4 is similar to that for methanol in CCl_4 (Fig.5(c)), indicating the validity of the fitting procedure.

Since the temperature dependent populations of the two conformers obey the Boltzmann distribution, the
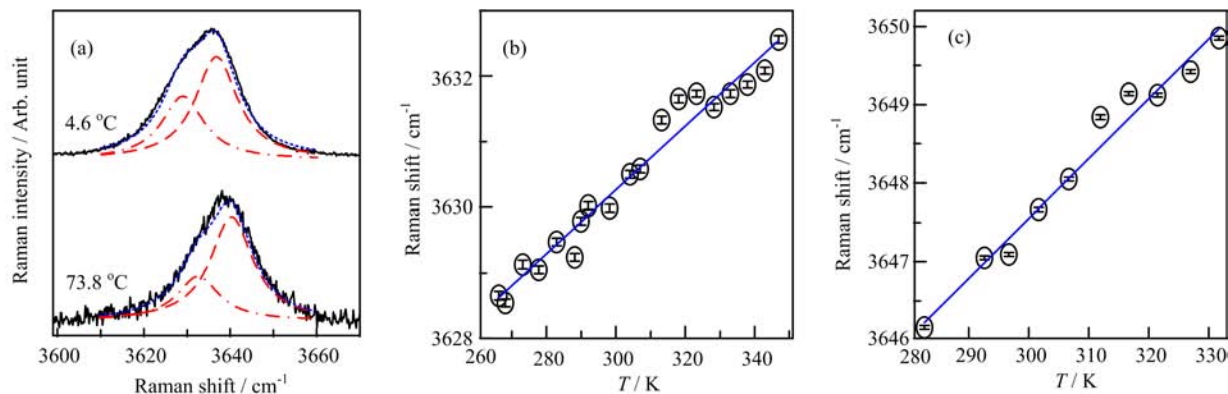
FIG. 5 (a) Raman spectra in the OH stretching vibration region of ethanol/CCl$_4$ at 4.6 and 73.8 °C, (b) temperature dependence of the OH stretching vibrational frequency of *gauche-* ethanol in CCl$_4$, (c) temperature dependence of the OH stretching vibrational frequency of methanol in CCl$_4$.

intensity ratio at temperature T can be described as the following formula:

$$\frac{I_{gauche}}{I_{trans}} = \frac{\sigma_{gauche}g_{gauche}}{\sigma_{trans}g_{trans}}\exp\left(\frac{-\Delta E}{k_{\rm B}T}\right) \qquad (1)$$

where I and σ are the spectral intensity and the Raman scattering cross section, respectively. g is the degeneracy factor, and it is 2 for *gauche-* and 1 for *trans-* conformer. ΔE is the energy difference between the two conformers.

Supposing the ΔE is not dependent on temperature, we can obtain ΔE and Raman scattering cross sections ratio ($\sigma_{gauche}/\sigma_{trans}$) by fitting $\ln(I_{gauche}/I_{trans})$-$1/T$ with the following linear equation:

$$\ln\frac{I_{gauche}}{I_{trans}} = \frac{-\Delta E}{k_{\rm B}T} + \ln\frac{g_{gauche}\sigma_{gauche}}{g_{trans}\sigma_{trans}} \qquad (2)$$

This equation is called as the van't Hoff relationship. Using this equation, the slope and the intercept of this linear equation offer the ΔE and the cross sections ratio $\sigma_{gauche}/\sigma_{trans}$. Through fitting the data from −6.9 °C to 73.8 °C, the ΔE and $\sigma_{gauche}/\sigma_{trans}$ are determined as −1.44±0.05 kcal/mol and 0.023±0.001, respectively. Thus the *gauche-* configuration seems more stable in energy. However, the ΔE is far from the data $\Delta E \approx 0.62$ kcal/mol from the previous FTIR of ethanol/CCl$_4$ [18]. Also the $\sigma_{gauche}/\sigma_{trans}$ is inconsistent with that of ∼0.667 from previous experimental result [9] and the present computation based on density functional theory. The experimental and the fitting errors are not responsible for the large discrepancy. Therefore, the contradiction indicates that the ΔE should be inconstant for different temperatures. The ΔE is an inconstant value because of the different intermolecular interactions at different temperatures, which is supported by the temperature dependent frequencies shown in Fig.5(b).

Through using the theoretical value of $\sigma_{gauche}/\sigma_{trans}$ as 0.667, the ΔE is obtained directly at each temperature with Eq.(1). Figure 6(a) shows the ΔE at
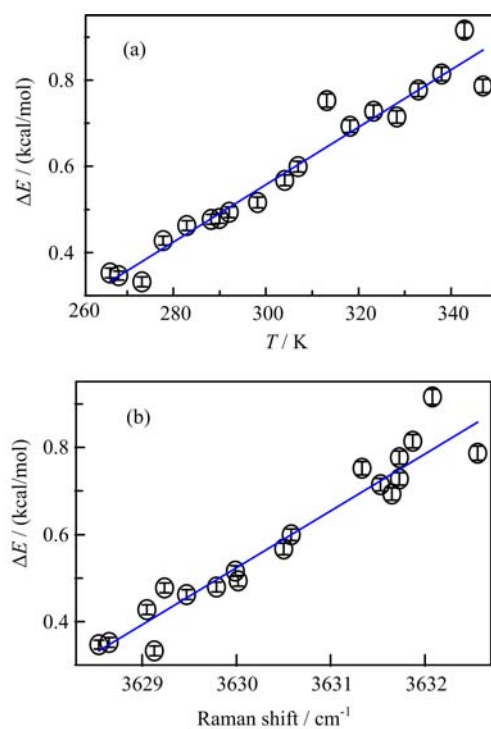

FIG. 6 (a) Temperature dependence of the energy difference between *gauche-* and *trans-* ethanol conformer in CCl$_4$, (b) relationship of Raman shift and the energy difference between *gauche-* and *trans-* ethanol conformer in CCl$_4$.

all the temperatures. The ΔE is dependent strongly on temperature and indeed inconstant. The average value of the ΔE in the present temperature range is 0.6±0.2 kcal/mol, which is close to the previous data, 0.62±0.21 kcal/mol [18]. The positive values indicate that the *trans-* conformer is more stable in energy. Moreover, the ΔE increases from 0.35 kcal/mol to 0.79 kcal/mol with a trend of 0.008 kcal/(mol·K) from −6.9 °C to 73.8 °C, thus the population of the *trans-* conformer is gained at higher temperature. The ΔE
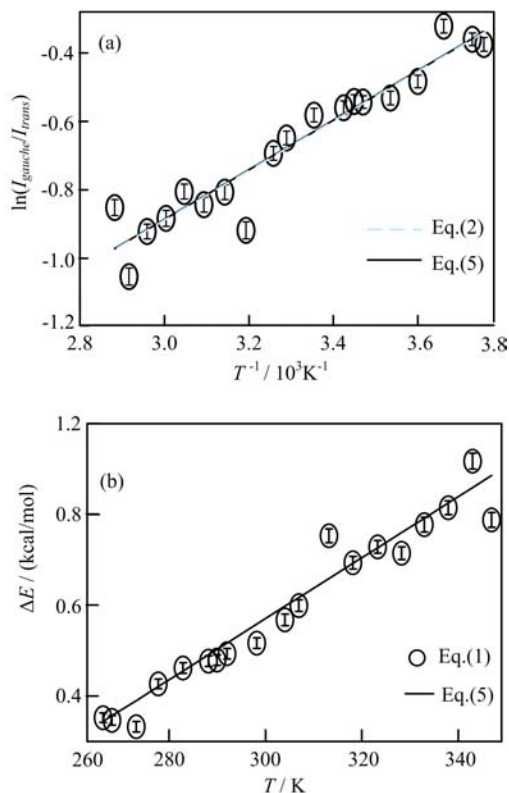
FIG. 7 (a) The plot of $\ln(I_{gauche}/I_{trans})$ *vs.* $1/T$ with the van't Hoff relationship (Eq.(2)) and Eq.(5). (b) The energy interval of ethanol conformers in CCl$_4$ derived from Eq.(1) and the fitting results with Eq.(5).
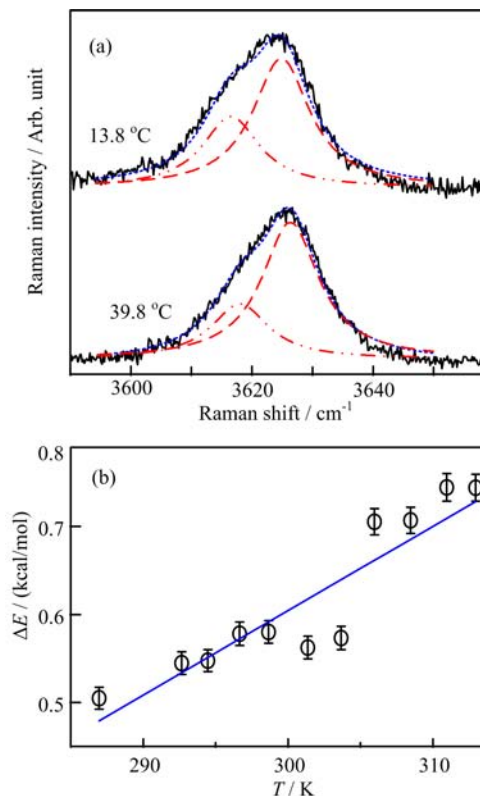

FIG. 8 (a) Raman spectra in the OH stretching vibration region of ethanol in CS$_2$ at 13.8 and 39.8 °C, (b) temperature dependence of the energy difference between *gauche-* and *trans-* ethanol conformer in CS$_2$.

presents the positive correlation with the OH stretching frequency of the *gauche-* ethanol, as shown in Fig.6(b). The increased OH stretching frequency demonstrates the weaker intermolecular interaction, which increases the population of the *trans-* ethanol.

According to the temperature dependent ΔE (Fig.6(a)), ΔE can be expressed as a linear function of temperature, as shown in Eq.(3).

$$\Delta E = \Delta E_{\mathrm{a}} + bT \tag{3}$$

where ΔE_{a} is the energy interval of ethanol conformers at the lowest temperature and b is the change rate of energy interval as temperature. Using this equation and Boltzmann distribution (Eq.(1)), the temperature dependent intensity ratio between *gauche-* and *trans-* conformer should obey the following relationship:

$$\ln \frac{I_{gauche}}{I_{trans}} = \frac{-(\Delta E_{\mathrm{a}} + bT)}{k_{\mathrm{B}}T} + \ln \frac{g_{gauche}\sigma_{gauche}}{g_{trans}\sigma_{trans}} \tag{4}$$

This equation could be simplified to the following equation:

$$\ln \frac{I_{gauche}}{I_{trans}} = \frac{-\Delta E_{\mathrm{a}}}{k_{\mathrm{B}}T} + \left(-\frac{b}{k_{\mathrm{B}}} + \ln \frac{g_{gauche}\sigma_{gauche}}{g_{trans}\sigma_{trans}} \right) \tag{5}$$

Similar to van't Hoff relationship (Eq.(2)), Eq.(5) also presents a linear relationship between $\ln(I_{gauche}/I_{trans})$ and $1/T$. Consequently, the experimental linear correspondence of $\ln(I_{gauche}/I_{trans})$ to $1/T$ does not directly reflect the validity of van't Hoff relationship in the solution C$_2$H$_5$OH/CCl$_4$. Eq(2) and Eq.(5) are both employed to fit the $\ln(I_{gauche}/I_{trans})$ at various temperatures, as shown in Fig.7(a). Although the fitting curves are the same, the fitting parameters are different. The parameters ΔE_{a} and b obtained from Eq.(5) can be applied to calculate the ΔE at different temperatures. It is found these ΔE agree with the values obtained from Eq.(1), as shown in Fig.7(b). Previously, the van't Hoff relationship was employed to analyze the energy interval of some two-state model [22, 38], however the intercept was not used to verify the availability of van't Hoff relationship.

In the ethanol/CS$_2$ solution the ΔE is also inconstant. We measured the Raman spectra of ethanol in CS$_2$ solution in the OH stretching vibration region from 13.8 °C to 39.8 °C. Figure 8(a) shows only the Raman spectra of ethanol/CS$_2$ at 13.8 and 39.8 °C for clarity. Also we decomposed all the spectra with two Lorentz bands. Based on the fitted spectra and the Boltzmann distribution, the energy difference ΔE is also calculated at each temperature, which is plot-

ted in Fig.8(b). The ΔE increases as the temperature with the slope $\sim$0.009 kcal/(mol·K) in ethanol/CS$_2$. The average value of ΔE in the ethanol/CS$_2$ solution is 0.6±0.1 kcal/mol, which is consistent with that in ethanol/CCl$_4$ solution. The similar ΔE is because of the similar intermolecular interactions in CS$_2$ and CCl$_4$, which are both nonpolar solvents and the relative dielectric constants are very close. The temperature dependent spectra of ethanol in C$_6$H$_{12}$ were also recorded, however the temperature dependent energies were not analyzed here because of the low signal-to-noise ratio.

IV. CONCLUSION

We employ Raman spectroscopy and theoretical calculations to investigate the populations of *trans-* and *gauche-* ethanol conformers in ethanol solutions with CCl$_4$ and CS$_2$.

To clearly observe the influence of intermolecular interactions on spectral shape of OH stretching band, the spontaneous Raman spectra of methanol in various organic solutions were recorded. In CHCl$_3$, *o*-xylene, *m*-xylene and *p*-xylene solvents, the asymmetric bandshape indicates that two kinds of intermolecular interactions occur between methanol and solvents. The symmetric profile of the OH stretching band observed in C$_6$H$_{12}$, CCl$_4$ and CS$_2$ demonstrates an unique intermolecular interaction exists. Hence the mixed solutions of ethanol in CCl$_4$ and CS$_2$ are selected as the benchmark to identify spectral contributions of the two ethanol conformers in the OH stretching region.

As suggested by the theoretical calculation at the level of B3LYP/6-311+G(d,p), the asymmetric profile of the OH stretching band of ethanol solutions are contributed by the *trans-* and *gauche-* conformers, and the *trans-* ethanol has the higher vibrational frequency of OH stretching. Through using the spectral intensity, the calculated Raman scattering cross section and the Boltzmann distribution, we estimated the energy differences ΔE between the *gauche-* and *trans-* conformer at various temperatures. It can be seen that the *trans-* ethanol is more stable in CCl$_4$ and CS$_2$ solutions. Moreover, the ΔE is increased with temperature, indicating that the weak intermolecular interactions between ethanol and solvents would enhance the population of the *trans-* ethanol.

V. ACKNOWLEDGMENTS

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