THE JOURNAL OF
PHYSICAL CHEMISTRY A

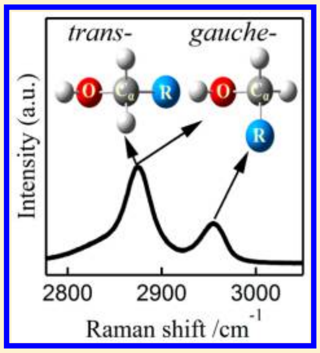
# Identification of Alcohol Conformers by Raman Spectra in the C−H Stretching Region

Lin Chen,[†] Weiduo Zhu,[†] Ke Lin,*[,†,‡] Naiyin Hu,[†] Yuanqin Yu,[§] Xiaoguo Zhou,[†,‡] Lan-Feng Yuan,[†] Shui-Ming Hu,[†] and Yi Luo[†,‡]

[†]Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, and [‡]Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China
[§]School of Physics and Material Science, Anhui University, Hefei, Anhui 230039, China

*Supporting Information*

**ABSTRACT:** The spontaneous polarized Raman spectra of normal and deuterated alcohols ($C_2$−$C_5$) have been recorded in the C−H stretching region. In the isotropic Raman spectra, a doublet of $-C_\alpha H$ stretching vibration is found for all alcohols at below 2900 $cm^{-1}$ and above 2950 $cm^{-1}$. By comparing the experimental and calculated spectra of various deuterated alcohols, the doublets are attributed to the $-C_\alpha H$ stretching vibration of different conformers. For ethanol, the band observed at 2970 $cm^{-1}$ is assigned as the stretching vibration of $-C_\alpha H$ in the $C_\alpha$−O−H plane of the *gauche*-conformer, while the band at 2895 $cm^{-1}$ is contributed from both the $-C_\alpha H_2$ symmetrical stretching vibration of the *trans*-conformer and the $-C_\alpha H$ stretching vibration out of the $C_\alpha$−O−H plane of the *gauche*-conformer. The population of *gauche*-conformer is estimated to be 54% in liquid ethanol. For the larger alcohols, the same assignments for the doublet are obtained, and the populations of *gauche*-conformers with plane carbon skeleton are found to be slightly larger than that of ethanol, which is consistent with results from molecular dynamics simulations.



## 1. INTRODUCTION

The alkyl groups exist widely in organic and biological molecules. The vibrational spectroscopy in the C−H stretching region is helpful to discriminate proteins,[1] to image tissues,[2] to interpret molecular interactions,[3] and to investigate dynamical processes.[4,5] The success of these applications relies on the correct spectral assignments. Taking the energy transfer process in liquid ethanol as an example, the time-resolved anti-Stokes Raman spectra were revealed that the stretching vibrational energy moved from the −OH group to the $-CH_2$ group and then reached the $-CH_3$ group.[4] This mechanism was established based on the existing spectral assignments in the C−H stretching region. Originally, the $-CH_2$ and $-CH_3$ stretching vibration bands were found to be separated in the Raman spectra of ethanol.[6,7] However, the Raman spectra[8] and the sum of frequency generation (SFG) spectra[9] of deuterated ethanol ($CH_3CD_2OH$ and $CD_3CH_2OH$) challenged the assignments. The new spectra demonstrated that the $-CH_2$ and $-CH_3$ vibrational bands were overlapped with each other.[8,9]

The controversial assignments in the C−H stretching region are due to the presence of strong spectral overlap. It is known that many Raman modes can present in this region, such as stretching vibrations of various alkys, alkyl symmetrical and asymmetrical stretching modes, and the alkyl bending overtone modes. Apart from these, the stretching modes can interact with bending overtone modes through the Fermi resonances. Previously, the spectral overlaps were eliminated through two approaches. The first one was to record Raman spectrum in gas phase instead of liquid to generate narrow bands due to the negligible intermolecular interactions. As shown in a recent Raman spectrum of gaseous methanol,[10] more bands in the C−H stretching region were indeed resolved. According to the quantum chemistry calculation, these bands originated from the methyl out-of-plane and in-plane asymmetrical vibrations, respectively. The second approach was to measure the spectra of the deuterated compounds, which allowed resolving vibrations of different alkyls. For ethanol molecule, only $-CH_2$ and $-CH_3$ vibration modes were observed in the C−H stretching region of $CD_3CH_2OH$ and $CH_3CD_2OH$, respectively.[8,9]

However, the presence of two possible conformers in alcohol molecules has made these two approaches powerless, since they cannot conquer and identify the spectral overlap from different conformers. In this context, the quantum chemistry calculation can play an important role. According to the calculations, the −CH stretching vibrations of *trans*- and *gauche*-ethanol behave differently. The $-CH_3$ asymmetric stretching vibration[11] and the overtone of $-CH_2$ bending vibration[12] of *gauche*-conformers can both contribute to the band at ~2985 $cm^{-1}$ in the Raman spectra of gaseous ethanol and $CD_3CH_2OH$, respectively. Although there is no consensus on the definite assignments, these studies suggest the significance of conformers in the C−H stretching region.

**Received:** December 31, 2014
**Revised:** March 15, 2015
**Published:** March 16, 2015

DOI: 10.1021/jp513027r
*J. Phys. Chem. A* 2015, 119, 3209−3217

There are 2, 5, 14, and 41 conformers in ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol, respectively. In addition, most of the conformers could be populated, since the energy differences among the conformers are small. For example, the population ratio of *trans*- to *gauche*-ethanol was 1:1.5 in the xenon solution,[11] which agreed with the theoretical ratio 1:1.6.[13] The population ratio was 14:24:28:19:15 for the Tt, Tg, Gt, Gg, and Gg′ conformers of *n*-propanol in the recent calculations at the level of DFT/B3LYP/6-311++G(d,p).[14] In these conformers, the geometry of the same alkyl groups was different as found in previous quantum chemistry calculations.[14,15] Taking the conformer rotating around the CO bond for example, the $-C_\alpha H_2$ group is different in *trans*- and *gauche*-alcohols. In the *trans*-conformers, the OH group and both $-C_\alpha H$ groups are in different planes, and in the *gauche*-alcohols, one $-C_\alpha H$ group and OH group are coplanar, as clearly illustrated in Figure 1.

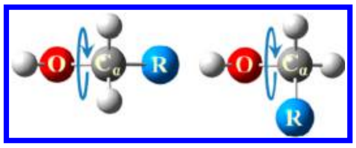


**Figure 1.** Geometries of *trans*-alcohol (left) and *gauche*-alcohol (right) conformers; R is alkyl group.

However, there is no direct experimental evidence to distinguish the *gauche*- and *trans*-conformers. Obviously, it is highly desirable to experimentally explore the possibility of identifying conformers in the C−H stretching region.

In this study, we measured the Raman spectra of ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol in the C−H stretching region. To eliminate spectral overlap, we first recorded the spectra of gaseous alcohol and the deuterated alcohols. Two new methods were also employed to further remove spectral overlaps. First, we recorded the isotropic Raman spectra to remove asymmetric vibration modes. Second, we measured the spectrum of crystal alcohol at low temperature, which gives very sharp bands. Furthermore, density functional theory calculation was used to assign the spectra of the deuterated alcohols. In the spectra of all deuterated alcohols, a doublet was observed, which was contributed from the $-C_\alpha H$ stretching vibration of *trans*- and *gauche*-alcohol. The frequency and the intensity of the doublet tell about the structure and the population of alcohol conformers associated with the CO rotation. In addition, the molecular dynamics simulations confirmed the established populations of the alcohol conformers from the doublet.

## 2. EXPERIMENT

The experimental setup is similar to that used in previous studies,[16,17] and we only describe it briefly here. In this study, the backscattering geometry was employed. All the experimental data were collected with a triple monochromator system (Acton Research, TriplePro) connected to a liquid nitrogen-cooled CCD detector (Princeton Instruments, Spec-10:100B). The excitation light was a stable CW laser (Coherent, Verdi-V5, 532 nm). The laser power of 3.5 and 0.4 W was employed to excite the liquid/gas sample and the solid sample, respectively. The laser was linearly polarized with a Glan-laser prism, and its polarization direction was controlled by a half-wave plate. The Raman shifts of the spectra were calibrated with the standard lines of a mercury lamp, and the spectral resolution was ~1.0 $cm^{-1}$.

Carbon tetrachloride ($CCl_4$, 99.5%), acetonitrile ($CH_3CN$, 99.8%), acetic acid ($CH_3COOH$, 99.5%), *n*-propanol (99.0%), *n*-butanol (99.5%), and *n*-pentanol (98.5%) were purchased from Sinopharm Chemical Reagent Co. Ethanol (99.8%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. $CH_3CD_2OH$ (98%), $CD_3CH_2OH$ (99%), and $CD_3CD_2OD$ (99%) were obtained from Sigma-Aldrich. $CD_3CHDOH$ (99.6%), $CH_3CD_2CD_2OH$ (99.8%), $CD_3CD_2CH_2OH$ (99.5%), $CH_3CD_2CD_2CD_2OH$ (99.4%), $CD_3CD_2CD_2CH_2OH$ (99.7%), and $CD_3CD_2CD_2CD_2CH_2OH$ (99.4%) were obtained from C.D.N Isotopes Inc. All the samples were used without further purification.

During the measurements of liquid samples, a heating bath (THD-2006, Ningbo) controlled the temperature (30 ± 0.1 °C) of the samples in a 10 × 10 mm quartz cuvette. For the gas phase measurements, the $CD_3CHDOH$ vapor was employed at room temperature.

The crystal ethanol was prepared by using a closed-cycle cryogenic cold head which can be cooled down to 4.2 K (Janis, SHI-4-5). A mixed sample of liquid $CD_3CH_2OH$ and $CD_3CD_2OD$ with a mole ratio of 1:1000 was used. Then the vapor of the mixed sample was deposited on a $BaF_2$ plate attached to the cold head at 5 K. After deposition, the temperature of the cool head was raised slowly to 140 K and then back to 5 K. After the annealing, the deposited ethanol transferred from amorphous state to crystal, which could be characterized from much sharper line profiles in the observed spectrum.

## 3. COMPUTATION

All calculations were performed with the Gaussian-09 program package.[18] The geometries of conformers of deuterated alcohols were optimized at the B3LYP level with the 6-311+G(d, p) and aug-PVQZ basis sets, respectively. The harmonic vibrational frequencies were calculated at the same level, and their isotropic Raman spectra were obtained subsequently with a scaled factor of 0.963. The structures of all the conformers are displayed in the Supporting Information. We use T/t and G/g to denote the dihedral angle of the conformers, which is 180° and 60°, respectively.[19] For example, the TGg′ *n*-butanol conformer indicates that the dihedral angle of $C_\delta C_\gamma{-}C_\beta C_\alpha$, $C_\gamma C_\beta{-}C_\alpha O$, and $C_\beta C_\alpha{-}OH$ is 180°, 60°, and −60°, respectively.

The molecular dynamics simulations were employed to analysis the conformer populations of ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol. The GROMACS simulation package[20] was used in *NPT* system. Each system consisted of 512 molecules in a cubic cell. The temperature and external pressure were fixed at 300 K and 1 atm, and they were controlled with the Nosé−Hoover thermostat[21] and Parrinello−Rahman barostat,[22] respectively. A cutoff of 1 nm was used for the LJ interactions, and the long-range electrostatic interactions were treated with the slab-adapted Ewald sum method.[23] The simulation for each system was carried out for 10−60 ns with a step of 2 fs.

## 4. RESULTS AND DISCUSSION

### 4.1. Isotropic Raman Spectra.

We recorded the polarized Raman spectra of all the samples, in which the polarization of Raman scattering light is parallel ($I_p$) or perpendicular ($I_v$) to that of excitation laser. The ratio between the two intensities $I_v$ and $I_p$ is equal to the depolarization ratio ($\rho$). The $\rho$ value is in the range from 0 to 0.75. The depolarization ratio can indicate the symmetry of vibrational mode. For the symmetric mode, $\rho$ is smaller than 0.75, while it equals to 0.75 for the asymmetric mode. Furthermore, we can calculate the so-called isotropic Raman spectrum by the relationship[24]

$$I_{\text{iso}} = I_p - \frac{4}{3}I_v \tag{1}$$

In this spectrum, the asymmetric vibrational bands disappear. Figure 2a shows the isotropic and parallel Raman spectra of carbon tetrachloride ($CCl_4$). It can be seen that only one $CCl_4$ symmetric stretching band (457 $cm^{-1}$) exists in the isotropic spectrum. Two $CCl_4$ asymmetric stretching bands (216 and 312 $cm^{-1}$) can be found in the parallel spectrum. Figures 2b and 2c show the isotropic and parallel Raman spectra of $CH_3CN$ and $CH_3COOH$, respectively. In both isotropic spectra, only one $-CH_3$ symmetric stretching band appears. It indicates that the isotropic spectra are helpful for the spectral assignment in the C−H stretching region.

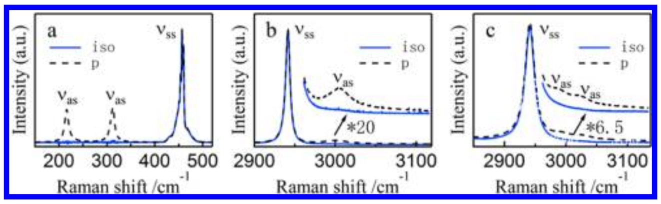


**Figure 2.** Isotropic and parallel Raman spectra of (a) $CCl_4$, (b) $CH_3CN$, and (c) $CH_3COOH$.

### 4.2. Raman Spectra of Ethanol Conformers.

*4.2.1. Isotropic Raman Spectra of $CH_3CH_2OH$, $CH_3CD_2OH$, and $CD_3CH_2OH$.* The vibrational spectra of liquid ethanol often display three bands at 2875, 2930, and 2970 $cm^{-1}$ in the C−H stretching region. The $-CH_2$ symmetric stretching vibration and the $-CH_3$ symmetric and asymmetric stretching vibrations were believed to contribute to these bands, respectively.[6,7] Several different assignments[8,9] were given from the spectra of deuterated ethanol molecules, such as $CH_3CD_2OH$ and $CD_3CH_2OH$. In these assignments,[8,9] both the $-CH_2$ and $-CH_3$ symmetric stretching modes were attributed to the band at 2875 $cm^{-1}$, and the Fermi resonance of the $-CH_3$ group gave rise to the band at 2930 $cm^{-1}$, while both $-CH_3$ asymmetric stretching vibration and the Fermi resonance of the $-CH_2$ group contributed to the band at 2970 $cm^{-1}$. It is noted that the spectral contributions of the ethanol conformers were completely neglected in these earlier studies.

It is well-known that both ethanol conformers can be populated at room temperature. For the gaseous ethanol, the population ratio of *trans-* to *gauche*-conformers was found to vary from 2:1 to 2:3 from different spectroscopies.[11,25] In liquid ethanol, the population of *gauche*-ethanol was found to be 50% from molecular dynamics simulations[26] or even 75% from neutron diffraction.[27] The contributions from ethanol conformers are thus necessary to consider when assigning the spectra in the C−H stretching region. This has been examined in a study on Raman spectra of gaseous ethanol. The $-CH_3$ asymmetric stretching vibration of the *gauche*-conformer is known to contribute to the band (~2985 $cm^{-1}$).[11] However, the same band (~2981 $cm^{-1}$) was still observed in the spectrum of gaseous $CD_3CH_2OH$, in which the spectral contribution of methyl group should not be presented. Consequently, this band was assigned as the Fermi resonance of the $-CH_2$ stretching vibration of the *gauche*-conformer.[12]

Similar to the previous spectra,[8] we have measured the polarized Raman spectra of liquid $CH_3CH_2OH$, $CH_3CD_2OH$, and $CD_3CH_2OH$ to generate the corresponding isotropic Raman spectra, as shown in Figure 3. As expected, only symmetric vibration Raman bands appear in these spectra. It can thus be concluded that the $-CH_3$ symmetric vibrations contribute to the bands at 2871, 2900, and 2934 $cm^{-1}$ in the isotropic spectrum of $CH_3CD_2OH$ (Figure 3a). Similarly, the $-CH_2$ symmetric vibrations contribute to the band at 2886 and 2970 $cm^{-1}$ in the isotropic spectrum of $CD_3CH_2OH$ (Figure 3b). The sum of the spectrum of $CH_3CD_2OH$ and $CD_3CH_2OH$ is roughly equal to the spectrum of $CH_3CH_2OH$ (Figure 3c). Furthermore, in the spectra of $CH_3CH_2OH$ and $CD_3CH_2OH$, the intensities of the band at 2970 $cm^{-1}$ are almost equal, which indicates that the $-CH_2$ symmetric vibration contributes to this band in the isotropic spectrum of $CH_3CH_2OH$.

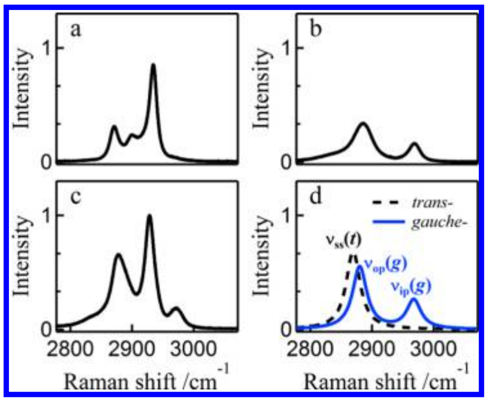


**Figure 3.** Experimental isotropic Raman spectra in the C−H stretching region of (a) $CH_3CD_2OH$, (b) $CD_3CH_2OH$, and (c) $CH_3CH_2OH$. The theoretical isotropic Raman spectra (d) of *trans*- and *gauche*-$CD_3CH_2OH$. All the vertical scales are the same.

As shown in Figure 3b, only a doublet at 2886 and 2970 $cm^{-1}$ is observed in the spectrum of $CD_3CH_2OH$. To assign this doublet, we have calculated the isotropic Raman spectra of *trans-* and *gauche*-$CD_3CH_2OH$ (Figure 3d). For the *trans*-conformer, only one Raman band appears at 2869 $cm^{-1}$ as contributed from $-CH_2$ symmetrical stretching vibration. For *gauche*-ethanol, a doublet at 2880 and 2968 $cm^{-1}$ is observed, which can be assigned to the two components of the $-C_\alpha H$ group, named as the out of the $C_\alpha-O-H$ plane $-C_\alpha H_{op}$ and in plane $-C_\alpha H_{ip}$, respectively. All vibration modes mentioned above are shown in Figure 4. Through comparing the experimental and theoretical spectra, the band at 2970 $cm^{-1}$ in the isotropic spectra of $CH_3CH_2OH$ and $CD_3CH_2OH$ may

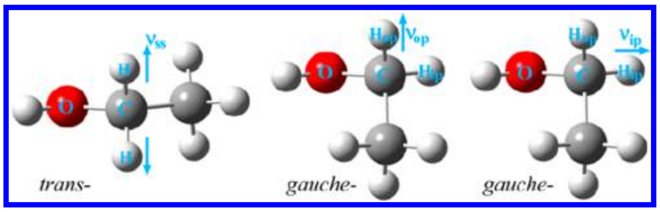


**Figure 4.** Methylene stretching vibration of *trans-* and *gauche*-$CD_3CH_2OH$.

arise from the $-C_{\alpha}H_{ip}$ stretching vibration of the *gauche*-conformer.

Previously, the band at 2970 $cm^{-1}$ in the parallel Raman spectra was assigned to $-CH_3$ asymmetric stretching vibration,[6,7] the overlap of the $-CH_3$ asymmetric stretching vibration and the Fermi resonance of the $-CH_2$ group,[8,9] the $-CH_3$ asymmetric stretching vibration of the *gauche*-conformer,[11] or the Fermi resonance of the $-CH_2$ group of the *gauche*-conformer.[12] Because the asymmetric vibration is absent in the isotropic spectra, the involvement of the $-CH_3$ asymmetric stretching vibration can be ruled out. The contributions from Fermi resonance of the $-CH_2$ symmetrical vibration[8,9,12] or the $-C_{\alpha}H_{ip}$ stretching vibration of the *gauche*-conformer still need to be clarified, which can be achieved by measuring the Raman spectra of $CD_3CHDOH$ and crystal $CD_3CH_2OH$.

*4.2.2. Raman Spectra of $CD_3CHDOH$.* As the $C_{\alpha}H$ bending, stretching frequencies, and their Fermi Resonance of $CD_3CHDOH$ are different from those of $CD_3CH_2OH$, we calculated vibrational frequencies of the first overtones of *trans*- and *gauche*-$CD_3CHDOH$. The theoretical $-C_{\alpha}H$ bending overtone Raman bands appear in the range of 2550−2750 $cm^{-1}$ (Figure 5), while a few bands can indeed be found in the experimental Raman spectrum of liquid $CD_3CHDOH$. Hence, the $-C_{\alpha}H$ bending overtone contributes to these weak bands, and in other words, the Fermi resonances of $-C_{\alpha}H$ bending overtones do not contribute to the doublet around 2900 $cm^{-1}$. Moreover in the spectrum of gaseous $CD_3CHDOH$, the doublet is more obvious as shown in Figure 5. According to the theoretical calculation, the $-CH_2$ symmetrical stretching vibration of *trans*-ethanol and $-C_{\alpha}H_{op}$ stretching vibration of the *gauche*-conformer give the band at 2895 $cm^{-1}$, and the $-C_{\alpha}H_{ip}$ stretching vibration of *gauche*-ethanol contributes to the other band at 2955 $cm^{-1}$. All these spectra demonstrate that the $-C_{\alpha}H$ stretching vibrations of *gauche*-ethanol indeed are different with those of *trans*-ethanol. Thus, the doublet in the Raman spectra can be used to identify the ethanol conformer.

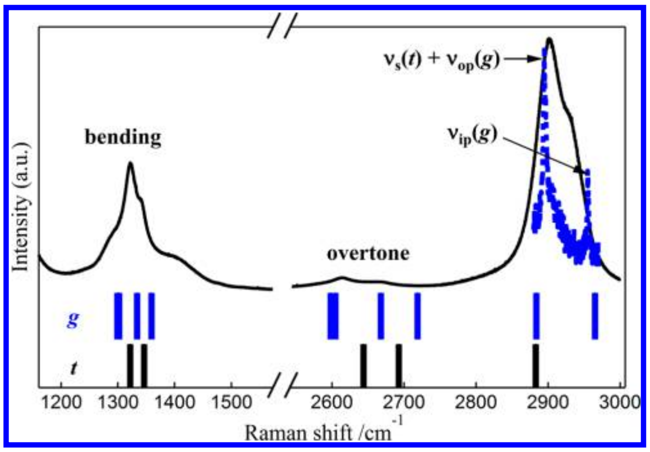


**Figure 5.** Calculated Raman spectra of *trans*-$CD_3CHDOH$ (black) and *gauche*-$CD_3CHDOH$ (blue) (vertical line). Experimental Raman spectra of liquid (solid line) and gaseous (dashed line) $CD_3CHDOH$.

*4.2.3. Raman Spectra of Crystal $CD_3CH_2OH$.* As the intermolecular interactions can influence the Fermi resonance,[28] we adjusted the molecular interactions through changing $CD_3CH_2OH$ from liquid to solid. Because the stretching vibrations of various $-CH_2$ groups couple with each other in pure crystal $CD_3CH_2OH$, we did not measure the spectrum of the pure crystal. We measured instead the parallel Raman spectrum of the crystal mixed with $CD_3CH_2OH$/$CD_3CD_2OD$ (1‰, mole fraction). In this case every $CD_3CH_2OH$ molecule is isolated by large number of $CD_3CD_2OD$ molecules, and the $-CH_2$ vibration coupling does not occur. Interestingly, there are more bands in the Raman spectrum of crystal ethanol. Two new bands appear at 2915 and 2932 $cm^{-1}$, which are consistent with the theoretical frequencies of the $-CH$ bending overtone bands of *gauche*- and *trans*-ethanol, respectively. The bands at 2869, 2880, 2896, and 2968 $cm^{-1}$ can be assigned as the $-CH_2$ symmetrical stretching vibration of the *trans*-conformer, $-C_{\alpha}H_{op}$ stretching vibration of the *gauche*-conformer, $-CH_2$ asymmetric stretching vibration of the *trans*-conformer, and $-C_{\alpha}H_{ip}$ stretching vibration of the *gauche*-conformer, respectively. Comparing the spectra of liquid and solid samples, the Fermi resonance bands disappear in the isotropic spectra of liquid $CD_3CH_2OH$. In the liquid, the first peak of the doublet results from the $-CH_2$ symmetrical stretching vibration of the *trans*-conformer and the $-C_{\alpha}H_{op}$ stretching vibration of the *gauche*-conformer, and the second peak of the doublet belongs to the $-C_{\alpha}H_{ip}$ stretching vibration of the *gauche*-conformer.

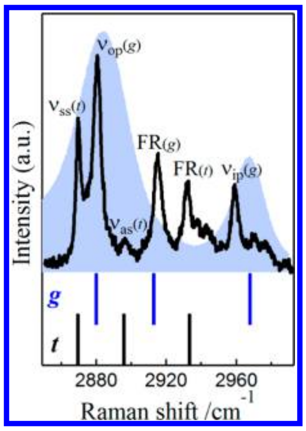


**Figure 6.** Parallel Raman spectrum in the C−H stretching region of crystal $CD_3CH_2OH$ in $CD_3CD_2OD$ at the temperature 5 K (solid line) and the isotropic Raman spectrum of liquid $CD_3CH_2OH$ (shaded curve). The theoretical Raman spectra (vertical line) of *trans*-$CD_3CH_2OH$ (black) and *gauche*-$CD_3CH_2OH$ (blue).

The spectra of $CD_3CHDOH$ and crystal $CD_3CH_2OH$ demonstrate that the band at 2970 $cm^{-1}$ does not result from the Fermi resonance of the $-CH_2$ symmetrical vibration, and it is assigned to the $-C_{\alpha}H_{ip}$ stretching vibration of *gauche*-ethanol. The doublet in the isotropic spectra of liquid $CD_3CH_2OH$ can thus be used to identify the *gauche*-conformer.

Rather than the −CH stretching modes, other vibration modes were employed to identify the ethanol conformers in the previous studies.[11,25,29−34] For example, $-CH_3$ rocking vibration of the *trans*-conformer and CC stretching vibration of the *gauche*-conformer contributed to the bands at 887 and 879 $cm^{-1}$ for ethanol in the xenon solution, respectively.[11] Furthermore, the *trans*- and *gauche*-conformers induced two separated bands in the −OH stretching region in the IR absorption spectra of ethanol in a nitrogen cryomatrix[29] and in the Raman spectra of jetted ethanol.[33] In this study, the doublet in the C−H stretching region of the isotropic Raman spectra of $CD_3CH_2OH$ offers a new spectral window to identify the ethanol conformer.

**4.3. Isotopic Raman Spectra of *n*-Propanol Conformers.** *n*-Propanol has five conformers, here they are denoted as Tt, Tg′, Gt, Gg, and Gg′. Their structures are given in Figure S1. Several spectroscopic tools have been used to identify the conformers. The rotational spectroscopy confirmed *trans*- (T) and *gauche*-*n*-propanol (G) in the vapor phase.[35] Recently, the same spectroscopy identified the Gt, Gg, and Gg′ conformers in the gaseous *n*-propanol.[36,37] The vibrational spectroscopy identified the *n*-propanol conformers in C−D stretching region,[14] O−H stretching region,[14,15,19,38−40] and fingerprint region.[40,41] For example, the $-C_\alpha D$ stretching band was used to identify the *gauche*-conformer of *n*-[1-D]propanol.[14] The bands in the −OH stretching region were employed to distinguish Tt, Tg, Gg′, and Gt conformers in diluted *n*-propanol/$CCl_4$ solution[38] and all the conformers in gaseous *n*-propanol.[39] Recently, the fingerprint region of IR absorption spectra helped to identify the T and G conformers of jetted *n*-propanol.[40] Based on these spectral studies, the populations of the conformers were obtained.[14,40,42] Through microwave spectroscopy, the population ratio of the four conformers Tt:Gt:Tg:Gg was estimated as 9:30:28:33.[42] The ratio was consistent with the theoretical value.[14] These spectroscopic studies indicate that the spectra of the conformers are different in various vibration region. However, to the best of our knowledge, there was no report about the C−H stretching vibration of the *n*-propanol conformers. Therefore, the characterization of *n*-propanol conformers in the C−H stretching region becomes interesting to us.

The theoretical isotropic Raman spectra of the five $CD_3CD_2CH_2OH$ conformers are shown in Figure 7. We divide the five conformers into two groups associated with the CO bond rotation. One group contains Tt and Gt conformers, which are named as *trans*-conformers. In this group, −OH group and both $-C_\alpha H$ groups are in the different plane. For the *trans*-conformers, both $-C_\alpha H$ bonds are almost equivalent because of the symmetrical structure. Therefore, both $-C_\alpha H$ stretching vibrations generate the $-CH_2$ symmetric and asymmetric stretching modes. Because of the absence of the asymmetric mode in isotropic spectra, only one band exists in the isotropic spectra of *trans*-conformers, as shown in Figure 7a. The $-CH_2$ symmetric stretching vibration contributes to the band at 2856 cm$^{-1}$. The other group contains Tg, Gg, and Gg′ conformers, which are named as *gauche*-conformers. In this group, one $-C_\alpha H$ group is coplanar with the −OH group, while the other $-C_\alpha H$ group is not in the plane of $C_\alpha$−O−H. For *gauche*-conformers, both $-C_\alpha H$ bonds generate two bands. The $-C_\alpha H_{op}$ and $-C_\alpha H_{ip}$ stretching vibration contributes to the bands below 2900 cm$^{-1}$ and above 2950 cm$^{-1}$, respectively, as shown in Figure 7b. Therefore, the doublet indicates *gauche*-*n*-propanol, which is the same with ethanol.

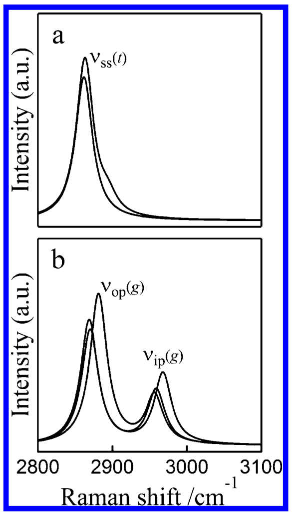


Figure 7. Calculated isotropic Raman spectra of (a) two *trans*- and (b) three *gauche*-$CD_3CD_2CH_2OH$. The same vertical scales are used.

The isotropic Raman spectrum of liquid $CD_3CD_2CH_2OH$ also presents the doublet, as shown in Figure 8a. Hence, the $-CH_2$ symmetrical stretching vibration of *trans*-propanol and the $-C_\alpha H_{op}$ stretching vibration of *gauche*-propanol are assigned to the first band at 2874 cm$^{-1}$ and the $-C_\alpha H_{ip}$ stretching vibration of *gauche*-propanol to the second band at 2955 cm$^{-1}$. Figure 8b shows the isotropic Raman spectrum of liquid $CH_3CH_2CH_2OH$. There is a shoulder peak at 2960 cm$^{-1}$, and its intensity roughly equals that of the band at 2955 cm$^{-1}$ for $CD_3CD_2CH_2OH$. Thus, the $-C_\alpha H_{ip}$ stretching vibration of *gauche*-conformers contributes to this shoulder. Traditionally, this band in the parallel Raman spectra was assigned as the $-CH_3$ asymmetric stretching vibration of liquid *n*-propanol,[43,44] but this asymmetrical stretching mode could be absent in the isotropic Raman spectra. In order to check the contribution of $-CH_3$ stretching vibration to the shoulder band at 2960 cm$^{-1}$, we measured the isotropic Raman spectrum of liquid $CH_3CD_2CD_2OH$, as shown in Figure 8c. Various $-CH_3$ symmetric vibrations contribute to all the bands. Because the band at 2969 cm$^{-1}$ is very weak in the spectrum of $CH_3CD_2CD_2OH$, the $-CH_3$ vibration contributes very little to the shoulder band at 2960 cm$^{-1}$ for $CH_3CH_2CH_2OH$. Again, the doublet represents the *gauche*-propanol in the isotropic Raman spectra of the $-C_\alpha H$ stretching vibration.

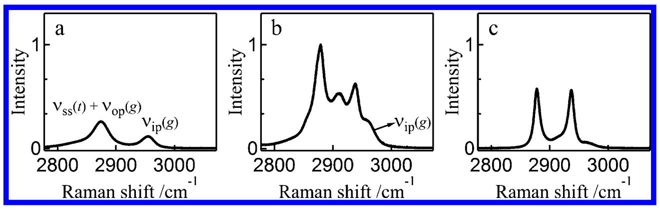


Figure 8. Experimental isotropic Raman spectra in the C−H stretching region of (a) $CD_3CD_2CH_2OH$, (b) $CH_3CH_2CH_2OH$, and (c) $CH_3CD_2CD_2OH$.

**4.4. Isotopic Raman Spectra of *n*-Butanol Conformers.** *n*-Butanol has 14 conformers, and their structures are displayed in Figure S2. The vibrational spectroscopies were used to identify these conformers in the fingerprint and the O−H stretching region. For example, the CO stretching band in IR spectra was employed to distinguish the conformers associated with $C_\gamma C_\beta$−$C_\alpha$O dihedral angle in liquid *n*-butanol.[45] The spectral region below 1600 cm$^{-1}$ of Raman and IR spectra helped to identify the TTt and TTg in the solid *n*-butanol, and all the conformers except the GG′*x* in the liquid and glassy *n*-butanol, where *x* was denoted as t, g, and g′.[46] The −OH stretching bands in FTIR spectra were applied to distinguish the conformers associated with $C_\beta C_\alpha$−OH dihedral angle in $CCl_4$ solution.[47] These studies suggested that the vibration spectra of conformers were different in various region. However, there was no report about the C−H stretching vibration of these conformers. Therefore, the identification of the conformers in the C−H stretching region becomes interesting to us.

The theoretical isotropic Raman spectra of the $CD_3CD_2CD_2CH_2OH$ conformers associated with CO rotation are displayed in Figure 9. One and two bands are observed in the isotropic spectra of *trans*- and *gauche*-conformers, respectively. Therefore, the doublet indicates the *gauche*-*n*-butanol. The $-CH_2$ symmetrical vibration contributes to the band in the spectra of *trans*-butanol. The $-C_\alpha H_{op}$ and $-C_\alpha H_{ip}$ stretching vibration of *gauche*-conformers contributes to the band below 2900 $cm^{-1}$ and above 2950 $cm^{-1}$, respectively.

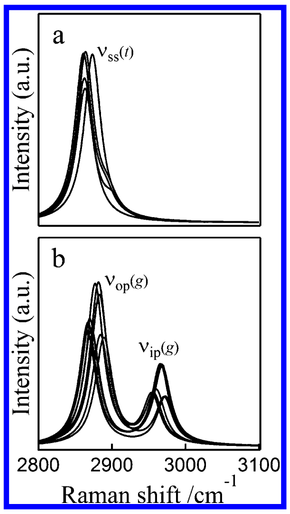


**Figure 9.** Calculated isotropic Raman spectra of (a) five *trans*- and (b) nine *gauche*-$CD_3CD_2CD_2CH_2OH$. The vertical scales are the same.

The isotropic Raman spectrum of liquid $CD_3CD_2CD_2CH_2OH$ also presents the doublet, as shown in Figure 10a. Therefore, the $-CH_2$ symmetrical stretching vibration of *trans*-butanol and the $-C_\alpha H_{op}$ stretching vibration of the *gauche*-conformer are assigned to the first band at 2876 $cm^{-1}$ and the $-C_\alpha H_{ip}$ stretching vibration of *gauche*-butanol to the second band at 2957 $cm^{-1}$. A shoulder band at 2962 $cm^{-1}$ is observed in the isotropic Raman spectrum of liquid *n*-butanol (Figure 10b); its intensity is roughly equal to that of the band at 2957 $cm^{-1}$ in the spectrum of $CD_3CD_2CD_2CH_2OH$. Thus, the shoulder band is assigned to the $-C_\alpha H_{ip}$ stretching vibration of *gauche*-butanol. However, the band above 2950 $cm^{-1}$ in the SFG spectrum was contributed from the $-CH_3$ asymmetric stretching vibration of *n*-butanol.[48] To confirm the contribution of $-CH_3$ group to the shoulder band at 2962 $cm^{-1}$, we recorded the isotropic Raman spectrum of liquid $CH_3CD_2CD_2CD_2OH$ (Figure 10c). In this spectrum, the band at 2965 $cm^{-1}$ is very weak, so the contribution of $-CH_3$ group is very little to the band at 2962 $cm^{-1}$. Again, the doublet or the band at 2957 $cm^{-1}$ represents *gauche*-*n*-butanol.

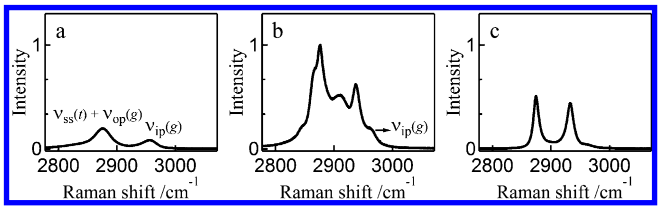


**Figure 10.** Experimental isotropic Raman spectra in the C−H stretching region of (a) $CD_3CD_2CD_2CH_2OH$, (b) $CH_3CH_2CH_2CH_2OH$, and (c) $CH_3CD_2CD_2CD_2OH$. All the vertical scales are the same.

### 4.5. Isotopic Raman Spectra of *n*-Pentanol Conformers.

*n*-Pentanol has 41 conformers, and the structures of these conformers are shown in Figure S3. The vibrational spectroscopy was employed to identify the conformers in the O−H stretching region and the skeleton stretching region. The −OH stretching band in FTIR absorption spectra was used to distinguish the *trans*- and *gauche*-conformer associated with CO rotation in the pentanol/$CCl_4$ solution.[30] The CC stretching bands in Raman spectra were applied to identify the *trans*-conformers associated with the CCCC axis.[49] Recently, the skeleton deformation and stretching bands in Raman spectra helped to identify the TTT, TTG, and TGG conformers.[50] To the best of our knowledge, the spectra of the *n*-pentanol conformers were ignored in the C−H stretching region. Therefore, here we again check the spectra of the conformers in the C−H stretching region.

Figure 11 shows the theoretical isotropic Raman spectra of $CD_3CD_2CD_2CD_2CH_2OH$ conformers associated with CO rotation. Similar to ethanol, *n*-propanol, and *n*-butanol, one band and two bands appear in the spectra of *trans*- and *gauche*-conformers, respectively. The $-CH_2$ symmetric stretching vibration contributes to the band for *trans*-*n*-pentanol. The $-C_\alpha H_{op}$ and $-C_\alpha H_{ip}$ stretching vibration contributes to the band below 2900 $cm^{-1}$ and above 2950 $cm^{-1}$ for *gauche*-*n*-pentanol, respectively. Therefore, the doublet indeed indicates the *gauche*-*n*-pentanol.

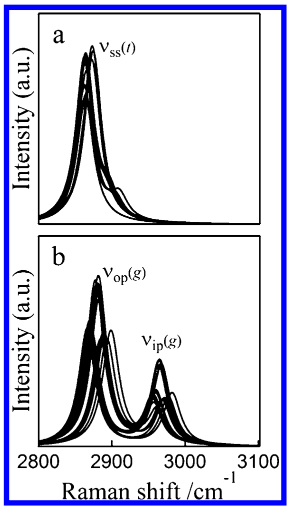


**Figure 11.** Calculated isotropic Raman spectra of (a) 14 *trans*- and (b) 27 *gauche*-$CD_3CD_2CD_2CD_2CH_2OH$ in the C−H stretching region. The vertical scales are the same.

The isotropic Raman spectrum of liquid $CD_3CD_2CD_2CD_2CH_2OH$ also presents a doublet (Figure 12a). Hence, the $-CH_2$ symmetric stretching vibration of *trans*-conformers and the $-C_\alpha H_{op}$ stretching vibration of *gauche*-conformers contribute to the first band at 2875 $cm^{-1}$ and the $-C_\alpha H_{ip}$ stretching vibration of *gauche*-conformers to the second band at 2956 $cm^{-1}$. In addition, the isotropic spectrum of *n*-pentanol also presents a shoulder band at 2961 $cm^{-1}$ (Figure 12b). As its intensity approximately equals to that of the band at 2956 $cm^{-1}$, the $-CH_{ip}$ stretching vibration of *gauche*-conformers contributes to the shoulder band. Moreover, this band in the SFG

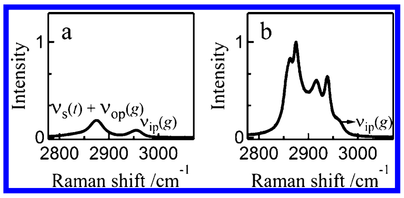


**Figure 12.** Experimental isotropic Raman spectra in the C−H stretching region of (a) $CD_3CD_2CD_2CD_2CH_2OH$ and (b) $CH_3CH_2CH_2CH_2CH_2OH$. The vertical scales are the same.

spectrum was attributed to the $-CH_3$ asymmetric stretching vibration.[51] However, the asymmetric vibration is absent in the isotropic Raman spectrum. In a word, the doublet or the band at 2956 cm$^{-1}$ represents the *gauche*-*n*-pentanol.

### 4.6. Relative Population of the *gauche*-Conformers.

All the Raman spectra present a doublet in the $C_\alpha$−H stretching region for the deuterated alcohols ($C_2$−$C_5$). The band above 2950 cm$^{-1}$ in the doublet belongs to the $-C_\alpha H_{ip}$ stretching vibrations of *gauche*-conformers. Figure 13a displays the theoretical frequencies of all these vibrations for each alcohol. In recent Raman study of alcohols in the low wavenumber region, it was found that the conformer with the plane carbon skeleton was dominant in liquid alcohols.[50] The frequencies of the $C_3$−$C_5$ alcohol conformers with this geometry are smaller than that of *gauche*-ethanol, as shown in Figure 13a. Thus, the Raman shift of the $-C_\alpha H_{ip}$ stretching band ($C_3$−$C_5$) should be smaller than that of *gauche*-ethanol, which is observed in the experimental Raman shifts of all the alcohols (Figure 13b). The consistency between experiment and theoretical calculation indicates again that the *gauche*-conformers contribute to the doublet.

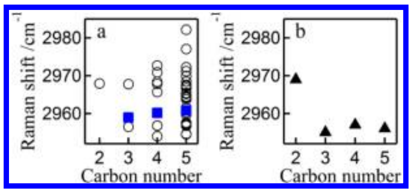


**Figure 13.** Carbon number dependent calculated frequencies of the $-C_\alpha H_{ip}$ stretching band of the *gauche*-conformers; the frequencies of the conformer with the plane carbon skeleton are indicated by blue squares (a). Carbon number dependent experimental frequencies of the $-C_\alpha H_{ip}$ stretching band of the deuterated alcohols (b).

As this doublet is contributed from two kinds of conformers, we can obtain their populations with eq 2

$$\frac{I_{2950\ \mathrm{cm}^{-1}}}{I_{2850\ \mathrm{cm}^{-1}}} = \frac{c\sigma_{\text{ip-}gauche}}{c\sigma_{\text{op-}gauche} + (1 - c)\sigma_{trans}} \tag{2}$$

where $I$ is the integral intensity from the spectral fitting with Lorentz function to the experimental Raman spectra, $c$ is the population of *gauche*-conformers, and $\sigma$ is the Raman scattering cross section. The theoretical scattering cross section ratio $\sigma_{trans}$:$\sigma_{\text{op-}gauche}$:$\sigma_{\text{ip-}gauche}$ is roughly 2:2:1 at the B3LYP/6-311+G-(d,p) and B3LYP/aug-PVQZ levels. Using this ratio, we obtain the populations of *gauche*-conformers in liquid alcohols, as shown in Table 1. Obviously, the *gauche*-conformers are dominant in all the alcohols. Moreover, the populations of *gauche*-conformers of the alcohols ($C_3$−$C_5$) are larger than that of ethanol. The 54% population of *gauche*-ethanol agrees well with that from previous molecular dynamics simulation.[26]

**Table 1. Population of *gauche*-Conformer in Alcohols Obtained through Raman Spectroscopy and Molecular Dynamics Simulation**

| | ethanol | *n*-propanol | *n*-butanol | *n*-pentanol |
|---|---|---|---|---|
| Raman | 54 | 67 | 70 | 68 |
| MD simulation | 50 | 63 | 60 | 60 |

Furthermore, we also performed the molecular dynamics simulations to calculate the populations of *gauche*-alcohols from ethanol to *n*-pentanol and are summarized in Table 1. The theoretical population is 50% in liquid ethanol, and the populations of *gauche*-conformers for other alcohols ($C_3$−$C_5$) are larger than that for ethanol. The theoretical populations agree well with the experimental ones.

## 4. CONCLUSIONS

The spontaneous Raman spectra of normal and deuterated alcohols ($C_2$−$C_5$) were recorded in the C−H stretching vibrational region. In all isotropic Raman spectra of the deuterated alcohols ($C_2$−$C_5$), a doublet of $-C_\alpha H$ stretching vibration is found for all alcohols at below 2900 cm$^{-1}$ and above 2950 cm$^{-1}$, respectively. Interestingly, the band intensity at above 2950 cm$^{-1}$ of normal alcohol is approximately equal to that of the deuterated molecule. The $-C_\alpha H$ stretching vibration is believed to contribute to the band, rather than the $-CH_3$ asymmetric stretching as previous assigned.

To identify the $-C_\alpha H$ stretching and the Fermi resonance of the $-C_\alpha H$ bending overtones, the Raman spectra of liquid/gaseous $CD_3CHDOH$ and the crystal $CD_3CH_2OH$/$CD_3CD_2OH$ have been measured. Apart from a very similar doublet around 2950 cm$^{-1}$, the Fermi resonance of the $-C_\alpha H$ bending overtones are observed in all the spectra. For $CD_3CHDOH$, the overtone bands locate in a range of 2550−2750 cm$^{-1}$, and for $CD_3CH_2OH$/$CD_3CD_2OH$, two overtone bands appear at 2915 and 2933 cm$^{-1}$. The doublet around 2950 cm$^{-1}$ is contributed from the $-C_\alpha H$ stretching.

With the aid of the calculated Raman spectra at the level of B3LYP/6-311+G(d,p), the first band at below 2900 cm$^{-1}$ of the doublet is contributed from both the $-C_\alpha H_2$ symmetrical stretching vibration of the *trans*-conformer and the $-C_\alpha H$ stretching vibration out of the $C_\alpha$−O−H plane of the *gauche*-conformer, and the second band at above 2950 cm$^{-1}$ is assigned to the $-C_\alpha H$ stretching vibration in the $C_\alpha$−O−H plane of the *gauche*-conformer. Using the spectral intensity of the doublet, the population of *gauche*-conformer is estimated to be 54%, 67%, 70%, and 68% from ethanol to *n*-pentanol, which is consistent with that from molecular dynamics simulation.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

All the conformers geometries of *n*-propanol, *n*-butanol, and *n*-pentanol; frequencies of the $-C_\alpha H_{ip}$ stretching vibration for *gauche*-alcohols. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail klin@ustc.edu.cn (K.L.).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research work was supported by the National Natural Science Foundation of China (Grants Nos. 91127042, 21103158, 21273211, and 21473171) and National key basic research special Foundation (Grant Nos. 2013CB834602 and 2010CB923300).

## REFERENCES

(1) Nevin, A.; Osticioli, I.; Anglos, D.; Burnstock, A.; Cather, S.; Castellucci, E. Raman Spectra of Proteinaceous Materials Used in Paintings: A Multivariate Analytical Approach for Classification and Identification. *Anal. Chem.* **2007**, *79*, 6143−6151.

(2) Meyer, T.; Bergner, N.; Medyukhina, A.; Dietzek, B.; Krafft, C.; Romeike, B. F. M.; Reichart, R.; Kalff, R.; Popp, J. Interpreting CARS Images of Tissue within the C—H-Stretching Region. *J. Biophotonics* **2012**, *5*, 729−733.

(3) Romero-Pastor, J.; Cardell, C.; Manzano, E.; Yebra-Rodríguez, Á.; Navas, N. Assessment of Raman Microscopy Coupled with Principal Component Analysis to Examine Egg Yolk-Pigment Interaction Based on the Protein C-H Stretching Region (3100−2800 cm$^{-1}$). *J. Raman Spectrosc.* **2011**, *42*, 2137−2142.

(4) Wang, Z.; Pakoulev, A.; Dlott, D. D. Watching Vibrational Energy Transfer in Liquids with Atomic Spatial Resolution. *Science* **2002**, *296*, 2201−2203.

(5) Iwaki, L. K.; Dlott, D. D. Ultrafast Vibrational Energy Redistribution within C-H and O-H Stretching Modes of Liquid Methanol. *Chem. Phys. Lett.* **2000**, *321*, 419−425.

(6) Perchard, J. P.; Josien, M. L. Vibrational Spectra of 12 Isotopic Species of Monomeric Ethanols. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1834−1855.

(7) Perchard, J. P.; Josien, M. L. Vibrational Spectra of 12 Isotopic Species of Auto-Associated Ethanols. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1856−1875.

(8) Yu, Y. Q.; Lin, K.; Zhou, X. G.; Wang, H.; Liu, S. L.; Ma, X. X. New C-H Stretching Vibrational Spectral Features in the Raman Spectra of Gaseous and Liquid Ethanol. *J. Phys. Chem. C* **2007**, *111*, 8971−8978.

(9) Gan, W.; Zhang, Z.; Feng, R.; Wang, H.-F. Identification of Overlapping Features in the Sum Frequency Generation Vibrational Spectra of Air/Ethanol Interface. *Chem. Phys. Lett.* **2006**, *423*, 261−265.

(10) Yu, Y. Q.; Wang, Y. X.; Lin, K.; Hu, N. Y.; Zhou, X. G.; Liu, S. L. Complete Raman Spectral Assignment of Methanol in the C-H Stretching Region. *J. Phys. Chem. A* **2013**, *117*, 4377−4384.

(11) Durig, J. R.; Deeb, H.; Darkhalil, I. D.; Klaassen, J. J.; Gounev, T. K.; Ganguly, A. The $r_0$ Structural Parameters, Conformational Stability, Barriers to Internal Rotation, and Vibrational Assignments for *trans* and *gauche* Ethanol. *J. Mol. Struct.* **2011**, *985*, 202−210.

(12) Pitsevich, G. A.; Doroshenko, I. Y.; Pogorelov, V. E.; Shablinskas, V.; Balevichus, V.; Kozlovskaya, E. N. Nonempiric Anharmonic Computations of IR Spectra of Ethanol Conformers in B3LYP/cc-pVQZ Approximation (Stretch C-H Vibrations). *Am. J. Chem.* **2012**, *2*, 218−227.

(13) Garden, A. L.; Paulot, F.; Crounse, J. D.; Maxwell-Cameron, I. J.; Wennberg, P. O.; Kjaergaard, H. G. Calculation of Conformationally Weighted Dipole Moments Useful in Ion−Molecule Collision Rate Estimates. *Chem. Phys. Lett.* **2009**, *474*, 45−50.

(14) Jarmelo, S.; Maiti, N.; Anderson, V.; Carey, P. R.; Fausto, R. C$_\alpha$-H Bond-Stretching Frequency in Alcohols as a Probe of Hydrogen-Bonding Strength: A Combined Vibrational Spectroscopic and Theoretical Study of n-[1-D] Propanol. *J. Phys. Chem. A* **2005**, *109*, 2069−2077.

(15) Wassermann, T. N.; Zielke, P.; Lee, J. J.; Cézard, C.; Suhm, M. A. Structural Preferences, Argon Nanocoating, and Dimerization of n-Alkanols as Revealed by OH Stretching Spectroscopy in Supersonic Jets. *J. Phys. Chem. A* **2007**, *111*, 7437−7448.

(16) Lin, K.; Zhou, X. G.; Luo, Y.; Liu, S. L. The Microscopic Structure of Liquid Methanol from Raman Spectroscopy. *J. Phys. Chem. B* **2010**, *114*, 3567−3573.

(17) Lin, K.; Hu, N. Y.; Zhou, X. G.; Liu, S. L.; Luo, Y. Reorientation Dynamics in Liquid Alcohols from Raman Spectroscopy. *J. Raman Spectrosc.* **2012**, *43*, 82−88.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09, revision A.1*; Gaussian, Inc.: Wallingford, CT, 2009.

(19) Lotta, T.; Murto, J.; Räsänen, M.; Aspiala, A. IR-Induced Rotamerization of 1-Propanol in Low-Temperature Matrices, and ab Initio Calculations. *Chem. Phys.* **1984**, *86*, 105−114.

(20) Hess, B.; Kutzner, C.; Van Der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *J. Chem. Theory Comput.* **2008**, *4*, 435−447.

(21) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695−1697.

(22) Parrinello, M.; Rahman, A. Polymorphic Transitions in Single Crystals: A New Molecular Dynamics Method. *J. Appl. Phys.* **1981**, *52*, 7182−7190.

(23) Yeh, I.-C.; Berkowitz, M. L. Ewald Summation for Systems with Slab Geometry. *J. Chem. Phys.* **1999**, *111*, 3155−3162.

(24) Hyde Campbell, J.; Fisher, J. F.; Jonas, J. Density and Temperature Effects on the Molecular Reorientation and Vibrational Relaxation in Liquid Methyl Iodide. *J. Chem. Phys.* **1974**, *61*, 346−360.

(25) Barnes, A. J.; Hallam, H. E. Infra-Red Cryogenic Studies. Part 5. Ethanol and Ethanol-d in Argon Matrices. *Trans. Faraday Soc.* **1970**, *66*, 1932−1940.

(26) Saiz, L.; Padro, J. A.; Guardia, E. Structure and Dynamics of Liquid Ethanol. *J. Phys. Chem. B* **1997**, *101*, 78−86.

(27) González, M. A.; Enciso, E.; Bermejo, F. J.; Bée, M. Glassy Dynamics in Supercooled-Liquid and Glassy Ethanol: A Molecular Dynamics Study. *Phys. Rev. B* **2000**, *61*, 6654−6666.

(28) Arencibia, A.; Taravillo, M.; Caceres, M.; Nunez, J.; Baonza, V. G. Pressure Tuning of the Fermi Resonance in Liquid Methanol: Implications for the Analysis of High-Pressure Vibrational Spectroscopy Experiments. *J. Chem. Phys.* **2005**, *123*, 214502.

(29) Aldiyarov, A.; Aryutkina, M.; Drobyshev, A.; Kurnosov, V. IR Spectroscopy of Ethanol in Nitrogen Cryomatrices with Different Concentration Ratios. *Low Temp. Phys.* **2011**, *37*, 524−531.

(30) Belhekar, A. A.; Agashe, M. S.; Jose, C. I. Conformational Equilibria in n-Alkanols. Infrared Spectral Deconvolution of the Unsymmetric Hydroxyl Band Profile. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1781−1784.

(31) Gardner, E. A.; Nevarez, A.; Garbalena, M.; Herndon, W. C. Infrared Spectra and Conformational Analysis of Anti and Gauche Deuterated Ethanol Isotopomers. *J. Mol. Struct.* **2006**, *784*, 249−253.

(32) Schiel, D.; Richter, W. Effect of the Internal Rotation of the OH Group on the OH Stretching Vibrational Raman Profile of Ethanol in the Gas Phase. *J. Chem. Phys.* **1983**, *78*, 6559−6562.

(33) Wassermann, T. N.; Suhm, M. A. Ethanol Monomers and Dimers Revisited: A Raman Study of Conformational Preferences and Argon Nanocoating Effects. *J. Phys. Chem. A* **2010**, *114*, 8223−8233.

(34) Coussan, S.; Bouteiller, Y.; Perchard, J. P.; Zheng, W. Q. Rotational Isomerism of Ethanol and Matrix Isolation Infrared Spectroscopy. *J. Phys. Chem. A* **1998**, *102*, 5789−5793.

(35) Abdurahmanov, A. A.; Rahimova, R. A.; Imanov, L. M. Microwave Spectrum of Normal Propyl Alcohol. *Phys. Lett.* **1970**, *32*, 123−124.

(36) Maeda, A.; De Lucia, F. C.; Herbst, E.; Pearson, J. C.; Riccobono, J.; Trosell, E.; Bohn, R. K. The Millimeter- and Submillimeter-Wave Spectrum of the *Gt* Conformer of *n*-Propanol (n-$CH_3CH_2CH_2OH$). *Astrophys. J., Suppl. Ser.* **2006**, *162*, 428−435.

(37) Kisiel, Z.; Dorosh, O.; Maeda, A.; Medvedev, I. R.; De Lucia, F. C.; Herbst, E.; Drouin, B. J.; Pearson, J. C.; Shipman, S. T. Determination of Precise Relative Energies of Conformers of *n*-

Propanol by Rotational Spectroscopy. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8329−8339.

(38) Krueger, P. J.; Mettee, H. D. Spectroscopic Studies of Alcohols: IV. Conformational Heterogeneity of 1-Propanol in Dilute $CCl_4$ Solution. *Can. J. Chem.* **1964**, *42*, 347−352.

(39) Richter, W.; Schiel, D. Raman Spectrometric Investigation of the Molecular Structure of Alcohols; Conformational Dynamics of Ethanol. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 548−552.

(40) Wassermann, T. N.; Suhm, M. A.; Roubin, P.; Coussan, S. Isomerization Around C−C and C−O Bonds in 1-Propanol: Collisional Relaxation in Supersonic Jets and Selective IR Photo-Isomerization in Cryogenic Matrices. *J. Mol. Struct.* **2012**, *1025*, 20−32.

(41) Tong, H.-J.; Yu, J.-Y.; Zhang, Y.-H.; Reid, J. P. Observation of Conformational Changes in 1-Propanol—Water Complexes by FTIR Spectroscopy. *J. Phys. Chem. A* **2010**, *114*, 6795−6802.

(42) Abdurakhmanov, A. A.; Veliyulin, E. I.; Ragimova, R. A.; Imanov, L. M. The Microwave Spectrum of *n*-Propanol. The Gauche-Gauche Conformer. *J. Struct. Chem.* **1981**, *22*, 28−33.

(43) Edwards, H. G. M.; Farwell, D. W.; Bowen, R. D. FT-Raman Spectra of *n*-Propanol and Selected Partially $^2$H-Labelled Analogues. *J. Mol. Struct.* **2007**, *832*, 184−190.

(44) Michniewicz, N.; Muszyński, A. S.; Wrzeszcz, W.; Czarnecki, M. A.; Golec, B.; Hawranek, J. P.; Mielke, Z. Vibrational Spectra of Liquid 1-Propanol. *J. Mol. Struct.* **2008**, *887*, 180−186.

(45) Crowder, G. A.; Townsend, M. J. Vibrational Spectra of 1-Butanol. *J. Mol. Struct.* **1977**, *42*, 27−30.

(46) Ohno, K.; Yoshida, H.; Watanabe, H.; Fujita, T.; Matsuura, H. Conformational Study of 1-Butanol by the Combined Use of Vibrational Spectroscopy and ab Initio Molecular Orbital Calculations. *J. Phys. Chem.* **1994**, *98*, 6924−6930.

(47) Czarnecki, M. A.; Wojtków, D.; Haufa, K. Rotational Isomerism of Butanols: Infrared, Near-Infrared and DFT Study. *Chem. Phys. Lett.* **2006**, *431*, 294−299.

(48) Lu, R.; Gan, W.; Wu, B.-h.; Zhang, Z.; Guo, Y.; Wang, H.-f C-H Stretching Vibrations of Methyl, Methylene and Methine Groups at the Vapor/Alcohol ($n$ = 1−8) Interfaces. *J. Phys. Chem. B* **2005**, *109*, 14118−14129.

(49) Baonza, V. G.; Taravillo, M.; Cazorla, A.; Casado, S.; Caceres, M. *n*-Pentanol at High Pressures: Rotational Isomerism in the Liquid Phase and the Liquid-Solid Phase Transition. *J. Chem. Phys.* **2006**, *124*, 044508.

(50) Pitsevich, G. A.; Doroshenko, I. Y.; Pogorelov, V. Y.; Kozlovskaya, E. N.; Borzda, T.; Sablinskas, V.; Balevicius, V. Long-Wave Raman Spectra of Some Normal Alcohols. *Vib. Spectrosc.* **2014**, *72*, 26−32.

(51) Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G. A.; Shen, Y.-R. Polar Ordering at the Liquid-Vapor Interface of n-Alcohols ($C_1$-$C_8$). *Chem. Phys. Lett.* **1995**, *232*, 407−413.