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Overlapping spectral features and new assignment of 2-propanol in the C–H stretching region

Yuanqin Yu,^a Yuxi Wang,^b Naiyin Hu,^b Ke Lin,^b Xiaoguo Zhou^b and Shilin Liu^{b*}



The vibrational spectra of gaseous and liquid 2-propanol in the C–H stretching region of 2800 ~ 3100 cm⁻¹ were investigated by polarized photoacoustic Raman spectroscopy and conventional Raman spectroscopy, respectively. Using two deuterated samples, that is, CH₃CDOHCH₃ and CD₃CHOHCD₃, the overlapping spectral features between the CH and CH₃ groups were identified. With the aid of depolarization ratio measurements and density functional theory calculations, a new spectral assignment was presented. In the gas phase, the band at 2884 cm⁻¹ was assigned to the overlapping of one CH₃ Fermi resonance mode and a CH stretching of gauche conformer. The bands at 2917 and 2933 cm⁻¹ were assigned to another two CH₃ Fermi resonance modes, but the latter includes weak contribution from CH stretching of trans conformer. The bands at 2950 and 2983 cm⁻¹ were assigned to CH₃ symmetric and antisymmetric stretching, respectively. The spectral features of liquid 2-propanol are similar to those in the gas phase except for the blue shift of CH and the red shift of CH₃ band positions, which can be attributed to the intermolecular interaction in the liquid state. The new assignments not only clarify the confusions in previous studies from different spectral methods but also provide the reliable groundwork on spectral application of 2-propanol in the futures. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: 2-propanol; overlapping; C–H stretching; spectral assignment; PARS

Introduction

Vibrational spectroscopy can be used as a valuable tool to detect the molecular structures and relevant dynamical process. This requires accurate correlation established between the observed bands and corresponding vibrational modes. Unfortunately, the application of vibrational spectroscopy is often hindered because of imprecise spectral assignments. Here, we report the overlapping spectral features of 2-propanol in the C–H stretching region, which were never identified in the previous studies from the spectral methods such as infrared (IR), liquid Raman, and sum frequency generation (SFG) spectroscopy. The present work is a continuation of our recent series that aims to give an explicit assignment on vibrational spectrum of alcohol molecules in the C–H stretching region and to provide reliable spectral basis in the other applications.^[1–3]

The C–H functional groups such as –CH, –CH₂, and –CH₃ exist widely in organic and biological molecules, and the vibration spectroscopy in the C–H stretching region of 2800 ~ 3100 cm⁻¹ is one of the extensively employed finger regions for analyzing various dynamical processes or imaging in biology and medicine studies.^[4–9] This benefits from the two main factors that the C–H stretching vibration is highly localized with no insignificant mixing of other vibrational modes and exhibits the large intensity both in IR and Raman measurements. Thus, the C–H stretching spectrum is relatively easy to be obtained and applied subsequently. However, from a spectroscopic view, clear understanding and explicit assignment in this region are quite difficult because of the congestion of various C–H vibrational modes, including the symmetric stretching, antisymmetric stretching, combination modes, and Fermi resonances. The latter is especially complex because it is sensitive to conformational and environmental factors.

Among all molecules containing C–H groups, alcohols are an important class of compounds widely used as solvents and as theoretical and experimental model systems to investigate intermolecular interaction, hydrogen bond effect, energy transfer mechanism, chemical reaction pathway, vapor/liquid interfacial properties, and so on.^[10–17] As we have reported recently, some assignments for the C–H stretching vibrational spectra are ambiguous or incorrect even for some simple molecules such as methanol and ethanol,^[1,2] and the incorrect spectral assignments have been applied to interpret many important dynamical processes.^[4,17–20] Compared with methanol and ethanol, the vibrational spectrum of 2-propanol is more complex because of the increased C–H groups. Although the extensive studies have been conducted to investigate the vibrational spectra of 2-propanol in the C–H stretching region, its assignment is still controversial at the present time. In 1963, Green performed a detailed assignment for the fundamental frequencies of 2-propanol in the range of 200 ~ 4000 cm⁻¹ by IR and liquid Raman techniques.^[21] Because the Fermi resonance interaction that commonly exists in the C–H stretching region of 2800 ~ 3100 cm⁻¹ was not

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considered, their assignment was not complete. In 2005, Wang *et al.* investigated the C–H stretching vibrational spectrum of 2-propanol at air/liquid interface by SFG spectroscopy and assigned it with the inclusion of Fermi resonance.^[22,23] Their assignment was adopted subsequently and applied to probing molecular structure at liquid/vapor interface in water/2-propanol binary mixtures by Kataoka *et al.*^[17] On the basis of spectral changes of the assigned CH₃ stretching bands at 2880 and 2974 cm^{−1}, Kataoka *et al.* observed that the methyl groups of 2-propanol lay down on the surface at low alcohol mole fraction and gradually twisted with increasing mole fraction. Obviously, their new founding was dependent on the spectral assignment of 2-propanol in the C–H stretching region.

Recently, Dobrowolski *et al.* interpreted the vibrational spectrum of 2-propanol in the C–H stretching region by an Ar-matrix IR technique.^[24] However, we notice that their IR assignment is in disagreement with that from SFG method at the air/2-propanol interface. For example, the same peak at 2880 cm^{−1} was assigned to the CH stretching vibration in matrix, whereas it was attributed to CH₃ stretching at the interface. The inconsistent assignment has brought the confusion on understanding the structure changes of 2-propanol at the interface in binary mixtures.^[17] Therefore, it is necessary to reexamine the vibrational spectrum of 2-propanol to provide a reliable assignment in the other applications. In this report, we measured the gas-phase Raman spectrum of 2-propanol in the C–H stretching region using a nonlinear spectral technique, called as polarized photoacoustic Raman spectroscopy (PARS), which is a combination of sensitive photoacoustic spectroscopy and stimulated Raman scattering. Compared with IR and liquid Raman as well as SFG spectra, the gas-phase Raman spectrum exhibits narrower and more separated peak shape and thus has its advantage in distinguishing the congested C–H stretching bands. This is due to the facts that Raman selection rule is different from that of IR, and gas-phase molecules are free of intermolecular interaction such as hydrogen bonding in the liquid state or interface. To the best of our knowledge, there are few reports on gas-phase Raman spectrum of 2-propanol, probably because of experimental difficulty in detecting the weak Raman photos in the gas phase, especially for the liquid sample with low saturation vapor pressure, such as 2-propanol. The PARS method used here has very high sensitivity and is particularly suitable to measure the gas-phase Raman spectrum of liquid sample.

With the help of isotope substitute and depolarization ratio measurements as well as density functional theory (DFT) calculation, we present the new assignments on the vibrational spectrum of gaseous 2-propanol in the C–H stretching region. Moreover, we recorded the Raman spectrum of liquid 2-propanol in the same region by a conventional spontaneous Raman method in order to provide more information about the impact of intermolecular interaction on the vibrational spectra, such as hydrogen bonding interaction.

Experimental and computational details

Normal 2-propanol (CH₃CHOHCH₃) is obtained from Sigma-Aldrich (>99.8%, GC grade), and isotope substituted 2-propanol, CD₃CHOHCD₃ (>98%) and CH₃CDOHCH₃ (>98%), are purchased from ICON isotopes. These samples are used without further purifications.

Polarized PARS

The basic theory and experimental setup of PARS has been fully described in previous papers.^[1–3,25,26] Here, only a short review is included in order to be complete. When the frequency difference between two temporally and spatially overlapped laser beams (one called pump beam and the other called Stokes beam) is resonant with a Raman-active vibrational transition, a stimulated Raman scattering process occurs, and a faction of ground-state molecules are transferred to the vibrationally excited state. These excited-state molecules are relaxed subsequently to ground state by collisions between the molecules. This will generate the local heat in the focused area of two laser beams and generate an excess pressure wave, which is detected by a microphone as the photoacoustic signal. The sensitivity of PARS is greatly increased in the contrast to direct measurement of weak Raman scattering photons. On the other hand, using polarized PARS, the Raman depolarization ratio can be accurately determined according to our developed I–θ curve method^[3] because the PARS intensity *I* is periodically dependent on the cross angle *θ* between the polarization directions of two laser beams. Although the intensity ratios of *θ* = 90° and *θ* = 0° is also the depolarization ratio, where *θ* = 90° and *θ* = 0° mean that the polarization directions of two laser beams are orthogonal and parallel to each other, the depolarization ratio in the present study is obtained by I–θ curve because of higher accuracy.

In PARS experiment, a 10 Hz and 10 ns second-harmonic output (532.1 nm) from pulsed Nd:YAG laser (line width, 1 cm^{−1}) is split into two beams by a common quartz wedge. One beam is used as a pump beam, and the other is entered into a dye laser system (Continuum, ND6000, 0.15 cm^{−1}) for generating a tunable Stokes beam (623–638 nm). The two beams are linearly polarized by two Glan–Taylor prisms and then focused in the center of the photoacoustic cell with a counterpropagating configuration. The generated photoacoustic signal is monitored by an oscilloscope to obtain the PARS intensity or averaged by a boxcar integrator to obtain the PARS spectrum. The energies of pump and Stokes beams are typically 10 and 6 mJ/pulse, respectively, and the sample pressure is kept at 5 Torr. The obtained PARS spectrum is normalized to the intensity of Stokes beam, and the wavelengths of both beams are calibrated by a laser wavelength meter with an accuracy of 0.005 nm. To obtain the accurate depolarization ratio with I–θ curve method, the polarization of the Stokes beam is fixed in the vertical direction, whereas those of pump beam is rotated by a λ/2 wave plate. The precision of depolarization ratio measurement with this experimental system is within the accuracy of 0.005 and checked by the *ν*₁ (2917 cm^{−1}) and *ν*₃ (3020 cm^{−1}) vibrational modes of methane. All measurements are carried out at room temperature and the same experimental conditions.

Liquid Raman spectroscopy

The Raman spectrum of liquid 2-propanol is recorded by a conventional spontaneous Raman experiment. The instrument and setup parameters are similar to those reported previously.^[27,28]

DFT calculations

All theoretical calculations are carried out at B3LYP/6-311++G(d,p) level by DFT method with GAUSSIAN09 software,^[29] including the optimized geometry, vibrational frequency, and total energy. The

potential energy distribution is also performed to obtain the detailed interpretation of the fundamental modes using the GAR2PED program written by Martin and Alsenoy.^[30] In order to better help the analysis of the experimental spectra, all of the calculated frequencies presented in the text and figure as well as in Table S1–S3 are scaled down by a factor of 0.973.^[31]

Results and discussions

Raman spectra of gaseous 2-propanol in the C–H stretching region

The polarized and depolarized Raman spectra of gaseous $\text{CH}_3\text{CHOHCH}_3$, $\text{CD}_3\text{CHOHCD}_3$, and $\text{CH}_3\text{CDOHCH}_3$ in the C–H stretching region from 2800 to 3100 cm^{-1} are recorded with PARS at both parallel ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$) polarization configurations, respectively, as presented in Fig. 1. It can be seen that there is a drastic change of Raman intensity under two polarization configurations. Because all the spectra are recorded under the same experimental conditions, including the laser power, sample gas pressure, and so on, the information on spectral contribution from different C–H groups can be directly obtained by comprising the intensities of normal and deuterated 2-propanol.

As shown in Fig. 1(a), the Raman spectrum of $\text{CH}_3\text{CHOHCH}_3$ shows several intense bands in the C–H stretching region. Obviously, for the first band at 2884 cm^{-1} , it contains contributions from CH_3 and CH groups because both of them exhibit important spectral intensities in the corresponding spectra of $\text{CH}_3\text{CDOHCH}_3$ and $\text{CD}_3\text{CHOHCD}_3$, respectively, as seen from Fig. 1(b) and (c). As a

result, the intensity of this band is much stronger than those in $\text{CD}_3\text{CHOHCD}_3$ and $\text{CH}_3\text{CDOHCH}_3$, and its band shape is also different from that in single deuterated species. Similarly, for the third band at 2933 cm^{-1} , it also contains the contributions of both CH_3 and CH groups although the CH band at 2934 cm^{-1} in $\text{CD}_3\text{CHOHCD}_3$ is much weaker than the CH_3 band at 2930 cm^{-1} in $\text{CH}_3\text{CDOHCH}_3$. These results show that the vibrational spectra from CH and CH_3 groups of gaseous 2-propanol overlap each other at two positions of 2884 and 2933 cm^{-1} . As mentioned earlier, in the previous studies on 2-propanol at air/liquid interface by SFG spectroscopy,^[17,22,23] the band at 2884 cm^{-1} was entirely attributed to CH_3 group, whereas the band at 2933 cm^{-1} was attributed to CH group. On the contrary, in the Ar-matrix IR study, the bands at 2884 cm^{-1} was attributed to CH group, whereas the band at 2933 cm^{-1} was attributed to CH_3 group.^[24] Here, our results clearly show that those two kinds of assignments are not complete.

From the spectrum of $\text{CH}_3\text{CHOHCH}_3$, it can also be seen that the second band at 2917 cm^{-1} , the fourth band at 2950 cm^{-1} , and the fifth broad band centered at 2983 cm^{-1} are contributed by CH_3 group because their spectral features are very similar to those in $\text{CH}_3\text{CDOHCH}_3$. However, an obvious shift of the band maximum to higher wavenumber can be observed from the spectra of $\text{CH}_3\text{CDOHCH}_3$ to $\text{CH}_3\text{CHOHCH}_3$. For instance, the band at 2899 cm^{-1} in $\text{CH}_3\text{CDOHCH}_3$ is shifted to 2917 cm^{-1} in $\text{CH}_3\text{CHOHCH}_3$ with a shift of 18 cm^{-1} , and the feature at 2967 cm^{-1} in $\text{CH}_3\text{CDOHCH}_3$ was shifted to 2972 cm^{-1} in $\text{CH}_3\text{CHOHCH}_3$ with a shift of 5 cm^{-1} . This indicates that the vibrations of CH and CH_3 groups are not entirely isolated within 2-propanol molecule but interfere with each other, which result in some subtle changes on the band positions, intensities, and other spectral features between the normal and deuterated species. However, the changes on these spectral details are not easy to be observed in the spectra of liquid state or air/liquid interface because of the band broadening, which is brought by the intermolecular interaction in the liquid or interface such as hydrogen bond. Because of no observation on these spectral details, the overlapped spectral features at air/2-propanol interface were not identified using SFG method, although an experiment on isotope substitution was also performed.^[17] These results indicate that gas-phase Raman spectroscopy has its advantage in resolving the complex vibrational spectra of complex molecules, which benefits from the fact that it exhibits more separated and narrower peak shape. As a result, more spectral details can be detected.

It is known that the depolarization ratio can be used as an important means to help the assignment of the observed Raman spectra. We determined the depolarization ratios of all the bands in $\text{CH}_3\text{CHOHCH}_3$, $\text{CD}_3\text{CHOHCD}_3$, and $\text{CH}_3\text{CDOHCH}_3$ according to the method of I– θ curve, as summarized in Table 1. It can be seen that the depolarization ratios are very small and even close to zero for all bands except for the two broad ones centered at 2981 cm^{-1} in $\text{CH}_3\text{CDOHCH}_3$ and 2983 cm^{-1} in $\text{CH}_3\text{CHOHCH}_3$, indicating that most bands belong to symmetric modes.

Calculated results

The geometric structures along with Raman spectra of normal 2-propanol and two deuterated species are calculated at B3LYP/6-311++G(d,p) level. As shown in Fig. 2, the 2-propanol has two stable conformers in the gas phase. In the trans conformer of C_s symmetry, the H-atom of the HOCH moiety are strictly in the trans orientation with a H–O–C–H dihedral angle of 180°, whereas in the gauche one of C_1 symmetry,

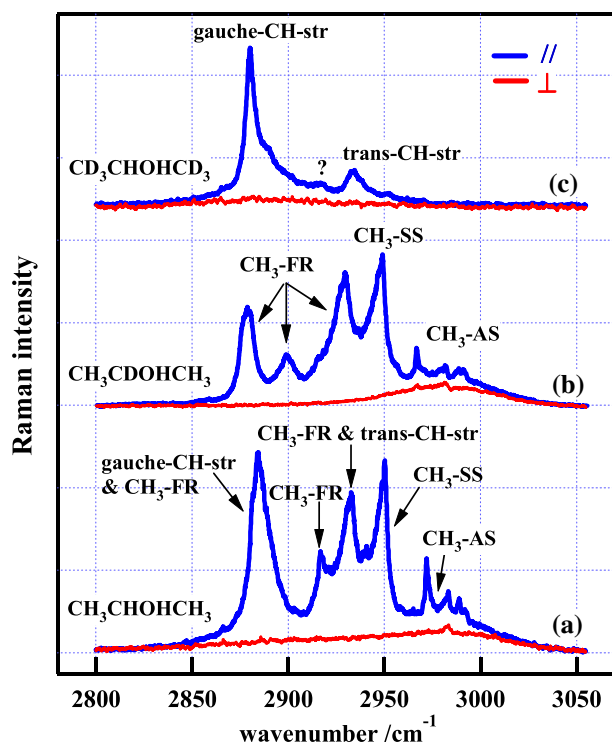
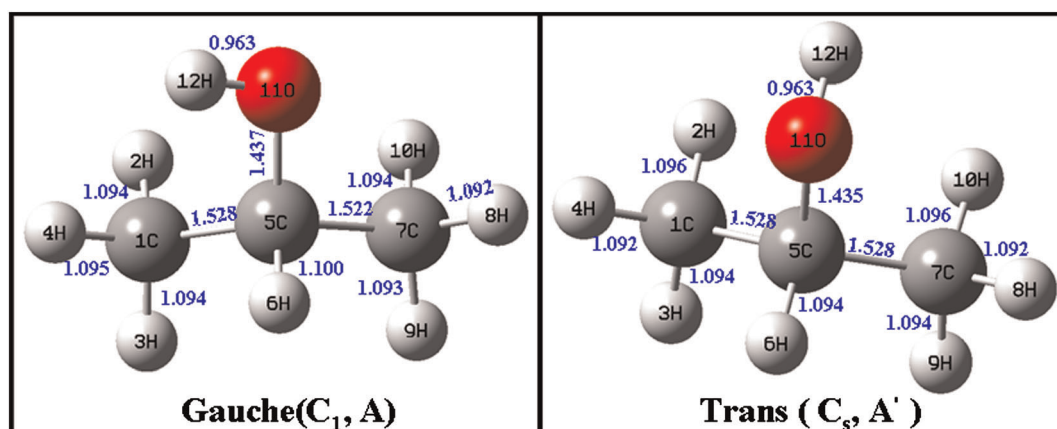


Figure 1. The polarized and depolarized Raman spectra of gaseous $\text{CD}_3\text{CHOHCD}_3$, $\text{CH}_3\text{CDOHCH}_3$, and $\text{CH}_3\text{CHOHCH}_3$ in the C–H stretching region under parallel (blue line, upper) and perpendicular (red line, lower) laser polarization configurations, respectively. CH-str: CH stretching; CH_3 -SS: CH_3 symmetric stretching; CH_3 -AS: CH_3 antisymmetric stretching, CH_3 -FR: CH_3 Fermi resonance. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

Table 1. Observed Raman frequencies (cm^{-1}) and depolarization ratios of 2-propanol in the gaseous and liquid phases, as well as their spectral assignments in the C–H stretching region

Molecule	Raman frequency/ cm^{-1}				Spectral assignment		
	ν^{gas}	ν^{liquid}	Δ^{a}	ρ^{gasb}	This work	Work of Lu <i>et al.</i> ^[22] and Wang <i>et al.</i> ^[23]	Work of Dobrowolski <i>et al.</i> ^[24]
$\text{CD}_3\text{CHOHCD}_3$	2880	2887	7	0.071	CH-str-gauche		
	2934	2940	6	0.110	CH-str-trans		
$\text{CH}_3\text{CDOHCH}_3$	2879	2869	–10	0.018	CH_3 -FR		
	2899	2891	–8	0.042	CH_3 -FR		
	2930	2920	–10	0.045	CH_3 -FR		
	2949	2936	–13	0.106	CH_3 -SS		
	2981	2972	–9	0.580	CH_3 -AS		
	(2963 ~ 2998)						
$\text{CH}_3\text{CHOHCH}_3$	2884	2879	–5	0.038	CH_3 -FR and CH-str-gauche	CH_3 -SS	CH-str
	2917	2911	–6	0.155	CH_3 -FR		CH_3 -FR and CH_3 -SS
	2933	2920	–13	0.075	CH_3 -FR and CH-str-trans	CH-str	CH_3 -FR and CH_3 -AS
	2950	2938	–12	0.077	CH_3 -SS	CH_3 -FR	CH_3 -SS
	2983	2973	–10	0.475	CH_3 -AS	CH_3 -AS	CH_3 -AS
	(2966 ~ 3000)						

^aThe difference of ν^{liquid} and ν^{gas} . ^bThe precision is ± 0.005 .

**Figure 2.** Geometry structures and labeling of atoms of 2-propanol in the two conformers. The plane in 2-propanol refers to 4H-1C-5C-7C-8H.

the H-atom adopts staggered configurations with a H–O–C–H dihedral angle of $+64^\circ$ or -64° (the gauche conformer has two spectrally undistinguished enantiomers). At the present theoretical level, the gauche conformer is more stable than the trans by an energy difference of 0.19 kcal/mol (the energy value is zero point corrected), which is more consistent with that of 0.18 kcal/mol from focal point calculations but larger than that of 0.02 kcal/mol from CCSD(T)/cc-pVTZ.^[24,32]

The calculated Raman spectra are presented in Fig. 3, where only the spectrum of normal 2-propanol in the selected regions of C–H bending and stretching are displayed. The details on the frequencies, Raman activity, and modes descriptions of normal and deuterated 2-propanol are listed in Table S1–S3. From Fig. 3, it is evident that there is a large frequency difference for CH group between gauche and trans 2-propanol, as marked with the character '■'. However, for CH_3 group, the frequency differences between two conformers are not changed significantly, although the corresponding vibrational modes have some variations according to the potential energy distribution analysis listed in Table S1–S3. On the other hand, it can be seen that the

overtone and combinations of CH_3 bending are very close to the CH_3 symmetric stretching fundamental. Therefore, the Fermi resonance interaction may be expected between them.

Spectral assignments of gaseous 2-propanol

Combined with isotope substitutions, theoretical calculations and depolarization ratio measurements, the explicit spectral assignments of gaseous 2-propanol, are presented in the C–H stretching region, as labeled in Fig. 1.

$\text{CD}_3\text{CHOHCD}_3$

In Fig. 1(c), two bands separated by 54 cm^{-1} can be found. According to the theoretical calculations (Table S2), the CH stretching mode of $\text{CD}_3\text{CHOHCD}_3$ is 2890 cm^{-1} for gauche conformer and 2968 cm^{-1} for trans one with a frequency difference of 78 cm^{-1} . We attribute the observed intense band at 2880 cm^{-1} to CH stretching of gauche $\text{CD}_3\text{CHOHCD}_3$ (gauche-CH-str) and the weak one at 2934 cm^{-1} to that of trans (trans-CH-str), as labeled

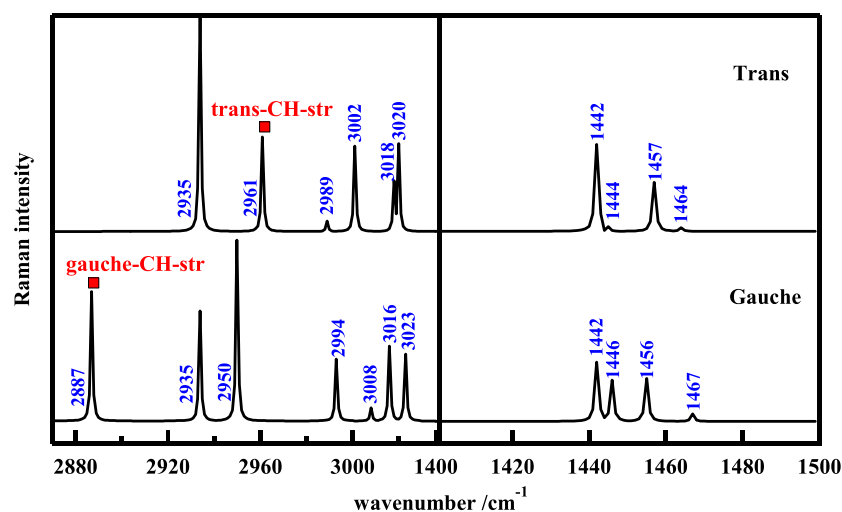


Figure 3. The calculated Raman spectra of normal 2-propanol in the C–H stretching and bending regions for trans and gauche conformers. The peaks marked with the character '■' are from CH group, and all of the other peaks are from CH₃ group.

in Fig. 1(c). According to the aforementioned assignments, one can see that, compared with the gauche CH stretching mode, the observed intensity of trans CH stretching mode at 2934 cm^{-1} (Fig. 1(c)) is much weaker than the calculated one at 2968 cm^{-1} (Table S2). This arises from two reasons. One is that the gauche conformer has a double multiplicity relative to the trans, and the other is that the energy of the gauche is lower than the trans by 0.19 kcal/mol calculated at B3LYP/6-311++G(d,p) level, leading to a larger abundance of the gauche. The CH stretching is generally located at about 2900 cm^{-1} according to earlier low-temperature Raman experiments on long-chain hydrocarbons containing CHD and CHD₂ groups.^[33] A recent SFG study on L-leucine at the air/water interface also presented a slight feature at 2902 cm^{-1} on the ssp spectra for the CH group.^[34] Here, the shift of CH stretching from 2900 to 2880 and 2934 cm^{-1} can be explained by the fact that the CH group is directly connected to the OH group in CD₃CHOHCD₃ with two different configurations. It can be seen that the CH band position may be slightly different in different molecules, we hope that our assignment on CD₃CHOHCD₃ molecule can shed some light on the vibrational spectra of other molecules containing CH group, especially 20 natural amino acids, which all have CH groups except for glycine.

From Fig. 1(c), it can be seen that the Raman spectrum of gaseous CD₃CHOHCD₃ is dominated by gauche 2-propanol. To further confirm this, we also record the Raman spectra of CH₃CHOHCH₃, CD₃CHOHCD₃, and CH₃CDOHCH₃ in the OH stretching region, as shown in Fig. 4, where two bands separated by about 21 cm^{-1} can be observed. Comparing Fig. 1(c) with Fig. 4, one can see that the intensity distributions of CH and OH stretching spectra are quite similar, one intense and one weak. According to the calculations, the intense band at 3658 cm^{-1} belongs to gauche conformer, whereas the weak one at 3637 cm^{-1} is trans. Thus, both CH and OH stretching spectra indicate that the gauche conformer is dominant in the Raman spectra of 2-propanol. This conclusion will further simplify the assignment for Raman spectra of deuterated CH₃CDOHCH₃ molecule in the following.

It should be mentioned that there is a small hidden peak at about 2917 cm^{-1} unassigned in the spectrum of gaseous CD₃CHOHCD₃, as shown in Fig. 1(c). This peak becomes more obvious in Raman spectra of liquid CD₃CHOHCD₃ (Fig. 5), and

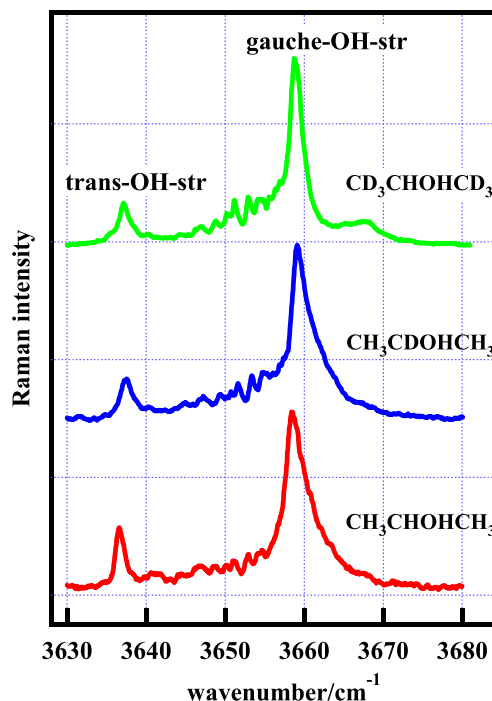


Figure 4. The Raman spectra of gaseous CD₃CHOHCD₃, CH₃CDOHCH₃, and CH₃CHOHCH₃ in the OH stretching region. OH-str: OH stretching.

thus it should not be from the impurity of the sample. Because the calculated CH and OH bending vibrations are 1329 and 1370 cm^{-1} in gaseous CD₃CHOHCD₃, the peak at 2917 cm^{-1} has no possibility from the CH and OH bending overtones or combinations. A possible explanation is that it is a plus of the CH bending overtone and low-frequency CD₃ torsion vibration (calculated at $1370 \times 2 + 186 = 2926\text{ cm}^{-1}$).

CH₃CDOHCH₃

As analyzed earlier, the vibrational spectra of 2-propanol is dominated by gauche conformer. On the other hand, the

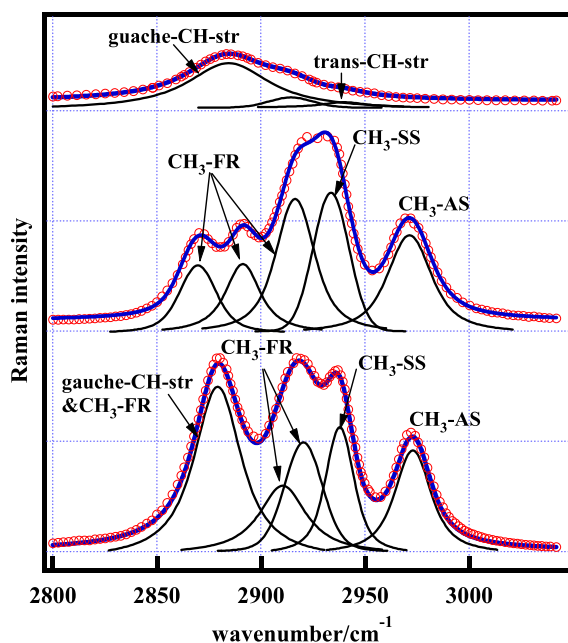


Figure 5. Raman spectra of liquid $\text{CD}_3\text{CHOHCD}_3$, $\text{CH}_3\text{CDOHCH}_3$, and $\text{CH}_3\text{CHOHCH}_3$ in the C–H stretching region (resolution 1 cm^{-1}). The solid lines are fittings with the Voigt profile.

calculations on $\text{CH}_3\text{CDOHCH}_3$ indicate that unlike the CH group the differences of CH_3 vibrational frequencies between gauche and trans conformers in the C–H stretching region are not significant and most are within $1\sim 6\text{ cm}^{-1}$ (Table S3). This value is much smaller than the intervals of $19\sim 32\text{ cm}^{-1}$ between observed peaks in the Raman spectrum of $\text{CH}_3\text{CDOHCH}_3$, as illustrated in Fig. 1(b) and Table 1. Therefore, we do not distinguish the contributions of two conformers during the spectral assignment for $\text{CH}_3\text{CDOHCH}_3$ molecule and take the more stable gauche conformer as example. The results show that this simplification is reasonable.

In Fig. 1 (b), the polarized Raman spectrum of $\text{CH}_3\text{CDOHCH}_3$ exhibits five bands at 2879, 2899, 2930, 2949, and 2981 cm^{-1} . The depolarization ratio measurements show that the first four bands belong to symmetric modes because their depolarization ratios are very small compared with 0.75. According to the theoretical calculations on gauche $\text{CH}_3\text{CDOHCH}_3$, there are two CH_3 symmetric stretching ($\text{CH}_3\text{-SS}$) modes at 2935 and 2950 cm^{-1} and four bending modes at 1440, 1446, 1454, and 1465 cm^{-1} , respectively. So we assign the fourth band at 2949 cm^{-1} to $\text{CH}_3\text{-SS}$, whereas we assign the first two bands at 2879 and 2899 cm^{-1} to overtones or combinations of CH_3 bending modes, which are enhanced by Fermi resonance interaction with $\text{CH}_3\text{-SS}$ because of the same symmetries and close frequencies, as labeled in Fig. 1(b). For the third band at 2930 cm^{-1} , we assign it to the overtone of CH_3 bending mode calculated at 1465 cm^{-1} ($1465\times 2=2930\text{ cm}^{-1}$), although it may also be from another $\text{CH}_3\text{-SS}$ calculated at 2935 cm^{-1} . This is because the Fermi resonance mode is often sensitive to the environmental factor, and we have observed that the third band at 2930 cm^{-1} becomes weak gradually in $\text{CH}_3\text{CDOHCH}_3$ -water binary mixtures with the increasing of the mole concentration of water (the data will be reported elsewhere). From the aforementioned assigned spectrum, it is clear that only relatively few overtones or combinations are involved in Fermi resonance, although several kinds of overtones or combinations can meet the Fermi resonance condition for gauche $\text{CH}_3\text{CDOHCH}_3$ of C_1 symmetry. Following the conventional labels, those overtones or combination of

CH_3 bending modes from Fermi resonance are denoted as $\text{CH}_3\text{-FR}$. With such multiple Fermi resonance coupling, the vibrational spectrum of $\text{CH}_3\text{CDOHCH}_3$ in the C–H stretching region presents the more complex spectral features than assigned previously.

In Fig. 1(b), there is still a broad band centered at 2981 cm^{-1} ($2963\sim 2998$) unassigned. One can see that this band is mainly depolarized, but some polarized peaks lie above it. It is known that the CH_3 group has two splitting antisymmetric stretching when its local symmetry no longer belongs to C_{3v} point group. One is the out-of-plane vibration with depolarized property, and the other is in-plane vibration with polarized property. Despite the symmetric properties of two splitting CH_3 vibrational modes are opposite their frequencies should be close degeneracy in the molecular systems such as 2-propanol studied here according to our recent results for methanol and ethanol.^[1,2] Thus, we see a picture that some polarized peaks at 2967, 2981, and 2988 cm^{-1} are superposed on the depolarized broad band centered at 2981 cm^{-1} , as shown in Fig. 1(b). Those polarized components correspond to in-plane CH_3 antisymmetric stretching ($\text{CH}_3\text{-AS}$) of $\text{CH}_3\text{CDOHCH}_3$, whereas the depolarized components correspond to out-of-plane one. In other words, the whole band at 2981 cm^{-1} belongs to $\text{CH}_3\text{-AS}$, which includes both out-of-plane and in-plane vibrations. This assignment is also consistent with the measured depolarization ratio of 0.58 and theoretical predictions.

The broad features of $\text{CH}_3\text{-AS}$ can be explained by the fact that the depolarized band consists of $\Delta J=0, \pm 1, \pm 2$ rotational transitions, whereas the polarized one mainly from $\Delta J=0$ transitions in the gaseous Raman measurement. In the following liquid Raman spectra (Fig. 5), the band at 2981 cm^{-1} becomes significantly narrower and stronger because the molecular rotations are quenched in the liquid state. Because of the same reason, those polarized peaks at 2967, 2981, and 2988 cm^{-1} , which can be regarded as rotational fine structures of in-plane $\text{CH}_3\text{-AS}$, are also quenched in corresponding liquid Raman spectra.

$\text{CH}_3\text{CHOHCH}_3$

With the spectra of both $\text{CD}_3\text{CHOHCD}_3$ and $\text{CH}_3\text{CDOHCH}_3$ assigned, it becomes easy to resolve that of $\text{CH}_3\text{CHOHCH}_3$. In detail, the band at 2884 cm^{-1} is attributed to the overlapping between one CH_3 Fermi resonance mode and a CH stretching of gauche 2-propanol. The bands at 2917 and 2933 cm^{-1} are assigned to another two CH_3 Fermi resonance modes, but the latter contains a weak contribution from the CH stretching vibration of trans 2-propanol. The band at 2950 and 2983 cm^{-1} are assigned to CH_3 symmetric and antisymmetric stretching modes. On the basis of the aforementioned assignments, some inconsistency on spectral assignments of 2-propanol in the C–H stretching region can be settled. The overlapped features identified in the present assignments will provide reliable spectral groundwork for the understanding of dynamical process of 2-propanol in the future and shed light on other molecules containing C–H groups, especially large biological molecules.

Raman spectra of liquid 2-propanol in the C–H stretching region

The Raman spectra of liquid normal and deuterated 2-propanol in the C–H stretching region of $2800\sim 3100\text{ cm}^{-1}$ are illustrated in Fig. 5. According to the spectral assignments in the gas phase, the individual peak positions are fitted using Voigt profile.^[35,36] It can be seen

that the spectral features in the liquid phase are very similar to those in the gas phase except for the band broadening and the changes of band positions and relative intensities. For example, the liquid $\text{CH}_3\text{CHOHCH}_3$ shows five bands located at 2879, 2911, 2920, 2938, and 2973 cm^{-1} , which correspond to those in the gas phase around 2884, 2917, 2933, 2950, and 2983 cm^{-1} , with red shift of 5, 6, 13, 12, and 10 cm^{-1} , respectively. Therefore, the gas-phase Raman spectral assignments can be directly transferable to liquid 2-propanol, although there are some changes on the band widths and positions as well as their relative intensities. The changes on relative intensities of CH_3 vibrational modes may be related to the effect of Fermi resonance because the Fermi resonance is very sensitive conformational and environmental factors.

Carefully comparing the gas-phase and liquid-phase Raman spectra between normal and deuterated species, one can find that the behaviors of band broadening and shifting are very different for CH_3 and CH groups in liquid 2-propanol. Obviously, the broadening of CH vibrations in liquid $\text{CD}_3\text{CHOHCD}_3$ is much larger than those of CH_3 vibrations in liquid $\text{CH}_3\text{CDOHCH}_3$. On the other hand, the band positions of CH and CH_3 groups are shifted to the opposite directions from the gas to liquid phases, blue shifting for CH and red shifting for CH_3 , as summarized in Table 1. For instance, the CH stretching is blue shifted by 7 cm^{-1} in $\text{CD}_3\text{CHOHCD}_3$, whereas the CH_3 symmetric stretching is red shifted by 13 cm^{-1} in $\text{CH}_3\text{CDOHCH}_3$. In addition, the intensity of CH stretching in liquid $\text{CD}_3\text{CHOHCD}_3$ is distinctly decreased compared with the gas phase. These spectral changes can be related to the intermolecular interactions in liquid 2-propanol such as hydrogen bonding. In previous studies on gaseous and liquid straight-chain 1-alcohol,^[1,2] only red shifts are observed for CH_2 and CH_3 groups from the gas to liquid phases, the branched-chain 2-propanol exhibits the blue and red shifts simultaneously. Further theoretical and experimental works are needed to explain these differences.

Conclusion

In this paper, the vibrational spectra of gaseous and liquid 2-propanol in the C–H stretching region are investigated with two different Raman spectroscopy and explicitly assigned with the aid of isotope substitution and depolarization ratio measurement as well as DFT calculations. The results show that the spectra from CH and CH_3 groups of 2-propanol molecule overlapped each other in the C–H stretching region. The new assignments not only clarify the confusions in the recent spectral studies from Ar-matrix IR technique and SFG spectroscopy but also provide the reliable groundwork for the spectra application of 2-propanol in the futures. Also, we hope that the assignments in this study can shed light on other molecules containing C–H groups, especially the large biological molecules.

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