The $\Delta\nu = 3$, 4, and 5 Vibrational Overtones and Conformations of the Hydroxyl Group of Isobutyl Alcohol

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Received: January 19, 2001; In Final Form: April 26, 2001

The O−H stretching $\Delta\nu = 3$, 4, and 5 vibrational overtone spectra of isobutyl alcohol (isobutanol, 2-methyl-1-propanol) are measured by using cavity ring-down spectroscopy (CRDS), where three bands are observed for each vibrational level. They are assigned to the O−H stretching vibrational absorption of the three kinds of conformations of the hydroxyl group and further confirmed by density function theory (DFT) calculations using highly accurate B3LYP/6-31+G(d,p) and 6-311+G(d,p) levels. The experimental mechanical frequencies ω_e, anharmonicities $\omega_e\chi_e$, and dissociation energies D are evaluated by the local mode theory. The band intensities of each band are obtained as well. The calculated O−H stretching $\Delta\nu = 1$, 3, 4, and 5 spectra are simulated by Lorentzian−Gaussian sum function in order to fit the experimental spectra. The molecular vibrational abundance and O−H stretching frequencies of different vibrations of the calculated molecular conformations are in agreement with the experimental results.

I. Introduction

Molecular conformation is an important aspect of stereochemistry. Isobutyl alcohol (isobutanol, 2-methyl-1-propanol) is one of the typical alcohols with a stereo structure similar to those of ethanol and propanol.[1] Because the energy difference among different conformations of the molecule is small, resolving such difference by its standard nuclear magnetic resonance (NMR) spectra is usually difficult.[2] However, the optical overtone spectra have higher resolving power to different molecular conformations due to the sensitivity of the overtone vibration to the local environment of X−H oscillators (X = C, N, or O).[3] Meanwhile, for higher frequencies, the overtone experiment can also be used to obtain information on molecular conformations that change on a time scale much shorter than the conventional NMR time scale.[4] Fang and Swofford[5] have studied successfully the molecular conformers of gas-phase ethanol by its vibrational overtones. Wong and Moore[6] have studied the molecular conformation of alkanes and alkenes in the gas phase by the overtone spectra. They found a bond length change of 0.001 Å for CH and a frequency shift of 69 cm^{-1} for the CH stretching $\Delta\nu_{\mathrm{CH}} = 6$ overtone spectrum, as compared to a frequency shift of 10 cm^{-1} for the fundamental. For the detection of even very weak absorptions such as overtone spectroscopy, several techniques, including photoacoustic laser spectroscopy,[7,8] long-path absorption spectroscopy,[9] and thermal lens spectroscopy,[10−12] have been used in past decades. Recently, the advanced CRDS technique has also shown great advantage in measurements for weak absorption of overtone spectroscopy,[13] especially for the absorption of overtone spectroscopy of 2-propanol[14] and 2-butanol.[15] Furthermore, it yields absolute quantitative spectroscopic measurements.[16]

For overtones of isobutyl alcohol, the O−H stretching $\Delta\nu = 5$ overtone vibration in the pure liquid was measured using thermal lens technique.[12] The O−H stretching $\Delta\nu = 4$ gaseous overtone spectrum was measured using an intracavity laser photoacoustic spectrometer,[17] which was assigned and predicted using the local mode model and the bond length overtone transition wavenumber correlation for the O−H oscillator, and the geometry optimizations and total energies of the five different conformations were calculated using both the ab initio HF/3-21G* and HF/6-31G** levels. Furthermore, for conformational studies of this molecule, the total and relative energies of the two conformers of trans C−C−O−H and gauche C−C−O−H of gauche,gauche-2-methyl-1-propanol (2Me-C−C−O) and the energy barrier of the internal rotation of C−C−O−H were calculated using the RHF/6-31G* level and single-point second-order Møller−Plesset (MP2) theory with the 6-31G* basis sets.[18] The total and relative energies of the two conformers of gauche,gauche-2Me-C−C−O−H (C−C−O−H trans) and gauche,trans-2Me-C−C−O−H (C−C−O−H trans) were calculated using the RHF/6-31+G*//6-31G*//3-21G, single-point MP2/6-31+G*, and MM2 calculations.[19] In this article, the higher-resolution overtone spectra of the O−H stretching $\Delta\nu = 3$, 4, and 5 vibrations of isobutyl alcohol in the gas phase are also measured using highly sensitive CRDS, which show the presence of the different conformations of the hydroxyl group, and all the stable conformational forms are calculated using DFT at highly accurate Becke3LYP/6-31+G(d,p) and 6-311+G(d,p) levels.

II. Experimental Section

The CRDS experimental setup is similar to that of our previous works.[14−16] The ring-down cavity is formed by two high-reflection concave mirrors, placed at a distance slightly less than 1 m. The mirrors are connected through bellows with a glass cell, which is filled with pure molecular sample at a pressure of ∼10 Torr. A tunable pulsed OPO laser system (Sunlite, Continuum) in the wavelength range of 944−960, 725−740, and 595−610 nm are used. The bandwidth of the

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10.1021/jp010214i CCC: \$20.00

laser radiation is less than 0.1 cm^{-1}. The laser light transmitted through the cavity is monitored using a photomultiplier tube (PMT), placed closely behind the cavity. The ring-down signal from the PMT is digitized on a programmable digitizer (7612D, Tektronix) with a 200 MHz sampling rate and a 8-bit vertical resolution. The characteristic ring down time is determined by fitting the natural logarithm of the ring-down exponential decay to a straight line and by using a weighted least-squares fitting algorithm. At each wavelength, we averaged 10 times. The empty cavity ring down time in our setup are about 1.5, 3, and 9 μs for the wavelength range of 944−960, 725−740 and 595−610 nm, respectively, which correspond to mirror effective reflection coefficients of 0.9978, 0.9989, and 0.9996, respectively.

The IR spectrum of the O−H stretching fundamental of isobutyl alcohol is measured in the regions of 3500−4000 cm^{-1} by using an FT-IR spectrometer (Impact 410, Nicolet company) with resolution 1 cm^{-1} and cumulative time 32, and the gas sample pressure is about 10 Torr.

The purity of isobutyl alcohol (99%, Beijing Chemical Company) was checked by GC runs.

III. Results and Discussion

The O−H stretching $\Delta\nu = 3$, 4, and 5 overtone spectra of isobutyl alcohol are shown in Figure 1, where three resolved vibrational bands of A, B, and C are found for each overtone transition. Bands A, B, and C have different band shapes, but they are almost identical in the $\Delta\nu = 3$, 4, and 5 spectra. The bands in the upper level overtone are farther separated than the one in the lower level overtone. The tendency of separation increases with the vibrational level ν. The band origins are measured by fitting the band shapes and calibrated by the standard water lines in the Hitran database 1996.[20] The errors of experimental spectra are estimated by statistics of multimeasurements. The three vibrational bands of the $\Delta\nu = 4$ overtone in the gas phase was reported,[17] and the relative measured errors of the band origins compared to our work are 1−8 cm^{-1}. Shifted frequencies in the $\Delta\nu = 5$ overtone due to hydrogen bonding in the pure liquid phase have also been reported.[12]

The band intensities of the O−H stretching vibrations of different conformations are obtained from the CRD spectra. The band intensity formula for absorption spectra[21] is expressed as

$$S_n = \int \sigma_n(\bar{\nu})\, d\bar{\nu} \qquad (1)$$

where $\sigma_n(\bar{\nu})$ is the absorption cross section (in cm^2) at band position $\bar{\nu}$ (in cm^{-1}). For CRDS,[13−15] the absolute absorption parameter $\alpha(\bar{\nu})$ is $1/c(1/\tau - 1/\tau_0)$, where c the speed of light, τ the ring-down time of molecular absorption, and τ_0 the ring-down time of the off-resonance baseline. From $\sigma_n(\bar{\nu}) = \alpha(\bar{\nu})/n$, $n = P/kT$, the equivalent formula of band intensity for CRDS

$$S_n = \frac{1}{P}\int \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) d\bar{\nu} \qquad (2)$$

with units in $cm^{-1}\ km^{-1}\ atm^{-1}$ at room temperature $T = 293$ K. The experimental band intensities of the overtones are determined by the integrated area of the whole band shape, obtained by extending the fitted band shapes as shown in Figure 1. When the band intensities of the different vibrational levels are compared in Table 1, the $\Delta\nu = 3$ overtone is 17 times stronger than that of $\Delta\nu = 4$, and the $\Delta\nu = 4$ overtone is 10 times stronger than that of $\Delta\nu = 5$. The relative ratio for the band intensities of the three bands A:B:C are near 47%:27%:26% for the $\nu = 4$ and 5 levels and near 49%:31%:20% for the $\nu = 3$ level. The band intensities of the whole absorption of isobutyl alcohol are nearly equal to those of 2-butanol[15] and larger by 20−30% than those of 2-propanol.[14]

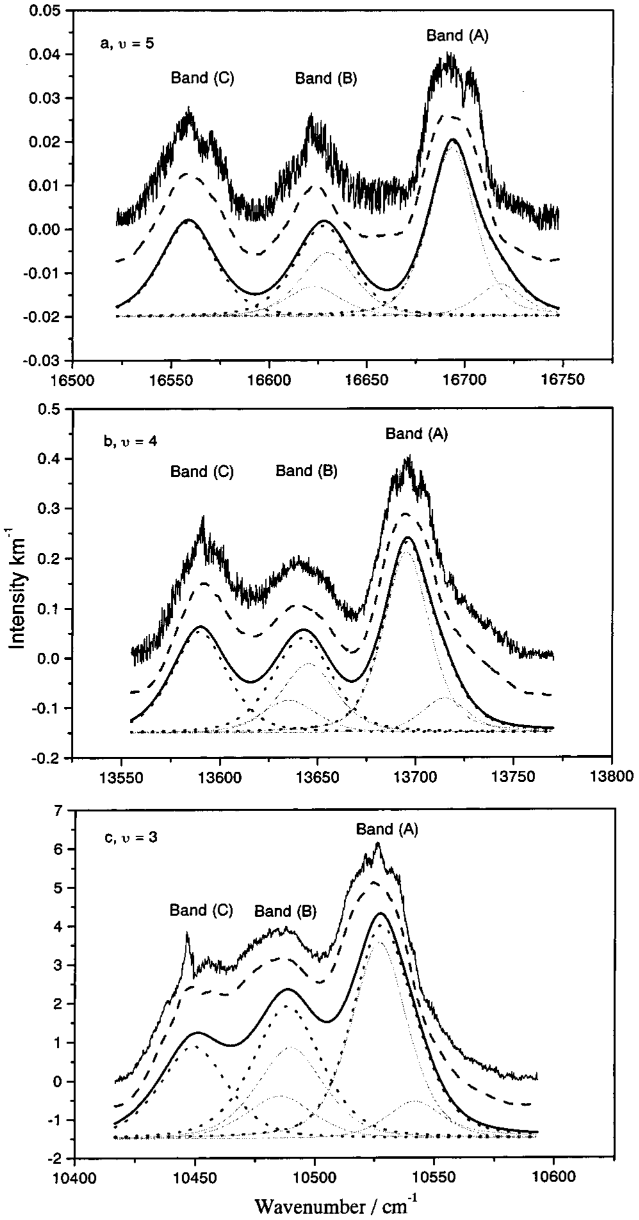

Figure 1. O−H stretching $\Delta\nu = 3$, 4, and 5 overtone spectra measured by CRDS for isobutyl alcohol. The dashed curves are smoothed spectra, the solid curves are the band shapes of the calculated spectra, the dotted curves are calculated three bands simulated by the sum function of Lorentzian−Gaussian, and the dash dotted curves are calculated spectra of conformations.

Because the O−H stretch in alcohols is, to a very good approximation, nearly a local mode,[22] each peak in the overtone spectra is assigned to O−H stretching vibration. Therefore, O−H anharmonic oscillators can be treated by the Birge−Sponer equation[23]

$$\Delta E_{\nu,0} = \nu(A + B\nu) \qquad (3)$$

where $\Delta E_{\nu,0}$ is the observed energy difference between the νth quantum level and the ground state, $\omega_e = A - B$ is the mechanical frequency, $\omega_e\chi_e = -B$ is the anharmonicity, and $D = -A^2/4B$ is the dissociation energy. The ω_e, $\omega_e\chi_e$, and D of

TABLE 1: Observed Band Origin, Band Intensity, Mechanical Frequencies ω_e, Anharmonicities $\omega_e\chi_e$, and Dissociation Energy *D* for the O−H Stretching Vibrations of Isobutyl Alcohol

molecule		$\nu_{OH} = 5$		$\nu_{OH} = 4$		$\nu_{OH} = 3$		$\nu_{OH} = 1$				
band[a]	conformation[b]	band origin (cm^{-1})	S_n[c]	band origin (cm^{-1})	S_n	band origin (cm^{-1})	S_n	deri. freq[d] (cm^{-1})	exp. freq. (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	*D* (kcal mol^{-1})
band A	form a form b	16 689±4	122 (±3%)	13 693±4	1140 (±3%)	10 525±4	17 480 (±3%)	3679.1±1.0		3850±1.0	85.3±0.2	119.0±0.6
band B	form c form d	16 623±4	68 (±3%)	13 640±4	646 (±3%)	10 486±4	11 020 (±3%)	3666.4±1.0	3674	3837±1.0	85.3±0.2	117.9±0.5
band C	form e	16 557±4	68 (±3%)	13 592±4	640 (±3%)	10 448±4	7600 (±3%)	3654.6±2.0		3826±2.0	85.7±0.8	117.2±0.5

[a] See Figure 1. [b] See Figure 2. [c] S_n band intensity in units of cm^{-1} km^{-1} atm^{-1}. [d] Frequencies derived from the spectral parameters of ω_e and $\omega_e\chi_e$ by local mode theory. [e] Frequency for the center of the O−H band in the FT-IR spectrum; see Figure 3.

the O−H stretching vibration for bands A−C evaluated from the above spectra are listed in Table 1. Up to now, the parameters of ω_e and $\omega_e\chi_e$ for some alcohols have been obtains by their overtones, including $\omega_e = 3855$ cm^{-1} and $\omega_e\chi_e = 86$ cm^{-1} for methanol,[24−26] $\omega_e = 3832-3846$ cm^{-1} and $\omega_e\chi_e = 85-86$ cm^{-1} for ethanol,[26] $\omega_e = 3831-3852$ cm^{-1} and $\omega_e\chi_e = 86$ cm^{-1} for 1-propanol,[26,27] $\omega_e = 3791-3831$ cm^{-1} and $\omega_e\chi_e = 83-86$ cm^{-1} for 2-propanol,[26,27] $\omega_e = 3798-3826$ cm^{-1} and $\omega_e\chi_e = 85$ cm^{-1} for 2-butanol,[15] and $\omega_e = 3814$ cm^{-1} and $\omega_e\chi_e = 86$ cm^{-1} for *tert*-butyl alcohol,[26] which are nearly identical with the values of isobutyl alcohol listed in Table 1. Therefore, we may conclude that the O−H vibration in alcohols fits into the local mode in general. However, it is noticed that the band profiles of the overtones of this molecule are different than those of other alcohols such as 1-propanol,[8,26,27] 2-butanol,[8,15] and *n*-butanol,[8] where the main two bands in the overtones were observed. The band profiles of the overtones are directly relevant to their O−H oscillator in the different geometric environment due to the conformations of isobutyl alcohol.[17]

To assign accurately to the overtones of isobutyl alcohol, we calculated the different conformations of the molecule by DFT using the GAUSSIAN 98 programs.[28] Indeed, the molecule exhibits different conformations because the hydroxyl functional group staggers between two C−H bonds and $-HMe_2$ groups rotate around C−C single bond. The conformations of isobutyl alcohol can be named according to different dihedral angles of $H_6O_1C_2C_3$ and $O_1C_2C_3H_9$, where trans (t) is near 180°, gauche (g) is near 60°, and gauche′ (g′) is near −60°, respectively. As shown in Figure 2, all the possible conformations are the following: form a Tt; form b, Tg (Tg′); form c), Gg (G′g′); form d, Gt (G′t); and form e, Gg′ (G′g). They are optimized by the accurate B3LYP methods using larger 6-31+G(d,p) and 6-311+G(d,p) basis sets,[29,30] and their corresponding frequencies are also calculated at the same levels. It is confirmed that the conformations are all stable, where Tg, Gg, Gt, and Gg′ conformers are mirror images of Tg′, G′g′, G′t, and G′g conformers, respectively. The distributions of these mirror images (named conformational enantiomers) and, hence, of exactly equal stability are, of course, equal. Therefore, there are five different stable conformations for isobutyl alcohol, compared with those of other alcohols such as the two different stable conformations for ethanol[5,8] and 2-propanol,[14] the five different stable conformations for 1-propanol,[27] the nine different stable conformations for 2-butanol,[15,31] and the 14 different stable conformations for 1-butanol.[32] The calculated total energies, relative energies, O−H bond lengths, O−H stretching harmonic frequencies, and IR intensities for the molecular conformations are listed in Table 2. As listed in the calculated results, the O−H stretching harmonic frequencies of the O−H trans conformations of form a and form b are closed to each other and larger by 10−25 cm^{-1} than those of the O−H gauche conformations in general. Meanwhile, in the O−H gauche conformations, the O−H stretching harmonic frequencies of form c and form d, whose hydroxyl axes parallel the methyl axis, are closed to each other and larger by 10 cm^{-1} than that of form e, whose hydroxyl axis parallels the carbonyl axis. The difference of 10 cm^{-1} for fundamental frequencies can be resolved in the high vibrational overtones because it is amplified *n* times in the $\nu = n$ overtone. In general, the conformations are classified as three kinds of the O−H trans forms, the O−H gauche forms whose hydroxyl axis parallels the methyl axis and the O−H gauche forms whose hydroxyl axes parallels the carbonyl axis, which correspond to the experimental three bands of the overtones. Therefore, band A is assigned to the O−H stretching overtone absorption of form a and form b, band B is assigned to the O−H stretching overtone absorption of form c and form d, and band C is assigned to the O−H stretching overtone absorption of form e. In ref 17, the three bands of the overtone were also assigned to the O−H stretching overtone absorption of the five conformations, but the order of their assignments were different from ours due to the lower accuracy

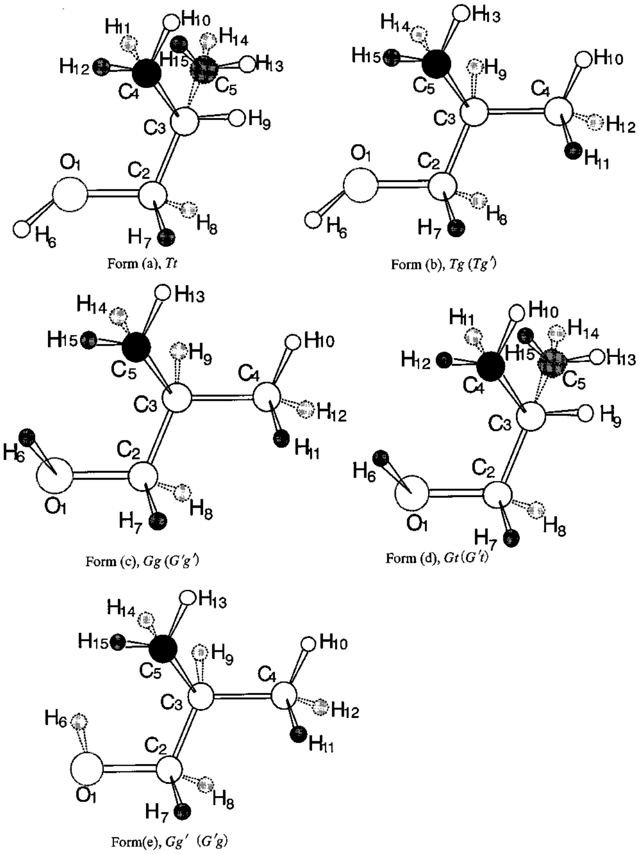
Form (a), *Tt*
Form (b), *Tg* (*Tg′*)
Form (c), *Gg* (*G′g′*)
Form (d), *Gt* (*G′t*)
Form(e), *Gg′* (*G′g*)

Figure 2. Stable conformations of isobutyl alcohol.

TABLE 2: Calculated Total Energy, Relative Energy, O−H Bond Length and Stretching Vibrational Frequencies, and the Percentage of the Conformations of Isobutyl Alcohol

	total energy[b] (Hartree)		relative energy (kcal mol^{-1})		O−H bond length (Å)		O−H str. harm. freq. (cal.)[c] (cm^{-1})		O−H str. IR inten. (km mol^{-1})		percentage[d]	
conformation[a]	calcd A[c]	calcd B[c]	calcd A	calcd B	calcd A	calcd B	calcd A	calcd B	calcd A	calcd B	calcd A	calcd B
form (a)	−233.555974	−233.607610	0.61	0.58	0.9647	0.9610	3845.3	3855.2	32.2	35.5	6%	6%
form (b)	−233.556949	−233.608535	0.00	0.00	0.9650	0.9613	3840.4	3850.3	29.2	33.3	34%	33%
form (c)	−233.556614	−233.608144	0.21	0.25	0.9652	0.9617	3835.3	3841.6	20.7	23.1	22%	22%
form (d)	−233.555838	−233.607467	0.70	0.67	0.9654	0.9618	3833.7	3840.1	21.7	23.4	11%	10%
form (e)	−233.556806	−233.608340	0.09	0.12	0.9661	0.9625	3822.2	3829.7	21.3	24.3	28%	29%

[a] See Figure 2. [b] Total energy including electronic energy and zero-point vibrational energy. [c] Calcd A using the B3LYP at the 6-31+G(d, p) level, and calcd B using the B3LYP at the 6-311+G(d, p) level. [d] Percentage of the conformations calculated by Boltzmann formula.

TABLE 3: Calculated O−H Stretching Frequencies of Different Vibrational Levels, Relative Integral Area *A*, and Simulated Half-Width *W* of Conformations of Isobutyl Alcohol

	calcd O−H stretching frequencies[b] (cm^{-1})						
conformation[a]	$\nu_{OH} = 1$	$\nu_{OH} = 2$	$\nu_{OH} = 3$	$\nu_{OH} = 4$	$\nu_{OH} = 5$	relative *A*[c] (km^{-1} cm^{-1})	simulated *W* (cm^{-1})
form a	3685	7199	10 542	13 715	16 718	(A) 16%	25
form b	3680	7189	10 527	13 695	16 693	(A) 84%	25
form c	3667	7164	10 490	13 645	16 630	(B) 68%	30
form d	3666	7161	10 485	13 639	16 623	(B) 32%	30
form e	3655	7138	10 449	13 590	16 570	(C) 100%	30

[a] See Figure 2. [b] O−H stretching frequencies of forms c−e calculated by the average of the harmonic frequencies of calcd A and calcd B and those of forms a and b calculated by the harmonic frequencies of calcd B combining local mode theory. [c] Relative integral area of each conformation calculated by the calculated relative band intensities.

of ab initio calculations. The assignments of this molecule are in agreement in general with the previous experimental assignments for ethanol,[5,8] where the high-energy band is assigned to the conformation with the O−H bond trans to the alkyl group and the low-energy band is assigned to the two equivalent conformations with the O−H group gauche to the alkyl group. But the two kinds of gauche conformations for isobutyl alcohol confirmed by the DFT calculations are not equivalent, and the two evident bands for the gauche conformations are observed successfully in the $\Delta\nu = 3$, 4, and 5 overtones.

In the precious ab initio calculations,[33−37] due to the low accuracy of calculations and no anharmonicities available, the calculated harmonic frequencies have to be scaled by an experiential factor in order to compare with the experimental fundamental frequencies. Furthermore, when different methods and different basis sets are used even for different molecules, their scaling factors are different. Fortunately, due to the highly accurate B3LYP method and much larger 6-31+G(d,p), 6-311+G(d,p) basis sets used in this study, the electron correlation for the molecule has been calculated accurately, and the calculated harmonic frequencies only without anharmonicities of the conformations are comparable with the experimental mechanical frequencies, where the calculated results at the 6-31+G(d,p) basis sets are smaller by 4−10 cm^{-1} than the experimental values and the calculated results at the 6-311+G(d,p) basis sets are larger by 3−5 cm^{-1} than the experimental values. We first obtain calculated fundamental frequencies from the calculated harmonic frequencies by detracting duple experimental anharmonicities without experiential scaling factor, and the difference between the calculations and experiments are the same as those of the above-mentioned harmonic frequencies. By using eq 3, we can also calculate the O−H stretching overtone frequencies of the conformations. For the experimental spectra to be fit well by the theoretical simulate spectra (discussed in next step), the calculated harmonic frequencies of forms a and b should be from the results at the 6-311+G(d,p) basis sets, and the calculated harmonic frequencies of forms c−e should be from the average data of the results at the 6-311+G(d,p) basis sets and those at the 6-31+G(d,p) basis sets. As listed in Table 3, the O−H stretching frequencies of the conformations at the $\Delta\nu = 1$, 2, 3, 4, and 5 vibrations are calculated using the above-mentioned harmonic frequencies. The calculated frequencies at the $\Delta\nu = 5$ overtone are larger by 5−29 cm^{-1} than the experimental values, and with the vibrational number decreasing, the difference between the calculated data and experimental ones decrease too.

According to thermal dynamics, the lower the total energy of conformation is, the more stable the conformation becomes. The stability order of the five forms should be b > e > c > a > d because relative energies of the forms calculated using the 6-311+G(d,p) basis sets are 0, 0.12, 0.25, 0.58, and 0.67 kcal mol^{-1}, respectively. Generally, the gauche,trans-2Me-C−C−O forms are 0.33−0.67 kcal mol^{-1} more stable than the gauche,gauche-2Me-C−C−O forms when dihedral angle C−C−O−H is fixed. On the other hand, when dihedral angle 2Me-C−C−O is fixed, the trans C−C−O−H forms are 0.12−0.25 kcal mol^{-1} higher than the gauche C−C−O−H forms. When the previous ab initio results were compared, the stability order of the five forms calculated by the HF/6-31G** levels was c (Gg defined in ref 17) > b (Ga) > a (Aa) > e (Gg′) > d (Ag).[17] Furthermore, the energy of form a was 0.16 kcal mol^{-1} higher than that of form d calculated using the MP2/6-31G(d) method in ref 18 and 0.21 kcal mol^{-1} higher than that of form c calculated using the MP2/6-31+G(d) method in ref 19, which are slightly larger than our results. The stability order of the five forms for isobutyl alcohol are also different from those of similar five forms of 1-propanol calculated by the B3LYP/6-31+G* method.[27] In addition, the relative percentage of the abundance of the molecular conformations follows the Boltzmann formula

$$\frac{N_i}{N_j} = \exp\left(-\frac{(E_i - E_j)}{kT}\right) \tag{4}$$

where N_i/N_j is the ratio of the two conformations; E_i and E_j are the total energies of the two conformations, respectively, and T is the room temperature of 293 K. From the calculated results, the percentage for form a (Tt), form b (sum of Tg and Tg′), form c (sum of Gg and G′g′), form d (sum of Gt and G′t), and form e (sum of Gg′ and G′g) is 6%, 33%, 22%, 9%, and 27%, respectively. The relative vibrational abundances of the conformations are relevant to both their relative energy abundances and relative vibrational transition strengths. In Table 2, the calculated IR intensities of the conformations are 23−36 km mol^{-1}, where the IR intensities of the O−H trans conformations are larger by about 10 km mol^{-1} than those of the O−H gauche forms. The calculated percentage of the vibrational abundances for forms a−e should be their relative energy abundances amplified by relative vibrational transition strengths, which is 8%, 40%, 20%, 8%, and 24%, respectively. The relative vibrational abundances (transition intensities) were also estimated from the Boltzman populations for the conformations in ref 17, but the data were not exact due to the lack of consideration of the conformational enantiomers, the difference of relative IR intensities of the O−H stretching bonds for the different conformations, and the calculated energies at the lower accuracy. In the spectra, the vibrational abundances of transitions correspond to the experimental band intensities. The percentage of the band intensities for the band A is 47−49%, corresponding to the sum of the calculated percentage of the vibrational abundances of form a and form b, 48%. The relative percentage of the band intensities for band B is 27−31%, corresponding to the sum of the calculated percentage of form c and form d, 28%. The percentage of the band intensities for band C is 20−26%, corresponding to the calculated percentage of form e, 24%. Therefore, the calculated percentage of the vibrational abundances for the conformations is in agreement with the experimental values of the corresponding bands, and difference between the calculated data and experimental ones is less than the experimental error for ±3%.

An isolated O−H stretching vibrational absorption band is of Lorentzian form imposing a Gaussian perturbation.[38] Because the O−H stretching frequencies of the conformations are closed to each other, the broad vibrational absorption in room temperature makes the overtones of the conformations overlap. The vibrational populations for each conformation in overtone absorptions have produced spectral band shape of each band. The sum of Gaussian and Lorentzian function can be used for fitting band shape,[15,38] which is as follows:

$$F(\gamma) = \frac{A}{2W\sqrt{\pi/2}}\, e^{-2(\gamma-\gamma_0)^2/W^2} + \frac{2A}{\pi}\,\frac{W}{4(\gamma-\gamma_0)^2 + W^2} \qquad (5)$$

where A is the integral area of the band in km^{-1} cm^{-1}, W is the half-width of the band in cm^{-1}, γ_0 is the band origin in cm^{-1}, and γ is the frequency in cm^{-1}. For the parameters of band shape function $F(\gamma)$ of each conformation in $\Delta\nu = 1$, 3, 4, and 5 vibrations listed in Table 3, γ_0 is from the calculated O−H stretching frequencies in the vibrations, the relative percentage of absorption integral area of each conformation is calculated by eq 4, and the integral area of bands A−C are obtained by experimental band intensities. The band shape function, $F_A(\gamma)$ for band A is sum of $F_a(\gamma)$ for form a, $F_b(\gamma)$for form b; $F_B(\gamma)$ for band B is sum of $F_c(\gamma)$ for form c, and $F_d(\gamma)$ for form d; $F_C(\gamma)$ for band C is equals $F_e(\gamma)$ for form e. The whole band shape function $F(\gamma)$ is the sum of $F_A(\gamma)$, $F_B(\gamma)$, and $F_C(\gamma)$. As shown in Figure 1, the smoothed curves of the original spectra are fitted by band shape function, where the simulated half-width W of O−H trans conformations is 25 cm^{-1}, those of O−H gauche conformations are 30 cm^{-1}, and the data are the same in different levels. The simulated calculated spectra in $\Delta\nu = 3$, 4, and 5 vibrations are similar to the experimental spectra, where the frequency difference between the simulated bands and experimental bands in the overtones is less than 5 cm^{-1}. It is also noticed that the parameters for the frequencies, relative population, and integral area of the bands in the simulated spectra are all from the calculated or experimental values; only simulated half-widths are variable parameters, and these simulated half-widths of 25−30 cm^{-1} are closed to the experimental half-widths of 30−35 cm^{-1} of *tert*-butyl alcohol at the $\Delta\nu = 3$, 4, and 5 vibrations.[26] Therefore, the simulated band shapes of the calculated spectra can reproduce reasonably the band shapes of the experimental spectra as a whole, a slight difference between the simulated spectra and experimental spectra is caused by the small difference between the calculated values and experimental ones. In ref 17, the predicted spectrum using the ab initio bond length-overtone transition wavenumber correlation for the O−H oscillator could not reproduce the experimental data; only tentative assignments could be suggested. In our work, the calculated spectrum in the $\Delta\nu = 1$ vibration can be also simulated by the band shape function $F(\gamma)$, where half-width W for each conformation is the same as that in the upper vibrational levels, and the O−H stretching frequencies and relative percentage of vibrational abundance of the five conformations are from the above-mentioned calculations. As shown in Figure 3, the three bands simulated by the five conformations have overlapped so heavily that they have merged into one peak, whose center frequency is 3677 cm^{-1}. Accordingly, the center frequency of the experimental fundamental spectrum is 3674 cm^{-1}. It is found that their band shapes are very similar, which show that the used band shape function of the Lorentzian−Gaussian sum function for spectra of simulation is reasonable.

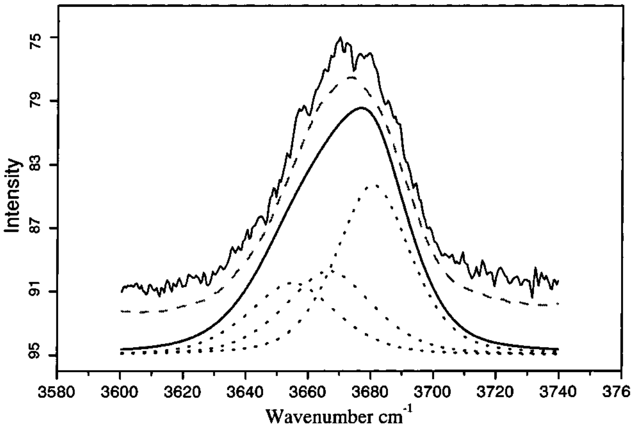

Figure 3. O−H stretching fundamental FT-IR spectrum of isobutyl alcohol. The dashed line is the smoothed spectrum, the solid line is the calculated spectrum, and the dotted curves are the calculated three bands simulated by the sum function of Lorentzian−Gaussian.

IV. Conclusion

The O−H stretching $\Delta\nu = 3$, 4, and 5 overtone spectra of isobutyl alcohol are studied by taking advantage of the CRDS technique. The resolved three bands in the overtones are assigned as the O−H stretching absorption of the three kinds of conformations of the hydroxyl group; the two bands in the low-energy region in particular are caused by the two kinds of nonequivalent gauche conformations confirmed by DFT calculations. The absolute band intensities of the bands in the overtones are obtained using the given band intensity formula for CRDS. The spectral parameters of the O−H oscillators are evaluated by local mode theory, which bridges the gap between experiment and theory. The present quantum chemistry DFT at highly accurate B3LYP/6-31+G(d,p) and 6-311+G(d,p) levels has been used to calculate all the stable conformations of the molecule and their O−H stretching frequencies. It is found that the calculated harmonic frequencies of the conformations can be compared directly to the experimental mechanical frequencies. It is the first time for us to obtain calculated fundamental frequencies by the calculated harmonic frequencies detracting duple experimental anharmonicities without experiential scaling factor. The calculated vibrational abundance, fundamental frequencies, and overtone frequencies are in agreement with the experimental values. The calculated spectra in the fundamental and overtones are simulated by the Lorentzian–Gaussian sum function, which are similar as the experimental spectra. In conclusion, the properties of the molecular conformations can be shown clearly by means of the experimental CRD overtone spectroscopy and theoretical DFT calculations, which is also a perfect example to show that the molecular vibrational spectroscopy and ab initio calculations have merged together without other experiential factor.

Acknowledgment. This work was supported by grants from the National Natural Science Foundation of China, Ministry of Science and Technology and Chinese Academy of Sciences.

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