4906 *J. Phys. Chem. A* **2000,** *104,* 4906−4911

Resolution Enhancement and Band Assignments for the First Overtone of OH(D) Stretching Modes of Butanols by Two-Dimensional Near-Infrared Correlation Spectroscopy. 3. Thermal Dynamics of Hydrogen Bonding in Butan-1-(ol-d) and 2-Methylpropan-2-(ol-d) in the Pure Liquid States

Mirosław A. Czarnecki* and Bogusława Czarnik-Matusewicz

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

Yukihiro Ozaki

Department of Chemistry, School of Science, Kwansei Gakuin University,
Uegahara, Nishinomiya 662-8851, Japan

Makio Iwahashi

Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara 228, Japan

Received: May 27, 1999; In Final Form: September 27, 1999

Two-dimensional (2D) near-infrared (NIR) correlation spectroscopy was used to study the temperature-induced changes in the hydrogen bonding of butan-1-(ol-d) and 2-methylpropan-2-(ol-d) in the pure liquid phase. The similarity between the 2D correlation spectra of both studied butanols and their nondeuterated analogues proves that the isotopic substitution in the hydroxyl group affects little the dynamic properties of the hydrogen bonding. This conclusion also confirms the heterospectral analysis, performed for the spectra of the deuterated samples and their nondeuterated counterparts. In the asynchronous spectra of 2-methylpropan-2-ol and its deuterated analogue, we identified new bands at 7040 and 5226 cm^{-1}, respectively, which are probably due to an intramolecular effect. Moreover, a heterospectral asynchronous plot develops a peak at (5286, 7085), not seen in the homospectral 2D plots of butan-1-(ol-d) and butan-1-ol, giving rise to an additional resolution enhancement. This new peak reveals different response to the temperature between the low frequency (gauche) rotamer of the butan-1-ol and the high frequency (trans) rotamer of butan-1-(ol-d). A lack of the asynchronous peak between the trans-rotamer of the butan-1-ol and the gauche-rotamer of butan-1-(ol-d) suggests that the deuterated butanol is less associated than the nondeuterated analogue. The 2D correlation method has appeared to be an excellent tool for reliable determination of the anharmonicity constants. The relevant values were calculated for all alcohols studied by 2D correlation approach. As expected, the anharmonicity constants are much lower for the deuterated alcohols as compared to the nondeuterated ones. A slight reduction of these values is observed upon going from the branched alcohols to the saturated straight chain alcohols. The extent of the self-association for the branched alcohols depends rather on the steric effects than the strength of hydrogen bonding interactions.

1. Introduction

Here we present the third paper dedicated to two-dimensional (2D) near-infrared (NIR) correlation study on self-association of butanols in the pure liquid phase. In two previous papers of this series 2D NIR correlation analysis of temperature-induced spectral variations for butan-2-ol (part 1)[1] and butanol-1-ol together with 2-methylpropan-2-ol (part 2)[2] were discussed. Owing to the resolution enhancement in 2D correlation spectra, we identified numerous peaks due to the free and associated OH groups, some of which had not been reported. The systematic assignments of all observed bands in the NIR region were based on several reasonable assumptions.[1] Interestingly, the splitting of the monomer band due to the rotational isomerism was observed for neat butan-2-ol, whereas in butan-1-ol this effect was seen only for the dilute solutions of CCl$_4$.[2] Hence, we concluded that the relative population of the rotational isomers was determined by the accessibility of the OH proton.[2] As shown, the dissociation of the polymeric species into monomers proceeds through the intermediate species.[1,2] Therefore, the changes in the population of the monomers are slower than those of any other species. Similar pattern of the temperature-induced intensity variations was also observed for *cis*-octadec-9-en-1-ol[3] and decan-1-ol.[4] Our 2D correlation studies on alcohols lead us to the conclusion that the degree of self-association decreases with increasing chain length (for the straight chain alcohols) and reduces upon branching.[4] Those tendencies are closely related with the strength of the hydrogen bonding for primary alcohols; the stronger hydrogen bonding, the higher extent of the self-association.[5]

The present study was undertaken in order to examine the effect of isotopic substitution in the hydroxyl group on the dynamic properties of hydrogen bonding. In this purpose we selected two deuterated analogues of recently reported butanols:

---

* Corresponding author. Faculty of Chemistry, University of Wrocław F. Joliot-Curie 14, 50−383 Wrocław, Poland. Fax: 48−71−3282348. E-mail: mcza@wchuwr.chem.uni.wroc.pl.

10.1021/jp991753e CCC: $19.00

butan-1-(ol-d) and 2-methylpropan-2-(ol-d).[2] Although there are some theoretical[6,7] and experimental[8,9] studies showing that the O−D···O interaction is weaker than O−H···O, the heterospectral 2D correlation analysis between the deuterated and nondeuterated samples gives an opportunity for the first direct comparison of these two types of hydrogen bonding. So far, only a few trials of the heterospectral correlation analysis were undertaken.[10−13] However, all those attempts were performed with one sample measured by two different spectral methods. In our case, we correlated the temperature-induced spectral variations for two different samples examined by the same spectroscopy method (FT-NIR). This type of the heterospectral correlation is particularly useful in establishing an ambiguous band assignments and has not been attempted yet.

The anharmonicity constants of the free and various associated species provide valuable information concerning the hydrogen bonding.[5] However, because of the uncertainty in the band assignments in the NIR region, these values are difficult to estimate. In this respect the 2D correlation method offers an excellent opportunity for very reliable determination of the anharmonicity constants. By correlating the fundamentals with the corresponding overtones or two different overtone regions, one can establish, with a high level of certainty, the bands having the same origin. In practice, the position of the synchronous 2D correlation peak yields the data necessary for the calculation of the anharmonicity constants. The relevant values were determined and discussed for all alcohols studied by 2D correlation approach.[1−4]

2. Experimental Section and Data Treatment

Butan-1-(ol-d) and 2-methylpropan-2-(ol-d) (spectroscopic grade) were purchased from Aldrich and used without further purification. All spectra were recorded from 8000 to 4000 cm^{-1} in a quartz cell of 1 cm thickness at a resolution of 4 cm^{-1}, and 300 scans were accumulated to achieve acceptable signal-to-noise ratio. The measurements were performed with a Nicolet Magna 760 spectrometer equipped with a PbSe detector, and the temperature was controlled with a precision of ±0.2° C. The spectra were corrected for the density change with temperature, and the integral intensity of the second overtone of the C−H stretching band was used as a reference.[14]

The 2D correlation spectra were calculated according to the generalized mathematical formalism proposed by Noda,[15,16] and the spectrum recorded at the lowest temperature was taken as a reference. The negative synchronous and asynchronous peaks were hatched. In a synchronous spectrum a positive peak at (ν_1, ν_2) indicates that the intensity changes at these two wavenumbers are in the same direction. As the asynchronous spectrum was multiplied by the sign of the companion synchronous spectrum,[1] a positive asynchronous cross-peak at (ν_1, ν_2) means that the spectral change at ν_1 occurs faster, as a function of increasing temperature, in comparison to ν_2. Negative synchronous and asynchronous peaks indicate the opposite. All the calculations were performed by using MATLAB 4.2 (Mathworks, Inc.).

3. Results and Discussion

Butan-1-(ol-d). Figure 1 shows FT-NIR spectra of butan-1-(ol-d) in the pure liquid phase measured over a temperature range of 20−85 °C with a step of 5 °C. A prominent band about 5270 cm^{-1} is assigned to the first overtone of the OD stretching mode in the monomers, whereas a feature near 4800 cm^{-1} is due to the associated species. Besides, one can see an intense band around 5500 cm^{-1} and a weak shoulder near 5350 cm^{-1}.

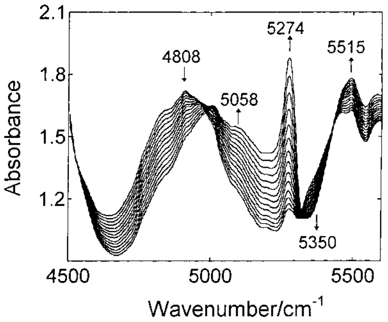

Figure 1. FT-NIR spectra of butan-1-(ol-d) in the pure liquid phase over the temperature range of 20−85 °C in the first overtone region. (↑: Intensity increase with temperature. ↓: Intensity decrease with temperature.)

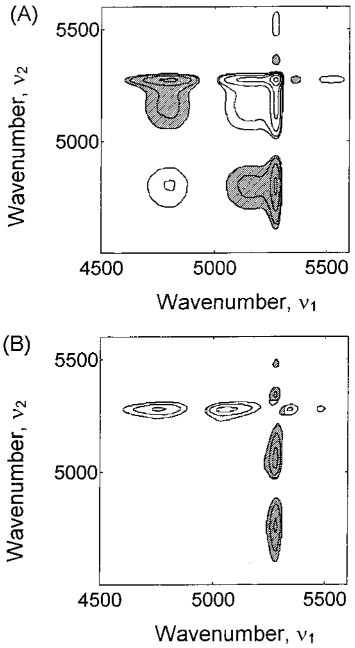

Figure 2. (A) Synchronous and (B) asynchronous 2D NIR correlation spectra of butan-1-(ol-d) in the temperature range of 20−85 °C. The negative peaks are hatched.

Figure 2 displays (A) synchronous and (B) asynchronous 2D FT-NIR correlation spectra of butan-1-(ol-d) in the pure liquid state from 20 to 85 °C. Except for the peaks at 5350 and 5500 cm^{-1}, the 2D correlation spectra of butan-1-(ol-d) and butan-1-ol (see Figure 2 in ref 1) are very similar, indicating the same mechanism of the thermal dissociation of the hydrogen-bonded species. The synchronous spectrum develops two autopeaks at (5274, 5274) and (4808, 4808). The negative cross-peak between them shows that the intensity changes at 4808 and 5274 cm^{-1} take place in the opposite direction. Two other cross-peaks are observed at (5274, 5357) and (5274, 5515). The corresponding asynchronous contour plot exhibits cross-peaks at (5278, 5477), (5278, 5338), (5058, 5278), and (4754, 5278), showing that the intensity change at 5278 cm^{-1} proceeds slower than intensity changes at any other wavenumber. This means that the thermal dissociation of the polymers into the monomers leads through the intermediate species. Two peaks at 4754 and 5058 cm^{-1} may be assigned to the linear O−D···O bonds and to the cyclic dimers, respectively. The positions and relative direction of the intensity changes suggest that the peaks at 5357 and 5515 cm^{-1} arise from the combination of the CH stretching mode (ν(C−H)) with the OD stretching modes due to the free ($\nu(\mathrm{O{-}D})_{\mathrm{free}}$) and associated species ($\nu(\mathrm{O{-}D})_{\mathrm{ass.}}$), respectively. The existence

TABLE 1: Assignments and Positions [cm^{-1}] of the NIR Bands Arising from the OD Stretching Modes of Various Species of Butan-1-(ol-d) and 2-Methylpropan-2-(ol-d) in the Pure Liquid State

	butan-1-(ol-d)		2-methylpropan-2-(ol-d)	
species	syn[a]	asy[b]	syn	asyn
monomer, second overtone	7772		7743	7750
combination ν(C−H) + ν(O−D)$_{\text{free}}$	5515	5477		
combination ν(C−H) + ν(O−D)$_{\text{associated}}$	5357	5338	5450	5429
monomer, first overtone, *trans*-rotamer		5286		
monomer, first overtone, gauche-rotamer	5274	5278		
monomer, first overtone			5253	5259
free terminal OH, linear polymers				5247
?				5226
cyclic dimers		5058		5064
linear and cyclic polymers[c]	4808	4754	4862	4817

[a] syn: synchronous. [b] asy: asynchronous. [c] Linear O−H···O.

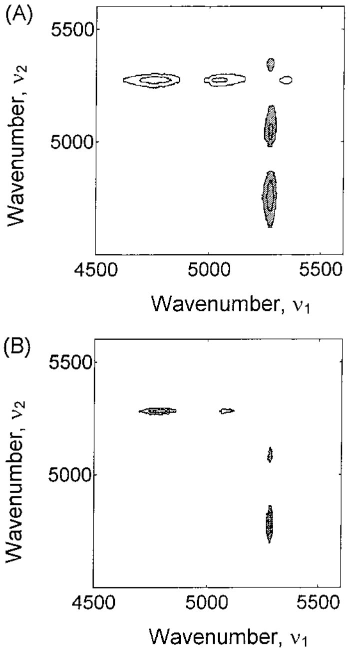

Figure 3. Asynchronous 2D NIR correlation spectra of butan-1-(ol-d) in the temperature ranges of (A) 20−50 °C and (B) 55−85 °C. The negative peaks are hatched.

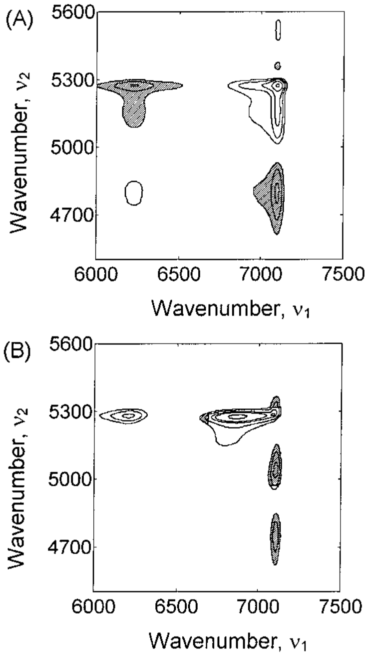

Figure 4. (A) Synchronous and (B) asynchronous 2D NIR correlation spectra of butan-1-ol vs butan-1-(ol-d) in the temperature range of 20−85 °C. The negative peaks are hatched.

of such combination bands is well evidenced for numerous alcohols.[17−20] The proposed assignments of various ν(OD) modes for both butanols in the NIR region are collected in Table 1. Note that the band positions obtained from the synchronous and asynchronous spectra are different. This difference is relatively small for the monomer band (4−6 cm^{-1}), whereas in the case of the polymer band it reaches 50 cm^{-1}. It has been recognized that the resolution enhancement gained in the 2D correlation spectra is accompanied by an error in the positions of the original spectral features.[21−23] In the case of the broad bands undergoing simultaneous frequency shift and width changes this error is expected to be serious.[23]

The more detailed insight into the mechanism of the thermal dissociation of the hydrogen bonding was achieved by 2D correlation analysis performed in narrower temperature intervals: 20−50 and 55−85 °C (Figure 3). Interestingly, at lower temperatures the asynchronous peaks at (4754, 5278) and (5058, 5278) are almost equal intensity, whereas at elevated temperatures the latter peak is hardly seen. It means that the cyclic dimers dissociate more easily with increase in temperature and hence, the changes in the population of the monomers and cyclic dimers occur more accordingly. The asynchronicity in Figure 3B is less significant as compared to that in Figure 3A, as revealed by irregular shapes of the peaks due to the random noise. Hence, we conclude that the spectral changes at higher temperatures happen at more similar rates.

Since the FT-NIR spectra of butan-1-ol and butan-1-(ol-d) were measured under the same experimental conditions, it was possible to correlate the temperature-dependent NIR spectra of both samples. This kind of heterospectreal correlation was performed for the first time. As expected, the synchronous spectrum (Figure 4A) is a combination of the spectra of butan-1-ol and butan-1-(ol-d) and does not include new features. A strong positive correlation occurs between the monomer bands of both butanols at (5274, 7097), the corresponding peak for the polymer band is located at (4808, 6220). The negative peaks correlate the monomer band of butan-1-ol and the polymer band of butan-1-(ol-d) at (4808, 7097) as well as the polymer band of butan-1-ol and the monomer band of butan-1-(ol-d) at (5274, 6220). Moreover, the monomer band of butan-1-ol develops the synchronous peaks with the combination modes of butan-1-(ol-d) at (5357, 7097) and (5515, 7097). The asynchronous spectrum (Figure 4B) exhibits peaks between the monomer band of butan-1-ol and the associated species of butan-1-(ol-d) at (4754,7101) and (5058, 7101). Similarly, the monomer band of butan-1-(ol-d) shows the asynchronicity with the polymer (5278, 6220) and cyclic dimer (5278, 6856) bands of butan-1-ol. Simultaneously, no meaningful asynchronicity appears between the peaks arising from the same species in the deuterated and nondeuterated samples. This fact gives a strong evidence for the similarity of the mechanism of the thermal dissociation of the hydrogen bonded species in both butanols.

Interestingly, the asynchronous spectrum (Figure 4B) develops a peak at (5286, 7085) although the features at 7085 and

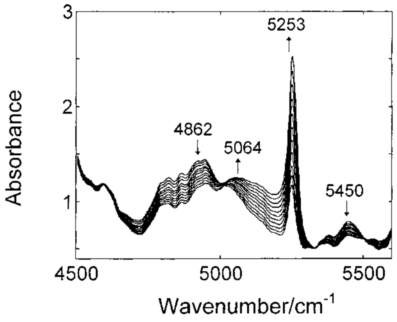

Figure 5. FT-NIR spectra of 2-methylpropan-2-(ol-d) in the pure liquid phase over the temperature range of 25−75 °C in the first overtone region. (↑: Intensity increase with temperature. ↓: Intensity decrease with temperature.)

5286 cm^{-1} do not appear in the 2D correlation plots of neat butan-1-ol and butan-1-(ol-d), respectively. This is a new example showing great potential of 2D correlation analysis in resolution enhancement. In the deconvoluted spectrum of butan-1-ol in CCl_4 (0.1 M) we observed a peak at 7084 cm^{-1}, that was assigned to the low frequency (gauche) rotational isomer of the free OH group.[2] Consequently, the feature at 5286 cm^{-1} was attributed to the high frequency (trans) rotamer of the OD group. Thus, this new asynchronous peak occurs between the trans-rotamer of the deuterated sample and the gauche-rotamer of the nondeuterated counterpart. In principle, one can expect an analogous peak between the gauche-rotamer of butan-1-(ol-d) and the trans-rotamer of butan-1-ol as well. The absence of this peak is probably due to low population of the latter species,[2] indicating the higher degree of the self-association in the pure butan-1-ol as compared to its deuterated analogue. This result is consistent with the other reports showing that the hydrogen bonding through the D is weaker than through the H.[6−9]

2-Methylpropan-2-(ol-d). In Figure 5 are exhibited FT-NIR spectra of 2-methylpropan-2-(ol-d) in the pure liquid phase over a temperature range of 25−75 °C. The most prominent peak about 5250 cm^{-1} can be assigned to the monomer band whereas the features below 5000 cm^{-1}, decreasing in intensity with temperature, arise from polymeric species. The synchronous and asynchronous spectra constructed from the data presented in Figure 5 are shown in Figures 6A and 6B, respectively. In the synchronous spectrum dominate the autopeak of the monomer band at (5253, 5253) and two negative cross-peaks at (4862, 5253) and (5253, 5450), showing that the monomer band changes its intensity in the opposite direction to the polymer and combination bands. The corresponding asynchronous contour plot develops peaks at (5247, 5259), (5064, 5259), (4817, 5259), and (5259, 5429). The peak at 4817 cm^{-1} is attributed to the linear O−D···O bonds in acyclic and cyclic polymers, whereas the feature at 5064 cm^{-1} is due to the bended hydrogen bonds in the cyclic dimers. A strong asynchronicity occurs between the peaks assigned to the free terminal OD group and the monomer band. The spectral changes at all wavenumbers are faster than the change at 5259 cm^{-1}; this observation is consistent with the result for 2-methylpropan-2-ol.[2] The sign of the synchronous and asynchronous peaks suggests that the intensity variation at 5450 cm^{-1} is due to the combination of ν(C−H) with $\nu(O{-}D)_{ass.}$, which agrees with the previous assignments.[17−20]

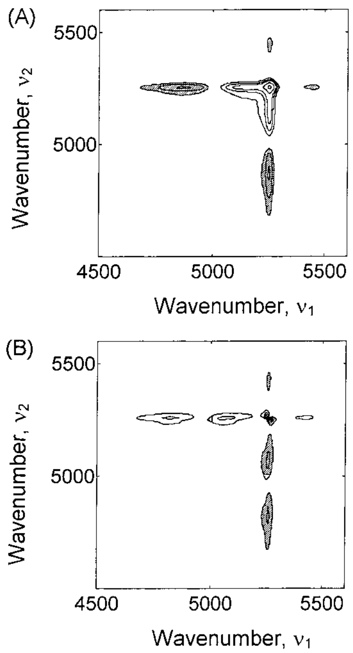

Figure 6. (A) Synchronous and (B) asynchronous 2D NIR correlation spectra of 2-methylpropan-2-(ol-d) in the temperature range of 25−75 °C. The negative peaks are hatched.

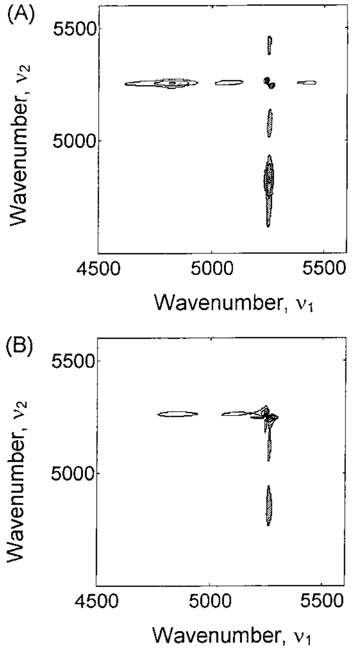

Figure 7. Asynchronous 2D NIR correlation spectra of 2-methylpropan-2-(ol-d) in the temperature ranges of (A) 25−50 °C and (B) 50−75 °C. The negative peaks are hatched.

Figures 7A,B show the asynchronous contour plots for 2-methylpropan-2-(ol-d) in temperature ranges of 25−50 and 50−75 °C, respectively. The spectrum calculated for the elevated temperatures reveals a new peak at (5226, 5247). The sign of this peak implies that the change in absorbance at 5226 cm^{-1} is slower than that of the free terminal OD groups in the open chain associates, suggesting that this feature is related to the monomer band. Thus, it cannot be due to the double excitation (simultaneous excitation by one quantum), reported for numerous self-associated alcohols,[20] as this phenomenon takes place in two OH(D) groups bonded together by a hydrogen bond. It seems that the band at 5226 cm^{-1} arises rather from an intramolecular effect than an intermolecular ones. Yet its exact origin cannot be derived from the present data.

The heterospectral 2D correlation between the dynamic spectra of 2-methylpropan-2-ol and 2-methylpropan-2-(ol-d) is shown in Figure 8. The synchronous spectrum develops the positive peaks between the monomer bands at (5253, 7070) and

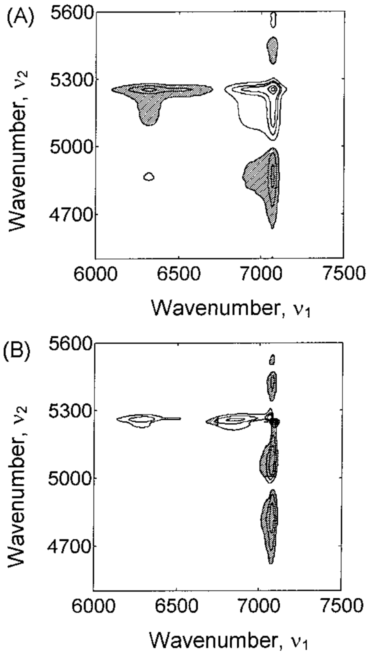

Figure 8. (A) Synchronous and (B) asynchronous 2D NIR correlation spectra of 2-methylpropan-2-ol vs 2-methylpropan-2-(ol-d) in the temperature range of 25−75 °C. The negative peaks are hatched.

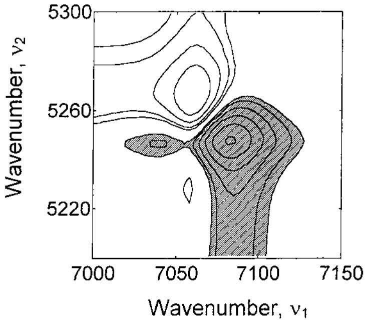

Figure 9. Expanded view of the asynchronous 2D NIR correlation spectra of 2-methylpropan-2-ol vs 2-methylpropan-2-(ol-d) in the temperature range of 25−75 °C. The negative peaks are hatched.

between the polymer bands at (4862, 6322). A negative peak correlates the monomer band of 2-methylpropan-2-ol and polymer band of 2-methylpropan-2-(ol-d) at (4862, 7070) as well as the monomer band of 2-methylpropan-2-(ol-d) and polymer band of 2-methylpropan-2-ol at (5253, 6322). Moreover, the monomer band of 2-methylpropan-2-ol shows a negative synchronous peak at (5450, 7070) with the combination mode of 2-methylpropan-2-(ol-d). The companion asynchronous spectrum reveals clear peaks between the monomer band of 2-methylpropan-2-ol and the polymer and cyclic dimer bands of 2-methylpropan-2-(ol-d) at (4817, 7078) and (5064, 7078), respectively. The same pattern is observed for the monomer band of 2-methylpropan-2-(ol-d); the corresponding peaks are located at (5259, 6295) and (5259, 6854). The features at (5247, 7081) and (5267, 7062) manifest the existence of the bands due to the free terminal OH(D) groups in open chain associates of 2-methylpropan-2-(ol-d) and 2-methylpropan-2-ol. The negative asynchronicity at (5429, 7078) confirms the assignment of the 5429 cm^{-1} peak to the combination of ν(C−H) with ν(O−D)$_{\text{ass.}}$ modes. A minor asynchronicity at (5226, 7058) reveals a new peak arising from 2-methylpropan-2-(ol-d). This peak is better seen in the expanded plot shown in Figure 9. Interestingly, the peak has its counterpart at (5247, 7040). The feature at 7040 cm^{-1} corresponds to the 5226 cm^{-1} peak in 2-methylpropan-2-(ol-d), and both bands have the same origin. The heterospectral 2D correlation analysis supports previously made band assignments for both butanols. Since no significant asynchronicity is found between the peaks arising from the same species in both samples, we speculate that the isotopic substitution in the hydroxyl group affects little the dynamic properties of the hydrogen bonding in 2-methylpropan-2-(ol-d).

TABLE 2: Position of the First (ν_{02}) and Second (ν_{03}) Overtones of the Free OH(D) Group together with the Anharmonicity Constants (X) for Selected Alcohols[a]

alcohols	ν_{02} [cm^{-1}]	ν_{03} [cm^{-1}]	X[cm^{-1}]
butan-1-ol[2]	7101	10386	−88.5
decan-1-ol[4]	7095	10379	−88.0
cis-octadec-9-en-1-ol[3]	7090	10380	−85.0
butan-2-ol[1]	7089	10379	−85.0
2-methylpropan-2-ol[2]	7070	10384	−85.5
butan-1-(ol-d)[b]	5274	7772	−46.5
2-methylpropan-2-(ol-d)[b]	5253	7743	−45.5

[a] The Values of X are estimated to be accurate within ±1 cm^{-1}. [b] Present study.

Anharmonicity. The positions of the synchronous peaks correlating the first (ν_{02}) and second (ν_{03}) overtones of the free OH group (not shown) were used for calculation of the anharmonicity constants ($X = \nu_{03}/3 - \nu_{02}/2$) for selected alcohols (Table 2). The estimated values of X, in different temperature ranges, for the free OH group have appeared to be independent of temperature. As expected, the deuterated alcohols have significantly smaller X than the nondeuterated ones. A slight increase in X for the saturated straight chain (nondeuterated) alcohols as compared to the values of X for the branched alcohols is observed. Note that the unsaturated *cis*-octadec-9-en-1-ol has an X similar to those of the branched alcohols. The values of X coincidence with the strength of the hydrogen bond; the higher the anharmoniciy, the stronger the hydrogen bond.[5] On the other hand, butan-2-ol and 2-methylpropan-2-ol have similar anharmonicity constants despite lesser extent of the self-association of the latter.[1,2,24−26] The same tendency is observed for butan-1-(ol-d) and 2-methylpropan-2-(ol-d). It means that the ability of the hydrogen bonding formation, expressed by the anharmonicity constant, can be considerably modified by steric effects.[5]

4. Summary

The temperature-induced changes in the FT-NIR spectra of neat butan-1-(ol-d) and 2-methylpropan-2-(ol-d) were explored by 2D correlation spectroscopy. The 2D correlation spectra of both studied samples are similar to those for butan-1-ol and 2-methylpropan-2-ol, indicating rather small isotopic effect on the dynamic properties of the hydrogen bonding. The population of the monomers increases at the expense of the polymeric species. However, this process proceeds through the intermediate species, such as cyclic dimers. For this reason, the changes in absorbance due to the monomer are slower than those due to any other species. With the increase in temperature, the cyclic dimers more easily dissociate into monomers.

For the first time we performed the heterospectral correlation between the dynamic spectra of the deuterated samples and their nondeuterated analogues. The analysis confirmed the band assignments made for both butanols individually. Additionally, in the asynchronous spectrum of butan-1-(ol-d) and butan-1-ol a new peak was found at (5286, 7085), not observed in the 2D correlation plots of each butanol separately. It means that during the heterospectral correlation analysis one can accomplish a further resolution enhancement. The peaks at 5286 and 7085 cm^{-1} were assigned to the trans- and gauche-rotamer of butan-1-(ol-d) and butan-1-ol, respectively. The lack of the asynchronous peak between the gauche- and trans-rotamers of butan-1-(ol-d) and butan-1-ol, respectively, is probably due to small population of the latter rotamer suggesting higher extent of the self-association in butan-1-ol. The heterospectral asynchronous plot for 2-methylpropan-2-(ol-d) and 2-methylpropan-2-ol reveals new bands at 5226 and 7040 cm^{-1}, for the time being the origin of these bands is not clear.

The positions of the relevant synchronous peaks were used for determination of the anharmonicity constants for a series of the normal and deuterated alcohols. These values appear to be considerably smaller for the deuterated alcohols as compared to nondeuterated analogues. The saturated straight chain alcohols have slightly higher anharmonicity constants than the branched alcohols. The butan-2-ol and 2-methylpropan-2-ol have similar anharmonicity despite the smaller extent of the aggregation of the latter. This result proves that for the branched alcohols the degree of self-association depends rather on steric effects than the strength of hydrogen bonding.

Acknowledgment. The authors acknowledge Hisashi Maeda (Kwansei Gakuin University) for assistance in measuring the NIR spectra. B. Czarnik-Matusewicz and M. A. Czarnecki gratefully acknowledge KBN for financial support (Grant 3 T09A 111 13).

References and Notes

(1) Czarnecki, M. A.; Maeda, M.; Ozaki, Y.; Suzuki, M.; Iwahashi, M. *Appl. Spectrosc*. **1998**, *52*, 994.

(2) Czarnecki, M. A.; Maeda, M.; Ozaki, Y.; Suzuki, M.; Iwahashi, M. *J. Phys. Chem. A* **1998**, *102*, 9117.

(3) Noda, I.; Liu, Y.; Ozaki, Y.; Czarnecki, M. A. *J. Phys. Chem.* **1995**, *99*, 3068.

(4) Czarnecki, M. A.; Ozaki, Y. *Phys. Chem. Chem. Phys.* **1999**, *1*, 797.

(5) Sandorfy, C. In *The Hydrogen Bond−Recent Developments in Theory and Experiments*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; Chapter 13, pp 615−654.

(6) Buckingham, A. D. *Trans. Faraday Soc*. **1960**, *56*, 753.

(7) Matsushita, E.; Matsubara, T. *Prog. Theor. Phys*. **1982**, *67*, 1.

(8) Broda, M. A.; Hawranek, J. P. *J. Mol. Struct*. **1994**, *321*, 137.

(9) Rospenk, M.; Koll, A.; Sobczyk, L. *J. Mol. Liquids* **1995**, *67*, 63.

(10) Noda, I. *Chemtracts: Macromol. Chem. Ed*. **1990**, *1*, 89.

(11) Noda, I.; Liu Y.; Ozaki, Y. *J. Phys. Chem*. **1996**, *100*, 8674.

(12) Czarnecki, M. A.; Wu, P.; Siesler, H. W. *Chem. Phys. Lett*. **1998**, *283*, 326.

(13) Schultz, C. P.; Fabian, H.; Mantsch, H. H. *Biospectrosc*. **1998**, *4*, 19.

(14) Czarnecki, M. A. *Appl. Spectrosc*. **1999**, *53*, 1392.

(15) Noda, I. *Appl. Spectrosc*. **1993**, *47*, 1329.

(16) Noda, I. Presented at the 2nd International Symposium on Advanced Infrared Spectroscopy, Durham, NC, 1996; Paper A-16.

(17) Luck, W. A. P.; Ditter, W. *Ber. Bunsen-Ges. Phys. Chem*. **1968**, *72*, 365.

(18) Fletcher, A. N.; Heller, C. A. *J. Phys. Chem*. **1967**, *71*, 3742.

(19) Fletcher, A. N.; Heller, C. A. *J. Phys. Chem*. **1968**, *72*, 1839.

(20) Bourderon, C.; Sandorfy, C. *J. Chem. Phys.* **1973**, *59*, 2527.

(21) Gericke, A.; Gadaleta, S. J.; Brauner, J. W.; Mendelsohn, R. *Biospectrosc*opy **1996**, *1*, 341.

(22) Czarnecki, M. A. *Appl. Spectrosc*. **1998**, *52*, 1583.

(23) Czarnecki, M. A. *Appl. Spectrosc.* **2000**, *54*. In press.

(24) Asselin, M.; Sandorfy, C. *J. Chem. Phys*. **1970**, *52*, 6130.

(25) Fletcher, A. N.*J. Phys. Chem*. **1972**, *76*, 2562.

(26) Forland, G. M.; Libnau, F. O.; Kvalheim, O. M.; Hoiland, H. *Appl. Spectrosc*. **1996**, *50*, 1264.