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.

Autorzy

Mirosław A. Czarnecki

Bogusława Czarnik-Matusewicz

Yukihiro Ozaki

M. Iwahashi

Rok wydania

2000

Czasopismo

Journal of Physical Chemistry A

Numer woluminu

104

Strony

4906-4911

DOI

10.1021/jp991753e

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

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.

Słowa kluczowe

Alcohols, Energy levels, Monomers, Noncovalent interactions, polymers