

# Vibrational study of anharmonicity, supramolecular structure, and hydrogen bonding in two octanol isomers



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## ARTICLE INFO

### Article history:

Received 2 February 2015

Received in revised form 22 April 2015

Accepted 4 May 2015

Available online 7 May 2015

### Keywords:

Infrared

Near-infrared

Anharmonicity

Hydrogen-bonding

Monohydroxy alcohols

Structural isomers

## ABSTRACT

Results from far-, mid-, and near-infrared spectroscopy are presented and combined with previous dielectric data on 2-ethyl-1-hexanol and 4-methyl-3-heptanol. This yields the electromagnetic absorption spectrum of the two monohydroxy alcohols, presented in terms of the imaginary part of the complex refractive index in a very wide frequency range. Low-frequency Raman measurements and far-infrared spectra hint at differences in the supramolecular structure of the two alcohols. By comparing the wavenumbers and amplitudes of the fundamental and the first overtone of the hydroxyl group's stretching vibration the temperature dependence of anharmonic effects and hydrogen bond cooperativity is studied.

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## 1. Introduction

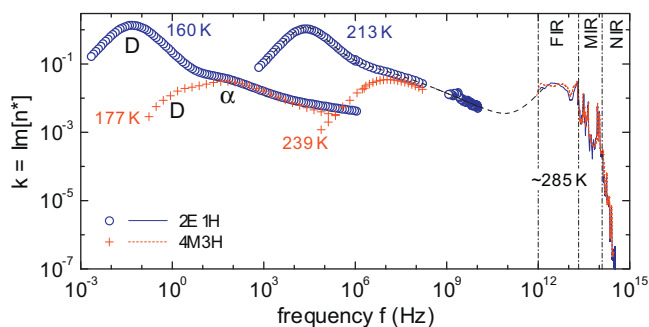
At the microscopic level hydrogen bonding can lead to a wealth of complex suprastructures that constantly break and reform. This thermally driven property governs the functionality of many bio-macromolecules. Relatively small hydrogen bonded molecules are currently under scrutiny as well, like for example sugars [1,2], pharmaceuticals [3], alcohols [4,5], and other substances of interest for the life sciences. The detailed nature of their supramolecular organization depends on the hydrogen bond strength and on molecular structure. Therefore, the study of isomeric species has been exploited for a long time using vibrational spectroscopy [6]. By focusing on the OH stretching vibration, the hydrogen-bonding partners can be accessed directly. This allows one to study the consequences of intra- and intermolecular hydrogen bonding [7,8] as well as that of hydrogen bond cooperativity [9]. The latter term refers to the observation that the addition of molecules to a hydrogen bonded network enhances the mutual bonding strength of its constituents and thus shifts the corresponding vibrational frequencies. The impact of hydrogen bond cooperativity is interesting to study in the condensed [10] as well as in the gas phase [11].

In the present work we focus on the liquid state of the isomeric octanols 2-ethyl-1-hexanol (2E1H) and 4-methyl-3-heptanol (4M3H). For the two monohydroxy alcohols previous studies inferred chain-like (in 2E1H) and ring-like (in 4M3H) supramolecular association patterns [12–19]. Here, we investigate these alcohols using far infrared (FIR), mid infrared (MIR), and near infrared (NIR) spectroscopy. To put the results for the absorption of electromagnetic radiation in perspective, we compile the dielectric spectra for the two alcohols [13,19] together with infrared results from previous [13,20] and the current study after transforming the data into a common format, the imaginary part,  $k$ , of the complex refractive index,  $n^* = n - ik$ . Here  $n$  designates the (real part of the) index of refraction. For nonmagnetic substances from  $n^{*2} = \epsilon^* = \epsilon' - i\epsilon''$  one derives  $k = \left[ \frac{1}{2}(\epsilon'^2 + \epsilon''^2)^{1/2} - \frac{1}{2}\epsilon' \right]^{1/2}$ . Using the Lambert–Beer law,  $A = \epsilon_{\text{IR}}cd = \ln(I_0/I)$ , and measuring the attenuated intensity,  $I = I_0 \exp(-\alpha d)$ , referring to the passage of a beam with intensity  $I_0$  through a sample of thickness  $d$ , the absorption coefficient  $\alpha = 4\pi k/\lambda = \epsilon_{\text{IR}}c$  and hence  $k$  can be obtained in a straightforward manner. Here  $\lambda$  is the wavelength,  $\epsilon_{\text{IR}}$  is the molar extinction coefficient, and  $c$  is the concentration of the absorbing species.

In Fig. 1 we plot  $k$  over a wide range of frequencies  $f$ . Focusing first on the low-frequency range ( $<0.1$  THz), one recognizes that the overall shape of  $k(f)$  looks similar for both alcohols. The large differences in the amplitudes of  $k$  for the two alcohols are due to

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**Fig. 1.** Temperature dependence of the imaginary part,  $k$ , of the complex index of refraction  $n^*$  for 2E1H and 4M3H comprising the frequency range below about 0.1 THz in which effects of orientational polarization dominate. Structural ( $\alpha$ ) and Debye ( $D$ ) relaxation peaks are marked for the low-temperature spectra. The dashed line is drawn to guide the eye. Infrared data are also represented in terms of  $k$  for the two alcohols at  $T \approx 285$  K. The vertical dashed-dotted lines separate the frequency intervals typically associated with the FIR, MIR, and NIR spectral ranges.

the effective addition of the molecular dipole moments if chain-like patterns prevail, like for 2E1H, or their near cancellation in ring-like supramolecular structures, like for 4M3H. Yet in the representation of Fig. 1 the spectra of the two monohydroxy alcohols look rather similar in the THz regime. Therefore, it is one of the goals of the present work to examine the impact of the different supramolecular structures of the two alcohol isomers on their infrared spectra in more detail.

First, we will present MIR data in the regime of the OH group's fundamental stretching vibration with the associated wavenumbers designated as  $\bar{\nu}^{(1)}$ . Consequently, the wavenumbers of the corresponding first overtone, appearing in the NIR spectral region, will be labeled as  $\bar{\nu}^{(2)}$ . The observation of overtones is per se an indication for anharmonicity, since overtones do not occur in a perfectly harmonic potential. Therefore, by comparing  $\bar{\nu}^{(1)}$  and  $\bar{\nu}^{(2)}$  the extent of anharmonicity may be inferred [21]. One usually distinguishes (i) so-called mechanical anharmonicity, referring to deviation from a parabolic shape of the vibrational potential and (ii) so-called electrical anharmonicity. The latter arises if the transition dipole moment changes non-linearly along its vibrational coordinate, see, e.g., [22]. While in studies of liquids the two contributions are often difficult to disentangle experimentally, in principle they should be considered separately, since they can either add up or at least partially compensate each other [23]. Furthermore, anharmonic effects are typically affected by the strength of hydrogen bonding [11,24,25] and by coupling of modes [26].

Finally, the FIR absorption and the Raman scattering of 2E1H and 4M3H are studied for wavenumbers up to about  $650\text{ cm}^{-1}$  with an interest in exploring whether and how the intermolecular stretching vibration,  $\nu_s(\text{O} \cdots \text{H})$ , along a hydrogen bond connecting two or more molecules reflects the different supramolecular structures of the two octanol isomers. Recently, a number of investigations on monohydroxy alcohols have focused on the difficult-to-access THz regime [27–29]. Nevertheless, while data on various alcohols have been published earlier, see, e.g., [30,31], FIR spectra for isomeric octanols are apparently not available.

## 2. Experimental details

The monohydroxy alcohol samples were purchased from Sigma–Aldrich with stated purities of  $\geq 99\%$  for 2E1H as well as for 4M3H (mixture of erythro and threo isomers) and used without further treatment.

The MIR measurements were conducted using a Varian Excalibur 3100 FT-IR spectrometer with a resolution of  $4\text{ cm}^{-1}$ .

Three droplets about 2 mm in diameter were dispersed between two optical AgCl windows with a diameter of 25 mm. This resulted in a film of about  $10\text{--}30\ \mu\text{m}$  thickness. The windows were fixed onto a cryogenic sample holder and inserted into a vacuum chamber that was pumped to a base-pressure of  $\sim 10^{-2}$  mbar. Two optical KBr windows of 49 mm diameter allowed the beam of light to pass through chamber and sample. The temperature was measured by a Pt100 sensor located at a distance of about 1 cm from the optical windows. The MIR spectra were corrected by subtracting a constant background, determined in the wavenumber range from  $2200$  to  $2350\text{ cm}^{-1}$  in which no significant absorbance occurs [32,33]. Then, the spectra were normalized by the CH peak intensity at  $2874\text{ cm}^{-1}$  in the 270 K spectrum. The analyzed NIR data were taken from previous work [13,20].

FIR measurements were performed using a Bruker Vertex 80v FT-IR spectrometer with a liquid helium cooled silicon bolometer detector from Infrared Laboratories. The monohydroxy alcohols were placed in a Bruker liquid cell with polycrystalline diamond windows of  $500\ \mu\text{m}$  thickness separated by a  $208\ \mu\text{m}$  thick polyethylene spacer. The temperature of the cell was kept constant at 293 K with a thermostat. The sample chamber was purged with dry nitrogen before and during measurement to reduce air humidity. For each spectrum 256 scans with a maximum resolution of  $2\text{ cm}^{-1}$  were averaged and then a sliding average of 25 data points was applied to minimize etalon (standing wave) effects.

Raman measurements were performed using an alpha 300 R/A/S confocal Raman microscope from WITec with a frequency-doubled Nd:YAG laser of  $532\text{ nm}$  wavelength as excitation source. The excitation beam was coupled into the microscope with a single-mode optical fiber and focused onto the liquid sample with a  $20\times$  objective (numerical aperture = 0.4). In a  $180^\circ$  geometry the Raman scattered light was collected by the same objective. Via a multimode fiber of  $50\ \mu\text{m}$  diameter and a diffraction grating of  $1800\text{ grooves/mm}$  the light was directed onto a back-illuminated electron multiplying charge-coupled device detector ( $200 \times 1600$  pixels, cooled to  $-60^\circ\text{C}$ ). For each sample 5 spectra with an integration time of 20 s and a spectral resolution of  $< 1\text{ cm}^{-1}$  were averaged.

## 3. Results and analysis

### 3.1. Mid-infrared spectroscopy

In Fig. 2(a) and (c) we present temperature dependent MIR spectra of 2E1H and 4M3H, respectively, in the wavenumber range from  $3000$  to  $3700\text{ cm}^{-1}$  corresponding to the region of the fundamental OH stretching vibration  $\nu(\text{OH})$  [32,34]. A broad absorbance band appears in this spectral range around  $\sim 3300\text{ cm}^{-1}$  that can be decomposed [34–36] into bands arising from strongly hydrogen bonded OH species conventionally designated [37] as  $\delta$  state and from weakly bonded proton donating hydroxyl groups labeled  $\gamma$  state. The absorbance of the  $\gamma$  state is small compared to that of the  $\delta$  state and becomes noticeable only as an asymmetrically broadened high-wavenumber flank of the  $\delta$  band. The absorbance of free OH groups ( $\alpha$  state) as well as that of weakly hydrogen bonded proton accepting hydroxyl groups ( $\beta$  state), strongly overlaps and usually a single absorbance band is found at wavenumbers close to  $3630\text{ cm}^{-1}$  [34,38,39]. Below room temperature the  $\alpha/\beta$  band is very faint indicating that only a small number of non- or weakly bonded OH groups exist.

Clear spectral changes emerge upon cooling the monohydroxy alcohols. Let us first turn to the  $\delta$  band positions,  $\bar{\nu}_\delta^{(1)}$ , that we have read off from the absorbance maxima of the data in Fig. 2(a) and (c). The results are presented in Fig. 3. For both

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