



# Chain length effects on the vibrational structure and molecular interactions in the liquid normal alkyl alcohols



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## ABSTRACT

Alkyl alcohols are widely used in academia, industry, and our everyday lives, e.g. as cleaning agents and solvents. Vibrational spectroscopy is commonly used to identify and quantify these compounds, but also to study their structure and behavior. However, a comprehensive investigation and comparison of all normal alkanols that are liquid at room temperature has not been performed, surprisingly. This study aims at bridging this gap with a combined experimental and computational effort. For this purpose, the alkyl alcohols from methanol to undecan-1-ol have been analyzed using infrared and Raman spectroscopy. A detailed assignment of the individual peaks is presented and the influence of the alkyl chain length on the hydrogen bonding network is discussed. A 2D vibrational mapping allows a straightforward visualization of the effects. The conclusions drawn from the experimental data are backed up with results from Monte Carlo simulations using the simulation package Cassandra.

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## 1. Introduction

The normal alcohols are a highly important class of chemicals. Their representatives find numerous applications in all industrial areas and in our everyday lives. For example, alcohols are used as reactants and solvents in the chemical industry [1–4], as (bio)fuels [5–8], as cleaning agents [9,10], and as germicides in the medical and health sector [11, 12]. In fundamental research, alcohols are commonly used as reference materials, e.g. to study molecular interactions [13,14] and phase behavior [15,16]. In this context, the thermophysical and chemical properties of alcohols are beneficial. Changing the length of the alkyl chain in alkanols allows a systematic variation of these properties as can be seen in Table 1. At the same time, the general chemical nature remains the same in a sense that all alkanols have a polar hydroxyl group to allow dipole-dipole interactions and hydrogen bonding, and a nonpolar alkyl chain. Consequently, at room temperature the normal alkanols span a wide range of the dielectric constant, see Table 1.

In the past two decades, spectroscopic methods entered new fields including process monitoring [17,18], environmental monitoring [19, 20], material and fluid characterization [21,22], medicine [23,24], and security [25,26]. As alcohols find applications in all these areas as well,

it is not surprising that the common *n*-alcohols have been extensively studied by all kinds of spectroscopy [27–34]. However, a look at the literature reveals that the efforts in a systematic investigation into the vibrational spectroscopy of *n*-alkanols are very limited. Most studies analyzed the individual short chain compounds methanol [28,35–39], ethanol [28,40], propanol [28], and butanol [29]. Some studies covered higher alkanols [30,31] or made comparisons between two or more different alcohol compounds [41–50]. A comparative investigation of all *n*-alkanols that are liquid at room temperature, i.e. from methanol (C1) to undecan-1-ol (C11), has not been performed to the best of our knowledge.

In the present study, we aim at closing this gap in the literature by performing a detailed vibrational analysis of all liquid *n*-alcohols. For this purpose, the experimental Raman and Infrared (IR) spectra are presented, analyzed, and interpreted. Conclusions on the chemical structure and intermolecular interactions are drawn and backed up by Monte Carlo simulations using the simulation package Cassandra [51]. The paper is organized as follows: the next section introduces the experimental and computational methods; Section 3 presents the results and discusses them; Section 4 concludes.

## 2. Materials and Methods

All chemicals had a purity of >99.5% and were used as received. The water content was determined by Karl-Fischer titration and the

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**Table 1**

Properties of the *n*-alkanols. The density and relative permittivity values are given for a temperature of 293.2 K.  $M$  = molar mass,  $\rho$  = density,  $T_m$  = melting temperature at atmospheric pressure,  $T_b$  = boiling temperature at atmospheric pressure,  $T_c$  = critical temperature,  $p_c$  = critical pressure,  $\epsilon_r$  = relative permittivity (dielectric constant).

	$M$	$\rho^{a,b}$	$T_m^b$	$T_b^b$	$T_c^b$	$p_c^b$	$\epsilon_r^{a,c}$
	g/mol	kg/dm <sup>3</sup>	K	K	K	bar	–
C1	32.04	0.79	175.6	337.8	513	81	33
C2	46.07	0.79	158.8	351.5	514	63	25.3
C3	60.10	0.80	146.7	370.3	536.9	52	20.8
C4	74.12	0.81	188.0	390.6	562	45	17.8
C5	88.15	0.81	194.7	411	580	39	15.3
C6	102.18	0.82	226.0	430	610.5	34.2	13.0
C7	116.20	0.82	238.3	448	633	30.6	11.8
C8	130.23	0.83	257.0	468	655	27.0	10.3
C9	144.26	0.83	268.0 <sup>d</sup>	485	672	25.3	8.8
C10	158.28	0.83	279.6	505	690	23.2	7.9
C11	172.31	0.83	288.5	516 <sup>e</sup>	704	21.5	6.6 <sup>f</sup>

<sup>a</sup> At  $T = 293.2$  K.

<sup>b</sup> Source: NIST Standard Reference Database Number 69.

<sup>c</sup> Source: CRC Handbook of Chemistry and Physics, 95th Edition.

<sup>d</sup> Source: Handbook of Data on Organic Compounds. Volume I. 3rd ed. CRC Press, Inc. Boca Raton, FL. 1994, p. V4: 3651.

<sup>e</sup> Source: Entry for CAS 112-42-5 in GESTIS-Stoffdatenbank of the IFA.

<sup>f</sup> Estimated from empirical equation of lower alcohols based on the value 5.98 given for 313.2 K.

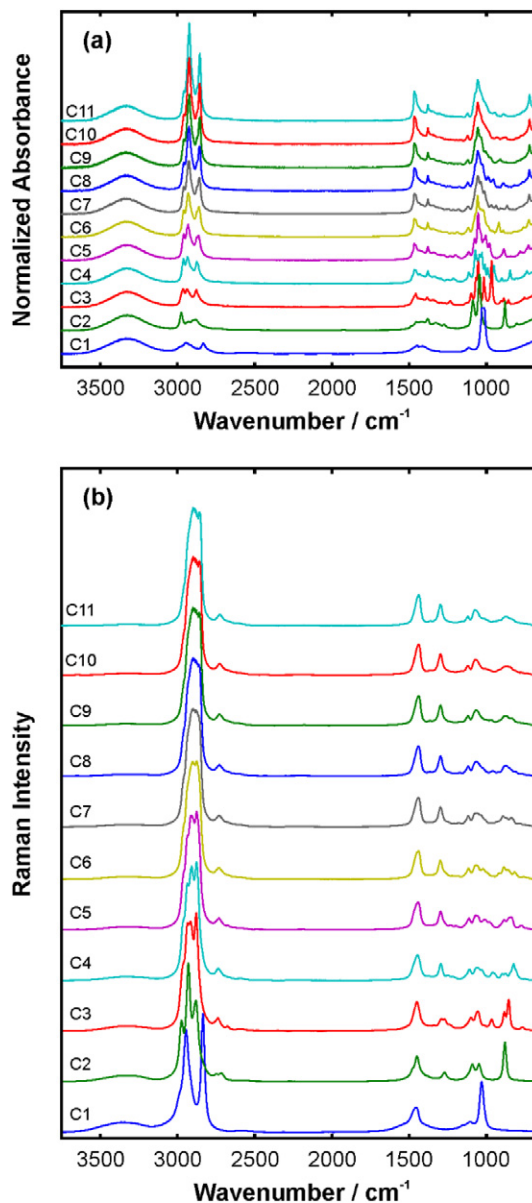
**Table 2**

Water content determined by Karl-Fischer titration.

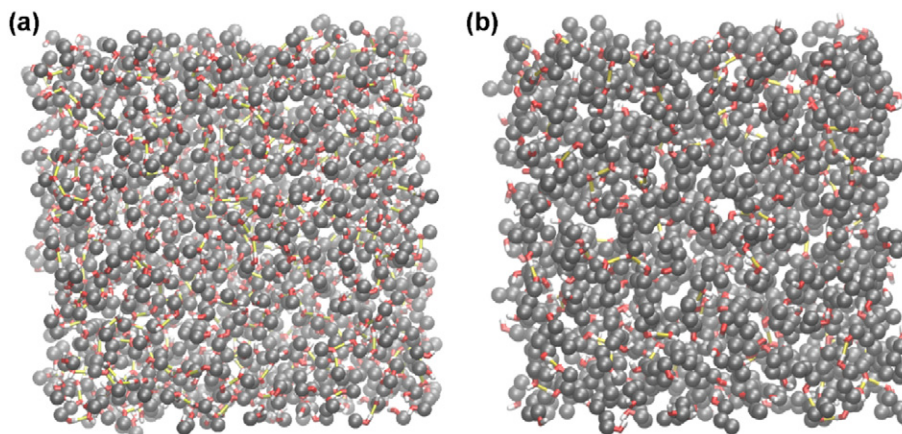
C1	348.9 ppm
C2	255.7 ppm
C3	404.7 ppm
C4	603.8 ppm
C5	386.8 ppm
C6	3254.3 ppm
C7	3324.1 ppm
C8	528.9 ppm
C9	5768.0 ppm
C10	331.8 ppm
C11	874.6 ppm

individual values are given in Table 2. All experiments were carried out at room-temperature (296 K).

The infrared spectra were recorded on an Agilent Cary 630 instrument equipped with a ZnSe ATR module (5 reflections at 45°). The spectra were recorded in the range 650–4000 cm<sup>-1</sup> with a nominal resolution of 2 cm<sup>-1</sup>. 32 scans were averaged in order to obtain an



**Fig. 2.** (a) Infrared and (b) Raman spectra of the eleven *n*-alkanols. The IR spectra are normalized with respect to the OH stretching band. The Raman spectra are normalized with respect to the strongest peak.



**Fig. 1.** View into a simulation box of (a) methanol and (b) *n*-propanol. The yellow lines represent hydrogen bonds.

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