Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectra-structure correlations in NIR region: Spectroscopic and anharmonic DFT study of *n*-hexanol, cyclohexanol and phenol

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ARTICLE INFO

Article history:
Received 3 October 2017
Received in revised form 8 January 2018
Accepted 13 January 2018
Available online xxxx

Keywords:
Near-infrared spectroscopy
Alcohols
Phenols
Quantum chemical calculation
Overtones
Combination modes
Time-independent vibrational Schrödinger equation
Spectra-structure correlation
Anharmonic spectra

ABSTRACT

We investigated near-infrared (7500–4000 cm^{-1}) spectra of *n*-hexanol, cyclohexanol and phenol in CCl_4 (0.2 M) by using anharmonic quantum calculations. These molecules represent three major kinds of alcohols; linear and cyclic aliphatic, and aromatic ones. Vibrational second-order perturbation theory (VPT2) was employed to calculate the first overtones and binary combination modes and to reproduce the experimental NIR spectra. The level of conformational flexibility of these three alcohols varies from one stable conformer of phenol through four conformers of cyclohexanol to few hundreds conformers in the case of *n*-hexanol. To take into account the most relevant conformational population of *n*-hexanol, a systematic conformational search was performed. Accurate reproduction of the experimental NIR spectra was achieved and detailed spectra-structure correlations were obtained for these three alcohols. VPT2 approach provides less reliable description of highly anharmonic modes, i.e. OH stretching. In the present work this limitation was manifested in erroneous results yielded by VPT2 for 2νOH mode of cyclohexanol. To study the anharmonicity of this mode we solved the corresponding time-independent Schrödinger equation based on a dense-grid probing of the relevant vibrational potential. These results allowed for significant improvement of the agreement between the calculated and experimental 2νOH band of cyclohexanol. Various important biomolecules include similar structural units to the systems investigated here. A detailed knowledge on spectral properties of these three types of alcohols is therefore essential for advancing our understanding of NIR spectroscopy of biomolecules.

1. Introduction[1]

Near-infrared (NIR) spectroscopy (12,500–4000 cm^{-1}; 800–2500 nm) has been growing in importance in science and technology over the last two decades [1–3]. In relation to other vibrational spectroscopies (mid-IR or Raman), NIR spectroscopy (NIRS) offers advantages such as simpler instrumentation and general versatility [1,4]. Numerous physicochemical studies i.e. on anharmonicity of molecular vibrations [3,5], molecular structure [3,6], intermolecular interactions [3,7,8], and hydrogen-bonding [3,9–13], solution chemistry [14] and microheterogeneity [15], solvent effects [16,17], etc., provide a good basis for applications of NIRS in analytical chemistry. NIRS appears to be very useful for qualitative and quantitative analysis of i.e. natural products [18], food [19], pharmaceuticals [20], medical samples [21] and medical tools [22]. Therefore, NIRS has become an important tool in a scientific or industrial laboratory.

Unfortunately, NIR spectra remain difficult for direct interpretation. The spectral information is intrinsically complex as a result of significant overlapping of overtones and numerous combination bands [23]. Therefore, applications of NIRS strongly rely on statistical data analysis [3]. As a result, NIRS is often used as a black-box tool. However, the field of applications of NIRS could be extended if the correlations between the molecular properties of a sample and its NIR spectrum were known in detail.

Quantum mechanical calculations are one of primary sources of an independent insight in the case of IR and Raman spectroscopies. The analysis of fundamental bands can be carried out by ordinary harmonic calculations [24]. On the other hand, the case of NIR spectra unequivocally requires an anharmonic approach. This imposes considerable requirements on the accuracy and computational affordability of calculations [2,25]. For a long time only the simplest molecules could be satisfactorily treated with fully anharmonic calculations. Therefore, our understanding of NIR spectra remains insufficient [1–3,26]. Advances in the theory of anharmonic methods and a rapid growth of available computational power over the years have allowed to push the limits in theoretical NIRS. Recent development of deperturbed and generalized VPT2 schemes [27], which combine good accuracy with relatively modest computational complexity and high versatility, should be noted. As a result, a growing number of NIR spectroscopic studies

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[1] This article is dedicated to Professor Yukihiro Ozaki from Kwansei Gakuin University on the occasion of his retirement, to honour his work which significantly advanced our knowledge on near infrared spectroscopy.

https://doi.org/10.1016/j.saa.2018.01.041
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aided by VPT2 calculations could be observed over the last two or three years [10,18,28–31]. Nowadays, the theoretical NIR spectra of fairly complex molecules, i.e. rosmarinic acid [18] or medium-chain fatty acids [32] can be successfully obtained.

The OH group strongly affects physicochemical properties of alcohols. The OH group can be attached to various types of molecular structures, i.e. normal or cyclic aliphatic chain or aromatic ring. The properties of this group, in particular its vibrational frequencies, strongly depend on the environment. For this reason, it is of high interest to establish detailed correlations between the structural factors of the three types of alcohols and their specific NIR spectral features. The first overtones of the free or weakly bonded OH are very pronounced in NIR spectra; therefore their spectral parameters (intensity, position, half-width) provide rich information on self-association and interactions with other molecules. It is relatively easy to study the OH stretching of the first overtone bands and so far many investigations focused on these bands [1,3,6,8–11,13]. In contrast, the other bands appearing in NIR region have not been used so often, despite carrying plentiful information on the structure and properties of these molecules [3,7] The complexity of NIR spectra has been the major hindrance in such studies. To overcome this problem it is necessary to establish detailed band assignments and obtain comprehensive spectra-structure correlations in a broad range of NIR (7500–3800 cm^{-1}). Here, we attempt to deeply analyze NIR spectra of medium-size alcohols which bear distinct structural differences. The OH group appears in variety of molecules, i.e. carbohydrates, nucleic acids; aliphatic OH group plays a role in the adsorption of proteins or nucleic acids [33,34], cyclic alcohols appear in metabolic paths [35,36], polyphenols in natural products act as radical scavengers [18], etc. The aim of the present work is to elucidate the differences between the NIR spectra for three major kinds of alcohols represented by *n*-hexanol, cyclohexanol and phenol, on the basis of anharmonic calculations. To achieve this aim we employ two different approaches. Firstly, second-order vibrational theory (VPT2) computations are used to simulate NIR spectra from 7500 to 4000 cm^{-1}. An analysis of the contributions from overtone and combination bands in various spectral subregions provides reliable band assignments. The limitations of VPT2 in describing highly anharmonic modes, such as OH stretching mode, clearly appears in the case of cyclohexanol. Secondly, in the latter case we perform a detailed study of the vibrational potential, vibrational levels and corresponding transition frequencies on the ground of numerical solving of time-independent Schrödinger equation.

2. Materials and Methods

2.1. Experimental

All samples were purchased from Wako Pure Chemical Industries Japan (*n*-hexanol, min. 97%; cyclohexanol, min. 98%; phenol, min. 99%) and dried by freshly activated molecular sieves (Wako Pure Chemical Industries Japan, 4 Å pore size). The NIR spectra were measured in 10,000–3700 cm^{-1} range on a Perkin Elmer Spectrum One NTS FT-NIR spectrometer operating in a transmittance mode. The solutions of 0.2 M in CCl_4 (Infinity Pure, min. 99.9%; Wako Pure Chemical Industries Japan; dried similar as above) were placed in rectangular quartz cell of optical path of 10 mm. Spectral measurements were performed at resolution of 4 cm^{-1}, resulting in an interpolated data spacing of 1 cm^{-1}, and 64 scans were accumulated. Each spectrum was recorded 3 times, preceded by a background collection (the spectrum of the solvent). The spectra were measured at a controlled temperature of 298 K. Baseline correction was performed by using the software which operates the spectrometer. No other spectral pre-treatment was applied.

2.2. Computational Details

All quantum mechanical calculations were carried out using Gaussian 09 Rev. E.01 software [37]. Conformational search (refer to Section 3.1 for detailed explanation), geometry optimization and anharmonic vibrational analysis were performed with the use of Density Functional Theory (DFT). Single-hybrid B3LYP density functional coupled with 6-31G(d,p) basis set for conformational searches, and SNST basis set for the subsequent computations were employed. The chosen methods have been reported to be very efficient and accurate in similar studies [10,25,28,30–32]. Superfine grids for integration and solving CPHF equations, and very tight convergence of geometry optimization were applied; with the exception of conformational searches (for which standard options were used). The calculations were carried out with conductor-like polarizable continuum model (CPCM) [38] of CCl_4 solvent and third formulation of Grimme's empirical correction for dispersion with Becke-Johnson damping (GD3BJ) [39]. To simulate NIR spectra of studied alcohols we performed fully anharmonic vibrational analysis by means of deperturbed/generalized vibrational second-order perturbation theory (DVPT2/GVPT2); [27] tightly coupled modes were not subjected to variational treatment. This computational procedure enabled us to obtain information on the first overtones and binary combinations. As shown [28,30–32], this approach is sufficient to capture the major features of NIR spectra without extensive calculations.

The vibrational frequencies and intensities were used for reconstruction of NIR bands for particular model structures in the same way as previously described [30,45]. The final theoretical NIR spectra were constructed as weighted-sum of calculated spectra of different conformational isomers (ref. Section 3.1) with respect to the calculated Boltzmann coefficients. The Boltzmann coefficients were derived from Gibbs free energies (B3LYP/SNST) corresponding to 298 K, additionally corrected by anharmonic zero-point energy (ZPE) values. This approach worked well with the exception of cyclohexanol case, which will be discussed in detail in Section 3.6.

The band assignments were performed with an aid of potential distribution analysis carried out in Gar2Ped software [40], after defining a non-redundant set of natural internal coordinates in accordance with Pulay et al. [41]

To enable accurate calculation of anharmonicity of OH stretching vibration, in the case where VPT2 calculation scheme gave erroneous results (cyclohexanol), an independent approach of numerical solving of time-independent Schrödinger equation (Eq. (1)) was employed:

$$\frac{\partial^2 \Psi(Q)}{\partial Q^2} = \left\{ \frac{2\mu}{\hbar^2} (V(Q) - E) \right\} \Psi(Q) \tag{1}$$

In Eq. (1) Q denotes the respective normal coordinate, Ψ the wave function, μ the reduced mass of the corresponding oscillator, V the potential energy, and E the energy eigenvalue. The scan of the potential energy over the OH stretching normal coordinate was performed from −0.4 to 2.0 Å with 0.005 Å/step. The harmonic analysis to determine the normal coordinate was carried out at B3LYP/6-311++G(3df,3pd) level, with preliminary geometry optimization using very tight convergence criteria, 10^{-12} SCF convergence level, superfine integration and CPHF grids and CPCM solvent model of CCl_4. The following grid-based energies were obtained with the use of 6-311G(d,p) basis set, all other parameters being equal to those listed above. The solution of the corresponding Schrödinger equation was performed by means of generalized Numerov's method, with seven-point numerical differentiation [42].

3. Results and Discussion

3.1. The Conformational Flexibility of Alcohols

The studied alcohols (Fig. 1a–c) differ notably in the levels of conformational flexibility. Phenol is the simplest case as it features only one stable conformer, with O—H bond in plane of the aromatic ring (Fig. S1 in Supplementary Material). Six-membered saturated ring of cyclohexanol takes four stable conformations, in which the OH group

Please cite this article as: K.B. Beć, et al., Spectra-structure correlations in NIR region: Spectroscopic and anharmonic DFT study..., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2018), https://doi.org/10.1016/j.saa.2018.01.041