

OH stretching frequencies in systems with intramolecular hydrogen bonds: Harmonic and anharmonic analyses

Jens Spanget-Larsen*, Bjarke K.V. Hansen, Poul Erik Hansen*

Department of Science, Systems and Models, Roskilde University, Universitetsvej 1, DK-4000 Roskilde, Denmark

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ABSTRACT

OH stretching wavenumbers were investigated for 30 species with intramolecularly hydrogen-bonded hydroxyl groups, covering the range from 3600 to ca. 1900 cm^{-1} . Theoretical wavenumbers were predicted with B3LYP/6-31G(d) density functional theory using the standard harmonic approximation, as well as the second-order perturbation theoretical (PT2) anharmonic approximations available with the Gaussian software package. The wavenumbers computed with the anharmonic procedures were found to be essentially linearly related to those obtained within the harmonic analysis. The theoretical wavenumbers were compared with experimental values taken from the literature, supplemented with values estimated from infrared (IR) absorption spectra recorded for the purpose of this study. An approximately linear relationship was established between the observed wavenumbers ν_{OH} and the results of the harmonic analysis. This is significant in view of the fact that the full anharmonic PT2 analysis requires orders-of-magnitude more computing time than the harmonic analysis. ν_{OH} also correlates with OH chemical shifts.

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1. Introduction

The concept of hydrogen bonding is of fundamental importance in many areas of chemistry and biology. Historically, infrared (IR) absorption spectroscopy has been the most important spectroscopic method in the study of hydrogen bonding. The wavenumber shift and half-height width of the OH stretching band are thus among the most important parameters in the characterization of hydrogen bonds with hydroxyl as the hydrogen donor [1–4]. However, assignment of the OH stretching band in the observed IR spectra is frequently problematic. The potential energy associated with the stretching motion of strongly hydrogen bonded OH groups may be highly anharmonic, leading to profound anharmonicity effects. Substantial anharmonic coupling with other vibrational modes may lead to distribution of the IR intensity over a large number of transitions, resulting in complex band structures covering a wide wavenumber range. In combination with inhomogeneous line broadening, this situation leads to IR bands which are broad and diffuse, and in some cases an OH band may not easily be identified in the experimental IR spectrum [5–9].

Vibrational transitions can frequently be predicted to a high degree of accuracy by quantum chemical calculations in the harmonic approximation, accounting for errors due to neglect of

anharmonic effects and other shortcomings by the application of empirical scaling procedures [10–18]. But these procedures tend to be misleading for strongly hydrogen bonded systems, where an explicit incorporation of anharmonic effects in the theoretical model seems to be required. On the other hand, a proper, multidimensional anharmonic treatment of such systems is extremely demanding, even for a small molecule like malonaldehyde enol (see f.inst. the recent studies by Bowman [19] and Suhm [20] and their co-workers). Szczepaniak et al. [21] introduced a simplified but remarkably efficient anharmonic analysis in their study of picolinic acid *N*-oxide, but unfortunately, general application of this procedure is not straightforward.

One attractive possibility is application of the fully automated second-order perturbation theoretical (PT2) approach developed by Barone [22], Carboniere et al. [23] and available in recent versions of the Gaussian software package [24] (option Freq = Anharmonic). The present paper presents the results of an application of this approach for a large number of intramolecularly hydrogen bonded systems, covering the range from weak to strong hydrogen bonds. OH stretching wavenumbers are predicted in the harmonic as well as in the PT2 anharmonic approximation for the following series of compounds: Salicylaldehyde (**1**), 2-hydroxyacetophenone (**2**), salicylate (**3**), methyl salicylate (**4**), 2-hydroxybenzamide (**5**), 2,6-dihydroxy-4-methylbenzaldehyde (**6**), 2,6-dihydroxyacetophenone (**7**), methyl 2,6-dihydroxy-4-methylbenzoate (**8**), 1,3,5-triacetyl-2,4,6-trihydroxybenzene (**9**), 2,2'-dihydroxybenzophenone (**10**), anthralin (**11**), 2-acetylcyclohexanone enol (**12**), dehydracetic acid (**13**), 5-acetyl Meldrums acid (2,2-dimethyl-5-acetyl-1,3-diox-

* Corresponding authors. Tel.: +45 46742710; fax: +45 46743011 (J. Spanget-Larsen), tel.: +45 46742432; fax: +45 46743011 (P.E. Hansen).

E-mail addresses: spanget@ruc.dk (J. Spanget-Larsen), poulerik@ruc.dk (P.E. Hansen).

ane-4,6-dione enol (**14**), malonaldehyde enol (**15**), nitromalonaldehyde enol (**16**), acetylacetone enol (**17**), dibenzoylmethane enol (**18**), (*o*-hydroxybenzoyl)benzoylmethane enol (**19**), malonamide enol (**20**), nitromalonamide enol (**21**), 2-acetylmalonamide enol (**22**), methanetricarboxamide enol (**23**), 2-cyanomalonamide enol (**24**), usnic acid (**25**), 2-hydroxythioacetophenone (**26**), thioacetylacetone enol (**27**), thiodibenzoylmethane enol (**28**), methanol (**29**), phenol (**30**), and the cage compound (*endo*, *endo*)-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diol (**31**). The assumed molecular constitutions are outlined in Scheme 1. The relationship between the OH stretching wavenumbers predicted in the different approximations is investigated, and correlations with observed wavenumbers are established.

2. Experimental

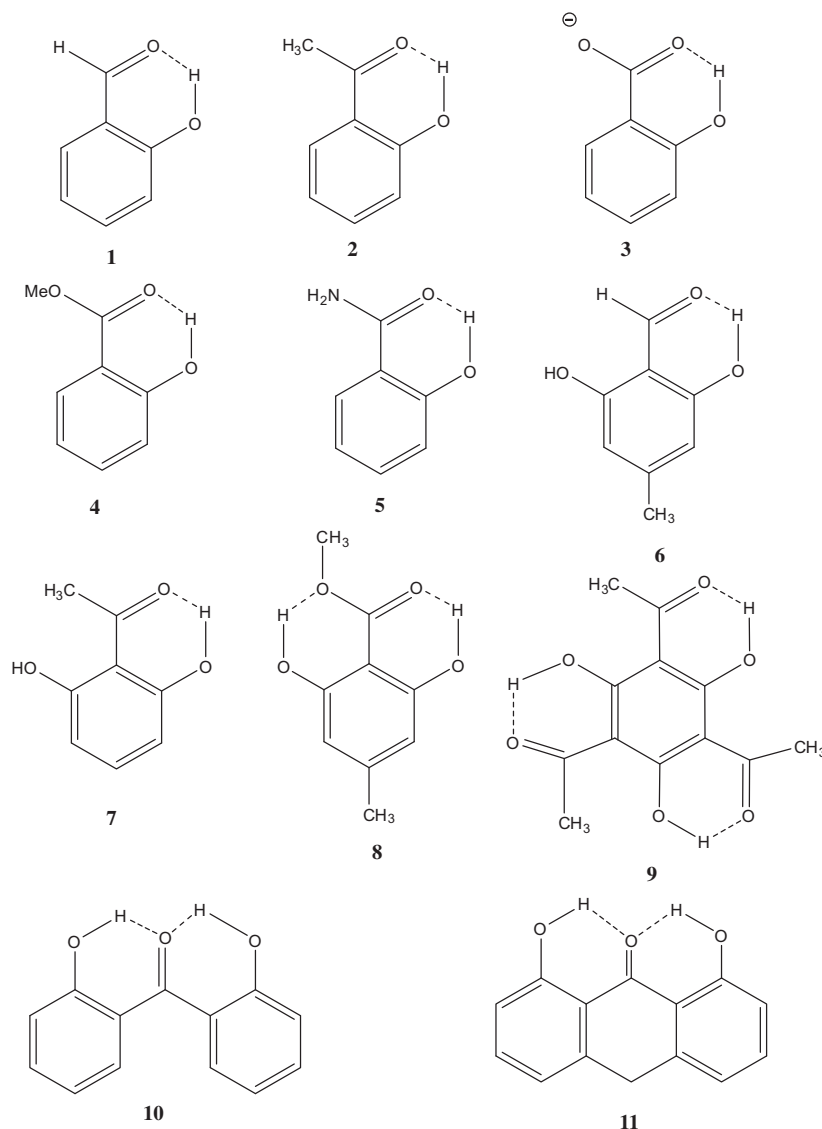
For the purpose of this investigation, the IR absorbance spectra of several compounds were recorded at room temperature on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer in the 4000–370 cm⁻¹ range with a resolution of 1 cm⁻¹ (average of 10 scans). **6**, **7**, **8**, **9**, and **11** were measured in CDCl₃ solution, and solid state KBr tablet spectra were recorded of **13**, **14**, and **21**, by using

standard procedures. **6**, **7**, **8**, **11**, and **13** were obtained from Aldrich; the sample of **11** was purified by column chromatography as previously described [25]. **9**, **14**, and **21** were synthesized and purified according to directions in the literature [26–28].

3. Calculations

All calculations were performed with the Gaussian 09 software package [24]. An initial series of calculations on malonaldehyde enol (**15**) with a variety of density functionals and basis sets indicated that the predicted OH stretching wavenumber depends significantly on the choice of functional and basis set. The results presented in this communication were obtained with the B3LYP [29,30] density functional and the standard basis set 6-31G(d) [24] which is consistent with the recommendations of Barone [22,23] for medium to large molecular systems. The calculations consider isolated molecules in the gas phase.

The molecular equilibrium geometries were determined for configurations with one or more intramolecular hydrogen bonds as indicated in Scheme 1 (phenomena associated with the hydrogen bonds involving NH₂ groups in **21** [31], **22**, and **23** are not a specific target of this investigation). The salicylate anion (**3**) was



Scheme 1. Structures of the compounds considered in this study.

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