Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Molecular Structure 741 (2005) 19–29

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Strong coupling effects in the polarized IR spectra of the chain hydrogen bond systems in 3-pyridinealdoxime and 4-pyridinealdoxime crystals: H/D isotopic *self-organization* effects in the IR spectra

Henryk T. Flakus*, Anna Michta

Institute of Chemistry, University of Silesia, 9 Szkolna Street, Pl40-006 Katowice, Poland

Received 21 October 2004; revised 10 January 2005; accepted 12 January 2005
Available online 3 March 2005

Abstract

This paper presents the results of our investigation with the polarized IR spectra of the hydrogen bond in the 3-pyridinealdoxime and 4-pyridnealdoxime crystals, and also in the crystals of the deuterium derivatives of these two compounds. In each case these spectra were measured for the two different crystalline faces at room temperature and at 77 K by a transmission method, using the polarized light. Theoretical analysis of the results concerned linear dichroic effects, and the H/D isotopic and temperature effects, observed in the solid-state IR spectra of the hydrogen and the deuterium bond, at the frequency ranges of the $\nu_{\text{O–H}}$ and the $\nu_{\text{O–D}}$ bands. Basic spectral properties of the crystals can be interpreted in a satisfactory quantitative way for a hydrogen bond linear dimer model in terms of the '*strong-coupling*' theory. This model explains not only a two-branch structure of the $\nu_{\text{O–H}}$ and the $\nu_{\text{O–D}}$ bands in the crystalline spectra, but also some essential linear dichroic effects in the band frequency ranges, for isotopically diluted crystals. Within the scope of our studies, the mechanism of the H/D isotopic *self-organization* processes (which take place in the crystalline hydrogen bond lattices) was also recognized. It was proved that for isotopically diluted crystalline samples of 3-pyridinealdoxime and 4-pyridnealdoxime, a non-random distribution of the protons and deuterons occurs exclusively in some restricted fragments (i.e. domains) of open chains of the hydrogen bonded molecules. Nevertheless, these co-operative interactions between the hydrogen bonds do not concern the adjacent fragments of the neighboring hydrogen bond chains in the lattice. The electronic structure of these compounds was considered as responsible for such co-operative effects of the hydrogen bonds.

Keywords: Hydrogen bond; Molecular crystals; Polarized IR spectra; H/D isotopic effects; Linear dichroic effects; Temperature effects; Model calculations; Isotopic dilution; H/D isotopic *self-organization* effects

1. Introduction

Infrared spectroscopy is still considered to be the most powerful tool for the hydrogen bond research. In this area the unique properties of the high-frequency $\nu_{\text{X–H}}$ bands, generated by the proton stretching vibrations in the X–H$\cdots$Y hydrogen bonds, are the subject of interest of many researchers, equally of theoreticians and experimentalists [1–5]. These bands are considered as the main attribute of the hydrogen bond, formed in molecular systems [1–5]. Theoretical models developed to quantitatively interpret the IR spectra of the hydrogen bonds, namely the so-called *strong-coupling* theory [6–8], which is the older one, and the most recent *relaxation* theory [9–12], see the source of these effects in anharmonic couplings, which involve the proton stretching vibrations and the low-energy X$\cdots$Y bond stretching vibrations. A unique dynamics of the hydrogen bridge atoms is considered by the two quantitative theoretical models, as responsible for the basic spectral properties, not only for single hydrogen bonds, but also for the simple aggregates like, e.g. the hydrogen bond dimers. Even for these latter systems, characterized by a relatively low degree of complexity, not an entire spectral behavior seems to be understood [6,7,10–16]. However, the greatest challenge in this area was to deliver the adequate theories, enabling description of the coupling mechanism in the hydrogen bond systems which are more complex than

---

* Corresponding author. fax: +48 32 2599 978.
E-mail address: flakus@ich.us.edu.pl (H.T. Flakus).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.01.043

dimers, the molecular crystals included. From these models the fine structure patterns of the ν_{X-H} and the ν_{X-D} bands in the crystalline spectra could be quantitatively interpreted.

The IR spectroscopy of hydrogen bonded molecular crystals in a polarized light seems to be the most promising experimental method for studying the diverse aspects of inter-hydrogen bond interactions in crystals. Measurements of the polarized IR spectra of spatially oriented hydrogen bond systems in the lattices of molecular crystals can deliver the data, allowing to estimate the vibrational transition moment directions to the excited states of the proton vibrations in the crystals, and also the symmetry of the proton vibration exciton states.

The solid state, however, is responsible for a substantial complication of the coupling mechanisms involving the hydrogen bond atom vibrations, thus implying a considerable growth in difficulty, when interpreting the hydrogen bond vibrational spectra of crystals. Therefore, elucidation of the nature of the inter- and the intra-hydrogen bond interactions, based on the polarized IR spectra, needs solution of a number of theoretical problems within one of the quantitative theoretical models, elaborated for interpretation of the hydrogen bond spectra. Unfortunately, very few researchers have undertaken this challenge so far. Thus, investigations of the polarized IR spectra of the hydrogen bonded molecular crystals, accompanied with an advanced theoretical interpretation, are extremely rare in literature.

Investigation of the polarized IR spectra of the hydrogen bonded crystals, performed in recent years, allowed revealing a number of new and highly non-conventional effects, not only spectral, but also of a thermodynamic nature. To the group of new spectral effects belong the diverse, non-traditional H/D isotopic effects in the IR spectra of the hydrogen bond in crystals [17,18]. A part of the recently revealed effects were considered as manifestation of non-conventional co-operative interactions in the area of the hydrogen bond thermodynamics. The so-called H/D isotopic *self-organization* effects depend on a non-random distribution of protons and deuterons between the hydrogen bridges, in the cyclic and chain systems of associated molecules, or in the mixed systems of the hydrogen and deuterium bonds in crystals [19–22]. Identification of these effects was only possible, when performing a quantitative analysis of the polarized IR spectra of the hydrogen bonded molecular crystals [20–22]. Although the basic principles of the H/D isotopic *self-organization* mechanism have recently been recognized for the cyclic dimeric systems of the hydrogen bonds [23], the nature of these co-operative interactions between the hydrogen bonds needs further intensive studies, especially for the open chain hydrogen bond systems. Spectra of the latter systems not always exhibited the effects, which might confirm a non-random distribution of protons and deuterons in their hydrogen bond lattices (e.g. the alcohol crystals) [20–22,24–26].

In this article we present the results of our studies on the IR polarized spectra of the hydrogen-bonded 3-pyridinealdoxime (**3-PA**) and 4-pyridinealdoxime (**4-PA**) crystals. The X-ray established structures of the both crystals are composed of the infinite *zig-zag*-type open chains of the hydrogen-bonded molecules, which build crystalline lattices [27,28]. Therefore, the two related isomeric molecular systems (their common structural formula is NC_5H_4 –CH =N–O–H) seemed to be the proper models to carry out the studies on the H/D *self-organization* effects in the crystalline hydrogen bond chain systems. Similarity of these two molecular structures might be considered as advantageous and facilitating interpretation of the spectra.

Investigation of the polarized IR spectra of the partially deuterated **3-PA** and **4-PA** crystals should provide valuable information about the H/D isotopic *self-organization* effects in these hydrogen bond chains. Presence, or absence of the linear dichroic effects, differentiating spectral properties of the longer- and the shorter-wave branch of the *residual* ν_{O-H} band, should allow recognition of the hydrogen isotope distribution scheme in the crystalline lattice. The *residual* ν_{O-H} bands in the IR spectra of partially deuterated samples is the attribute of the hydrogen bond protons not replaced by deuterons. Absence of the dichroic effect would indicate a totally random distribution of the protons and the deuterons. On the other hand, if positive identification of polarization effects in the 'residual' ν_{O-H} band were confirmed, it should prove a non-random distribution of the hydrogen isotopes, due to the H/D isotopic *self-organization* effects.

Full understanding of the problem should be preceded by theoretical studies on the generation mechanism of the hydrogen bond spectra for the **3-PA** and **4-PA** crystals. At this stage of our knowledge, investigation of these non-conventional co-operative effects may demand simultaneous developing of theoretical models, useful for quantitative interpretation of the crystalline IR spectra. Spectral studies on the H/D isotopic *self-organization* effects might facilitate solving the nature of the vibrational exciton coupling mechanism, which involves the crystalline hydrogen bonds and is responsible for generation of the fine structure of the ν_{O-H} band.

2. Crystalline structures of 3-pyridinealdoxime and 4-pyridinealdoxime

The **3-PA** crystal is orthorhombic and belongs to the space group $Pna2_1$, $Z=4$, $a=19.014$ c, $b=3.8296$ Å, $c=8.1179$ Å. The O–H···N hydrogen bonded **3-PA** molecules form infinite chains, displayed along the *a* axis, with the hydroxyl group protons attached to the pyridine ring nitrogen atoms [27].

The **4-PA** crystal is orthorhombic and belongs to the space group $P2_12_12_1$, $Z=4$, $a=15.750$ Å, $b=7.434$ Å,