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Strong vibronic coupling effects in polarized IR spectra of the hydrogen bond in *N*-methylthioacetamide crystals

Henryk T. Flakus [a,*], Wioleta Śmiszek-Lindert [a], Katarzyna Stadnicka [b]

[a] *Institute of Chemistry, University of Silesia, 9 Szkolna Street, Pl-40-006 Katowice, Poland*
[b] *Department of Chemistry, Jagiellonian University, 3 Ingardena Street, Pl-30-060 Cracow, Poland*

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Abstract

This paper presents the investigation results of the polarized IR spectra of the hydrogen bond in crystals of *N*-methylthioacetamide. The spectral studies were preceded by the determination of the crystal X-ray structure. The spectra were measured at 283 K and at 77 K by a transmission method, using polarized light. Theoretical analysis of the results concerned the linear dichroic effects, the H/D isotopic and temperature effects, observed in the solid-state IR spectra of the hydrogen and of the deuterium bond at the frequency ranges of the $\nu_{\mathrm{N-H}}$ and the $\nu_{\mathrm{N-D}}$ bands, respectively. The main spectral properties of the crystals can be interpreted satisfactorily in terms of the simple quantitative theory of the IR spectra of the hydrogen bond, i.e., the "*strong-coupling*" theory on the basis of the hydrogen bond centrosymmetric dimer model. The spectra revealed that the strongest vibrational exciton coupling involved the closely spaced hydrogen bonds, each belonging to a different chain of associated *N*-methylthioacetamide molecules. The crystal spectral properties, along with an abnormal H/D isotopic effect in the spectra, were found to be strongly influenced by vibronic coupling mechanisms in these dimers. These mechanisms were considered as responsible for the activation in IR of the totally symmetric proton stretching vibrations in the dimers. On analyzing the spectra of isotopically diluted crystalline samples of *N*-methylthioacetamide, it was proved that a non-random distribution of the protons and deuterons took place in the hydrogen bond lattices. In an individual hydrogen-bonded chain in the crystals distribution of the hydrogen isotope atoms H and D was fully random. The H/D isotopic "*self-organization*" mechanism, of a vibronic nature, involved a pair of hydrogen bonds from a unit cell, where each hydrogen bond belonged to a different chain of the associated molecules.

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1. Introduction

For over six decades the infrared spectroscopy has constituted a mighty tool in the field of hydrogen bond research. IR spectra provide an ample source of information about the physical–chemical properties of the hydrogen bonds, mainly on the complex dynamics of these systems [1–4]. Major problems and difficulties in obtaining a full information about the hydrogen bonds based on the IR spectra, are related with the comprehension of the interaction mechanisms taking place inside the hydrogen bonds, as well as among them, in associated molecular systems. This concerns fine mechanisms of dynamical coupling between motions of nuclei and electrons in single hydrogen bonds and in their larger, mutually coupled systems. The mechanisms of the dynamical coupling have been considered as a basic source of the unique IR spectral properties of the hydrogen bond [5].

So far, two quantitative theories of the IR spectra of hydrogen bond have been elaborated: (i) the "*strong-coupling*" theory [6–8] and the newer one, so-called "*relaxation*" theory [9–11]. Both main theories represent a purely

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

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vibrational approach to the problem of the description of the spectral properties of the hydrogen bond. Their source is found in the strong anharmonic coupling mechanisms of the hydrogen bonded system normal vibrations, characterized by different frequencies. The basic mechanism of the coupling in the X–H…Y hydrogen bridges concerns the high frequency proton stretching vibrations (marked by the symbol ν_{X-H}) and the low-energy X…Y hydrogen bridge stretching vibrations (the vibration symbol $\nu_{X\cdots Y}$). Both theories explain how the anharmonic coupling of the vibrations with different frequencies of atoms forming hydrogen bridge systems determines the fine structure of the ν_{X-H} high frequency bands of the proton stretching vibrations in IR spectra. Inversely, a quantitative analysis of the fine structure of bands ν_{X-H} constitutes the basis for the comprehension of the complex mechanisms of dynamical couplings, characterizing the single hydrogen bond, as well as the hydrogen bond aggregate systems [6–11].

IR spectroscopy in polarized light of hydrogen-bonded molecular crystals plays an important role in the hydrogen bond research. The IR spectra measurements concern the hydrogen bonds systems that are spatially ordered and oriented with respect to the polarization plane of the incident beam of radiation. The spectra obtained in this way can provide an abundant data system on the intra- as well as the inter-hydrogen bond interaction mechanisms. Unfortunately, so far only a few researchers have made a systematic experimental and theoretical research in the field of polarized spectra in the IR range of the hydrogen-bonded molecular crystals. The lack of comprehensive and systematic research in this branch in the nearby past was probably due to the fact that the crystalline state contributes its own new effects to the very complex mechanisms of the hydrogen bond IR spectra generation. It poses some new, serious problems to be solved in the interpretation of the crystalline system spectra, though unmistakable benefits, in spite of the significant benefits this experimental method provides for the oriented monocrystalline samples.

As a result of the intensive research in the field of measurements and the quantitative theoretical interpretation of the hydrogen bond IR spectra of molecular crystals, our knowledge about the hydrogen bond as a natural phenomenon has been expanded markedly. Firstly, the role of vibrational–electronic interactions in the hydrogen-bonded systems and their influence on their spectral properties in IR was noted. One of the consequences of the mentioned vibronic coupling were the spectral effects of the vibrational dipole selection rule breaking for IR transitions, of centrosymmetric hydrogen bonds dimers [12]. As a result of the activity of this kind of coupling mechanisms the totally symmetric proton stretching vibrations undergo spectral activation in IR, e.g. in centrosymmetric carboxylic acid, dimer spectra are responsible for the appearance of the suitable bands connected with the excitation of the proton's totally symmetric vibrations [11–13].

The studies of polarized IR spectra of the hydrogen-bonded molecular crystals allowed us to find a new type of spectral H/D isotopic effects, i.e., the so-called "*self-organization*" isotopic effects. These non-conventional spectral effects were interpreted as a manifestation of a new sort of dynamical co-operative interactions in the hydrogen bond systems in molecular crystal lattices [14]. In some cases, the consequence of these interactions could be a non-random distribution of protons and deuterons between the hydrogen bridges of partially deuterated molecular crystals, having different proton to deuteron concentration ratios. This is most probably the main reason for the appearance of anomalous isotopic dilution effects in the IR spectra of the hydrogen bond in the molecular crystals [14,15].

The H/D isotopic "*self-organization*" effects were observed in the majority of the crystal spectra, exhibiting a lattice structure composed of cyclic dimers of the hydrogen bonds [16], as well as in the case of crystals, whose lattices contain infinitely long chains of the hydrogen bonds [17,18]. In the latter case, the effects of the isotopic dilution point to the various ways of the H/D isotopic "*self-organization*" processes proceed in the lattices of chain-linked systems of the hydrogen bonds. However, their relation with the electronic structure of the associated molecules remains unclear.

An especially large magnitude of the vibronic coupling effects in IR spectra of the hydrogen bond was found for crystals with the N–H…S hydrogen bonds in their lattices. This is undoubtedly due to the electronic properties of the sulfur atoms. According to the results of earlier investigations, the hydrogen bonds with the sulfur atoms as proton acceptors, are characterized by a series of peculiar properties, including highly non-conventional H/D isotopic effects, observed in the IR spectra of the crystalline systems [16]. Regarding the molecular crystals, in which the N–H ⋯ S hydrogen bond centrosymmetric dimers were present in their lattices, strong effects of the vibrational selection rule breaking in their IR spectra were also noticed, referring to the totally symmetric proton stretching vibrations in the dimers [12,16].

In this article, we present the results of our study of the IR polarized spectra of *N*-methylthioacetamide crystals. Due to the molecular structure, the molecules of this compound should associate, forming infinitively long N–H…S hydrogen bond chains. At the onset of our research it was expected that the unique properties of the N–H…S hydrogen bonds in the lattice of these crystals could be a source of some highly irregular H/D isotopic effects in the crystalline spectra. However, it was assumed that some properties of these sulfur-containing hydrogen bonds might also fundamentally influence the energy value magnitude of the dynamical co-operative interactions between these hydrogen bonds in the lattice. They might somehow even change the typical scheme of the course of the H/D isotopic "*self-organization*" processes in the isotopically diluted crystals. Then all these N–H…S hydrogen bond properties would strongly influence the intensity distribution patterns of the ν_{N-H} and ν_{N-D} bands in the crystalline IR spectra.

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