

“Reversal” exciton coupling effect in the IR spectra of the hydrogen bond cyclic dimers; polarized IR spectra of 3-hydroxy-4-methyl-2(3H)-thiazolethione crystals

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Abstract

This paper presents the results of our investigation of the polarized IR spectra of the hydrogen bond in crystals of 3-hydroxy-4-methyl-2(3H)-thiazolethione. These spectra were measured at room temperature and at 77 K by a transmission method using polarized light. The spectral studies were preceded by re-determination of the crystal X-ray structure. Theoretical analysis of the results concerned linear dichroic effects, the H/D isotopic and temperature effects observed in the solid-state IR spectra of hydrogen and deuterium bonds at frequency ranges of the $\nu_{\text{O-H}}$ and the $\nu_{\text{O-D}}$ bands, respectively. Basic spectral properties of the crystals can be interpreted satisfactorily in terms of the “strong-coupling” theory, when based on a hydrogen bond dimer model. This model sufficiently explains not only the two-branch structure of the $\nu_{\text{O-H}}$ and the $\nu_{\text{O-D}}$ bands and the temperature-induced evolution of the crystalline spectra, but also the linear dichroic effects observed in the band frequency ranges. A vibronic mechanism responsible for promotion of the symmetry forbidden transition in the IR for the totally symmetric proton stretching vibrations in centrosymmetric hydrogen bond dimers was analyzed. The crystal spectral properties were successfully interpreted on assuming a “reversal” Davydow-splitting effect expressed by changing of the vibrational exciton interaction energy sign for hydrogen bond dimers in the lattice. These effects were ascribed to a considerable elongation of the dimeric O–H...S bonds in the crystal due to the large atomic radius of sulfur determining the dimer geometry.

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1. Introduction

For many years, infrared spectroscopy has been considered to be a powerful tool in the area of hydrogen bond research. IR spectra of hydrogen bond systems provide an abundant source of information about physical and chemical properties of hydrogen bonds, mainly about the complex dynamics of these systems [1–4]. The crucial problems in providing a complete data system about hydrogen bonds on the basis of polarized IR spectra are connected with a deeper understanding of the coupling mechanisms, both of intra- and inter-hydrogen bonds, in the associated molecular systems. This mainly concerns the subtle dynamical coupling mechanisms involving atomic and

also electronic movements in single hydrogen bridges and also in coupled hydrogen bonded systems like simple molecular aggregates, or even molecular crystals. The above mentioned dynamical coupling mechanisms are considered as the basic source of the unique spectral properties of hydrogen bonds in the IR frequency range [5].

Two quantitative theoretical models of IR spectra of hydrogen-bonded systems have been published so far: (i) the “strong coupling” theory [6–8] and the novel one; (ii) the so-called “relaxation” theory [9–13]. Both theories represent a pure vibrational approach to the formal description of spectral properties of hydrogen bonds. In the two models the source of the hydrogen bond spectra generation is attributed to the strong dynamic anharmonic coupling of the hydrogen bond normal vibrations characterized by different frequencies. The basic coupling mechanism in the X–H...Y hydrogen bond involves the high-frequency protonic stretching vibrations (labeled by

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the ν_{X-H} symbol) and the low-energy hydrogen bond $X \cdots Y$ stretching vibrations (denoted by the $\nu_{X \cdots Y}$ symbol). These theoretical models explain how the anharmonic coupling of different frequency vibrations determines the fine structure pattern of the high-frequency proton stretching vibration bands ν_{X-H} , in IR spectra of hydrogen-bonded molecular systems. Whereas a quantitative analysis of the fine structure pattern of the ν_{X-H} band enables the understanding of the complex hydrogen bond dynamics, which characterizes both single hydrogen bonds and more complex hydrogen bond aggregates.

In spite of a thorough elaboration of these two sophisticated theoretical models aimed at a quantitative description of the hydrogen bond system spectral properties, some effects observed in IR spectra of even such simple hydrogen bonded complexes as cyclic centrosymmetric dimers still remain unexplained. This could be connected with some mechanisms governing the hydrogen bond dynamics, which are beyond the reach of these two models. On the other hand, over the last four decades these two theoretical approaches have succeeded in interpreting a number of hydrogen bonded dimeric system IR spectra. These advanced theoretical models have inspired a fast development of new, effective experimental methods in the hydrogen bond research.

A great future role in the hydrogen bond research is attributed to the IR spectroscopy in a polarized light of hydrogen bonded molecular crystals. When applying this method to measuring the crystalline spectra, the linearly polarized infrared beam interacts with spatially oriented hydrogen bond systems of a crystalline lattice. The spectra obtained in this way can provide complete information concerning the interaction mechanisms, both acting in the inter- and intra-hydrogen bond systems. On the other hand, not many researchers have undertaken systematic experimental and theoretical studies concerning the measuring and interpreting of polarized IR spectra of hydrogen bonded molecular crystals. Over the past decades, the lack of broad and systematic studies in this field was probably due to the fact that the solid-state was responsible for the occurrence of some new sub-mechanisms, contributing to the basic complex mechanism of the IR spectra generation for hydrogen bonded systems. Recognition of these non-conventional effects gives rise to new, significant problems to be solved in the IR crystal spectra interpretation, despite the unquestionable advantages resulting from the measuring of the polarized IR spectra of the hydrogen bond in molecular crystals.

The quantitative theoretical interpretation of the polarized IR spectra of hydrogen bonds in molecular crystals may extend our knowledge about hydrogen bond as a natural phenomenon. Firstly, one has to emphasize the role of vibronic interactions in hydrogen bonded systems and of their influence on spectral properties of the system in the IR frequency range. One of these effects, related to the above mentioned vibronic coupling, is the breaking of the vibrational dipole selection rules for IR transitions in the case of centrosymmetric dimeric systems of hydrogen bonds [14]. This type of coupling mechanism is responsible for the activation of the excitation of the transition in IR, leading to the totally symmetric proton stretching

vibration excited state in centrosymmetric dimers of hydrogen bonds. As a consequence, some new bands in the IR spectra corresponding to this excitation may appear [14,15]. Such an effect has been found in many dimeric hydrogen bonded systems, for instance, in IR spectra of carboxylic acid dimeric systems [16–19].

Another non-conventional spectral behavior, revealed when investigating the polarized IR spectra of hydrogen-bonded molecular crystals, is a new kind of H/D isotopic effects the so-called H/D isotopic “*self organization*” effects. They were interpreted as a manifestation of relatively strong dynamical cooperative interactions taking place in the hydrogen bond systems of molecular crystals lattices. In some cases, these interactions could be the result of a non-random distribution of protons and deuterons between hydrogen bridges in molecular crystals. This distribution is characterized by a wide variation range of the deuterium substitution rates in the hydrogen bonds. In these circumstances the abnormal spectral effects of isotopic dilution in hydrogen bonded molecular crystal spectra may appear [20–22].

The so-called H/D isotopic “*self-organization*” effects were observed in the IR spectra of molecular crystals with hydrogen bond cyclic dimers as lattice structural units [15–19] and in molecular crystals characterized by infinite open chains of hydrogen bonds in their lattices [23–26]. In the latter case the observed isotopic dilution effects in crystalline spectra suggested that different paths of the H/D isotopic “*self-organization*” might appear in the lattices formed by hydrogen bonded chains, depending on the electronic structure of the associated molecules [23–26].

A surprisingly large magnitude of vibronic coupling effects, observed in the IR spectra of hydrogen bonds was revealed when investigating the polarized spectra of N–H \cdots S hydrogen bonds in lattices in some molecular crystals. These effects were undoubtedly connected with the electronic properties of the sulfur atoms. The results of earlier studies showed that hydrogen bonds, involving the sulfur atoms as acceptors of protons, are characterized by a number of specific properties. Among them were some non-conventional H/D isotopic effects observed in the IR spectra of the crystal system [15]. In the case of IR spectra of crystals characterized by cyclic dimers of N–H \cdots S hydrogen bonds in their crystal lattices a strong vibrational selection rule breaking was also observed responsible for the activation of the excitation of the totally symmetric proton stretching vibrations [14,15].

In this article we present the results of our studies of the polarized IR spectra of 3-hydroxy-4-methyl-2(3H)-thiazolethione (3H4MTT) crystals. In the solid-state molecules of this compound associate, forming centrosymmetric dimers, were linked by relatively long O–H \cdots S hydrogen bonds. When starting these studies it was expected that the unique properties of the O–H \cdots S hydrogen bonds in the crystal lattices might be the source of strong vibronic effects, as well as of some non-conventional H/D isotopic effects, substantially influencing IR spectra of the crystals. Moreover, we realized that properties of the sulfur atom containing hydrogen bonds could considerably effect the energy value of dynamical

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