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Investigation of Polarized Infrared Spectra of the Hydrogen Bond in Molecular Crystals. New Spectral Effects in the Vibrational Spectroscopy of Hydrogen Bonded Systems

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A review of the experimental as well as of the theoretical studies, performed on the area of the infrared spectroscopy of hydrogen bonded molecular crystals, is given. Discussion of some physical phenomena is presented, responsible for basic spectral effects registered in the infrared spectra, as breaking of vibrational dipole selection rules in the IR spectra, linear dichroic as well as temperature effects, observed in the frequency range of the proton stretching vibrations. Also some newly recognized H/D isotopic effects for hydrogen bonded systems are presented, deduced from a quantitative analysis of the polarized spectra in the IR, namely the so called isotopic "*self-organization*" effects and the "*long-range*" H/D isotopic effects.

Key words: hydrogen bond, molecular crystals, polarization spectra in the IR, model calculations, band shape analysis, H/D isotopic effects, linear dichroism effects, temperature effects, Fermi resonance, H/D isotopic "*self-organization*" effects, "*long-range*" H/D isotopic effects

1. Introduction

Studies of the hydrogen bond have lasted more than 70 years. During this time a large number of articles have been published, concerning investigations performed with the use of diverse research methods, starting from methods of the classical physical chemistry and ending on advanced spectroscopic methods. Based on these studies, theoretical models were subsequently proposed, aiming to explain not only the hydrogen bond nature, but also mechanisms of generation of some effects, observed in the IR spectra of hydrogen bonded systems [1–5]. On the other hand, the progress in the theory has inspired a further development of the hydrogen bond research.

Experimental data obtained by IR spectra of hydrogen bonded systems are of particular importance, when investigating fine mechanisms of inter-hydrogen bond interactions in associated molecular systems. Familiar spectral effects in the IR spectroscopy, attributed to the hydrogen bond, allowed considering this kind of spectroscopy as a powerful tool in the hydrogen bond research [1–5]. These effects basically depend: (i) on a considerable low-frequency shift of $\nu_{X\text{-}H}$ bands, generated by excitation of the proton stretching vibrations in hydrogen bonds, (ii) on a considerable increase of the band integral intensities (even by 2 orders of magnitude) and (iii) on a band widening, very often accompanied by band fine structures [1–3].

Subsequently developed theories of IR spectra of the hydrogen bond were confronted with the necessity of explanation of the source of the basic spectral effects, attributed to hydrogen bonds. In the vibrational spectroscopy the fine structure of $\nu_{\text{X-H}}$ bands is of main interest, as all the modern theoretical models have considered it as closely connected with the hydrogen bond atom dynamics, not only in single hydrogen bonds but also in hydrogen bond aggregates [1–4]. In recent years many theories for interpretation of spectral properties appeared, however, in our review we are going to restrict ourselves to most recent models, which can quantitatively interpret the fine structures of IR spectra of hydrogen bond systems. The Stepanov theory allowed for the first time to understand the mechanism of the $\nu_{\text{X-H}}$ band generation, proposing a scheme qualitatively resembling the Franck-Condon principle for forming band vibrational structure patterns in electronic spectra of molecules [6–8]. This approach essentially influenced the understanding of the very nature of the $\nu_{\text{X-H}}$ band contour forming mechanism in the IR spectra. In the Stepanov theory, the role of the quick motion was played by the proton stretching vibrations, that determined the potential energy for the low-energy stretching vibrations of the hydrogen bridge X....Y [6–8]. Similarly as for the Franck-Condon model, optical transition occurs between vibrational levels of these two coupled motions, belonging to two potential curves, mutually shifted not only vertically, but also horizontally. This approach became a starting point to other latter and more sophisticated theoretical models, able to interpret satisfactorily quantitatively the band fine structure pattern. In this way these theoretical models were helpful in elucidation of fine mechanisms of dynamic interactions in hydrogen bond systems.

The first quantitative theory of the hydrogen bond IR spectra, the so-called "*strong-coupling*" theory, was presented in the mid 60-ties [9,10]. This theory has treated the vibrational motions of the $\nu_{\text{X-H}}$ high and the $\nu_{\text{X....Y}}$ low frequency as strongly anharmonically coupled, but separable in the spirit of the adiabatic approximation of Born-Oppenheimer [11]. Such an approach allows for, at least semi-quantitatively, explaining not only the spectra of systems characterized by single hydrogen bonds, but also the spectra of simple hydrogen bond aggregates, like in carboxylic acid dimers formed in the gaseous phase, along with reproduction of the H/D isotopic effects in the spectra [9,10,12–14]. However, when analyzing numerical reproduction of experimental spectra, performed in the limits of the "*strong-coupling*" model, some doubts might appear, concerning the precision of the band contour simulation routines. This was because of the band calculation procedure, assuming that each elementary transition subband, participating in the $\nu_{\text{X-H}}$ and the $\nu_{\text{X-D}}$ band formation, was represented by the *"delta"-Dirac* function [9,10,12–14]. Other theoretical models, especially stochastic models, developed to interpret diffused spectra of some weak and some medium strength hydrogen bonds, appeared to be rather non-sufficient for interpretation of structured bands, and in this way for resolving of the interaction mechanisms in hydrogen bond systems [15–18].

The state of the art of IR spectrometers in mid 60-ties generally strongly restricted the possibilities of performing advanced spectral experiments, included measurements of polarized crystalline spectra. Therefore, some general doubts remained, whether the experiment and theoretical treatment of the spectra obtained did not loose some essential effects, concerning not only the spectroscopy, but also the physical chemistry of the hydrogen bond.

2. The state of the art of the research on polarized IR spectra for hydrogen bonded crystals at mid 70-ties

Although at the beginning of 70-ties computer aided Fourier-transform IR spectrometers allowed obtaining of IR spectra in much more sophisticated experiments (*e.g.* using polarized light) than those, measured using grating spectrometers of the older generation, only few research groups have answered for this challenge. One of the first trials of experimental studies, aiming to obtain polarized spectra of the hydrogen bond in solid-state samples, were performed by Ratajczak and co-workers at the Wrocław University, when studying effects of ferroelectricity [19,20]. However, much more precise investigations on the hydrogen bond crystalline spectra, performed by Marechal and co-workers in Grenoble, seem to be of particular importance. They carefully studied spectra of selected model hydrogen bonded crystalline systems (of formic and acetic acid crystals and crystals of deuterium derivatives of these compounds) [21–25]. The main aim of their works was to provide most reliable results, helpful in further development of the theory of the IR spectra of hydrogen bonds. Experimental studies of the Marechal group had inspired a series of theoretical works on the area of the IR spectroscopy of hydrogen bonded molecular crystals in the next years.

Investigation of the polarized IR spectra of molecular crystals theoretically might provide some new and decisive results concerning the rules, governing spectral properties of hydrogen bonds. In lattices of hydrogen bonded molecular crystals there may exist a wealth variety of hydrogen bond arrangement patterns, dimeric cyclic systems of hydrogen bonds, as well as the open-chain hydrogen bond systems included. These latest systems do not appear in the gaseous phase.

Measurements of IR spectra performed for spatially oriented molecules of a crystalline lattice, with utilizing of polarized light, might provide highly valuable information about the exciton effects in the spectra, about the complex structure of the measured bands and about the symmetry of the exciton states of a crystal. An optimum choice of proper crystalline system first of all demands a well-developed fine structure of the spectrum of a selected molecular crystal, in the frequency ranges of the $\nu_{X\text{-}H}$ and $\nu_{X\text{-}D}$ bands. Of cause, the X-ray structure of the selected crystal should earlier be known.

Some very serious problems concern theoretical quantitative interpretation of the IR spectra of hydrogen bonded molecular crystals. A successful quantitative interpretation of crystalline spectra most probably needs the developing of theoretical models, in order to incorporate to the theory of the hydrogen bond spectra the influence of interactions between hydrogen bond systems in the solid state. First of all the problem of an influence of the crystal space-symmetry on the vibrational selection rules must be solved. Also some methods of dealing with an infinite number of associated molecules and hydrogen bonds from a crystalline lattice must by solved and some reasonable models of the lattice, restricted to a limited number of hydrogen bonds have to be elaborated. A proper theoretical model for describing of spectral properties of hydrogen bonded molecular crystals should also include some elements of the exciton theory of the solid state.

The first trial of a quantitative interpretation of the IR spectra of monoclinic crystals, with four molecules in the unit cell, hydrogen bonded as two centrosymmetric dimers, was presented by Wójcik [26]. However, this work was restricted to the interpretation of spectra measured in non-polarized light, as no suitable polarized spectra of proper model system were available in that time. Therefore, the theory could not be reliably confronted with the experiment, also because the Dirac "*Delta*"-functions were used for reproduction of the experimental spectra in model calculations.

3. Theory of the hydrogen bond IR spectra for the formic and acetic acid crystals

Next steps in developing of theoretical models for quantitative interpretation of IR polarized crystalline spectra aimed to elaborate a theory, based on the "*strong-coupling*" mechanism [9,10], for interpretation of spectral properties of formic and acetic acid crystals. These crystals, each with four molecules in one unit cell, belong to the orthorhombic system. In this case the hydrogen bonds form infinite open chains. The crystalline IR spectra were measured by Marechal and co-workers [21–25], spectra of deuterium derivatives included.

The theory proposed by Flakus, being an extended "*strong-coupling*" model, took into the account a strong, non-adiabatic anharmonic coupling between the proton vibration in each of the four hydrogen bonds in one unit cell, with the low-energy stretching vibrations of each O....O hydrogen bond. From this model mathematical formulas were derived for the vibrational selection rules in the hydrogen bond crystalline spectra, allowing for a theoretical reconstitution of the experimental spectra. A new way of simulation of the $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ band contour shapes has also been proposed, based on utilizing of the single band shape function of the $(\cosh x)^{-1}$ – type, instead of the Dirac function. It allowed obtaining a more spectacular and a more reliable reproduction of the hydrogen and the deuterium bond spectra, measured for the formic and the acetic acid crystals [27,28]. In these studies an approach in interpretation of "*semi-polarized*" spectra of the formic and the acetic acid crystals was applied, taking into account the fact that the spectra were measured in particular conditions, when non-polarized IR beam was perpendicular with respect to the investigated crystal monocrystalline layer. The model calculation results have shown the adequacy of interpretation of the IR spectra of this kind of hydrogen bonded crystals, based on the "*strong-coupling*" modified theory.

4. Theory of crystalline spectra of dimeric N-H...S bonded systems

Simultaneously performed theoretical studies concerned theoretical interpretation of some highly abnormal spectral effects, mainly some H/D isotopic effects, registered in the spectra of 2-mercaptobenzothiazole and 2-mercaptopyridine (2-thiapyridone) crystals, belonging to the monoclinic and to the orthorhombic systems, respectively [29]. In these crystalline lattices there are four N–H...S hydrogen bonds in each unit cell. A highly non-regular H/D isotopic effect in the spectra, depended on a very strong narrowing of the $\nu_{\text{N-D}}$ band (practically reduced to one narrow spectral line), in relation the $\nu_{\text{N-H}}$ bandwidth, in the spectra of each investigated solid state system [30]. A theoretical model proposed, being a modification of the most recent "*strong-coupling*" theory, assumed a linear dependence of the "*C*" vibrational resonance interaction integral, for the vibrationally excited hydrogen bonds in a cyclic dimer, upon the low-energy totally symmetric stretching vibrations of the hydrogen bonds N–H...S [29] $C = C_0 + C_1 Q_1$, where C_0 and C_1 denote the developing coefficients and Q_1 is the vibration normal coordinate. This approach allowed *via* model calculations to satisfactorily reproduce the $\nu_{\text{N-H}}$ and the $\nu_{\text{N-D}}$ band shapes in the spectra of 2-mercaptobenzothiazole crystals.

Nevertheless, the model calculations performed for the 2-mercaptobenzothiazole crystal hydrogen bond spectra, and also for spectra of some other crystalline systems with cyclic dimers of hydrogen bonds in their lattices, other N–H...S bonded crystals included, have suggested that in this way an unexpected spectral effect has been recognized. It appeared that an almost ideal reproduction of the $\nu_{\text{N-H}}$ band contour was possible only in the one particular case, when making an unorthodox assumption, depending on taking into the account of the forbidden transition to the excited state of the totally symmetric proton vibrations of the A_g–symmetry. Activation of the spectrally forbidden transition was considered as co-responsible for the $\nu_{\text{N-H}}$ band structure generation mechanism.

Model calculations have suggested that the forbidden transition, promoted by a mechanism, non-understood in that time, participated in the band generation mechanism with a comparable probability with the symmetry-allowed transition to the A_u – state. The assumption concerning the vibrational selection rule breaking effect, allowed for numerical reproduction of the longer-wave branch of the $\nu_{\text{N-H}}$ band. Nevertheless, the hypothetical, forbidden transition practically did not participate in the $\nu_{\text{N-D}}$ band generation process. According to these calculations, it appeared to be almost a band connected solely with the allowed transition in the centrosymmetric dimer [29]. The theoretical model, supported by the model calculations, expressed a not fully pronounced idea of an influence of coupling mechanisms between the protonic and the electronic motions in cyclic hydrogen bond dimers, on vibrational dipole selection rules. It also emphasized the necessity of taking into account of the electronic effect on the IR spectra of hydrogen bonds in molecular crystals [29].

In literature concerning IR spectroscopy of the hydrogen bonds, the model calculations performed to interpret quantitatively the polarized spectra of the formic acid, acetic acid and 2-mercaptobenzothiazole crystals were the first and at least partially successful trials in this area of the hydrogen bond research.

5. Vibrational transition selection rule breaking effects in the centrosymmetric hydrogen bond dimer spectra

Further efforts aimed to elaborate a theoretical model able to explain, that time only a hypothetical effect of breaking of vibrational selection rules, in the IR spectra of centrosymmetric dimers of hydrogen bonds. These works were preceded by quantum-chemical calculations, aimed to estimate the influence of the protonic stretching motion on the electron charge distribution in a hydrogen bond [31]. Simultaneously new articles have appeared by Marechal and Auvert, that have experimentally proved a complex nature of the $\nu_{\mathrm{O\text{-}H}}$ and the $\nu_{\mathrm{O\text{-}D}}$ bands in the adipic acid crystal spectra, with the help of spectroscopy in polarized light [32,33]. It appeared, that two easily distinguishable spectral branches in each band differ one with respect another by their dichroic properties and in a different way evaluate with decreasing temperature [32,33]. In this way the hypothesis, concerning a complex structure of the $\nu_{\mathrm{O\text{-}H}}$ band and the promotion of the forbidden transition in the spectra of centrosymmetric hydrogen bond dimers, was strongly supported by the experiment.

The theoretical model of this phenomenon, proposed by Flakus, considered a non-adiabatic vibronic coupling in a centrosymmetric dimer of hydrogen bonds [34]. In a relatively simple mechanism, only the proton stretching vibrations were taken into account, along with the electronic motions in the hydrogen bonds, mainly on the proton-acceptor atom nonbonding orbitals. The vibronic coupling in the dimer was considered in the limits of the Herzberg-Teller model, in its linear term approximation [11]. Also the proton stretching vibration anharmonicity was considered in the model, as well as the resonance interactions between the vibrationally excited hydrogen bonds in the dimer were taken into account. Under these assumptions, a matrix coupling Hamiltonian was derived, related to the excited state of the proton vibrations. A consequence of the vibronic coupling hamiltonian for the dimer was, that due this coupling the proton normal vibrations were not still characterized by precisely defined symmetries, A_g or A_u. Therefore, the vibrational dipole selection rules could be weakened, which seemed to be a very non-conventional effect in the IR spectroscopy. In the consequence the forbidden transition to the A_g excited state might be activated, with its intensity and its dichroic properties "*borrowed*" from the symmetry allowed vibrational transition of the non-totally symmetric proton vibrations in a dimer.

The promotion mechanism of the forbidden transition in the IR may be treated as a "*reversion*" of the familiar Herzberg-Teller mechanism, responsible for activation of the forbidden transition, in the electronic spectra of aromatic molecules [11]. According to the model, the forbidden transition becomes spectrally active, due to the vibronic mechanism, which results in mixing of the dimer protonic normal vibrations of different symmetries [34]. Therefore, the forbidden transition promotion effect could be treated as the first known case in the IR spectroscopy of breaking of the vibrational symmetry based dipole selection rules. In this approach the hydrogen bond IR spectra represent the vibronic effect magnitude case, being an intermediate between that governing the electronic spectra of molecules from the UV and VIS spectroscopy and that estimated from the IR spectra of the majority of non-associated molecules. At this point it seems worth to remind that vibrational spectra of molecules are basically of a vibronic origin. The vibronic model proposed sees this phenomenon as a consequence of the following three coinciding effects: of the polarization of the hydrogen bond electronic cloud in a dimer, by the vibrating protons, of the proton vibration anharmonicity and of the resonance interaction of the dimer hydrogen bonds [34]. This effect has no counterpart in the "*common*" IR spectra of isolated molecules. The vibronic model also succeeded in explaining of the forbidden transition probability diminution in the $\nu_{\text{X-D}}$ bands of the dimeric system spectra. This effect most probably results from a lower deuteron vibration anharmonicity effects for deuterium bonds. Also spectral differences concerning N–H...O and N–H...S bonded dimers were explained by the model, as related to different proton acceptor atom electronic properties, namely to the O and the S atom polarization property differences [29,30,34].

6. Quantitative interpretation of the adipic acid crystal polarized IR spectra

Incorporation of the idea of the symmetry-forbidden transition promotion in the IR to the "*strong-coupling*" theory formalism, allowed interpreting quantitatively the polarized IR spectra of the hydrogen bond in adipic acid crystals [35], along with isotopic, temperature and polarization effects, measured recently by Auvert and Marechal [32,33]. In this way the selection rule breaking effect appeared to be a reliable physical phenomenon in the vibrational spectroscopy of hydrogen bonded molecular crystals, with cyclic centrosymmetric dimers of hydrogen bonds in sites of their lattices.

7. Polarized spectra of hydrogen bonded imidazole crystals

Based on the results of experimental studies performed by Excoffon and Marechal on hydrogen bonded imidazole crystals [36–39], the problem of adequacy of the "*strong-coupling*" mechanism was analyzed, in order to explain the observed in the crystalline spectra extremely strong H/D isotopic and temperature effects. The lattice of the imidazole crystal is formed by infinite, open chains of hydrogen bonded molecules with four molecules and four hydrogen bonds in each unit cell and with the site-symmetry governed by the C_i group. In this case the inversion center operation exchanges imidazole molecules belonging to two adjacent chains. In the imidazole crystal spectra an extremely abnormal H/D isotopic effect was observed, characterized by an extremely strong narrowing of the $\nu_{\text{N-D}}$ band in relation to a wide and complex $\nu_{\text{N-H}}$ band. With regard to this isotopic effect, the imidazole crystals exhibit a similar spectral properties as the previously discussed crystals, with cyclic dimers of the N–H...S bonds in their lattices (2-mercaptobenzothiazole), although in the imidazole crystal cyclic dimers of hydrogen bonds do not exist [29].

For a quantitative interpretation of the imidazole crystal spectral properties an extended theoretical model was proposed, assuming an extremely strong exciton coupling between the hydrogen bonds from an unit cell belonging to two adjacent chains, related by the inversion center operation. A much weaker interaction was assumed for another pairs of the hydrogen bonds from an unit cell, related by the screw-axis or the glide-plane operation. The strongest coupling case was formally expressed by a linear dependence of the resonance interaction integral upon the totally symmetric coordinate of the low-frequency hydrogen bond stretching vibration. The derived "*strong-coupling*" hamiltonian for the four hydrogen bonds contained in the unit cell represented essential spectral properties of the imidazole crystal. It described a non-adiabatic coupling of the proton high-frequency and of the hydrogen bond low-frequency stretching vibrations of the four allowed symmetries A_g, A_u, B_g and B_u, in the four hydrogen bond system. Solving of the matrix eigenvalue equation demanded diagonalization of very large energy matrices, *e.g.* 1001 × 1001. The model calculations allowed for, satisfactory enough reproduction of the experimental spectra of imidazole crystals in the frequency range of the $\nu_{\text{N-H}}$ band, along with the basic H/D isotope effect in the IR spectra, observed in the $\nu_{\text{N-D}}$ band [40–42]. The model calculations also confirmed the presence of the selection rule breaking effects in the spectra of hydrogen bond centrosymmetric dimeric system [40–42].

In addition, the problem of generation of an extremely intense overtone band of the bending "*out-of-plane*" proton vibrations in spectra of imidazole crystals has been solved. Also mechanisms responsible for appearance of the overtone band fine structure and a strong temperature impact on the band intensity was identified [42]. This mechanism was not considered as connected with a typical Fermi resonance, but with a resonance of the proton stretching and the proton "*out-of-plane*" bending vibrations in bent N–H...N hydrogen bonds in the crystal. The source of this resonance could be found in kinematic interactions, due to the "*G*" kinematic coefficient matrix advantageous structure, for non-linear hydrogen bonds [42,43]. Therefore, the overtone band properties were found to be a specific and a purely crystalline spectral effect, as resulting from dynamic interaction between the proton stretching and the proton bending vibrations in the non-axial N–H...N hydrogen bonds in the imidazole crystal.

8. "*Long-range*" H/D isotopic effects in the hydrogen bond IR spectra

A quantitative analysis of the imidazole crystal IR spectra and of the crystalline spectra of its various deuterium isotopomers allowed identifying a new kind of H/D isotopic spectral effects of the hydrogen bond. These effects, *i.e.* the so called "*long-range*" H/D isotopic effects are connected with an influence of the hydrogen or the deuterium atoms, belonging to skeletons of the associating molecules, on the fine structure of the $\nu_{\text{X-H}}$ and the $\nu_{\text{X-D}}$ bands and on their other spectral properties. The analysis concerned the spectra of imidazole deuterium derivative crystals, differing by the number and distribution of deuterium atoms in imidazole molecular skeleton rings. The model calculations have shown that the relative intensity of the longer-wave branch of the $\nu_{\text{N-D}}$ band depends upon the deuterium atom distribution pattern in the imidazole rings. Such effects seemed to be unexpected if based on a totally vibrational hydrogen bond vibration model, in the limits of the theory of normal vibrations by Wilson, Decius and Cross [43]. In this formalism the C–H bond stretching vibrations should not mix with the proton stretching vibrations, due to a non-advantageous structure of the "*G*" kinematic coefficient matrices, with no cross-terms for these two vibrational motions.

To explain the "*long-range*" isotopic effect in the imidazole crystal spectra, a vibronic model was proposed by Flakus and Machelska for describing of centrosymmetric non-cyclic hydrogen bond dimer spectral properties. I this case not only the proton or the deuteron motions couple with electronic movements, but the coupling mechanism also concerns the stretching vibrations of the C–H or the C–D bonds. A dynamic coupling of these latter vibrations with the proton or the deuterium motions is facilitated *via* a coupling with electronic motions on delocalized π orbitals of the imidazole rings. From the derived vibronic model it resulted that when in the hydrogen bonds and in the molecular skeletons are identical hydrogen isotope atoms, the selection rule breaking effects should be the strongest ones. Replacement of subsequent hydrogen atoms weakens the forbidden band promotion mechanism along with the increasing deuterium substitution rate in the imidazole rings [44]. When discussing the deuterium bond spectral properties for he crystal, the forbidden transition probability depends on the symmetry of the deuterium distribution pattern in the molecules. From this it results an appropriate symmetry of the skeleton electronic cloud perturbation, resulting from the totally symmetric C–D bond stretching vibrations, occurring with the participation of the deuterium atoms of these isotopomers [44].

However, in [44] only one kind of "*long-range*" isotopic effects was analyzed, depending on the influence of the hydrogen isotope atoms on the magnitude of the forbidden transition promotion effect, in the IR spectra of centrosymmetric hydrogen bonded dimeric systems. Further studies, mainly experimental ones, have shown that also another "*long-range*" isotopic effect in these spectra, remaining fairly non-regular and therefore non-understandable, influenced the $\nu_{\text{X-H}}$ band fine structures. This statement was justified by a very low number of experimental works, devoted to studies of such H/D isotopic effects.

9. Abnormal effects of isotopic dilution in the spectra of hydrogen bonded crystals

Next problem concerning the hydrogen bond spectral properties appeared quite unexpected. Measurements of IR spectra of dimeric systems of hydrogen bonds in the solid state, for samples of a high deuterium substitution rate in hydrogen bonds, a non-conventional effect was identified, depending on a practical invariance of "*resi-*

dual" $\nu_{\text{X-H}}$ band shapes, accompanying the increasing H/D isotope exchange rate. This effect seemed to contradict totally the contemporary theories of the IR spectra of hydrogen bond in dimers, *i.e.* to the "*strong-coupling*" theory [9,10] and to the "*linear response*" or the "*relaxation*" theory [45–49]. Both theories have connected the shape of the dimeric spectra with vibrational exciton interactions between the hydrogen bonds in dimers. Exciton interactions seemed to be the coresponsible factors for the dimeric $\nu_{\text{X-H}}$ band shape forming mechanism. In monomeric hydrogen bonds exciton interactions vanish, therefore, the spectra of monomer hydrogen bonds should significantly differ from spectra of hydrogen bond dimer systems. Thus, the dimeric spectra should be wider, as in this case the $\nu_{\text{X-H}}$ bands, split due to exciton interactions. However, it must be emphasized that in all the recent studies in the hydrogen bond area, a silent assumption was made that during the H/D isotopic exchange, the hydrogen isotope atoms were fully randomly distributed in the dimer hydrogen bonds. So far there were no arguments against this assumption, as the hydrogen and the deuterium bond energies and many of other properties were estimated to be fairly identical [1–3].

The assumption about the random distribution of hydrogen isotopes was strongly supported by recent studies on the effect of the isotopic dilution of alcohol crystals on their "*residual*" $\nu_{\text{O-H}}$ band shapes [50,51]. At this point it seems worth to add that the crystal lattice of alcohol is formed by infinite open chains of the O–H...O hydrogen bonds. These studies had confirmed on the experimental way and also justified on a basis of a proper theoretical model, the variation of the $\nu_{\text{O-H}}$ band contour shape, accompanying the isotopic dilution of alcohol crystals. The conclusion of these studies was, that the spectra of the hydrogen bond in isotopically diluted alcohol crystals varied in accordance to the model, assuming a random distribution of protons and deuterons in the crystal hydrogen bond chains. Unfortunately, the articles [50,51] influenced for many years the way of understanding of the isotopic effects concerning hydrogen bonds.

Explanation of the observed spectral phenomenon, concerning the isotopically diluted samples, demanded formulation of a hypothesis about a new kind of H/D isotopic effects for the hydrogen bond. In the proposed model it was assumed, that symmetric, cyclic hydrogen bond dimers of the "*HH*" or the "*DD*"-type (with two identical hydrogen isotope atoms) are thermodynamically more stable in comparison with the non-symmetric "*HD*"-type dimers, containing two different hydrogen isotopes. This hypothetical effect might be considered as a new and a specific kind of co-operative effects concerning hydrogen bond systems. It means that in the ground electronic and in the ground proton stretching vibration state, the symmetric dimers of the "*HH*" or the "*DD*"-type are the dominating forms, independently from the H/D isotope exchange rate. Therefore, the "*residual*" $\nu_{\text{X-H}}$ band shapes do not change in conditions of increasing deuteration rate in hydrogen bond dimeric system crystalline samples, for the identical hydrogen and deuterium bond energies of a system. That time this assumption had found no deeper justification in the theory.

Evolution of "*residual*" ν_{N-H} band shapes in the IR spectra of 2-mercaptobenzothiazole crystals (which contain cyclic dimers of N–H...S hydrogen bonds in their lattices), predicted by the model, when assuming a random distribution of protons and deuterons in the dimer hydrogen bonds, is shown in Fig. 1. Based on the "*strong-coupling*" model calculations for 2-mercaptobenzothiazole dimers, evolution of the "*residual*" ν_{N-H} band contour shapes was simulated as a function of an assumed ΔG value (ΔG is the Gibbs thermodynamic potential) for the hydrogen isotope exchange reaction for the dimers: 1/2 "*HH*" + 1/2"*DD*" = "*HD*".

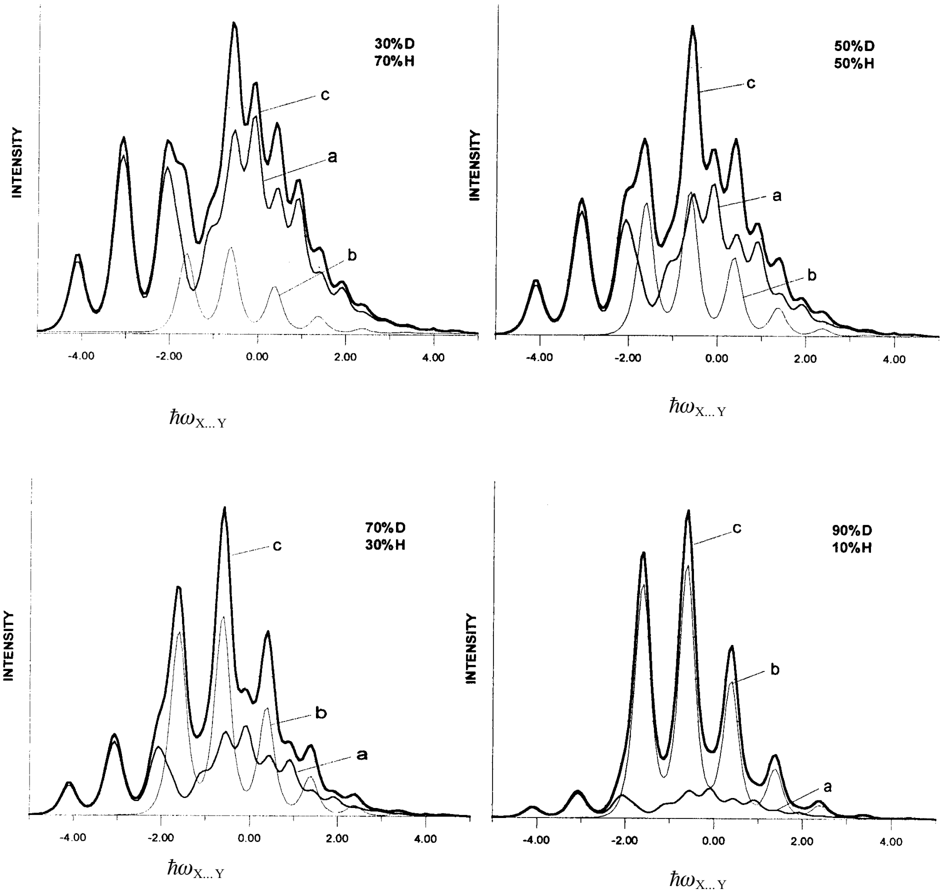


Figure 1. Evolution of the "*residual*" ν_{N-H} band shape for 2-mercaptobenzothiazole dimers accompanying to isotopic dilution, predicted on the basis of the "*strong-coupling*" model. A fully random distribution of protons and deuterons between the dimer hydrogen bonds was assumed [52]:

a. Spectrum of monomer N–H...S hydrogen bonds from 2-mercaptobenzothiazole dimers.

b. The ν_{N-H} band shape from the spectra of 2-mercaptobenzothiazole dimers calculated using the "*strong-coupling*" model, which reproduces the experimental spectrum.

c. Superposition of the "*a*" and "*b*" spectra.

These calculations aimed to estimate such a minimum ΔG value, for which the calculated "*residual*" $\nu_{\text{N-H}}$ band contour remains invariant at room temperature, independently from concentration of deuterons in 2-mercaptobenzothiazole samples. It was found that the lowest ΔG value, fulfilling this demand, was approximately 1.5 kcal, in relation to one mole of the "*HD*"-type dimers [52]. The additional hydrogen bond dimer stabilization energy appeared to be typical for co-operative interaction energies, for mutually interacting hydrogen bond systems [4]. The predicted by model calculation evolution of the "*residual*" $\nu_{\text{N-H}}$ band contour shape in spectra of 2-mercaptobenzothiazole dimers, related with the increasing ΔG value for the isotope exchange relation, is presented in Figs. 2a and 2b.

At this stage the source of these co-operative interactions, called as isotopic "*self-organization*" effects, are undoubtedly dynamic interactions in the dimer hydrogen bonds and not interactions in the static systems. This statement seemed to be justified just by an influence of the hydrogen isotope mass distribution in the dimer on the dynamic co-operative interaction mechanism.

On this stage of studies on isotopic "*self-organization*" effects, the hypothesis has been supported by the model calculations only. Therefore, the mechanism of these interactions could not be resolved precisely at that time. At this point it is worth to add, that the choice of a theory, able to interpret quantitatively the dimeric system spectra, had no basic influence on the model calculation general conclusion. To make the idea of the isotopic "*self-organization*" mechanism more reliable, some precisely and precautionary planed experiments had to be done, in order to confirm the appearance of these co-operative interactions by another method, than solely by model calculations.

The most promising studies, potentially able to deliver a most complete data system concerning this problem, seems to be the IR absorption spectroscopy in polarized light, applied for investigations of thin monocrystalline layers of cyclic dimeric hydrogen bonded systems. Unfortunately, the literature available, concerning the IR spectroscopy of hydrogen bonded crystalline systems, contains data concerning an extremely restricted number of crystals. Nevertheless, even in these cases the problem of the linear dichroism for $\nu_{\text{X-H}}$ band frequency ranges was treated rather marginally, as the aim of these studies was more general [53–56]. Even if the polarized IR spectra were studied for some hydrogen-bonded crystals, the analysis of the linear dichroic effect was restricted rather to the X–H bond orientation impact on the dichroic properties for $\nu_{\text{X-H}}$ bands [53–56]. The analysis performed of the hydrogen bond crystalline spectra was only of a qualitative character, basically not aided by model calculations. In all these cases the dichroic band properties in the entire measured spectra, in the full available range of the mid-IR , were analyzed. Most frequently, a particular attention was paid to the Davydow-splitting effects for each band, which along with the analysis of dichroic properties, supported the vibrational analysis calculations for the molecular systems. The general aim of these investigations of crystalline spectra was not an investigation of polarization, isotopic and temperature effects precisely enough, to obtain some new key data of so high quality, allowing on this basis developing of the theory of IR spectra of hydrogen bonds. Some doubts also

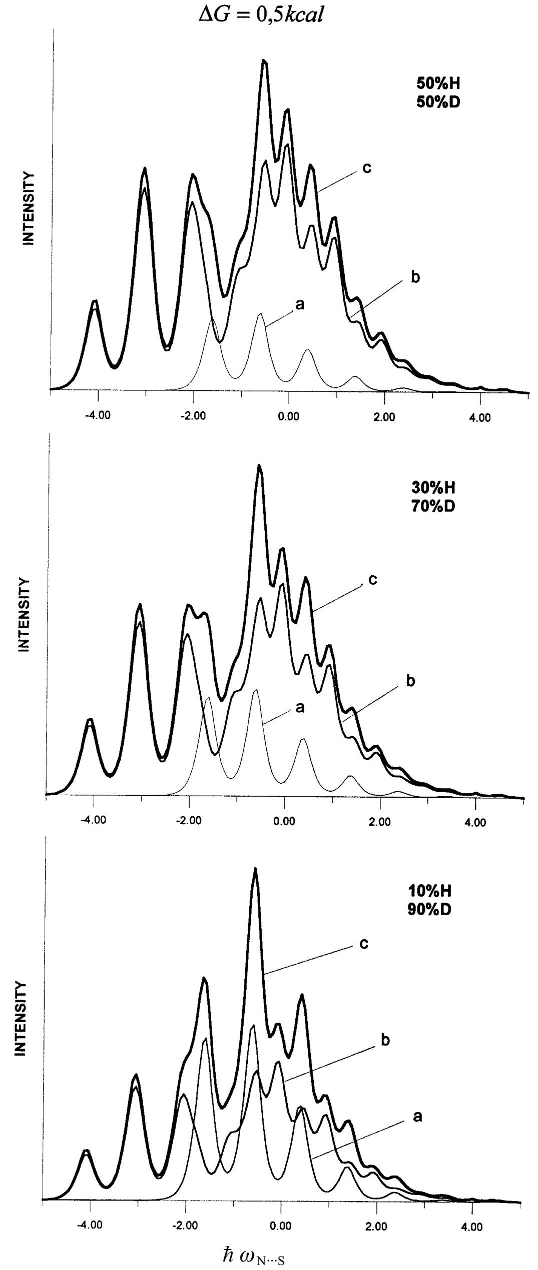


Figure 2a. Evolution of the "*residual*" $\nu_{\text{N-H}}$ band shape for 2-mercaptobenzothiazole dimers when assuming a difference in the "*HH*" and "*HD*"-type dimer hydrogen bond energy, for $\Delta G = 0.5$ kcal. It is easy to notice changes in the "*residual*" $\nu_{\text{N-H}}$ band shape accompanying to the increasing deuterium substitution rate.

appeared when analyzing the choice of crystal systems for studies of the polarized spectra, as their spectral properties seemed to be rather a non-optimum for an advanced research on the interaction mechanism in hydrogen bond aggregate systems. This

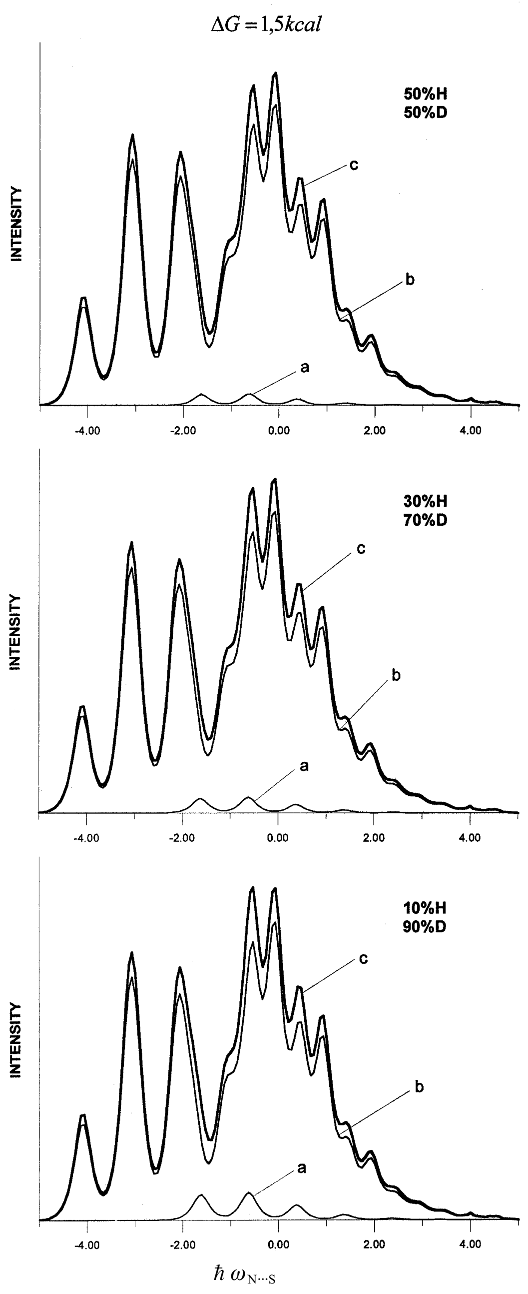


Figure 2b. The result of similar calculations for ΔG = 1.5 kcal. The "residual" $\nu_{N\text{-}H}$ band shape for 2-mercaptobenzothiazole dimers remains unchanged when the H/D isotope exchange rate increases.

statement can be justified by the fact that $\nu_{X\text{-}H}$ and $\nu_{X\text{-}D}$ bands were characterized by rather poor fine structure patterns [53–56]. At this point it also seems worth to add that no review article has appear so far, even in the latest monographs, devoted to experimental studies and to theoretical investigations on polarized IR spectra of hydrogen bonded molecular crystals. This fact seems to be connected rather not with experimental difficulties, when measuring polarized spectra, but with some unsolved theoretical problems, appearing when practically interpreting polarized spectra of hydrogen bonded crystals in a quantitative way.

In the historical view, when investigating the H/D isotopic effects in spectra of the hydrogen bond in molecular crystals, the authors most frequently restricted themselves to measurements of the $\nu_{\text{X-D}}$ bands only. The problem of the "*residual*" $\nu_{\text{X-H}}$ band properties practically found no its counterpart in the published articles. Therefore, it became necessary to perform systematic studies on the problem for a considerably large number of crystalline systems, aiming to obtain their polarized IR spectra for the frequency ranges of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ bands, the "*residual*" $\nu_{\text{X-H}}$ bands included. On this stage of studies it was unknown, whether the isotopic "*self-organization*" effects are the attribute of cyclic, dimeric systems of hydrogen bonds, or in contradiction to the results of recent works [50,51], these effects also concerned to open-chain hydrogen bond systems. The "*residual*" $\nu_{\text{X-H}}$ band term means the $\nu_{\text{X-H}}$ band measured for non-totally deuterated samples.

The problem of the mechanism of the isotopic "*self-organization*" effects for cyclic hydrogen bond dimers found last time its solution. These co-operative effects result from the hydrogen bond dynamics in the dimers. The additional stabilization energy of symmetric cyclic hydrogen bond dimers of the "*HH*" or the "*DD*"-type results from the Herzberg-Teller vibronic coupling between the totally symmetric proton vibrations, with the electronic motions in the dimers. These strongly anharmonic proton vibrations were found responsible for an additive effective polarization of the electronic cloud of the dimer hydrogen bonds and thus an additive bonding effects might appear for symmetric dimers. It was proved that the proton and the deuteron vibrations, in non-symmetric dimers of the "*HD*"-type, are unable to introduce such contribution to the energy of hydrogen bonds [57].

10. Systematic experimental studies on polarized IR spectra of hydrogen bonded molecular crystals

During last four years Flakus and co-workers investigated polarized IR spectra of about forty hydrogen bonded crystalline systems. Among them crystals with centrosymmetric, cyclic dimers of hydrogen bonds made *ca*. 60%. The other crystals contained infinite open chains of hydrogen bonds in their lattices. In each case the deuterium-bonded derivative was synthesized and crystal spectra for this isotope derivative were measured. Spectra were recorded at room temperature and at temperature of liquid nitrogen. The crystals were selected and the experimental results were analyzed under the scope of the following aims:

1. Investigation of the vibrational selection rule breaking effects in the hydrogen bond spectra, for crystals containing cyclic hydrogen bond dimers in their lattices. Mea-

surements of small differences in dichroic properties between the longer and the shorter branches of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ bands in the spectra.

2. Experimental studies on the isotopic "*self-organization*" effects in the spectra of isotopically diluted crystals, for systems with cyclic hydrogen bond dimers in their lattices. Similar studies for crystals of structure formed by infinite open chains of hydrogen bonds were also planed.
3. Estimation of the model calculation adequacy for the quantitative interpretation of hydrogen bond spectra of molecular crystals in the frequency ranges of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ bands.
4. Investigation of H/D "*long-range*" isotopic effects in IR spectra of hydrogen bonded crystals.
5. Analysis of the influence of electronic properties of associating molecules on the IR hydrogen bond spectra of crystals. Studies on coupling effects concerning hydrogen bond protons and the aromatic ring electrons.
6. Experimental studies on temperature induced evolution of IR spectra of the hydrogen bonds in crystals.

10.1 Studies on the vibrational selection rule breaking effect

Based on the results of investigations of polarized IR spectra performed for *ca.* 25 crystalline systems, containing cyclic hydrogen bond dimers in their lattices, the breaking effects of vibrational dipole selection rules appeared to be a common property of the spectra. In each case a better or worse pronounced two-branch structure of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ bands was observed with an individual intensity ratio of the two branches of a band for each crystal [58–63]. A complex structure of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ bands found its additional confirmation in slight polarization effect, differentiating the spectral properties of each band spectral branches in a small, but measurable degree [32,33,58–65]. The selection rule breaking effect appeared to be temperature sensitive, which was most probably connected with defects in the lattices, generated when the crystallization from melt was chosen as the method of growing crystals suitable for the spectral experiment [35]. The forbidden transition effect promotion magnitude appeared to be strongly dependent on electronic properties of the associating molecules. This statement can be illustrated by the following examples. In the spectra of aromatic acid crystals (benzoic acid, 1- and 2-naphthoic acid) the longer-wave branch of the $\nu_{\text{O-H}}$ bands is characterized by an extremely high intensity, when compared with the longer-wave branch properties [61,66]. Separation of the carboxyl groups from aromatic rings by methylene groups (phenylacetic acid, 1- and 2-naphthylacetic acids) results in a decrease by 3–4 times of the longer-wave branch of these bands [63,68]. Surprisingly, for trans-cinnamic acid, with carboxyl group separated from the phenyl ring by the -CH=CH- group, the longer-wave branch is very intense, similarly like in the spectra of benzoic acid crystals [61,69]. It also appeared that electronic properties of the proton acceptor atoms effect the magnitude of the forbidden transition promotion effect in spectra of hydrogen bond dimeric systems. It was found that for dimers linked by N–H...S bonds (2-mercaptobenzothiazole) the symmetry forbidden longer-wave branch of the $\nu_{\text{N-H}}$ band was about three times more intense than the respective branch of the $\nu_{\text{N-H}}$ band in spectra of dimers with N–H...O hydrogen bonds (2-hydroxybenzothiazole) [62]. In all the cases the observed spectral effects, connected with breaking of the selection rules for all investigated crystalline systems, remain in a good agreement with predictions of the theoretical model of this phenomenon [34]. In Figs. 3a and 3b polarized spectra of hydrogen bonded crystals of

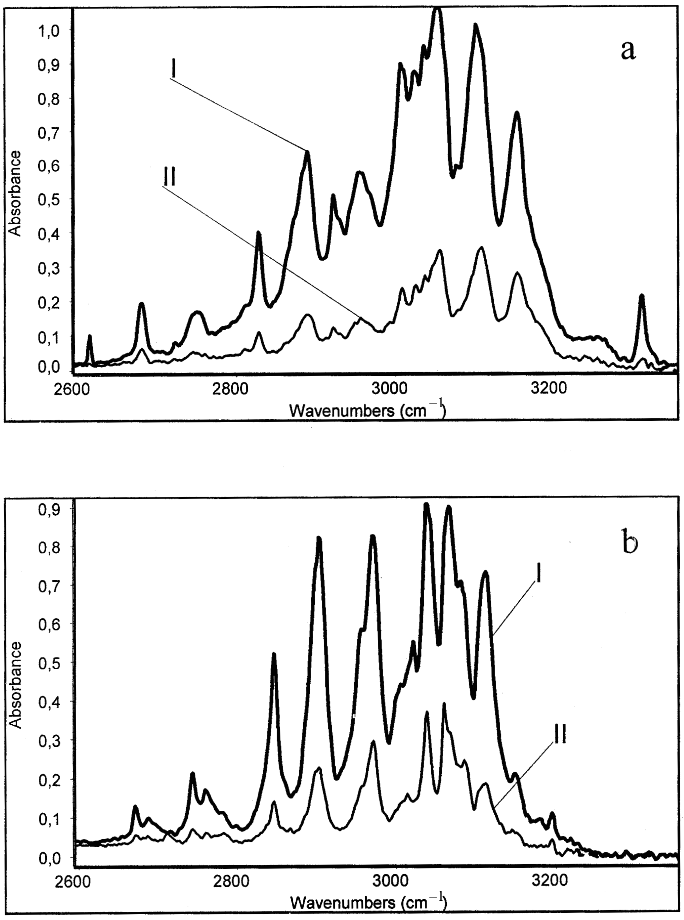


Figure 3a. The polarized spectra of 2-hydroxybenzothiazole and 2-mercaptobenzothiazole crystals measured at 77 K in the $\nu_{\text{N-H}}$ band frequency range, taken from [62]:

a. Spectra of the 2-hydroxybenzothiazole crystal. The IR beam of normal incidence with respect to the "*ac*" plane was used. The component spectra were obtained for the two orientations of the electric field vector *E*:

(I). *E* parallel to the "*a*" axis,

(II). *E* perpendicular to the "*a*" axis (parallel "*c**" axis).

b. Spectra of the 2-mercaptobenzothiazole crystal. The beam of normal incidence with respect to the "*ab*" crystalline face.

(I). *E* parallel to the "*b*" axis,

(II). *E* perpendicular to the "*b*" axis (parallel to the "*a*" axis).

Spectra (I) and (II) were drawn on a common scale.

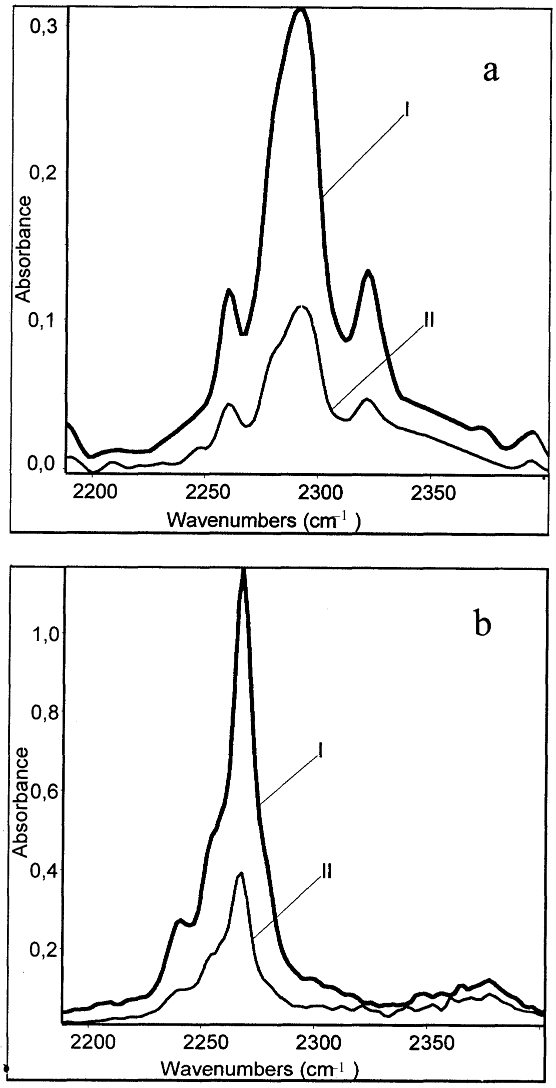


Figure 3b. The $\nu_{N\text{-}D}$ bands in the polarized crystalline spectra of the deuterium derivatives of 2-hydroxybenzothiazole (HBT) and 2-mercaptobenzothiazole (MBT) crystals measured at 77 K [62]. Other experimental conditions and the presentation of the spectra are identical to those given for Fig. 3a.

2-hydroxybenzothiazole and 2-mercaptobenzothiazole have been presented, characterized by an extremely strong H/D isotopic effect [62].

In Figs. 4a and 4b the results of model calculations, aiming to reconstitute the $\nu_{N\text{-}H}$ and $\nu_{N\text{-}D}$ band structures, based on the "*strong-coupling*" model, have been shown [62]. These results strongly support the hypothesis concerning the forbidden transition activity as co-responsible in generation of the $\nu_{N\text{-}D}$ band fine structure. The forbidden transition sub-band is absent in the $\nu_{N\text{-}D}$ band contours.

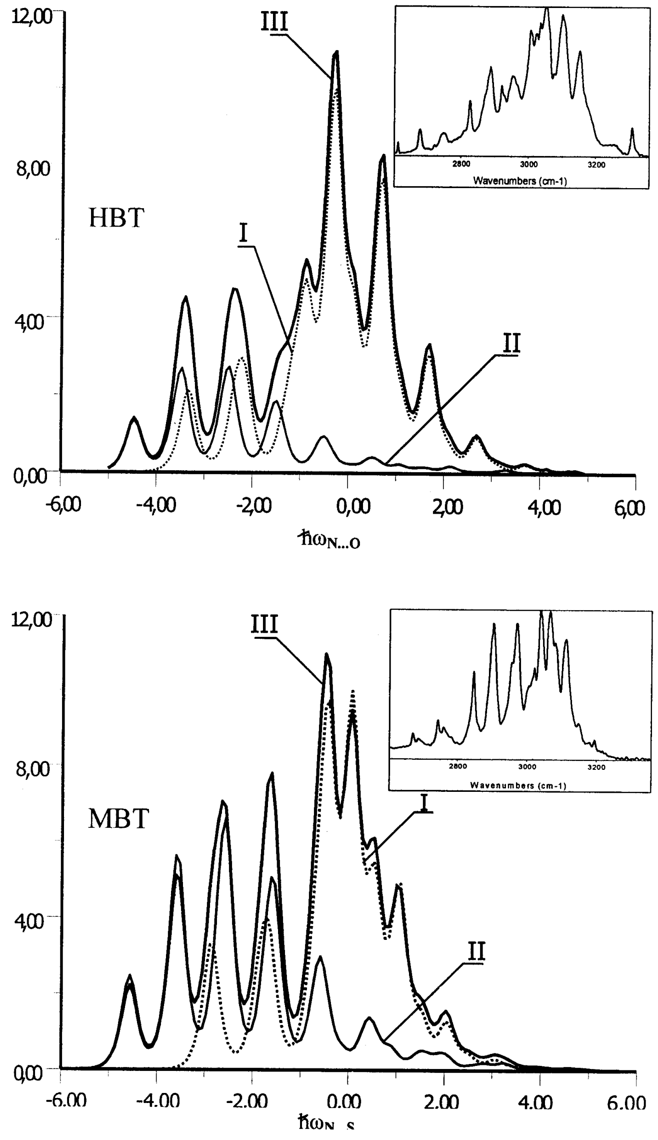


Figure 4a. Theoretical reconstitution of the most intense $\nu_{N\text{-}H}$ band components from the low-temperature spectra of HBT and MBT crystals. (I) The "plus" dimeric band reconstituting the symmetry-allowed transition, (II) the "minus" dimeric band reproducing the forbidden transition and, (III) the superposition of the "plus" and "minus" bands taken with their statistical weight parameters F^{-} and F^{-}. The experimental spectrum is presented at the right upper edge of each sub-picture [62].

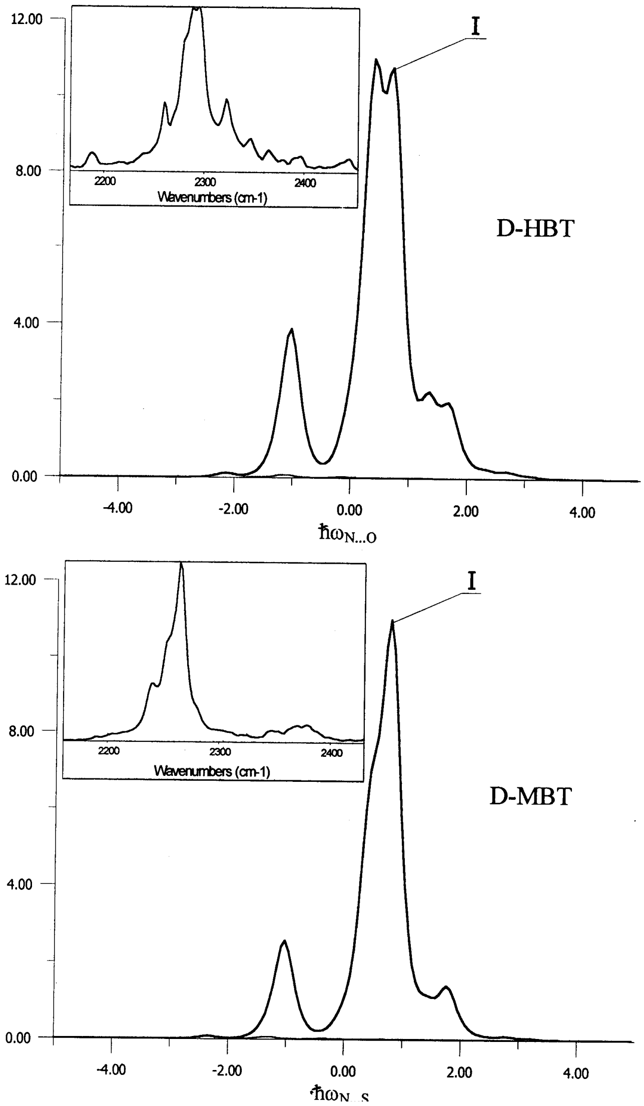


Figure 4b. Theoretical reconstitution of the most intensive $\nu_{N\text{-}D}$ band components from the low-temperature spectra of HBT and MBT crystals. (I) The “plus” dimeric band [62]. The experimental spectrum is presented at the left upper edge of each sub-picture.

10.2 Investigation of isotopic “self-organization” effects in IR spectra of hydrogen bonded crystals

Isotopic “*self-organization*” effects were studied for two groups of crystalline systems, *i.e.* for crystals with cyclic, centrosymmetric hydrogen bond dimers in their lattices and for crystals with infinite open chains of hydrogen bonds forming their X-ray structures. In each case the observed spectral effect of isotopic dilution appeared to be different.

1. For crystals with dimeric structures of the hydrogen bond lattices, spectra of isotopically diluted crystalline samples, measured in the frequency range of "*residual*" $\nu_{X\text{-}H}$ bands remained almost unchanged, when compared with the corresponding spectra of "*pure*" substances [58–63,66,68]. Although *ca.* 25 crystalline systems were investigated, no individual example has been found, for which the isotopic dilution transformed a dimeric spectrum of a crystal, towards a monomer spectrum one. This fact confirmed, that the dominating forms of the hydrogen bond dimers are the symmetric dimers of the "*HH*" and of the "*DD*"-type, with two identical hydrogen isotope atoms in both hydrogen bonds of a dimer. The isotopic "*self-organization*" effect in the crystalline spectra of partially deuterated samples of 2-hydroxybenzothiazole and 2-mercaptobenzothiazole, taken from [62], are shown in Fig. 5.
2. In the case of the second group of crystals two different kinds of the isotopic dilution effect were observed. For crystals of 4-mercaptopyridine [64], pyrazole [65],

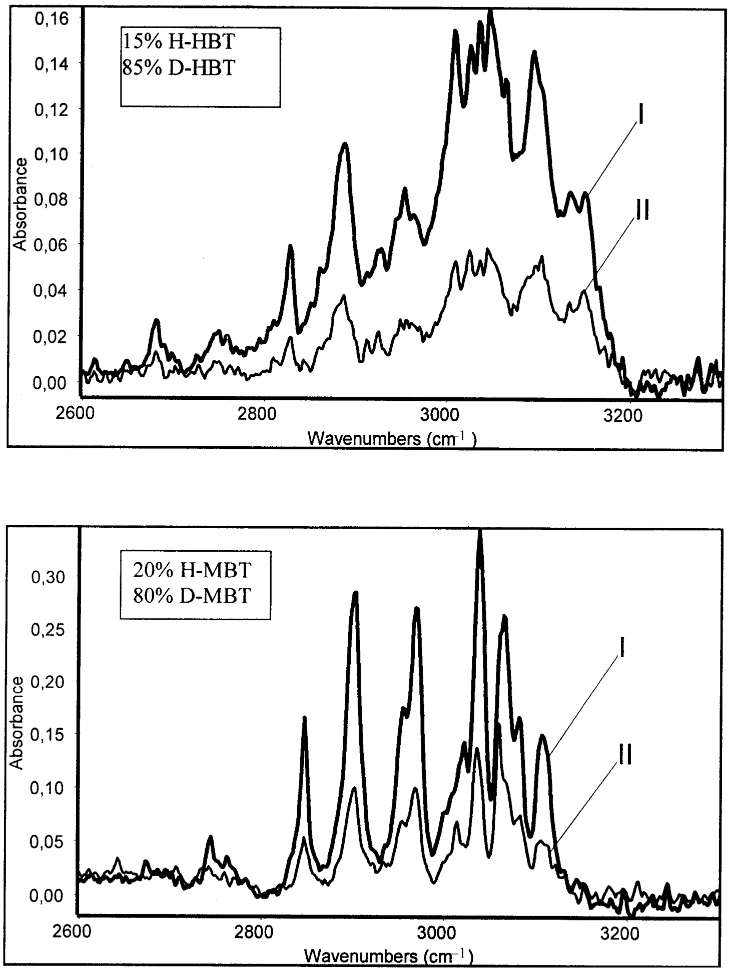


Figure 5. The "*residual*" $\nu_{N\text{-}H}$ bands from the crystalline spectra of the partially deuterated samples of 3-hydroxybenzothiazole and 2-mercaptobenzothiazole [62]. Other experimental conditions and the presentation of the spectra are identical to those given for Fig. 3a.

indazole and for the high-temperature form of 4-hydroxypyridine it was found that the "*residual*" $\nu_{\text{X-H}}$ bands remained unchanged for a wide value range of the isotopic dilution ratio. The isotopic "*self-organization*" effect was also confirmed by the observed linear dichroic effect, depending on a differentiation of spectral properties of the two spectral branches of "*residual*" $\nu_{\text{X-H}}$ bands. For a "*zig-zag*" structure of each chain, the proton vibrations "*in phase*" and "*out-of-phase*" differ by the transition moment vector direction. From this result the different dichroic properties of the two branches of each $\nu_{\text{X-H}}$ band. If despite of the increasing isotopic dilution rate the band shapes and its polarization properties remain unchanged, it means that the remaining protons are grouped in domains, in some fragments of the chains. This conclusion simply results from the fact that the discussed polarization effects in the $\nu_{\text{X-H}}$ bands, as well the Davydow-splitting effect magnitude remain unchanged, independently from the increasing deuterium content in the crystalline samples. This effect is shown in Figs. 6a and 6b, on the example of pyrazole crystal spectra.

The observed polarization effect for the "*residual*" $\nu_{\text{X-H}}$ bands delivers the strongest support for the idea of isotopic "*self-organization*" processes for chain systems of hydrogen bonds in crystals. The Davydow-splitting effect in spectra of isotopically diluted crystals is an attribute of closely spaced hydrogen bond systems.

Among experimental methods, IR spectroscopy in polarized light seems to be the optimum one to study this problem. It seems rather very hard to propose another research method able to investigate the very nature of vibrational exciton couplings in the domains of hydrogen bonds in open chains, occupied by identical hydrogen isotope atoms. It is easy to deduce that in this sub-group of crystals there are aromatic rings in molecular structures and the protons are linked directly to heteroatoms of the aromatic rings. It suggests a basic role of vibronic couplings in isotopic "*self-organization*" process mechanisms.

Properties of the another sub-group of the open-chain structure crystals fairly remain the recently described effects of the isotopic dilution in alcohol crystal spectra, mainly depending on disappearance of the Davydow-splitting effects. This effect was ascribed to a random distribution of protons and deuterons in the hydrogen bonds [50,51]. Very similar effects were observed in polarized spectra of 3-hydroxypyridine crystals [67] and also in spectra of the low-temperature form of 4-hydroxypyridine and 6-hydroxyquinoline crystals [69]. In these latter cases protons were much more separated from the aromatic rings when compared with the situation of protons in the first sub-group of structures, as these protons were linked with oxygen atoms in hydroxyl groups. Therefore, the hydroxyl group protons much less weakly couple with the aromatic ring π-electrons. Another possibility of a non-effective coupling of the hydrogen bonds in chains may result from a low polarizability of electrons occupying non-delocalized π-orbitals, restricted to one bond only (*e.g.* the carboxyl group). These regularities seem to emphasize a role of vibronic interactions as a source of isotopic "*self-organization*" mechanisms. These effects remain in agreement with predictions of a general vibronic model, explaining the mechanism of the isotopic "*self-organization*" effects in cyclic hydrogen bond dimers [57].

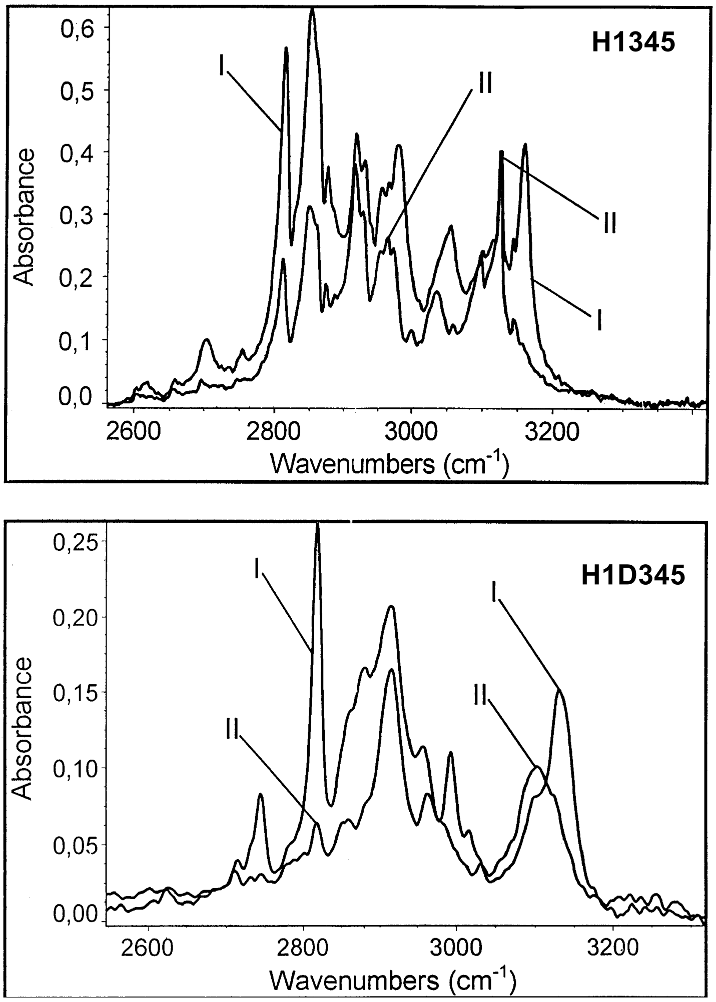


Figure 6a. Polarized absorption IR spectra of the hydrogen bond in crystals of pyrazole "*H1345*" and pyrazole "*H1D345*", measured at the frequency range of the $\nu_{N\text{-}H}$ band [65]. The IR beam was oriented perpendicularly to the "*ac*" plane. The band polarized components were measured for two different orientations of the electric field vector *E*:

{I} *E* parallel to the "*c*"-axis,

{II} *E* perpendicular to the "*c*"-axis (parallel to the "*a*"-axis).

10.3 "Strong-coupling" model in the quantitative interpretation of IR spectra of hydrogen bonded crystals

For a majority of the analyzed crystal spectra, their quantitative interpretation was performed on the basis of a properly modified version of the "*strong-coupling*" theory, which has shown a full adequacy and usefulness of this relatively simple model. Although this model in its basic version appeared more than 30 years ago, it many

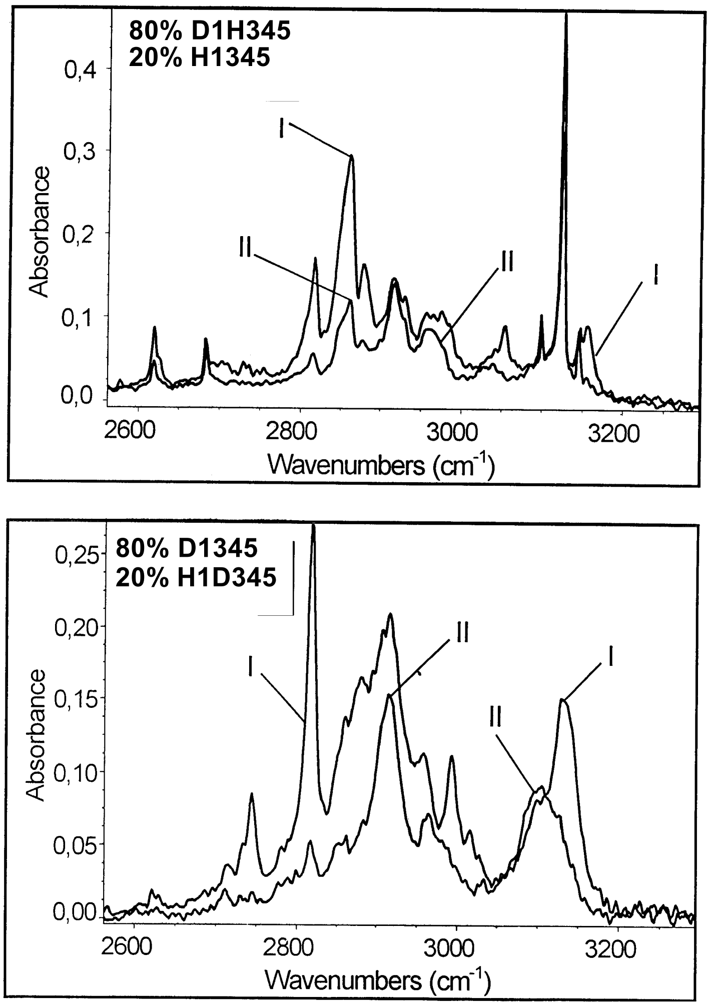


Figure 6b. "*Residual*" $\nu_{\text{N-H}}$ bands in spectra of isotopically diluted solid-state spectra of pyrazole "*H1345*" and pyrazole "*H1D345*" [65]. The same experimental conditions as for Fig. 6a.

times succeeded in a quantitative reconstitution of the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ band shapes in IR spectra of crystals [35,40–44,58–63,66]. The novel, but much more complex "*relaxation*" model [45–49] was not utilized in a practical interpretation of crystalline spectra due to its complexity. On the other hand, main elements of the "*strong-coupling*" mechanism were incorporated to the general formalism of the "*relaxation*" theory. When quantitatively interpreting polarized IR spectra of crystals, couplings of hydrogen bonds in lattices with their environment become negligible and the "*strong-coupling*" mechanism dominates over other "*relaxation*" sub-mechanisms, taken into account in the most general "*relaxation*" theory [45,46].

10.4 “Long-range”H/D isotopic effects in IR spectra of hydrogen bonded crystals

“*Long-range*” H/D isotopic effects in IR spectra of the hydrogen bond were recently investigated for the following crystalline systems: 1. pyrazole crystal and for crystals of its deuterium derivatives [65], 2. benzoic acid and its d_5 deuterium derivative crystals [61], 3. 1-naphthoic acid crystals and crystals of its derivative [66], 4. crystals of 2-naphthoic acid and crystals of its derivative [66], 5. phenylacetic acid and d_7 and the d_2 derivative crystals [64], 6. malonic acid and the d_2 derivative crystals, 7. succinic acid and the d_4 derivative crystals.

In Fig. 7 typical “*long-wave*” H/D isotopic effects were shown, on the example of IR spectra of benzoic acid crystals. (Also see Figs. 6a and 6b).

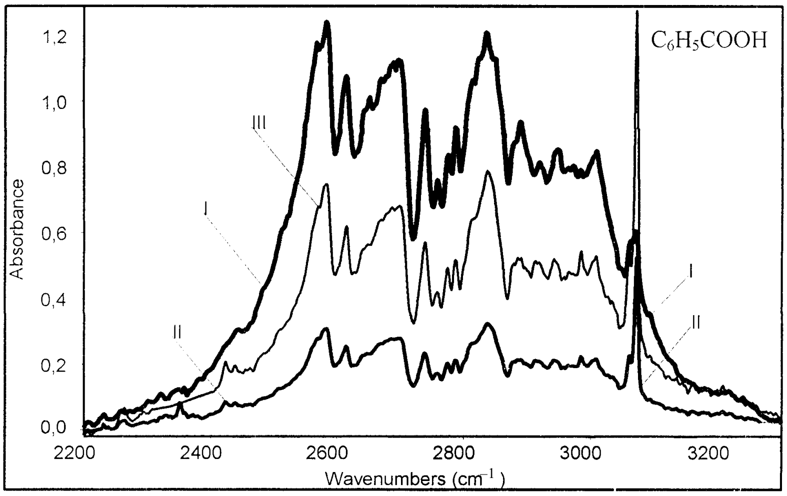
In the case of solid-state spectra no major changes in the $\nu_{\text{O-H}}$ band contour shapes were identified, due to replacing hydrogen atoms of methylene groups by deuterium atoms. For succinic acid crystal spectra some noticeable effects could be observed, especially in the longer-wave branch of the $\nu_{\text{O-H}}$ band [69]. Perhaps this effect is connected with electron-vibrational coupling in a flat molecular skeleton of succinic acid. Strongest ones “*long-range*” H/D isotopic effects were observed in the spectra of the hydrogen bond of benzoic acid crystals [61], of pyrazole [65] and for 1-naphthoic and 2-naphthoic acid crystals [66]. In the case of the above listed aromatic carboxylic acid crystals, deuterium substitution of the hydrogen atoms in aromatic rings, leads to essential changes in their fine $\nu_{\text{O-H}}$ band structure patterns, basically depending on a considerable multiplication of their band fine structure elements, when the band envelopes remain unchanged. This effect might be ascribed to a yet not understood effect of an effective diminution of the low-energy $\nu_{\text{O....O}}$ hydrogen bond vibration quantum for the crystals. In the case of the phenylacetic acid crystals the “*long-range*” H/D isotopic effects in the IR spectra were practically non-identified [63].

Very strong changes were also found in the fine structures of the $\nu_{\text{N-H}}$ and $\nu_{\text{N-D}}$ bands in pyrazole crystal spectra [65] due to the “*long-range*” isotopic effects. In conclusion, a preliminary hypothesis could be accepted, that “*long-wave*” H/D isotopic effects probably result from some yet non-recognized coupling mechanisms, concerning proton or deuteron stretching vibrations with electronic motion in associating molecules. These mechanisms seem to be most effective when the protons remain in a closest connection with aromatic ring electrons of molecular skeletons.

10.5 Effect of the molecular electronic structure on IR spectra of the hydrogen bond

Investigations of the hydrogen bond crystalline spectra performed by Flakus and co-workers for *ca.* 40 solid-state systems have shown that the electronic structure of associating molecules considerably influenced spectral properties of hydrogen bonds formed between them. To these effects belong:

1. Electronic structure impact on the vibrational selection rule breaking effects in IR spectra of hydrogen bonded dimeric systems, in the frequency range of the $\nu_{\text{X-H}}$ and the $\nu_{\text{X-D}}$ bands [53,54,56,59,62]. In the case of easy-polarizable hydrogen bonds, coupled with π delocalized bond systems, the selection rule breaking effects were



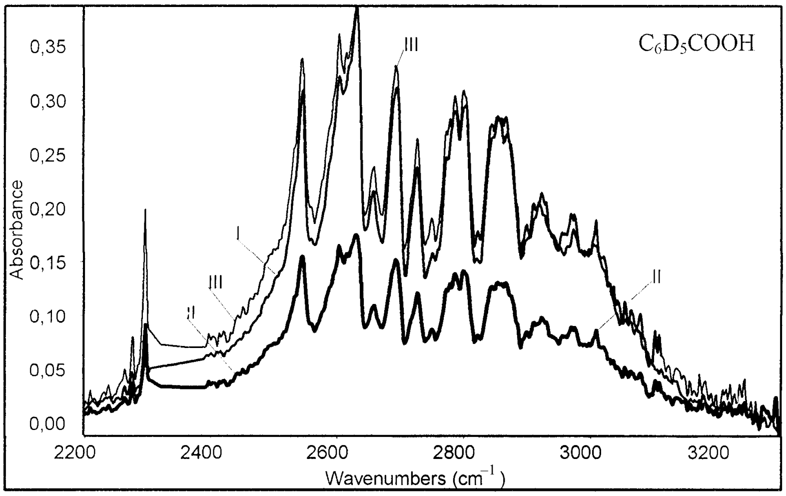


Figure 7. Polarized IR spectra of benzoic acid and its d_5 derivative crystals for the $\nu_{\text{O-H}}$ band frequency range [63] measured at 77 K. The IR beam was oriented perpendicularly to the "*ab*" plane. The band polarized components were measured for two following orientations of the incident light electric field vector *E*:

{I} *E* parallel to the "*b*"-axis,

{II} *E* perpendicular to the "*b*"-axis (parallel to the "*a*"-axis).

(III) The spectrum (II) normalized to common scale with the spectrum (I).

found to be the strongest ones. Also electronic properties of the proton acceptor atoms strongly influence the vibrational selection rules of cyclic dimeric systems of hydrogen bonds (*e.g.* the spectra of 2-mercaptobenzothiazole and 2-hydroxybenzothiazole crystals) [62].

2. The influence of the heterocyclic molecule size on the $\nu_{\text{X-H}}$ band fine structures (2-mercaptothiazoline, 2-mercapto-1-methylimidazole crystals in comparison with 2-mercaptobenzothiazole crystals) [55,58].

3. The effect of the molecular electronic structure on the "*long-range*" H/D isotopic effects in the IR spectra of hydrogen bonded solid-state systems [56,59,61,63].

The electronic effects have not been considered so far, when interpreting IR spectra of hydrogen bonds in molecular crystals. The models utilized recently were fully vibrational ones. Taking the electronic effect into the account, makes this approach to some extent similar to the Zundel model, proposed to describe spectra of easily polarizable hydrogen bonds [70].

11. Conclusions

Vibrational IR spectroscopy in polarized light opens new horizons in the hydrogen bond research. It allowed identification of new spectral effects that were expressed by the vibrational selection rule breaking for hydrogen bonded crystalline systems. By investigating of H/D isotopic effects in IR spectra of hydrogen bonded systems, of a new kind of co-operative interaction in hydrogen bonded crystalline systems, the so-called isotopic "*self-organization*" effects could be identified in spectra of partially deuterated solid-state samples. These latter effects, of an undoubted potential biological importance, seem to be worth of intensive studies in the nearest future. Measurements of IR polarized spectra in a wide temperature range also seem to be a proper method of investigation of complex H/D isotopic effects, the "*long-range*" H/D isotopic effects included. All these results of experimental and theoretical studies on the hydrogen bonded crystal vibrational spectra, done in few recent years, makes these studies potentially the most promising research method of the hydrogen bond in the nearest future.

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