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"Long-distance" H/D isotopic self-organization phenomena in scope of the infrared spectra of hydrogen-bonded terephthalic and phthalic acid crystals

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ABSTRACT

This paper deals with the experimental and theoretical studies of abnormal properties of terephthalic acid (TAC) and phthalic acid (PAC) crystals manifested in the H/D isotopic exchange. The widely utilized deuteration routine appeared to be insufficiently effective in the case of the h_6-TAC isotopomer. In the case of the d_4-TAC derivative the isotopic exchange process occurred noticeably more effectively. In contrast, both isotopomers of PAC, h_6 and d_4, appeared much more susceptible for deuteration. A theoretical model was elaborated describing "long-distance" dynamical co-operative interactions involving hydrogen bonds in TAC and PAC crystals. The model assumes extremely strong dynamical co-operative interactions of hydrogen bonds from the adjacent $(COOH)_2$ cycles. This leads to an additional stabilization of h_6–TAC molecular chains. The interaction energies affect the chemical equilibrium of the H/D isotopic exchange. The model predicts a differentiated influence of the H and D atoms linked to the aromatic rings on to the process. In this approach the totally-symmetric C—H bond stretching vibrations and the proton stretching totally symmetric vibrations couple with the π-electronic motions. It was also shown that identical hydrogen isotope atoms, H or D, in whole TAC molecules, noticeably enlarge the energy of the dynamical co-operative interactions in the crystals, in contrast to the case of different hydrogen isotopes present in the carboxyl groups and linked to the aromatic rings. The "long-distance" dynamical co-operative interactions in PAC crystals were found of a minor importance due to the electronic properties of PAC molecules.

1. Introduction

Infrared spectra of H-bonded systems, recorded in the υ_{X-H} band frequency region, connected with the proton stretching vibrations, are highly susceptible to the influence of numerous external physical factors such as strong coupling, relaxation mechanism, vibronic interactions, Davydov-type vibrational exciton interactions, etc. [1–5]. The υ_{X-H} band fine structure patterns are also related to the molecular electronic structure as well as to the chemical character of the H-bonded molecular aggregates [6–8].

Quantitative theoretical models [9–14], which were subsequently developed over the last six decades, were able to solve only some selected theoretical problems concerning the spectra. However, the most advanced quantitative theories, each individual of a purely vibrational nature, namely the "strong coupling" [16–17] and the "linear response" (or the so-called "relaxation") [18,19] theories, are still unable to convincingly explain some peculiar effects observed in the IR spectra of even so simple H-bond aggregates like centrosymmetric cyclic dimers of hydrogen bonds.

The most valuable data set, allowing for an essential extension of our knowledge about the mechanisms of the hydrogen bond IR spectra generation, may be obtained by measuring of the polarized IR spectra of spatially oriented monocrystalline layers. Despite of the notable progress, which was made on this scientific area, the wealth and the diversity of the υ_{X-H} bands fine structure patterns found in the polarized crystalline IR spectra, related different mutual arrangements of hydrogen bonds in crystal lattices, are actually still considered as a real challenge for the theory. However, the solid-state also remains a significant source of additional spectra complications. In the case of crystalline IR spectra, the Davydov-type vibrational exciton interactions [20] involving hydrogen bonds, connected with the presence of translationally non-equivalent $(COOH)_2$ cycles in each unit cell, cannot be totally neglected. Investigation of linear dichroic effects in the υ_{X-H} band frequency range allows obtaining the most complete information about the transition moment directions of vibrational transitions

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contributing in the generation of the υ_{X-H} band fine structure patterns. On the other hand, the spectra measurements performed in wide temperature ranges enable verifying of the validity of the subsequently developed theoretical models.

The latest IR spectral studies of H-bonded molecular crystals have shown that vibronic interactions should be considered as the key factor responsible for the observed complexity of the υ_{X-H} and υ_{X-D} band fine structures patterns. A close correlation between the spectra characteristics and the molecular aggregate electronic properties allows discarding of the purely vibrational approach in the interpretation of hydrogen bonds spectra.

The contemporary IR spectroscopic studies of hydrogen bonds in molecular crystals have opened a new patch on this scientific area. H-bonded molecular systems in the solid-state are known for the rich diversity of their internal structures. The molecular associated systems most widely encountered in the nature are linked together forming infinitely long H-bonded chains, or forming molecular cyclic dimers. Extremely rare structural motif found in carboxylic acid crystals concerns the chain linkage of molecules occurring via single hydrogen bonds [21,22].

The so-called H/D isotopic "self-organization" phenomena [23] belong to the effects in the hydrogen bond research area, which were revealed during the two-decades lasting studies of the IR spectra of H-bonded crystals. They depend on a non-random distribution of protons and deuterons in the hydrogen bond lattices of crystals isotopically diluted with deuterium. The dynamical co-operative interactions involving hydrogen bonds are the source of these phenomena [7,8,23]. On analysing the results of these works a unique relation between the way of the spatial arrangement of the hydrogen isotope atoms, H and D, in the hydrogen bond network and the molecular electronic properties has been found. The spectral properties of monocarboxylic acids, with the centrosymmetric hydrogen bond cycles present in the crystal lattices, have been analysed to verify the validity of the formerly introduced theory of the dynamical co-operative interactions involving hydrogen bonds. On analysing the results of the latest studies of monocarboxylic acid IR spectra one can expect that as the consequence of the H/D isotopic "self-organization" mechanism the atoms of the different hydrogen isotopes, H and D, are non-randomly distributed in the lattices. They are grouped together in local domains, found in the centrosymmetric $(COOH)_2$ and $(COOD)_2$ cycles. The existence of the cycles with the HD mixed hydrogen isotope content was found practically non-detectable by measuring of the IR spectra of isotopically diluted of carboxylic acid crystals [24–26].

IR spectra of monocarboxylic acid crystals, with infinitely long chains of associated molecules in their lattices, in some cases are different when compared with the spectra of the carboxylic acid crystals with cyclic hydrogen bond dimers in $(COOH)_2$ cycles and in other cases, are fairly similar to them. The comparison of the HCOOH and the CH_3COOH crystal spectra has suggested that the spectra generation processes, the band fine structure patterns were basically determined by the electronic structure of the associating molecules. The H/D isotopic exchange phenomena and the spatial distribution of the different hydrogen isotopes, H and D (i.e., the H/D isotopic "self-organization" phenomena) were found to be also influenced by the molecular electronic properties [27,28].

It seems noteworthy to remark that in the case of linearly associated molecular systems there is no one way of occurring of the H/D isotopic "self-organization" processes. The inter-hydrogen bond dynamical co-operative couplings may involve the moieties from each individual molecular chain, or in the other case, from pairs of the closely-spaced hydrogen bonds from the different adjacent molecular chains in a lattice. The first case is typical for pyrazole [29] and of 4-thiopyridone [30] and formic acid [27] crystals, and the second case is characteristic for acetic acid [28] as well as for the vast diversity of thioamide and amide crystals [31,32].

Dicarboxylic acids constitute the particular group of H-bonded compounds, since isolated hydrogen bond dimers are absent in their crystal lattices. In this case complex structures exist, in which the associated molecules in the solid- state are linked together by means of the $(COOH)_2$ cycles forming infinitely long chains. On analysing the up-to-date recorded spectra of aliphatic dicarboxylic acid crystals [20,24,25,26] it seemed true that the "dynamical co-operative interaction" effects in these spectra were basically restricted to the domains localized on single $(COOH)_2$ cycles in each individual molecular chain. One could also expect that the IR spectra of discussed TAC and PAC crystals, due to the existence of aromatic rings in the molecular skeletons, should be generally similar to the formerly analysed monocarboxylic, arylic acid and arylacrylic acid crystalline spectra [6].

One may intuitionally expect that in the case of dicarboxylic acid crystals the H/D isotopic "self-organization" processes are followed by some abnormal physical phenomena resulting from the electronic structure of the associating molecules, namely from a vibronic coupling mechanism involving the proton stretching vibrations in the cycles and the electronic motions in the molecular skeletons. These phenomena are also predicted to strongly depend of the electronic properties of the substituent atomic groups. Therefore, the analysis of the spectral properties of systems characterized by extremely differentiated electronic structures enable us to obtain the most complete spectral data set for the further theoretical interpretation of the problem [6,27,28].

In the case of dicarboxylic acid crystals, the spectral analysis of molecular systems based on the π-electronic cores (particularly on these based on the 1,4-phenylene and 1,2-phenylene rings), allows us to expect some extremely strong and abnormal spectral effects in the υ_{X-H} and the υ_{X-D} bands frequency regions. In these circumstances one can also suspect of the presence of extremely strong hydrogen bonds in the crystals in contrast to the corresponding properties of the diverse dicarboxylic acid crystals analysed yet. For this reason the investigation of the TAC and PAC crystal IR spectra seems to be justified. The TAC and PAC molecules are linked together by $(COOH)_2$ cycles forming infinitely long chains [34–38]. In Fig. 1 the X-ray structures of TAC and PAC crystals are presented.

The extreme physical and chemical properties of TAC in the solid state, namely its very high melting point value acts in support of this project. However, it excludes recording of the polarized IR spectra of TAC crystals by utilizing of the familiar experimental method widely used in our previous studies [23–32]. Therefore, our experimental studies will be restricted to recording of polycrystalline spectra of the title compounds.

2. Experiment

Two isotopomers of TAC acid, h_6-TAC (HOOC-C_6H_4-COOH) and d_4-TAC (HOOC-C_6D_4-COOH), were the commercial substances (Sigma-Aldrich). Two isotopomers of PAC, h_6-PAC (HOOC-C_6H_4-COOH) and d_4-PAC (HOOC-C_6D_4-COOH), also originated from the same source. They were used for our studies without further purification. In order to obtain the D-bonded d_2-TAC and d_2-PAC derivative solid-state samples, samples of the h_6-TAC and h_6-PAC derivative were dissolved in mixture of D_2O and THF (tetrahydrofuran) and then evaporated under reduced pressure. Due to the very low solubility of TAC and PAC in pure water the H/D isotopic exchange process had to be performed in the environment of the mixture of D_2O and THF [39,40]. An addition of THF essentially enlarges the solubility of these two compounds in water. The isotopic exchange procedure was standardized. In each case 25 mg sample of a given individual compound was treated with 5 ml of THF and 5 ml of D_2O. In these circumstances the differentiation of the investigated properties of the compounds were most visibly pronounced in the spectra. The IR spectra were recorded using the FT-IR NICOLET Magna 560 spectrometer by using of the technique of KBr pellets (5 mg of TAC or PAC and 150 mg KBr for a pellet). In each isotopomer case, the final spectra were obtained by averaging of 10 spectra, where each individual spectrum was measured by a separate isotopic exchange process. The approximate frequency ranges in which the υ_{C-H} (~3000 cm^{-1})