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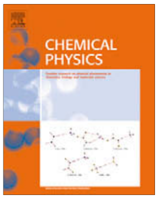

Effects of dynamical couplings in hydrogen bond systems in the polarized IR spectra of 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde crystals

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ABSTRACT

This paper presents the investigation results of the polarized IR spectra of 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde crystals measured at 293 and 77 K. Analysis of the results concerned the linear dichroic, H/D isotopic and temperature effects observed in the spectra of the hydrogen and deuterium bond at the frequency ranges of the $\nu_{\text{O-H}}$ and the $\nu_{\text{O-D}}$ bands, respectively. The main spectral properties of the crystals were interpreted in terms of the "*strong-coupling*" theory on the basis of the hydrogen bond 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 molecules. The reason for two different crystalline systems, are characterized by almost identical $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ band shapes, is explained. It was proved that a random distribution of the protons and deuterons took place in the lattices of the isotopically diluted crystals.

1. Introduction

Over the last six decades IR spectroscopy has been considered to be a powerful tool in investigating hydrogen bonds. The spectral studies mainly concern the middle frequency range of IR where the $\nu_{\text{X-H}}$ bands, ascribed to the proton stretching vibrations in the X–H···Y hydrogen bonds, appear [1–5]. Complex fine structure patterns of the $\nu_{\text{X-H}}$ bands are highly susceptible to influences exerted by diverse interaction mechanisms such as the intra- and inter-hydrogen bond ones [1–5].

According to the contemporary quantitative theories of IR spectra of hydrogen bonded systems these bands are treated as an abundant source of information about the complex dynamics of hydrogen bonds. In terms of these theories, strong anharmonic couplings involving motions of different forms and of different energies are considered to be responsible for the generation of the main spectral properties of hydrogen bond systems. To understand the spectral properties of the hydrogen bond systems the so-called "*strong-coupling*" [6–8] and the "*relaxation*" theory [9,10] played an important role. These theoretical models allowed us to succeed in the quantitative interpretation of the IR spectra of the hydrogen bond in simple molecular aggregates like dimers [7,11–13] as well as in hydrogen-bonded molecular crystals [14–16].

The H/D isotopic effects obtained due to IR spectroscopy have been used to verify the validity of theoretical models subsequently introduced for the quantitative interpretation of vibrational spectra of hydrogen bond systems [6–10]. From earlier spectral studies of hydrogen bond dimers it resulted that mechanisms non-revealed yet might also co-decide about the generation of the system spectra [17,18]. It seemed that IR spectroscopy in polarized light, applied for investigation of crystalline spectra should provide essential data in this matter. Polarized IR spectra of molecular crystals measured for spatially oriented lattices of hydrogen bonds seem to be the source of the a complete data system concerning the inter- as well as the intra-hydrogen bond interactions in the systems. However, the solid-state introduces its own new effects considerably complicating the crystal spectra interpretation, related to the inter-hydrogen bond couplings in the excited vibrational state. Overcoming these interpretation problems may allow us to extend our knowledge about the coupling mechanisms, involving motions of diverse forms in hydrogen bond systems.

Recent studies of polarized IR spectra of the hydrogen bond in diverse crystalline systems have exhibited a rich diversity of their spectral properties and have allowed us to reveal a number of new, non-conventional effects in the spectra. These new effects were found when model calculations, mainly performed in terms of the so-called "*strong-coupling*" theory [6–8], were applied to the quantitative interpretation of the crystalline spectra. Among these effects are the so-called H/D isotopic "*self-organization*" effects, identified in the polarized IR spectra of isotopically diluted

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hydrogen-bonded molecular crystals [19,20]. They result from a non-random distribution of protons and deuterons in the hydrogen bridge systems in lattices of isotopically diluted molecular crystals. It looks as if some non-identified "*attraction*" forces appear, which involve identical hydrogen isotope atoms in coupled hydrogen bond systems. Therefore, the invariability of the ν_{X-H} proton stretching vibration bands, registered independently of the increasing concentrations of deuterons in a crystalline sample could be observed in the spectra of isotopically diluted crystalline samples. The latter effect is the result of the newly revealed mechanisms governing the inter-hydrogen bond co-operative interaction in molecular crystals, i.e., the so-called *dynamical co-operation interaction* mechanisms [19,20]. Vibronic coupling in hydrogen bonded molecular systems is considered to be the most probable source of these interactions [19,20]. In the spectral studies of H/D isotopic effects for hydrogen bonded systems carried out so far the problem of the influence of the isotopic dilution on to the IR spectra was treated as rather marginal. This was the result of the studies performed in the past, which significantly influenced later investigations in this area [21–23].

Detailed studies of the *dynamical co-operative interaction* mechanisms performed for diverse solid-state systems have proved that the H/D isotopic "*self-organization*" processes did not occur in one precisely defined way. This remark mainly concerns a particular group of hydrogen-bonded molecular crystals in whose lattices hydrogen bonds form infinitely long chains. It appeared that in relation to the electronic structure of the associating molecules, the H/D isotopic "*self-organization*" processes, provided they take place, might proceed in two different ways. In the first one they may involve the adjacent hydrogen bonds in each individual chain. In the other case, pairs of closely-spaced hydrogen bonds participate, where each moiety in an individual pair belongs to another chain.

The first group of crystals comprises crystals of pyrazole [24], imidazole [25] and 4-thiopyridone [26]. These molecules contain large delocalized "π"-electronic systems. Surprisingly, also formic acid crystals belong to this group [27]. This way of the occurrence of the discussed processes is evidenced by the fact that linear dichroic effects are retained. This in turn depends on the differentiation of the dichroic properties of the two opposite branches of the ν_{X-H} "*residual*" bands in the polarized spectra of isotopically diluted crystals. Also the intensity distribution pattern of these bands, characteristic of linear hydrogen bond dimers, supports this conclusion.

The second group comprises crystals of N-methylthioacetamide [28], N-methylacetamide [29] and crystals of acetic acid [30]. For these latter systems the distribution of protons and deuterons in the hydrogen bridge chains appeared to be fully random. This was deduced from the disappearance of the *Davydow-splitting* effects [31,32] in the ν_{X-H} "*residual*" bands in the spectra of the isotopically diluted crystals, attributed to the *in-chain* exciton couplings. Also the fine structure intensity pattern of these bands, similar to the one observed for cyclic hydrogen bond dimers appears in these spectra. In this case no essential differences in the dichroic properties between the opposite ν_{X-H} "*residual*" band branches can be observed [28,29]. This fact supports the hypothesis about the inter-chain H/D isotopic "*self-organization*" in this group of crystals.

In this article, we present the polarized IR spectra of 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde crystals. Aiming at their quantitative interpretation in the initial theoretical approach it seems possible that the process proceeds in two different ways. The lattices of both these crystals are composed with infinite hydrogen bond chains, differing however, from one another in their space-symmetry groups and in the mutual hydrogen bond arrangement. Therefore, these systems seemed to pose interesting objects for the investigation of the H/D isotopic "*self-organization*" process mechanisms in relation to the electronic structure of the associated molecules and the space-symmetry of the crystals.

One may expect that the substituent atomic groups, O–H and CHO, linked to the benzene rings in two different positions, 1,3- and 1,4-, can significantly influence the electronic properties of O–H···O hydrogen bonds in these crystalline systems. In this way they may affect the magnitude of the *dynamical co-operative interaction* energies since these mechanisms are basically of a vibronic nature [19,20]. Therefore, one can expect that the H/D isotopic "*self-organization*" processes occur in two different ways for these two different isomeric system crystals. Similar electronic properties of the two akin molecular systems may facilitate a fully quantitative interpretation of the crystal spectra and therefore, might allow for a deeper insight into the very nature of the H/D isotopic "*self-organization*" processes in hydrogen bond systems [19,20].

2. X-ray structures of 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde

Crystals of 3-hydroxybenzaldehyde (3-HBA) belong to the orthorhombic system. Space-symmetry group is $Pna2_1 = C_{2v}^9$. The *Factor-group* is C_{2v}. Melting point is 100–103 °C. A unit cell contains four molecules ($Z = 4$). The crystal lattice is composed of infinitely long chains of associated 3-HBA molecules of a "*zig-zag*" form, linked by O–H···O hydrogen bonds. These molecular chains elongate along the "*c*" axis direction. The lattice constants are: $a = 18.858(7)$ Å, $b = 3.864(1)$ Å, $c = 8.190(7)$ Å and $\alpha = \beta = \gamma = 90°$ [33]. A view of the 3-HBA crystal lattice is shown in Fig. 1.

Crystals of 4-hydroxybenzaldehyde (4-HBA) are monoclinic. The space-symmetry group is $P2_1/c = C_{2h}^5$ and $Z = 4$. The crystal *Factor-group* is C_{2h}. The unit cell parameters determined at 295 K are: $a = 6.453(5)$ Å, $b = 13.810(8)$ Å, $c = 7.044(6)$ Å, $\alpha = \gamma = 90°$, $\beta = 107.94(9)°$. 4-HBA molecules are linked by O–H···O hydrogen bonds forming infinitely long "*zig -zag*"-type chains elongating along the "*b*" axis [34]. Fig. 2 presents the arrangement of the hydrogen-bonded 4-HBA molecules in the lattice of 4-HBA crystal.

3. Experimental

3-Hydroxybenzaldehyde (3-HBA) and 4-hydroxybenzaldehyde (4-HBA) (the general chemical formula HO–C_6H_4–CHO), used for our studies were the commercial substances (Sigma–Aldrich). The samples were used without their further purification.

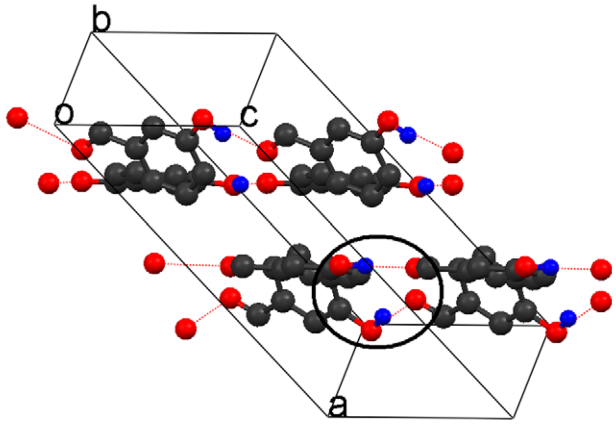

Fig. 1. View of a unit cell in the crystal lattice of 3-hydroxybenzaldehyde. A pair of the closely-spaced O–H···O hydrogen bonds governed by the C_{2v} site-symmetry group is marked by an ellipse.