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INVESTIGATION OF DAVYDOV SPLITTING IN THE IR SPECTRA OF CRYSTALLINE DICARBOXYLIC ACIDS

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In the present paper the collective (vibrational) excitations in molecular crystals were studied. Since the corresponding molecular interactions are characterized by a small radius, the investigation results are important for the molecular and nanoelectronics problem solving.

The paper includes the investigation results of resonance (Davydov) splitting of the methylene CH_2 group rocking vibrations in the IR absorption spectra of even homologues of crystalline dicarboxylic $HOOC(CH_2)_nCOOH$ acids (crystal space group $P2_1/a$). Temperature dependence of the Davydov splitting value for the series of rocking vibration bands of methylene groups in the spectral range 700-1100 *cm^{-1} was investigated for homologues with the number of carbon atoms* $n = 4$-10 *using the polarized IR spectroscopy in the wide temperature range* 100-300 *K. Interpretation of the series of rocking vibration bands of methylene groups in the IR absorption spectra of even homologues of crystalline dicarboxylic acids is performed. Based on the theoretical calculation of normal modes and the assignment of observed absorption bands to vibrations of different symmetry types it was shown, that in the spectra of the studied acids the series of rocking vibration bands may be interpreted as the vibration of $(n - 2)$ methylene groups connected by the collective interaction, in contrast to the case of normal paraffins where all the methylene groups are involved in rocking vibrations. Dependence of the Davydov splitting value on the number of methylene groups is analyzed, and shown that this value increases proportionally to the methylene chain length.*

Keywords: *DAVYDOV SPLITTING, DICARBOXYLIC ACIDS, IR SPECTRA, NORMAL MODES, ABSORPTION.*

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1. INTRODUCTION

Investigation of the collective molecular (electronic and vibrational) excitations in molecular crystals, which are the excitations of a small radius, is an important problem in molecular and nanoelectronics, and description of the molecular dynamic systems depends on its solution. Moreover, solution of such a problem promotes the development of new investigation methods of molecular systems in non-equilibrium state.

The aim of the present work is to study Davydov splitting of vibrations in the IR absorption spectra of different homologues of crystalline dicarboxylic acids.

To achieve the aim we have solved the following tasks:
– assignment of the IR absorption bands, which are observed in the spectral range 700-1000 cm^{-1}, to the separate vibrations of the series of the methylene group rocking vibrations is performed; and comparison of the obtained results with the experimental and theoretical data for crystalline *n*-paraffins [1] is carried out.
– dependence of the Davydov splitting value in the vibrational spectra of the crystalline dicarboxylic acids on the symmetry of the crystal space group, on the methylene chain length and the temperature is studied.

2. EXPERIMENT

Polarized IR absorption spectra of monocrystals (which are stable at room temperature) of even homologous series of $HOOC(CH_2)_nCOOH$ dicarboxylic acids (where $n = 4, 6, 8, 10$ is the number of CH_2 groups in molecule) were measured in the frequency range of the methylene group rocking vibrations (700-1000 cm^{-1}) using the double-beam spectrophotometer UR-20 (Karl Zeiss, Jena) at the temperatures 100 and 300 K. Monocrystal samples were grown by the cooling of the melt placed between two KBr plates. Homogeneity of the obtained samples and orientation of the crystal axes were checked using the polarizing microscope. According to the polarization and the X-ray structure analysis data the obtained monocrystal layers have the orientation, which is parallel to the crystal face (ab). Polarized IR radiation was perpendicular to the monocrystal surface. Two mutually perpendicular orientations of the electric field vector of an incident IR radiation E ∥ a and E ∥ b were used. For comparison the spectra of the powdered sodium salts of azelaic and sebacic acids ($n = 7$ and 8, respectively) were investigated as well.

3. RESULTS AND DISCUSSION

Even and odd homologues of dicarboxylic acids are crystallized in the monoclinic syngony with two or four molecules in the unit cell [2, 3]. Molecules in a crystal are coupled to infinite chains via the hydrogen $(COOH)_2$ bonds between the end groups. Long axis of a chain is inclined at the certain angle to the crystal axis *c*. Chain packing is described by the orthorhombic Vand's subcell with two $(CH_2)_2$ groups in a cell. Symmetry of molecules of even homologues of dicarboxylic acids is C_{2h}, and of the odd ones is C_{2v}. Symmetry of molecules of sodium salts of dicarboxylic acids is C_s [2].

Series of the methylene group rocking vibrations conditioned by the coupled vibrations of equal CH_2 groups of a fully extended methylene chain appears in the IR absorption spectra of the aliphatic-bonded crystals in the form of the narrow band series of mean intensity. The number of bands in the series is equal to the number of CH_2 groups. In accordance with the selection rule for molecules with C_{2h} symmetry in the IR absorption spectra only $n/2$ symmetry vibrations of Au appear, other $n/2$ vibrations of B_g symmetry appear only in the combination scattering spectra. In the case of molecules of odd homologues with C_{2v} symmetry only the B_2 symmetry vibrations appear in the IR absorption spectra, while other vibrations of A_2 symmetry are forbidden in the IR spectra. In Tables 1 and 2 we present the band frequencies of the series of rocking vibrations observed in the IR spectra of crystalline *n*-paraffins and dicarboxylic acids. The most intensive

band of the series with a center on the frequency 720 cm^{-1} corresponds to the synchronous vibrations of all CH_2 groups and is denoted as P_1. Other bands of this vibration series of smaller intensity are denoted as P_2, P_3, P_4, P_5, ..., P_α [1] and correspond to the coupled vibrations of CH_2 groups with different phase difference between the adjacent CH_2 groups. Symbol α belongs to the so-called α-CH_2 group, which is directly attached to the end group of molecules of investigated homologous series.

Table 1 – *Band frequencies of the series of methylene group rocking vibrations (cm^{-1}) (A)*

Even *n*-paraffins (C_{2h}) Triclinic syngony, Z = 1					Even dicarboxylic acids (C_{2h}) Monoclinic syngony, Z = 2,4										
n	P_1	P_3	P_5	P_7	*n*	P_1	P_3	P_5	P_α	P_1	P_3	P_5	P_7	P_α	Polarization
77 K					300 K					100 K					
2	733	–	–	–	2	–	–	–	802*	–	–	–	–	–	–
4	720	798	–	–	4	734	–	–	901	734 740	– –	– –	– –	– 904	E ‖ b E ‖ a
6	721	747	868	–	6	722 726	797 798	– –	– 914	722 727	797 797	– –	– –	– 917	E ‖ b E ‖ a
8	721	731	793	–	8	721 725	756 755	856 857	– 905	720 726	754 754	855 856	– –	– 906	E ‖ b E ‖ a
10	721	725	758	840	10	721 727	737 737	795 796	– 907	721 729	737 737	793 794	892 892	– 910	E ‖ b E ‖ a
					*M. Suzuci, T. Shimanouchi, *J. Mol. Spectr.* **283**, 394 (1968)										
Note: data of Ref. [2] is used					Na sebacate (C_s)										
					8	720	748	856	920	720	748	856	–	920	–

As appears from the data of Tables 1 and 2, the band frequencies of rocking vibrations, observed in the IR absorption spectra of crystalline dicarboxylic acids with *n* carbon atoms in a methylene chain, correspond to the band frequencies of this series observed in the IR absorption spectra of crystalline *n*-paraffins with (n – 2) methylene groups. One might reasonably suppose, that in the case of even dicarboxylic acids not all methylene groups participate in the coupled rocking vibration (the model of coupled oscillators), but only (n – 2) of such groups. Two residual CH_2 groups, which are the nearest to the polar end COOH groups, have another local field, and, consequently, another vibration frequency, which does not depend on the methylene chain length. It was shown before [3], that because of the methylene chain deformation nearby the dimer $(COOH)_2$ ring a carbon atom of the nearest to this ring α-CH_2 methylene group protrudes a few degrees from the plane formed by the carbon atoms of a methylene chain that leads to the change in the force constants and vibration frequency of this group. We have to note, that the number of IR absorption bands observed in the series of rocking vibrations in spectra of dicarboxylic acids and their salts correlates with the corresponding symmetry of molecules in a crystal.

Based on the analysis of the IR absorption spectra, the band with the frequency 902 cm^{-1} belongs to the α-CH_2 group rocking vibrations. We should also note the increase in the band intensity of the series of rocking vibrations in the spectra of crystalline dicarboxylic acids (with $n > 3$) in comparison with the spectra of crystalline *n*-paraffins [5]. We have also observed only the weak temperature dependence of the mentioned bands while cooling the crystal to 100 K that indicates the conservation of the fully extended trans conformation of a methylene chain in the given temperature range.

Table 2 – *Band frequencies of the series of methylene group rocking vibrations (cm^{-1}) (B)*

Odd *n*-paraffins (C_{2v}) Orthorhombic syngony, Z = 2								Odd dicarboxylic acids (C_{2v}) Monoclinic syngony, Z = 4							
n	P_1	P_2	P_3	P_4	P_5	P_6	P_7	*n*	P_1	P_2	P_3	P_4	P_5	P_α	Polarization
77 K								100 K							
1	747	–	–	–	–	–	–	0	–	–	–	–	–	943	
3	722 728	759 –	858 –	– –	– –	– –	– –	1	756	–	–	–	–	893	
5	727	(732)	766	(834)	925	–	–	3	722	736	836	–	–	902	
7	722 727	(725) –	736 –	770 –	824 –	(889) –	957 –	5	729	722	873	–	–	904	
Note: data of Ref. [2] is used								Na azelaate (C_s)							
								7	717 726	726 –	740 –	775 –	823 830	896 –	E ‖ b E ‖ a

This paper mostly focuses on the investigation of the Davydov splitting value in the IR absorption spectra of crystalline dicarboxylic acids. As known, the Davydov splitting phenomenon is observed in vibrational spectra of the crystals, the unit cell of which contains some chemically identical, but oriented at some angle to each other, molecules, and is conditioned by the resonant interaction of such molecules in the lattice. It follows from the theory, that the number of components of Davydov multiplet [4] is equal to the number of molecules in the unit cell, and the multiplet components are polarized along the direction of the crystal axes. Splitting value is determined by the value of matrix element of the molecular interaction energy and depends on the distance between adjacent molecules in the unit cell that in our case corresponds to the distance between long axes of molecules of dicarboxylic acids. It was earlier reported in [5-7] about the Davydov splitting investigation in the IR absorption spectra of *n*-paraffins, α- olefines and *n*-carboxylic acids. It was shown, that analysis of the temperature dependence of the Davydov splitting value is the suitable investigation method of the crystal lattice dynamics of aliphatic compounds with the different chain length [6, 7].

In this paper the investigation results of Davydov splitting in the IR absorption spectra of crystalline dicarboxylic acids with even number of carbon atoms in a methylene chain are presented for the first time. Corresponding frequencies and polarization ratios of the splitting components

observed in the IR spectra of different crystalline dicarboxylic acids are given in Tables 1 and 2. As seen from Table 1 the largest splitting value (of the order of some inverse centimeters) is observed for the rocking vibration P_1. We have also to note that the splitting value increases slightly with the chain length and is equal to 4 and 6 cm^{-1} for the acids with $n = 4$ and 10, respectively. Such dependence is the same as that in the spectra of carboxylic acids [6], though in the spectra of investigated dicarboxylic acids the given effect is more pronounced, since crystalline dicarboxylic acids are formed by infinite chains of molecules coupled by the hydrogen bonds. We should also mention that the splitting value increases with the temperature decrease that correlates with the decrease in the distance between methylene chains at low temperatures.

One more feature of Davydov splitting in the IR absorption spectra of crystalline dicarboxylic acids is that the given effect is not observed in crystals of even homologous series, in spite of the fact that their unit cell contains two translation-nonequivalent molecules [8]. To explain this fact it is necessary to take into account that in accordance with the X-ray data in crystalline dicarboxylic acids of odd series the fully extended conformation of methylene chain is broken. The chain plain is rotated on the angle of ~ 30 degrees around the $C\text{-}C_\alpha$ bond. We suppose that planarity distortion in the case of dicarboxylic acids of odd series and appearance of steric difficulties lead to the increase in the distance between methylene chains in comparison with its value in crystalline acids of even series, where molecules keep their plain conformation.

Our investigation results are well agreed with those presented in [9].

4. CONCLUSIONS

1. Assignment of the series of rocking vibration bands of a methylene chain in the IR absorption spectra of dicarboxylic acids and their salts is performed.
2. It was shown, that in the case of dicarboxylic acids only $(n - 2)$ CH_2 groups participate in collective vibrations of a methylene chain in contrast to the case of crystalline *n*-paraffins, where the series of rocking vibration bands is conditioned by the collective vibrations of total number of n methylene groups.
3. It was shown, that in the case of crystalline dicarboxylic acids of even series the Davydov splitting of rocking vibration bands is observed in the IR absorption spectra, and the splitting value changes subject to the homologue number and the temperature.
4. In the case of crystalline dicarboxylic acids of odd homologous series Davydov splitting in the IR absorption spectra is not observed even at 100 K that is connected with the substantial deformation of methylene chains in these crystals.
5. Since molecular interactions, which condition the appearance of collective excitations, are characterized by a small radius the investigation results are important for the problem solving both of spectroscopy of molecular crystals and molecular and nanoelectronics.

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