



# An insight into the disorder properties of the $\alpha$ -cyclodextrin polyiodide inclusion complex with $\text{Sr}^{2+}$ ion: Dielectric, DSC and FT-Raman spectroscopy studies

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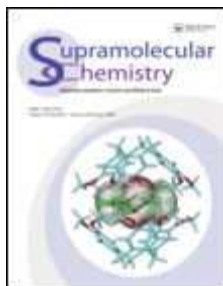
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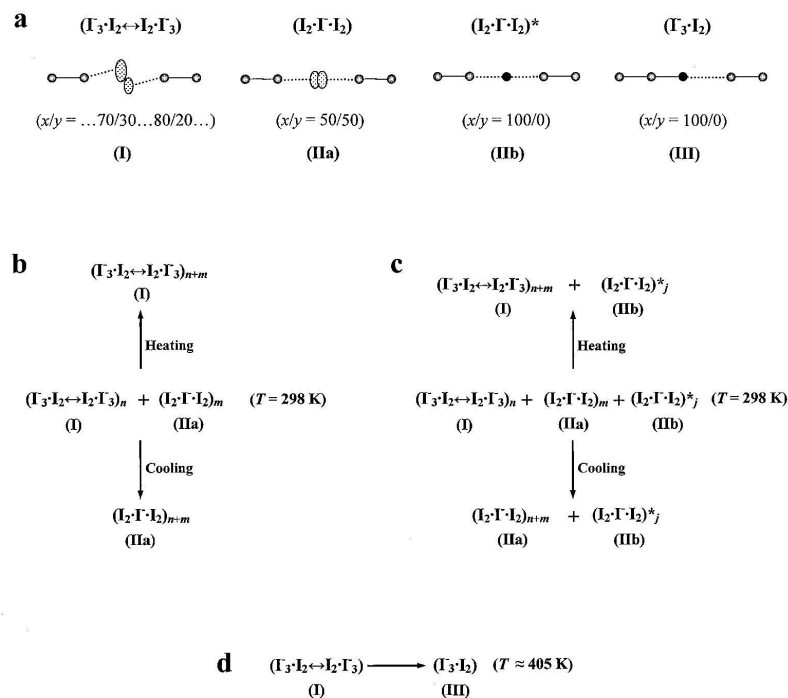
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Keywords:	Cyclodextrin inclusion complexes, Dielectric relaxation, Disorder phenomena, Pentaiodide transformations, Raman scattering



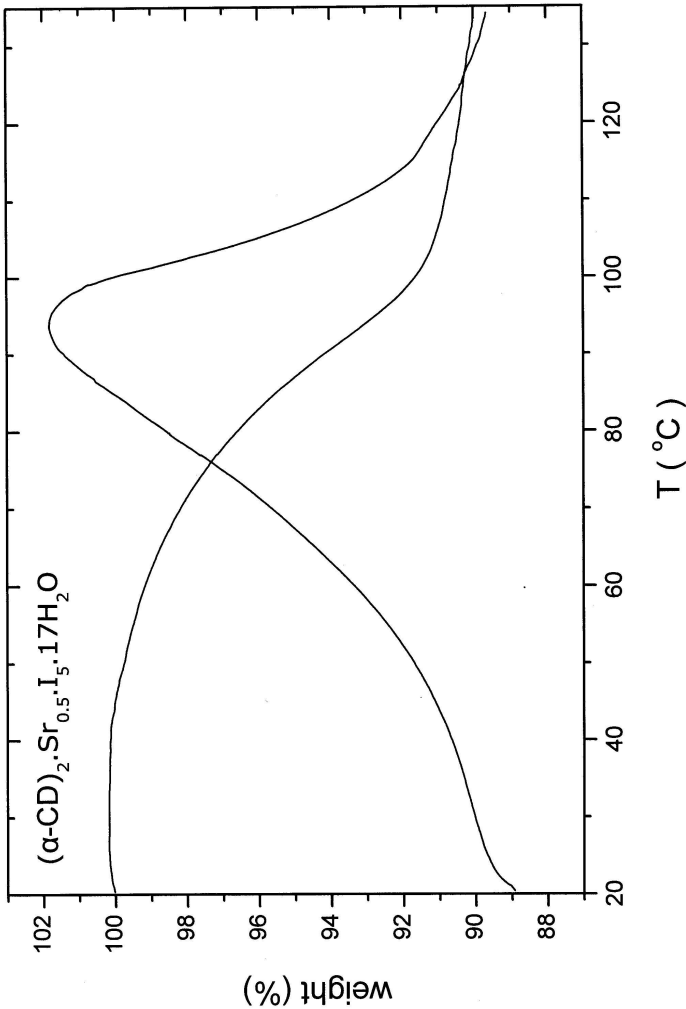


Figure 1



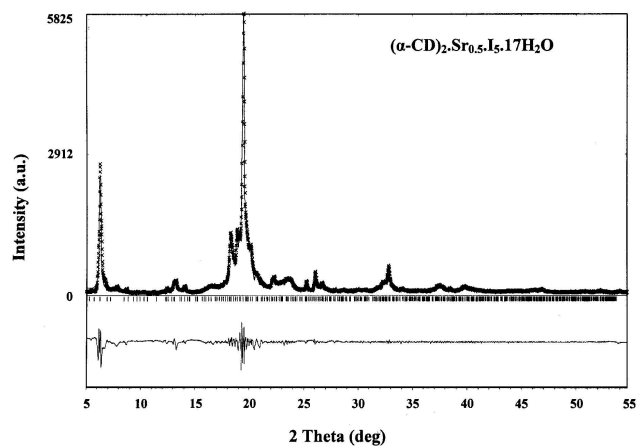
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Figure 2



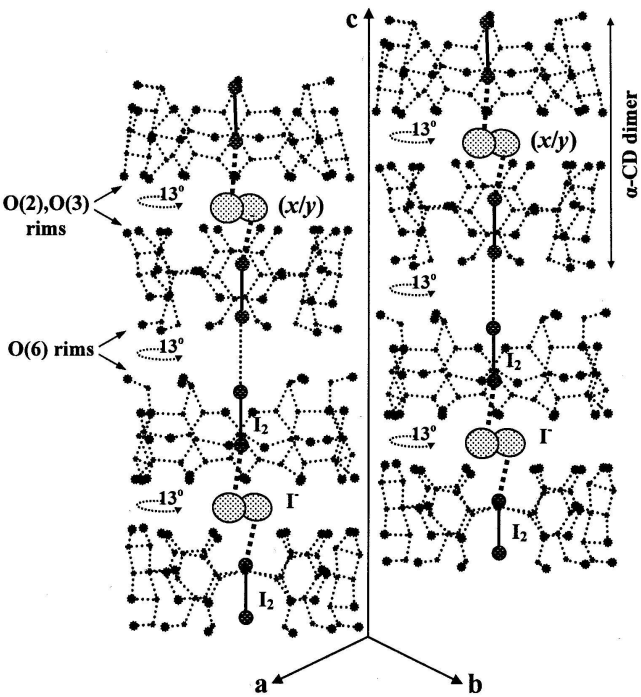
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Figure 3



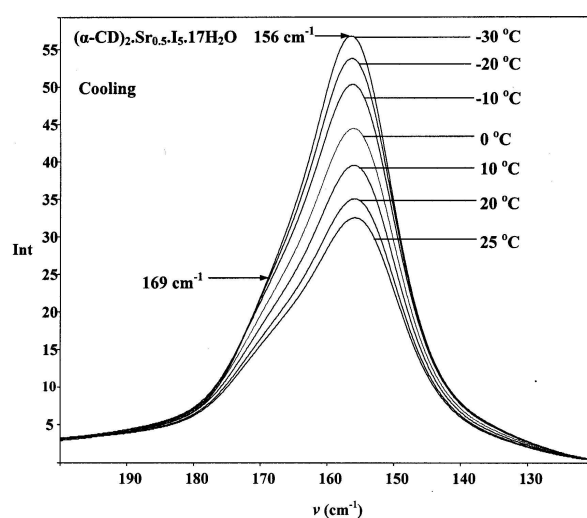
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Figure 4



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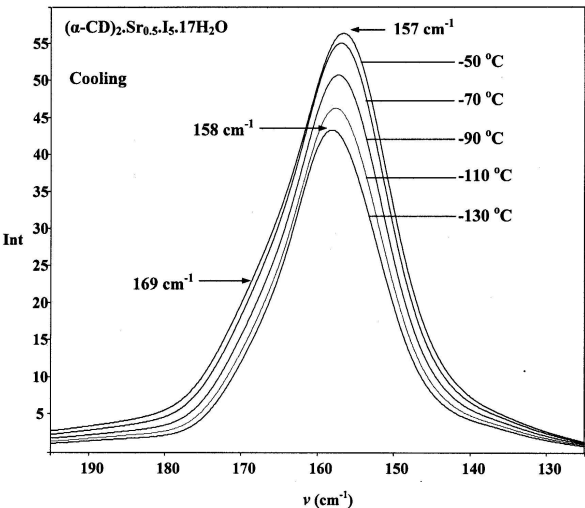
Figure 5a



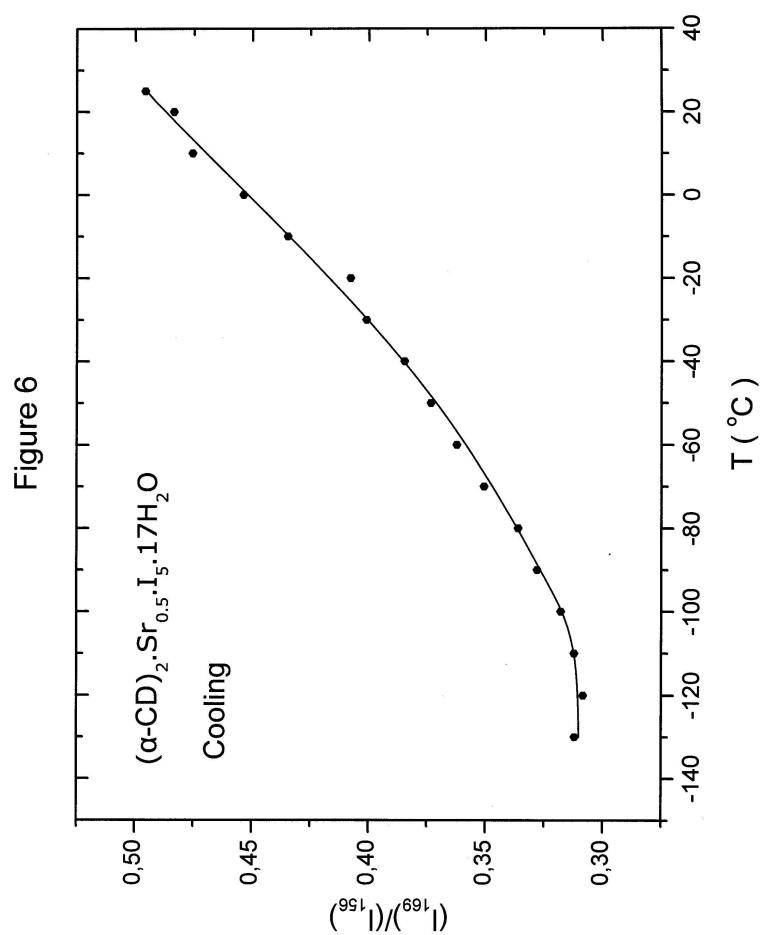
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Figure 5b

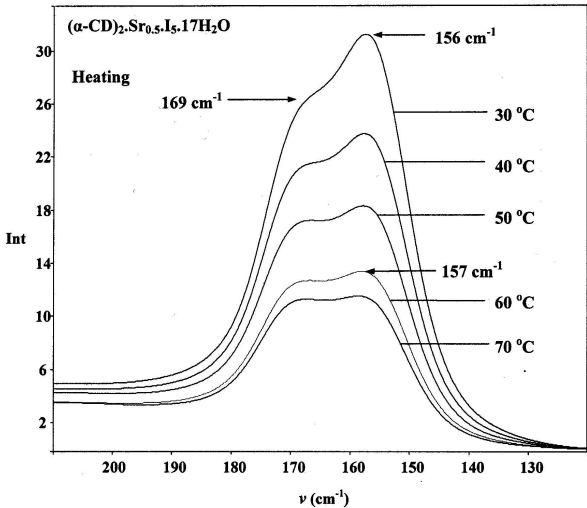


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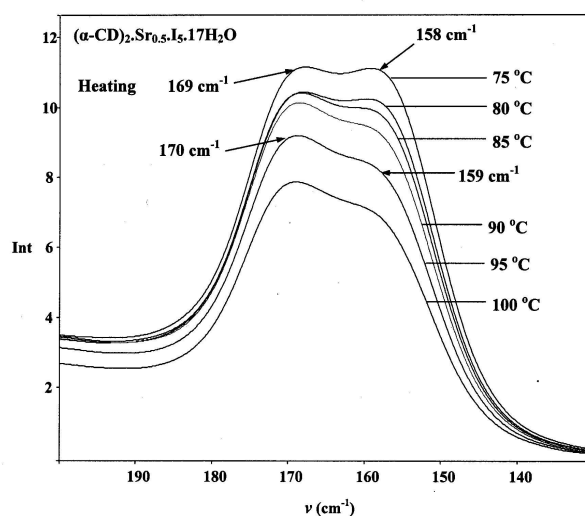
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Figure 7a



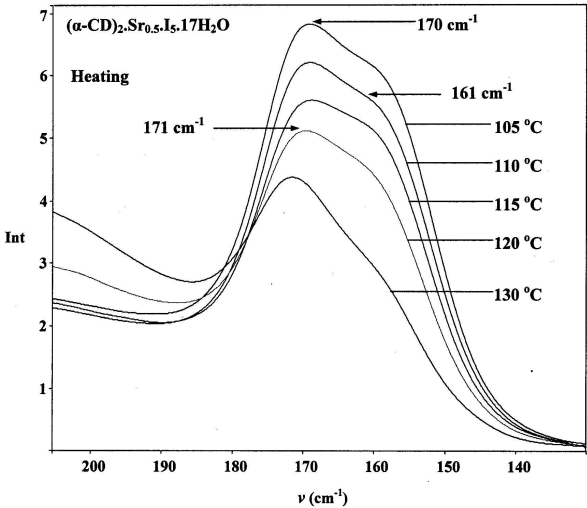
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Figure 7b

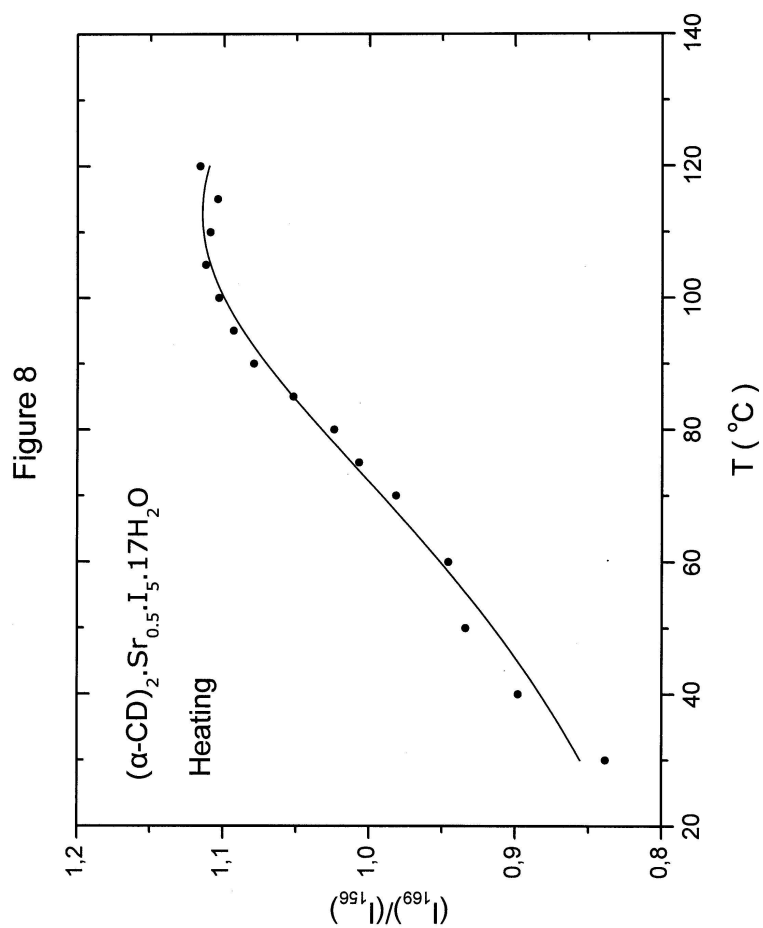


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Figure 7c

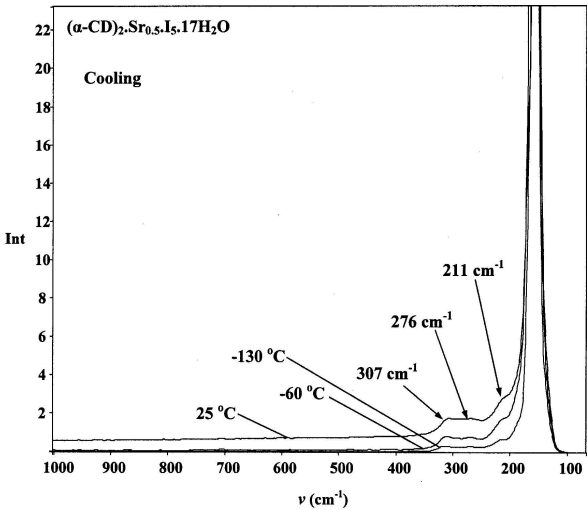


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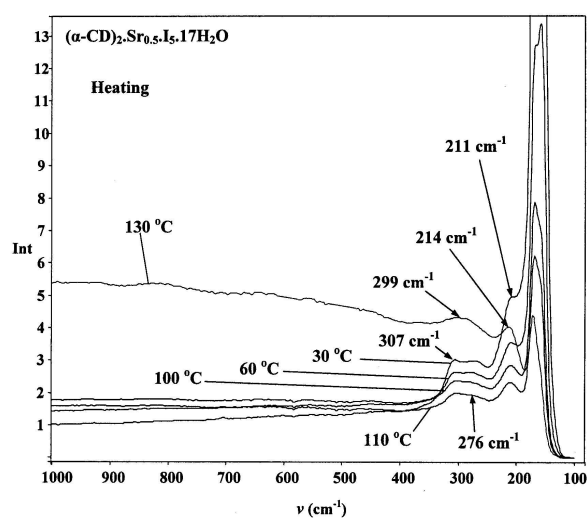
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Figure 9a



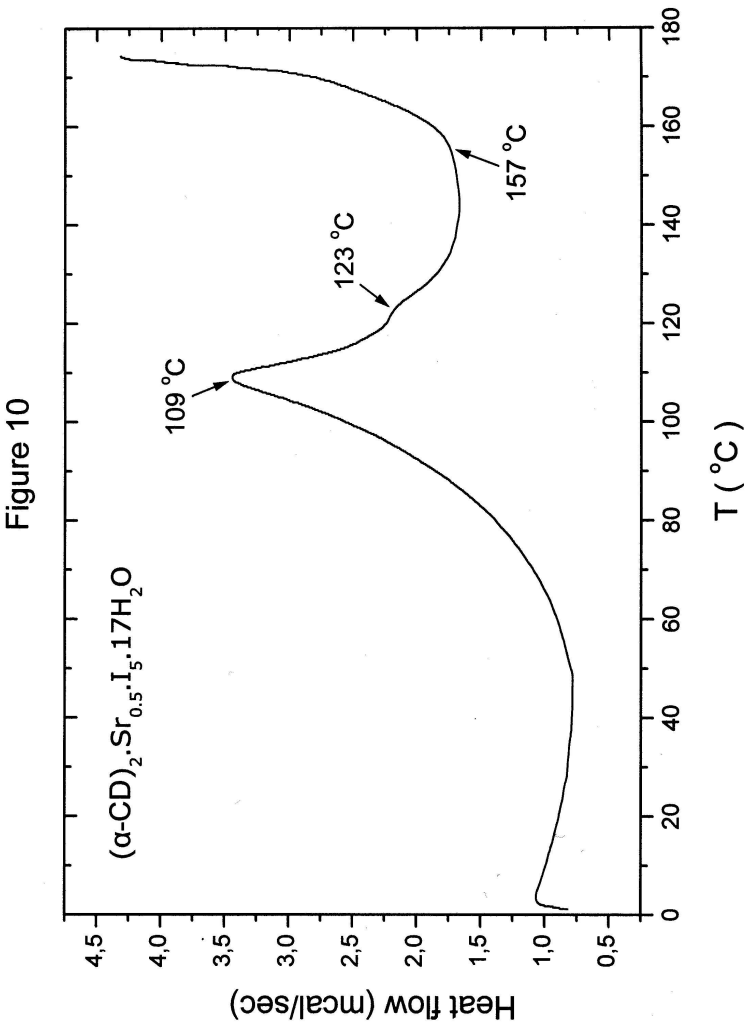
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Figure 9b

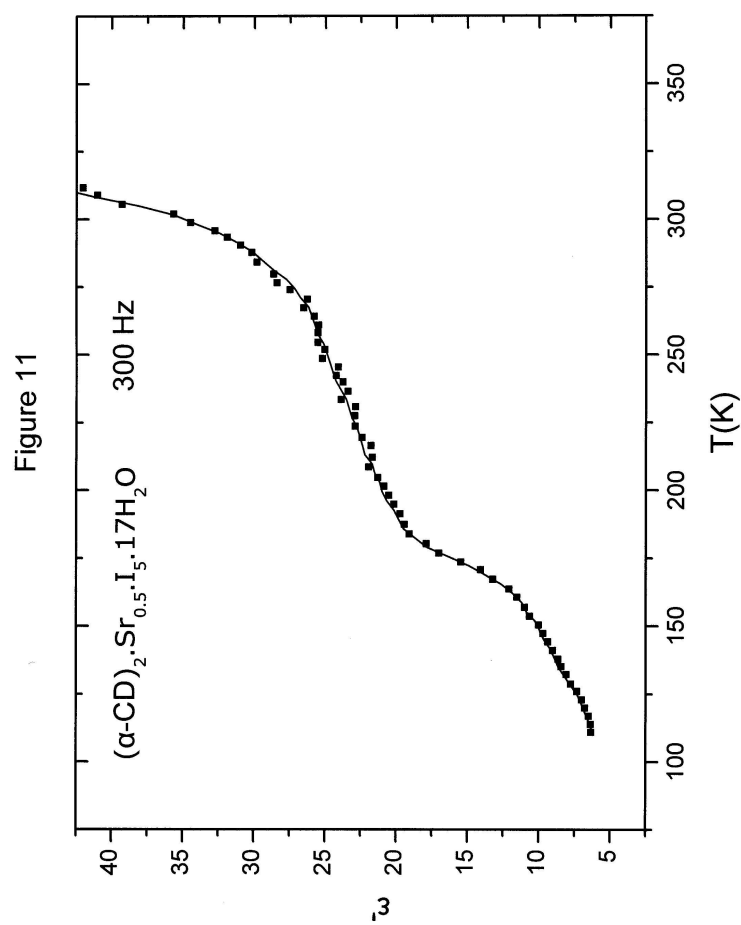


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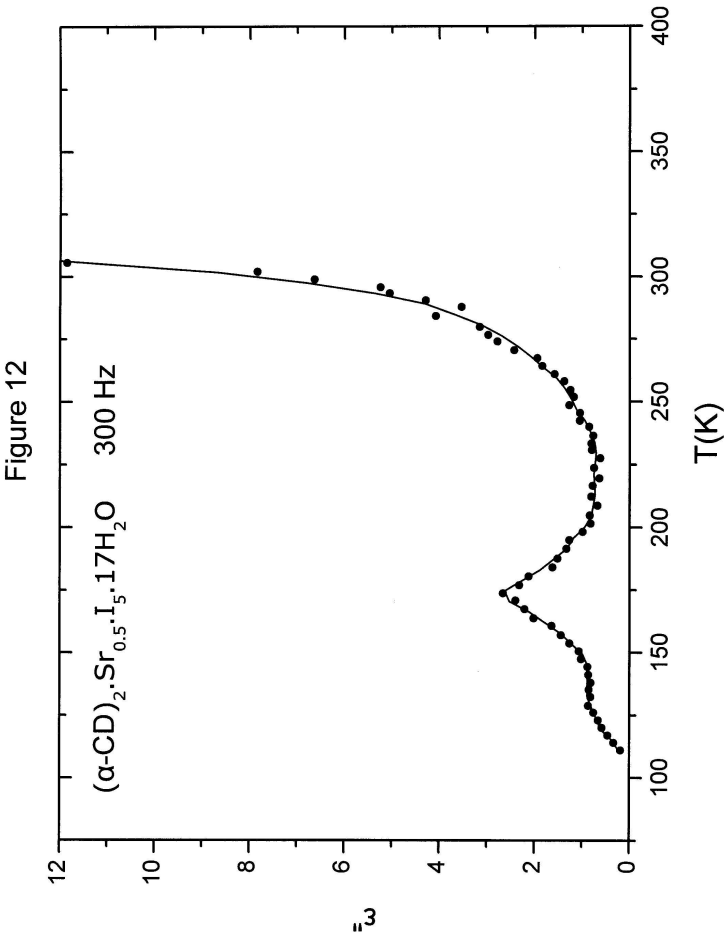




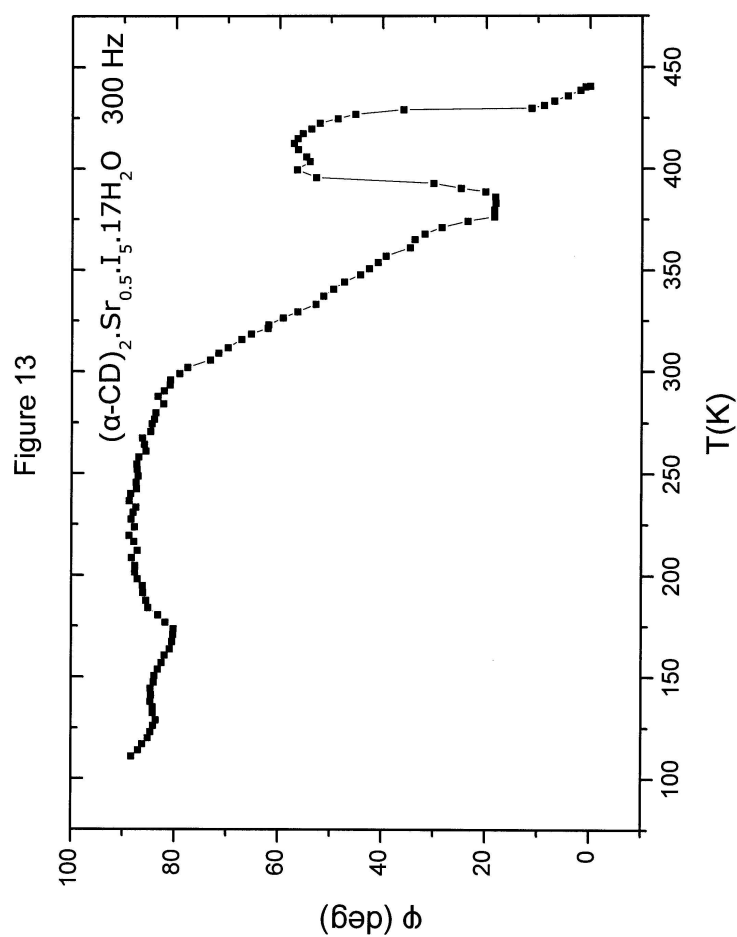
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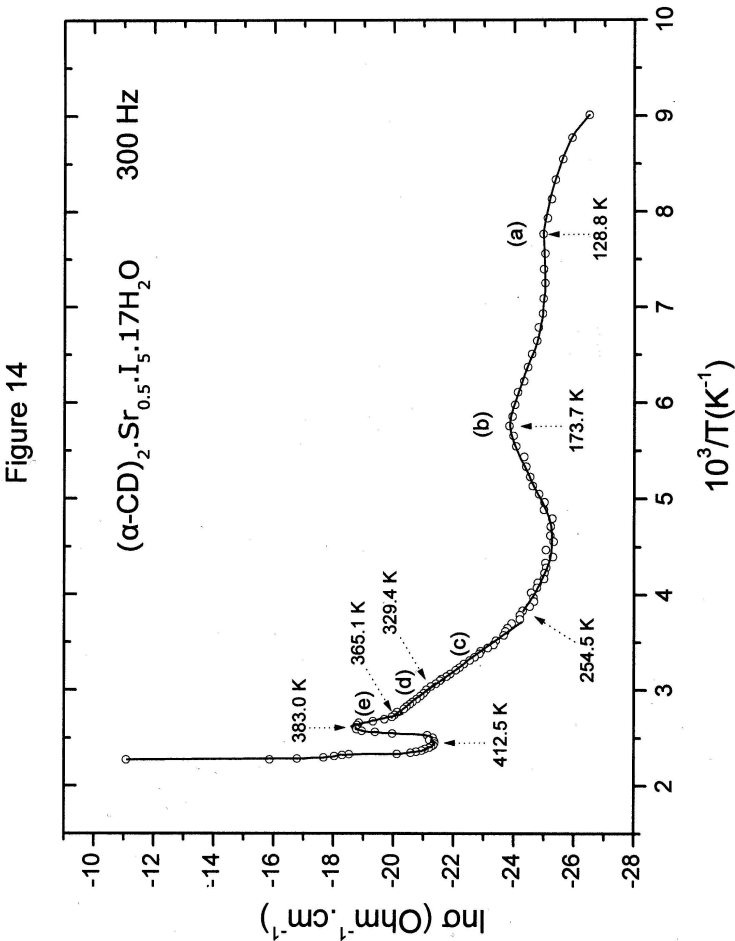
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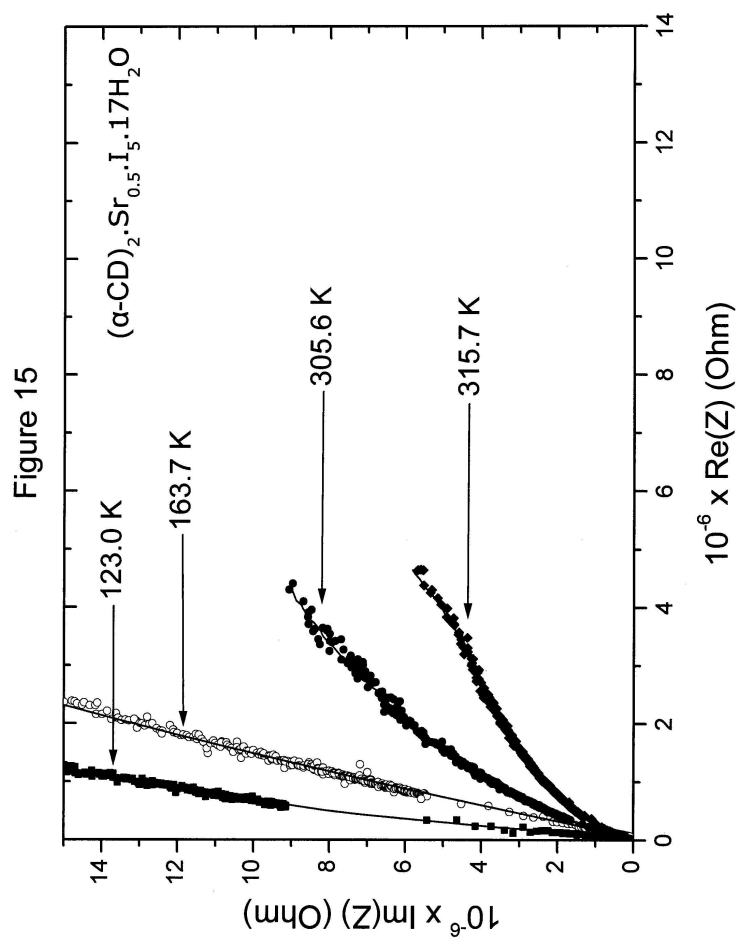
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**An insight into the disorder properties of the  $\alpha$ -cyclodextrin polyiodide inclusion complex with  $\text{Sr}^{2+}$  ion: Dielectric, DSC and FT-Raman spectroscopy studies**

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**Abstract.**

At  $T < 250$  K, the polyiodide inclusion complex  $(\alpha\text{-cyclodextrin})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  displays two separate relaxation processes due to both the frozen-in proton motions in an otherwise ordered H-bonding network and the order-disorder transition of some normal H-bonds to flip-flop ones. At  $T > 250$  K, the ac-conductivity is dominated by the combinational contributions of the disordered water network, the mobile  $\text{Sr}^{2+}$  ions, the polyiodide charge-transfer interactions and the dehydration process. The evolution of the Raman spectroscopic data with temperature reveals the coexistence of four discrete pentaiodide forms. In form (I) ( $\text{I}_3\cdot\text{I}_2 \leftrightarrow \text{I}_2\cdot\text{I}_3$ ), the occupancy ratio ( $x/y$ ) of the central  $\text{I}^-$  ion differs from 50/50. In form (IIa) ( $\text{I}_2\cdot\text{I}\cdot\text{I}_2$ )  $x/y = 50/50$ , whereas in its equivalent form (IIb) ( $\text{I}_2\cdot\text{I}\cdot\text{I}_2$ )\* as well as in form (III) ( $\text{I}_3\cdot\text{I}_2$ ),  $x/y = 100/0$  (indicative of full occupancy). Via slow cooling and heating the inverse transformations (I)  $\rightarrow$  (IIa) and (IIa)  $\rightarrow$  (I) occur, respectively.

**Keywords:** Cyclodextrin inclusion complexes; Dielectric relaxation; Disorder phenomena; Pentaiodide transformations; Raman scattering;



## 1. Introduction

The single crystal X-ray analysis of the polyiodide inclusion complexes of  $\alpha$ -cyclodextrin ( $\alpha$ -CD) with a series of metal ions ( $M^{n+}$ ) (1-3), has revealed that they comprise systems of particular interest due to their complicated structural chemistry. More specifically, the crystalline water molecules as well as the  $M^{n+}$  ions (in most cases) act as space-fillers between the neighboring  $\alpha$ -CD stacks (composed of head-to-head arranged dimers) producing along with the vicinal hydroxyl groups a whole network of electrostatic and hydrogen-bonding interactions. Furthermore, the endless polyiodide chains that are embedded in the  $\alpha$ -CD cavities and consist of weakly interactive  $I_5$  ions, not only have they been used as models for the blue amylose-iodine complex (2,3) but they have also presented remarkable electrical properties due to electron delocalization between their I atoms.

In recent years (4-6), we have investigated the  $\alpha$ -cyclodextrin polyiodide complexes with  $Cd^{2+}$  and  $Na^+$  ions (named ( $\alpha$ -CD)-Cd and ( $\alpha$ -CD)-Na, respectively) using a wide variety of experimental techniques that enabled valuable insights into the chemical changes as a function of temperature (120-450 K). Interestingly, dielectric spectroscopy has proven to be very sensitive to the rotational (flip-flop H-bonds (7-9)) and translational ( $H_2O$  molecules distributed over different sites) motion of the dipolar groups in the corresponding hydrogen-bonding networks, providing further evidence for dislocations of the metal ions and for enhanced polyiodide charge-transfer phenomena at elevated temperatures. On the other hand, FT-Raman spectroscopy has offered quite sound information about the coexistence of the different pentaiodide structural features  $I_2 \cdot I \cdot I_2$  and  $I_3 \cdot I_2 \leftrightarrow I_2 \cdot I_3$  at room temperature (which depend on the occupancy ratio  $x/y$  of the central I anion and are analytically described in Figure 1a) and their impressive interconversions (exhibited in Figures 1b, c and d) during the cooling and heating of the crystals. Finally, thermal analysis (DSC, STA) effectively detected both the gradual removal (dehydration process) of the interstitial water molecules with various energy contents and the degradation of polyiodide moieties due to the sublimation of iodine.

These findings explicitly indicate that the aforementioned inclusion complexes are excellent models for the elucidation of principal forces, dynamic properties and charge transport mechanisms in the water clusters of biological systems (10-14), in the building blocks of many polyiodide materials (15) and in the cyclodextrin complex formation processes (16,17). Despite the fact that the individual nature of each counterion appears

to have a strong influence on the resultant crystalline form (1-3) it also appears to affect in a unique manner (along with slight variations in experimental conditions during synthesis and crystallization) the following: (i) the extent of the relevant disorder phenomena in the corresponding hydrogen bonding networks (4-6) and (ii) the obtained configuration of the solid polyiodide structures (15,18). Thus, in the present contribution we expand our experimental studies to one more  $\alpha$ -CD polyiodide inclusion complex with  $\text{Sr}^{2+}$  ion (named **( $\alpha$ -CD)-Sr**) relying on the combinational application of dielectric relaxation, FT-Raman spectroscopy and thermal analysis. Our main aim is not only a thorough interpretation of the respective physicochemical properties (dipolar orientational correlations, polyiodide structural conversions, electron interactions and thermal dissociations) but also a valid corroboration of our preliminary conclusions.

## 2. Experimental

$\alpha$ -Cyclodextrin and solid iodine were obtained from Fluka Chemica whereas strontium iodide ( $\text{SrI}_2$ ) was obtained from Alfa Aesar. 5.50 g of  $\alpha$ -CD (5.66 mmol) were dissolved in distilled water (40 mL) at room temperature under **continuous stirring (full dissolution)**. Then 0.195 g of strontium iodide (0.571 mmol) and 0.22 g of solid iodine (0.866 mmol) were simultaneously added to the solution which was heated up to 70 °C for 20-25 min. The hot solution was quickly **filtered through a folded filter paper** into an empty beaker (100 mL) which was covered with Teflon and then immersed in a Dewar flask (500 mL) containing water at the same temperature. After two days, very fine thin needles of **( $\alpha$ -CD)-Sr** were grown with golden luster and uniform composition. These were **isolated by filtration** and dried in air.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) of the crystals were conducted using a NETZSCH-STA 409 EP Controller TASC 414/3 (reference  $\text{Al}_2\text{O}_3$ ). The sample (65.90 mg) was heated in the temperature range of 20-135 °C with a heating rate of 5 °C·min<sup>-1</sup>. The C content of **( $\alpha$ -CD)-Sr** was determined microanalytically on a LECO CS 230 analyzer (combustion analysis), whereas the Sr content was measured on a Perkin Elmer Optima 5300 DV ICP-OES (inductively coupled plasma-optical emission spectrometer).

The experimental X-ray powder diffraction pattern was obtained with a Siemens D 5000 diffractometer using CuK $\alpha$ 1 radiation ( $\lambda = 1.54059 \text{ \AA}$ ) at 40 kV, 30 mA and a graphite crystal monochromator. The diffraction data were collected in the  $2\theta$  range of  $5-55^\circ$  with a constant step of  $0.015^\circ$  and a dwell time of 7s/step. The calculation of the simulated X-ray powder diffraction pattern of  $(\alpha\text{-CD})_2\cdot\text{Cd}_{0.5}\cdot\text{I}_5\cdot 27\text{H}_2\text{O}$  (2,3) and the Rietveld refinement of the lattice parameters were performed by the computer program POWDERCELL 2.4 developed by Nolze and Kraus (19-23).

The differential scanning calorimetry method (Perkin Elmer DSC-4 instrument) was applied using a thermal analysis data station (TADS) system for all calorimetric measurements. Known weights (10-15 mg) of  $(\alpha\text{-CD})\cdot\text{Sr}$  were sealed into aluminum pans and then heated from 0 up to  $170^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ , under a dynamic nitrogen atmosphere. The instrument was calibrated using indium at the same scanning rates.

For the dielectric spectroscopy experiment a pressed pellet of powdered sample (542.5 mg), 20 mm in diameter with thickness 1.05 mm was prepared with a pressure pump (Riken Powder model P-1B) at room temperature. Two platinum foil electrodes were pressed at the same time with the sample. The electrical measurements were taken using a low-frequency (0-100 kHz) dynamical signal analyzer (DSA-Hewlett-Packard 3561A) at the temperature range of 110-440 K. The data can be transferred to a PC through an HP 82335 Interface Bus (IEEE-488), where they can be stored and analysed by a software program (2plt-1996). The complex permittivity  $\epsilon^*$ , impedance  $Z^*$ , conductivity  $\sigma^*$  along with the phase shift  $\varphi$  and the respective Argand diagrams ( $\epsilon''$  versus  $\epsilon'$  and  $Z''$  versus  $Z'$ ) can be calculated and plotted as a function of both temperature and applied frequency. An analytical description of the process is given in previous articles (24,25).

The Raman spectra were obtained at  $4 \text{ cm}^{-1}$  resolution from  $3500 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$  with a data point interval of  $1 \text{ cm}^{-1}$  using a Perkin-Elmer NIR FT-spectrometer (Spectrum GX II) equipped with an InGaAs detector. The laser power and spot (Nd: YAG at 1064 nm) were controlled to be constant at 50 mW during the measurements and 400 scans were accumulated. Two experiments were performed in the temperature ranges of: (a)  $(-130)\text{-}25^\circ\text{C}$  (cooling) and (b)  $30\text{-}130^\circ\text{C}$  (heating), with different samples. During the cooling process the sample was enclosed in a glassy NMR tube and held at a constant temperature ( $\pm 1^\circ\text{C}$ ) by means of a low temperature cell (Ventacon).

The temperature variation was controlled with a Ventacon Winchester instrument equipped with a CALCOMMS 3300 autotune controller.

### 3. Results and discussion

#### 3.1. Characterization of the synthesized inclusion complex

The thermogravimetric (TG) and differential thermal analysis (DTA) curves of ( $\alpha$ -CD)-Sr from room temperature to 135 °C (heating rate: 5 °C·min<sup>-1</sup>) are shown in Figure 2. The number of water molecules per dimer was calculated from the weight loss (10.10 %) in the temperature range of ~ 46-133 °C, where the dehydration process gradually takes place. The result is in agreement with ~ 17 water molecules per  $\alpha$ -cyclodextrin dimer. Furthermore, we have carried out the % C and % Sr elemental analysis of ( $\alpha$ -CD)-Sr in order to achieve a more complete determination of its general composition and this is explained in the following discussion. It has been shown that the  $\alpha$ -CD polyiodide inclusion complexes with metal ions display at least four different crystalline forms that strongly depend on the nature of the counterion and its coordination scheme (1-3). Among other cations, cadmium and strontium ions were classified into those which induce a tetragonal crystalline form with space group  $P4_22_12$ . Taking into account the fact that the single crystal X-ray analysis of ( $\alpha$ -CD)-Cd at room temperature (2,3) revealed that cadmium ions were twofold disordered with 0.5 Cd<sup>2+</sup> per  $\alpha$ -CD dimer (general composition ( $\alpha$ -CD)<sub>2</sub>·Cd<sub>0.5</sub>·I<sub>5</sub>·27H<sub>2</sub>O) in the present case the elucidation of the statistical distribution of Sr<sup>2+</sup> ions in relation to the  $\alpha$ -CD dimers appears to be crucial. The elemental analysis provided the following data: C, 29.86 % and Sr, 1.63 %. The corresponding % C, % Sr calculated values are 29.51 %, 1.49 % for 0.5 Sr<sup>2+</sup> per dimer (Sr to C ratio 1:19.80) and 29.08 %, 2.95 % for 1.0 Sr<sup>2+</sup> per dimer (Sr to C ratio 1:9.86). It becomes apparent that the obtained experimental values as well as the experimental Sr to C ratio (1:18.32) approach to the respective calculated ones for a twofold disordered strontium ion (0.5 Sr<sup>2+</sup> per dimer) indicating that the general composition of ( $\alpha$ -CD)-Sr can be described as ( $\alpha$ -CD)<sub>2</sub>·Sr<sub>0.5</sub>·I<sub>5</sub>·17H<sub>2</sub>O.

For the X-ray powder diffraction method (XRPD), a few grams of needle-shaped ( $\alpha$ -CD)-Sr crystals were finely hand-pulverized aiming at reducing the greater volume fraction of certain crystal orientations (texture) in the powdered sample. The

experimental XRPD pattern was collected at room temperature covering the  $5-55^\circ 2\theta$  range, in order to carry out a Rietveld refinement of the lattice parameters. Figure 3 shows the experimental XRPD pattern of **( $\alpha$ -CD)-Sr** and the Rietveld refinement of this profile (POWDER CELL 2.4 software) with the tetragonal  $P4_22_12$  structure of **( $\alpha$ -CD) $_2$ ·Cd $_{0.5}$ ·I $_5$ ·27H $_2$ O (2,3):  $R_p = 10.17\%$ ,  $R_{wp} = 16.28\%$ ,  $R_{exp} = 10.96\%$  and  $\chi^2 = 2.206$ . We obtained the following lattice parameters  $a = b = 19.9281(5)$  Å and  $c = 30.8151(7)$  Å which are in very good agreement with the unit cell constants reported by Noltemeyer and Saenger (2,3). At this point we clarify that some experimental reflection intensities vary from the corresponding ones of the simulated XRPD pattern due to the following reasons: (i) most of the pentaiodide units in **( $\alpha$ -CD)-Sr** display different configurations from those described in the single crystal of **( $\alpha$ -CD)-Cd** as it becomes evident from the FT-Raman spectroscopy study, (ii) in **( $\alpha$ -CD)-Sr**, the degree of hydration per dimer (17 H $_2$ O) is lower than that of **( $\alpha$ -CD)-Cd** (27 H $_2$ O) indicating that the crystalline water molecules of these systems are neither expected to occupy equivalent lattice positions nor to present identical spatial correlations, and (iii) an inevitable though little contribution of preferred orientation effects. Nevertheless, the observed isomorphism between **( $\alpha$ -CD)-Sr** and **( $\alpha$ -CD)-Cd** reveals that the  $\alpha$ -CD molecules of the former are arranged coaxially with the crystallographic  $c$  axis (Figure 4) exhibiting a rotation to each other by  $13^\circ$  as in the case of the latter complex (2,3). This structural feature is consistent with the formation of wide enough interstices between the  $\alpha$ -CD stacks. These interstices accommodate 17 water molecules per  $\alpha$ -CD dimer along with the twofold disordered Sr $^{2+}$  ions (2). Finally, the total absence of any hump (indicative of amorphous material) in the experimental XRPD pattern proves the purity of the synthesized inclusion complex (single phase compound).**

### 3.2. Disorder in polyiodide moieties

A preliminary comparison of the present FT-Raman spectroscopy results to those obtained from our previous investigations (5,6) reveals that **( $\alpha$ -CD)-Sr** displays a rather similar behaviour to that of **( $\alpha$ -CD)-Na** (Figure 1c) during the cooling and heating processes. More specifically, at room temperature (25 °C) there is a strong band at 156 cm $^{-1}$  (Figure 5a) which is ascribed to the symmetric coupling of the  $\nu_1$  stretching vibration of the outer I-I bonds in a (I $_2$ ·I·I $_2$ ) configuration (form (IIa) according to

Figure 1a) and an **easily distinguished** shoulder at  $169\text{ cm}^{-1}$  which is attributed to the  $\nu_1$  symmetric vibrational mode of a weakly coordinated  $\text{I}_2$  unit in a  $(\text{I}_3\cdot\text{I}_2 \leftrightarrow \text{I}_2\cdot\text{I}_3)$  configuration (form (I) according to Figure 1a) (15,18,26-32). As the temperature is lowered to  $-130\text{ }^\circ\text{C}$  (Figures 5a, b), the band at  $156\text{ cm}^{-1}$  is slightly shifted to the higher frequency of  $158\text{ cm}^{-1}$  and presents an intensity enhancement in relation to the shoulder at  $169\text{ cm}^{-1}$  which becomes so weak that it is barely identifiable. These experimental data are consistent with the pentaiodide structural transformation  $(\text{I}) \rightarrow (\text{IIa})$  which is a consequence of the fact that the occupancy ratio of the disordered  $\Gamma$  ions in form (I) gradually changes from an initial value of, for example, ...60/40...70/30... to the final value of 50/50 (form (IIa)) as the crystals are slowly cooled. Figure 6 exhibits the variation of the intensity ratio  $I_{169}/I_{156}$  as a function of temperature. From 25 to  $-110\text{ }^\circ\text{C}$ , this ratio decreases due to the continuous transformation  $(\text{I}) \rightarrow (\text{IIa})$ . In the range of  $(-130)-(-110)\text{ }^\circ\text{C}$ , it remains almost invariant indicating that the aforementioned transformation is completed and that there is a very small population of  $(\text{I}_3\cdot\text{I}_2)$  ions (form (III) according to Figure 1a) that does not display any configurational conversion with temperature retaining the **hardly distinguished** shoulder at  $169\text{ cm}^{-1}$ .

Complementary information is provided by the FT-Raman spectra of  $(\alpha\text{-CD})\text{-Sr}$  in the temperature range of  $30\text{-}130\text{ }^\circ\text{C}$  (Figures 7a, b and c). Initially, there is a strong band at  $156\text{ cm}^{-1}$  and an **easily distinguished** shoulder at  $169\text{ cm}^{-1}$ . As the temperature is raised the band at  $169\text{ cm}^{-1}$  becomes more intense in comparison to that at  $156\text{ cm}^{-1}$  and accompanying this relative intensity change there is also a small position shift of the former band to the frequency of  $171\text{ cm}^{-1}$  and of the latter band to the frequency of  $161\text{ cm}^{-1}$ . These phenomena are caused by the transformation  $(\text{IIa}) \rightarrow (\text{I})$  which implies a progressive change of the occupancy ratio of the  $\Gamma$  ions in the initial ( $25\text{ }^\circ\text{C}$ ) form (IIa), from 50/50 to the value of ...60/40...70/30... and so on. Similar changes also happen to the occupancy ratio of the  $\Gamma$  anions in the initial ( $25\text{ }^\circ\text{C}$ ) form (I) (e.g....60/40...70/30...  $\rightarrow$  ...70/30...80/20...). Thus, it appears to be explicit that as the temperature increases the vario-occupancy ratio of the disordered ions  $\Gamma$  in the pentaiodide forms (I) and (IIa), presents the tendency to take the value of 100/0 (indicative of full occupancy). The disordered  $\Gamma$  ions in form (I) will become well-ordered earlier than those in form (IIa), according to the disorder - order transition  $(\text{I}) \rightarrow (\text{III})$  (Figure 1d). This effect takes place via a charge-transfer interaction (as evident from dielectric measurements) between the central  $\Gamma$  ion (Lewis base donor) and one of the two  $\text{I}_2$  molecules (Lewis



acid acceptors). The fact that the shoulder at  $161\text{ cm}^{-1}$  is retained up to the end of the experiment suggests that there is an important percentage of **pentaiodide ions that is described by the  $(\text{I}_2\cdot\text{I}\cdot\text{I}_2)^*$  configuration (form (IIb)) according to Figure 1a** and remains unaffected during the slow heating of the sample. Figure 8 shows that the temperature dependent intensity ratio  $I_{169}/I_{156}$  continuously increases from 30 to  $100\text{ }^\circ\text{C}$  due to the gradual transformation  $(\text{IIa}) \rightarrow (\text{I})$ . Above  $100\text{ }^\circ\text{C}$ , this ratio remains almost constant revealing that all the  $(\text{I}_2\cdot\text{I}\cdot\text{I}_2)$  ions of form (IIa) have been transformed into those of form (I), **whereas the  $(\text{I}_2\cdot\text{I}\cdot\text{I}_2)^*$  ions of form (IIb) still exist in the crystal lattice**. The initial very small population of  $(\text{I}_3\cdot\text{I}_2)$  ions (form (III)) that has been detected during cooling is also expected to present no configurational conversions with temperature rise.

The characteristic Raman-active (symmetric stretch) band  $\nu''_1$  of the  $\text{I}_3$  ions at approximately  $107\text{ cm}^{-1}$  (27,28,33) does not appear as a result of the limited frequency range of the spectrometer ( $\geq 100\text{ cm}^{-1}$ ). Nevertheless, in Figures 9a and b, we observe its progressive overtones at  $211\text{ cm}^{-1}$  ( $2\nu''_1$ ,  $2 \times 107$ ) and  $307\text{ cm}^{-1}$  ( $3\nu''_1$ ,  $3 \times 107$ ) whose intensity variation obviously follows the intensity variation of the band at  $169\text{ cm}^{-1}$  ( $\nu'_1$ ) as a function of temperature in both cooling (up to the final temperature of  $-130\text{ }^\circ\text{C}$ ) and heating (up to the selected temperature of  $110\text{ }^\circ\text{C}$ ) processes. This spectral behaviour as well as the existence of the combination band at  $276\text{ cm}^{-1}$  ( $\nu''_1 + \nu'_1$ ,  $107 + 169$ ), comprise further assurances that the  $\nu''_1$  and  $\nu'_1$  fundamental transitions originate from a single chemical species ( $\text{I}_3\cdot\text{I}_2$ ,  $\text{I}_3\cdot\text{I}_2 \leftrightarrow \text{I}_2\cdot\text{I}_3$ ). Interestingly, at the high temperature of  $130\text{ }^\circ\text{C}$  (Figure 9b) additional information is drawn allowing a probe into both the local and long-range order fluctuations of the polyiodide moieties. More specifically, as it can be observed the broadened  $3\nu''_1$  band exhibits a downshift to the frequency of  $299\text{ cm}^{-1}$  indicating a downshift of the non-detectable parent fundamental band  $\nu''_1$  at  $\sim 107\text{ cm}^{-1}$ . This phenomenon is attributed to the initiation of the sublimation of iodine which is directly related to the band at  $214\text{ cm}^{-1}$  (characteristic of the sublimating  $\text{I}_2$ ) (15) and results in the breaking of the  $(\text{I}_3\cdot\text{I}_2)$ ,  $(\text{I}_3\cdot\text{I}_2 \leftrightarrow \text{I}_2\cdot\text{I}_3)$  and  $(\text{I}_2\cdot\text{I}\cdot\text{I}_2)^*$  chain compounds into  $\text{I}_3$  and  $\text{I}_2$  (26,31,34). This process increases both the  $\text{I}_3$  chain population and the  $\text{I}_2$  sublimating population at the expense of pentaiodide units explaining the enhanced intensities of the  $3\nu''_1$  and  $214\text{ cm}^{-1}$  bands in relation to those of the bands at  $161\text{ cm}^{-1}$  ( $\nu_1$ ) and  $171\text{ cm}^{-1}$  ( $\nu'_1$ ). Moreover, we strongly believe that the shift of the  $\nu''_1$  and  $3\nu''_1$  vibrational modes of  $\text{I}_3$  ions to lower frequencies is a result of both the emerging  $\text{I}_3\cdots\text{I}_3$  excitonic interactions along the chain length (head-to-tail arrangement of transition

dipole moments) and the  $\Gamma_3$  thermal tension (34,35). The latter phenomenon may also play a key role in the observed broadening of the  $3\nu''_1$  band. Concerning the combination band ( $\nu''_1 + \nu'_1$ ), it weakens and becomes obscured by the  $3\nu''_1$  band as a result of the important reduction of ( $\Gamma_3 \cdot I_2$ ) and ( $\Gamma_3 \cdot I_2 \leftrightarrow I_2 \cdot \Gamma_3$ ) units due to the sublimation of iodine. Finally, the band at  $214\text{ cm}^{-1}$  seems to obscure the  $2\nu''_1$  overtone which is also expected to present a frequency downshift and make an essential contribution to the intensity of the former band. At this point, the fact that at even higher temperatures the total degradation of the polyiodide chains takes place is also emphasized.

**In summary, the present work, via the temperature-dependent FT-Raman spectroscopy, sheds light on the relatively unknown mechanisms of ion transport at the atomic scale by detecting a series of detailed snapshots of the disordered  $\Gamma$  ions during the underlying pentaiodide interconversions. Within this perspective, this system could be used as a model for the elucidation of the charge-transfer processes in a variety of biological materials that display a vario-degree of ion disorder under different experimental conditions. Apart from the above findings, the employment of Raman technique also reveals that the endless polyiodide chains of ( $\alpha$ -CD)-Sr consist of four discrete pentaiodide substructures at room temperature.** This should not appear unfamiliar to the reader since it is widely shared among chemists that the real crystals present deviations from the ideal picture of a periodical perfect repetition of a unit cell (36). Even though, we have credibly demonstrated that the occupancy ratio ( $x/y$ ) of the disordered central  $\Gamma$  ions seems to be exclusively responsible for the predominant pentaiodide form during the thermal variation of the sample, it is clear that some significant questions remain concerning the nature of this disorder. A detailed crystallographic study over a range of temperatures by a specialist can effectively determine the evolution of the atomic displacement parameters (ADPs) in order to achieve a successful discrimination between dynamic, static and thermal vibrational disorder (36-39). Although, a discussion of this particular topic is beyond the scope of the present work, we believe that dynamic phenomena make a fundamental contribution to the temperature dependent distribution of the electronic density of  $\Gamma$  ions. In such a case, the lifetime of the ground state of the interconverting pentaiodide species is expected to be longer than the Raman vibrational scale ( $10^{-13}$  sec) (40). Furthermore, it is worth stressing that the small position shifts of the two initial bands ( $156$  and  $169\text{ cm}^{-1}$ ) to higher wavenumbers during cooling ( $156 \rightarrow 158\text{ cm}^{-1}$ ) and heating ( $156 \rightarrow 161\text{ cm}^{-1}$  and  $169 \rightarrow 171\text{ cm}^{-1}$ ) may arise from small



geometrical transformations involving not only slight decrements in the  $I_2$  bond lengths (attenuation of donor-acceptor interactions, increased  $I_2$  force constant) (15,41) but changes in the bond angles of the pentaiodides as well. According to the *ab initio* calculations of Sharp and Gellene (42) the highly bent ( $C_{2v}$  symmetry) and the linear ( $D_{\infty h}$  symmetry)  $I_2 \cdot I_2$  ions present a symmetric stretch of the outer I-I bonds at 157.4 and 165  $cm^{-1}$ , respectively. Additionally, both the Resonance Raman spectroscopy studies of starch-iodine samples by Teitelbaum et al. (26) and of ( $\alpha$ -CD)-Cd and ( $\alpha$ -CD)-Li single crystals by Mizuno et al. (28) have shown that the linear  $I_2 \cdot I_2$  chain compounds exhibit the aforementioned vibrational mode in the narrow range of 161-163  $cm^{-1}$ . Taking into consideration these results, the shift of the band at 156  $cm^{-1}$  to the frequency of 161  $cm^{-1}$  with temperature rise (Figures 8a, b and c) can be interpreted in terms of a gradual conversion of a  $C_{2v}$  point group symmetry to a  $D_{\infty h}$  one.

### 3.3. Thermal stability

The DSC trace of ( $\alpha$ -CD)-Sr recorded with a scan rate of 10  $^{\circ}C \cdot min^{-1}$  is shown in Figure 10. The strong endothermic peak at 109  $^{\circ}C$  and the **easily distinguished** shoulder at 123  $^{\circ}C$  are directly related to the removal of the two kinds of water molecules which coexist in the crystal lattice. More specifically, the former peak corresponds to the gradual evaporation of the water molecules with a higher energy content than those, whose evaporation is responsible for the latter peak. This discrimination can be explained by taking into account the differences traced in the local environments of the water molecules. At room temperature, some of them are neatly coordinated (tightly bound state) with fully occupied positions whereas, others are positionally disordered (easily movable state) exhibiting extensive thermal motions and less favorable hydrogen bond geometries (3,7-9,43). Via the slow heating of the crystals, the relative populations of the two kinds of water molecules change inversely as a function of temperature (the disordered  $H_2O$  molecules increase whereas the well ordered ones decrease). During the dehydration process the loss of the disordered water molecules is expected to take place at lower temperatures than the loss of the well ordered water molecules. The strong peak at 109  $^{\circ}C$  is consistent with an enthalpy change  $\Delta H$  which is greater than the one in the case of the shoulder at 123  $^{\circ}C$ , revealing that as the temperature is being raised there is an enormous increment of the disorder in

the interstitial water arrangement and only a small percentage of H<sub>2</sub>O dipoles remains in the tightly bound state.

The upward baseline at  $T > 157\text{ }^{\circ}\text{C}$  is interpreted in terms of the sublimation of iodine that involves the gradual degradation of the  $\Gamma_5$  ions and the subsequent effusion of the sublimed iodine molecules resulting in the rupture of the grain boundaries. This process should not be related to the decomposition of the  $\alpha$ -cyclodextrin molecules since the latter begins at temperatures higher than  $250\text{ }^{\circ}\text{C}$  (44). In our previous studies we examined a series of  $\beta$ -CD polyiodide complexes with various metal ions (25,45-47) and we found that the sublimation of iodine took place at lower temperatures ( $130\text{-}135\text{ }^{\circ}\text{C}$ ) than in the present case. This happens because: (i) the neighboring  $\Gamma_5$  ions in ( $\alpha$ -CD)-Sr are weakly interactive (electron delocalization) whereas, the neighboring  $\Gamma_7$  ions in the  $\beta$ -CD systems are non interactive, and (ii) the  $\alpha$ -CD cavities are narrower than those of  $\beta$ -CDs indicating much more stronger C-H $\cdots$ I dispersion forces (3).

### 3.4. Disorder in the hydrogen-bonding network

Dielectric relaxation spectroscopy (DRS) is a powerful method for the detection of all the electrical conduction mechanisms within a whole series of materials. In the present case the data were analyzed in terms of the complex permittivity  $\epsilon^*$ , the complex impedance  $Z^*$ , the phase shift  $\varphi$  (or phase angle) and the complex conductivity  $\sigma^*$ . Complex permittivity  $\epsilon^*$  is defined as follows (48-50):

$$\epsilon^*(f) = \epsilon'(f) - j\epsilon''(f) \quad (1)$$

where the real part  $\epsilon'$  is directly related to the variations of the total polarization, the imaginary part  $\epsilon''$  (loss factor) expresses the energy dissipation within the sample,  $f$  is the frequency of the applied electric field and  $j = \sqrt{-1}$ . Complex impedance  $Z^*$  is described by the following relation:

$$Z^*(f) = Z'(f) - jZ''(f) \quad (2)$$

Generally, the complex plane plots imaginary  $Z''$  versus real  $Z'$ , are used in order to gain valuable information about the relaxation processes that take place in the systems under investigation. In the rare case of a single relaxation time  $\tau$ , a perfect semicircle is formed (Debye relaxation) whose diameter corresponds to the resistance of the material and its center is localized on the real axis. When there is a distribution of relaxation

times, a semicircular arc appears (Cole-Cole relaxation) having its center lying below the real axis. The complex impedance  $Z^*$  and the complex permittivity  $\varepsilon^*$  are interrelated as (50):

$$\varepsilon^*(f) = \frac{1}{j\omega C_o Z^*(f)} \quad (3)$$

where  $\omega = 2\pi f$  is the angular frequency,  $C_o = \varepsilon_o A_c / l$  is the capacitance of the empty measuring cell of electrode area  $A_c$  and electrode separation length  $l$ . The quantity  $\varepsilon_o$  is the dielectric permittivity of free space ( $8.854 \cdot 10^{-12}$  F/m).

The phase difference  $\varphi$  (also known as phase shift or phase angle) between the applied voltage  $V^*(t)$  and the resulting current  $I^*(t)$  is given by the relation (50):

$$\varphi = \tan^{-1} \left( \frac{Z''(f)}{Z'(f)} \right) \quad (4)$$

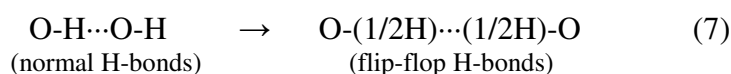
while the complex conductivity  $\sigma^*$  is represented by the following expression (49):

$$\sigma^*(f) = \sigma'(f) + j\sigma''(f) \quad (5)$$

being related to the complex permittivity  $\varepsilon^*$  and the complex impedance  $Z^*$  as (49,50):

$$\sigma^*(f) = j\omega \varepsilon_o \varepsilon^*(f) = \frac{1}{Z^*(f)} \quad (6)$$

Concerning the polycrystalline **( $\alpha$ -CD)-Sr**, DRS reveals that at low temperatures this system presents a different dielectric behaviour from that of the previously investigated **( $\alpha$ -CD)-Cd** and **( $\alpha$ -CD)-Na** complexes (4-6). More specifically, in the temperature range of 110-250 K what becomes obvious is the presence of two sigmoid curves in the  $\varepsilon'(T)$  variation (inflection points  $\varepsilon' = 7.8$  at  $T = 128.8$  K and  $\varepsilon' = 15.5$  at  $T = 173.7$  K, Figure 11), of two loss peaks in the  $\varepsilon''(T)$  variation ( $\varepsilon''_{1\max} = 0.9$  at  $T = 128.8$  K and  $\varepsilon''_{2\max} = 2.7$  at  $T = 173.7$  K, Figure 12) and of two topical minima in the  $\varphi(T)$  variation ( $\varphi_{1\min} = 83.6^\circ$  at  $T = 128.8$  K and  $\varphi_{2\min} = 80.2^\circ$  at  $T = 173.7$  K, Figure 13). These experimental data indicate two separate relaxation processes which result in important changes in the sample polarization and are directly related to the motions of the water molecules and the hydroxyl groups in the crystal lattice. The transition temperature  $T_{\text{trans}} = 173.7$  K is consistent with the order-disorder transition of some normal hydrogen bonds to those of flip-flop type according to the following scheme:



Flip-flop hydrogen bonds are characterized by the existence of H-atoms that are dynamically disordered in two energetically near equivalent positions (entropically favoured). This type of H-bonds has been originally detected in the single crystal of  $\beta$ -CD $\cdot$ 11H<sub>2</sub>O at room temperature by means of neutron diffraction analysis carried out by Betzel et al. (8).

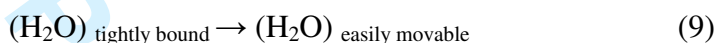
The relaxation peak at 128.8 K (Figure 12) can be interpreted in terms of a frozen-in disorder which is associated with the persistence of a certain percentage of molecular motions in the hydrogen-bonding network of ( $\alpha$ -CD)-Sr. Such a behaviour can be explained by taking into consideration the results of the low-temperature neutron diffraction study of  $\beta$ -CD $\cdot$ 11D<sub>2</sub>O carried out by Zabel et al. (9). This work demonstrated that at the temperature of 120 K, all the existing flip-flop H-bonds had been transformed into those of normal type with the exception of a four-membered ring which consisted of flip-flop H-bonds and was positioned at the junction of several homodromic rings and infinite chains. The above phenomenon was attributed to an energetical advantage at 120 K over an entropy advantage at room temperature. Furthermore, Hanabata and co-workers (51) conducted a calorimetric study of  $\beta$ -CD $\cdot$ 11H<sub>2</sub>O and reported a first-order phase transition at 226 K along with a glass transition behaviour of the sample at ~150 K which was correlated with the frozen-in disorder of the proton configurations engaged in the four-membered ring. Finally, the dielectric investigation of  $\beta$ -CD $\cdot$ 11H<sub>2</sub>O by Pathmanathan et al. (52) exhibited apart from the order-disorder transition (7) at 209.8 K, a relaxation peak of the imaginary part  $\epsilon''$  at 109 K which was attributed to the occurrence of localized molecular motions in an otherwise rigid matrix. Thus, in the present case the relaxation peak at 128.8 K comprises strong evidence for the formation of a flip-flop ring in the low temperature region despite the complete ordering (glasslike state) in the rest hydrogen-bonding network. The exact structural characteristics of such a ring can only be determined via a detailed single crystal neutron diffraction study of ( $\alpha$ -CD)-Sr and for this reason we do not proceed to any further interpretation. However, the fact that ( $\alpha$ -CD)-Sr presents similar behaviour to  $\beta$ -cyclodextrin undecahydrate and not to the ( $\alpha$ -CD)-Cd and ( $\alpha$ -CD)-Na complexes (single relaxation peaks at  $T < 250$  K) (4-6) is a matter of concern.

Above the temperature of ~250 K, the conductance of ( $\alpha$ -CD)-Sr increases enormously resulting in very high values of  $\epsilon'$  and  $\epsilon''$  that have no significance in the conventional dielectric sense (53). Therefore, we turn our attention to the temperature dependence of the ac-conductivity  $\sigma$  which provides valuable information about all the

different charge transport properties that appear in the range of 110-440 K. In the  $\ln\sigma$  versus  $1/T$  plot (Figure 14) the broad bell-shaped curve (a) at 128.8 K corresponds to the frozen-in disorder in the hydrogen-bonding network, whereas the broad bell-shaped curve (b) at 173.7 K is caused by the order-disorder transition (7). The linear part (c) in the range of 254.5-329.4 K exhibits an Arrhenius behaviour according to the semiconduction equation (54,55):

$$\sigma = \sigma_o \exp\left[-\frac{E_a}{kT}\right] \quad (8)$$

with activation energy  $E_a = 0.37$  eV ( $\sigma_o$  is the pre-exponential factor,  $k$  the Boltzmann's constant and  $T$  the absolute temperature). This exponential variation of the conductivity is a consequence of the gradual transformation:



which takes place along with the strontium ions' movements as it becomes evident from the impedance diagram of Figure 15. The appearance of the semicircular arcs reveals that the behaviour of the complex impedance  $Z^*$  in the present case can be described by the Cole-Cole formalism (56,57):

$$Z^*(\omega) = \frac{Z_s - Z_\infty}{1 + (j\omega\tau)^{1-\alpha}} \quad (10)$$

where  $Z_s$  is the static or the dc resistance  $R_{dc}$ ,  $Z_\infty$  is the impedance at high frequency and  $\alpha$  represents a measure of the distribution of relaxation times. During the heating process, the radii of the semicircular arcs decrease since the thermally activated processes (7) and (9) involve a continuous increment of the positionally disordered protons,  $\text{H}_2\text{O}$  molecules and OH-groups causing a progressive reduction of the grain interior resistance. Furthermore, the remarkably increased degree of disorder in the hydrogen-bonding network due to energy gain with temperature rise, implies the cleavage of certain H-bond geometries and the initiation of a proton hopping process described as Grotthuss mechanism (58-60). The generation of the linear response in the low frequency region at  $\sim 315.7$  K is associated with the onset of space charge in the material (61,62), an effect which is directly related to the release of  $\text{Sr}^{2+}$  ions and their successive oscillations with the frequency of the applied alternative field. This diffusive process is so much slower than any other diffusive process in the crystal lattice (hydrogen bond dynamics occur in a time scale of  $10^{-11}$ - $10^{-6}$  s (43,59,63)) and therefore it is responsible for the appearance of the aforementioned linear response.

The linear part (d) in the temperature range of 329.4-365.1 K also follows the semiconduction equation (8) with  $E_a = 0.34$  eV. This activation energy is slightly lower than that of the linear part (c) since the progressive dehydration process reduces the number of the reorientated H<sub>2</sub>O dipoles (easily movable state) in the interstices (first endothermic peak in Figure 10). Surprisingly, the linear part (e) in the range of 365.1-383 K, presents an activation energy with the very high value of 1.16 eV. This experimental feature reveals that there is a population of H<sub>2</sub>O molecules which remains in the tightly bound state (fully occupied sites) as the temperature is raised, due to the existence of very strong intermolecular interactions in the corresponding local environments (this population is responsible for the endothermic shoulder in Figure 10). Above 365.1 K, these rigid hydrogen-bonding arrangements are perturbed resulting in a considerable mobility of the involved water molecules and an unexpected increasing rate of the ac-conductivity which does not seem to be essentially affected by the simultaneous dehydration in this temperature range. It is noteworthy, that the enormous increase of  $\sigma$  up to 383 K, is consistent with the abrupt decrease of  $\varphi$  up to the same temperature (Figure 13) revealing that the sample conductance is being dominated by the disorder phenomena in the hydrogen-bonding network. At  $T > 383$  K, the ac-conductivity decreases rapidly due to the fact that the dehydration process starts to have a significant impact on the electrical properties leading to both the extensive breakdown of the water network and the attenuation of the proton conduction. Moreover, the continuous removal of the water molecules from the crystal lattice gradually minimizes the contribution of the strontium ions that act as localized charges. The remarkable increment of the ac-conductivity at  $T > 412.5$  K, is caused by the sublimation of iodine which provides conduction paths along the polyiodide chains resulting in an enhanced connectivity between the neighboring building blocks and important electron delocalization (long-range Coulomb attraction of excited electron and hole) (34,35,64). This phenomenon is also responsible for the rapid drop of the phase shift  $\varphi$  at  $T > 412.5$  K (Figure 13). The topical minimum value of  $\varphi$  (54.1°) at 403.5 K is attributed to the structural transition (I)  $\rightarrow$  (III) which a certain number of pentaiodide units undergo. This transition is analytically described in Figure 1d and was originally detected in the case of ( $\alpha$ -CD)-Cd (5).



#### 4. Concluding remarks

Interestingly, at  $T < 250$  K the dielectric behaviour of ( $\alpha$ -CD)-Sr is similar to the one of  $\beta$ -CD undecahydrate and significantly different from that of the previously investigated  $\alpha$ -CD polyiodide complexes with  $\text{Cd}^{2+}$  and  $\text{Na}^+$  ions. The relaxation peak at 128.8 K indicates the persistence of localized proton motions (frozen-in disorder) in the glasslike state (complete ordering in the rest H-bonding network) of ( $\alpha$ -CD)-Sr, whereas the relaxation peak at 173.7 K is consistent with the transition of some normal H-bonds to those of flip-flop type. At  $T > 250$  K, the ac-conductivity  $\sigma$  increases abruptly due to the gradual transformation  $(\text{H}_2\text{O})_{\text{tightly bound}} \rightarrow (\text{H}_2\text{O})_{\text{easily movable}}$  (also confirmed via DSC measurements) and the mobility of the released  $\text{Sr}^{2+}$  ions. Above 383 K the ac-conductivity drops rapidly since the dehydration process starts to have an important impact on the electrical properties leading to both the extensive breakdown of the water network and the minimization of metal ions' contribution. Furthermore, the enormous increment of the ac-conductivity at  $T > 412.5$  K is attributed to the sublimation of iodine. Concerning the polyiodide moieties of ( $\alpha$ -CD)-Sr, four discrete pentaiodide structural features were found to coexist at room temperature (298 K) depending on the occupancy ratio ( $x/y$ ) of the central I ions. In the  $(\text{I}_3 \cdot \text{I}_2 \leftrightarrow \text{I}_2 \cdot \text{I}_3)$  units (form (I))  $x/y \neq 50/50$  (e.g. ...60/40...70/30...). The  $(\text{I}_2 \cdot \text{I} \cdot \text{I}_2)$  units can be classified as the two equivalent forms (IIa) and (IIb). In (IIa)  $x/y = 50/50$ , whereas in (IIb)  $x/y = 100/0$  (a ratio indicative of full occupancy). Finally, in the  $(\text{I}_3 \cdot \text{I}_2)$  units (form (III)) the I ion is well ordered (100/0) forming with the one of the two  $\text{I}_2$  molecules, a triiodide ion. As the crystals are slowly cooled the transformation (I)  $\rightarrow$  (IIa) takes place, whereas during the heating process the inverse transformation (IIa)  $\rightarrow$  (I) occurs. These phenomena are caused by the changes in the corresponding occupancy ratios ( $x/y$ ) as the thermal variation of the sample proceeds. At 403.5 K, a certain number of  $\text{I}_5$  ions undergo the disorder-order transition (I)  $\rightarrow$  (III). The initial (298 K) forms (IIb) and (III) remain unaffected by temperature.

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## Figure Captions

Figure 1. The four discrete pentaiodide forms that have been detected in  $(\alpha\text{-CD})_2\cdot\text{Cd}_{0.5}\cdot\text{I}_5\cdot 26\text{H}_2\text{O}$  (**( $\alpha\text{-CD}$ )-Cd**) and  $(\alpha\text{-CD})_2\cdot\text{NaI}_5\cdot 8\text{H}_2\text{O}$  (**( $\alpha\text{-CD}$ )-Na**) (5,6): a) In form (I) the occupancy ratio  $x/y$  of the disordered central  $\text{I}^-$  ion is different from 50/50 (e.g. ...70/30...80/20...). In form (IIa) the occupancy ratio of the  $\text{I}^-$  ion is 50/50. In form (IIb) the  $\text{I}^-$  ion is well ordered and equidistant from the two  $\text{I}_2$  units. The value of 100/0 does not have any physical sense and is used to illustrate full occupancy. In form (III) the central  $\text{I}^-$  anion is well ordered forming with the one of the two  $\text{I}_2$  units an  $\text{I}_3^-$  ion. b) In **( $\alpha\text{-CD}$ )-Cd** the transformation (I)  $\rightarrow$  (IIa) takes place during cooling, whereas the inverse one (IIa)  $\rightarrow$  (I) happens during heating. c) **( $\alpha\text{-CD}$ )-Na** displayed similar behaviour to the one of **( $\alpha\text{-CD}$ )-Cd** further presenting the form (IIb) which remained unaffected by temperature. d) At  $\sim 405$  K, both systems exhibit the disorder-order transition (I)  $\rightarrow$  (III) via a charge-transfer interaction between the  $\text{I}^-$  ion and one of the two  $\text{I}_2$  units.

Figure 2. Simultaneous thermogravimetry (TGA) and differential thermal analysis (DTA) of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$ , with a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$ .

Figure 3. Rietveld refinement pattern of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$ . Black crosses: experimental pattern, solid line: refined model. The curve at the bottom is the difference between the observed and calculated intensities in the same scale. Black vertical lines indicate the positions of the allowed reflections.

Figure 4. The crystalline structure of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  based on the single crystal X-ray crystallography analysis of the isomorphous  $(\alpha\text{-CD})_2\cdot\text{Cd}_{0.5}\cdot\text{I}_5\cdot 27\text{H}_2\text{O}$  (tetragonal  $\text{P4}_22_12$ ), carried out by Noltemeyer and Saenger (2,3). The  $\alpha\text{-CD}$  stacks are strictly linear and arranged coaxially with the crystallographic  $c$  axis, leaving large spaces between them. The disordered  $\text{I}^-$  anions are presented as spotted ellipsoids, whereas the well-ordered  $\text{I}$  atoms are presented as small spotted spheres.

Figure 5. Raman spectra of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  during cooling, in the temperature ranges of: (a)  $(-30) - 25^\circ\text{C}$  and (b)  $(-130) - (-50)^\circ\text{C}$ .

Figure 6. The temperature dependence of the Raman intensity ratio  $(\text{I}_{169})/(\text{I}_{156})$  of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  during the cooling process.

Figure 7. Raman spectra of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  during heating, in the temperature ranges of: (a)  $30 - 70^\circ\text{C}$ , (b)  $75 - 100^\circ\text{C}$  and (c)  $105 - 130^\circ\text{C}$ .

Figure. 8. The temperature dependence of the Raman intensity ratio  $(\text{I}_{169})/(\text{I}_{156})$  of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  during the heating process.

Figure 9. Raman spectra of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  in the extended frequency range of 100-1000  $\text{cm}^{-1}$  : a) at the representative temperatures of 25, -60 and -130 °C during cooling and b) at the representative temperatures of 30, 60, 100, 110 and 130 °C during heating.

Figure 10. DSC thermogram of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  with a heating rate of 10 °C/min.

Figure 11. Temperature dependence of the real part  $\varepsilon'$  of the dielectric constant of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  at 300 Hz.

Figure 12. Temperature dependence of the imaginary part  $\varepsilon''$  of the dielectric constant of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  at 300 Hz.

Figure 13. Temperature dependence of the phase shift  $\varphi$  of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  at 300 Hz.

Figure 14. Temperature dependence of the ac-conductivity  $\sigma$  ( $\ln\sigma$  vs.  $1/T$ ) of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  at 300 Hz.

Figure 15. Impedance plot of  $(\alpha\text{-CD})_2\cdot\text{Sr}_{0.5}\cdot\text{I}_5\cdot 17\text{H}_2\text{O}$  at the representative temperatures of 123.0, 163.7, 305.6 and 315.7 K.