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Investigation of hydrogen bonds properties in the terephthalic acid crystal, using molecular dynamics method



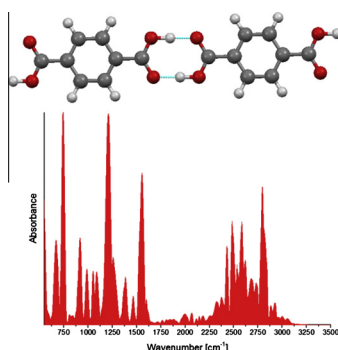
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HIGHLIGHTS

- The acid and its deuterated forms were studied by Car–Parrinello molecular dynamics.
- The power and theoretical infrared spectra were calculated for the different systems.
- The theoretical infrared spectra were compared with the experimental data.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to perform calculations using the method of Car–Parrinello molecular dynamics, leading to the optimized geometry of the molecules of 1,4-benzenedicarboxylic acid (terephthalic acid) in crystals, for the hydrogen form and three variants of substitution of deuterium atoms inside a carboxyl group. Based on the results, trajectories and dipole moments were calculated, what makes possible to simulate vibrations in different systems, and to make calculation of theoretical infrared spectra and atomic power spectra. Theoretical results were compared with the experimental spectra, which verifies the correctness of the method and also was compared with the results obtained by quantum-mechanical calculations using DFT for the isolated dimer. Comparison of the spectra of different forms, allowed for in-depth analysis of the effect of isotopic substitution on the frequency of vibrations and shapes of bands, and confirm the presence of possible coupling effects and intra- and intermolecular interactions. Comparison with the DFT results for the dimer show influence of the crystal structure on the spectra.

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Introduction

Hydrogen bond (HB) is still one of the most investigated subjects, due to its great importance in many chemical areas. It has strong effect on the micro- and macroscopic physicochemical

properties of matter [1–4] and also it is involved in stabilization of the chemical structures and important biological processes [5–9]. Spectroscopic methods provided many useful information which made possible to better know HB properties, but only a combination of spectroscopic and computational methods [10–12] made possible to obtain complementary information to understand this very complicated interaction.

In the cyclic dimers of carboxylic acids, many factors are affected on the nature of the HB [13]. Calculations of the vibrational spectra

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of the HB system are complicated due to large anharmonicity and proton delocalization [14]. The commonly used models of the cyclic dimer, describing the shape of the HB band in IR spectroscopy, assumed that it is the result of: (a) strong anharmonic coupling of the O–H stretching vibration with the stretching vibration of HB [15–18], (b) the Fermi resonance [19], appearing between the O–H stretching vibration and the first overtone of the O–H bending vibration [20], and (c) Davydov coupling [18,21,22] occurring between a pair of isoenergetic hydrogen bonds in the cyclic dimer. The calculations which are presented in this paper, also take into account the coupling between the vibrations of O–H bonds in the crystal, which is a factor that strongly influences the HB properties. Such interactions are very important considering the fact that very often the hydrogen bonds are most important for holding together organic crystals. Understanding this is extremely important for the development of modeling, starting from crystals of small size to large structures of macromolecules [23]. The progress of computational methods leads to increasing compatibility of the HB models with real systems.

Car and Parrinello are the creators of new kind molecular dynamics (CPMD) [24], where the main idea is the best use of quantum-mechanical time-scale separation of fast electrons and slow nuclei motions. This is achieved by converting the quantum-classical problem in a purely classical (in two separable time scales), on expense of losing information about the physical time in the quantum network [24–26]. The great advantage of the CPMD method is the possibility of quantum chemical description of the system, with effects on the HB factors, such as the crystal periodicity and thermal fluctuations [27,28], which are not included in other computational methods, such as DFT [29,30]. In the present paper, the results of the CPMD calculations for the terephthalic acid crystal and DFT calculations for its cyclic dimer have been compared. Also we performed study of the isotopic substitution effect, on the spectra. CPMD is recently used to simulate IR spectra of hydrogen-bonded crystals [31,32].

Terephthalic acid is an aromatic organic compound, which is involved in controlling the processes of some chemical reactions in organisms, such as being an antioxidant for protection against damage of internal organs, and myocardial infarction. It is used widely in industry for the production of high tensile strength polyester fibers. It occurs in nature in the form of white crystals. Its molecular weight is 166.13 g/mol, and density 1.522 g/cm³. Its melting point is 573 K, and at temperature 675 K is sublimed. It is weakly soluble in water and in organic liquids. It crystallizes in the triclinic system. The unit cell which belongs to the space group P₁, contains one molecule of the acid [33,34]. Terephthalic acid has two polymorphic forms. Our study concerns one of them because it is more stable as a result of its higher density and second form tended to become rarer on storage [34]. Lattice parameters of the unit cell of the studied crystal acid are:

$$a = 7.73 \text{ \AA} \quad b = 6.443 \text{ \AA} \quad c = 3.749 \text{ \AA} \quad \alpha = 92.75^\circ \\ \beta = 109.15^\circ \quad \gamma = 95.95^\circ$$

Computational methods

Calculations performed using the CPMD package were aimed to determine the optimal geometry of the structure of the crystal with four different isotopic substitutions. Consequently, we calculated the appropriate trajectories and dipole moments. The obtained results enabled us to simulate vibrations of the system, leading to theoretical power spectra and infrared spectra. As a model system four terephthalic acid molecules were used, which corresponds to 72 atoms. They form two hydrogen-bonded dimers I and II as shown in Fig. 1. Inside the unit cell are two pairs of hydrogen bonds. In the two other model systems, hydrogen atoms in the carbonyl group were substituted by deuterium atoms forming isotopomer structures. In the first model system positions I-H1, H6, H1', H6' and the second I-H1, H6', II-H1, H6' were substituted.

All dynamic calculations were performed using the BLYP functional [35]. To describe the electronic structure of the core we used Goedecker pseudopotentials [36], while for the valence electrons Bloch plane wave basis set [37] with the parameter CUTOFF 120 Ry. Optimization of geometry was done with an accuracy 10⁻⁶, what permitted to achieve the trajectories. Dipole moment was calculated at tenth iteration of the optimized geometry. In order to determine the trajectories, 220,000 iterations of trajectories were carried for each of the system, with time step equal 2 a.u. (0.049 fs). Such large number of steps were required because it was necessary to omit first 70,000 steps in the calculated trajectories, to stabilize the system. In addition, the geometry optimization was performed for the isolated dimer using DFT method, with functional B3LYP and 6-31++G** basis set.

Experimental section

Infrared spectra were measured for the hydrogen form of terephthalic acid, and for deuterated crystals with deuterium atoms replacing hydrogen atoms in the carboxylic groups. This substitution has been obtained by heating a suspension of terephthalic acid crystals in tetrahydrofuran with the addition of heavy water, followed by vacuum evaporation. Due to low solubility of terephthalic acid, efficiency of the isotopic exchange process was low. Only partially isotopically substituted acid was obtained. ATR technique was used for the spectroscopic measurements, which were done on Thermo Scientific Nicolet IR200 spectrometer.

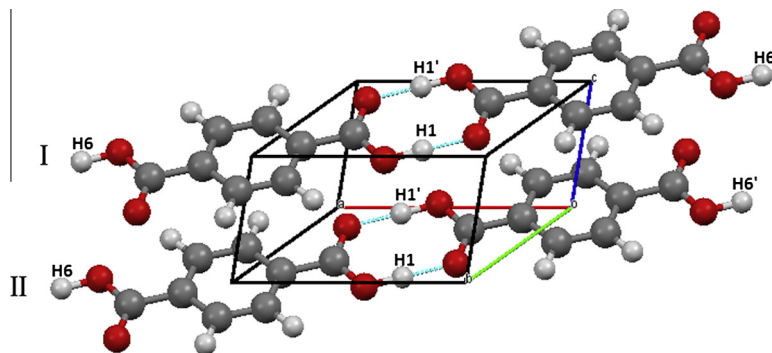


Fig. 1. Model system of terephthalic acid crystal.

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