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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
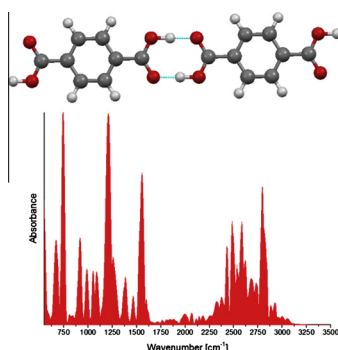
ABSTRACT

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/cm^3. 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 P$\bar{1}$, 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:

$$a = 7.73 \text{ Å} \quad b = 6.443 \text{ Å} \quad c = 3.749 \text{ Å} \quad \alpha = 92.75°$$
$$\beta = 109.15° \quad \gamma = 95.95°$$

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 of 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.
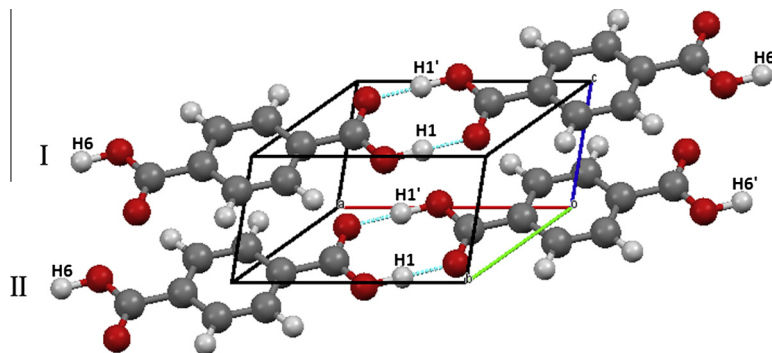

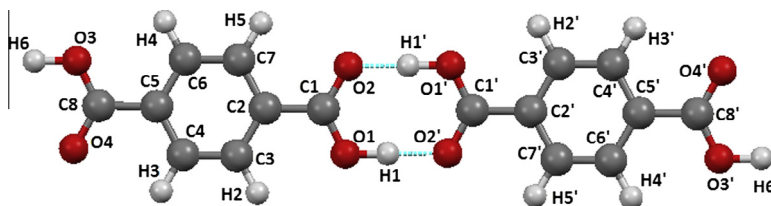**Fig. 1.** Model system of terephthalic acid crystal.

Fig. 2. Labeling of atoms used in descriptions of bond lengths and angles.

Results and discussion

Geometry analysis

Comparison of crystallographic data with the geometry optimized structures were made. Fig. 2 shows geometry of terephthalic acid dimer and labeling used in descriptions of bond lengths and angles.

In a model system, there are four molecules which are identical with each other, due to the presence of the inversion. Therefore the description is limited to the parameters for one of them. Crystallographic data are simultaneously the output coordinates for the atoms which geometry has been optimized. The obtained values of bond lengths and angles for all atoms were averaged due to loss of identity as a result of optimization. The results are summarized in Tables 1 and 2, together with the crystallographic data.

The analysis of the results leads to the conclusion that the calculated geometry, which was obtained by optimization with the CPMD package, does not differ significantly from the crystallographic data. Theoretical bond lengths are in good agreement with those experimentally determined. Differences vary between 0 and 0.05 Å. Angles, after geometry optimization using CPMD package, are in most cases reproduced very well, however, some exceptions are observed, mainly in the angles formed by the carbon atoms connected to the hydroxyl groups. It may be caused by limitations of the method as well as to the uncertainty of determination of the positions of hydrogen atoms by X-ray diffraction.

Results of the geometry optimization in the isolated dimer (DFT method) are much worse. In this case, the calculated lengths of the O—H bonds are in larger disagreement with the crystallographic

data (0.108 Å), two times more than for the CPMD calculations performed for the crystal.

Experimental infrared spectra of terephthalic acid

In the IR spectrum of the hydrogen form the widest range, located at 2400–3100 cm^{-1}, comes from stretching vibrations of the O—H groups, which are engaged in the formation of hydrogen bonds. This is confirmed by the presence of the band shifted to lower wave numbers compared with the bands of non-hydrogen-bonded hydroxyl groups. Also large half-width of the band, close to 700 cm^{-1}, and the presence of fine structure are evidences of hydrogen bond formation. Obtaining partially isotopically substituted form of the acid is manifested by a decrease in intensity of the O—H band, and the appearance at lower wave numbers a new band, derived from O—D vibration. Spectra of hydrogen-bonded and partially dueterated crystals are shown in Fig. 3.

Theoretical infrared spectra of terephthalic acid

Fig. 4a shows the experimental spectrum of terephthalic acid crystal, Fig. 4b the theoretical infrared spectrum of the crystal

Table 1
Bond lengths in terephthalic acid, obtained from crystallographic data and from theoretical calculations.

Description	Crystallographic data (Å) [34]	Averaged bond lengths obtained from geometry optimization using the CPMD method (Å)	Bond lengths from geometry optimization using DFT method (Å)
O1—H···O2′	2.608	2.582	2.637
O1—H1	1.080	1.030	1.007
O1—C1	1.272	1.329	1.322
O2=C1	1.262	1.250	1.237
C1—C2	1.484	1.480	1.490
C2—C3	1.401	1.401	1.404
C3—C4	1.370	1.386	1.392
C4—C5	1.406	1.400	1.403
C5—C6	1.401	1.401	1.403
C6—C7	1.370	1.386	1.392
C7—C2	1.406	1.399	1.402
C5—C8	1.484	1.479	1.491
O3—C8	1.272	1.330	1.357
O3—H6	1.080	1.030	0.972
C8=O4	1.262	1.249	1.216
C3—H2	1.080	1.082	1.084
C4—H3	1.080	1.081	1.084
C6—H4	1.080	1.082	1.084
C7—H5	1.080	1.081	1.084

Table 2
Angles formed by atoms in terephthalic acid obtained from crystallographic data and from theoretical calculations.

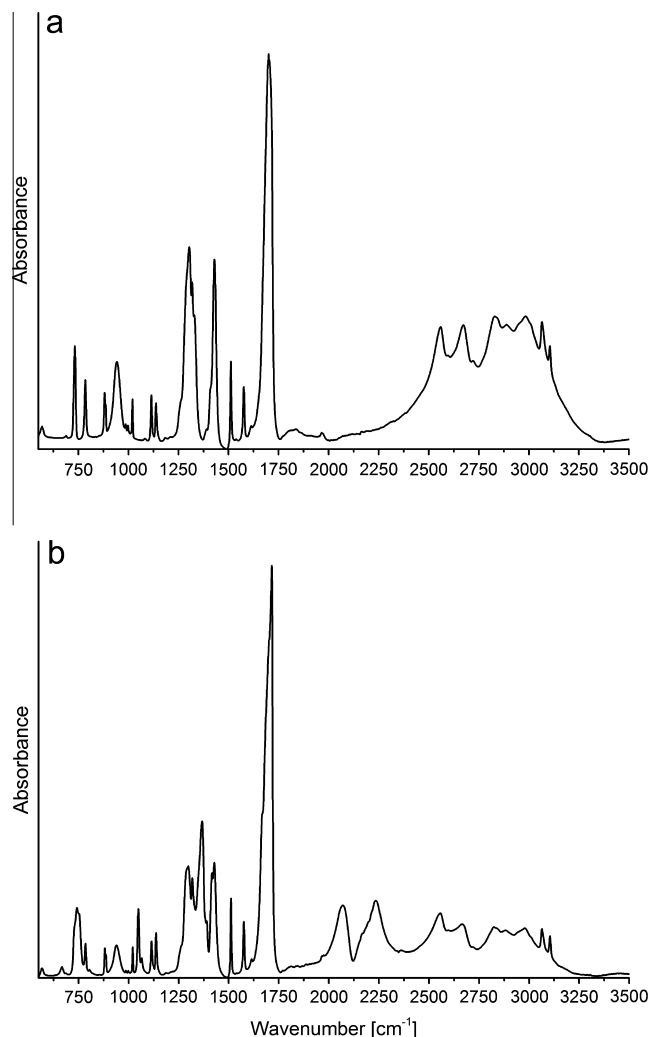| Description	Crystallographic data (°) [34]	Average values of angles from geometry optimization using the CPMD method (°)	The values of the angles from geometry optimization using the DFT method (°)
O1—H1···O2′	179.97	175.51	179.98
H1—O1—C1	115.70	110.74	110.53
O1—C1—O2	123.52	123.21	123.51
O1—C1—C2	117.00	114.90	114.60
O2—C1—C2	119.47	121.89	121.89
C1—C2—C3	119.39	118.85	121.23
C1—C2—C7	120.15	120.62	118.70
C3—C2—C7	120.46	120.54	120.06
C2—C3—C4	119.40	119.68	119.86
C2—C3—H2	120.33	119.84	119.62
H2—C3—C4	120.27	120.48	120.53
C3—C4—C5	120.13	119.79	120.08
C3—C4—H3	119.94	120.44	120.99
H3—C4—C5	119.92	119.77	118.93
C4—C5—C6	120.46	120.53	120.07
C4—C5—C8	120.15	120.61	118.00
C6—C5—C8	119.39	118.86	121.94
C5—C6—C7	119.40	119.68	119.84
C5—C6—H4	120.33	119.84	119.81
H4—C6—C7	120.27	120.49	120.35
C6—C7—C2	120.13	119.79	120.09
C2—C7—H5	119.92	119.77	119.03
C6—C7—H5	119.94	120.44	120.89
C5—C8—O3	117.00	114.92	113.12
C5—C8—O4	119.47	121.89	124.76
O3—C8—O4	123.52	123.19	122.13
C8—O3—H6	115.70	110.76	106.76

Fig. 3. Experimental spectrum of the hydrogen form (a) and partially deuterated form (b) of terephthalic acid.

and Fig. 4c the atomic spectrum of hydrogen atoms in the hydroxyl groups. Power spectrum and atomic power spectra were calculated using the Fourier transformation (FT) of the trajectory autocorrelation function, and the vibrational spectrum was obtained from FT of the dipole autocorrelation function. FT calculations have been performed with CPMD additional scripts. Theoretical spectrum, shown in Fig. 4b, exhibits all calculated bands in the frequency range 2000–3250 cm^{-1}. Spectrum in Fig. 4c contains all bands calculated for vibrations of hydrogen atoms in the hydroxyl groups, also these which are inactive in infrared spectra. Analyzing infrared spectra, similarities between experimental and theoretical spectra can be found in the positions of the bands and in their shapes. Theoretical IR spectrum does not reproduce well band at 3050 cm^{-1}. Power spectrum of the O—H vibrations has low intensity in the range about 3050 cm^{-1}, therefore the band at 3050 cm^{-1} can be attributed to the C—H groups in aromatic ring.

Spectra of isotopically substituted terephthalic acid

Fig. 5a presents experimental IR spectrum of partially deuterated terephthalic acid. Theoretical IR and atomic power spectra of partially deuterated crystals I-D1, D1′/II-H1.H1′ and I-H1, D1′/II-D1, H1′ are presented in Fig. 5b,c and d,e, respectively.
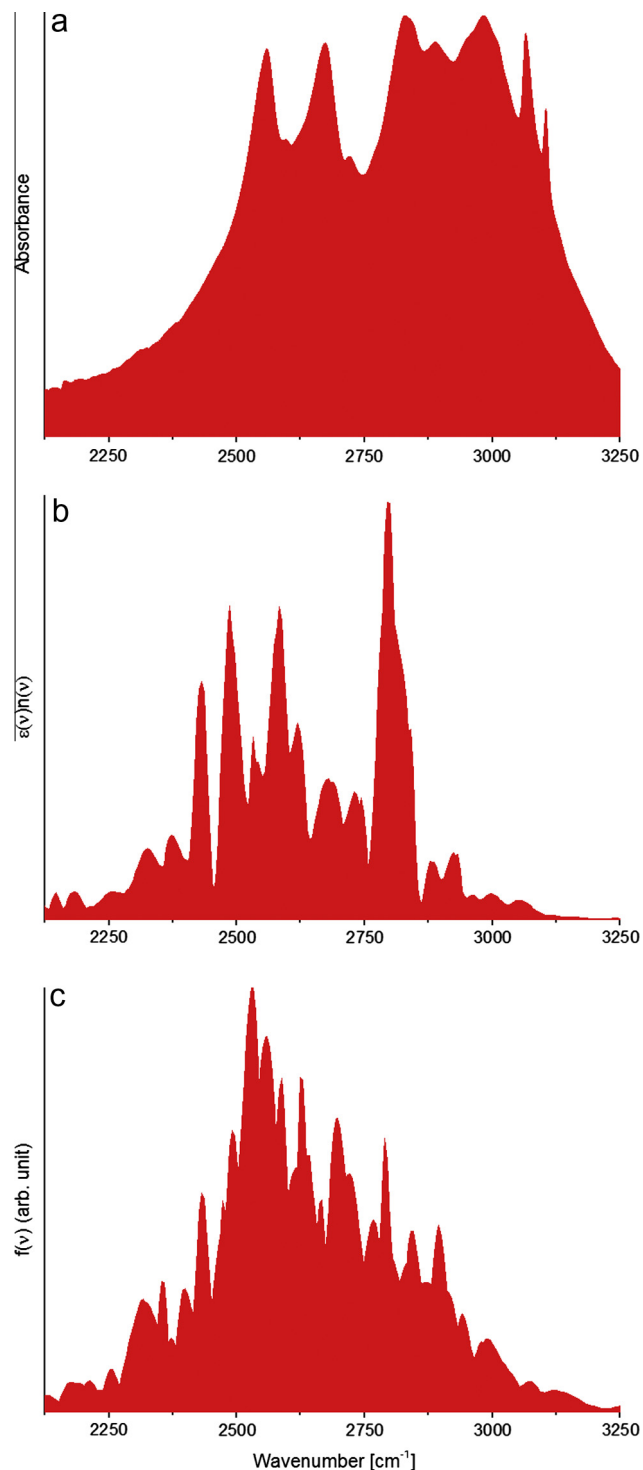

Fig. 4. Experimental spectrum of terephthalic acid crystal (a), theoretical infrared spectrum of the crystal (b) and atomic spectrum of hydrogen atoms in the hydroxyl groups (c).

Although in the theoretical infrared spectra bands positions are shifted to lower wave numbers compared with the experimental spectrum, an analogy to the experimental one can be found in their shapes. Comparing the calculation results with the experimental data shows that the effect of the revaluation of the oscillator strength is caused by mass renormalization of vibrating system by introducing a fictitious mass of the electrons. The fictitious electron mass makes the nuclei effectively heavier. This is different for
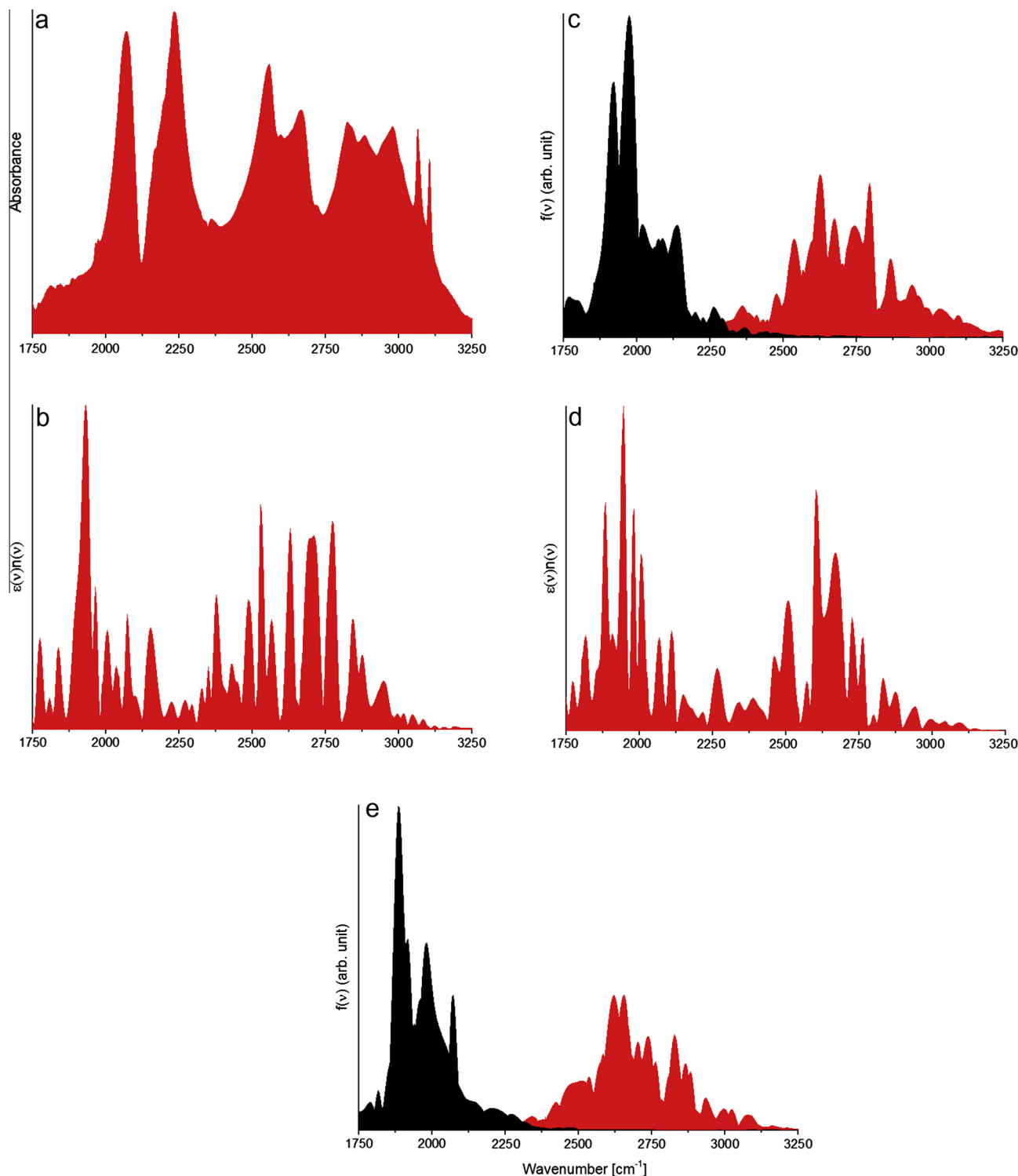
Fig. 5. Experimental IR spectrum of partially deuterated terephthalic acid (a); theoretical IR spectrum (b) and atomic power spectrum (c) of the I-D1, D1′/II-H1.H1′ crystal; and theoretical IR spectrum (d) and atomic power spectrum (e) of the I-H1, D1′/II-D1, H1′ crystal. In atomic power spectra of hydrogen atoms highlighted in red color and deuterium atoms in black color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mass-dependent quantities such as velocity or dipole time–correlation functions and the resulting power and infrared spectra, respectively, are sensitive to mass rescaling. This is particularly apparent of those modes that involve significant hydrogen or oxygen motion [39,40]. Frequency shift induced by finite μ values has been analyzed numerically for compressed MgO at high temperature by Tangney and Scandolo [41]. The red shift effect observed

calculated for the $\mu = 400$ a.u. was 10–15% compared to reference frequency values determined from the Born–Oppenheimer approximation. If $\mu = 100$ a.u. this effect reduces to 5%. This strong effect contrasted to a covalent solid like crystalline silicon at ambient conditions [41], where the red shift is of the order of 1% with $\mu = 800$ a.u. The mass renormalization also effects the calculation of physical temperature of the system [41] from the average

kinetic energy of the nuclei using usual equipartition theorem estimator [42–44]. The temperature is systematically too low if the mass renormalization effect is not taken into account. It is important to note that partially deuterated terephthalic acid crystal includes homogenous hydrogen or deuterium-bonded dimers H1, H1′ or D1, D1′ and mixed dimers H1, D1′ or D1, H1′.

In the area of O—H stretching vibrations band shape is very similar to the spectrum of the hydrogen form, which indicates the presence of homogenous non-deuterated dimers. Two intensive bands, which come from O—D vibrations, are located at lower frequencies, which is consistent with the quantum-chemical model $\left(\frac{v_{OH}}{v_{OD}} \approx \sqrt{2}\right)$ [18,38]. Recent works show that this ratio is different from $\sqrt{2}$ due the anharmonic effect of the slow mode of the hydrogen bond. The reasons of the deviations were discussed in a several papers [46,47,49].

The band at 2250 cm^{-1} is not reproduced well. This fact may be caused by imperfection of the calculation method or the presence of interactions between another types of dimers, not considered in the present calculations.

The differences between the theoretical and experimental spectra can be caused by various factors. Effect on the location and shape of the theoretical band has a fictional mass of electrons. This effect was discussed above. The inverse Fourier transform of the autocorrelation function of the dipole moment is a product of the extinction coefficient and refractive index. Therefore, experimental spectra cannot be directly compared with the theoretical ones. This is only possible if the refractive index of the sample does not depend on the wavelength. The basic physical mechanism responsible for the energy and intensity distributions is an anharmonic-type coupling between the high-frequency X—H(D) stretching vibration and the low-frequency hydrogen bond X···Y stretching vibration also Fermi resonance between the X—H(D) stretching fundamental and the first overtone of X—H(D) in-plane bending in each H bond of the system. These effects were discussed in detail by a number of authors [45–48]. Used in the calculations the Goedecker's pseudo potential probably not very well describes near and far-ranged interactions between corresponding vibrations in the crystal. It is also probably one of the reasons of not very good reproduction of the IR band at 2250 cm^{-1}.

Power spectrum again contains information about all vibrations, also inactive in IR, related to hydrogen and deuterium atoms in hydroxyl groups. Comparing them with the IR spectra allows to separate vibrations coming exclusively from hydrogen bonds, separately for vibrations O—H and O—D.

Conclusions

Analysis of corresponding angles and bonds lengths obtained by optimizing the geometry of terephthalic acid crystal, leads to the conclusion that the resulting CPMD geometry is in very good agreement with the experiment, giving much better results than for DFT calculation for the isolated dimer.

Comparison of theoretical infrared spectra of terephthalic acid with the experimental spectrum shows that most important characteristic features have been preserved. It is possible to approximately attribute each band, and to find equivalents in their fine structure, even if they are slightly shifted towards lower frequencies.

The obtained theoretical results are excellent source of information, which is the complement to experimental results, giving the opportunity of detailed analysis and interpretation of experimental spectra.

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