Computer simulation and study of the IR spectra of irradiated polymer materials

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Abstract. Within the framework of MDDP the calculations of IR spectra have been performed for the initial polyethylene terephthalate (PET) and its state with the cation which satisfactorily describing experimental data. The calculations were made using the MDDP (modified neglect of diatomic differential overlap), implemented in the program MOPAC 2012. A feature of the method is that the overlap integrals are replaced by the δ-function, single-site Coulomb and exchange integrals are calculated by atomic parameters Slater-Condon. In recent years the studies of the structure and physico-chemical properties of polyethylene terephthalate and composites made on it basis have got the intensive development. Comparison of calculations with experimental data gives their satisfactory agreement.

1. Introduction

It is known that many physical and chemical properties of polymers, including optical, depend on the type and internal structure of the material, its energy characteristics, manufacturing conditions, the parameters of external loads, etc. In recent years the studies of the structure and physico-chemical properties of polyethylene terephthalate and composites made on it basis have got the intensive development.

At present PET is one of the basic polymeric materials, from which are made nuclear membranes having wide application in industry [1, 2].

The basis for preparing these membranes is the irradiation polyethylene terephthalate films (thickness of 10 to 300 microns) by heavy ions (argon, xenon, Gold et al.) followed by etching and obtaining pores with diameter of 10 to 300 nm and with a density of 10^9 cm^{-2}.

In the theoretical studies, one of the main methods for studying the structure of molecules is the method of IR-spectroscopy, because, as a rule, the absorption spectra of substances in the 500–500 cm^{-1} are investigated where you can explore the bands are the most characteristic for molecular structures [3 – 5].

This method is rather informative method of analysis and identification of organic compounds [6 – 9]. In this paper, the studies of the IR spectra in the unirradiated and irradiated polyethylene terephthalate films have been carried out.

2. Calculation procedure

The calculations were made using the MDDP (modified neglect of diatomic differential overlap), implemented in the program MOPAC 2012. As models were used PET chains for the ground state and the state with the cation. A feature of the method is that the overlap integrals are replaced by the □-function, single-site Coulomb and exchange integrals are calculated by atomic parameters Slater-Condon. Two-center electron-electron integrals are asymptotically Coulomb, and at zero internuclear distance, they tend to the corresponding single-center integrals. The skeleton repulsion is calculated from the selected formula (asymptotically Coulomb forces) with optimized parameters. The problem with this is that in one integral is summed nuclear-nuclear repulsion and attraction of the nuclei; in the electronic cores of another nucleus. In addition, it is also taken into account repulsion of the cores themselves.

3. Results

In the result of calculations it was obtained that for the initial state and variant with the cation, the location of the peaks in the frequency spectrum is the same. Meanwhile, their amplitudes vary considerably. Comparison of the experiments with the initial and with the cation gives good agreement.

Figures 1 and 2 show the calculated and experimental infrared (IR) spectra of polyethylene terephthalate (non-irradiated and irradiated).

Tables 1 and 2 show the results of calculations and interpretation of the absorption bands on the basis of the calculation is given. We took into account only those bands that were in the spectral range 2000 – 400 cm-1 and the moment of transition which was greater than 1.0 (approximately 15% of the total).
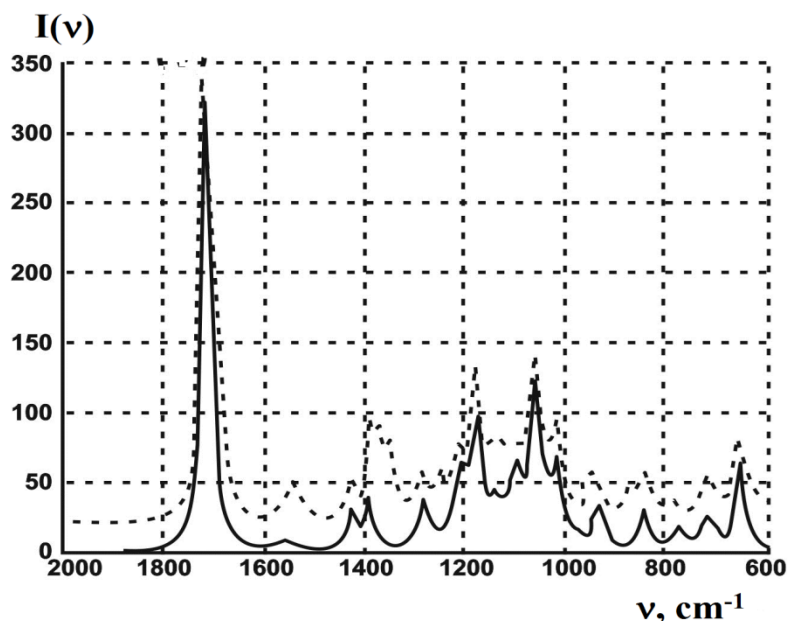

Figure 1. The IR spectra of PET (initial – solid curve and with cation – dotted line).

The following notation is used: d – bending vibration, v – stretching vibration, (C = O) – a carbon atom of a carbonyl group, (C = C) – the carbon atoms of the vinyl group, ar – vibration of benzene rings, i – the group is inside molecule.

Since the calculation only gives a line spectrum, then for comparison with the experiment, he is subjected by additional processing – calculate the convolution integral, with so called instrument function that simulates broadening of the observed lines due to the finite width of the entrance slit and the thermal motion:

$$I(\nu) = \sum_i \int I_0(\nu_i) F(\nu - \nu_i) d\nu,$$

where $I_o(\nu_i)$ is the intensity of the i-th band line spectrum, $F(\nu - \nu_i)$ is the instrument function, which is usually taken either as Gauss function or Lorentz; $I(\nu)$ is the resulting intensity. As a result the weak bands are hiding under the "tails" of the more powerful. The convolution integral is calculated using specially written programs and package MATLAB. We used the function of the Lorentz with a half width 10 cm^{-1}. For comparison of theoretical calculations with the experiment were used the data of the work [10] for forming membranes in PET films irradiated xenon ions with energy of 450 MeV and a dose of $3 \cdot 10^9$ cm^{-2}.
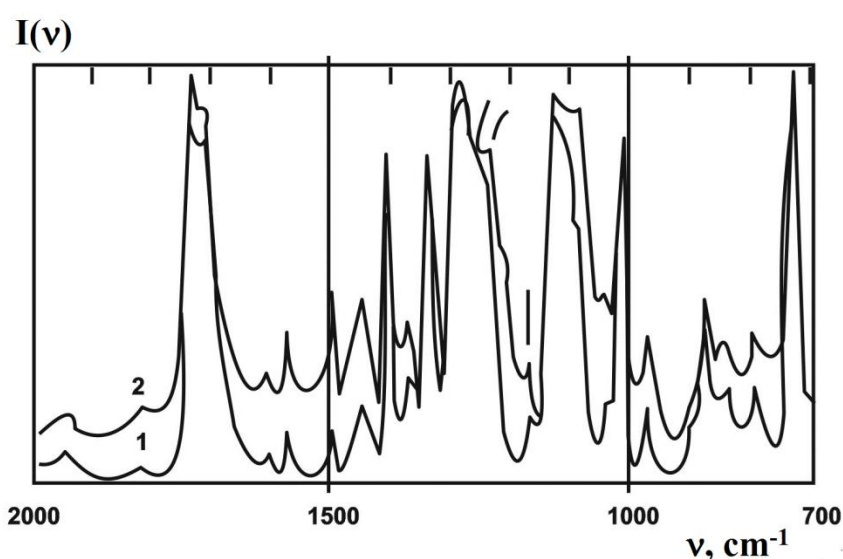

Figure 2. The experimental IR spectra of PET (initial and irradiated).

Table 1. Parameters IR spectra for initial polyethylene terephthalate.

Frequency (sm^{-1})	Moment of transition	Type of transition	Frequency (sm^{-1})	Moment of transition	Type of transition
715	1.35	d COC	1179	2.79	v CC + d CCH
776	1.20	d HCH	1189	1.44	v CC +v CO
937	1.78	d CCC ar	1210	2.65	d HCH
1040	1.28	d CCC ar	1292	2.24	Vv CC + v CCar
1054	1.06	d COCH	1393	1.34	d CCC ar
1058	1.72	d CCC ar	1429	1.35	d CCC ar
1061	5.04	d COC	1710	3.03	v C=O
1165	1.31	d CCH + vd CCC	1.712	2.87	v C=O
1066	0.93	vd COC + d CCH	1714	11.15	v C=O
1092	1.16	v CC + v CO	1717	2.70	v C=O
1101	1.76	d CCH	1719	6.42	v C=O
1131	1.10	d COC	1720	2.17	v C=O
1143	1.36	d CCH	1721	5.83	v C=O
1173	3.23	d CCC + d CCO			

The film thickness was 38 micrometers, density - 1.39 g/cm^3 (Figure 2). In the first approximation, it was believed that xenon ions in the first stage of passage knock out an electron from a macromolecule of polyethylene terephthalate that corresponds to PET with cation. The figure shows that the majority of experimental and theoretically calculated bands in the frequency range 1800 – 700 cm $^{-1}$ is the same (in particular frequency bands with 1719; 1429; 1393; 1292; 1189; 1101; 937; 776; 715). However, it should be noted that by the intensity peaks are not always quantitatively described in terms of this model due to changes in the ratio of the middle and end of fragments.

Table 2. Parameters of IR spectra of PET with the cation.

Frequency (sm^{-1})	Moment of transition	Type of transition	Frequency (sm^{-1})	Moment of transition	Type of transition
714	1.11	d CCO	1146	1.15	v CC ar + d CCH ar
721	1.15	d CCO + d CCH	1177	2.23	v CC + d CCH
729	1.13	d CCO	1179	1.24	v CC ar + d CCH
790	1.03	d OCC + d OCCH	1181	1.19	d HCH
878	1.48	v CO + v CC	1185	1.44	v CC
944	1.22	d CCCC ar	1189	1.12	d HCH
951	0.94	d CCCC ar	1190	0.95	v CC +d CCO
953	1.15	d CCCCCC ar	1209	1.58	d HCH
1006	0.97	d CCO + d CCH	1226	1.14	d HCH
1013	0.92	d OCH	1252	1.93	v CC + d CCO
1021	1.87	v CO	1307	1.17	v CO + v CC
1022	1.56	v CO + d HCH	1355	4.75	v CO + v CC
1043	1.05	v CC ar	1376	4.30	v CO + v CC ar
1045	1.02	v CO + d HCH	1396	3.04	v CO +v CC ar
1054	1.28	v CO	1430	1.07	v CC ar + d CCC ar
1060	2.25	v CC + v CO + d COC	1528	1.17	v CC ar
1062	2.10	d OCH + d HCH	1545	2.10	v CC ar
1062	2.01	v CO	1693	7.00	v C=O + v CO
1067	1.71	v CC + d CCO	1700	6.78	v C=O
1074	1.27	v CC ar	1711	6.49	v C=O
1090	0.95	v CC + v CO	1718	4.01	v C=O
1099	1.09	v CC + v CO	1721	5.31	v C=O
1102	1.33	v CO + d OCH	1729	5.52	v C=O
1114	1.07	v CO +d OCH	1733	5.64	v C=O
1138	1.73	v CC + d CCC ar			

However, in our view, the model and the results are satisfactory for predicting features of the vibrational spectra of molecules of polyethylene terephthalate and other polymeric materials.

4. Conclusion
1. IR spectra calculations for polyethylene terephthalate for the initial state and a state with a cation were made.
2. Comparison of calculations with experimental data gives their satisfactory agreement.

Acknowledgments

References
[1]   Charlesby A 1954 Atomic radiation and polymers (Pergamon, New York)
[2]   Lunkwitz K, Lappan U, Fuchs B, Scheler U 2004 J. Fluor. Chem. 125 (5) 863
[3]   Smith A A 1982 Applied Infrared Spectroscopy: Per. from English (M: Mir) 328
[4]   Bellamy L 1963 Infrared spectra of complex molecules (M: Izdat.in.lit) 489
[5]   Tarutino L I, Pozdnyakov FO 1986 Spectral analysis of polymers (L: Chemistry) 534
[6]   Hummel D O 1997 Polymers, additives, surfactants and their mixtures: Computer-based search with special FTIR libraries: Pap.12th Eur. Symp. Polym. Spectrosc. (ESOPS-12), Lyon, Macromol. Symp., **119** 65 – 77
[7]   Tlebayev K B, Kupchishin A I, Kusainov A T, Pivovarov S P and Aryutkin K N 2011 Radiation-thermal processes in polytetrafluoroethylene (Almaty: Ed. KazNPU. Abaya Ltd. "Kama") 271
[8]   Kamanina N, Iskandarov M O and Nikitich A A 2003 Technical Physics Letters **29** 16 29 – 37
[9]   Tarasevich BN 2012 Basics of IR spectroscopy with Fourier transform Training in Training (Manual, M.) 200
[10] Takahashi S, Yoshida M, Asano M et al. 2004 NIM. **B 217** 435