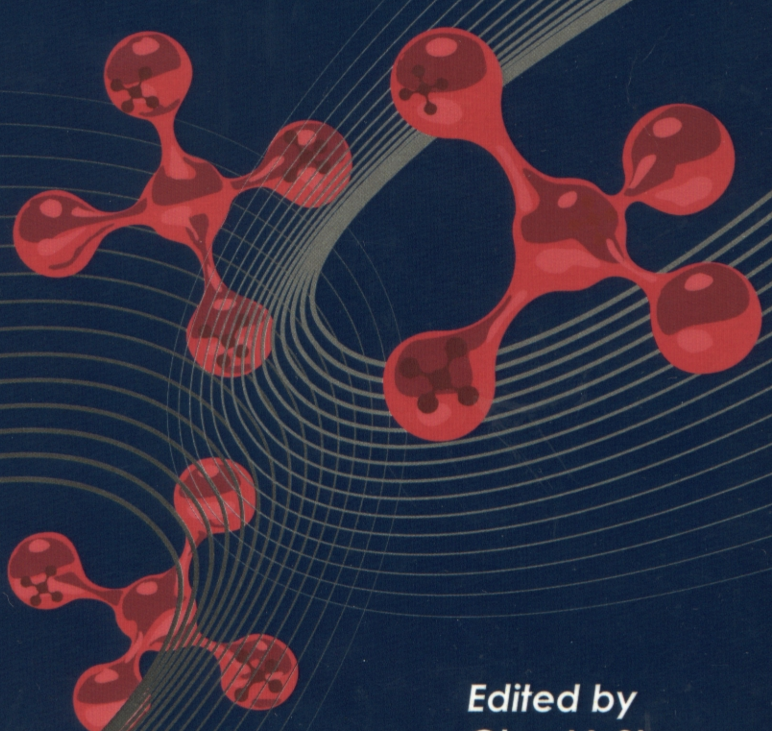
On the borders of physics, chemistry, biology, medicine and agriculture

research and development

VOLUME II



Edited by
Oleg V. Stoyanov
Ewa Kłodzińska
Gennady E. Zaikov

ON THE BORDERS OF PHYSICS, CHEMISTRY, BIOLOGY, MEDICINE AND AGRICULTURE
RESEARCH AND DEVELOPMENT

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Institute for Engineering
of Polymer Materials and Dyes

Toruń 2014

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ISBN 978-83-63555-33-7

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Typesetted by Jacek Leszczyński
Cover design REKPOL

Printing and binding REKPOL

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Semiempirical and DFT modeling of the IR spectra of benzoyl peroxide derivatives

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Abstract

The infrared spectra of the benzoyl peroxide symmetrical derivatives $(4\text{-R-PhCOO})_2$ with R: NO_2-, CF_3-, CF_3O-, I-, Br-, Cl-, F-, H-, CH_3-, CH_3O- were studied by the semiempirical methods. There is a linear relationship between the frequencies of the normal vibrations of the experimental and calculated (PM6, PDDG and AM1) spectra for this series of peroxides. The effect of the DFT level on the normal vibrations frequencies of C = O group of benzoyl peroxide was estimated. The best reproduction of these frequencies is observed in the case of BLYP calculation method with 6-311G (d, p) basis set.

Keywords: *benzoyl peroxide, diacyl peroxides, infrared spectra, molecular modeling, semiempirical methods, DFT-methods*

Aims and background

The methods of the molecular spectroscopy rightfully occupy one of the leading places in the study of the peroxide compounds structure. The IR spectroscopy is successfully used to establish the structure of the synthesized peroxides as well as for their identification and kinetic studies [1]. The IR spectra play the role of indicator of the oxidative stability and peroxide value in the foods oxidative modification [1]. An important feature of the IR spectroscopy is the absence of damaging effects of the infrared light quanta on the peroxide molecule. This method allows one to investigate peroxides in any aggregate state. Analytical capabilities of the infrared spectroscopy in the study of processes involving diacyl peroxides are possible due to the presence in peroxides extremely characteristic frequency of the intensity ratio and "doublet" form in the 1750 - 1820 cm^{-1}, which corresponds to the absorption of carbonyl group of the diacyl peroxide fragment (-C (O)-O-O-C (O) -).

There are two absorption bands belonging to the ν(C=O) in the spectra of symmetric diacyl peroxides that explained by the resonant interaction of carbonyl groups [2], as well as the in-phase (ν_s) and antiphase (ν_{as}) vibrations of the C=O groups [3]. The bands that belong to the group vibration absorption molecular fragments as a whole with the traditional interpretation of the assignment of bands in the IR spectrum were allocated for aliphatic peroxides - within 1132 - 1180 and 1045 - 1076 cm^{-1}, heterocyclic – 1265 ± 10 and 1070 ± 10 $cм^{-1}$ aromatic – 1048 – 1074 $cм^{-1}$. The largest differences are observed in assigning of the absorption bands of the peroxide fragment -O-O-, which most researchers refer to the strip in the area of 850 ± 15 cm^{-1} [4].

The development of quantum chemistry and the growth of computing power have led to the fact that modern semiempirical, DFT and ab initio methods of the quantum chemistry can significantly improve the speed and accuracy of calculations of various physical and chemical characteristics of the objects or processes and in many cases allow to achieve precise agreement with the experimental data [5]. This makes it possible to predict the molecular force constants and frequencies of normal vibrations. The second derivative of the total energy of the molecule on the internal coordinates and on the electric field determines the intensity of the IR absorption [6]. Calculation of normal vibrations allows estimating the contributions of various fragments of the molecule in the distribution of potential energy at different frequencies. Comparison of experimental and calculated vibration spectra significantly simplifies the correct assignment of the bands to a certain type of vibrations. Calculated methodology successfully used to determine the characteristic frequencies of the peroxides with unknown individual IR spectra [7, 8].

The aim of this study is the assessment of opportunities of DFT and semiempirical methods for the reproduction and prediction of the diacyl peroxides IR spectra. The paper presents the results of IR spectra molecular modeling of the benzoyl peroxide symmetrical derivatives $(4\text{-R-PhCOO})_2$, R: NO_2-, CF_3-, CF_3O-, I-, Br-, Cl-, F-, H-, CH_3-, CH_3O- by the semiempirical (AM1, PM6, PDDG) methods. The IR spectra of the benzoyl peroxide were investigated also at the DFT level.

Experimental

Parameters of the molecular geometry, electronic structure and thermodynamic properties of the benzoyl peroxide (BPO) molecule and its symmetrical derivatives were calculated by the GAUSSIAN 09 [9]. The molecular geometry optimization of all objects was carried out at the first stage of the work. The calculation of harmonic frequencies of vibrations and thermodynamic parameters were performed after that. The stationary points obtained after the molecular geometry optimization were identified as minima, as there were no negative values of analytic harmonic vibration frequencies for them. The reaction center of the peroxide compounds is a peroxide bond -O-O-. Therefore, selection criterion for the quantum chemical calculation method was the best reproduction of the peroxide moiety molecular geometry.

To solve the problem of choosing the optimal method for molecular geometry optimization and calculation of infrared spectra of BPO and its symmetrical derivatives the evaluation parameters of the structure of these compounds and the strength of peroxide bond were performed by semiempirical (AM1 [10], PM6 [11], PDDG [12]) and DFT methods (BLYP [13], B1LYP [14], B3LYP [12], B971 [15], B972 [16], BHandHLYP [17], M06HF [18], O3LYP [19], PBE1PBE [20], PBEh1PBE [21], X3LYP [22]). The solvent effect was taken into account in the CPCM approximation [23]. Visualization of the calculated IR spectra was carried out using Chemcraft 1.6 [24].

The experimental IR spectra of the benzoyl peroxide (Fig. 1) and its derivatives in CH_2Cl_2 used in the study were taken from [4]. The following symmetric diacyl peroxides: $(4\text{-}NO_2\text{-}C_6H_4\text{-COO})_2$, $(4\text{-}CF_3\text{-}C_6H_4\text{-COO})_2$, $(4\text{-}CF_3O\text{-}C_6H_4\text{-COO})_2$, $(4\text{-I-}C_6H_4\text{-COO})_2$, $(4\text{-Br-}C_6H_4\text{-COO})_2$, $(4\text{-Cl-}C_6H_4\text{-COO})_2$, $(C_6H_5\text{-COO})_2$, $(4\text{-}CH_3\text{-}C_6H_4\text{-COO})_2$,$(4\text{-}CH_3\text{-O-}C_6H_4\text{-COO})_2$ have been investigated.

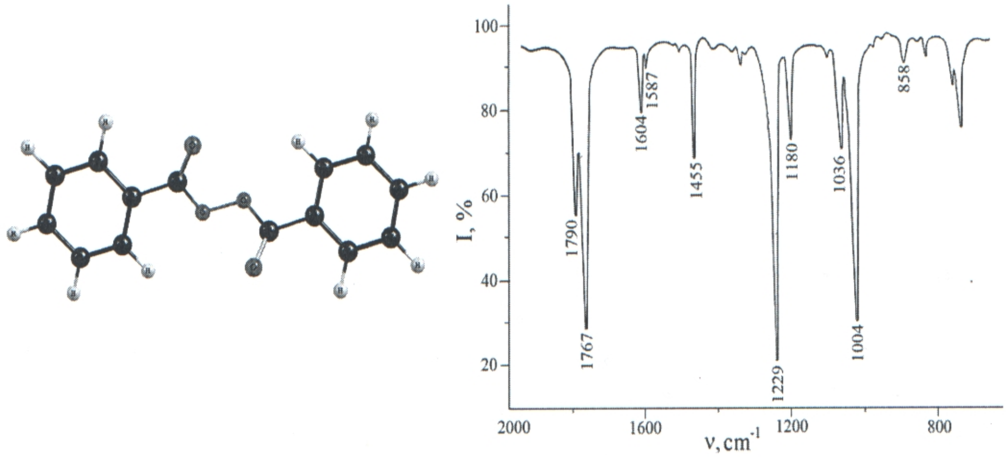
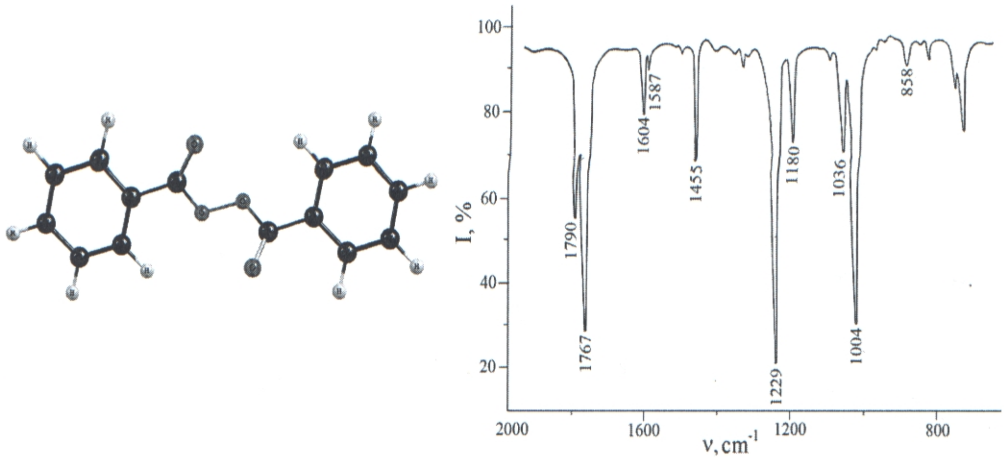


Fig. 1. Structural model of the benzoyl peroxide (PM6 method) and its experimental IR spectrum in CH_2Cl_2, [ROOR] = 0.14 mol/dm^3, thickness 0.058 mm (according to the Ref. [4])

Results and discussion

The equilibrium configuration of the benzoyl peroxide molecule was obtained by the PM6, AM1 and PDDG semiempirical methods using the CPCM solvation model (Table 1). The equilibrium configuration geometry of the benzoyl peroxide was used in the calculation of IR spectra.

Calculation results listed in Table 1 show the best reproduction of the C=O group normal vibrations frequencies in the case of PM6 calculation method application.



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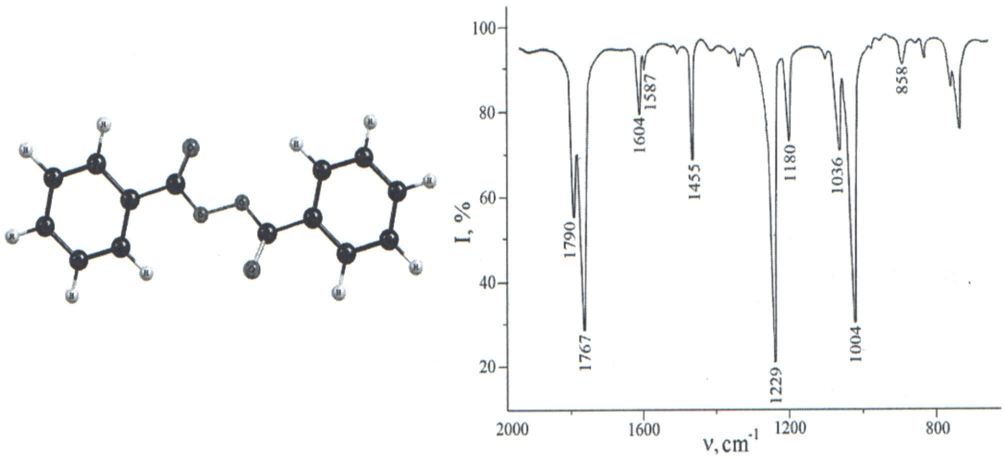

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Table 1. Parameters of the benzoyl peroxide molecular geometry in CH_2Cl_2

Parameters	Experiment [4, 25, 26]	PM6/CPCM	AM1/CPCM	PDDG/CPCM
C=O, Å	1.190	1.205	1.230	1.216
O–O, Å	1.460	1.423	1.292	1.440
C–O, Å	1.380	1.408	1.406	1.367
O-O-C, °	111.0	109.8	114.5	113.0
C-O-O-C, °	91.0	101.5	91.5	105.9
μ, D	1.60	1.53	1.71	1.88
ν_{as}(C=O), cm^{-1}	1767	1800	2065	1993
ν_{s}(C=O), cm^{-1}	1790	1808	2076	2004

Liner relationships between the experimental (ν_{exp}) and calculated (ν_{calc}) values of the normal vibrations are observed for the BPO IR spectra (Fig. 2). These relationships are described by equations (1) - (3) for PM6, PDDG and AM1 quantum chemical calculation methods respectively.

$$\nu_{exp} = (195 \pm 26) + (0.79 \pm 0.02) \cdot \nu_{calc}, n = 19, R = 0.995 \quad (1)$$

$$\nu_{exp} = (119 \pm 29) + (0.82 \pm 0.02) \cdot \nu_{calc}, n = 19, R = 0.995 \quad (2)$$

$$\nu_{exp} = (195 \pm 26) + (0.79 \pm 0.02) \cdot \nu_{calc}, n = 19, R = 0.995 \quad (3)$$

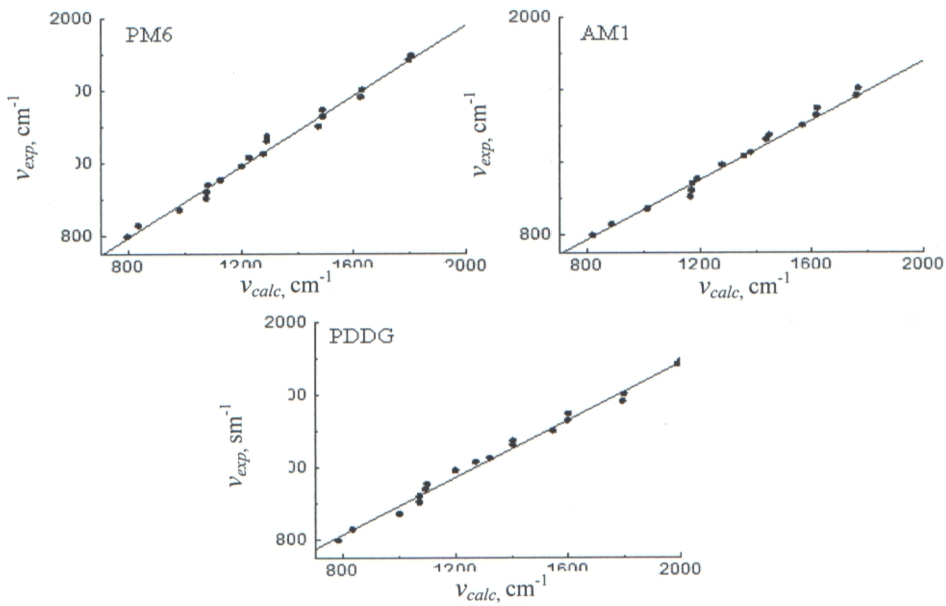

Fig. 2. Relationships between the experimental (ν_{exp}) and calculated (ν_{calc}) normal vibrations frequencies of the benzoyl peroxide IR spectrum in CH_2Cl_2 (CPCM solvation model)

The influence of the structure of the benzoyl peroxide symmetrical derivatives (R-PhC(O)-O-O-C(O)Ph-R) on the position of the carbonyl groups absorption band in the IR spectra has been also investigated. Calculations were carried out in the approximation of AM1, PM6 and PDDG semiempirical methods. The best correspondence between the experimental and calculated parameters is observed in the case of PM6 method (Table 2). Introduction of electron-donor substituents into the structure of benzoyl peroxide leads to a shift of the normal vibrations mode of C = O groups towards the field of short waves, while shift of the mode towards the region of long waves is observed in the case of electron- acceptor substituents in peroxide molecule.

Table 2. The normal vibrations frequencies of the C = O groups (ν(C = O), cm^{-1}) of the BPO derivatives R-PhC(O)-O-O-C(O)Ph-R

R-	Experiment [4]		PM6		AM1		PDDG	
	ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
NO_2-	1780	1801	1851	1847	2101	2090	2029	2021
CF_3-	1776	1798	1849	1845	2100	2090	2027	2020
CF_3O-	1771	1795	1846	1843	2098	2087	2025	2018
I-	1771	1792	1846	1842	2099	2088	2024	2017
Br-	1772	1792	1846	1842	2099	2088	2024	2017
Cl-	1765	1793	1845	1841	2098	2088	2023	2016
F-	1767	1790	1843	1841	2097	2087	2023	2016
H-	1767	1790	1844	1840	2097	2087	2023	2016
CH_3-	1762	1785	1841	1838	2097	2086	2022	2015
CH_3O-	1759	1781	1837	1834	2096	2086	2018	2012

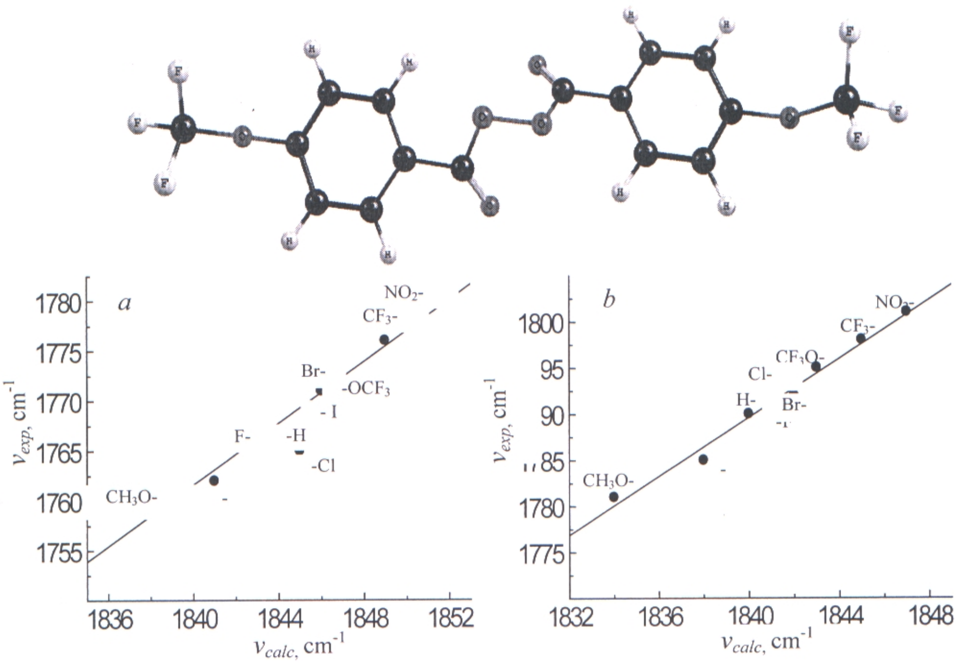

Fig. 3 Structural model of $(4\text{-}CF_3O\text{-}C_6H_4\text{-}COO)_2$ (PM6 method) and dependence of the normal antisymmetric (a) and symmetric (b) vibration frequencies of carbonyl groups obtained experimentally (ν_{exp}) and calculated by the PM6 method (ν_{calc}) for the benzoyl peroxide derivatives

There is a linear dependence between experimental (ν_{exp}) and calculated by the PM6 method (ν_{calc}) values of the normal vibrations frequencies of carbonyl groups of the benzoyl peroxide derivatives (Fig. 3).

These linear dependences (Fig. 3) in the linear regression analysis are described by the following equations:

$$\nu_{exp} = (-1072 \pm 297) + (1.54 \pm 0.16) \cdot \nu_{calc}, n = 10, R = 0.959 \qquad (4)$$

$$\nu_{exp} = (-1141 \pm 187) + (1.59 \pm 0.10) \cdot \nu_{calc}, n = 10, R = 0.984 \qquad (5)$$

Thus, among of the used semiempirical methods only PM6 provides a mathematical model for predicting of the normal vibrations frequencies position of the carbonyl group in the IR spectrum of the benzoyl peroxide symmetric derivatives.

The positions of the normal vibrations mode of carbonyl groups can be used as an analytical signal of qualitative and quantitative analysis of this class of peroxides by IR - spectroscopy. DFT methods are promising for computer structural chemistry of peroxide compounds because they with sufficient accuracy reproduce parameters of the molecular geometry and electronic structure of peroxides [5]. The opportunity of different DFT methods to reproduce the values of the normal vibrations frequencies of the benzoyl peroxide C = O group was estimated. The calculations were performed using the 6-311G (d, p) basis set in all cases. The results are listed in Table 3.

Table 3. The effect of the DFT level on the normal vibrations frequencies of the benzoyl peroxide C = O group

Method	ν_{as}, cm^{-1}	ν_s, cm^{-1}	$\Delta\nu^*$, cm^{-1}	$\Delta\nu_{as}^{**}$, cm^{-1}	$\Delta\nu_s^{***}$, cm^{-1}
Experiment [4]	1767	1790	23	0	0
BLYP	1739	1762	23	28	28
B1LYP	1839	1864	25	72	74
B3LYP	1827	1852	25	60	62
O3LYP	1832	1853	21	65	63
X3LYP	1834	1859	25	67	69
B971	1837	1862	25	70	72
B972	1857	1888	31	90	98
PBEH1PBE	1868	1894	26	101	104
PBE1PBE	1868	1894	26	101	104
BHandHLYP	1926	1953	27	159	163
M06HF	1938	1966	28	171	176

$*\Delta\nu = \nu_s - \nu_{as}$

$**\Delta\nu_{as} = \nu_{as}^{calc} - \nu_{as}^{exp}$

$***\Delta\nu_s = \nu_s^{calc} - \nu_s^{exp}$

An appropriate correspondence of the calculated and experimental values of $*\Delta\nu = \nu_s - \nu_{as}$ is observed for all DFT methods under consideration. The best reproduction of the normal vibrations frequencies of C = O group is observed in the case of the BLYP method.

Conclusions

IR spectra of the benzoyl peroxide and its symmetrical derivatives $(4\text{-R-PhCOO})_2$, R: NO_2-, CF_3-, CF_3O-, I-, Br-, Cl-, F-, H-, CH_3-, CH_3O- have been calculated by the semiempirical and DFT methods. There is a linear dependence between the frequencies of normal vibrations experimentally obtained and calculated (PM6, PDDG and AM1) spectra of the benzoyl peroxide. Among the used semiempirical methods, only PM6 provides an appropriate mathematical model for predicting of the position of the carbonyl group normal vibrations frequencies in the

IR spectra of the benzoyl peroxide symmetrical derivatives. The values of the normal vibrations frequencies of C = O group of the benzoyl peroxide were calculated on the different DFT levels. It was found that the best reproduction of the experimental values was observed in the case of BLYP calculation method with the 6-311G (d, p) basis set.

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ISBN 978-83-63555-33-7

978-83-63555-20-7

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978-83-63555-31-3