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PREDICTION OF DIPROPYL SULFONE PROPERTIES BY DENSITY FUNCTIONAL THEORY METHODS: CONFORMATIONAL ANALYSIS AND SIMULATED IR SPECTRUM

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In this work, the conformational and vibrational analysis of dipropyl sulfone in its isolated gaseous state with identification of all stable conformers, their energy and degeneracy, relative population determined by Boltzmann distribution, as well as IR spectra have been performed by density functional theory (DFT) methods. Several DFT methods and basis sets were tested. It was demonstrated that the various local and hybrid DFT functionals such as well-known B3LYP, regardless of the size of basis sets, completely fail in the prediction of correct molecular structures, let alone the IR spectra. It was found that only long-range corrected hybrid density functionals, combined with decently sized basis sets are capable to predict correct values of dihedral angles between non-bonded atomic groups: the most important coordinates in conformational analysis. Thus, wB97XD/6-311++G(2df,2pd) method/basis set combination appears to be the best method for the titled system both in terms of geometry and IR spectra prediction. A detailed analysis of the potential energy surface revealed the existence of 28 distinct conformers with various populations at 298 *K*, which have significant impact in the simulated IR spectra. The linear scaling equation (LSE) fitting methodology was successfully adopted for the calibration of wavenumbers and achievement of the best match between theoretical and experimental absorption regions of functional groups in sulfones. Moreover, in the construction of the simulated IR spectra, the Lorentzian broadening of each calculated mode with different full widths at half maximum was considered to obtain extinction coefficients, thus more realistic $\varepsilon(\nu)$ dependency, that is directly comparable with experimental spectra. The authenticity of the results obtained have been verified by comparison with existing experimental literature data on sulfones.

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***Keywords*:** sulfone, density functional theory, IR spectra, molecular statistics.

Introduction. The development of computational methods in recent decades has greatly increased the accuracy of electronic structure calculations and the prediction of many properties of molecules based on them: a stable molecular structure, energy, IR spectra, etc. [1]. On one hand, the desired accuracy of electronic structure calculations can be achieved using higher levels of theory and basis sets, but, on the other, this requires larger computational resources, especially for large molecules. One way to avoid complex calculations is to find a sufficient method/basis set

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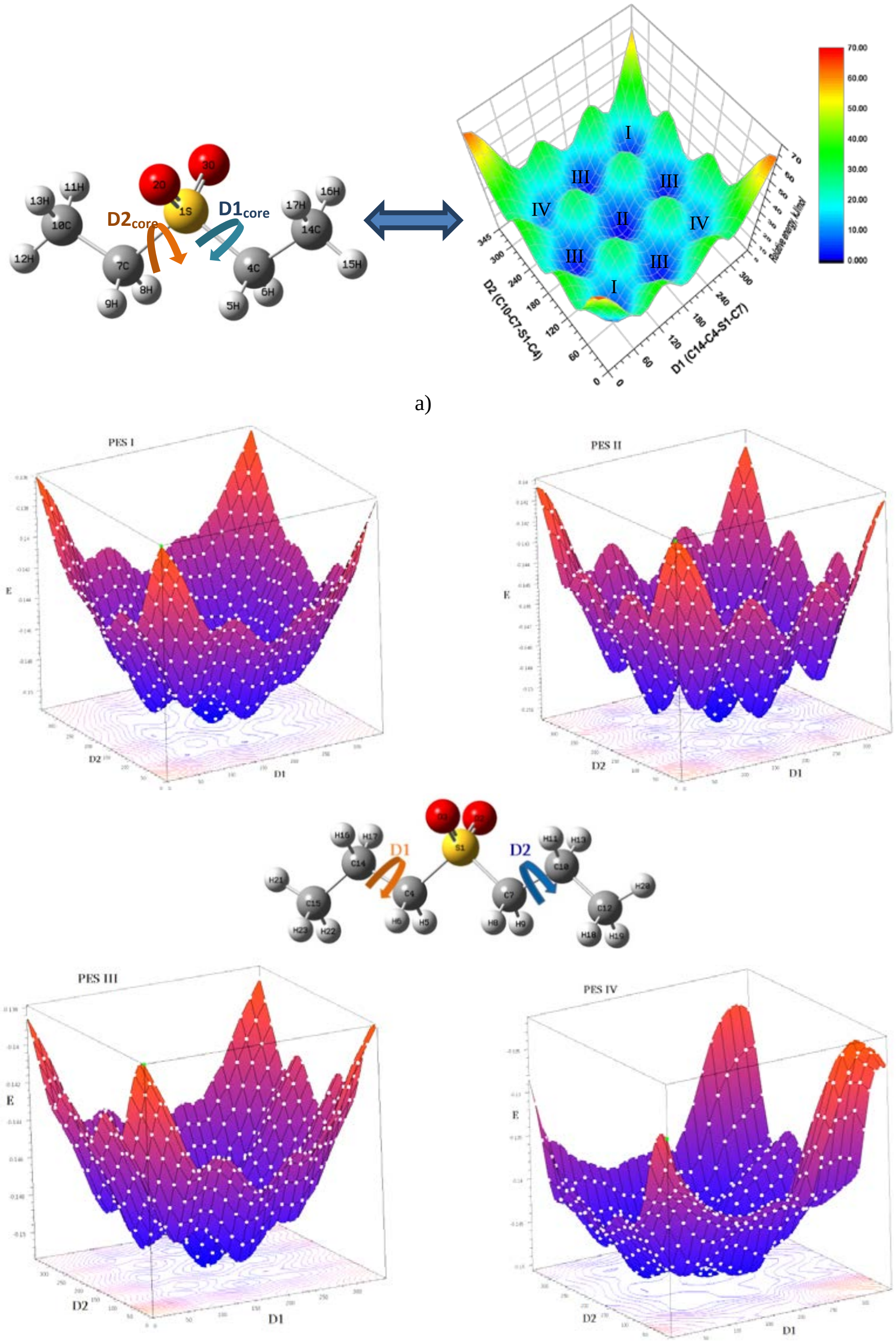
combination for model molecules and to extrapolate it to further homologues of this class of compounds.

Among quantum chemical methods, attracting considerable attention, density functional theory (DFT) methods provide quite accurate computational models. Up to date new density functionals continue to appear, taking the performance of DFT to unprecedented levels [2]. Depending on the goals of computation the local density approximation (LDA), pure, hybrid, double-hybrid and dispersion-corrected functionals are available. The search for an efficient DFT method/basis combination is based not only on its predictive ability of appropriate geometry obtained from optimization procedure, but also on an accurate calculation of vibrational spectra. As is well known, theoretical vibrational wavenumbers are usually calculated using the harmonic oscillator model, so the overestimation is always expected. Therefore, the correction of theoretically calculated data can be achieved by applying various scaling procedures based on the minimization of the errors (root mean square, etc.) [3].

Sulfones are a promising class of dipolar aprotic solvents, which are used in various fields of science and chemical technology [4–7]. Despite the widespread use of sulfones, more precise experimental and theoretical studies were carried out for the first homologues, in particular for dimethyl sulfone (DMSO2) [4, 7, 8]. Recently, the full conformational analysis of diethyl sulfone (DESO2) by DFT methods has been performed and optimized structures and IR spectra of both stable conformers and transition states have been determined [9, 10].

To establish a link between the various properties of alkyl sulfones and their structural features, a systematical theoretical study of sulfone series is necessary. In this aspect, the main goal of the present study was the development of a combined methodological approach directed towards correct evaluation of structural flexibility and thermodynamic stability of molecules, their statistics and features like electronic structure, bond lengths and angles, infrared spectra, etc. based solely on quantum chemical DFT calculations. In this work, the strategy chosen was assessed on the example of dipropyl sulfone (DPSO2) molecule, the next homologue of alkyl sulfones: the conformational and population analysis, the prediction of molecular properties, especially IR spectrum, which is previously unreported, were performed with appropriate DFT methods. Among various DFT methods examined in our study, surely, the proposed wB97XD/6-311++G(2df,2pd) method/basis combination appears as a method of choice. The results were compared with available experimental results for similar molecules.

Computational Methodology. All quantum chemical calculations, including conformational and vibrational analysis, were performed using Gaussian 09 computational package [11]. First, in order to establish all stable conformers of DPSO2 it was necessary to construct potential energy surfaces for relevant molecular coordinates. The initial input geometries of DPSO2 molecules were constructed based on 4 stable conformations of DESO2 [10], by replacing the terminal hydrogen atom with one methyl group on each side. Potential energy surface (PES) calculations were carried out along the coordinate of the two dihedral angles as defined by D1(C15C14C4S1) and D2(C12C10C7S1) in the range of 0 to 345° at an increment of 15°, while the two core dihedral angles D(C14C4S1C7) and D(C10C7S1C4) were kept constant with values consistent with those of corresponding DESO2 conformations (Fig. 1).



a)

b)

Fig. 1. Relaxed optimization results for corresponding dihedral angles: a) potential energy surface of DESO2, calculated by RHF/6-311++G(d,p) method [9]; (b) four potential energy surfaces of DPSO2 conformers, calculated by AM1 semiempirical method.

Thus, the total number of calculations is 4×24×24=2304 optimizations at this stage, and the computational effort needed is huge – AM1 semiempirical method was employed for this task.

All resulted local and global minima along the PES were subjected to complete geometry optimizations by AM1, RHF and DFT methods with different basis sets. During the optimization procedure the opt=verytight convergence criterion was used. To ensure that real minima were obtained and to generate IR spectra, vibrational calculations were also run with the same method/basis set combination as for the geometry optimization. The absence of an imaginary frequency confirmed the real minimum structure.

In selected cases, to identify all conformers and obtain the valid IR spectra, additional pure, hybrid, and dispersion-corrected functionals (DFT methods) were employed for calculations: BLYP (pure), B3LYP, cam-B3LYP, B3PW91, MPW1PW91, PW91PW91 (hybrid), wB97, wB97X (LC hybrid functionals), wB97XD (dispersion-corrected), LC-BLYP, LC-wPBE (long range corrected). All these methods have been used in combination with various Pople/Dunning basis sets as 6-31+g(d), 6-311++G(2df,2pd), aug-cc-pVTZ etc.

To calibrate the calculated harmonic IR frequencies, scaling procedures such as single overall scale factor (OSF) and a linear scaling equation (LSE) were tested [2]. The estimation of scaling coefficients for vibrational frequencies were performed by minimizing the root mean square error (RMSE) between the calculated and experimental values for DMSO2 molecule in the gas phase.

LabTalk and C Programming languages in Origin 8.5 program were used to write and execute scripts to perform data analysis and plotting, calculation of energetic states populations according to Boltzmann distribution, Lorentzian broadening of IR modes of ensembles, etc.

Results and Discussion.

Potential Energy Surfaces. In order to find out all stable DPSO2 conformers, it was necessary to analyze the potential energy surface, which is a graphical relationship between energy of a molecule and its geometry. As is known, the number of minima typically grows exponentially with the number of internal variables, so the global optimization problem is an extremely difficult task for a multidimensional function [1]. To solve this task, the following approach was selected in this study: 4 stable conformations of DESO2 from our previous study [9] were taken as starting geometries, then the two terminal hydrogen atoms (those in trans position) were replaced with one methyl group each. Afterwards, conformational searching was done, performing a stepwise rotation around two C–C bonds consequently (dihedral angles D1(C15C14C4S1) and D2(C12C10C7S1)) leaving dihedral angles D(C14C4S1C7) and D(C10C7S1C4) frozen (Fig. 1). For the linear alkanes, it is known in advance that trans conformations in general are favored over gauche [12].

Four PES maps for DPSO2 originating from parent DESO2 structures, as calculated by the AM1 semi-empirical method, are given in Fig. 1. After careful examination of the conformational space of DPSO2 nine minima were discovered for three maps and eleven minima for the remaining one. Thus, in total 38 minima (local and global) were obtained, as expected. But taking into account the degenerate states of DPSO2 molecule (with the same structures and energies) only 28 distinct conformers exist in reality. The analysis of PES I revealed 6, PES II – 4, PES III and PES IV – 9 unique conformers each. The distinct structures with notations, DPSO2 degeneracies (g_2) related to the corresponding PES region, the degeneracies (g_1) of initial DESO2 structures, the calculated total degeneracies ($g_1 \times g_2$) and number of conformers are presented in Tab. 1. Thus, in total 101 minima were found on the entire PES plot (DESO2, DPSO2 combined), while only 28 of them represent unique molecular structures.

Table 1

The distinct structures of DPSO2 with notations, their degeneracies (g_2), degeneracies (g_1) of initial DESO2 structures, the calculated total degeneracies ($g_1 \times g_2$), and the total number of DPSO2 conformers in PES

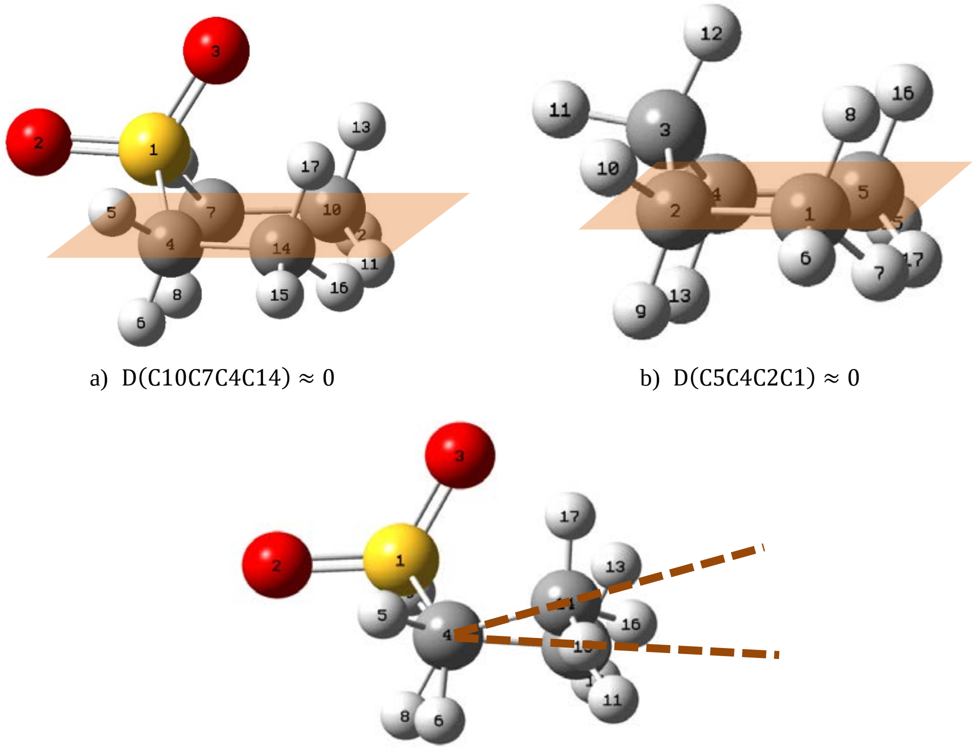
PES №	g_1 (DESO2)	Distinct structures of DPSO2	g_2 (DPSO2)	$g_1 \times g_2$	Number of structures in PES
I	2	1_2	2	4	18
		1_3	2	4	
		1_6	2	4	
		1_1	1	2	
		1_5	1	2	
		1_9	1	2	
II	1	2_1	2	2	11
		2_2	4	4	
		2_3	4	4	
		2_5	1	1	
III	4	3_1 ⋮ 3_9	1 ⋮ 1	4 ⋮ 4	36
IV	4	4_1 ⋮ 4_9	1 ⋮ 1	4 ⋮ 4	36

Then, using the same semi-empirical method, the positions of the energy minima on the PES corresponding to the equilibrium structures of the stable conformers were fully optimized removing all dihedral constraints. It should be noted that not all structures were identified as stable at this stage of optimization by AM1 method, since the “DESO2 core” of molecule collapses for some cases. Due to these instability issues and also that the AM1 is not suitable for quantitative treatment in general, it was necessary to try various high-level ab initio and DFT methods. These were successfully employed to reliably identify all minima observable on PES, geometry optimization and further analysis.

Computational Methods Assessment. The first challenge that arose was to find a suitable high-level computational method that would give reliable geometric structures for all conformers.

First issue with very popular DFT methods we encountered was the incorrect prediction of some dihedral angles already in starting DESO2 molecule. Our calculations have shown, that some DFT methods such as B3LYP and B3PW91, as well as MPW1PW91, BLYP, PW91PW91 result in mispredictions regarding to dihedral angle in one of conformers (gauche) of DESO2 (Fig. 2, a), i.e. these methods predict that all carbon atoms lie in the same plane $\mathrm{D(C10C7C4C14)} \approx 0^{\circ}$.

To identify the underlying issue additional calculations were performed for n-pentane molecule (gauche conformer), for which is well-known non-zero value of dihedral angle: four carbon atoms do not lie in the same plane (in contrast to cyclohexane) [12]. Calculations with aforementioned DFT methods resulted in close-to-zero values for corresponding angles, i.e. the weakness of these methods for predicting long-range interactions was confirmed (Fig. 2, b). It is worthy to mention, that the expansion of the basis sets did not improve the results in any manner.



a) $\mathrm{D(C10C7C4C14)} \approx 0$

b) $\mathrm{D(C5C4C2C1)} \approx 0$

c) $\mathrm{D(C10C7C4C14)} \neq 0$

Fig. 2. Representation of DESO2 conformer IV (a) and pentane gauche (b) with incorrect structures (zero dihedral angle), and real structure with non-zero dihedral angles (c).

Then, the performance of cam-B3LYP, wB97, wB97X, wB97X-D, LC-BLYP, LC-wPBE, RHF, and MP2 methods in the calculations of long-range interactions was assessed. Satisfactory results, i.e. non-zero dihedral angle values $\mathrm{D(C10C7C4C14)} \neq 0$ in all cases were obtained for DESO2 molecule (see Tab. 2). It is noteworthy that ab initio methods, even classic RHF, has an advantage in predicting the molecule structure in comparison with widespread used B3LYP/DFT method.

Table 2

The calculated dihedral angle in DESO2 conformer (IV) by various ab initio and DFT methods

Method	D(C10C7C4C14)
B3LYP, B3PW91, MPW1PW91, BLYP, PW91PW91	≈ 0
cam-B3LYP	7.0
wB97	17.5
wB97X	15.5
wB97X-D	16.9
LC-BLYP	16.0
LC-wPBE	17.7
RHF	10.0
MP2	19.4

Next issue encountered was the identification of all 9 geometries in PES IV conformational space, which manifested itself in terms of destabilization of DESO2 core (conformation IV [9]) in DPSO2 molecule after switching to fully unconstrained optimization from “frozen” internal coordinates, as was described above. The structures in other 3 quadrants were optimized without issues by nearly all computational methods. This is due to the much more “crowded” structure of particular DPSO2 conformations, where too much overlap between neighboring hydrocarbon groups occurs, but mainly due to insufficient long-range interaction energies, which would otherwise hinder the internal rotations and stabilize molecular structure. In this context, among DFT methods tested cam-B3LYP, wB97 and its extension, combined with expanded basis set provided much better results. Only utilizing wB97XD/6-311++G(2df,2pd) combination it was possible to obtain all predicted structures in the PES IV quadrant of DPSO2.

Another major goal of this study was to simulate the theoretical IR spectrum of DPSO2: to calculate the IR absorption of substance in an exceptionally theoretical manner, based on quantum chemical and statistical analysis, which further can be directly matched with experimentally determined one. It is worthwhile to note that concerning the vibrational analysis of sulfur-organic molecules Barnes et.al have shown that among DFT methods cam-B3LYP, M06-2X, wB97X-D, and PBE0 with 6-311++G(2df,2pd) and triple-zeta Dunning’s basis sets predict the harmonic IR spectra in close agreement with the experimental spectrum [13], while most of other popular DFT methods completely fail. Thus, there is an overlap of methods with our study, showing that particular methods provide good results both from geometrical and spectral accuracy considerations. Therefore, only cam-B3LYP, wB97XD with aug-cc-pVTZ/6-311++G(2df,2pd) expanded basis sets were selected for further evaluation.

Due to the lack of experimental IR spectra of DPSO2 in literature and relatively large size of molecule, next approach was followed: a search was performed for an efficient method/basis combination for predicting the theoretical IR spectrum for the first homologue DMSO2, the model molecule. The choice was made by the applying various scaling procedures based on the minimization of errors of theoretically predicted IR frequencies in comparison with the experimentally recorded IR spectrum of DMSO2 in the gas phase [7] (the NIST WebBook [14]), and its further extrapolation to other homologues of this class of compounds.

A linear regression algorithm was employed to find the best correlation between calculated and experimental IR frequencies of DMSO2. In essence it provides the linear fitting parameters between the two, while keeping the RMSE values to minimal. Theoretically calculated IR harmonic frequencies of DMSO2 can be scaled using both a single overall scale factor (OSF) and a linear scaling equation (LSE) [2]. Obviously using a linear equation instead of a single scaling factor gives more accurate frequency calibration and smaller errors.

This procedure is based on establishing a linear relationship between the calculated and experimental wavenumbers of a molecule:

$$\nu_{exp} = k\nu_{cal} + b, \tag{1}$$

where ν_{exp} is experimental, ν_{cal} is calculated wavenumbers, k is the slope and b is the y-intercept.

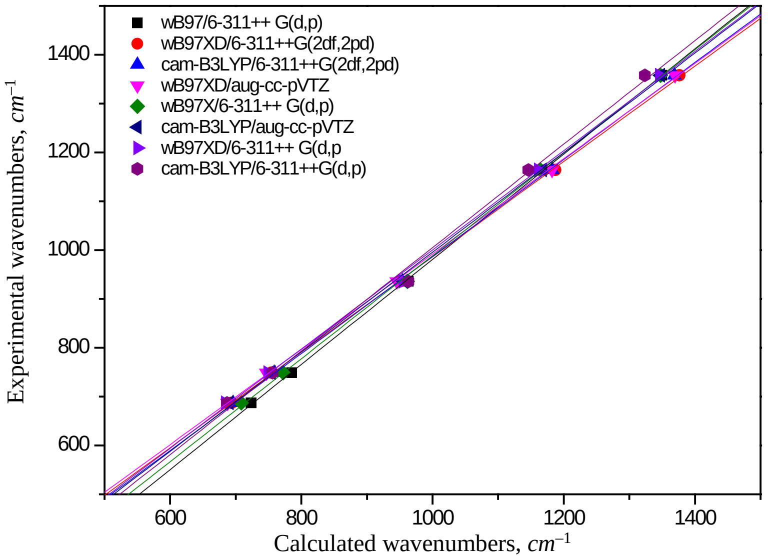


Fig. 3. Linear regression fitting of the experimental wavenumbers versus calculated wavenumbers by various DFT methods for dimethyl sulfone molecule.

The scaling procedure was carried out for the 0–1500 cm^{-1} “fingerprint” wavenumber range of DMSO2, which includes the vibrational modes of anti-symmetric and symmetric SO_2 stretch, CH_3 deformation, antisymmetric and symmetric SC stretch, and SO_2 bend [7]. Fitting results for different method/basis set combinations are depicted in (Fig. 3, Tab. 3). The values of k and b thus obtained were used to recalculate the theoretical DFT wavenumbers, further discussion is based on these scaled values only.

Considering the DMSO2 vibrational spectrum, among the all methods tested the following DFT method/basis combinations have given the acceptable results (RMSE<4 cm^{-1}): wB97XD/6-311++G(2df,2pd); wB97XD/aug-cc-pVTZ; cam-B3LYP/6-311++G(2df,2pd), and wB97/6-311++G(d,p). However despite the smallest value of RMSE in the case of wB97/6-311++G(d,p) it was not capable to stabilize DPSO2 (PES IV) structure. Moreover, some of its non-corrected IR peak wavenumbers for DMSO2 were underestimated in comparison with experimental values, which is unphysical. Both issues were probably caused by not large enough basis set choosen, nevertheless it fell out of further consideration. Thus, only 3 methods remain, capable of correctly predicting DMSO2 experimental spectrum. As can be seen (Fig. 4), there is a good agreement between the experimental IR spectrum of DMSO2 in the gas phase and linearly scaled calculated spectra by the selected DFT methods.

Table 3

The root mean square errors (RMSE), coefficients k and b obtained in the scaled wavenumbers of the DMSO2 modes by the linear scaling equation (Eq. 1) for various DFT methods

DFT method	*k*	*b*, cm^{-1}	RMSE, cm^{-1}
wB97/6-311++G(d,p)	1.07663	–95.48603	3.2424
wB97XD/6-311++G(2df,2pd)	0.97668	9.47251	3.3326
cam-B3LYP/6-311++G(2df,2pd)	0.99340	–6.57655	3.8741
wB97XD/aug-cc-pVTZ	0.97596	16.09653	4.0594
wB97X/6-311++G(d,p)	1.05446	–65.99861	6.3304
cam-B3LYP/aug-cc-pVTZ	1.01933	–23.61442	8.4638
wB97XD/6-311++G(d,p)	1.01515	–14.70476	9.4459
cam-B3LYP/6-311++G(d,p)	1.05953	–54.38533	15.6167

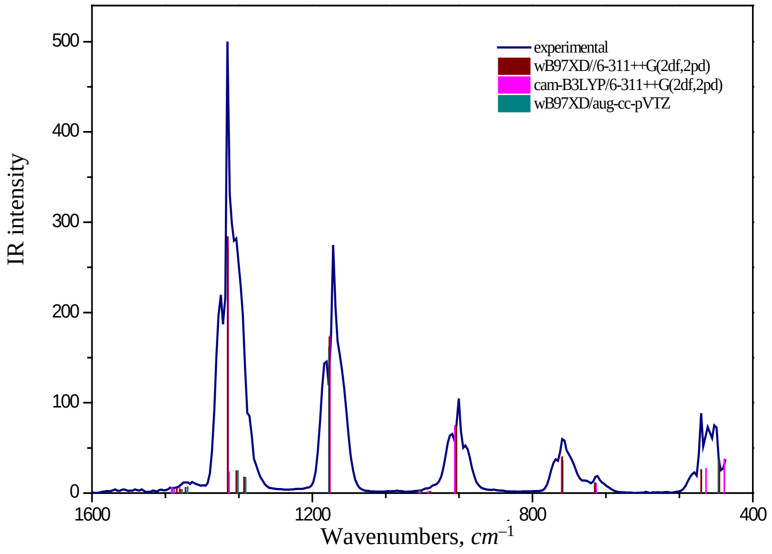


Fig. 4. Comparison of experimental IR spectrum of DMSO2 in gas phase and linear scaled calculated spectra by various DFT methods.

Thus, of all the methods discussed, taking into account both the value of root mean square error obtained by DMSO2 IR analysis (c.a. 3.3326 cm^{-1} compared to experimental values), and the improved structural stability of DPSO2 conformers (discussed above), the method of choice proposed is the wB97XD/6-311++G(2df,2pd) method/basis combination.

Structural and Spectral Parameters of DPSO2. Thus, the wB97XD/6-311++G(2df,2pd) method was chosen as optimal to obtain the geometry of all stable conformers and for simulated IR spectrum of DPSO2, which was performed in the following steps:

i. first of all, the geometries of all stable conformers were optimized;

ii. the energy, structural parameters and the relative populations (based on Boltzmann distribution) of these conformers were calculated;

iii. vibrational spectra of all DPSO2 conformers were calculated;

iv. to scale the calculated frequencies, the coefficients of linear fit obtained for DMSO2 were applied;

v. finally, Lorentzian broadening of each modes was constructed, considering Boltzmann distribution, degeneracy and temperature in order to obtain simulated spectra, which is to compared with experimental results.

As it was proven in previous sections the only sufficient method/basis set combination both in terms of structural stability and vibrational spectrum accuracy is wB97XD/6-311++G(2df,2pd). All 28 distinct conformers (101 in total) of DPSO2 obtained from PES analysis were successfully optimized at this level of theory utilizing a very strict opt=verytight criterion, parameters including total molecular energies, geometrical parameters, vibrational frequencies and intensities, zero-point energies, etc. were obtained. From the analysis of DPSO2 PES landscape degeneracies for individual structures have been obtained (Tab. 4). This, combined with exact total energies from wB97XD/6-311++G(2df,2pd) outputs made it possible to perform population analysis of DPSO2 gas state at a given temperature.

The Boltzmann distribution was used to predict the relative populations (P_i) of stable DPSO2 conformations according to equation:

$$P_i = \frac{g_i e^{-\varepsilon_i/k_B T}}{\sum_i g_i e^{-\varepsilon_i/k_B T}}\,, \tag{2}$$

where ε_i is the potential energy of i-th conformers, g_i is its degeneracy, k_B is the Boltzmann constant, and T is the absolute temperature (was taken 298.15 K). To predict Boltzmann probabilities a script was written, that collects the required total energies and degeneracies for all individual conformers, then calculates the relative populations for each according to the equation.

The absolute and relative gas-phase energies for all 28 conformers of DPSO2, their degeneracy and relative populations, according to the Boltzmann distribution, calculated at wB97XD/6-311++G(2df,2pd) level are reported in Tab. 4. As can be seen the energy differences among all these minima can reach up to 17 kJ/mol. If compared to the value of thermal energy at the same temperature ($RT = 2.48$ kJ/mol) it is concluded that the highest states are “unreachable” and remain highly unoccupied, as is evident from the figures in table. Indeed, along the full conformational space there are regions where the molecular structure of

DPSO2 molecule is very compact and repulsion forces between neighboring groups become pronounced, especially in PES IV in the DPSO2 case.

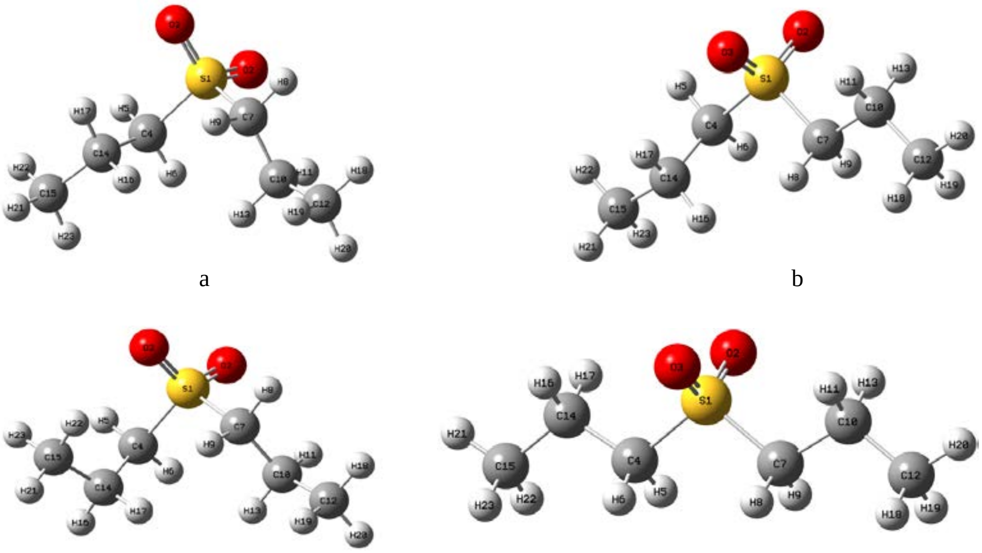
Table 4

The absolute and relative energies of all 28 conformers of DPSO2 in the gas phase, their degeneracy (g) and relative populations (P), according to the Boltzmann distribution, calculated at wB97XD/6-311++G(2df,2pd) level

Conformer №	*g*	*E, Hartree*	*ΔE, kJ/mol*	*P*
1	2	–785.728558	0	0.20381
2	4	–785.727900	1.73	0.20305
3	1	–785.727676	2.32	0.04004
4	4	–785.727094	3.84	0.08647
5	4	–785.726817	4.57	0.06448
6	4	–785.726764	4.71	0.06096
7	4	–785.726647	5.02	0.05386
8	4	–785.726573	5.21	0.04980
9	4	–785.726319	5.88	0.03805
10	4	–785.726131	6.37	0.03118
11	2	–785.725949	6.85	0.01286
12	2	–785.725742	7.39	0.01033
13	4	–785.725522	7.97	0.01636
14	4	–785.725468	8.11	0.01545
15	4	–785.725436	8.20	0.01494
16	2	–785.725435	8.20	0.00746
17	4	–785.725347	8.43	0.01359
18	4	–785.725333	8.47	0.01339
19	4	–785.725245	8.70	0.01220
20	4	–785.725211	8.79	0.01177
21	4	–785.725127	9.01	0.01077
22	4	–785.724955	9.46	0.00897
23	4	–785.724507	10.64	0.00558
24	4	–785.724312	11.15	0.00454
25	4	–785.724193	11.46	0.00400
26	4	–785.724123	11.64	0.00372
27	4	–785.723499	13.28	0.00192
28	4	–785.722095	16.97	0.00043

Also, surprisingly the trans- conformation (Fig. 5, d) does not have the lowest gas-phase energy, as it traditionally is discussed in similar cases, such as *n*-alkanes and tetrahedral-carbon molecules [12]. The population calculated is only 4%, which stems on the one hand from the degeneracy of this conformation (g=1), on the other hand due to its relatively high energy. Almost 50% of the total population relate to the three dominant conformations with 20.4%, 20.3% and 8.6%, respectively. The optimized structures of these conformers with the lowest energy are shown in Fig. 5.

In Tab. 5 are summarized some important geometrical parameters of these structures: bond lengths, angles, dihedral angles, and dipole moments. In any case, it will be further discussed, the values of relative populations for all individual structures proved to be helpful in the construction of simulated IR spectrum of gas phase.



a b c d

Fig. 5. DFT/wB97XD/6-311++G(2df,2pd) optimized three dominant conformers of DPSO2: a) P = 20.4 % (№ 1); b) P = 20.3 % (№ 2); c) P = 8.6 % (№ 4); d) trans conformer (№ 3).

For the vibrational analysis of DPSO2 spectra, it is worth noting that DPSO2 molecule contains 23 atoms, therefore, there are 3N–6=63 vibrational modes, since 28 conformers were identified, in total 28·63=1764 modes must be taken into account. First the wB97XD/6-311++G(2df,2pd) calculated frequencies must be scaled with some factor, in order to provide a sensible match with expected experimental spectrum. As it was discussed in previous sections, this was done with reasonable accuracy for DMSO2 homologue utilizing LSE procedure, and the values for linear fitting equation were obtained. Since the experimental DPSO2 spectrum is not presented in literature, the scaling factors cannot be obtained via similar procedure, instead they are taken from DMSO2 data. This is an appropriate approach, since there are no functional group differences in homologous series.

Table 5

DFT/wB97XD/6-311++G(2df,2pd) calculated geometrical parameters of low-energy conformers

	№ 1 (1_5)	№ 2 (3_5)	№ 4 (1_2)	№ 3 (2_5)
R(S1O2), *Å*	1.4431	1.4431	1.4434	1.4442
R(S1O3), *Å*	1.4433	1.444	1.4432	1.4439
A(C4S1C7)	105.4943	104.4891	105.3813	103.4066
D(C14C4S1C7)	59.6236	64.3005	51.4948	–178.285
D(C10C7S1C4)	58.6647	178.4931	60.4686	178.2954
D(C15C14C4S1)	172.8079	172.0504	65.6181	–179.8555
D(C12C10C7S1)	170.8976	179.5936	174.8547	179.2361
Dipole moment, *D*	5.1324	4.7167	5.0396	4.3116
Population	0.20381	0.20305	0.08647	0.04004
Relative Energy, *kJ/mol*	0.0	1.73	3.84	2.32

Also, the calculated IR intensities for all the modes must be scaled to take into account the data obtained from population analysis. Here the corresponding intensities are multiplied via probability values of individual structures, thus the "weight" of each conformation in total spectrum is considered. Since these "weights" are temperature-dependent variables in accordance to Boltzmann's distribution function, therefore the IR spectrum-gas temperature dependence is obtained automatically.

This IR spectrum, corrected in both frequencies and intensities domains, is further processed to achieve the broadening of absorption peaks, which can then be compared with experimental one. This is accomplished via Lorentzian function, where the peak center position ($\bar{\nu}_c$) and area (A) are taken from corrected modes data, and the full width at half maximum (FWHM) (w) is considered adjustable to obtain the best match.

To obtain real intensity/wavenumber dependency for a given region of wavenumbers 1764 Lorentzian functions (total modes of all conformers) must be summed, each with own arguments:

$$\varepsilon(\bar{\nu}) = \sum_{i=1}^{Nmods} \frac{2A_i}{\pi} \cdot \frac{w}{4\left(\bar{\nu}-\bar{\nu}_{c,i}\right)^2 + w^2} \ , \tag{3}$$

where $\bar{\nu}_c$, w and A represent center (wavenumber), width and area of the absorption peak respectively. The offset is set to zero.

To cope with the construction of such a large number of mathematical functions a simple program in Origin 8.5 C scripting language was written, which collects all the corrected peak data (areas, positions in spectrum) and for an arbitrarily chosen FWHM generates the true absorption spectrum in the terms of molar extinction – wavenumbers relationship.

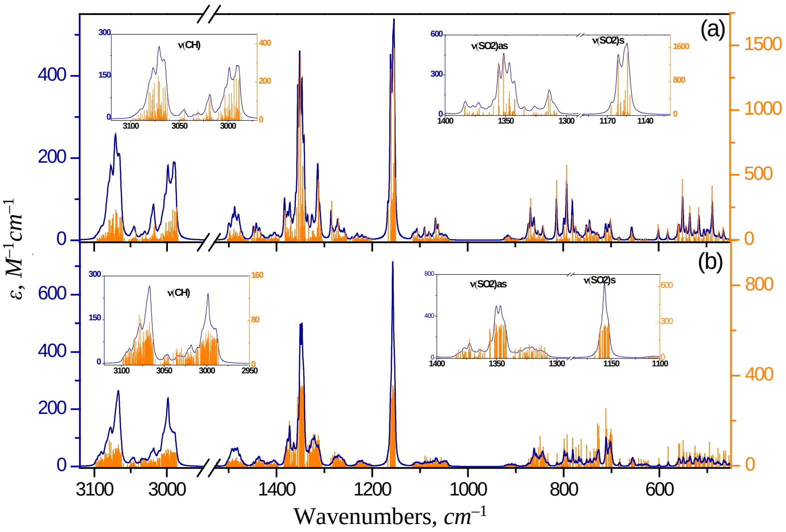


Fig. 6. Simulated IR spectra of DPSO2 with Lorentzian broadening (FWHM = 3 cm^{-1}). Energy distributions (a) by Boltzmann at 298 K and (b) equiprobable for all conformers. Inset graphs: zoomed part in CH and SO_2 stretching vibrations region of DPSO2.

Fig. 6 represents the weighted peak data in accordance with Boltzmann distribution (a) and for comparison with equal probabilities only (b), accompanied with Lorentzian-broadening simulated spectra. For the most IR-active SO_2 symmetric and antisymmetric stretching vibrations present around 1150 cm^{-1} and 1350 cm^{-1} regions, it can be observed that the temperature has a significant influence on the spectrum. Indeed, the contribution of individual conformations in IR spectra is highly unequal, as expected from the figures in Tab. 2, therefore the most prominent peaks observed in Fig. 6, a belong to mainly to the 3 most populated states out of 28, while the remaining peaks contribute to the overall spread and broadening only. Also, it can be observed that in comparison to Fig. 6, b there is a splitting of the main peaks in simulated spectrum due to the same reasons, which will appear as a “shoulder” in experimental spectrum.

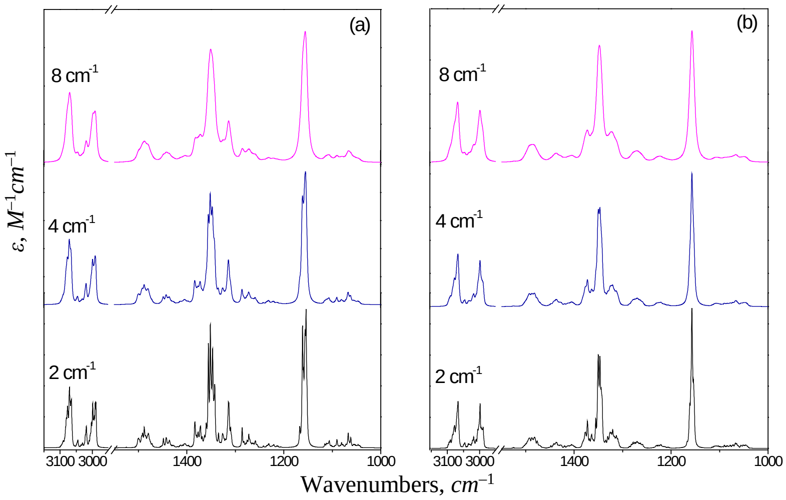


Fig. 7. Simulated IR spectra of DPSO2 with Lorentzian broadening of various FWHM (2, 4, 8 cm^{-1}) with Boltzmann distribution (a) and equal distribution (b) of all conformers.

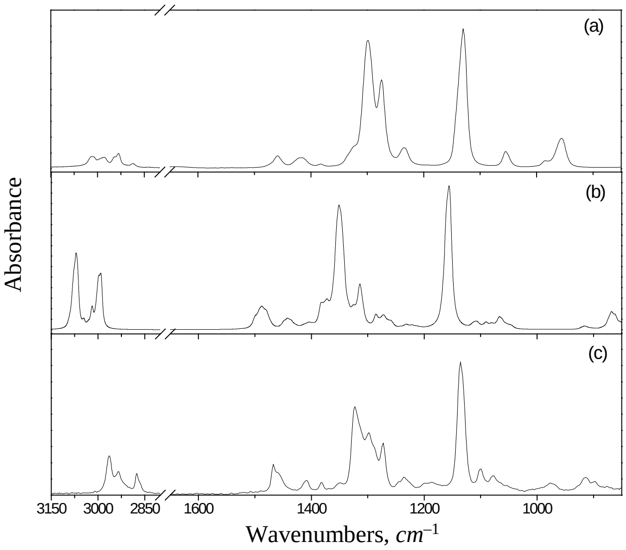


Fig. 8. Simulated IR spectrum of DPSO2 (b) and experimental FTIR ATR spectra of pure liquid ethyl methyl sulfone (a) and dibutyl sulfone/CCl_4 mixture (0.3 *mol*/*L*) (c).

In order to obtain extinction coefficients, i.e. more realistic $\varepsilon(\nu)$ dependency, that is directly comparable with experimental spectra in the construction of the simulated IR spectra, the Lorentzian broadening of each calculated mode with different FWHM values was considered (Fig. 7). Among the simulated IR spectra with various FWHM the one with 8 cm^{-1} was chosen to compare with experimental spectra (Fig. 8).

From the experimental IR spectra of DPSO2 homologues EMSO2 and DBSO2 it can be observed that in SO_2 absorption region the main peaks are rather unsymmetrical, which is a result of multiple non-equal overlapping contributions underneath, akin to the spectra we predicted for DPSO2 (Fig. 8, b). There appears to be a somewhat upshifted in wavenumbers in simulated spectrum of DPSO2, compared to empirical ones. This is expected, since IR calculations in our work are done for the gas phase isolated molecules, while FTIR spectra are given for condensed state. Therefore, the inconsistency is only superficial. The overall shape and spectral features are practically undistinguishable from experimentally recorded ones of homologues (Fig. 8 a, c). Thus, the general methodology of analysis presented, the model of the DPSO2 gas-state and its simulated IR spectra are proved to be precise.

Conclusion. A reliable strategy for the computational treatment of systems with conformational flexibility is proposed in this work, the performance assessment is conducted on the example of DPSO2 molecule. Several DFT methods and basis set combinations were systematically probed, downsides of few mainstream methods were revealed.

It is proven that DFT wB97XD/6-311++G(2df,2pd) method is suitable for accurate calculations.

Complete potential energy surface of isolated DPSO2 molecule is examined. In total 101 stable conformers are found with various degeneracy states, from which 28 unique structures are identified. Their absolute energies, degeneracies, IR spectra, other important structural parameters, calculated by various DFT methods, are presented. Linear fitting coefficients for the correction of theoretically calculated IR wavenumbers (i.e. scaling factors) are given.

The structures of 4 dominant DPSO2 conformers ($P > 50\%$ at 298 K) and their impact on IR spectrum, based on population analysis, are established. The simulated IR spectrum of DPSO2 is constructed considering Boltzmann distribution of states for all conformers, as well as Lorentzian broadening of each vibrational mode. The resulted spectrum is shown to be in excellent agreement with experimental ones of homologues.

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ԴԻՊՐՈՊԻԼՍՈՒԼՖՈՆԻ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ԿԱՆԽԱՏԵՍՈՒՄԸ ԽՏՈՒԹՅԱՆ ՖՈՒՆԿՑԻՈՆԱԼԻ ՏԵՍՈՒԹՅԱՆ ՄԵԹՈԴՆԵՐՈՎ. ԿՈՆՖՈՐՄԱՑԻՈՆ ԱՆԱԼԻԶ ԵՎ ՍԻՄՈՒԼԱՑՎԱԾ ԻԿ ՍՊԵԿՏՐ

Սույն աշխատանքում իրականացվել է մեկուսացված դիպրոպիլսուլֆոնի կոնֆորմացիոն և տատանողական սպեկտրների վերլուծություն բոլոր կայուն կոնֆորմերների, դրանց էներգիաների և վերասերման աստիճանների, հարաբերական բնակեցվածության ըստ Բոլցմանի բաշխման և ԻԿ սպեկտրների նույնականացմամբ՝ օգտագործելով խտության ֆունկցիոնալի տեսության (DFT) մեթոդները:

Փորձարկվել են DFT մի քանի մեթոդներ և բազիսային հավաքածուներ:

Ցույց է տրվել, որ տարբեր լոկալ և հիբրիդային DFT ֆունկցիոնալները, ինչպիսին է ամենահայտնի B3LYP-ը, անկախ բազիսային հավաքածուի չափսերից, ի վիճակի չեն կանխատեսել ճշգրիտ մոլեկուլային կառուցվածքները, ինչպես նաև ԻԿ սպեկտրները:

Պարզվել է, որ միայն հեռու կարգի փոխազդեցությունները ներառող հիբրիդային խտության ֆունկցիոնալները, համակցված բավարար չափի բազիսային հավաքածուի հետ, ի վիճակի են կանխատեսել ճշգրիտ երկնիստ անկյունները չկապված ֆունկցիոնալ խմբերի միջև, որոնք ամենակարևոր կոորդինատներն են կոնֆորմացիոն վերլուծության համար:

Ցույց է տրվել, որ wB97XD/6-311++G(2df,2pd) մեթոդ/բազիսային հավաքածու համադրությունը լավագույն մեթոդն է նշված համակարգի համար թե′ երկրաչափության, թե′ ԻԿ սպեկտրների կանխատեսման տեսակետից:

Պոտենցիալ էներգիայի մակերևույթի մանրամասն վերլուծությունը բացահայտեց 28 տարբերակվող կոնֆորմերների առկայությունը տարբեր բնակեցվածությամբ 298 *Կ* ջերմաստիճանում, ինչը զգալի ազդեցություն ունի սիմուլացված ԻԿ սպեկտրներում:

Գծային մասշտաբավորման հավասարման մեթոդաբանությունը հաջողությամբ կիրառվել է ալիքային թվերի կալիբրման և սուլֆոնների ֆունկցիոնալ խմբերի տեսական և փորձարարական կլանման մարզերի լիարժեք համապատասխանության հասնելու համար:

Բացի այդ, սիմուլացված ԻԿ սպեկտրների կառուցման ժամանակ հաշվի է առնվել յուրաքանչյուր մոդի լորենցիան ընդլայնումը՝ էքստինկցիայի գործակիցների, և հետևաբար, ավելի իրատեսական $\varepsilon(\nu)$ կախվածության ստացման նպատակով, որն ուղղակիորեն համեմատելի է փորձարարական սպեկտրների հետ:

Ստացված արդյունքների հավաստիությունը հաստատվել է՝ սուլֆոնների վերաբերյալ առկա փորձարարական գրականական տվյալների հետ համեմատությամբ:

З. Х. ПАПАНЯН, Л. С. ГАБРИЕЛЯН

ПРОГНОЗИРОВАНИЕ СВОЙСТВ ДИПРОПИЛСУЛЬФОНА МЕТОДАМИ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ: КОНФОРМАЦИОННЫЙ АНАЛИЗ И СИМУЛИРОВАННЫЙ ИК СПЕКТР

В данной работе проведен конформационный и колебательный анализ дипропилсульфона в его изолированном газообразном состоянии с идентификацией всех стабильных конформеров, их энергии и вырожденности, относительной заселенности по распределения Больцмана, а также ИК-спектров методами теории функционала плотности (DFT). Протестированы несколько методов и базисных наборов DFT.

Продемонстрировано, что различные локальные и гибридные функционалы DFT, такие как хорошо известный B3LYP, независимо от размера базисных наборов, совершенно не в состоянии предсказывать правильные молекулярные структуры, не говоря уже об ИК-спектрах. Обнаружено, что только дальнодействующие скорректированные гибридные функционалы плотности в сочетании с базисными наборами достаточного размера способны предсказывать правильные значения двугранных углов между несвязанными атомными группами – наиболее важными координатами в конформационном анализе.

Таким образом, комбинация wB97XD/6-311++G(2df,2pd) метод/базисного набора представляется лучшим методом для указанной системы как с точки зрения предсказания геометрии, так и ИК-спектров.

Детальный анализ поверхности потенциальной энергии выявил существование 28 различных конформеров с разной заселенностью при температуре 298 *K*, которая оказывает существенное влияние на симулированные ИК-спектры.

Методология уравнения линейного масштабирования (LSE) успешно применена для калибровки волновых чисел и достижения наилучшего соответствия между теоретическими и экспериментальными областями поглощения функциональных групп в сульфонах. Кроме того, при построении симулированных ИК-спектров учитывалось лоренцево уширение каждой расчетной моды с различной шириной на полувысоте для получения коэффициентов экстинкции, т.е. более реалистичную зависимость $\varepsilon(\nu)$, непосредственно сравнимую с экспериментальными спектрами.

Достоверность полученных результатов подтверждена сравнением с экспериментальными литературными данными, полученными для сульфонов.