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FOURIER SPECTRUM OF THE INTEGRAL DIPOLE MOMENT OF A NUMBER OF AMINO ACIDS SUPERCOMPUTER MODELS

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Abstract. In order to analyze molecular vibrations, a method based on the calculation of the Fourier frequency spectrum of supercomputer amplitude-time realizations of the integral dipole moment in supercomputer simulation of glycine, Diphenyl-L-alanine, and tryptophan has been implemented. Under conditions of a zero external electromagnetic field, the frequency spectra of natural local vibrations of the atomic subsystem of the molecule were established to be the results of spectral analysis of these realizations. The spectra were verified by comparison with the known literature data on quantum chemical computing, computer simulation and experimental spectroscopy. It was shown that the proposed complex and technique made it possible to efficiently calculate reliable spectra of local amino acid vibrations. The results obtained may be useful for the development of prototypes of hybrid semiconductor microelectronic devices with built-in biomolecular components.

Keywords: amino acid, hybrid biomolecular electronics, computer modeling, molecular oscillation

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ФУРЬЕ-СПЕКТР ИНТЕГРАЛЬНОГО ДИПОЛЬНОГО МОМЕНТА СУПЕРКОМПЬЮТЕРНЫХ МОДЕЛЕЙ РЯДА АМИНОКИСЛОТ

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Аннотация. Реализован метод анализа молекулярных колебаний, основанный на вычислении Фурье-спектра частот суперкомпьютерных амплитудно-временных реализаций интегрального дипольного момента при суперкомпьютерном моделировании аминокислот глицина, дифенил-L-аланина и триптофана. Спектры верифицированы путем сопоставления с известными литературными данными квантовохимических вычислений, компьютерного моделирования и экспериментальной спектроскопии. Показано, что предложенные комплекс и методика позволяют эффективно вычислять достоверные спектры локальных колебаний атомной подсистемы молекулы. Полученные результаты полезны при разработке прототипов гибридных полупроводниковых микроэлектронных приборов с встроенными биомолекулярными компонентами.

Ключевые слова: аминокислота, гибридная биомолекулярная электроника, компьютерное моделирование, молекулярные колебания

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Introduction

Hybrid semiconductor microelectronic devices with built-in molecular components constructed in recent years include novel transistors, photodiodes and LEDs, biosensors, organosilicon hybrids and other devices [1–6]. Built-in biomolecular components (BMCs) have been represented by DNA, proteins, peptides and other molecules in numerous studies [5–8]. The unique functionality that such BMCs offer for microelectronics (including such industries as energy, electrical engineering, communications) cannot be replicated by any other means. Preserving the biological function of proteins and the transfer characteristics of charge carriers, constructing BMCs with a sufficiently large interface area, immobilization and structural properties of both single molecules and their clusters, crystals, film and bulk structures are all critical factors for successful integration of BMCs in electronic components (see, for example, review [9]). However, despite considerable efforts in this undoubtedly promising field, most of the existing problems are yet to be solved or even formulated consistently, Many fundamental challenges hindering the development of hybrid microelectronics remain to be addressed. From the standpoint of electrodynamics and electronics, biomolecules are primarily viewed not as carriers of biological functions but rather as physical oscillators with special properties of dynamic states localized in the spatial structure and over the amplitude spectrum in the frequency domain.

There are two main approaches to constructing such oscillators: the first one involves proteins and the second one amino acids (AA); both approaches come with the challenges and opportunities that vary widely for different hybrid devices. Protein BMCs are much more complicated than simple physical oscillators, as they have a larger number of atoms, more diverse secondary/higher structures with larger parameter values, and may contain inclusions other than amino acid residues. Protein BMCs have many conformational and structural differences, so they can only be accurately reproduced by statistical models. Amino acids of biomolecular components characterized by high repeatability of structures generally appear to be not only simpler but also more versatile.

Twenty-two naturally occurring amino acids making up all proteins in living cells are built have been well described physically, are environmentally safe, can be obtained in pure form, and their production is relatively simple and cheap. Peptide chains composed of amino acid residues serve as the main building blocks in biomolecular complexes. However, studies into hybrid devices have paid far less attention to these structures than to protein molecules built from them. The integral electron dipole moment (EDM) of amino acids is an informative and convenient parameter for potential applications in electronics, serving for monitoring the conformational dynamics in adsorbed states and solutions, for electrical potentials and temperature dependences, interaction energies with the solid surface, etc. For example, computer simulation of alanine oligopeptides (Ala 2-Ala 20) of different sizes in an aqueous medium and vacuum yielded a large amount of data on the most probable conformational states of the molecule and the EDM values under certain (variable) external conditions [10]. The aggregate patterns of the variation in EDM were comprehensively described in [10] from a physical standpoint, with the results obtained consistent with the literature.

Quantum mechanics methods are considered to be the most accurate for obtaining the vibrational frequencies of isolated free protein molecules: for example, this is the density functional theory (DFT) implemented in the GAUSSIAN software package (which is, however, very complex). Moreover, empirical fitting of numerical parameters is typically required in such simulation of vibrational spectra to adjust the calculated frequencies of normal vibrations and the intensities of vibrational transitions.

Hybrid semiconductor microelectronic devices need more effective approaches to simulating the nonequilibrium dynamics of bound molecules in the adsorbed state or in solutions in nonequilibrium states are needed. Supercomputer time-domain simulations of EDM magnitude [10] had long durations, which can nevertheless be considered acceptable for recording sufficiently accurate Fourier frequency spectra. Indeed, high resolution of the lines in the Fourier spectrum is achieved when a sufficiently large (of the order of 10^5–10^6 and above) number of oscillation periods is recorded throughout the time-domain simulations.

Accordingly, this paper set out to test the proposed method for sufficiently long time-domain simulation of integral EDM magnitude with subsequent Fourier analysis.

Molecular dynamics simulation

Molecular dynamics simulation was aimed at computing the integral EDM amagnitude over a time domain based on a solution of Newton's equations for each atom of the molecular system:

$$m_a \ddot{\mathbf{r}}_a = -\frac{\partial}{\partial \dot{r}_a} U_{total}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N),\ a = 1, 2, ..., N, \quad (1)$$

where m_a is the atomic mass, $\ddot{\mathbf{r}}_a$ is the acceleration, U_{total} is the integral over all components of the system's potential energy, depending on the mutual positions of all atoms and calculated at the location of the given atom.

The trajectories obtained for the motion of atoms in the force field of the empirical atom-atom potential provided a detailed microscopic picture of the internal thermal mobility of the macromolecule. The equations of motion (1) were represented in finite-difference form in the program for time-step calculations. The coordinates and velocities of all particles were set at the initial moment of time to calculate new values of the acting forces, coordinates and velocities of particles at each time step. The temperature was found as the mean kinetic energy per one degree of freedom of the system:

$$T(t) = \frac{1}{3Nk_B}\sum_{i=1}^{n} m_i \mathbf{v}_i^{\,2}, \mathbf{v}_i = \frac{d\mathbf{r}_i}{dt}, \tag{2}$$

where N is the molecule's total number of degrees of freedom, $N = 3n - 6$ (n is the total number of atoms); k_B is the Boltzmann constant.

The total momentum and angular momentum are preserved in an isolated system; the total energy of an adiabatically isolated system is also preserved, and the temperature is obtained by averaging its instantaneous values $T(t)$ (see Eq. (2)) over a given time domain.

The potential energy of the molecule was given in the following form:

$$U_{total} = \sum_{bonds} k_b (b - b_0)^2 + \sum_{angle} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} k_\varphi [1 + \cos(n\varphi - \delta)] +$$
$$+ \sum_{impropers} k_\omega (\omega - \omega_0)^2 + \sum_{Lennard-Jones} (-E_{\min}) \cdot \left[\left(\frac{R_{\min_{ij}}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min_{ij}}}{r_{ij}} \right)^{6} \right] + \varepsilon_{14} \frac{q_i q_j}{\varepsilon_0 r_{ij}}, \tag{3}$$

where b, b_0 are the stretching ratios of molecular bonds; θ, θ_0 are the angles relative to the plane; φ, δ are twist angles; ω, ω_0 are the irregular dihedral angles; $R_{\min}$ is the distance between the ith and the jth atoms at which the interaction energy becomes zero; the parameter $E_{\min}$ is the potential energy minimum of the Lennard–Jones interaction, $E_{\min} = U_{LJ}(R_{\min})$ (U_{LJ} is the Lennard–Jones potential); ε_{14} is a parameter representing a dimensionless scale factor, $\varepsilon_{14} = 1$, except for the modified interaction 1–4, when a pair of atoms is separated by a sequence of three covalent bonds (so that atoms can also participate in the interaction at a twist angle); r_{ij} are the distances between the ith and the jth atoms; q is the atomic charge; ε_0 is the dielectric constant, k_b, k_θ, k_φ, k_ω are the interaction coefficients.

The atomic interactions in Eq. (3) include stretching of the bonds and their twisting at a dihedral angle (proper and improper dihedrals).

The probability ω_τ of a given microscopic state with the energy E_τ depended only on the energy value, and was given by the Gibbs distribution:

$$\omega_\tau = \frac{1}{Z} e^{-E_\tau / k_B T}, \tag{4}$$

where τ is the number of the probability.

The normalization constant Z was chosen provided that the sum of probabilities be equal to 1; it took the form

$$Z = \sum_{\tau} e^{-E_\tau / k_B T}.$$

The instantaneous values of the EDM at each time step were calculated by summing the partial moments:

$$\boldsymbol{\mu} = \sum_{n=1}^{N} q_n \mathbf{r}_n. \tag{5}$$

Notably, summation in Eq. (1) is carried out for all charges in the molecule accounting for their individual position vectors. The sequence of $\boldsymbol{\mu}(t)$ values in expression (5) corresponded to instantaneous values of the integral EDM of the molecule obtained by time-domain simulation.

Running the computational algorithm for systems with a large number of atoms turned out to be a complex data-intensive problem. For this reason, we developed a specialized software system for supercomputer simulations including the Avogadro, Visual Molecular Dynamics and NAMD packages, as well as additional programs written in Python.

Software system for supercomputer simulations

The RSC-Tornado cluster of the Supercomputer Center at Peter the Great St. Petersburg Polytechnic University was used to develop the system. This cluster with a peak performance of 10^{15} teraflops contains 668 dual-processor nodes (Intel Xeon E5 2697 v3), 56 of which have two NVIDIA K40 GPU accelerators [11].

Fig. 1 shows a block diagram of the computational algorithm developed and adapted for the RSC-Tornado supercomputer cluster, intended for preparing and performing the molecular dynamics simulation and spectral processing of the data, and visualizing the results.

The following steps were taken to start the computations within the proposed algorithm: the initial parameters of the force field were set, the coordinates of atoms were determined in a specific molecular model, the equations accounting for the medium parameters of the molecules and representing the parameters of the physical/mathematical model of the vibrational system were formulated.

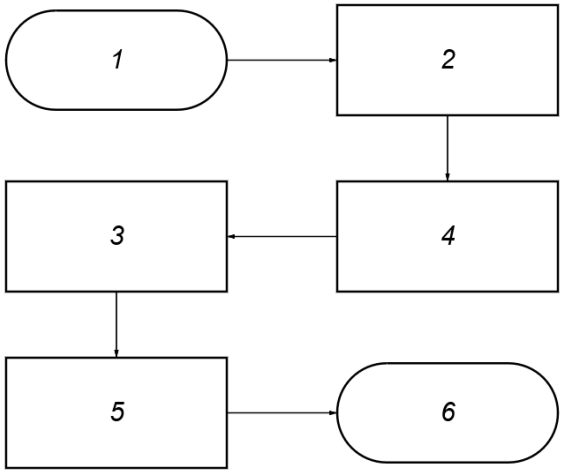

Fig. 1. Block diagram for the algorithm for preparing and performing molecular dynamics simulation, as well as analyzing the computational data obtained: *1*: experimental parameters are determined, *2*: functions of the force field parameters are set, *3*: coordinates of the atoms of amino acid molecules are determined, *4*: medium parameters of amino acid molecules are accounted for, *5*: frequency analysis of dipole moments of amino acid molecules is performed, *6* : results are visualized

Avogadro and Visual Molecular Dynamics (VMD) software was used to construct the models of molecular systems. The Avogadro software can generate files containing the coordinates of atoms of various biological molecules, including amino acids, as well as perform preliminary optimization of the molecular structure geometry. Avogadro was used to generate the input files with the atomic coordinates for glycine (Gly), diphenyl-L-alanine (FF) and tryptophan (TRP) molecules. The VMD software can generate structural files based on the topology of molecular bonds, add water molecules and salt ions, visualize molecular systems, calculate the energy and dipole moments of conformationally mobile molecules.

Fig. 2 schematically shows the structural formulas of glycine, diphenyl-L-alanine and tryptophan molecules used in the simulations.

Glycine was chosen for the study because it is the simplest organic aliphatic amino acid; for this reason, it can be used as reference for monitoring the most common types of vibrations in amino acids. Diphenyl-L-alanine and tryptophan belong to the class of aromatic α-amino acids. The chemical structure of diphenyl-L-alanine can be represented as the alanine amino acid where two hydrogen atoms are replaced by a phenyl group. Tryptophan contains an aromatic indole ring, rendering it hydrophobic. The structure of tryptophan can be represented as two radical residues: indole (an aromatic heterocyclic compound formed by two fused rings: benzene and pyrrole) and alanine connected by a C–C carbon bond. Both molecules are based on alanine, making it possible to compare the vibrational frequencies; in this case, the differences in the vibrational spectra can be attributed to the aromatic group.

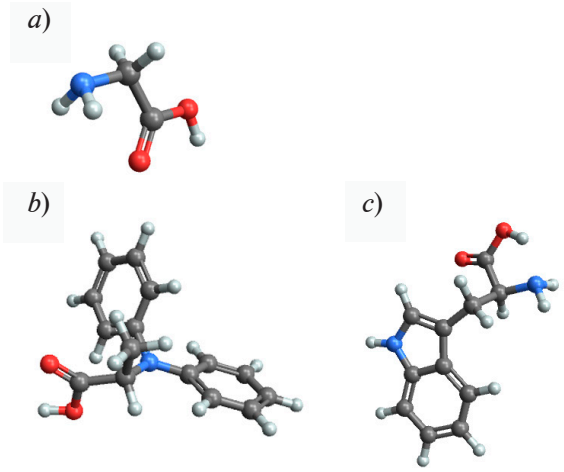

Fig. 2. Structural formulas of glycine (*a*), diphenyl-L-alanine (*b*) and tryptophan (*c*) molecules. The hydrogen, carbon, oxygen and nitrogen atoms are colored in gray, black, red and blue, respectively

The molecular model of each amino acid from the experimental set was placed in a virtual cell that was a water box. The size of the box varied from 20 to 30 E, depending on the sizes and positions of biomolecules, and the cells formed a periodic sequence. The dissolution of molecules was simulated by the TIP3W water model, corresponding to three atoms of a water molecule at three points of interaction with the molecule. Such models provide high computational efficiency and are used in many applications for molecular dynamics simulation. This water model was implemented in the CHARMM force field where the Lennard–Jones parameters are assigned to hydrogen atoms in addition to the oxygen parameters in the water molecule.

NaCl salt ions at a concentration of 0.15 mol/l were added to water unit cells containing amino acid molecules to construct models close to real systems. In this case, the maximum number of ions per molecule in the water box was about 30. Similar methods were verified in the experiments described in [12–15].

Molecular simulation was carried out with the CHARMM27 force field superimposed using the NAMD v.2.14 (Nanoscale Molecular Dynamics) package in four stages:

minimization of energy,

heating of the system,

finding the equilibrium values of kinetic and integral potential energy,

molecular dynamics simulation.

The NAMD package used the Charm++ parallel programming framework, which has a high parallelization efficiency for supercomputing. Periodic boundary conditions were imposed, the cutoff radii were set (for non-bonded interactions with the switching function), starting from 9 E and up to 12 E (detailed simulation parameters are given in Table 1). The instant when the system reached was simulated imposing the conditions for energy minimization, slow heating of the system (0.01 K per 1 fs) and stabilization of the conformational state of molecules. Stable states of molecules were obtained as a result of energy minimization; these are necessary to subsequently calculate the integral EDM of amino acid molecules in vacuum or in solution.

We calculated the EDM of a single amino acid molecule in aqueous solution stabilized with sodium ions.

The simulation stage was initiated with a special script with instructions. This script (along with the configuration files necessary for molecular dynamics simulation) was sent to the local directory of the cluster. All the necessary files were transferred using the SSHFS (Secure SHell File System) package for LINUX systems. The set of necessary files included a script to initiate the simulation, a .pdb file containing the coordinates of all the atoms in the molecular system, a .psf file containing a description of molecular bonds, as well as four namd configuration files for minimization and stabilization of energy.

Table 1

Parameters used in the simulation

Parameter	Value
Frame recording range, fs	1–20
Simulation time, ps	100–2000
Temperature, K	300
Pressure, bar	1.01325
Non-valent interactions, Å	18
Verlet list, Å	20
List update step, PHz	1
Number of frames, thousand	100
Weight of dcd coordinate file, Gb	0.015–20.0

Note. The NPT particle ensemble, CHARMM force field and explicit aqueous solvent were used.

The computational time ranged from several to hundreds of hours, depending on the number of atoms and the level of output power. The coordinates of the atoms in the molecular system were analyzed as output data at each instant in the simulation. The size of the coordinate file for each recorded frame ranged from 14 MB for vacuum systems to 20 GB for large solvent systems. The analysis of oscillation frequencies was performed using the VMD IR Spectral Density Calculator package. This package can analyze the atomic coordinates from the .dcd velocity file and build the spectral density plots for the variation in the dipole moment of the selected atoms. The distribution of the vibrational energy density over the frequency spectrum was computed via the time-domain simulation of instantaneous EDM magnitude for each molecule. A structural file and a file with sets of atomic coordinates of the molecular system were loaded into the program for this purpose. The sample was set over biomolecule atoms (excluding salt ions and water molecules), the temperature at which the simulation was performed, the coordinate step corresponding to the step in the simulation configuration file, and the upper-bound frequency of computations in the range of 6000 cm^{-1}. A file containing the frequencies and spectral densities of vibrations was generated as a result of calculations. Vibrations of amino acid molecules were visually monitored in the VMD program.

An original algorithm written in Python was used for further analysis of the computational data, combined with the Pandas Big Data software package. This algorithm allowed to process .csv files and generate a data set convenient for performing various operations on table rows and columns.

Frequency spectrum of time-dependent integral dipole moment for the amino acids considered

Fig. 3 shows the instantaneous values of the total integral EDM and its projections on the coordinate axis as a function of time, illustrating the spatial and angular configuration of the molecule in dynamics

EDM projections on the coordinate axes, dip_*x*, dip_*y*, dip_*z*, vary in magnitude relatively slowly, becoming correlated over time; the absolute value of the integral EDM remains approximately constant in the region of relatively low frequencies. This likely points to relatively slow nonlocal (including rotational) motions of the molecule as an approximately single structure provided that the conformational structure is preserved over a long period. Time-domain simulations of the total integral EDM (see Fig. 3) produce vibrations at significantly higher frequencies. The corresponding frequency spectra are shown in Fig. 4. They have a quasi-discrete character and a stable peak structure, so the predominant frequencies could be detected and interpreted with respect to local intramolecular vibrations in the atomic subsystem.

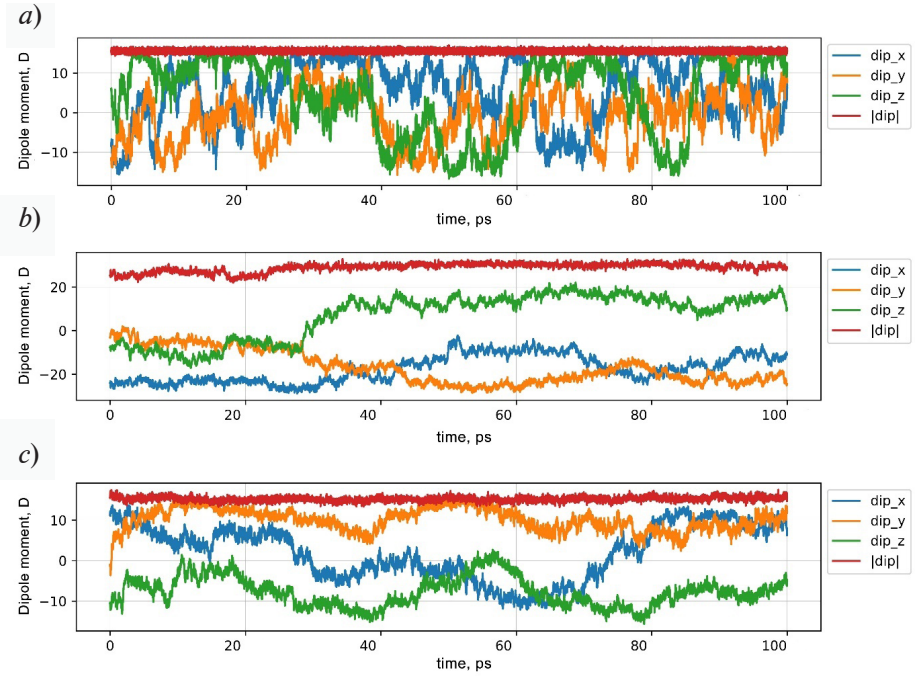

Fig. 3. Integral EDM for glycine(*a*), diphenyl-L-alanine (*b*) and tryptophan (*c*) amino acid molecules, as well as the corresponding projections of the EDM vector on the coordinate axis as a function of time (temperature of 300 K)

The obtained simulation results are given in Table 2 along with the natural vibrations and the data from the available literature. Fig. 5 shows the typical spatial configuration of some vibrations, corresponding to different spectral frequencies for the tryptophan molecule.

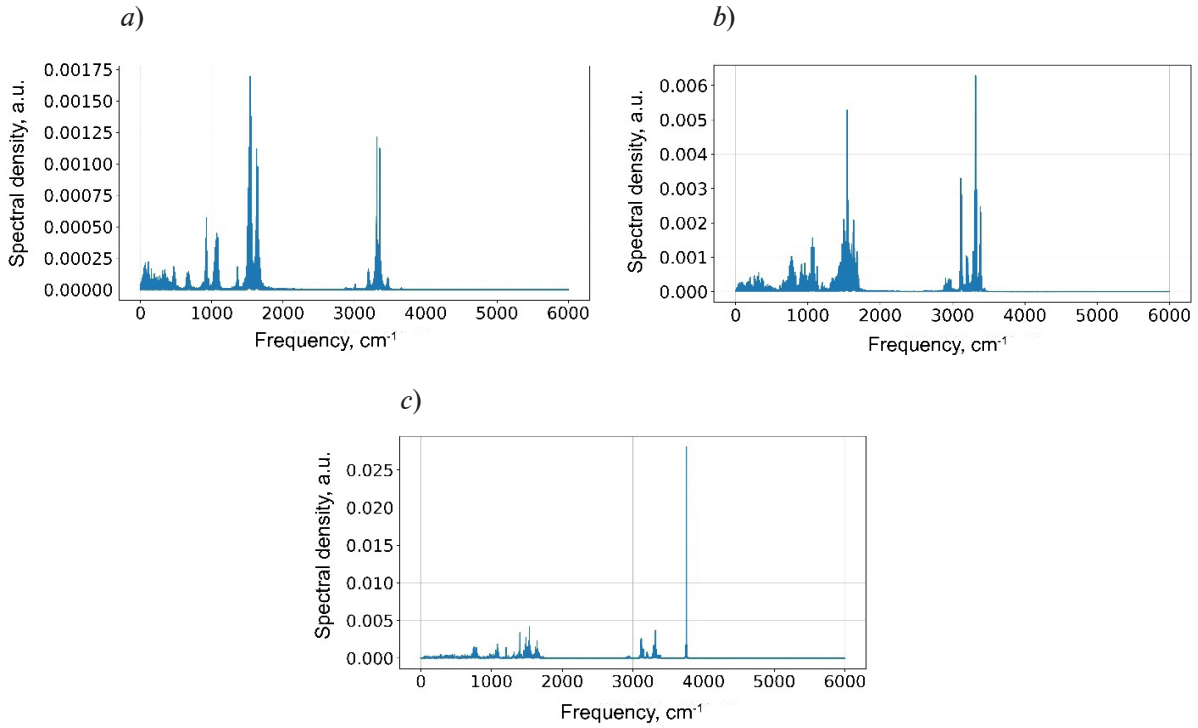

Fig. 4. Fourier transforms for time-domain simulation of total integral EDM for glycine (*a*), diphenyl-L-alanine (*b*) and tryptophan (*c*) amino acids

Table 2

Comparison of computed spectral components for three amino acids with the literature data

Bond, vibration type	Vibrational frequency of bond, cm^{-1}					
	Computational data			Literature data and source		
	TRP	FF	GLY	TRP	FF	GLY
Hydrogen	38–200	57–201	43–210	40–215 [16]	59–216 [16]	22–233 16]
$CC^{\alpha}N$, deformation	240–242	278	–	238–269 [17]	258, 278 [17]	–
CO_2, torsional	–	260	–	–	258, 261 [18]	–
NH_3^+	337–341	301–334	322–357	325–347 [17]	293, 324 [18]	356 [18]
COO^-, bending	582–597	479, 542–564 640–659	459, 543–563	499–655 [16]	535–647 [16, 19]	504–607 [16]
TRP $\delta_{o.o.p.}$, $\{\nu_4\}$ ring	683–687	–	–	660–692 [20]	–	–
νCC, $\{\nu_1\}$ ring breathing	745–766	–	–	716–795	–	–
δCH_2 + t pyrrol	844–874	–	–	790–828 [20]	–	–
δCOO^-, ωCOO νCC	–	–	677	–	–	679 [20]
OCO^-	–	748–770	–	–	778 [20]	–
δCOO–, νCC, νCN	–	846	–	–	837–859 [19]	–
νCC, δCOO^-	–	–	855	–	–	882–916 [20]
νCC, νCN, r CH_3	–	892, 949–955	–	–	913–931 [19, 20]	–
C–C	–	–	922–928	–	–	930, 988 [18, 20]
C–N	1036–1053 1060–1098	1039–1062 1134	1009–1061 1158	1018–1137 [18]		
C–O/OH	1202–1208	1200–1225	1229	1200–1300 [17]		
C–N (amide III)	1321	1338	–	1200–1340 [17, 21]		
CH_2/COO–	1401, 1486	1494	1362	1343/1330 [17]		
N–H (amide II)	1536	1541–1548	1526–1552	1530–1580 [17, 21]		
NH_2/NH_3 scissoring vibrations	1620–1647	1606–1642	1629–1646	1604–1660 [17]		
Valent C–H	2948	2887–2979	3013	2810–2900 [23]		
Asymmetric NH (amide A)	3117–3122, 3205–3227, 3295–3332	3116, 3192–3206, 3318, 3384	3199, 3314, 3356, 3472	3300 [23]		
Stretching O–H	3747–3765	–	3670	3700 [23]		

TRP, FF, GLY correspond to tryptophan, diphenyl-L-alanine and glycine molecules.

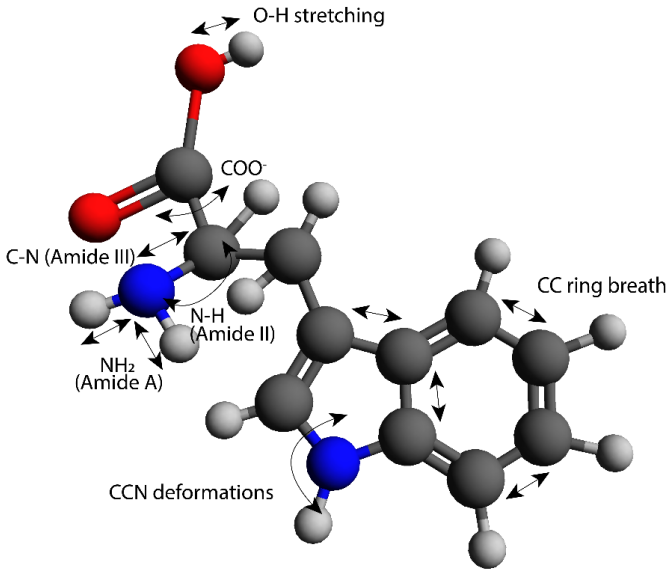

Fig. 5. Schematic images of some local vibrational motions in a tryptophan molecule

Discussion

The frequencies of natural local vibrations obtained by time-domain simulation of the instantaneous total integral EDM lie in the far infrared range of electromagnetic radiation. The entire set almost completely coincides with the results well-known from the literature (both statistically and in detail), obtained by experimental spectroscopy and computational methods in a wide frequency range.

As evident from Table 2, the computational values of the frequency are in excellent agreement with the experimental ones. For example, the best agreement for glycine amino acids is observed in the high-frequency range (from 988 cm^{-1}), with predominant vibrations of glycine anion, as well as valence vibrations of the C-C bond of the molecular skeleton. The main contributionIn the range from 1083 to 1154 cm^{-1} is made by the vibration of the C—N bond. Data agreement is observed for all three amino acids considered. Almost complete agreement is also observed for the three amino acids in the region of 1200—1300 cm^{-1}, where two spectral vibrational bands are present. These are C—O valence vibrations and (less intense band) deformational vibrations of the OH group. In addition, this frequency domain may include wagging vibrations of the CH_2— group. According to the literature data, vibrations of the C_α—H bond may be present at the boundary of this frequency domain (~1337 cm^{-1}), however, our simulations did not reveal any spectral density peak at this frequency.

The best agreement with respect to frequencies was observed for such bonds as N—H (amide II), scissoring vibrations of NH_2/NH_3 bonds, asymmetric NH (amide A). No 'excessive' vibrations that would not correspond to the known modes were detected in the computational frequency spectra. For example, according to $(3n - 6)$ golden rule, a glycine molecule should have a set of 24 natural frequencies. The values we obtained correspond closely to this requirement (see Table 2). The same agreement was obtained for the FF and TRP amino acids.

Assessing the overall results, we can conclude that the good agreement with the experimental data we obtained is clear evidence for the efficiency of the computational approach developed.

There are also some discrepancies between the computational values and the known frequencies of local modes, which may be due to factors such as the initial states of the molecules and their environments, including the presence of solvent molecules or salt ions. Molecules of water with salt ions dissolved in it can shift the frequency due to spontaneous formation of atomic complexes and the electric field of the ionic environment.

Conclusion

We have developed a supercomputer software system including the Avogadro, Visual Molecular Dynamics and NAMD software packages, as well as additional programs written in Python. The system was implemented at the RSC-Tornado supercomputer cluster at Peter the Great Polytechnic University and used for simulations of integral EDM magnitude over a long time domain (up to 100 ps). The frequency spectra of glycine, diphenyl-L-alanine and tryptophan amino acids were obtained in vacuum and in a salt aqueous solution with a zero external electromagnetic field.

Glycine, diphenyl-L-alanine and tryptophan amino acids in vacuum and in salt aqueous solutions, along with polyalanines, are of interest for further studies due to their unique structural and functional properties, as well as the possibilities provided for comparing the results obtained with available data.

The procedure and the results obtained were verified by benchmarking analysis and comparison with the known characteristics given in the literature, including density functional theory simulations based on methods of quantum chemistry. Fourier analysis of these simulations was used to obtain the frequency spectra of local self-oscillations for three selected amino acid molecules: glycine, diphenyl-L-alanine and tryptophan. The method, the software package and the results obtained were verified by comparing the frequency spectra with the data available in the literature. As evident from analysis, the method proposed and tested is effective for reliably computing the local vibrational spectra of amino acids. In contrast with quantum mechanical approaches, the method offers simpler computations for the dynamics of bound nonequilibrium molecules in the adsorbed state and in solution. The data obtained useful for developing prototype hybrid devices for semiconductor microelectronics with built-in biomolecular components. The software system can be used for supercomputer simulations of more complex and representative molecular scenarios. In particular, we intend to adopt this approach to simulate the dynamics of molecules located in an external high-frequency electromagnetic field.

The results were obtained using the resources of the Supercomputer Center at Peter the Great St. Petersburg Polytechnic University (www.scc.spbstu.ru).

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