SUPERCOMPUTER DYNAMICAL MODELS OF GLYCINE, TRYPTOPHAN AND DIPHENYL-L-ALANINE IN THE ELECTRICAL FIELDS OF TERAHERTZ AND INFRARED SPECTRAL RANGES

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Abstract. In the paper, a method for analyzing molecular oscillations of the glycine, tryptophan and difenilalanine amino acids in the electric fields of the THz/IR frequency ranges has been implemented with Fourier-frequency spectrum calculation of the integral dipole moment amplitude-time realizations obtained by supercomputer modeling. The achieved results inhibited new possibilities of applying this method, supplemented the understanding of the dynamic properties of biomolecules. The method and the data obtained can be recommended in the development of nanobiotechnologies, bioelectronics, and hetero hybrid microelectronic devices with embedded biomolecular components.

Keywords: molecular dynamics, simulation, amino acid, biomolecular electronics, glycine, tryptophan, diphenylalanine

СУПЕРКОМПЬЮТЕРНЫЕ ДИНАМИЧЕСКИЕ МОДЕЛИ ГЛИЦИНА, ТРИПТОФАНА И ДИФЕНИЛАЛАНИНА В ЭЛЕКТРИЧЕСКИХ ПОЛЯХ ТЕРАГЕРЦОВОГО И ИНФРАКРАСНОГО СПЕКТРАЛЬНЫХ ДИАПАЗОНОВ

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Аннотация. В статье реализован метод анализа молекулярных колебаний аминокислот глицина, триптофана и дифенилаланина в электрических полях терагерцового и инфракрасного диапазонов, основанный на вычислении Фурье-спектра частот амплитудно-временных реализаций интегрального дипольного момента, полученных суперкомпьютерным моделированием. Результаты показали новые возможности применения данного метода, дополнили представления о динамических свойствах биомолекул; использованный метод и полученные данные можно рекомендовать при разработке нанобиотехнологий, биоэлектронных и гетерогенных гибридных микроэлектронных приборов с встроенными биомолекулярными компонентами.

Ключевые слова: молекулярная динамика, компьютерное моделирование, аминокислота, биомолекулярная электроника, глицин, триптофан, дифенилаланин

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Introduction

Intramolecular and intermolecular vibrations of protein molecules, playing a crucial role in biological processes, are the focus of much attention in research and technical applications, including spectroscopy, development of bioelectronic and hybrid micro- and nanoelectronic heterogeneous semiconductor devices with embedded organic components, etc. [1−7].

Biomolecules, including amino acids, have the properties of a complex of coupled oscillators in a uniquely wide frequency range of the electromagnetic field, including such spectral ranges as giga- and terahertz (GHz and THz, respectively), infrared (IR), visible and ultraviolet (UV) [8−10]. Compared with large protein molecules, amino acids are characterized by a higher statistical repeatability of the structure, a stable set of dynamic parameters, and extensive functionality. This can serve as a basis for creating components for hybrid microelectronic devices controlled by electrical signals. Well-systematized, distributed and local vibrations appear in the zero external electromagnetic field in the THz and IR spectra of amino acids, due to normal-mode dynamics [11−14]. Internal local intramolecular electric fields are induced by multipoles of normal vibrational modes, mainly dipoles. Accordingly, the molecule is a multi-frequency system of coupled oscillators, whose activity in the zero external field is determined by stored and incoming energy.

Such vibrations generate an internal self-consistent electric field with the largest amplitude up to approximately 1 V/nm at the frequencies of intramolecular resonances at normal temperature, due to the spatial redistribution of charges. The energy of internal multipoles of biomolecules in the gas phase and in solution can be effectively changed by an external electromagnetic field, DC or AC at selective frequencies, which determines conformational transitions, variations in multipole moments and the intensity of forced vibrations.

It is assumed in theoretical and experimental (THz−IR) spectroscopy that the absorption of the energy of the irradiating electromagnetic field occurs during local intramolecular vibrations related to the primary structure, as well as during non-local vibrations of the secondary and higher structures [7, 12, 15, 16]. Spectroscopy is mainly aimed at recording spectrally selective absorption of irradiation energy, but this technique does not allow to monitor the rearrangement of the entire complex of intramolecular oscillators.

Supercomputer simulation was performed in our earlier study [17] by the molecular dynamics method, accompanied by a comparative study of the frequency spectra of the integral dipole moment for the glycine, diphenyl-L-alanine and tryptophan amino acids via time-domain simulation at zero external electromagnetic field. The Fourier spectra of the local normal vibrations of amino acids were verified in our previous study by comparison with the data available from computer modeling and experimental spectroscopy. The effectiveness of the developed experimental technique was also validated.

Computer simulation of nonequilibrium molecular dynamics in an external electromagnetic field allows to develop the theory of spectroscopy, monitor the conformational dynamics and local vibrations of amino acids, peptides and large proteins, construct biotechnologies, prototypes of bioelectronic and heterogeneous hybrid micro- and nanoelectronic semiconductor devices with embedded organic components, and much more [18].

According to the simulation data, the linear dipole response of the oscillators corresponds to the external electric field strengths up to ~0.5 V/nm, i.e., significantly less than the internal field [15, 19, 20].

While there are vast amounts of data from theoretical and experimental studies on the effects of external electromagnetic fields on protein molecules, there is still insufficient information about forced local vibrations of amino acids in the mid-IR and near-IR ranges. The ratio of free and forced components upon excitation at selective frequencies is also insufficiently studied. Supercomputer simulation of molecular dynamics in [1], supplemented by taking into account the AC external field of the IR-range, was performed for the glycine amino acid in an aqueous solution. The study detected for the first time the resonant and transient effects of forced asymmetric NH_2 vibrations (Amide A) and C−N vibrations with wavenumbers amounting to, respectively, about 3335.62 and 1042.37 cm^{-1}.

This article adopts the technique [1] for comparative analysis of molecular dynamics in glycine, tryptophan and diphenylalanine amino acids in an AC electric field with a frequency tunable in the range of 20−6000 cm^{-1}.

Amino acids were chosen for such comparative studies due to the peculiarities of the structure and functional properties of molecules, the possibility of comparing the results obtained with known data, as well as the potential of the new data for development and search for prototypes of bioelectronic and heterogeneous hybrid microelectronic devices with embedded biomolecular components.

Technique for simulating the molecular dynamics of amino acids in the electric field of THz−IR ranges

The Avogadro package was used to generate the input files with the atomic coordinates of glycine (GLY), tryptophan (TRP) and diphenylalanine (FF) 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. A Newton dynamics equation was solved for each atom of the system, , atomic coordinates, force field parameters, system temperature, pressure, etc. were determined by time steps. As a result, instantaneous values of the atomic coordinates and velocities were obtained, which were then used to calculate the time dependences of integral electric dipole moments (EDM) $\mu(t)$ were by summing the partial moments:

$$\mu(t) = \sum_{n=1}^{N} q_n \left[\mathbf{r}_n(t) - \mathbf{r}_n(0) \right], \tag{1}$$

where $\mathbf{r}_n(0)$ is the radius vector of the spatial position of the charge q_n at time $t = 0$; $\mathbf{r}_n(t)$ is its instantaneous value.

The sequence of time-dependent values of the integral EDM $\mu(t)$ (see Eq. (1)) was a superposition of local vibrations of intramolecular atomic oscillators.

The RSC-Tornado cluster of the Supercomputer Center at Peter the Great St. Petersburg Polytechnic University was used to perform the computations. 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 [17]. This allowed to accumulate effective databases of time-domain simulations of integral EDM of molecules with a maximum duration of up to 2 ns, with the smallest sampling step of up to 1 fs, providing high-resolution Fourier spectra in acceptable time (no more than 100 machine hours). The SPbPU computing system included Avogadro, Visual Molecular Dynamics and NAMD packages, as well as additional original programs written in Python. In addition to the simulation technique described in more detail in [17], an AC electric field of the (THz−IR) frequency range is introduced, similar to the one used in [21]. Following the majority of the studies on this subject, we assumed that the force acting on intramolecular charges from the AC magnetic field is small (significantly less than the electric one), and the electromagnetic field was given only by the electric component. The electric field $\mathbf{E}(t)$ had a planar polarization along the coordinate axes x, y, z with components $[E00]$, a symmetrical square wave and an amplitude relative to the zero line from 0 to 0.5 V/nm. Consequently, the applied field was significantly smaller than the internal electric field in the molecule. There is only one known study where a similar electric square wave, but with much lower frequency, was generated to study the dynamic properties of liquid water in the frequency range of 20−500 GHz with an amplitude ranging from 0.05 to 1.00 V/nm [22].

Fig. 1 shows the distribution of the external field and the first three harmonics of its Fourier spectrum. The frequency of the applied field could be varied within wide limits by varying the number of sampling points in the square wave period and the values of the sampling frequency. Euler's formula can be used to represent each harmonic by a circular polarization, or a superposition of two waves rotating in opposite directions, one of which can be synchronous with the rotation of the dipole moment vector.

Fourier analysis of the frequency spectrum of time-domain simulations of the integral dipole moment in an electric field was performed using the VMD IR Spectral Density Calculator package, which also allowed calculating the coordinates of atoms from the .dcd velocity file.
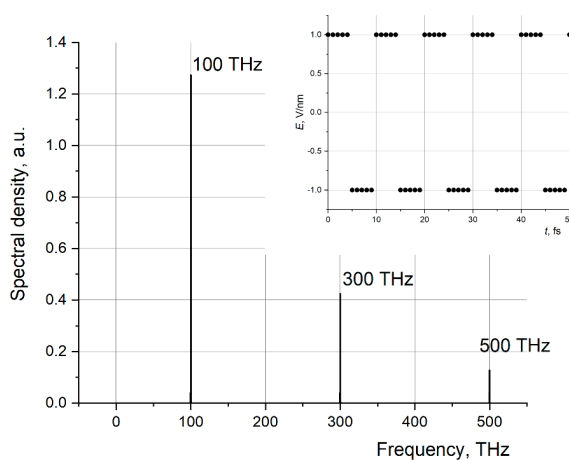

Fig. 1. Fragment of calculated Fourier spectrum of external electric field
with a fundamental harmonic frequency of 100 THz.
The inset shows the plot of the applied AC electric field $E(t)$

Dynamic characteristics of amino acids in an electric field
of (THz−IR)-bands

Typical time dependences of the instantaneous values of the total integral EDM and its projections on the coordinate axis, showing the spatial and angular configuration and dynamics of glycine, diphenyl-alanine and tryptophan molecules in a zero electric field, were presented in [17]. The time-domain simulation of the integral EDM was dominated by high frequencies characteristic of local vibrations and remained approximately constant in the region of relatively low frequencies. The projections of the EDM on the axis of rectangular coordinates fluctuated relatively slowly in amplitude, pointing to non-local collective motions of the molecule maintaining its conformational structure over long periods.

Fig. 2 shows typical time dependences of the integral EDM for the glycine and tryptophanamino acids in an aqueous solution with an electric field applied at a frequency of 100 THz with a rectangular pulse envelope. The electric field was absent in the first 500 ps ($E = 0$), then it was switched on for periods of 500 or 1000 ps (see Fig. 2). The field was switched off at the end of the pulse ($E = 0$). Evidently, the amplitude of forced local vibrations occurring during the action of the field increases especially intensely at the resonant frequencies of the field coinciding with the frequencies of normal modes.
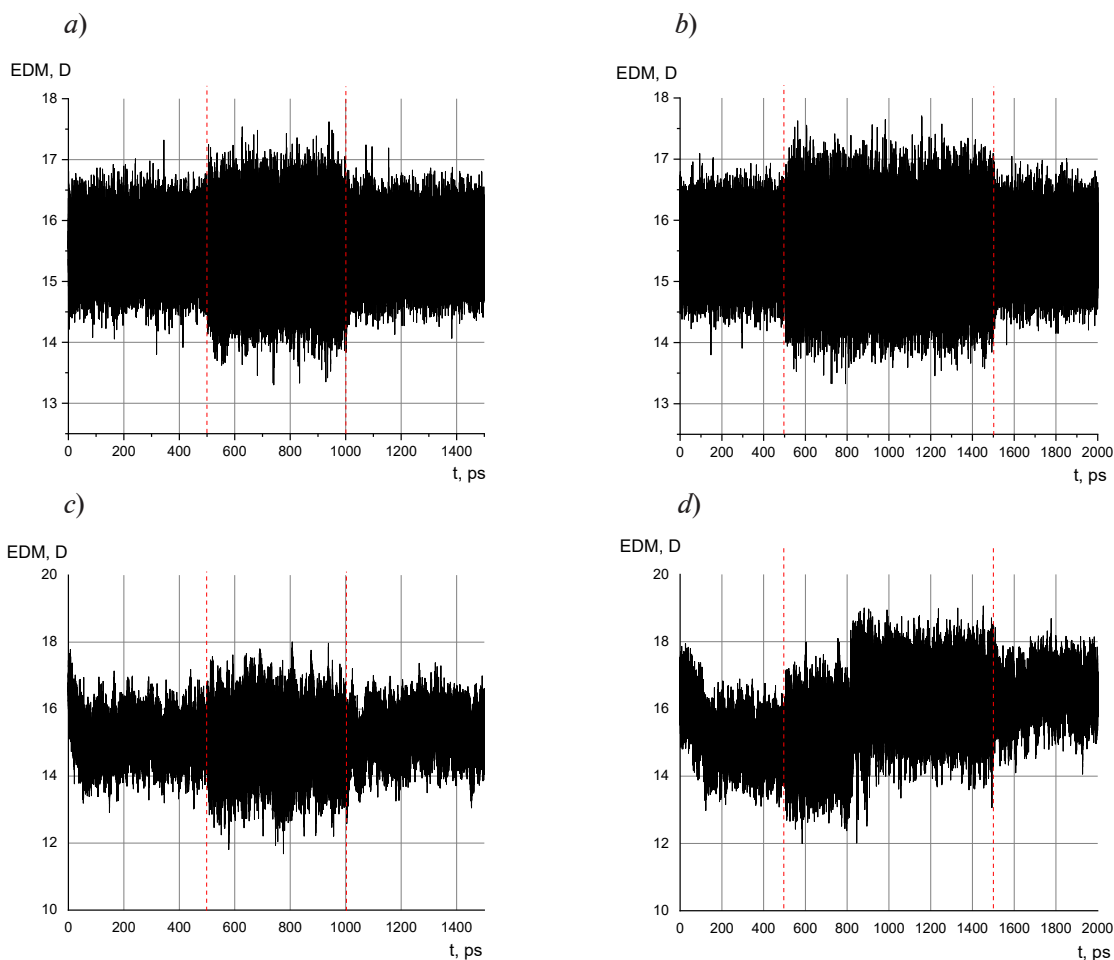

Fig. 2. Time-domain simulations of integral EDM for glycine (*a*, *b*) and tryptophan (*c*, *d*) amino acid molecules in square-wave pulsed electric field (pulse durations of 500 ps (*a*, *c*) and 1000 ps (*b*, *d*)) with an amplitude of approximately 0.4 V/nm, at a resonant frequency of 100 THz (Amide A, 3333 cm^{-1}). The time instants when the electric field was switched on and off are shown by red dashes. Fig. 2,*d* shows an abrupt conformational transition at $t = 800$ ps.

The data processing technique, described for the first time in [1], allowed to determine such parameters of the local oscillator as the frequency band Δf and the Q factor (given for example in Fig. 2). For this purpose, the distributions (see Fig. 2) were first transformed depending on the time when the vibrational energy W was proportional to the square EDM; next, the rise and fall time constants τ were determined for the pulses $W(t)$. Since the leading edges of the field pulses lasted no longer than the sampling step (1 fs, see the inset in Fig. 1), it was possible to determine the time constants and transient dynamic characteristics of local oscillators with great accuracy. It was found that the resonant modes of the local oscillator of the normal asymmetric NH_2 vibrations of tryptophan (Amide A), as well as glycine, corresponded to $\tau \approx 10^{-10}$ s, frequency bands $\Delta f \approx 10$ GHz and $Q \approx 10^4$. The given parameter values were preserved for the pulse durations varied within the limits shown in Fig. 2. Apparently, such local oscillators can be considered independent or weakly related to the collective conformational dynamics at lower frequencies. Along with local resonances, rare abrupt changes in the mean value of the integral EDM were observed in the presence of a field, which can be associated with spontaneous conformational transitions. Similar transitions were also detected during VMD visualization of the molecular structure.

The next stage of the analysis is applying the Fourier transform to the time-domain simulations of the integral EDM of molecules (shown for example in Fig. 2), and constructing the frequency spectra.

Non-local collective or conformational motion occurs in the region of gigahertz frequencies and the adjacent part of the terahertz range. Time-domain simulations of the integral EDM and calculations of the frequency spectra revealed both non-resonant and resonant excitation scenarios of molecular oscillators by an electric field in this range. Fig. 3 shows typical spectra of non-resonant and resonant scenarios in the THz frequency range.

Conformational dynamics of biomolecules in this frequency range is associated to a greater extent with the motion determined by hydrogen bonds and secondary structure. It was established, for example, that low-energy vibrations in the range of wave numbers from 300 to 500 cm^{-1} can point to the presence of secondary structures in linear and cyclic peptides [12]. It was also found in the literature that spectral peaks of collective vibrations form a dense continuum of selected frequencies in the range of 20−200 cm^{-1} [12, 20].

Table 1 compares the calculated resonant frequencies with the values of such frequencies known from the literature for glycine (GLY), tryptophan (TRP) and diphenyl-L-alanine (FF) molecules.

A large number of resonant scenarios given in Table 1 shows that the simulation results yield good agreement with the known data for high spectral densities in the frequency range of 20−200 cm^{-1}, likely related to collective vibrations involving hydrogen bond chains. There are groups of local eigenmodes in the spectra located higher in frequency in the ranges of 200−1800 cm^{-1} and 2800−3700 cm^{-1}; they are considered in detail in [17] for a zero external
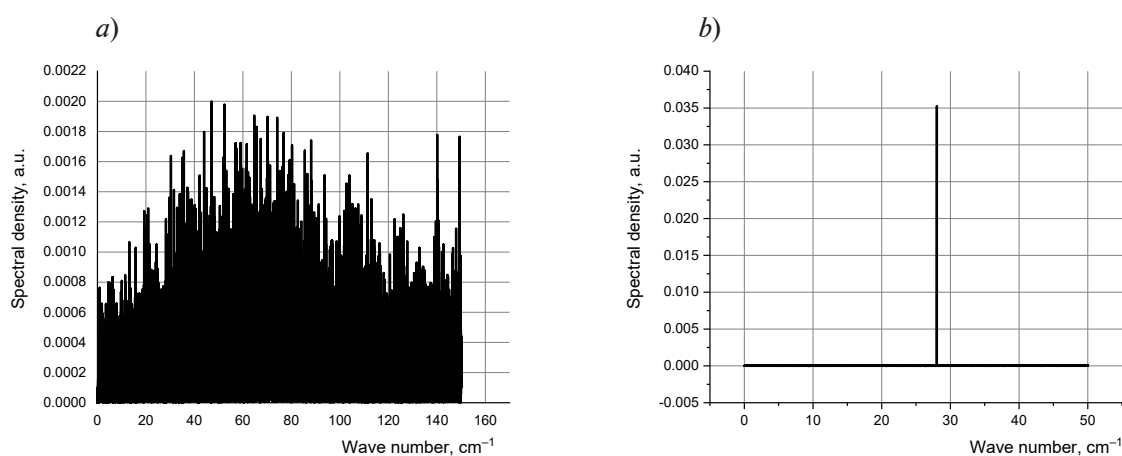

Fig. 3. Typical Fourier spectra of non-local vibrations in an AC electric field
of the THz range. Non-resonant (glycine, 144.67 cm^{-1}) (a)
and resonant (tryptophan, 28.03 cm^{-1}) (b) interactions are shown

field. Such frequency spectra of natural vibrations at $E_{ampl} = 0$ are shown in Figs. 4−6 for comparison with the spectra of forced local vibrations. The latter in these high-frequency groups, obtained by the Fourier transform of time-domain simulations of the integral EDM with a plane-polarized electric field applied as a symmetrical square wave with a deviation amplitude from the zero line $E_{ampl} = \pm 0.43$ V/nm, are also shown in Figs. 4−6. The data are given for glycine, tryptophan and diphenyl-*L*-alanine molecules.

The data shown in Figs. 4−6 allow to construct an interpretation corresponding to forced local intramolecular vibrations excited by both the main and third field harmonics.

Discussion

The obtained spectral dependences had a quasi-discrete character in all spectral ranges, a stable peak structure and a wide range of resonant and non-resonant scenarios of forced harmonic vibrations. In cases of resonances, the energy of all recorded vibrations was mainly concentrated in the resonant peak, and a significant (by an order of magnitude or more) increase in amplitude of the selected type of vibration occurred during the transition from natural to forced vibrations. The resonant frequencies correspond to non-local types of vibrations in the THz range (see Table 1, range of 20−200 cm^{-1}) and local normal modes in the IR range (see Figs. 4−6, range of 980−6000 cm^{-1}). Local resonances correspond to the frequency values of 100, 33.3 and 31.0 THz, non-resonant scenarios to 125, 83.3 and 29.4 THz. An intermode energy transfer is observed at the frequency of the main harmonic of 29.4 THz, or 980 cm^{-1} (see Fig. 4,*a* and Table 2) to the right at higher frequencies, mainly for the Amide A 3335.6 cm^{-1} mode (glycine, Fig. 4); partial absorption at resonance and energy transfer to Amide A and O−H 3758.57 cm^{-1} modes [1, 17] (tryptophan, Fig. 5); absorption at the irradiation frequency and resonance excitation at the C−C 980 cm^{-1} mode corresponds to the known mode of 981.08 cm^{-1} [17, 29] (diphenylalanine, Fig. 6).

Table 1

Comparison of computational results (CR) with the literature data (LD)
(THz frequency range)

Resonant frequency, cm^{-1}					
GLY		TRP		FF	
CR	LD	CR	LD	CR	LD
22.00	22.00 [1]	28.03	28.00 [1]	–	–
37.06	37.00 [8]	31.14	30.33 [8, 23]	–	–
52.45	52.33 [3]	39.71	39.67 [8]	41.69	41.67 [8]
58.73	58.67 [3]	46.85	46.83 [24]	–	–
61.09	61.00 [8]	47.65	47.67 [23, 25]	–	–
68.07	68.00 [3]	60.65	60.67 [23, 26]	–	–
76.86	76.67 [25]	61.32	61.33 [24]	66.45	66.33 [23]
77.21	77.00 [3]	75.47	75.33 [8, 23]	67.25	67.33 [8]
80.18	80.00 [23]	–	–	–	–
84.23	84.33 [3]	–	–	84.23	84.33 [23]
86.86	86.67 [27]	85.53	85.67 [23]	90.64	90.67 [23]
90.15	90.00 [23]	–	–	92.14	92.00 [8]
133.49	133.33 [3]	121.74	122.00 [3]	–	–
135.59	135.83 [27]	–	–	138.98	138.67 [8]
166.78	166.67 [3]	158.84	158.67 [3]	–	–

The glycine, tryptophan and diphenyl-*L*-alanine biomolecules considered are abbreviated as GLY, TRP, FF.
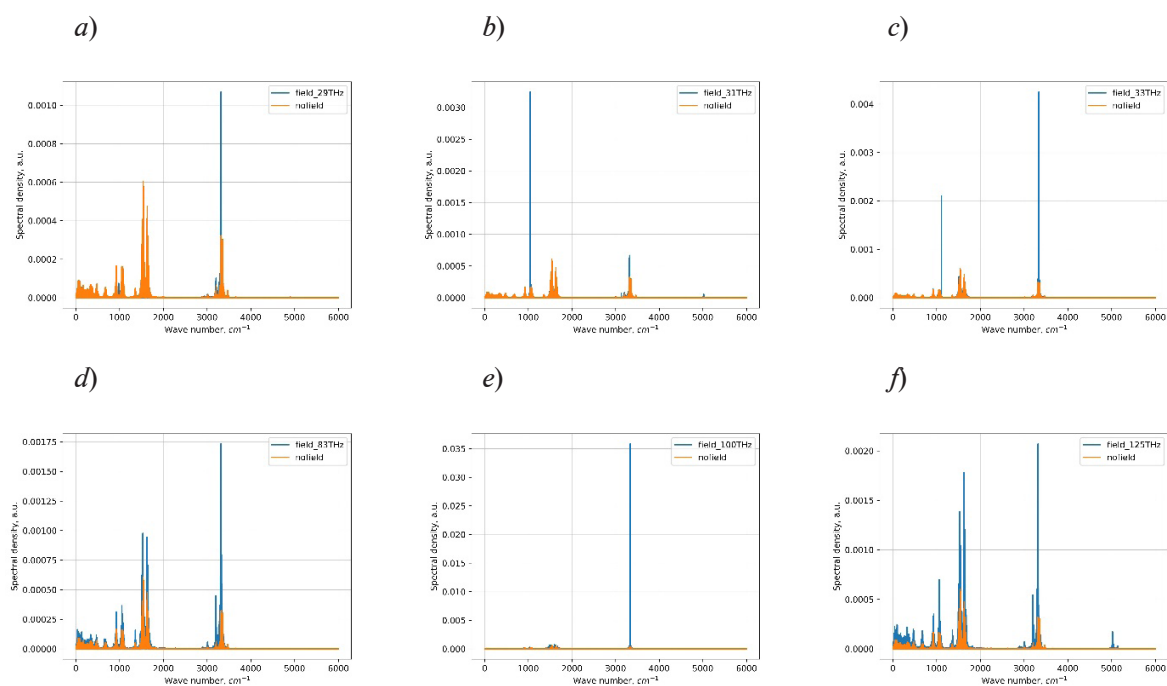
Fig. 4. Comparison of forced local (blue curves) and natural (orange curves) vibrations of glycine. The first ones were obtained by Fourier transform of time-domain simulations of integral EDM with a plane-polarized electric field applied as a symmetrical meander square wave with a deviation amplitude from the zero line $E_{ampl} = \pm 0.43$ V/nm, $E_{ampl} = 0$ for the second ones. The frequencies and wave numbers of the fundamental harmonic of the applied field are given in Table 2.
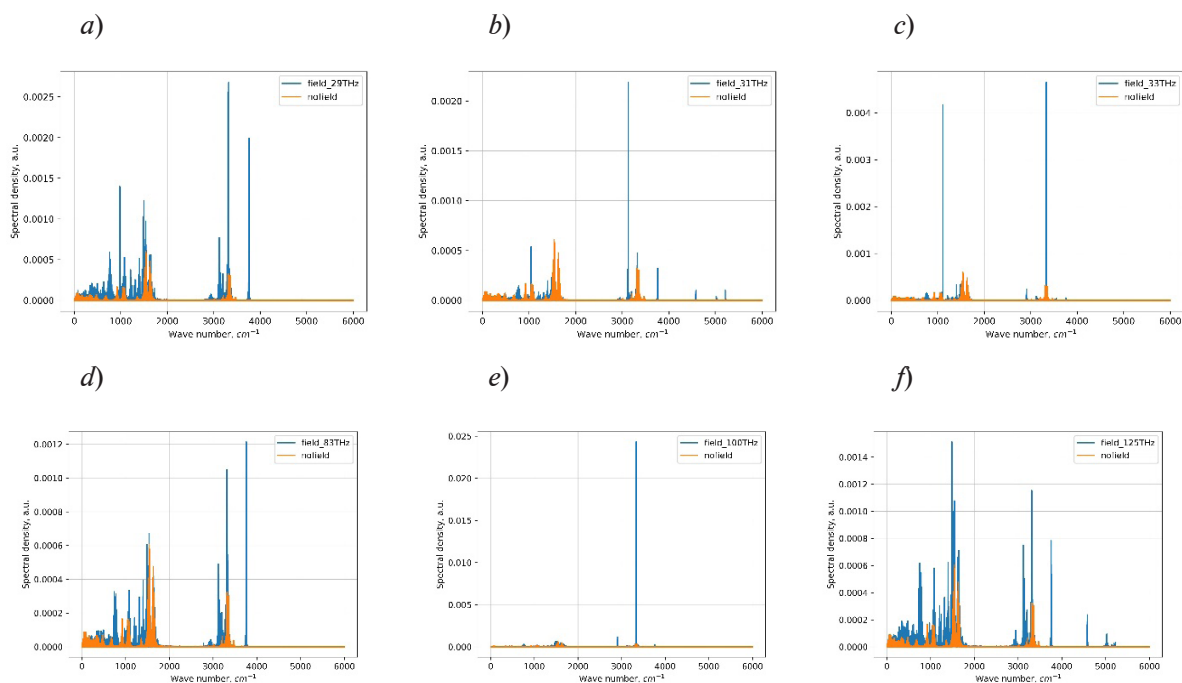

Fig. 5. Same comparison as in Fig. 4, but for tryptophan (see also Table 2)
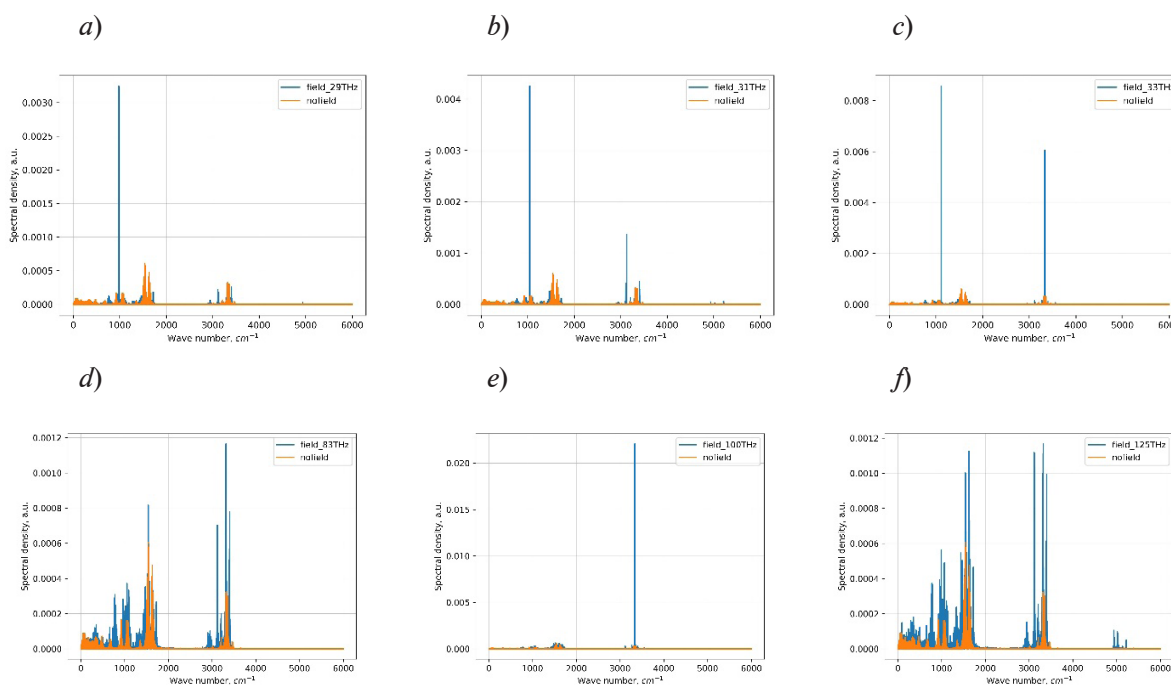
Fig. 6. Same comparison as in Figs. 4, 5, but for diphenylalanine (see also Table 2)

Upon irradiation at the frequency of the main harmonic 31.26 THz, or 1042 cm^{-1} (see Fig. 4,*b*; 5,*b*; 6,*b* and Table 2), resonances of the C−N 1042 cm^{-1} mode were observed at the 3rd harmonic N−H 3127.15 cm^{-1} [4, 21], as well as two resonances simultaneously: C−N and N−H at the 1st and 3rd harmonics [17, 30]. Two resonances were obtained simultaneously at the main harmonic frequency of 3.33 THz, or 1111 cm^{-1} (see Fig. 4,*c*; 5,*c*; 6,*c* and Table 2) for each of the three types of amino acid molecules: the first for the C−N modes in the main harmonic, the second for Amide A in the 3rd harmonic [17, 30]. In the case of irradiation at a frequency of 83.34 THz, or 2778 cm^{-1} (see Fig. 4,*d*; 5,*d*; 6,*d* and Table 2), resonant scenarios were not detected, almost all lines of the free local vibration spectrum were excited, stretching O−H 3758.57 cm^{-1} and Amide A 3333 cm^{-1} modes were predominant. The most pronounced resonant absorptions for all three molecules in the asymmetric N−H (amide A) [21] mode were observed under irradiation at the fundamental harmonic at a frequency of 100 THz, or 3333 cm^{-1} (see Fig. 4,*e*; 5,*e*; 6,*e* and Table 2). In the cases shown in Fig. 4,*f*; 5,*f*; 6,*f*, non-resonant excitations were observed at a frequency of 125 THz, or 4167 cm^{-1} (see Table. 2), distributed over the entire mode spectrum, and there was no increase in the vibrational energy at the irradiation frequency, but vibration peaks appeared at neighboring frequencies, where free vibrations were not represented.

Table 2

**Frequencies and wave numbers of fundamental harmonic of applied electric
field with deviation amplitude from zero line E_{ampl} = ±0.43 V/nm**

Figure	Frequency, THz	Wavenumber, cm^{-1}
4,*a*; 5,*a*; 6,*a*	29.40	980
4,*b*; 5,*b*; 6,*b*	31.26	1042
4,*c*; 5,*c*; 6,*c*	33.33	1111
4,*d*; 5,*d*; 6,*d*	83.34	2778
4,*e*; 5,*e*; 6,*e*	100.0	3333
4,*f*; 5,*f*; 6,*f*	125.0	4167

Conclusion

Supercomputer molecular dynamics was used for time-domain simulation of integral EDM with a THz and IR-range electric field applied. The frequency spectra of forced local vibrations of glycine, tryptophan, and diphenylalanine in vacuum and in an aqueous-salt solution, as well as the parameters of transient dynamic processes in an external high-frequency electromagnetic field were calculated by Fourier transform method. The mode of forced vibrations close to resonant ones was detected, threshold values of the field at which the transition to the nonlinear mode occurs were established. The theory of forced vibrations in linear resonant mode was used to calculate the Q-factors of oscillators and the vibrational frequency bands at various normal modes. Resonant and frequency-band effects of distributed and local molecular oscillators in an electric field, detected by computer simulation, expand the understanding of the dynamics of atomic groups in amino acid structures. As a result, a wide range of forced vibration scenarios was obtained, illustrating in detail the diverse dynamics of amino acid molecules and complementing the known data, including THz and IR spectroscopy.

The developed technique and the results obtained will be useful for applications in nanobio-technologies, bioelectronic and heterogeneous hybrid microelectronic devices with embedded biomolecular components.

The tested software package can be used for more supercomputing more complex and representative molecular scenarios, for example, internal vibrations in molecular clusters and crystals.

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