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Computer resonance dynamics of a glycine molecule in an infrared electric field

© E.K. Nepomnyashchaya, M.A. Baranov, O.Yu. Tsybin

Peter the Great Saint-Petersburg Polytechnic University, St. Petersburg, Russia
E-mail: baranovma1993@gmail.com

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The supercomputer software-computer complex of molecular dynamics is supplemented with an external alternating electric field. Along with nonresonant influences, the mode of resonant excitation of normal vibration modes in the molecules of the amino acid glycine was studied when an electric field was set in the form of a symmetrical meander in the IR frequency range. The technique expands the possibilities of studying the structure, dynamics, and functions of biomolecules, as well as methods for developing hybrid micro and nanoelectronic devices.

Keywords: biomolecules, molecular modeling, electronics, molecular vibrations.

Intramolecular vibrations are of fundamental importance for biological functions of protein molecules and are observed in fundamental and applied research (spectroscopy, studies into hybrid semiconductor microelectronic devices with embedded organic components, etc. [1–3]).

Computer nonequilibrium dynamics of biomolecules in an external electromagnetic field provides an opportunity to develop the spectroscopy theory further, identify conformational dynamics, determine dielectric characteristics, etc. [4,5]. Vibrational processes (especially those occurring in protein molecules under far and middle IR electromagnetic influences) remain understudied. In the present study, we use supercomputer simulations to examine resonance and transition effects emerging when an IR electric field affects glycine amino acid molecules in a solution.

The authors of [6] devised a supercomputer software-computer complex (SCC) and examined the frequency spectrum of amplitude-time realizations of the integral dipole moment of glycine, diphenyl-L-alanine, and tryptophan amino acids in zero external electromagnetic field. This SCC included Avogadro, Visual Molecular Dynamics, and NAMD application packages and additional proprietary software written in Python. Fourier spectra of natural local vibrations of amino acids were verified by comparing them with the results of computer simulation and experimental spectroscopy performed earlier. The calculation procedure was found to be reliable.

In the present study, the mentioned SCC is supplemented with an external alternating electric field with a frequency falling within the 3–240 THz range (with wave numbers of normal modes of local intramolecular vibrations around 100–8000 cm^{-1} , respectively). Computational resources of the supercomputing center of Peter the Great St. Petersburg Polytechnic University („RSK-Tornado“ cluster) were used. This cluster with a peak performance of 10^{15} TFLOPS features 668 dual-processor nodes (Intel Xeon E5 2697 v3),

56 of which are fitted with two NVIDIA K40 computational accelerators [6]. The molecular system contained a glycine amino acid molecule and molecules of water (model TIP3W) and NaCl salt. Water and salt molecules were added in order to simulate the dynamics of amino acids in a near-natural environment. The Newtonian equation of motion was solved for each atom of the system; the coordinates of atoms, force field parameters, temperature of the system, pressure, etc., were determined in time steps. The obtained instantaneous values of coordinates and velocities of atoms were then used to calculate time dependences $\boldsymbol{\mu}(t)$ of the electric dipole moment (EDM) by summing over partial moments:

$$\boldsymbol{\mu}(t) = \sum_{n=1}^N q_n [\mathbf{r}_n(t) - \mathbf{r}_n(0)]. \quad (1)$$

Here, $\mathbf{r}_n(0)$ is the radius vector of the spatial position of charge q_n at time $t = 0$, and $\mathbf{r}_n(t)$ is the current value. The sequence of values of the amplitude-time realization of integral EDM $\boldsymbol{\mu}(t)$ (1) was a superposition of local vibrations of intramolecular atomic oscillators. The smallest time step was 1 fs, and the maximum length of realizations was 2 fs.

The Fourier analysis of realizations $\boldsymbol{\mu}(t)$ in VMD („IR Spectral Density Calculator“) provided a quasi-discrete frequency spectrum with a stable structure of peaks, thus allowing us to interpret forced local intramolecular vibrations in the atomic subsystem in an external electric field. An atomically weak field was set in the form of a symmetrical meander with different packet durations and a plane spatial polarization over coordinate axes x , y , z with components [A00] and amplitude A varying from 0 to $\pm 0.5 \text{ V} \cdot \text{nm}^{-1}$. The field frequency was varied within a wide range by adjusting the number of sampling points in a meander period and the sampling frequency. Since a

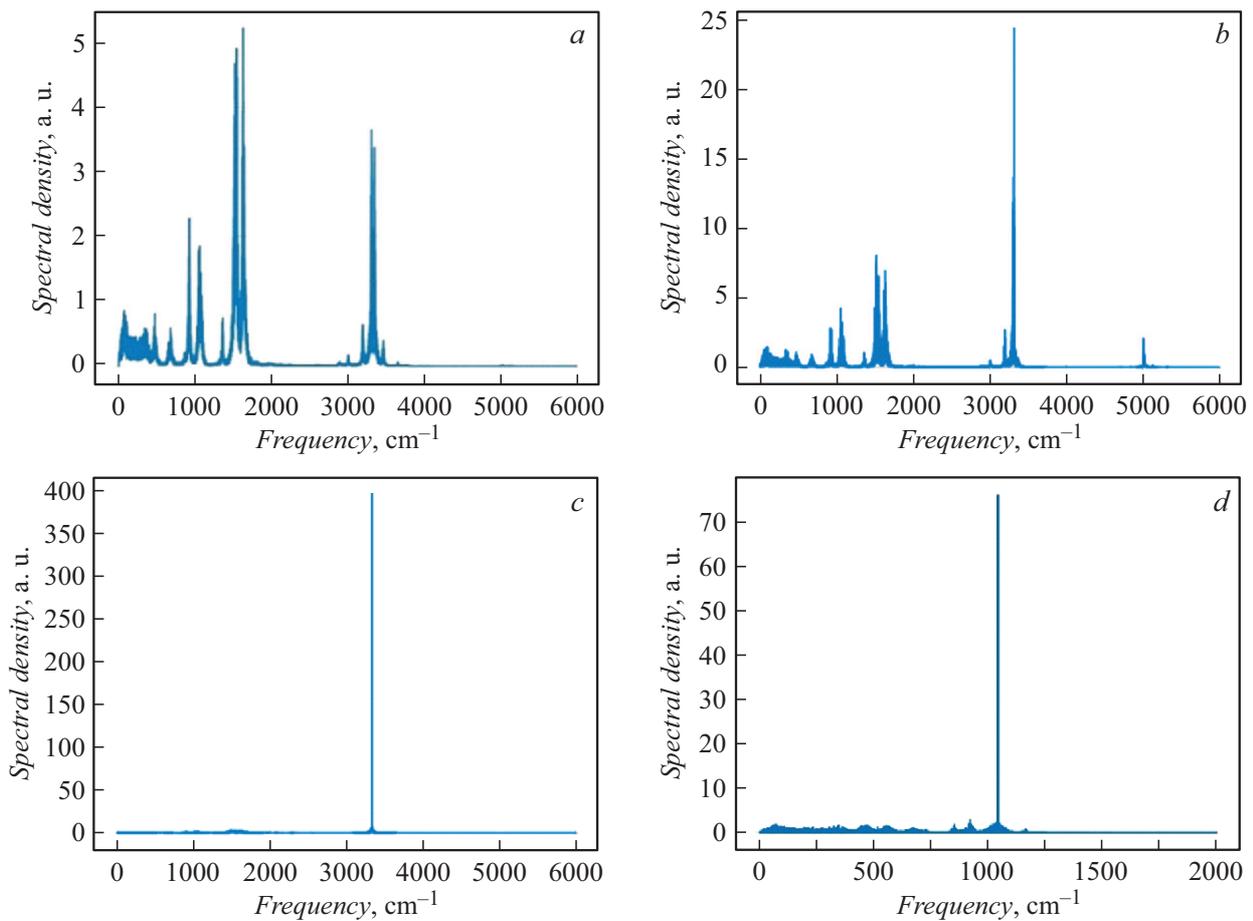


Figure 1. Fourier spectrum of amplitude-time realizations of the integral EDM of a glycine molecule in an aqueous solution at $T = 300$ K and $E = 0$ (a), in nonresonance electric field $f_E = 125$ THz (4167 cm^{-1}) (b), and in resonance electric fields $f_E = 100$ THz (3333 cm^{-1}) (c) and $f_E = 31$ THz (1042 cm^{-1}) (d).

well-studied glycine molecule was chosen for examination, we had an opportunity to compare the results with literature data and ensure the highest possible reliability of calculation and analysis procedures.

Figure 1 presents the frequency spectra of intramolecular vibrations obtained via Fourier spectral decomposition of amplitude-time realizations of the integral EDM of glycine in zero field at $E = 0$ (a) and in nonresonance (b) and resonance (c, d) fields. An external field of a nonresonance frequency induced a several-fold enhancement of the amplitudes of peaks with the closest frequencies (Fig. 1, b). In the resonance case, when the fundamental frequency of the applied field matched the local vibration frequency, the amplitude of the chosen vibration type increased significantly (by an order of magnitude or more). The shape of the spectrum revealed that almost the entire detected energy of vibrations was concentrated in the resonance peak.

The determined resonance frequencies fit valence local vibrations of the type of asymmetric NH_2 vibrations (amide A) and C–N vibrations with wave numbers around 3335.6 and 1042.37 cm^{-1} , respectively. The resonance peak

amplitude increased linearly with meander amplitude within the range from 0 to ± 0.4 $\text{V} \cdot \text{nm}^{-1}$. A nonlinear regime was established in higher-intensity fields. Similar results were obtained for diphenyl-L-alanine and tryptophan molecules. The following parameters may be introduced to characterize forced resonance in the linear quasi-harmonic oscillator regime: time constant of relaxation (i.e., buildup and decay of the energy of local vibrations) τ , frequency band $\Delta f = 1/\tau$, and quality factor $Q \approx f/\Delta f$. When setting a rectangular envelope of a meander packet, we determined the values of τ by examining the fronts of an integral EDM pulse (Fig. 2).

The approximation of pulses $D^2(t)$ corresponded to exponential dependences of the energy variation in the course of vibration buildup and decay. The values of $\tau \approx 10^{-10}$ s, frequency band $\Delta f \approx 10$ GHz, and quality factor $Q \approx 10^4$ of a local oscillator of the normal mode of asymmetric NH_2 vibrations corresponded to the plots shown in Fig. 2 and other similar resonance regimes.

The discussed implementation of the procedure for simulation of dynamic parameters of amino acids is consistent with a linear nature of superposition of local normal

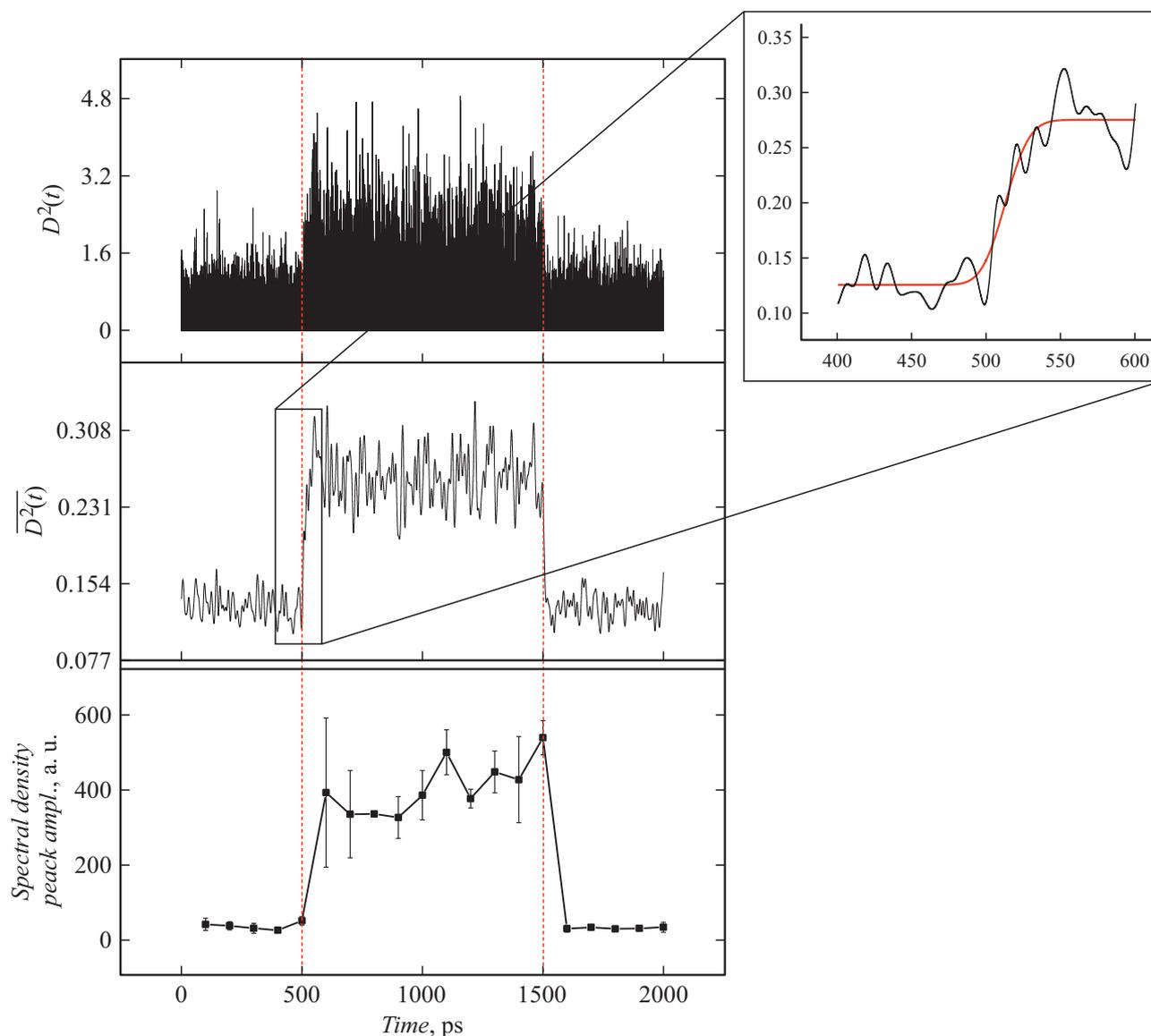


Figure 2. Time dependence of the square of amplitude $D(t)$ of the high-frequency EDM component (upper panel), the same dependence averaged with a period of 5 ps (middle panel), and histogram of the resonance peak (lower panel). The approximation of the $D^2(t)$ pulse front is shown in the inset. The moments of switching a meander packet at a frequency of 100 THz (3333 cm^{-1}) on (500 ps) and off (1500 ps) are indicated.

vibration modes and a nonuniform distribution of the energy of coupled quasi-harmonic oscillators over a wide frequency spectrum. Regimes of resonance excitation of forced vibrations in glycine, diphenyl-L-alanine, and tryptophan amino acid molecules in an electric field at far and middle IR frequencies were revealed, and the linear section and the threshold of switching to a nonlinear regime were identified. Typical parameters of transient dynamic processes (including relaxation time constants, the frequency band, and quality factors of molecular oscillators) were calculated. The proposed method and the obtained results widen the opportunities for supercomputer research into the structure and dynamics of biomolecules in an electric field and into their functions

in heterogeneous hybrid micro- and nanoelectronic devices.

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Conflict of interest

The authors declare that they have no conflict of interest.

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