Russian Supercomputing Days

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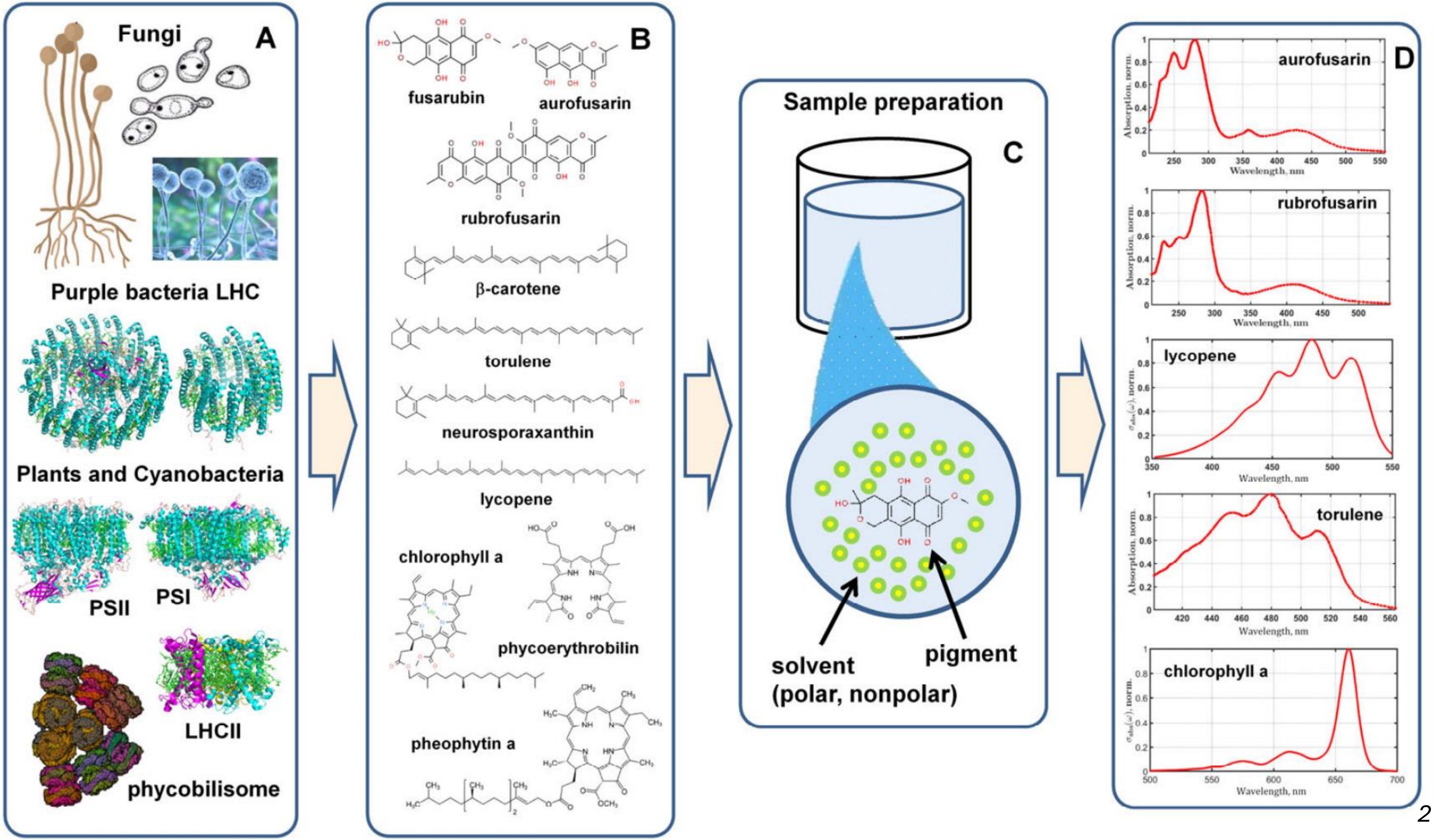
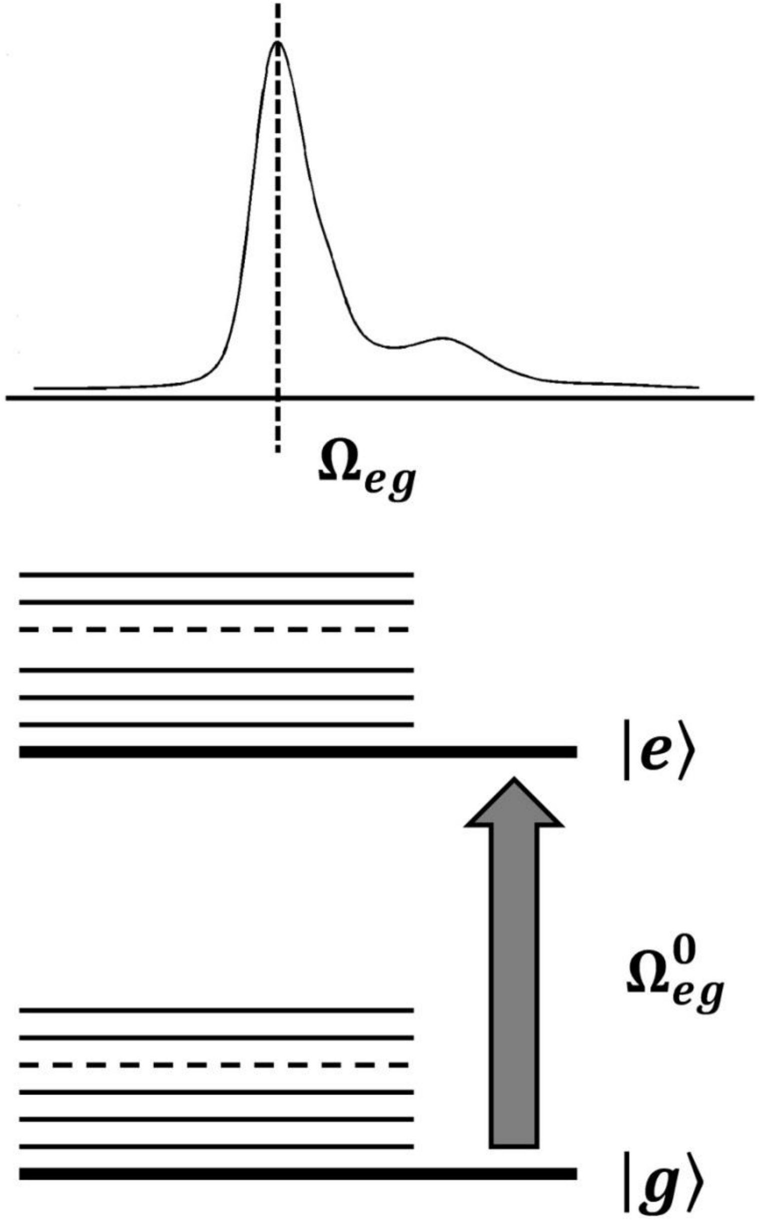
ИОФ РАН

Evolutionary optimization in semiclassical quantum modeling of the optical properties of organic pigments

Kurkov Vasily Andreevich, Denis D. Chesalin, Roman Y. Pishchalnikov



A
Fungi
Purple bacteria LHC
Plants and Cyanobacteria
PSII
PSI
LHCII
phycobilisome
B
fusarubin
aurofusarin
rubrofusarin
β-carotene
torulene
neurosporaxanthin
lycopene
chlorophyll a
phycoerythrobilin
pheophytin a
Sample preparation
C
solvent
(polar, nonpolar)
pigment
D
aurofusarin
rubrofusarin
lycopene
torulene
chlorophyll a
Wavelength, nm
Absorption, norm.



The Hamiltonian of the system :

$$H_{total} = H_g + H_e + H_{VB}$$

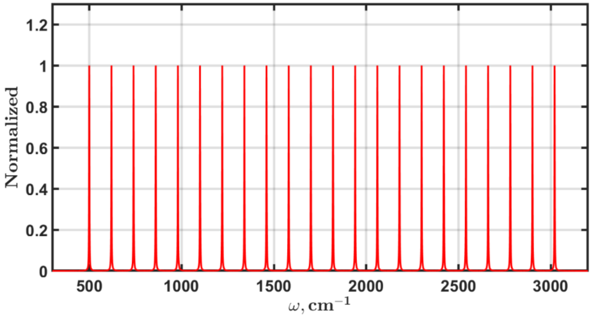
The electronic Hamiltonian :

$$H_g(q) = \sum_j^N \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right)$$

$$H_e(q) = \hbar\omega_{eg}^0 + \sum_j^N \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j + d_j)^2 \right)$$

Spectral density function :

$$C''(\omega) = \sum_j \frac{2S_j \omega_j^3 \omega \gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}$$

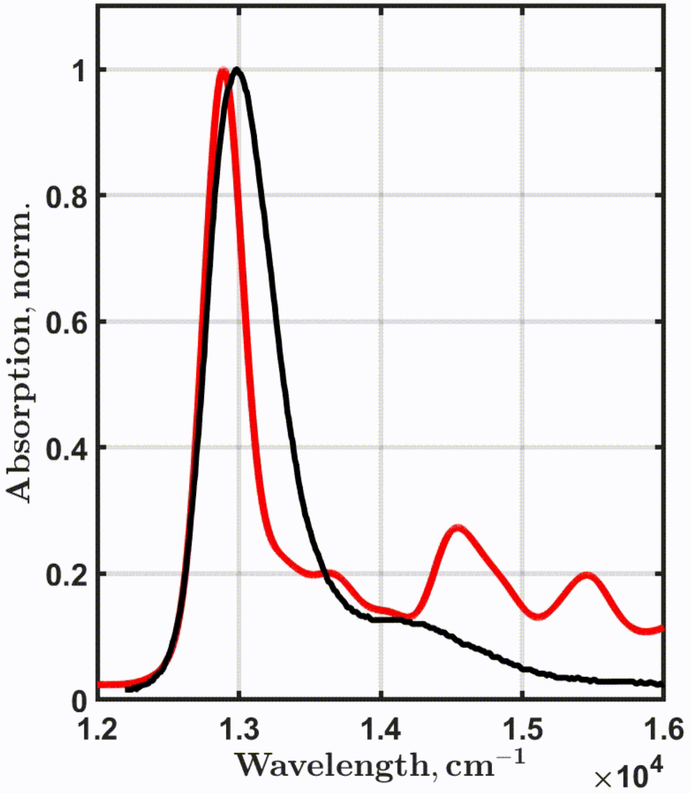


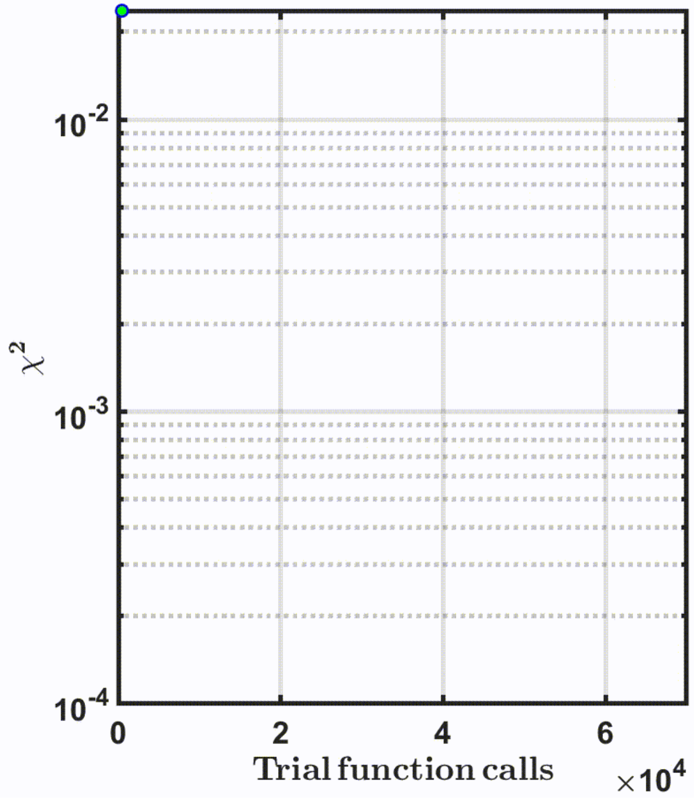
Lineshape function:

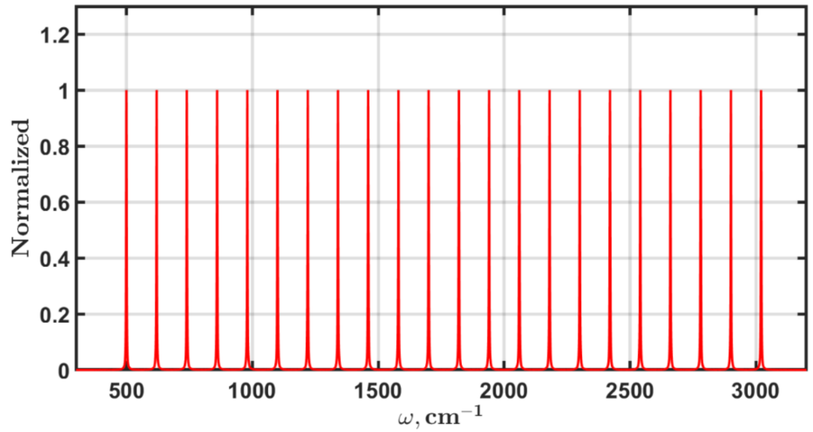
$$g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{1 - \cos \omega t}{\omega^2} \coth(\beta\hbar\omega/2) C''(\omega) - \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\sin(\omega t) - \omega t}{\omega^2} C''(\omega)$$

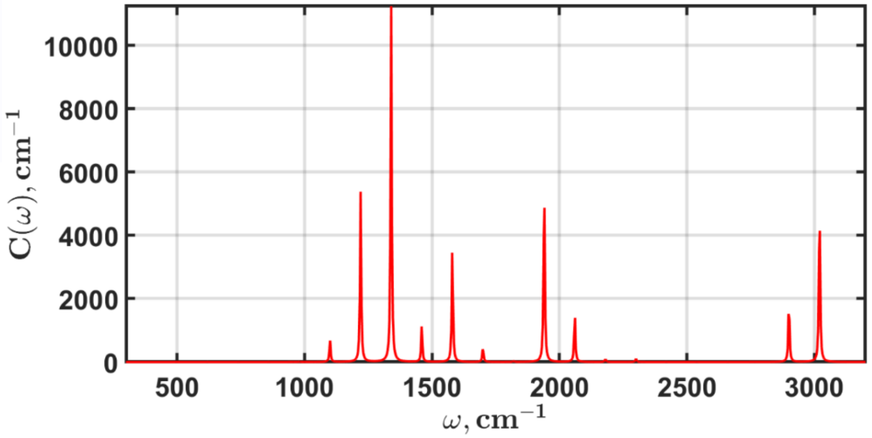
Absorption spectrum:

$$\sigma_{abs}(\omega) = \frac{1}{\pi} Re \int_0^{\infty} dt\, e^{i(\omega - \Omega_{eg})t} e^{-g(t)} e^{-\frac{1}{2}(\Delta t)^2}, \quad \Delta = FWHM/2\sqrt{2 \cdot ln2}$$







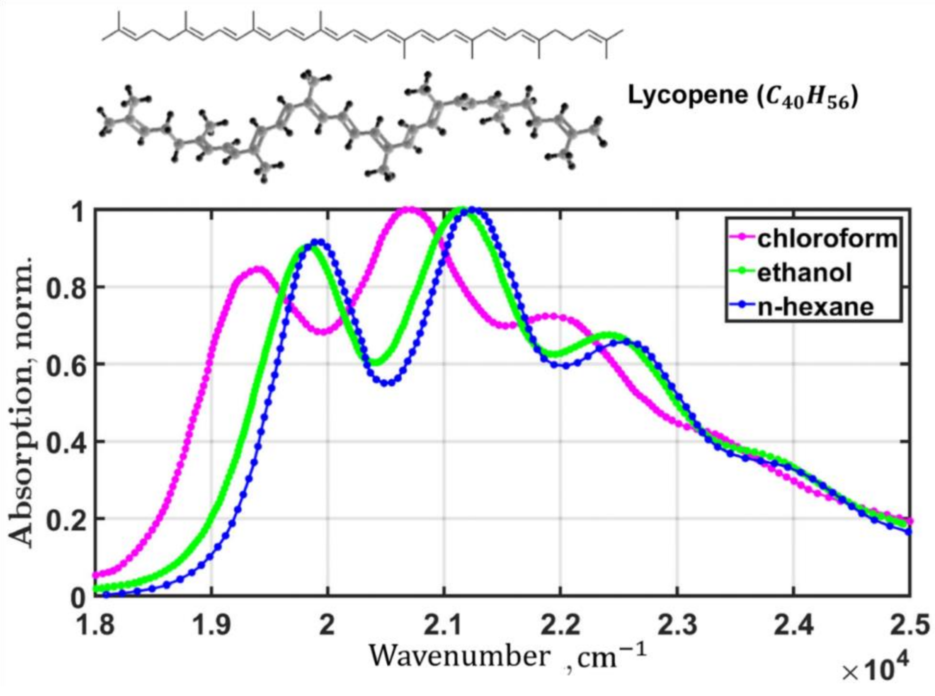


Input parameters:

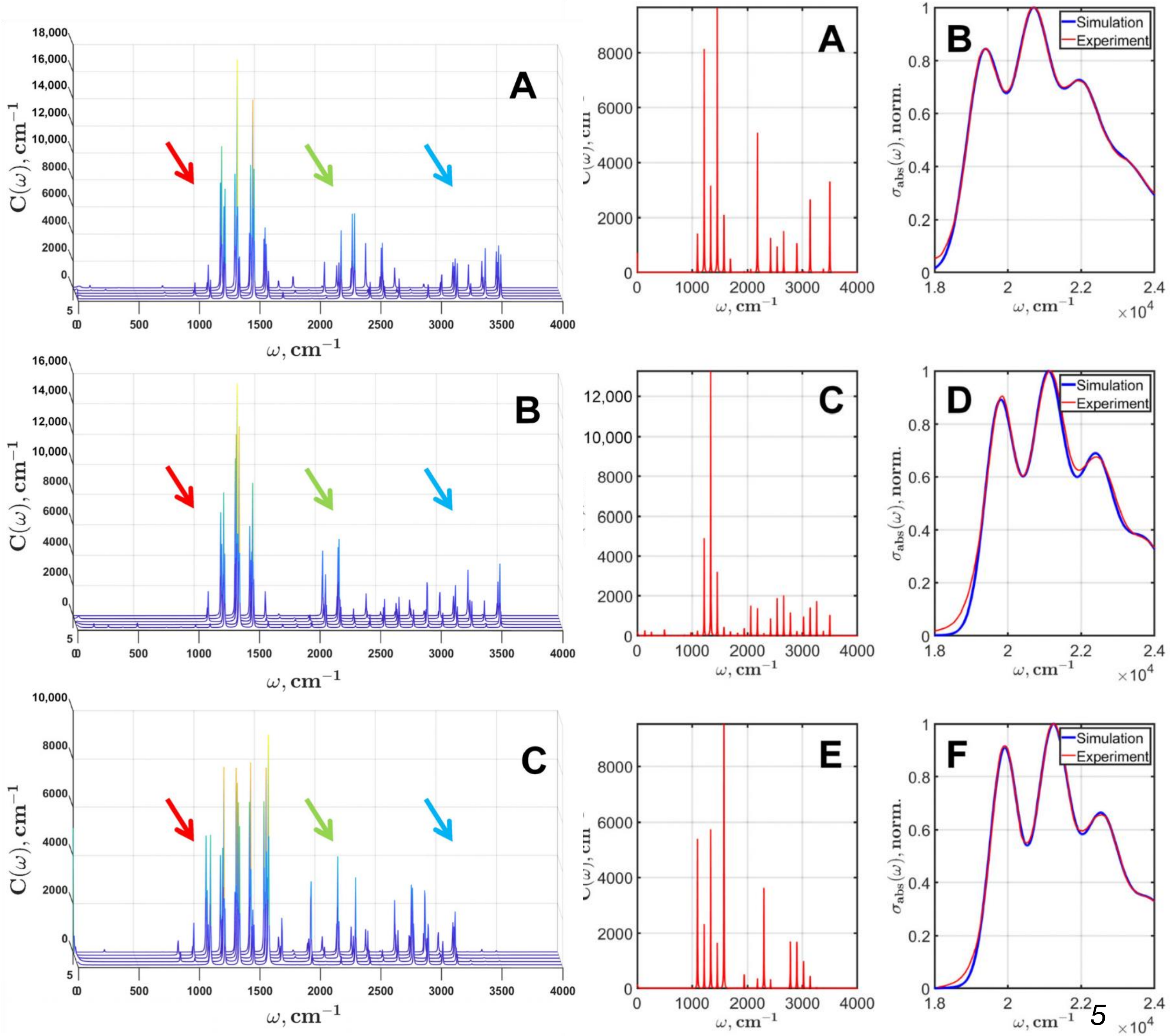
Ω_{eg}

$FWHM$

$\{\omega_j, S_j, \gamma_j\}$

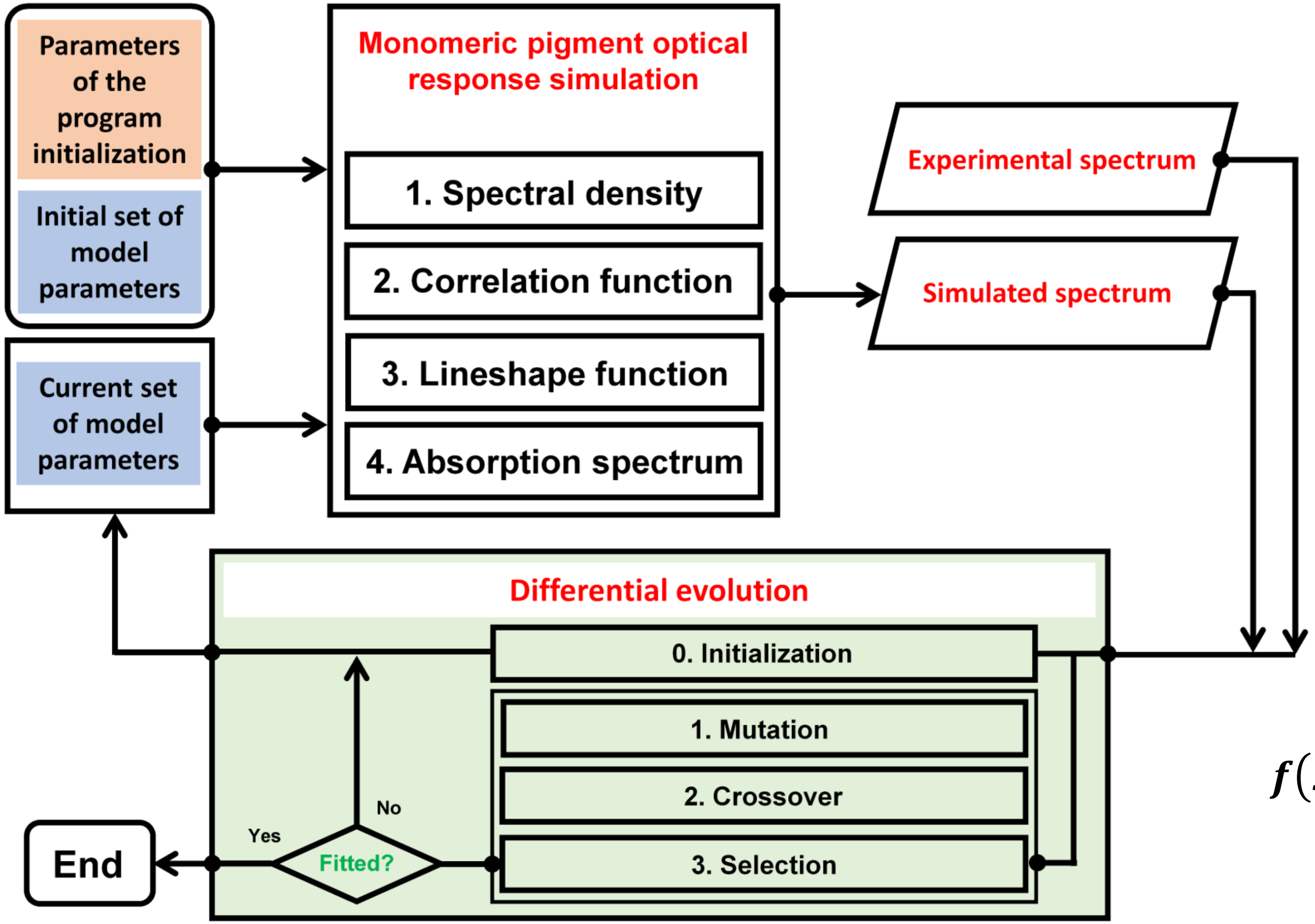

Lycopene ($C_{40}H_{56}$)
chloroform
ethanol
n-hexane
Absorption, norm.
Wavenumber ,cm^{-1}
×10^4

6


A
B
C
D
E
F
C(ω), cm^{-1}
ω, cm^{-1}
$\sigma_{abs}(\omega)$, norm.
Simulation
Experiment
×10^4

5

Differential Evolution algorithm



F – weighting factor (contribution of the difference of two random vectors)

Cr – *crossover probability (replacing the coordinate of the base vector with the coordinate of the mutant one)*

$G_0(\omega_n)$ - *the spectrum of the sum of Gaussians with an arbitrary set of parameters*

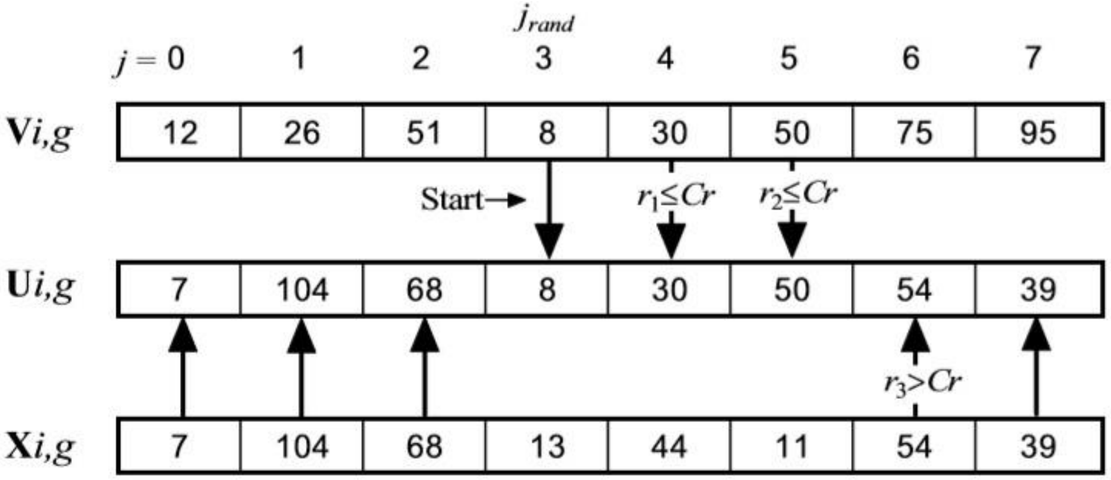
$G(\omega_n, x_i^g)$ - *the current result of modeling the desired spectrum*

$$f(x_i^g) = \frac{1}{N}\sum_{n=1}^{N}\left(G_0(\omega_n) - G(\omega_n, x_i^g)\right)^2$$

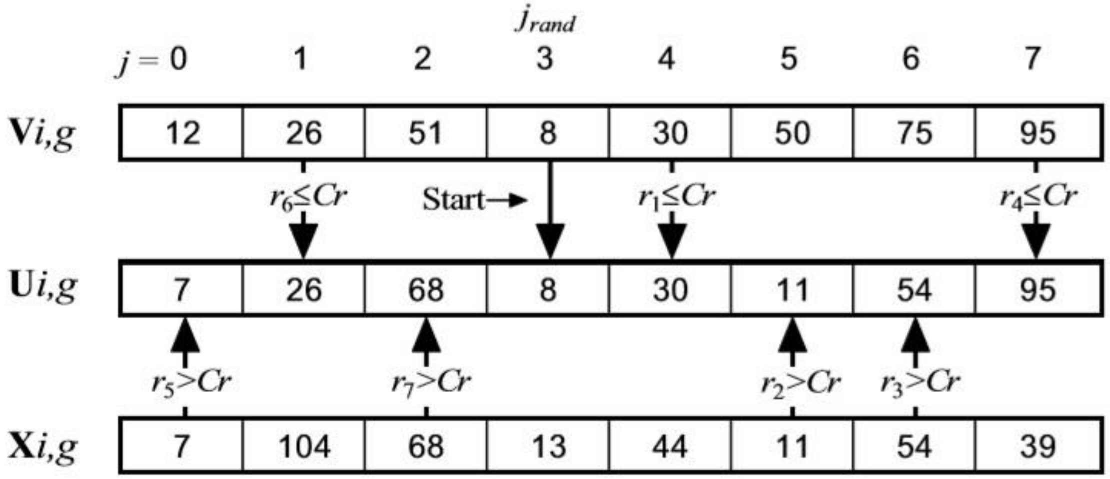
v_{ji}^{g} - the mutant vector; u_{ji}^{g} - trial vector; x_{ji}^{g} - the base vector.

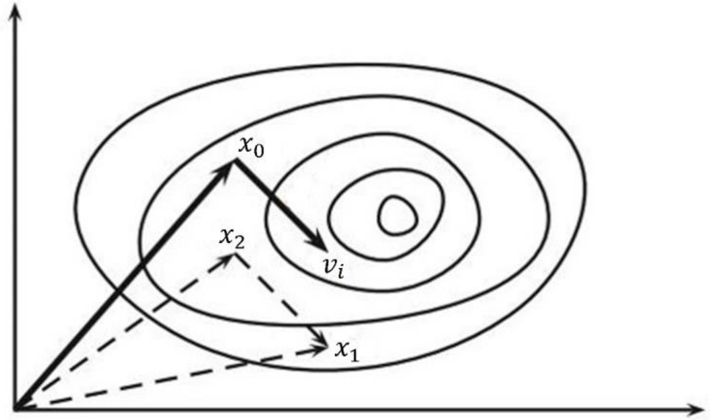
$$\left(rand_{ji}(0,1) \leq Cr\right)\ OR\ (j = j_{rand}) \longrightarrow u_{ji}^{g} = v_{ji}^{g}.$$

Exponential crossover



Binomial crossover





$$\mathbf{v}_i^g = \mathbf{x}_{best}^g + F\left(\mathbf{x}_{r1}^g - \mathbf{x}_{r2}^g\right)$$

$$\mathbf{v}_i^g = \mathbf{x}_{r0}^g + F\left(\mathbf{x}_{r1}^g - \mathbf{x}_{r2}^g\right)$$

$$\mathbf{v}_i^g = \mathbf{x}_{r0}^g + F\left(\mathbf{x}_{best}^g - \mathbf{x}_{r0}^g\right) + F\left(\mathbf{x}_{r1}^g - \mathbf{x}_{r2}^g\right)$$

$$\mathbf{v}_i^g = \mathbf{x}_{best}^g + F\left(\mathbf{x}_{r1}^g - \mathbf{x}_{r2}^g\right) + F\left(\mathbf{x}_{r3}^g - \mathbf{x}_{r4}^g\right)$$

$$\mathbf{v}_i^g = \mathbf{x}_{r0}^g + F\left(\mathbf{x}_{r1}^g - \mathbf{x}_{r2}^g\right) + F\left(\mathbf{x}_{r3}^g - \mathbf{x}_{r4}^g\right)$$

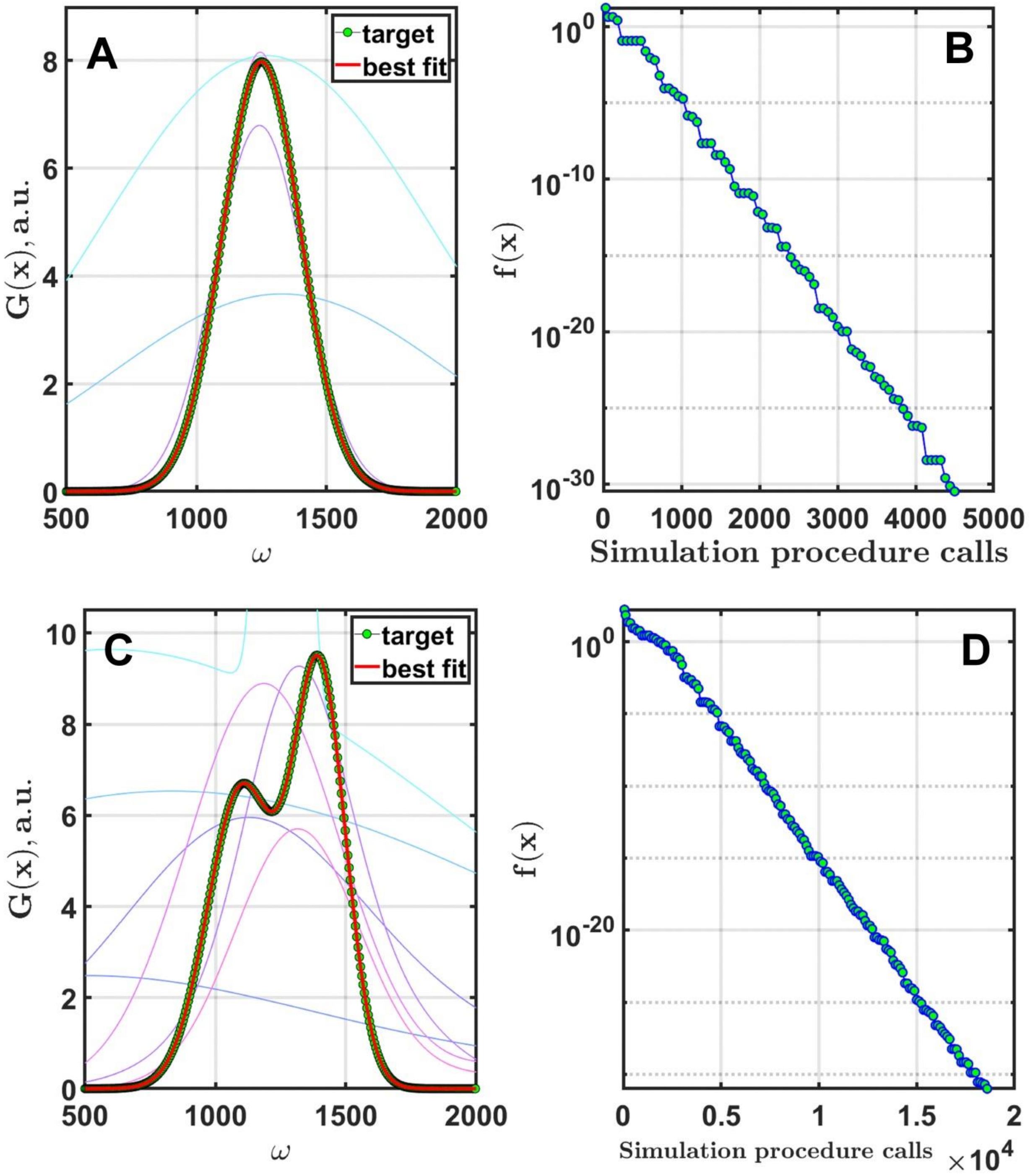


Figure 1. Fitting of two spectrum-like curves simulated with one (A) and two (C) Gaussian functions. Thin colored lines are the current best results for the first eight generations of optimization. The overall convergence dynamics are shown in (B) and (D).

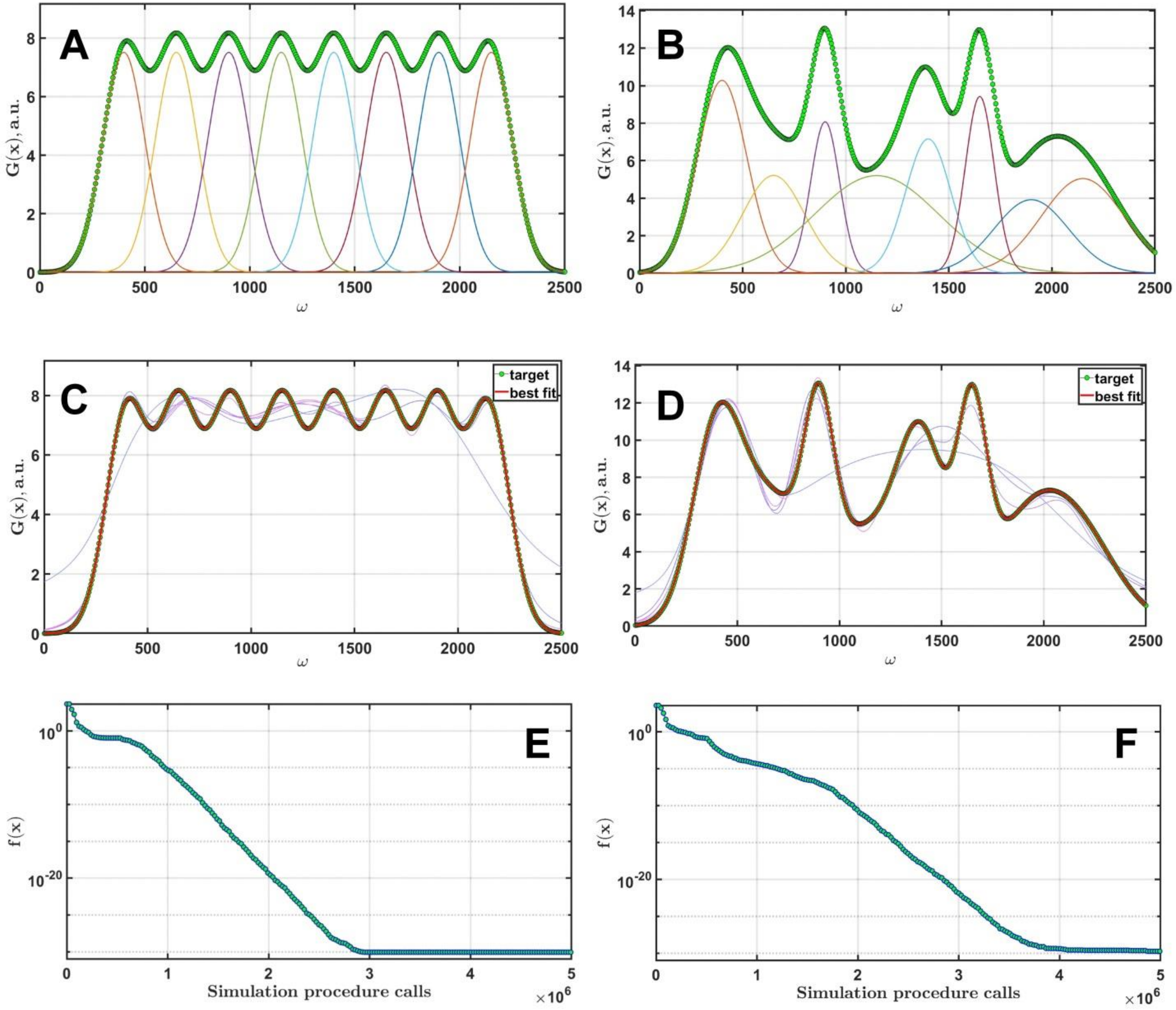


Figure 3. Fitting of a simulated spectrum-like curve consisting of 8 identical Gaussian functions (A) and a curve consisting of 8 Gaussians with different parameters for each function (B). The target curves are calculated using the same set of frequencies. The results of the successful fits are presented for both cases (C and D). Thin lines indicate the current best curves after immediately after beginning of the optimization. The convergence dynamics are presented in (E and F).

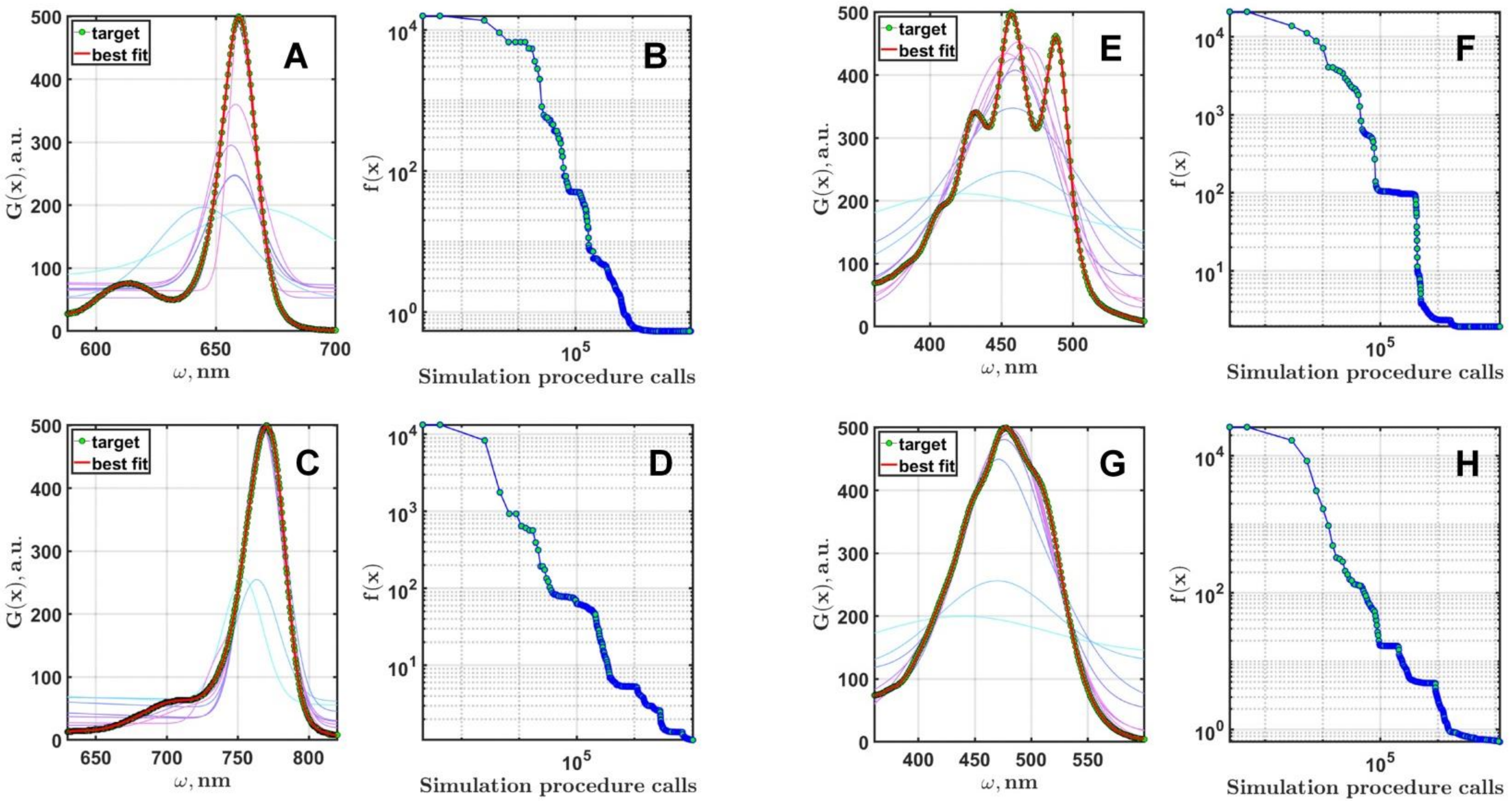
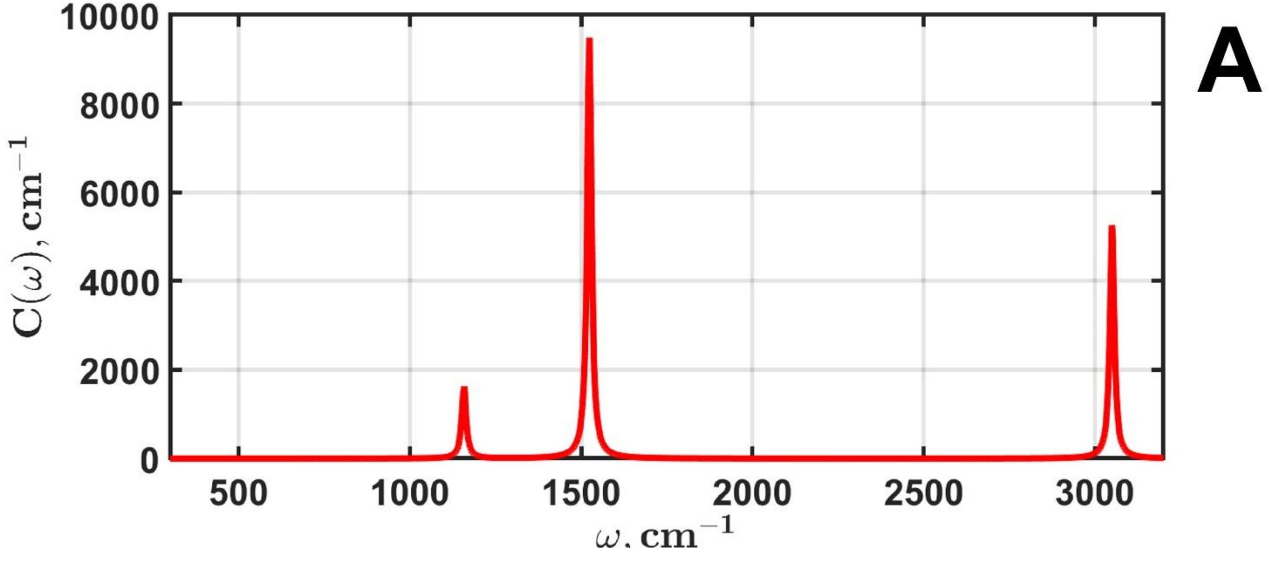


Figure 8. The results of the fitting for Chl *a* (A), BChl *a* (C), Spheroidene (E), and Spheroidenone (G). The thin lines indicate the best spectra after first seven generations of the optimization process. The corresponding convergence dynamics are shown in (B,D,F,H) on logarithmic scales.



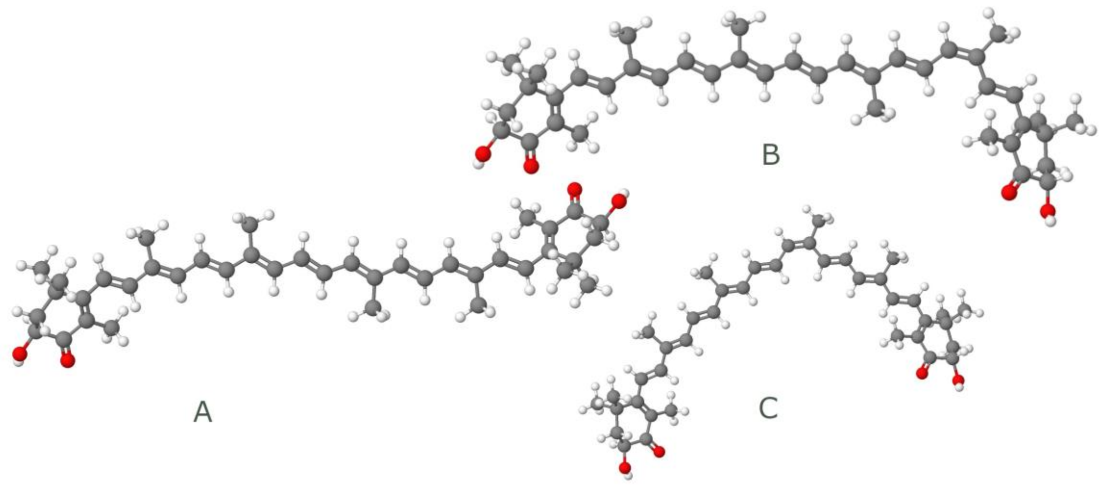


Рис. 1. Структурные формулы изомеров кантаксантина; *транс-* (A), *цис*-9 (B), *цис*-13 (C).

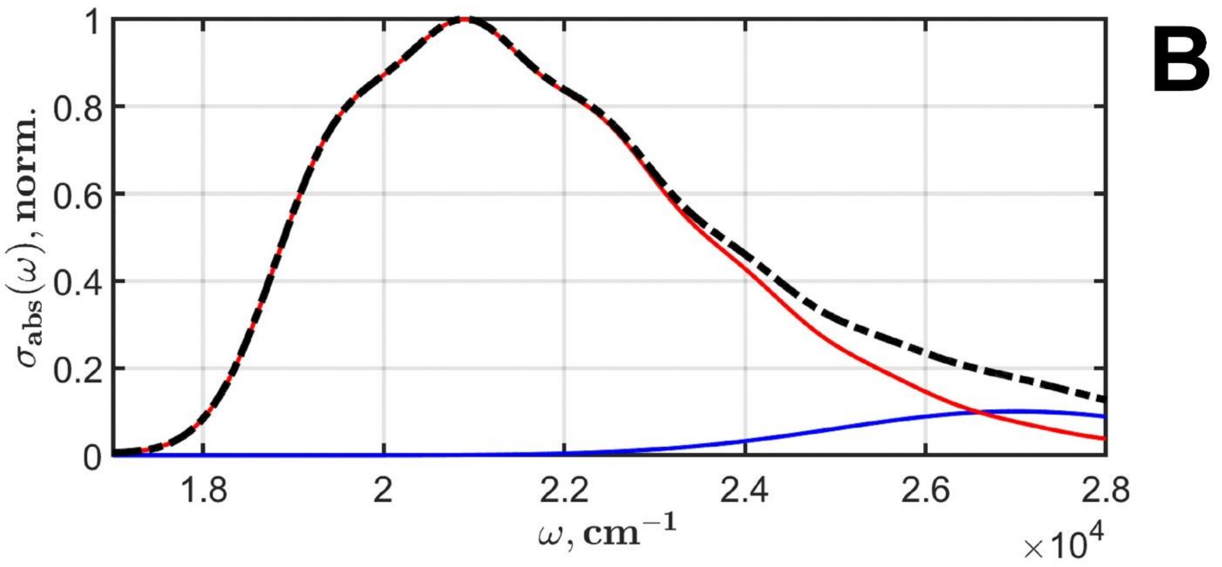
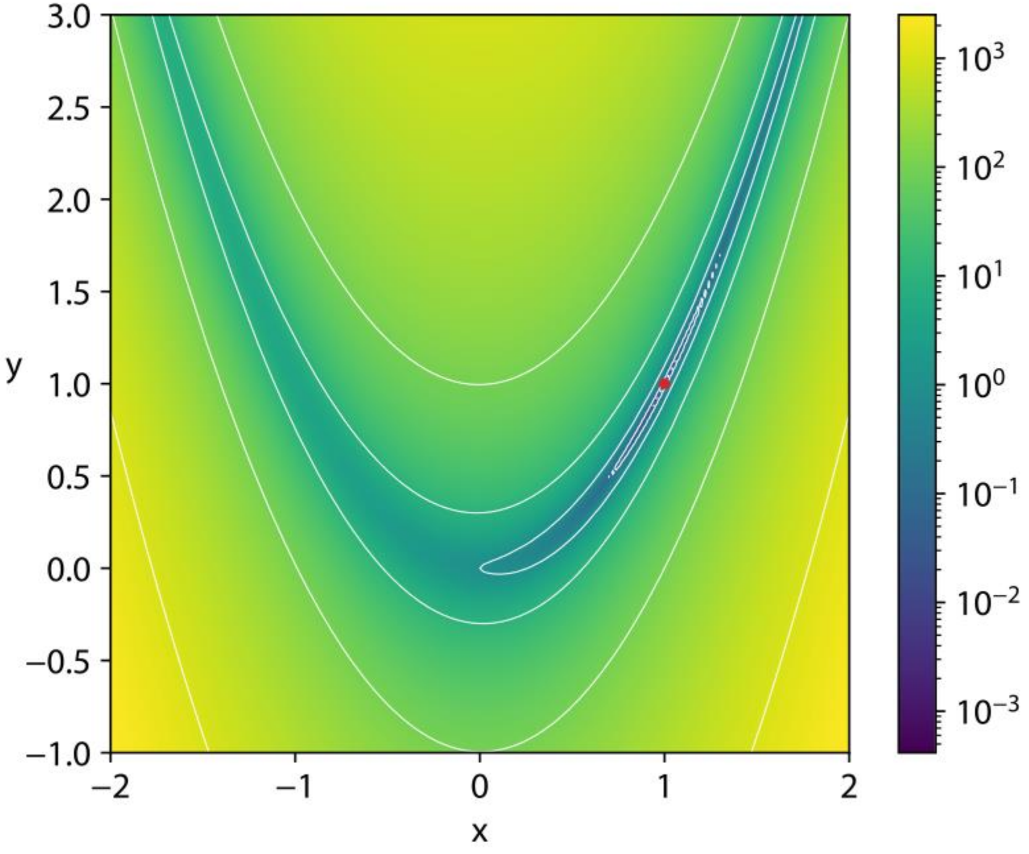
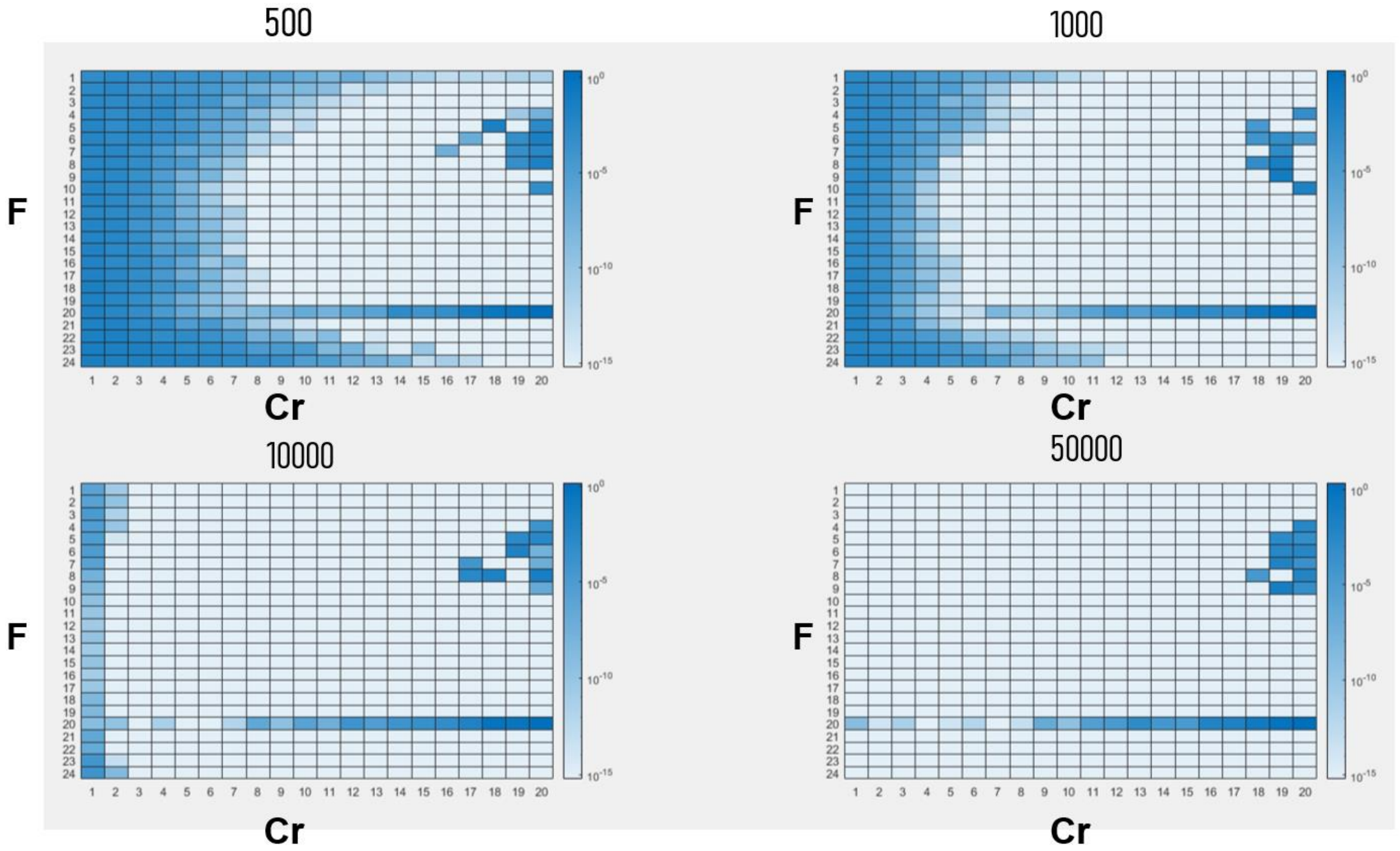


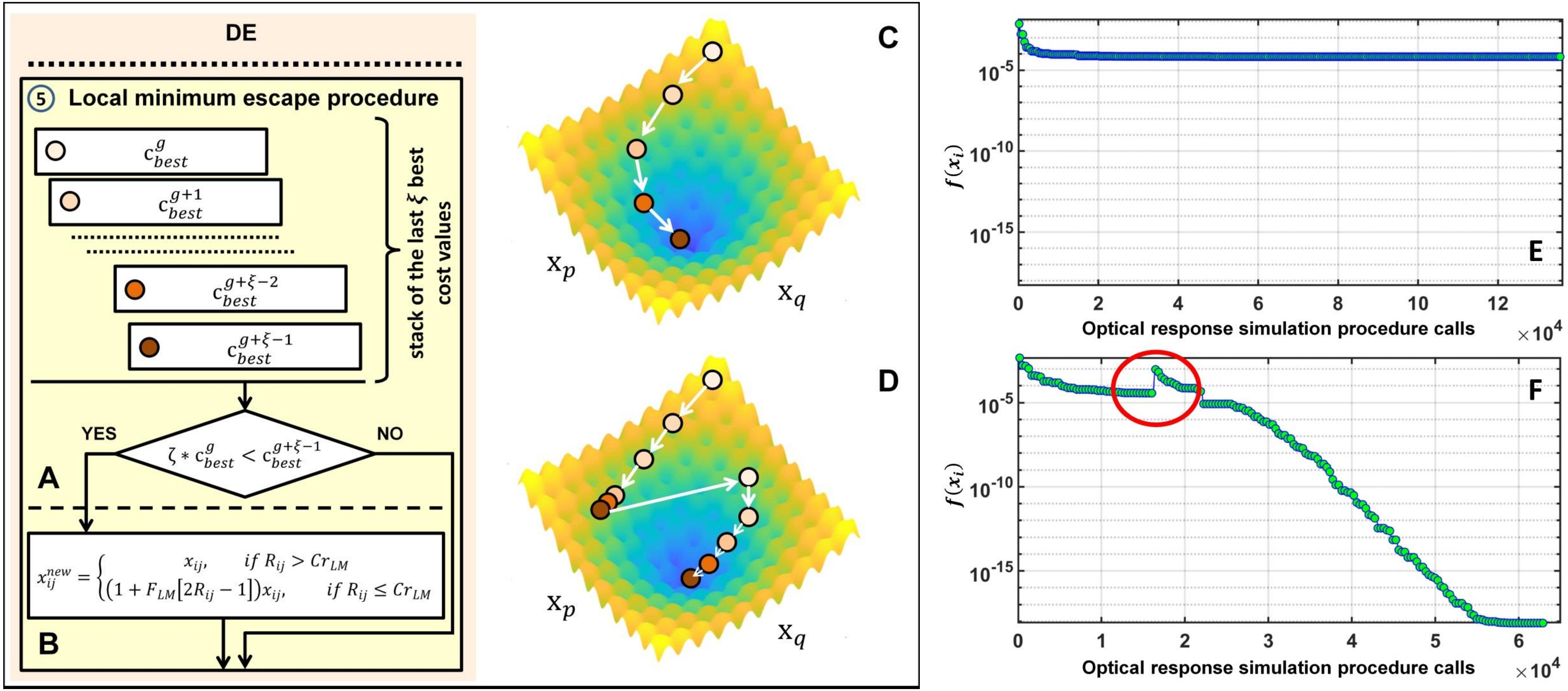
Рис. 2. Функция спектральной плотности, рассчитанная с учетом двух вибронных мод и одного обертона: $\nu_1 = 1524\ \mathrm{cm}^{-1}$, $\nu_2 = 1158\ \mathrm{cm}^{-1}$ и $2\nu_1 = 3048\ \mathrm{cm}^{-1}$ (A); смоделированный спектр поглощения каротиноида, соответствующий электронному переходу $|S_2\rangle \to |S_2\rangle$. Профиль поглощения представляет собой сумму вкладов *транс-* и *цис*-переходов (B).

Rosenbrock function

$$f(\boldsymbol{x}) = \sum_{i=1}^{n-1} \left[100\left(x_{i+1} - x_i^2\right)^2 + \left(1 - x_i\right)^2 \right]$$






DE
5 Local minimum escape procedure
c_{best}^{g}
c_{best}^{g+1}
$c_{best}^{g+\xi-2}$
$c_{best}^{g+\xi-1}$
stack of the last ξ best cost values
YES
NO
$\zeta * c_{best}^{g} < c_{best}^{g+\xi-1}$
A
$x_{ij}^{new} = \begin{cases} x_{ij}, & if\ R_{ij} > Cr_{LM} \\ (1 + F_{LM}[2R_{ij} - 1])x_{ij}, & if\ R_{ij} \le Cr_{LM} \end{cases}$
B
C
D
x_p
x_q
E
F
$f(x_i)$
Optical response simulation procedure calls
$\times 10^4$

$$f(x_i) = An + \sum_{i=1}^{n} \left[x_i^2 - A\cos(2\pi x_i) \right]$$

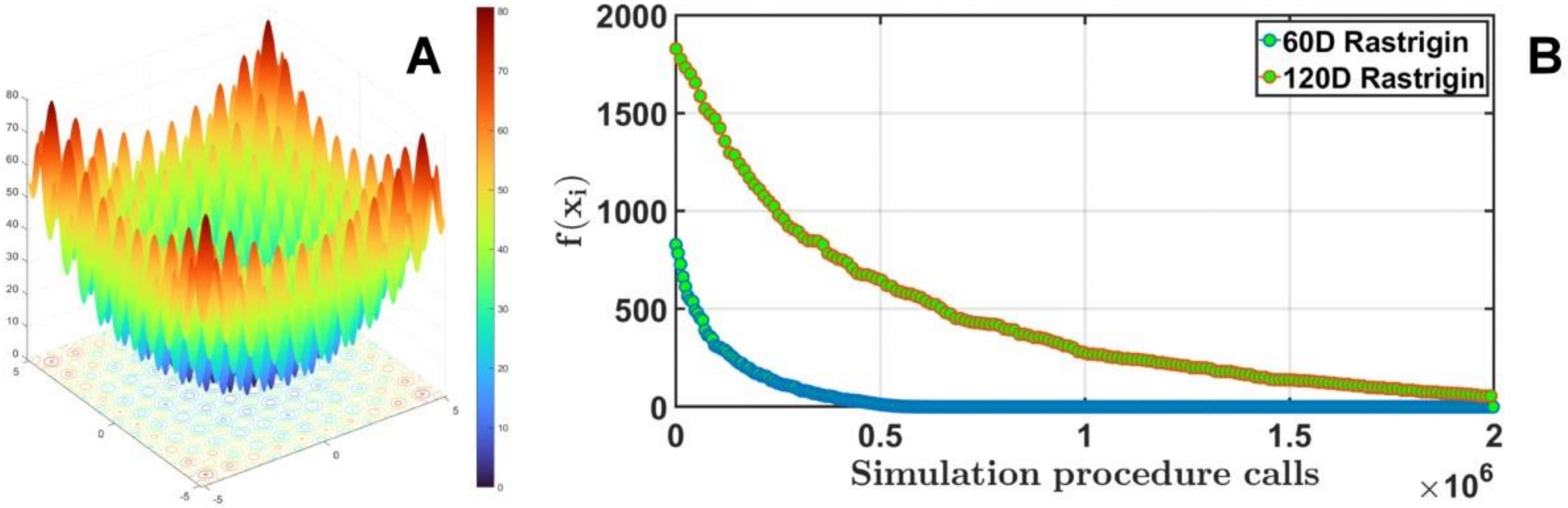


Fig. 1. 2D Rastrigin benchmark function (A). Evolution of 60D and 120D Rastrigin function (B).

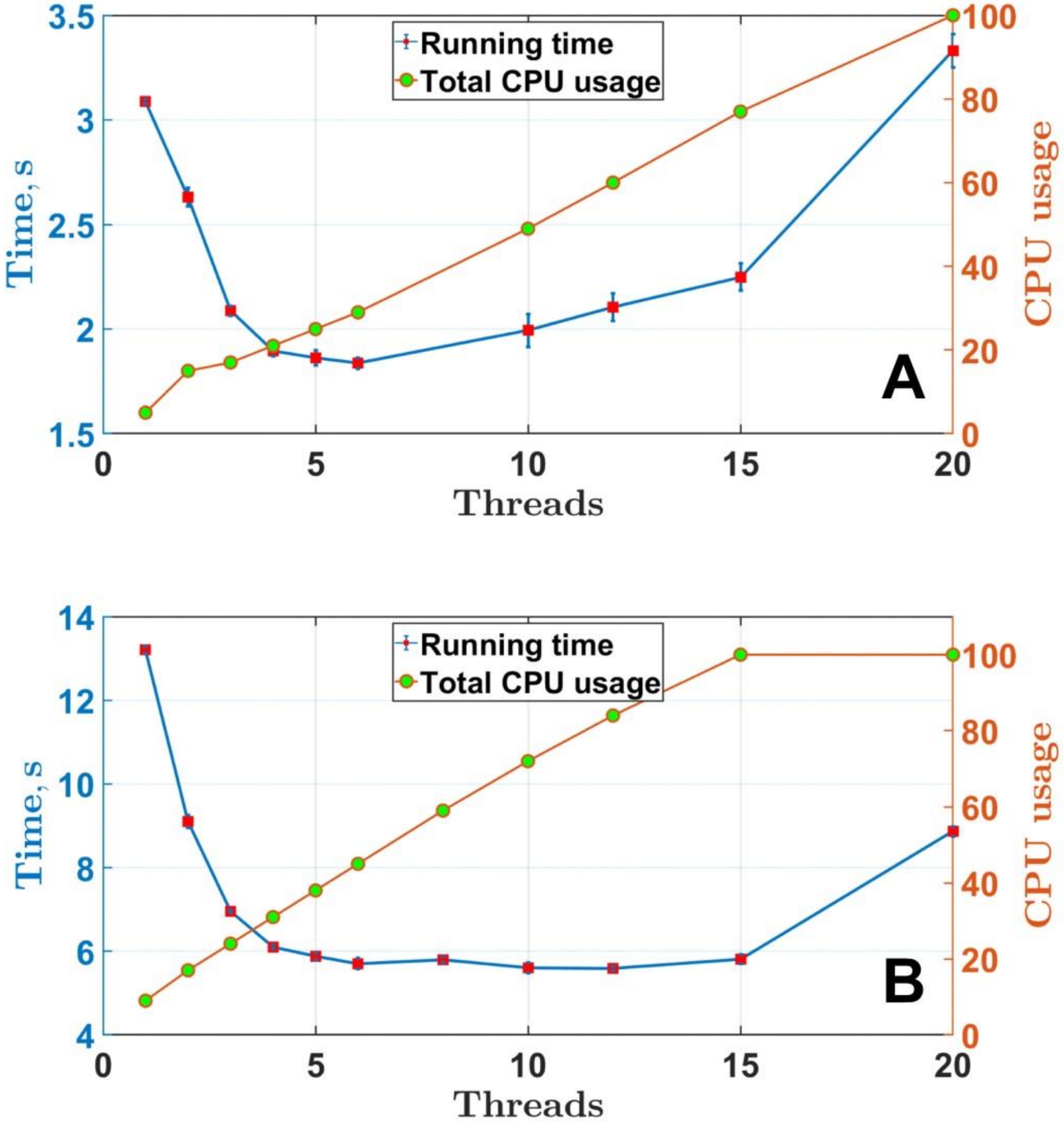


Fig. 2. Total execution time of the optimization program depending on the number of thread passed to mpiexec (blue line). The corresponding percentage of the CPU usage during optimization is shown by red line. The target functions are 60D (A) and 120D (B) Rastrigins.

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