

Supporting information for
Monitoring Molecular Vibronic Coherences in a
Bichromophoric Molecule by Ultrafast X-Ray
Spectroscopy

Daniel Keefer^{a,†}, Victor M. Freixas^{b,†}, Huajing Song^c, Sergei
Tretiak^c, Sebastian Fernandez-Alberti^b, and Shaul Mukamel^{a,*}

^aDepartments of Chemistry and Physics and Astronomy,
University of California, Irvine, California 92697-2025, USA

^bDepartamento de Ciencia y Tecnologia, Universidad Nacional de
Quilmes/CONICET, B1876BXD, Bernal, Argentina

^cTheoretical Division, Los Alamos National Laboratory, Los
Alamos, New Mexico 87545, United States

[†]These authors contributed equally

*E-Mail: smukamel@uci.edu, serg@lanl.gov

November 17, 2020

Computational details

The AIMC method is implemented within the non-adiabatic excited state molecular dynamics (NEXMD) framework [1, 2, 3]. It allows the simulation of the photoexcitation and subsequent non-adiabatic electronic and vibrational energy relaxation and redistribution in large multichromophoric conjugated molecules involving several coupled electronic excited states. Excited states energies [4, 5, 6], gradients [7, 8] and non-adiabatic couplings [9, 10, 11] are calculated *on-the-fly* at the configuration interaction singles (CIS) level of theory using the semiempirical Austin model 1 Hamiltonian [12] by means of the Collective Electronic Oscillator (CEO) approach [13, 14, 15]. More details concerning the NEXMD implementation and parameters can be found elsewhere [1, 2, 16].

Cloning events took place whenever the Ehrenfest approximation failed throughout these initial Ehrenfest simulations, leading to the correct outcome of the process. The additional computational cost is justified only if cloning events represent a significant contribution to the final accuracy of the results. Therefore, they must be restricted to situations in which certain cloning criteria are fulfilled. Following our previous works [1, 17], three cloning criteria were applied in order to identify situations in which the average Ehrenfest force loses its physical meaning due to events of wave function bifurcation after the nuclear wave function leaves the non-adiabatic coupling region. Therefore, at least two electronic excited states should be significantly populated with their corresponding adiabatic forces moving the nuclei in a bifurcated way. In order to limit the cloning events and avoid their exponential growth, a threshold for each cloning criterion is imposed [1]. The first criterion monitors the number of electronic excited states significantly populated during an Ehrenfest trajectory n by using the distribution width W_n (participation ratio) for the expansion of the electronic wave function in terms of adiabatic states ($|\varphi_n(t)\rangle = \sum_I a_I^n(t)|\phi_I^n(t)\rangle$) defined as:

$$W_n = \frac{1}{\sum_i^N |a_i^n|^4} . \quad (\text{S1})$$

W_n varies between 1 and N , the total number of electronic excited states considered. While $W_n \approx 1$ indicates a complete localization of $|\varphi_n(t)\rangle$ on a single $|\phi_I^n(t)\rangle$, $W_n \approx N$ indicates its spread among all $|\phi_I^n(t)\rangle$. Cloning events are limited to values of $W_n > \delta_1$. In the present work $N = 2$, therefore a value of $\delta_1 = 1.5$ is in between these two limits indicating that both states are significantly populated.

The second criterion monitors situations in which the average Ehrenfest force \mathbf{F}_M^n mismatches with the force \mathbf{F}_{max}^n that correspond to the most populated state by using the generalized angle between them, defined as:

$$\Theta_n = \arccos \left(\frac{2 \mathbf{F}_M^n \cdot \mathbf{F}_{max}^n}{|\mathbf{F}_M^n|^2 + |\mathbf{F}_{max}^n|^2} \right) . \quad (\text{S2})$$

Cloning events are limited to values of $\Theta_n > \delta_2$. In the present work, we have tested that a value $\delta_2 = 5^\circ$ results in an average of approximately seven cloning events per original Ehrenfest trajectory, guaranteeing a minimal statistical contribution of any subsequent cloning event to the full quantum wave function.

The third criterion limits cloning events to regions of phase space where the electronic states are not strongly coupled, limiting the rate of basis set

growth. Since it depends on the non adiabatic couplings, which can be very spiky, it has required an update in order to gain reproducibility respect to its previous formulation. However, this has no impact on the results since it only differentiates strong coupling and low coupling regimes, and differences between them are of several orders of magnitude.

The more cloning events we have the better the configuration space is mapped and, therefore, simulations become closer to the exact solution. The convergence of AIMC results has been tested against the different threshold values selected to limit the cloning events (unpublished results) and the robustness of the AIMC simulations has been confirmed. A new variation of the third criterion has been considered in the present work. Herein, we redefine it in order to restrict cloning events to situations in which:

$$\left| \frac{2\rho_I}{\rho_M} \cos(\theta_I - \theta_M) \dot{\mathbf{R}} \cdot \mathbf{d}_{IM} \right| \leq \delta_3, \quad (\text{S1})$$

where M represents the excited state with the higher population, ρ_I and θ_I are the modulus and phase corresponding to the electronic amplitude a_I , $\dot{\mathbf{R}}$ is the nuclear velocity in the center of the wave function and \mathbf{d}_{IM} is the non-adiabatic coupling between states I and M :

$$\mathbf{d}_{IM} = \langle \phi_I | \nabla_{\mathbf{R}} | \phi_M \rangle. \quad (\text{S2})$$

In this work we used a threshold value $\delta_3 = 0.005$ a.u.t.⁻¹. Besides, for each of the initial Ehrenfest simulations, a maximum of 16 cloning events were permitted. As a result, a total of 2718 cloning events were obtained.

AIMC is an extension of the Multi-configurational Ehrenfest method (MCE) [18] in which the molecular wave function is expanded in a basis of trajectory-guided Gaussian basis functions (TBF) as described in eq. 1 and 2. The nuclear parts $|x_n(t)\rangle$ are coherent states [19] given by Gaussian functions centered in the Ehrenfest trajectories with coordinates \mathbf{R}_n and momenta \mathbf{P}_n :

$$\begin{aligned} |\chi_n(\mathbf{R}, t)\rangle &= \\ &= \left(\frac{2\alpha}{\pi} \right)^{\frac{N_{dof}}{4}} \times \exp \left(-\alpha (\mathbf{R} - \mathbf{R}_n)^2 + \frac{i}{\hbar} \mathbf{P}_n (\mathbf{R} - \mathbf{R}_n) + \frac{i}{\hbar} \gamma_n(t) \right), \quad (\text{S3}) \end{aligned}$$

where N_{dof} is the number of nuclear degrees of freedom of the system, α is a width parameter and $\gamma_n(t)$ is a phase. According to previous works [20], α was set as 4.7 Bohr⁻² for hydrogen atoms, 22.7 Bohr⁻² for carbon atoms, 19.0 Bohr⁻² for nitrogen atoms, 12.2 Bohr⁻² for oxygen atoms and 7.4 Bohr⁻² for chlorine atoms. The Min-Cost algorithm was used to identify and track the state swaps due to trivial unavoided crossings as described in [21].

The expectation values of the energy splitting between two excited states K and L was approximated according to:

$$\begin{aligned} \Delta E_{KL} &= \frac{1}{2} \sum_{m,n} \left(E_K^{(m)} - E_L^{(m)} + E_K^{(n)} - E_L^{(n)} \right) \langle \chi_m | \chi_n \rangle \times \\ &\quad \sum_{I,J} \left(a_I^{(m)} \right)^* a_J^{(n)} \langle \phi_I^{(m)} | \phi_J^{(n)} \rangle, \quad (\text{S4}) \end{aligned}$$

where $E_K^{(m)}$ is the energy corresponding to the excited state K in configuration m and we have used the generalized zero-order bra-ket averaged Taylor expansion [22].

The expectation value of the kinetic energy along a specific direction \mathbf{e} was calculated according to:

$$K_{\mathbf{e}} \equiv \left\langle \Psi \left| -\frac{\hbar^2}{2} \mathbf{e} \cdot \nabla_{\mathbf{R}} M^{-1} \mathbf{e} \cdot \nabla_{\mathbf{R}} \right| \Psi \right\rangle, \quad (\text{S5})$$

where M here refers to the masses of the nuclei. This expression can be written as:

$$K_{\mathbf{e}} = -\frac{\hbar^2}{2} \sum_{m,n} M^{-1} \left[-\alpha + \alpha^2 (\mathbf{e} \cdot (\mathbf{R}_n - \mathbf{R}_m))^2 - \frac{1}{4\hbar^2} (\mathbf{e} \cdot (\mathbf{P}_n + \mathbf{P}_m))^2 \right] \times \langle \chi_m | \chi_n \rangle \sum_{I,J} \left(a_I^{(m)} \right)^* a_J^{(n)} \langle \phi_I^{(m)} | \phi_J^{(n)} \rangle. \quad (\text{S6})$$

In this work we used \mathbf{e} as the direction of the expectation value of the coupling between excited states S_1 and S_2 , which was approximated as:

$$\mathbf{d}_{KL} = \frac{1}{2} \sum_{m,n} \left(\mathbf{d}_{KL}^{(m)} + \mathbf{d}_{KL}^{(n)} \right) \langle \chi_m | \chi_n \rangle \times \sum_{I,J} \left(a_I^{(m)} \right)^* a_J^{(n)} \langle \phi_I^{(m)} | \phi_J^{(n)} \rangle, \quad (\text{S7})$$

where $\mathbf{d}_{KL}^{(m)}$ is the non-adiabatic coupling between excited states K and L and we have used the generalized zero-order bra-ket averaged Taylor expansion.

Finally, figure S1 shows the overlap between \mathbf{d}_{12} at 20 fs and the electronic normal modes corresponding to the excited state S_1 . Here we can see that the coupling overlaps with a bundle of ~ 5 high frequency vibrations with frequencies between the range of 1650-1880 cm^{-1} .

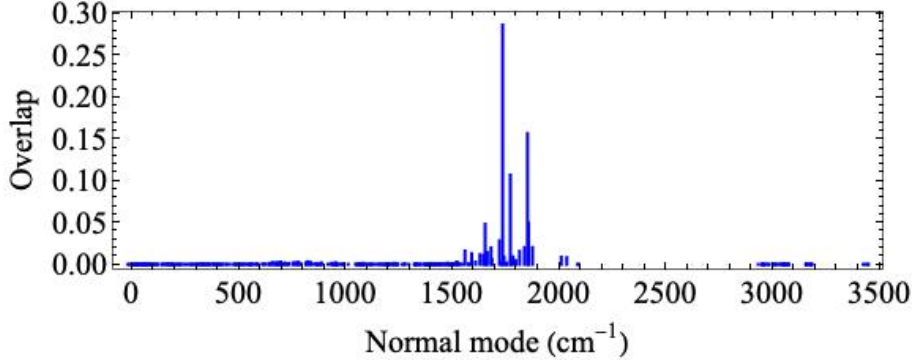


Figure S1: **Overlap** of \mathbf{d}_{12} and the electronic normal modes calculated at the minimum energy configuration of the excited state S_1 .

Trajectory Averaging

To calculate the signal of the trajectory ensemble (Fig. 3 in the main manuscript), first the signal in each individual trajectory was calculated according to equation (4) of the main manuscript. The average signal was then calculated by

summing over all of them with equal weights. This corresponds to an incoherent average over initial conditions, but including the overlaps between clones that belong to the same initial condition. In the present example, the relative phases of initial conditions was set to zero, where preliminary tests of randomly assigning them have shown no impact on the final result. Note that due to the high number (360) nuclear degrees of freedom, the nuclear overlaps between configurations belonging to different initial conditions, collected from a ground state conformational sampling at 300K, are negligible.

Additional Trajectories

Three additional trajectories are presented here that exhibit different features than the ones in the main text. This completes the overview over the trajectory ensemble, where all of them can be classified according one of the five presented examples.

A trajectory where multiple cloning events (9 in total) occur is shown in Fig. S2. Despite all the cloning events, meaning that the evolution in both electronic states is not well described by their mean field, the coherence and the signal is strong for the complete 500 fs.

Trajectory 4 (Fig. S3) exhibits a strong vibronic coherence throughout the dynamics. Population transfer occurs immediately, around 250 fs and after 400 fs. This corresponds to the times where the energy difference ΔE_{12} is close to zero, the coherence magnitude is highest, and the signal is strongest. The coherence is never lost, despite the trajectory passing strong coupling regions several times.

Fig. S4 depicts a trajectory where the strong initial coherence is lost after 150 fs. The coherence magnitude decays along with the signal, and ΔE_{12} never gets close to zero again. The loss of coherence happens despite the absence of cloning events in this trajectory.

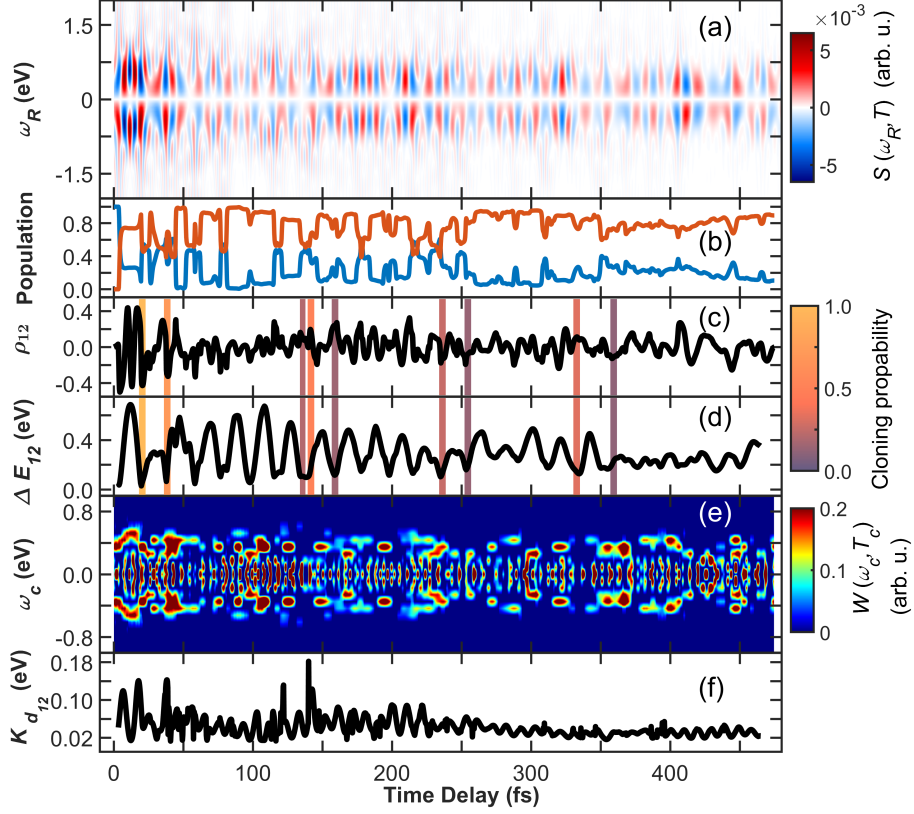


Figure S2: **Coherence in trajectory 5 of the heterodimer** simulated by the AIMC protocol. **(a)**: TRUECAR signal according to equation (4) in the main manuscript. **(b)**: Population in the S_2 and S_1 electronic states. **(c)**: Coherence ρ_{12} between the S_2 and S_1 state according to equation (3) in the main manuscript. **(d)**: Energy splitting between the two participating electronic states. **(e)**: Wigner spectrogram equation (5) in the main text, which is extracted from the TRUECAR signal in (a) by taking a temporal trace at $\omega_R = 0.4$ eV. **(f)**: Kinetic energy along the direction of the coupling.

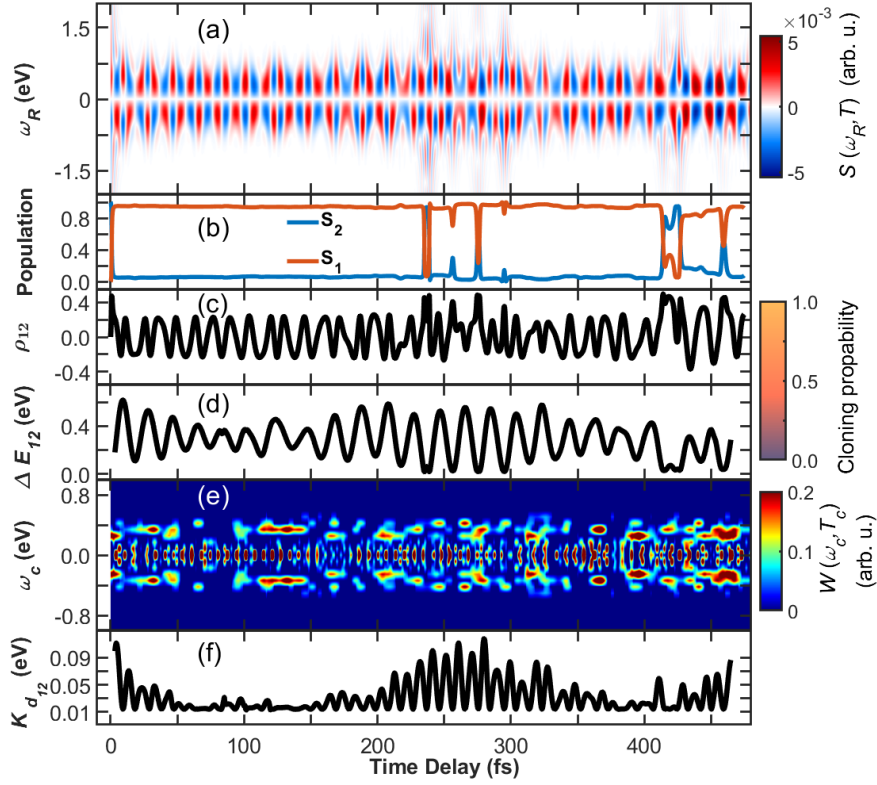


Figure S3: **Coherence in trajectory 3 of the heterodimer** simulated by the AIMC protocol. **(a)**: TRUECAR signal according to equation (4) in the main manuscript. **(b)**: Population in the S_2 and S_1 electronic states. **(c)**: Coherence ρ_{12} between the S_2 and S_1 state according to equation (3) in the main manuscript. **(d)**: Energy splitting between the two participating electronic states. **(e)**: Wigner spectrogram equation (5) in the main text, which is extracted from the TRUECAR signal in (a) by taking a temporal trace at $\omega_R = 0.32$ eV. **(f)**: Kinetic energy along the direction of the coupling.

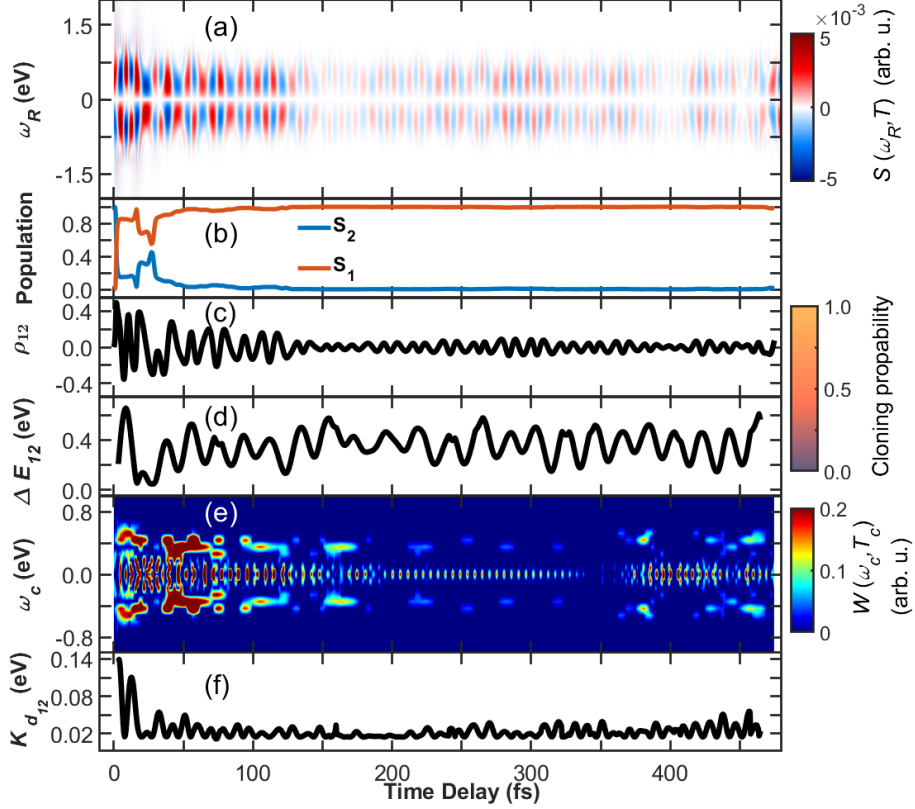


Figure S4: **Coherence in trajectory 4 of the heterodimer** simulated by the AIMC protocol. **(a)**: TRUECARs signal according to equation (4) in the main manuscript. **(b)**: Population in the S_2 and S_1 electronic states. **(c)**: Coherence ρ_{12} between the S_2 and S_1 state according to equation (3) in the main manuscript. **(d)**: Energy splitting between the two participating electronic states. **(e)**: Wigner spectrogram equation (5) in the main text, which is extracted from the TRUECARs signal in (a) by taking a temporal trace at $\omega_R = 0.49$ eV. **(f)**: Kinetic energy along the direction of the coupling.

References

- [1] Victor M Freixas, Sebastian Fernandez-Alberti, Dmitry V Makhov, Sergei Tretiak, and Dmitrii Shalashilin. An ab initio multiple cloning approach for the simulation of photoinduced dynamics in conjugated molecules. *Physical Chemistry Chemical Physics*, 20(26):17762–17772, 2018.
- [2] Tammie R Nelson, Alexander J White, Josiah A Bjorgaard, Andrew E Sifain, Yu Zhang, Benjamin Nebgen, Sebastian Fernandez-Alberti, Dmitry Mozyrsky, Adrian E Roitberg, and Sergei Tretiak. Non-adiabatic excited-state molecular dynamics: Theory and applications for modeling photo-physics in extended molecular materials. *Chemical Reviews*, 120(4):2215–2287, 2020.
- [3] Walter Malone, Benjamin Nebgen, Alexander White, Yu Zhang, Huajing Song, Josiah A Bjorgaard, Andrew E Sifain, Beatriz Rodriguez-Hernandez, Victor Manuel Freixas, Sebastian Fernandez-Alberti, et al. Nexmd software package for non-adiabatic excited state molecular dynamics simulations. *Journal of Chemical Theory and Computation*, 2020.
- [4] Sergei Tretiak and Shaul Mukamel. Density matrix analysis and simulation of electronic excitations in conjugated and aggregated molecules. *Chemical reviews*, 102(9):3171–3212, 2002.
- [5] Vladimir Chernyak, Michael F Schulz, Shaul Mukamel, Sergei Tretiak, and Eugene V Tsiper. Krylov-space algorithms for time-dependent hartree–fock and density functional computations. *The Journal of Chemical Physics*, 113(1):36–43, 2000.
- [6] Sergei Tretiak, Christine M Isborn, Anders MN Niklasson, and Matt Challa-combe. Representation independent algorithms for molecular response calculations in time-dependent self-consistent field theories. *The Journal of chemical physics*, 130(5):054111, 2009.
- [7] Filipp Furche and Reinhart Ahlrichs. Adiabatic time-dependent density functional methods for excited state properties. *The Journal of chemical physics*, 117(16):7433–7447, 2002.
- [8] S Tretiak and V Chernyak. Resonant nonlinear polarizabilities in the time-dependent density functional theory. *The Journal of chemical physics*, 119(17):8809–8823, 2003.
- [9] Matteo Tommasini, V Chernyak, and S Mukamel. Electronic density-matrix algorithm for nonadiabatic couplings in molecular dynamics simulations. *International Journal of Quantum Chemistry*, 85(4-5):225–238, 2001.
- [10] Vladimir Chernyak and Shaul Mukamel. Density-matrix representation of nonadiabatic couplings in time-dependent density functional (tddft) theories. *The Journal of Chemical Physics*, 112(8):3572–3579, 2000.
- [11] Robert Send and Filipp Furche. First-order nonadiabatic couplings from time-dependent hybrid density functional response theory: Consistent

- formalism, implementation, and performance. *The Journal of chemical physics*, 132(4):044107, 2010.
- [12] Michael JS Dewar, Eve G Zoebisch, Eamonn F Healy, and James JP Stewart. Development and use of quantum mechanical molecular models. 76. am1: a new general purpose quantum mechanical molecular model. *Journal of the American Chemical Society*, 107(13):3902–3909, 1985.
- [13] Shaul Mukamel, Sergei Tretiak, Thomas Wagersreiter, and Vladimir Chernyak. Electronic coherence and collective optical excitations of conjugated molecules. *Science*, 277(5327):781–787, 1997.
- [14] Sergei Tretiak, Vladimir Chernyak, and Shaul Mukamel. Recursive density-matrix-spectral-moment algorithm for molecular nonlinear polarizabilities. *The Journal of chemical physics*, 105(19):8914–8928, 1996.
- [15] Sergei Tretiak, Wei Min Zhang, Vladimir Chernyak, and Shaul Mukamel. Excitonic couplings and electronic coherence in bridged naphthalene dimers. *Proceedings of the National Academy of Sciences*, 96(23):13003–13008, 1999.
- [16] VM Freixas, Sergei Tretiak, Dmitry V Makhov, Dmitrii V Shalashilin, and Sebastian Fernandez-Alberti. Vibronic quantum beating between electronic excited states in a heterodimer. *The Journal of Physical Chemistry B*, 124(19):3992–4001, 2020.
- [17] Victor M Freixas, Daneilis Ondarse-Alvarez, Sergei Tretiak, Dmitry V Makhov, Dmitry V Shalashilin, and Sebastian Fernandez-Alberti. Photoinduced non-adiabatic energy transfer pathways in dendrimer building blocks. *The Journal of chemical physics*, 150(12):124301, 2019.
- [18] Dmitry V Makhov, Christopher Symonds, Sebastian Fernandez-Alberti, and Dmitrii V Shalashilin. Ab initio quantum direct dynamics simulations of ultrafast photochemistry with multiconfigurational ehrenfest approach. *Chemical Physics*, 493:200–218, 2017.
- [19] Dmitrii V Shalashilin and Mark S Child. The phase space ccs approach to quantum and semiclassical molecular dynamics for high-dimensional systems. *Chemical physics*, 304(1-2):103–120, 2004.
- [20] Alexis L Thompson, Chutintorn Punwong, and Todd J Martínez. Optimization of width parameters for quantum dynamics with frozen gaussian basis sets. *Chemical Physics*, 370(1-3):70–77, 2010.
- [21] Sebastian Fernandez-Alberti, Adrian E Roitberg, Tammie Nelson, and Sergei Tretiak. Identification of unavoided crossings in nonadiabatic photoexcited dynamics involving multiple electronic states in polyatomic conjugated molecules. *The Journal of chemical physics*, 137(1):014512, 2012.
- [22] Dmitry V Makhov, William J Glover, Todd J Martinez, and Dmitrii V Shalashilin. Ab initio multiple cloning algorithm for quantum nonadiabatic molecular dynamics. *The Journal of chemical physics*, 141(5):054110, 2014.