Ab initio simulation of laser-induced electronic and vibrational coherence

Jannis Krumland,¹ Matheus Jacobs,¹ and Caterina Cocchi¹,²,†

¹Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
²Institute of Physics, Carl von Ossietzky Universität Oldenburg, 26129 Oldenburg, Germany

(Dated: December 22, 2021)

We introduce an efficient quantum-seciemiclasmal method based on time-dependent density-functional theory (TDDFT) for the parameter-free simulation of laser-induced electronic and vibrational coherences in condensed matter and their subsequent decay on the femtosecond timescale. With the example of (extended) carbon-conjugated molecules, we show that an ensemble-averaging approach with initial configurations taken from a nuclear quantum distribution remedies many of the shortcomings of the quantum-classical combination of real-time TDDFT and Ehrenfest molecular dynamics, naturally introducing a damping of electronic coherence and ultrafast non-adiabatic coupling between excited states. The number of required simulations decreases with the size and rigidity of the investigated compounds so that computational costs remain moderate even for large systems for which the mean-field approach shines. This work paves the way towards first-principles simulations of coherent nonlinear spectroscopy without empirical parameters, as an independent counterpart to corresponding experimental results.

Advances in experimental techniques based on nonlinear spectroscopy have enabled tracking ultrafast coupled electronic-vibrational motion in real time on its natural timescale [1–5], triggering interest in complementary time-resolved simulations from first principles [6]. Within a growing variety of approaches to non-adiabatic ab initio molecular dynamics [7], mean-field techniques [8] remain appealing thanks to their excellent numerical scalability. Among them, the Ehrenfest scheme – the classical-nuclei limit of the time-dependent self-consistent field approximation [9] – is particularly attractive as it can be straightforwardly coupled to real-time time-dependent density functional theory (RT-TDDFT), whereby the quantum-mechanical electronic subsystem explicitly evolves in time, also granting access to well-resolved electron dynamics. Notably, in the last decade, the RT-TDDFT+Ehrenfest approach has been successfully employed to rationalize charge-transfer dynamics in sizeable complexes [10–14].

The direct time propagation of the electronic subsystem in the framework of RT-TDDFT makes straightforward the explicit inclusion of an exciting laser field in the simulation, elevating the targeted system to a non-stationary excited state. Thus, all electronically coherent features arising from the system not being in an eigenstate of its Hamiltonian are naturally captured, including linear-response polarization, as well as quantum interferences between different excited states. However, in this context, there are some problems associated with the classical limit taken for the nuclei in the single-trajectory RT-TDDFT+Ehrenfest (STE) scheme. Laser-initiated electron dynamics remain overly coherent when the nuclei have always well-defined positions and momenta. Moreover, the neglect of zero-point energy (ZPE) is hard to justify in organic systems, in which it is much higher than thermal energy due to the low mass of the constituent atoms. Initial nuclear configurations taken from adiabatic classical molecular dynamics simulations or a Boltzmann distribution function thus grossly underestimate fluctuations in nuclear positions and momenta. By mapping nuclear wavefunctions into phase space with a Wigner transform [15], it is possible to directly compare the magnitudes of thermal and quantum-mechanical fluctuations showing that ZPE alone roughly corresponds to a classical temperature of about 900K in organic compounds [16].

In this letter, we show the potential of the multi-trajectory RT-TDDFT+Ehrenfest (MTE) approach with random initial configurations from quantum distributions for the ab initio simulation of creation and subsequent decay of electronic and vibrational coherence by laser irradiation. We contrast the results obtained for prototypical organic molecules, such as benzene and coronene, against corresponding single-trajectory simulations and ensemble-averaged calculations with fixed nuclei. This comparison highlights the role of nuclear motion, which redistributes oscillator strength in the optical absorption spectra through non-adiabatic couplings between excited states. These processes are particularly evident when considering nonlinear response. The population dynamics are mainly encoded in the second order, and corresponding simulations resemble established methods of simulating non-adiabatic dynamics, but naturally feature also transient contributions related to coherences between excited states. Finally, we consider the nuclear motion triggered by electronic excitations, demonstrating the ability of the proposed approach to simulate wavepacket motion, which follows an almost classical time evolution for fully symmetric modes, while becoming non-trivial for the less symmetric ones.

MTE simulations are initialized by generating a set of nuclear coordinates and momenta by sampling a zero-temperature Wigner distribution for the normal modes of the molecules, thus accounting for ZPE (see Supple-
mentary Material, Sec. S1). For every configuration, a STE calculation is performed, sub jceting the molecule to a laser pulse with a system-specific carrier frequency marking the center of the frequency band. A weak pulse is chosen to avoid problems with the adiabatic approximation to the dynamical exchange-correlation potential, which works best if the electronic system remains close to the ground state \([17,18]\).

A central quantity in this analysis is the ensemble-averaged electronic dipole moment, creating a macroscopic polarization in extended samples, which, in turn, gives rise to an emitted electric field. Furthermore, oscillations of the induced dipole moment are an indicator of (electronic) coherence. In benzene, where the linear absorption spectrum \([19]\) is reproduced remarkably well by the employed adiabatic local-density approximation \([20]\), a laser pulse in resonance with the strong \(1^1E_{1u} \leftrightarrow 1^1A_{1g}\) excitation at 6.9 eV causes merely short-lived dipole oscillations [Fig. 1b], upper panel]: A monoexponential fit to the decaying envelope yields a dephasing time, \(T_{01}\), of only 2.5 fs. The first-order density matrix after the pulse, which gives rise to the induced dipole moment, is, in this case,

\[
\hat{\rho}^{(1)}(t) \sim \exp(i\omega_{01} t - t/T_{01})|0\rangle\langle 1|,
\]

where \(|0\rangle\) and \(|1\rangle\) represent the \(1^1A_{1g}\) and \(1^1E_{1u}\) states with energies \(E_0\) and \(E_1\), respectively, and \(\omega_{01} = (E_1 - E_0)/\hbar\). In contrast to the exponential decay, no damping is observed in the single-trajectory case (grey curve), corresponding to an expression of \(\hat{\rho}^{(1)}(t)\) identical to Eq. (1) except for the missing decaying part in the exponential.

The fast damping of the induced dipole moment in benzene results from the small size of this molecule and its correspondingly high flexibility and excitation energy. In larger and more rigid conjugated molecules like coronene [Fig. 1b], inset], the decay is slower, occurring over tens of femtoseconds [Fig. 1b, center panel]. Here, the laser carrier frequency is set to 3.7 eV [Fig. 1b], dashed red curve], close to the absorption onset of the molecule. An initial transient polarization during laser irradiation produces a maximum of the envelope at 8 fs; this is a dispersive rather than absorptive feature, associated with the real part of the polarizability. Furthermore, a beating pattern can be spotted on the tail end of the curve, which is absent in the STE simulation (faint curve). On a technical note, we highlight that the dipole moment statistically converges much faster for coronene than for benzene (see Sec. S4 and Fig. S5), i.e., fewer trajectories are required for the former, likely owing to its bigger size and larger rigidity. Symmetry is another important aspect to consider: Both benzene and coronene belong to the \(D_{6h}\) point group and thus are highly symmetric. As a consequence, neither of them showcases the common experimental scenario of molecules or molecular ensembles with few or even no symmetries. In this case, much less selection rules are in effect \([21,22]\), leading to richer vibronic dynamics involving a manifold of bright electronic states and coupled vibrational modes. As an example, we note that only 2 out of the 30 vibrational modes in benzene are totally symmetric \([23]\) and, therefore, allowed to couple to electronic excitations within the Franck-Condon (FC) approximation. In a molecule without symmetries, such constraints are absent.

In light of these considerations, we study the dynamics in a less symmetric conjugated molecule, which we obtain by isoelectronically replacing one CH group on the edge of coronene by an N atom [Fig. 1b], inset]. The carrier frequency of the laser is set to 3.9 eV, slightly above the absorption onset [Fig. 1b], dashed blue curve]. Already in the single-trajectory dynamics, we notice a persistent beating pattern in the induced dipole moment [Fig. 1b], bottom panel]. This is a fingerprint of the large number of optically active states participating in the dynamics, which still predominantly take place within the linear regime, resulting from a density matrix of the form

\[
\hat{\rho}^{(1)}(t) \sim \sum_{m=1}^{M} \rho_{0m} \exp(i\omega_{0m} t)|0\rangle\langle m|,
\]

involving a total of \(M\) excited states within the frequency band of the laser. The coefficients \(\rho_{0m}\) depend on the coupling strength between the electric field and the \(|0\rangle \rightarrow |m\rangle\) transition. As for coronene, the ensemble-averaged dipole decays over time, supplying the exponents in Eq. (2) with a real-valued part, \(i\omega_{0m}t - i\omega_{0m}t - t/T_{0m}\). From the induced dipole moments, we are able to calculate within a limited frequency band the optical absorption spectrum (Sec. S1), for which related nuclear-ensemble-based methods were already employed in the past \([24,26]\). The match of theoretical and experimental linewidths found in previous work validates our simulated real-time dynamics, as these widths are closely related to the decay of polarization.

In the spectrum of pristine coronene, the so-called \(β\)-band \([24]\), corresponding to the bright \(1^1E_{1u} \leftrightarrow 1^1A_{1g}\) excitation, exhibits some structure at the low-energy end as well as a shoulder at the high-energy side [Fig. 1b]], in agreement with experimental results \([28,29]\). Comparing to linear-response calculations of the molecule in equilibrium (Fig. S1), the peak is red-shifted as a sign of FC-type vibronic coupling, corresponding to a nonvanishing curvature in the FC region (i.e., the vertical projection of the ground-state distribution onto the excited-state surfaces). The finite oscillator strength at 3.1 eV is a consequence of Herzberg-Teller (HT) vibronic coupling. Like the bright \(1^1E_{1u} \leftrightarrow 1^1A_{1g}\) excitation, the \(1^1B_{2u} \leftrightarrow 1^1A_{1g}\) one, corresponding to the so-called \(α\)-band, arises from transitions between the doubly degenerate highest occupied and lowest unoccupied molecular orbitals. However, it is strictly forbidden in the FC approximation as the two equivalent configurations involving degenerate frontier orbitals are superposed destructively. However, symmetry-breaking fluctuations of the nuclear positions due to ZPE give rise to a non-zero transition dipole moment: the excitation borrows intensity from the \(1^1E_{1u} \leftrightarrow 1^1A_{1g}\) one, which is made possible
Compared to the pristine counterpart, the N-doped coronene absorbs less in the considered energy window. The main peak has a more pronounced tail at the high-energy end, which can be traced back to optical activation of previously dark states, a consequence of the substitution-related lowering of symmetry (Fig. S1). The $p$-band is no longer visible, but this is likely due to negligible laser power in the corresponding spectral region. Instead, some additional dark states at 3.3 eV come into play, drawing some intensity from the main absorption band. As the laser is not centered on the peak, the induced dipolar oscillations are rather weak [Fig. 1a]). This, in turn, leads to a higher number of trajectories required for the statistical convergence of the dipole moment (Fig. S5); the higher amount of bright states and FC-coupled vibrational modes can play a role in this regard, too.

We performed additional calculations with the same nuclear ensemble, but keeping the atoms fixed, which is closely related to the snapshot-based nuclear-ensemble approach [24, 25]. The analysis of these results allows us to assess the role of nuclear momentum in the coupled dynamics. We highlight two differences in the resulting spectra [Fig. 1b]), blue vs. turquoise curves: (i) The main absorption features are smeared out when the nuclear motion is enabled; when it is disabled, peaks are more defined. Such details in the spectra arise from the long-term time evolution, which in this case is damped by the nuclear motion. (ii) Considering the dominant peak at 3.5 eV [Fig. 1b]), the nuclear motion leads to a redistribution of oscillator strength from higher to lower energy. In the time domain, this is reflected in stronger mid-term dipolar oscillations (40-60 fs time window, not shown). We attribute both phenomena – mid-term increase and long-term decrease of dipolar oscillations due to nuclear motion – to non-adiabatic coupling: Population is transferred from weakly bright states at 3.8 eV to the strongly bright ones at 3.6 eV, and finally to the dark states below the absorption onset. Such processes are mediated by nuclear momentum and thus missing in static-nuclei calculations.

The populations of many-body states are not directly accessible in the adopted approach, but indications can be inferred from the time-resolved fluorescence, which we calculate from the dipole moment by performing short-time Fourier transforms of the individual dipole moments (Sec. S1) [30]. The ensemble-averaged result remains constant after some initial temporary polarization during laser irradiation, if nuclei are frozen [Fig. 2a), top panel]; no population is transferred to other states, as anticipated. By enabling nuclear motion, other frequency components are mixed in over time at the expense of the optically targeted state, mainly resulting from an energetically lower state at 2.7 eV (lower panel). However, also higher states participate: Those close to 6 eV have
FIG. 2. a) Time- and frequency-resolved dipole moment. The white dashed lines indicate the spectral range of the laser. b) Slow components of the dipole moment, resolved in $x$ and $y$ directions (dashed and solid lines, respectively), defined according to the axis in the left inset. The grey bar marks the interval of laser irradiation. The right inset schematically illustrates the occurring time evolution, involving two excited states with different dipole moments.

particularly large oscillator strengths and thus fluoresce notably, despite their population being rather low.

The phenomena considered up to this point are related to coherences between ground state and excited states, which are accessible within the linear regime. The excited-state dynamics are mainly contained in the second-order response. We are concerned with excited-state populations and coherences,

$$\hat{\rho}^{(2)}(t) \sim \rho_{mn} \exp(i\omega_{mn}t)|m\rangle\langle n|,\quad (3)$$

where $|m\rangle$ and $|n\rangle$ are both excited states. The coherences ($m \neq n$) tend to have oscillation periods $\omega_{mn}$ similar to those of interatomic vibrations and have been conjectured to play a key role in energy transport in certain photosynthetic complexes [31–36]. The second-order response additionally contains second-harmonic and Raman terms, both involving the ground state. All of these superposed processes can be partially separated by means of phase-cycling [37] or low-pass filtering (Sec. S3), exploiting the fact that second-harmonic processes (as well as linear ones) entail a distinctively fast time evolution.

We investigate the excited-state dynamics occurring in N-substituted coronene after excitation with a pulse centered at 3.9 eV. Due to the lack of inversion invariance in the system, the second-order contributions tend to be dipolar in character, which is not possible in centrosymmetric systems such as pristine coronene. Thus, in the N-substituted molecule we find a non-zero second-order dipole after laser irradiation [blue curves in Fig. 2b)]. For a brief period after the excitation, coherence between excited states is maintained, as evident in the initial dip, corresponding to a single oscillation cycle. Afterwards, this evolution is taken over by an incoherent buildup of dipole moment on a timescale of about 100 fs, associated with the population transfer between states. Unsurprisingly, this effect is absent in the fixed-nuclei simulations [turquoise curves in Fig. 2b)]. The final dipole moment after 100 fs differs significantly in the two scenarios in terms of magnitude and orientation (Fig. 2b), right inset): with enabled nuclear dynamics, it points towards the N atom, indicating an electron transfer to its site after excitation of the delocalized $\pi$-conjugated network.

The dipole moment does not always reflect the excited-state dynamics as unambiguously as in this case. In general, one can resort to other observables directly related to the electron density, such as partial charges or higher multipole moments. Compared to other methods for computing non-adiabatic dynamics, the focus is shifted away from potential-energy surfaces (PES) towards a real-space representation based on the charge density. Further conclusions can be drawn from direct simulations of third-order spectroscopy, which is fairly straightforward with RT-TDDFT or related real-time methods [38–42].

Finally, we analyze vibrational coherence established by the electronic excitation. This corresponds to the harmonic wavepacket motion after an instantaneous elevation to a harmonic excited-state PES and is characterized by an essentially classical time evolution [43]. Thus, such motion does not need to be viewed necessarily as arising...
from quantum interference, even though the term “coherence” tends to invoke such associations \[44\]. In the following, we consider benzene as an example. As mentioned above, this molecule only has two totally symmetric modes that can couple to electronic excitations within the FC approximation. One of them is the breathing mode around 1600 cm\(^{-1}\), while the other one is a C-H stretching mode, which, however, is not stimulated effectively by the \(\pi - \pi^*\) transition at 6.9 eV. In STE, which yields only FC-type dynamics, the nuclear motion is thus induced predominantly in the breathing mode. For MTE, we visualize the induced nuclear density (Fig. 3), which is the probability distribution of the nuclei relative to the ground state (Sec. S1). For the breathing mode (upper panel), we find an approximately harmonic time evolution. At the maxima, there are adjacent regions of density accumulation and depletion, reflecting a wavepacket having left the FC region of the excited-state surface, while minima mark instances of return. The corresponding classical trajectory is given by the superposed sine function (dashed line). We note that due to its mean-field nature, MTE does not include wavepacket splitting, but rather describes dynamics through a single, averaged nuclear wavepacket. However, these different descriptions appear similarly in the nuclear density if a ground-state reference is subtracted, as done here.

In MTE, modes without the complete symmetry of the structure gain energy too, like the C=C stretching mode around 1600 cm\(^{-1}\), which transforms as \(e_2g\). Vibrations of this symmetry activate otherwise dark \(\Pi^1 \leftrightarrow 1^1A_1g\) excitations through HT-type coupling \[45\]. This type of post-FC effect can be seen as a fin-gerprint of electron-nuclear correlation, as it requires a \(Q\)-dependent transition dipole moment and thus parametrically \(Q\)-dependent electronic wavefunctions, with \(Q\) being normal-mode coordinates (Sec. S1). In this case, the intuitive picture of a Gaussian wavepacket prepared on an excited-state PES is invalid, and the observed nuclear dynamics are qualitatively different (Fig. 3 lower panel). Particularly, perfect overlap between the wavepacket and the “hole” left behind in the ground state is never recovered. There is a stationary redistribution of nuclear density from the center to the outskirts of the oscillator, plus a superposed harmonic oscillation, which is damped over time. Notably, such a time evolution cannot be accurately represented by a single trajectory and thus, does not fit into the picture of essentially classical wavepacket motion.

In summary, we have presented the combination of RT-TDDFT+Ehrenfest and quantum sampling of initial conditions as a tool for \(ab\ initio\) simulations of laser-induced ultrafast coherent dynamics applied to molecular systems. This efficient approach naturally includes electronic dephasing effects without empirical parameters and is capable of describing transitions between close-lying excited states. Furthermore, it can be employed to determine the laser-induced nuclear dynamics such as coherent wavepacket motion of Franck-Condon-coupled vibrational modes, or non-classical nuclear dynamics associated with purely Herzberg-Teller-active excitations. While the considered molecules are medium-sized, the computational efficiency and scalability of RT-TDDFT+Ehrenfest allow for the application to much more extended systems. Indeed, MTE in itself can yield rather poor results for small molecules, most likely because ground- and excited state surfaces often differ quite substantially therein \[46\]. We assume the validity of the proposed scheme to increase with system size for several reasons: (i) Duschinsky rotations and vibrational frequency shifts tend to be much smaller; (ii) a revival of electronic coherence due to the wavepacket returning to the FC region – which MTE does not seem to capture properly – becomes unlikely, as the overlap has to occur simultaneously among an increasing amount of FC-coupled vibrational modes \[47\]; (iii) the excitation-induced perturbation of the electron density becomes smaller in relation to the total density, enhancing the validity of the adiabatic approximation assumed for the dynamical exchange-correlation potential.

In future work, we aim to couple the proposed approach to \(ab\ initio\) simulations of nonlinear spectroscopies \[41, 48, 49\]. The statistical aspect naturally leads towards machine learning techniques \[50, 51\], which possibly can be exploited to further reduce computational costs, pushing the size limit of the modelled systems and helping to save power and to enhance efficiency. Further methodological progress can be possibly made by introducing coupling between trajectories during the time evolution, through which wavepacket splitting can be included \[52, 54\].
We are thankful to Dr. Michele Guerrini, Katherine R. Herperger, and Dr. Mariana Rossi for fruitful discussions, and to Dr. Ralph Ernstorfer for posing the question that stimulated this research. This work was funded by the German Research Foundation (DFG), project number 182087777 – CRC 951, by the German Federal Ministry of Education and Research (Forschungseinrichtungen Programm III), and by the State of Lower Saxony (Forschungen für Niedersachsen). Computational resources were provided by the North-German Supercomputing Alliance (HLRN), project bep0076.

[1] S. Mukamel, Multidimensional femtosecond correlation spectroscopies of electronic and vibrational excitations, Annu. Rev. Phys. Chem. 51, 691 (2000).
[2] D. M. Jonas, Two-dimensional femtosecond spectroscopy, Annu. Rev. Phys. Chem. 54, 425 (2003).
[3] M. Cho, Coherent two-dimensional optical spectroscopy, Chem. Rev. 108, 1331 (2008) pMID: 18363410, https://doi.org/10.1021/cr078377b.
[4] P. Hamm and M. Zanni, Concepts and Methods of 2D Infrared Spectroscopy (Cambridge University Press, 2011).
[5] E. Collini, 2d electronic spectroscopic techniques for quantum technology applications, J. Phys. Chem. C 125, 13096 (2021), https://doi.org/10.1021/acs.jpcc.0c06293.
[6] I. Conti, G. Cerullo, A. Nenov, and M. Garavelli, Ultrafast spectroscopy of photovoltaic molecular systems from first principles: Where we stand today and where we are going, J. Am. Chem. Soc. 142, 16117 (2020).
[7] B. F. E. Curchod and T. J. Martínez, Ab initio nonadiabatic quantum molecular dynamics, Chem. Rev. 118, 3305 (2018) pMID: 29465231, https://doi.org/10.1021/acs.chemrev.7b00423.
[8] J. C. Tully, Mixed quantum–classical dynamics, Faraday Discuss. 110, 407 (1998).
[9] E. J. Heller, Time dependent variational approach to semiclassical dynamics, J. Chem. Phys. 64, 63 (1976), https://doi.org/10.1063/1.431911.
[10] C. Andrea Rozzi, S. Maria Falke, N. Spallanzani, A. Ru-bio, E. Molinari, D. Brida, M. Mairi, G. Cerullo, H. Schramm, J. Christoffers, and C. Lienau, Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system, Nature Commun. 4, 1602 (2013).
[11] S. M. Falke, C. A. Rozzi, D. Brida, M. Mairi, M. Amato, E. Sommer, A. D. Sio, A. Rubio, G. Cerullo, E. Molinari, and C. Lienau, Coherent ultrafast charge transfer in an organic photovoltaic blend, Science 344, 1001 (2014).
[12] C. A. Rozzi, F. Troiani, and I. Tavernelli, Quantum modeling of ultrafast photoinduced charge separation, J. Phys.: Condens. Matter. 30, 013002 (2017).
[13] J. Zhang, H. Hong, C. Lian, W. Ma, X. Xu, X. Zhou, H. Fu, K. Liu, and S. Meng, Interlayer-state-coupling dependent ultrafast charge transfer in mos2/ws2 bilayers, Adv. Sci. 4, 1700086 (2017).
[14] M. Jacobs, J. Krumland, A. M. Valencia, H. Wang, M. Rossi, and C. Cocchi, Ultrafast charge transfer and vibronic coupling in a laser-excited hybrid inorganic/organic interface, Adv. Phys.: X 5, 1749883 (2020) https://doi.org/10.1080/23746149.2020.1749883.
[15] E. Wigner, On the quantum correction for thermodynamic equilibrium, Phys. Rev. 40, 749 (1932).
[16] M. Barbatti and K. Sen, Effects of different initial condition samplings on photodynamics and spectrum of pyrrole, Int. J. Quantum Chem. 116, 762 (2016).
[17] L. Lacombe and N. T. Maitra, Developing new and understanding old approximations in tddft, Faraday Discuss. 224, 382 (2020).
[18] L. Lacombe and N. T. Maitra, Minimizing the time-dependent density functional error in ehrenfest dynamics, J. Phys. Chem. Lett. 12, 8554 (2021) pMID: 34464148, https://doi.org/10.1021/acs.jpclett.1c02020.
[19] E. Koch and A. Otto, Optical absorption of benzene vapour for photon energies from 6 ev to 35 ev, Chem. Phys. Lett. 12, 476 (1972).
[20] K. Yabana and G. F. Bertsch, Time-dependent local-density approximation in real time: Application to conjugated molecules, Int. J. Quantum Chem. 75 (1999).
[21] D. C. Harris and M. D. Bertolucci, Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy (Courier Corporation, 1989).
[22] C. Cocchi, D. Prezzi, A. Ruini, M. J. Caltas, and E. Molinari, Anisotropy and size effects on the optical spectra of polycyclic aromatic hydrocarbons, J. Phys. Chem. A 118, 6507 (2014) pMID: 24984100, https://doi.org/10.1021/jp503054j.
[23] E. B. Wilson, The normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule, Phys. Rev. 45, 706 (1934).
[24] M. Barbatti, J. A. A. Aquino, and H. Lischka, The uv absorption of nucleobases: semi-classical ab initio spectra simulations, Phys. Chem. Chem. Phys. 12, 4959 (2010).
[25] R. Crespo-Otero and M. Barbatti, Spectrum simulation and decomposition with nuclear ensemble: formal derivation and application to benzene, furan and 2-phenylfuran, Theo. Chem. Accounts 131, 1237 (2012).
[26] K. Lively, G. Albareda, S. A. Sato, A. Kelly, and A. Rubio, Simulating vibronic spectra without born-oppenheimer surfaces, J. Phys. Chem. Lett. 12, 3074 (2021) pMID: 33750137, https://doi.org/10.1021/acs.jpclett.1c00073.
[27] J. M. Hollas, Polyyclic Hydrocarbons (Springer, Berlin, 1964).
[28] K. Ohno, T. Kajiwara, and H. Inokuchi, Vibrational analysis of electronic transition bands of coronene, Bull. Chem. Soc. Jpn. 45, 996 (1972) https://doi.org/10.1246/bcsj.45.996.
[29] F. Cataldo, O. Ursini, G. Angelini, and S. Iglesias-Groth, On the way to graphene: The bottom-up approach to very large pahs using the scholl reaction, Fuller. Nanotub 19, 713 (2011) https://doi.org/10.1016/j.nanotube.2010.494787.
[30] G. U. Kuda-Singappulige, A. Wildman, D. B. Lingerfelt, X. Li, and C. M. Aikens, Ultrafast nonradiative decay of a dipolar plasmon-like state in naphthalene, J. Phys. Chem. A 124, 9729 (2020) pMID: 33181013, https://doi.org/10.1021/acs.jpca.0c09564.
[31] T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E.
