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# Ultrafast coherent photoexcited dynamics in a trimeric dendrimer probed by X-ray stimulated-Raman signals†

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The photoinduced ultrafast coherent inter-chromophore energy redistribution in a triarylamine trimer is explored using nonadiabatic excited state molecular dynamics followed by simulations of X-ray Raman signals. The nitrogen centered system ensures strong interchromophore interactions and, thus, the presence of coherences. Nevertheless, the multitude of non-deterministic photoinduced pathways during the ultrafast inter-branch migration of the excitation results in random confinement on some branches and, therefore, spatial exciton scrambling and loss of phase information at long times. We show that the vibronic coherence dynamics evolving into the incoherent scrambling mechanism on ultrafast 50 fs timescale, is accurately probed by the TRUECARs X-ray stimulated Raman signal. In combination with previous results, where the technique has revealed long-lived coherences in a rigid heterodimer, the signal is most valuable for detecting ultrafast molecular coherences or their absence. We demonstrate that X-ray Raman spectroscopy is a useful tool in the chemical design of functional molecular building blocks.

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## Introduction

Dendrimers are highly branched multichromophoric conjugated macromolecules with well-defined structural arrangements.<sup>1–3</sup> Their highly polarizable and spatially extended  $\pi$ -electron manifold controls their highly tunable photoexcited dynamics and potential applications. The efficiency of light harvesting and subsequent electronic and vibrational (vibronic) energy redistribution depends on the type of their constituent chromophore units, their structural organization in the connected branches, symmetry, and the energy funneling through different nonradiative relaxation channels.<sup>4</sup>

The energy transfer between dendritic branches can involve coherent<sup>5</sup> or incoherent<sup>6</sup> hopping mechanisms. While coherent processes involve in-phase evolution of spatially delocalized electronic wavefunctions, incoherent hopping-like mechanisms ultimately lead to a random exciton self-trapping and spatial scrambling on different units.<sup>7–12</sup> The competition between

these two processes reflects the relative strengths of electronic couplings and thermal fluctuations.

Coherences can have either pure electronic or vibronic origin.<sup>13,14</sup> Electronic coherences are evaluated through the calculation of the pure dephasing time,<sup>15,16</sup> *i.e.*, the dephasing of the off-diagonal elements of the density matrix involving a mechanism which erodes the phase relationship between states without changing their population. On the other hand, vibronic coherences require the calculation of the full quantum wavefunction of electrons and nuclei as well as the corresponding nonadiabatic couplings between states.<sup>14</sup> Often, vibronic dynamics funnel the energy transfer through specific vibrational modes that modulate the wavelike localized – delocalized motion of the electronic wavefunction.<sup>11</sup> That is, the nonequilibrium dynamics of such selected excited vibrations is observed as ultrafast beatings of electronic populations.<sup>17–24</sup>

The choice of the dendrimer's branching unit allows a direct control of the inter-branch interactions and, therefore, the coherence between branches. This has significant effects on its spectroscopic properties. Nitrogen-centered dendrimers have been shown to induce stronger interactions and electronic delocalizations compared to benzene-centered ones.<sup>5,10,25</sup> The fast decay observed in ultrafast fluorescence anisotropy measurements performed on a triarylamine trimer supports the fact that coherence processes must be taken into account.<sup>25</sup> The photoexcitation and subsequent electronic and vibrational energy redistribution in large conjugated dendrimers involve dynamics in coupled excited states and multiple events like

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transient localization and delocalization of the wavefunction, coherent and incoherent inter-chromophore energy transfers, exciton self-trapping and internal conversion processes.<sup>26</sup> Such dynamics imply the passages through conical intersections that require quantum methods beyond Born–Oppenheimer approximation.<sup>27,28</sup>

Understanding coherence in dendrimers is a crucial challenge toward utilization of underpinning physical process for tailored chemical design. Over the past decade, sophisticated 2D electronic spectroscopy techniques<sup>29,30</sup> have been developed to provide time-resolved signatures of coherences.<sup>31</sup> More recently, X-ray free electron laser (XFEL) beam sources that offered unprecedented spatial, temporal and spectral resolutions,<sup>32</sup> making them novel probes of ultrafast chemical dynamics.<sup>33,34</sup> Pioneering experimental probes such as stimulated Raman transitions between electronic states<sup>35</sup> or (time-resolved) X-ray scattering-based measurements<sup>36,37</sup> have been demonstrated.

The theoretical design of new signals, and the prediction of their capabilities on molecular systems with distinct dynamics, is an important step in ultrafast X-ray sciences due to the extremely high cost and difficulty of the corresponding experiments. One promising signal that has been put forward recently, is the Transient Redistribution of Ultrafast Electronic Coherences in Attosecond Raman Signals (TRUECARS).<sup>38,39</sup> It uses a hybrid broadband + narrowband off-resonant X-ray probe field at delay time  $\tau$  after the pump pulse that initiates a stimulated Raman process between two electronic states. The hybrid field – requiring precise phase control between the two pulses – can alternatively be substituted by a single stochastic XFEL pulse in a covariance-based measurement.<sup>40</sup> In either case, the signal is free from the usually dominating population dynamics and is finite only when there is a nuclear wavepacket overlap between electronic states. At short times, these coherences can be unique signatures of passages through conical intersections, since they are created due to wavepacket bifurcation. The signal is also a good indicator of whether the coherences survive multiple nonadiabatic passages, or whether they are destroyed by decoherence processes. We have previously simulated TRUECARS for the photoinduced dynamics in a rigid heterodimer, demonstrating that the signal can adequately monitor the experimentally observed long-living coherence surviving multiple conical intersection passages for several hundred femtoseconds at room temperature.<sup>41</sup>

In the present study, we perform excited state nonadiabatic molecular dynamics simulations of the triarylamine trimer depicted in Fig. 1a using the *ab initio* multiple cloning approach (AIMC).<sup>42,43</sup> The three equivalent branches of the dendrimer are connected by a nitrogen center that enhances the interaction and delocalization between states. According to previous ultrafast fluorescence anisotropy measurements, its fast decay cannot be reproduced using the Förster energy transfer model and coherences must be taken into account.<sup>25</sup> This implies using sophisticated computational techniques that consider transient strong coupling regimes and wavefunction delocalizations. Using information from AIMC calculations, we then simulate the non-linear X-ray TRUECARS signal to monitor the

interplay between coherent and incoherent inter-chromophore energy redistribution regimes. Due to the fast energy exchange between the three branches, it is expected that coherences only persist during a few tens of femtoseconds, making this dendrimer an ideal system to test the capacity of AIMC and the TRUECARS signal to monitor coherences.

## Results

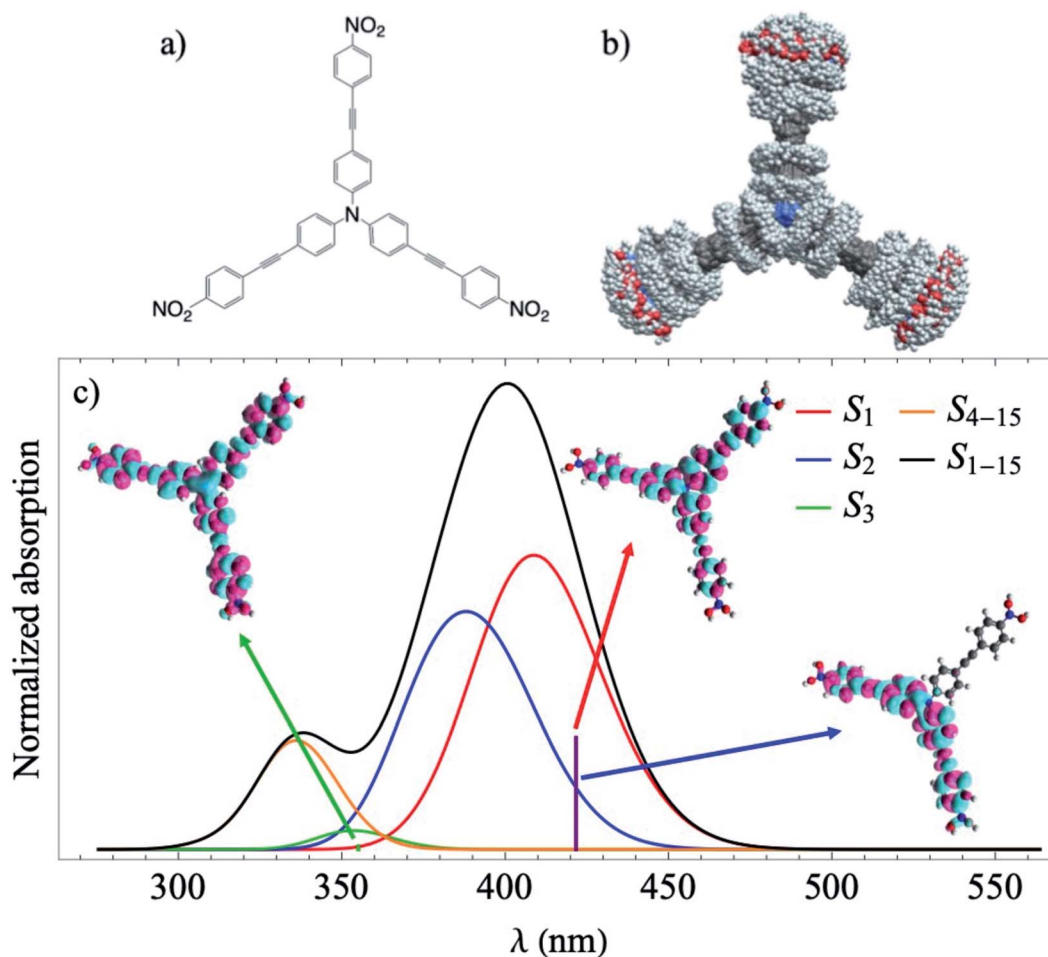
We start with conformational sampling of the triarylamine trimer using equilibrated ground state molecular dynamics. It shows that phenylene ethynylene units can freely rotate at room temperature (Fig. 1b). Fig. 1c displays the simulated absorption spectra with separated contributions from different excited states  $S_1$ – $S_{15}$ . The energies and spatial distribution of electronic transition densities of  $S_1$ ,  $S_2$  and  $S_3$  reflect the 3-fold symmetry, that is,  $S_1$ ,  $S_2$  are degenerate at ground state minimum, while  $S_3$  is fully delocalized at higher energy as shown by the respective orbital plots in the insets of Fig. 1c. The validity of the electronic structure method for phenylene–ethynylene dendrimer in question is justified by a good agreement with the experimental absorption spectra<sup>25</sup> and consistency with the Frenkel exciton Hamiltonian typically used for these systems.

The time evolution of the expectation values of the electronic state populations<sup>42,44</sup> are shown in Fig. 2a. According to Fig. 1c, an initial laser excitation at 388 nm populates the excited states  $S_1$  and  $S_2$  with a negligible contribution from  $S_3$ . An efficient energy transfer to  $S_1$  then takes place within the first 100 fs. Different processes take place during that time. An exponential decay from  $S_2$  to  $S_1$  is concomitant with a damped oscillatory interchange between these states. These two behaviors of the population transfer are due to two different effects introduced by the energy transfer between these states. To analyze them, the increase of  $S_1$  population in time has been fitted to the equation:

$$f(t) = a + \frac{b-a}{2} \left\{ \exp\left(-\frac{t}{\tau_1}\right) + \frac{1}{2} \left[ 1 + \cos\left(2\pi\frac{t}{T}\right) \right] \exp\left(-\frac{t}{\tau_2}\right) \right\}. \quad (1)$$

The parameters from this fitting are given in supplementary Table S1.† On one hand, after each crossing of the  $S_2/S_1$  seam, the molecular system follows different pathways on either the  $S_1$  or  $S_2$  potential energy surfaces. The nuclear motion on the  $S_1$  state moves the molecular system away to regions of low coupling, while the nuclear motion on  $S_2$  keeps it lingering in the regions of strong coupling, which facilitates subsequent relaxation to  $S_1$ . This behavior, previously reported in other branched dendritic molecules,<sup>45,46</sup> leads to the ultimate exponential decay of the initial  $S_2$  electronic population to  $S_1$ . It is represented by the pure decoherence time  $\tau_1 = 5.42$  fs that corresponds to the decoherence time  $\tau = 4.94$  fs obtained from the pure dephasing rate  $D_{12}$  calculated using the autocorrelation function within linear response theory<sup>44,45</sup> (eqn S14†). The corresponding curve is shown in supplemental Fig. S3.† On the other hand, the direction of energy transfer between  $S_2$  and  $S_1$ , represented by the non adiabatic couplings (NACR), does not





**Fig. 1** (a) Chemical structure of the triarylamine trimer; (b) superposition of structural snapshots obtained from ground state molecular dynamics at ambient conditions, the color convention followed for the atomic species is: white for hydrogen, gray for carbon, blue for nitrogen and red for oxygen; (c) simulated absorption spectrum (black) with separated contributions (colors) from the different excited states. Vertical lines mark values obtained at ground state minimum, and the corresponding spatial distribution of electronic transition densities of  $S_1$ ,  $S_2$  and  $S_3$ , calculated for the ground state energy minimum, are shown in the insets. The oscillator strength corresponding to  $S_3$  vertical line was magnified by 3 orders of magnitude.

involve a random participation of all vibrational motions, but of a reduced set of vibrational modes with periods of  $\sim 20$  fs (see Fig. S4c<sup>†</sup>). This manifests in Fig. 2a as oscillation patterns of the  $S_2$  and  $S_1$  electronic populations with periods of  $\sim 20$  fs, which therefore are associated to vibronic coherences with the vibronic decoherence time  $\tau_2 = 23.31$  fs.

Localization patterns of the transition densities associated with intra- and inter-branch energy transfers are mediated by thermal fluctuations at room temperature within the same electronic state or by energy transfers between different electronic states. Therefore, the time evolution of the electronic populations shown in Fig. 2a is not necessarily related to inter-branch energy transfer. This is evident from Fig. 2b that shows the average fraction of electronic transition density localized on the different branches. The formal definition of fraction of transition density is provided in the ESI (eqn S11<sup>†</sup>). In each trajectory we label the three branches as A, B, and C according to their decreasing order of fraction of transition density at  $t = 0$ . During the first  $\sim 100$  fs, the excess of electronic energy leads

to an ultrafast inter-branch migration. The absence of an energy gradient leads to an ultrafast energy redistribution among iso-energetic branches. Thus, we observe a final scrambling of the spatial electronic transition density due to incoherent dynamic mechanisms governed by thermal fluctuations. This process competes with the concerted evolution of the nuclear wavepackets in  $S_1$  and  $S_2$  that modulates the strength and longevity of the vibronic coherence. Considering coupling as one third of the energy splitting between  $S_1/S_2$  and  $S_3$  calculated at ground state minimum, a value of  $1484 \text{ cm}^{-1}$  was obtained. The strength of the thermal fluctuations, calculated as the full width at half maximum of the excitation energy, results in  $2000 \text{ cm}^{-1}$  and  $2250 \text{ cm}^{-1}$  for  $S_1$  and  $S_2$  respectively. That is, thermal fluctuations compete with coupling by randomly distorting the equivalent branches and breaking their symmetry, which leads to persistent interbranch exciton exchanges throughout the simulations. Despite that, the coupling is large enough to guarantee certain initial coherence.



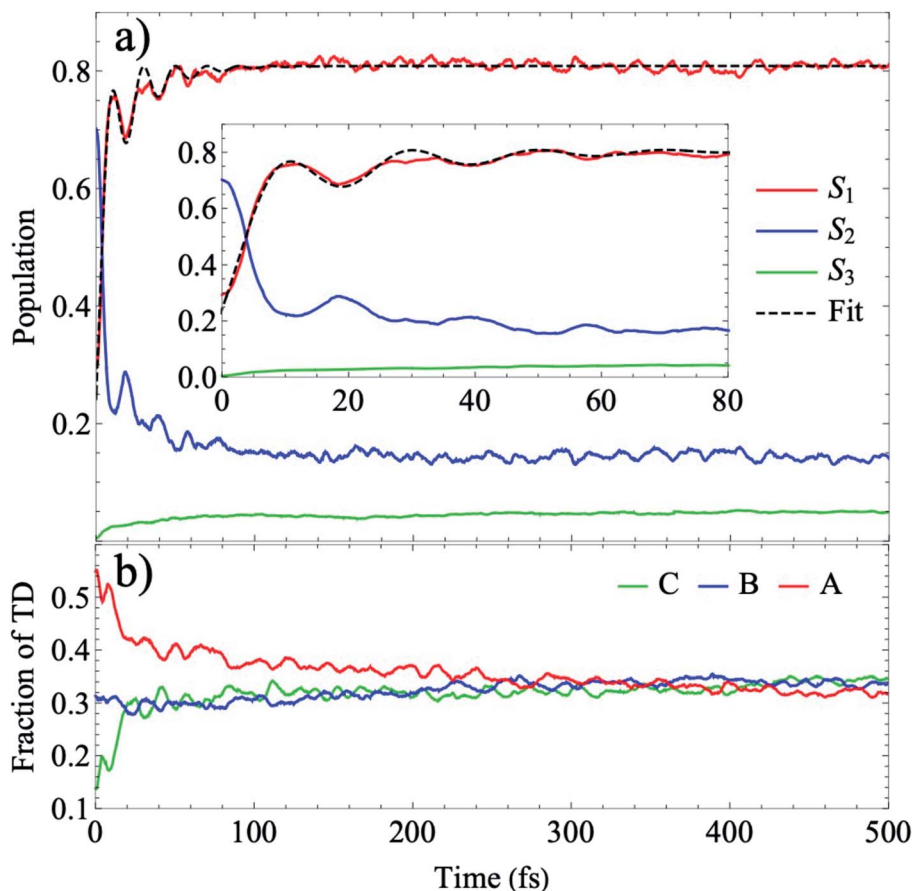


Fig. 2 (a) Time evolution of the electronic populations averaged over the ensemble of AIMC simulations according to the expectation values calculated according to (eqn S18†). The inset shows the oscillations of  $S_1$  and  $S_2$  at earlier times. The dashed black line is the fit to the  $f(t)$  function given by eqn (1); (b) time evolution of the mean fraction of electronic transition density localized on the different branches. For each trajectory we label the three branches as A, B, and C according to their decreasing order of fraction of transition density at  $t = 0$ .

It is worth pointing out that previous studies using the trajectory surface hopping protocol, in a similar system but with a benzene being the branching center, totally miss the oscillation patterns observed in this work.<sup>47</sup> This difference is attributed to partially stronger couplings introduced by the nitrogen-center that increase the interaction and delocalization between states, as well as the superior AIMC method able to properly describe coherent dynamics in contrast with ad hoc nature of trajectory surface hopping method. In order to clarify this issue, surface hopping simulations of the triarylamine trimer were performed. Results are shown in supplemental Fig. S4.† The evolution in time of  $S_1$  and  $S_2$  populations do not reproduce the oscillation patterns shown in Fig. 2a, pointing out the limitation of this method to properly evidence vibronic coherences.

Our analysis of individual trajectories indicates that the spatial scrambling corresponding to the ensemble-average values shown in Fig. 2b is due to random transfers between linear branches rather than to a complete delocalization of the wavefunction across the entire molecule. This is clearly evident from Fig. 3 that shows results for AIMC trajectory 1, which is typical for the majority of trajectories in the ensemble. We observe that population exchanges between  $S_1$  and  $S_2$  states

involve sudden changes in the transition density spatial localization. While transient delocalizations take place at the moments of energy transfer between states and induce energy transfer between different branches, the final result is a random exciton self-trapping on one or two branches, with the fraction of transition density not necessarily related to the initial order. Since the identity of the branches is defined at  $t = 0$ , the random exciton self-trapping reflects as a deceiving equivalence between the fraction of transition density on the branches at the end of the simulation, as shown in Fig. 2b. The electronic transition density matrices that correspond to the different snapshots indicated in Fig. 3a, are depicted in supplemental Fig. S5.† In agreement with Fig. 3a, we can observe a transient delocalization of the electronic transition density within the branches A and B at 6.4 fs, accompanied by a population exchange between  $S_1$  and  $S_2$ . Subsequently, the transition density is localized on the branch A and a new transient delocalization between the branches A and C takes place at  $t = 22.6$  fs. The excitation finally relaxed to  $S_1$  and becomes localized on the C branch.

Thus, the successive transient couplings between states through multitude of non-deterministic photoinduced pathways involve delocalizations of pairs of different branches that



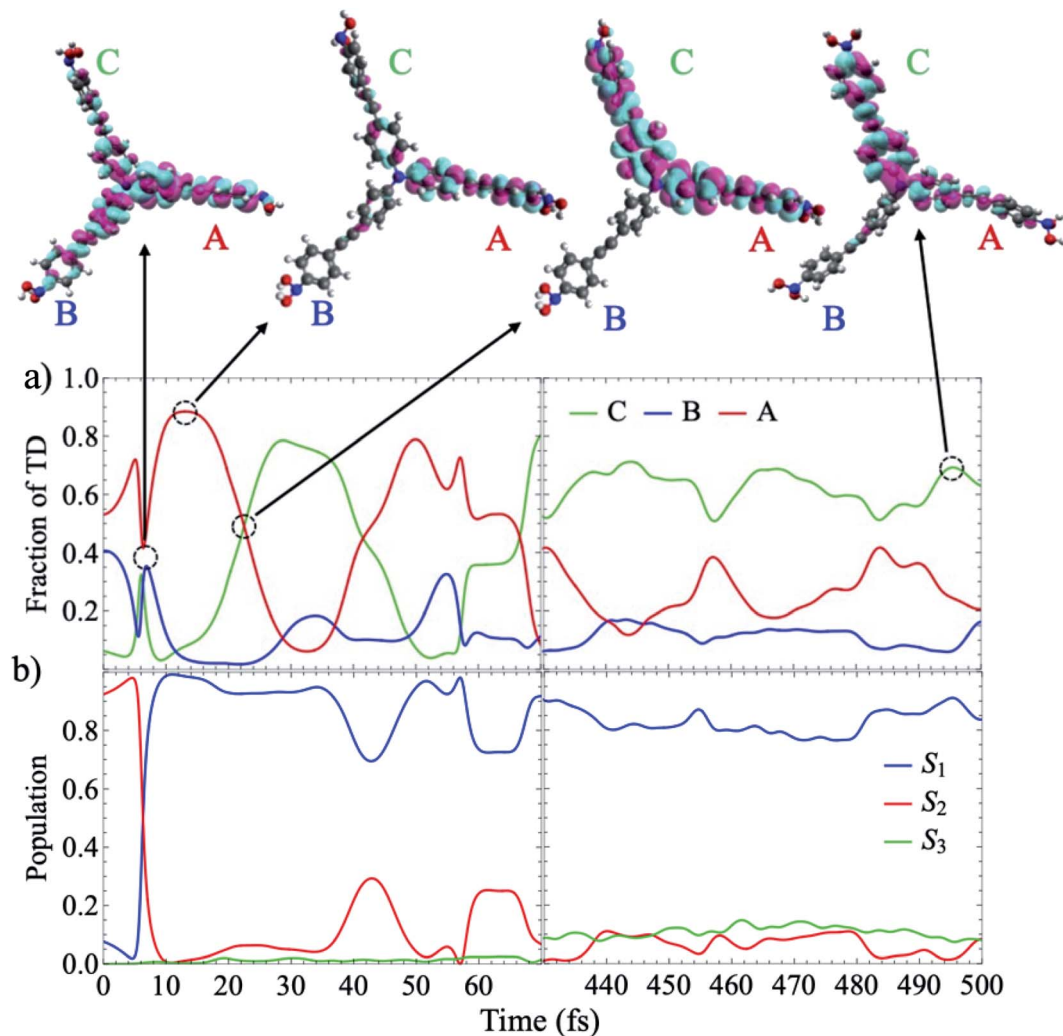


Fig. 3 Dynamics in a typical trajectory 1. (a) Temporal evolution of the fraction of transition density over each branch. Labels A, B, and C are assigned according to the decreasing order of fraction of transition density at  $t = 0$ . Selected snapshots of the transition densities in real space are also shown. (b) Concomitant electronic population evolution for the same AIMC trajectory.

ultimately leads to an exciton self-trapping on one within a random molecular scrambling. Furthermore, as shown in supplemental Fig. S6,<sup>†</sup> these transient couplings driving the vibronic dynamics are assisted by a reduced set of high-frequency normal modes.

We next examine the possibility to probe the coherence dynamics of the triarylamine trimer with the TRUECARS X-ray stimulated Raman signal, given by:

$$S(\omega_R, \tau) = 2\mathcal{I} \int_{-\infty}^{\infty} dt e^{i\omega_R(t-\tau)} \varepsilon_0^*(\omega_R) \varepsilon_1(t-\tau) \times \langle \Psi(t) | \hat{\alpha} | \Psi(t) \rangle, \quad (2)$$

where  $\varepsilon_0$  and  $\varepsilon_1$  are broadband and narrowband pulses,  $\omega_R$  is the observed Raman frequency, and  $\mathcal{I}$  denotes the imaginary part. The time-dependent polarizability  $\langle \alpha \rangle$  is taken to be constant in the nuclear space, following the original formulation,<sup>38</sup> so each matrix element factorizes into the wavepacket overlap between the involved electronic states given in eqn (5).

The probe fields are kept off-resonant with any real valence-to-core transitions. Otherwise the populations will start to contribute and dominate the coherences. We have previously found that an ideal scenario to maximize the experimental cross-section is to choose the central frequency near a valence-to-core resonance, while still staying off-resonant (pre resonant).<sup>40,41</sup> Our molecule, shown in Fig. 1a, offers carbon, nitrogen and oxygen species as potential candidates. Another possibility to enhance the intrinsically weak coherence contribution and overcome potential loss channels like ionization or Auger–Meitner decay, is to use tailored light fields that steer the molecular wavepacket motion by coherent control.<sup>48</sup>

X-ray TRUECARS initiates a stimulated Raman process between electronic states, similar to Raman spectroscopy between vibrational levels in the visible domain.<sup>33</sup> Only the ensemble average over all trajectories is experimentally observable. It is however useful to first discuss individual trajectories to gain insight about the underlying mechanisms. One example is depicted in Fig. 4 for a representative trajectory



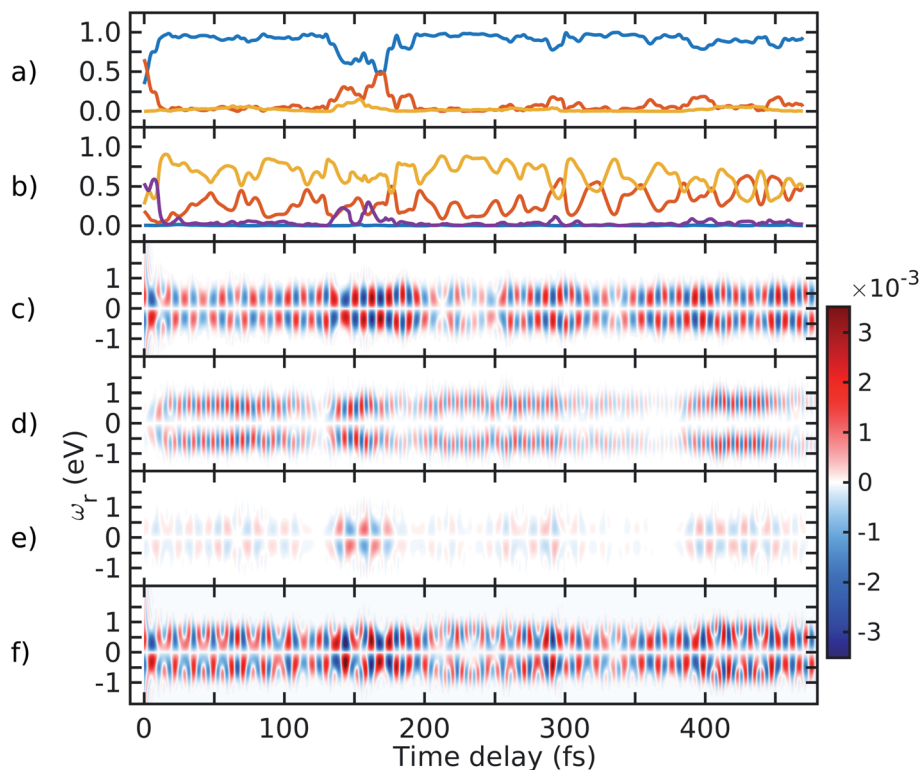


Fig. 4 Dynamics and TRUECARs signal in trajectory 2. (a) Populations in the  $S_1$  (blue),  $S_2$  (red) and  $S_3$  (yellow) states. (b) Fraction of transition density in branch A (purple), B (yellow), C (red) and around the central nitrogen (blue). (c) Frequency-dispersed TRUECARs signal (eqn (2)) for the coherence  $\rho_{12}$  between  $S_1$  and  $S_2$ . (d and e) same as (c) for  $\rho_{13}$  and  $\rho_{23}$ . (f) Total TRUECARs signal for trajectory 2 given by the sum of (c–e).

2. Following an initial population transfer from  $S_2$  to  $S_1$ , there is a free 100 fs evolution period. At 150 fs, the molecule again enters a region of strong nonadiabatic coupling, with population exchange between all three states (although  $S_3$  is only slightly affected). The transition density fractions in Fig. 4b exhibit the typical fluctuations, with the majority of excitation being located in branches B and C after a short redistribution period at the beginning of the dynamics.

Since three electronic states are involved, there exist three coherences  $\rho_{12}$ ,  $\rho_{13}$  and  $\rho_{23}$ . A TRUECARs signal according to eqn (2) can be calculated for each of these coherences, and their sum gives the total signal of the trajectory. According to Fig. 4, the contribution from the  $\rho_{12}$  coherence is the strongest. Interestingly, it is not only strong during the times when the molecule enters strong coupling regions – around 150–200 fs – but also in between. This suggests a concerted wavepacket evolution in the electronic states, where cloning events do not necessarily lead to decoherence. The signal contribution from the  $\rho_{13}$  coherence is only slightly weaker, and is located at the higher Raman shifts, in agreement with the larger  $S_3$ – $S_1$  energy difference compared to  $S_2$ – $S_1$ . The  $\rho_{23}$  contribution is the weakest, as these two states are much less populated than  $S_1$  throughout the dynamics. The signal exhibits considerable magnitude only around 150 fs, where both  $S_2$  and  $S_3$  get significantly populated intermediately.

Trajectory 2 illustrates the characteristics of a large fraction of trajectories in the ensemble. The domination of the  $\rho_{12}$

contribution to the signal (given degeneracy of  $S_1$  and  $S_2$  states due to molecular symmetry), as well as the trapping of transition density in two of the three branches, is typical. Three additional trajectories shown in supplemental Fig. S7–S9† exhibit the largest differences to give insight about the variance within the ensemble. Individual features – like the magnitude of

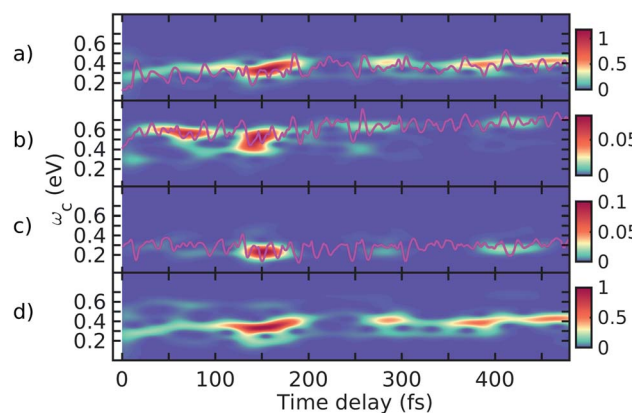


Fig. 5 Spectrogram of the TRUECARs signal (eqn (6)), dissected into the three contributions. (a) Spectrogram of the  $\rho_{12}$  coherence signal in Fig. 4c. (b) Spectrogram of the  $\rho_{13}$  coherence signal in Fig. 4d. (c) Spectrogram of the  $\rho_{23}$  coherence signal in Fig. 4e. The pink lines show the energy splitting between the corresponding adiabatic states as extracted from the AIMC simulations. (d) Spectrogram of the total signal in Fig. 4f.



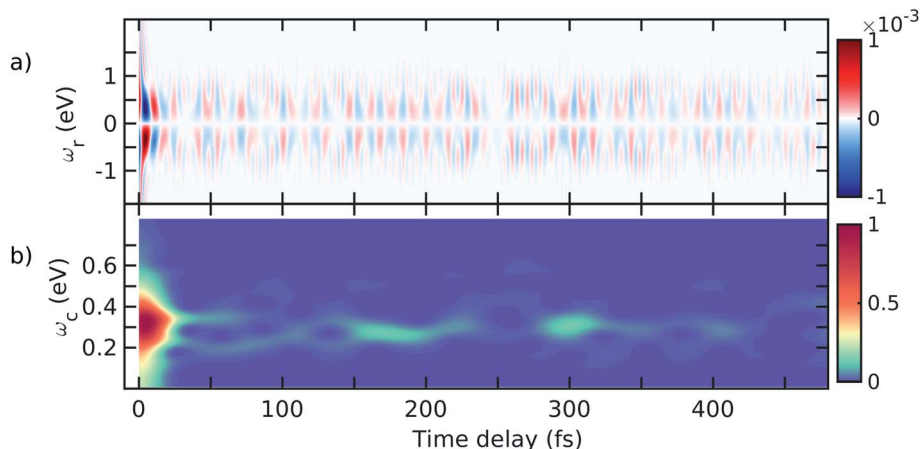


Fig. 6 (a) TRUECARs signal (eqn (2)) of the ensemble, obtained by averaging the over all 300 trajectories. (b) Spectrogram of the TRUECARs signal (eqn (6)).

population transfer, the relative magnitude of the coherence contributions or the branches where the transition density is eventually trapped – may vary, but the qualitative structure persists.

The spectrogram of the TRUECARs signal  $I(\omega_c, \tau)$ <sup>39</sup> (eqn (6)) gives the vibronic coherence distribution and corresponds to the energetic splitting of the adiabatic electronic states.  $I(\omega_c, \tau)$  is depicted in Fig. 5 for trajectory 2, dissected into the three coherences similar to Fig. 4. The spectrogram of each contribution correctly reproduces the energy splitting of the involved adiabatic electronic states, with  $S_2$ – $S_1$  and  $S_3$ – $S_2$  oscillating between 0 and 0.4 eV, and  $S_3$ – $S_1$  oscillating between 0.4 and 0.8 eV. Both contributions are visible in the total spectrogram depicted in Fig. 5d, with the dominating feature around 0.3 eV and the weaker  $S_3$ – $S_1$  signal at higher  $\omega_c$ . The spectrograms along other trajectories (not shown) are very similar.

In Fig. 6, we present the total TRUECARs signal averaged over all 300 trajectories. Surprisingly, even though the individual trajectories exhibit persisting coherences throughout the dynamics, the total signal is strong only in the very beginning and rapidly decays. This is in agreement with Fig. 2, where the population transfer as well as the transition density relocalization complete over after 50–100 fs. The spectrogram shown in Fig. 6 exhibits the main feature centered around 0.3 eV, with additional weak features stemming mainly from the  $\rho_{13}$  coherence at higher Raman shifts. This dynamics is in a stark contrast to the rigid heterodimer previously investigated,<sup>41</sup> where the experimentally observed long-living coherences are correctly reproduced in the ensemble-averaged TRUECARs signal. In the present molecule, we observe a rapid decay of the coherence, corresponding to the incoherent scrambling of the transition density across all three arms. This corroborates that TRUECARs can be a powerful tool in the molecular design of future optoelectronic devices on the basis of such dendritic or multi-chromophoric building blocks, where coherent electronic evolution is advantageous for conversion efficiencies. As demonstrated here, TRUECARs can directly monitor whether or not such coherence properties are present in a given molecule.

## Conclusions

The photoexcitation and subsequent inter-branch energy redistribution of the triarylamine trimer shown in Fig. 1a have been simulated using AIMC that treats decoherences in a natural way beyond the Born–Oppenheimer dynamics on several excited states. The photophysics of this trimer results in a competition between coherent and incoherent energy transfers between branches. An initial ultrafast coherent dynamics is followed by incoherent mechanisms governed by thermal fluctuations that ultimately lead to a random molecular scrambling. Successive transient couplings creates multitude of non-deterministic photoinduced pathways involving delocalizations of pairs of different branches that ultimately leads to an exciton self-trapping on one within a random molecular scrambling. This is a consequence of the fact that thermal fluctuations compete with coupling differentially and randomly distorting the equivalent branches, which leads to persistent interbranch exciton exchanges throughout the simulations. Despite that, the coupling seems to be relatively large enough to guarantee certain initial coherence. Two distinct coherences, *i.e.*, pure electronic and vibronic coherences, can be distinguished at earlier times. Vibronic couplings principally involve asymmetric motions in two of the three branches per time and are related to specific high-frequency bond-stretching vibrational modes (supplemental Fig. S6†).

We have calculated the TRUECARs X-ray stimulated Raman signal for all individual trajectories as well as the ensemble average of the AIMC dynamics. TRUECARs is an unambiguous probe of molecular vibronic coherences as it is free from the usually dominating population background. The signal is strong only at the very beginning of the dynamics and rapidly decays within the first 50 femtoseconds, reproducing the incoherent scrambling dynamics of the photoexcited triarylamine trimer. This is different from previous results on a bichromophoric heterodimer,<sup>41</sup> where TRUECARs has revealed long-living coherences that were also experimentally observed. This demonstrates the unique capability of near-future XFEL



experiments in monitoring coherent molecular dynamics, and thereby help in the chemical design of molecular building blocks for optoelectronic materials that benefit from these coherences. While coherent TRUECARs, as calculated here, requires phase control of the two pulses in the hybrid probe field, the information is equally accessible by a covariance-based measurement with an existing single stochastic XFEL pulse.<sup>40</sup>

## Methods

### AIMC simulations

The *ab initio* multiple cloning (AIMC)<sup>42,43</sup> technique is an extension of the Multiconfigurational Ehrenfest (MCE) method<sup>49–51</sup> that uses trajectory-guided Gaussian basis functions (TBF). Independent Ehrenfest trajectories, *i.e.* configurations  $\psi_n(t)$  are used as a basis set to represent the full time-dependent quantum-mechanical wavefunction of electrons and nuclei:

$$|\Psi(t)\rangle = \sum_n c_n |\psi_n(t)\rangle \quad (3)$$

with:

$$|\psi_n(t)\rangle = |\chi_n\rangle \left( \sum_I a_I^{(n)}(t) |\phi_I^{(n)}\rangle \right) \quad (4)$$

where  $\chi_n(t)$  and  $\phi_I^{(n)}$  are the nuclear and electronic components, respectively.

$\chi_n(t)$  are coherent states<sup>52,53</sup> given by frozen Gaussian functions centered in the Ehrenfest trajectories. In the original versions of MCE and AIMC,<sup>51</sup>  $\phi_I^{(n)}$  are adiabatic states. However, photoinduced dynamics in large conjugated molecules like dendrimers can involve unavoided crossings between states whose nonadiabatic couplings have sharp peaks strongly localized in configurational space.<sup>54–56</sup> In these situations, the adiabatic states change abruptly within the Gaussian width and the molecule should follow the diabatic pathways. Otherwise, unphysical intramolecular energy redistributions can occur. To address this issue, we use time-dependent diabatic electronic states, defined to coincide with adiabatic states in the center of each Gaussian,<sup>54–56</sup> as detailed elsewhere.<sup>51</sup>

Ehrenfest trajectories evolve on an average potential energy surface that can lead to unphysical nuclear motions if the intramolecular energy redistribution follows different relaxation pathways dominated by several electronic states whose forces are very different. In these situations, the original wavefunction branches out into multiple parts, each following a specific pathway. AIMC quantifies them by using a set of cloning criteria.<sup>42,57</sup> When these criteria are met, the original Ehrenfest trajectory splits into two new trajectories that continue their dynamics with the same nuclear wave function at the moment of cloning event but different electronic populations in order to be independently propagated on different potential energy surfaces. Such cloning events introduce decoherence in a natural way for wavefunctions moving on sufficiently different potential energy surfaces. More details and technical aspects of the AIMC method can be found elsewhere.<sup>42,43,57,58</sup>

The AIMC method is implemented within the nonadiabatic excited state molecular dynamics (NEXMD) framework.<sup>42,59,60</sup> It is worth mentioning that the *ab initio* from AIMC comes from historical reasons and the method can be adapted either to TDDFT<sup>61</sup> or semiempirical calculations as is the case of NEXMD. The NEXMD implementation has been specifically developed to deal with photoinduced dynamics in large multichromophoric conjugated molecules involving several coupled electronic excited states. Excited states energies,<sup>62–64</sup> gradients<sup>65,66</sup> and nonadiabatic couplings<sup>67–69</sup> are calculated on-the-fly at the configuration interaction singles (CIS) level of theory using the semiempirical Austin Model 1 (AM1) Hamiltonian<sup>70</sup> with the Collective Electronic Oscillator (CEO) approach.<sup>71–73</sup> In our previous studies we have tested this approach for a number of dendritic chromophores, where we have found semi-quantitative agreement with experimental data and higher level electronic structure methodologies.<sup>45–47,59,62</sup> Furthermore, the accuracy of this AIMC implementation has been previously tested on photoinduced nonadiabatic energy transfer pathways dynamics in poly(phenylene ethynylene) dendrimer building blocks.<sup>74</sup>

AIMC trajectories start by vertical excitation of 300 initial configurations equispaced in time obtained from a 1 ns equilibrated ground state molecular dynamics simulation. This simulation was performed at ambient conditions ( $T = 300$  K) using the Langevin thermostat with a friction coefficient  $\gamma = 2.0$  ps<sup>-1</sup> and a time step of 0.5 fs starting from an initial structure that has been previously minimized using the generalized amber force field<sup>75</sup> followed by a subsequent second minimization using AM1. The initial excited states were populated according to a Franck–Condon window given by  $g_i(r, R) = f_i \exp[-T^2(E_{\text{laser}} - E_i)^2]$  where  $f_i$  and  $E_i$  are the oscillator strength and energy of excited state *I*, and  $E_{\text{laser}}$  is the energy of a Gaussian laser pulse  $f(t) = \exp(-t^2/2T^2)$ , centered at 388 nm that corresponds to the maximum of the absorption for the S<sub>2</sub> state, and  $T = 42.5$  fs, *i.e.*, a FWHM = 100 fs. AIMC trajectories were run at constant energy and with a 0.05 fs time step. Gaussian widths were taken from the optimized parameters reported by Thompson *et al.*<sup>76</sup> Details on the cloning criteria and thresholds can be found in the ESI.†

The coherence between any two electronic states *K* and *L* can be extracted from AIMC simulations as:

$$\rho_{KL} = \frac{1}{2} \sum_{m,n} c_m^* c_n \langle \chi_m | \chi_n \rangle \sum_I \left[ (a_K^{(m)})^* a_L^{(n)} \langle \phi_L^{(m)} | \phi_I^{(n)} \rangle + (a_L^{(m)})^* a_K^{(n)} \langle \phi_I^{(m)} | \phi_K^{(n)} \rangle \right]. \quad (5)$$

It includes coherences between the electronic and the nuclear subsystem, each carrying their own phases. Their joint information is required to obtain a TRUECARs signal, and their state is accounted for in the molecular wavefunction when calculating  $\rho_{KL}$ .

### TRUECARs signal spectrogram

The TRUECARs signal given by eqn (2), was calculated with the broadband 500 attosecond pulse  $\varepsilon_0$  and the narrowband 3 fs





pulse  $\varepsilon_1$ . A powerful analysis tool that is experimentally available for the TRUECARs signal is its spectrogram  $I$ .<sup>39</sup> This is a post-processing analysis using a gating function  $E_{\text{gate}}$  convoluted with a TRUECARs signal trace  $S(t)$  at constant Raman shift  $\omega_R$  (integration over positive or negative  $\omega_R$  is also possible, while integration over the whole  $\omega_R$  range yields zero). It is given by:

$$I(\omega_c, \tau_{\text{coh}}) = \left| \int_{-\infty}^{\infty} d\tau S(\tau) E_{\text{gate}}(\tau - \tau_{\text{coh}}) e^{-i\omega_c \tau} \right|^2 \quad (6)$$

and yields the transient frequency pattern of the signal oscillations.

## Data availability

The data that supports the findings of this study are available within the ESI† and from the corresponding author upon reasonable request.

## Author contributions

S. T., S. F.-A. and S. M. designed the project. V. M. F. and S. F.-A. performed AIMC simulations. D. K. calculated the signals and the Wigner spectrograms. All authors analyzed and interpreted the results. V. M. F. and D. K. prepared the figures. The manuscript was written with contributions from all authors. All authors were involved in the scientific discussion of the results of the paper. V. M. F. and D. K. contributed equally.

## Conflicts of interest

There are no conflicts to declare.

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