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Collective Optical Excitations and Photoexcited-Carrier Dynamics in the Na₂₀@C₂₄₀ Core-Shell Nanostructure

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Abstract: Finite metal clusters and fullerene cages lie between molecular and classical plasmonic regimes, where collective polarization, discrete electron-hole transitions, and orbital hybridization coexist. We use adiabatic real-time time-dependent density functional theory to examine the optical response and post-pulse electronic dynamics of isolated Na₂₀, isolated C₂₄₀, and the Na₂₀@C₂₄₀ core-shell model. The isolated Na₂₀ calculation exhibits a dominant dipole-active feature at 2.73 eV with coherent contributions from several off-resonant electron-hole transitions and a dipole-like induced density. We interpret it as a finite-size plasmon-like resonance with mixed and potentially fragmented character, rather than as a classical localized surface plasmon. The C₂₄₀ cage supports several mixed molecular-polarization resonances, with the clearest plasmon-like signature among the examined modes at 5.59 eV. In the composite, the shell polarization is antiphase with the Na-centered response at 2.73 eV and suppresses the net dipole, whereas the 5.70 eV response is predominantly an in-phase, shell-localized polarization. Time-dependent energy decompositions show coherent redistribution from collective Coulomb-driven motion toward resonant electron-hole channels, accompanied by finite-system beating and recurrence. Hot-carrier distributions are concentrated mainly on C₂₄₀ at the end of the propagation. It should be noted that these quantities are internal descriptors within a frozen-ion mean-field simulation of a closed quantum system, and do not correspond to extractable carrier yields or irreversible lifetimes.

Keywords: finite-size plasmons; core-shell coupling; molecular plasmon; RT-TDDFT; hot-carrier distributions

1. Introduction

Plasmonic and molecular-scale nanostructures can concentrate optical energy and generate nonequilibrium electronic populations through collective and single-particle excitation channels.¹⁻⁴ In extended metals, nonradiative plasmon decay produces energetic electrons and holes conventionally termed hot carriers, with potential relevance to photocatalysis,⁵⁻⁶ photodetection,⁷⁻⁸ photovoltaics,⁹⁻¹⁰ and so on. In finite clusters, discrete levels, strong state mixing, and recurrences make the boundary between a collective mode and a particle-hole excitation less sharp. In this work, hot-carrier distributions denote the nonthermal changes in electron and hole occupations extracted from the real-time time-dependent density functional theory (RT-TDDFT) density matrix, the term does not imply a thermalized population or an experimentally extractable yield.

Conventional plasmonic materials are dominated by Au and Ag. Their strong optical responses are accompanied by interband screening and intrinsic optical losses, motivating the study of alternative plasmonic platforms.¹¹⁻¹² Sodium is an instructive simple-metal candidate because its delocalized s electrons exhibit nearly free-electron-like behavior, avoiding the complex d-band screening present in noble metals.¹³⁻¹⁶ In parallel, carbon-based structures with extended π conjugation, including polycyclic aromatic hydrocarbons (PAHs),¹⁷⁻²³ conjugated polyene chains,²⁴⁻²⁷ and fullerenes,²⁸⁻³¹ can support molecular excitations with varying collective character. A sodium cluster inside a fullerene cage is therefore a useful model for testing how finite-size metallic polarization, molecular excitation, charge transfer, and orbital hybridization interact at an atomically defined interface.

Earlier work predicted transfer of approximately six electrons from Na₂₀ to C₂₄₀, substantial hybridization between Na-derived and fullerene states, and plasmon-mediated resonant intercluster Coulombic decay in the photoionization continuum.³²⁻³³ These results preclude treating the system as a neutral Na₂₀ cluster inside a passive cage. They also motivate a complementary time-domain question: after a finite optical pulse, how do the core- and shell-resolved polarization, coherent dephasing and nonthermal occupations evolve within the core-shell system?

Addressing this question requires an atomistic treatment of electronic response, while recognizing that a finite RT-TDDFT propagation is not a complete theory of irreversible relaxation. Quantum confinement, nonlocal screening, orbital hybridization, and intercomponent charge transfer can all reshape a plasmon-like response.³⁴⁻³⁷ RT-TDDFT supplies the time-dependent Kohn-Sham (KS) response under an applied field. We then use RHODENT, an open-source modular Python package for processing RT-TDDFT output,³⁸ to reconstruct the density-matrix response and calculate spectra, induced densities, transition contribution maps (TCMs), energy decompositions, and hot-carrier distributions.³⁹⁻⁵² In the adiabatic frozen-ion form used here, the underlying RT-TDDFT calculation describes coherent mean-field electronic dynamics but omits

explicit electron-electron collisions beyond the adiabatic functional, electron-phonon scattering, nuclear motion, environmental damping, and carrier extraction.^{39, 53}

Here, we compare isolated Na₂₀ and C₂₄₀ fragments frozen in the optimized composite geometry with Na₂₀@C₂₄₀. We resolve the finite-pulse response in the time domain, focusing on the phase relation between core and shell polarization, coherent redistribution between plasmon-like collective and near-resonant transition channels, and the excitation-energy dependence of fragment-projected hot-carrier distributions. This combination of frequency-domain and finite-pulse analysis provides an atomistic account of how plasmon-like polarization is screened, coherently dephased, and redistributed into nonthermal electron-hole occupations in a lightweight simple-metal@carbon model, while retaining explicit limits on collectivity, charge transfer, and carrier extraction.

2. Computational details

All calculations are performed using the GPAW (version 24.6.0) package⁵⁴⁻⁵⁵ and the Atomic Simulation Environment (ASE) package.⁵⁶ The KS wave functions are expanded using a linear combination of atomic orbitals (LCAO) basis set⁵⁷ within the projector augmented-wave (PAW) theory.⁵⁸ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁵⁹ is employed for both ground-state and time-dependent calculations. The *dzp* basis set is used for C, while the *p*-valence basis set is used for Na, which is important to capture plasmon resonances.

The initial Na₂₀@C₂₄₀ geometry is taken from previous theoretical studies³³ and further optimized with the Broyden-Fletcher-Goldfarb-Shanno (BFGS)⁶⁰ optimizer implemented in ASE until the maximum residual force is below 0.05 eV Å⁻¹. The density and potentials are represented on a real-space grid with a spacing of 0.20 Å. Open (non-periodic) boundary conditions are applied, and a vacuum region of at least 8 Å is included in all directions to avoid spurious interactions between periodic images. The Fermi-Dirac smearing with a width of 0.05 eV is used to facilitate self-consistent field (SCF) convergence. The maximum number of SCF iterations is set to 500, and the density convergence threshold is set to 1×10⁻¹². The isolated Na₂₀ and C₂₄₀ reference geometries are extracted from the optimized composite without further relaxation, so their comparison isolates electronic coupling at a fixed geometry. The optimized geometries of the Na₂₀, C₂₄₀, and Na₂₀@C₂₄₀ are shown schematically in Figure 1.

The excited-state calculations are performed using the RT-TDDFT method. The same exchange-correlation functional, basis sets, grid spacing, and boundary conditions as those used in the ground-state calculations are adopted. To obtain the linear optical response, each system is perturbed by a weak sinc-shaped electric field polarized along the *z* direction. The time-dependent perturbation is written as

$$v(t) = s_0 \frac{\sin(\omega_c(t - t_0))}{\omega_c(t - t_0)}, t > 0, \quad (1)$$

where s_0 is the field strength, ω_c is the cutoff frequency, and t_0 is the time offset. The Fourier transform of this pulse is approximately rectangular, allowing excitation of all transitions below the cutoff energy while suppressing higher-energy responses. In this work, the cutoff energy is set to 9 eV and the field strength is chosen as 1×10^{-6} a.u., ensuring that the response remained in the linear regime. The time offset is set as

$$t_0 = \left(n + \frac{1}{4}\right) T_c, \quad (2)$$

where $T_c = 2\pi/\omega_c$ is the oscillation period associated with the cutoff frequency. In this work, $n = 5$ is used as a compromise between including most of the pulse within the simulation window and maintaining stable early-time propagation.³⁸ Absorption spectra are obtained by Fourier transforming the time-dependent dipole moment, and Gaussian broadening with $\sigma = 0.1$ eV is applied to produce smooth spectra.

To investigate the real-time plasmon dynamics, selected resonances are excited using ultrafast Gaussian laser pulses.³⁹⁻⁴⁰ The electric field is written as

$$E(t) = E_0 \cos(\omega_0(t - t_0)) \exp\left(-\frac{(t - t_0)^2}{\tau^2}\right), \quad (3)$$

where E_0 is the field amplitude, ω_0 is the central excitation frequency, $t_0 = 10$ fs is the pulse center, and $\tau = 3.72$ fs is the temporal width. The corresponding full widths at half maximum are approximately 6.2 fs in the time domain and 0.59 eV in the frequency domain. The total propagation time is 150 fs. The isolated Na₂₀ is excited at 2.73 eV, isolated C₂₄₀ at 4.53 and 5.59 eV, and Na₂₀@C₂₄₀ nanostructure at 2.73 and 5.70 eV.

The RT-TDDFT outputs are post-processed with RHODENT package³⁸ to obtain TCMs, time-dependent stored energies, induced charge densities, and fragment-projected hot-carrier distributions. The stored energy is decomposed into kinetic and Hartree-exchange-correlation (H_{XC}) contributions, as well as into resonant and non-resonant electron-hole transition channels. The relevant theoretical derivations and computational procedures are described in detail in previous studies.^{38, 61} Occupation distributions are averaged over the time interval from 120 to 125 fs, whereas the spatial distributions are shown at 120 fs. These times define post-pulse analysis windows within a coherent, closed-system propagation and should not be interpreted as experimental carrier lifetimes. Structural visualization and numerical data processing are performed using VESTA,⁶² Numpy,⁶³ Scipy,⁶⁴ and Matplotlib.⁶⁵

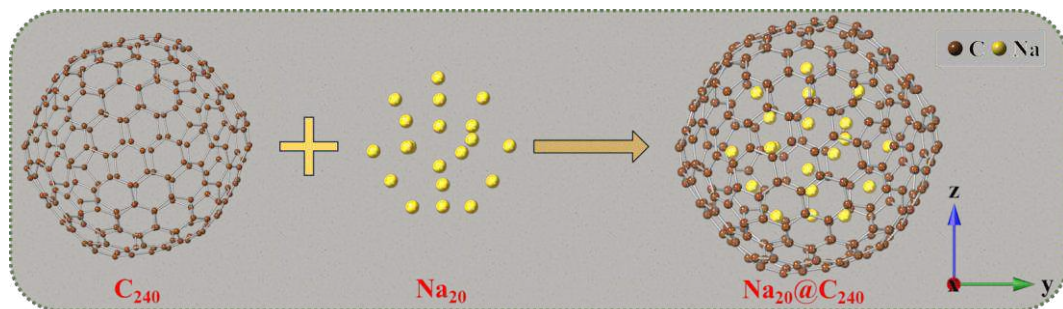


Fig. 1 Optimized $\text{Na}_{20}@\text{C}_{240}$ geometry and the frozen-fragment reference structures used for the optical comparison. Brown and yellow spheres denote C and Na atoms, respectively. The isolated C_{240} (left) and Na_{20} (middle) structures are extracted from the optimized composite without further relaxation; the encapsulated structure is shown at right in the same orientation.

3. Results and discussion

The optimized $\text{Na}_{20}@\text{C}_{240}$ structure is shown in Figure 1, with the Na atoms occupying the interior of the C_{240} cage. To enable a controlled optical comparison, the isolated Na_{20} and C_{240} references are extracted from this composite geometry and are not relaxed again. Consequently, differences between the frozen fragments and $\text{Na}_{20}@\text{C}_{240}$ primarily reflect electronic coupling, screening, and hybridization at a common geometry rather than an additional change in fragment shape. Figure 1 also establishes the spatial core and shell assignments used for later projections.

3.1 Finite-size collective response of the Na_{20}

Figure 2a shows the calculated spectrum of the Na_{20} fragment. Its strongest feature occurs at 2.73 eV, with weaker structures at higher energy. This geometry-specific dominant peak should not be interpreted as a universal, isolated classical localized surface plasmon resonance (LSPR). Experimental spectra across small neutral sodium clusters establish collective surface plasmon response but also show substantial size-, shape-, and temperature-dependent structure.⁶⁶ For neutral Na_{20} in particular, theory attributes the observed multippeak response to coupling between a collective surface mode and discrete particle-hole transitions, i.e., Landau fragmentation.⁶⁷⁻⁶⁸ The TCM and induced density are therefore used here to assess whether the 2.73 eV feature contains a finite-size plasmon-like collective component, not to impose a pure single-mode picture.

The inset of Figure 2a resolves why the 2.73 eV feature is described as mixed but plasmon-like. Its TCM is not confined to a single spot on the resonant diagonal: several constructive contributions arise from occupied levels between approximately -1.5 and 0 eV and unoccupied levels below about 1 eV, including pairs whose KS energy differences are smaller than 2.73 eV. Their common sign indicates coherent addition to the dipole response. The induced density shows two extended regions of opposite sign on opposite sides of the Na cluster along the field direction, rather than density localized around one bond or one atom. Distributed transition participation plus a cluster-scale

dipolar density supports a pronounced Coulomb-coupled collective component. It does not prove a pure collective eigenmode: finite Na_{20} can retain substantial collective oscillator strength while that strength is fragmented and mixed with individual transitions.⁶⁷⁻⁶⁸ We therefore refer to this feature as a Na_{20} -derived finite-size plasmon-like resonance with mixed character.

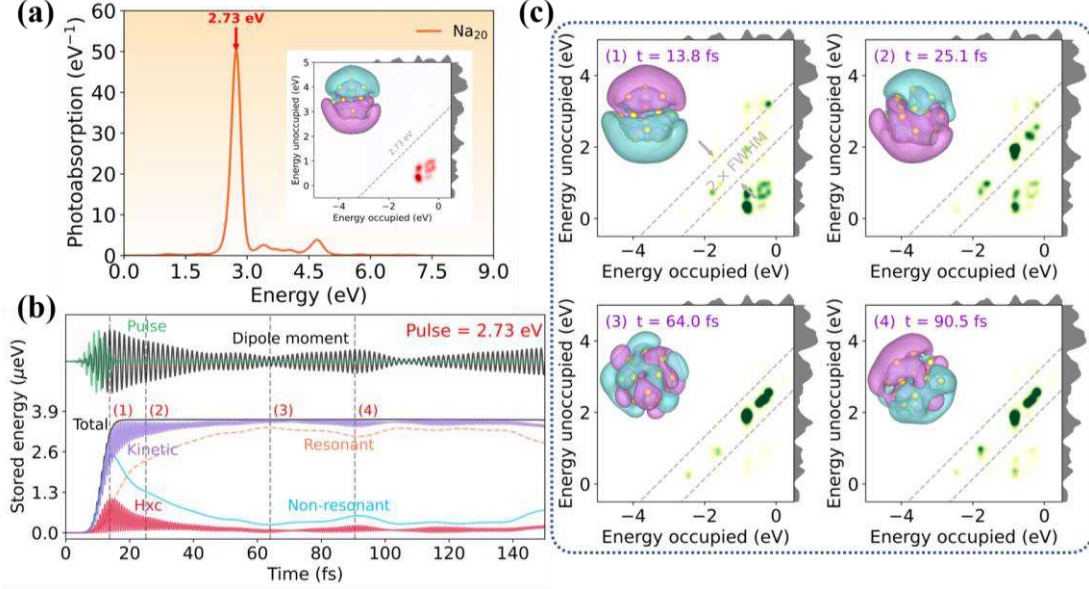


Fig. 2 Optical response and coherent post-pulse dynamics of the frozen Na_{20} fragment. (a) Photoabsorption spectrum from 0 to 9 eV. The red arrow identifies the dominant 2.73 eV feature. The inset combines its frequency-domain TCM with the induced density: occupied-state energy is on the horizontal axis, unoccupied-state energy on the vertical axis, and energies are referenced to the Fermi level. Red and blue TCM features are constructive and destructive contributions to the dipole response, respectively. The dashed diagonal line denotes resonant KS transitions with energy differences equal to the excitation energy $\hbar\omega$. The gray marginal curves show the occupied and unoccupied state densities, and the cyan/magenta isosurfaces show opposite signs of the induced density. (b) Response to the 2.73 eV Gaussian pulse. The upper trace shows the incident field (green) and induced dipole (gray); the lower trace shows total stored energy (black), kinetic energy (purple), H_{xc} energy (red), resonant energy (orange dashed), and non-resonant energy (cyan). Vertical markers identify $t = 13.8, 25.1, 64.0,$ and 90.5 fs. (c) Energy-resolved TCMs and induced densities at those four times. The paired dashed lines delimit the near-resonant band used in the energy decomposition. A common TCM color normalization is used for all four snapshots, so changes in intensity and redistribution toward or away from the resonant band can be compared directly.

We next excite the 2.73 eV finite-size plasmon-like feature with a resonant Gaussian pulse (Figure 2b). The induced dipole moment persists after the field and exhibits pronounced beating rather than monotonic exponential decay. In the present finite, frozen-ion electronic model, this behavior reflects coherent exchange between a dipole-active collective component and discrete electron-hole channels. It should not be interpreted as an experimental plasmon lifetime or as evidence that a dissipative system would rebuild the same coherent oscillation at late times.

The total electronic energy rises during the pulse and then remains constant, as required for a closed propagation without a bath. Near-resonant channels contain

electron-hole pairs whose KS energy differences lie within the stated resonance windows (single-particle excitation), whereas non-resonant channels represent transitions coupled through the induced field. Early in the response, a large fraction of the energy is associated with non-resonant channels. This indicates that the laser pulse initially drives a collective motion formed by coherent coupling among multiple off-resonant electron-hole transitions. Later, weight is coherently redistributed toward near-resonant channels, while oscillatory back-transfer remains visible. The kinetic and H_{XC} decomposition provides a complementary diagnostic. H_{XC} energy measures the Coulomb-driven part of the time-dependent response and can therefore track loss and recurrence of collective polarization. Its oscillatory, nonzero late-time behavior confirms that the finite system does not undergo one-way irreversible relaxation in the present model.

The four common-scale snapshots in Figure 2c connect the time traces to transition-space and real-space changes. At 13.8 fs, near the end of the pulse, the induced density is strongly hemispheric and the energy TCM contains intense weight outside the near-resonant band. At 25.1 fs, the density reverses sign along the driving direction and the dominant TCM spots reorganize, consistent with the first large dipole beating cycle. By 64.0 fs, when the induced dipole moment is near to zero, the density is more spatially fragmented and the strongest TCM weight lies closer to the near-resonant band. At 90.5 fs, non-resonant energy is partially revived, accompanied by changes in the induced density and the TCM pattern, which demonstrates back-transfer among discrete channels rather than one-way damping. These snapshots support plasmon-assisted formation of nonthermal electron-hole occupations together with coherent finite-system recurrence, not irreversible hot-carrier relaxation.

Overall, the 2.73 eV feature has a pronounced dipole-active, plasmon-like collective component. The closed RT-TDDFT dynamics show collisionless plasmon dephasing, hot-carrier occupation formation, and coherent recurrence among discrete transition channels rather than one-way conversion into a thermal bath.

3.2 Collective optical properties of the C₂₄₀

We next examine the collective optical properties of the isolated C₂₄₀. The calculated photoabsorption spectrum is shown in Figure 3a. In contrast to the Na₂₀, the C₂₄₀ displays a much richer absorption profile in the energy range of 0-9 eV. Several absorption peaks with different intensities are observed, reflecting the more complex electronic structure of the fullerene-like carbon cage. As a result, optical excitations in the C₂₄₀ generally involve multiple molecular orbital transitions and may exhibit mixed collective and single-particle character.

To identify the nature of the representative absorption peaks, we select several resonance energies marked by arrows in Figure 3a, analyze their TCMs and induced charge densities, as shown in Figures 3b-f. The red arrow indicates the strongest absorption peak, whereas the blue arrows denote other prominent resonances. Similar

to the analysis of the Na_{20} , the TCMs provide microscopic information on how individual electron-hole transitions contribute to the optical response. In particular, collective plasmon-like excitations are expected to involve coherent contributions from multiple transitions, including those whose energy differences are smaller than the excitation energy. In contrast, a single-particle-dominated excitation is usually characterized by transition contributions concentrated near the resonant transition line.

Figures 3b-f show a graded evolution rather than a binary separation between plasmonic collective and single-particle excitations. At 1.89 and 2.73 eV, the TCMs are dominated by only a few discrete spots, while the induced densities show dipole-like distributions across the cage. These modes may contain molecular polarization but have limited visible transition participation. At 4.53 eV, multiple electron-hole pairs contribute across an extended region, with constructive contributions predominantly reside in the off-diagonal part and destructive contributions largely confined to the diagonal domain, and the density exhibit partial upper-lower separation. At 5.59 eV, the constructive region is broader and the induced density displays the clearest two hemisphere separation across the full cage, giving the strongest qualitative molecular plasmon-like signature of the selected modes. At 6.89 eV, a few near-diagonal features dominate and the density is again more locally modulated, so the response is predominantly single-particle-like.

The direct comparison of Figures 3d and 3e explains the spectral intensity difference. At 4.53 eV, the TCM contains both positive and negative contributions, indicating partial cancellation among different electron-hole transitions. This cancellation reduces the net dipole even though several electron-hole pairs participate. Its induced density is correspondingly less uniform, with a hemispheric component superimposed on smaller cage-scale modulations. In contrast, at 5.59 eV, constructive contributions extend over a wider range, while the destructive signal becomes weaker. The induced density forms a clearer positive-negative separation across the cage. Such enhanced coherent addition accounts for the largest absorption peak in Figure 3a and corroborates the assignment of the 5.59 eV mode to the strongest molecular plasmon-like component among those examined excitations.

The selected C_{240} modes also contain collective contributions, but their character differs from the Na_{20} -derived response. In C_{240} , delocalized π electrons are constrained by molecular symmetry and discrete level structure, so collective polarization and individual orbital transitions are strongly mixed. The comparison is therefore between degrees and spatial patterns of collectivity, not between a classical metal plasmon and purely molecular single-particle excitations.

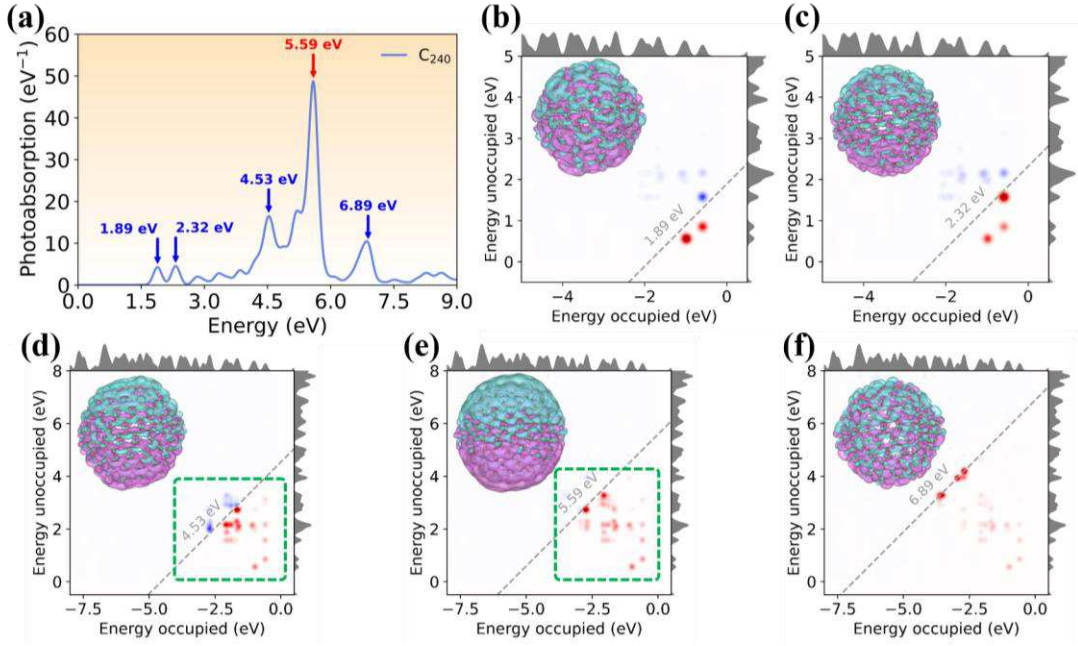


Fig. 3 Frequency-domain response of the frozen C_{240} shell. (a) Photoabsorption spectrum from 0 to 9 eV. The red arrow marks the strongest peak at 5.59 eV, blue arrows mark the 1.89, 2.32, 4.53, and 6.89 eV features selected for comparison. (b-f) TCMs and induced densities at (b) 1.89, (c) 2.32, (d) 4.53, (e) 5.59, and (f) 6.89 eV. Panels b and c show relatively sparse transition participation, panel d contains competing constructive and destructive channels, panel e combines broad constructive participation with the clearest hemispheric dipolar separation, panel f is concentrated more closely around discrete near-resonant transitions.

To examine how the two C_{240} resonances evolve after a finite pulse, we compare 4.53 and 5.59 eV excitation in Figure 4. In both cases the induced dipole moment persists and displays an amplitude envelope produced by beating among discrete frequencies. For 4.53 eV (Figure 4a), the envelope nearly collapses after the initial response and subsequently revives around the later times, producing a visibly irregular sequence. For 5.59 eV (Figure 4c), the dipole is stronger and remains appreciable across the simulated window, although its envelope also modulates. The denser set of participating C_{240} transitions makes these beats less regular than in the small Na_{20} fragment.

The stored-energy traces provide a model-internal diagnostic. At both excitation energies, the total electronic energy rises during the pulse and then remains constant because the propagation contains no explicit dissipative bath. The resonant term contains most of this conserved total after the pulse, while the non-resonant and H_{XC} components continue to oscillate. At 4.53 eV, these two collective response diagnostics are comparatively small. At 5.59 eV, they are visibly larger over much of the trajectory and exchange weight with the resonant component. Because resonant and non-resonant terms are present already during the pulse, the response is mixed from the outset rather than undergoing a sequential conversion of an initially pure plasmon. Furthermore, the larger non-resonant and H_{XC} participation at 5.59 eV supports a stronger molecular plasmon-like component than at 4.53 eV.

The snapshots in Figures 4b and 4d show how the time traces are expressed microscopically. The resonant contributions are already present at early times. As the propagation proceeds, weight is redistributed between non-resonant and resonant electron-hole channels while the induced density retains oscillatory dipolar structure. Multiple diagonal and off-diagonal TCM features remain visible throughout. The synchronized changes in density sign, TCM weight, H_{XC} energy, and dipole envelope demonstrate coherent redistribution among KS transition channels. They do not establish irreversible thermalization or an experimental hot-carrier lifetime.

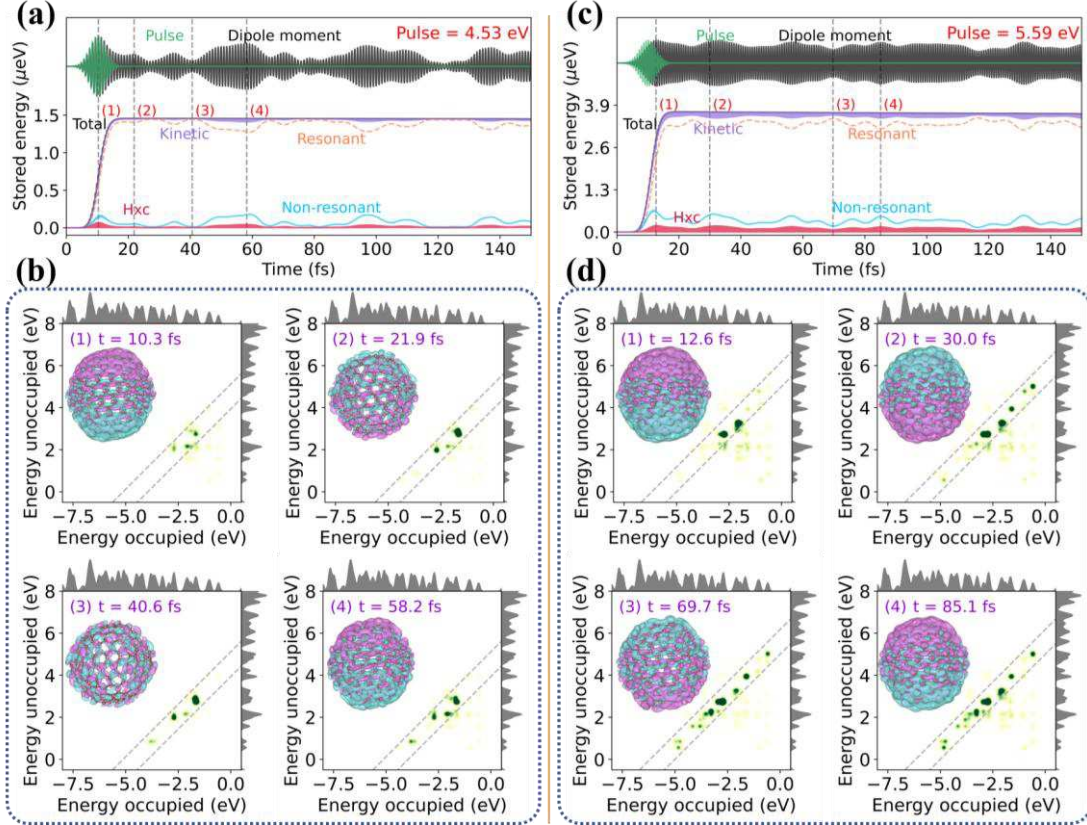


Fig. 4 Coherent time-domain response of the frozen C_{240} at two representative resonances. (a) Response to a 4.53 eV Gaussian pulse. The upper trace shows the pulse and induced dipole, and the lower trace shows total, kinetic, H_{XC} , resonant, and non-resonant stored-energy components. Vertical markers identify $t = 10.3, 21.9, 40.6$, and 58.2 fs. (b) TCMs and induced densities at those times. (c) Corresponding response to a 5.59 eV pulse, with markers at $t = 12.6, 30.0, 69.7$, and 85.1 fs. (d) TCMs and induced densities at those times.

The isolated C_{240} supports several dipole-active excitations with mixed collective and single-particle character. The 5.59 eV feature has the strongest collective contribution among the selected C_{240} resonances, followed by the 4.53 eV feature. These modes provide the high-energy parent response that couples to the Na-derived subsystem in the composite.

3.3 Coherent electronic dynamics in the Na₂₀@C₂₄₀ core-shell nanostructure

Figure 5a shows the calculated Na₂₀@C₂₄₀ spectrum and marks six representative features. Relative to the isolated fragments, the 2.73 eV Na-derived feature is strongly attenuated, the shell-associated peak shifts from 5.59 to 5.70 eV and becomes the dominant composite response, and the surrounding spectral weight is redistributed. These changes are consistent with core-shell screening, orbital hybridization, and Coulomb coupling.

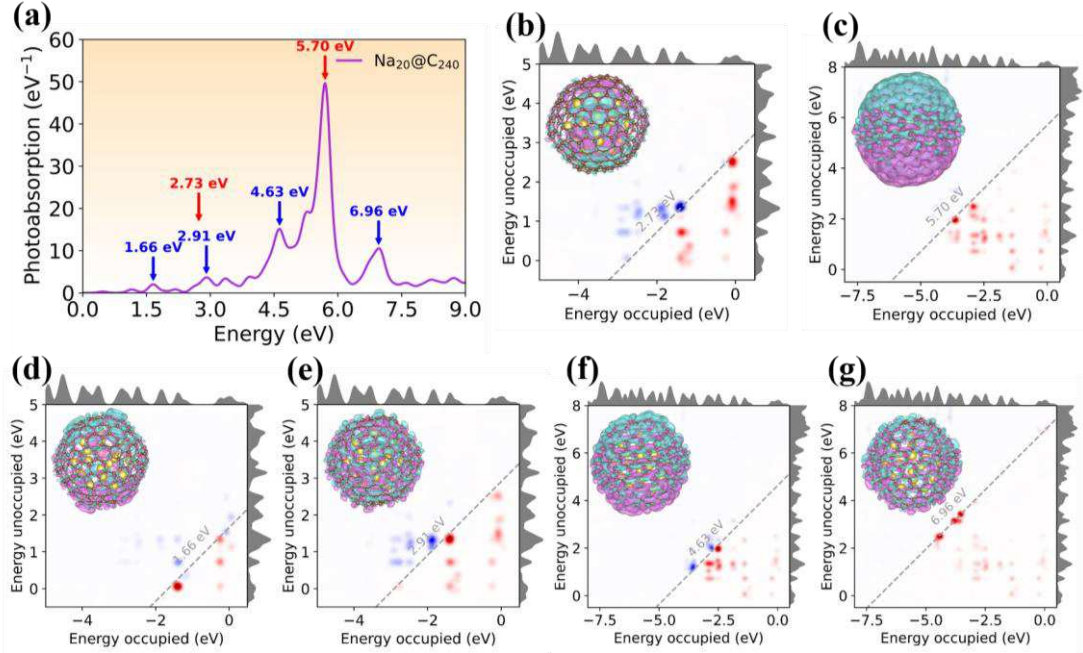


Fig. 5 Frequency-domain optical response of Na₂₀@C₂₄₀. (a) Photoabsorption spectrum from 0 to 9 eV. Red arrows select the 2.73 and 5.70 eV resonances for time-domain analysis, and blue arrows mark additional features at 1.66, 2.91, 4.63, and 6.96 eV. (b-g) TCMs and induced densities at (b) 2.73, (c) 5.70, (d) 1.66, (e) 2.91, (f) 4.63, and (g) 6.96 eV.

Figures 5b-g resolve the microscopic diversity behind the composite spectrum. At 1.66 eV (Figure 5d), the TCM is dominated by a small number of electron-hole pairs and the induced density is spatially mottled over both the core and shell. The 2.91 eV map (Figure 5e) contains a pronounced destructive near-resonant contribution together with several constructive channels, again producing a mixed core-shell density. At 4.63 eV (Figure 5f), constructive and destructive features occupy a broader energy window and the density begins to display a larger-scale shell polarization. At 6.96 eV (Figure 5g), the dominant TCM features lie closer to the resonant diagonal, consistent with a larger single-particle contribution. Across the spectrum, therefore, plasmon-like and single-particle-like components coexist rather than forming a strict monotonic sequence.

The two resonances selected for time propagation show the clearest contrast (Figures 5b-c). At 2.73 eV, the TCM contains strong contributions of both signs: a destructive feature lies near the resonant diagonal while constructive weight is distributed over additional pairs. In real space, the Na-centered density has a dipole-

like component, but the induced density on the inner shell is predominantly opposite in sign on the corresponding side. This antiphase core-shell polarization cancels much of the total dipole and explains why the Na-derived spectral feature is weak in Figure 5a. At 5.70 eV, constructive contributions extend over numerous C₂₄₀-like pairs and the induced density forms a much clearer hemispheric separation across the cage. The weaker Na response is predominantly in phase, producing a bright shell-dominated mode. In plasmon hybridization language, there are an antiphase screened branch and an in-phase bright branch.^{16, 69-70} We refrain from assigning a simple bonding-antibonding eigenpair, as the parent responses are not a near-degenerate two-mode basis and the composite states are strongly mixed with molecular and potential charge transfer channels.

To identify the fragment origin of the response in Figure 6, we employed the Voronoi-based transition projections implemented in RHODENT. In this scheme, the atomic Voronoi cell is defined as the region of space closer to a given atom than to any other atom. For fragment A, where A denotes either Na₂₀ or C₂₄₀, the union of the corresponding atomic Voronoi cells defines the spatial domain Ω_A . The projection weight of the KS orbitals is then

$$w_{nn'}^A = \int_{\Omega_A} \psi_{n'}^*(\mathbf{r}, 0) \psi_n(\mathbf{r}, 0) d\mathbf{r}. \quad (4)$$

At frequency ω , let $S_{ia}(\omega)$ denote the signed contribution of the occupied-to-unoccupied transition $i \rightarrow a$ to the absorption TCM, as obtained from the transition dipole and the Fourier transformed electron-hole density matrix. Positive and negative values correspond to constructive and destructive contributions, respectively. Figure 6 uses the one-sided occupied-state projection

$$T_A^{\text{occ}}(\varepsilon_{\text{occ}}, \varepsilon_{\text{unocc}}; \omega) = \sum_{i,a}^{f_i > f_a} w_{ii}^A S_{ia}(\omega) G_{\sigma}(\varepsilon_{\text{occ}} - \varepsilon_i) G_{\sigma}(\varepsilon_{\text{unocc}} - \varepsilon_a), \quad (5)$$

where G_{σ} is the Gaussian broadening function; the same $\sigma = 0.10$ eV is used for all maps. The signed fragment share reported in Figure 6 is

$$C_A^{\text{occ}}(\omega) = 100\% \frac{\sum_{i,a}^{f_i > f_a} w_{ii}^A S_{ia}(\omega)}{\sum_{i,a}^{f_i > f_a} S_{ia}(\omega)}. \quad (6)$$

Because the denominator is the signed total response, $C_A^{\text{occ}}(\omega)$ is not a probability and may lie outside $\pm 100\%$ when constructive and destructive fragment contributions cancel. Importantly, the factor w_{ii}^A is applied only to the occupied, hole-side state. The present projection therefore identifies the spatial origin of the occupied-state component of the optical response, but not the destination of the excited electron.

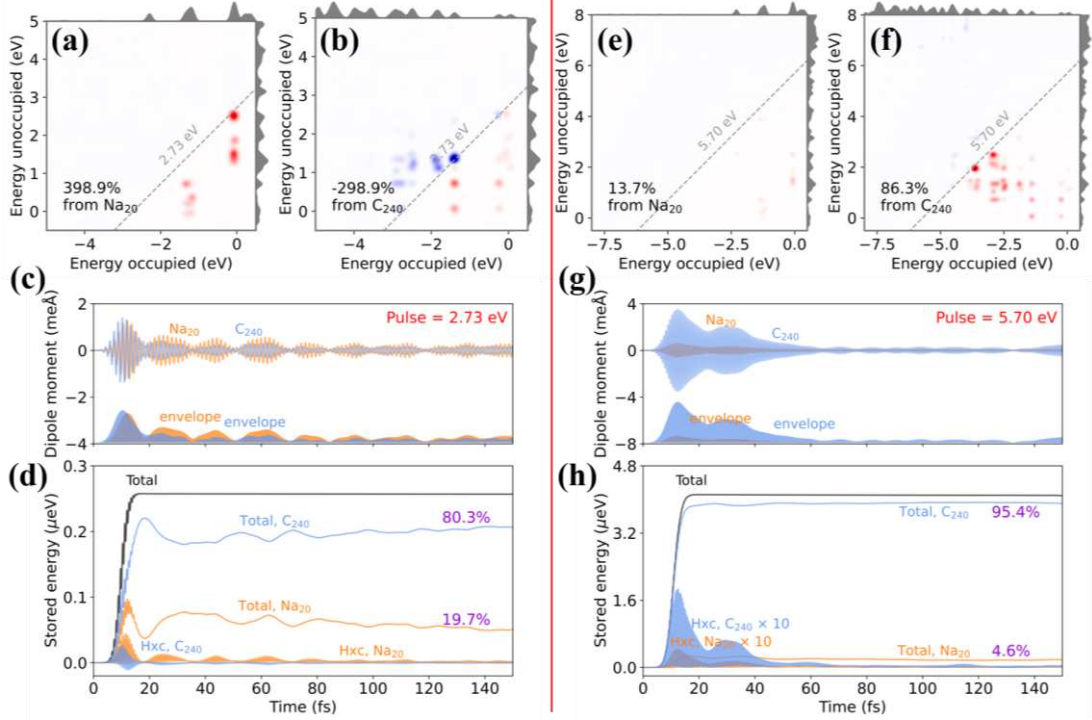


Fig. 6 Fragment-projected response of $\text{Na}_{20}@\text{C}_{240}$ at 2.73 and 5.70 eV. (a-b) One-sided TCM projections at 2.73 eV in which each signed transition contribution is weighted only by the occupied-state Voronoi character on (a) Na_{20} or (b) C_{240} . (c) Na_{20} - and C_{240} -projected dipole traces after 2.73 eV excitation, shaded Hilbert-transform envelopes emphasize their relative amplitudes and antiphase beating. (d) Corresponding fragment-partitioned total and H_{XC} stored energies. (e,f) Occupied-origin TCM projections at 5.70 eV. (g) Projected dipoles at 5.70 eV, where the C_{240} envelope dominates and the Na_{20} component is weak. (h) Fragment-partitioned total and H_{XC} stored energies. The H_{XC} traces are multiplied by 10 only for visibility.

At 2.73 eV, Figure 6a contains a large constructive Na-origin contribution, whereas Figure 6b contains a comparably large destructive C-origin contribution. Their normalization by the small residual total gives 398.9% and -298.9%, and they are neither probability nor independently measurable fragment observable. At 5.70 eV, Figures 6e-f show the opposite amplitude hierarchy. The Na-origin TCM is weak on the common scale, and the C-origin map retains the visible transition pattern, giving signed shares of 13.7% and 86.3%.

The time traces in Figures 6c-d provide an independent view of the 2.73 eV cancellation. The Na_{20} and C_{240} dipoles have comparable early-time envelopes but oscillate predominantly out of phase. Their sum is therefore much smaller than either signed component, and both envelopes show later beating. After their early oscillatory exchange, the chosen Voronoi partition assigns 80.3% of the late-time stored electronic energy to C_{240} and 19.7% to Na_{20} . At 5.70 eV (Figures 6g-h), the C_{240} dipole envelope is much larger than the Na_{20} envelope and the C_{240} total energy quickly becomes dominant, yielding a late-time C_{240} partition of 95.4%. The H_{XC} curves, displayed at tenfold scale in Figure 6h, remain small and oscillatory after the pulse.

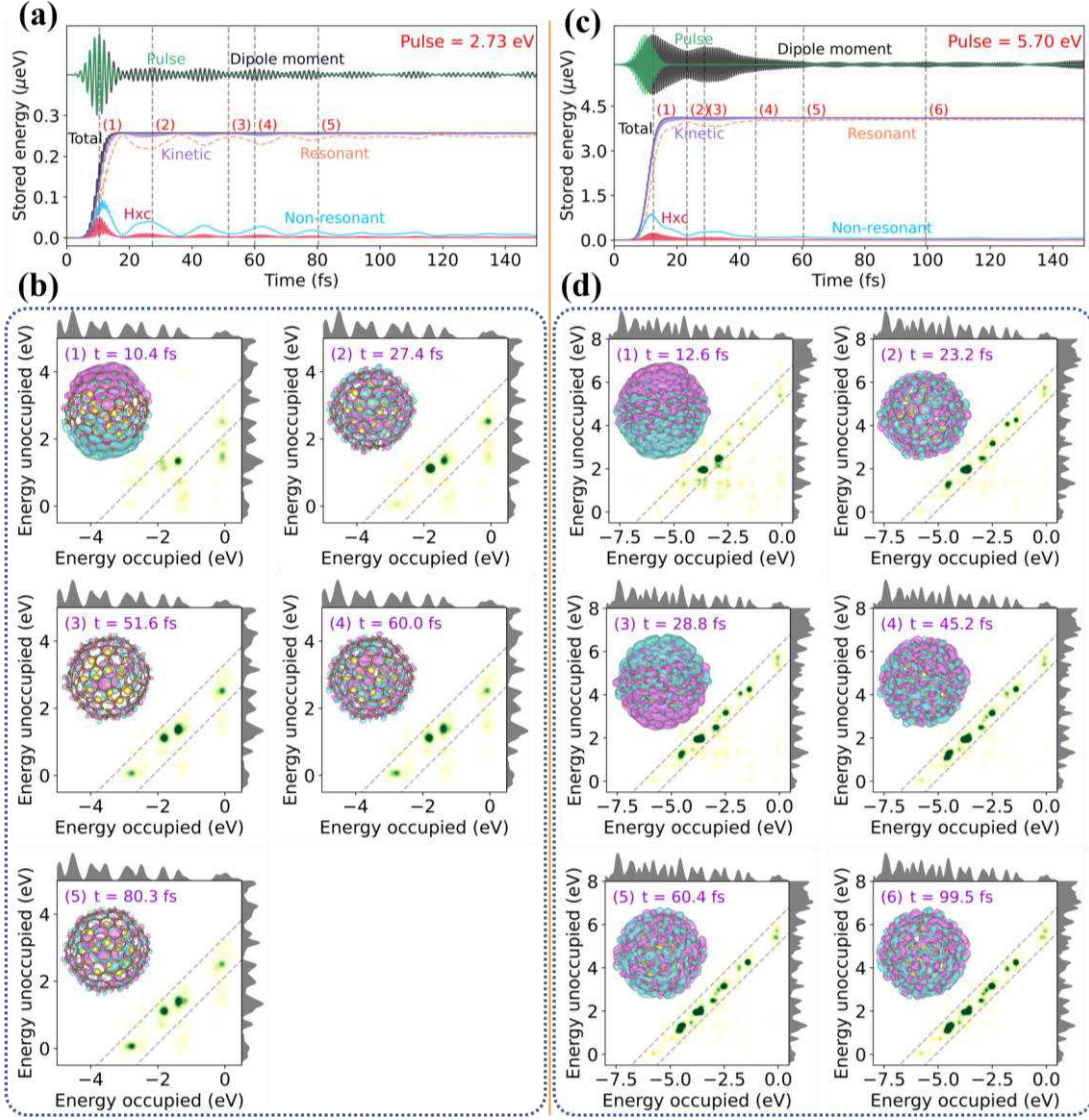


Fig. 7 Coherent time-domain response of $\text{Na}_{20}@\text{C}_{240}$ at 2.73 and 5.70 eV. (a) Following the 2.73 eV Gaussian pulse, the upper trace shows the pulse and total induced dipole, and the lower trace shows total, kinetic, H_{XC} , resonant, and non-resonant stored energies. Vertical markers select $t = 10.4, 27.4, 51.6, 60.0$, and 80.3 fs. (b) TCMs and induced densities at those times. (c) Corresponding 5.70 eV response, with selected times $t = 12.6, 23.2, 28.8, 45.2, 60.4$, and 99.5 fs. (d) TCMs and induced densities at those times.

Figure 7 compares the total dynamics without imposing a fragment partition. Under 2.73 eV excitation (Figure 7a), the H_{XC} and non-resonant energies rise together with the resonant term during the pulse, confirming that the screened composite response is hybridized from its formation. After about 20 fs, the resonant energy accounts for most of the conserved total, whereas the H_{XC} and non-resonant components display smaller revivals. The total dipole correspondingly loses its initial envelope but retains weak oscillations. Under 5.70 eV excitation (Figure 7c), the deposited energy is much larger on the plotted scale, the resonant term becomes dominant rapidly, and the H_{XC} and non-resonant components fall to small residual values after their early maxima. The dipole envelope decays strongly over the first

several tens of femtoseconds and then exhibits weak late-time recurrence. In this closed mean-field model, these changes diagnose coherent loss of macroscopic polarization and redistribution toward resonant nonthermal occupations, not irreversible dissipation.

The snapshot sequences in Figures 7b and 7d provide a spatial and transition-resolved view of the same process. At 2.73 eV, the 10.4 fs density contains a pronounced but spatially mixed core-shell dipole. At 27.4 fs the sign pattern has reversed and multiple TCM spots contribute both within and outside the resonant band. The 51.6, 60.0, and 80.3 fs snapshots retain a complex core-shell density while the strongest TCM intensity becomes progressively concentrated in a few near-resonant features, and smaller off-band features track the energy revivals. At 5.70 eV, the early 12.6 fs density is nearly hemispheric over the shell. The 23.2 and 28.8 fs maps show rapid sign reversal and local modulation, while the later 45.2, 60.4, and 99.5 fs maps remain shell distributed with evolving phase. Their TCMs form a sequence of strong spots along the near-resonant band plus weaker surrounding contributions.

3.4 Hot-carrier distributions and excitation-energy-dependent localization in $\text{Na}_{20}@\text{C}_{240}$

Figure 8 reports hot-carrier distributions calculated by post-processing the RT-TDDFT density matrices. The physical quantities are nonthermal KS occupation changes. The hole distribution records depletion in the occupied state block, whereas the electron distribution records population in the unoccupied state block, with energies referenced to the Fermi level. The plotted distributions describe internal occupation changes produced by the finite pulse, not absolute carrier yields, Fermi-Dirac temperatures, or populations already extracted into an external acceptor.

The energy-resolved curves in Figures 8a and 8d are visibly structured rather than thermal. For 2.73 eV excitation, discrete hot-hole peaks below the Fermi level are accompanied by electron peaks mainly within a few electronvolts above it. Corresponding structures are separated approximately by the photon energy but do not form a rigidly shifted copy because the pulse has finite bandwidth and the composite levels are hybridized and discrete. The 5.70 eV pulse accesses a substantially broader energy window, producing multiple hole and electron peaks over most of the plotted range and a larger vertical scale. The gray curves above the panels are the ground-state densities of states and indicate where available KS levels support the occupation changes. In the present closed-system sense, these curves quantify energy-resolved nonthermal electron-hole populations generated during coherent plasmon dephasing.

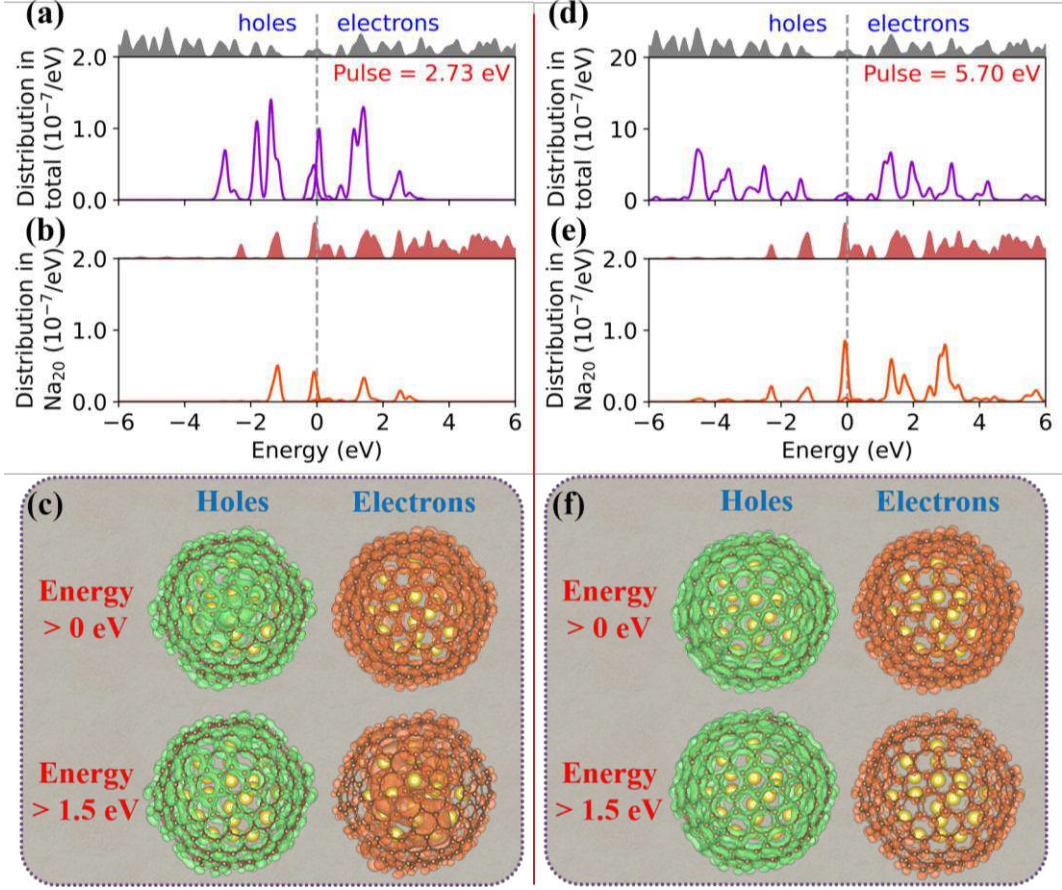


Fig. 8 Energy- and real-space hot-carrier distributions. (a) Total hot-hole and hot-electron distributions after 2.73 eV excitation. The gray curve above the axis is the total density of states. (b) Corresponding Na_{20} -projected distributions, with the Na_{20} -projected density of states in red above the axis. (c) Spatial distributions of the corresponding electron and hole occupation weights for thresholds of 0 and 1.5 eV relative to the Fermi level. The isovalues are 3×10^{-11} and 2×10^{-11} a.u., respectively. (d) Total hot-hole and hot-electron distributions after 5.70 eV excitation. (e) Corresponding Na_{20} -projected distributions. (f) Spatial distributions of the corresponding electron and hole occupation weights for thresholds of 0 and 1.5 eV relative to the Fermi level. The isovalue is 2.5×10^{-10} a.u. for all panels.

Figures 8b and 8e isolate the Na_{20} -weighted portions of the same distributions. At 2.73 eV, the Na-projected signal contains pronounced hole features below the Fermi level and smaller electron features above it, showing that the low-energy screened mode retains substantial Na character on the occupied side. At 5.70 eV, the Na-projected curves remain much smaller than the total curves and consist of several narrow features, consistent with a predominantly shell-driven excitation with residual hybridized Na character. The red curves above these panels are the Na-projected densities of states and help locate the KS energy regions that carry Na weight. Because hot holes and hot electrons are projected from different density-matrix blocks, unequal integrated Na weights are not by themselves a time-dependent net charge.

The real-space maps in Figures 8c and 8f complement the energy curves. When all states beyond the Fermi boundary are included (0 eV threshold), both the hole and electron isosurfaces extend over the cage. However, the hole maps exhibit more

pronounced and spatially continuous weight inside the cage than the corresponding electron maps, particularly under 2.73 eV excitation. This observation is consistent with the stronger Na_{20} -projected hole features in Figure 8b, although the interior density should not be interpreted as being exclusively localized on Na because the core and shell states are hybridized. The electron density at this threshold is comparatively concentrated on the carbon cage. Applying the 1.5 eV threshold removes contributions from states close to the Fermi level and produces a more energy-selective spatial pattern. The remaining hole density is distributed predominantly over the cage, whereas the high-energy electron maps retain more pronounced interior region features for the 2.73 eV excitation. The threshold dependence therefore suggests that a substantial part of the interior hole weight originates from occupied states relatively close to the Fermi level, while interior electron character persists within the higher-energy unoccupied manifold. Under 5.70 eV excitation, shell-distributed character remains substantial for both carrier types, consistent with the shell-dominated optical response.

Figure 9 shows the hot-carrier distributions as a function of pulse frequency from 2.5 to 6.0 eV. On the logarithmic vertical scale, the black curve representing the full-system carrier population, exhibits a local maximum near 2.8 eV, decreases to a broad minimum around 3.7 eV, and subsequently rises to its global maximum near 5.6 eV. The low- and high-energy enhancements approximately coincide with the Na-derived screened response and the shell-dominated bright resonance, respectively. The orange Na -projected electron and cyan Na -projected hole curves are both one to two orders of magnitude below the total because they contain only the Na-weighted part of the composite occupations. At the low-energy edge, the Na-projected hole weight is larger. The curves cross near 2.87 eV, after which the Na-projected electron weight is generally larger.

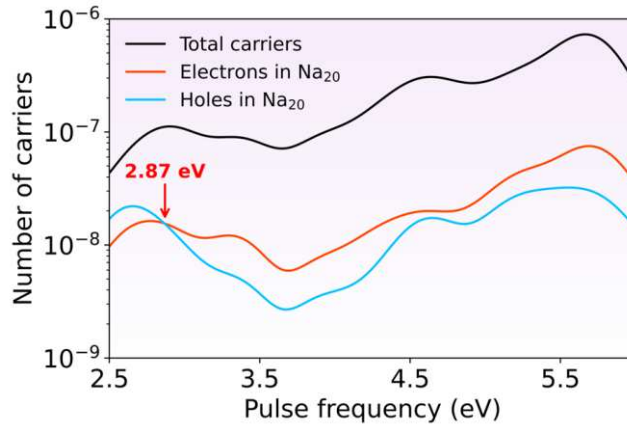


Fig. 9 Hot-carrier weights as functions of pulse frequency from 2.5 to 6.0 eV. The black curve is the full-system electron-hole population, while the orange and cyan curves are the Na_{20} -projected electron and hole weights, respectively.

Above approximately 4 eV, both Na-projected curves increase with the total response, but the electron curve follows the total more closely and reaches the larger high-energy maximum. This behavior is consistent with broader Na character among the unoccupied states sampled by the pulse than among the depleted occupied states. Importantly, the black curve is the full-system carrier population and is not the sum of the two Na-projected curves. Their crossover near 2.87 eV therefore indicates a change in the relative localization of Na-projected electrons and holes, rather than zero net charge transfer or a reversal of the charge-transfer direction.

4. Conclusions

We employed adiabatic RT-TDDFT to investigate the optical response and post-pulse electronic dynamics of $\text{Na}_{20}@\text{C}_{240}$, using the frozen Na_{20} and C_{240} fragments extracted from the optimized composite as reference systems. By combining photoabsorption spectra, TCMs, induced charge densities, time-dependent stored-energy decompositions, and fragment-projected hot-carrier distributions, we established a unified transition-space, real-space, and time-domain description of the coupled core-shell response.

For the isolated Na_{20} fragment, the dominant 2.73 eV feature contains a significant dipole-active, finite-size plasmon-like collective component. Its distributed TCM contributions and cluster-scale dipolar induced density distinguish it from a purely localized single-particle transition. Nevertheless, the discrete electronic structure of Na_{20} and the possible fragmentation of its oscillator strength preclude interpreting this feature as a unique classical LSPR. The C_{240} supports excitations of mixed collective and single-particle character. Among the investigated C_{240} modes, the 5.59 eV resonance displays the clearest molecular plasmon-like signature, as indicated by its comparatively broad constructive transition participation and shell-scale dipolar polarization.

Encapsulation substantially modifies these parent responses. At 2.73 eV, the Na-centered plasmon-like polarization induces an oppositely phased response on the C_{240} shell, leading to strong cancellation and suppression of the total dipole. At 5.70 eV, the response is dominated by an in-phase, shell-localized bright polarization, with only a weak Na contribution. These contrasting phase relations demonstrate that the optical response of $\text{Na}_{20}@\text{C}_{240}$ cannot be understood as a simple superposition of the isolated-fragment spectra. Instead, it emerges from the combined effects of electrostatic screening, orbital hybridization, intercomponent Coulomb coupling, and the ground-state electronic structure of the composite. The time-domain analysis further reveals coherent plasmon dephasing and redistribution of electronic energy from Coulomb-coupled collective motion toward near-resonant KS electron-hole channels. Because the simulated system is finite and electronically closed, this redistribution is accompanied by beating and partial recurrence rather than irreversible relaxation. At the end of the propagation window, both the partitioned stored energy and the

nonthermal hot-carrier distributions are concentrated predominantly on C₂₄₀, particularly under 5.70 eV excitation. The crossover between the Na-projected electron and hole weights near 2.87 eV provides an excitation-energy-dependent localization descriptor. However, it does not by itself establish a reversal of net interfragment charge transfer.

Overall, this work demonstrates how the excitation energy can tune the phase relationship, spatial localization, and transition-channel composition of the plasmon-associated electronic response in an atomically defined simple-metal@carbon nanostructure. The present results therefore provide a microscopic basis for selecting excitation energies that selectively excite core-derived or shell-dominated response channels. Such excitation-energy control may help guide the design of endohedral fullerene-based and related core-shell nanostructures in which optical energy is preferentially localized within a selected spatial region or electronic subsystem.

Authors contributions

Y. F conceived the idea and directed the project. H. L and N. G did DFT and TDDFT calculations. H. L and Y. F analyzed the data and wrote the manuscript. All the authors revised the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration

The Artificial Intelligence GPT-5.6 model was employed to assist with grammatical improvement, expression optimization and textual consistency polishing. No artificial intelligence tool was used to generate core scientific conclusions and data processing.

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