Attosecond tracking of light absorption and refraction in fullerenes

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The collective response of matter is ubiquitous and widely exploited, e.g. in plasmonic, optical and electronic devices. Here we trace on an attosecond time scale the birth of collective excitations in a finite system and find distinct new features in this regime. Combining quantum chemical computation with quantum kinetic methods we calculate the time-dependent light absorption and refraction in fullerene that serve as indicators for the emergence of collective modes. We explain the numerically calculated novel transient features by an analytical model and point out the relevance for ultra-fast photonic and electronic applications. A scheme is proposed to measure the predicted effects via the emergent attosecond metrology.

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I. INTRODUCTION

The last decade has witnessed the emergence of the attosecond science opening a window on sub-femtosecond processes that take place in atoms and molecules [1–4] (see Refs. [5–8] for reviews). Increased interest is currently focused on many-body effects and condensed matter systems [9–11] where many degrees of freedom may interfere. The hallmark of extended systems is the collective, dielectric linear response [12] that determines for example the light propagation [13,14] and the energy and momentum loss of traversing charged particles [15,16]. On a fundamental level, the dielectric response describes how the particles cooperatively act as to screen the interparticle Coulomb interaction. Obviously, this collective motion builds up on a time scale on which the effective interparticle interaction changes qualitatively (even in sign) [17]. This was impressively demonstrated by terahertz spectroscopy for a semiconductor-based electron-hole plasma [18] evidencing that the electron-electron interaction develops from its unscreened to a fully screened form on a time scale of the order of the inverse plasma frequency (several femtoseconds). This collective response is marked by a giant plasmon absorption peak of order of the inverse plasma frequency (several eV) [24] that was investigated experimentally [20,21]. Also C60 is readily available, very stable, and has an ionization potential of ≈7.5 eV and an electron affinity of 2.2 eV. It also exists in a well-studied crystalline form (fullerite) [23]. The collective response is marked by a giant plasmon resonance at ≈ 22 eV [24] that was investigated experimentally in the solid [25,26] and the gas phase [27]. Considerable efforts were devoted to clarify quantitatively the experiments [28,29]. It was not until recently however that the existence of a second plasmon peak at higher energy (≈39 eV) but with a lower oscillator strength was experimentally confirmed [30,31]. Theoretically, the presence of two collective modes follows from a classical dielectric shell model [32,36]. The quantitative description, as we are seeing here, is a challenging task, however. Quantum mechanical approaches utilize either the tight-binding (TB) model for the valence electrons [24] or the jellium shell model [31,37,39]. The linear response to an external electric field is calculated either using

that at a time \( t = 0 \) an XUV attosecond pulse ionizes C60 and the change in the absorption at a time delay \( \tau_D \) thereafter is recorded, as sketched in Fig. 1. For negative \( \tau_D \), we obtain the absorption of C60 and for large (few femtoseconds) \( \tau_D \), we expect the steady-state absorption of C60. Equilibration in the limit \( t \rightarrow \infty \) proceeds via electronic, plasmonic and finally ionic channels, each having a distinct time scale; the ions are frozen at the \( \alpha_s \) timescale. We focus on the plasma frequency \( (\omega_p) \) regime where the absorption and refraction show strong modulations [22]. The change of \( \omega_p \), for \( t > 0 \) is evident from a qualitative consideration of the square root dependence on the density: The valence band of C60 accommodates 240 electrons (originating from the 2s and 2p states of each carbon atom) that form 180 \( \sigma \)-type and 60 \( \pi \)-type molecular orbitals [20]. The highest occupied molecular orbital (HOMO) is five-fold degenerate. Its complete depletion by the XUV pulse reduces the number of particles by 4%, or red-shifts the collective response by 2%. As theoretically quantified below, even a single-photoionization event has a significant impact on the plasmon dynamics.

II. THEORETICAL FORMULATION

C60 has a size below 1 nm [21], its electronic and optical properties for \( t < 0 \) and \( t \rightarrow \infty \) are well-documented [20,21]. Also C60 is readily available, very stable, and has an ionization potential of \( \approx 7.5 \) eV and an electron affinity of 2 eV. It also exists in a well-studied crystalline form (fullerite) [23]. The collective response is marked by a giant plasmon resonance at \( \approx 22 \) eV [24] that was investigated experimentally in the solid [25,26] and the gas phase [27]. Considerable efforts were devoted to clarify quantitatively the experiments [28,29]. It was not until recently however that the existence of a second plasmon peak at higher energy (\( \approx 39 \) eV) but with a lower oscillator strength was experimentally confirmed [30,31]. Theoretically, the presence of two collective modes follows from a classical dielectric shell model [32,36]. The quantitative description, as we are seeing here, is a challenging task, however. Quantum mechanical approaches utilize either the tight-binding (TB) model for the valence electrons [24] or the jellium shell model [31,37,39]. The linear response to an external electric field is calculated either using
the random phase approximation (RPA) for the polarization propagator \( \chi \) (in the case of the TB \[24\] and some of the density-functional-based (DFT) models \[38,39\]), or by implementing the time-dependent DFT (TDDFT) \[31,32,40\]. Until now TDDFT seems to deliver the best agreement with experiments, however, the theory describes correctly either the presence of the high energy plasmon resonance or, with the help of an adjustable parameter, the position of the lower energy plasmon resonance \[31,40\]. Here we develop an approach that rests on three steps: 1. We utilize quantum chemical ab-initio techniques to capture accurately the stationary, single-particle electronic structure. 2. These states are expressed in a basis appropriate for many-body calculations which we perform within the linear response theory (i.e., the random phase approximation) to obtain the steady-state collective response. 3. With both quantities at hand we perform quantum kinetic calculations within the density matrix formalism to formalize the time and the frequency dependent polarizability \( \alpha(E, t = \tau_0) \). The imaginary and the real part of \( \alpha(E, t) \) deliver then respectively the time-dependent absorption and refraction properties of the sample \[22\].

We showed recently \[41,43\] that the wave function \( \Psi_n(\vec{r}) \) of the valence band electrons with an energy \( \epsilon = \epsilon_{nl} \), as obtained from first principle calculations, is expressible to a good approximation as a product of a radial part \( R_n(r) \) (having \( n - 1 \) nodes) and an angular part described by spherical harmonics \( Y_{lm}(\Omega) \) with \( l, m \) being the orbital and magnetic quantum numbers \( \vec{r} \equiv (r, \Omega) \) identifies the electron position, cf. Ref. \[44\] \[38,41\]. This procedure is shown \[41\] to be valid for C\(_{48}\)N\(_{12}\), B\(_{85}\), C\(_{60}\), C\(_{240}\), C\(_{540}\), C\(_{200}\)H\(_{20}\), and Au\(_{24}\). Thus, the theory presented below is readily applicable to these systems; for the sake of clarity the discussion is restricted to C\(_{60}\), however. For C\(_{60}\) the two occupied radial subbands \( \epsilon_{n=1} \) and \( \epsilon_{n=21} \) are separated by approximately 17.5 eV. The HOMO-LUMO gap as determined by our ab-initio calculations \( E_g \approx 5.5 \) eV as well as some structural information are encapsulated in the energy spectrum \( \epsilon_{nl} \) (cf. \[44\]). These data allow us to perform the mapping of the unperturbed system to the single-particle Hamiltonian \( \hat{H}_0 \) with the states \( \phi_{nl} \equiv \phi_{nlm} = R_n(r)Y_{lm}(\Omega) \) and the spectrum \( \epsilon_{nl} \). These single particle states are then taken as the basis to express the density operator \( \hat{\rho} \). Our theoretical description of the charge dynamics is based on the resulting density matrix \( \rho \).

We are interested in two types of external perturbations \( \hat{V}^{\text{ext}} \) that trigger the evolution: (i) a broad band, low-intensity light pulse probing the plasmonic response and (ii) a sudden change in the population upon a single ionization of C\(_{60}\) by the attosecond XUV pulse. Formally, the latter change is described by a time-dependent occupation function \( f_{nl}(t) \). To simulate the plasmonic response, we employ the Heisenberg equation of motion for the density matrix \( \hat{\rho} \), the mean-field approximation and the linear response to the external driving. The relaxation within a time \( \tau \) due to collisions we treat within the particle-conserving relaxation time approximation \[45\]. This approach has been successfully tested for a variety of systems \[18,46,49\]. It should be emphasized, however, that we are interested in the dynamics at times much shorter than \( \tau \). The equation of motion for \( \hat{\rho} \) reads as

\[
\frac{\partial \hat{\rho}}{\partial t} + \frac{i}{\hbar} \left[ \hat{H}_0 + \hat{V}^{\text{ind}} + \hat{V}^{\text{ext}}, \hat{\rho} \right] = \frac{\hat{\delta}^\text{e.c} - \hat{\rho}}{\tau}.
\]

The induced potential \( \hat{V}^{\text{ind}} \) has to be determined self-consistently from the induced charge density as derived from the change in the density operator \( \hat{\rho} \) [to find \( \hat{\rho} \) we need \( \hat{V}^{\text{ind}} \) in Eq. \[1\]]. \( \hat{\delta}^{\text{e.c}} \) is the local equilibrium density operator. The corresponding locally relaxed density \( \hat{\rho}^{\text{re}}(r, t) \) is the distribution that, at any given instant, would be in equilibrium in the presence of \( \hat{V}^{\text{ext}} \) and \( \hat{V}^{\text{ind}} \) while satisfying the charge conservation \[45\]. Technically, we express \( \hat{\rho} \) in the basis \( \{ \phi_n(\vec{r}) \} \) and expand to first order around the equilibrium, i.e. \( \rho_{\alpha\beta}(t) = \langle \alpha | \hat{\rho}(t) | \beta \rangle = f_\alpha(t)\delta_{\alpha\beta} + \delta\rho_{\alpha\beta}(t); \quad \rho_{\alpha\beta}^{\text{re}}(t) = \langle \alpha | \hat{\rho}^{\text{re}}(t) | \beta \rangle = f_\alpha(t)\delta_{\alpha\beta} + \pi^\text{re}_{\alpha\beta}(t)\delta_{\mu\alpha\beta}(t) \), where \( \pi^\text{re}_{\alpha\beta}(t) = \frac{\delta\rho_{\alpha\beta}(t) - f_\alpha(t)\delta_{\alpha\beta}}{\epsilon_{\alpha\beta} - \epsilon_{\epsilon}} \) and \( \delta_{\epsilon\epsilon} \) is the matrix corresponding to the local chemical potential (full details are given in Appendix[A]).

Application of an external linearly-polarized electric field with an amplitude \( E_0 \), polarization direction \( \vec{e} \), and frequency \( \omega \), that corresponds to \( \hat{V}^{\text{ext}}(t) = -e\vec{r} \cdot \vec{e} E_0 e^{-i\omega t} \) (\( e \) is the electron charge), leads to the change of the density matrix \( \delta\rho(t) \) which in linear response is governed by the two-times response function \( \chi(t, t') \), i.e. \( \delta\rho(t) = \int_{-\infty}^t dt' \chi(t, t') \hat{V}^{\text{ext}}(t') \). The induced dipole moment derives from \( \tilde{\hat{P}}(t) = \text{Tr} [\vec{e}\delta\hat{\rho}(t)] \). For spherical molecules, reducing all quantities to their radial components, we find (see Appendix[B])

\[
P(t) = -\frac{4\pi}{3} e^2 E_0 \int_{-\infty}^t dt' \, \vec{r}^T \chi(t, t') \vec{r} e^{-i\omega t'},
\]

where the elements of \( \vec{r} \) are \( r_{n+1} = r_{n+1} = \langle \vec{r} | r \rangle \). Introducing the dimensionless, Fourier-transformed response function \( \hat{\chi} = \hat{\rho} / \rho_0 \) (\( \rho_0 \) is the fullerene average radius and \( \epsilon_0 \) is the vacuum permittivity)

\[
z(\omega, t) = \frac{e^2}{3\epsilon_0 r_0} \int_0^\infty dt' \, e^{i\omega t'} \chi(t, t - \tau) \tau^4,
\]

we find

\[
P(\omega; t) = -4\pi r_0^3 \epsilon_0 E_0 e^{-i\omega t} \vec{r} \cdot z(\omega, t).
\]
density in two different radial channels are still coupled via the interband components can be then neglected when calculating to \(\alpha\) by one. On the same approximation level Eq. (3) simplifies analytically for ,,spherical" molecules) we find that the intraband components are hardly influenced by the interband components and the induced fields like in concentric nanoshells \([50]\).

For an insight into the numerical results we construct an analytical model based on the following: For C\(_{60}\) (and generally for \(\alpha\) a.u.) (a) we included in Appendix A. In such a consideration the dynamics of the electron states in the same subband having the value of \(l\) is the number of electrons in the \(n\)-th radial subband and the unoccupied \(N\) band. For C\(_{60}\), calculation of spatial distributions of the induced charge densities \(\rho_{\text{in}}\) and \(\rho_{\text{out}}\) is explicitly defined in Appendix [A]. In this approximation (and with the time-dependent DFT results \([37, 40]\]. There is also a weak low energy contribution at \(\approx 9\) eV. Such structures in the absorption have been attributed to single-electron transitions \([20, 28]\). Our calculated resonance has a collective character and is energetically in the proximity of the single-electron excitations making it difficult for an observation via absorption. As well-established \([22]\), the peaks in the absorption (refraction) are symmetric (antisymmetric) with respect to reflection at the respective central frequency.

The approximation including only intraband collective excitations, i.e. considering the stationary solution of Eq. (4), gives a very good description of the main peak in the spectrum (see Fig. 2), but misses the higher energy plasmon. The last is caused by interband collective excitations (i.e. governed by \(z_{12}\) and \(z_{21}\)) that are still influenced strongly by the interband character and is energetically in the proximity of the single-electron excitations making it difficult for an observation via absorption. As well-established \([22]\), the peaks in the absorption (refraction) are symmetric (antisymmetric) with respect to reflection at the respective central frequency.

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citation is evident. Its radial structure is determined by the
product $R_2(r)R_3(r)$ and has therefore one node located in the
middle of the fullerene cage. The angular dependence of the
modes in and out of the depicted plane is governed by their
dipolar character. The radial structure of the density oscillation
at the main plasmon peak shows a constructive superposition
of the radial electronic radial density of the first $|R_1(r)|^2$
and the second $|R_2(r)|^2$ radial channels that oscillate in phase.
In contrast, we observe an out-of-phase oscillation of the den-
sities in different channels at 9 eV. Both cases are collective
infraband electronic excitations.

IV. TRANSIENT DYNAMICS

Having assessed successfully the steady-state response we
move on to the attosecond transient dynamics. We focus on
the setup shown in Fig. 1. At $t = 0$ the XUV pulse with en-
ergy $\omega > \omega_p$ and a duration $< 100$ as changes the population
swiftly in C$_{60}$ by ejecting one electron. To access the transient
absorption or refraction let us assume the photoelectron is
emitted at $t = 0$ from the second radial band leaving C$_{60}^+$ (we
find similar results for multiple XUV ionization). For all time
moments before the ionization the time-dependent response
$\alpha(E, t < 0)$ is equal to its steady-state value $\alpha_{C_{60}}(E)$ for
C$_{60}$. At $t > 0$ we solve for the dynamics of $\alpha(E, t)$, which for
long times approaches the steady-state value $\alpha_{C_{60}^+}(E)$ for C$_{60}^+$.
The results in Figs. 3(a) and 3(b) illustrate the change in the imaginary (absorption) and real (refraction) parts of the polari-
zability by evaluating $\Delta\alpha(E, t) = \alpha_{C_{60}}(E, t) - \alpha_{C_{60}^+}(E)$.
The transient dynamics shows a rich structure evolving over
approximately 2 fs. For 1 fs the remainder of the vanishing
difference between $\alpha(E, t)$ and $\alpha_{C_{60}^+}(E)$ is still visible
in Figs. 3(a) and 3(b). For $t < 100$ as the response is basic-
ally determined by that of C$_{60}$, i.e., it takes around 100 as
for C$_{60}^+$ to start responding collectively and it attains its full,
steady state response for $t > 1$ fs. The reason of this iner-
tia is the finite mass of the carriers. Three marked general
transient features can be distilled from Fig. 3. The dispersive
hump starting around 200 as is due to the sudden change in
the population (and hence the wide frequency perturbation)
brought about by the shortness of the XUV pulse. Further-
more, in addition to the relaxation to the steady-state response
we observe an oscillatory behavior in time with a certain fre-
cency. This behavior is most obvious around $\omega_p$ (cf. Fig. 3).
The origin of these oscillations is comprehensible from a con-
sideration of the response of the fullerene molecule in the
lowest approximation: As we demonstrated by Eq. (4) the re-
response resembles two coupled damped harmonic oscillators.
For photon frequencies $\omega$ close to the main peak position
the model can even be further simplified and the spectra are
determined approximately by the dynamics of a single driven
damped harmonic oscillator with the frequency correspond-
ing to the main peak position. Hence, the feature in the re-
response we can now understand from the known properties of
the driven, damped harmonic motion. On a short time scale
this dynamics is governed by a combined decay and oscilla-
tions with a frequency around $2\omega_p$, which is clearly observed in
the full-fledge calculations shown in Fig. 3(c) for Im $\alpha(E, t)$
at $E = 24.6$ eV (time period corresponding to $2\omega_p$ is indicated
by a horizontal double-arrow line for comparison). The dyna-
mics of Im $\alpha(E, t)$ for fixed energy $E = 38.8$ eV in the
vicinity of the higher energy peak is contributed to by more
frequencies because the higher energy plasmon is strongly influ-
enced by the main plasmon. However, oscillations correspond-
ing to $2\omega$ are also seen.

V. SUMMARY

We developed a framework for the attosecond collective re-
response in finite systems with spherical symmetry and applied
it to fullerenes. The predicted marked features in the transient
absorption and refraction should be accessible with current at-
tosecond metrology. The discovered attosecond dynamics in
the optical response points to new opportunities for optoelec-
tronic devices at the sub-femtosecond time scale.
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Appendix A: Derivation of the linear response equations

The transient time and energy-dependent polarizability \( \alpha(t,E) \) is governed, to a first order (linear response), by the two-time response function \( \chi(t,t') \). For the determination of \( \chi(t,t') \) we setup a calculational scheme based on the solution of the Heisenberg equation of motion for the density matrix \( \hat{\rho} \) under the influence of the external field \( V_{\mathrm{ext}}^{\nu} \) in the mean-field approximation that leads to Eq. (1). In the basis \( \{ \phi_n \} \) we find the density matrix elements as \( \rho_{nlm,n'l'm'} = \langle nlm|\hat{\rho}|n'l'm' \rangle \). From the change in the density matrix \( \delta \rho_{nlm,n'l'm'} \), we calculate the change in the charge density

\[
\delta n(\vec{r}) = \sum_{lm} \delta n_{lm}(r) Y_{lm}(\theta, \phi),
\]

(A1)

where

\[
\delta n_{lm}(r) = \sum_{n'n''} s_{n'n''}(r) \delta n_{lm}'',
\]

(A2)

\[
s_{n'n''}(r) = R_{n'}(r) R_{n''}(r),
\]

(A3)

\[
\delta n_{lm}''' = \sum_{l'm',l''m''} y^{l'm'}_{lm,l''m''} \delta \rho_{nlm,n'l'm'},
\]

(A4)

\[
y^{l'm'}_{lm,l''m''} = \int d\Omega Y^*_{lm}(\Omega) Y_{l''m''}(\Omega) Y_{l'm'}(\Omega)
\]

\[
\times \left( \frac{(2l'+1)(2l''+1)}{4\pi(2l+1)} \right) C^{lm}_{l'0,l''0} C^{l'm'}_{l''m''}
\]

(A5)

\( C^{lm}_{l'm',l''m''} \) are Clebsch-Gordan coefficients. The change in the charge density determines the induced potential \( V_{\mathrm{ind}} \) leading thus to a self-consistent procedure.

In the basis \( \{ \phi_n \} \) the Heisenberg equation of motion for the density matrix \( \{ \phi_n \} \) reads:

\[
\frac{\partial \rho_{nlm,n'l'm'}(t)}{\partial t} = -\frac{i}{\hbar} \left[ (\varepsilon_{nlm} - \varepsilon_{n'l'm'}) + \frac{\hbar}{\tau} \right] \rho_{nlm,n'l'm'}
\]

\[
-\frac{i}{\hbar} \sum_{n''l''m''} (\rho_{nlm,n'l'm'} V_{nlm,n''l''m''} - \rho_{nlm,n''l''m''} V_{nlm,n'l'm'} + \rho_{nlm,n'l'm'} V_{nlm,n''l''m''})
\]

\[+ \frac{\delta \rho_{nlm,n'l'm'}}{\tau} \] A6

Here \( \varepsilon_{nlm} \) are the single particle energies (cf. Ref. [44]). The matrix elements of the Coulomb potential are cast as

\[
V_{nlm,n'l'm'} = \langle nlm|\hat{V}_{\mathrm{ind}} + \hat{V}_{\mathrm{ext}}^{n'l'm'} \rangle
\]

(A7)

\[
= V_{nlm,n'l'm'}^{\mathrm{ind}} + V_{nlm,n'l'm'}^{\mathrm{ext}},
\]

where

\[
V_{nlm,n'l'm'}^{\mathrm{ext}} = \sum_{l'm''} y^{l'm'}_{lm,l''m''} V_{l'm''}^{\mathrm{ext},nn'}
\]

(A8)

and

\[
v^{n'm'}_{l''m''} = \int_0^\tau d\tau s_{n'm'}(r) V_{l''m''}^{\mathrm{ext}}(r).
\]

(A9)

Upon solving the Poisson equation (see Appendix B) we find for the matrix elements of the potential \( V_{\mathrm{ind}}^{n'}(\vec{r}) = e\Phi(\vec{r}) \) induced by the change in the charge density \( \delta n(\vec{r}) \) the following expression

\[
V_{nlm,n'l'm'}^{\mathrm{ind}} = \frac{e^2}{\epsilon_0} \sum_{n_1n_2} \sum_{l'm''} y^{l'm'}_{lm,l''m''} y^{n'n''}_{l'm''} \delta n_{n_1n_2} l'm''.
\]

(A10)

The coefficients \( g_{n'n'',n_1n_2} \) are defined in Appendix B by Eq. (B13).

We are interested in the linear response and expand therefore the density matrix around the equilibrium distribution \( \rho_0^{nlm} \) as

\[
\rho_{nlm,n'l'm'} = \rho_0^{nlm} + \delta \rho_{nlm,n'l'm'}
\]

(A11)

Thus, \( \delta \rho_{nlm,n'l'm'} \) is a small perturbation. The elements of the local equilibrium density matrix including the lowest order correction with respect to the equilibrium density matrix are given then by [45]

\[
\delta \mu^{l'n'n'n''}_{nlm,n'l'm'} = \int_0^\tau d\tau s_{n'm'}(r) \delta \rho^{l'n'n''}_{nlm,n'l'm'} + \frac{\delta \rho_0^{nlm} - \rho_0^{nlm} \delta \rho^{l'n'n''}_{nlm,n'l'm'}}{\varepsilon_{nlm} - \varepsilon_{n'n'}.}
\]

(A12)

Here the components of the chemical potential can be expressed as

\[
\delta \mu^{l'n'n'n''}_{nlm,n'l'm'} = \sum_{l''m''} y^{l'm'}_{lm,l''m''} \delta \mu^{n'n''}_{l''m''}.
\]

(A13)

We require density conservation, meaning that \( n^{l'n'n''}_{lm} = n^{l'n'n''}_{l'm'} \) which in turn leads to

\[
\delta n^{l'n'n''}_{lm} = \sum_{l''m''} M^{l'n'n''}_{lm,l''m''} \delta \mu^{n'n''}_{l''m''}.
\]

(A14)

where

\[
M^{l'n'n''}_{lm,l''m''} = \frac{\sum_{l'm''} y^{l'm'}_{lm,l''m''} y^{l'm'}_{l'm''} \delta \rho^{l'n'n''}_{l'm''} \delta \rho^{l'n'n''}_{l'm''}}{\varepsilon_{nlm} - \varepsilon_{n'n'}.}
\]

(A15)

In general, \( \delta \mu^{l'n'n''}_{l'm'} \) is determined from Eq. (A14) by solving a system of linear equations for each pair of indexes.
This step of the calculation is significantly simplified by neglecting the energy splitting of the multiplet with the same \( l \), i.e. by writing \( \varepsilon_{nlm} = \varepsilon_{nlm'} = \varepsilon_{nl} \), and therefore \( f_{nlm} = f_{nlm'} = f_{nl} \), which is a good approximation for “spherical” molecules such as \( C_{60} \), as confirmed by the ab-initio calculations. Adopting this approximation we conclude that (cf. Appendix C):
Inserting the definition (A25) into Eq. (A22), changing the order of integration in the second term on the right hand side, comparing again with Eq. (A25) and making use of the dipole approximation, we get the following integral equation for the response function:

\[
\sum_{n_1 n_2} \chi_{n'n'' n_1 n_2}(t, t') \tilde{r}_{n_1 n_2} = \Pi_{n'n''}(t, t') \tilde{r}_{n'n''} + \int_t^t \! dt' \frac{e^2}{\epsilon_0} \sum_{n_1 n_2 \to n_3 n_4} g_{n'n'', n_1 n_2} \chi_{n_1 n_2 n_3 n_4}(t'', t') \tilde{r}_{n_3 n_4} \tag{A26}
\]

\[
+ \int_t^t \! dt'' \sum_{n_1 n_2} \chi_{n'n'' n_1 n_2}(t'', t') \tilde{r}_{n_1 n_2},
\]

where the matrix elements \( \tilde{r}_{n'n''} \) are given by \( \tilde{r}_{n'n''} = \frac{1}{\epsilon_0} \int r^2 dr \, s_{n'n''}(r) r \) and are calculated by us using the radial functions for C_{60} from our \textit{ab-initio} calculations. Here we have also taken into account that in the dipole approximation the identity \( V_{\text{ext}, n_1 n_2 \tilde{r}_{n'n''}} = V_{\text{ext}, n'n''} \tilde{r}_{n_1 n_2} \) holds. The corresponding time- and frequency-dependent response function is determined then by

\[
z_{n'n''}(\omega, t) = \frac{e^2 g}{\epsilon_0} \int_0^\infty dT \, e^{i \omega T} \sum_{n_1 n_2} \chi_{n'n'' n_1 n_2}(t, t - T) \tilde{r}_{n_1 n_2}, \tag{A27}
\]

where \( g = 1/(3r_0) \) and \( \epsilon_0 \) is the vacuum permittivity. Here \( r_0 \approx 6.745 a_0 \) is the average radius of the C_{60} atomic cage, where \( a_0 \) is the Bohr radius. After inserting Eq. (A26) into Eq. (A27) we arrive at the following system of integral equations for each frequency value \( \omega \):

\[
z_{n'n''}(\omega, t) = \int_{-\infty}^t \! dt' e^{i \omega (t-t')} \tilde{r}_{n'n''}(t, t') \sum_{n_1 n_2} \chi_{n'n'' n_1 n_2}(t, t - T) \tilde{r}_{n_1 n_2}
\]

\[
+ \int_{-\infty}^t \! dt' e^{i \omega (t-t')} \sum_{n_1 n_2} \chi_{n'n'' n_1 n_2}(t, t - T) \tilde{r}_{n_1 n_2} z_{n_1 n_2}(\omega, t'),
\]

\[
+ \int_{-\infty}^t \! dt' e^{i \omega (t-t')} I_{n'n''}(t, t') z_{n'n''}(\omega, t'), \quad n', n'' = 1, 2;
\]

where \( \tilde{g}_{n'n'', n_1 n_2} = g_{n'n'', n_1 n_2} / g \) and

\[
W_{n'n''}(t, t') = \frac{e^2 g}{\epsilon_0} \Pi_{n'n''}(t, t'). \tag{A29}
\]

Here \( \Pi_{n'n''} \) and \( I_{n'n''}(t, t') \) are given by Eq. (A23) and Eq. (A24), respectively, with \( l = 1 \). The system of equations (A28) is solved numerically. It can be shown (see section E) that the time- and frequency-dependent dipolar polarizability can be written as

\[
\alpha(\omega, t) = -r_0^3 \sum_{n'n''} \tilde{r}_{n'n''} \frac{z_{n'n''}(\omega, t)}{n(n-1)}. \tag{A30}
\]

Appendix B: Calculation of the induced potential and its matrix elements

Here we determine the electrostatic potential \( \Phi(\vec{r}) \) induced by the change of the density in the spherical layer \( n(\vec{r}) \). The Poisson equation

\[
\Delta \Phi(\vec{r}) = -\frac{e}{\epsilon_0} n(\vec{r}) \tag{B1}
\]

has then to be solved (SI units are used in this work). Its solution can be written using the Green’s function \( G(\vec{r}, \vec{r}') \)

\[
\Phi(\vec{r}) = -\frac{e}{\epsilon_0} \int G(\vec{r}, \vec{r}') n(\vec{r}') d^3 \vec{r}', \tag{B2}
\]

where

\[
G(\vec{r}, \vec{r}') = -\frac{1}{4\pi |\vec{r} - \vec{r}'|}. \tag{B3}
\]

Using the spherical geometry of the problem we apply the following decomposition for the Green’s function:

\[
\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{l=0}^\infty \sum_{m=-l}^l \frac{4\pi}{2l + 1} Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi'), \tag{B4}
\]

where \( r_\rho = \max\{r, r'\} \) and \( r_\rho = \min\{r, r'\} \). Then we get the following expression for the potential

\[
\Phi(\vec{r}) = \frac{e}{\epsilon_0} \int d^3 \vec{r}' \sum_{l=0}^\infty \sum_{m=-l}^l \frac{1}{2l + 1} \frac{r_\rho^l}{r_\rho^{l+1}} Y_{lm}(\theta, \phi) \times Y_{lm}^*(\theta', \phi') n(\vec{r}'). \tag{B5}
\]
To proceed further we decompose \( n(r') \) in spherical harmonics

\[
n(r, \theta, \phi) = \sum_{l,m} n_{lm}(r) Y_{lm}(\theta, \phi),
\]

where the radial-dependent angular components of the density can be found as

\[
n_{lm}(r) = \sum_{n',n''} s_{n'n''}(r) n^l_{lm},
\]

with

\[
s_{n'n''}(r) = R_{n''}(r) R_{n''}(r),
\]

and finally expressed via the components of the density matrix \( \rho_{nlm,n'l'm'} \)

\[
n^l_{lm} = \sum_{n'n''} y_{lm,l'm'n'm'}^l \rho_{nlm,n'l'm'}.
\]

After inserting Eq. (B6) with Eq. (B7) into Eq. (B5) we get

\[
\Phi(r) = \sum_{n'n''} \sum_{l=0}^{\infty} n^l_{lm} \int_0^1 \ldots \int_{r'} dw' \ldots dw'' \ s_{n'n''}(r'),
\]

where

\[
I^n_{lm}(r') = \frac{1}{2l+1} \int_0^1 \ldots \int_0^1 \frac{\ldots \int_{r'} dw' \ldots dw''}{r''} \ s_{n'n''}(r').
\]

The determination of the induced electrostatic potential entails the knowledge of the elements of the density matrix because the calculation of the matrix elements \( \langle n'l'm'|\Phi(r)|n''l''m'' \rangle \) as

\[
\Phi_{nlm,n'l'm'} = \frac{e}{\epsilon_0} \sum_{n1n2} \sum_{I\bar{I}} y_{l'm'n'm'}^l \ h_{n'1n2} n_{1I} n_{2\bar{I}},
\]

where \( y_{l'm'n'm'} \) is given by Eq. (A5) and

\[
g_{l'n'n',n1n2} = \int_0^1 \ldots \int_0^1 s_{n'n''}(r) I^n_{lm}(r).
\]

The values of all matrix elements entering Eq. (B13) are obtained numerically using the radial functions for \( C_{60} \) from our ab-initio calculations.

As explained above, for \( C_{60} \) we may adopt the approximation of a spherical layer with the width of the layer \( d \) being smaller than the radius of the layer \( d \ll r_0 \). This enables us to write

\[
g_{l'n'n',n1n2} = g_l \left( \delta_{n1n2} \delta_{n'n'n} \hat{g}_{l'n'n',n1n2} + \delta \hat{g}_{l'n'n',n1n2} \right),
\]

where

\[
g_l = \frac{1}{2l+1},
\]

\[
\hat{g}_{l'n'n',n1n2} \approx 1 \quad \text{and} \quad \hat{g}_{l'n'n',n1n2} \ll 1 \quad \text{so that the second term in Eq. (B14) can be neglected to a leading order of } d/r_0.
\]

Appendix C: Chemical potential calculation

With \( \varepsilon_{nlm} = \varepsilon_{nlm'} \equiv \varepsilon_{nl} \) and \( \omega^0_{nlm} = \omega^0_{nlm'} \equiv \omega^0_{nl} \), Eq. (A15) can be written as

\[
M^l_{lm,l'm'} = -\sum_{l''m''} \omega^0_{nlm'} y_{l'm'n'm''}^l y_{l'm'n'm''}^l,
\]

The last sum on the right hand side of this equation we evaluate using the following property of the Clebsch-Gordan coefficients

\[
\sum_{m1,m2} C_{jm1j2m2}^j C_{jm'1j2m'2} = \delta_{j'j} \delta_{mm'}. \quad (C2)
\]

Therefore we make use of the definition \( A5 \) and rewrite

\[
y_{l'm'n'm''}^l y_{l'm'n'm''}^l = (-1)^{m+m} y_{l'm'n'm''}^l y_{l'm'n'm''}^l.
\]

Summing over \( m' \) and \( m'' \) and using Eq. (C2) we find

\[
\sum_{m',m''} y_{l'm'n'm''}^l y_{l'm'n'm''}^l = \delta_{l'l} \delta_{m,m} K_{l'l'},
\]

where \( K_{l'l'} \) is given by Eq. (A18). With this finding Eq. (C1) simplifies to

\[
M^l_{lm,l'm'} = \delta_{l'l} \delta_{m,m} M^l_{l'm''}, \quad (C5)
\]

where \( M^l_{l'm''} \) is defined by Eq. (A17). Equation (A14) can then be simplified to

\[
\delta_{l'l} \delta_{m,m} M^l_{l'm''} = M^l_{l'm''} \delta_{l'l'} \delta_{m,m} \quad (C6)
\]

and after dividing this by \( M^l_{l'm''} \) we get finally Eq. (A16).

Appendix D: Approximate stationary solutions

Utilizing the spherical shell approximation \( (d/r_0 \ll 1) \) we find \( \hat{g}_{n1n2n1n2} \ll 1 \) and \( \hat{r}_{n1n2} \ll 1 \) for \( n1 \neq n2 \) whereas \( \hat{g}_{n1n2n1n1} \approx 1 \) and \( \hat{r}_{n1n1} \approx 1 \). As a consequence it follows from Eq. (A28) that the intraband components \( z_{11}(\omega, t) \) and \( z_{22}(\omega, t) \) of the response function are only weakly influenced by the interband components \( z_{12}(\omega, t) \) and \( z_{21}(\omega, t) \). Therefore, we obtain an approximate solution by solving the equation system (A28) considering only the intraband terms. This leads to a system of two coupled equations for \( z_{11}(\omega, t) \) and \( z_{22}(\omega, t) \).

The equilibrium population of levels is determined by the energetic order of the states. The expressions for \( W_{nn}(t, t') \) and \( I_{nn}(t, t') \) can thus be written approximately as

\[
W_{nn}(t, t') = \omega_{nn}^2 \frac{e^\frac{1}{2}(t'-t) \sin \left[ \omega_{nn}^2 (t' - t) \right]}{\omega_{nn}^3}, \quad (D1)
\]

\[
I_{nn}(t, t') = \frac{1}{e^\frac{1}{2}(t'-t) \cos \left[ \omega_{nn}^2 (t' - t) \right]}, \quad (D2)
\]
\[ \omega_{p,n} = \sqrt{\frac{\omega_{F,n}^2 + e^2 N_n}{\omega_{F,n} - E_g} \frac{1}{e^2 m_0 \ell}}. \]  
\[ \text{(D3)} \]

\( N_n \) is the number of electrons in the \( n \)-th radial subband. \( h \omega_{F,n} \) are the energy distances between the highest occupied state in the \( n \)-th radial subband and the unoccupied state in the same subband having the value of \( \ell \) that is greater by one. This energy distance can be written as

\[ h \omega_{F,n} = \sqrt{2N_n \frac{\hbar^2}{2m_0 \ell^2}} + E_g, \]  
\[ \text{(D4)} \]

where the first term on the right hand side determines the corresponding energy gap between the highest occupied state and the lowest unoccupied state for \( N_n \) free electrons in a thin spherical layer with the radius \( r_0 \) and \( E_g \) is an additional band gap appearing for the real “spherical” molecule \( C_{60} \).

With kernels determined by Eqs. (D11) and (D2) the system of integral equations for \( z_{11}(\omega,t) \) and \( z_{22}(\omega,t) \) can be reduced to two coupled ordinary differential equations, each of which describes the plasmon dynamics in the respective radial band:

\[ \frac{d^2}{dt^2} z_{11}(\omega,t) + \left( \frac{1}{\tau} - 2i\omega \right) \frac{dz_{11}(\omega,t)}{dt} + \left( \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{F,1}^2 - \omega^2 - i\frac{\omega}{\tau} \right) z_{11}(\omega,t) \]
\[ + \omega_{p,1}^2 \tilde{g}_{11,22} z_{22}(\omega,t) = -\omega_{p,1}^2. \]  
\[ \text{(D5)} \]

\[ \frac{d^2}{dt^2} z_{22}(\omega,t) + \left( \frac{1}{\tau} - 2i\omega \right) \frac{dz_{22}(\omega,t)}{dt} + \left( \omega_{p,2}^2 \tilde{g}_{22,22} + \omega_{F,2}^2 - \omega^2 - i\frac{\omega}{\tau} \right) z_{22}(\omega,t) \]
\[ + \omega_{p,2}^2 \tilde{g}_{22,11} z_{11}(\omega,t) = -\omega_{p,2}^2. \]  
\[ \text{(D6)} \]

Here we made use of the fact that the corrections to \( \tilde{r}_{11} = \tilde{r}_{22} = 1 \) are of a second order in \( d/r_0 \) and can be neglected. Then the time- and frequency-dependent dipolar polarizability is expressed as

\[ \alpha(\omega,t) = -r_0^3 \left[ z_{11}(\omega,t) + z_{22}(\omega,t) \right]. \]  
\[ \text{(D7)} \]

The stationary solution of the system (4) can be found as

\[ z_{11}(\omega) = \frac{1}{D} \left[ \omega_{p,1}^2 \omega_{p,2}^2 \tilde{g}_{11,22} \right] \]
\[ \times \left( \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{F,1}^2 - \omega^2 - i\frac{\omega}{\tau} \right), \]  
\[ \text{(D8)} \]

\[ z_{22}(\omega) = \frac{1}{D} \left[ \omega_{p,1}^2 \omega_{p,2}^2 \tilde{g}_{11,22} \right] \]
\[ \times \left( \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{F,1}^2 - \omega^2 - i\frac{\omega}{\tau} \right), \]  
\[ \text{(D9)} \]

where \( \tilde{g}_{11,22} = \tilde{g}_{22,11} \) and

\[ D = \left( \omega_{p,2}^2 \tilde{g}_{22,22} + \omega_{F,2}^2 - \omega^2 - i\frac{\omega}{\tau} \right) \]
\[ \times \left( \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{F,1}^2 - \omega^2 - i\frac{\omega}{\tau} \right) \]
\[ - \omega_{p,1}^2 \omega_{p,2}^2 \left( \tilde{g}_{11,22} \right). \]  
\[ \text{(D10)} \]

The stationary frequency-dependent dipolar polarizability is given then by

\[ \alpha(\omega) = -r_0^3 \left[ z_{11}(\omega) + z_{22}(\omega) \right]. \]  
\[ \text{(D11)} \]

The plasmon frequencies as derived from Eq. (D11) differ from the zeros of denominator (for \( 1/\tau = 0 \)). Since \( \omega_{p,1}^2 - \omega_{F,2}^2 < \omega_{p,1}^2 \tilde{g}_{11,11} - \omega_{p,2}^2 \tilde{g}_{22,22} \) we find two possible frequencies \( \omega_+ \) and \( \omega_- \) such that

\[ \omega_+^2 = \omega_p^2 + \frac{1}{\omega_p^2} \left( \omega_{p,1}^2 \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{F,1}^2 \omega_{F,1}^2 \tilde{g}_{22,22} \right), \]  
\[ \text{(D12)} \]

\[ \omega_-^2 = \frac{1}{\omega_p^2} \left( \omega_{p,1}^2 \omega_{p,2}^2 \tilde{g}_{22,22} + \omega_{F,2}^2 \omega_{F,2}^2 \tilde{g}_{11,11} \right), \]  
\[ \text{(D13)} \]

where

\[ \omega_p^2 = \omega_{p,1}^2 \tilde{g}_{11,11} + \omega_{p,2}^2 \tilde{g}_{22,22}. \]  
\[ \text{(D14)} \]

The amplitude of the peak centered around the frequency \( \omega_- \) has much smaller value because it contains terms of the order \( (\omega_{p,2}^2 \tilde{g}_{11,11} - \omega_{p,1}^2 \tilde{g}_{22,22}) \). From Eq. (D14) we get \( \omega_+ = 25.4 \text{ eV} \) and \( \omega_- = 8 \text{ eV} \). Comparing the results found so with those without making the above approximations confirms the accuracy of the approximate expressions for the peak positions.

**Appendix E: Time- and frequency-dependent dipolar polarizability**

Given the time-dependent perturbation of the system density \( \delta n(\tilde{r},t) \) the induced dipole moment \( \tilde{P}(t) \) is determined then by

\[ \tilde{P}(t) = e \int \tilde{r} \delta n(\tilde{r},t) d^3\tilde{r}. \]  
\[ \text{(E1)} \]

Inserting here Eqs. (A1) and (A2) we find

\[ \tilde{P}(t) = e \int \tilde{r} \sum_{n,n'} \delta n_{n,n'}(r) \sum_{lm} \delta n_{l,m}(t) Y_{lm}(\theta, \phi) d^3\tilde{r}. \]  
\[ \text{(E2)} \]

The components \( \delta n_{l,m}(t) \) can be calculated once we have the components \( V_{lm}^{\text{ext}, n, n'}(t) \) of the external perturbation and the response function \( \chi_{n',n,n',n}^{(2)}(t, t') \) using Eq. (A25).

If we consider the response of the system to an external spatially homogenous time-dependent electric field \( \tilde{E}(t) \), it is enough to consider only the dipolar components of the response function, i.e. the components with \( l = 0 \). We may
select the $z$-axis to be parallel to the electric field. Then the external potential reads:

$$V_{\text{ext}}(\vec{r}, t) = -e z E(t).$$ \hspace{1cm} (E3)

Considering the angular components of this potential we conclude that only the component with $l = 1$ and $m = 0$ does not vanish:

$$V_{\text{ext}}^{10}(\vec{r}, t) = -2\sqrt{\frac{\pi}{3}} e r E(t).$$ \hspace{1cm} (E4)

As a consequence in Eq. (E2) only terms with $l = 1$ and $m = 0$ survive and we infer that the induced dipole $\vec{P}(t)$ moment is directed parallel to the electric field $\vec{E}(t)$. Its magnitude is given by

$$P(t) = -\frac{4\pi \varepsilon_0^2}{3} \int_{-\infty}^{t} dt' \sum_{n'n''; n_1 n_2} \tilde{r}_{n'n''} \chi_{n'n''; n_1 n_2}(t, t') \times \tilde{r}_{n_1 n_2} E(t'),$$ \hspace{1cm} (E5)

where

$$\tilde{r}_{n'n''} = \frac{1}{r_0} \int r^2 dr s_{n'n''}(r) r.$$

(E6)

For a perturbation with an electric field $E(t) = E_0 e^{-i\omega t}$ at a particular frequency $\omega$ we derive using Eq. (A27) the expression

$$P(\omega; t) = -4\pi \varepsilon_0^3 \sum_{n'n''} \tilde{r}_{n'n''} z_{n'n''}^* (\omega, t) E_0 e^{-i\omega t}. \hspace{1cm} (E7)$$

The time- and frequency-dependent dipolar polarizability $\alpha_{\text{SI}}(\omega, t)$ in SI units is then found to be equal to

$$\alpha_{\text{SI}}(\omega, t) = -4\pi \varepsilon_0^3 \sum_{n'n''} \tilde{r}_{n'n''} z_{n'n''} (\omega, t). \hspace{1cm} (E8)$$

In literature, however, the polarizability is more frequently expressed as polarizability volume (as it happens naturally when using Gauss units): $\alpha = \frac{1}{4\pi \varepsilon_0} \alpha_{\text{SI}}$. Using this definition we end up with

$$\alpha(\omega, t) = -r_0^3 \sum_{n'n''} \tilde{r}_{n'n''} z_{n'n''} (\omega, t).$$ \hspace{1cm} (E9)

We note that the factors $z_{n'n''}(\omega, t)$ are dimensionless.

For $d/r_0 \ll 1$ and considering only the lowest order contribution we conclude $\tilde{r}_{n'n''} \approx \delta_{n'n''}$ and therefore

$$\alpha(\omega, t) \approx -r_0^3 \sum_n z_{nn}(\omega, t).$$ \hspace{1cm} (E10)

With this expression we can describe the approximate response given only by the intraband excitations.

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[1] S. Haessler, J. Caillat, W. Boutu, C. Giovanetti-Teixeira, T. Rachon, T. Auguste, Z. Diveki, P. Breger, A. Maquet, B. Carre, R. Taieb, and P. Salieres, Nat. Physics 6, 200 (2010).

[2] D. Shafir, Y. Mairesse, D. M. Villeneuve, P. B. Corkum, and N. Dudovich, Nat. Physics 5, 412 (2009).

[3] P. Eckle, M. Smoliariski, P. Schupl, J. Biegert, A. Staudte, M. Schoeffler, H. G. Muller, R. Doerner, and U. Keller, Nat. Physics 4, 565 (2008).

[4] E. Goulielmakis, M. Schultz, M. Hofstetter, V. S. Yakovlev, J. Gagnon, M. Uiberacker, A. L. Aquila, E. M. Gullikson, D. T. Attwood, R. Kienberger, F. Krausz, and U. Kleineberg, Science 320, 1614 (2008).

[5] P. B. Corkum and F. Krausz, Nat. Physics 3, 381 (2007).

[6] F. Krausz and M. Ivanov, Rev. Mod. Phys. 81, 163 (2009).

[7] M. F. Kling and M. J. Kravking, Annu. Rev. Phys. Chem. 59, 463 (2008).

[8] T. Popmintchev, M.-C. Chen, P. Arpin, M. Murnane, and H. C. Kapteyn, Nat. Photonics 4, 822 (2010).

[9] T. Rohwer, S. Hellmann, M. Wiesenmann, C. Sohr, A. Stange, B. Slomski, A. Carr, Y. Liu, L. M. Avila, M. Kallane, S. Mathias, L. Kipp, K. Rossnagel, and M. Bauer, Nature (London) 471, 490 (2011).

[10] M. Schultz, M. Fieß, N. Karpowicz, J. Gagnon, M. Korbman, M. Hofstetter, S. Neppi, A. L. Cavaliere, Y. Komminos, T. Mercouris, C. A. Nicolaides, R. Pazourek, S. Nagele, J. Feist, J. Burgdorfer, A. M. Azzeer, R. Ernstorfer, R. Kienberger, U. Kleineberg, E. Goulielmakis, F. Krausz, and V. S. Yakovlev, Science 328, 1658 (2010).

[11] A. L. Cavaliere, N. Mueller, T. Uphues, V. S. Yakovlev, A. Balatskus, B. Horvath, B. Schmidt, L. Bluemel, R. Holzwarth, S. Hendel, M. Drescher, U. Kleineberg, P. M. Echenique, R. Kienberger, F. Krausz, and U. Heinzmann, Nature (London) 449, 1029 (2007).

[12] G. Mahan, Many particle physics (Physics of Solids and Liquids) (Kluwer Acad./Plenum, New York, 2000).

[13] S. Maier, Plasmonics: Fundamentals and Applications (Springer, New York, 2007).

[14] M. L. Brongersma and V. M. Shalaev, Science 328, 440 (2010).

[15] R. F. Egerton, Electron Energy Loss Spectroscopy in the Electron Microscope (2nd Edition) (Plenum, New York, 1996).

[16] R. F. Egerton, Rep. Prog. Phys. 72, 016502 (2009).

[17] H. Haug and A.-P. Jauho, Quantum kinetics in transport and optics of semiconductors (Springer, Berlin, 1996).

[18] R. Huber, F. Tauser, A. Brodschelm, M. Bichler, G. Abstreiter, and A. Leitenstorfer, Nature (London) 414, 1658 (2001).

[19] H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl, and R. E. Smalley, Nature (London) 318, 162 (1985).

[20] G. Orlandi and F.negri, Photochem. Photobiol. Sci. 1, 289 (2002).

[21] M. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of fullerene and carbon nanotubes (Acad. Press, San Diego, 1996).

[22] K. D. Bonin and V. V. Kresin, Electric-dipole polarizabilities of atoms, molecules and clusters (World Scientific, Singapore, 1997).

[23] W. Kratschmer, L. D. Lamb, F. K., and D. Huffman, Nature (London) 347, 354 (1990).

[24] G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev.
Lett. 67, 2690 (1991).
[25] P. L. Hansen, P. J. Fallon, and W. Krätschmer, Chem. Phys. Lett. 181, 367 (1991).
[26] E. Sohmen, J. Fink, and W. Krätschmer, Z. Phys. B 86, 87 (1992).
[27] I. V. Hertel, H. Steger, J. de Vries, B. Weisser, C. Menzel, B. Kamke, and W. Kamke, Phys. Rev. Lett. 68, 784 (1992).
[28] R. Bauernschmitt, R. Ahlrichs, F. H. Hennrich, and M. M. Kappes, J. Am. Chem. Soc. 120, 5052 (1998).
[29] J. Berkowitz, J. Chem. Phys. 111, 1446 (1999).
[30] A. Reinköster, S. Korica, G. Prümper, J. Viefhaus, K. Godenhuis, O. Schwarzkopf, M. Mast, and U. Becker, J. Phys. B 37, 2135 (2004).
[31] S. W. J. Scully, E. D. Emmons, M. F. Gharaibeh, R. A. Phaneuf, A. L. D. Kilcoyne, A. S. Schlachter, S. Schippers, A. Muller, H. S. Chakraborty, M. E. Madjet, and J. M. Rost, Phys. Rev. Lett. 94, 065503 (2005).
[32] G. Mukhopadhyay and S. Lundqvist, Il Nuovo Cimento B 27, 1 (1975).
[33] P. Lambin, A. A. Lucas, and J.-P. Vigneron, Phys. Rev. B 46, 1794 (1992).
[34] D. Östling, P. Apell, and A. Rosén, Europhys. Lett. 21, 539 (1993).
[35] D. Östling, S. P. Apell, G. Mukhopadhyay, and A. Rosén, J. Phys. B 29, 5115 (1996).
[36] B. Vasvari, Z. Phys. B 100, 223 (1996).
[37] M. J. Puska and R. M. Nieminen, Phys. Rev. A 47, 1181 (1993).
[38] K. Yabana and G. F. Bertsch, Phys. Scr. 48, 633 (1993).
[39] V. Ivanov, G. Kashenok, R. Polozkov, and A. Sotovyov, JETP 96, 658 (2003).
[40] M. E. Madjet, H. S. Chakraborty, J. M. Rost, and S. T. Manson, J. Phys. B 41, 105101 (2008).
[41] Y. Pavlyukh and J. Berakdar, Chem. Phys. Lett. 468, 313 (2009).
[42] Y. Pavlyukh and J. Berakdar, Phys. Rev. A 81, 042515 (2010).
[43] Y. Pavlyukh and J. Berakdar, J. Chem. Phys. 135, 201103 (2011).
[44] See Supplemental Material at [URL will be inserted by publisher] for the details of the calculated electronic structure of C_{60}.
[45] N. D. Mermin, Phys. Rev. B 1, 2362 (1970).
[46] K. Morawetz, P. Lipavsky, and M. Schreiber, Phys. Rev. B 72, 233203 (2005).
[47] A. Borisov, D. Sanchez-Portal, R. D. Muio, and P. M. Echenique, Chem. Phys. Lett. 387, 95 (2004).
[48] F. J. García de Abajo, Rev. Mod. Phys. 82, 209 (2010).
[49] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 43, 689 (2011).
[50] C. Radloff and J. Halas, Nano Lett. 4, 1323 (2004).
[51] S. P. Apell, P. M. Echenique, and R. H. Ritchie, Ultramicroscopy 65, 53 (1996).
[52] G. Pal, Y. Pavlyukh, W. Hübner, and H. C. Schneider, Eur. Phys. J. B 79, 327 (2011).
[53] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, Singapore, 1988).