High Harmonic Generation of Soft X-Rays by Carbon Nanotubes

Ofir E. Alon,[1] Vitali Averbukh,[1] and Nimrod Moiseyev[1,2]

[1]*Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

[2]*Minerva Center for Non-Linear Physics of Complex Systems, Technion-Israel Institute of Technology, Haifa 32000, Israel*

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We extend the method for the formulation of selection rules for high harmonic generation spectra [Phys. Rev. Lett. **80**, 3743 (1998)] beyond the dipole approximation and apply it to single-walled carbon nanotubes interacting with a circularly polarized laser field. Our results show that the carbon nanotubes can be excellent systems for a selective generation of high harmonics, up to the soft x-ray regime.

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There is a very limited number of possibilities by which one can obtain coherent x-rays [1]. The interest in short-wavelength sources stimulated numerous experimental investigations of harmonic generation spectra of noble gases in intense linearly polarized laser fields (see [2], and references therein). The recent experimental successes in the field [3,4] emphasize the possibility of application of high harmonics in spectroscopy and other areas. One property which would have made the harmonic radiation particularly useful is the selectivity of the generation of high harmonics. In order to achieve a selective generation of high harmonics, one has to devise a system possessing a very high order spatiotemporal symmetry [5]. To the best of our knowledge, such systems cannot be found among the planar molecules discussed in Ref. [5]. Here we show that the interaction of nanotubes and circularly polarized incident radiation is characterized by this type of symmetry and can lead to the generation of the high order harmonics in a selective fashion. Thus, already the first high harmonic emitted by a nanotube can fall within the desired soft x-ray range.

The approach to the formulation of the selection rules developed by us previously [5] for the description of planar systems is based on the dipole approximations with respect to both the incident and emitted waves and is not valid for the spatially extended target systems, such as nanotubes. In fact, the dipole approximations can be misleading even in the case of atomic targets sufficiently distorted by the incident fields. For example, an exact symmetry analysis would show that the selection rules for the harmonic generation in the crossed beam setup proposed recently by Tong and Chu [6] are only approximate. Therefore, let us first present a general and exact method for the formulation of the selection rules for high harmonic generation and then proceed with applying it to the harmonic generation by single-walled carbon nanotubes.

High harmonic generation (HHG) is a process in the course of which a target (e.g., atomic or molecular) system emits high harmonics of the incident laser frequency. According to classical electrodynamics, the intensity of lth harmonic, $I(l\omega)$, in HHG spectra is associated with the corresponding Fourier component of the time-dependent electron flux $\vec{J}(\vec{r},t)$ [7],

$$\begin{aligned} I(l\omega) &\propto |\vec{A}_l \times \vec{k}|^2, \\ \vec{A}_l &\propto \int_0^\infty dt \int_{-\infty}^\infty d^3r\, \vec{J}(\vec{r},t) e^{-i(l\omega t - \vec{k}\cdot\vec{r})}, \end{aligned} \tag{1}$$

where ω is the incident radiation frequency and $\vec{k}$ is the harmonic wave vector. Note that, in Eq. (1), $\vec{A}_l$ stands for the (immeasurable) vector potential of the emitted field of the frequency $l\omega$. The (measurable) magnetic and electric fields propagating along the direction of the wave vector $\vec{k}$ are obtained from $\vec{A}_l$ by vector multiplication: $\vec{H}_l = i\vec{A}_l \times \vec{k}$, $\vec{E}_l = \frac{ic}{l\omega}\vec{k} \times (\vec{A}_l \times \vec{k})$.

When dealing with microscopic or mesoscopic systems behaving according to the laws of quantum mechanics, one has to use the quantum mechanical expression for the flux [8], $J(\vec{r},t) = \mathrm{Re}(\Psi^* \hat{\vec{v}} \Psi)$, where $\hat{\vec{v}}$ is the electron velocity operator. The most appropriate choice for the wave function Ψ, when regarding the symmetries of the system in space and time, is Floquet wave function [5,9], which is periodic in time apart from a phase factor. Its time-periodic part, $\Phi(\vec{r},t)$, is an eigenfunction of Floquet Hamiltonian:

$$\begin{aligned} \hat{\mathcal{H}} &= \frac{\hbar}{i}\frac{\partial}{\partial t} + \frac{[\hat{\vec{p}} - e\vec{A}(\vec{r},t)]^2}{2m} + V(\vec{r}), \\ \hat{\mathcal{H}}\Phi(\vec{r},t) &= \varepsilon\Phi(\vec{r},t). \end{aligned} \tag{2}$$

The vector potential $\vec{A}(\vec{r},t)$ for the incident plane wave propagating along the z axis is

$$\vec{A}(\vec{r},t) = \frac{E_0}{\omega}[\cos(\omega t - kz), \alpha \sin(\omega t - kz), 0], \tag{3}$$

where E_0 is the incident field strength, the wave vector $\vec{k} = (0,0,k)$, and α is equal to 0 and ± 1 for linear and right or left circular polarizations, respectively.

Floquet theory can be applied if the incident radiation pulse is many optical cycles long [10]. The Floquet expression for the vector potential of the lth harmonic emitted in the incident field propagation direction is

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$$\vec{A}_l \propto \langle\langle \Psi(\vec{r},t)\,|\hat{\vec{A}}_l|\Psi(\vec{r},t)\rangle\rangle + \langle\langle \Psi^*(\vec{r},t)\,|\hat{\vec{A}}_l^{\dagger^*}\,|\Psi^*(\vec{r},t)\rangle\rangle,$$
$$\hat{\vec{A}}_l = \hat{\vec{v}}e^{-il(\omega t-kz)}, \qquad \hat{\vec{A}}_l^{\dagger^*} = \hat{\vec{v}}^* e^{-il(\omega t-kz)}, \tag{4}$$

where $\hat{\vec{v}} = \frac{1}{m}[\hat{\vec{p}} - e\vec{A}(\vec{r},t)]^2$ is the electron velocity operator, and the double bracket notation $\langle\langle\cdots\rangle\rangle$ stands for the integration over spatial coordinates and over one field period in time. Note that expression (4) is not based on the dipole approximation with respect to either an incident or emitted wave. Taking into account the spatial dependence of the waves enables us to study the HHG by targets extended along the propagation direction of the radiation.

In order to discuss the selectivity of HHG quantitatively, one has to derive the selection rules for the spectrum of the emitted photons with energies equal to $l\hbar\omega$, $l = 1, 2, \ldots$. The selection rules can be found in the following way: One has to find all of the symmetry operations of the time-dependent Hamiltonian (2). Such symmetries will most likely be associated with transformations in space *and* time and will be referred to as dynamical symmetries (DS's). If all of the DS operators commute with each other, it is enough to verify the invariance of the vector potential operators, $\hat{\vec{A}}_l$ [Eq. (4)], under all of the DS operations. Only those harmonics, for which at least *one* of the vector potential operators, $\hat{\vec{A}}_l$, is invariant under *all* of the DS operations, will be present in the HHG spectrum. The higher the order of the DS present in the system, the more selective is HHG. In the following we will show that the interaction of a single-walled carbon nanotube with a circularly polarized laser field can be characterized by DS of a very high order.

Carbon nanotubes are a recently synthesized allotropic form of carbon (see Ref. [11] for a review of their physical properties). Single-walled carbon nanotubes, to which we will restrict our attention, can be viewed as cylinders made of graphite sheets. The infinite order translational symmetries of the graphite lattice can transform into various finite order symmetries once the graphite sheet plane is transformed into the nanotube cylinder. The order and character of the resulting symmetries depend on the way the graphite sheet boundaries are connected with each other to form the cylinder. The nanotubes are classified by a pair of indices, (n, m), such that the $(n, 0)$ (zigzag) and (n, n) (armchair) tubes possess achiral structure, while a $(n, 0 < m < n)$ tube is chiral [11].

The two basic symmetry operations for a general nanotube relevant for our study can be taken as a revolution about the highest order screw axis and the translation. Expressed in cylindrical coordinates, they are

$$S_{N,R} = (\varphi \to \varphi + \psi, z \to z + \tau),$$
$$T_\infty = (z \to z + z_0), \tag{5}$$

where the screw axis parameters (ψ is the chiral rotation angle, τ is the screw axis basic translation, N is the order of the screw axis which is equal to the number of hexagonal units in a unit cell, and R is the number of rotations around the nanotube axis after N successive operations) and the nanotube period, z_0, are functions of its indices (n, m) (for their dependencies, see, e.g., Ref. [11]).

Consider, for example, the chiral nanotube with indices $(8, 2)$. In this case, $\psi = \frac{3}{28}2\pi$ and $\tau = \frac{2}{28}z_0$. Therefore, after $N = 28$ successive operations of $S_{28,3}$, a general point, Q, on the nanotube perimeter is transformed to an equivalent point, Q', at a distance $2z_0$ from Q, after having completed three rotations around the nanotube axis.

Recently, Slepyan *et al.* [12] predicted that the HHG by armchair nanotubes interacting with an intense radiation linearly polarized along the nanotube axes is a highly efficient process. In this paper we concentrate on HHG due to the interaction of general nanotubes with an electromagnetic field propagating along the nanotube axes and polarized circularly in the perpendicular plane. The reason is that this mode of interaction brings about the highest order DS's. The corresponding Floquet Hamiltonian [Eq. (2)] possesses the following DS's:

$$\hat{P}_{N,R} = \left(\varphi \to \varphi + \psi, z \to z + \tau, t \to t + \frac{k\tau}{\omega} + \alpha\frac{\psi}{\omega}\right),$$
$$\hat{P}_\infty = \left(z \to z + z_0, t \to t + \frac{kz_0}{\omega}\right). \tag{6}$$

Equations (6) are just the spatial transformations dictated by the symmetry of the nanotube potential [Eqs. (5)] and compensated by the appropriate translations in time. The order of $\hat{P}_{N,R}$ symmetry operation is equal to N for both left and right circular polarizations, i.e., it is the same for $\alpha = 1$ and $\alpha = -1$. The symmetries [Eqs. (6)] correspond, of course, to the fixed positions of nuclei. In the following it is assumed that the carbon nuclei do not change their positions during the interaction with the laser pulse and regard them as frozen in their field-free equilibrium positions.

In order to determine which harmonics are emitted by nanotubes during the interaction with circularly polarized radiation, it is sufficient to check the invariance of the $\hat{A}_{l,\pm} = \hat{A}_{l,x} \pm i\hat{A}_{l,y}$ operators [see Eq. (4)] under the above two DS's. It turns out that the $\hat{A}_{l,\pm}$ operators are invariant under $\hat{P}_\infty$ for *any* harmonic order n. The $\hat{P}_{N,R}$ DS operation, on the other hand, leaves invariant the vector potential operators only for those harmonics with $l = 1$, $N \pm 1$, $2N \pm 1, \ldots$, and $pN \pm 1, \ldots$. The $(pN + 1)$, $p = 1, 2, \ldots$ harmonics are circularly polarized as the incident field, while the $(pN - 1)$,

$p = 1, 2, \ldots$ harmonics are circularly polarized in the opposite direction.

The order of the screw axis, N, of an achiral nanotube is equal to twice the order of its rotation axis, n. Consequently, the selection rule for HHG by achiral nanotubes is $l = 2pn \pm 1$. For example, the $(10, 0)$ zigzag-type nanotube and the $(10, 10)$ armchair-type nanotube emit only the 19th, 21st, 39th, 41st, ... harmonics of the incident laser frequency. For such a value of N and incident radiation wavelength of 1 μm, the first emitted harmonic wavelength, λ_{19}, is about 53 nm.

The chiral nanotubes can possess screw axes of much higher orders than the achiral ones, which leads to a much more selective HHG by these systems. For example, for the chiral $(8, 2)$ single-walled carbon nanotube, the $(pN \pm 1)$ selection rule implies that the first emitted harmonics are the 27th and 29th. In such a case, the wavelength of the first harmonic, generated by a circularly polarized 1 μm incident radiation, is about 37 nm. The $(8, 3)$ chiral nanotube, possessing only a slightly different diameter but considerably higher order symmetry, would generate the first high harmonics of orders 193 and 195.

Our discussion of the selectivity of HHG by single-walled carbon nanotubes has been limited so far to the formulation of the selection rules. It is important, however, to estimate the intensities of the symmetry-allowed harmonics emitted by these systems. To this end, let us consider a model of HHG by nanotubes based on the tight-binding approximation to the tube electronic structure [11] and the dipole approximation with respect to the incident and emitted waves. In contrast to our symmetry arguments, which are generally valid, this approach is justified only for the low frequency laser fields, such that the fundamental and harmonic wavelengths are larger than the unit cell length. The Floquet Hamiltonian is represented in the basis of tight-binding Bloch states,

$$\Psi_p^k(\rho_0, \varphi, z) = \sum_{q=-\infty}^{\infty} e^{ikz_{p,q}} \cdot 2p_z(\rho_0, \varphi - \varphi_p^{(0)}, z - z_{p,q}),$$
$$z_{p,q} = z_p^{(0)} + (p + q)z_0, \qquad p = 1, 2, \ldots, 2N, \tag{7}$$

where $\{\varphi_p^{(0)}, z_p^{(0)}\}$ are the positions of carbon atoms in the zeroth unit cell and k is the quasimomentum, $-\frac{\pi}{z_0} < k \leq \frac{\pi}{z_0}$. Only those field-free Hamiltonian matrix elements which involve the same or adjacent atomic orbitals are nonzero. The interaction term represented in the length gauge is diagonal,

$$\langle \Psi_p^k | \frac{1}{2} eE_0\rho_0(e^{i\omega t}e^{i\varphi} + e^{-i\omega t}e^{-i\varphi}) | \Psi_{p'}^k \rangle$$
$$= \frac{1}{2} eE_0\rho_0(e^{i\omega t}e^{i\varphi_p^{(0)}} + e^{-i\omega t}e^{-i\varphi_p^{(0)}})\delta_{p,p'} \tag{8}$$

The solution of the time-dependent Schrödinger equation leads to the Floquet-Bloch functions which are eigenstates of the translation by a unit cell length, z_0:

$$\Phi_j^k(t)(\rho_0, \varphi, z) = \sum_{p=1}^{2N} C_{j,p}^k(t)\Psi_p^k(\rho_0, \varphi, z). \tag{9}$$

The corresponding quasienergies are functions of quasimomentum, $\varepsilon_j = \varepsilon_j(k)$. The single-electron Fourier components of the time-dependent dipole moment, corresponding to a specific Floquet-Bloch state, are

$$d_{\pm,k}^{(j)}(n\omega) = \langle\langle \Phi_j^k(t) | e\rho_0 e^{i\omega nt} e^{\pm i\varphi} | \Phi_j^k(t) \rangle\rangle. \tag{10}$$

In order to take into account the generation of harmonics by the electrons filling a number of quasienergy bands, we average the Fourier components of dipole moment arising from the ith Floquet-Bloch state, $d_{\pm,k}^{(i)}(n\omega)$, over the quasimomenta and sum them over the filled bands:

$$d_{\pm}(n\omega) = \frac{z_0}{2\pi N} \sum_{j=1}^{N} \int_{k=-\pi/z_0}^{\pi/z_0} dk\, d_{\pm,k}^{(j)}(n\omega). \tag{11}$$

This procedure is equivalent to the Hartree approximation to the multielectron Floquet-Bloch wave function [13]. Because of the chosen normalization of the Hartree wave function, the resulting harmonic components of the dipole moment, $d_{\pm}(n\omega)$, are analogous to the single-atom, single-electron response in calculations of HHG by atomic gases. The model described above, while not being very precise, should give a correct order of magnitude estimate for the harmonic intensities.

In the present calculations we restrict our attention to the intensities low enough so that the ionization is weak. On the basis of the work by Lenzner *et al.* [14] we take the appropriate threshold intensity as $I = 10^{14}$ W/cm^2. The significant ionization is expected to take place above this threshold, which cannot be accounted for by the presented model. Besides causing irreversible damage to the nanotube sample, the breakdown would be accompanied by the free electron generation having a negative effect on the propagation of the emitted harmonics. The HHG spectra of the armchair $[(5, 5), \rho_0 \approx 6.5$ a.u.], the zigzag $[(9, 0), \rho_0 \approx 6.7$ a.u.], and the chiral $[(8, 2), \rho_0 \approx 6.9$ a.u.] single-walled carbon nanotubes interacting with the electric field of the frequency 0.037 a.u. ($\approx$1.0 eV, $\lambda \approx 1.2$ μm) and the strength 0.05 a.u. (corresponding to the intensity of 9×10^{13} W/cm^2) are shown in Fig. 1. The cutoff in the nanotube HHG spectra is not sharp and appears at the maximal variation of the interaction energy, $n_{\text{cutoff}} = 2eE_0\rho_0/\hbar\omega$. Such cutoff is characteristic of the multicenter ringlike systems driven by circularly polarized field when the interaction energy is much higher than the energy differences of the field-free system [15]. The three nanotubes possess about the same diameter (and hence

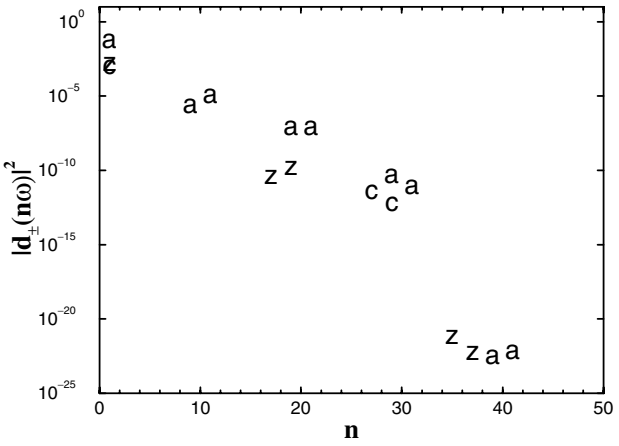

FIG. 1. HHG spectra of the armchair $(5,5)$ ("a"), the zigzag $(9,0)$ ("z") and the chiral $(8,2)$ ("c") nanotubes.

about the same value of the interaction energy) which leads to the similar cutoff positions at about $n_{\text{cutoff}} = 20$.

In the case of the armchair nanotube, the absolute values of the Fourier components of the time dependent dipole moment in the plateau region are of the same order of magnitude as those obtained by Kulander and co-workers in the atomic case for the linear polarization of the incident field at the intensities close to 10^{14} W/cm^2 [16]. The $(9,0)$ zigzag nanotube exhibits lower intensities of the plateau harmonics, while the first pair of harmonics emitted by $(8,2)$ chiral nanotube is in the cutoff region.

In conclusion, the interaction of a parallel nanotube array with a circularly polarized laser beam can lead to the selective generation of high harmonics in the soft x-ray range. The considered $(5,5)$ armchair nanotube gives rise to the HHG spectrum which is both selective and efficient enough to be of interest to experimentalists. The chiral nanotubes represent the first example of realistic physical systems for which all harmonics, except the very high ones, are forbidden by symmetry. This high selectivity, however, is expected to show up only at intensities higher than 10^{14} W/cm^2. The feasibility of HHG by nanotubes at such intensities depends on the breakdown thresholds for these materials.

From a practical point of view, the nanotube targets lack a number of serious drawbacks which are characteristic of the molecular ones. Unlike molecules, the nanotubes can be oriented in space just as solid targets. Arrays of nanotubes parallel to each other can be achieved by present day methods [17]. Efforts are being made to prepare the ropes containing the nanotubes of a single definite symmetry [18]. The chemical bonding between carbon atoms in nanotubes is rather strong which means that their deformation and dissociation in intense fields take place on longer time scales than that of aromatic molecules. The lack of light hydrogen atoms in nanotubes contributes to the same stability effect.

Besides the potential significance for the generation of the coherent, almost monochromatic, high frequency radiation, the selective HHG by carbon nanotubes can be used for the structural analysis of the nanotube samples. The relative strengths of the harmonics allowed for different nanotubes can provide information about the relative abundances of the various symmetry species in a nanotube sample. This information would be of great value given that other means of analysis, such as scanning tunneling microscopy, do not allow at present an unambiguous determination of the nanotube indices.

The general framework for the formulation of the selection rules for HHG beyond the dipole approximation developed in this paper can be applied to the study of selectivity of HHG by other systems which are extended along the incident beam propagation direction and emit low wavelength radiation.

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