Optical High Harmonic Generation in C_{60}

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High harmonic generation (HHG) requires a strong laser field, but in C_{60} a relatively weak laser field is sufficient. Numerical results presented here show that, while its low order harmonics result from the laser field, its high order ones are mainly from the multiple excitations. Since high order harmonics directly correlate with electronic transitions, the HHG spectrum accurately measures transition energies. Therefore, C_{60} is not only a promising material for HHG, but may also present an opportunity to develop HHG into an electronic structure probing tool.

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High harmonic generation (HHG) in atoms has attracted tremendous attention [1]. HHG is a potential light source with its time scale as short as several hundred attoseconds. The underlying mechanism is now well established both experimentally and theoretically. The highest harmonic is determined by $(\hbar\Omega)_{\max} = I_p + 3.17U_p$, where I_p is the atomic ionization potential and $U_p = e^2E^2/4m\omega^2$ is the ponderomotive energy of the electron. Here e and m are the electron charge and mass, respectively. E is the amplitude of the electric field and ω is the incident laser frequency. The general feature of these harmonics is that very sharp spikes with similar amplitude form a plateau, followed by an abrupt cutoff determined by the above equation. Comparatively, investigations of HHG in nanostructures and larger molecular systems are very limited [2,3], but multiple excitation channels and charge delocalizations in these systems are advantageous to HHG; C_{60} is a good example and it already shows a large off-resonant third harmonic generation $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of about 10^{-12} esu [4]. Its 5th order harmonic can be generated with a weak laser intensity of 10^{10} W/cm^2 [5]. To this end, no further experiment has been done beyond the 5th order [6]. Therefore, a theoretical investigation at this time is very appropriate [3,6].

In this Letter, we perform a dynamical simulation to study HHG in C_{60}. We find that due to the multiple excitations, high order harmonics in C_{60} can be easily generated even with a weak laser field. Similar to HHG in atoms, low order harmonics directly result from the laser field, but high order harmonics mainly come from the multiple electronic excitations whose energy positions directly correlate with electronic transitions. We suggest this correlation may allow one to develop HHG into a tool to probe the electronic states. The optimal experimental conditions to observe HHG in C_{60} are also investigated.

C_{60} has the highest I_h point symmetry. We describe it by the Hamiltonian [7]

$$H_0 = -\sum_{\langle ij\rangle,\sigma} t_{ij}(c^\dagger_{i,\sigma}c_{j,\sigma} + \text{H.c.}) + \frac{K_1}{2}\sum_{\langle i,j\rangle}(r_{ij} - d_0)^2 + \frac{K_2}{2}\sum_i d\theta^2_{i,5} + \frac{K_3}{2}\sum_i (d\theta^2_{i,6,1} + d\theta^2_{i,6,2}) \quad (1)$$

where $c^\dagger_{i,\sigma}$ is the electron creation operator at site i with spin $\sigma(=\uparrow\downarrow)$ [8] and the summation $\langle ij\rangle$ over $i(j)$ runs from 1 to 60 with $i \neq j$. The first term on the right hand side represents the electron hopping, and the last three terms on the right hand side are the lattice stretching, pentagon-hexagon, and hexagon-hexagon bending energies, respectively [9]. $t_{ij} = t_0 - \alpha(|\mathbf{r}_i - \mathbf{r}_j| - d_0)$ is the hopping integral between nearest-neighbor atoms at positions $\mathbf{r}_i$ and $\mathbf{r}_j$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here t_0 is the average hopping constant, and α is the electron-lattice coupling constant. By fitting the energy gap, bond lengths and normal mode frequencies, You *et al.* [7] have determined the above parameters as $t_0 = 1.91$ eV, $\alpha = 5.0$ eV/Å, $K_1 = 42$ eV/Å^2, $K_2 = 8$ eV/rad^2, $K_3 = 7$ eV/rad^2, and $d_0 = 1.5532$ Å. We will fix these parameters in the high harmonic generation calculations.

The laser field is simulated by

$$H_I = -e\sum_{i\sigma}\mathbf{E}(t)\cdot\mathbf{r}_i n_{i\sigma}, \quad (2)$$

where $|\mathbf{E}(t)| = F\sin^2(\pi t/\tau)\sin(\omega t)$ [10] and $n_{i\sigma}$ is the electron number operator at site i. Here F, ω, τ, e, and t are the field amplitude, laser frequency, pulse duration or width, electron charge, and time, respectively. We numerically solve the Liouville equation for the electron density matrices [8], $-i\hbar\partial\langle\rho^\sigma_{ij}\rangle/\partial t = \langle[\rho^\sigma_{ij}, H]\rangle$, where $H = H_0 + H_I$, and $\rho^\sigma_{ij} = c^\dagger_{i\sigma}c_{j\sigma}$ is the density matrix operator. The dipole is defined as $\mathbf{d}(t) = \langle\Sigma_{i\sigma}\mathbf{r}_i n_{i\sigma}\rangle$, and the dipole acceleration $\ddot{\mathbf{d}}(t)$ (the second derivative of dipole with respect to time) is computed either directly from $\mathbf{d}(t)$ or from $\ddot{\mathbf{d}}(t) = \langle\Sigma_{i\sigma}\ddot{\mathbf{r}}_i n_{i\sigma} + 2\dot{\mathbf{r}}_i\dot{n}_{i\sigma} + \mathbf{r}_i\ddot{n}_{i\sigma}\rangle$, each of which gives numerically same results. Since the harmonic generation spectrum is proportional to the Fourier form of the

dipole acceleration, we Fourier transform $\ddot{\mathbf{d}}(t)$ to the frequency space $\ddot{\mathbf{d}}(\Omega)$ by

$$\ddot{\mathbf{d}}(\Omega) = \int_0^\tau \ddot{\mathbf{d}}(t) e^{i\Omega t} dt, \tag{3}$$

where Ω is the emitted photon frequency. In atoms, Ω can be written as $\Omega = n\omega$, where n is the harmonic order and is often an integer [1,11]. In our system, n can be fractional (see below). Since C_{60} has a three-dimensional structure, the amplitude of the HHG is a vector-sum over its three components as

$$\ddot{d}(\Omega) = \sqrt{(\ddot{d}_x(\Omega))^2 + (\ddot{d}_y(\Omega))^2 + (\ddot{d}_z(\Omega))^2}, \tag{4}$$

where $\ddot{d}_x(\Omega)$, $\ddot{d}_y(\Omega)$, and $\ddot{d}_z(\Omega)$ are the Fourier components along the x, y, and z directions, respectively.

In atoms, the density of states (DOS) is low, thus one needs a strong laser to generate HHG. But in C_{60}, the DOS is higher and there are many multiple excitation channels. Consequently, HHG in C_{60} is relatively easier. For instance, even with a weak laser intensity Kafafi *et al.* were able to generate the 5th order harmonic [5]. We choose a weak laser intensity of 0.02 eV/Å. Previous results in atoms show that in order to efficiently excite HHG, it is necessary to excite the system at off resonance. We choose the laser frequency of 0.4 eV, which is about one-seventh of the first dipole-allowed transition gap from $H_u \rightarrow T_{1g}$ (HOMO $\rightarrow$ LUMO + 1) and is away from any major resonance. We select the pulse duration of $\tau = 32$ laser field cycles. The results are presented in Fig. 1(a), where the x axis denotes the harmonic order and the y axis represents the logarithmic of Fourier-transformed dipole accelerations. We see high order harmonics all the way up to the 31st order. Since our photon energy is roughly at 1/7th of the first dipole-allowed transition, the 7th order harmonic is substantially enhanced while the 5th order one is suppressed [12]. The spectrum naturally breaks into two regions at the 7th order. For those harmonics below the 7th order, they form a typical pattern of harmonic generation, where harmonic orders, as a result of the inversion symmetry in C_{60}, are odd integer numbers such as 1 and 3, except peak a. We find that peak a comes from the lattice vibrational excitations associated with the A_g, H_g, and T_{1u} normal modes, which can be independently verified by switching off the lattice [13]. Consistent with previous studies [14], the widths of those integer order harmonics are inversely proportional to the laser pulse duration.

Above the 7th order, the harmonics are not exactly at odd harmonic orders, but instead they appear rather randomly. This is very puzzling if compared with atomic HHG where most harmonic orders are integer numbers [11]. However, C_{60} is not alone, and similar harmonics have been reported in benzene and ring-shaped molecules [15]. We decide to simply change the harmonic orders to the energy scale [see the top x axis in Fig. 1(a)], which is a crucial step to fully understand those irregular peaks, but this alone is still not enough to explain those peaks.

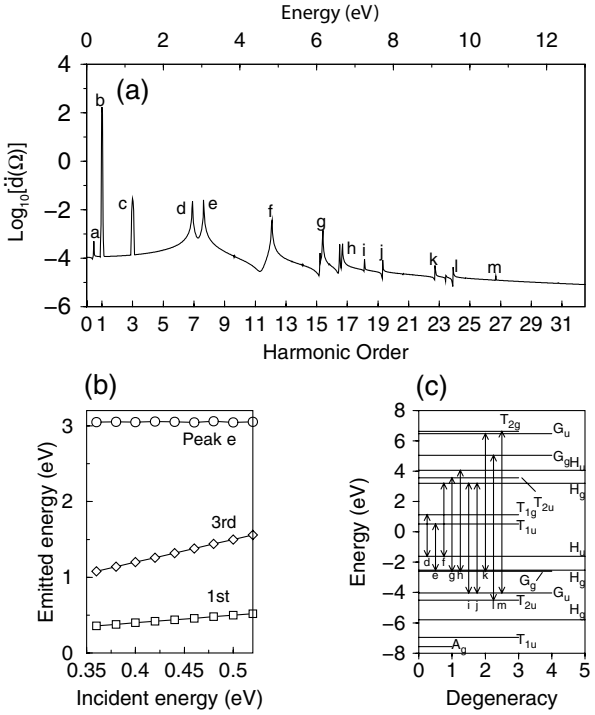

FIG. 1. (a) Harmonic generations in C_{60}. The laser energy is 0.4 eV, pulse duration is 32 laser cycles, and field strength is 0.02 eV/Å. Peak a results from the lattice vibration. Peaks b, c, and d are at the 1st, third, and seventh orders, respectively. Above the 7th order, harmonics mainly result from the intrinsic electronic excitations. (b) The emitted photon energy versus the incident energy. The circles, diamonds, and squares denote peak e, the third harmonic, and the first harmonic, respectively. (c) Assignment of peaks from d to m (see letters below arrows) to their respective transitions (double-arrow lines). The H_u (HOMO) is at -1.6158 eV and the T_{1u} (LUMO) is at 0.5255 eV.

Motivated by a previous resonant inelastic x-ray scattering (RIXS) study [16], we find a familiar concept in RIXS is useful for HHG. In RIXS, an x-ray photon first excites a core electron to unoccupied bands and leaves a core hole behind. In the decay process, when the electron recombines with the core hole, it emits a photon. If the emitted photon is from the elastic scattering, its energy is the same as the incident photon energy and increases linearly with the incident energy. On the other hand, if the photon results from the normal fluorescence or intrinsic electronic states, its energy is unchanged with respect to the incident photon energy. Here we can apply the same idea to HHG. By changing the incident laser frequency, we find that emitted energies of those low integer order harmonics [squares and diamonds in Fig. 1(b)] move linearly with the incident photon energy. Those squares and diamonds represent the 1st and 3rd harmonic peak positions, respectively, and have different slopes of 1 and 3. By contrast, for those high order harmonics, their energy positions are almost invariant with respect to incident wavelengths (see empty circles for peak

e). Here peak e is a representative example and other peaks behave similarly. Such invariance demonstrates that those high order harmonics are intrinsic to the system. Thus, they should be explainable from the electronic energy spectrum.

We illustrate the electronic energy levels in Fig. 1(c). As shown above that peak d is from the transition $H_u \rightarrow T_{1g}$, we start with peak e of Fig. 1(a). By comparing its energy of 3.05 eV with the electronic states, we find that only one transition can match this energy. That is the second dipole-allowed transition from $H_g \rightarrow T_{1u}$ (HOMO $-$ 1 to LUMO). In Fig. 1(c) we use a double-arrow line labeled by e to highlight this transition. This is very encouraging, but will this work for other peaks? We try another peak f and we find it corresponds to $H_u \rightarrow H_g$ (HOMO to LUMO + 2). A complete analysis of all the peaks reveals a truly insightful picture behind those irregular peaks: These high order harmonics are a result of multiple electron transitions. The double-arrow lines in Fig. 1(c) represent the transitions, with letters below the arrows denoting their respective peaks. For instance, the highest peak m corresponds to the transition from the lowest G_u to the highest T_{2g}. Such an accurate one-to-one correspondence between harmonic peaks and electronic transitions may pave the way to develop the HHG emission spectroscopy into an electronic state probing tool. Such a tool is within reach of current experiments. It requires more than one laser frequency, but the frequency conversion is already achievable for a long time, for instance using the second harmonic generations. Therefore, we believe HHG in C_{60} is not only a good potential light source but also a test case for a new tool of electronic structures.

We want to explore the possibility of observing HHG experimentally. Key experimental parameters to affect HHG include laser frequency, duration, and intensity. We investigate them separately below. (i) Laser frequency. From the HHG in atoms, it is clear that an off-resonant excitation is essential, but to see how far the laser frequency should be off resonance in C_{60}, we take peak j as an example. We compute the ratio of the intensity of the peak to the background baseline [17]. Since the baselines before and after the peak may be different, we denote these differences by the error bars in Fig. 2(a). Figure 2(a) shows the logarithmic ratio versus the incident laser frequency. One sees that the overall dependence is a decaying function [18], which explains the significance of off-resonant excitation. At 0.1 eV, there is no major resonant transition associated with this energy; harmonic j is huge, about 1 order of magnitude higher than its background. However, as far as one increases energy to 0.2 eV, a low harmonic, peak e, is resonant and overshadows peak j. Consequently the amplitude of peak j reduces sharply. A similar pattern repeats itself at 0.45, 0.8, and 1.0 eV, where the resonance occurs for low order harmonics. One notices that the optimal laser frequencies are around 0.1, 0.3, and 0.6 eV. (ii) Pulse duration. Consistent with previous studies [19], we find that for a shorter pulse, the harmonic peaks are broader, while a longer pulse reduces the background spectra and allows better resolution of the peaks. Our results show that the HHG in C_{60} is less sensitive to the duration than that in atoms. (iii) Laser intensity. The laser intensity has an important effect on HHG (see L'Huiller *et al.* in [1]). Figure 2(b) illustrates explicit dependences for a low order harmonic d and a high order harmonic m. We see that their dependences are qualitatively similar, but their quantitative dependences are slightly different. In the low field $F < 0.06$ eV/Å, $\ddot{d}_d \sim F^{0.98}$, and $\ddot{d}_m \sim F^{0.8}$, indicating that these harmonic generations proceed with multiple excitations. In the high field $F > 0.06$ eV/Å, $\ddot{d}_d \sim F^7$, and $\ddot{d}_m \sim F^{5.2}$. Note that only low order harmonics such as peak d increase with the same order numbers (7 for d), and the powers of higher order ones are lower than their orders [20]. We should mention that our present calculation does not include the ionization and possible fragmentation since our laser intensity is kept low [21]. Thus our formalism is essentially the same as the one employed by other groups [22]. When the laser intensity becomes stronger, one should consider both the multiphoton ionization and fragmentation. The effects of the ionization were already investigated by Bhardwaj *et al.* and they found that the $U_{\max}$ is higher than $3.2U_p$ [23]. We should also add that since our model includes only π electrons, all the HHG's come from π electrons. With the inclusion of high lying σ states, even higher order harmonic generations are expected [3]. As Bandrauk and Yu showed, the maximal emitted photon energy is well beyond the $I_p + 3.17U_p$ limit [24]. Therefore, we conclude the current experimental conditions should be adequate to generate HHG in C_{60} [23].

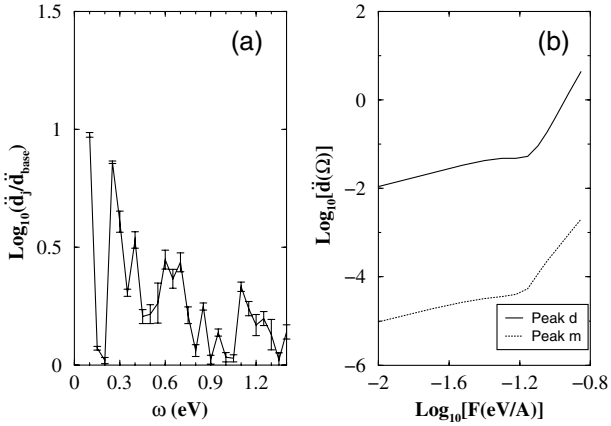

FIG. 2. (a) Efficiency of generating peak j as a function of the laser frequency. $\ddot{d}_j$ and $\ddot{d}_{\mathrm{base}}$ are the amplitudes of peak j and the background baseline, respectively. The error bars represent the difference between two baselines before and after peak j. The pulse duration and field strength are same as those in Fig. 1. (b) Intensity dependence of harmonics d and m. The power of the high harmonic m is lower than its order. The pulse duration and frequency are same as those in Fig. 1.

In conclusion, we investigate high harmonic generations in C_{60}. Because of the multiple electron excitations, HHG can be generated by a relatively weak laser. We find that low order harmonics are almost always at integer numbers, but high order harmonics are not exactly at those integer numbers. These high harmonics mainly result from the intrinsic electronic states. An accurate match between the harmonic peak positions and electronic transition energies suggests that those HHG spectra may be a useful tool to probe electronic states. Optimal experimental conditions to generate harmonics are investigated at the end.

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