PRL **99,** 113901 (2007) PHYSICAL REVIEW LETTERS week ending 14 SEPTEMBER 2007

Information Content of High Harmonics Generated from Aligned Molecules

S. Ramakrishna and Tamar Seideman*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

(Received 1 December 2006; published 10 September 2007)

We derive an expression for the harmonic signal from nonadiabatically aligned molecules that accounts for both electronic and rotational motions. We identify a single approximation, which converts the expression into a physically transparent and computationally convenient form. Our analytical result gives explicitly the time dependence of the harmonic spectra, thus explaining the observations of a class of recent experiments. Moreover, it points to new opportunities for generating insights into the structure and dynamics of molecular systems through harmonic generation experiments from aligned molecules. This includes information regarding the rotational and electronic dynamics of isolated systems, as well as regarding the decoherence and relaxation in molecules subject to a dissipative environment.

DOI: 10.1103/PhysRevLett.99.113901 PACS numbers: 42.65.Ky, 33.15.Mt, 33.20.Sn, 33.80.Wz

High harmonics generation (HHG) from prealigned molecules has been the topic of rapidly growing experimental [1–11] and theoretical [4,12–23] interest since the pioneering experiments of [3] that demonstrated the possibility of using harmonic spectra to explore the underlying electronic wave functions. HHG is well understood in terms of a 3-step process [24], wherein ionization takes place close to the maximum of the electric field, generating a free-electron wave packet in the continuum that follows the electric field oscillations. If the field is linearly (or close to linearly) polarized, the electron will revisit the core, with the most energetic recollisions taking place near the second zero of the laser electric field after the electron release. Possible consequences of the recollision are elastic or inelastic scattering events or a recombination, whereby photons at harmonics of the generating field are emitted. The intuitive picture of [24] was quantified by an analytical strong-field theory [25] and substantiated by a large number of numerical calculations [26]. The application of the recollision event as an intramolecular diffraction tool, to probe the electronic structure and dynamics, is particularly inviting in molecules. It requires, however, that the molecule be prealigned.

Molecular alignment by moderately intense laser pulses can be realized adiabatically [27] or nonadiabatically [28] (see [29,30] for a recent and an early review, respectively) but in the context of HHG the latter route presents major advantages [5,8,10]. Here, a short (with respect to rotational periods) pulse generates a broad rotational wave packet via sequential angular momentum nonconserving transitions. Such wave packets can be shown to align at a controllable time delay with respect to the pulse peak and, subsequent to dephasing, undergo a coherent revival process [31]. In systems where the classical rotation is stable (linear and symmetric top molecules), the initial alignment is precisely reconstructed at multiples of the rotational period, exhibiting partial revivals at system-dependent fractions of the period.

The fascinating physics of HHG from nonadiabatically aligned molecules, along with potential applications both as a spectroscopy and as a control tool, has fueled a large number of experiments on this topic within the past 2–3 years [3–11]. Theoretically, much insight was generated by a 2-scattering-centers model, wherein a diatomic molecule is described as two point emitters located at the two nuclei, leading to an interference pattern between electrons diffracted from the two sources [13,14]. More recently, considerable progress has been made on accurate description of the bound electronic wave function [19]. To date, however, all studies focused entirely on the electronic part of the time-dependent dipole, either neglecting the rotations and assuming a fixed orientation of the molecule or averaging the electronic dipole over a distribution of aligned molecules. While both approaches are valuable, neither can describe the experimentally observed time dependence of the harmonic signal. Empirically it was found that the observed structure follows in most cases the expectation value of $\cos^2\theta$. In some cases, however, depending on the molecule and on the harmonic order, $\langle\sin^2 2\theta\rangle$ or a combination of both geometric functions was found to correspond better to the observable [6,8].

One objective of the present work is to fill in the gap in our understanding of HHG from aligned molecules by deriving an analytical expression for the time evolution of the observable. A second objective is to propose that harmonic signals provide potentially more information about molecular systems than what has been envisioned so far, not only regarding the electronic structure, but also regarding the rotational dynamics of aligned molecules. To meet these objectives we derive a closed form expression for the harmonic spectrum that properly accounts for the rotational, as well as the electronic wave function, and examine its structure subject to a single approximation. The analytical solution provides *explicitly* the time dependence of the harmonics, thus illustrating the origin of the temporal structure observed experimentally and its dependence on the harmonic order. It reinterprets observations previously assumed to evolve as $\langle\cos^2\theta\rangle$, showing that the correct behavior is of the $\langle\cos^4\theta\rangle$ form. More interestingly, it points to the molecular parameters that determine the temporal structure. Formulation of our theory in terms of the density operator introduces the possibility of studying HHG from aligned molecules in dissipative media (such as dense gases) and simplifies calculations at nonzero rotational temperatures. We expect our result to provide complementary insights to previous numerical work in application to existing experiments, which have focused on linear systems. In addition, the present formulation applies to arbitrary molecular symmetries and hence to polyatomic systems and dynamical processes.

The rotational-electronic wave packet is written as

$$\Psi(t) = \sum_{JM} C^J_M(\tau)|0JM\rangle e^{iI_p t} + \sum_{J_c M_c}\int d^3k\, C^{J_c}_{M_c}(\vec{k},t)|\vec{k}J_cM_c\rangle e^{iI_p t}, \qquad \hbar = 1, \tag{1}$$

where $|0JM\rangle = |0\rangle|JM\rangle$, $|\vec{k}J_cM_c\rangle = |\vec{k}\rangle|J_cM_c\rangle$, $|0\rangle$ is the electronic ground state, $|\vec{k}\rangle$ denotes the electronic continuum states, and I_p is the ionization potential. The $|\vec{k}\rangle$ incorporate the effect of the strong HHG pulse on the electronic continuum and account for the journey of the ionized electron in the field. The $|0\rangle$ can incorporate the strong-field effect on the bound state, which amounts to a gradual depletion, but neglect of this effect was shown to be a successful approximation [25], as the continuum carries most of the physics. J and M are the total angular momentum and its projection onto the space-fixed z axis, and a subscript c denotes the ion core indices. The expansion coefficients C^J_M are the probability amplitudes of the states $|0JM\rangle$ in the wave packet, $C^J_M = \langle 0JM|\Psi\rangle$, and similarly $C^{J_c}_{M_c}$. τ in Eq. (1) denotes time with respect to the alignment pulse whereas t denotes time with respect to the HHG pulse. The $C^J_M(\tau)$ are determined by the alignment pulse and the molecular rotational constants and are not modified by the HHG pulse [32]. They contain the information about the rotational wave packet dynamics and evolve on the time scale of the wave packet rotations. The $C^{J_c}_{M_c}(\vec{k},t)$ contain the continuum dynamics induced by the HHG field and evolve on the electronic time scale. Equation (1) applies to the case of a linearly polarized alignment pulse and a linear molecule that is sufficiently heavy to behave as a rigid rotor on the time scale of relevance. This has been the case in experimental studies of HHG from nonadiabatically aligned molecules published to date [3–11]. The general case is addressed elsewhere. The harmonic spectrum is given as the Fourier transform of the component of the time-dependent dipole moment along the direction of polarization of the observed harmonics, denoted $\hat{n}$,

$$\langle\Psi(t)|\vec{\mu}\cdot\hat{n}|\Psi(t)\rangle = \sum_{J_cM_c}\sum_{JM}\int d^3k\, C^{J*}_M(\tau)C^{J_c}_{M_c}(\vec{k},t) \times \langle 0JM|\vec{\mu}\cdot\hat{n}|\vec{k}J_cM_c\rangle + \text{c.c.}, \tag{2}$$

where the continuum coefficients are determined through

$$\begin{aligned} i\dot{C}^{J_c}_{M_c}(\vec{k},t) = {}& (E^{J_c} + E_k + I_p)C^{J_c}_{M_c}(\vec{k},t) \\ & - \sum_{JM} C^J_M(\tau)\langle\vec{k}J_cM_c|\vec{\mu}\cdot\vec{\varepsilon}(t)|0JM\rangle \\ & - i\nabla_k C^{J_c}_{M_c}(\vec{k},t)\cdot\left(\frac{\partial\vec{k}}{\partial t}\right), \end{aligned} \tag{3}$$

E^{J_c} is the rotational energy associated with $|J_cM_c\rangle$, and E_k is the electronic energy of the continuum. Using Eqs. (2) and (3), neglecting E^{J_c} with respect to I_p ($E^{J_c} \sim 10^{-5}I_p$ for O_2, for instance), and using the closure relation,

$$\sum_{J_cM_c}\langle\hat{R}|J_cM_c\rangle^*\langle\hat{R}'|J_cM_c\rangle = \delta(\hat{R}-\hat{R}') \tag{4}$$

one obtains

$$\begin{aligned} \langle\Psi(t)|\vec{\mu}\cdot\hat{n}|\Psi(t)\rangle = {}& i\sum_{JJ'M} C^{J*}_M(\tau)C^{J'}_M(\tau)\int d\hat{R}\, Y^*_{JM}(\hat{R})Y_{J'M}(\hat{R}) \\ & \times\int d^3k\langle 0|\vec{\mu}\cdot\hat{n}|\vec{k}\rangle \\ & \times\int^t dt'\varepsilon(t')\langle\vec{k}'|\vec{\mu}\cdot\hat{\varepsilon}|0\rangle e^{-iS(t,t')} + \text{c.c.}, \end{aligned} \tag{5}$$

where the electric field is written as $\vec{\varepsilon}(t) = \hat{\varepsilon}\varepsilon(t)$ and $\hat{R}$ denote the Euler angles of rotation of the molecular axis with respect to the polarization vector. The time-dependent phase in Eq. (5) is $S(t,t') = \int_{t'}^{t} dt''(E_{k''} + I_p)$ and $\vec{k}' = \vec{k}(t')$, $\vec{k}'' = \vec{k}(t'')$. [Within the familiar strong-field approximation, $\vec{k}' = \vec{k} + \vec{A}(t) - \vec{A}(t')$, where $\vec{A}(t) = -\int^t \vec{\varepsilon}(t')dt'$.] Equation (5) can be recast as

$$\langle\Psi(t)|\vec{\mu}\cdot\hat{n}|\Psi(t)\rangle_T = \int d\hat{R}\,\rho_T(\hat{R};\tau)F_{\text{elect}}(\hat{R},t) + \text{c.c.}, \tag{6}$$

where ρ_T is the rotational density operator at time τ, which is understood to have been propagated by the Liouville equation from an initial rotational distribution at temperature T and incorporates the effects of the aligning pulse. Explicitly,

$$\rho_T(\hat{R};\tau) = \left|\sum_{JM} C^J_M(\tau)Y_{JM}(\hat{R})\right|^2, \tag{7}$$

and

$$\begin{aligned} F_{\text{elect}}(\hat{R},t) = {}& i\int d^3k\langle 0|\vec{\mu}\cdot\hat{n}|\vec{k}\rangle \\ & \times\int^t dt'\varepsilon(t')\langle\vec{k}'|\vec{\mu}\cdot\hat{\varepsilon}|0\rangle e^{-iS(t,t')}. \end{aligned} \tag{8}$$

Equation (6) converts the problem into a product of an electronic factor and a rotational factor, integrated over angles, where the rotational factor serves as a weight function for electronic overlap elements computed at fixed orientations of the molecular axis with respect to the polarization axis. Equation (6) is physically transparent and intuitively expected. It was taken as an ansatz in Refs. [16,17], but the rigorously derived rotational factor of Eq. (7) differs from the one in [16,17], as the latter confines the molecular rotation to a plane. Equations (5) and (6) amount to a separation of the dipole into an electronic and a rotational part.

To derive an analytical expression for the time dependence of the harmonics and provide insight into their information content, we proceed by exploring the angular dependence of the electronic factor. For simplicity we consider first the case where the HHG field is polarized parallel to the alignment field, and the harmonic signal measured is polarized along the fields polarization axis. Expanding the continuum state in partial waves in terms of the laboratory frame and transforming into the molecular frame (in which the bound state is computed) we have

$$\begin{aligned}\langle\vec{Q}|\vec{k}(t)\rangle &= \sqrt{\frac{2}{\pi}}\sum_{lm_lk_l} i^l D^{l*}_{k_lm_l}(\hat{R})Y^*_{lm_l}(\hat{k})\Phi_{lk_l}(E_k,\vec{Q},t)\\ &= \sqrt{\frac{2}{\pi}}\sum_{lk_l} i^l Y_{lk_l}(\hat{R})\Phi_{lk_l}(E_k,\vec{Q},t), \qquad (9)\end{aligned}$$

where $\vec{Q}$ denotes the electronic coordinates with respect to the molecular frame, l is the electronic angular momentum with projections m_l and k_l onto the polarization and molecular axes, respectively, and $\Phi_{lk_l}(E_k,\vec{Q},t)$ is the corresponding partial wave. In deriving the second equality we assume $\hat{k}\parallel\hat{\varepsilon}$, that is, the momentum of the strong-field driven electron is along the polarization vector. This assumption is not necessary but simplifies the notation and is consistent with stationary state integration results [21]. Thus,

$$\langle\Psi(t)|\vec{\mu}\cdot\hat{n}|\Psi(t)\rangle_T = \int d\hat{R}\rho_T(\hat{R};\tau)\Big\{\cos^2\theta\sum_{ll'k_l}Y_{lk_l}(\hat{R})Y^*_{l'k_l}(\hat{R})F_{\parallel}(l,l',k_l,t) + \sin^2\theta\sum_{ll'k_l}Y_{lk_l}(\hat{R})Y^*_{l'k_l}(\hat{R})F_{\perp}(l,l',k_l,t)\Big\} + \text{c.c.}, \qquad (10)$$

where the purely electronic function $F_{\parallel(\perp)}$ is given as

$$\begin{aligned}F_{\parallel(\perp)}(l,l'k_l,t) = \frac{2}{\pi}i^{l-l'+1}&\int dk\langle 0|\mu_{\parallel(\perp)}|\Phi_{lk_l}\rangle\\ &\times\int^t dt'\varepsilon(t')\langle\Phi_{l'k_l}|\mu_{\parallel(\perp)}|0\rangle e^{-iS(t,t')}. \qquad (11)\end{aligned}$$

Equation (11) has the same physical content and mathematical structure as the time-dependent dipole moment evaluated in studies of HHG from atoms [25,26]. Here the strong-field theory of [25] has been particularly popular, due to its insight and computational simplicity, but recent work has advanced the description of the ground state [19]. The recombination matrix element in this term, the prefactor to the time integral, contains the information about the scattering of the electron from the atomic constituents and incorporates the interference of electron waves that may arise from the availability of several scattering centers, discussed in [3–19,21,22]. The temporal factors account for the journey of the driven electron subject to the field, discussed, e.g., in [25]. It is important to note that Eqs. (10) and (11) can be computed with any method of describing the bound and continuum electronic wave functions. Although in principle the l summation is infinite, in practice the dipole element with the ground electronic state favors the lowest l waves. The partial wave dominating the sum depends, however, on the symmetry of the ground state.

For homonuclear diatomics, l, l' are either even or odd and for most ground states the projection of the electronic angular momentum onto the molecular axis vanishes. In this case the product of spherical harmonics in the first term of Eq. (10) is $Y_{l0}Y^*_{l'0} = \sum_n f_n\cos^{2n}\theta$, whereas the same product in the second term is $Y_{l\pm1}Y^*_{l'\pm1} = \sin^2\theta\sum_n g_n^{\pm}\cos^{2n}\theta$. For ground states with ±1 projection of the electronic angular momentum, such as O_2, the two series are reversed. For a σ_g orbital the parallel component, $\mu_{\parallel}$ in Eq. (10), typically dominates, and one expects the harmonic signal to behave as a rapidly converging power series in $\cos^2\theta$. For the specific case of N_2, we find numerically that the lowest order term, $\cos^2\theta F_{\parallel}(1;1;0;t)$, dominates. It follows that the HHG signal of N_2 evolves rigorously as $\langle\cos^4\theta\rangle(\tau)$. This result reinterprets a large number of observations of the HHG from aligned N_2, where the time dependence was fitted to $\langle\cos^2\theta\rangle(\tau)$. We note, however, that (apart from a shift of the baseline) $\langle\cos^4\theta\rangle(\tau)$ and $\langle\cos^2\theta\rangle(\tau)$ are very similar. The above analysis indicates that, for a π_g orbital, both parallel and perpendicular components in Eq. (10) are non-negligible, and hence the pattern would vary with the incoming electron energy, reflecting the balance between at least two terms of different time dependence. For O_2 we find numerically that a term proportional to $\langle\cos^4\theta\sin^2\theta\rangle$ plays a significant role, while the lowest order term allowed is $\propto\langle\cos^2\theta\sin^2\theta\rangle$. Numerical results of Eq. (10), shown in Fig. 1, compare well with the observations of [6,8]. Our analysis explains why for N_2 all previous numerical results, including ones based on crude description of the electronic dynamics, were found in good agreement with measurements, whereas for O_2 it proved more difficult to reproduce observations. It explains also the marked sensitivity of the signal to the harmonic order in the O_2 case and its insensitivity in the N_2 case. Finally, our results can be used to predict the time evolution of HH generated from different classes of linear molecules ahead of detailed calculations.

Equations (10) and (11) suggest the ability of HH signals to trace different moments of the alignment, depending on

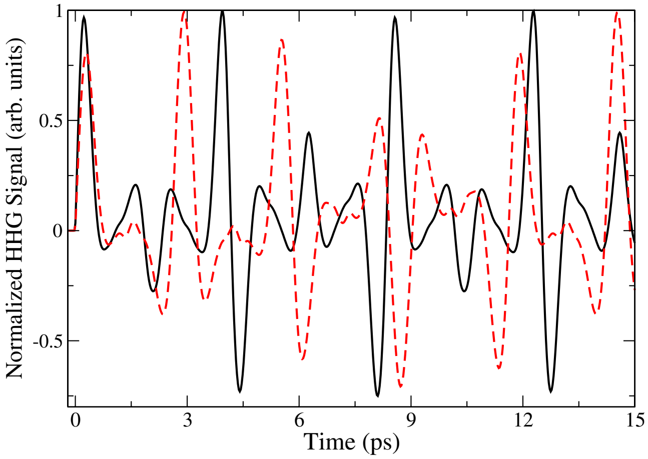

FIG. 1 (color online). The computed 23rd harmonic of N_2 (solid line) and O_2 (dashed line) at a rotational temperature of $T = 30$ K. The alignment pulse is Gaussian with duration 250 fs and a peak intensity of 2.4×10^{13} W cm^{-2}, and the HHG peak intensity is 2.0×10^{14} W cm^{-2} at 800 nm.

the harmonic order and the field parameters. We remark that the conventional measure of wave packet alignment, $\langle \cos^2\theta \rangle$, probes only second order ($J \longrightarrow J \pm 2$) rotational coherences, but strong-field-aligned wave packets contain the much richer higher order coherences. HHG spectra may thus provide new information about the evolution of rotational wave packets, which is silent in conventional observables. It is worth noting that rotational coherences contain valuable information about both the molecular system [33] and the medium in which it evolves [34].

In summary, we derived a rigorous framework for calculation of HH signals from aligned molecules that accounts for both the electronic and the rotational wave packet dynamics as well as for their correlation. The former was intensively discussed in the recent literature whereas the latter is new and fascinating. By providing a closed form expression for the time dependence of the signal, the formalism explains the observations of a large number of experiments over the past 3 years. Interestingly, it points to the information content of such experiments regarding the rotational coherences of the target molecule, hence suggesting a broad class of new applications of HHG.

We are grateful to Professors M. Murnane and H. Kapteyn for raising our interest in the topic of this contribution, to Dr. T. Dutoi for interesting discussions, and to the US Department of Energy (Grant No. DE-FG02-04ER15612) for generous support.

*t-seideman@northwestern.edu

[1] R. Velotta *et al.*, Phys. Rev. Lett. **87**, 183901 (2001).
[2] N. Hay *et al.*, Phys. Rev. A **65**, 053805 (2002).
[3] J. Itatani *et al.*, Nature (London) **432**, 867 (2004).
[4] R. de Nalda *et al.*, Phys. Rev. A **69**, 031804(R) (2004).
[5] M. Kaku *et al.*, Japan. J. App. Phys. **43**, L591 (2004).
[6] T. Kanai *et al.*, Nature (London) **435**, 470 (2005).
[7] K. Miyazaki and M. Kaku *et al.*, Phys. Rev. Lett. **95**, 243903 (2005).
[8] J. Itatani *et al.*, Phys. Rev. Lett. **94**, 123902 (2005).
[9] C. Vozzi *et al.*, Phys. Rev. Lett. **95**, 153902 (2005).
[10] C. Vozzi *et al.*, J. Phys. B **39**, S457 (2006).
[11] G. H. Lee *et al.*, J. Korean Phys. Soc. **49**, 337 (2006).
[12] M. Lein *et al.*, Phys. Rev. Lett. **88**, 183903 (2002).
[13] M. Lein *et al.*, Phys. Rev. A **66**, 023805 (2002).
[14] M. Lein *et al.*, Phys. Rev. A **67**, 023819 (2003).
[15] B. Zimmermann *et al.*, Phys. Rev. A **71**, 033401 (2005).
[16] X. Zhou *et al.*, Phys. Rev. A **71**, 061801 (2005).
[17] X. Zhou *et al.*, Phys. Rev. A **72**, 033412 (2005).
[18] M. Lein *et al.*, J. Mod. Opt. **52**, 465 (2005).
[19] S. Patchkovskii *et al.*, Phys. Rev. Lett. **97**, 123003 (2006).
[20] A.-T. Le, X.-M. Tong, and C. D. Lin, Phys. Rev. A **73**, 041402(R) (2006).
[21] C. B. Madsen and L. B. Madsen, Phys. Rev. A **74**, 023403 (2006).
[22] C. D. Lin and X. M. Tong, J. Photochem. Photobiol., A **182**, 213 (2006).
[23] C. C. Chirila and M. Lein, Phys. Rev. A **73**, 023410 (2006).
[24] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[25] M. Lewenstein *et al.*, Phys. Rev. A **49**, 2117 (1994).
[26] K. C. Kulander *et al.*, in *Atoms in Intense Radiation Fields*, edited by M. Gavrila (Academic, New York, 1992); for a review see, P. Agostini and L. F. DiMauro, Rep. Prog. Phys. **67**, 813 (2004).
[27] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
[28] T. Seideman, J. Chem. Phys. **103**, 7887 (1995).
[29] For a recent review, see T. Seideman and E. Hamilton, Adv. At. Mol. Phys. **52**, 289 (2006).
[30] For a review see, H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003).
[31] T. Seideman, Phys. Rev. Lett. **83**, 4971 (1999).
[32] The HHG pulse does not drive rotational excitation (although its duration could suffice to that end in some of the published experiments, due to the high intensity) because the ionization this pulse induces is rapid compared to the stimulated J-changing transitions.
[33] P. M. Felker, J. Chem. Phys. **96**, 7844 (1992).
[34] S. Ramakrishna and T. Seideman, Phys. Rev. Lett. **95**, 113001 (2005).