A numerical ab initio study of harmonic generation from a ring-shaped model molecule in laser fields

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When a laser pulse impinges on a molecule which is invariant under certain symmetry operations selection rules for harmonic generation (HG) arise. In other words: symmetry controls which channels are open for the deposition and emission of laser energy—with the possible application of filtering or amplification. We review the derivation of HG selection rules and study numerically the interaction of laser pulses with an effectively one-dimensional ring-shaped model molecule. The harmonic yields obtained from that model and their dependence on laser frequency and intensity are discussed. In a real experiment obvious candidates for such molecules are benzene, other aromatic compounds, or even nanotubes.

I. INTRODUCTION

Harmonic generation (HG) from atoms (L’Huillier & Balcou 1993), molecules (Liang et al. 1994), clusters (Donelly et al. 1996), and solids (von der Linde et al. 1995) as a short-wavelength source is of great practical relevance. In recent years a huge amount of publications were devoted to “harmonic engineering,” under which we subsume either the study of phase matching during the propagation of the emitted light through gaseous media (Gaarde et al. 1998), generation of attosecond pulses using varying ellipticity (Antoine et al. 1997), multi-color studies (Milosevic et al. 2000), or HG from thin crystals (Faisal & Kaminski 1996 and 1997). Experimental results on HG from cyclic organic molecules were also reported in the literature (Hay et al. 2000a and 2000b). However, the authors made no attempt to verify theoretically predicted selection rules. In the well established physical picture of HG one assumes that an electron tunnels out of the atom or ion, moves in the laser field and eventually rescatters with its parent (or other) ion where it might recombine—leading to an emission of a photon with several times the fundamental frequency (Becker et al. 1997). Assuming such a viewpoint one can easily explain prominent features of HG spectra such as the famous cut-off at $I_p + 3\cdot 17 U_p$ in the single atom case (where $I_p$ is the ionization energy and $U_p$ is the ponderomotive energy, i.e., the cycle-averaged quiver energy of the electron in the laser field). For a general overview on harmonic generation in laser fields see the recent review by Salières et al. (1999).

Fortunately, to derive the selection rules for harmonic emission only symmetry considerations are necessary (Alon et al. 1998). We now briefly summarize this approach. Let us consider a Hamiltonian which is periodic in time, i.e., $H(t) = H(t + \tau)$. Such a Hamiltonian might describe an electron in a long laser pulse where the pulse envelope is sufficiently adiabatic. The time-dependent Schrödinger equation (TDSE) reads (we use atomic units $\hbar = e = m = 1$ throughout, if not noted otherwise)

$$\left[H(t) - i\frac{\partial}{\partial t}\right] \Psi_E(r, t) = 0. \tag{1}$$

According to the Floquet theorem (see, e.g., Faisal 1987) we can write $\Psi_E(r, t) = \psi_E(r, t) \exp(-iEt)$ with $\psi_E(r, t) = \psi_E(r, t + \tau)$ leading to the Schrödinger equation

$$H_F(t)\psi_E(r, t) = E\psi_E(r, t), \quad H_F(t) = H(t) - i\frac{\partial}{\partial t} \tag{2}$$

with $E$ the so-called quasi energy and $H_F$ the Floquet Hamiltonian. Since $\psi_E(r, t)$ is periodic in time it might be expanded in a Fourier series $\psi_E(r, t) = \sum_n \exp[-in(\omega t + \delta)]\Psi_E^{(n)}(r)$. This Floquet approach is a well-known method in multiphoton physics (Gavrila 1992) and a widely used numerical simulation technique also (Potvliege 1998). In order to derive the HG selection rules we now assume (for reasons which will become clear soon) that the system is in a single and non-degenerate Floquet state $\psi_E$. The HG spectra (HGS) peak no. $n$ is present only if the Fourier transformed dipole moment $\mu(r)$ does not vanish for the frequency $n\omega$,
\[
\int dt \exp(-i\omega t) \int d^3 r \, \Psi_\epsilon^*(r, t) \mu(r) \Psi_\epsilon(r, t) \neq 0.
\]

Now let us suppose we worked out a symmetry operation \( \mathcal{P} \) under which the Floquet Hamiltonian is invariant, \( \mathcal{P} H_F(t) \mathcal{P}^{-1} = H_F(t) \). It follows that (in the case of non-degenerated Floquet states \( \psi_\epsilon \), see assumption above) \( \mathcal{P} \psi_\epsilon = a \psi_\epsilon \) holds. Here \( a \) is a phase factor, \(|a| = 1\). For convenience, we rewrite (3) as

\[
\langle \langle \psi_\epsilon | \mu(r) \exp(-i\omega t) | \psi_\epsilon \rangle \rangle = \langle \langle \psi_\epsilon | \mu(r) \exp(-i\omega t) | \psi_\epsilon \rangle \rangle \neq 0
\]

where the double brackets indicate spatial and temporal integration [this is the so-called extended Hilbert space formalism, see, e.g., Sambe (1973)]. The HG selection rule can be derived from

\[
\langle \langle \psi_\epsilon | \mu(r) \exp(-i\omega t) | \psi_\epsilon \rangle \rangle = \langle \langle \mathcal{P} \psi_\epsilon | \mathcal{P} \mu(r) \exp(-i\omega t) \mathcal{P}^{-1} | \mathcal{P} \psi_\epsilon \rangle \rangle
\]

leading to

\[
\mu(r) \exp(-i\omega t) = \mathcal{P} \mu(r) \exp(-i\omega t) \mathcal{P}^{-1}.
\]

The last step in (3) is not possible if \( \psi_\epsilon \) is not a pure Floquet state. In the next Section we apply (3) to derive the selection rule for HG from ring-shaped molecules. Here, for the sake of illustration, we rederive the selection rule for a single atom with spherically symmetric potential \( V(r) \) and linearly (in \( x \)-direction) polarized laser field \( \mathbf{E}(t) = \hat{E}_x \sin \omega t \). The Floquet Hamiltonian \( H_F(t) = -\frac{1}{2} \nabla^2 + V(r) + \hat{E}_x \sin \omega t - i \hbar \) is invariant under the transformation \( x \rightarrow -x \) and \( t \rightarrow t + \pi/\omega \). If we look for harmonics polarized in the \( x \)-direction we have \( \mu(r) = x \) and from (3) \( x \exp(-i\omega t) = -x \exp[-i\omega(t + \pi/\omega)] \) follows \( \exp(-i\pi) = -1 \). Therefore only odd harmonics are generated.

The paper is organized as follows: in Section II we introduce our model and the selection rule which holds in its case. In Section III we present and discuss our numerical results. Finally, in Section IV we give a summary and an outlook.

II. A SIMPLE ONE-DIMENSIONAL MODEL FOR RING-LIKE MOLECULES

The time-dependent Schrödinger equation (TDSE) for a single electron in a laser field \( \mathbf{E}(t) \) and under the influence of an ionic potential \( V(r) \) reads in dipole approximation and length gauge

\[
i \frac{\partial}{\partial t} \Psi(r, t) = \left( -\frac{1}{2} \nabla^2 + V(r) + \mathbf{E}(t) \cdot \mathbf{r} \right) \Psi(r, t).
\]

(7)

The dipole approximation is excellent since in all the cases studied in this paper the wavelength of the laser light is much greater than the size of the molecule.

If we force the electron to move along a ring of radius \( \rho \) in the \( xy \)-plane \( V(r) \) becomes \( V(\varphi) \) where \( \varphi \) is the usual polar angle. With an electric field of the form \( \mathbf{E}(t) = \hat{E}(t) \left[ \xi \cos(\omega t) \hat{e}_x + \sqrt{1 - \xi^2} \sin(\omega t) \hat{e}_y \right] \), where \( \hat{E}(t) \) is a slowly varying envelope, \( \omega \) is the laser frequency, and \( \xi \) is the ellipticity parameter, the TDSE (7) becomes effectively one-dimensional (1D) in space and reads

\[
i \frac{\partial}{\partial t} \Psi(\varphi, t) = \left( -\frac{1}{2\rho^2} \frac{\partial^2}{\partial \varphi^2} + V(\varphi) + \hat{E}(t) \rho \left[ \xi \cos(\omega t) \cos \varphi + \sqrt{1 - \xi^2} \sin(\omega t) \sin \varphi \right] \right) \Psi(\varphi, t).
\]

(8)

In case of circularly polarized light (\( \xi = 1/\sqrt{2} \)) this simplifies to

\[
i \frac{\partial}{\partial t} \Psi(\varphi, t) = \left( -\frac{1}{2\rho^2} \frac{\partial^2}{\partial \varphi^2} + V(\varphi) + \frac{\hat{E}(t) \rho}{\sqrt{2}} \cos(\varphi - \omega t) \right) \Psi(\varphi, t).
\]

(9)

We now assume that the potential \( V(\varphi) \) has an \( N \)-fold rotational symmetry, \( V(\varphi + 2\pi/N) = V(\varphi) \). Then, with the help of (3), we can easily derive the selection rule for HG in the system described by the TDSE (7). The transformation \( (\varphi \rightarrow \varphi + 2\pi/N, \ t \rightarrow t + 2\pi/N \omega) \) leaves the corresponding Floquet Hamiltonian invariant. For, e.g., anti-clockwise polarized emission \( \mu(r) = \rho \exp(i\varphi) \) holds, and from (3) we have
leading to \( n = Nk + 1, k = 1, 2, 3, \ldots \). For the clockwise emission one finds accordingly \( n = Nk - 1 \). Thus we expect pairs of HG peaks at \( kN \pm 1 \) (Alon et al. 1998).

The TDSE (8) or (9) can be easily solved ab initio on a PC. We did this by propagating the wavefunction in time with a Crank-Nicholson approximant to the propagator \( U(t + \Delta t, t) = \exp[-i\Delta t H(t + \Delta t/2)] \) where \( H(t) \) is the explicitly time-dependent Hamiltonian corresponding to the TDSE (8). Our algorithm is fourth order in the grid spacing \( \Delta \varphi \) and second order in the time step \( \Delta t \). The boundary condition is \( \Psi(0, t) = \Psi(2\pi, t) \) for all times \( t \).

### III. NUMERICAL RESULTS AND DISCUSSION

We now present results from single active electron (SAE)-runs with \( \rho = 2.64 \) (bond length and radius of benzene \( C_6H_6 \)) and an effective model potential

\[
V(\varphi) = -\frac{V_0}{2}[\cos(N\varphi) + 1]
\]

with \( N = 6 \) and \( V_0 = 0.6405 \). This leads to an electronic ground state energy \( E_0 = -0.34 \) which is the experimental ionization potential for removing the first electron in benzene (see, e.g., Talebpour et al. 1998 and 2000). Note, that in our simple model we have no continuum but discrete states only. The first six excited states are located at \(-0.27 \) (two-fold degenerated), \(-0.07 \) (two-fold degenerated), \( 0.16 \) (non-degenerated), \( 0.48 \) (non-degenerated), \( 0.85 \) (two-fold degenerated), \( 1.48 \) (two-fold degenerated). The energy levels of our model resemble, apart from an overall downshift and the removal of degeneracies of certain states, those of the isoperimetric model where \( V_0 = 0 \), the energy levels are given by \( E_m = m^2/2\rho^2 \), \( m = 0, 1, 2, \ldots \) with the states \( m \neq 0 \) two-fold degenerated. Therefore, the energy level spacing, and thus typical electronic transitions, are different from those in real benzene. However, it is not our goal to present quantitatively correct results for laser benzene-interaction in this paper but we rather want to demonstrate some of the underlying principles of HG from ring-shaped molecules in general.

In Fig. 1a we present HGS for a \( q = 240 \) cycle pulse of the shape \( \hat{E}(t) = \hat{E}\sin^2(\omega t/2q) \) with an electric field amplitude \( \hat{E} = 0.5 \) a.u. and frequency \( \omega = 0.18 \). In Fig. 1b, the result for linear polarization \( \xi = 1 \) is shown, in Fig. 1b the result for circular polarization \( \xi = 1/\sqrt{2} \). To obtain those plots we evaluated the Fourier transformed dipole in \( x \)-direction, i.e., \( \langle (\Psi(t)\rho\cos(\varphi)\exp(-i\omega t)|\Psi(t)) \rangle \). In the \( \xi = 1 \)-case the dipole with respect to \( y \) is clearly zero while in the circular case there is simply a phase shift of \( \pi/2 \) with respect to the dipole in \( x \). As expected, in the linearly polarized field all odd harmonics are emitted whereas in the circular case only the harmonics \( 6k \pm 1, k = 1, 2, \ldots \) are visible. Other emission lines are many orders of magnitude weaker. Those lines can form band-like structures which are interesting in itself. However, in this paper we focus only on the laser harmonics. They dominate the HGS, at least as long as no resonances are hit.

In Fig. 2 the emitted yield of the fundamental and the first four harmonics (5th, 7th, 11th, 13th) in a circularly polarized laser pulse are presented as a function of the laser frequency. The pulse length \( T = 8378 \) a.u. (corresponding to \( \approx 200 \) fs) and peak field strength \( \hat{E} = 0.2 \) a.u. (corresponding to \( 1.4 \times 10^{15} \) W/cm\(^2\)) were held fixed. The frequency is plotted in units of the smallest level spacing of the model molecule, i.e., the energy gap between first excited and ground state, which is in our case \( \Omega = 0.34 - 0.27 = 0.07 \). For laser frequencies \( \omega < \Omega \) we do not find the 7th or higher harmonics. The 11th and 13th harmonic show an overall decrease with increasing laser frequency whereas the fundamental, the 5th and the 7th stay relatively constant in intensity. For frequencies \( \omega < 2.5\Omega \) there is a complicated dependency of the harmonic yield on \( \omega \). All harmonics show a local maximum around \( 1.3\Omega \). However, at that frequency one apparently hits a resonance since the harmonic peaks become broad and show a substructure (see left inlay in Fig. 2). In the interval \( 2 < \omega/\Omega < 2.5 \) the fundamental drops whereas the 7th harmonic increases in strength. Note that the 7th harmonic is anti-clockwise polarized, like the incident laser field, whereas the 5th is polarized in the opposite direction. For frequencies \( \omega > 2.5\Omega \) the behavior becomes more smooth apart from another resonance near \( 3.8\Omega \). In general, the HGS look clean for sufficiently high frequencies and far away from resonances (like in the right inlay of Fig. 2). A rich substructure near resonances is visible in the HGS (cf. inlay for \( \omega = 2\Omega \)).

In Fig. 3 harmonic yields for the fixed frequency \( \omega = 2.8\Omega \) as a function of the field amplitude \( \hat{E} \) are shown. The higher harmonics (11th–19th) appear only for higher field strengths whereas fundamental, 5th and 7th are rather weakly dependent on the field strength. The anti-clockwise polarized harmonics (polarized like the incident laser light, drawn thick) tend to overtake the clockwise polarized ones (drawn thin) at higher laser intensities. However, \( \hat{E} = 0.6 \) corresponds already to a laser intensity \( 1.3 \times 10^{16} \) W/cm\(^2\) where a real benzene molecule would probably break.
It is interesting to study the scaling of the TDSE with respect to the size of the molecule. If one scales the molecule radius like $\rho' = \alpha \rho$, the TDSE remains invariant if $t' = \alpha^2 t$, $V' = V/\alpha^2$, $E' = E/\alpha^3$, $\omega' = \omega/\alpha^2$ is chosen. From this and our numerical result that laser frequencies $> \Omega$ are preferable for clean HGS we learn that molecules bigger than benzene are more promising candidates for HG with realistic laser frequencies [from Nd ($\omega = 0.04$ a.u.) to KrF ($\omega = 0.18$ a.u.)].

One might object that electron correlation could spoil the selection rule because in reality it is not only a single electron which participates in the dynamics. However, Alon et al. (1998) have proven that this is not the case. This is due to the fact that (i) the electron interaction part of the Hamiltonian is still invariant under the transformation $P$, and (ii) $P$ commutes with the (anti-) symmetrization operator. Even approximate theories or numerical techniques like time-dependent Hartree-Fock or density functional theory do not spoil the selection rule since they involve only functionals which depend on scalar products of single particle orbitals, all invariant under the transformation $P$ (Ceccherini & Bauer 2001).

IV. SUMMARY AND OUTLOOK

In this paper we demonstrated numerically HG from a model molecule with discrete rotational symmetry which is subject to a circularly polarized laser pulse. In particular the harmonic emission from an effectively 1D model with $N = 6$ (i.e., a simple model for benzene) as a function of laser frequency and intensity was discussed. It was found that for frequencies below the characteristic level spacing $\Omega$ HG is strongly affected by resonances. The situation relaxes for higher frequencies. For the efficient generation of higher harmonics laser frequencies $> \Omega$ and rather strong fields are necessary. In such fields real aromatic compounds probably ionize and dissociate already.

Numerical studies for a more realistic, effectively 2D model molecule will be presented elsewhere (Ceccherini & Bauer 2001).

In order to obtain short wavelength radiation it is desirable to have either $k$ or $N$ in the selection rule $kN \pm 1$ as big as possible. From our numerical results we infer that it is probably hard to push efficiently towards high $k$ without destroying the target molecule. For that reason, in a real experiment nanotubes are promising candidates because $N$ can be of the order of 100 or more (Dresselhaus et al. 1998), and, moreover, HG should be even more efficient when the laser propagates through the tube. However, it remains the problem of the proper alignment of the laser beam and the symmetry axis of the molecule. Crystals might be better candidates in that respect.

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FIG. 1. HGS for a 240 cycle sin$^2$-shaped pulse with an electric field amplitude $\hat{E} = 0.5$ a.u. and frequency $\omega = 0.18$. The polarization was (a) linear ($\xi = 1$) and (b) circular ($\xi = 1/\sqrt{2}$). In (a) odd harmonics up to $n = 23$ dominate whereas in (b) the harmonics obey the selection rule $6k \pm 1, k = 1, 2, \ldots$, i.e., the 5th, 7th, 11th, 13th, 17th, 19th harmonics are visible.

FIG. 2. Fundamental and harmonic yield vs. laser frequency $\omega$ in units of the smallest level spacing $\Omega = 0.07$. Laser field intensity and pulse length was kept fixed. The anti-clockwise polarized fundamental, 7th, and 13th are plotted thick, the clockwise polarized 5th and 11th are drawn thin. The inlays show spectra (harmonic yield vs. harmonic order) for three particular frequencies (indicated by arrows). See text for further discussion.

FIG. 3. Harmonic and fundamental yields for fixed frequency $\omega = 2.8\Omega$ but different field amplitude $\hat{E}$. The inlays show spectra (harmonic yield vs. harmonic order) for three particular $\hat{E}$ (indicated by arrows). See text for further discussion.
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