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Xia, Yuqing and Jaron-Becker, Agnieszka, "Mollow sidebands in high order harmonic spectra of molecules." (2016). *Physics Faculty Contributions*. 103.
[https://scholar.colorado.edu/phys_facpapers/103](https://scholar.colorado.edu/phys_facpapers/103)
Mollow sidebands in high order harmonic spectra of molecules

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Abstract: Novel feature of high order harmonic generation process for molecules is presented for several molecules at their equilibrium geometries. The high order harmonic spectra reveal additional sidebands for each odd harmonic, which are a consequence of the resonant coupling of two valence orbitals, a mechanism analogous to Mollow triplets known from quantum optics. Strong modification of the high order harmonic generation process is illustrated with time frequency analysis in which there appear additional minima dependent on the Rabi frequency for the corresponding transition. The orbital coupling further leads to the modification of the electron dynamics which is presented using total electron density difference maps.

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OCIS codes: (020.2649) Strong field laser physics; (020.4180) Multiphoton physics; (191.4190) Multiphoton processes; (190.7110) Ultrafast nonlinear optics; (190.4160) Multi-harmonic generation.

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The nonperturbative interaction between atoms, molecules or solids and an intense laser fields results, among other phenomena, in high-order harmonic generation (HHG) [1,2]. In one of the most extreme cases, the upconversion of the fundamental driver frequency via HHG has recently led to the generation of coherent soft X-ray laser light [3]. The radiation is emitted as isolated bursts or in trains of attosecond pulses of light [4–7]. While the process is often studied in neutral atoms, more recently HHG generation from plasma containing atomic ions has been observed as well [8, 9]. HHG process has been also proposed as a spectroscopic tool to image static and dynamic properties of molecules [10–16]. The analysis of HHG itself as well as its spectroscopic applications is often based on approximations such as the semiclassical treatment of the electron-field interaction and the single-active electron approximation. Accordingly, our basic understanding of HHG relies on the three-step model [17], in which the electron is first tunnel ionized, then driven by the field and finally recombines with the parent ion leading to the emission of light in a form of integer harmonics of the fundamental driver laser frequency. In recent years it however has been shown that, in particular in the case of molecules, the generated harmonic spectra often incorporate more features than predicted by this basic picture. For example, the relevance of multi-electron contributions for the interpretation of experimental data on the ellipticity of high-order harmonics from nitrogen molecules has been demonstrated [18–21]. This results from the fact that in molecules often there are several orbitals energetically close together in the neutral as well as the cation. Therefore, the emission of electrons from different orbitals or the coupling between different orbitals becomes more likely. In particular, if the laser field is resonant with a transition, a coherent superposition of states can be formed during the pulse. It is known from atomic and model studies that resonant HHG and HHG from a coherent superposition of states can affect the spectrum [22–27], as resonant harmonics may form their own plateau and cutoff, the temporal characteristics of the corresponding harmonics may change and even transitions via autoionizing states may be involved. Besides fundamental interest, such studies are also motivated by experimental studies on plasma ablation [28].

In this article we predict and analyze the presence of sidebands of the ‘usual’ odd harmonics due to the interaction of molecules with intense laser radiation. They appear when the driver wavelength is tuned to the transition between one of the inner valence orbitals and a hole in the highest occupied molecular orbital (HOMO) and is, hence, most prominent in the interaction of open shell molecules with intense laser radiation. The mechanism is analogous to that responsible for Mollow sidebands in quantum optics [29]. Similar sidebands have been identified before for the HOMO-LUMO transition in the simplest molecular ion, H$_2^+$, in the regime of charge resonance enhanced ionization at large internuclear distances [30,31]. According to the results of our calculations the phenomenon is however more general and occurs for many open shell molecules at equilibrium geometry. In particular, in the general case charge resonance effects [31] do not have to be induced and the phenomenon appears due to straightforward coupling of orbitals of different types of symmetry. Furthermore, the coupling of the orbitals and related transition introduces an additional time scale, that is related to a nonadiabatic dynamics and induces dynamical localization of the electron within the molecule. All of the results
are not described by the standard 'strong field approximation' approaches for multi-electron molecular systems [14, 18, 32–36] and show how excitations during the HHG process can lead to nonadiabatic internal dynamics which strongly affects the HHG spectra.

In order to calculate the response of a molecule, including multi-electron effects, to an intense laser field, we make use of the time-dependent density functional theory (TDDFT). In the past this theoretical approach has been applied successfully to determine optical properties of molecules and clusters [37] as well as high-order harmonic generation [38–40]. It is based on a solution of the Kohn-Sham equations:

\[ i \frac{\partial}{\partial t} \phi_k(r,t) = -\nabla^2 \phi_k(r,t) + (V_{KS}[\rho(r,t)] + U(r,t)) \phi_k(r,t) \]  

(1)

where 

\[ \rho(r,t) = \sum_k \phi_k^*(r,t) \phi_k(r,t) \]  

(2)

is the density of the non-interacting particles, \( \phi_k \) are the so-called Kohn-Sham orbitals, \( V_{KS} \) contains correlation and exchange interactions, and \( U(t) \) denotes the interaction of the Kohn-Sham orbitals with the external laser field. In the present calculations we have implemented the adiabatic local density approximation and the so called LB94 functional [41]. We have further used the approximation of Linear Combination of Atomic Orbitals for Molecular Orbitals (LCAO-MO) to represent the molecular wavefunction. In our application the Kohn-Sham equations are solved on a space-time grid for the interaction of the molecule, initially in its ground state, with an intense short laser pulse. The space-time grid had a time step size of 0.03 a.u. and a grid step size of 0.3 a.u.

In Fig. 1 we present a comparison of HHG spectra with (a) and without (b) the presence of sidebands. In the corresponding calculations we have considered the nitrogen molecular ion aligned parallel (a) and perpendicular (b) to the polarization vector of the electric field of a laser at 400 nm wavelength and an intensity of \( 2 \times 10^{14} \) W/cm\(^2\). The pulse length was 15 fs and the pulse shape trapezoidal. While the spectrum for the perpendicularly aligned molecular ion shows the traditional spectrum consisting of odd harmonics only (b), there are first and second order sidebands for each of the harmonics when the molecular ion is aligned along the polarization axis of the laser field (a).

The sidebands appear in between harmonic frequencies and may be also termed "fractional" harmonics. For the present laser parameters they are related to the transition between HOMO-2 (\( \sigma_u, E = -0.8799 \) a.u.) to HOMO (\( \sigma_g, E = -0.7763 \) a.u.) in this open shell molecule, which are approximately separated by the energy of a single 400 nm photon. The intensity of the sidebands is surprisingly high, which can be attributed to a rather significant transition dipole matrix element describing the coupling between these two molecular states. The mechanism responsible for the sidebands is analogous to that for Mollow sidebands in quantum optics [29]. In the insets on the right we present enlarged views of a part of the spectra. This clearly shows the relation between the separation of the first and second order sideband peaks in the spectrum and the Rabi transition frequency \( \Omega_r = |d_{ij}| \cdot E \), where \( d_{ij} \) and \( E \) are correspondingly the transition matrix element for transition between states \( i \) and \( j \), and the electric field.

The close relation of the present sideband structure to Mollow sidebands, known in quantum optics, is supported by the results presented in Fig. 2. In that Figure we present the dependence of the displacement of the first (solid line with circles) and the second-order (dashed line with squares) sidebands of the 9th harmonic in \( N^+_2 \), aligned parallel to the polarization axis, on the electric field strength. The displacement is determined as half of the energy difference between the right and the left sideband of the harmonic. The displacements of the sidebands scales linearly with the electric field strength and are in agreement with the (perturbative) Rabi frequency of the corresponding transition (solid and dashed lines with stars). Thus, the peak positions of
the sidebands in the present results show indeed the same intensity dependence as the Mollow sidebands.

The results in Fig. 1 involve the transition between the same type of orbitals as in the previously studied case of H$_2^+$ [30]. However, in the previous study the sidebands occurred for the interaction of the molecular ion at larger internuclear distances, in the regime of charge resonance enhanced ionization [31]. In contrast, here the effect shows up for the interaction of the molecular ion with the field at equilibrium distance showing that the phenomenon is more general than considered before.

Mollow sidebands in high harmonic generation have so far been predicted for the coupling between orbitals of $\sigma$-symmetry only. However, in general, the phenomenon appears for the coupling between molecular orbitals of different type of symmetry as well. Since the symmetry of the orbitals governs the alignment dependence of the transition matrix element, the strengths of the respective fractional harmonics depends on the alignment between the molecular axis with respect to the polarization vector. For example, fractional harmonics due to the coupling between orbitals of $\pi_u$ (HOMO-1) and $\sigma_g$-symmetry (HOMO) in N$_2^+$ are induced for the interaction with a 800 nm laser pulse and perpendicular alignment of the molecule. The respective results of our calculations for the HHG spectrum in Fig. 3 clearly reveal the occurrence of the Mollow sidebands at these parameters. We may note parenthetically that for these laser parameters there is no coupling induced and, hence, no sidebands are observed for the molecular ion aligned along the polarization axis (not shown).

The strong coupling between the orbitals does not only leave its footprints in the high har-
Fig. 2. Shift of the first (red solid line with circles) and second-order (red dashed line with circles) Mollow sidebands for the 9th harmonic in N$_2^+$, aligned parallel to the polarization direction, as function of the electric field strength. Also shown is the Rabi frequency (green solid line with stars) and twice the Rabi frequency (green dashed line with stars) for the transition between HOMO-2 ($\sigma_u$) and HOMO ($\sigma_g$). Other laser parameters are the same as in Fig. 1.

Fig. 3. High harmonic spectrum of N$_2^+$ aligned perpendicular to the polarization axis of a 60 fs laser pulse at 800 nm and $2 \times 10^{14}$ W/cm$^2$. The inset provides an enlarged view of part of the spectrum.

monic spectra, but does strongly influence the dynamics of the electron density. More specifically, the emergence of sidebands comes along with profound variation of the electron dynamics inside the molecule as well as during its excursion in the continuum throughout the harmonic generation process. Firstly, the molecular orbital coupling leads to a laser induced nonadiabatic electron dynamics in the molecule, where the electron instead of directly following the changes in the oscillating electric field experiences lags and dwells at one of the nucleus for longer than a half period of the laser field cycle. The time scale of the corresponding localization of the electron is governed, as the location of the fractional harmonics in the spectrum, by the transition frequency, i.e. Rabi frequency, and can therefore be controlled via the laser parameters. This nonadiabatic dynamics can be visualized in our calculations via the difference of the time-dependent total density of the propagated molecular wavepacket and the initial total
electron density. After integration over the two spatial dimensions transversal to the molecular axis, we present the resulting total density difference, $\rho(z,t) - \rho(z,t_0)$, for $\text{N}_2^+$ as a function of the electron position along the internuclear axis and as a function of time in Fig. 4. The laser parameters and the orientation of the molecular axis (along the electric field vector) are the same as for the results in Fig. 1. For the purpose of comparison the electric field is shown in an inset at the top of each panel. We present changes in the density difference for the case where coupling and nonadiabatic dynamics is present (a) and for the case without coupling where one can observe, typical, adiabatic dynamics (b).

The result in Fig. 4(a) clearly shows that in the Rabi flopping regime the electron density does not swap adiabatically from one side of the molecular ion to the other every half cycle of the electric field. Instead, dynamical localization islands can be observed along the internuclear axis. However, also the electron density localized at nuclei shows nonadiabatic behavior. In contrast for adiabatic case (b) one can typically observe changes in electron density primarily around the nuclei. The frequency of the associated nonadiabatic oscillation is estimated to be approximately equal to the Rabi frequency of the transition between the states.

This nonadiabatic electron dynamics in the molecule further leads to modifications of the traditional semiclassical picture of HHG, as can be seen from the time frequency analysis in
Fig. 6. High harmonic spectra showing fractional harmonics for (a) NO$_2$ at 400 nm, $10^{14}$ W/cm$^2$, and 40 fs pulse length, (b) CO$^+_2$ at 350 nm, $10^{14}$ W/cm$^2$ and 34 fs, and (c) C$_2$H$_4^+$ at 400 nm, $10^{14}$ W/cm$^2$ and 18 fs.

Fig. 5. Wavelet analysis has been performed using the Gaussian window with the width equal to 3 harmonic orders, using the following formula,

$$d(\omega, t) = \int d(\tau) \exp\left(-\frac{(\tau - t)^2}{2\sigma^2}\right) \exp(-i\omega\tau) d\tau.$$  \hspace{1cm} (3)

In contrast to the typical wavelet analysis for high harmonic generation, which exhibits the return of the electron and harmonic emission via short and long trajectories, shown for comparison in Fig. 5 (b), the generation of the frequencies in the harmonic spectrum as a function of time related to fractional harmonics becomes more complex (see panel a). Obviously, any interpretation in terms of classical paths becomes cumbersome in this case. Instead, the time-frequency pattern is modulated by the nonadiabatic dynamics and temporal variation of the electron localization inside the molecule and, not surprisingly, shows an additional oscillating variation of the pattern with the time scale related to the Rabi frequency for transition between HOMO and HOMO-2 in the nitrogen molecular ion. For illustration of the time scale in Fig. 5 (a) the calculated HOMO population is shown superimposed over the lower part of spectrum.

Before concluding, we emphasize that the present findings are not restricted to the nitrogen molecular ion. Indeed, from the results of our calculations we observe the appearance of fractional harmonics in other larger open shell molecules as well. In Fig. 6 we present examples of harmonic spectra for the neutral triatomic open shell molecule NO$_2$ (a), the triatomic open shell molecular ion CO$_2^+$ (b) and the polyatomic molecular ion C$_2$H$_4^+$ (c). For each of these molecules the Mollow sidebands can be induced using wavelengths around 400 nm between different type...
of orbitals: $6\alpha_1$ (HOMO, $E=-0.2016$ a.u.) - $4\beta_2$ (HOMO-1, $E=-0.3136$ a.u.) (NO$_2$), $1\pi_g$ (HOMO, $E=-0.8208$ a.u.) - $1\pi_u$ (HOMO-2, $E=-0.9633$ a.u.) (CO$_2^+$), $1\beta_3$ (HOMO-3, $E=-0.7195$ a.u.) (C$_2$H$_4^+$). The orientation of the molecule versus the polarization direction is shown in inserts in Fig. 6. In each case the harmonic spectrum has been obtained for the molecule in its equilibrium configuration. The coupling between the orbitals is strongest in CO$_2^+$, leading to the appearance of strong sidebands, while the transition between the orbitals is weakest for NO$_2$. Therefore, in the latter case the sidebands do not occur as separate peaks in the spectrum, but in contrast rather lead to a broadening of each of the odd harmonic peaks.

Finally, we may note that the present results are based on a microscopic study of molecular high-order harmonic generation. Inclusion of macroscopic effects (focal averaging and propagation), which are sometimes important for the analysis of experimental data, are very challenging for theoretical analysis of molecular high-order harmonic generation. However, the results presented in Fig. 2 provide us with the opportunity to comment on the effect of intensity averaging. As discussed above, the position of the sidebands scales linearly with the electric field strength. On the other hand, high-order harmonic generation is a strongly nonlinear process in itself. Therefore, small intensity variations in the focal averaging will lead to a drastic reduction of the harmonic yield, while the position of the sidebands varies slightly only. We may therefore expect that an intensity average will not affect the present results much. Conclusions about propagation effects cannot be done based on the present results and are beyond the scope of the present ab-initio studies.

In conclusion, we have shown that Mollow sidebands occur in high harmonic spectra of open shell molecules at equilibrium geometries. The sidebands are due to a driving laser induced one-photon coupling (Rabi flopping) between one of the inner valence orbitals and the HOMO. The phenomenon is found and illustrated for parallel as well as perpendicular transitions, di-, tri- and polyatomic molecules. Moreover we illustrate the coupling of different type of orbitals, and different orientations of the molecule. Thus, it is shown that Mollow sidebands are much more general than the previously studied case of stretched H$_2^+$ in the regime of charge resonance enhanced ionization. Furthermore, the time-dependent electron density and the time-frequency analysis have shown that the appearance of the sidebands comes along with a nonadiabatic electron dynamics and localization in the molecule as well as a breakdown of the traditional semiclassical picture of high harmonic generation and a description using strong field approximation [14, 18, 32–36].

Presented results represent a novel interesting property of HHG for open shell multi-electron molecules. Experimental studies and corresponding measurements may provide information about dipole transition matrix elements. In addition, the effect can also modify HHG based dynamical imaging of the chemical reactions [15], recently performed for open shell molecules [42, 43]. Many interesting chemical reactions studied vigorously due to their applications and relevance for atmospheric, combustion, polymerization research as well as plasma chemistry and biochemistry, contain free radicals which are open shell molecules and can be considered for generation of Mollow sidebands.

Acknowledgments

This work was supported via grants from the U.S. National Science Foundation (NSF) (Grant No. PHY-1068706 and Grant No. PHY-1125844). This work utilized the Janus supercomputer, which is supported by the National Science Foundation (NSF) (Grant No. CNS-0821799) and the University of Colorado, Boulder. This work also used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation (NSF) (Grant No. ACI-1053575).