XUV lasing during strong-field assisted transient absorption in molecules

Timm Bredtmann,1 Szczepan Chelkowski,2 André D. Bandrauk,2 and Misha Ivanov1,3

1Max-Born-Institut, Max-Born-Strasse 2A, D-12489 Berlin, Germany
2Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1
3Department of Physics, Imperial College London, South Kensington Campus, SW7 2AZ, London, UK

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Using ab-initio non-Born-Oppenheimer simulations, we demonstrate amplification of XUV radiation in a high-harmonic-generation type process using the example of the hydrogen molecular ion. A small fraction of the molecules is pumped to a dissociative Rydberg state from which IR-assisted XUV amplification is observed. We show that starting at sufficiently high IR driving field intensities the ground state molecules become quasi-transparent for XUV radiation, while due to stabilization gain from Rydberg states is maintained, thus leading to lasing from strongly driven Rydberg states. Further increase of the IR intensity even leads to gain by initially unexcited molecules, which are quickly excited by the driving IR pulse.

High-order harmonic generation (HHG) in gases is a table-top technique producing attosecond pulses from the vacuum ultraviolet to the soft x-ray region and beyond [1], opening, in particular, the field of attosecond science [2]. Its challenge, however, is the low conversion efficiency. One option to address this challenge is to rely on phase matching, see e.g. [3–6]. Alternatively, HHG may be enhanced at the single atom/molecule level by enhancing the first step of the HHG process – ionization – seeding it with single attosecond pulses or pulse trains, see e.g. [7–11]. Here, we focus on the recombination step in HHG and explore the possibility of IR-assisted stimulated XUV recombination from Rydberg states, leading ideally to exponential growth of the XUV signal with the particle density, as opposed to quadratic growth in standard HHG (Figure 1(a)). While HHG is a coherent process, it begins as spontaneous: no incident field is originally present at the HHG frequencies to stimulate the emission. As the generated high-frequency light is accumulated in the medium, it may start to stimulate both emission and absorption at these new frequencies. Whether these stimulated transitions would lead to loss or self-seeded XUV light amplification depends on the dynamics of a quantum system. Crucially, the strong IR driving field alters and controls its response, see e.g. [12–17] for some striking examples of what such a control field can achieve.

If an effective population inversion is created between the states during or after the interaction with the strong IR driving field, light emitted at the corresponding transition frequencies can be amplified. Parametric amplification might also be possible, with the energy transferred from the driving field to the XUV field via nonlinear interaction with the medium. This mechanism was suggested [18–19] as explanation of HHG amplification reported in Ref. [18], see also Ref. [20]. Our ab-initio simulations include both possibilities.

Excitations of Rydberg states during high harmonic generation occur e.g. due to frustrated tunnelling [21–22], via field-induced Freeman resonances [23] or due to the lower harmonics of the IR radiation generated in the medium. It may play an important role during HHG in dense gases. Here, however, we model Rydberg excitation as a separate step. This choice allows for a systematic analysis of the parameter ranges involved. Likewise, we split the generation of the primary harmonic seed light and its amplification into separate stages, i.e. the XUV seed is added explicitly in the simulations. This choice allows us to look at the transient absorption setup, where an XUV probe can be moved relative to the dressing IR driver, leading to amplification of the XUV probe. Moreover such splitting could also help one to exploit the full potential of XUV amplification [24].

Specifically, we consider the molecular medium H$_2^+$, which consists of a nuclear wavepacket from the electronic ground state $\sigma_g 1s$ into the dissociative Rydberg state $\sigma_g 2p$ (Figure 1(c)) via a two-photon transition, with the intermediate state $\sigma_a 1s$. Next, a time-delayed combination of a strong IR driving field (Figure 1(b), black) and a weak XUV probe pulse (red), which stimulates non-resonant absorption or emission, interacts with both the ground state and the small fraction of excited dissociating molecules. Short duration of the time-delayed probe allows one to think of a transient, time-dependent electronic spectrum for the dissociating molecules.

Figure 1(d) sketches the key absorption and emission channels for the XUV probe pulse (red arrows) with and without the strong IR field (black arrows). In the absence of the IR pulse, XUV absorption is the only channel both for the unexcited (left) and the excited (right) molecules. We show that adding the IR field to the probe XUV attenuates absorption from the unexcited molecules, while IR-assisted XUV stimulated recombination of the excited molecules to lower states leads to amplification of the XUV pulse accompanied by the absorption of many IR
photons. The amplified windows in the XUV range depend on the internuclear distance and may be controlled by timing of the pump pulse and the XUV–IR pair.

Two comments are in order: First, the amplifier may strongly attenuate XUV absorption while assisting IR acceleration (see Fig. 1b). Second, we find that even if the number of excited molecules is much less than the number of unexcited ones, IR-assisted XUV amplification can still occur, reminiscent of ‘lasing without inversion’ (see e.g. [25–29]).

We solve numerically the 3-body, Non-Born-Oppenheimer time-dependent Schrödinger equation for the model molecule H$_2^+$ (atomic units, a.u., $\hbar=m_e=1$ are used):

$$\frac{\partial \Psi(z,R,t)}{\partial t} = H(z,R,t)\Psi(z,R,t),$$

where

$$H(z,R,t) = -\beta \frac{\partial^2}{\partial z^2} - \frac{1}{m_p} \frac{\partial^2}{\partial R^2} + \frac{1}{R} + V_C(z,R) + \kappa z E(t),$$

with

$$\beta = \frac{2m_p + m_e}{4m_p m_e}, \quad \kappa = 1 + \frac{m_e}{2m_p + m_e}$$

and the soft core potential

$$V_C(z,R) = \frac{-1}{\sqrt{(z-R/2)^2 + 1}} + \frac{-1}{\sqrt{(z+R/2)^2 + 1}}$$

is the three body Hamiltonian after separation of the center-of-mass motion. Both the nuclei and the electron are restricted to one dimension (see e.g. [30]). Here, $z$ is the electron coordinate and $R$ is the internuclear distance.

The electric field for each pulse is defined via the vector potential $A(t)$ [31]. Sine-squared functions are used for the envelopes of the $A(t)$ for each pulse, as in [31, 32]. The carrier envelope phase $\phi$ for all pulses (as defined in Ref. [31]) is set to $\pi/2$, i.e., a sine pulse is used. The total pulse durations are $T_{IR} = 5.3$ fs [2.7 fs full width at half maximum (FWHM)] for IR and $T = 2.7$ fs [1 fs full width at half maximum (FWHM)] for both the VUV pump and the XUV seed. Figure 1(b). While intensities of the 800 nm IR driving pulse and of the 134 nm VUV pump pulse are systematically varied, the intensity of the XUV seed with variable central frequency $\Omega_{XUV}$ is set to $I_{XUV} = 5 \times 10^{12}$ W/cm$^2$, which was tested to yield stable numerical results while being in the linear response regime.

The total wavefunction of the system is $\Psi(z,R,t) = \Psi_{IR}(z,R,t) + \Delta \Psi_{XUV}(z,R,t)$. Here $\Psi_{IR}(z,R,t)$ is the wavefunction of the IR dressed system, which also includes the effect of the pump pulse, and $\Delta \Psi_{XUV}(z,R,t)$ is the perturbation due to the weak XUV probe. The induced dipole moment is

$$\langle \Psi(t)|\hat{d}|\Psi(t)\rangle = \langle \Psi_{IR}(t)|\hat{d}|\Psi_{IR}(t)\rangle + \langle \Delta \Psi_{XUV}(t)|\hat{d}|\Delta \Psi_{XUV}(t)\rangle + \langle \Delta \Psi_{XUV}(t)|\hat{d}|\Delta \Psi_{XUV}(t)\rangle,$$

where $\hat{d}$ is the dipole operator. The first term on the right describes the non-linear response to the strong IR field alone, without any assistance from the XUV. Thus, it does not include any XUV stimulated processes and contains only spontaneous HHG-type emission during radiative recombination. The second and third terms describe stimulated emission/absorption of XUV radiation by the IR dressed system, the subject of this paper. The last term depends quadratically on the weak XUV probe field and may thus be neglected for sufficiently low XUV intensities. For increased numerical stability, we use the dipole accelerations $a(t) = -\langle \Psi(t)|[H,Z]\Psi(t)\rangle$ and
\[ a_{IR}(t) = -\langle \Psi_{IR}(t) | [H, [H, z]] | \Psi_{IR}(t) \rangle. \]

Hence, to identify stimulated absorption and emission of the XUV probe, we calculate the frequency resolved linear response of the IR dressed system to the XUV probe pulse as

\[ D_{XUV}(\Omega) = \frac{1}{\Omega^2} \int dt e^{i\Omega t} (a(t) - a_{IR}(t)), \]

technically removing the contribution of the standard HHG-type emission. The numerical propagation is carried out until the end of the XUV probe pulse. The XUV probe absorption/emission is related to the out-of-phase component of \( D_{XUV}(\Omega) \) with respect to the spectral amplitude of the XUV pulse, \( E_{XUV}(\Omega) \). The XUV probe absorption signal is

\[ S_{XUV}(\Omega) \propto \frac{\text{Im}(E_{XUV}(\Omega) D_{XUV}(\Omega))}{\int d\Omega |E_{XUV}(\Omega)|^2}. \]

Figure 2(a) explores the possibility of light amplification from the excited molecules (\( |\sigma_g 2p\rangle \), left) and the reponse of the ground state molecules (\( |\sigma_g 1s\rangle \), right) for a highly non-resonant XUV probe-pulse for the intensity range \( I_{IR} = 1 \times 10^{13} \text{ W/cm}^2 \) - \( 9 \times 10^{15} \text{ W/cm}^2 \) of the IR driving field for time-delays \( \Delta_{IR} = 3 \text{ fs} \) and \( \Delta_{XUV} = 2.4 \text{ fs} \), c.f. Figure 1(b). The central frequency of the XUV probe is set to \( \Omega_{XUV} = \Omega_{se} + 7\Omega_{IR} = 20.4 \text{ eV} \), where \( \Omega_{IR} \) is the central frequency of the 800 nm IR pulse and \( \Omega_{se} = 9.5 \text{ eV} \) denotes the transition frequency \( |\sigma_g 2p\rangle \rightarrow |\sigma_g 1s\rangle \) for the employed delay-time. First, we assume complete population transfer to the excited state \( |\sigma_g 2p\rangle \) at time zero. While there is only XUV absorption below \( I_{IR} = 5 \times 10^{13} \text{ W/cm}^2 \), we identify three regimes for higher IR intensities, see Figure 2(b) which shows the integrated XUV transient absorption spectrum, \( \int S_{XUV}(\Omega) d\Omega \), both for the excited state (red) and the ground state molecules (blue). For comparison, the corresponding integrated signal strength without the IR driving field is indicated by the horizontal arrows.

In regime (I), strong negative absorption from the excited state molecules yields a first amplification maximum at \( I_{IR} = 1 \times 10^{14} \text{ W/cm}^2 \). This gain from the excited state molecules is accompanied by comparable XUV
light absorption from the ground state molecules. In regime (II), rapid IR-induced depletion of the excited state reduces amplification from excited molecules and XUV absorption from the ground state molecules dominates. Starting with intensities $I_{IR}=2 \times 10^{15} \text{ W/cm}^2$ (regime (III)), one enters the stabilization regime for the excited states [21, 22], resulting in striking XUV light amplification with maximum at $I_{IR}=3 \times 10^{15} \text{ W/cm}^2$, being even stronger than in regime (I). At the same time, the ground state molecules become quasi-transparent due to rapid depletion.

For intensities beyond $I_{IR}=4 \times 10^{15} \text{ W/cm}^2$, lasing is even observed from the molecules which were initially prepared in the electronic ground state. This is likely due to IR-induced transient population of Rydberg states through frustrated tunneling [21, 22]. At these intensities, the gain from molecules initially in the electronic ground state adds to the stronger amplification of molecules which were prepared in the Rydberg state $\sigma_{4p}$. This gain without nominal population inversion is stable over a large range of XUV-probe time-delays $\Delta_{XUV}$ (Figure 2(c)). Moreover, it is stable over a large range of XUV pulse durations (Supplementary Material), i.e. is robust with respect to possible XUV pulse reshaping during macroscopic light propagation through the molecular medium.

Figure 3 explores, for the full pump-probe scenario, the dependence of the integrated XUV transient absorption signal both on the delay of the IR driving field, $\Delta_{IR}$, and on the central frequency of the XUV seed, $\Omega_{XUV}$. The pump intensity is set to $I_{\text{pump}}=3 \times 10^{14} \text{ W/cm}^2$, exciting 18% of the ground state molecules to electronic state $\sigma_{4s1s}$ and 16% to the dissociative Rydberg state $\sigma_{5p}$. The remaining parameters are identical to Figs. 2(a)+b(h). Even with 83% of the molecules residing in the two lowest electronic states, tunable XUV light amplification is demonstrated. The control of the internuclear distance $R$ through the pump-probe time delay $\Delta_{IR}$ allows the effective amplification of XUV pulses with central frequencies $\Omega_{XUV}$ ranging from the pump carrier frequency ($\Omega_{XUV}=9.25 \text{ eV}$) up to at least $\Omega_{XUV}=22 \text{ eV}$. Importantly, starting with time-delays $\Delta_{IR}=11 \text{ fs}$, the broad amplification windows centered around $\Omega_{XUV}=11 \text{ eV}$ and $\Omega_{XUV}=17 \text{ eV}$ become independent of internuclear distance and hence no longer depend on the pump-probe synchronization.

Finally, Figure 3(b) determines the pump intensities needed such that the overall gain in the full pump-probe simulations matches the absorption from the ground state molecules in the absence of both the VUV pump and the IR pulse. The results are indicated by the vertical arrows, black for XUV seeds centered at $\Omega_{XUV}=15.7 \text{ eV}$ for long internuclear distances using delays $\Delta_{IR}=14.9 \text{ fs}$, and red for central frequency $\Omega_{XUV}=18.8 \text{ eV}$ for short internuclear distances using $\Delta_{IR}=3.9 \text{ fs}$. The corresponding populations after the pump pulse in the state $\sigma_{4p}$ are 8% for $\Omega_{XUV}=15.7 \text{ eV}$ (black) and 15% for $\Omega_{XUV}=18.8 \text{ eV}$ (red).

In conclusion, we have shown that absorption of multiple IR photons from the strong laser field can be accompanied by amplification of weak XUV light incident on the $\text{H}_2^+$ molecule. Amplification is enabled by excitation to a dissociative Rydberg state and controlled by molecular dynamics. The XUV absorption from this excited Rydberg state is suppressed in favour of IR-assisted, stimulated XUV recombination into the lower-lying bound states of the molecule. The process takes advantage of the stability of excited electronic states, with the strong-IR-driven wavefunction oscillating as a nearly free Kramers-Henneberger-like quasi-bound wavepacket [33, 36].

While for IR intensities below $I_{IR}=2 \times 10^{15} \text{ W/cm}^2$ strong absorption of the ground state molecules constitutes the limiting factor, we have established a high intensity regime (regime (III), Figure 2(b)), in which rapid ionization makes the overall response of the ground state molecules quasi-transparent. At the same time, considerable stabilization of Rydberg states yields overall gain even at small degrees of excitation. It is shown that exciting merely 10%-15% of the molecules suffices for the overall gain to match the overall absorption of a sample of unexcited molecules in the absence of the IR pulse.

For intensities beyond $I_{IR}=4 \times 10^{15} \text{ W/cm}^2$ lasing of the initially unexcited molecules is observed, adding to the considerably stronger gain from the molecules prepared by the pump pulse. This is most likely due to IR-induced transitions to Rydberg states through frustrated tunneling [21, 22]. This amplifier is operates over wide spectral windows, controlled by the internuclear distance via the pump-probe time delay.

Concerning the synchronization of the pulses, amplification occurs for a range of IR-XUV time-delays of about 3 fs, much longer than the XUV half-cycle. Thus, phase matching carrier oscillations of the XUV-IR pair within one XUV half-cycle is not required. For the pump step, deviations of at least 1 fs are tolerated. Moreover, for specific but broad ranges of central XUV frequencies, e.g. around $\Omega_{XUV}=17 \text{ eV}$, no pump-probe synchronization is necessary for pump-probe delays $>11 \text{ fs}$, until at least 50 fs. Hence, for such frequency windows, the external addition of both the pump pulse and the XUV-seed may become obsolete in dense gases, resulting in self-seeded amplification, with excitation to Rydberg states originating either via multi-photon transitions induced by the VUV radiation generated in the medium, or through frustrated tunneling [21, 22].

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FIG. 4. Influence of the XUV probe pulse duration, $T$, on the XUV transient absorption spectrum, $S_{\text{XUV}}(\Omega)$, from excited $\sigma_g 2p$ molecules, for $I_{\text{IR}} = 5 \times 10^{15}$ W/cm$^2$, $\Delta_{\text{IR}} = 3$ fs and $\Delta_{\text{XUV}} = 1.9$ fs and $\Omega_{\text{XUV}} = 20$ eV. (a) From top to bottom: Electric field of the IR and XUV probe pulses with durations $T = 2.75$ fs (blue, corresponding to the durations used in the main part of the text), $T = 5.5$ fs (green), $T = 8.25$ fs (red), $T = 11$ fs (cyan). (b) XUV transient absorption spectra, $S_{\text{XUV}}(\Omega)$, for the XUV pulses from (a), shown in corresponding colors.