Molecular Rydberg Laser without inversion

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Using ab-initio simulations, we demonstrate amplification of XUV radiation in a high-harmonic generation type process in the hydrogen molecular ion. A small fraction of the molecules is pumped with 9 eV photons to a dissociative Rydberg state from which IR-assisted XUV amplification is observed up to 22 eV. We show that starting at IR driving field intensities of $2 \times 10^{15}$ W/cm$^2$, the hitherto dominant XUV absorption of the ground state molecules becomes quasi transparent while, due to stabilisation, strong gain from Rydberg states is maintained, thus leading to Rydberg lasing without inversion. We also show that the amplified windows in the XUV range depend on the internuclear distance and may be controlled by proper timing of the pump pulse and the IR driving field.

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 main 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 of 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, initially it is spontaneous: no incident field is originally present at the HHG frequencies to stimulate the emission. However, as the generated coherent high-frequency light is accumulated in the medium, it may start to stimulate emission and absorption at these new frequencies. This corresponds to self seeded amplification. Whether these stimulated transitions would lead to XUV light amplification or not 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 striking examples of what such control 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 of HHG might also be possible, with the energy transferred from the driving field via nonlinear interaction with the system. 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.

While self-seed amplification [18] and excitations to Rydberg states could and likely will occur during HHG in dense gases, either due to frustrated tunneling [21], multi-photon, or collisional excitation, we fully model both the pump step and the XUV seed explicitly. This allows a systematic analysis of the involved parameter ranges. Furthermore, a splitting of primary harmonic-seed-light generation and its amplification into individual stages that can be optimized separately is expected to exploit the full potential of XUV amplification [22].

Specifically, we consider the molecular medium H$_2^+$: starting from the electronic ground state $\sigma_g 1s$, a short femtosecond pulse (Figure 1(b), blue) prepares through a two photon transition via the state $\sigma_u 1s$ a nuclear wavepacket in the dissociative Rydberg state $\sigma_u 2p$ (Figure 1(c)). 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 two-color pulse allows one to think of a transient, time-dependent electronic spectrum for the excited 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 strong 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 in the excited molecules leads to amplification of the XUV pulse. Furthermore, the amplified windows in the XUV range depend on the internuclear distance and may be controlled by proper timing of the pump pulse and the IR driving field.
are used):
\[ i \frac{\partial \Psi(z, R, t)}{\partial t} = H(z, R, t)\Psi(z, R, t), \]
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
\[ \beta = \frac{2m_p + m_e}{4m_pm_e}, \quad \kappa = 1 + \frac{m_e}{2m_p + m_e}. \]
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 full 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. [23]). Here, z is the electron coordinate and R is the internuclear distance.

The electric field for each pulse is defined via the vector potential \( A(t) \) [24]. Sine-squared functions are used for the envelopes of the \( A(t) \) for each pulse, as in Refs. [24, 25]. The carrier envelope phase \( \phi \) for all pulses (as defined in Ref. [24]) is equal to \( \pi/2 \), i.e., a sine pulse is used. The total durations of the pulses are \( T_{IR} = 5.3 \text{ fs} \) [2.7 fs full width at half maximum (FWHM)] for IR and \( T = 2.7 \text{ fs} \) [1 fs full width at half maximum (FWHM)] for both the VUV pump and the XUV seed. 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 \( I_{XUV} = 5 \times 10^{12} \text{ W/cm}^2 \), which was tested to yield stable numerical results while being in the linear response regime.

To calculate the linear response of the IR dressed system to the weak XUV seed, we note that the total wavefunction 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, including 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
\[ \langle \hat{\Psi}(t)|\hat{d}|\Psi(t)\rangle = \langle \Psi_{IR}(t)|\hat{d}|\Psi_{IR}(t)\rangle + \langle \Psi_{IR}(t)|\hat{d}|\Delta \Psi_{XUV}(t)\rangle + \langle \Delta \Psi_{XUV}(t)|\hat{d}|\Psi_{IR}(t)\rangle + \langle \Delta \Psi_{XUV}(t)|\hat{d}|\Delta \Psi_{XUV}(t)\rangle, \]
where \( \hat{d} \) is the dipole operator. The first term on the right describes the non-linear response to the strong IR field alone. The second and third terms describe the linear response of the IR dressed molecular system to the weak XUV probe, i.e. stimulated emission/absorption of XUV radiation by the IR dressed system, the subject

Three comments are in order: First, the considered amplifier may operate over a wide spectral range since it is based on a non-resonant process and is thereby not limited to specific atomic or molecular resonances. Second, we find that even if the number of excited molecules is much less than the number of unexcited ones, IR-assisted XUV amplification still occurs. Third, the condition of phase matching of the conventional HHG is replaced by the less stringent condition of the group velocity matching between the IR driver and the XUV seed.

We solve numerically the complete, 3-body, Non-Born-Oppenheimer time-dependent Schrödinger equation for the model molecule H$_2^+$ (atomic units, a.u., \( e=\hbar=m_e=1 \)
of this paper. The last term depends quadratically on the weak XUV probe field and may thus be neglected for sufficiently low XUV intensities. Furthermore, for increased numerical stability, we use the dipole accelerations $a(t) = -E(t) - \langle \Psi(t) | \frac{d}{d\tau} | \frac{d}{d\tau} \Psi(t) \rangle$ and $a_{IR}(t) = -E_{IR}(t) - \langle \Psi_{IR}(t) | \frac{d}{d\tau} | \frac{d}{d\tau} \Psi_{IR}(t) \rangle$. Hence, we calculate the frequency resolved linear response of the IR dressed system with respect to the weak XUV probe pulse as

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

thereby removing the contributions of the standard HHG-type emission, unaltered by the weak XUV probe. The numerical propagation is carried out until the end of the XUV probe pulse. Finally, 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 [26]

$$S_{XUV}(\Omega) \propto \frac{\text{Im}(E_{XUV}(\Omega) D_{XUV}(\Omega))}{\int d\Omega |E_{XUV}(\Omega)|^2},$$

FIG. 2. (a) XUV transient absorption spectra $S_{XUV}(\Omega)$ from excited state molecules (left) and ground state molecules (right) for variable IR intensities $I_{IR}$ with $\Delta_{IR} = 3$ fs, $\Delta_{XUV} = 2.4$ fs (c.f. Figure 1(b)) and central XUV frequency $\Omega_{XUV} = 20.4$ eV. Here, a $\delta$-Pulse excitation is assumed yielding complete excitation to the excited state at $t=0$ fs. (b) Corresponding integrated signals, $\int S_{XUV}(\Omega) d\Omega$, as function of the intensity of the IR driving field for excited state (red) and ground state (blue) molecules identifying three amplification regimes. Values without the IR pulse are indicated by the horizontal arrows. (c) Dependence of integrated signals from excited state molecules on XUV-probe delay-time for $I_{IR} = 5 \times 10^{13}$ W/cm$^2$.

FIG. 3. Full pump-probe simulations: (a) Integrated XUV transient absorption spectrum, $\int S_{XUV}(\Omega) d\Omega$, as function of the central frequency of the XUV seed, $\Omega_{XUV}$, and the time delay of the IR driving field, $\Delta_{IR}$. The pump intensity is set to $I_{pump} = 3 \times 10^{13}$ W/cm$^2$, exciting 16% of the molecules to the dissociative Rydberg state $\sigma_g 2p$. In all simulations, the intensity of the IR driving field is set to $I_{IR} = 3 \times 10^{15}$ W/cm$^2$ and the delay of the XUV seed is $\Delta_{XUV} = 2.4$ fs. (b) Integrated signals as function of pump intensity, $I_{pump}$, with central XUV frequency $\Omega_{XUV} = 15.7$ eV for large internuclear distances ($\Delta_{IR} = 14.9$ fs) (black) and for $\Omega_{XUV} = 20.4$ eV for short internuclear distances ($\Delta_{IR} = 3.9$ fs) (red).

Figure 2(a) explores the possibility of light amplification from the excited molecules ($\sigma_g 2p$, left) and the reponse of the ground state molecules ($\sigma_g 1s$, right) for a highly non-resonant XUV probe-pulse for the intensity range $I_{IR} = 1 \times 10^{13}$ W/cm$^2$ - $9 \times 10^{15}$ W/cm$^2$ of the IR driving field for time-delays $\Delta_{IR} = 3$ fs and $\Delta_{XUV} = 2.4$ fs, c.f. Figure 1(b). The central frequency of the XUV probe is set to $\Omega_{XUV} = \Omega_{ge} + 7\Omega_{IR} = 20.4$ eV, where $\Omega_{IR}$ is the central frequency of the 800 nm IR pulse and $\Omega_{ge} = 9.5$ eV denotes the transition frequency $|\sigma_g 2p \rangle \rightarrow |\sigma_g 1s \rangle$ for the employed delay-time. Here, a $\delta$-pump pulse excitation is assumed yielding complete population transfer to the excited state $\sigma_g 2p$ at time zero. While there is only XUV absorption below $I_{IR} = 5 \times 10^{13}$ W/cm$^2$, we identify three regimes for higher intensities of the IR driver. This is illustrated in Figure 2(b) which shows these three regimes in the integrated XUV transient absorption spectrum, $\int S_{XUV}(\Omega) d\Omega$, both for the excited state (red) and the ground state molecules (black). For comparison, the corresponding integrated signal strength without the IR driving field is indicated by the hori-
horizontal arrows. In regime (I), strong negative absorption from the excited state molecules yields a first amplification maximum at $I_{IR}=1\times10^{14}$ 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 strongly dominates. Starting with intensities $I_{IR}=2\times10^{15}$ W/cm$^2$ (regime (III)), one enters the stabilization regime for highly excited states [21], resulting in striking XUV light amplification with maximum at $I_{IR}=3\times10^{15}$ W/cm$^2$, being even stronger than in regime (I). At the same time, the response of the ground state molecules becomes quasi-transparent due to the lack of stabilization and rapid ionization. For intensities beyond $I_{IR}=4\times10^{15}$ 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]. At these intensities, the gain from molecules initially in the electronic ground state adds to the considerably stronger amplification of molecules which were prepared in the Rydberg state $\sigma_g2p$. 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 large ranges of XUV pulse durations (Supplementary Material), i.e. with respect to XUV pulse reshaping occurring in the 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 $I_{pump}=3\times10^{13}$ W/cm$^2$, exciting 18% of the ground state molecules to electronic state $\sigma_g1s$ and 16% to the dissociative Rydberg state $\sigma_g2p$. The remaining parameters are identical to Figs. 2(a)+(b). Even with 83% of the molecules residing in the two lowest electronic states, tunable XUV light amplification is demonstrated. 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 ($\Omega_{XUV}=9.25$ eV) up to at least $\Omega_{XUV}=22$ eV.

Starting with time-delays $\Delta_{IR}=11$ fs, the broad amplification windows centered around $\Omega_{XUV}=11$ eV and $\Omega_{XUV}=17$ eV become independent of internuclear distance and hence no longer depend on the pump-probe synchronization. Finally, Figure 3(b) shows that the molecular medium starts to lase at pump intensities around $I_{pump} = 1.5 \times 10^{13}$ W/cm$^2$, corresponding to population transfer of about 5%, as illustrated for XUV seeds with central frequencies $\Omega_{XUV}=20.4$ eV (red) and $\Omega_{XUV}=15.7$ eV (black) for short and long internuclear distances, respectively. The overall gain can of course be controlled by increase of the pump intensity $I_{pump}$, thereby enhancing the number of molecules in the excited electronic state $\sigma_g2p$.

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 molecular quantum system $H_2^+$. In our case, 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 fact that, for the excited state, the wavefunction of the strong-IR-driven excited electronic state oscillates as nearly free, in a Kramers-Henneberger-like quasi-bound wavepacket [27–29], including IR-induced excitations to higher lying Rydberg states.

While for IR intensities below $I_{IR}=2\times10^{15}$ 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 around 5%. For intensities beyond $I_{IR}=4\times10^{15}$ W/cm$^2$ lasing of the initially unexcited molecular medium is observed, adding to the considerably stronger gain from molecules prepared by the pump pulse. This is most likely due to IR-induced transitions to Rydberg states through frustrated tunneling [21]. This amplifier is non-resonant and operates over wide spectral windows, controlled by the internuclear distance via the pump-probe time delay. Concerning the synchronization of the pulses, it is shown that deviations of roughly 3fs are tolerated for the time-delay of the XUV seed with respect to the IR driving field, thereby replacing the challenging issue of phase matching by the less stringent group velocity matching of the IR driver and the XUV seed. 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 $\Omega_{XUV}=17$ eV, no pump-probe synchronization is necessary for pump-probe delays > 11 fs until at least 40 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 where the excitation to Rydberg states is created by multi-photon transitions by VUV radiation created in the medium or through frustrated tunneling [21], as also shown in this Letter.

Even though distinctly different, our scheme has nevertheless similarities to parametric wave-mixing schemes in strongly driven systems [12–17]. However, none of these schemes uses ionization and dissociation-controlled population inversion for excited molecular ensembles. The
excitations investigated here may also have been created in the course of the experiment presented in Ref. [18] being the origin of the observed amplification.

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FIG. 4. Influence of the length of the XUV probe pulse, $T$, on the XUV transient absorption spectrum, $S_{\text{XUV}}(\Omega)$, from excited $\sigma_g^2p$ molecules for parameters $I_{\text{IR}} = 5 \times 10^{15}$ 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 IR field and of 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.