Extreme UV generation from molecules in intense Ti:Sapphire light

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Introduction
The use of ultrashort intense infrared light to study atomic and molecular dynamics on femtosecond timescales has been extremely successful. This technique, particularly in the pump-probe mode, has enabled an analysis in the time domain of molecular conformation changes and the study of excited-state vibrational dynamics. Very recently the prospect of resolving and manipulating electronic dynamics by creating high-frequency optical pulses has been advanced. To realise spatial and temporal resolution of electronic transitions within a molecule requires intense coherent light that switches on attosecond (10^-18 s) timescales with wavelengths in the extreme ultraviolet or soft x-ray spectrum, λ=0.1–10 nm.

One of the most promising schemes for producing such light is through high-harmonic generation from intense Ti:Sapphire lasers interacting with gas-phase atoms and molecules. The CCLRC-Central Laser Facility, Imperial College and Oxford are leading participants in a large UK consortium developing sub-femtosecond and attosecond pulses using the controlled generation of high-frequency light in atomic and molecular systems. The process of high-harmonic generation from IR light can be considered to have three distinct steps. Firstly, the initial molecular orbital is polarized and pulled away from the parent core by the external field to form a coherent continuum state, which then evolves within the laser field and finally, a few femtoseconds later driven by the field reversal, it returns to interact with the molecular core. In the ensuing collision the electron releases energy by bremsstrahlung during its passage across the molecule. Experiments have shown that the nonlinear medium, the molecule, has a critical role in forming, evolving and scattering the electronic wave packet, and hence in the generation of extreme UV light.

A feature of molecules that are hydrogenated or deuterated is that, for IR stimulation, the hydrogen vibrational relaxation time is comparable with the cycle time of the field, and hence the excursion time of the continuum wave packet. In previous work, we have shown that this vibration is extremely important for the process of ionization in light molecules and in this work we show that it carries over to the process of harmonic generation. We study the quantal vibration effect in both long and short pulses and for both isotopes of hydrogen. In order to simplify the physics and isolate the important mechanisms, we consider the simple one-electron molecular ion and the single-molecule response for the spectral density.

Quantum vibration effects in 25 fs pulses
We simulate the dynamics of H_2^+ and HD^+ by direct solution of the time-dependent Schrödinger equation for the electronic and nuclear motion for the interaction of intense femtosecond pulses. On these timescales the rotational motion, even for such light molecules, is frozen. Therefore it is a reasonable assumption that the nuclear alignment is fixed during the pulse interaction and that rotation can be neglected. In terms of vibrational relaxation, and since the nuclei are light, vibration will be important over femtosecond timescales. Although homonuclear diatomics are IR-inactive, in an intense field one can create vibrational excitation through continuum coupling. To show the effect of vibration, consider first a approximation in which the nuclei are infinitely massive so they maintain their positions at a fixed bond length of R=2 a.u., throughout the process. A typical result for the single-molecule response for a 10 cycle, λ=750nm pulse is shown in Figure 1. The spectrum has a characteristic plateau that is in rough agreement with the classical cut-off. In the classical model the maximum photon energy depends on the ionization potential of the molecule (I_0=31.7 eV) and ponderomotive energy corresponding to an intensity of I=4.5x10^{14} W cm^{-2} (U_p=23.6 eV). In this case, and under the assumption of fixed nuclei, only 1% of the molecules are ionized. A more realistic simulation, including quantal vibration, shows that 38% of the H_2^+ molecules are ionized. For the heavier isotope, HD^+ the yield is lower at 26% and closer to the infinite mass approximation. Our simulation shows that quantum vibration gives dramatically different results for ionization yields.

![Figure 1](image1)

**Figure 1.** Simulation for frozen vibration showing the harmonic generation spectrum from the hydrogen molecular ion with fixed molecular bond length (R=2 a.u.). Indicated on the Figure is the classical cut-off frequency, which depends on the ionization potential (I_0) and ponderomotive energy (U_p). The incident pulse is 10 cycles, λ=750nm, with intensity, I=4.5x10^{14} W cm^{-2}.

![Figure 2](image2)

**Figure 2.** Simulation with quantal vibration. The harmonic generation spectrum from the hydrogen molecular ion, including quantal vibration. The incident pulse is the same as that used for the results in Figure 1.
The corresponding harmonic generation spectrum including quantum vibration for the same 10 cycle, $\lambda=750\text{nm}$ pulse with intensity, $I=4.5\times10^{14}\text{ W cm}^{-2}$, is shown in Figure 2. The spectrum of Figure 1 shows very significant inadequacies in the infinite mass approximation in qualitative and quantitative terms when compared with the quantum simulation (Figure 2). The molecule is much more efficient at high harmonic generation than one would conclude based on the infinite mass approximation. For example, around the 40th harmonic the quantum vibration amplifies the intensity by a factor of 100 in comparison with Figure 1. Furthermore, the classical cut-off law is no longer a reliable guide to the range of the plateau in Figure 2. Indeed the spectral density shows strong yields around 5nm, corresponding to the 150th harmonic, not replicated by Figure 1.

The primary reason for these quantal features is that molecular vibration assists the ionization process occurring via dynamic tunnelling ionization\(^6\). One could cite this as an extreme example of phonon-assisted tunneling. Another factor is the quantum enhancement of bremsstrahlung due to nuclear wave packet expansion and dispersion increasing the cross section for electron-ion scattering. Additional quantal effects are visible in the structure of the spectral lines. A closer analysis of the spectrum, see Figure 3 upper diagram, around the 45th harmonic shows that the sidebands of the triplet are prominent and well resolved. This is further evidence of strong continuum coupling. Conversely the fixed nuclei results show sharp central lines with very weak sidebands. We note that the small permanent dipole moment of HD\(^+\) gives even harmonics for all harmonics. Around the 85th harmonic (Figure 3 lower) the even harmonics are present for both species indicating polarization during the pulse rise – a feature of high intensity and short pulse rise time.

Conclusions

The simulations show that quantal vibration enhances the high-harmonic yield from hydrogen and deuterium molecules for intense femtosecond IR pulses. The spectral line shapes, sidebands and intensities of the harmonics show quantum features and can be calculated to high precision for arbitrary IR pulses. This will provide a useful tool for attosecond pulse design. For few-cycle IR pulses the molecular expansion is suppressed and the classical cut-off formula gives a reasonable limit for the harmonic plateau. The yields (intensities) of extreme UV light from these light dimers would be rather low in comparison with heavier multi-electron systems, although the a smaller ionization potential will limit the extent of the plateau. Diatomic molecules such as O\(_2\) and N\(_2\) relax slowly in comparison with heavier multi-electron systems, although this will provide a useful tool for attosecond pulse design. For few-cycle IR pulses the molecular expansion is suppressed and the classical cut-off formula gives a reasonable limit for the harmonic plateau. The yields (intensities) of extreme UV light from these light dimers would be rather low in comparison with heavier multi-electron systems, although this will provide a useful tool for attosecond pulse design. For few-cycle IR pulses the molecular expansion is suppressed and the classical cut-off formula gives a reasonable limit for the harmonic plateau. The yields (intensities) of extreme UV light from these light dimers would be rather low in comparison with heavier multi-electron systems, although this will provide a useful tool for attosecond pulse design.

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