Complicated high-order harmonic generation due to the falling edge of a trapezoidal laser pulse

H Ahmadi¹, M Vafaee² and A Maghari¹

¹ Department of Physical Chemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran
² Department of Chemistry, Tarbiat Modares University, PO Box 14115-175, Tehran, Iran

E-mail: m.vafaee@modares.ac.ir

1 Department of Physical Chemistry, School of Chemistry, University of Tehran, Tehran, Iran
2 Department of Chemistry, Tarbiat Modares University, PO Box 14115-175, Tehran, Iran

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Abstract
High-order harmonic generation (HHG) is investigated for H₂⁺ and its isotopologues under seven and ten-cycle trapezoidal laser pulses at an 800 nm wavelength and I = 4 × 10¹⁴ W cm⁻² intensity. We numerically solved the full-dimensional electronic time-dependent Schrödinger equation (TDSE) with and without the Born–Oppenheimer approximation (BO). We show that contribution to the HHG spectrum from the trailing edge of a trapezoidal laser pulse can result in a redshift and complexity in the total HHG spectrum. This effect can be removed by considering different laser pulse durations and nuclear motion that is not possible for sin² and Gaussian laser pulses. We have resolved the contributions to the redshift and other patterns in the HHG spectra into the different electronic and vibrational channels and the interference thereof.

Keywords: high-order harmonic generation, time-dependent Schrödinger equation, non Born–Oppenheimer approximation, ultra-short intense laser pulse, dissociation, ionization

1. Introduction
The non-perturbative interaction of intense laser pulses with atoms and molecules gives rise to the generation of highly energetic photons; this is known as high-order harmonic generation (HHG) [1, 2]. HHG is interpreted through a three-step model proposed by Corkum [3] and extended by Lewenstein et al. [4]. First, an electron tunnels into the continuum when the Coulomb potential of the system is significantly modified by the laser pulse. Then, the electron moves away from the ion core while under the influence of the half-cycle of the laser field. After the field reverses, it comes back to the core. Finally, the electron may recombine with its parent ion, leading to photon emission at high frequencies which are multiples of the frequency of the driving laser. HHG is used to produce single isolated or trains of attosecond laser pulses which are necessary for the real-time observation of electronic dynamics [5]. The HHG spectrum from a system under investigation provides sub-femtosecond resolution of time-dependent structural features [6–10]. For example, from amplitude [11] and frequency [12] modulations in the HHG spectrum, molecular internuclear distance can be obtained.

The HHG process in molecules is more complex than that in atoms due to nuclear motion, two-center interference and different orientations of a molecule with respect to the laser field. We mention some recent works on the effect of nuclear motion on the HHG as follows. Experiments on H₂ and D₂ [7, 13, 14], and CH₄ and CD₄ [7] show that HHG is more suppressed for lighter isotopes than heavier because of the faster nuclear motion. The nuclear motion can shorten the length of attosecond laser pulse trains [15] and can produce an isolated attosecond laser pulse because of long-trajectory suppression [16, 17]. It has been reported that even-order harmonics are produced from the superposition of two electronic states at large internuclear distances as a result of the system’s symmetry breaking [18]. It has also been shown that in the presence of nuclear motion, like in H₂⁺ and H₂, the energy difference between the lowest bonding and anti-
bonding electronic states decreases for large internuclear distances. Thus, the lowest anti-bonding electronic state can have a significant contribution on the HHG spectrum [19]. The two-center interference minimum disappears at large internuclear distances where recombination to the first excited (anti-bonding) state becomes important [20]. The suppression of long trajectories and the HHG yield at different intensities due to nuclear motion are also reported [21].

By considering nuclear movement and laser pulse duration, Bian et al observed only the redshift of the HHG spectrum for a \( \text{sin}^2 \) laser pulse [12]. For laser pulses with \( \text{sin}^2 \) and Gaussian envelopes having only rising and falling parts, the blueshift or redshift of harmonics relative to odd harmonic orders occur inevitably at the rising and falling parts, respectively (for more details, see [12] and references therein). In practice, it is more difficult to observe only the redshift than the blueshift. At some conditions for \( \text{sin}^2 \) and Gaussian laser pulses, depending on the pulse duration and the type of the isotope and laser pulse intensity, both blueshift and redshift of harmonics can be present, leading to a broadening of the harmonics if the HHG happens comparably at both the rising and falling edges of the laser pulse [12]. Therefore, the HHG spectrum certainly changes in the case of \( \text{sin}^2 \) and Gaussian laser pulses.

In this work, we investigate the effect of nuclear movement on the HHG spectrum under trapezoidal laser pulses, mainly focused on the laser falling part. We address some questions for different isotopologues under trapezoidal laser pulses not already introduced and answered; these are as follows. Would the rising and falling parts of a trapezoidal laser pulse affect the HHG? To what extent are the effects dependent on the type of the isotopologue? What molecular electronic and vibrational components contribute to the effects? Finally, how could we control the shape of HHG spectrum due to the corresponding effects?

For the trapezoidal laser pulses, we show that the redshift of harmonics may occur depending on the isotope and pulse duration. It is shown that the effect of the laser falling part on the HHG spectrum could be even removed and therefore controlled for a trapezoidal laser pulse which is not possible for \( \text{sin}^2 \) and Gaussian laser pulses as mentioned above.

We resolve the redshifts and complexities of the HHG spectra into different electronic and vibrational states and their interferences. Similarly, decomposing the HHG into different electronic [19, 20] and vibrational [18] states has been reported but here we apply them to resolve the observed redshifts. We show that not only individual electronic and vibrational states are involved in the redshifts but also their interferences are significant and should be taken into account.

To our knowledge, resolving the redshifts into their components has not been reported, even for \( \text{sin}^2 \) and Gaussian laser pulses. To see whether the nuclear motion affects the HHG, we performed the calculations for both fixed and freed nuclei. For the latter, we used different isotopologues in order to have a better understanding of the effects of the nuclear movement on the observed complexities in the HHG.

Here, the full-dimensional electronic time-dependent Schrödinger equation (TDSE) beyond the Born–Oppenheimer approximation (NBO) is solved numerically for \( \text{H}_2^+ \), \( \text{D}_2^+ \) and \( \text{X}_2^+ \) (X is a virtual isotopologue of H being 10 times heavier).

The full-dimensional electronic TDSE within the Born–Oppenheimer approximation (BO) for \( \text{H}_2^+ \), which is indicated throughout the article by \( \text{H}_2^+ \) (BO), is also solved to compare with the NBO results. The equilibrium internuclear distance within the BO is set to \( R_{eq} = 1.96 \text{ au} \). Calculations have been done with seven and ten-cycle laser pulses of 800 nm wavelength with \( I = 4 \times 10^{14} \text{ W cm}^{-2} \) intensity. We suppose that molecular ions are aligned in such a way that their internuclear–distance axis is parallel to the laser polarization direction. Nowadays the molecular alignment in strong laser fields is readily feasible and it is applied in several experiments [6, 9, 22–27]. We use atomic units throughout the article unless stated otherwise.

### 2. Computational methods

The time-dependent Schrödinger equation for \( \text{H}_2^+ \) (\( \text{D}_2^+ \)) with electron cylindrical coordinates \((z, \rho)\) with respect to the molecular center of mass and internuclear distance \(R\), for both \(z\) and \(R\) parallel to the laser polarization direction, can be read (after elimination of the center-of-mass motion and ignoring molecular rotation) as [28, 29]

\[
\frac{\partial \psi(z, \rho, R; t)}{\partial t} = \hat{H}(z, \rho, R; t) \psi(z, \rho, R; t). \tag{1}
\]

In this equation, \( \hat{H} \) is the total electronic and nuclear Hamiltonian which is given by

\[
\hat{H}(z, \rho, R; t) = -\frac{2m_N + m_e}{4m_Nm_e} \left[ \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial z^2} \right] + \frac{1}{m_N} \frac{\partial^2}{\partial R^2} + \hat{V}_e(z, \rho, R; t), \tag{2}
\]

with

\[
\hat{V}_e(z, \rho, R, t) = -\frac{1}{\sqrt{(z + \frac{R}{2})^2 + \rho^2}} - \frac{1}{\sqrt{(z - \frac{R}{2})^2 + \rho^2}} + \frac{1}{R} \left( \frac{2m_N + 2m_e}{2m_N + 2m_e} \right) \varepsilon_{0} f(t) \sin(\omega t). \tag{3}
\]

In these equations, \( \varepsilon_{0} \) is the laser peak amplitude, \( m_e \) and \( m_N \) are the masses of the electron and single nuclei, \( \omega \) is the angular frequency and \( f(t) \) is the laser pulse envelope, which rises linearly during the first two cycles, then is constant for a few cycles and decreases during the last two cycles. For example, the shape of the ten-cycle laser pulse used in this work is shown in figure 1.

The TDSE is solved using unitary split-operator methods [30, 31] with an 11-point finite difference scheme through a general nonlinear coordinate transformation for both electronic and nuclear coordinates which is described in more detail in our previous works [32–34]. The grid points for the \( z, \rho, \) and \( R \) coordinates are 500, 83, and 210, respectively. The finest grid size values in this adaptive grid schemes are 0.13,
0.2, and 0.025, respectively for the $z$, $\rho$, and $R$ coordinates. The grids extend up to $z_{\text{max}} = 98$, $\rho_{\text{max}} = 25$, and $R_{\text{max}} = 16$. The HHG spectra are calculated as the square of the wind- 
owed Fourier transform of the dipole acceleration $a_z(t)$ in the electric field direction ($z$) as 

$$ S(\omega) = \int_0^T <\psi|a_z(t)|\psi> H(t) \exp[-i\omega t] \, dt^2, \quad (4) $$

where 

$$ H(t) = \frac{1}{2} [1 - \cos(2\pi \frac{t}{T})], \quad (5) $$

is the Hann window function and $T$ is the total pulse duration. The Hann window function brings the dipole acceleration smoothly to zero at the end of the laser interaction. There are some non-decaying components (such as the coherence between other excited states and the ground state [35]) in the dipole acceleration that lasts even after the laser pulse is off. Furthermore, to perform a discrete Fourier transform it is also necessary for the signal to be periodic which is satisfied by the introduction of a window function. Otherwise unphysical patterns are to appear after performing a Fourier transform. Therefore, the Hann window function reduces the unphysical features and long-lived effects in the dipole acceleration on the HHG spectrum as the Hann window transform is applied over the finite time by artificially cutting the dipole acceleration in equation (4).

To obtain the contributions of different vibrational and electronic states to the total HHG spectrum, we first decompose the total wavefunction as [20]

$$ \psi(z, \rho; R; t) = \sum_{n=1}^{4} c_n(R; t) \psi_n(z, \rho; R) + \psi_{\text{res}}(z, \rho; R; t). \quad (6) $$

$\psi_n(z, \rho; R)$’s are the four lowest Born–Oppenheimer electronic wavefunctions of the system and $c_n(R; t) = \langle \psi_n(z, \rho; R) | \psi(z, \rho; R; t) \rangle_{z, \rho}$ which is integrated over the $z$ and $\rho$ electronic coordinates. The wavepacket $\psi_{\text{res}}(z, \rho; R; t)$ is the residual part of the $\psi(z, \rho; R; t)$ including the higher excited states and electronic continuum states. In equation (6), $c_i(R; t) = c_i(R; t)$, $c_2(R; t) = c_2(R; t)$, $\psi_1(z, \rho; R) = \psi_1(z, \rho; R)$ and $\psi_2(z, \rho; R) = \psi_2(z, \rho; R)$ and $\psi_3(z, \rho; R)$ are the ground and first excited electronic wavefunctions, respectively, corresponding to the $1s_{\sigma_g}$ and $2p_{\sigma_u}$ states. If we substitute equation (6) to equation (4) and retain the dominant terms, we arrive at [20]

$$ S_{\text{tot}} \approx S_{\text{g}}(\omega) + S_{\text{d}}(\omega) + 2[A_{\text{g}}^g(\omega) \times A_{\text{d}}(\omega)], \quad (7) $$

where $S_{\text{g}}(\omega) = |A_{\text{g}}(\omega)|^2$ and $S_{\text{d}}(\omega) = |A_{\text{d}}(\omega)|^2$ and $A_{\text{g}}(\omega)$ and $A_{\text{d}}(\omega)$ denote the recombination to the $1s_{\sigma_g}$ and $2p_{\sigma_u}$ states, respectively and the term $2[A_{\text{g}}^g(\omega) \times A_{\text{d}}(\omega)]$ corresponds to the electronic interference term (EIT) between these two electronic states [20]. In this work, the second ($\psi_2(z, \rho; R)$) and third ($\psi_3(z, \rho; R)$) excited electronic states are not considerably populated (both reach maximum $\sim 1.4\%$ while the population of the first excited state reaches up to $40\%$) during the interaction and therefore the corresponding terms $S_{\text{g}}(\omega)$ and $S_{\text{d}}(\omega)$ are negligible and consequently have been ignored.

We also decompose the $S_{\text{g}}(\omega)$ into the bound and dissociative parts as

$$ S_{\text{g}}(\omega) = S_{\text{b}}(\omega) + S_{\text{d}}(\omega) + 2[A_{\text{g}}^b(\omega) \times A_{\text{d}}(\omega)], \quad (9) $$

in which the bound term $S_{\text{b}}(\omega) = S_{\text{b}}^{\text{num}}(\omega)$ and $A_{\text{b}}(\omega) = A_{\text{b}}^{\text{num}}(\omega)$ in which $S_{\text{g}}^{\text{b}}(\omega) = |A_{\text{g}}^b(\omega)|^2$ with

$$ A_{\text{g}}^b(\omega) = \sum_{\nu=0}^{n-1} \int 2Re <c_{\nu}(t)\psi_{\nu}(R)|\psi_{\text{res}}(z, \rho; R) > |a_{\nu}(t)|^2 \, dt, \quad (10) $$

which is the sum over the vibrational states with the vibrational quantum number $\nu$ and $c_{\nu}(t) = \langle \psi_{\nu}(R)|c_{\nu}(R; t)\rangle>$. The dissociative term $S_{\text{d}}(\omega) = |A_{\text{d}}(\omega)|^2$ with $A_{\text{d}}(\omega) = A_{\text{d}}(\omega) - A_{\text{d}}(\omega)$. The last term in equation (9), $2[A_{\text{g}}^b(\omega) \times A_{\text{d}}(\omega)]$, corresponds to the vibrational interference term (VIT) between the bound and dissociative terms of the $1s_{\sigma_g}$ state. The time profile of harmonics is obtained by the Morlet-wavelet transform of dipole acceleration $a_{\nu}(t)$ via [36, 37]

$$ w(\omega, t) = \frac{\omega}{\sqrt{\pi \omega^2}} \times \int_{-\infty}^{\infty} a_{\nu}(t') \exp[-i\omega(t' - t)] \exp \left[-\frac{\omega^2(t' - t)^2}{2\sigma^2}\right] dt'. \quad (11) $$

We set $\sigma = 2\pi$ in this work as used in [36].

Figure 1. The ten-cycle laser pulse shape with a two-cycle linear turn-on, followed by a constant intensity, and a two-cycle linear turn-off at the 800 nm wavelength ($\omega = 0.057 \text{ au}$) and $I = 4 \times 10^{-14}$ W cm$^{-2}$ intensity.
3. Results and discussion

The HHG spectra of $\text{H}_2^+$, $\text{D}_2^+$, $\text{X}_2^+$ and BO $\text{H}_2^+$ ($\text{H}_2^+(\text{BO})$) obtained under seven-cycle 800 nm laser pulses of $I = 4 \times 10^{14}$ W cm$^{-2}$ intensity are shown in figure 2. For better visualization, the range of 1–29 and 31–59 harmonics of the spectra are shown in the left and right panels, respectively. Generally, below saturation intensity, the intensity of the HHG spectra is higher for lighter isotopologues having a higher ionization probability. However, harmonics are suppressed more for a lighter isotopologue with a larger nuclear motion than those of a heavier one [21]. This attenuation effect is more pronounced for higher harmonic orders in a short-trajectory branch having longer return times (we neglected the long-trajectory branch because of its higher suppression than that of the short-trajectory one). Therefore we see in the right panel of figure 2 that some parts of the HHG spectrum of $\text{X}_2^+$ are higher than those of $\text{D}_2^+$ and even $\text{H}_2^+(\text{BO})$ shows higher intensity compared to the three other isotopologues (see [21] for more details). For the fixed-nuclei approximation case ($\text{H}_2^+(\text{BO})$), only odd harmonics are seen while for NBO cases, although odd harmonics are dominant at low orders, the HHG signals are complicated. For the $\text{X}_2^+$ isotopologue, small redshifts in harmonics relative to odd harmonics are seen which are more discernible for higher harmonics. For the $\text{D}_2^+$ and $\text{H}_2^+$ cases, the patterns of the redshift are complicated and the HHG spectra broaden for most harmonic orders.

To demonstrate the origin of redshifts discussed above, we plotted the temporal dependence of harmonic orders for both BO and NBO cases in figure 3. As can be seen, mostly short trajectories contribute to the HHG because long-trajectory suppression is considerable due to the wavepacket spreading and also nuclear motion [21]. For laser pulses of $\sin^2$ and Gaussian envelopes, we can attribute the rising and falling parts to the laser pulse. The blueshift and redshift of harmonics occur in rising and falling parts, respectively (see [12], and references therein). Bian et al showed that the HHG occurs mostly at the laser falling part because of the nuclear motion and enhanced ionization, giving rise to the redshift of harmonics [12]. In this work, we used trapezoidal envelopes having a two-cycle rising and a two-cycle falling part. As it is seen in figure 3, for $\text{H}_2^+$, $\text{D}_2^+$ and $\text{X}_2^+$, there are three relatively intense peaks between the 5–7 laser cycles, i.e. in the falling part of the laser pulse, while there is not any significant peak between the 0–2 optical cycles for the laser rising part. For $\text{X}_2^+$, we see several intense peaks before five optical cycles and therefore the redshifts from the laser falling part become less important in comparison with $\text{H}_2^+$ and $\text{D}_2^+$ and for $\text{D}_2^+$.
similarly the redshifts are less than those in $H_2^+$. To see whether the redshifts are due to the laser falling part, we plotted the HHG spectra of three isotopologues in figure 4 which is similar to figure 2 but here the Fourier transform is integrated over the first five optical cycles to remove the contribution of the last two-cycle falling part of the laser pulse. As it is obvious, the HHG spectra have been smoothed and complicated features, already seen in figure 2, are not seen in figure 4 and also the redshifts have been decreased.

If we choose a longer trapezoidal laser pulse (without changing the optical cycles of the rising and falling parts of the laser pulse), we expect that the contribution of the laser falling part becomes less as the HHG process occurs mostly before the laser falling part especially for the lighter isotopologues with faster nuclear motions and more population depletion. To show this, we calculated the HHG spectra for ten-cycle laser pulses (as shown in figure 1) with other laser parameters similar to those of figure 2. The results are shown in figure 5 with their corresponding time profiles depicted in figure 6. As can be seen in figure 5, the redshifts are small in comparison with figure 2 and for $H_2^+$ we can say that no redshift is observed but for $D_2^+$ and $X_2^+$ small redshifts are seen. Figure 6 shows that for $H_2^+$ and $D_2^+$ most HHG occurs before the pulse falling part. The intensity of the harmonic peaks decreases for $H_2^+$ and $D_2^+$ at time $t > 6.5$ o.c. and at $t > 7.5$ o.c., respectively. The population of $H_2^+$ ($D_2^+$) is depleted from 0.8 at $t = 6.5$ o.c. (7.5 o.c.) to 0.15 (0.45) at the end of the ten-cycle laser pulse. Therefore, these population depletions are responsible for the suppression of the HHG at the last two-cycle laser pulse in figure 6. For $X_2^+$, the population depletion is minimal due to the slow nuclear motion not allowing the nuclei to reach large internuclear distances where enhanced ionization occurs. Therefore the HHG has considerable intensity in the falling part of the laser pulse. Figure 6 shows that for $X_2^+$ there are three HHG peaks having redshift at the falling part of the laser pulse (between 8–10 optical cycles) and there are twelve HHG peaks without redshift before the falling part (between 2–8 optical cycles) which reduce and cover the contribution of the three peaks with redshift into the total HHG spectrum as we do not observe any redshift in the total HHG spectrum of $X_2^+$ in figure 5. In figure 7, the ionized outgoing wavepacket (IOW) probability density in the $z$ direction as a function of the internuclear distance for the ten-cycle laser pulse is shown for $H_2^+$, $D_2^+$ and $X_2^+$. This figure shows that the ionization occurs for $D_2^+$ and $H_2^+$ mostly at large internuclear distances where charge-resonance enhanced ionization happens. It must be noted for figure 7 that we calculated the IOW probability density from the boundary on the electronic $z$ coordinate by virtual detector methods [32]. The nuclei in this IOW are mainly under the influence of the Coulomb repulsion of each other. Therefore, we expect that the internuclear distance of the IOW increases between the ionization time and the time to reach the virtual detector. This increase of the internuclear distance is more for a smaller internuclear distance. Therefore, if we want to introduce the IOW probability density in figure 7 as the ionization probability, it is relatively deformed and shifted to larger internuclear distances.

The time-dependent population as a function of the internuclear distance is also shown in figure 8 for the $H_2^+$, $D_2^+$ and $X_2^+$ for the ten-cycle laser pulse. The probability of finding the molecule at larger internuclear separations

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**Figure 4.** The same as figure 2, but the Fourier transform is done over the first five optical cycles (set $T = 5$ o.c. in equation (4)).

**Figure 5.** The same as figure 2, but for a ten-cycle laser pulse shown in figure 1.
increases in time which is more for the lighter isotopologues. The intensity decrease of the harmonic peaks in figure 6 for $\text{H}_2^+$ ($t > 6.5$ o.c.) and $\text{D}_2^+$ ($t > 7.5$ o.c.) is consistent with finding the molecule at large internuclear distances (figure 8) where the ionization (figure 7) and therefore the population depletion is at its maximum.

In order to figure out the contributions of the different electronic and vibrational states into the redshifts observed in figure 2 for the seven-cycle laser pulse, we plotted separately the recombination to the dominant electronic states, $1s\sigma_g$ and $2p\sigma_u$, and different vibrational states ($\psi_{\nu_I}$) of the $1s\sigma_g$ state which are depicted in figures 9–11 for $\text{X}_2^+$, $\text{D}_2^+$ and $\text{H}_2^+$, respectively. We should note that for figures 9–11 we have depicted harmonic orders greater than 19 to focus mainly on the recombination of the continuum electron into bound states. Transitions between bound electronic states also lead to the generation of harmonic orders up to the ionization potential $I_p$ (in this work $I_p = 1.1$ corresponding to the harmonic order $\sim 19$), leading to further complexity of harmonic orders below the $I_p$ which was not intended in this work. In figure 9(a) for $\text{X}_2^+$, the spectra of $S_g$ and $S_u$ have nearly the same magnitude and thus we can conclude that the EIT has no significant effect. It is also observed for recombinations to the $1s\sigma_g$ and $2p\sigma_u$ states that $S_g$ is dominant over $S_u$ for almost high harmonic orders but at low harmonic orders $S_u$ is slightly higher (figure 9(b)). As $S_g$ is dominant for most
harmonic orders, we therefore focus on its components, $S_b$ and $S_d$, to find out their contribution in the redshifts seen in figure 2. As can be seen in figure 9(c), $S_d$ is much lower than $S_b$ and consequently the dissociative part of $S_g$ has an insignificant portion. In addition, $S_g$ and $S_b + S_d$ have overlapped in figure 9(b), so we can say that the VIT is negligible which is also deduced from equation (9). Therefore the vibrational components of $S_b$ should be the source of the redshifts observed for $X_2^+$. To find out how many vibrational states contribute to $S_b$, we compared different $S_{b,n}$ with the $S_b$ and found that $S_{b,10}$ matches well with the $S_b$, i.e. mainly up to ten vibrational states contribute to the $S_b$. Therefore the lowest vibrational states ($\nu \leq 9$) mainly contribute to the $S_{tot}$ and the higher-lying vibrational states ($\nu > 9$) have little contribution. It was expected because of the heavy nuclei of $X_2^+$ which makes the nuclear motion slower and thus the nuclear wavepacket cannot reach large internuclear distances at these seven and ten-cycle laser pulses; therefore the high vibrational states are not significantly populated. We also already observed that $S_d$ (figure 9(c)) was also very weak which is consistent with the contribution of the lowest bound vibrational states discussed above. If we compare $S_{b,5}$ and $S_{b,10}$ in figure 9(d), the redshifts are larger for the $S_{b,10}$ demonstrating that the redshifts in the HHG spectra originate from the contribution of the higher vibrational states of the $1s\sigma_g$ state. The patterns of the HHG spectra for $S_{b,5}$ to $S_{b,10}$ is similar to those of $S_d$ and only the HHG signals have been intensified, with no extra shift compared to what is observed for $S_{b,5}$.

Now we investigate contributions of decomposed components of the total HHG spectrum for $D_2^+$ in figure 10 as applied for the $X_2^+$. The $D_2^+$ is much lighter than $X_2^+$ and therefore we expect faster nuclear dynamics and different coupled electron–nuclear dynamics. By comparing $S_g + S_u$ and $S_{tot}$ in figure 10(a), it can be deduced that the EIT is not important for low harmonic orders but has a pronounced effect on high ones ($>39$), leading to considerable modulations on the signal. The EIT weakened the signal, partially around odd-order harmonics and remarkably around even-order harmonics. In figure 10(b), for low harmonic orders ($<39$), the intensities of $S_g$ and $S_u$ differ considerably which is the reason why the EIT is insignificant at these harmonic orders. But for harmonics greater than 39, $S_g$ and $S_u$ have almost close signal magnitude and this is while, as mentioned above, the EIT is more noticeable for these harmonic orders. One of the important points observed for $S_g$ and $S_u$ is that the redshifts occur for both components. The $2p\sigma_u$ state is an anti-
of vibrational states contributing to the HHG indicates that the EIT has increased the signal for low harmonic orders but has decreased it for high ones (figure 11(a)). The signal $S_g$ is higher than $S_p$ for harmonic orders 39–53 and the redshifts are seen for both $S_g$ and $S_p$ in figure 11(b). Due to the faster nuclear motion of $H_2^+$ relative to $D_2^+$ and $X_2^+$, the molecular ion can reach large internuclear distances in which charge-resonance enhanced ionization occurs and leads to considerable population in the $2p\sigma_u$ state. Unlike $X_2^+$ and $D_2^+$, $S_d$ shows comparable intensity as $S_b$ and even for some high harmonic orders is higher than $S_b$ as shown in figure 11(c). Comparing $S_g$ with $S_b + S_d$ in figure 11(b) shows that the VIT could change (weaken or enhance) the HHG spectrum not observed for $D_2^+$ and $X_2^+$. In figure 11(d), as the number of vibrational states that contribute to $S_b$ increases, the peaks close to odd harmonics are being slightly redshifted and the HHG spectrum near the even harmonics gets more intense.

For the case of the ten-cycle laser pulse, all the HHG components, $S_{tot}$, $S_g$, $S_u$, $S_p$, $S_d$ and $S_b$’s show only odd harmonic orders with very small redshift compared to those observed for the seven-cycle laser pulse in figure 2. The contribution of the above-mentioned decomposed components for each isotopologue is similar (only around odd harmonic orders) to those observed and mentioned in figures 9–11. The only difference seen is that the VIT is insignificant for the ten-cycle laser pulse case, even for the $H_2^+$.

## 4. Conclusion

We solved numerically the full-dimensional electronic time-dependent Schrödinger equation for $H_2^+$ and its isotopologues with and without Born–Oppenheimer approximation under seven and ten-cycle trapezoidal laser pulses of 800 nm wavelength and $I = 4 \times 10^{14}$ W cm$^{-2}$ intensity. The effects of the falling part of the trapezoidal laser pulses and the control of these effects on the HHG spectrum were investigated by considering different pulse durations and isotopologues. We showed that the HHG spectrum is significantly affected by the falling edge of a trapezoidal laser pulse. The redshift and complexity caused by the trailing edge of the trapezoidal laser pulse can be controlled and even removed by considering different laser pulse durations and nuclear motion. We resolved the contributions to the redshift and other patterns in the HHG spectra into the different electronic and vibrational channels and the interference thereof.

In the case of the fixed-nuclei calculation, only odd harmonic orders are generated but for the case of the freed
nuclei (beyond the Born–Oppenheimer approximation), the HHG spectra change depending on the isotopologue. The results show that considerable redshifts appear for a shorter laser pulse (seven cycles) in the presence of nuclear motion, originating mainly from the last two-cycle falling part of the laser pulse. Whereas, by considering a longer laser pulse (ten cycles), the redshifts and complexity of the HHG spectra are considerably reduced and controlled because the HHG at the falling part of the laser pulse has a little contribution on the total HHG spectrum. For D$_2^+$ and H$_2^+$ under ten-cycle laser pulses, the HHG is suppressed considerably at the laser falling part due to the population depletion.

In order to get insight into the underlying components of the complicated patterns observed for the seven-cycle trapezoidal laser pulses, the HHG spectrum was decomposed into different components representing recombinations to different electronic states $1\sigma_u$ and $2\sigma_u$. We also decompose recombination to the ground electronic state $1\sigma_g$ into the bound ($S_b$) and dissociative ($S_d$) components. For the heaviest isotopologue, X$^2\Sigma^+$, mostly the ground electronic state and low vibrational states contribute to the HHG spectrum and the high harmonic orders show a redshift coming mainly from the high vibrational states of the $1\sigma_g$ state. For isotopologues D$_2^+$ and H$_2^+$, recombination to the first excited electronic state $2\pi_u$ becomes also significant and the interference term (EIT) between the $1\sigma_g$ and $2\pi_u$ states plays an important role and changes the HHG signal, remarkably around even-order harmonics. More vibrational states contribute to the HHG signal for lighter isotopologues indicating that larger inter-nuclear distances have become accessible during the interaction due to the faster nuclear motion. With increasing the number of vibrational states, the HHG signal of odd harmonic orders becomes slightly redshifted and that of the even-order harmonics gets more intense. The dissociation part $S_d$ and VIT seems to be noticeable for the H$_2^+$.

Another way that we can suppress the effect of the falling laser pulse on the HHG spectrum is to use enough high laser peak intensities, instead of a longer laser pulse; this is not considered in this work. We should note that, at very high laser intensities or longer laser rising parts, the blueshift of harmonics at the laser rising part may arise which should be considered.

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