

High harmonic generation in H_2^+ and HD^+ by intense femtosecond laser pulses: A wave packet approach with nonadiabatic interaction in HD^+

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Abstract. We have theoretically investigated the high harmonic generation (HHG) spectra of H_2^+ and HD^+ using a time-dependent wave packet approach for the nuclear motion with pulsed lasers of peak intensities (I_0) of 3.5×10^{14} and 4.5×10^{14} W/cm², wavelengths (λ_L) of 800 and 1064 nm, and pulse durations (T) of 40 and 50 fs, for initial vibrational levels $v_0 = 0$ and 1. We have argued that for these conditions the harmonic generation due to the transitions in the electronic continuum by tunnelling or multiphoton ionization will not be important. Thus, the characteristic features of HHG spectra in our model arise only due to the nuclear motions on the two lowest field-coupled electronic states between which both interelectronic and intramolecular (due to intrinsic dipole moments, for HD^+) radiative transitions can take place. For HD^+ , the effect of nonadiabatic (NA) interaction between the two lowest Born–Oppenheimer (BO) electronic states has been taken into account and comparison has been made with the HHG spectra of HD^+ obtained in the BO approximation. Even harmonics and a second plateau in the HHG spectra of HD^+ with the NA interaction and hyper-Raman lines in the spectra of both H_2^+ and HD^+ for $v_0 = 1$ have been observed for higher value of I_0 or λ_L . Our calculations indicate reasonable efficiencies of harmonic generation even without involving the electronic continuum.

Keywords. High harmonic generation; H_2^+ ; HD^+ ; wave packet; nonadiabatic interaction.

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1. Introduction

High harmonic generation (HHG) in atoms and molecules [1–8] has attracted much attention in the last two decades. In addition to the fundamental aspects of dynamics of the

process, its application to the production of coherent radiation in the extreme ultraviolet (XUV) or soft X-ray range and generation of very high-energy attosecond (as) pulses have been widely discussed [5].

Many workers have studied the HHG spectra of H_2^+ by solving the time-dependent Schrödinger equation (TDSE) for the electronic motion with fixed nuclei approximation [6,7]. But one cannot generally expect to obtain reliable HHG spectra from fixed or clamped nuclei calculations [8]. Moiseyev *et al* [9] were the first to investigate the contribution of nuclear motion to the HHG spectra of H_2^+ in intense long-pulse laser fields, using time-independent non-Hermitian Floquet ansatz for such motion, and taking into account only the multiphoton dissociation channels. Recently, Sarkar *et al* [10,11] have studied the HHG in H_2^+ and HD^+ with continuous wave (CW) lasers using time-independent Hermitian Floquet approach for the nuclear motion of the molecular ions without invoking any tunnelling or multiphoton ionization.

In this paper, we investigate the HHG spectra of the single-electron diatoms H_2^+ and HD^+ for different intensities and wavelengths of linearly polarized intense short laser pulses. The time-dependent wave packet approach for the nuclear motion has been adopted without considering the conventional electron recollision model [12]. In our model, any tunnelling ionization resulting in Coulomb explosion [13,14] is not involved, the sole (bound) electron remains on a bonding or antibonding MO (molecular orbital), and does not become free [1].

In experiments with short laser pulses of the order of a few femtosecond, the use of the Floquet ansatz, which is strictly applicable to a periodic Hamiltonian only, cannot be justified and the time-dependent wave packet propagation technique is required. One of the important differences of this method compared to the time-independent Floquet approach [9–11] is that the rotation of the molecule, with a time-scale of the order of picosecond, is not relevant and even harmonics in the HHG spectra of the heteronuclear diatom HD^+ should be observed.

In the present work, we have taken laser peak intensities (I_0) of 3.5×10^{14} and 4.5×10^{14} W/cm², with wavelengths (λ_L) of 800 and 1064 nm, yielding the Keldysh parameter [15] $\gamma [= \omega_L(2I_P/I_0)^{1/2}$ (in a.u.)] = 0.41–0.62, where ω_L is the laser (angular) frequency and I_P is the ionization potential. As $\gamma < 1$, it seems that tunnelling ionization may be significant making the electron moves far away from the nuclei. But, it may be stressed here that the Keldysh parameter is actually adopted for the tunnelling ionization of an one-electron atomic system. It even ignores the structure of a multielectron atom [16]. It may be stressed here that, for H_2^+ or HD^+ , the tunnelling ionization probability strongly depends on the internal vibrational levels of the ion. This has been clearly demonstrated by Feuerstein and Thumm [17], and Roudnev and Esry [18]. Considering the electronic and nuclear motions together, they have shown that, for $I_0 < 5 \times 10^{14}$ W/cm² and $\lambda_L \simeq 800$ nm, dissociation strongly dominates over tunnelling ionization for H_2^+ or HD^+ in the two lowest vibrational levels ($v_0 = 0$ and 1), while the tunnelling ionization resulting into Coulomb explosion becomes more and more important as the vibrational quantum number increases. As in this work, we have confined our HHG calculations for $I_0 = 3.5 \times 10^{14}$ and 4.5×10^{14} W/cm² only with $v_0 = 0$ and 1, the contribution of the tunnelling ionization process would not be important and the hyper-Rayleigh or the hyper-Raman process will be the main

mechanism for HHG. Thus, the present results indicate the contribution of nuclear motion on the HHG process when only transition between the two lowest electronic states is involved.

The importance of tunnelling ionization for HHG from a higher vibrational level is evident from the work of Chelkowski *et al* [13] who calculated the harmonic spectra from $v_0 = 6$ of H_2^+ , considering one-dimensional nuclear motion and three-dimensional electron motion. They showed that the electronic motion far from the nuclei does occur in such case, and this can be important for HHG when an initial excited vibrational level is taken. It is relevant to note that in their case the transitions leading to the electronic continuum are important for the initial excited vibrational level $v_0 = 6$ even though the Keldysh parameter $\gamma > 1$ ($\simeq 1.50$ in their case).

It may also be noted here that in the present study, the laser peak intensities are comparatively higher than those in our previous works [10,11] for H_2^+ and HD^+ in which the time-independent Hermitian Floquet ansatz for HHG was used. As mentioned earlier, that situation was more appropriate for CW lasers of moderate intensities. But, in the wave packet approach, with femtosecond laser pulses, higher laser peak intensities are necessary to get efficient and significant range of harmonic spectra, because of the much shorter interaction time.

In this work, the nonadiabatic (NA) interaction or coupling in HD^+ , arising due to the effect of nuclear motion on the charge-resonance (CR) [6,19] Born–Oppenheimer (BO) electronic states ($1s\sigma_g, 2p\sigma_u$), has been taken into account. Nuclear motion mixes the two CR states and the heteronuclearity (unequal nuclear masses) of HD^+ causes the symmetry breaking [20,21]. We have considered the nuclear motion and also all the radiative transitions between the two lowest electronic states arising due to transition as well as intrinsic (for HD^+) dipole moments [10].

In an earlier work [11], we have shown that the higher excited electronic states play some roles on HHG in H_2^+ for time-independent CW lasers. In the present study, with short pulsed lasers, the transitions occurring during the laser pulse time are predominantly the electronic transitions between the two lowest states of H_2^+ or HD^+ . The nuclear wave packet is simply transferred between the surfaces of the two lowest electronic states only and does not get enough time to be transferred to the higher excited electronic states [19] whose threshold energy is about 10.2 eV higher than the threshold energy of the two lowest states [11]. Thus, for such short laser pulses, the interaction process reduces to electronic transitions between the two surfaces ($1s\sigma_g, 2p\sigma_u$) for H_2^+ and (GS, ES) for HD^+ , with the internuclear separation corresponding to the coordinate R of the wave packet. The system is capable of undergoing multiphoton dissociation involving the two states. In our model, multiphoton absorption of n laser photons (n is an integer) between the two electronic states, followed by coherent emission of one high-energy photon to the initial level, like the laser-induced nonperturbative $(n + 1)$ hyper-Rayleigh or hyper-Raman scattering [4,22] via continuum, gives rise to HHG in H_2^+ or HD^+ .

In §2, the theory and formulation of HHG are presented using the time-dependent wave packet propagation method. In §3, different laser parameters and the molecular data used in this study are discussed. In §4, the HHG spectra obtained for H_2^+ and HD^+ are illustrated and discussed. Finally, in §5, a brief conclusion is given.

2. Theory and formulation

The intensity $\sigma(\omega)$ of the emitted radiation generating the harmonic spectra of a single molecule is obtained by Fourier transform of the time-dependent dipole moment $d(t)$,

$$\sigma(\omega) = \left| \int_0^T e^{-i\omega t} d(t) dt \right|^2. \quad (1)$$

Here, T is the incident laser pulse duration and ω is the emitted photon frequency. The time-dependent expectation value $d(t)$ of the dipole moment $\mu(R)$, arising from the nuclear motion, in the length form and length gauge, is defined as

$$d(t) = \langle \Psi(R, t) | \hat{\epsilon} \cdot \mu(R) | \Psi(R, t) \rangle, \quad (2)$$

where $\Psi(R, t)$ is the nuclear radial wave packet, $\mu(R)$ is the electronic transition (as well as intrinsic for a heteronuclear system) dipole moment (vector) operator, $\hat{\epsilon}$ is the unit polarization vector of the linearly polarized incident laser field, and R denotes the nuclear radial coordinate of the diatom.

We solve the TDSE for the nuclear coordinate (R) in the basis of two lowest electronic states (in a.u.),

$$i \frac{\partial \Psi(R, t)}{\partial t} = H(R, t) \Psi(R, t), \quad (3)$$

where

$$H(R, t) = -\frac{1}{2M} \frac{\partial^2}{\partial R^2} + V(R, t) \quad (4)$$

and

$$V(R, t) = V_0(R) + V_1(R, t). \quad (5)$$

Here, M is the reduced mass of the molecule and $V_0(R)$ is the intramolecular potential. $V_1(R, t)$, the interaction potential of the molecule with the pulsed laser field $\mathbf{E}(t)$, is given by

$$V_1(R, t) = -\mathbf{E}(t) \cdot \mu(R). \quad (6)$$

It may be mentioned here that the rotational time period (\sim ps) of the diatom is orders of magnitude larger than the laser pulse duration T (\sim fs) used by us, and so we have neglected the rotational degree of freedom of the molecule.

We use the split operator technique along with the fast Fourier transform (FFT) for solving the TDSE to propagate an initial stationary wave function on the ground electronic state vibrational level (v_0) to a sufficiently large time (much greater than T). The nuclear vibrational wave packet at time $t + \Delta t$ can be obtained from the wave packet at time t by the operation

$$\Psi(R, t + \Delta t) = e^{-iH(R,t)\Delta t} \Psi(R, t). \quad (7)$$

Following the work of Charron *et al* [23], and Bhattacharya and Bhattacharyya [24], we have solved the TDSE for the nuclear motion at each R and t .

We have used a linearly polarized laser field

$$\mathbf{E}(t) = \hat{\mathbf{e}} E_0 f(t) \cos(\omega_L t), \quad (8)$$

where E_0 is the peak field amplitude and $f(t)$ is the pulse shape. We have chosen the pulse envelope function $f(t)$ to have a $\sin^2\{\pi t/(2t_r)\}$ [4,13,25] rise (turn-on) and fall (turn-off) ramps with rise and fall time $t_r = 5$ fs. A flat (constant) top of 30 or 40 fs between the ramps with a total pulse duration of 40 or 50 fs has been taken.

The mixing of the two asymptotically degenerate BO electronic states $1s\sigma_g$ and $2p\sigma_u$ by the NA interaction in HD^+ results in nondegenerate electronic states GS (ground state) and ES (excited state) with an asymptotic splitting of about 29.84 cm^{-1} (energy difference of the D($1s$) and H($1s$) atoms) [20,21]. The potential energies of GS and ES are obtained by the diagonalization of the electronic Hamiltonian matrix with the inclusion of the NA coupling terms (beyond the BO dynamics) [20].

3. Calculations

We have calculated the HHG spectra of H_2^+ and HD^+ for laser peak intensities (I_0) of 3.5×10^{14} and $4.5 \times 10^{14} \text{ W/cm}^2$, laser wavelengths (λ_L) of 800 nm (Ti:sapphire laser) and 1064 nm (Nd:YAG laser), and laser pulse durations (T) of 40 and 50 fs, and molecular initial vibrational levels $v_0 = 0$ and 1. For comparison, we have also computed the HHG spectra of HD^+ with the BO approximation [$HD^+(\text{BO})$].

The BO potentials of the ground ($1s\sigma_g$) and the first excited ($2p\sigma_u$) electronic states of H_2^+ as well as the NA potentials of the ground (GS) and excited (ES) electronic states of HD^+ are taken from Carrington and Kennedy [20], and Moss and Sadler [21]. The electronic transition ($1s\sigma_g \rightarrow 2p\sigma_u$) dipole moments of H_2^+ are given by Bates [26]. The electronic transition (GS \rightarrow ES) and intrinsic (GS \rightarrow GS, ES \rightarrow ES) dipole moments of HD^+ are obtained also from Bates [26], using the method given in the Appendix of Ghosh *et al* [27]. The potential energies and the dipole moments of H_2^+ and HD^+ are depicted in Sarkar *et al* [10]. It may be mentioned here that, unlike the neutral HD molecule [8], which has a very small permanent dipole moment of about $1.54 \times 10^{-3} \text{ D}$ [28], the HD^+ molecular ion has a large permanent dipole moment of about 0.87 D [29] (both the values are for $v_0 = 0$, $J = 0$ of the diatom).

4. Results and discussions

We have illustrated in figures 1–8 the relative harmonic intensities of the HHG spectra of H_2^+ and HD^+ as a function of the harmonic order for different laser peak intensities (I_0), wavelengths (λ_L), pulse durations (T), and molecular initial vibrational levels (v_0). The harmonic intensities are normalized to have the same value at the fundamental frequency (ω_L). We observe that the harmonic spectra, in general, exhibit the characteristic features of (at least) one plateau followed by a cut-off, though the cut-off is not sharp. This may possibly be the consequence of the HHG process not being dependent, in our model, on the electron moving very far from the nuclei and hence the effective ionization energy $I_P + 3.17U_P$ dependent cut-off need not occur, where $U_P = I_0/(4\omega_L^2)$ (in a.u.) is the ponderomotive energy.

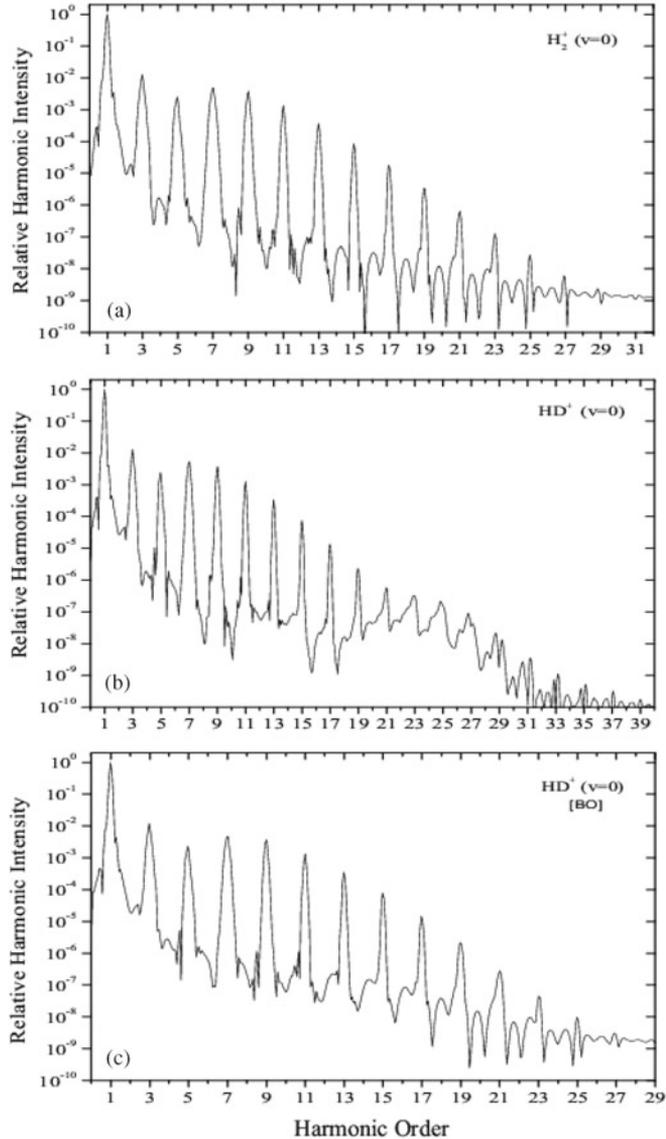


Figure 1. The relative harmonic intensity of HHG spectra as a function of harmonic order with $I_0 = 3.5 \times 10^{14}$ W/cm², $\lambda_L = 1064$ nm, and $T = (5-40-5)$ fs for (a) H_2^+ , (b) HD^+ , and (c) $HD^+(BO)$ at $v_0 = 0$. The harmonic intensities are normalized to have the same value at the fundamental frequency.

Figures 1 and 2 show the HHG spectra of H_2^+ , HD^+ , and $HD^+(BO)$ for $I_0 = 3.5 \times 10^{14}$ and 4.5×10^{14} W/cm² respectively, with $\lambda_L = 1064$ nm, $T = (5-40-5)$ fs (here 1 o.c. = 3.5 fs), and $v_0 = 0$. We find that the harmonic spectra of H_2^+ and $HD^+(BO)$ are quite similar but in the spectra of HD^+ , there is a second plateau at higher harmonic orders. This

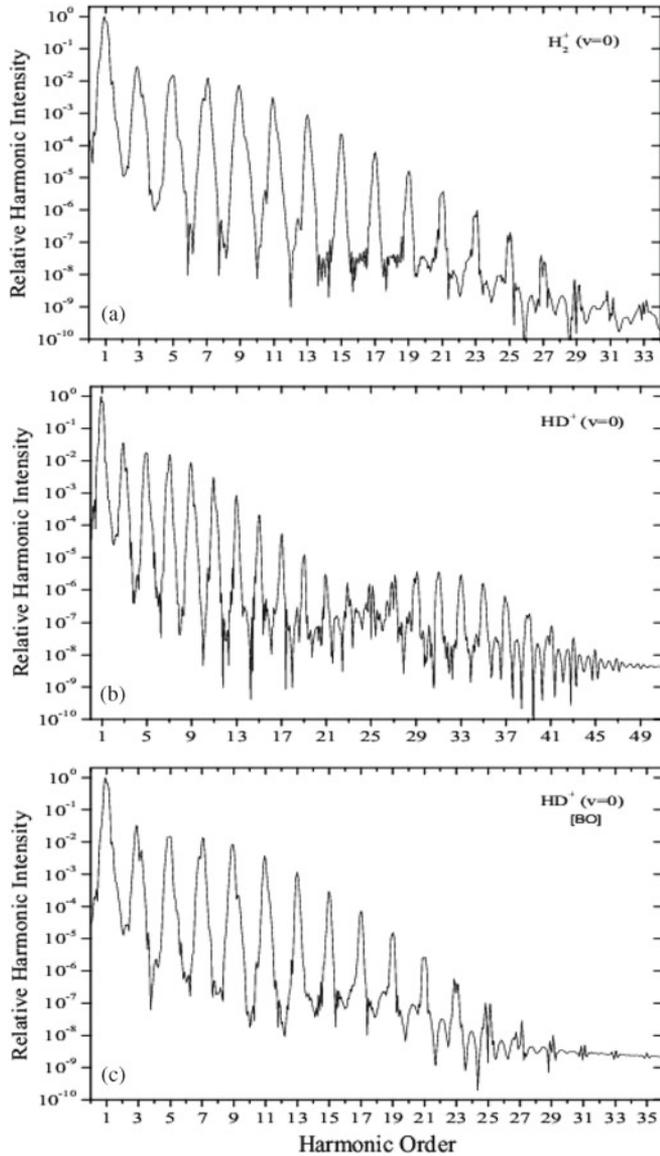


Figure 2. Same as figure 1 except that $I_0 = 4.5 \times 10^{14} \text{ W/cm}^2$.

second plateau arises from the nonadiabatic effects in HD^+ and causes the HHG spectra of HD^+ to extend to much higher orders compared to H_2^+ or $HD^+(BO)$.

In figures 3 and 4, the harmonic spectra of H_2^+ , HD^+ , and $HD^+(BO)$ are drawn for $I_0 = 3.5 \times 10^{14}$ and $4.5 \times 10^{14} \text{ W/cm}^2$ respectively, with $\lambda_L = 800 \text{ nm}$, $T = (5-30-5)$ fs (here 1 o.c. = 2.7 fs), and $v_0 = 0$. Here again, we observe that the HHG spectra of H_2^+ and $HD^+(BO)$ are similar whereas for HD^+ , there is a second plateau at high-order harmonics for only $I_0 = 4.5 \times 10^{14} \text{ W/cm}^2$ (figure 4b).

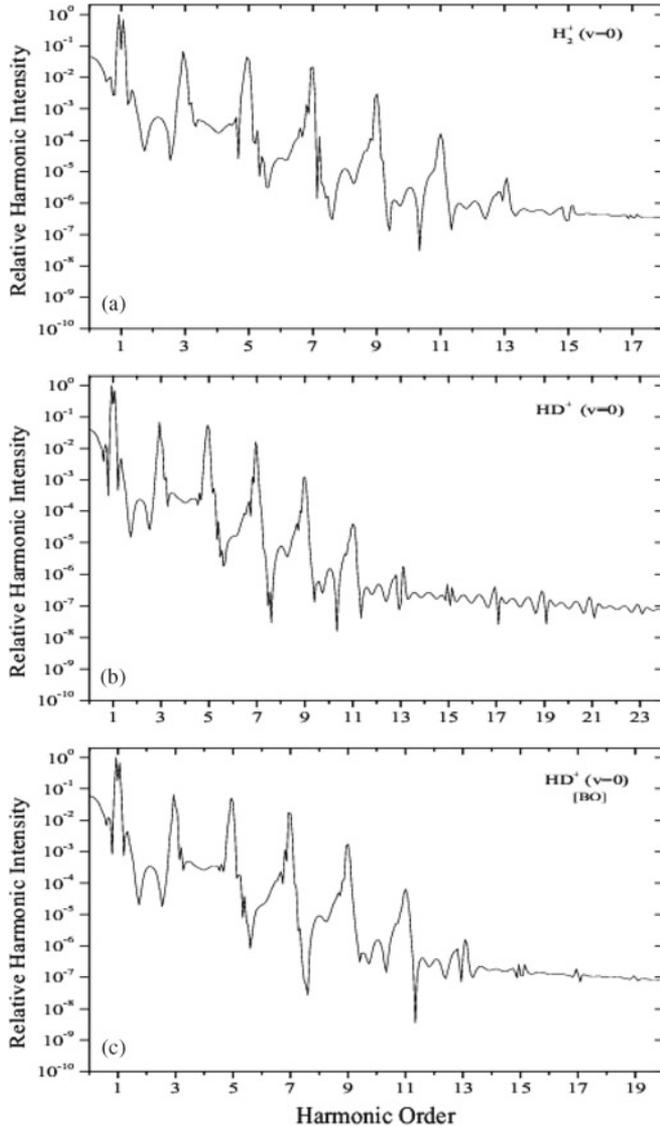


Figure 3. Same as figure 1 except that $I_0 = 3.5 \times 10^{14}$ W/cm², $\lambda_L = 800$ nm, and $T = (5-30-5)$ fs.

Figures 5 and 6 illustrate the harmonic spectra of H_2^+ , HD^+ , and $HD^+(BO)$ for $I_0 = 3.5 \times 10^{14}$ and 4.5×10^{14} W/cm² respectively, with $\lambda_L = 1064$ nm, $T = (5-40-5)$ fs, and $\nu_0 = 1$. When comparing the corresponding spectra in figures 1 and 2 for $\nu_0 = 0$, we find that the intensity of the harmonic spectra at high orders is enhanced for $\nu_0 = 1$. The similarity of the spectra of H_2^+ and $HD^+(BO)$, and a second plateau of HD^+ are observed for the vibrationally excited initial level as well.

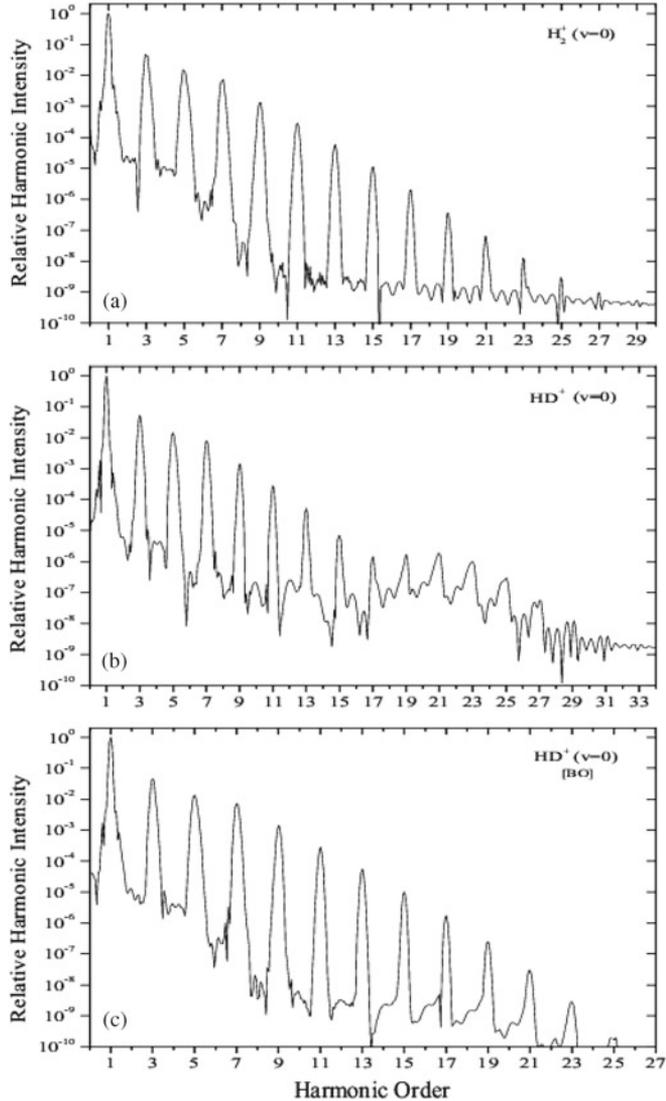


Figure 4. Same as figure 3 except that $I_0 = 4.5 \times 10^{14} \text{ W/cm}^2$.

In figures 7 and 8, the HHG spectra of H_2^+ , HD^+ , and $HD^+(BO)$ are shown for $I_0 = 3.5 \times 10^{14}$ and $4.5 \times 10^{14} \text{ W/cm}^2$ respectively, with $\lambda_L = 800 \text{ nm}$, $T = (5\text{-}30\text{-}5) \text{ fs}$, and $\nu_0 = 1$. Here also, a second plateau for HD^+ occurs for only higher values of I_0 (figure 8b).

The absence of the second plateau for lower values of I_0 ($3.5 \times 10^{14} \text{ W/cm}^2$) and λ_L (800 nm) (figures 3b and 7b) can be explained as follows. The second plateau (for HD^+) occurs at high harmonic orders. For lower values of I_0 and λ_L (higher ω_L), the harmonic spectra would not be much enhanced (due to the lower values of the transition dipole

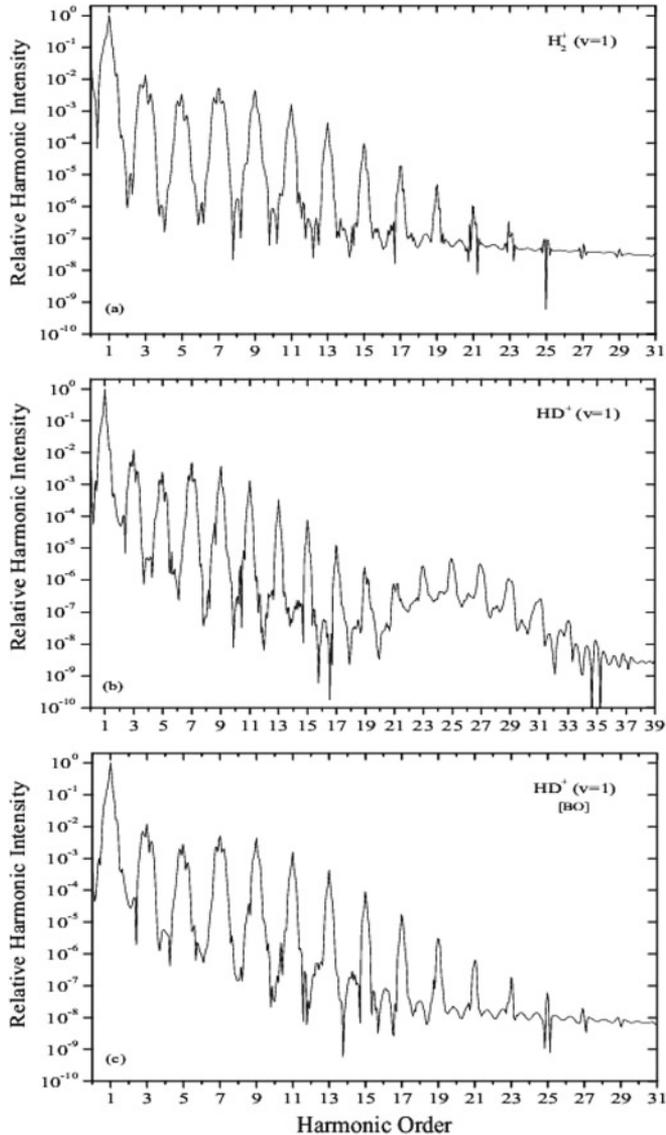


Figure 5. Same as figure 1 except that $\nu_0 = 1$.

matrix elements) and extended enough (due to less number of laser photons absorbed) to the higher harmonic orders to produce the second plateau due to the nonadiabatic interaction in HD^+ .

The range of the harmonic spectra is influenced by the laser peak intensity, wavelength, pulse shape, and pulse duration. From figures 1–8, we find that when I_0 or λ_L increases for the same value of T , the harmonic intensities also increase and the plateau extends to higher order [2] for both $\nu_0 = 0$ and 1 because, in our model, as I_0 or λ_L increases

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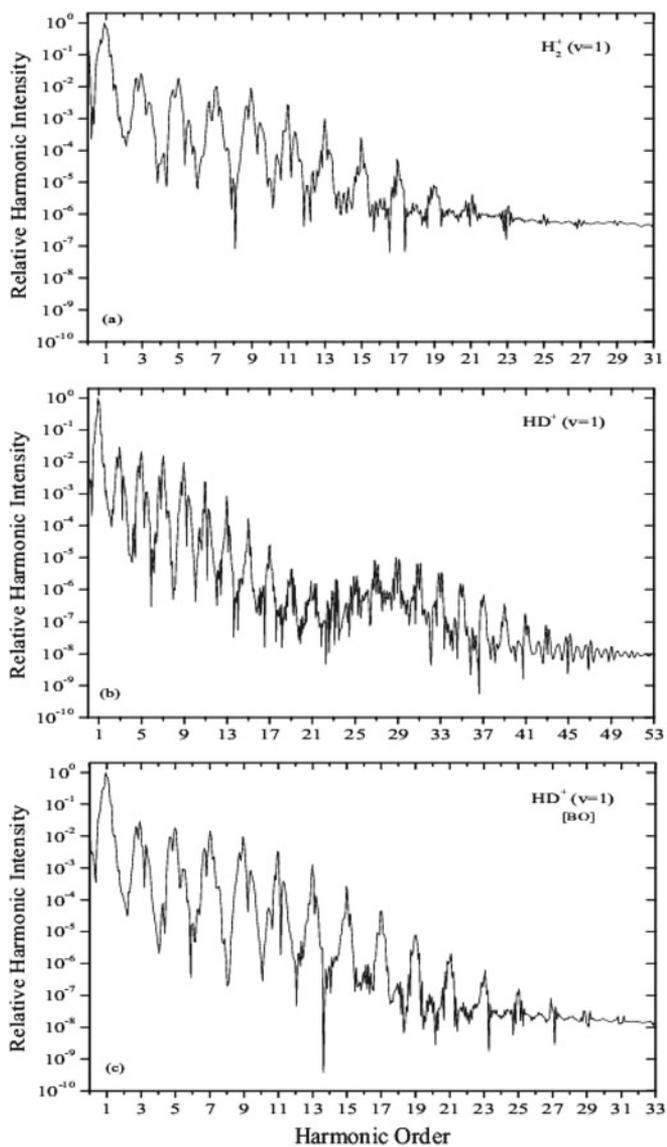


Figure 6. Same as figure 2 except that $v_0 = 1$.

(ω_L decreases), more and more laser photons n (of lower photon energy ω_L), would be absorbed into the continua of the molecular electronic states, after (nonperturbative) multiphoton excitation and de-excitation processes, followed by the final emission of a single high-energy coherent (not spontaneous or a laser) harmonic photon (with sum frequency of $n\omega_L$), giving rise to higher and longer HHG spectra. The harmonic spectra would be enhanced due to the increase of transition dipole matrix elements with increase in I_0 (till

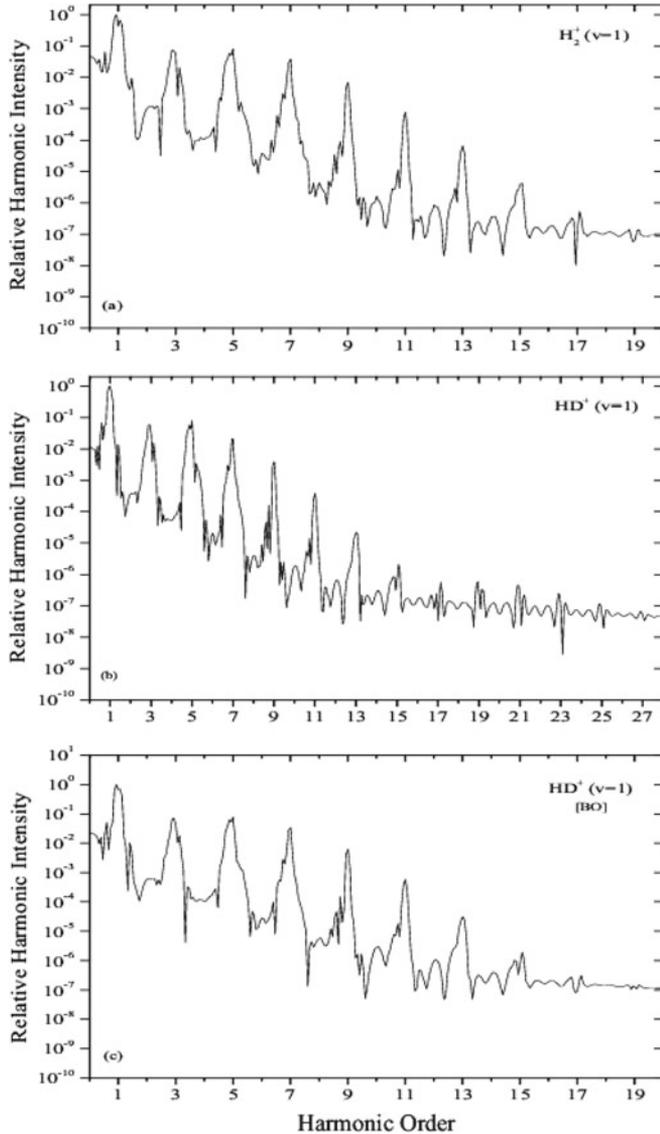


Figure 7. Same as figure 3 except that $\nu_0 = 1$.

saturation is reached) and would be extended due to the increase of n for higher values of I_0 or λ_L (smaller ω_L).

We may mention here that a \sin^2 pulse of the same λ_L , I_0 , and T (40 or 50 fs) was found to yield less efficient and smaller range of harmonic spectra [30] because the interaction time of the molecule with the peak intensity of a \sin^2 pulse is much less than that of a flat (constant) top pulse (with turn-on and turn-off time) of the same pulse duration.

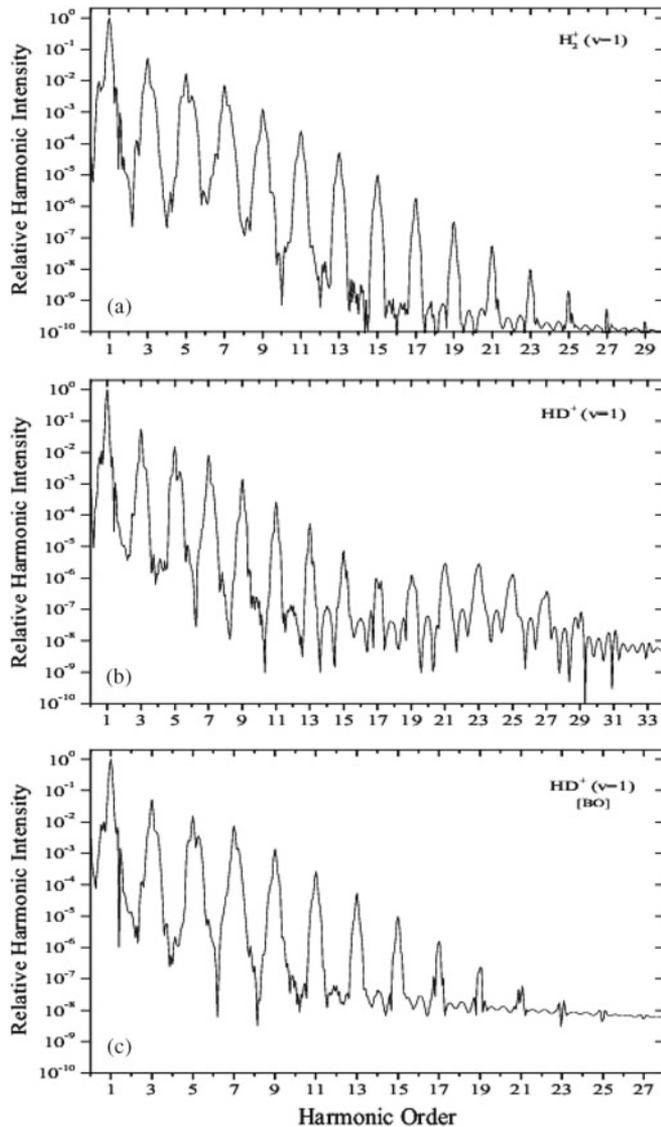


Figure 8. Same as figure 4 except that $v_0 = 1$.

In the systems studied, the HHG spectra for $v_0 = 1$ (figures 5–8) exhibit significant hyper-Raman lines (HRL) [4] on the two sides of the low odd harmonics for the laser intensities and wavelengths considered by us. The HRL are located at $(2n + 1)\omega_L \pm \Delta\omega_{v_0, v_0 \pm 1}$, where n is the harmonic order and $\Delta\omega_{v_0, v_0 \pm 1}$ is the energy difference between the perturbed initial (v_0) and final ($v = v_0 \pm 1$) vibrational levels of the molecular ions. Here, HRL arise because of the strong mixing of the initial $v_0 = 1$ level with the final adjacent $v = 0$ and 2 levels in the intense laser fields. We do not observe any significant HRL in the harmonic spectra for the initial vibrational level $v_0 = 0$ (figures 1–4). This

is due to the comparatively weak mixing of the initial vibrational level $v_0 = 0$ with the final excited vibrational levels $v = 1$ and 2 . Dutta and Bhattacharyya [31] have recently performed close-coupling calculations for the overlap of laser-induced resonances with different vibrational states of HD^+ using lasers of moderate intensities and wavelength of 800 nm. It has been shown, in Table I of their paper, that the area of overlap of the initial state $v_0 = 1$ with the resonance closest in energy to it is much less than that between the initial state $v_0 = 0$ and the corresponding resonance state. This means that the mixing of the initial level $v_0 = 1$ with the final adjacent level $v = 0$ or 2 is more than that of the initial level $v_0 = 0$ with the final level $v = 1$ or 2 . These findings would be more relevant at the laser intensities considered in the present work.

Another notable feature is the presence of even harmonics in the spectra of HD^+ for higher values of I_0 or λ_L . The even harmonics are much weaker than the odd harmonics at low harmonic orders, but become more pronounced at the higher harmonic orders [8]. We do not observe notable even harmonics in the spectra of $\text{HD}^+(\text{BO})$ (as that of H_2^+), though $\text{HD}^+(\text{BO})$ has intrinsic dipole moments which, in principle, should be capable of generating such harmonics. The harmonic spectra are enhanced and extended to higher harmonics for higher values of I_0 or λ_L (smaller value of ω_L). The even harmonics in the spectra of HD^+ are observable in the high harmonic orders for higher values of I_0 or λ_L . This can be ascertained in all the figures presented for HD^+ except for figures 3b and 7b which are drawn for lower values of I_0 (3.5×10^{14} W/cm²) and λ_L (800 nm), though the even harmonics are not as pronounced as the odd harmonics (in the higher harmonic orders).

The differences in the harmonic spectra of HD^+ with that of $\text{HD}^+(\text{BO})$ can be explained as follows. The nonadiabatic (nonradiative) interaction in HD^+ causes symmetry breaking [20,21] of the asymptotically degenerate states $1s\sigma_g$ and $2p\sigma_u$ of H_2^+ or $\text{HD}^+(\text{BO})$, and by mixing of these states, two asymptotically nondegenerate states GS and ES of HD^+ are formed. The transition (GS \rightarrow ES) and intrinsic (GS \rightarrow GS, ES \rightarrow ES) dipole moments of HD^+ drastically differ from those of $\text{HD}^+(\text{BO})$ (or H_2^+ for only the transition dipole moment) due to the nonadiabatic interaction. The electronic transition dipole moment between the two asymptotically degenerate CR states ($1s\sigma_g$ and $2p\sigma_u$) of $\text{HD}^+(\text{BO})$ diverges as $R/2$ (like H_2^+), while that between the two nondegenerate electronic states (GS and ES) (figure 1 of ref. [10]) of HD^+ vanishes at large R (figure 2a of ref. [10]). The intrinsic dipole moments of $\text{HD}^+(\text{BO})$ diverge as $-R/6$ for both the $1s\sigma_g$ and $2p\sigma_u$ states, while those of HD^+ blow up as $-2R/3$ for GS and $R/3$ for ES at large R (figure 2b of ref. [10]). For $\text{HD}^+(\text{BO})$, the dipole matrix elements of the strong, diverging transition dipole moment ($\sim R/2$) predominate the dipole matrix elements of the less diverging intrinsic dipole moments ($\sim -R/6$). Thus, the intrinsic dipole moments are less effective for generating recognizable even harmonics in the HHG spectra of $\text{HD}^+(\text{BO})$. For HD^+ , the dipole matrix elements of the strong, diverging intrinsic dipole moments ($\sim -2R/3$ for GS, $\sim R/3$ for ES) dominate the dipole matrix elements of the non-diverging transition dipole moment (~ 0), and also survive for absorption of large number of laser photons (n) for higher values of I_0 or λ_L leading to the generation of a second plateau with significant even (and odd) harmonics at the higher harmonic orders. It follows that the generation of the even harmonics is due to the nonadiabatic effects on the intrinsic as well as the transition dipole moments of a heteronuclear diatom. Thus, due to the nonadiabatic interaction (beyond the BO dynamics) [8], we find the presence of even harmonics and a second

plateau at the higher harmonic frequencies in the HHG spectra of HD^+ for higher values of I_0 or λ_L .

It is worth mentioning here that the harmonic spectra presented in this paper represent the response of a single molecular ion interacting with a pulsed laser field. HHG is really a coherent emission process from all the molecular ions in a macroscopic medium. The actual emission observed in an experiment depends on the phase matching of the single molecular spectra. Under conditions of low pressure and weak focus typically encountered in experiments, the phase-matched results would not differ dramatically from the single-molecule results [2].

5. Conclusion

Our theoretical calculations demonstrate that harmonics of considerably high orders are generated with significant efficiencies in single-electron diatoms like H_2^+ , HD^+ , even without tunnelling ionization and subsequent recollision of the free electron with the residual nuclear species in the presence of laser field. The recollision model was the general physical picture proposed [12] for HHG in atoms [3,4] and subsequently extended to neutral molecules and molecular ions [3,5–8]. While in these works, interaction between the recolliding electronic and the residual nuclear (ionic) wave packets were found to be crucial for HHG, our present work emphasizes the role of nuclear motion for lower vibrational levels of the simplest one-electron diatoms, at least over a limited laser peak intensity range.

Our time-dependent nuclear wave packet propagation technique enables us to find the dependence of harmonic spectra on the laser parameters, such as, peak intensity, wavelength, pulse duration, and pulse shape as well as on the molecular initial vibrational level. The calculations of the HHG spectra of HD^+ with and without NA couplings show that these couplings do play important roles in the heteronuclear diatom, particularly in enhancing the intensities of the relatively high order harmonics. Such calculations are also useful for interpreting the presence of even harmonics in the harmonic spectra of HD^+ , and the relative importance of the intrinsic dipole moments and the NA couplings in their generation. Our work can also explain the occurrence of HRL in the HHG spectra of H_2^+ and HD^+ for the initially excited molecular vibrational level.

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