



# Optical preparation and manipulation of ground-state coherent vibrational wavepackets of varying constituents in HD<sup>+</sup>

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MS received 12 October 2018; revised 2 March 2019; accepted 1 April 2019

**Abstract.** We have numerically explored different optical schemes for manipulating the composition of a coherent vibrational wavepacket on the ground electronic state of the HD<sup>+</sup> ion. This was achieved by simulating the impulsive interaction of one or more ultrashort laser pulses with stationary eigenstates of HD<sup>+</sup>. Such a study highlights the use of various laser fields for the preparation of a molecular ion vibrational wavepacket, with variable constituents, in its ground electronic state. We have investigated different control scenarios through proper optimisation of the laser parameters and plausible interpretations of the results were proposed.

**Keywords.** Ultrashort; wavepacket; control; HD<sup>+</sup>; coherent.

**PACS Nos** 42.50.Hz; 33.80.Wz; 33.20.Tp

## 1. Introduction

The exposure of a molecular system in a stationary vibrational state to an intense ultrashort laser pulse will result in the formation of a wavepacket which is a superposition of a number of stationary states. The availability of a few intense cycle laser pulses has greatly facilitated the experimental study of wavepacket formation in molecules through such impulsive excitation. Ultrashort pulse techniques are also required for the characterisation and real-time mapping of such wavepackets. The development of these techniques has also paved the way for possible quantum control over molecular dynamics. Right from the beginning, the prospect of control over the preparation of quantum states has been a major incentive for theoretical and experimental studies of laser-induced molecular dynamics. Such control over the preparation of quantum states and their subsequent alteration will facilitate further advancement in the field of photophysics and photochemistry as well as in quantum information science. In recent years, the fascinating possibility of modulating the composition and spatial structure of a wavepacket, at will, has attracted much attention. The scheme of time- and phase-resolved interaction of the laser with the evolving wavepacket should

allow the opportunity to effectively interfere with the inherent nuclear dynamics of the molecules.

The technique of wavepacket generation and its monitoring using femtosecond laser pulses dates back from the early 1990s. Mokhtari *et al* [1] and Khundkar and Zewail [2] were one of the leading groups to have adopted this technique to prepare the transition state of a chemical reaction and then monitor the wavepacket evolution to extract information about the nuclear dynamics. The wavepacket, once generated, continues to evolve on the field-free potential surface after the pulse is over. However, due to the anharmonicity of the potential, the different stationary states involved in the superposition in a bound wavepacket begin to dephase and at some large times the wavepacket may exhibit recurrences. The revival of the wavepacket form in such recurrences may be either fractional or complete [3,4]. The wavepacket revival structures were thoroughly investigated for the D<sub>2</sub><sup>+</sup> molecular system [5–7]. In [8], real-time mapping of the wavepacket dynamics of the HD<sup>+</sup> molecular ion was performed experimentally. The wavepacket dephasing and revival patterns were observed. A quantum mechanical simulation was able to match the observed structure. Such observation of the nuclear motion was the stepping

stone for eventual attempts aimed at wavepacket shape alteration by ultrashort laser pulses. More recently, the generation of wave packet in the cubical billiard and its time evolution for various closed orbits was investigated in [9]. It is also relevant to mention that the sub-Planck structure in mesoscopic quantum systems can be realised in the temporal evolution of vibrational wave packets, as has been predicted in [10].

The question of selectivity in the context of laser manipulation of nuclear motion continues to be a fascinating problem. Although laser-driven control of quantum systems has now been studied for many years, it is only recently that the possibility of manipulation of non-stationary wavepackets to increase the contribution of a particular constituting vibrational level has been addressed.

A promising method of gaining control over the population distribution of the constituting eigenstate in vibrational wavepackets at the preparation stage is to expose an initial stationary state to a sequence of multiple phase-locked laser pulses [11]. The time delay between the pulses causes the accumulated phases of the sets of vibrational eigenstates to be different and allows interference between them. Results obtained from a series of experimental investigations showed that the interferences between the multiple wavepackets generated by time-delayed phase locked laser pulses may actually allow a wavepacket with arbitrary superposition of vibrational eigenstates to be selectively prepared [12–14]. This method, named wavepacket interferometry (WPI), has been reviewed in detail in [15]. Apart from the controlled variation of the population distribution of the quantum systems, WPI is also useful for accessing the amplitude and phase information of the wavepackets. The information extracted from the wavepackets can play a significant role in quantum information processing based on molecular systems. It is of interest to note that WPI has been implemented in gas phase experiments and has also been applied to the condensed phase. A series of recent experiments combining WPI along with coherent anti-Stokes Raman scattering (CARS) was used for the coherent control and manipulation of vibrational and ro-vibrational wavepackets in the solid parahydrogen crystal [16–19].

A complementary method of controlling the wavepacket shapes by population redistribution between the vibrational levels is to perturb the molecular system with an intense laser field in operation for only a few femtoseconds [20–29]. The high field strength along with the broad spectral bandwidth of the laser pulse can set up multiple hyper-Raman transitions between the different eigenstates constituting the wavepacket. This can induce internal rearrangement between the constituent eigenstates through a multitude of optical pathways.

The ultimate aim is to attain field-induced stopping or collapsing of a nuclear wavepacket to a selected stationary state.

Niikura *et al* [20] were the first to report the possibility of quenching of nuclear wavepackets launched by a pump pulse on the ground electronic state of the  $D_2^+$  ion, with a second, time-delayed, intense ultrashort laser pulse. Their results showed that by varying the delay time between the pump pulse and the control pulse, it was possible to alter the wavepacket constitution by driving the population to a specific vibrational level in the wavepacket. Later, many other groups have concentrated on this particular technique of controlling the wavepacket motion. The objective of such studies has been to gain a better understanding of the dependence of the processes on the experimental parameters with an eye on improving the performance with respect to the ultimate goal. Niederhausen and Thumm [21] reported the results of a detailed investigation on the vibrational quenching of nuclear wavepackets by laser pulses. Very recently, their predictions regarding the control of vibrational dynamics in  $H_2^+$ , obtained from a simple two-electronic state model, were compared with the three-dimensional simulation results [22]. In [23], numerical simulations were performed to investigate the heating and cooling of vibrational populations brought about by an ultrafast laser field. It was shown in [24] that by using a few cycle laser pulses, it is possible to selectively enhance the contribution of the odd or even numbered vibrational states alternatively in the wavepacket. This pattern of population redistribution closely resembles the arrangement of squares in a chessboard. Subsequently, efforts were directed towards the extension of this technique to tackle modern challenges of encoding quantum information [25]. The underlying idea that emerged unanimously from all these studies was that the mechanism behind the quenching of nuclear wavepackets is impulsive Raman transitions mediated via an excited electronic state.

A quasiclassical model (QCM), different from the one discussed above, was proposed in [26] for nuclear wavepacket generation and the manipulation of such wavepackets. The results from this method were in excellent agreement with that of the quantum mechanical simulations. In this method, the wavepacket is modelled as a non-interacting classical ensemble of molecules and the propagation of the classical ensemble on the particular electronic potential corresponds to the wavepacket evolution.

This method of controlling vibrational wavepackets has gained an impetus through recent experimental investigations. Very recently, an experiment was conducted on molecular iodine showing effective control of the eigenstate populations within a wavepacket using

a time-delayed near-infrared pulse [27]. The alternate increase and decrease of populations of each vibrational level on the variation of interpulse delay time was interpreted to arise from laser-induced interferences between the multiple optically connected pathways between the different eigenstates constituting the wavepacket. The mechanism of a strong laser-induced interference was theoretically investigated for a two-electronic state model of I<sub>2</sub> [28].

A similar type of experiment was performed in [29] where non-resonant laser pulses were employed to redistribute the vibrational populations of the wavepacket in D<sub>2</sub><sup>+</sup> ion generated through the tunnel ionisation of D<sub>2</sub>. The probing of the modulated wavepacket was performed by measuring the D<sub>2</sub><sup>+</sup> photodissociation yield.

The primary motivation of this work is to optically manipulate the generation of constitutionally different vibrational wavepackets in the ground electronic state of HD<sup>+</sup> by the impulsive interaction of ultrashort laser pulses with stationary eigenstates of HD<sup>+</sup> [30]. For this, we propose different intuitive schemes, both single and multipulse, to effectively control both the generation and the constitution of the wavepackets. In the multipulse schemes, a second laser field is introduced to influence the vibrational distribution generated by a single pulse. This second pulse may be either phase differing or time-delayed in relation to the first pulse. The generated wavepackets can be made to have unimodal or multimodal type of vibrational distributions depending on the configuration of the exciting pulses.

a correct description of the two distinguishable and non-degenerate asymptotic atomic states arising from HD<sup>+</sup> dissociation.

In the case of the polar HD<sup>+</sup> molecular ion, in order to take into account all possible permanent dipole moment-induced intraelectronic radiative couplings without invoking the rotational state expansion, the ground and excited electronic states are subdivided into groups of different parities, even (e) and odd (o) [30–34], respectively. Thus, the Schrödinger equation is solved by propagating a four-component wavepacket expanded on the basis of the two lowest electronic states for HD<sup>+</sup>:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \Psi_{G_e}(R, t) \\ \Psi_{G_o}(R, t) \\ \Psi_{E_e}(R, t) \\ \Psi_{E_o}(R, t) \end{pmatrix} = H(R, t) \begin{pmatrix} \Psi_{G_e}(R, t) \\ \Psi_{G_o}(R, t) \\ \Psi_{E_e}(R, t) \\ \Psi_{E_o}(R, t) \end{pmatrix} \quad (1)$$

with

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + V(R, t). \quad (2)$$

Here,  $m$  is the reduced mass of the nuclei and  $R$  is the internuclear separation.  $V(R, t)$  is the potential matrix, in the four-component basis, including both the diagonal internuclear potentials and the off-diagonal interstate as well as intrastate radiative couplings resulting from the external electromagnetic fields. The solution of the time-dependent Schrödinger equation essentially starts with an initial stationary wavefunction of arbitrarily defined parity. The potential matrix for the HD<sup>+</sup> system takes the form

$$V(R, t) = \begin{pmatrix} V_G(R) & -\mu_{GG}(R) \cdot E(t) & 0 & -\mu_{EG}(R) \cdot E(t) \\ -\mu_{GG}(R) \cdot E(t) & V_G(R) & -\mu_{EG}(R) \cdot E(t) & 0 \\ 0 & -\mu_{EG}(R) \cdot E(t) & V_E(R) & -\mu_{EE}(R) \cdot E(t) \\ -\mu_{EG}(R) \cdot E(t) & 0 & -\mu_{EE}(R) \cdot E(t) & V_E(R) \end{pmatrix}. \quad (3)$$

## 2. Theory

We have conducted a theoretical investigation on the formation and control of vibrational wavepackets in the ground electronic state of the HD<sup>+</sup> molecular ion in the presence of one or more intense ultrashort near-infrared laser fields. These calculations essentially involve the solution of the time-dependent Schrödinger equation for the nuclear motion. A simple two-electronic state model has been invoked for this purpose. The two lowest electronic states denoted as GS and ES, respectively, are obtained from the Born–Oppenheimer molecular states 1sσ<sub>g</sub> and 2pσ<sub>u</sub>, by including the non-adiabatic g–u symmetry breaking coupling term between them, arising from the mass asymmetry of the heteronuclear ion, in the full Hamiltonian [31,32]. This gives

The  $R$ -dependent permanent dipole moments in the two-electronic states are represented as  $\mu_{GG}(R)$  and  $\mu_{EE}(R)$ , while  $\mu_{EG}(R)$  is the  $R$ -dependent transition dipole moment.

The wavepacket dynamics in the presence of either a single pulse or a pair of phase-differing pulses or a pair of time-delayed pulses was numerically calculated by starting from an initial stationary state eigenfunction. The pulses with sine squared field envelope shapes were applied. The electric field, when two pulses are used, may be expressed as

$$E(t) = E_1^0 f_1(t) \cos(\omega_1 t) + E_2^0 f_2(t) \cos(\omega_2 t + \phi), \quad (4)$$

where

$$f_1(t) = \sin^2 \left\{ \frac{\Pi t}{2\sigma_1} \right\} \quad \text{for } t = 0 - 2\sigma_1 \quad (5)$$

and

$$f_2(t) = \sin^2 \left\{ \frac{\Pi(t - 2\sigma_1 - \tau)}{2\sigma_2} \right\} \quad \text{for } t \geq 2\sigma_1 + \tau. \quad (6)$$

Here,  $\tau$  is the delay time between the two pulses acting on the evolving wavepackets. This delay time is the time between the end of the first pulse which generates a wavepacket on the ground electronic state of  $\text{HD}^+$  and the start of the second pulse (often referred to as the control pulse).  $E_1^0$  and  $E_2^0$  are the peak magnitudes of the electric field of the laser pulses and  $2\sigma_{1,2}$  is the total pulse duration. The relative phase between the pair of pulses is denoted by  $\phi$ . The time delay would be zero when two phase different pulses of the same wavelength are simultaneously applied. When only a single pulse is in operation, the second term in eq. (4) would be absent.

The population in the different bound vibrational levels at any particular time can be obtained by calculating the overlap integral of the final bound nuclear wavepacket component of the GS state at that time with the field-free eigenfunctions of different vibrational levels. The expression for obtaining the vibrational populations is given by

$$|\langle \Psi_v(R) | \Psi_{(G)}(R, t) \rangle_R|^2. \quad (7)$$

### 3. Results and discussions

In the beginning, we present the characteristics of the coherent wavepackets generated in the ground electronic state of  $\text{HD}^+$  by exposing the molecule in a specific initial stationary vibrational state to an intense ultrashort laser field for a few femtoseconds. The wavelengths of the laser field were chosen as 800 and 1064 nm. Although the conventional methods of preparation of the  $\text{HD}^+$  system from its neutral precursor usually generate a vibrational state distribution of the molecular ion, it is possible to prepare a single stationary state of the  $\text{HD}^+$  ion, and its experimental feasibility has been discussed in [35].

We have used the conventional two lowest electronic states model for wavepacket generation and hence photodissociation remains the only loss process in our calculations. This seems to be a valid approximation, as the *ab-initio* calculation considering both the nuclear as well as the electronic motion [36] have clearly shown that for a wavelength of 800 nm and the range of IR pulse durations used by us, ionisation from the lower vibrational levels ( $v = 0-2$ ) is completely negligible. Thus, it can be safely inferred that, in our case, ionisation will not play a significant role in the generation of wavepackets by our short-duration pulses.

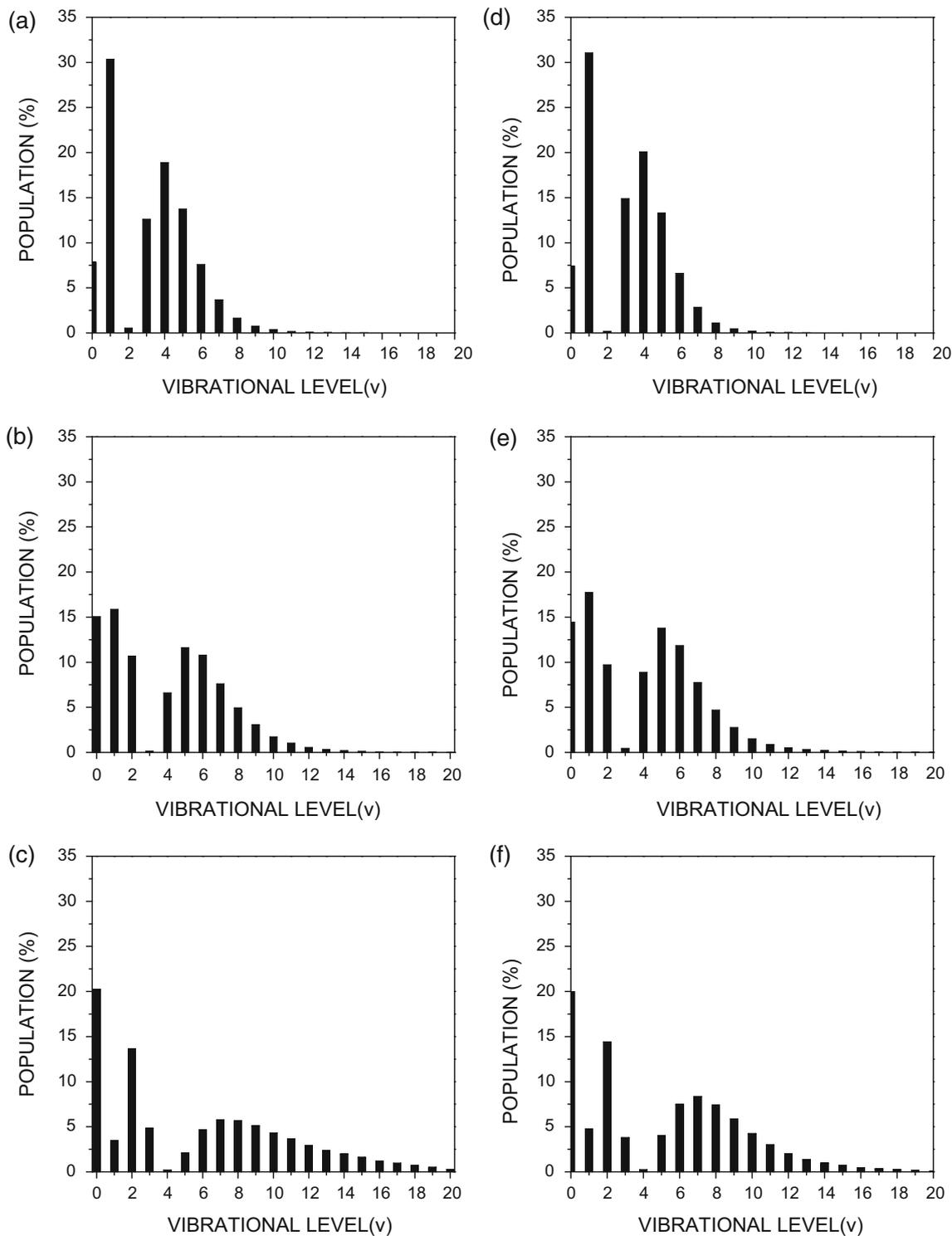
Figure 1 demonstrates the effect of pulse duration on the vibrational distributions of ground electronic state

coherent wavepackets generated in  $\text{HD}^+$  under impulsive excitation of the  $v = 2$  state by 800 nm laser. For this, the vibrational distributions in the residual wavepackets at the end of the pulse for three different pulse times have been plotted. The peak intensity of the exciting laser pulse was  $I^0 = 5 \times 10^{14} \text{ W/cm}^2$ . From the results displayed in figure 1a, it is evident that a bimodal vibrational distribution is obtained for the shortest pulse length of 7.3 fs with a node at  $v = 2$ . For this type of intense pulse, an increase of the pulse time from 7.3 to 9.7 (figure 1b) and 12.1 fs (figure 1c) induces a change of the position of the node in the distribution from  $v = 2$  to  $v = 3$  and 4, respectively, along with a broadening of the distribution width. This is because the release of wavepacket portions through the laser-induced avoided crossings becomes greater for comparatively larger pulse durations, allowing these portions to traverse regions of larger internuclear separation leading to a broadening of vibrational distribution [23].

Thus, the application of the laser field initiates a population transfer from the initial  $v = 2$  state to the neighbouring vibrational levels. When the pulse duration is 7.3 fs (figure 1a), before a retransfer of population to the  $v = 2$  level can begin, the pulse effectively ends. This results in a depopulated  $v = 2$  state in the final population distribution in the  $v$  space (figure 1a). For slightly longer pulses, the population from the other  $v$ 's, e.g.  $v = 3, 4$  starts to decrease with a subsequent increase of population in the  $v = 2$  state. When the pulse duration is 9.7 fs, the time was appreciable enough for the entire population from the  $v = 3$  level to be transferred, thus causing a shift of the node from the  $v = 2$  to  $v = 3$  level (figure 1b). When the pulse time is 12.1 fs, the additional time allows the complete depopulation of the  $v = 4$  level and a small gain of population for the  $v = 3$  level (figure 1c). Thus, the node in the vibrational distribution can be selectively controlled through proper adjustment of the pulse duration.

We have also repeated the simulation for a 1064 nm laser field. The pattern of vibrational distribution (figures 1d–1f) closely resembles the patterns obtained for an 800 nm laser field. However, for higher wavelength, i.e. 1064 nm, the probability of ionisation from the lower vibrational states may not be completely negligible. Hence, the simulated results for the residual bound population, without explicitly invoking the ionisation channels, may be slightly overestimated.

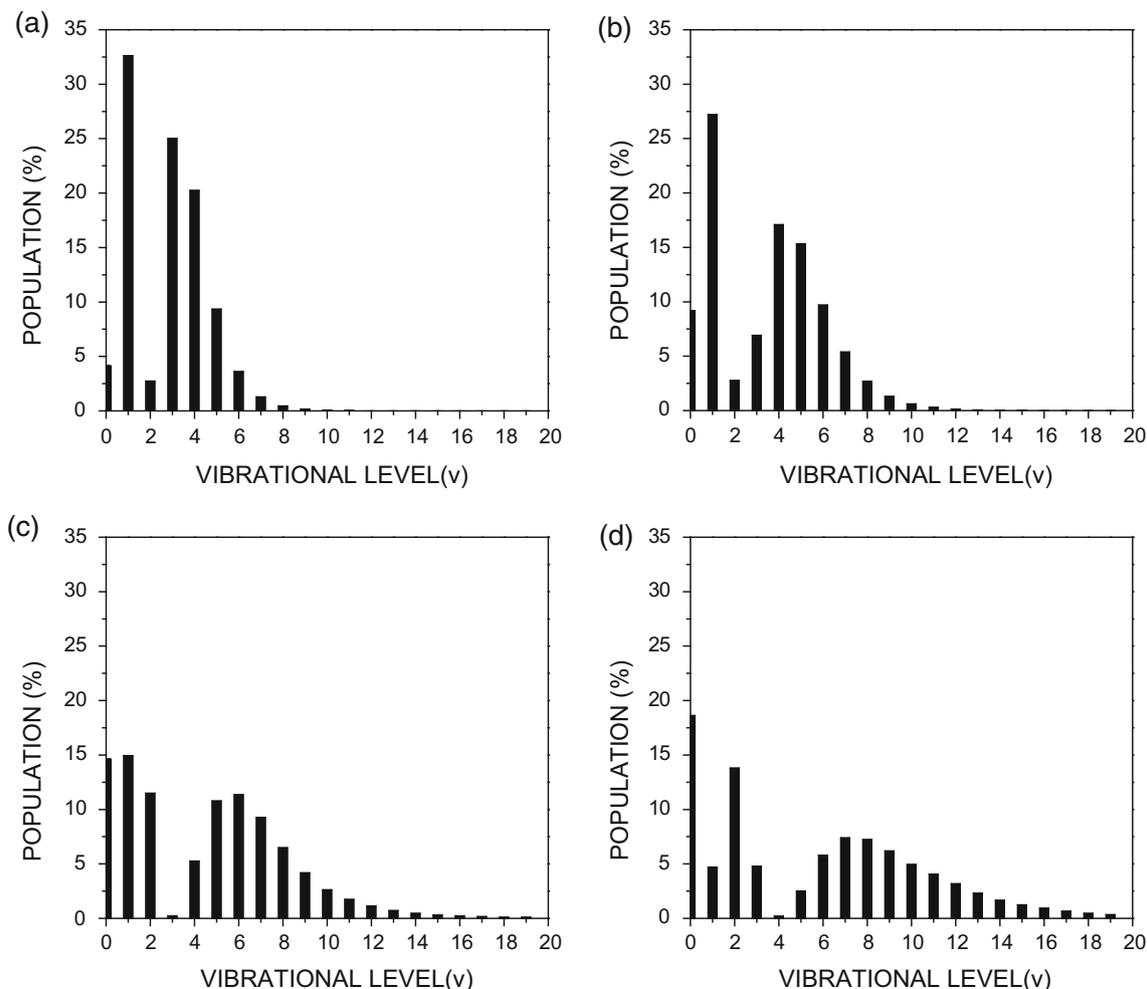
To investigate whether the nuclear mass plays any substantial role in determining the spatial extent of the population distribution in the  $v$  space, we have performed a similar calculation for the  $\text{D}_2^+$  system. The presence of identical and non-identical constituents introduces a significant difference in nuclear mass in  $\text{D}_2^+$  and  $\text{HD}^+$ , respectively. The results for a 800 nm laser



**Figure 1.** Vibrational distribution in the residual wavepackets, starting from the initial state  $v = 2$ , for three different pulse times, 7.3 fs in (a) and (b), 9.7 fs in (c) and (d) and 12.1 fs in (e) and (f), respectively. The peak intensity of the laser field is  $I^0 = 5 \times 10^{14} \text{ W/cm}^2$  with a wavelength of 800 nm for (a)–(c) and 1064 nm for (d)–(f), respectively.

field of peak intensity  $I^0 = 5 \times 10^{14} \text{ W/cm}^2$  at four different pulse times (7.3, 9.7, 12.1 and 14.5 fs) are presented in figures 2a–2d. A comparison to  $\text{HD}^+$  reveals that the wavepacket for the heavier  $\text{D}_2^+$  requires more

time for effectively producing a similar distribution of vibrational states. For example, a shift of the node from  $v = 2$  to  $v = 3$  occurs at a pulse time of 12.1 fs (figure 2c) for  $\text{D}_2^+$  as against 9.7 fs (figure 2b) for  $\text{HD}^+$ .



**Figure 2.** Vibrational distribution in the residual wavepackets of  $D_2^+$  starting from the initial state  $v = 2$  for four different pulse times 7.3, 9.7, 12.1 and 14.5 fs in (a), (b), (c) and (d), respectively. The peak intensity of the laser field of 800 nm wavelength is  $I^0 = 5 \times 10^{14}$  W/cm<sup>2</sup>.

It is to be noted that due to the non-identical constituents in heteronuclear  $HD^+$ , it has a permanent dipole moment that makes  $HD^+$  sufficiently different from its homonuclear counterpart  $D_2^+$ . It is also to be noted that for the  $HD^+$  system, additional pathways are set off due to the presence of permanent dipole moments. In  $D_2^+$ , the two lowest electronic states become coupled through transition dipole-mediated coupling by the absorption or emission of only an odd number of photons. In  $HD^+$ , due to the presence of permanent dipole moments, additionally, the two lowest electronic states can become optically coupled by the absorption or emission of an even number of photons. Moreover, due to the presence of permanent dipole moments, optically allowed transitions within the same electronic state opens new excitation pathways in  $HD^+$ . This permanent dipole-mediated interelectronic and intra-electronic transitions in  $HD^+$  increase the number of pathways compared to that in  $D_2^+$ . However, it is to

be noted that the radiative couplings due to the permanent dipole moments become strong only at a large internuclear distance (greater than around 9.5 a.u.). The vibrational wavepackets generated in the ground electronic state of  $HD^+$  are essentially present at an internuclear distance lower than 9.5 a.u. As a result, due to the absence of appreciable wavepacket components at a large internuclear distance, the strong radiative coupling due to permanent dipole moments do not seriously influence the spatiotemporal evolution of the coherent wavepackets, and cannot cause an appreciable change of the distribution of the bound vibrational levels in the ground electronic state of  $HD^+$ , compared to its homonuclear counterpart  $D_2^+$ .

In our previous work [30], it has been argued that the wavepacket motion on a field-distorted potential surface would determine the nature of population distribution among different vibrational levels. The greater peak intensity of the laser field would cause a larger

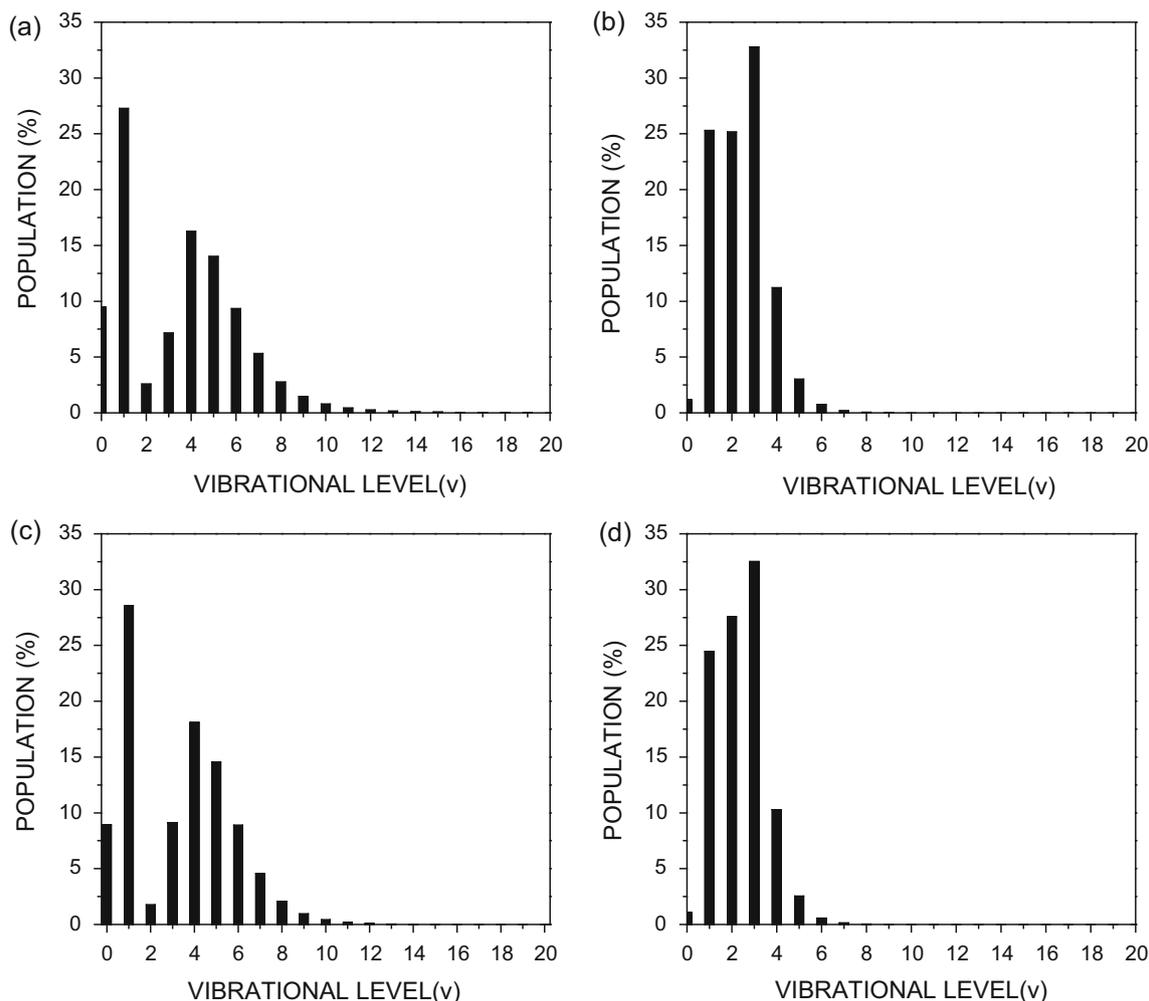
gap between the adiabatic potentials. This allows the wavepacket components to be released in larger proportions, thereby accelerating the extent of outward movement of the wavepacket. In the next few paragraphs we would like to elaborate on the question of the effect of field strength modulation (which can be made to occur through the phase variation of a single pulse, or between a pair of pulses) on the nature of vibrational distribution of the generated coherent wavepacket.

The resulting time variation of the field intensity due to the variation of carrier envelope phase of a single laser pulse can change the time of opening of the gap between the adiabatic potentials, but has little influence over the size of the gap. As a result, the simple phase variation at any particular field intensity does not have a major effect on the outward movement of the wavepacket and, consequently, the vibrational distribution does not undergo

any major changes on the CEP variation of the laser field.

For a better way of controlling the vibrational constitution of the wavepacket, we have explored the possible effects produced by the simultaneous action of a pair of pulses of the same wavelength. Here also, we have used both the 800 as well as 1064 nm carrier wavelength of the laser field. The relative phase between the two pulses can be used as control parameters for changing the pattern of distribution over the vibrational states. The variation of the relative phase difference between two simultaneous pulses of similar characteristics facilitates the generation of any arbitrary peak intensity of the laser field.

Some of our results are represented in figure 3. Two laser pulses of wavelength 800 (1064) and peak intensity  $I^0 = 1 \times 10^{14}$  W/cm<sup>2</sup> are simultaneously introduced to act on an initial stationary state  $v = 2$ . When the pulses



**Figure 3.** Vibrational distribution in the residual wavepackets of  $\text{HD}^+$  starting from the initial state  $v = 2$ , obtained on application of a pair of laser pulses of 9.7 fs duration and peak intensity  $I^0 = 1 \times 10^{14}$  W/cm<sup>2</sup> for each pulse with phase difference: (a)  $\phi = 0.0\pi$ , (b)  $\phi = 0.5\pi$ , (c)  $\phi = 0.0\pi$  and (d)  $\phi = 0.5\pi$ , respectively. The wavelength of both laser fields is 800 nm for (a) and (b) and 1064 nm for (c) and (d), respectively.

are in the same phase, a bimodal distribution with a node at  $v = 2$  is generated (figures 3a and 3c). However, as the relative phase  $\phi$  between the two pulses starts to increase, the contribution of the original vibrational level, in this case  $v = 2$ , in the modified wavepacket begins to increase. This gradually gives rise to a unimodal distribution with a peak at  $v = 3$  when  $\phi = 0.5\pi$  as shown in figures 3b and 3d. Thus, it is apparent that the variation of the relative phase between two simultaneous laser pulses can be used to control the wavepacket motion and hence the vibrational distribution within the wavepacket. When  $\phi = 0$  (figures 3a and 3c), due to the enhanced field strength, the wavepacket can travel towards the larger internuclear separation region thereby accounting for a population distribution ranging over a large number of vibrational levels and a bimodal distribution in  $v$ -space. The change of the relative phase to  $\phi = 0.5\pi$  limits the spatial extension of the wavepacket within a narrower range of internuclear separation ( $R$ ) due to the relatively lower field strength, thereby leading to the shrinkage of vibrational distribution. Due to the more localised wavepacket, the corresponding vibrational distribution becomes unimodal in nature.

From our discussion it is evident that the two-pulse scheme can be used as an effective method for controlling the vibrational distribution formed due to wavepacket motion on a field-induced reshaped potential. The independent variation of the relative phase actually modulates the field strength experienced by the molecule. This in turn has a strong effect on the nature of vibrational distributions which are determined basically by the extent of wavepacket motion.

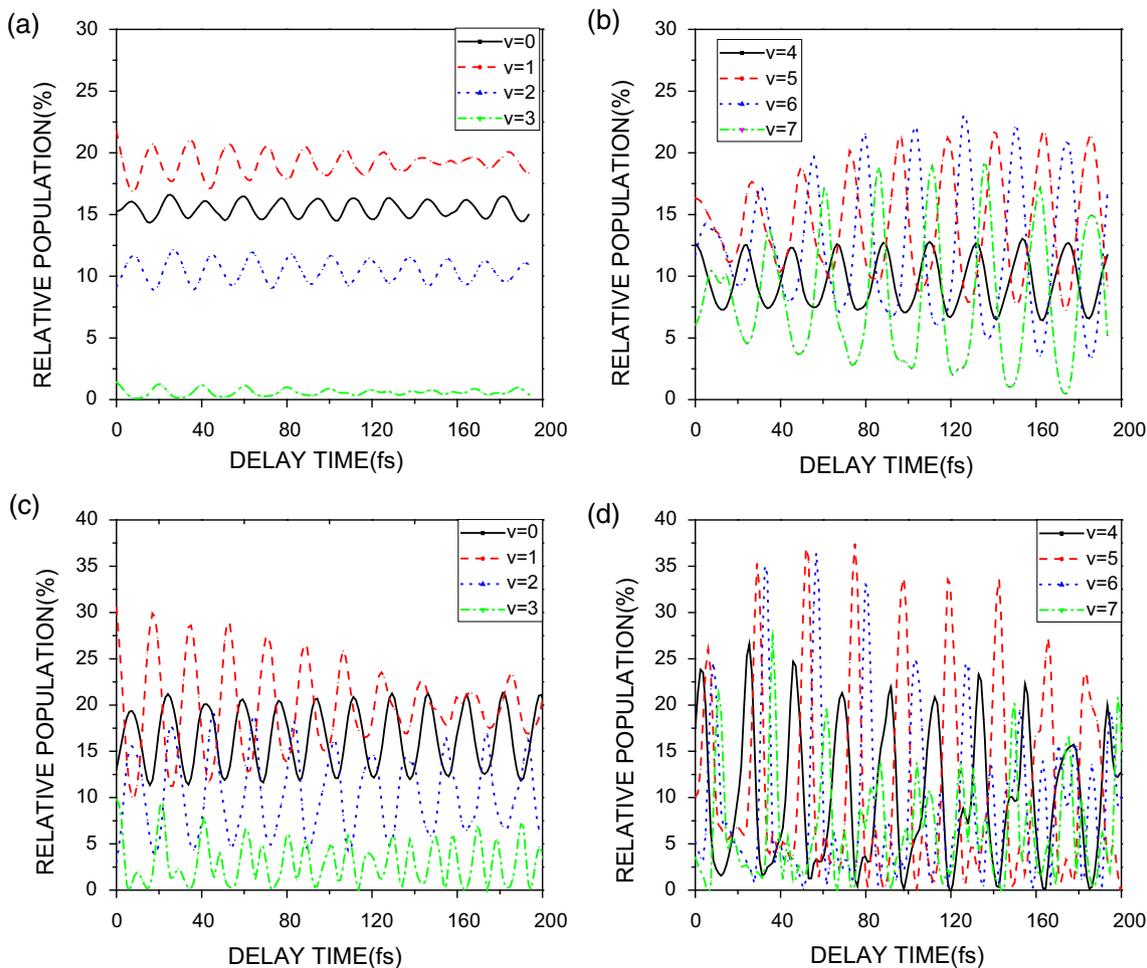
We now discuss the possibility of exercising control by employing an alternative multipulse scheme where a time-delayed intense ultrashort control laser of 800 nm wavelength acts on a wavepacket having a bimodal vibrational distribution. The initial wavepacket was prepared by using a 1064 nm laser field of 9.7 fs duration and  $5 \times 10^{14}$  W/cm<sup>2</sup> peak intensity on the  $v = 2$  stationary state. The resulting bimodal population distribution is displayed in figure 1e. The control laser of two different peak intensities  $I^0 = (1, 5) \times 10^{13}$  W/cm<sup>2</sup> acts on this wavepacket for a total duration of 13.3 fs (550 a.u.). In figure 4, the relative populations of each eigenstate ( $v = 0, 1, 2, 3$ , etc.) after the end of the control pulse has been plotted against the delay time  $\tau_c$  with a time delay grid of 100 a.u. ( $\sim 2.4$  fs). This pulse duration was kept short so that the population loss through dissociation was minimal.

It is evident from figures 4a and 4b that a low-intensity ( $I^0 = 1 \times 10^{13}$  W/cm<sup>2</sup>) control pulse effectively manipulates only a selected portion of the initial population distribution. By applying this pulse, the population of the lower vibrational levels ( $v = 0-3$ ) remains more or

less unchanged (figure 4a). However, significant oscillations in populations for the higher vibrational levels from  $v = 4-7$  to the right of the node at  $v = 3$  are found to occur. In other words, the control pulse initiates a redistribution of population between selected portions of the spectrum of vibrational levels. This is because the field strength is not sufficiently strong to induce population transfer between the lower-lying vibrational levels. The population maxima are periodically repeated with time intervals equal to the time period of vibrations for each level, by varying  $\tau_c$ . This periodicity is maintained for almost the entire range of delay time that has been scanned. Although the efficiency of population transfer to a particular vibrational level is comparatively lower for this type of low-intensity control pulse, it provides a framework for attaining vibrational selectivity by acting over a portion of the ensemble of molecular states present in the wavepacket.

The oscillatory pattern of the variation of population amplitudes of different vibrational levels, as functions of the interpulse delay time between the pump and the control pulse (figure 4), has been interpreted by several groups as occurring due to quantum interferences between multiple optically connected pathways leading to the same final state [14,27]. The relative phases between the different eigenstates constituting the wavepacket change during its evolution. This is manifested in the change of shape of the wavefunction as it moves on the field-free potential surface. These changes in turn affect the phase relationship between the time-dependent amplitudes of different optically connected pathways of Raman-like transitions between various vibrational states. Thus, through proper variation of the timing of the control pulse, the quantum mechanical interference can be controlled, and this is reflected in the oscillatory enhancement of the contribution of a particular eigenstate in the modified wavepacket [27].

However, in the case of a laser field of higher peak intensity ( $I^0 = 5 \times 10^{13}$  W/cm<sup>2</sup>), as shown in figures 4c and 4d, both the low- and high-lying vibrational levels in the entire population distribution respond to the sufficiently strong control pulse in a significant way. In fact, by further increasing the field strength, population redistribution starts to occur by a greater extent among the lower-lying vibrational levels. However, when the laser field is very strong, selectivity is attained at the expense of population loss through photodissociation [23]. The variation of relative populations with delay time follows a complicated pattern due to the emergence of minor peaks between two major crests (figure 4d). As a result, the overall dependence of the variation of relative populations in the final wavepacket with  $\tau_c$ , for  $I^0 = 5 \times 10^{13}$  W/cm<sup>2</sup>, is significantly different and

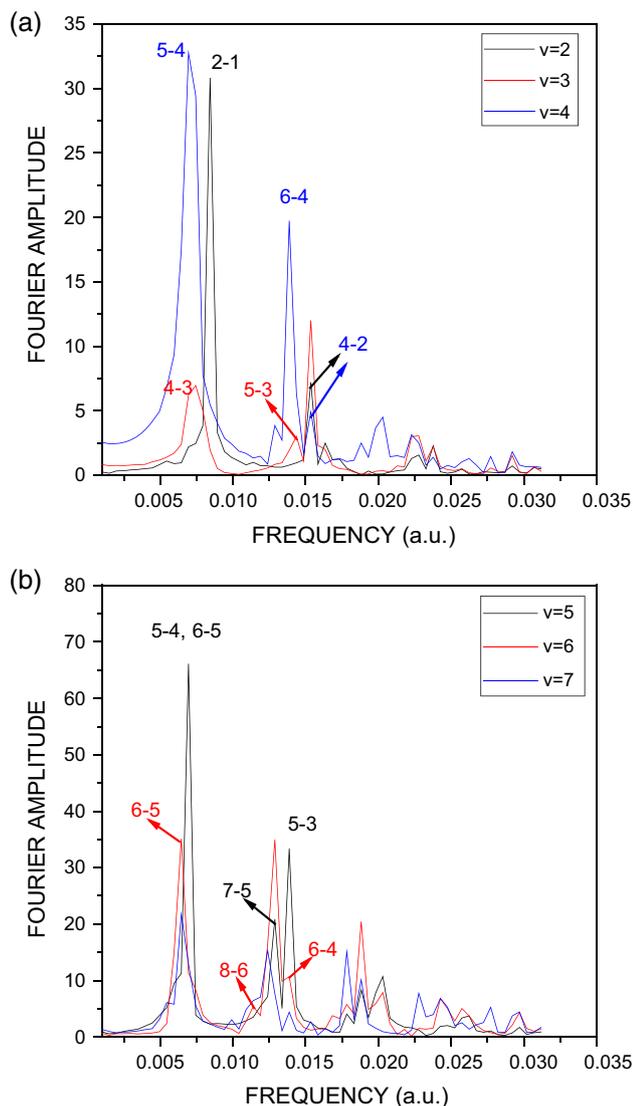


**Figure 4.** The plot of variations of relative population in different vibrational levels of an initial wavepacket prepared in figure 1e due to the application of a control pulse of 800 nm wavelength and  $2\sigma = 13.3$  fs for  $I^0 = 1 \times 10^{13}$  W/cm<sup>2</sup> in (a) and (b) and  $I^0 = 5 \times 10^{13}$  W/cm<sup>2</sup> in (c) and (d), respectively, plotted against the delay time between the generating and the control pulse. The relative populations of  $v = 0-3$  and  $4-7$  are represented separately for each  $I^0$  in (a), (c) and (b), (d), respectively.

more complex from that of the lower intensity case ( $I^0 = 1 \times 10^{13}$  W/cm<sup>2</sup>) in figure 4b.

Fourier transformation of the relative populations of individual vibrational levels (plotted as functions of interpulse delay time in figures 4c and 4d) for  $I^0 = 5 \times 10^{13}$  W/cm<sup>2</sup> is represented in figures 5a and 5b. The plots reveal, in addition to the major frequency component corresponding to  $\Delta v = \pm 1$ , the presence of secondary peaks associated with higher frequency transitions, i.e.  $\Delta v = \pm 2, \pm 3$ , etc. The involvement of these higher-order transitions, along with the usual first-order transitions, during population redistribution is instrumental for the emergence of minor peaks between well-separated maxima. Similar signatures of higher-order Raman-like transitions were also observed for heavier molecular systems like iodine [27]. The broad peaks, along with secondary side peaks arising

from the Fourier transform of the relative populations of the individual eigenstates, can be correlated to the energy separations between two vibrational levels corresponding to  $\Delta v = \pm 1, \pm 2$ , etc. as have been depicted in figures 5a and 5b. For the  $v = 3$  level (figure 5a), the amplitude of the peak corresponding to  $\Delta v = \pm 2$  is greater in magnitude than that of  $\Delta v = \pm 1$ . Initially, the population of the  $v = 2$  and  $4$  levels, before the application of the control pulse, were low in comparison with  $v = 1$  and  $5$  (figure 1e). Hence during population redistribution, the contributions from  $v = 1$  and  $5$ , in enhancing the population of the  $v = 3$  levels at selected delay times would be probably more than that of the immediate neighbouring  $v$ 's ( $v = 2, 4$ ). This is reflected in the Fourier transform results with the height of the second-order peaks being greater than the first-order peaks.



**Figure 5.** Fourier transformed results for figures 4c and 4d for  $v = 2-4$  in (a) and  $v = 5-7$  in (b).

Such secondary periodicities remain absent for the lower intensity case, as can be seen from figures 4a and 4b. Fourier transformation of the relative populations of the individual vibrational levels (plotted as a function of the delay time in figure 4) for lower intensity, i.e.  $I^0 = 1 \times 10^{13}$  W/cm<sup>2</sup>, shows the presence of only a single frequency component (results not shown). This particular frequency constituent corresponds to energy separations between the adjacent vibrational levels involved, i.e.  $\Delta v = \pm 1$ . This explains the well-maintained periodicity in the variation of relative populations of each vibrational level with changes in delay time (see figure 4b).

The curves for the variation of relative populations with interpulse delay time demonstrate that specific

vibrational levels from a range of levels can be selectively depopulated and the position of the depopulated state in the  $v$  space can be controlled by the timing of the control pulse. An analysis of the Fourier transform of population curves in frequency space provides a qualitative understanding of the mechanism behind the complicated oscillatory behaviour of relative populations of different vibrational components of the wavepacket with interpulse delay time.

#### 4. Conclusion

In this work, we have discussed the numerical results for controlling the characteristic constitution of a vibrational wavepacket generated on the ground electronic state of a HD<sup>+</sup> ion as well as its subsequent change by a delayed control pulse. We did not implement the conventional route of wavepacket preparation by tunnel ionisation from a neutral molecule. Instead, the wavepacket generation was controlled through the impulsive interaction of one or more ultrashort laser pulses with a stationary eigenstate of HD<sup>+</sup>. We have computed the effects of both single as well as two pulsed laser fields with different relative phases on the stationary eigenstates of the HD<sup>+</sup> molecular ion on the formation of vibrational wavepackets of different constitutions. We also studied the effects of nuclear mass on the vibrational distribution by comparing the results for HD<sup>+</sup> with D<sub>2</sub><sup>+</sup>. We have shown how the variation of time delay between the generating and the control laser can be used to change the vibrational constitution of a wavepacket. Our investigations revealed a control scenario where, by changing the control field intensities, different ranges of constituting vibrational levels in the initial coherent wavepacket can be manipulated.

#### Acknowledgement

One of the authors (SC) thanks the CSIR, New Delhi (Government of India) for the financial support during the execution of this work.

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