

The long-term evolution of D_2^+ nuclear wave-packet with interaction of intense femtosecond laser pulse

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Abstract: We investigate the long-term evolution of D_2^+ nuclear wave-packet after interacting with a 5fs, 800nm laser pulse at an intensity of $0.5 \cdot 10^{14} \text{W/cm}^2$. The nuclear wave-packet evolves in field-free condition for very long time after the laser pulse. The collapse and revival of nuclear wave-packet is studied. The scale of the classical time ($\sim 25\text{fs}$), the revival time ($\sim 580\text{fs}$) and the super-revival time ($\sim 12\text{ps}$) are determined from the simulation as well as the calculation. The constituents of long-standing nuclear wave-packet are also analyzed.

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1. Introduction

The interaction of the molecules with strong femtosecond laser pulses is of particular interest, since the laser pulse duration is comparable to the vibrational period [1]. The H_2^+ (D_2^+) molecular ion is of fundamental interest in atomic and molecular physics. It represents the simplest three-body molecular system in the presence of strong laser field. As a consequence, a number of experiments and simulations have been performed on an H_2^+ target, as compared to the complexity in the case of H_2 target. Irrespective of the target however, a number of interesting phenomena have been observed in the molecular hydrogen ion system, including bond-softening [2], bond-hardening [3], quantum encoding [4] and Coulomb explosion from a critical internuclear separation [5,6].

Femtosecond time-resolved Coulomb explosion by now is a frequently used technique to study dynamical processes in molecules. Recent the techniques of femtosecond laser [7] and Cold-target reaction microscopes (COLTRIMS) [8] have made it possible to trace electronic and nuclear motion in real time and also to achieve control over the nuclear wave-packet motion using femtosecond laser pulses [9,10]. Numerous theoretical studies of chirped pulse excitation have been performed, discussing effects as molecular dissociation in strong fields [11], population transfer in molecules [12], nonadiabatic dynamics [13], control of wave-packet evolution [14,15] or cold-molecule formation [16]. Experiments were performed on small molecules addressing phenomena as strong field dissociation [17], tailoring of wave packets [18], or high harmonic control [19]. Those works provide comprehensive understanding of coherent control of neutral molecular and molecular ions [20].

The evolution of quantum interference effects of nuclear wave packet created by an ultrashort laser pulse in a molecular system is an interesting topic (see e.g., the overview [21] and references therein). In the system quantum interference at an intersection of two potential energy curves could cause the nuclear vibration probability to oscillate. Later on, such interference was invoked to explain unexpectedly long-lived rotational and vibrational states in dissociative systems. The analysis on a molecular system makes clear that quantum wave-packet interference plays a decisive role in the molecular dissociation process. In this paper, we take attention on the long-term evolution of D_2^+ after interacting with an intense femtosecond laser pulse. Through solving time-dependent Schrödinger equation, we propagate the nuclear wave-packet as long as few nonaseconds and trace the evolution of vibration states. The phenomenon of nuclear wave-packet revivals will be investigated in the time domain and frequency domain. The constituents of nuclear wave-packet are also analyzed. Those findings provide a potential pathway of coherent control for a molecular system. The method using time-resolved Coulomb explosion to trace the evolution of nuclear wave-packet is suggested.

2. Method

We solve the time-dependent Schrödinger equation of hydrogen molecular ion (D_2^+) system numerically on a grid using the Crank-Nicholson split-operator method [22]. The molecular ion D_2^+ is described in a reduced dimensionality collinear model, which is described in terms of the electronic coordinate z relative to the center of mass of the nuclei and the inter-nuclear distance R . Atomic units (a. u.) ($\hbar = m_e = e = 1$) are used unless stated otherwise throughout this paper. The total Hamiltonian of D_2^+ system consists of the time-dependent field-free Hamiltonian $H_0(R, t)$ and the interaction term $V(z, t)$:

$$H(z, R, t) = H_0(R, t) + V(z, t), \quad (1)$$

$$H_0(R, t) = T_i + T_{el} + 1/R + V_{ei}, \quad V(z, t) = -zE(t), \quad (2)$$

where T_{el} and T_i are the electron and nuclear kinetic energy operator respectively, V_{ei} is the soft-core Coulomb potential, and $E(t)$ is the electric field of laser pulse. The interaction of the electron with the laser field is given in dipole approximation in the length gauge. The linear polarized laser field is used, therefore only the coordinates in the laser polarization plane play a decisive role. In order to simplify the calculation, the rotation of molecular ion is not taken into consideration. The form of the soft-core Coulomb potential is given by $V_{ei} = -1/\sqrt{z_-^2 + 1} - 1/\sqrt{z_+^2 + 1}$, with $z_{\pm} = z \pm R/2$. The electric field waveform of laser pulse is described with $E(t) = \varepsilon_0 e^{-t^2} \cos(\omega t + \varphi_0)$, where ε_0 is the laser field strength, ω is the carrier frequency and φ_0 is the carrier-envelope phase (CEP). The model includes the non-Born-Oppenheimer coupling between the electronic and nuclear motion. In the calculation, we imply the time step $\Delta t = 1$ and space step $\Delta r = 0.05$ in the range of $R = 0.05$ to $R = 20$. Due to the computation limitation, we can propagate the nuclear wave-packet up to few nanoseconds after femtosecond laser pulses. The probability density of nuclear wave-packet is calculated through:

$$|\varphi(R, t)|^2 = \sum_k \rho_{kk} |\phi_k(R)|^2 + \sum_{k \neq m} \rho_{km}(t) \phi_k(R) \phi_m^*(R), \quad (3)$$

where ρ_{km} is time-dependent density matrix:

$$\rho_{km}(t) = a_k a_m^* e^{-i\omega_{km}t}, \quad \omega_{km} = \omega_k - \omega_m. \quad (4)$$

Thus the probability density includes two parts. One is the diagonal terms, which is time independent. Another part is coherent time-dependent off diagonal terms. The components of wave-packet are analyzed through Fourier transform of the temporal evolution of the expectation inter-nuclear distance.

3. Results and discussions

Figure 1 illustrates the coherent nuclear wave-packet evolution of D_2^+ up to 4ps, which is following the vertical transition from D_2^+ from ground vibration state $v = 0$. In the simulation we use a laser pulse with an intensity of $0.5 \cdot 10^{14} \text{W/cm}^2$ in a duration of 5 fs (Full Width at Half Maximum) at the wavelength of 800nm. The CEP φ_0 is zero in the simulations. The laser duration is chosen less than the classical time in order to resonantly excite the vibration states. The laser intensity is chosen to avoid the strong double ionization channel. The population density history represents the time evolution of a coherent superposition of states.

From Fig. 1, one can find that in the region $t < 100\text{fs}$ the dissociation channel is observed. In the time region of $450 \leq t \leq 650$ fs, the probability density exhibits a 25 fs revival modulation with maximum contrast around 550 fs, which is the result of vibrational revival and is consistent with recent experiments findings [9]. Between $200 \leq t \leq 350$ fs a half fractional revival is also observed and the period is about 12 fs. One can find the detailed

features in subplots (a) and (b). After a few oscillations, the anharmonicity of the potential curve, i.e., the nonequal spacing of the vibrational levels, leads to the collapse of the wave packet. For $720 \text{ fs} < t < 920 \text{ fs}$, there is another fractional revival wave-packet. Here the wave-packet consists essentially of two copies of the initial one, each shifted against the other by half of the vibrational period. Dynamical interference between these two counter-propagating waves produce a frequency doubled periodic pattern compared to the fundamental vibrational. The vibrational wave-packet revives again in the time region of $920 \text{ fs} < t < 1300 \text{ fs}$. In general, collapse and revival phenomena are due to a de-phrasing and re-phrasing of a quantum system.

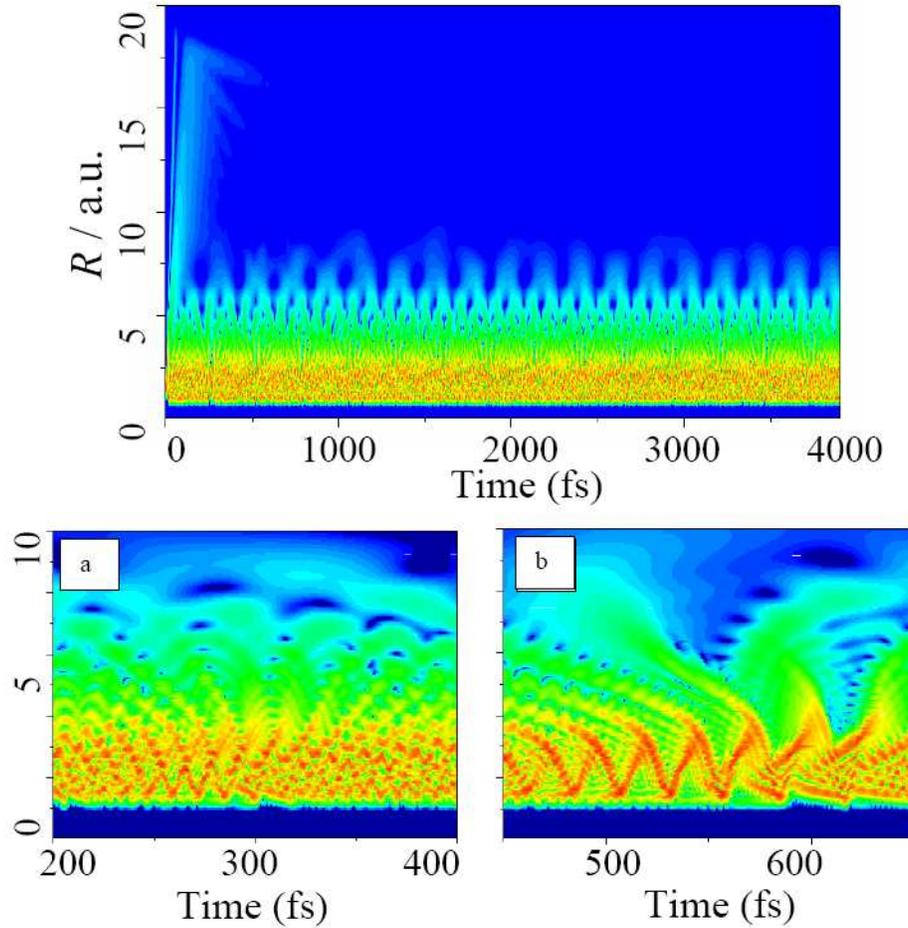


Fig. 1. Nuclear wave-packet propagation of D_2^+ in a laser pulse in (5 fs, 800nm) at the intensity of $0.5 \cdot 10^{14} \text{ W/cm}^2$. The figure presents the time evolution of probability density $|\varphi(R,t)|^2$. The subplots (a) and (b) show the half fractional revival in the time range of $200 \leq t \leq 400$ and the fully revival in the time range of $450 \leq t \leq 650$ respectively. The figures are plotted as logarithmic color scale.

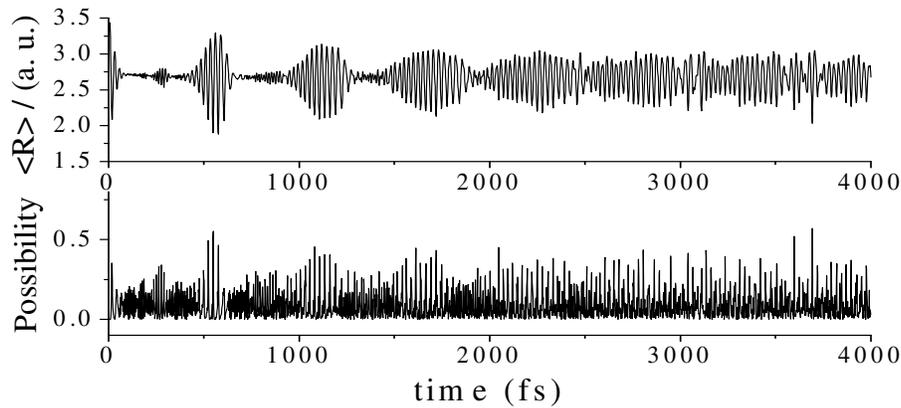


Fig. 2. The expectation inter-nuclear value $\langle R \rangle$ (top) and the temporal history of the auto-correlation function $|\langle \varphi(t=0) | \varphi(t) \rangle|^2$ (bottom) from the starting time to about 4ps.

The revival patterns substantially overlap, resulting in constructive and destructive interferences, as indicated in Fig. 1. Then the revival patterns no longer represent individual full revivals, but their superposition gives rise to new structures. The anharmonicity of the vibrational potential provides an auxiliary and independent mechanism for revivals in the molecular vibration. We also illustrate the expectation inter-nuclear value $\langle R \rangle$ and the auto-correlation function $|\langle \varphi(R, t=0) | \varphi(R, t) \rangle|^2$ from the starting time to about 4ps in Fig. 2. The time history of the expectation inter-nuclear value $\langle R \rangle$ can provide more direct information of the wave-packet evolution.

In order to have a look on the long-term evolution of nuclear wave-packet, the time history of the expectation inter-nuclear value $\langle R \rangle$ up to 500ps is shown in Fig. 3. Surprisingly, one can find that the vibrational states can still revive. The inset (a) in Fig. 3 indicates that the interference stripes reappear, indicating a restored fractional periodicity of the wave-packet motion after about 12 ps. Already after a few oscillations, i.e., the non-equal spacing of the vibrational levels populated by the laser pulse, leads to the de-phasing, or collapse of the wave-packet, reflected in the apparent degeneration of the vibrational structures. However, after about every 12ps, the stripes reappear, indicating a restored periodicity of the wave-packet motion. The inset (b) in Fig. 3 shows the vibration period of the revival state is still about 25fs. This phenomenon is known as a quantum wave-packet super-revival [21]. Therefore, a longtime coherence is preserved in this interaction process.

A localized wave packet is excited with an energy spectrum which is tightly spread around a large central value of the vibrational number v_0 , i.e., $v_0 \gg \Delta v \gg 1$. In this case, we can expand the individual energy eigenvalues of $E(v)$ using Talor formula,

$$E_v = E(v_0) + E'(v_0) \cdot (v - v_0) + \frac{E''(v_0)}{2} \cdot (v - v_0)^2 + \frac{E'''(v_0)}{6} \cdot (v - v_0)^3 + \dots \quad (5)$$

Thus, the time-dependence of each individual vibrational eigenstate is through the factors,

$$e^{-E_v t} \equiv \exp(-i\omega_0 t - 2\pi i(v - v_0)t / T_{cl} - 2\pi i(v - v_0)^2 t / T_{rev} - 2\pi i(v - v_0)^3 t / T_{Super} - \dots), \quad (6)$$

where $T_{cl} = 2\pi/|E'(v_0)|$ is the classical time, $T_{rev} = 2\pi/|E''(v_0)/2|$ is the revival time, and $T_{Super} = 2\pi/|E'''(v_0)/6|$ is the super-revival time. Theoretically, they can be calculated with,

$$T_{cl}(v) = \frac{2\pi}{\left|3\omega_e y_e (v + \frac{1}{2})^2 - 2\omega_e x_e (v + \frac{1}{2}) + \omega_e\right|}, \quad (7)$$

$$T_{rev}(v) = \frac{2\pi}{\left|3\omega_e y_e (v + \frac{1}{2}) - \omega_e x_e\right|}, \quad T_{Super}(v) = \frac{2\pi}{\left|\omega_e y_e\right|}, \quad (8)$$

where ω_e is the hamonicity constant, $\omega_e x_e$ and $\omega_e y_e$ are the anharmonicity constants. Taking those parameters from [23], the classical time is about 21fs, the revival time is about 560fs, and the super-revival time is about 11.6ps for D_2^+ system. Here T_{cl} is corresponding to the vibration period, T_{rev} gives the revival period and T_{Super} represents the high-order super-revival time.

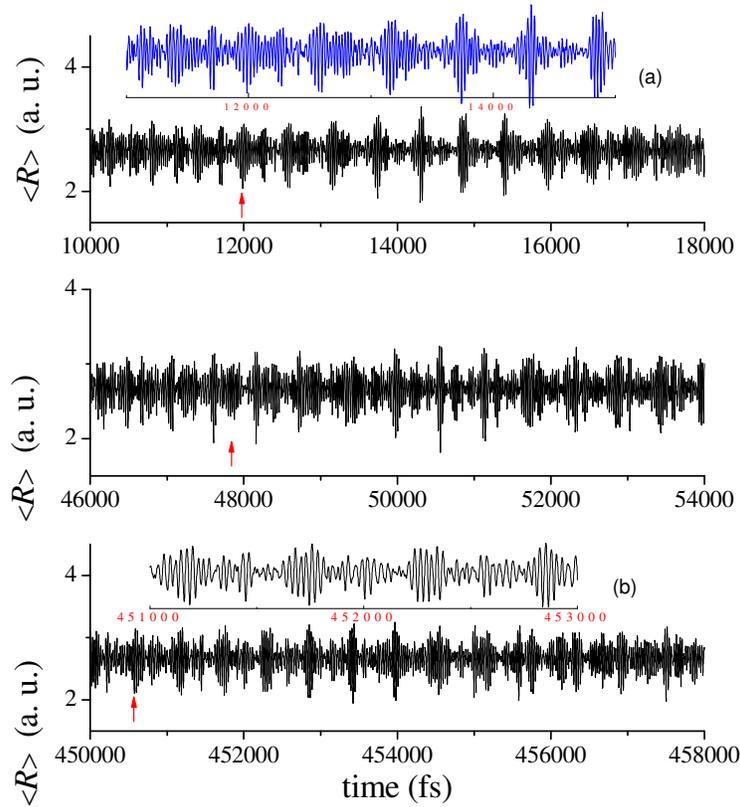


Fig. 3. The expectation inter-nuclear value $\langle R \rangle$. From top to bottom, those figures give the temporal history of the expectation inter-nuclear values in three different time region. The insets (b) shows the zoom-out patterns. The inset (a) shows that the first super-revival time is about 12ps. The inset (b) shows the vibration period of the revival wave-packet is about 25fs.

For systems with purely quadratic energy dependence on a single quantum number, there are no independent time scales longer than the revival time, and the pattern of fractional and

full revivals will repeat itself indefinitely with the T_{rev} time scale. However, for a realistic system, with higher order terms in the expansion in Eq. (5), the super-revival time T_{super} becomes very important. In this case, the qualitatively new patterns of revival behavior, with periodicities in the motion of the packet characterized by periods which are fractions of T_{rev} , giving a self-similar structure to the auto-correlation function plots for $t > T_{rev}$. The wave-packet behavior on the T_{super} time scale is similar to that of the fractional revival structures seen on the T_{rev} scale, with integral multiples of T_{super} appearing, explicitly due to the presence of the third-derivative term. According our simulation, we can roughly give about $T_{cl} \approx 25$ fs, $T_{rev} \approx 580$ fs and $T_{super} \approx 12$ ps for the interaction system. The simulated results are consist with the calculated values.

The Fourier transform spectrum of the evolution possibility of the nuclear wave-packet is performed, which is indicated in Fig. 4. The frequency components present in the vibrational wave-packet are beats between vibrational states ν and $\nu \pm 1$, $\nu \pm 2$, $\nu \pm 3$. The Fourier amplitudes thus return a message of vibrational population. One can see that the largest population is through the selection rule of $\Delta\nu = 1$.

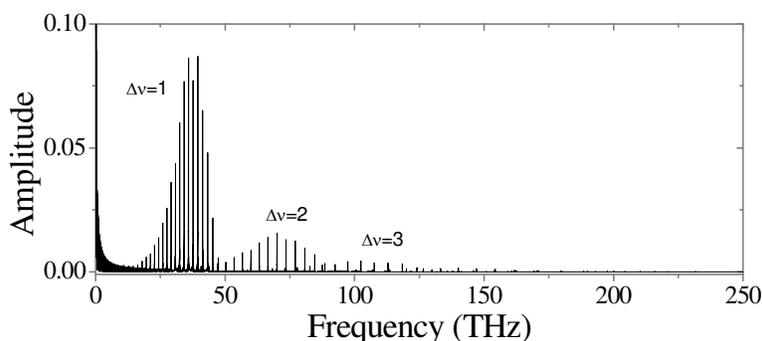


Fig. 4. The Fourier spectrum of the nuclear wave-packet

Especially for the Franck–Condon distribution, known to overestimate the population of the higher excited vibrational states, the series of different $\Delta\nu$ are seen to overlap each other. In particular, contributions from higher $\Delta\nu > 2$ series are seen to reach into the range of frequencies for $\Delta\nu = 2$, even reach into the range of frequencies for $\Delta\nu = 1$. Clearly, without the presence of an external perturbation after the laser pulse, the population possibility is explicitly time-independent. The nuclear wave function will evolve on the adiabatic binding D_2^+ $1s\sigma_g$ potential curve. The anharmonicity of the potential results in a quick de-phasing of the wave-packet and only after a long propagation time the vibrational states overlap in-phase, leading to wave function revivals and fractional revivals.

Even without laser fields, nonadiabatic transitions take place frequently in chemistry of electronically excited states. Here, nonadiabatic effect is directly taken into account to nuclear wave-packet dynamics in the simulations and indeed nonadiabatic nuclear wave-packet dynamics is crucial in the molecular science.

4. Conclusions and applications

In a real experiment only the kinetic energy release after a probe pulse is measurable, which can be mapped using Coulomb's law to reconstruct the evolution of the probability density $\rho(R,t) = |\phi(R,t)|^2$. In a general application, the laser pulse duration shorter than the vibrational motion establishes a time-dependent variation of the refractive index in a Raman-active molecular medium. By employing the vibrational mode of a hydrogen molecular ion, it may be possible to spectrally broaden and self-compress, potentially to the laser sub-cycle

level. The long-term evolution of nuclear wave-packet can also be retrieved using Coulomb explosion imaging pump-probe scheme method. The full vibration states involved in the evolution can be measured. Besides, intense laser chemistry is now under strong focus, where laser-induced nonadiabatic couplings between electronic and nuclear wave-packets are expected to frequently take place again in a very short time scale. The coupling between the electronic and nuclear wave-packets will be great interesting for both theory and experiment in the future.

In summary, we have investigated the long-term evolution of D_2^+ nuclear wave-packet after interacting with strong femtosecond laser field. The vibrational states revive a very long time after the interaction. The classical time, the revival time and the super-revival time for this system are simulated and calculated respectively. We find that the classical time, the revival time and super-revival time of the nuclear wave-packet is about 25fs, 580fs and 12ps respectively. Those time scales can be measured through precisely Coulomb explosion pump-probe imaging techniques. The components of the vibrational wave-packet are analyzed. We find that different Δv are seen to overlap each other. The goal of ultrafast coherent control of smallest hydrogen molecular ion is close at hand with the current advanced technique of ultrashort pulse lasers.

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