Nonspreading wave packets of diatomic molecules: Generation and control

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(Received 14 March 2000; published 21 March 2001)

A circularly polarized electric field is used to create a trap that can guide the rotational motion of diatomic molecules. Theoretical analyses and numerical calculations support the existence of trapped nonspreading wave packets rotating with an electric field. Optimal coherent control of the rotational motion of diatomic molecules can be achieved by manipulating the nonspreading wave packets with a circularly polarized electric field whose amplitude and frequency are changed adiabatically.

DOI: 10.1103/PhysRevA.63.043420 PACS number(s): 33.80.Rv, 31.15.−p, 03.65.Ge

The development of new techniques for manipulating microscopic states of atomic and molecular systems has been of fundamental importance in a broad span of research fields, such as Bose-Einstein condensation, controlling chemical reactions, nanotechnology, etc. Various schemes employing electric and magnetic fields have been proposed to achieve these goals. In the field of optical control of molecular systems, it was recently reported [1], through a quasiclassical study, that strong lasers with rotating polarization can guide molecular rotation and propel molecules into high-angular-momentum states. Proposed applications of this method include isotope separation and selective breaking of molecular bonds. Such an optical centrifuge for molecules has recently been demonstrated experimentally [2]. In this paper, we assert that optimal control of the rotational motion of molecules can be attained by preparing the molecules initially in a nonspreading wave packet (NSWP) state and manipulating the NSWP with a circularly polarized (CP) electric field. We provide an explicit, albeit approximate, expression for the NSWP of diatomic molecules placed in a CP field, and suggest a scheme to generate and control the NSWP. Numerical calculations of the two-dimensional Schrödinger equation demonstrate the efficient performance of this scheme.

The atomic counterpart of the NSWP has already attracted considerable attention [3–7]. Theoretical studies have revealed the existence of nondispersive electronic wave packets in Rydberg atoms irradiated by a CP electromagnetic wave. These wave packets have been called “Trojan” wave packets [4], because they are similar to the Trojan asteroids moving in the Sun-Jupiter system. The system has also been regarded as the realization of Bohr’s planetary atom, in which an electron moves without spreading along a Kepler orbit around a nucleus [5]. Because, by their quantum nature, localized wave packets are subject to dispersion as they evolve, the presence of an external CP field (and a magnetic field [6]) is crucial to prevent the electronic wave packet from spreading. A similar phenomenon occurs in diatomic molecules under the influence of a CP field; specific wave packets in diatomic molecules do not undergo dispersion or distortion in shape as they evolve. Just as the electronic NSWP of Rydberg atoms is likened to a planet orbiting a heavier star, the NSWP of diatomic molecules discussed here could be considered as a microscopic realization of a binary star rotating around its center of mass.

The nondispersive coherent property of the NSWP of diatomic molecules is of special interest in implementing an efficient control scheme. Once a diatomic molecule is launched into the NSWP state, its rotational motion can be guided by a CP field, and an adiabatic change in the frequency of the CP field can carry the molecule to a target rotational state without destroying the coherent property of the NSWP. Generation of a NSWP from an angular momentum eigenstate will be addressed in the latter part of the paper. Here we illustrate the scheme using the diatomic molecule HF, which has a permanent dipole moment. One may be able to apply the present control technique to molecules that do not possess permanent dipole moments at the cost of higher laser intensity by taking advantage of their field-induced dipole moments and the interaction between the induced dipole moments and the laser fields [1,8].

When a diatomic molecule is assumed to rotate in the plane in which a CP field oscillates, the Hamiltonian can be written in reduced units [9,10] as

\[ H = \frac{1}{2} \left( p_\phi^2 + \frac{p_r^2}{r^2} \right) + V(r) - \frac{B}{\sqrt{2}} r \cos(\phi - \Phi(t)) , \]

where, for simplicity, the dipole moment function is assumed to be linear in \( r \), and the interatomic vibration is modeled by the Morse potential \( V(R) = D \left[ e^{-2a(R-R_e)} - 2 e^{-a(R-R_e)} \right] \), which in the reduced units is written as \( V(r) = (1/2) [ e^{-2(r-r_e)} - 2 e^{-r} ] \) with \( r = aR \) and \( r_e = aR_e \), where \( R \) and \( R_e \) are the interatomic distance and its equilibrium value, respectively, and \( a \) describes the steepness of the potential. In the reduced units employed here, energy and time are measured, respectively, in units of \( 2D \) and \( 1/\omega_0 \), where \( D \) is the dissociation energy, \( \omega_0 = a \sqrt{2Dm_{\text{red}}} \) is the harmonic frequency of the Morse oscillator, and \( m_{\text{red}} \) is the reduced mass of the molecule. The dimensionless field amplitude \( B \) is related to the electric field strength of the laser field \( E_0 \) by \( B = q_e E_0 / (2aD) \), where \( q_e \) is the effective charge, in terms of which the dipole moment is expressed as \( d = q_e R \). The symbol \( \phi \) in Eq. (1) stands for the rotational angle of the molecule, and the instantaneous frequency of the

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CP field is given by $\Omega_{\text{inst}} = d\Phi/dt$. When the system is quantized, Planck’s constant is replaced by its dimensionless counterpart, $h_{\text{eff}} = h/\sqrt{2Dm_{\text{red}}} = \hbar\omega_0/2D$. For HF, $\alpha = 2.22\text{ Å}^{-1}$, $R_0 = 0.917\text{ Å}$, $q_e = 0.309\text{ a.u.}$, and $D = 6.125\text{ eV}$, giving $\hbar\omega_0 = 513\text{ meV}$, $r_e = 2.035$, and $h_{\text{eff}} = 0.0419$. Numerical calculations of the two-dimensional Schrödinger equation were performed in the laboratory frame by the split operator method [11] using a maximum $512\times512$ grid in Cartesian coordinates.

In order to provide a quick insight into the nature of the NSWP, we start by presenting an approximate form for the NSWP in the presence of a fixed-frequency CP field with $\Phi(t) = \Omega_0 t$:

$$\psi(r, \phi) = N \exp[-\kappa_r(r-r_0)^2/2h_{\text{eff}}] \times \exp[-\kappa_\phi(\phi-\phi_0)^2/2 + ip\phi_0(\phi-\phi_0)]/h_{\text{eff}},$$

where $N$ is a normalization factor, $\phi_0 = \Phi(0) = 0$, $p_{\phi_0} = r_0^2\Omega_0$, and $r_0$ is determined by the equation

$$-\frac{dV(r_0)}{dr} + \Omega_0^2 r_0 + \frac{B}{\sqrt{2}} = 0.$$  

The NSWP of Eq. (2) has the mean angular momentum $\langle \hat{\rho}_\phi \rangle = (\langle -ih_{\text{eff}}\partial/\partial \phi \rangle)r_0^2\Omega_0$. Note that $r_0$ satisfying Eq. (3) is the stable equilibrium internuclear separation of a diatomic molecule rotating with the same frequency as the CP field while aligned along the field direction, i.e., the equilibrium between the Morse force, the centrifugal force, and the field driving force at $\phi = \Phi(t)$. Confinement in the radial direction of the above NSWP can thus be easily understood as long as the molecule stays at the radial potential minimum and rotates in phase with the CP field. A detailed theoretical derivation of Eq. (2) and optimal selection of the parameters $\kappa_r$ and $\kappa_\phi$ will be presented below.

Propagating the wave packet of Eq. (2) according to the Schrödinger equation, we clearly observe in Fig. 1 that the wave packet moves along a circular orbit in phase with the CP field without dispersion for a long period of time. At the field parameters chosen, leakage dissociation of the wave packet through tunneling is negligible, and Poincaré surface sections show that the classical dynamics of the system is quasi-periodic almost in the entire phase space except near the thin separatix layers and the high-energy states. Therefore, chaotic diffusion of the quasi-classical trajectories corresponding to low-energy wave packets is inhibited by nearby Kolmogorov-Arnold-Moser tori, and dissociation mediated by the chaotic diffusion can be neglected. The stability of the NSWP can be checked by monitoring the quantity $P_A(t) = \int \int |\psi|^2 r dr d\phi$, where the integration is restricted to the region $r, -0.5 \leq r \leq r_0 + 0.5$ and $-\pi/4 \leq \phi - \Phi(t) \leq \pi/4$, for each integer $n$ of the field cycle. It was found that $P_A(nT_0)/P_A(0)$ fluctuates around 1 within 4% and does not fall below 0.961 up to the time limit ($t = 2 \times 10^3 T_0$) investigated, where $T_0$ is the optical period.

![FIG. 1. Time evolution of a nonsparking wave packet with parameters $r_0 = 2.058$, $\phi_0 = 0$, and $p_{\phi_0} = r_0^2\Omega_0$. $B = 0.002$ ($I = 4.1 \times 10^{11} \text{ W/cm}^2$) and $\Omega_0 = 2\pi/T_0 = 0.1$ (frequency $= 413.8 \text{ cm}^{-1}$, $T_0 = 80.6 \text{ fs}$). (a) $t = 0$. (b) $t = (20 + 1/3) T_0$. (c) $t = (50 + 2/3) T_0$. (d) $t = 100 T_0$. Dimensionless reduced units are used for the coordinates $x$ and $y$.](image)

As can be seen from Fig. 1, our NSWP does not vibrate in the radial direction, i.e., it corresponds to a vibrationally cold molecule. For theoretical analyses, we may thus ignore the time variation in $r$ and set $r = r_0$, and separate the angular and radial components of the motion. The trapping mechanism in the angular direction can then be conveniently described in the rotating frame defined by

$$\theta = \phi - \Phi(t), \quad p_\theta = p_{\phi} - r_0^2\dot{\Phi}(t),$$

and the new Hamiltonian governing the angular motion in this frame takes the form

$$K = \frac{p_\theta^2}{2r_0^2} - \frac{B}{\sqrt{2}} r_0 \cos \theta + r_0^2\dot{\Phi}(t) \theta.$$  

The above canonical transformation can be carried out with the help of the generating function $F_z(\phi, p_\theta) = p_{\phi} \phi - \Phi(t) + r_0^2\dot{\Phi}(t) \phi + A(t)$, where $A(t)$ is chosen such that $(\dot{r}_0^2/2)\dot{\Phi}^2(t) + r_0^2\dot{\Phi}(t) \Phi(t) + A = 0$. It should be noted immediately that Eq. (5) has the form of the prototype Hamiltonian accompanying the so-called bucket dynamics [10]. The potential term in Eq. (5) creates a well (trap) in angular space as shown in Fig. 2.

Before we proceed to discuss the implication of the bucket dynamics for controlling the molecular rotational motion, let us consider the case of a CP field with the fixed frequency $\Omega_0$ to derive the NSWP of Eq. (2). In this case, the third term on the right-hand side of Eq. (5) vanishes, and
two types of classical motion are possible depending on the value of \( K \): rotation if \( B r_0 / \sqrt{2} < K \), and libration (around \( \theta = 0 \)) if \( -B r_0 / \sqrt{2} < K < B r_0 / \sqrt{2} \). It is the librational motion that is associated with the angular trapping of the NSWP. The Schrödinger equation for the Hamiltonian of Eq. (5) can be cast into Mathieu’s equation [12], and the Mathieu functions, corresponding to the system’s eigenstates, are the desired NSWPs. If the potential well in Eq. (5) is deep enough, it can be expanded by power series in \( \theta \) and approximated by the first quadratic term for calculating the ground state. The ground state so obtained yields a Gaussian function that corresponds to the angular part of the NSWP of Eq. (2), where \( \kappa_\phi \) was determined to be \( \kappa_\phi = (B r_0^3) 1/2 / 2^{1/4} \) from this consideration. The approximate form for the radial part of Eq. (2) can be calculated similarly by expanding the radial potential quadratically about the equilibrium \( r_0 \) determined by Eq. (3). The appropriate value for \( \kappa_r \) can then be obtained from the resulting Gaussian ground state wave function. If the field is weak and the frequency not too high, \( \kappa_r \) is calculated to be \( \kappa_r = 1 \).

In analogy with the vibrational excitation [10,13,14], we can use the same physical argument of bucket dynamics to describe the control of the angular momentum of a molecule by using a CP field with properly chirped frequencies. Since the rotational frequency is normally lower than the vibrational frequency for molecules in low-energy states, the frequency of the chirped CP field used here is relatively lower than that required for vibrational excitation control. We consider here a linearly chirped CP field whose frequency increases as \( \Omega_{\text{inst}} = d^2 \Phi/t = \Omega_0 (1 + \gamma t) \), where the parameter \( \gamma \) defines the rate of the chirping. In this case, the potential term in Eq. (5) creates in phase space a trapped region whose angular momentum, when viewed in the laboratory frame, increases as \( p_\phi = p_\phi + r_0^2 \Omega_0 (1 + \gamma t) \) [see Eq. (4)] [9,10]. The wave packet initially prepared in the NSWP state \( (\langle \hat{p}_\phi \rangle = 0) \) will be guided by the trap and gain angular momentum until the chirping is terminated. If, instead, a negatively chirped CP field is used, the angular momentum of the NSWP will be lowered. Figure 2(b) indicates that for the wave packet to be successfully guided by the moving trap, the frequency of the CP field should be changed slowly to guarantee the existence of the potential well. This imposes on the chirping rate the adiabatic condition \( |\gamma| < B/r_0 \Omega_0 \sqrt{2} \)

[under this condition the potential of Eq. (5) has a local minimum].

Displayed in Fig. 3 is the time evolution of the wave packet initially prepared in the NSWP state, Eq. (2), in the presence of the chirped CP field. The frequency of the CP field is increased (decreased) linearly from \( \Omega_0 = 0.1 \) to \( \Omega_1 = 0.2 \) (\( \Omega_1 = 0.05 \)) during the interval \( T_c = 50 T_0 \), and then set at the fixed value \( \Omega_1 \). The chirping rate is given by \( \gamma = (\Omega_1 / \Omega_0 - 1) / T_c \), and the amplitude of the CP field is held constant during the process. At \( t = T_c \), the phase of the positively chirped CP field advances by \( \Delta \Phi = \int_0^{T_c} \Omega_{\text{inst}} dt = 75 \times 2 \pi \). At this moment, the wave packet returns to the original angular position \( (\phi = 0) \), as can be seen in Fig. 3(a), after completing 75 rotations. In the case of Fig. 3(c), the rotation number is \( 37 + 1/2 \), and the wave packet appears at \( \phi = \pi \). At the end of the chirping process, the mean angular momentum of the state reaches \( \langle \hat{p}_\phi \rangle = r_1 \Omega_1 \), where \( r_1 \) is the new equilibrium point decided by Eq. (3) with \( \Omega_1 \) substituted for \( \Omega_0 \).

The efficiency of the control scheme can be measured by calculating the partial norm \( P_A(t) \) defined earlier. It is found that \( P_A(T_c) / P_A(0) = 1.003 \) for the wave packet in Fig. 3(a) and 0.993 for that in Fig. 3(c), which demonstrates the high efficiency of the control scheme.

We next discuss how to generate the NSWP. If the initial wave packet is not prepared in the NSWP state, the control

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**FIG. 2.** Angular potential (in reduced units) of Eq. (5) in the rotating frame for the cases of (a) a fixed-frequency CP field and (b) a linearly chirped CP field with \( \gamma > 0 \).

**FIG. 3.** Controlled evolution of a nonspreading wave packet by a chirped CP field with amplitude \( B = 0.002 (t = 4.1 \times 10^{11} \text{ W/cm}^2) \). The initial frequency of the field is \( \Omega_0 = 2 \pi / T_0 = 0.1 \) (frequency = 413.8 cm\(^{-1} \)), and the chirping is terminated at \( T_c = 50 T_0 \) (\( T_c = 4.03 \text{ ps} \)). The initial wave packet was prepared as in Fig. 1(a). Wave packet (a) at \( t = T_c \) for positive chirping (\( \Omega_1 = 0.2 \)), and (b) at one field cycle (\( T_f = 2 \pi / \Omega_1 \)) later than (a). Wave packet (c) at \( t = T_c \) for negative chirping (\( \Omega_1 = 0.05 \)), and (d) at one field cycle (\( T_f = 2 \pi / \Omega_1 \)) later than (c). Dimensionless reduced units are used for the coordinates \( x \) and \( y \).
scheme described above will only lead to partial trapping of the wave packet. Thus, a generation scheme for the NSWP is necessary to complement the control scheme. We here wish to create, in particular, a NSWP from the initial state

$$\psi(r, \phi) = Ne^{-\kappa(r-r_0)^2/2h_{\text{eff}}^2}e^{im\phi},$$

(6)

where \(m\) is an integer and \(r_0\) is calculated from Eq. (3) with \(B=0\) and \(\Omega_0 = m\hbar_{\text{eff}}/r_0^2\). This wave function approximately corresponds to the two-dimensional Morse eigenstate with the vibrational quantum number \(\nu = 0\) and the angular momentum quantum number \(m\). Using the unitary operator \(\hat{U} = e^{i\hat{\phi}(t)\hat{\hbar}_{\text{eff}}^2/m^2}\), or equivalently the generating operator \(\hat{F}(\hat{\phi}, \hat{\rho}_\phi) = [\hat{\rho}_\phi - \Phi(t)]\hat{\rho}_\phi + i\hbar_{\text{eff}}(2\ln2\pi)/\hbar_{\text{eff}}\) [15], we can make a canonical transformation in Hilbert space similar to Eq. (4). Here, the insignificant term \(A(t)\) has been dropped for convenience. If \(\Phi(t) = \Omega_{\phi,t}\), the state of Eq. (6) is transformed into a state whose angular momentum quantum number is \(m = 0\) in the new rotating frame, while the vibrational quantum number remains unaltered.

To transform this state into a NSWP state, we turn on the CP field in an adiabatic manner [1, 4–7]. A theoretical explanation of this process and its validity can be provided by the quantum adiabatic theorem which states that, if the time variation in a Hamiltonian is adiabatic, the number of zeros, or nodes, of an eigenfunction does not change during the whole process of the adiabatic transformation [16]. This means that the following quantity is a quantum adiabatic invariant [17]:

$$\oint P dq = mh,$$

(7)

where \(P = (\hbar/\imath)\partial \ln \psi/\partial q\), and \(m\) is the number of nodes of the wave function or the quantum number with \(m = 0\) for the ground state. Since our initial state in the rotating frame has zero nodes \((m = 0)\), it can be predicted that the state at an arbitrary later time will be the ground state of the instantaneous Hamiltonian, as long as the process is maintained to be adiabatic. This proves that the adiabatic turn-on of the CP field creates a NSWP, which is the ground state of the Hamiltonian (5), from the wave function of Eq. (6). If the CP field is switched on rather rapidly, we may end up with a wave packet that contains not only the ground state but also some excited states as its components. This can give rise to distortion of the resulting wave packet as it evolves.

The generation scheme for the initial state with \(m = 10\) is illustrated in Fig. 4, in which a Gaussian turn-on of the field amplitude in the form \(B(t) = B_0e^{-(t-T_{\text{on}})^2/2}\) with \(a = 5 \times 10^{-8}\) and \(T_{\text{on}} = 200\) is used. At the final stage of the turn-on process \((t = T_{\text{on}})\), 85% of the initial wave function is captured in the region used to define \(P_A(t)\), i.e., \(P_A(T_{\text{on}}) = 0.85\). When applied along with the control scheme, this generation scheme could provide a useful strategy for an efficient control of the rotational state of a molecule that is initially in an angular momentum eigenstate. Finally, we mention that the designed rotational states and their controlled evolution may be detected experimentally by sending probing laser pulses with suitable delays to interrogate the rotational and vibrational states of the molecule [2]. An example is provided by the powerful pump and dump technique [18], which can be used to measure the rotational and vibrational distributions of the molecule.

In conclusion, it has been shown that nonspreading wave packets of diatomic molecules can be generated and controlled by a circularly polarized electric field with properly chosen amplitude and frequency. An approximate expression for the NSWP has been provided, and the underlying mechanism of the generation and control schemes for the NSWP has been explained theoretically. Numerical calculations of the Schrödinger equation demonstrate the efficient performance of the scheme.

[3] See, for example, the focus issue of Opt. Express 1, No. 7 (1997).


