

Proposal for laser purification in molecular vibrational cooling using zero-width resonances

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Intense-field molecular photodissociation offers the possibility to define resonances of zero width for particular intensities at given wavelengths. We show how a laser pulse can be shaped to fulfill, at all times, the conditions leading to a zero width for a particular resonance originating from a field-free vibrational state. The solution of the time-dependent Schrödinger equation confirms that only this state survives after the pulse is off. This is the basis for a purification procedure leading to population left only in a single state chosen at will. The illustrative example is H_2^+ .

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Purification, to get a single vibrational (or rotational) state out of an ensemble of initial ones, is an important issue in the laser control of molecular dynamics. In particular, molecular rovibrational cooling is a major challenge which necessitates a selective preparation of a single rovibrational state starting from an initial distribution, either thermal or resulting from photoassociation [1]. Among other techniques, vibrational cooling has experimentally been achieved referring to blackbody-radiation-assisted lasers [2,3] or optical pumping by broadband femtosecond lasers [4]. In particular, methods involving photoassociation of ultracold atoms are able to produce translationally cold tightly bound molecules in a given electronic state. Additional sequences of shaped laser pulses are used to transfer most of these molecules in their ground vibrational state. All these processes involve a decay mechanism which describes the unavoidable entropy flow, a key concept in purification [5].

For this purpose, we have recently proposed an adiabatic vibrational population transport mechanism using exceptional points (EPs) corresponding to two coalescing resonances for a specific laser wavelength and intensity [6]. A chirped pulse encircling the EP monitors the vibrational transfer between two adjacent resonances originating from field-free vibrational states $v + 1$ and v . The residual populations, after the pulse is over, could then be transferred step by step to state $v = 0$, using successive pulses. Contrary to a stimulated Raman adiabatic passage (STIRAP) technique which, by itself, is not fully appropriate for the purification purpose as it does not offer a dissipative channel where the entropy goes, this cooling strategy clearly involves a dissociative process. But it suffers from a compromise to ensure the underlying adiabatic transport. In particular, a long pulse duration to fulfill the requirement of adiabaticity may have, as a consequence,

an important depletion of the overall molecular population through photodissociation. A much more robust purification technique that we propose in this Rapid Communication is to start from a given vibrational distribution and to appropriately shape a single laser pulse, such as to efficiently photodissociate all vibrational states, with the exception of one. The entropy flow is merely associated with the photodissociation process. The mechanism we are referring to when shaping such a pulse is the adiabatic and continuous transport of the vibrational state we aim to protect against dissociation on infinitely long-lived so-called zero-width resonances (ZWRs).

More precisely and unexpectedly, for certain critical field intensities, the photodissociation rate vanishes for a given wavelength, leading, thus, to a ZWR either in continuous-wave (cw) [7,8] or in pulsed regimes [9]. The situation is very similar to that met in the predissociation of diatomic molecules. The criteria to produce the occurrence of ZWRs have been derived by Bandrauk and Child [10] within a semiclassical formulation. We have previously shown [11] that it is possible to produce ZWRs even at very low intensities so that the photodissociation rate is unexpectedly (but not trivially) low. The present Rapid Communication is devoted to the potentiality of ZWRs as a basic mechanism in purification strategies. The approach is to test, through the solution of the time-dependent Schrödinger equation (TDSE), the results obtained via approximate treatments, such as the Floquet theory which, in principle, is valid for cw fields [12] or the semiclassical formalism [10,13,14].

H_2^+ is taken as an illustrative example. Our model describes a field-aligned molecule in one spatial dimension (the internuclear distance R) involving but two electronic states $|g\rangle$ and $|u\rangle$ (ground and first excited, respectively). The frozen rotation assumption is validated by considering short pulse durations (at most 120 fs) we refer to hereafter as compared to the H_2^+ rotational period (of about 7 ps). The wave function is written

$$|\Psi(R, t)\rangle = \chi_g(R, t)|g\rangle + \chi_u(R, t)|u\rangle, \quad (1)$$

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with nuclear wave-function solutions of the TDSE,

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \chi_g(R,t) \\ \chi_u(R,t) \end{bmatrix} = \left(T_N + \begin{bmatrix} V_g(R) & 0 \\ 0 & V_u(R) \end{bmatrix} - \mu(R)\mathcal{E}(t) \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \right) \begin{bmatrix} \chi_g(R,t) \\ \chi_u(R,t) \end{bmatrix}. \quad (2)$$

T_N is the nuclear kinetic-energy operator. $V_g(R)$ and $V_u(R)$ are the Born-Oppenheimer potentials. $\mu(R)$ is the electronic transition dipole moment between states $|g\rangle$ and $|u\rangle$. $\mathcal{E}(t)$ is the linearly polarized laser electric-field amplitude of the form $\mathcal{E}_0 \cos(\omega t)$ with a wavelength $\lambda = 2\pi c/\omega$. If the intensity of the field ($I \propto \mathcal{E}_0^2$) is such as to allow only for a single-photon absorption, the Floquet wave function can be written

$$\begin{bmatrix} \chi_g(R,t) \\ \chi_u(R,t) \end{bmatrix} = e^{-iE_F t/\hbar} \begin{bmatrix} \varphi_g(R) \exp i\omega t \\ \varphi_u(R) \end{bmatrix}. \quad (3)$$

E_F is called a quasienergy. $\varphi_g(R)$ and $\varphi_u(R)$ satisfy the two coupled equations,

$$[T_N + V_g(R) + \hbar\omega - E_F]\varphi_g(R) - 1/2\mathcal{E}_0\mu(R)\varphi_u(R) = 0, \quad (4)$$

$$[T_N + V_u(R) - E_F]\varphi_u(R) - 1/2\mathcal{E}_0\mu(R)\varphi_g(R) = 0. \quad (5)$$

Solutions with Siegert outgoing-wave boundary conditions produce complex quasienergies of the form $E_R - i\Gamma_R/2$, where Γ_R is the resonance width related to its decay rate.

As already pointed out in previous papers [7–9], these rates can go through zero at some laser-field intensities for given frequencies. An analytical explanation can be provided using the semiclassical theory of photodissociation of a diatomic molecule [13]. This formalism deals with the so-called field-dressed adiabatic potentials $V_{\pm}(R)$ resulting from the diagonalization of the molecule-field interaction. The semiclassical formalism predicts [10,14] that, if the following two conditions,

$$\int_{R_+}^{R_0} dR k_+(R) + \int_{R_0}^{R_t} dR k_+(R) + \chi = \left(\tilde{\nu}_+ + \frac{1}{2} \right) \pi, \quad (6)$$

and

$$\int_{R_-}^{R_0} dR k_-(R) + \int_{R_0}^{R_t} dR k_+(R) = \left(\tilde{\nu} + \frac{1}{2} \right) \pi \quad (7)$$

are simultaneously fulfilled, the outgoing scattering amplitude in the lower (open) adiabatic channel V_- is zero, resulting in photodissociation quenching. In Eqs. (6) and (7), $k_{\pm}(R) = \hbar^{-1}[2m(E - V_{\pm}(R))]^{1/2}$, m being the reduced nuclear mass. R_{\pm} are the two left turning points of V_{\pm} potentials, R_t is the right turning point of V_+ , and R_0 is the diabatic crossing point resulting from field dressing. With integers $\tilde{\nu}_+$ and $\tilde{\nu}$, these conditions lead to Bohr-Sommerfeld quantization. They mean that there is coincidence of two energies: one of the upper adiabatic potentials, with a phase correction χ , which in weak coupling is $-\pi/4$ [14], and a second of a potential made of two branches. On the left of R_0 , the potential is the lower adiabatic potential $V_-(R)$, whereas, beyond this point, it is the upper adiabatic potential $V_+(R)$. For a weak coupling, this is practically the diabatic attractive potential $V_g(R)$.

The specific choice of the photon frequency dressing the adiabatic potentials, which is at the origin of such

coincidences, picks out the couple of electronic states which take part in the ZWR process. This is why, in terms of potentials, only two among the manifold of excited electronic states are retained in Eq. (2). In addition, only single-photon processes are taken into account in Eqs. (4) and (5) following converged calculations for the relatively modest intensities that are referred to. In Fig. 1, we show an example of the loci of critical parameters leading to ZWRs originating from states $v = 8$ and $v = 9$ of H_2^+ , as resulting from Floquet formalism. It is worthwhile noting that, within this wavelength and intensity window, ZWRs are very close to being along a straight line in the parameter plane. The linear fit used in the calculations for these loci,

$$I(10^{13} \text{ W/cm}^2) = a\lambda(\text{nm}) + b \quad (8)$$

is also displayed. For ZWRs originating from $v = 8$, the coefficients are found to be $a = -0.0153$ and $b = 6.5867$. An interesting observation is that the semiclassical estimate for the critical wavelength with an intensity close to zero is 430 nm [11], to be compared with 431 nm derived from TDSE. But the most important point is that the requirement for adiabatic transport from the field free $v = 8$ state to its corresponding ZWRs can completely be fulfilled as the ZWRs are reached at almost zero-field intensity and continuously are followed with increasing strength.

The implementation of the purification scheme is illustrated on the example of the ZWR originating from the field-free vibrational state $v = 8$, referring to a full quantum dynamical simulation based on wave-packet propagation, solution of the TDSE [Eq. (2)]. The laser pulse is chirped, such as to combine at each time the wavelength and intensity corresponding to the following of the ZWR, as obtained from the Floquet theory, in Fig. 1. Within the hypothesis of an initial ensemble of vibrational states, or of an initial coherent vibrational superposition, the expectation is that, when the molecule is exposed

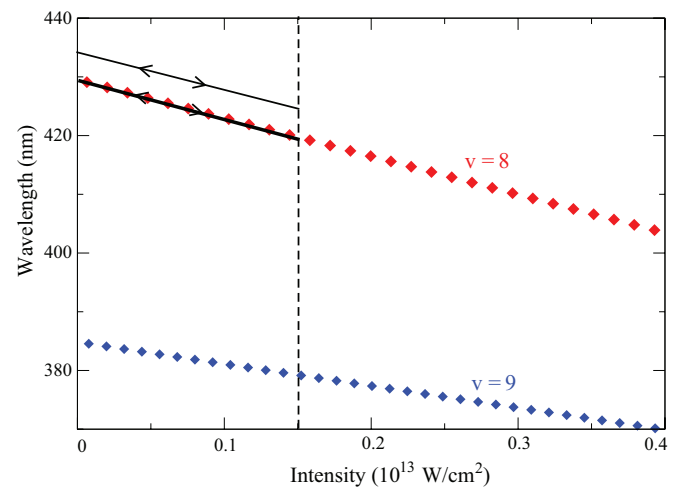


FIG. 1. (Color online) The loci of ZWRs in the laser parameter plane for $v = 8$ and $v = 9$. The solid diamonds are the Floquet results, whereas, the solid lines represent the linear representations used for the pulse chirping. The arrows indicate the front and back directions of the chirp along the pulse. The maximum intensity (corresponding to a given ZWR) used in the calculations $I_{\max} = 0.1459 \text{ MW/cm}^2$ is indicated by the vertical dotted line.

to such a field, the initial population of its $v = 8$ vibrational state will be preserved against dissociation, whereas, all other vibrational states are depleted. Apart from the chirp strategy, additional control parameters concern the time shaping of the pulse envelope. In particular, the total pulse duration τ has to be long enough to ensure complete dissociation of all levels $v' \neq 8$. A long duration pulse is also consistent with the adiabaticity requirement of the population transfer from the field free $v = 8$ vibrational level to its corresponding ZWR as supported by the Floquet model. The pulse rise and fall-off durations are still other control parameters we will have to take into account while monitoring adiabatic transports.

The wave packet is numerically propagated using a third-order split-operator technique to solve Eq. (2) with an initial condition,

$$|\Psi_v(R, t = 0)\rangle = \chi_{g,v}(R)|g\rangle, \quad (9)$$

where $\chi_{g,v}(R)$ stands for the field-free vibrational state v accommodated by the $V_g(R)$ electronic potential. The observables are the time-dependent populations calculated by projecting the wave packet on field-free vibrational states,

$$P_{v,v'}(t) = |\langle \chi_{g,v'}(R) | \Psi_v(R, t) \rangle|^2. \quad (10)$$

Figure 2 displays the results for a first set of control parameters, namely, the chirp scheme following the ZWR of $v = 8$ (Fig. 1) and an initial guess for the trapezoidal pulse envelope with a total duration of $\tau = 70$ fs and equal rise and fall-off times of 10 fs. Only three adjacent levels $v = 7, 8, 9$ are retained for the discussion. Panels (a)–(c) correspond to population decays $P_{v,v'}(t)$ for an initial state v , respectively, equal to 7, 8, or 9. The overall observation is that, as expected, the population of $v = 8$ is rather well protected against dissociation, whereas, those of neighboring levels $v = 7$ and 9 are decaying very

fast. More quantitatively, at the end of the pulse, the survival probability of state $v = 8$ is $P_{8,8}(\tau) = 0.53$ [panel (b)], those of $v = 7$ or 9 being less than 0.05 [panels (a) and (c)]. An already comfortable contrast $P_{8,8}/P_{9,9}$ of about 10 is reached showing the selectivity of the strategy but still remains the question concerning the additional control that can be exerted on the pulse envelope to improve this first finding. An obvious answer appears to be the increase in the total pulse duration τ , the expectation being that, for a longer τ , the population of $v = 9$ will continue on decreasing to zero, whereas, the one of $v = 8$ is still protected. The other control knobs at our disposal, i.e., the switch on and off profiles, may be used to ensure better adiabaticity, that is, better protection of the $v = 8$ population from decay. Actually, from Fig. 2(b), it is clear that the $v = 8$ population is subject to decay mainly during the pulse rise and fall-off periods. It is also during these ramps that the $v = 8$ population is partly transferred to $v = 7$ and 9 ($P_{8,7}$ reaches values up to 0.06 at times corresponding to the end of the rise ramp). These observations are well-known signatures of nonadiabaticity. A way to minimize them is to increase the ramp durations. The relative values of the rise, plateau, and fall-off durations could, of course, be obtained by a three-parameter genetic algorithm. Even more simply, after a few attempts, we produce a laser pulse illustrated in Fig. 3(b), which almost leads to the expected result. Figure 3 illustrates our full control strategy with a total pulse duration $\tau = 120$ fs, long enough to produce almost complete decay of neighboring level populations ($v = 7, 9$) and ramp durations of 53 fs for an even better protection of $v = 8$. There is a slight regular decrease in the probability to remain in state $v = 8$. But now, 75% of the molecules are left in state $v = 8$ when the pulse is over. Of course, the probabilities calculated during the pulse cannot be taken as an indication of the adiabaticity of the process since the wave function may have significant components on different vibrational resonances. However, it is rewarding to see that, at the end of the pulse, the only nonvanishing probability is in $v = 8$. The contrast $P_{8,8}/P_{9,9} = 0.75/0.02$ has now reached a value as important as 37, which means very efficient purification. A simple STIRAP

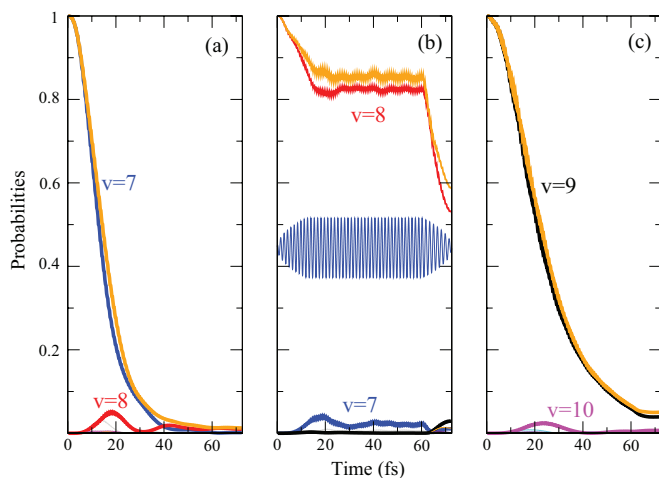


FIG. 2. (Color online) Decaying populations when starting at time $t = 0$ either from $v = 7$ [panel (a)], $v = 8$ [panel (b)], or $v = 9$ [panel (c)]. The pulse, shown in blue [panel (b)], has parameters devised, such as to follow the ZWR line of the state $v = 8$ with a total duration of 70 fs and ramps of 10 fs. The populations remaining in $v = 7$, $v = 8$, $v = 9$, and $v = 10$, respectively, are indicated by blue, red, black, and magenta solid lines. The orange solid curve represents their sum, i.e., the probability to remain in the initial field-free bound state.

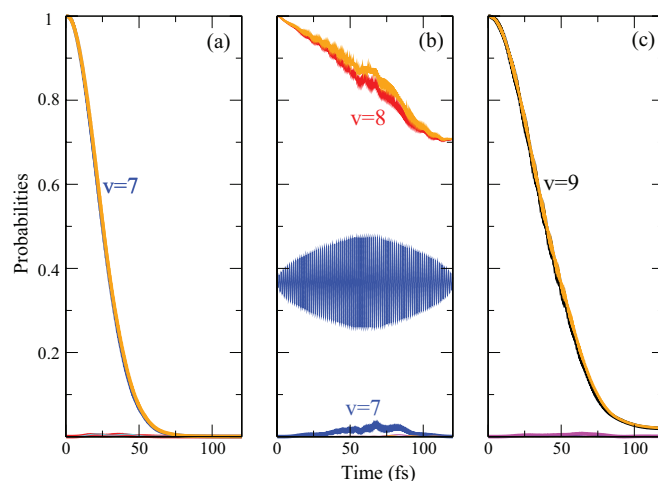


FIG. 3. (Color online) Same as in Fig. 2, except that the pulse now has a duration of 120 fs with ramps of 53 fs.

could then be used to transport the population to the ground vibrational state, if desired.

To further check the sensitivity of the strategy with respect to pulse parameters and, thus, its experimental feasibility, we perform calculations by slightly changing the chirp parameters a and b in Eq. (8), whereas, maintaining the pulse envelope displayed in Fig. 3. Even for ZWRs, loci presenting deviations up to 2 nm with respect to the corresponding TDSE estimates (Fig. 2) photodissociation quenching of $v = 8$ is still observed with a final nondissociated population $P_{8,8}$ of about 0.55, to be compared with 0.75 for the optimal case.

In conclusion, we show how the occurrence of ZWRs in the context of laser-induced photodissociation can be exploited as a purification strategy based on appropriately chirped laser pulses. This is an example where the specificity of resonances derived from a purely adiabatic Floquet model is used in a wave-packet propagation scheme aiming at quantum purification control. We emphasize that, due to continuous adiabatic transport of the initial field-free state on its corresponding ZWRs at all times (intensities starting from zero), the strategy does not suffer from a possible nonadiabatic contamination as has recently been discussed in the context of EPs [15]. The present results go much beyond

some previous works where either only the passage through ZWRs at fixed wavelength was at the basis of a filtering [9] or only ZWRs were used as a last step in a cooling process based on EPs [16]. Our study has, however, been limited to two electronic channels with no account of the rotation. Although the introduction of this degree of freedom can significantly affect the dissociation rates [17], we have previously shown [9] that, through a shift in the critical intensities, which can be explained as due to a scaling law, the zero-width phenomenon persists even when introducing further channels needed to account for the rotation. Within these model limitations, it is important to emphasize that the proposed strategy is robust, generic, and experimentally feasible. A convenient choice of laser parameters (wavelength, intensity) seems always possible to produce ZWRs originating from any given field-free vibrational level of a two electronic state curve-crossing situation. Figure 1 exemplifies two such cases for $v = 8$ and $v = 9$. The chirp amplitudes under consideration (less than 10%) are within experimental reach, and the required field strengths are also rather modest (less than 0.5×10^{13} W/cm²) with pulse durations not exceeding 120 fs. Finally, the model is generic enough to be transposed to other molecular species, such as Na₂ where ZWRs have already been demonstrated theoretically [16].

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