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Proposal for a laser control of vibrational cooling in Na₂ using resonance coalescence

O. Atabek¹, R. Lefebvre^{1,2}, M. Lepers³, A. Jaouadi^{1,3}, O. Dulieu³, and V. Kokoouline^{3,4}

¹*Institut des Sciences Moléculaires d'Orsay, CNRS, Bât 350, Univ. Paris-Sud, 91405 Orsay France*

²*U.F.R. de Physique Fondamentale et Appliquée,
Université Pierre et Marie Curie, 75321 Paris, France*

³*Laboratoire Aimé Cotton, CNRS, Bât. 505, Univ. Paris-Sud, 91405 Orsay, France*

⁴*Department of Physics, University of Central Florida, Orlando, FL 32816, USA **

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With a specific choice of laser parameters resulting into a so-called exceptional point (EP) in the wavelength-intensity parameter plane, it is possible to produce the coalescence of two Floquet resonances describing the photodissociation of the Na₂ molecule, which is one of the candidates for the formation of samples of translationally cold molecules. By appropriately tuning laser parameters along a contour encircling the exceptional point, the resonances exchange their quantum nature. Thus a laser controlled transfer of the probability density from one field-free vibrational level to another is achieved through adiabatic transport involving these resonances. We propose an efficient scenario for vibrational cooling of Na₂ referring to cascade transfers involving multiple EPs and predicted to be robust up to a 78% rate against laser-induced dissociation.

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Progress made during the last two decades in the cooling of quantum gases at ultracold temperatures down to the quantum degenerate regime has opened a possibility to study small molecules at the level of individual quantum rovibrational and hyperfine states [1, 2]. An important step in the experimental developments is the achievement of the deterministic manipulation of quantum states of small molecules, the formation of pre-selected quantum states and the control of the coupling between them. The variety of robust experimental techniques [3, 4] which are currently being developed may later be used as a tool set for many-body physics, high precision measurements and technological applications. Ultracold alkali-metal molecules are most often prepared in a distribution of vibrational levels of the singlet electronic ground state, or of the lowest triplet state. An important challenge is to create dense samples of ultracold molecules in a selected single quantum state. At present, there are several different techniques used to create and manipulate well-defined rovibrational and/or hyperfine states of diatomic molecules at ultralow temperatures, *e.g.* photoassociation (PA) [5], stimulated Raman adiabatic passage (STIRAP) [6–9], black-body radiation-assisted laser cooling [10, 11], or optical pumping by a broadband femtosecond laser [12, 13].

In this work we propose an alternative way for a deterministic manipulation of vibrational states of alkali-metal diatomic molecules, relying on adiabatic transfer of population using chirped picosecond laser pulses, blue-detuned with respect to an atomic transition frequency. The procedure is based on the coalescence of two resonances into a single one described in the Floquet formalism [14]. By coalescence we mean a situation of energetically degenerate resonances with, in addition, identical wave-functions. The laser-controlled vibrational transfer scenario consists in applying an electromagnetic field which couples the ground or a metastable electronic molecular state to an excited one. The induced resonances are identified through a series of complex eigenenergies of the Hamiltonian of the system, their imaginary part being related to their dissociation lifetime. With an appropriate choice of the laser parameters (intensity, wavelength) which is called an exceptional point (EP) [15, 16] of the parameter space, it is possible [17] to achieve a degeneracy of two such energies. By defining a loop encircling the EP in the laser parameter plane, the probability density of a field-free vibrational level is transferred to a lower one through the continuous adjustment of the energy and the width of a single resonance along the contour [18, 19]. Optimal times for a laser pulse to follow the loop are determined to ensure an adiabatic transfer. The proposed scheme is general. In the case of the Na₂ molecule chosen here, we demonstrate that the amount of molecules surviving to laser-induced photodissociation is as high as 78%, suggesting that this scheme is robust.

We consider the example of the Na₂ molecule in an excited vibrational level of its $a^3\Sigma_u^+(3^2S + 3^2S)$ lowest triplet electronic state (referred to as state u). The formation of ultracold sodium molecules has been demonstrated in Ref. [20], and therefore the present application represents a realistic situation. The same technique can be applied to other diatomic molecules, especially to alkali dimers, with only small changes due to the similarities of their potentials. The laser-controlled vibrational transfer scenario consists in applying an electromagnetic field with wavelength around 560 nm that couples state u with the $(1)^3\Pi_g(3^2S + 3^2P)$ excited electronic state, labeled g below.

Hereafter we refer to a model describing a rotationless field-aligned molecule in one spatial dimension (the internuclear distance R) and involving only two electronic states $|u\rangle$ and $|g\rangle$ whose Born-Oppenheimer (BO) potential energy curves $V_u^{BO}(R)$ and $V_g^{BO}(R)$ are displayed in Fig. 1a, b. Among all electronic states of Na₂, the chosen $|u\rangle$ and $|g\rangle$ states present a favorable curve crossing situation at the laser wavelengths used to couple them (Fig. 1c). The frozen rotation assumption can be validated by considering the long rotational periods of Na₂ (estimated as hundreds of ps) as compared with the pulse durations under consideration (less than 2 ps). The time-dependent wave function of the system is expanded on these two states

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

with the unknown functions χ_u , χ_g accounting for the field-assisted nuclear dynamics. When the interaction of the molecule with an electromagnetic field with leading frequency ω is described by a time-periodic Hamiltonian, applying the Floquet ansatz, the two-component solution of the time-dependent Schrödinger equation (TDSE) can be written as

$$\begin{bmatrix} \chi_u(R, t) \\ \chi_g(R, t) \end{bmatrix} = e^{-iE_F t/\hbar} \begin{bmatrix} \phi_u(R, t) \\ \phi_g(R, t) \end{bmatrix} \quad (2)$$

where E_F is the Floquet quasi-energy. The periodicity in time of $\phi_k(R, t)$ ($k = u, g$) allows us to expand these functions in Fourier series

$$\phi_k(R, t) = \sum_{n=-\infty}^{+\infty} e^{in\omega t} \varphi_k^n(R). \quad (3)$$

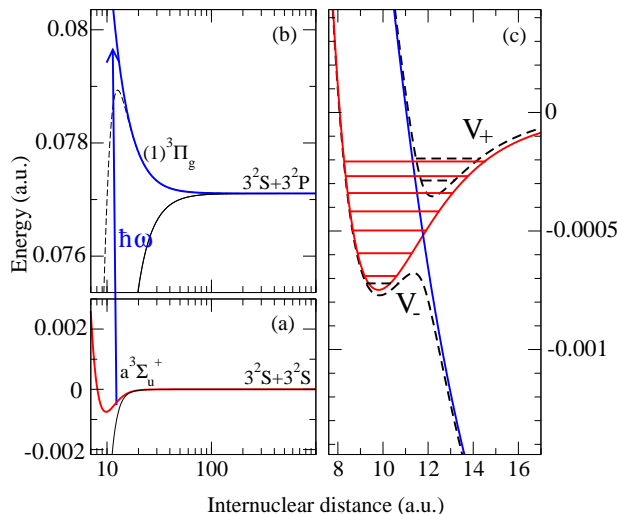


FIG. 1. (Color online) Na₂ potential curves in field-free (a,b) and field-dressed representations (c) with the absorption of a photon ($\hbar\omega = 0.0808$ a.u. or wavelength $\lambda = 564$ nm) and the laser field intensity ($I = 0.35$ GW/cm²). V_{\pm} (black dashed lines) are the adiabatic potentials with their corresponding levels (dashed horizontal lines).

Finally, adopting the length-gauge and the long-wavelength approximation for the matter-field coupling, the Fourier components $\varphi_k^n(R)$ are given as solutions of the set of coupled differential equations resulting from the TDSE, exemplified by the general form, for all n [14]

$$\left[T + V_{u,g}^{BO} + n\hbar\omega - E_F \right] \varphi_{u,g}^n - 1/2 \mathcal{E}_0 \mu(R) \left[\varphi_{g,u}^{n-1} + \varphi_{g,u}^{n+1} \right] = 0, \quad (4)$$

where $T = (-\hbar^2/(2\mathcal{M}))(d^2/dR^2)$ is the usual radial kinetic energy operator and \mathcal{M} is the reduced mass. The transition between the u and g states is governed by the R -dependent molecular transition dipole moment $\mu(R)$ [21, 22]. The laser is characterized by the linearly-polarized electric field $\mathcal{E}(t) = \mathcal{E}_0 \cos(\omega t)$, the wavelength $\lambda = 2\pi c/\omega$ and the intensity $I \propto \mathcal{E}_0^2$. Solutions with boundary conditions appropriate for resonance calculations [14] produce complex quasienergies of the form $E_F = E_R - i\Gamma_R/2$, where Γ_R is the resonance width related to its decay rate. The single photon processes are described using the two diabatic channels u and g , with field-dressed potentials $V_u(R) \equiv V_u^{BO}(R)$, $V_g(R) \equiv V_g^{BO}(R) - \hbar\omega$ (Fig.1c), and with wave functions $\varphi_u^0(R)$ and $\varphi_g^{-1}(R)$, designated briefly as $\varphi_u(R)$ and $\varphi_g(R)$. It is of course possible, for each value of the coordinate R , to obtain, through a linear transformation, the functions associated with the adiabatic potentials $V_-(R)$, $V_+(R)$ (Fig.1c) resulting from the diagonalization of the diabatic potential matrix after accounting for the matter-field interaction [23].

The adiabatic potentials are very useful for the interpretation of resonances induced by high-intensity electromagnetic fields, which fall in two categories [26]: (i) the *Feshbach-type* (FT) resonances associated with the levels of the $V_+(R)$ potential well interacting with the continuum of the $V_-(R)$ potential; (ii) the *shape-type* (ST) resonances associated with the levels of the $V_-(R)$ potential, decaying through or above the barrier and still interacting with $V_+(R)$ by residual non-adiabatic kinetic couplings. The horizontal lines in Figure 1c indicate positions of bound and quasi-bound levels obtained after solving the Schrödinger equation for the corresponding one-channel adiabatic (black) or diabatic (red) potential curves. The dashed lines are zeroth order approximations for FT and ST resonances (respectively accommodated by V_+ and V_-). The energy of FT resonances increases with intensity, as the adiabatic potentials split further and further; these resonances ultimately merge with the vibrational levels of $V_+(R)$ of vanishing width. Increasing the intensity has an opposite effect on ST resonances. As a consequence of the barrier lowering of the $V_-(R)$ potential, their energy is decreasing, while their width increases.

EPs result from the coalescence (*i.e.*, complex energy degeneracy) of FT and ST resonances [24]. In order to locate them, we calculate the resonance energies as a function of intensity for various values of the wavelength [17, 24]. Our best estimate (within two digits of accuracy) for the parameters leading to coalescence of $(v+1, v)$ pairs with $v = 2$ or 3 taken as an illustrative example of this wavelength region, is $\lambda_{EP} = 562.53$ (or 558.43) nm and $I_{EP} = 0.332$ (or 0.353) GW/cm². For $\lambda \leq \lambda_{EP}$ the widths of the FT and ST resonances as a function of intensity, exhibit an avoided crossing, while the energies cross each other at the EP. The reverse situation occurs for $\lambda \geq \lambda_{EP}$, which is a general morphological signature of an EP [24]. A workable control scheme consists in applying a chirped pulse which

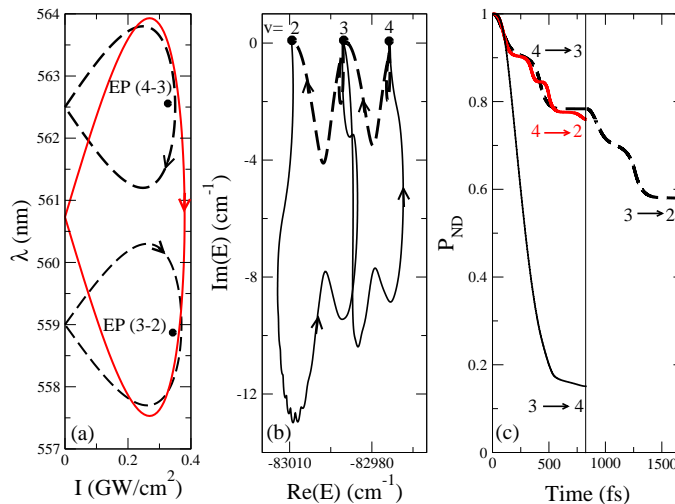


FIG. 2. (Color online) (a) Laser pulses encircling either single EPs (black, dashed lines) or two EPs (red solid line), (b) Energy trajectories for the down $v = 4, 3, 2$ (dashed lines) or up $v = 2, 3, 4$ (solid lines) transfers, (c) Survival probabilities after 800 fs adiabatic pulses for two vibrational quanta transfers ($v = 4$ to 2): Using either a single 800 fs pulse with multiple EP cascade transfers (red solid line) or two 800 fs pulses successively transferring from $v = 4$ to 3 and $v = 3$ to 2 (black dashed lines). Is also indicated the survival probability for the single quantum up transfer $v = 3$ to 4 (black solid line). The end of the first pulse is indicated by the thin vertical line.

adiabatically transfers the probability density from one field-free vibrational level to another, following a contour around the EP in the laser parameter plane [18], as shown in Fig.2a. Adiabaticity refers here to a strategy consisting in the transport of a field-free vibrational level on a single laser-induced resonance, following it in time until it changes its label and ends up into another single vibrational level, when the field is over. This requires a laser pulse duration t_f that exceeds an intrinsic time scale of the system, related here to a typical energy separation ΔE_v within the vibrational spectrum, *i.e.*, $\hbar/\Delta E_v$ [25]. The laser bandwidth is narrow enough to avoid resonance mixing, except in the vicinity of the EP, where a strategy consisting in an adiabatic (energy) separation of a two-dimensional sub-space built on the pair of resonances participating to the EP, from all the others, should be applied. The resulting penalty, when taking a long duration laser pulse, is a possible depletion of molecular bound states. It is thus very important to reach a compromise between adiabaticity and the requirement for a dissociation not to be complete along the contour. We have built such contours with an intensity and a wavelength obeying to a simple relation

$$I = I_{max} \sin(\phi/2), \quad \lambda = \lambda_0 + \delta\lambda \sin(\phi), \quad (5)$$

to encircle either a single EP or simultaneously the two EPs, as shown in Fig. 2a, aiming in single or double vibrational quantum transfers. The parameter ϕ is continuously and linearly changing with time from 0 (at $t = 0$) to 2π (at $t = t_f$). It is important to emphasize the experimental feasibility of such picosecond laser pulses in the visible domain, with a chirped wavelength centered on 560 nm, variations not exceeding 1% and a rather modest intensity, less than 0.5 GW/cm². The robustness of the method results from the fact that the requirement is solely to encircle the EP, without any specific consideration on the precise shape of the loop itself. This is compatible with some uncertainty on the EP position and also with a default to alignment of the molecules. Actually, molecules not aligned along the laser polarization direction, would experience, for a given intensity, a lower radiative interaction which may be compensated by a loop extending to higher intensity regions. Fig. 2 shows the loops in the parameter plane (a) and the resulting trajectories in the energy plane (b). The trajectories going from $v = 2$ to 3 and $v = 3$ to 4 on one hand, and those going from $v = 4$ to 3 and $v = 3$ to 2 on the other hand, involve quite different rates, in agreement with the previous analysis of ST and FT resonances.

In order to estimate the fraction of non-dissociated molecules left after the pulse is over, we refer to the adiabatic Floquet theory [26, 27]. This assumes that the chirped laser pulse envelope and its frequency vary sufficiently slowly with time such that the overall fraction of non-dissociated molecules P_{ND} is given by [26]

$$P_{\text{ND}}(t) = \exp \left[-\hbar^{-1} \int_0^t \Gamma_R(t') dt' \right]. \quad (6)$$

Here, $\Gamma_R(t)$ is associated with the relevant Floquet quasi-energy calculated using the instantaneous field parameters at time t . We present in the left panel of Fig. 2c P_{ND} for two cases: either starting from $v = 3$ to reach $v = 4$, or the reverse process, for a laser duration $t_f \simeq 800$ fs compatible with adiabatic transport. The results differ drastically. As already mentioned, the interpretation relies on the nature of the instantaneous resonance states created during the pulse. In the first case, the resonances involved in the adiabatic transport from $v = 3$ to $v = 4$ are ST, with large values of the decay rate. For the transfer $v = 4$ to $v = 3$ the situation is opposite, involving FT resonances. Therefore there is a better chance to preserve the molecules from dissociating when the transfer amounts to a decrease of the vibrational quantum number.

The ultimate goal for this and future similar studies is molecular vibrational cooling using a purification scheme to obtain a single ro-vibrational state, by successive transfers starting, for instance, from an initial distribution originating from photoassociation and involving a few excited vibrational levels. In this respect two strategies could be evoked. A realistic scheme would be to consider several chirped pulses, encircling a single EP at a time, monitoring thus the vibrational transfer between two adjacent resonances $v + 1$ and v . Such a pulse will only affect the other vibrational populations v' in terms of a decay in the dissociation continuum, without any interstate transfer. The residual populations, after the first pulse is over, could then be transferred, step by step, to state v (with ultimately $v = 0$) using successive pulses, encircling the corresponding relevant EPs. Staging this two-pulse strategy for the pairs $v = (4, 3)$ and $v = (3, 2)$ ends up in a two vibrational quantum transfer from $v = 4$ to 2. The efficiency is about 58% as indicated in Fig. 2c. But a more direct strategy would be to shape a single chirped pulse to encircle several EPs between successive resonances allowing cascade transfers from $v + n$ to v . For our typical example, the result displayed in Fig. 2c leads to a much better efficiency of 78%. Finally, this last technique would present an evident advantage over others, such as STIRAP, which manipulate only two vibrational populations at a time, with restrictions due to propensity rules. In addition, STIRAP is not fully appropriate for cooling purposes as it does not offer a dissociation channel where the entropy goes.

A crucial result of this work is that at the end of the pulse more than 78% of the molecules survive the dissociation. The importance of this result can be understood by comparing with a similar vibrational transfer control in lighter molecular systems such as H_2^+ [17]. Due to a much higher density of levels, resonance coalescence in Na_2 are obtained for much lower laser intensities. As a result the resonances participating in the adiabatic transfer process have widths of the order of ten cm^{-1} while, in the case of H_2^+ , they reach a thousand of cm^{-1} , leading thus to a much better protection against dissociation for Na_2 . However, a high density of levels requires longer pulse durations, for the adiabaticity to be safely implemented. More precisely, 50 fs pulse is long enough for an adiabatic transfer in H_2^+ , whereas about 1 ps is necessary for the same adiabaticity to be achieved in Na_2 , which is thus submitted to laser interaction (inducing its dissociation) for a duration about 20 times longer than H_2^+ . Despite this fact, the long lifetimes of Na_2 Feshbach resonances on which the vibrational transfer relies are such that 78% of Na_2 molecules remain non-dissociated at the end of the pulse, as compared to only 10% in the case of H_2^+ . It is worth noticing that there are other lifetime-limiting processes competing with the photodissociation, namely spontaneous emission (for the $(1)^3\Pi_g$ state) and the dimer-atom inelastic collisions between Na and Na_2 . The Na_2 lifetimes associated with these processes are much larger than 1 ps, of the order of a few ns for the spontaneous emission and a few seconds for inelastic atom-dimer collisions.

We have shown that selective vibrational transfer leading to vibrational cooling is possible using resonance coalescence (exceptional points) in laser-induced photodissociation/photoassociation of a molecular system using a rather simple experimental technique. This is illustrated for the case of Na_2 with realistic laser parameters. We emphasize that the population is selectively transferred from one vibrational state to another, except for a fraction (about 20%) that has decayed in the dissociation continuum. The proposed scheme can be applied to other molecular species like Cs_2 or Rb_2 , because the wavelength and the amplitude of the applied electric field are two parameters giving considerable freedom to manipulate the resonance quasienergies originating from a rather high density of vibrational levels.

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* O. Atabek: osman.atabek@u-psud.fr

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