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Selective coherent control of the lifetime of a resonance state with laser pulses

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It is shown that new possibilities for control of the lifetime of a system in a resonance state emerge when the density of resonances overlapping and interfering with the target resonance increases. When using a control scheme combining two pump laser pulses, it is found that increasing the density of resonance states overlapping with the target one increases the selectivity of the scheme applied, and leads to achieve a remarkably higher degree of control. Lifetime enhancements by factors up to 20 are obtained when this selectivity is applied. The underlying reasons for such strong enhancements are analyzed and explained in the light of the equations of the model applied. Application of this strategy to control and enhance the lifetime of a system in excited states is envisioned. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823983>]

I. INTRODUCTION

The design of coherent control strategies of molecular processes has been explored in several fields of chemistry and physics over nearly the last three decades.^{1–22} The basis of coherent control consists of manipulating constructive and destructive interference of quantum pathways between the initial and final target states. Consequently, the control schemes proposed are typically based on quantum interference mechanisms that are induced and controlled by means of laser pulses.^{3–22} Photodissociation, molecular reactions, and radiationless transitions are among the various processes whose control has been pursued.

It has been discussed that the occurrence of periodic vibrational revivals along time of molecular wave packets can be used to control photochemical processes.^{21,23–25} However, due to coupling of the system with the environment an initial coherent superposition of system vibrational states tends to dephase with time, and the onset of wave packet decoherence appears. Decoherence suppresses the wave packet revivals and then the possibility of controlling the photochemical process. Several strategies have been designed to control wave packet decoherence, in order to avoid it or to delay it as much as possible.^{26,27} Among the schemes proposed, one is based on controlling the quantum interference that occurs between overlapping resonances of the system populated by a coherent superposition created by a laser pulse, by varying the relative amplitude of the resonances.^{28–30} An extensive discussion and an analytical treatment of the preparation and decay evolution of a superposition of overlapping resonances are presented in Ref. 28(a).

The effect of interference between overlapping resonances excited in a coherent superposition was also used recently to suggest a scheme to control the lifetime of a single overlapping resonance within the superposition created.³¹

The control scheme is based on the novel finding that the lifetime of an overlapping resonance is no longer an intrinsic property of the resonance state, as it is the case of an isolated resonance, but instead it strongly depends on the amplitudes of the other overlapping resonances populated in the superposition.³¹ This effect allows one to control the survival probability and the associated lifetime of a specific resonance state by simply modifying the relative amplitudes of the excited resonances overlapping with the target resonance in the superposition prepared.

The control scheme was applied to a realistic three-dimensional wave packet model of the predissociation decay dynamics of $\text{Br}_2(B, v' = 27)\text{--Ne}$ in its ground van der Waals (vdW) resonance, which overlaps with practically only one orbiting resonance in the lower $v' - 1 = 26$ vibrational manifold of Br_2 .³² In a first scheme proposed the relative amplitudes of the two overlapping resonances were modified by changing the width of the pump pulse used to create the resonance superposition.³¹ Later on, a more flexible control scheme using a combination of two pump laser pulses, each pulse exciting one of the two resonances, was suggested. By varying the ratio of intensities and the delay time between the two pulses, a strong enhancement of the resonance lifetime, by a factor of up to three, was achieved.³³

The regime of two overlapping resonances of $\text{Br}_2(B, v' = 27)\text{--Ne}$ is the simplest overlapping regime we can have, being very suitable to understand how the proposed control scheme works.³¹ The counterpart, however, is that this sparse overlapping regime limits to a large extent the possibilities of control of the scheme. Indeed, as discussed previously (see the discussion around the general equation (Eq. (7) of Ref. 31), the larger is the number of resonances overlapping (and interfering) with the target resonance, the higher can be the degree of control achieved on the resonance survival probability and lifetime. It is also noted that the enhancement of the ability of control when the density of overlapping resonances increases has been shown and

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discussed as well in the context of control of the decay of the whole coherent superposition of resonances prepared.^{29,30} Thus, investigating in detail how the degree of control of a single resonance lifetime can be increased when we change to a denser overlapping regime is a most interesting issue, and is the main goal of the present work.

The $\text{Br}_2(B, v')\text{--Ne}$ system presents the interesting advantage that for vibrational levels $v' > 27$ we can find the situation of higher density of overlapping resonances. It has been shown that for $v' > 27$ the ground vdW resonance of $\text{Br}_2(B, v')\text{--Ne}$ overlaps with a spectrum of several vdW resonances corresponding to the $v' - 1$ manifold and located below the $\text{Br}_2(B, v' - 1) + \text{Ne}$ dissociation threshold.^{34,35} Thus, by simply changing the vibrational level v' in $\text{Br}_2(B, v')\text{--Ne}$, it is possible to compare the behavior of a given control scheme in the cases of the very sparse overlapping regime of $v' = 27$ (with only two overlapping resonances) and of a denser overlapping regime ($v' > 27$). For this latter case the $v' = 35$ vibrational level has been chosen in this study in order to investigate how the degree of control can be increased when we change to a stronger overlapping regime.

The ground vdW resonance of $\text{Br}_2(B, v' = 35)\text{--Ne}$ is optically excited through the transition $\text{Br}_2(B, v' = 35)\text{--Ne} \leftarrow \text{Br}_2(X, v'' = 0)\text{--Ne}$. Then the resonance decays to the dissociation continuum following vibrational predissociation, $\text{Br}_2(B, v' = 35)\text{--Ne} \rightarrow \text{Br}_2(B, v_f < v') + \text{Ne}$.^{34–38} The calculated excitation spectrum associated with the ground vdW resonance of $\text{Br}_2(B, v' = 35)\text{--Ne}$ is displayed in Fig. 1. The main peak in the spectrum located at the energy -56.34 cm^{-1} (relative to the $\text{Br}_2(B, v' = 35, j' = 0) + \text{Ne}$ dissociation threshold) is associated with the ground vdW resonance of $\text{Br}_2(B, v' = 35)\text{--Ne}$, labeled as (v', gr) in the figure. The spectrum displays several other peaks and bumps at lower and higher energies than that of the main peak, which correspond to vdW resonances of the $v' - 1$ lower manifold that overlap between them and also with the v' ground res-

onance. Previous variational calculations of the zeroth-order energies of these $v' - 1$ resonances (see Table II of Ref. 35) allow one to identify the overlapping resonances associated with the main peaks of the spectrum. These resonances are those in the range $n = 5\text{--}13$, and their corresponding zeroth-order energies are -64.22 (for $n = 5$), -62.80 , -60.76 , -59.57 , -57.75 , -54.79 , -54.23 , -51.36 , and -50.99 cm^{-1} (for $n = 13$), respectively.

The $v' = 35$ excitation spectrum displays a remarkably denser regime of $v' - 1$ resonances overlapping with the v' ground resonance than in the $v' = 27$ case. In this situation new possibilities for control are expected to open up. In fact, a study of the control of the lifetime of the $\text{Br}_2(B, v' = 35)\text{--Ne}$ ground resonance by applying the control scheme using a single pulse of variable width has been recently reported.³⁹ That work indeed confirmed that the interference pattern found both in the survival probability of the v' ground resonance and in the transient population curves for appearance of $\text{Br}_2(B, v < v')$ products is more intense for $v' = 35$ than in the $v' = 27$ case, as a result of the larger number of $v' - 1$ overlapping resonances interfering with the v' one. It is stressed that the v' ground resonance survival probability and the $\text{Br}_2(B, v < v')$ appearance probabilities are observable quantities.^{38,40}

However, the more flexible control scheme using two pulses³³ (or even more) is expected to exploit better the new possibilities for control that appear with the denser overlapping regime. One of these possibilities is to select different $v' - 1$ overlapping resonances to be excited with the second pump laser pulse, which will probably lead to a different pattern of interference with the v' ground resonance, and to a correspondingly different degree of control. Another possibility is to use more than two pump laser pulses, for instance three ones, where the second and third pulses would excite different combinations of two energies associated mainly with $v' - 1$ resonances overlapping with the v' resonance excited with the first pulse, which is expected to enhance remarkably the intensity of interference and of control. The purpose of the present work is to explore these new possibilities of control. In addition, the effect of the control scheme applied on the survival probabilities of the $v' - 1$ overlapping resonances will be analyzed as well for the first time.

The paper is organized as follows. Section II describes briefly the methodology used. Section III presents and discusses the results. Some conclusions are given in Sec. IV.

II. METHODOLOGY

Optical excitation of the system to the $\text{Br}_2(B, v' = 35)\text{--Ne}$ ground vdW resonance and the subsequent predissociation of the complex was simulated with a three-dimensional wave packet method previously described in detail.³⁴ The wave packet is expanded on the basis of $\text{Br}_2(B, v)$ vibrational states v , and ten states, $v = v', v' - 1, v' - 2, \dots, v' - 9$ were used in the expansion. Details of the computation of the energies and wave functions of the v' and $v' - 1$ vdW resonances were given elsewhere.^{34,35} An empirical potential-energy surface is used.^{34,36}

FIG. 1. Calculated excitation spectrum associated with the ground vdW resonance of $\text{Br}_2(B, v' = 35)\text{--Ne}$. The energy axis is relative to the $\text{Br}_2(B, v' = 35, j' = 0) + \text{Ne}$ dissociation threshold. The arrows indicate the position of the zeroth-order energies of the $v' - 1$ vdW resonances $n = 5\text{--}13$, and of the $v' = 35$ ground (gr) vdW resonance.

In this work, three different pump laser electric fields have been applied, namely, one involving a single laser pulse, $E_1(t)$, one involving a combination of two laser pulses, $E_2(t)$, and a third one involving a combination of three laser pulses

$$E_1(t) = Ae^{-(t-t_1)^2/2\sigma^2} \cos \omega_1 t, \quad (1)$$

$$E_2(t) = Ae^{-(t-t_1)^2/2\sigma^2} \cos \omega_1 t + Ae^{-(t-t_2)^2/2\sigma^2} \cos \omega_2 t \quad (2)$$

and

$$E_3(t) = Ae^{-(t-t_1)^2/2\sigma^2} \cos \omega_1 t + Ae^{-(t-t_2)^2/2\sigma^2} \cos \omega_2 t + Ae^{-(t-t_3)^2/2\sigma^2} \cos \omega_3 t. \quad (3)$$

All the pulses involved in the three electric fields of Eqs. (1)–(3) were assumed to have the same intensity A and the same full width at half maximum (FWHM), related to σ , which in the time domain is FWHM = 200 ps, and corresponds to a spectral width of FWHM = 0.15 cm⁻¹. This narrow spectral width implies that each pulse excites a very narrow, nearly monochromatic distribution of energies. The phases of the pulses of the fields of Eqs. (1)–(3) have been assumed to be zero. It is well known that the relative phase between the two or three pulses is an additional control parameter that may have an impact on the control scheme outcome,^{18,20} and varying it is expected to have an effect also on the present interference mechanism between overlapping resonances and thus on their lifetime.

The frequency ω_1 in the three electric fields is the photon frequency required to excite the energy of the main peak of the excitation spectrum, -56.34 cm⁻¹. Thus, the pulse centered at ω_1 is the one exciting the Br₂(B, $v' = 35$)–Ne ground vdW resonance. The ω_2 and ω_3 frequencies are the photon frequencies required to excite the energies of peaks of the spectrum mainly associated with $v' - 1$ vdW resonances. While the energy excited with ω_1 is always the same (-56.34 cm⁻¹, associated with the v' ground resonance), depending on the specific simulation the peak energies excited with ω_2 and ω_3 will change in order to excite different $v' - 1$ resonances. In the simulations reported here three peak energies have been excited with the pulses centered at ω_2 and ω_3 , namely, -60.76, -57.75, and -54.23 cm⁻¹, indicated by the arrows labeled with $n = 7, 9$, and 11, respectively, in Fig. 1. These three peaks are the most intense ones closest in energy to the main peak of the spectrum, which is expected to involve a stronger overlapping of the corresponding $v' - 1$ resonances with the v' ground resonance. It is noted that in the present overlapping regime several $v' - 1$ resonances (and also the v' ground resonance) will contribute to each peak energy, although one of them will provide the main contribution.

In the three fields $E_1(t)$, $E_2(t)$, and $E_3(t)$ the time t_1 is always fixed at $t_1 = 0$, while t_2 and t_3 are fixed at $t_2 = t_3 = 120$ ps, which implies that in all the simulations the center of the second and third pulses is delayed by 120 ps from the center of the first pulse. It has been found³³ that the delay time between pulses is a parameter that affects dramatically the degree of control achieved on the resonance lifetime, and that can be optimized for each target resonance. It is stressed,

however, that in the present work no attempt has been made to optimize the delay time between pulses chosen.

III. RESULTS AND DISCUSSION

A. Simulations applying the single pulse electric field

When the electric field $E_1(t)$ is applied, a wave packet $\Phi(t)$ is created with a very narrow distribution of energies around the energy of the main peak of the spectrum. This wave packet contains contributions of several v' and $v' - 1$ overlapping resonances. Let us denote by ψ_{gr} and ψ_n the wave functions associated with the v' ground resonance and with the different $v' - 1$ resonances labeled by the n index, respectively. The survival probability associated with each of these resonances can be expressed as $I_{gr}(t) = |\langle \psi_{gr} | \Phi(t) \rangle|^2$ for the v' ground resonance and $I_n(t) = |\langle \psi_n | \Phi(t) \rangle|^2$ for the different $v' - 1$ resonances. Such survival probabilities obtained with the $E_1(t)$ field are shown in Fig. 2. No interference pattern, or at most a very weak, practically negligible one is displayed by the probability curves despite that several v' and $v' - 1$ resonances are populated. The practical absence of interference pattern is due to the very narrow spectral width of the wave packet prepared, which closely approaches the single energy component situation, and a single energy component does not interfere with itself.

It is noted that if the system was excited with a delta-function pulse (instead of with a narrow bandwidth pulse, as done here), all the v' and $v' - 1$ resonances having appreciable Frank-Condon factors with the ground state would be populated. Previous works using a single pump pulse with increasing bandwidth indicate that the lifetime of the v' ground resonance decreases remarkably as the spectral width of the pulse increases, due to the interference of the increasing number of overlapping resonances populated.^{31,39} Thus, it is expected that the v' ground resonance lifetime would reach a minimum for a delta-function excitation.

FIG. 2. Survival probabilities of the v' ground resonance and of the $v' - 1$ resonances $n = 5$ –12 calculated when the single pulse electric field $E_1(t)$ is applied.

The most interesting feature of the survival probabilities of Fig. 2 is that they provide information on the population of the different $v' - 1$ resonances at the energy of the v' ground resonance, and therefore provide an estimate of the extent to which they overlap. The figure shows that the strongest overlapping with the v' resonance occurs for the $v' - 1$ resonances $n = 9, 11, 8, 7$, and 10 (following this order), while overlapping of the v' resonance with the $v' - 1$ resonances $n = 5, 6$, and 12 is practically negligible. This result confirms that the three peak energies labeled as $n = 7, 9$, and 11 in Fig. 1 are the best candidates to be excited in order to induce a stronger interference with the v' ground resonance and to achieve a higher degree of control over its lifetime.

B. Simulations applying the two pulse electric field

When the two pulse electric field $E_2(t)$ is applied, two different peak energies are now excited (along with a narrow distribution of energies around them) in the superposition created. These two energy components of the wave packet, and therefore the v' and $v' - 1$ overlapping resonances contributing to them, can now interfere. The survival probability of the v' ground resonance, $I_{gr}(t)$, has been calculated when the second pulse centered at ω_2 excites the three energies associated mainly with the $v' - 1$ resonances $n = 7, 9$, and 11 , and they are plotted in Fig. 3(a). The $I_{gr}(t)$ survival probability obtained with the single pulse field $E_1(t)$ is also shown for comparison.

All the $I_{gr}(t)$ curves obtained with the $E_2(t)$ field show a strong pattern of interference. This interference pattern is characterized by a constant time separation between the peaks of the $I_{gr}(t)$ curves, which is inversely proportional to the separation of the two peak energies populated by the two pulses of the $E_2(t)$ field. The constant time separation between peaks in the $I_{gr}(t)$ curves found for the peak energies excited by the second pulse corresponding to $n = 7, 9$, and 11 are ~ 7 , ~ 24 , and ~ 15 ps, respectively. These time separations correspond to the separations of ~ 4.4 , ~ 1.4 , and ~ 2.1 cm^{-1} between the energies of the v' ground resonance and the $v' - 1$ resonances $n = 7, 9$, and 11 , respectively. The $E_2(t)$ field survival probability curves reach remarkably higher intensities and extend to longer times than the survival probability obtained with the single pulse field. Indeed, the single pulse probability decays completely at 200 ps, while the $E_2(t)$ curves reach up to 300 ps. While the $n = 7$ and 11 curves are very similar in intensity and temporal spreading, the $n = 9$ $I_{gr}(t)$ probability reaches a substantially higher intensity and temporal spreading, as a result of stronger interference between the corresponding excited v' and $v' - 1$ resonances.

Lifetimes τ associated with the four $I_{gr}(t)$ survival probabilities of Fig. 3(a) have been obtained by fitting the $I_{gr}(t)$ curves to the function

$$I_{gr}(t_j) = B \int_{-\infty}^{t_j} CC(t) [\exp(-(t_j - t)/\tau)] dt, \quad (4)$$

with $CC(t)$ being the cross-correlation curve of the laser pulse used to excite the v' ground resonance, and B being an amplitude scaling parameter.^{34,38} The fits obtained for three of the

FIG. 3. (a) Survival probabilities of the v' ground resonance obtained when the single pulse electric field $E_1(t)$ is applied, and when the two pulse field $E_2(t)$ is applied exciting the energies -60.76 cm^{-1} , -54.23 cm^{-1} , and -57.75 cm^{-1} mainly associated with the $n = 7, 11$, and 9 resonances, respectively, with the second pulse of the field. (b) Survival probabilities and their corresponding fits obtained with Eq. (4) for the v' ground resonance when the $E_1(t)$ field is applied, and when the $E_2(t)$ field is applied exciting the energies -54.23 cm^{-1} and -57.75 cm^{-1} mainly associated with the $n = 11$ and 9 resonances, respectively, with the second pulse of the field.

curves are shown in Fig. 3(b). The lifetime estimated for the single pulse $I_{gr}(t)$ survival probability is $\tau = 3.8$ ps, while the lifetimes obtained for the $E_2(t)$ field $I_{gr}(t)$ probabilities are $\tau = 43$ and 44 ps for excitation of the $n = 7$ and 11 peak energies, respectively, and $\tau = 61$ ps for the $n = 9$ peak energy. Thus, the v' ground resonance lifetime is strongly enhanced by a factor of about 11 when the energies associated with the $v' - 1$ resonances $n = 7$ and 11 are populated, and the factor of lifetime enhancement increases further up to 16 when the $n = 9$ peak energy is excited. Clearly the magnitude of control achieved on the lifetime enhancement increases remarkably when it is possible to select different overlapping resonances to interfere with the target resonance.

As previously discussed,^{31,33} for $\text{Br}_2(B, v' = 27)\text{-Ne}$ the two pulse electric field creates a superposition of

essentially two v' and $v' - 1$ overlapping resonances

$$\Phi(t) = a_{gr}(t)\psi_{gr}(t) + a_n(t)\psi_n(t). \quad (5)$$

In this case the survival probability associated with the $v'\psi_{gr}$ resonance can be expressed as

$$\begin{aligned} I_{gr}(t) &= |\langle \psi_{gr} | \Phi(t) \rangle|^2 \\ &= |a_{gr}(t)\langle \psi_{gr} | \psi_{gr}(t) \rangle + a_n(t)\langle \psi_{gr} | \psi_n(t) \rangle|^2 \\ &= |a_{gr}(t)|^2 |\langle \psi_{gr} | \psi_{gr}(t) \rangle|^2 + |a_n(t)|^2 |\langle \psi_{gr} | \psi_n(t) \rangle|^2 \\ &\quad + a_{gr}(t)a_n(t)^* \langle \psi_{gr} | \psi_{gr}(t) \rangle \langle \psi_n(t) | \psi_{gr} \rangle \\ &\quad + a_{gr}(t)^* a_n(t) \langle \psi_{gr}(t) | \psi_{gr} \rangle \langle \psi_{gr} | \psi_n(t) \rangle, \end{aligned} \quad (6)$$

where the last three terms are responsible for the interference pattern. There is a similar equation to Eq. (6) for $I_n(t) = |\langle \psi_n | \Phi(t) \rangle|^2$. Since for $v' = 27$ there is only one $v' - 1$ resonance ψ_n , in order to control the interference terms of Eq. (6) we can only modify the a_{gr} and a_n amplitudes of the superposition $\Phi(t)$, which was done by different means using electric fields with one pulse of variable width³¹ and two pulses.³³ However, in the denser overlapping regime of $v' = 35$ there are now available different $v' - 1$ resonances ψ_n to be excited with the second pulse of the electric field, creating the superposition

$$\Phi(t) = a_{gr}(t)\psi_{gr}(t) + \sum_n a_n(t)\psi_n(t). \quad (7)$$

Thus, in addition to vary the a_{gr} and a_n amplitudes, now it is possible to modify the overlapping factors $\langle \psi_{gr} | \psi_n(t) \rangle$ in the expression of $I_{gr}(t)$ by selecting different ψ_n resonances for excitation. The larger is the overlapping between ψ_{gr} and ψ_n , the larger will be the effect of the interference terms on $I_{gr}(t)$, and the degree of control achieved. This is why interference is stronger in the $I_{gr}(t)$ curve of Fig. 3 obtained for the $n = 9$ peak energy, because the overlapping between ψ_{gr} and ψ_9 is the largest (see Fig. 2). Then, the denser overlapping regime allows for selective control over a new element of the $I_{gr}(t)$ survival probability, namely, the overlapping factor $\langle \psi_{gr} | \psi_n(t) \rangle$, in addition to the amplitudes of the resonances in the coherent superposition.

As mentioned above, several v' and $v' - 1$ resonances contribute to each peak energy excited. It means that each pulse of the $E_2(t)$ field populates several $v' - 1$ resonances ψ_n [instead of only one as in Eq. (5)] with different weights [see Eq. (7)]. Thus, with only two pulses we can achieve interference of the v' resonance with several $v' - 1$ resonances, leading to a large number of interference terms [many more than three ones as in Eq. (6)] affecting the $I_{gr}(t)$ survival probability. This increases dramatically the intensity of interference and the degree of control, and explains the large factors 11 and 16 of lifetime enhancement achieved without optimization of other parameters.

C. Simulations applying the three pulse electric field

Simulations have been carried out applying the $E_3(t)$ electric field involving three pump pulses. In particular, two different situations have been investigated, namely, one where

FIG. 4. Survival probabilities of the v' ground resonance obtained when the three pulse electric field $E_3(t)$ is applied, exciting with the second and third pulses the energies -60.76 cm^{-1} and -57.75 cm^{-1} mainly associated with the $v' - 1$ resonances $n = 7$ and 9 , respectively, and also exciting with the second and third pulses the energies -57.75 cm^{-1} and -54.23 cm^{-1} mainly associated with the $v' - 1$ resonances $n = 9$ and 11 . The survival probability obtained for the v' ground resonance by applying the $E_1(t)$ field is also shown in the figure for comparison.

the ω_2 and ω_3 pulses excite the peak energies mainly associated with the $n = 7$ and 9 resonances (-60.76 and -57.75 cm^{-1}), respectively, and another one where those pulses excite the peak energies of the $n = 9$ and 11 resonances (-57.75 and -54.23 cm^{-1}), respectively. The survival probability $I_{gr}(t)$ calculated in the two cases is shown in Fig. 4, along with the survival probability obtained with the single pulse field $E_1(t)$ for comparison.

As expected, the curves of Fig. 4 display a more intense interference pattern and a longer temporal spreading than the survival probabilities of Fig. 3. This is the result that a larger number of $v' - 1$ resonances overlapping with the v' resonance are now simultaneously excited, which leads to a remarkably larger number of interference terms affecting the shape of the $I_{gr}(t)$ probability. The lifetimes associated with the survival probabilities of Fig. 4 are correspondingly longer, being $\tau = 70 \text{ ps}$ for the $I_{gr}(t)$ curve obtained when the energies associated with the $n = 7$ and 9 resonances are excited, and $\tau = 73 \text{ ps}$ when the energies excited correspond to the $n = 9$ and 11 resonances. Thus, in this case the v' ground resonance lifetime is enhanced by nearly a factor of 20 with respect to the situation when a single pulse electric field is used.

It should be noted that the survival probabilities of Fig. 4 display now two different constant time separations between peaks. The two time separations are directly related to the two energy separations between the three peak energies that are populated by the three pulse field $E_3(t)$. It is also worth noting that the largest lifetime enhancement, up to 73 ps , is obtained when we excite the energies associated mainly with the $n = 9$ and 11 resonances. These two resonances are those leading also to the largest lifetime enhancements (up to 61 and 44 ps , respectively) when they are excited separately. This result indicates that selectivity still operates when a combination of

FIG. 5. (a) Survival probabilities calculated for the v' ground resonance and for the $v' - 1$ resonances $n = 5$ –12 when the $E_2(t)$ field is applied exciting with the second pulse of the field the energy -57.75 cm^{-1} mainly associated with the $v' - 1$ resonance $n = 9$. (b) Same as (a) but for the case when the energy -54.23 cm^{-1} , mainly associated with the $v' - 1$ resonance $n = 11$ is excited with the second pulse of the field. The survival probability obtained for the v' ground resonance by applying the $E_1(t)$ field is shown in the two panels for comparison.

two energies mainly associated with $v' - 1$ resonances are populated simultaneously with the $E_3(t)$ field, and that different combinations of two such energies will produce different control outcomes.

D. Survival probabilities of the $v' - 1$ resonances

It is very interesting to analyze also the behavior of the $I_n(t)$ survival probabilities of the different $v' - 1$ resonances ψ_n when the energy excited by the second pulse of the electric field $E_2(t)$ is varied. Figure 5 shows the survival probabilities $I_{gr}(t)$ and $I_n(t)$ for the resonances $n = 5$ –12 for two different situations, namely, when the second pulse of $E_2(t)$ excites the peak energies mainly associated with the $n = 9$ and 11 resonances. The $I_{gr}(t)$ curve obtained with the single pulse field $E_1(t)$ is also shown in the two cases for comparison.

Figure 5 displays the interesting finding that all the $I_{gr}(t)$ and $I_n(t)$ survival probabilities present a similar interference pattern with the same time separation between peaks. While this was expected because it is determined by the energy separation $\omega_1 - \omega_2$, the interesting feature found in the two panels of the figure is that the interference patterns of all the survival probabilities are nearly in phase, that is, the peaks of the different $I_{gr}(t)$ and $I_n(t)$ curves nearly coincide. This result is likely due to the narrow spectral width of the two pump pulses. This finding may have two important implications. One is of experimental interest. Indeed, when probing experimentally the survival probability of $\text{Br}_2(B, v' = 35)$ –Ne at the energy of the maximum of the excitation spectrum, where the v' resonance overlaps strongly with several $v' - 1$ resonances (see Fig. 2), since the interference patterns of all the v' and $v' - 1$ resonances are similar and nearly in phase, the interference pattern of the system survival probability probed is very likely to survive and to be observed. The other implication involves the appearance of an additional parameter of control. Since the time separation between the peaks in the interference pattern of the different survival probabilities depends on the $\omega_1 - \omega_2$ separation, we can control it by selecting different peak energies to be excited with the ω_2 pulse. Control on the periodicity of the interference peaks can be used to make more effective further excitation of the system to other electronic or vibrational states, as in the case of the vibrational revivals.²³

As expected, Fig. 5 shows that the strongest interference effects are displayed by the v' and $v' - 1$ survival probabilities that are populated simultaneously by the two pulses of $E_2(t)$. In this sense, the strongest enhancement of intensity and time spreading is found for the $I_{gr}(t)$, $I_8(t)$, and $I_9(t)$ (and to a lesser extent the $I_7(t)$) survival probabilities in Fig. 5(a), and for the $I_{gr}(t)$ and $I_{11}(t)$ (and to a lesser extent the $I_{10}(t)$) survival probabilities in Fig. 5(b). When the system is excited to a given energy (or to a narrow bandwidth around this energy), for instance, the energy -56.34 cm^{-1} of the maximum of the excitation spectrum, several v' and $v' - 1$ overlapping resonances contribute to this energy, and the interference effects of their corresponding survival probabilities will add together. By means of interference we are enhancing the lifetime not only of the v' ground resonance, but also of some of the $v' - 1$ resonances contributing to the above energy. Thus, the interesting implication is that in a denser overlapping regime, the final lifetime enhancement of the survival probability of the system at that energy can be remarkably larger than that associated only with the target v' ground resonance survival probability.

E. Population curves for appearance of Br_2

The behavior of the time-dependent probability curves of appearance of the $\text{Br}_2(B, v < v')$ product fragments has also been investigated. Such probability curves are calculated by accumulating the wave packet probability in the asymptotic region where the Br_2 –Ne complex can be considered dissociated (for Ne and Br_2 separations larger than $20.0a_0$), for the different vibrational manifolds v of the $\text{Br}_2(B, v < v')$

FIG. 6. Population curves for appearance of $\text{Br}_2(B, v < v' = 35)$ products vs time, for excitation of the $\text{Br}_2(B, v' = 35)\text{-Ne}$ complex using the single pulse, the two pulse, and the three pulse electric fields. When the two pulse field is used, $\text{Br}_2(B, v < v')$ population curves are shown when the second pulse excites the energies associated mainly with the $v' - 1$ resonances $n = 7, 9$, and 11 . When the three pulse field is applied, $\text{Br}_2(B, v < v')$ population curves are shown when the second and third pulses populate the energies associated mainly with the $v' - 1$ resonances $n = 7$ and 9 , respectively, and $n = 9$ and 11 , respectively. Fits to the $\text{Br}_2(B, v = v' - 2)$ population curves, used to estimate associated lifetimes in all cases, are also shown in the figure.

product. In the case of the $\text{Br}_2(B, v' = 35)\text{-Ne}$ ground resonance the $\Delta v' = -1$ dissociation channel is energetically closed, and therefore only the $v \leq v' - 2$ vibrational states can be populated. The difference between the survival probability curve $I_{gr}(t)$ and the $\text{Br}_2(B, v < v')$ appearance probability curves is that only a single resonance (the v' ground one)

contributes to $I_{gr}(t)$, while all the populated v' and $v' - 1$ vdW resonances will contribute to the appearance probabilities. Thus, substantial changes in the shape of the $\text{Br}_2(B, v < v')$ appearance probability curves can be expected as the number and nature of the $v' - 1$ resonances populated is varied. In Fig. 6, the $\text{Br}_2(B, v < v')$ appearance population curves

for $v = v' - 2, v' - 3, \dots, v' - 6$ calculated by applying the electric fields with a single pulse, two pulses, and three pulses, are shown.

Interestingly, in general the $\text{Br}_2(B, v < v')$ appearance curves obtained with the two and three pulse fields show an interference pattern. Such a pattern is displayed by the population curves corresponding to all the different $\Delta v'$ dissociation channels. As in the case of the $I_{gr}(t)$ survival probabilities of Figs. 3 and 4, the intensity of the pattern is larger as the overlapping between the v' and the $v' - 1$ resonances excited is stronger (the strongest overlapping occurring with the $n = 9$ resonance), and as the number of $v' - 1$ resonances populated increases, when the three pulse electric fields are used. The constant time separations of the patterns of Fig. 6, namely, a single time separation with the two pulse fields and two different time separations with the three pulse fields, are the same as those found in the $I_{gr}(t)$ survival probabilities. The main difference between the interference patterns of Fig. 6 and those of Figs. 3 and 4 is that the intensity of the former ones is dramatically smaller, and they have been mostly washed out.

The reason why the interference pattern is mostly washed out in the $\text{Br}_2(B, v < v')$ product probability curves is related to the fact that the different v' and $v' - 1$ resonances contributing to the $\text{Br}_2(B, v < v')$ curves have different predissociation lifetimes, and therefore different time scales for dissociation through the $\Delta v'$ channels to produce $\text{Br}_2(B, v < v')$ fragments. These different time scales cause a dephasing in time of the maxima and minima of the interference patterns of the different resonances contributing to the $\text{Br}_2(B, v < v')$ curves, which leads to almost disappearance of the pattern in the product probability curves. This situation is in sharp contrast with that of the $I_{gr}(t)$ survival probabilities of the different v' and $v' - 1$ resonances, whose interference patterns are nearly in phase, as discussed above (see Fig. 5). However, the result that the interference pattern is still able to survive in the $\text{Br}_2(B, v < v')$ product curves seems to support strongly the chances to observe the (nearly in phase) pattern of the $I_{gr}(t)$ survival probability curves of Fig. 5.

As mentioned above, in a regime of relatively strong overlapping like that of $\text{Br}_2(B, v' = 35)\text{-Ne}$, the $\text{Br}_2(B, v < v')$ population curves are an average of contributions from all the v' and $v' - 1$ resonances excited. This has two main implications. The first implication is that the lifetime associated with the $\text{Br}_2(B, v < v')$ curves is an average of the predissociation lifetimes of all the resonances contributing to the product curves, and therefore this lifetime is no longer directly related only to the lifetime of the v' ground resonance, as it happens when the v' ground resonance is isolated, not overlapping with other vdW resonances.

The second implication, derived from the above one, is that the lifetime for $\text{Br}_2(B, v < v')$ product appearance can be modified and control to some extent by changing the number and nature of the $v' - 1$ vdW resonances populated with the second (and third) pulse(s). It is noted, however, that this type of lifetime control for $\text{Br}_2(B, v < v')$ product appearance is rather unrelated to the mechanism of interference between overlapping resonances. The $\text{Br}_2(B, v = v' - 2)$ curves of Fig. 6 have been fitted to a convolution function^{34,38} (shown

in Fig. 6) in order to estimate the corresponding lifetimes. The lifetimes obtained are $\tau = 7.3$ ps when the single pulse field is used, $\tau = 31, 40$, and 25 ps when the two pulse field is used and the energies mainly associated with the $v' - 1$ resonances $n = 7, 9$, and 11 are excited with the second pulse, respectively, and $\tau = 41$ and 43 ps when the three pulse field is used and the energies mainly associated with the $v' - 1$ resonances $n = 7$ and 9 and $n = 9$ and 11 are excited with the second and third pulses, respectively. Indeed such $\text{Br}_2(B, v = v' - 2)$ appearance lifetimes are quite different from the lifetimes found for the corresponding $I_{gr}(t)$ survival probabilities of the v' resonance, due to the contributions of the $v' - 1$ resonances. A substantial variation of the appearance lifetime, from 7.3 to 43 ps, is found by using second and third pulses and selecting different additional energies to be excited corresponding to different $v' - 1$ resonances.

The curves of Fig. 6 show another interesting result. By increasing the number of overlapping resonances populated by the second and third pump pulses, and also by increasing the magnitude of the overlapping between them, leads to an increase of the proportional weight of the population of $\text{Br}_2(B, v)$ in the lower vibrational levels $v < v' - 2$. This is particularly clear for the $v' - 3$ population. It thus appears that increasing the overall overlapping between the resonances populated favors the vibrational deactivation of the $\text{Br}_2(B, v)$ fragment produced. It should be worth to investigate further this point, since it might have potential interest in the cooling of the internal excitation of molecules.⁴¹⁻⁴⁴

IV. CONCLUSIONS

This work shows that moving to a denser regime of overlapping resonances opens up new possibilities for control of a system lifetime in a target resonance, using a control scheme with two (or more) pump laser pulses of simple experimental application. In particular, increasing the available number of resonances overlapping with the target resonance allows one to be more selective when choosing the resonance(s) interfering with the target one, which also increases the degree of control achieved. A higher density of overlapping resonances also involves remarkably stronger interference effects, leading to a very large lifetime enhancement for the target resonance by a factor of up to 20, without any optimization of other parameters of the control scheme. The present results and conclusions are general to any system with a regime of overlapping resonances where Eq. (7) is valid and an external field like $E_2(t)$ or $E_3(t)$ can be applied.

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¹S. A. Rice and M. Zhao, *Optical Control of Molecular Dynamics* (Wiley, New York, 2000).

- ²M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley, New York, 2003).
- ³D. Tannor and S. Rice, *J. Chem. Phys.* **83**, 5013 (1985).
- ⁴D. J. Tannor, R. Kosloff, and S. Rice, *J. Chem. Phys.* **85**, 5805 (1986).
- ⁵P. Brumer and M. Shapiro, *Chem. Phys. Lett.* **126**, 541 (1986).
- ⁶E. D. Potter, J. L. Herek, S. Pedersen, Q. Liu, and A. H. Zewail, *Nature (London)* **355**, 66 (1992).
- ⁷W. S. Warren, H. Rabitz, and M. Dahleh, *Science* **259**, 1581 (1993).
- ⁸D. J. Tannor and A. Bartana, *J. Phys. Chem. A* **103**, 10359 (1999).
- ⁹P. Anfinrud, R. de Vivie-Riedle, and V. Engel, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 8328 (1999).
- ¹⁰R. B. Gerber, M. V. Korolkov, J. Manz, M.-Y. Niv, and B. Schmidt, *Chem. Phys. Lett.* **327**, 76 (2000).
- ¹¹R. J. Levis, G. M. Menkir, and H. Rabitz, *Science* **292**, 709 (2001).
- ¹²E. Skovsen, M. Machholm, T. Ejdrup, J. Thøgersen, and H. Stapelfeldt, *Phys. Rev. Lett.* **89**, 133004 (2002).
- ¹³M. Wollenhaupt, A. Assion, D. Liese, C. Sarpe-Tudoran, T. Baumert, S. Zamith, M. A. Boucheme, B. Girard, A. Flettner, U. Weichmann, and G. Gerber, *Phys. Rev. Lett.* **89**, 173001 (2002).
- ¹⁴C. Daniel, J. Full, L. González, C. Lupulescu, J. Manz, A. Merli, S. Vajda, and L. Wöste, *Science* **299**, 536 (2003).
- ¹⁵C. Petersen, E. Péronne, J. Thøgersen, and H. Stapelfeldt, *Phys. Rev. A* **70**, 033404 (2004).
- ¹⁶G. Vogt, G. Krampert, P. Niklaus, P. Nuernberger, and G. Gerber, *Phys. Rev. Lett.* **94**, 068305 (2005).
- ¹⁷B. J. Sussman, D. Townsend, M. I. Ivanov, and A. Stolow, *Science* **314**, 278 (2006).
- ¹⁸Y.-C. Han, K.-J. Yuan, W.-H. Hu, T.-M. Yan, and S.-L. Cong, *J. Chem. Phys.* **128**, 134303 (2008).
- ¹⁹T. Bayer, M. Wollenhaupt, C. Sarpe-Tudoran, and T. Baumert, *Phys. Rev. Lett.* **102**, 023004 (2009).
- ²⁰I. Znakovskaya, P. von den Hoff, S. Zhrebtssov, A. Wirth, O. Herrwerth, M. J. J. Vrakking, R. de Vivie-Riedle, and M. F. Kling, *Phys. Rev. Lett.* **103**, 103002 (2009).
- ²¹H. Goto, H. Katsuki, H. Ibrahim, H. Chiba, and K. Ohmori, *Nat. Phys.* **7**, 383 (2011).
- ²²H. Li, A. D. Bristow, M. E. Siemens, G. Moody, and S. T. Cundiff, *Nat. Commun.* **4**, 1390 (2013).
- ²³S. Meyer and V. Engel, *J. Phys. Chem. A* **101**, 7749 (1997).
- ²⁴C. Meier and J. A. Beswick, *J. Chem. Phys.* **121**, 4550 (2004).
- ²⁵H. Katsuki, H. Chiba, B. Girard, C. Meier, and K. Ohmori, *Science* **311**, 1589 (2006).
- ²⁶G. Katz, M. A. Ratner, and R. Kosloff, *Phys. Rev. Lett.* **98**, 203006 (2007).
- ²⁷M. P. A. Branderhorst, P. Londero, P. Wasylczyk, C. Brif, R. L. Kosut, H. Rabitz, and I. A. Walmsley, *Science* **320**, 638 (2008).
- ²⁸(a) M. Shapiro, *J. Phys. Chem. A* **102**, 9570 (1998); (b) E. Frishman and M. Shapiro, *Phys. Rev. Lett.* **87**, 253001 (2001).
- ²⁹P. S. Christopher, M. Shapiro, and P. Brumer, *J. Chem. Phys.* **123**, 064313 (2005); T. Grinev, M. Shapiro, and P. Brumer, *J. Chem. Phys.* **137**, 094302 (2012).
- ³⁰T. Grinev, M. Shapiro, and P. Brumer, *J. Chem. Phys.* **138**, 044306 (2013).
- ³¹A. García-Vela, *J. Chem. Phys.* **136**, 134304 (2012).
- ³²A. García-Vela, *J. Chem. Phys.* **129**, 094307 (2008).
- ³³A. García-Vela, *J. Phys. Chem. Lett.* **3**, 1941 (2012).
- ³⁴A. García-Vela and K. C. Janda, *J. Chem. Phys.* **124**, 034305 (2006).
- ³⁵A. García-Vela, *J. Chem. Phys.* **126**, 124306 (2007).
- ³⁶M. Nejad-Sattari and T. A. Stephenson, *J. Chem. Phys.* **106**, 5454 (1997).
- ³⁷T. A. Stephenson and N. Halberstadt, *J. Chem. Phys.* **112**, 2265 (2000).
- ³⁸J. A. Cabrera, C. R. Bieler, B. C. Olbricht, W. E. van der Veer, and K. C. Janda, *J. Chem. Phys.* **123**, 054311 (2005).
- ³⁹A. García-Vela, *Chem. Phys. Lett.* **563**, 30 (2013).
- ⁴⁰J. M. Pio, M. A. Taylor, W. E. van der Veer, C. R. Bieler, J. A. Cabrera, and K. C. Janda, *J. Chem. Phys.* **133**, 014305 (2010).
- ⁴¹N. Balakrishnan, R. C. Forrey, and A. Dalgarno, *Phys. Rev. Lett.* **80**, 3224 (1998).
- ⁴²E. Bodo, F. A. Gianturco, and A. Dalgarno, *J. Chem. Phys.* **116**, 9222 (2002).
- ⁴³J. M. Hutson, M. Beyene, and M. L. González-Martínez, *Phys. Rev. Lett.* **103**, 163201 (2009).
- ⁴⁴A. García-Vela, I. Cabanillas-Vidosa, J. C. Ferrero, and G. A. Pino, *Phys. Chem. Chem. Phys.* **14**, 5570 (2012).