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Quantum Interference Control of an Isolated Resonance Lifetime in the Weak-Field Limit

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Abstract

Resonance states play an important role in a large variety of physical and chemical processes. Thus, controlling the resonance behavior, and particularly a key property like the resonance lifetime, opens up the possibility of controlling those resonance mediated processes. While such a resonance control is possible by applying strong-field approaches, the development of flexible weak-field control schemes that do not alter significantly the system dynamics still remains a challenge. In this work, one such control scheme within the weak-field regime is proposed for the first time in order to modify the lifetime of an isolated resonance state. The basis of the scheme suggested is quantum interference between two pathways induced by laser fields, that pump wave packet amplitude to the target resonance under control. The simulations reported here show that the scheme allows for both enhancement and quenching of the resonance survival lifetime, being particularly flexible to achieve large lifetime enhancements. Control effects on the resonance lifetime take place only while the pulse is operating. In addition, the conditions required to generate the two interfering quantum pathways are found to be rather easy to meet for general systems, which makes the experimental implementation straightforward and implies a wide applicability of the control scheme.

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Introduction

Coherent control of a quantum system aimed at steering its dynamical evolution towards a desired target has been a goal pursued for a long time[1,2]. Control strategies have been developed for different molecular processes like photodissociation,[3–6] molecular reactions,[7–13] radiationless transitions,[14,15] and decoherence.[16–21] Several control targets have been pursued. Some of them are the enhancement of the yield of a specific chemical reaction pathway among the different competing ones,[6–13] and the minimization (or even suppression) of intramolecular vibrational redistribution (IVR) and decoherence mechanisms of coherent superposition states.[16–21] This latter control target is directly related to the development of quantum computing.

The use of external strong fields able to induce changes in the molecular Hamiltonian has been an essential feature in the development of very successful control schemes.[9–12] An advantage of the strong-field control approaches is that no additional excitation to other electronic states than those involved in the process under control is needed. A disadvantage is that undesired multiphoton ionization and fragmentattion of the system may occur. An alternative is to develop control schemes in the weak-field regime.[22] Weak-field control schemes typically rely on the manipulation of interference between two or more quantum pathways leading to the same final state.[23] One of these pathways is the process to be controlled. Thus, developing a control scheme essentially consists of finding one or more additional pathways that can interfere with the process of interest, and whose signal intensity can be manipulated in order to control their interference with the target process.

Resonance states are intriguing objects of quantum nature that share features of both bound and continuum states. One of these features is that resonances have a finite lifetime that can vary remarkably by several orders of magnitude for different resonance states. Another interesting feature of resonances is that they can be located at places where no bound states are present, for instance, embedded in a continuum. Such features make resonances ideal intermediate or doorway states from which some molecular processes can be activated. From this point of view, it

would be highly desirable to be able to modify and control the lifetime of a specific resonance of interest. Such a control would involve controlling the molecular process mediated by that resonance state. Clearly, this is possible by using strong fields that modify the potential-energy surface supporting the resonance state and its coupling to the continuum states. However, it would also be very interesting to develop flexible weak-field control schemes to control the resonance lifetime that do not alter the nature of the system and its dynamics.

Recently, weak-field control schemes have been proposed to modify the lifetime of a specific resonance that overlaps with other resonance states, when they are populated in a coherent superposition.[24–27] Such control schemes are based on the finding[24] that the lifetime of a specific overlapping resonance state depends strongly on the amplitudes of the other overlapping resonances populated in the superposition. The reason of this dependence is that the resonances overlapping with the target resonance subject to control interfere with it, and the intensity of this interference mechanism can be controlled by modifying the amplitudes of the different overlapping resonances in the superposition state prepared. Control of the intensity of the resonance interference allows one to control the resonance lifetime. The control schemes proposed were applied to control the resonance decay in the vibrational predissociation dynamics of the Ne-$Br_2(B, v')$ van der Waals (vdW) complex, which is a system reach in overlapping resonances. Previous works have addressed the control of the lifetime of a whole superposition state of overlapping resonances (instead of a single resonance state), by varying the amplitude coefficient of the different overlapping resonances within the superposition.[3,21,28,29] It was also shown in a recent work that postpulse coherent control of transient photofragment distributions can be achieved by means of laser phase modulation, when a superposition of overlapping resonances is prepared in Ne-$Br_2(B)$.[30]

Now, a most interesting question is whether one can also control the lifetime of an isolated (nonoverlapping) resonance state in the weak-field regime. For an isolated resonance, its lifetime is an intrinsic property (related to the intrinsic width

of the resonance) when the whole resonance bandwidth is populated. As mentioned above, it can be modified in the presence of intense laser pulses (strong-field regime) that change the nature of the system Hamiltonian. In the weak-field regime the lifetime of an isolated resonance can be also modified to some extent by varying the bandwidth of the laser pulse used to populate the resonance. More specifically, for an isolated resonance with a given energy width, it is possible to change the "intrinsic lifetime" achieved when the whole resonance width is populated, to a somewhat different value if only part of the resonance spectral width is excited with a narrow enough bandwidth pulse. The maximum lifetime increase that can be obtained in this way is that corresponding to populating a narrow bandwidth that includes only the longest-lived energy components of the resonance state. Therefore, the effects of control over the lifetime with this approach are rather limited. In addition, application of this control method is typically restricted to rather broad resonances, because for narrow resonances pulses with very long time durations (and very narrow bandwidths) must be used in order to be effective.

Thus, a weak-field scheme that allows a larger degree of control over the lifetime, and that can be applied to a general resonance regardless its width size, is desirable. In this work, such a flexible control scheme is suggested for the first time, and it is demonstrated that the lifetime of an isolated resonance can be controlled in the weak-field regime with the aid of interference. This is shown by applying the proposed control scheme to the decay dynamics of the Ne-$Br_2(B, v' = 16)$ ground intermolecular resonance (*i.e.*, the lowest energy resonance in the spectrum of intermolecular vdW resonances of the $v' = 16$ vibrational manifold), which is an isolated resonance state.

Theoretical background

Upon laser excitation, Ne-$Br_2(X, v'' = 0) + h\nu \rightarrow$ Ne-$Br_2(B, v' = 16)$, the ground vdW resonance of Ne-$Br_2(B, v' = 16)$ is populated. Then the resonance excited decays to the fragmentation continuum through vibrational predissociation, Ne-

$Br_2(B, v' = 16) \rightarrow Ne + Br_2(B, v_f < v')$. This process has been studied in detail both experimentally[31,32] and theoretically.[33–36] The process of Ne-$Br_2(B, v' = 16)$ excitation with a laser pulse and the subsequent predissociation of the complex was simulated with a full three-dimensional wave packet method (assuming zero total angular momentum for the system), described in detail elsewhere.[24,34] The pump laser electric field applied for the $X \rightarrow B$ excitation has a Gaussian form

$$\mathcal{E}_{pump}(t) = \mathcal{E}_0 e^{-(t-t_0)^2/2\sigma_0^2} \cos(\omega_0 t + \phi_0), \quad (1)$$

where ω_0 is the photon frequency required to excite the Ne-$Br_2(B, v' = 16)$ ground resonance, and the phase ϕ_0 is taken to be $\phi_0 = 0$. The temporal full width at half maximum (FWHM) of the pulse (related to σ_0) is FWHM= 10 ps, which corresponds to a spectral width of FWHM= 3 cm^{-1}. The maximum pulse amplitude used is $\mathcal{E}_0 = 1.0 \times 10^{-6}$ a.u., which corresponds to a maximum pulse intensity of about 3.5×10^4 W/cm^2, within the weak-field regime.

It is noted that the lifetime calculated with the present theoretical model for the decay of the Ne-$Br_2(B, v' = 16)$ ground resonance is 69 ps, while the corresponding lifetime estimated experimentally is 68 ± 3 ps.[32] This good agreement with the experimental lifetime implies that both the three-dimensional wave packet method and the potential surfaces used in the present simulations are quite realistic in order to describe this resonance decay process. The Ne-$Br_2(B, v' = 16)$ ground resonance is separated from the first excited intermolecular resonance by $\sim$ 17 cm^{-1}. The linewidth associated with a lifetime of 69 ps is much narrower than that energy separation, which implies that indeed the ground resonance is well isolated. In addition, with the above pump pulse bandwidth (FWHM= 3 cm^{-1}) it is ensured that the Ne-$Br_2(B, v' = 16)$ ground resonance is the only resonance state populated.

Now, a second quantum pathway that populates the Ne-$Br_2(B, v' = 16)$ ground resonance in an alternative way to the $X \rightarrow B$ excitation described above, and that therefore can interfere with it, is required. Such a pathway can be generated by applying a second pulse (or actually a pulse train) that induces a $B \rightarrow E$ transition to the E excited electronic state of Ne-Br_2. More specifically, the control pulse train

would pump wave packet amplitude from the Ne-$Br_2(B, v' = 16)$ ground resonance to the ground intermolecular resonance state of the Ne-$Br_2(E, v)$ system. Once population is generated in the Ne-$Br_2(E, v)$ ground resonance, the radiative coupling also induces the reverse transition $E \rightarrow B$ (stimulated emission) between the ground resonances of Ne-$Br_2(E, v)$ and Ne-$Br_2(B, v' = 16)$, and this completes the alternative pathway required to populate the Ne-$Br_2(B, v' = 16)$ resonance. Thus, amplitude in the Ne-$Br_2(B, v' = 16)$ ground resonance is now generated through two different quantum pathways, namely the $X \rightarrow B$ transition on the one side (pathway A), and the $B \rightarrow E$ and $E \rightarrow B$ combined transitions on the other side (pathway B), and the corresponding amplitudes will interfere. A schematic picture of the two interfering pathways A and B is displayed in Fig. 1. It should be emphasized that pathway A to the Ne-$Br_2(B, v' = 16, n' = 0)$ ground resonance operates only during the relatively short duration (FWHM= 10 ps) of the pump pulse of eqn (1). After this pulse is over, only the control pulse of eqn (2) inducing pathway B operates, making possible a continuous flow of wave packet amplitude through the $B \rightarrow E$ and $E \rightarrow B$ transitions.

The control pulse train applied is a sum of Gaussian pulses, and has the form

$$\mathcal{E}(t) = \sum_{k=1}^{N} \mathcal{E}_k e^{-(t-t_k)^2/2\sigma_k^2} \cos(\omega_1 t + \phi_k), \qquad (2)$$

where ω_1 is the photon frequency required for the transition between the ground resonances of Ne-$Br_2(B, v' = 16)$ and Ne-$Br_2(E, v)$. In the simulations reported here different control pulse trains have been used with different combinations of N, $\mathcal{E}_k$, t_k, and σ_k, but in all cases $\phi_k = 0$, $\forall k$. Details of the potential-energy surface used for the E electronic state and of the wave packet method applied in that state (the same as that applied in the B state) have been given elsewhere.[27]

The control strategy underlying the design of the above alternative pathway is to generate a reservoir of wave packet amplitude in the Ne-$Br_2(E, v)$ ground resonance, that can be used to induce and control interference with the amplitude pumped to the Ne-$Br_2(B, v' = 16)$ resonance under control through the $X \rightarrow B$ transition. In this way, the survival probability of the Ne-$Br_2(B, v' = 16)$ ground resonance, and

therefore the associated lifetime, can be modified and controlled. The use of weak fields to induce both the $X \rightarrow B$ and the $B \rightarrow E$ (and the subsequent $E \rightarrow B$) transitions might lead to think that the intensity of the interference produced could not be enough as to cause appreciable effects in the survival probability of the target resonance. Indeed, a weak $\mathcal{E}_{pump}(t)$ field will not pump a large amount of amplitude to the Ne-$Br_2(B, v' = 16)$ resonance, out of which also a rather small amount of amplitude will be excited to the Ne-$Br_2(E, v)$ ground resonance by the weak $\mathcal{E}(t)$ control field, out of which the final amplitude producing the interference is generated through the $E \rightarrow B$ transition. This control scheme, however, depends on two factors that, under certain conditions, can favor a substantial increase of the transfer of wave packet amplitude through the $B \rightarrow E$ and $E \rightarrow B$ transitions, even using weak fields.

The first factor is the dependence of the intensity of the $B \rightarrow E$ and $E \rightarrow B$ transitions on the Franck-Condon factor between the Ne-$Br_2(B, v' = 16)$ and Ne-$Br_2(E, v)$ resonances. Since in this work the ground intermolecular resonance is involved in both cases, the overlap between them is maximal (~ 0.99) because the two associated wave functions have a very similar shape, and the Franck-Condon factor depends essentially on the overlap between the $(B, v' = 16)$ and (E, v) vibrational states of Br_2, $\chi^B_{v'=16}$ and χ^E_v, respectively. Then, by properly choosing the (E, v) vibrational state, it is possible to maximize the Franck-Condon factor and therefore the transfer of amplitude in the $B \rightarrow E$ and $E \rightarrow B$ transitions. The $< \chi^B_{v'=16} | \chi^E_v >$ overlap can be positive or negative, and this sign contributes as a phase in the interference mechanism that can be used as a control parameter, as we shall see below. The second factor is related to the duration of the lifetime of the target resonance in the absence of control field. Indeed, if this lifetime is not very short, the control field will have time enough to transfer a sufficiently large amount of wave packet amplitude to the reservoir of the intermediate Ne-$Br_2(E, v)$ resonance state through the alternative quantum pathway, as to produce an interference intense enough to make possible the control of the resonance survival

probability. In this sense, a threshold is expected for the resonance lifetime, below which (very short lifetimes) the control scheme will become inefficient, while above which the scheme will work increasingly better as the resonance lifetime increases. It is noted that the above conditions favoring the control efficiency, namely an appreciable Franck-Condon factor between the target resonance and the intermediate state in the alternative quantum pathway, and not a very short lifetime of the target resonance, are quite generally met in many molecular systems, and therefore they do not seem to restrict much the applicability of the control scheme.

Results and discussion

In the simulations carried out, the intermediate state of the alternative pathway consisting of the $B \rightarrow E$ and $E \rightarrow B$ transitions is the Ne-$Br_2(E, v)$ ground resonance of the $v = 4$, 5, and 6 vibrational states of $Br_2(E)$. The corresponding $< \chi^B_{v'=16} | \chi^E_v >$ overlap for $v = 4$, 5, and 6 is -0.16, -0.026, and 0.20, respectively. Thus, these three vibrational states v provide the possibility to investigate the cases of overlap between the Ne-$Br_2(B, v' = 16)$ resonance and the Ne-$Br_2(E, v)$ intermediate state of similar and appreciable magnitude but different sign ($v = 4$ and 6), and also of small magnitude ($v = 5$). It is noted that ideally, for a general system, the intermediate state of the alternative pathway should be a bound state in order to act as a reservoir of wave packet amplitude, such that the amplitude generated does not decay in time. In the case of Ne-$Br_2(E)$ the intermolecular states are resonances. However, for low vibrational states $v \leq 6$, the lifetime of the ground resonance of Ne-$Br_2(E, v)$ is much longer than that of the Ne-$Br_2(B, v' = 16)$ resonance under control, and this $(E, v \leq 6)$ intermediate state can be considered as a bound state in practice.

In Fig. 2 the results obtained for $v = 4$ are displayed. In this case, three different control fields $\mathcal{E}(t)$ have been used, namely one consisting of a four pulse train ($N = 4$), and another two consisting of a six pulse train ($N = 6$). The envelopes of the three pulse trains are shown in Fig. 2(a). The parameters of the four pulse

train control field are $\mathcal{E}_1 = 2.0 \times 10^{-5}$ a.u. (which corresponds to an intensity of about 1.4×10^7 W/cm^2), $\mathcal{E}_2 = 8.0 \times 10^{-6}$ a.u., $\mathcal{E}_3 = 4.8 \times 10^{-6}$ a.u., $\mathcal{E}_4 = 2.0 \times 10^{-6}$ a.u., FWHM$_1$ = 80 ps, FWHM$_2$ =FWHM$_3$ =FWHM$_4$ = 85 ps, $t_1 = 45$ ps, $t_2 = 200$ ps, $t_3 = 405$ ps, and $t_4 = 620$ ps. The parameters of the six pulse train (a) are $\mathcal{E}_1 = 2.3 \times 10^{-5}$ a.u. (which corresponds to an intensity of about 1.9×10^7 W/cm^2), $\mathcal{E}_2 = 9.0 \times 10^{-6}$ a.u., $\mathcal{E}_3 = 5.9 \times 10^{-6}$ a.u., $\mathcal{E}_4 = 4.2 \times 10^{-6}$ a.u., $\mathcal{E}_5 = 3.0 \times 10^{-6}$ a.u., $\mathcal{E}_6 = 2.5 \times 10^{-6}$ a.u., FWHM$_1$ =FWHM$_2$ =FWHM$_3$ =FWHM$_4$ =FWHM$_5$ =FWHM$_6$ = 85 ps, $t_1 = 35$ ps, $t_2 = 175$ ps, $t_3 = 320$ ps, and $t_4 = 475$ ps, $t_5 = 640$ ps, and $t_6 = 840$ ps. The parameters of the six pulse train (b) are $\mathcal{E}_1 = 2.26 \times 10^{-5}$ a.u. (which corresponds to an intensity of about 1.8×10^7 W/cm^2), $\mathcal{E}_2 = 9.7 \times 10^{-6}$ a.u., $\mathcal{E}_3 = 7.2 \times 10^{-6}$ a.u., $\mathcal{E}_4 = 5.8 \times 10^{-6}$ a.u., $\mathcal{E}_5 = 4.9 \times 10^{-6}$ a.u., $\mathcal{E}_6 = 4.7 \times 10^{-6}$ a.u., FWHM$_1$ = 110 ps, FWHM$_2$ = 115 ps, FWHM$_3$ = 130 ps, FWHM$_4$ = 140 ps, FWHM$_5$ = 150 ps, FWHM$_6$ = 200 ps, $t_1 = 35$ ps, $t_2 = 175$ ps, $t_3 = 320$ ps, and $t_4 = 475$ ps, $t_5 = 640$ ps, and $t_6 = 840$ ps. Again, with all the above pulse trains only the Ne-Br$_2(E, v)$ ground resonance is populated within the v vibrational manifold. In Fig. 2(b) the survival probabilities calculated when no control field is applied and by applying the above three control fields, are displayed.

The survival probability calculated without control field can be nicely fitted to an exponential decay function $e^{-t/\tau}$ convoluted with the $\mathcal{E}_{pump}(t)$ pump laser pulse cross-correlation function,[24] and the lifetime τ obtained from this fit is $\tau = 69$ ps, in excellent agreement with the experimental estimate of 68 ± 3 ps (29), as mentioned above. The three control fields of Fig. 2(a) allow one to increase the survival probability, and therefore the associated lifetime, of the Ne-Br$_2(B, v' = 16)$ ground resonance by means of (constructive) interference. The four pulse train and the six pulse train (a) have been tailored by performing a systematic search in order to enhance the target resonance lifetime by a factor of two and three, respectively. Indeed, these two survival probabilities can be fitted by convoluted exponential functions (also shown in Fig. 2(b)) with associated lifetimes $\tau = 138$ and 207 ps, respectively. This result indicates the large degree of control allowed by the scheme.

The calculated survival probabilities display oscillations that reflect the number of Gaussian pulses composing the pulse train of the control field. The magnitude of these oscillations can be greatly diminished by increasing the overlap between the Gaussian pulses in the pulse train. No serious attempt to do this has been carried out in this work, since it affects rather little the lifetime enhancement achieved.

The most interesting result of Fig. 2(b) is that obtained with the six pulse train (b), which makes possible to enhance the resonance survival up to $\sim$ 1200 ps, keeping its population at a value around the maximum one reached with the $\mathcal{E}_{pump}(t)$ pulse (for the sake of simplicity no attempt was made to reach the exact maximum value of the survival probability, but this indeed can be achieved by increasing only slightly the amplitude of the pulses in the train). Once the control field is over, the survival probability of the target resonance decays. It is noted that the duration of the six pulse train (b) has been arbitrarily chosen. A longer pulse train could be used, causing a survival of the target resonance longer than 1200 ps. The maximum limit for lifetime enhancement and the conditions under which it can be reached remain to be determined. The important implication of this result is that, by using a weak control field, the target resonance population can be kept at about the maximum value achieved with the $\mathcal{E}_{pump}(t)$ pulse during the time range that the control field is applied, inducing constructive interference between the two quantum pathways.

It is interesting to analyze the shape of the control pulse trains applied (Fig. 2(a)), and how it changes as the resonance survival is gradually enhanced. All the pulse trains of Fig. 2(a) display a similar and rather simple shape, consisting of a first pulse with higher amplitude, followed by a series of pulses with lower, decreasing amplitude. The first pulse of the train covers the time range during which the target resonance is populated by the pump pulse, reaching its maximum population. This feature, along with the higher amplitude of this first pulse, aims at maximizing the generation of a reservoir of wave packet amplitude in the intermediate Ne-$Br_2(E, v)$ ground resonance. Once the reservoir of amplitude in the (E, v) intermediate vibronic state is generated to a large extent by the first pulse, the following pulses

of the train may have a lower amplitude. Regarding the change of shape of the pulse train associated with resonance survival increase, Fig. 2(a) shows that the amplitude of the first pulse increases rather little in the different pulse trains. More interestingly, the increase of the amplitude of the second and further pulses of the train is not large either, particularly when comparing the six pulse trains (a) and (b). Again, the reason is that the reservoir of amplitude has been generated previously to a large extent by the first pulse. The implication is that only rather moderate increases in the amplitude of the pulse train are required in order to achieve large enhancements of the resonance survival probability. It is also noted that although simple Gaussian pulse trains have been used here for simplicity, the scheme would work with other type of pulse shapes, as long as a reservoir of wave packet amplitude is generated at the beginning of the pulse train, as discussed above. However, single Gaussian pulses (instead of a pulse train) were also used, and they were found to be less flexible and efficient than the pulse train in order to achieve a larger degree of lifetime control.

In order to investigate the effect of the overlap between the target resonance and the intermediate vibronic state on the control of the resonance survival, Fig. 3 compares the survival probabilities obtained when the Ne-$Br_2(E, v)$ intermediate state with $v = 4$, 5, and 6 are used, and the four pulse train of Fig. 2(a) is applied in the three cases. The curve for $v = 4$ is the same as that shown in Fig. 2(b). The survival probability curve obtained for $v = 5$ is practically indistinguishable from the survival probability calculated without control field. This result is not surprising, and is due to the small overlap $< \chi^B_{v'=16}|\chi^E_{v=5} >= -0.026$. Thus, overlaps $< 3\%$ are very small as to cause appreciable control effects on the resonance survival. Interestingly, the survival probability corresponding to $v = 6$ leads to a decrease of the resonance survival, and therefore of the associated lifetime. Such a decrease of the survival appears to be related to the different sign of the overlap $< \chi^B_{v'=16}|\chi^E_{v=6} >= 0.20$ with respect to the sign of the overlap $< \chi^B_{v'=16}|\chi^E_{v=4} >= -0.16$. The different sign of the 0.20 overlap appears to introduce a different phase in the wave packet am-

plitude transferred to the Ne-$Br_2(E, v)$ ground resonance, that causes destructive interference with the amplitude of the Ne-$Br_2(B, v' = 16)$ resonance. This result indicates that indeed the control process is induced by an interference mechanism, and that by choosing different intermediate vibronic states it is possible to control the sign of interference (constructive or destructive), which allows one to produce either enhancing or quenching of the resonance survival.

It is also interesting to note that, with the same control field used in Fig. 3, the effects of enhancing the resonance survival are substantially more intense than the effects of quenching it, despite that the magnitude of the overlap of $v = 6$ (0.20) is somewhat larger than that of the $v = 4$ overlap (-0.16). This is another manifestation of an interference effect. If $a(t)$ and $b(t)$ denote the wave packet amplitudes generated in the Ne-$Br_2(B, v' = 16)$ ground resonance through the two interfering quantum pathways at a given time, the resonance survival probability is $P_{surv}(t) = |a(t)|^2 + a^*(t)b(t) + a(t)b^*(t) + |b(t)|^2$. When the sign of both $a(t)$ and $b(t)$ is the same, the four terms of $P_{surv}(t)$ add up with positive sign, and the contribution of the constructive interference to the effect of control on the enhancement of $P_{surv}(t)$ is maximal. However, when $a(t)$ and $b(t)$ have different sign, the effect of destructive interference produced by the terms $a^*(t)b(t)$ and $a(t)b^*(t)$ is cancelled out to some extent by the always positive term $|b(t)|^2$, and the net effect of control on $P_{surv}(t)$ becomes less intense than in the case of constructive interference. As a consequence, control is easier and its effects are more intense for enhancing the resonance survival and the associated lifetime than for quenching them. This can be viewed as rather an advantage of the control scheme, since typically the desired process is the enhancement of the resonance lifetime.

The possibility of quenching the Ne-$Br_2(B, v' = 16)$ resonance lifetime has been further explored by using the intermediate Ne-$Br_2(E, v = 6)$ ground resonance and a three pulse train with an envelope shown in Fig. 4(a). The parameters of this pulse train are $\mathcal{E}_1 = 3.0 \times 10^{-5}$ a.u. (which corresponds to an intensity of about 3.2×10^7 W/cm^2), $\mathcal{E}_2 = 2.3 \times 10^{-5}$ a.u., $\mathcal{E}_3 = 1.9 \times 10^{-5}$ a.u., FWHM_1 =FWHM_2 = 25 ps,

FWHM$_3$ = 35 ps, t_1 = 15 ps, t_2 = 40 ps, and t_3 = 90 ps. The survival probability obtained with the above pulse train is displayed in Fig. 4(b). This curve can be fitted with a convoluted exponential function with an associated lifetime $\tau = 43$ ps (also shown in the figure), which implies a reduction of the target resonance lifetime by almost a factor of two.

The experimental realization of the interference control scheme proposed in this work should be quite straightforward. In fact, the transition Ne-Br$_2(B, v') + h\nu \rightarrow$ Ne-Br$_2(E, v)$ between the two ground resonances of the (B, v') and (E, v) manifolds, which is the basis of the second quantum pathway required for interference, has been used experimentally (with $v \leq 7$, as in the present simulations) in order to probe the decay of the Ne-Br$_2(B, v')$ ground resonance.[31,32,37] In the above experiments the ground resonance of both Ne-Br$_2(B, v')$ and Ne-Br$_2(E, v)$ is prepared with a distribution of total angular momenta J (corresponding to a temperature of a few K). Thus, the experimental results prove that the $(B, v') \rightarrow (E, v)$ transition (and therefore the $(E, v) \rightarrow (B, v')$ estimulated emission) of pathway B is feasible for both the cases of $J = 0$ (as in the present simulations) and $J > 0$. Therefore, generating the alternative quantum pathway is a realistic possibility for the present system. The pulse train needed to this purpose is a weak control field with a simple shape, which should be easy to produce experimentally. In addition, only moderate overlaps ($\sim 20\%$) between the target resonance and the intermediate vibronic state are needed to produce large control effects on the resonance lifetime, as shown by the current results. The above conditions should also be rather easy to meet for a general system, where favorable Franck-Condon factors between the target and the intermediate states could be determined by spectroscopic studies.

Conclusions

In conclusion, this work reports for the first time a powerful coherent control scheme to modify the survival probability and associated lifetime of an isolated resonance state. The key feature of the approach is the interference between two

quantum pathways that populate simultaneously the target resonance, one of them induced by a pump laser field, and the other one induced by a second control field, both fields belonging to the weak-field regime of intensity. The interference control scheme allows one both to enhance and to quench the resonance lifetime, through constructive or destructive interference of the resonance state amplitude produced by the two quantum pathways, respectively. In particular, the scheme appears to be quite flexible in order to achieve large enhancements of the resonance lifetime, by tailoring the control field pulses. Conditions required to apply the control scheme, namely a simple shape of the control fields needed and relatively low Franck-Condon factors between the target resonance and the intermediate vibronic state required to produce the alternative, interfering quantum pathway, are found to be rather easy to meet in general, implying that the experimental implementation of the scheme should be quite straightforward. Thus, a wide applicability of the control scheme proposed to isolated resonances of a large variety of molecular and cluster systems is envisioned.

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FIGURE CAPTIONS

Fig. 1 Schematic picture of the two interfering pathways, A and B, induced by the electric fields of eqn (1) and (2), respectively. Pathway A induces the transition from the ground intermolecular resonance ($n'' = 0$) of Ne-$Br_2(X, v'' = 0)$ to the Ne-$Br_2(B, v' = 16)$ ground resonance ($n' = 0$), while pathway B induces the transition from Ne-$Br_2(B, v' = 16, n' = 0)$ to the ground resonance Ne-$Br_2(E, v, n = 0)$, used as intermediate state. The indexes n'', n', and n are used to denote the three ground intermolecular resonances involved in the process, in the X, B, and E electronic states, respectively.

Fig. 2 (a) Temporal profiles of the envelopes of the three different pulse trains composed of four and six Gaussian pulses, and used as the control field to reach the Ne-$Br_2(E, v = 4)$ ground resonance as intermediate state of the $B \rightarrow E$ and $E \rightarrow B$ alternative pathway transitions. (b) Survival probablities of the Ne-$Br_2(B, v' = 16)$ ground resonance calculated with no control field, and using the three control fields of Fig. 2(a). Two of the survival probability curves are fitted to an exponential decay function convoluted with the pump laser pulse cross-correlation function, from which the corresponding lifetime is obtained. See the text for details.

Fig. 3 Survival probablities of the Ne-$Br_2(B, v' = 16)$ ground resonance obtained with no control field, and using the four pulse train of Fig. 2(a) as the control field when the Ne-$Br_2(E, v)$ ground resonance with $v = 4$, 5, and 6 is used as intermediate state of the $B \rightarrow E$ and $E \rightarrow B$ alternative pathway transitions.

Fig. 4 (a) Temporal profile of the envelope of the three pulse train used as the control field to reach the Ne-$Br_2(E, v = 6)$ ground resonance as intermediate state of the $B \rightarrow E$ and $E \rightarrow B$ alternative pathway transitions. (b) Survival probablities of the Ne-$Br_2(B, v' = 16)$ ground resonance calculated with no control field, and using the control field of Fig. 4(a). A fit to an exponential function

convoluted with the pump laser cross-correlation function is also shown in the figure, from which a lifetime of $\tau = 43$ ps is estimated.

Fig. 1

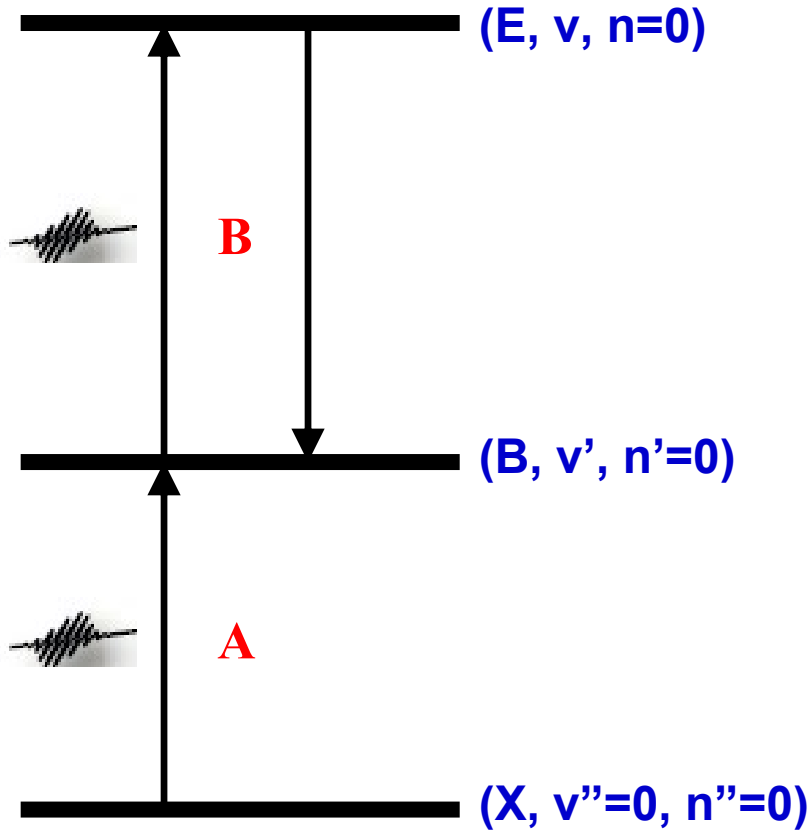

Fig. 2

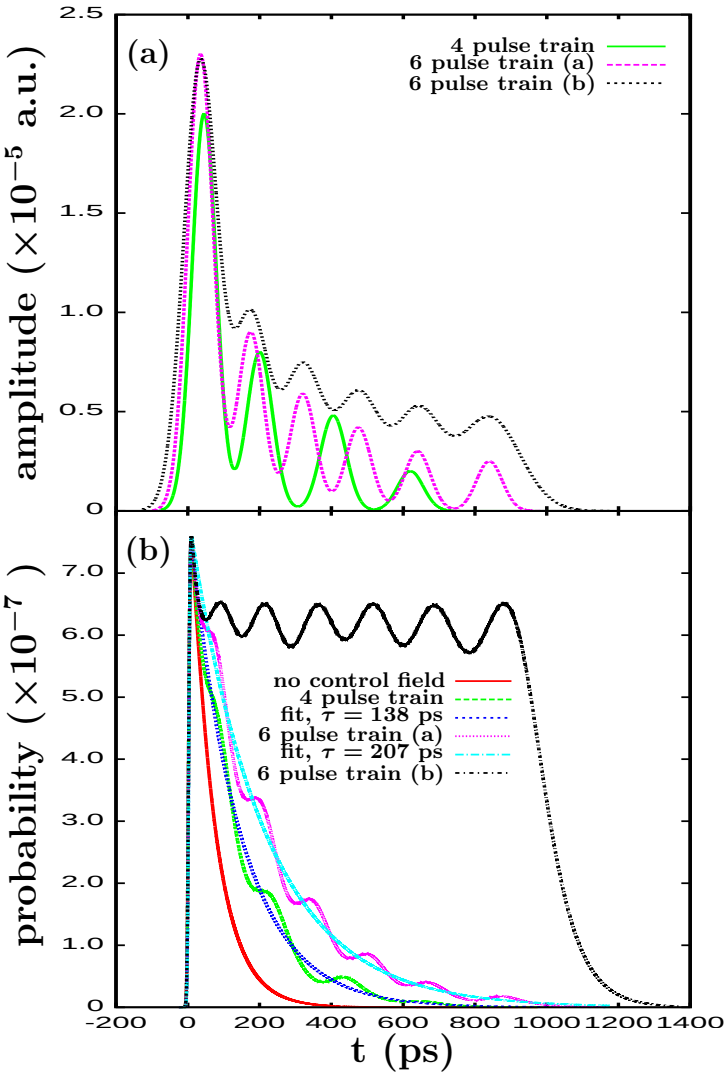

Fig. 3

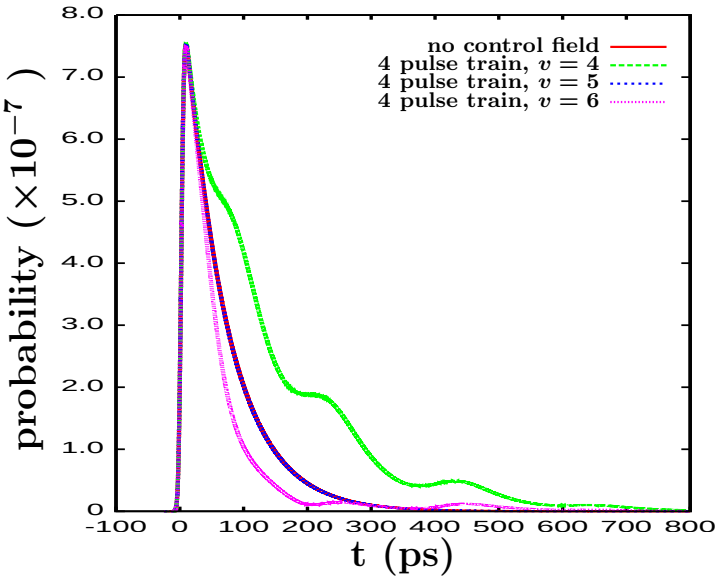

Fig. 4