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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JULY 2012

Impact Factor: 7.46 · DOI: 10.1021/jz300707g

1 AUTHOR:

Alberto García-Vela
Spanish National Research Council

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

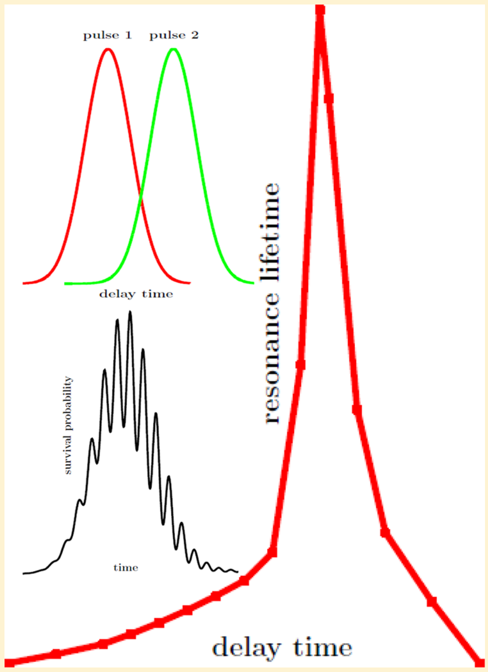
pubs.acs.org/JPCL

Strong Enhancement of the Lifetime of a Resonance State by Using a Combination of Two Laser Pulses

A. García-Vela*

Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain

ABSTRACT: The lifetime of a resonance state overlapping with a second resonance is shown to be strongly enhanced (by a factor of 3) by combining two pump pulses to simultaneously excite the two resonances. Such an enhancement is produced by interference effects occurring between the two coherently excited overlapping resonances. A high degree of control on the intensity of interference, and thus on the resonance lifetime enhancement, is found to be achieved by varying the delay time between the pulses and their relative intensities.



SECTION: Spectroscopy, Photochemistry, and Excited States

The subject of quantum coherent control of molecular processes has motivated a great deal of research in the last years.[1−13] The control schemes proposed are typically based on quantum interference mechanisms that are induced and controlled by means of laser pulses.[3−14] Several processes have been the object of control, such as molecular reactions, radiationless transitions, and photodissociation.

Vibrational revivals along the time of coherent superpositions of molecular vibrational states have been characterized in different systems[14−16] and can be used to control photochemical reactions.[17] Decoherence of these vibrational wave packets suppresses the revivals, and thus control of such decoherence becomes a fundamental issue.[18] One of the schemes suggested to control vibrational decoherence exploits the quantum interference effects that occur between overlapping resonances of the system populated by a coherent superposition created by a laser pulse.[19−21] By varying the amplitude coefficients of the overlapping resonances within the superposition, it is possible to control the interference between such resonances.

More recently, a scheme based on the interference between overlapping resonances was also suggested to modify and control the lifetime of a system in a specific single resonance state within the superposition prepared.[22] It was shown in that work that the lifetime of an overlapping resonance is no longer an intrinsic property of the resonance state, as in the case of an isolated resonance, which allows the possibility of exerting control on it. In the scheme applied, a laser pulse of variable width was used to modify the weight of the different overlapping resonances in the coherent superposition. The control scheme was applied to a realistic model of the predissociation decay dynamics of $Br_2(B,v' = 27)$−Ne in its ground van der Waals (vdW) resonance, which overlaps with some vdW orbiting resonances correspoding to the lower $v' - 1$ vibrational manifold of Br_2. Extensive control of the system lifetime in the ground vdW resonance was found to be achievable.

In the present work, a more flexible and efficient control scheme of a resonance lifetime is proposed. It is based on combining the action of two pump laser pulses, instead of using a single pump pulse as in the previous work.[22] The efficiency of

Received: May 31, 2012
Accepted: July 9, 2012

the new scheme is illustrated by applying it again to control the decay dynamics of $Br_2(B,v' = 27)$−Ne in its ground vdW resonance.

Upon laser excitation of Br_2−Ne to the $(B,v' = 27)$ excited vibronic state, $Br_2(B,v' = 27)\text{−Ne} \leftarrow Br_2(X,v'' = 0)\text{−Ne}$, the ground vdW resonance of $Br_2(B,v' = 27)$−Ne is populated. Then the excited resonance decays to the fragmentation continuum through vibrational predissociation of the complex, $Br_2(B,v' = 27)\text{−Ne} \rightarrow Br_2(B,v_f < v') + \text{Ne}$.[23−26] It has been shown[26−28] that the $Br_2(B,v' = 27)$−Ne ground vdW resonance overlaps with a sparse spectrum of $v'−1$ vdW orbiting resonances located above the $Br_2(B,v' − 1)$−Ne dissociation threshold.

The excitation spectrum of the $Br_2(B,v')$−Ne ground vdW resonance was calculated previously,[28] and it is shown in Figure 1. The spectrum displays a main peak located at -61.80 cm^{-1},

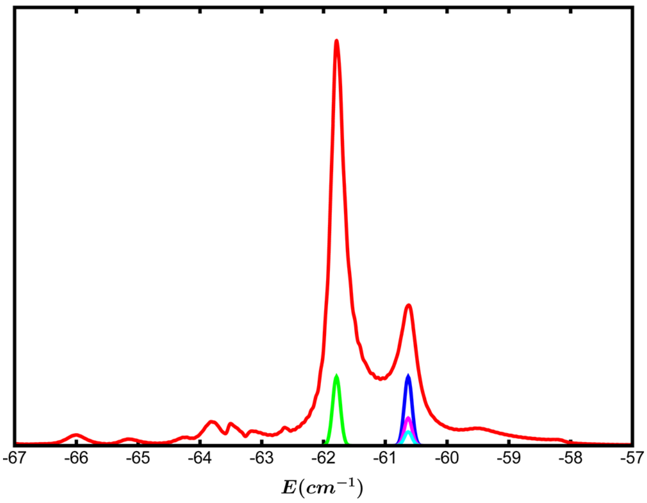


Figure 1. Calculated excitation spectrum associated with the ground vdW resonance of $Br_2(B,v' = 27)$−Ne (ref 28). The energy axis is relative to the $Br_2(B,v' = 27,j' = 0)$ + Ne dissociation threshold. The Gaussian spectral profiles of the pump pulses used to excite the two resonances are also displayed in the figure for the three sets of relative intensities applied in the simulations, $A_2 = bA_1$, with $b = 0.2$, 0.4, and 1.0.

associated with the v' ground vdW resonance, and several other overlapping peaks associated with $v' − 1$ orbiting resonances. The second most intense feature in the spectrum is a peak at -60.63 cm^{-1} that overlaps with the main peak. Actually, the previous results[22] indicated that interference of the v' ground resonance occurs with appreciable intensity only with the $v' − 1$ orbiting resonance associated with this secondary peak. Using spectral methods, the lifetimes associated with these two v' and $v' − 1$ resonances were previously estimated[28] to be 21.2 and 12.2 ps, respectively.

The new control scheme proposed in this work consists of using a combination of two pump laser pulses (assumed to be Gaussian) to create a coherent superposition of the above two overlapping resonances in the v' and $v' − 1$ manifolds. One pump pulse would excite the v' ground resonance, while the other pulse would excite the $v' − 1$ orbiting resonance. Thus, the pump laser electric field applied is

$$E(t) = A_1 e^{-(t-t_1)^2/2\sigma^2} \cos \omega_1 t + A_2 e^{-(t-t_2)^2/2\sigma^2} \cos \omega_2 t \tag{1}$$

where ω_1 and ω_2 are the photon frequencies required to excite the v' and $v' − 1$ resonances, respectively. Although it is not a requirement of the control scheme, for simplicity it was assumed to be the same width (related to σ) for the two pump pulses, which specifically corresponds to fwhm = 200 ps. However, the intensities A_1 and A_2 and the centers t_1 and t_2 of the two pulses are allowed to be different. Specifically, simulations have been carried out for three different sets of relative intensities, namely, $A_2 = 0.2A_1$, $A_2 = 0.4A_1$, and $A_2 = A_1$. The Gaussian envelopes of the spectral bandwidth of the two pulses are displayed in Figure 1 for the above three combinations of relative intensities. It is noted that for a pulse with a temporal fwhm = 200 ps, the corresponding spectral width is fwhm = 0.15 cm^{-1}, and therefore the spectral bandwidths of the two pump pulses do not overlap. Thus each pulse essentially excites a single resonance.

The phase of the two pulses of the field of eq 1 has been assumed to be zero. It is well-known that the relative phase between the two pump pulses is an additional control parameter that may have an impact on the control scheme outcome,[11,13] and varying it is expected to also have an effect on the control of the present interference mechanism between overlapping resonances and thus on their lifetime. For the sake of simplicity of the analysis, in this work the control parameters have been restricted to the delay time and the relative intensities between the two pump pulses. However, it should be very interesting to explore the effect of varying the relative phase between the pulses as an additional control parameter. Another interesting possibility involving the single pump pulse control scheme previously reported[22] is to combine the variation of both the intensity and the phase of the pump pulse in order to optimize the pulse shape. Work in these two directions is currently under way.

A number of theoretical works applying control schemes using two or more laser pulses has been reported. They include control of molecular excitation with a sequence of pulses,[3] and control of molecular dissociation using two pump pulses by creating interfering dissociating wave packets,[11,29,30] or by dynamic Stark effect.[31,32] Similarly, experiments using two pulses in order to control molecular dissociation by Stark effect,[10] or to control interference between free electron wave packets[6] and molecular wave packets[14,29,30] have also been carried out.

The electric field $E(t)$ of eq 1 creates a coherent superposition of the v' (ψ_1) and $v' − 1$ (ψ_2) resonances

$$\Phi(t) = a_1(t)\psi_1(t) + a_2(t)\psi_2(t) \tag{2}$$

Now we can express the survival probability associated with the ψ_1 resonance as

$$\begin{aligned} I_1(t) &= |\langle\psi_1|\Phi(t)\rangle|^2 \\ &= |a_1(t)\langle\psi_1|\psi_1(t)\rangle + a_2(t)\langle\psi_1|\psi_2(t)\rangle|^2 \\ &= |a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2 + |a_2(t)|^2|\langle\psi_1|\psi_2(t)\rangle|^2 \\ &\quad + a_1(t)a_2(t)^*\langle\psi_1|\psi_1(t)\rangle\langle\psi_2(t)|\psi_1\rangle \\ &\quad + a_1(t)^*a_2(t)\langle\psi_1(t)|\psi_1\rangle\langle\psi_1|\psi_2(t)\rangle \end{aligned} \tag{3}$$

There is a similar equation to eq 3 for $I_2(t) = |\langle\psi_2|\Phi(t)\rangle|^2$.

The first term of the second right-hand side of eq 3 is the square of the autocorrelation function of ψ_1. This is actually the definition of the survival probability for an isolated, non-

dx.doi.org/10.1021/jz300707g | J. Phys. Chem. Lett. 2012, 3, 1941−1945

overlapping resonance. However, in the survival probability of resonance ψ_1, there are contributions of three additional terms. These are interference terms arising from two conditions simultaneously fulfilled, namely, that resonances ψ_1 and ψ_2 overlap ($\langle\psi_1|\psi_2(t)\rangle \neq 0$), and that the ψ_2 resonance is populated ($a_2(t) \neq 0$). As long as the coeffiecients a_1 and a_2 of the superposition of eq 2 can be systematically modified, the effects of the interference terms can be controlled in order to change the survival probability and the associated lifetime of the system in resonance ψ_1 (or ψ_2). One obvious way to change the a_1 and a_2 amplitudes is to change the intensities A_1 and A_2 of the pulses exciting the two resonances.

Another dynamic and flexible way to modify the weight of the two interfering resonances in the superposition is to vary the delay time, $\Delta t = t_2 - t_1$, between the pulses. Indeed, by varying Δt, one can control with high sensitivity the amount of population of the two resonances excited at a given time, which is determined by the degree of overlapping of the two pulses in time and by the decay time of the resonances. The overlapping of the two pump pulses in time is illustrated in Figure 2 for

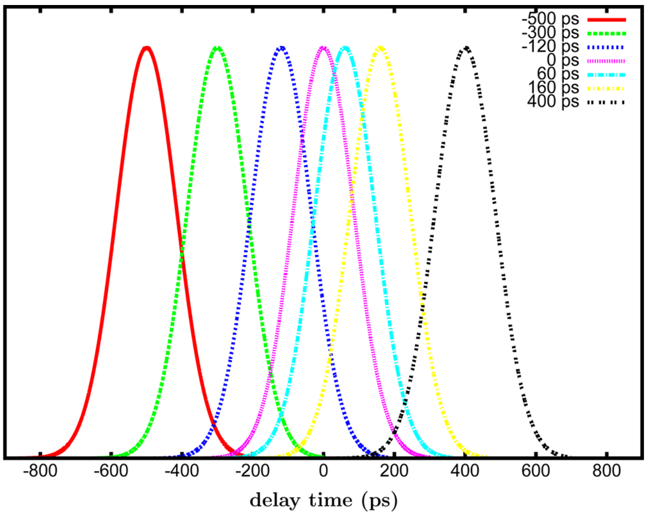


Figure 2. Gaussian temporal profiles of the two pump pulses for different delay times $\Delta t = t_2 - t_1$ between them. The center of one of the pulses is always fixed at $t_1 = 0$ ps.

several delay times Δt. In the simulations, the center of the pulse exciting the v' ground resonance is fixed at $t_1 = 0$ ps, while the center of the other pump pulse is varied from −500 to 500 ps. The delay times $\Delta t = -500$ and 500 ps correspond to practically zero overlap between the pulses (see Figure 2), which implies that excitation of the two resonances is practically independent and does not coincide in time.

The process of $Br_2(B,v')$−Ne ← $Br_2(X,v'' = 0)$−Ne excitation with a laser pulse and the subsequent predissociation of the complex was simulated with a three-dimensional wave packet method that was described in detail elsewhere.[26] Then, following eq 3, the survival probability associated with the $Br_2(B,v' = 27)$−Ne ground vdW resonance is calculated as $I_1(t) = |\langle\psi_1|\Phi(t)\rangle|^2$.[2] Details of the computation of the resonance wave function ψ_1 were given earlier.[22,26] The lifetime of the system, τ, is obtained by applying the same procedure used to estimate the experimental lifetimes,[25,26] namely, by fitting $I_1(t)$ to the function

$$I_1(t_j) = A \int_{-\infty}^{t_j} CC(t)[\exp(-(t_j - t)/\tau)]\, dt \tag{4}$$

with $CC(t)$ being the laser cross-correlation curve and A being an amplitude scaling parameter.

The lifetimes obtained by fitting $I_1(t)$ with eq 4 for the three ratios of the two pulse intensities and the different delay times between pulses applied are plotted in Figure 3. As mentioned

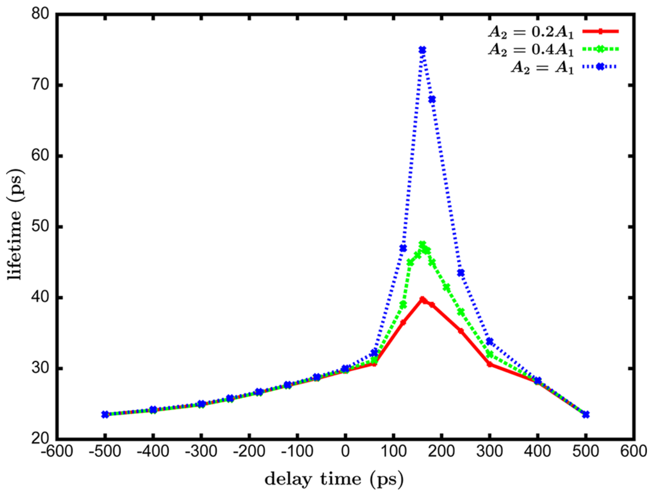


Figure 3. Resonance lifetimes obtained for the ground vdW resonance of $Br_2(B,v' = 27)$−Ne for different delay times and A_2/A_1 intensity ratios of the pump pulses.

above, for $\Delta t = -500$ and 500 ps, the separation between the two pump pulses is sufficiently large as to consider that in practice the v' ground vdW resonance ψ_1 is excited alone, without coinciding in time with appreciable enough population of the ψ_2 resonance. Thus, the lifetime found in these two limiting situations, namely, 23.5 ps, is that corresponding to excitation only of ψ_1 with a pulse of fwhm = 200 ps.[22] Figure 3 shows that the ψ_1 lifetime can increase remarkably from this minimum value by varying both Δt and the ratio between the intensities A_1 and A_2 of the two pulses. Indeed, in the present simulations, the ψ_1 lifetime is enhanced up to the value of 75.0 ps, i.e., by a factor of 3, for $\Delta t = 160$ ps and $A_2 = A_1$. Moreover, a larger enhancement of the lifetime could be achieved if the A_2 intensity is increased further. In this sense, it is stressed that optimization of the laser field applied in order to maximize the lifetime enhancement was not intended in the present work. Such optimization could be achieved by means of optimal control techniques.[1] The main goal of this study has been to investigate whether extensive control of the resonance lifetime can be achieved with high sensitivity just by changing two parameters that are typically straightforwardly varied in an experiment, like the delay time and the ratio of intensities between the two pump pulses.

The behavior of the lifetime displayed in Figure 3 when Δt and the A_2/A_1 ratio are modified can be inderstood by analyzing the corresponding survival probabilities $I_1(t)$ (see Figure 4). In Figure 4a, the survival probabilities for $A_2 = 0$ (i.e., excitation of resonance ψ_1 without excitation of ψ_2), and for $\Delta t = 160$ ps and $A_2 = 0.2A_1$, $A_2 = 0.4A_1$, and $A_2 = A_1$ are shown. The case of $A_2 = 0$ implies that $a_2(t) = 0$ in the superposition of eq 2, which leads to $I_1(t) = |a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2$. This survival probability decays monotonically as an exponential function, as displayed in the figure. For the three cases of $A_2 \neq 0$, now $a_2 \neq$

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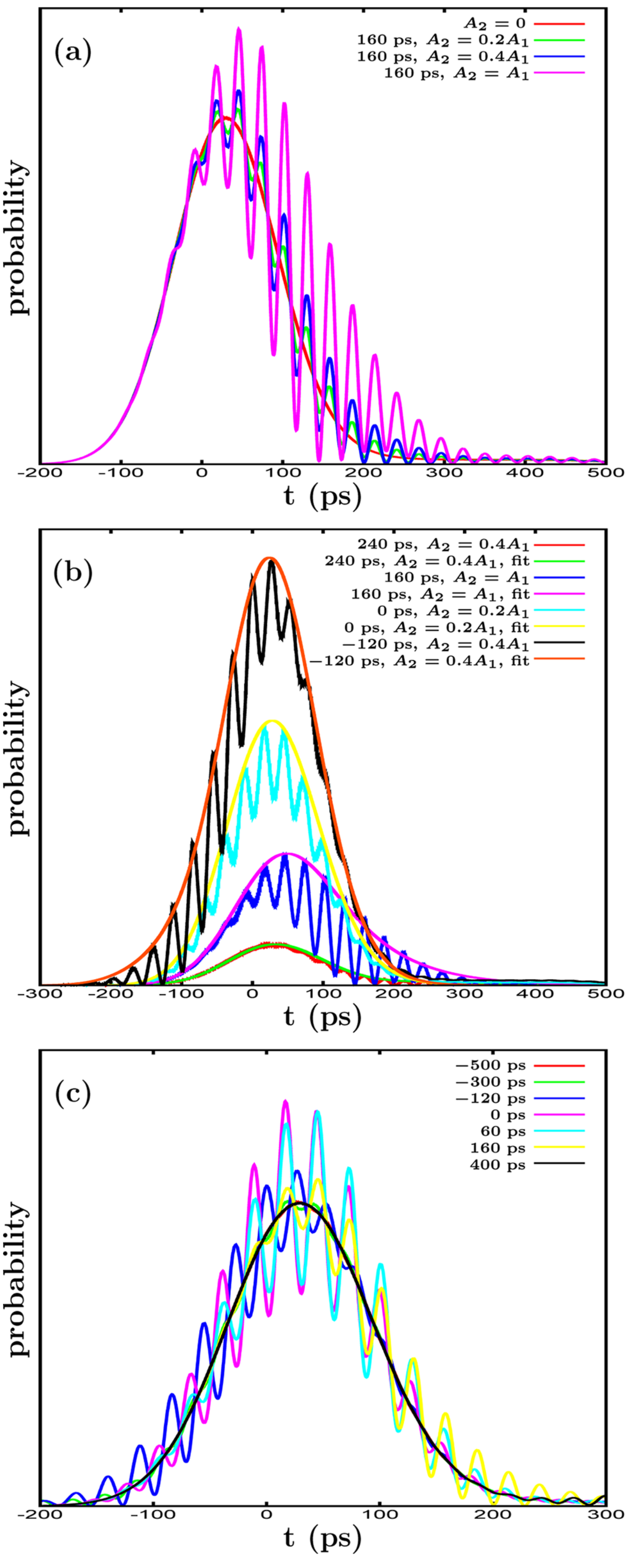

Figure 4. (a) Survival probabilities calculated for $A_2 = 0$ (excitation of resonance ψ_1 only), and for the delay time $\Delta t = 160$ ps and the three intensity ratios $A_2 = 0.2A_1$, $A_2 = 0.4A_1$, and $A_2 = A_1$. (b) Typical survival probabilities calculated for several delay times and pulse intensity ratios along with their corresponding fits obtained with eq 4 in order to find the resonance lifetime. The curves have been rescaled for convenience. (c) Survival probabilities calculated for different delay times in the case of $A_2 = 0.4A_1$.

0, and the three last terms of the second right-hand side of eq 3 become nonzero and add to the $|a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2$ term. These additional interference terms cause the undulation pattern exhibited by the $I_1(t)$ curves and the lifetime enhancement. The time separation between maxima of adjacent undulations is ∼27 ps, which corresponds to an energy separation of ∼1.2 cm^{-1}, which is the separation between the two overlapping and interfering ν' and $\nu' - 1$ resonances located at −61.80 cm^{-1} and −60.63 cm^{-1}, respectively (see Figure 1). As the A_2 intensity increases with respect to A_1, the a_2 amplitude in eq 2 increases correspondingly, causing an enhancement of the contributions of the interference terms to $I_1(t)$ (see eq 3). As a result, the intensity of the undulation pattern becomes increasingly larger (Figure 4a) and thus the corresponding lifetime becomes increasingly longer (Figure 3). In Figure 4b, the $I_1(t)$ curves calculated for different delay times and A_2/A_1 ratios are shown along with their corresponding fits from which the lifetimes were obtained.

After discussing the behavior of the lifetime with the A_2/A_1 ratio, it is interesting to analyze the effect of the delay time between the pulses. Figure 3 shows that the intensity of the interference effects produced by the different A_2/A_1 ratios is not homogeneously distributed for all the delay times studied. Indeed, there is a range, 60 ps ≤ Δt ≤ 300 ps, where the interference effects and the resulting lifetimes are maximized, reaching a peak at Δt = 160 ps. In this Δt range where the intensity of interference becomes large, an increase of the A_2 pulse intensity leads to important enhancements of the lifetime, as should be expected. Outside this range of delay times, the intensity of interference effects appears to decrease substantially, leading to a remarkably smaller enhancement of the resonance lifetime, which in addition is practically unaffected by increasing the A_2 intensity.

As the delay time is varied, the region of overlap between the two pulses changes (see Figure 2), and a correspondingly changing undulation pattern appears in the survival probability curve over the pulses overlap region. This behavior is illustrated by the $I_1(t)$ curves of Figure 4c. The maximum intensity of the interference pattern occurs over the time region of $I_1(t)$ where overlap between the pulses is maximum (i.e., around the intersection point of the two pulse temporal profiles). Complete overlap between pulses occurs for Δt = 0 ps, and in this case the undulation pattern spreads over the whole $I_1(t)$ curve. On the contrary, for delay times $|\Delta t|$ > 300 ps, overlap between pulses is small or nearly zero, producing a rather weak or absent interference pattern on $I_1(t)$, consistent with the relatively small enhancement of the lifetime displayed in Figure 3 for those cases.

One might think, in principle, that complete overlap between pulses (for Δt = 0 ps) would provide the maximum intensity of interference, and therefore of lifetime enhancement. Actually the intensity of the undulation pattern becomes largest for Δt = 0 ps (Figure 4c). However, the results of Figure 3 show that the region of largest lifetime enhancement is 60 ps ≤ Δt ≤ 300 ps, reaching the maximum lifetime for Δt = 160 ps. This region of Δt roughly coincides with the region of time decay of the $I_1(t)$ curve (which depends on the temporal width of the pulse used to excite resonance ψ_1). Indeed, for delays 60 ps ≤ Δt ≤ 300 ps, the region of maximum overlap between pulses occurs at times within the range of time decay of $I_1(t)$. Thus, the implication is that the impact of the interference effects between overlapping resonances on the lifetime enhancement is maximized as long as such effects occur mainly during the time decay of the target

dx.doi.org/10.1021/jz300707g | J. Phys. Chem. Lett. 2012, 3, 1941−1945

resonance survival probability, which is the time region that determines the resonance lifetime.

The present results and discussion can be generalized to any system supporting (at least) two overlapping resonances. In this sense, the $Br_2(B,v' = 27)$−Ne system is just a convenient choice that provides these conditions and can be realistically modeled. The results of Figures 3 and 4 indicate that the lifetime enhancement and the intensity of the interference pattern are strong enough as to be experimentally observed. Such an experiment would require two pump pulses of similar characteristics to those applied here, and a probe pulse with a similar width to the pump pulse used to excite resonance ψ_1 in order to probe the $I_1(t)$ survival probability. It is noted that the present control scheme with two pump laser pulses is expected to be easier to implement experimentally than the previous scheme using a single pump pulse of variable width.[22]

In summary, this work demonstrates that the lifetime of a resonance overlapping with another resonance can be strongly enhanced by using two pump pulses to excite simultaneously the two resonances. Lifetime enhancement is produced by effects of interference between the two overlapping resonances excited. The intensity of the interference effects, and thus the lifetime enhancement, can be controlled with a high sensitivity by varying two typical experimental parameters like the delay time between the two pump pulses and their intensities.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: garciavela@iff.csic.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by Ministerio de Ciencia e Innovación, Spain, Grant No. FIS2010-18132, the Consolider program, Grant No. CSD2007-00013, and the COST Action program, Grant No. CM1002. Computer time granted by the Centro de Supercomputación de Galicia (CESGA) is acknowledged.

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