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Active control of the lifetime of excited resonance states by means of laser pulses

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Quantum control of the lifetime of a system in an excited resonance state is investigated theoretically by creating coherent superpositions of overlapping resonances. This control scheme exploits the quantum interference occurring between the overlapping resonances, which can be controlled by varying the width of the laser pulse that creates the superposition state. The scheme is applied to a realistic model of the Br_2(B)-Ne predissociation decay dynamics through a three-dimensional wave packet method. It is shown that extensive control of the system lifetime is achievable, both enhancing and damping it remarkably. An experimental realization of the control scheme is suggested.
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I. INTRODUCTION

Quantum coherent control of molecular processes has been the subject of a great interest in the last years.[1–9] Control schemes usually exploit quantum interference effects typically induced by laser excitation.[3–10] Several control targets have been pursued, among them control of the yield of specific molecular reaction pathways[4–9] and control of radiationless transitions and decoherence of initially excited molecular states.[11–14] This latter topic has potential applications in numerous fields, including quantum information processing and quantum computing.[15]

One of the strategies proposed to control the survival of initially excited molecular states is based on the quantum interference effects that occur between overlapping zeroth-order resonances of the system when a coherent superposition of such resonances is created.[12–14] By optimizing the coefficients of the different overlapping resonances in the superposition prepared (e.g., by means of pulse shaping), it is possible either to minimize or to maximize the lifetime of the initial superposition state, and this has been successfully achieved for a number of model systems.[12–14] The presence of overlapping resonances in a large variety of molecular systems makes this control scheme widely applicable.

The above scheme was typically applied to control the lifetime of the whole resonance superposition created in the system. However, in several situations it would be most interesting to control the survival of the system in a specific excited resonance state rather than in the whole superposition of resonances (e.g., in the fields of quantum information and state to state selective chemistry). In practice this would be equivalent to modify and control the lifetime of a given resonance state. The aim of the present work is to explore such a possibility by exploiting the effect of quantum interference between overlapping resonances first reported in Ref. 12 and further applied to control of decoherence of superposition states.[13,14]

Weakly bound van der Waals (vdW) complexes of the type $X_2(B, v')$-Rg (X= halogen atom, Rg=rare gas atom) are known to possess a range of v' vibrational states where some of the v' vdW resonances overlap with some of the vdW resonances corresponding to the lower $v' - 1$ vibrational manifold. This feature makes those systems ideal candidates for the present purpose. More specifically, in this work the $Br_2(B, v')$-Ne complex in its ground vdW resonance has been chosen to investigate how the system lifetime can be modified when different superpositions of this v' ground resonance and of the $v' - 1$ vdW resonances are prepared.

The paper is organized as follows. In Sec. II the underlying theory is briefly described. The results are presented and discussed in Sec. III. Finally, some conclusions are given in Sec. IV.

II. THEORY

Upon laser excitation of Br_2-Ne from the ground state to the (B, v') excited vibronic state, $Br_2(B, v')$-Ne $\leftarrow$ $Br_2(X, v'' = 0)$-Ne, the ground vdW resonance of $Br_2(B, v')$-Ne is populated. Then the excited resonance decays to the fragmentation continuum through vibrational predissociation of the complex, $Br_2(B, v')\text{-Ne} \rightarrow Br_2(B, v_f < v') + \text{Ne}$.[16–19] It has been shown[19,20] that there are three different overlapping regimes between the ground vdW resonance of $Br_2(B, v')$-Ne and the vdW resonances of the lower $v' - 1$ manifold, depending on the location of v'. For $v' < 23$ the v' ground resonance is isolated and does not overlap with any $v' - 1$ vdW resonance. For $23 \leq v' \leq 27$ the v' resonance overlaps with a sparse spectrum of $v' - 1$ orbiting resonances located above the $Br_2(B, v' - 1)$-Ne dissociation threshold. The third regime occurs for $v' > 27$, where the v' ground resonance overlaps with a denser spectrum of $v' - 1$ resonances located below the $Br_2(B, v' - 1)$-Ne dissociation limit. These three regimes are schematically shown in Fig. 1. In this work, simulations have been carried out for two v' states corresponding to the two first overlapping regimes, namely $v' = 16$ (nonoverlapping

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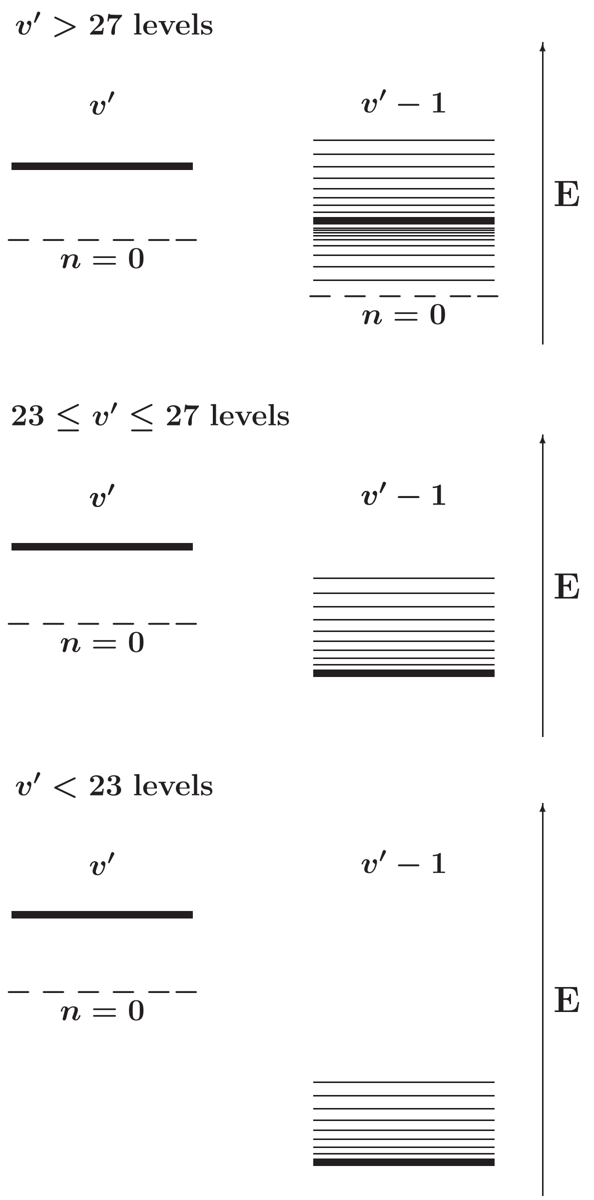

FIG. 1. Schematic representation of the relative position of the ground vdW resonance of $Br_2(B, v')$-Ne with respect to the spectrum of vdW resonances of the lower vibrational manifold $v' - 1$ for three regions of v' levels, $v' > 27$, $23 \leq v' \leq 27$, and $v' < 23$. The thick solid lines represent the Ne + $Br_2(B, v, j = 0)$ ($v = v'$, $v' - 1$) dissociation limit of each manifold. The thin solid lines are resonance energy levels within the $v' - 1$ manifold. The dashed lines labeled as $n = 0$ represent the ground resonance state of the corresponding vibrational manifold. The arrows indicate the direction of increasing energy.

resonance regime) and $v' = 27$ (sparse overlapping resonance regime), both of which were studied experimentally.[18]

A coherent superposition of $Br_2(B)$-Ne zeroth-order resonances ψ_n consisting of the v' ground resonance and $v' - 1$ vdW resonances is prepared with a laser pulse,

$$\Phi = \sum_n a_n \psi_n, \tag{1}$$

where each zeroth-order resonance is a wave packet that can be expressed in terms of the system eigenstates φ_E as

$$\psi_n = \int dE |\varphi_E\rangle\langle\varphi_E|\psi_n\rangle, \tag{2}$$

where φ_E are continuum eigenfunctions fulfilling $\langle\varphi_E|\varphi_{E'}\rangle = 2\pi\hbar\delta(E - E')$. It is noted that due to the use of a finite temporal width laser pulse, the a_n coefficients of Eq. (1) are time-dependent.

The time evolution of both the resonances and the wave packet created is given by

$$\psi_n(t) = \int dE |\varphi_E\rangle\langle\varphi_E|\psi_n\rangle e^{-iEt/\hbar}, \tag{3}$$

$$\Phi(t) = \sum_n a_n(t) \int dE |\varphi_E\rangle\langle\varphi_E|\psi_n\rangle e^{-iEt/\hbar}. \tag{4}$$

If the ψ_i and ψ_n resonances overlap, then

$$\langle\psi_i|\psi_n\rangle = \int dE \langle\psi_i|\varphi_E\rangle\langle\varphi_E|\psi_n\rangle \neq 0, \tag{5}$$

which implies that $\langle\psi_i|\varphi_E\rangle \neq 0$ and $\langle\psi_n|\varphi_E\rangle \neq 0$ at least for one φ_E state.

Now, the survival probability of the system in resonance ψ_i can be expressed as

$$I_i(t) = |\langle\psi_i|\Phi(t)\rangle|^2 = \left|\sum_n a_n(t)\langle\psi_i|\psi_n(t)\rangle\right|^2$$
$$= \sum_{n,n'} a_n^*(t) a_{n'}(t) \langle\psi_n(t)|\psi_i\rangle\langle\psi_i|\psi_{n'}(t)\rangle, \tag{6}$$

which in terms of the φ_E eigenstates, by applying Eqs. (2)–(5), becomes

$$I_i(t) = \left|\sum_n a_n(t) \int dE \langle\psi_i|\varphi_E\rangle\langle\varphi_E|\psi_n\rangle e^{-iEt/\hbar}\right|^2$$
$$= \sum_{n,n'} a_n^*(t) a_{n'}(t) \int dE' \int dE \langle\varphi_{E'}|\psi_i\rangle\langle\psi_i|\varphi_E\rangle\langle\psi_n|\varphi_{E'}\rangle$$
$$\times \langle\varphi_E|\psi_{n'}\rangle e^{-i(E-E')t/\hbar}. \tag{7}$$

The above equations show that if the ψ_i and ψ_n resonances overlap then $I_i(t)$ depends on interference terms of the type $a_n^*(t)a_i(t)$ (and the complex conjugate). The larger is the number of ψ_n resonances overlapping with ψ_i, the larger will be the number of interference terms affecting $I_i(t)$. Thus, by changing the amplitude of the coefficients a_i and a_n, the interference terms (and therefore the associated interference effects) can be modified and controlled, allowing one to control the survival probability and associated lifetime of the system in the resonance ψ_i. Modifying the amplitude of the coefficients a_i and a_n can be achieved by changing the width of the pulse that creates the superposition of resonances.

The process of $Br_2(B, v')$-Ne $\leftarrow$ $Br_2(X, v'' = 0)$-Ne excitation with a laser pulse and the subsequent predissociation of the complex was simulated with a three-dimensional wave packet method which has been described in Ref. 19. Then the survival probability $I_i(t)$ associated with $Br_2(B, v')$-Ne in the ground vdW resonance is calculated following Eq. (6) as $I_i(t) = |\langle\psi_i|\Phi(t)\rangle|^2$ for different widths of the pump pulse. The system is represented in Jacobi coordinates (r, R, θ), where r is the Br–Br bond length, R is the distance between Ne and the Br_2 center-of-mass, and θ is the angle between the vectors associated with the two radial coordinates. In these coordinates, and assuming zero total angular momentum for the system, the Hamiltonian can be expressed as

$$\hat{H} = -\frac{\hbar^2}{2\mu_{I_2}}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_{Br_2-Ne}}\frac{\partial^2}{\partial R^2} + \left(\frac{1}{2\mu_{I_2} r^2} + \frac{1}{2\mu_{Br_2-Ne} R^2}\right)\hat{j}^2 + V(r, R, \theta), \quad (8)$$

where μ_{I_2} and μ_{Br_2-Ne} are the reduced masses corresponding to I_2 and Br_2-Ne, respectively, $\hat{j}$ is the angular momentum operator associated with θ, and $V(r, R, \theta)$ is the interaction potential of the $Br_2(B)$-Ne complex. Now, in order to compute the ψ_i wave function associated with the zeroth-order $Br_2(B, v')$-Ne ground vdW resonance it was expressed as

$$\psi_i(r, R, \theta) = \chi_v^{(j)}(r) \sum_{n,j} c_{n,j}^{(v)} \phi_n^{(v)}(R) P_j(\theta), \quad (9)$$

where $\chi_v^{(j)}(r)$ is a rovibrational eigenstate of $Br_2(B)$, $\phi_n^{(v)}(R)$ are radial basis functions, and $P_j(\theta)$ are normalized Legendre polynomials. The radial functions were obtained by calculating the eigenfunctions of the reduced Hamiltonian $\hat{H}_{vv}(R, \theta) = \langle \chi_v^{(j=0)}(r)|\hat{H}|\chi_v^{(j=0)}(r)\rangle$ for several fixed angles θ, and then orthogonalizing these eigenfunctions through the Gram-Schmidt procedure. Resonance energies and wave functions were obtained by representing the Hamiltonian $\hat{H}$ in the basis set of Eq. (9) and diagonalizing. The basis set consisted of 1 vibrational state ($v = v' = 16$ and 27), 22 radial functions $\phi_n^{(v)}(R)$, and 25 Legendre polynomials (with even j).

The corresponding lifetime of the system, τ, is obtained following the same procedure used to estimate the experimental lifetimes,[18,19] namely by fitting $I_i(t)$ to the function

$$I_i(t_j) = A \int_{-\infty}^{t_j} CC(t)[\exp(-(t_j - t)/\tau)]dt, \quad (10)$$

being $CC(t)$ the laser cross-correlation curve and A an amplitude scaling parameter. It is noted that the v' ground resonance is separated from the v' first excited vdW resonance by $\sim$17 cm^{-1}. As will be seen below, even the pulse with the largest bandwidth used in the simulations cannot cover that gap and to populate the v' first excited resonance. Thus, the superposition of $Br_2(B)$-Ne resonances prepared by the different laser pulses (assumed to be Gaussian) consists of a single v' resonance (the ground one) and a number of $v' - 1$ resonances that depends on the pulse bandwidth.

III. RESULTS AND DISCUSSION

A. The $v' = 16$ isolated resonance case

In the case of $v' = 16$ four different pump pulses have been used with a temporal full width at half maximum (FWHM) of 100, 50, 30, and 10 ps. These pulses have a corresponding spectral FWHM ranging from 0.3 cm^{-1} for the 100 ps pulse to 3.0 cm^{-1} for the 10 ps pulse, and a spectral full width (FW, i.e., the energy range covered by the pulse with nonzero intensity) of $\sim$0.8 and $\sim$8.0 cm^{-1} for the 100 and 10 ps pulses, respectively. The $Br_2(B, v')$-Ne excitation energy (which determines the center of the superposition bandwidth) coincides with the $v' = 16$ ground resonance energy (i.e., the energy of the maximum of the calculated excitation spectrum), namely -63.45 cm^{-1} relative to the $Br_2(B, v' = 16)$-Ne dissociation threshold.

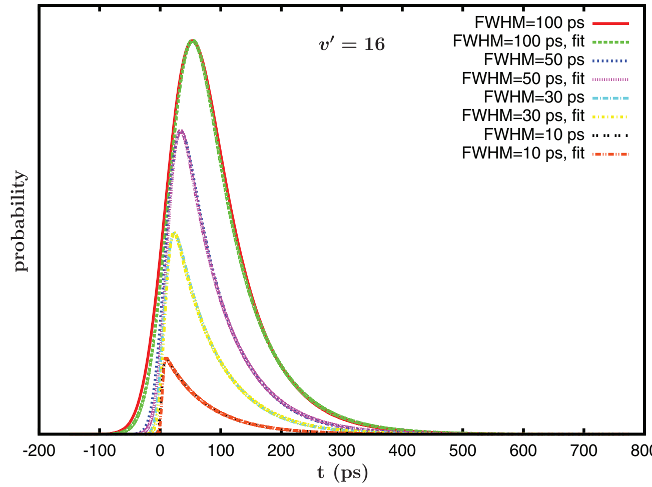

FIG. 2. Survival probability associated with $Br_2(B, v' = 16)$-Ne in the ground vdW resonance obtained with four different pump laser pulses, along with the corresponding fit. The curves have been rescaled for convenience.

Since the $Br_2(B, v' = 16)$-Ne ground vdW resonance is isolated no superposition of resonances can be created and therefore no interference effects are possible. The survival probabilities calculated with the above four pulses are shown in Fig. 2 along with their corresponding fits. The lifetimes obtained for the pulses with FWHM = 100, 50, 30, and 10 ps are 72.0, 71.0, 70.7, and 70.0 ps, respectively. As expected in this isolated resonance case, the lifetime changes very little with increasing spectral bandwidth of the pump pulse. The slight decrease of 2 ps in the lifetime is due to the slight increase of the population in the off resonance energy components of the excitation spectrum (with somewhat lower lifetimes associated) as the pulse spectral width increases. It is noted that the $Br_2(B, v' = 16)$-Ne ground resonance lifetime obtained experimentally with a pulse with FWHM = 15 ps was 74 $\pm$ 8 ps.[18] The excellent agreement between the present calculations and experiment indicates that the system is realistically modeled in the current simulations.

B. The $v' = 27$ overlapping resonance case

For the $v' = 27$ state ten different pump pulses were used, with a FWHM ranging from 200 ps to 2.5 ps. The spectral widths range from FWHM = 0.15 cm^{-1} (FW $\simeq$ 0.4 cm^{-1}) for the 200 ps pulse to FWHM = 12.0 cm^{-1} (FW $\simeq$ 32.0 cm^{-1}) for the 2.5 ps pulse. The effect of the excitation energy is also investigated in this case by exciting the system to three different energies, namely the $v' = 27$ ground resonance energy, -61.80 cm^{-1} (relative to the $Br_2(B, v' = 27)$-Ne dissociation threshold), -61.90 cm^{-1} (-0.10 cm^{-1} off resonance), and -62.22 cm^{-1} (this is the zeroth-order resonance energy, -0.42 cm^{-1} off resonance). The excitation spectrum of the $Br_2(B, v' = 27)$-Ne ground vdW resonance was calculated previously, and a number of $v' - 1$ vdW orbiting resonances overlapping with the v' ground resonance were identified.[21] This spectrum is displayed in Fig. 3, where the arrows indicate the position of the three excitation energies considered in this work.

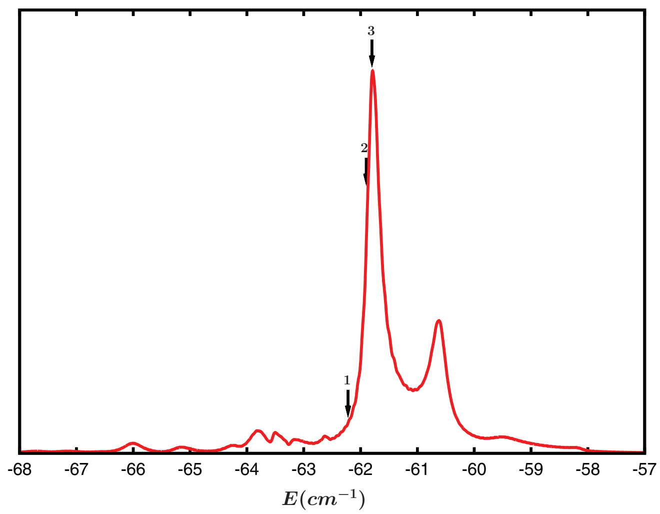

FIG. 3. Calculated excitation spectrum associated with the ground vdW resonance of $Br_2(B, v' = 27)$-Ne (Ref. 21). The energy axis is relative to the $Br_2(B, v' = 27, j' = 0)$ + Ne dissociation threshold. The arrows 1, 2, and 3 indicate the positions of the off resonance energies −62.22 and −61.90 cm^{-1}, and of the on resonance energy −61.80 cm^{-1}, respectively.

The survival probabilities calculated with several pulses for the off resonance excitation energy −62.22 cm^{-1} are shown in Fig. 4 along with the corresponding fits. The lifetimes obtained with all the pulses for the three excitation energies are collected in Table I and plotted in Fig. 5. The −62.22 cm^{-1} energy is rather far from the resonance energy, and therefore the curves of Fig. 4 corresponding to the narrow band 200 and 100 ps pulses display typical features of a continuum, with very short lifetimes. As the pulse bandwidth increases, population of energies closer to the resonance energy increases as well, causing the lifetime to increase. Most interestingly, for pulse widths between 20 and 15 ps a pattern of undulations due to quantum interference appears. The pattern appears when the pulse bandwidth is broad enough as to populate appreciably the $v' - 1$ resonances that overlap with the v' resonance, inducing interference between them. This begins to occur for pulses with FWHM < 20 ps, for which the spectral widths are FWHM > 1.5 cm^{-1} and FW > 4.0 cm^{-1} (see the excitation spectrum of Fig. 3). When the survival probability exhibits undulations the lifetime is obtained by fitting the survival probability envelope covering all the undulations, since the probability decays to zero only when the intensity of the undulations vanishes. The present pattern is qualitatively similar to the pattern of quantum beats observed experimentally in the individually detected time-dependent population of each eigenstate within a wave packet of I_2 vibrational eigenstates.[10]

TABLE I. Lifetimes τ obtained from the survival probabilities of $Br_2(B, v' = 27)$-Ne in the ground vdW resonance calculated with different pump laser pulses for three excitation energies.

Pulse FWHM (ps)	τ (ps), on resonance	τ (ps), off resonance (−0.10 cm^{-1})	τ (ps), off resonance (−0.42 cm^{-1})
200	23.5	10.9	0.2
100	21.3	18.3	0.4
50	20.3	19.5	9.4
40	20.1	19.6	13.0
30	19.9	19.3	16.2
20	19.7	18.7	17.5
15	19.3	18.6	18.3
10	18.4	18.1	18.0
5	15.9	15.9	15.8
2.5	14.1	14.1	14.1

After appearing, the pattern changes if the pulse bandwidth is further increased (going from FWHM = 15 ps to 2.5 ps) because the a_i and a_n coefficients of the superposition excited are modified, which changes the $a_n^* a_i$ interference terms in Eqs. (6) and (7). For this excitation energy the effect is that the lifetime reaches a maximum of 18.3 ps for the 15 ps pulse, and then for shorter pulses the intensity of the interference undulations decreases, causing the lifetime to decrease. When the pulse FWHM becomes shorter than 15 ps only the superposition coefficients of $v' - 1$ resonances nonoverlapping with the v' resonance increase, while the coefficients of the v' and $v' - 1$ overlapping resonances begin to decrease, damping the interference mechanism and the system lifetime.

It should be noted that in Ref. 21, the most intense feature of the spectrum, located at −61.79 cm^{-1} and with a lifetime estimated of 21.2 ps was identified in that work as a $v' - 1$ orbiting resonance. The present results indicate that such an assignment was wrong, and that the resonance at −61.79 cm^{-1} is actually the v' ground resonance instead of a $v' - 1$ orbiting resonance. The reason for avoiding the assignment of such spectral feature to the v' ground resonance was that the lifetime estimated experimentally using a pulse of FWHM = 15 ps was <10 ps,[18] far from the 21.2 ps obtained theoretically. The current theoretical results find lifetimes between 18.3 and 19.3 ps for a 15 ps pulse (see Table I). A possible explanation for this discrepancy between theory and experiment for $v' = 27$ (in addition to the approximations of the theoretical model) could be that the experiment was carried out at a somewhat off resonance excitation energy.

The spectrum of Fig. 3 shows a second most intense feature associated with a $v' - 1$ orbiting resonance located at −60.63 cm^{-1} and overlapping with the v' ground resonance, and some other $v' - 1$ resonance features also overlapping with the v' one with much smaller spectral intensity. The time separation between the maxima of the undulations in the interference pattern of Fig. 4 is ∼27 ps, which corresponds to an energy separation between resonances of ∼1.2 cm^{-1}. Not surprisingly, this is the energy separation between the v' and $v' - 1$ resonances located at −61.79 and −60.63 cm^{-1}, respectively, and producing the two most intense features in the spectrum. Thus the pattern of Fig. 4 is produced by interference of the v' ground resonance with a single $v' - 1$ orbiting resonance located at −60.63 cm^{-1}. For longer times than those shown in Fig. 4 some undulations can also be identified as produced by interference of the v' resonance with other $v' - 1$ overlapping resonances, albeit with very small intensity.

For the other two excitation energies of $Br_2(B, v' = 27)$-Ne the behavior of the survival probabilities and lifetimes with the pulse width is qualitatively similar to that previously discussed. Indeed, for narrow band pulses the lifetimes increase as the range of energies excited becomes closer to the

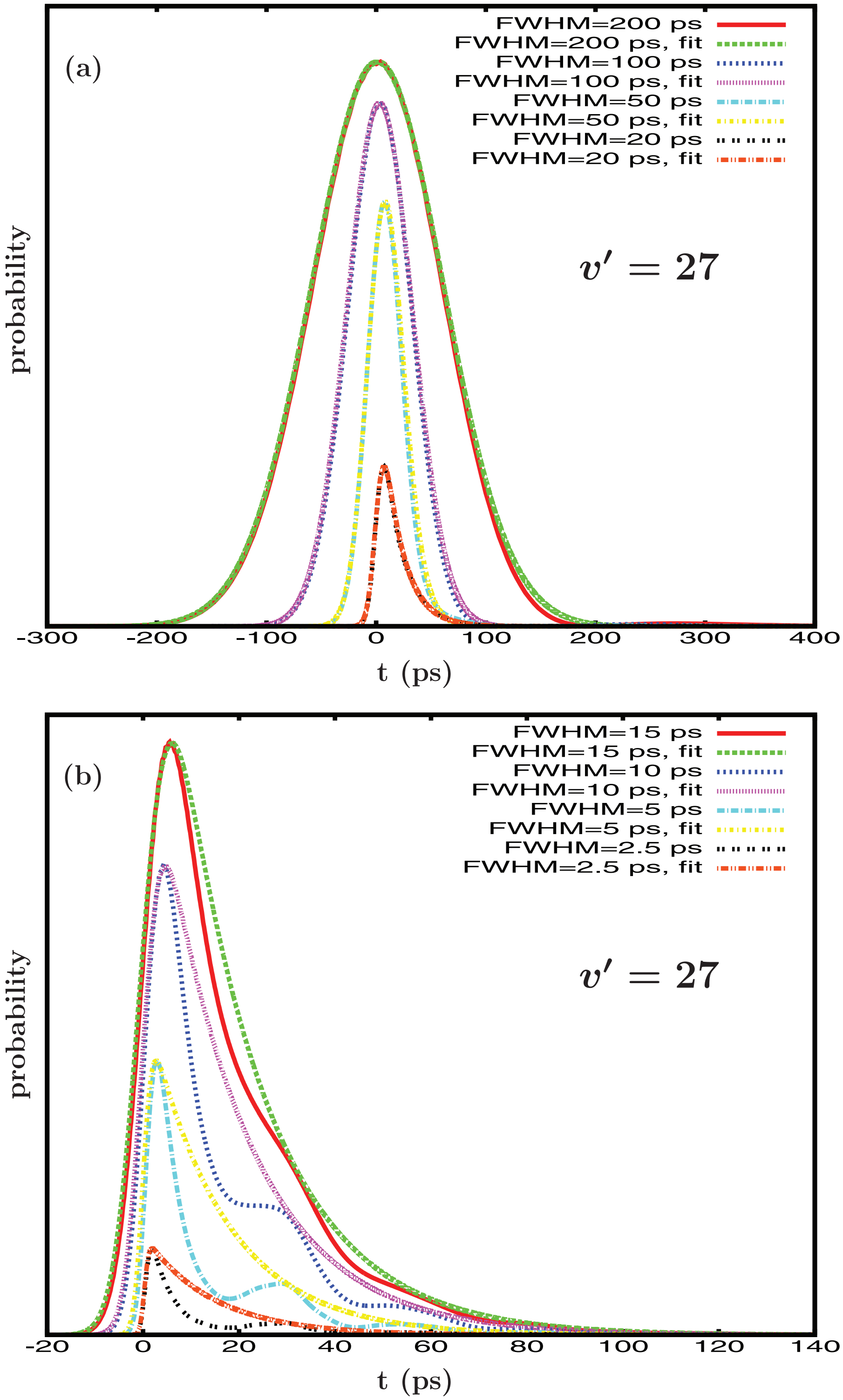

FIG. 4. Survival probability associated with $Br_2(B, v' = 27)$-Ne in the ground vdW resonance obtained with different pump laser pulses by exciting the system to the -62.22 cm^{-1} off resonance energy, along with the corresponding fit. The curves have been rescaled for convenience.

resonance energy. When the resonance energy is excited, with increasing pulse bandwidth the lifetime can only decrease because increasingly off resonance spectral components are populated. Similarly as before, for the 20 ps pulse an interference pattern appears. The interference pattern produced by a given pulse is very similar for the three excitation energies, although it becomes more intense and pronounced (leading to a longer lifetime) as the excitation energy approaches the resonance energy. The reason is that, as the center of the wave packet created approaches the resonance energy, the population of the two resonances that essentially interfere in the v' and $v' - 1$ manifolds increases, enhancing the interference effects. For pulses with FWHM $\leq$ 15 ps the survival probabilities and lifetimes obtained become practically the same for the three excitation energies. This convergence is achieved because when the spectral width of the wave packet is broad

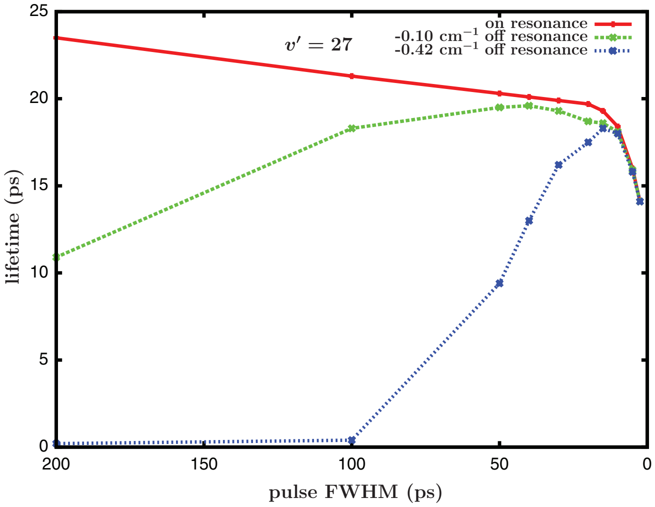

FIG. 5. Plot of the lifetimes obtained from the survival probabilities of $Br_2(B, v' = 27)$-Ne in the ground vdW resonance calculated with different pump laser pulses for three excitation energies.

enough, differences of 0.1 or 0.42 cm^{-1} in the position of the center of the wave packet bandwith affects very little the interference effects.

C. Formal rationalization of the results

At this point some remarks shoud be made. The survival probabilities shown in Fig. 4 (and also those calculated for the other two excitation energies for $v' = 27$) were computed in all cases with Eq. (6) by projecting out the corresponding resonance superposition onto the same single ψ_i zeroth-order resonance wave function, namely that of the $Br_2(B, v' = 27)$-Ne ground vdW resonance. One might think in principle that in an environment of overlapping resonances, the v' resonance wave function ψ_i may contain a strong character of the overlapping $v' - 1$ resonance located around -60.63 cm^{-1}. Then the survival probabilities (and the associated interference patterns) obtained with Eq. (6) for ψ_i would not correspond essentially to a single resonance (the v' ground one), but rather to the two mainly overlapping v' and $v' - 1$ resonances. Were this the case, the interference pattern should appear in the survival probability as soon as the bandwidth of the wave packet created covers the bandwidth of ψ_i. The excitation spectrum shows that the bandwidth of ψ_i is FW ~ 2 cm^{-1}, and thus even for the off resonance excitation energy -62.22 cm^{-1} the bandwidth of the 20 ps pulse (with FW = 4 cm^{-1}) should be more that enough as to produce the undulation pattern in the survival probability. However, Fig. 4(a) shows that for the 20 ps pulse the survival probability exhibits no interference pattern at all. This result is a strong indication that the present overlapping regime is not a strong one, and ψ_i and its associated survival probabilities of Fig. 4 correspond essentially to a single resonance, the v' ground resonance. The interference pattern appears only when the pump pulse bandwidth becomes broad enough as to populate significantly the $v' - 1$ resonance (for FWHM < 20 ps), but still in that case the survival probabilities of Fig. 4 correspond essentially to a single resonance.

The results found in this work can be rationalized in a more formal way with the aid of Eq. (6). As discussed above, the results show that essentially only one $v' - 1$ resonance interferes with the v' ground vdW resonance and causes the undulation pattern in the survival probability curves. Thus, for the sake of simplicity we can assume to a very good approximation that the resonance superposition created by the different pump pulses only contains these two resonances

$$\Phi(t) = a_1(t)\psi_1(t) + a_2(t)\psi_2(t), \tag{11}$$

with ψ_1 and ψ_2 being the v' and $v' - 1$ resonances, respectively. Now, following Eq. (6) we can express the survival probabilty associated with the ψ_1 resonance as

$$\begin{aligned} I_1(t) &= |\langle\psi_1|\Phi(t)\rangle|^2 = |a_1(t)\langle\psi_1|\psi_1(t)\rangle + a_2(t)\langle\psi_1|\psi_2(t)\rangle|^2 \\ &= |a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2 + |a_2(t)|^2|\langle\psi_1|\psi_2(t)\rangle|^2 \\ &\quad + a_1(t)a_2^*(t)\langle\psi_1|\psi_1(t)\rangle\langle\psi_2(t)|\psi_1\rangle \\ &\quad + a_1^*(t)a_2(t)\langle\psi_1(t)|\psi_1\rangle\langle\psi_1|\psi_2(t)\rangle, \end{aligned} \tag{12}$$

where, using Eqs. (3) and (5),

$$\langle\psi_1|\psi_n(t)\rangle = \int dE\langle\psi_1|\varphi_E\rangle\langle\varphi_E|\psi_n\rangle e^{-iEt/\hbar}, n = 1, 2. \tag{13}$$

There is a similar equation to Eq. (12) for $I_2(t) = |\langle\psi_2|\Phi(t)\rangle|^2$.

In the case of an isolated resonance (like the present $Br_2(B, v' = 16)$−Ne case), both $a_2(t)$ and $\langle\psi_1|\psi_2(t)\rangle$ are zero, and therefore the last three terms of the second right hand of Eq. (12) become zero. The survival probability $I_1(t)$ then consists of the single term $|a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2$, which is essentially the square of the autocorrelation function of the resonance wave function ψ_1, i.e., the traditional definition of the survival probability of a single isolated resonance. This survival probability is known to have an exponential decay.

When a superposition of two overlapping resonances is prepared (as in the present $Br_2(B, v' = 27)$−Ne case), and $a_2(t) \neq 0$ and $\langle\psi_1|\psi_2(t)\rangle \neq 0$, the contributions of the last three terms of the second right hand of Eq. (12) are nonzero and add to the exponential decay of the $|a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2$ term, producing the undulation pattern found in the survival probability for pulses with FWHM < 20 ps (for which the condition $a_2(t) \neq 0$ is fulfilled with enough intensity). In a not strong overlapping regime of the two resonances, as in the present case (see Fig. 3), the term $\langle\psi_1|\psi_2(t)\rangle$ is remarkably smaller than the term $\langle\psi_1|\psi_1(t)\rangle$. The implication is that most of the undulation pattern of the $I_1(t)$ survival probability is due to the interference terms $a_1(t)a_2^*(t)\langle\psi_1|\psi_1(t)\rangle\langle\psi_2(t)|\psi_1\rangle$ and $a_1^*(t)a_2(t)\langle\psi_1(t)|\psi_1\rangle\langle\psi_1|\psi_2(t)\rangle$ (in comparison with the contribution of the $|a_2(t)|^2|\langle\psi_1|\psi_2(t)\rangle|^2$ term).

Let us suppose now that we are again in the $Br_2(B, v' = 27)$ −Ne case, but populating only the ψ_1 resonance, that is, $a_1(t) \neq 0$ and $a_2(t) = 0$. This is what happens for pulses with FWHM > 20 ps. Despite that $\langle\psi_1|\psi_2(t)\rangle \neq 0$, the three terms of the second right hand of Eq. (12) become zero again, and we are in the same situation as in the isolated resonance regime, i.e., the survival probability decays monotonically as an exponential function, as shown in Fig. 4(a). Thus, Eq. (12) [and in general Eqs. (6) and (7)] shows clearly that in order to produce an interference pattern in the survival probability, the two requirements that are to be fulfilled simultaneously are $\langle\psi_1|\psi_2\rangle \neq 0$ (resonance overlapping condition) and $a_2(t) \neq 0$, in addition to $a_1(t) \neq 0$ (population of the overlapping resonance condition). By changing the amplitude of a_1 and a_2 it is possible to control the interference effects on the survival probability of the system in resonance ψ_1, and therefore the lifetime that the system survives in this resonance.

The main implication of the present results is that, while the resonance lifetime is an intrinsic property of an isolated, nonoverlapping resonance state, this is not so in the case of an overlapping resonance. If a superposition of resonances like that of Eq. (11) is prepared with nonoverlapping resonances ($\langle\psi_1|\psi_2\rangle = 0$), the lifetime of the system in this superposition will be an average of the lifetimes of resonances ψ_1 and ψ_2 that will depend on the coefficients a_1 and a_2. However, the survival probability and associated lifetime of each resonance state, $I_1(t) = |\langle\psi_1|\Phi(t)\rangle|^2 = |a_1(t)|^2|\langle\psi_1|\psi_1(t)\rangle|^2$ and $I_2(t) = |\langle\psi_2|\Phi(t)\rangle|^2 = |a_2(t)|^2|\langle\psi_2|\psi_2(t)\rangle|^2$, is the same as if each resonance was populated alone instead of within a superposition, regardless of the value of the coeffiecient of the other resonance in the superposition. In contrast, the onset of interference between overlapping resonances causes that the survival probability and the lifetime of a given resonance do depend on the coefficients of the other overlapping resonances in the superposition, as shown by Eq. (12).

D. Experimental realization of the control scheme

It is most convenient to rewrite the survival probability of Eq. (12) in terms of its contributions coming from the different energy components populated by the coherent superposition created by the pump pulse. This can be done by defining the coefficients

$$c_E^{(n)} = \langle\varphi_E|\psi_n\rangle. \tag{14}$$

The $c_E^{(n)}$ coefficients are an intrinsic property of each resonance ψ_n, related to its resonance width and reflected in its excitation spectrum. With the above definition we can write

$$\langle\psi_i|\psi_n(t)\rangle = \int dE c_E^{(i)*} c_E^{(n)} e^{-iEt/\hbar} \tag{15}$$

and then

$$|\langle\psi_1|\psi_1(t)\rangle|^2 = \int dE \int dE' \left|c_E^{(1)}\right|^2 \left|c_{E'}^{(1)}\right|^2 e^{-i(E-E')t/\hbar}, \tag{16}$$

$$|\langle\psi_1|\psi_2(t)\rangle|^2 = \int dE \int dE' c_E^{(1)*} c_E^{(2)} c_{E'}^{(1)} c_{E'}^{(2)*} e^{-i(E-E')t/\hbar}, \tag{17}$$

$$\langle\psi_1|\psi_1(t)\rangle\langle\psi_2(t)|\psi_1\rangle = \int dE \left|c_E^{(1)}\right|^2 \int dE' c_{E'}^{(2)*} c_{E'}^{(1)} e^{-i(E-E')t/\hbar}, \tag{18}$$

$$\langle\psi_1(t)|\psi_1\rangle\langle\psi_1|\psi_2(t)\rangle = \int dE \left|c_E^{(1)}\right|^2 \int dE' c_{E'}^{(1)*} c_{E'}^{(2)} e^{i(E-E')t/\hbar}, \tag{19}$$

which gives

$$\begin{aligned} I_1(t) = \int dE \Bigg\{ \left|c_E^{(1)}\right|^2 \Bigg[|a_1(t)|^2 \int dE' \left|c_{E'}^{(1)}\right|^2 e^{-i(E-E')t/\hbar} \\ + a_1(t) a_2^*(t) \int dE' c_{E'}^{(1)} c_{E'}^{(2)*} e^{-i(E-E')t/\hbar} \\ + a_1^*(t) a_2(t) \int dE' c_{E'}^{(1)*} c_{E'}^{(2)} e^{i(E-E')t/\hbar} \Bigg] \\ + |a_2(t)|^2 \int dE' c_E^{(1)*} c_E^{(2)} c_{E'}^{(1)} c_{E'}^{(2)*} e^{-i(E-E')t/\hbar} \Bigg\}. \end{aligned} \tag{20}$$

Each coefficient $c_E^{(1)}$ corresponds to a single energy component E of resonance ψ_1. Thus, following Eq. (20), the contribution of each energy component E of ψ_1 to the survival probability is $|c_E^{(1)}|^2\{[...] + |a_2(t)|^2|c_E^{(2)}|^2\}$, where [...] denotes the sum of the three terms between square brackets in Eq. (20). This leads to the interesting result that the contribution of each single energy component of ψ_1 to the survival probability contains the effects of the interference terms. Such a result has two important implications. One of them is that it confirms that the interference pattern found in the survival probability corresponds to the single resonance which is the target of control, as discussed above. Or in other words, while the occurrence of interference requires the population of a superposition of overlapping resonances, however, the effects of interference manifest in observables associated with single resonances of the superposition like the survival probability of the system in a given resonance.

The other implication is closely related to the important issue of the experimental realization of the present control scheme. Experimental detection of the survival probabilities obtained with Eq. (6) would involve using a narrow band probe pulse that promotes to the detection state only a wave packet similar to that associated with the target resonance ψ_i. As shown by Eq. (20), the contributions to the survival probability of all the energy components of this wave packet are susceptible to manifest the interference effects of Fig. 4. In a regime of sufficiently separated and not strongly overlapping interfering resonances (as the present case), the survival probability measured in the above conditions would correspond essentially to the i target resonance, with only a small contamination of the overlapping resonances, as discussed above. Furthermore, any possible contamination of overlapping resonances can be minimized by narrowing the bandwidth of energy components of the wave packet probed, and Eq. (20) shows that the intereference effects will still be observed in the survival probability measured. It is noted that narrow band probe pulses have been recently used to detect experimentally interference effects in the time-dependent population of individual I_2 vibrational eigenstates within a wave packet.[10] In summary, the experimental realization of the current control scheme would consist of a time-resolved pump-probe experiment, where the pump pulse would change both in width and frequency, while the probe pulse would be a narrow band pulse with fixed frequency and width adjusted to probe the target resonance ψ_i.

It is interesting now to point out similarities and differences between the present work and previous ones. In previous studies[12–14] control of the survival probability of a system prepared in a resonance superposition was explored. Here the object of control is also the survival probability of the system in a wave packet, namely a single resonance ψ_i out of the whole resonance superposition created. The novelty is that the ψ_i wave packet is associated with a given single resonance state of the system (with its properties and characteristics). It also has a remarkably smaller bandwidth than the whole resonance superposition. This can imply important differences on the effects of control. Apart from the interference effects between overlapping resonances, the lifetime of a system in a resonance superposition is expected to approach the average of the lifetimes of the resonances populated in the superposition. For a single resonance, however, the effects of control will depend in general rather strongly on specific properties of the resonance, such as width, position, and how many and which other resonances overlap with it. Thus, the ability to control the survival probability of a system can be remarkably increased by selecting different resonances.

IV. CONCLUSIONS

Quantum control of the lifetime of a system in an excited resonance state is explored by creating coherent superpositions of overlapping resonances with laser pulses of different width. The scheme of control is applied to a realistic three-dimensional wave packet model of the $Br_2(B)$-Ne predissociation decay dynamics. The present results show that by changing the pulse width the system lifetime in a resonance can be dramatically modified, both by increasing it from nearly zero to ∼18 ps and by damping it from 24 ps to 14 ps, depending on the excitation energy, which becomes an additional degree of control in combination with the pulse width. Control of the resonance lifetime is possible due to interference between the overlapping resonances in the superposition, which appears to cause the lifetime of an overlapping resonance to be a nonintrinsic property of the resonance state, in contrast to the situation of isolated, nonoverlapping resonances. This work thus demonstrates realistically the possibility to control extensively the survival probability and lifetime of a system in a single excited resonance overlapping with other resonances. A feasible experimental realization of this control scheme is suggested.

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