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Coherent control of a resonance lifetime with laser pulses

A. García-Vela *

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

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ABSTRACT

Quantum control of the lifetime of the $Br_2(B, v' = 35)$—Ne ground van der Waals resonance is investigated theoretically by creating coherent superpositions of $v' - 1$ resonances overlapping with the v' resonance. This control scheme exploits the quantum interference occurring between the overlapping resonances, which is controlled by varying the width of the laser pulse creating the superposition state. For $v' = 35$ the v' resonance overlaps more strongly and with a higher number of $v' - 1$ resonances than in the previously studied $v' = 27$ case. It is found that as a consequence of this stronger overlapping regime, the effects of control over the resonance lifetime become more intense.

1. Introduction

Achievement of quantum coherent control of molecular processes has been pursued with great interest in the last years [1–21]. The control schemes typically applied have exploited the quantum interference mechanisms induced and controlled by external optical fields. Processes like photodissociation, molecular reactions, and radiationless transitions are among the various objects of the control strategies investigated.

Among the control schemes suggested, one of them exploits the quantum interference effects that take place between overlapping resonances of the system populated by a coherent superposition created by a laser pulse [22–24]. By modifying the amplitude coefficients of the overlapping resonances within the superposition, the mechanism of interference between resonances can be controlled, which allows control over the survival probability and lifetime of the superposition created.

Recently, two schemes based on the interference between overlapping resonances were suggested to modify and control the lifetime of a system in a specific single resonance state within the superposition prepared. In the first control scheme, a laser pulse of variable width was used to modify the population of the different overlapping resonances in the coherent superposition [25]. The 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 [26–29]. It has been shown that the $Br_2(B, v' = 27)$—*Ne* ground vdW resonance overlaps with some vdW orbiting resonances of the lower $v' - 1$ vibrational manifold of Br_2, and mainly with one $v' - 1$ orbiting resonance located $\sim 1.2\ cm^{-1}$ higher in energy than the v' ground resonance [30,31]. A similar situation of a v' ground resonance overlapping with $v' - 1$ orbiting resonances was also found in the case of the $I_2(B, v' = 60, 61)$—He vdW complex [32]. An extensive degree of control of the $Br_2(B, v' = 27)$—*Ne* ground resonance lifetime was achieved with this scheme [25]. It was found that the lifetime of an overlapping resonance is no longer an intrinsic property of the resonance state, as it is the case of an isolated resonance, and this feature allows one the possibility to control it.

A second, more flexible control scheme was further suggested. This scheme used a combination of two laser pulses, one of them to excite the $v' = 27$ ground resonance and the other one to excite the $v' - 1$ orbiting resonance separated by $\sim 1.2\ cm^{-1}$ [33]. In this case the time delay and the ratio of intensities between the two pulses were used as the parameters varied to exert control by modifying the population of the two resonances, and therefore the mechanism of interference between them. A strong enhancement of the v' ground resonance lifetime, by a factor of three, was achieved with this scheme.

In this work the aim is to apply the single pulse scheme in order to control the lifetime of the ground vdW resonance state of $Br_2(B, v')$—Ne, now in the $v' = 35$ vibrational mainfold. The main difference of $v' = 35$ with respect to $v' = 27$ is that the $Br_2(B, v' = 35)$—Ne ground resonance overlaps more strongly and with several $v' - 1$ resonances (instead of mainly with a single $v' - 1$ resonance, as in $v' = 27$). Thus, the goal of the current work is to explore the effect of this stronger overlapping regime on the control scheme.

The Letter is organized as follows. In Section 2 the theoretical method is briefly described. The results are presented and discussed in Section 3. Some conclusions are given in Section 4.

2. Methodology

The ground vdW resonance of $Br_2(B, v' = 35)$—Ne is populated by laser excitation of Br_2—Ne to the $(B, v' = 35)$ excited vibronic state, $Br_2(B, v' = 35)$–Ne $\leftarrow Br_2(X, v'' = 0)$–Ne. The excited

* Fax: +34 915854894.
E-mail address: garciavela@iff.csic.es

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resonance then decays to the fragmentation continuum through vibrational predissociation of the complex, $Br_2(B, v'=35)$–Ne → $Br_2(B, v<v')$ + Ne [26–29]. It was found in previous works [29,30] that the $Br_2(B, v'=35)$—Ne ground vdW resonance overlaps with a relatively dense spectrum of $v'-1$ vdW resonances located below the $Br_2(B, v'-1)$–Ne dissociation threshold.

The excitation process $Br_2(B, v'=35)$–Ne ← $Br_2(X, v''=0)$–Ne with a laser pulse and the subsequent predissociation of the complex were simulated using a three-dimensional wave packet method which was described in detail elsewhere [29]. An empirical potential-energy surface is used [31]. Although some *ab initio* potential-energy surfaces for vdW complexes have been reported in the last years [34,35], the use of empirical potentials in studies of photodissociation dynamics of vdW clusters has been a usual practice [36–38], and in general has led to a good description of the experimental observations [29,33].

The theoretical basis of the control scheme applied in the current work has been presented in detail previously [25], so it will be just briefly reviewed here. A coherent superposition of $Br_2(B)$—Ne resonances ψ_n consisting of the v' ground resonance and the $v'-1$ manifold vdW resonances overlapping with the v' ground one is prepared with a laser pulse,

$$\Phi = \sum_n a_n \psi_n. \quad (1)$$

Let us denote the v' ground resonance wave function by ψ_i. Now, the survival probability of the system in resonance ψ_i can be expressed as

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

Eq. (2) shows that if the ψ_i and ψ_n resonances overlap, *i.e.*, $\langle\psi_i|\psi_n(t)\rangle \neq 0$, then $I_i(t)$ depends on interference terms of the type $a_n^*(t)a_j(t)$ (and the complex conjugate), where j can be $j=i$ or $j=n\neq i$. The larger is the number of ψ_n resonances overlapping with ψ_i, the larger will be the number of interference terms affecting $I_i(t)$. Therefore, by changing the amplitude coefficients a_n of the superposition of Eq. (1), the interference terms, and thus the interference effects, can be modified and controlled, allowing one to control the survival probability and associated lifetime of the system in resonance ψ_i. The a_n coefficients can be modified by changing the width of the pulse that creates the Φ superposition. The lifetime of the system, τ, is obtained by fitting $I_i(t)$ to the function

$$I_i(t_j) = A\int_{-\infty}^{t_j} CC(t)[\exp(-(t_j-t)/\tau)]dt, \quad (3)$$

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

3. Results and discussion

Pump pulses with ten different widths were used, ranging from a full width at half maximum (FWHM) FWHM = 200 ps to FWHM = 2.5 ps. The spectral width range from FWHM = 0.15 cm^{-1} and a spectral full width (FW, i.e., the energy range covered by the pulse with nonzero intensity) FW ∼ 0.4 cm^{-1} for the 200 ps pulse, to FWHM = 12.0 cm^{-1} and FW∼ 32.0 cm^{-1} for the 2.5 ps pulse. In addition to the effect of varying the pulse width, the effect of the excitation energy is also investigated. Indeed, the system is excited to three different energies, namely the $v'=35$ ground resonance energy, −56.34 cm^{-1} (relative to the $Br_2(B, v'=35)$—Ne dissociation threshold), −58.02 cm^{-1} (−1.68 cm^{-1} off resonance), and −59.76 cm^{-1} (this is the zeroth-order resonance energy, −3.42 cm^{-1} off resonance). It is noted that the v' ground resonance is separated from the v' first excited vdW resonance by ∼ 17 cm^{-1}. Therefore, even the pulse with the largest bandwidth used in the simulations (that with FWHM = 2.5 ps) cannot cover that gap and 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.

The calculated excitation spectrum of the $Br_2(B, v'=35)$—Ne ground vdW resonance is shown in Figure 1. The arrows indicate the position of the three excitation energies (on and off resonance) for which the simulations have been carried out. The spectrum shows that there are several $v'-1$ vdW resonances overlapping significantly with the $v'=35$ ground resonance, and also between them.

The survival probabilities $I_i(t)$ calculated with several pulses for excitation to the resonance energy −56.34 cm^{-1} are shown in Figure 2. The lifetimes obtained by fitting the survival probabilities with Eq. (3) are collected in Table 1 for all the pulses and the three excitation energies. These lifetimes are also plotted in Figure 3.

For the pulses with FWHM = 200 and 100 ps the survival probability displays a shape consistent with the convolution of the Gaussian pump pulse and the $v'=35$ ground resonance exponential decay associated with a resonance lifetime of $\tau \simeq 11$ ps (see Table 1). These two pulses have rather narrow spectral widths with FW∼ 0.4 and 0.8 cm^{-1}, respectively, and thus they populate essentially only the v' ground resonance. The slight decrease of τ from 10.7 to 10.6 ps is due to the slight increase of population of off resonance energy components when changing from the 200 ps to the 100 ps pulse.

A qualitative change appears when the 50 ps pulse is used, in the form of a weak and broad bump located around $t=79$ ps. The bump becomes more pronounced as the width of the pulse gradually decreases to 40, 30, and 20 ps. As already found in the case of $v'=27$ [25,33], this bump or undulation is produced by interference between the $v'=35$ ground resonance and some of the $v'-1$ vdW resonances overlapping with it. Indeed, as the bandwidth of the pump pulse increases, some a_n coefficients of $v'-1$ resonances become nonzero in Eqs. (1) and (2), and interference with the v'

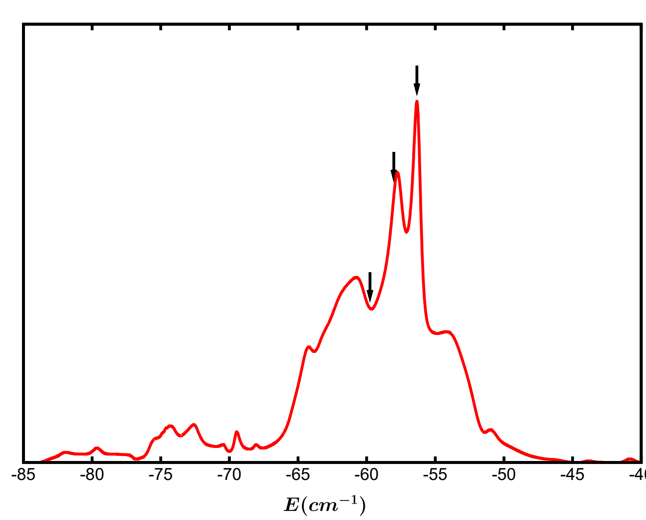

Figure 1. Calculated excitation spectrum associated with the ground vdW resonance of $Br_2(B, v'=35)$–Ne. The energy axis is relative to the $Br_2(B, v'=35, j'=0)$ + Ne dissociation threshold. The arrows indicate the positions of the off resonance energies −59.76 and −58.02 cm^{-1}, and of the resonance energy −56.34 cm^{-1}.