Enhancement of the degree of control of photofragment distributions by laser phase modulation

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Abstract

The possibility of enhancing the degree of control of a transient photofragment distribution achieved by means of laser phase modulation is explored. Such a control is exerted through interference between overlapping resonances which are populated in a superposition by the laser field. It is found that by varying the central frequency of the pump laser across the energy range of the resonance superposition created, the effects of laser phase modulation on the resonance interference mechanism change remarkably, causing significant variations on the photofragment distribution. Knowledge of these variations can be used to increase and optimize the control effects of the scheme applied. The results presented here show that the intensity of the phase modulation control effect on the fragment distribution can be increased by more than double. Thus, varying the laser carrier frequency as an additional control parameter makes the control scheme more efficient and flexible.

Keywords: Coherent control, Overlapping resonances, Interference, Photodissociation, Fragment distributions

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1 INTRODUCTION

A large variety of molecular processes are governed by resonance states.^[1,2] Among them, some examples are photodissociation processes like electronic,^[3] vibrational,^[4,5] and rotational^[6] predissociation of a molecular system, as well as low-temperature reactive^[7–12] and nonreactive^[13–20] molecular collisions. Control of such molecular processes has been pursued for a long time.^[21–39] In the case of resonance-mediated processes, modifying the behavior of the resonance state (or states) governing the process appears as a natural control strategy. Modification of the behavior of a resonance essentially involves modification of the resonance properties such as the lifetime (which determines the duration of the process) and the product fragment state distributions produced upon resonance decay (which determine the outcome of the process).

Weak-field coherent control (vs. strong-field control) has the advantage of preserving the inherent dynamics of the system. Strategies to control the resonance lifetime based on quantum interference have been suggested for overlapping and isolated resonances in the weak-field regime.^[40–43] However, weak-field control of the product fragment distributions is a more challenging problem. It has been proven theoretically that for closed systems, phase control of the asymptotic, long-time final photofragment state distributions is not possible in the weak-field regime.^[44] Indeed, that proof showed that asymptotic product distributions are independent on the laser phase, and thus phase modulation cause no effects on the final fragment distributions. The reason is that the laser phase distribution is a complex exponential function of the pulse frequencies, and since the fragment state distributions are square magnitudes, this complex function cancels out. Thus the only dependence of the final state distribution on the laser field is through the spectral profile, and control of the asymptotic distribution is possible only by changing that profile. In this sense, a control scheme has been suggested that modifies the final, asymptotic fragment state distribution, based on varying the shape of the spectral profile (albeit keeping its bandwidth fixed) through interference between two pulses delayed

in time, that overlap in the frequency domain.^[45,46]

While no laser phase modulation control of the asymptotic fragment distribution is possible, however, control of the transient distribution can be achieved by modulation of the laser phase in some conditions. It has been shown that when a superposition of nonorthogonal, interfering states, like overlapping resonances, is prepared, transient weak-field phase control of the time-dependent populations of some electronic states in different systems is possible during a postpulse time window.^[47,48] More recently, the first computational demonstration of coherent control of the transient state distribution of photodissociation fragments, based on pure phase modulation of the pump pulse in the weak-field regime, was reported for a polyatomic molecule supporting overlapping resonances.^[49,50] Phase control effects on the transient fragment distribution were demonstrated by varying the chirp rate of the pump pulse applied, and such effects were found to persist for a long-time window after the pulse is over. As discussed previously,^[50] the control scheme is based on the interference occurring between the system overlapping resonances, and on how the interference mechanism changes when the pulse chirp is varied.

The possibility of enhancing the degree of control achieved by laser phase modulation is an important aspect which was not addressed in the previous works.^[49,50] Such an enhancement is expected to be associated with specific ways of interference between the overlapping resonances.^[51] For a given chirp rate of the pulse (which determines the temporal sequence in which the different overlapping resonance components are excited by the pump pulse), a factor which also determines the mechanism of resonance interference is the central or carrier frequency of the pulse, since it determines the relative amplitudes excited in the different resonances by the pulse applied. Varying this central frequency should have an impact on the resonance interference mechanism, and therefore on the control of the transient fragment distribution. Thus, the goal of the present work is to investigate how the variation of this parameter of the pulse affects the enhancement of the degree of control achieved on the transient product distribution. To this purpose, the specific process subject of

this study is the vibrational predissociation of the Ne-Br₂(*B*) van der Waals (vdW) complex, as done earlier,^[49,50] because this system is rich in overlapping resonances.

2 THEORETICAL BACKGROUND

Upon excitation Ne-Br₂(*X*, $v'' = 0$) + $h\nu \rightarrow$ Ne-Br₂(*B*, v') with a laser pulse with a given bandwidth, a superposition of resonances of Ne-Br₂(*B*, v') is populated. The labels v'' and v' denote the vibrational states of Br₂ in the *X* and *B* electronic states, respectively. Then the resonances decay to the fragmentation continuum through vibrational predissociation, Ne-Br₂(*B*, v') $\rightarrow$ Ne + Br₂(*B*, $v_f < v'$). This process has been studied in detail both experimentally^[52,53] and theoretically^[4,5]. Excitation of Ne-Br₂(*B*, v') and subsequent predissociation was simulated with a full three-dimensional wave packet method (assuming $J = 0$) described in detail elsewhere^[4,40]. In order to assess the quality of the model applied, it is noted that the lifetime calculated with the present model for the decay of the Ne-Br₂(*B*, $v' = 16$) ground intermolecular resonance was found to be 69 ps^[42], while the corresponding lifetime estimated experimentally is 68 ± 3 ps^[53]. Such a good agreement indicates that both the three-dimensional wave packet method and the potential surfaces used in the present simulations are realistic enough in order to describe this resonance decay process.

The simulations will focus on excitation of the Ne-Br₂(*B*, $v' = 27$) ground intermolecular resonance. It has been shown^[5,40] that this resonance overlaps with some orbiting resonances of Ne-Br₂(*B*, $v = v' - 1 = 26$). These orbiting resonances lie above the Ne + Br₂(*B*, $v' - 1 = 26$, $j' = 0$) dissociation threshold, and are supported by centrifugal barriers. The excitation spectrum associated with the Ne-Br₂(*B*, $v' = 27$) ground intermolecular resonance is displayed in Figure 1. The main peak located at -61.8 cm⁻¹ corresponds to the Ne-Br₂(*B*, $v' = 27$) ground resonance, while the other two peaks at the energies -60.63 and -59.5 cm⁻¹ correspond to two $v = 26$ orbiting resonances overlapping with each other and with the Ne-Br₂(*B*, $v' = 27$) ground resonance. There are other less intense peaks in the

spectrum associated with some other $v = 26$ orbiting resonances.

Excitation of $\text{Ne-Br}_2(B, v' = 27)$ is carried out by applying a pump pulse with a fixed Gaussian frequency distribution centered around ω_0 (which is the frequency required to excite a given energy of the spectrum of Figure 1), including a quadratic spectral phase function with chirp parameter β_0 . The electric field applied in the excitation takes the form

$$\mathcal{E}(t) = \mathcal{E}_0 \text{Re} \left[\sqrt{\frac{\tau_0^2}{\tau_0^2 - i\beta_0}} \exp \left(-\frac{(t - t_0)^2}{2\tau^2} - \frac{i\beta(t - t_0)^2}{2} - i\omega_0(t - t_0) \right) \right], \quad (1)$$

with a linear chirp rate β and a pulse duration τ related to τ_0 and β_0 via

$$\beta = \frac{\beta_0}{(\tau_0^4 + \beta_0^2)}, \quad (2)$$

and

$$\tau^2 = \tau_0^2 \left(1 + \frac{\beta_0^2}{\tau_0^4} \right). \quad (3)$$

The value $\tau_0 = 2.12$ ps was used in the above equations. For a transform-limited pulse ($\beta_0 = \beta = 0$) the above value of τ_0 corresponds to a temporal full width at half maximum (FWHM) of the pulse of $\tau_{\text{FWHM}} = \tau\sqrt{8\ln 2} = \tau_0\sqrt{8\ln 2} = 5$ ps. 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/cm², within the weak-field regime. The values $\beta_0 = 0$ ps² (no chirp), $\beta_0 = 75$ ps² (positive chirp), and $\beta_0 = -75$ ps² (negative chirp) have been used for the pulses applied in the simulations.

Figure 2A shows the Gaussian envelope of the laser pulse $\mathcal{E}(t)$ for the two values $\beta_0 = 0$ and $\beta_0 = 75$ ps² of the chirp parameter used in the present calculations (the corresponding envelope for $\beta_0 = -75$ ps² is the same as for $\beta_0 = 75$ ps²). As seen from the figure, the maximum temporal range covered by the pulse with $\beta_0 = 75$ and $\beta_0 = -75$ ps² is 100 ps. In Figure 2B the spectral profile $|\mathcal{E}(\omega)|^2$ associated with the pulses of Figure 2A is displayed. The spectral FWHM of $|\mathcal{E}(\omega)|^2$ is 4 cm⁻¹, and the full bandwidth of the profile covers ~ 12 cm⁻¹. This bandwidth covers all the spectrum of Figure 1.

In previous works where the goal was to study the effect of varying the magnitude of the chirp,^[49,50] the frequency ω_0 of the pump pulse applied was always fixed

to reach the energy -61.8 cm^{-1} of the $\text{Ne-Br}_2(B, v' = 27)$ ground intermolecular resonance. In the present work the goal is different. Then the strategy applied consists of keeping fixed the chirp rate (which is the usual situation of an experiment), and shifting gradually the central energy excited by the pump pulse to higher energies, starting from -61.8 cm^{-1} . The total shift of the central energy excited applied in the simulations is 3 cm^{-1} , namely from -61.8 to -58.8 cm^{-1} . This leads to a gradual increase of the population excited to the two $v = 26$ orbiting resonances at the expense of a decrease of the $v' = 27$ ground resonance population. This allows to investigate how preparing different superpositions of the overlapping resonances with the pump pulse affects the intensity of interference between them, and therefore the degree of control achieved on the transient fragment distribution produced.

3 RESULTS AND DISCUSSION

When a pump pulse is applied with specific values of the chirp parameter β_0 and carrier frequency ω_0 , the normalized vibrational populations of the $\text{Br}_2(B, v_f)$ product fragment are calculated as

$$P_{v_f}^{\text{norm}}(t) = \frac{P_{v_f}(t)}{\sum_{v_f} P_{v_f}(t)}, \quad (7)$$

with $v_f = v' - 1, v' - 2, \dots$. These $P_{v_f}(t)$ populations include the contributions of all the energies of the spectrum of Figure 1 populated by the pulse in the superposition prepared, and are equivalent to the transient populations measured in a time-resolved experiment. The transient vibrational populations for $v_f = v' - 1$ and $v' - 2$ at times $t \geq 0$ are shown in Figure 3 for the three different values of β_0 , and for four energy shifts of the central energy of the pulse spectral profile $|\mathcal{E}(\omega)|^2$ with respect to the energy -61.8 cm^{-1} of the $\text{Ne-Br}_2(B, v' = 27)$ ground intermolecular resonance.

For all the energy shifts ΔE the transient populations of Figure 3 show postpulse variations once the pulse applied is over (for $t \geq 100$), as expected from previous results.^[49,50] The most interesting result is that the magnitude of the variations in the populations increases remarkably with increasing ΔE . The increase of the

population of the $v = 26$ orbiting resonances (and the corresponding decrease of the $v' = 27$ ground resonance population) in the superposition created, produced by increasing ΔE causes a change in the mechanism of interference between the different overlapping resonances, producing a change of the postpulse variations in the transient populations. The interesting implication is that the changes in the interference mechanism are intense enough as to produce a remarkable enhancement of the magnitude of the postpulse variations in the populations.

In the following the effect of varying ΔE on increasing the magnitude of the postpulse variations in the transient populations will be analyzed in more detail. Figure 3 shows that the effect appears to be very similar in the populations of both $v_f = v' - 1$ and $v' - 2$. Thus, for simplicity only the $v_f = v' - 1$ population will be analyzed. To this purpose, the magnitude $P(t) = (P_{v_f}^{norm,(a)}(t) - P_{v_f}^{norm,(b)}(t))/P_{v_f}^{norm,(a)}(t)$ is defined, where $P_{v_f}^{norm,(a)}(t) = P_{v_f}^{norm,\beta_0=0,\Delta E}(t)$ and $P_{v_f}^{norm,(b)}(t) = P_{v_f}^{norm,\beta_0=\pm 75ps^2,\Delta E}(t)$. This quantity is very convenient because it provides the effects of interference (in percentage) on the transient populations when β_0 is varied from 0 to 75 (or -75) ps^2 for different ΔE energy shifts. While the absolute values of $P_{v_f}^{norm,\beta_0=0,\Delta E}(t)$ and $P_{v_f}^{norm,\beta_0=\pm 75ps^2,\Delta E}(t)$ change with ΔE (see Figure 3), the main advantage of the relative magnitude $P(t)$ is that it allows a comparison on equal foot of the interference effects produced by varying ΔE .

The $P(t)$ functions obtained for different energy shifts when $P_{v_f}^{norm,(b)}(t) = P_{v_f}^{norm,\beta_0=75ps^2,\Delta E}(t)$ are shown in Figure 4 for times $t \geq 100$ ps, namely once the positively chirped pulse is over. The figure thus displays the postpulse interference effects produced. As expected from previous results,^[49,50] $P(t)$ and therefore the interference effects vanish at long times, as the population excited to the overlapping resonances gradually decays in time. However, before reaching this asymptotic behavior the curves show clear interference effects, mainly in the time window between 100 and 200 ps, but also with still appreciable intensity up to nearly 500 ps. The most interesting result is a trend of gradual change of the sign of the main peak of the curves, which goes from $\sim -8\%$ at around 150 ps for $\Delta E = 0$ to $\sim 12\%$ at 120

ps for $\Delta E = 3.0 \text{ cm}^{-1}$. A corresponding gradual change of sign of the curves takes place also for $t > 200$ ps.

The change of sign in the curves of Figure 4 occurs because the absolute intensity of $P_{v_f=v'-1}^{norm, \beta_0=0, \Delta E}(t)$, which is smaller than that of $P_{v_f=v'-1}^{norm, \beta_0=75\text{ps}^2, \Delta E}(t)$ for $\Delta E = 0$, becomes gradually larger as ΔE increases ($P(t)$ is calculated as a difference between those two populations). Actually this change is already appreciated in the populations of Figure 3, and is caused by increasing the relative population of the $v = 26$ orbiting resonances with respect to that of the $v' = 27$ ground resonance in the superposition prepared. Thus, in the present case by shifting the central energy of the pump pulses by 3 cm^{-1} , the interference effects caused by the chirp of the pulse are indeed enhanced, causing a variation of the $v_f = v' - 1$ transient population from $\sim -8\%$ to $\sim 12\%$, *i.e.*, a total range of variation of $\sim 20\%$ vs. the variation of $\sim -8\%$ obtained with $\Delta E = 0$. The degree of control achieved is therefore increased by more than double. In addition, the time position of the peaks of each curve of Figure 4 in the time window $100 - 200$ ps also changes with ΔE , going from ~ 150 ps for $\Delta E = 0$, to ~ 190 ps for $\Delta E = 1.6 \text{ cm}^{-1}$, and finally to ~ 120 ps for $\Delta E = 3.0$, which provides some flexibility to the control scheme.

The $P(t)$ curves calculated when a negatively chirped pulse ($\beta_0 = -75 \text{ ps}^2$) is applied for different ΔE shifts are shown in Figure 5. A similar trend as in Figure 4 of gradual change of the sign of the relative postpulse variations of the transient populations with increasing ΔE is found. While the qualitative behavior of these curves is similar to that found in Figure 4, still some differences are displayed. Such differences are not surprising because a negative chirp affects the mechanism of interference between resonances in a different way as a positive one. The change of sign of the main peak intensity requires here a much smaller shift of only $\Delta E = 0.4 \text{ cm}^{-1}$ to go from $\sim -8\%$ (for $\Delta E = 0$) to $\sim 4\%$. The total range of variation of the interference effects, $\sim 12\%$, is also somewhat smaller in this case. An interesting difference with the positive chirp situation is that in Figure 5 the curves display two main peaks in the time range $100 - 200$ ps, namely one around 150 ps and a second

one around 200 ps, and the behavior of these peaks with ΔE is rather different. The peak around 150 ps first changes sign from negative to positive, and then changes back to negative sign by increasing further ΔE . By contrast, the peak around 200 ps only changes sign from positive to negative with increasing ΔE . Thus, while negative chirp in general produces somewhat less intense postpulse variations in the transient populations when ΔE is varied, however it produces remarkable variations at different times, which complements the increase of the degree of control achieved with positive chirp.

The results of Figure 4 and 5 can be summarized as follows. When the carrier frequency of the pump laser field samples the energy range of the overlapping resonance superposition created, different combinations of relative populations of those resonances are prepared. The behavior of the interference mechanism between the resonances will be different as the relative populations change, and thus the effects of phase modulation on the transient populations will also be different. Therefore, the result of varying the laser carrier frequency is to disclose the whole range of possible effects of laser phase modulation (both in intensity and nature) on the transient photofragment distribution. Clearly, knowledge of this range of effects makes the application of the control scheme more efficient and flexible.

4 CONCLUSIONS

Control of transient product photofragment distributions through interference between overlapping resonances induced by laser phase modulation is investigated. More specifically, the possibility of enhancing the degree of control achieved by laser phase modulation is explored by shifting the carrier frequency of the pump laser field across the energy range of the superposition of overlapping resonances created. The effect of this shift is to vary the relative population of the different overlapping resonances, which changes the mechanism of interference between them and therefore the effect of laser phase modulation on the transient photofragment distribution. It is found that by properly handling this change in the interference mechanism, varying

the laser carrier frequency, it is possible to increase and optimize the degree of control achieved both for positive and negative laser chirps with respect to the situation where only a single fixed carrier frequency is chosen. In the case studied here the results show that the degree of control can be enhanced by more than double. Thus the present findings allow for a more efficient and flexible application of the laser phase modulation control scheme of photofragment distributions. Experimental application should be straightforward.

ACKNOWLEDGMENTS

This work was funded by the Ministerio de Economía y Competitividad (MINECO, Spain), Grant No. CTQ2015-65033-P, and COST Action program, Grant Nos. CM1401 and CM1405. The Centro de Supercomputación de Galicia (CESGA, Spain) is acknowledged for the use of its resources.

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FIGURE CAPTIONS

FIGURE 1 Excitation spectrum associated with the $\text{Ne-Br}_2(B, v' = 27)$ ground inter-molecular resonance. The energy axis is relative to the $\text{Ne} + \text{Br}_2(B, v' = 27, j' = 0)$ dissociation threshold.

FIGURE 2 (A) Temporal profiles of the pump pulse applied with two values of the chirp parameter β_0 . (B) Spectral profile of the pump pulses of the upper panel.

FIGURE 3 Time-dependent normalized vibrational population of the $\text{Br}_2(B, v_f)$ fragment produced in the $v_f = v' - 1$ and $v' - 2$ final vibrational states, upon predissociation of a $v' = 27$ and $v' - 1$ $\text{Ne-Br}_2(B)$ resonance superposition prepared with a pump laser pulse with three different chirp parameters β_0 and for four values of the shift ΔE of its central energy.

FIGURE 4 Calculated $P(t)$ functions defined as $P(t) = (P_{v_f}^{norm, \beta_0=0, \Delta E}(t) - P_{v_f}^{norm, \beta_0=75\text{ps}^2, \Delta E}(t)) / P_{v_f}^{norm, \beta_0=0, \Delta E}(t)$ for different values of the shift ΔE .

FIGURE 5 Same as in Figure 4 but for $P(t)$ defined as $P(t) = (P_{v_f}^{norm, \beta_0=0, \Delta E}(t) - P_{v_f}^{norm, \beta_0=-75\text{ps}^2, \Delta E}(t)) / P_{v_f}^{norm, \beta_0=0, \Delta E}(t)$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5