Communication: Control of the fragment state distributions produced upon decay of an isolated resonance state

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Control of the fragment state distributions produced upon decay of a resonance state is achieved by using a weak laser field consisting of two pulses with a varying time delay between them. It is shown that specific product fragment states can be significantly favored or quenched. The efficiency and flexibility of the control method are found to increase with increasing resonance width. The control scheme is completely independent of the specific system to which it is applied, which makes its applicability universal. Published by AIP Publishing.

Quantum coherent control of molecular processes has become a research field of growing interest in the last two decades.1–17 Controlling a specific molecular process involves exerting control over the different observables associated with that process. Among the observables of interest to be controlled are the time scale of the process, the opening/closing of specific molecular reaction channels and the final product distributions. Different control strategies have been developed with the goal of achieving the above specific control targets in a variety of molecular processes.

Resonance states are interesting objects that can act as intermediate or doorway states from which some molecular processes can be activated. Thus, controlling the decay process of a given resonance would imply to control the molecular process mediated by that resonance state. The two essential observable properties associated with the decay of a resonance state are its lifetime and the final product state distributions. Thus, exerting control over these two properties of the resonance decay would provide a high degree of control on the process mediated by the resonance of interest. Schemes to control the lifetime of a single resonance state have been developed for the cases of both overlapping and isolated resonances.20 Control strategies have also been proposed to modify the product fragment state distributions produced by the decay of a superposition of resonances.21–24 It would also be desirable to have available a flexible scheme to control the fragment state distributions produced by the decay of a single, isolated resonance state.

It has been shown for atomic and diatomic systems that the relative populations of the different states excited within a superposition can be modified in the weak field, one-photon limit by using a combination of two subsequent laser pulses with a varying time delay between them.8,25,26 As discussed below, the condition required is that the two pulses overlap in a certain range of their spectral domain, because this causes the appearance of an interference term that modulates the spectral profile of the laser field, thus modifying the relative populations within the superposition. Modification of the relative populations of the components of a superposition causes the variation of the final fragment state distributions produced upon photodissociation of the superposition prepared. In this work, it is shown for the first time that the above effect can be used in order to achieve a flexible control of the final photofragment state distributions produced upon decay of a single, isolated resonance state. The flexibility of the control scheme is demonstrated by applying it to the decay of several resonances of different width of the Ne-Br$_2$(B, $v'$) polyatomic complex, a system rich in different types of resonances.

Upon laser excitation, Ne-Br$_2$(B, $v'$ = 0) + hν → Ne-Br$_2$(B, $v'$), an intermolecular resonance is populated, and then it decays to the fragmentation continuum through vibrational predissociation, Ne-Br$_2$(B, $v'$) → Ne + Br$_2$(B, $v_f$ < $v'$). This process has been studied in detail both experimentally27,28 and theoretically.29–32 The process of Ne-Br$_2$(B, $v'$) excitation with a laser field and the subsequent predissociation of the complex was simulated with a full three-dimensional wave packet method (assuming $J = 0$) described in detail elsewhere.18,30 It is noted that the lifetime calculated with the present theoretical model for the decay of the Ne-Br$_2$(B, $v'$ = 16) ground intermolecular resonance has been found to be 69 ps,30 while the corresponding lifetime estimated experimentally is 68 ± 3 ps.26 This good agreement with the experimental lifetime implies that both the three-dimensional wave packet method and the potential surfaces used in the present simulations are quite realistic in order to describe this resonance decay process.

The pump laser field used here to excite the resonance state is a combination of two Gaussian pulses,

$$E_{\text{pump}}(t) = E_0 e^{-\left(t-t_1\right)^2/2\sigma^2} \cos[\omega_1(t-t_1) + \phi_1]$$

$$+ E_0 e^{-\left(t-t_2\right)^2/2\sigma^2} \cos[\omega_2(t-t_2) + \phi_2],$$

(1)

where $\omega_1$, $\omega_2$ and $t_1$, $t_2$ are the frequency and time centers, respectively, of the two pulses. For simplicity, the phases are taken to be $\phi_1 = \phi_2 = 0$, and the amplitudes of the pulses are assumed to be equal, $E_0 = 1.0 \times 10^{-10}$ a.u., which corresponds to a maximum pulse intensity of about $3.5 \times 10^4$ W/cm$^2$, within the weak-field regime.

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The frequency amplitude profile \( \tilde{E}_{\text{pump}}(\omega) \) of the laser field of Eq. (1) can be calculated as the Fourier transform,

\[
\tilde{E}_{\text{pump}}(\omega) = \int_{-\infty}^{\infty} E_{\text{pump}}(t)e^{i\omega t}dt.
\]  

(2)

For a laser field consisting of Gaussian functions like \( E_{\text{pump}}(t) \), the integral of Eq. (2) can be performed analytically, and after some algebra it is found that

\[
\tilde{E}_{\text{pump}}(\omega) = \frac{1}{2}\left[\left(e^{-\sigma^{2}(\omega^{2} + \omega_{1}^{2})/2} + e^{-\sigma^{2}(\omega^{2} + \omega_{2}^{2})/2}\right)e^{i\omega t_{1}}
\right.
\]

\[
+ \left(e^{-\sigma^{2}(\omega^{2} + \omega_{1}^{2})/2} + e^{-\sigma^{2}(\omega^{2} + \omega_{2}^{2})/2}\right)e^{i\omega t_{2}},
\]

(3)

or in more compact form

\[
\tilde{E}_{\text{pump}}(\omega) = A(\omega, \omega_{1})e^{i\omega t_{1}} + B(\omega, \omega_{2})e^{i\omega t_{2}}.
\]  

(4)

Now, the spectral profile \( |\tilde{E}_{\text{pump}}(\omega)|^{2} \) of the field \( E_{\text{pump}}(t) \) that determines the relative populations of the energy components of the resonance excited is

\[
|\tilde{E}_{\text{pump}}(\omega)|^{2} = A^{2}(\omega, \omega_{1}) + B^{2}(\omega, \omega_{2})
\]

\[
+ A(\omega, \omega_{1})B(\omega, \omega_{2})\left[e^{i\omega(t_{2} - t_{1})} + e^{-i\omega(t_{2} - t_{1})}\right]
\]

\[
= A^{2}(\omega, \omega_{1}) + B^{2}(\omega, \omega_{2}) + 2A(\omega, \omega_{1})
\]

\[
\times B(\omega, \omega_{2})\cos[\omega(t_{2} - t_{1})].
\]  

(5)

The term \( 2A(\omega, \omega_{1})B(\omega, \omega_{2})\cos[\omega(t_{2} - t_{1})] \) of Eq. (5) is an interference term that modulates the shape of \( |\tilde{E}_{\text{pump}}(\omega)|^{2} \) (without changing its spectral bandwidth) by varying the time delay \( \Delta t = t_{2} - t_{1} \) between the two pulses of \( E_{\text{pump}}(t) \). As pointed out above, the condition for this term to be nonzero is that the factor \( A(\omega, \omega_{1})B(\omega, \omega_{2}) \) be nonzero, which implies that the bandwidths of the two pulses of the field of Eq. (1) must overlap in a certain range of frequencies. The most important implication of Eq. (5) is that the appearance of the interference term is independent of the system and the specific resonance state to which the laser field is applied, which makes this control scheme of universal application.

A resonance can be defined as a state whose behavior and properties depend strongly on energy. One of these properties is the fragment state distribution produced upon predissociation of the resonance energy components excited by the laser field. This is the case of the two pulses of \( E_{\text{pump}}(t) \) used here, both with a temporal full width at half-maximum (FWHM) of \( \tau_{\text{FWHM}} = \sigma \sqrt{8 \ln 2} = 100 \text{ ps} \).

In Fig. 1(a), the spectral profile associated with the \( \tau_{\text{FWHM}} = 100 \text{ ps} \) pulse laser field is shown for different time delays \( \Delta t \) between the two pulses of \( E_{\text{pump}}(t) \). For all the time delays, the spectral profile \( |\tilde{E}_{\text{pump}}(\omega)|^{2} \) varies as a function of \( \Delta t \), as shown below.

The field \( E_{\text{pump}}(t) \) of Eq. (1) has been applied to excite three intermolecular resonances of \( \text{Ne-Br}_{2}(B, v') \) with different widths, associated with the \( v' = 16 \) and 27 vibrational manifolds of \( \text{Br}_{2}(B) \). For simplicity, the same central frequency \( (\omega_{1} = \omega_{2}) \) has been chosen for the two pulses of \( E_{\text{pump}}(t) \), although this is not a requirement of the control scheme. In this way the overlap between the spectral bandwidths of both pulses is complete, and \( |\tilde{E}_{\text{pump}}(\omega)|^{2} \), the control scheme. In this way the overlap between the spectral bandwidths of both pulses is complete, and |\( \tilde{E}_{\text{pump}}(\omega)|^{2} \)
delays, the bandwidth remains fixed, covering a narrow range of ~0.6 cm\(^{-1}\) (from ~62.1 to ~61.5 cm\(^{-1}\)). While for \(\Delta t = 0\) the profile is plain, for \(\Delta t \neq 0\) it displays oscillations due to the interference term \(2A^2(\omega, \omega_\Delta) \cos(\omega \Delta t)\). The separation between the maxima of the oscillations is proportional to \(1/\Delta t\). Thus, as \(\Delta t\) increases, the number of oscillations in the profile increases as well. For very large \(\Delta t\), the \(\cos(\omega \Delta t)\) factor becomes a rapidly oscillating function, and the shape of the profile approaches that of the \(\Delta t = 0\) profile. In this limiting cases of \(\Delta t = 0\) and large \(\Delta t\), similar outcomes regarding the final fragment state distributions are expected. It is also noted that since \(\cos(-\omega |\Delta t|) = \cos(\omega |\Delta t|)\), the same profile is obtained for equal time delays between the pulses, regardless of their sign.

The decay of the Ne-Br aggregate (B, \(v' = 27, n' = 0\)) resonance has been simulated by applying the \(E_{\text{pump}}(t)\) laser field with different \(\Delta t\) time delays between the pulses. The normalized vibrational populations of the Br\(_2\) (B, \(v\)) product fragment are calculated as

\[ \rho_{v,v}(t) = \frac{P_{v,v}(t)}{\sum_{v'} P_{v',v}(t)}, \]

with \(v_f = v' - 1, v' - 2, \ldots\). The \(P_{v,v}(t)\) populations associated with the dominant dissociation channel, which in this case is \(v_f = v' - 2\) because the \(v_f = v' - 1\) channel is nearly closed,\(^{30}\) are displayed at times \(t \geq 0\) in Fig. 1(b) for different \(\Delta t\).

The asymptotic \(\rho_{v,v}(t)\) populations exhibit a variation as \(\Delta t\) is modified, as a result of the modification of the corresponding spectral profile [see Fig. 1(a)]. The variation of the populations shows an oscillating behavior as \(\Delta t\) increases from \(\Delta t = 0\). As commented above, when \(\Delta t\) becomes large the asymptotic population approaches a similar value to that obtained for \(\Delta t = 0\), as confirmed by the result found for \(\Delta t = 500\) ps. The overall variation of the population is 0.018, from 0.663 for \(\Delta t = 100\) ps to 0.645 for \(\Delta t = 400\). Since the sum of all the \(\rho_{v,v}(t)\) is normalized to unity, i.e., \(\sum_{v'} \rho_{v,v}(t) = 1\) at every \(t\), the total variation of the difference \(\rho_{v,v}(t)\) populations is 1.8%. The remaining normalized populations for \(v_f = v' - 1, v' - 3,\) and \(v' - 4\) vary correspondingly to compensate the 0.018 variation of the \(v_f = v' - 2\) population. In relative terms, variations of specific populations are larger than 1.8%. Indeed, the \(v_f = v' - 2\) population varies about 2.8% (0.028 \(\pm\) 0.018/0.645), while the \(v_f = v' - 1\) population varies about 11% (it changes from 0.103 to 0.114 for \(\Delta t = 100\) and 400, respectively).

The Ne-Br aggregate (B, \(v' = 27, n' = 0\)) resonance is a rather narrow one. It is interesting to investigate how the present control scheme behaves as the resonance width changes. For this purpose, the first excited intermolecular Ne-Br aggregate (B, \(v' = 27, n' = 1\)) resonance has been chosen. This resonance is located at the energy ~44.87 cm\(^{-1}\) (i.e., about 17 cm\(^{-1}\) above the \(n' = 0\) resonance) and has associated a lifetime of 6.3 ps, which means that it is more than three times broader than the \(n' = 0\) resonance. The \(n' = 1\) resonance overlaps very weakly with some \(v' - 1\) orbiting resonances, so it can be considered as essentially an isolated resonance. Here two pulses with a temporal width of \(\Delta t = 15\) ps each have been used in the \(E_{\text{pump}}(t)\) field. The excitation spectrum of the \(n' = 1\) resonance along with the spectral profile of the laser field applied with different \(\Delta t\) are shown in Fig. 2(a).

The \(E_{\text{pump}}(t)\) populations associated with the dominant dissociation channel (\(v_f = v' - 1\)) obtained for different \(\Delta t\) are shown in Fig. 2(b). An oscillating behavior of the population variation similar to that found for the \(n' = 0\) resonance is also displayed in Fig. 2(b). The total variation of the \(v_f = v' - 1\) population is 0.055, from 0.711 to 0.656 for \(\Delta t = 10\) and 15 ps, respectively, which involves a total change of 5.5%, larger than that obtained for \(n' = 0\). The specific \(v_f = v' - 3\) asymptotic population changes from 0.094 for \(\Delta t = 15\) ps to 0.063 for \(\Delta t = 30\) ps which implies a relative variation of about 50% for this population. Thus the control scheme appears to be more efficient as the resonance width increases.

In order to confirm the above trend, simulations have been carried out for the Ne-Br aggregate (B, \(v' = 16, n' = 0\)) ground intermolecular resonance, which has an associated lifetime of 69 ps,\(^{20}\) and therefore is about ten times narrower than the Ne-Br aggregate (B, \(v' = 27, n' = 1\)) resonance. To this purpose, a field \(E_{\text{pump}}(t)\) with two pulses with a temporal width \(\Delta t = 200\) ps and different time delays between them has
been applied. The total variation of the dominant channel \(B(\nu_f = \nu' - 1)\) fragment population found (not shown) is very small, 0.000 26 (or 0.026%), from 0.936 19 to 0.936 45 for \(\Delta t = 200\) and 400 ps, respectively, which comes to support the trend that as the resonance is narrower, the control scheme becomes more inefficient. For broader resonances, a stronger dependence of the fragment distributions on energy becomes more likely, and then the effects on the distributions of changing the shape of \(|\tilde{E}_{\text{pump}}(\omega)|^2\) become more pronounced. It appears, however, that the degree of control achieved over the fragment distributions can be related, to a large extent, to the specific decay mechanism of the resonance of interest. Further investigation of this point should be very interesting. It is also noted that for sufficiently broad resonances, the control method could become more flexible by using different central frequencies, \(\omega_1 \neq \omega_2\), then \(\Delta \omega = \omega_2 - \omega_1\) becoming an additional control parameter.

One most interesting finding is that by choosing appropriately the time delay between pulses, it is possible to favor a specific final state of the fragments. This is shown in Fig. 3 for the case of the Ne-Br \((B, \nu' = 27, n' = 1)\) resonance. For \(\Delta t = 10\) ps, the \(\nu_f = \nu' - 1\) population increases, while the \(\nu_f = \nu' - 2, \nu' - 3,\) and \(\nu' - 4\) populations decrease, as compared to the populations found for \(\Delta t = 0\). The larger decrease occurs in the case of the \(\nu_f = \nu' - 2\) population. However, when \(\Delta t = 15\) ps, the \(\nu_f = \nu' - 1\) population decreases (relative to the \(\Delta t = 0\) result) and the \(\nu_f = \nu' - 2, \nu' - 3,\) and \(\nu' - 4\) populations increase, but now the larger increase corresponds to the \(\nu' - 3\) population (by about 42%, from 0.066 to 0.094). Thus, by changing slightly \(\Delta t\), from 0 to 10 and 15 ps in this case, a specific final state of the dissociation fragments can be remarkably quenched (\(\nu_f = \nu' - 2\)) or favored (\(\nu_f = \nu' - 3\)). This additional possibility of control is a consequence of the oscillating behavior of the variation of the final distributions combined with the specific energy dependence of these distributions.

In summary, this work demonstrates that the fragment state distributions produced upon decay of a resonance state can be controlled by using a weak laser field consisting of two pulses overlapping spectrally and with a certain time delay between them. Control is based on interference between the two pulses. Specific product fragment states can be favored or quenched. The efficiency and flexibility of the control scheme are found to increase with increasing resonance width. The present findings are general for any isolated resonance state, regardless of the specific system involved. Experimental application of this control strategy should be straightforward.

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