Measurement-assisted Coherent Control
Jiangbin Gong and Stuart A. Rice
Department of Chemistry and The James Franck Institute,
The University of Chicago, Chicago, Illinois 60637
(Dated: November 6, 2018)

Two advantageous roles of the influence of measurement on a system subject to coherent control are exposed using a five-level model system. In particular, a continuous measurement of the population in a branch state in the Kobrak-Rice extended stimulated Raman adiabatic passage scheme is shown to provide a powerful means for controlling the population transfer branching ratio between two degenerate target states. It is demonstrated that a measurement with a large strength may be used to completely shut off the yield of one target state and that the same measurement with a weak strength can dramatically enhance the robustness of the controlled branching ratio against dephasing.

I. INTRODUCTION

Interest in coherent control of atomic and molecular processes has grown rapidly in recent years. One of the prominent goals is the manipulation of quantum interference effects to enhance the yield of a particular wanted final state while suppressing the yield of another. An example of this class of operations is enhancement of the yield of one product of a reaction while suppressing the yield of a competing product. In this case, and in others as well, a quantum system under control is typically not measured until the desired unitary evolution ends. The advantages and disadvantages of the influence of measurement on the system in a variety of coherent control scenarios remain unexplored.

We note that the inhibition or acceleration of a quantum process under observation, the so-called quantum Zeno and anti-Zeno effects, demonstrate that the role of measurement in quantum dynamics can be dramatic. Although the quantum Zeno effect was first derived in terms of wavefunction collapse induced by a measurement, recent studies have shown that introducing the concept of wavefunction collapse is unnecessary for describing the quantum Zeno and anti-Zeno effects. That is, a measurement apparatus, even in the case of obtaining a null result, always disturbs the system’s Hamiltonian and can therefore strongly affect the quantum dynamics without involving our consciousness, a view that is adopted in this paper.

In this paper we describe two interesting and advantageous roles of measurement in coherent control, using a well-studied model of selective photochemistry, namely, the Kobrak-Rice extended five-level stimulated Raman adiabatic passage scheme. That model is also the basis for the Chen-Shapiro-Brumer strong field control approach to selective photochemistry. In particular, it is shown that a continuous measurement of population in a so-called “branch state” with a large measurement strength provides a powerful means for manipulating the nonadiabatic coupling and therefore the useful quantum interference between two particular adiabatic states. The resultant control over the population transfer branching ratio between two degenerate product states is extraordinary insofar as (1) the yield of one of the two target states may be completely shut off while the yield of the other target state is still considerable, and (2) the intermediate state is unpopulated during the population transfer. Further, we show that the same measurement with a weak strength can dramatically enhance the stability of the controlled branching ratio under adverse situations, such as in the presence of strong dephasing modelled by stochastic energy level fluctuations. These results are of broad theoretical and experimental interest. Indeed, the measurement-assisted coherent control of the branching ratio between two unmeasured product states can be regarded as a third aspect of measurement effects that complements the quantum Zeno and anti-Zeno effects.

FIG. 1: A schematic diagram of the Kobrak-Rice five-level model for the control of population transfer branching ratio between two degenerate states $|3\rangle$ and $|4\rangle$, with the branch state $|5\rangle$ subject to a continuous population measurement.
II. EXPLOITING MEASUREMENT EFFECTS: STRONG MEASUREMENT LIMIT

A schematic diagram of the Kobrak-Rice five-level model is shown in Fig. 1. The initial state $|1\rangle$ is coupled with the intermediate state $|2\rangle$ by a pump pulse, while state $|2\rangle$ is coupled with two degenerate product states $|3\rangle$ and $|4\rangle$ by a Stokes pulse. Due to the degeneracy of states $|3\rangle$ and $|4\rangle$, altering their population transfer branching ratio (denoted by $B$) cannot be achieved unless we introduce the “branch state” $|5\rangle$ that is also coupled with states $|3\rangle$ and $|4\rangle$ by a third “branching pulse”. All the laser fields are on resonance with the respective transitions $|1\rangle \leftrightarrow |2\rangle$ and are assumed to be Gaussian, with their pulse duration sufficiently short that, except for one case discussed below, the natural lifetimes of all the five states can be taken as infinitely. To be specific, the associated Rabi frequencies (assumed to be real) [see Fig. 1] are chosen to be $\Omega_P = \Omega_P \exp[-(t - T)^2 / T^2]$, $\Omega_{S3,S4} = \Omega_{S3,S4} \exp[-t^2 / T^2]$, and $\Omega_{B3,B4} = \Omega_{B3,B4} \exp[-0.5(t - 0.5T)^2 / T^2]$, where the pump and Stokes pulses have been counter-intuitively ordered $\mathcal{H}$. The characteristic magnitude of the various peak Rabi frequencies is represented by $\Omega$. The branch state is also subject to a continuous population measurement by coupling it to a continuum. Within the framework of the slowly varying continuum approximation $\mathcal{H}$, the disturbance of the system by the continuous measurement can be described by a finite and controllable lifetime of state $|5\rangle$, $\mathcal{H}$, with a decay rate constant (denoted $\Gamma$) to be tuned via the strength of the system-probe interaction. However, because $\mathcal{H}$ is not on-resonance Hamiltonian in the absence of branch state measurement, the eigenvalues and eigenvectors of $\mathcal{H}$ written as $\mathcal{H} = \mathcal{H}_r + \mathcal{H}_f$, where $\mathcal{H}_r$ denotes the on-resonance Hamiltonian in the absence of branch state measurement,

$$\mathcal{H}_r = \begin{bmatrix} 0 & \Omega_P & 0 & 0 & 0 \\ \Omega_P & 0 & \Omega_{S3} & \Omega_{S4} & 0 \\ 0 & \Omega_{S3} & 0 & 0 & \Omega_{B3} \\ 0 & \Omega_{S4} & 0 & 0 & \Omega_{B4} \\ 0 & 0 & \Omega_{B3} & \Omega_{B4} & 0 \end{bmatrix},$$

(1)

and $\langle k | \mathcal{H}_f | j \rangle = -i \Gamma \delta_{kj} \delta_{5}^{j}$ is due to the continuous measurement. The eigenvalues and eigenvectors of $\mathcal{H}_r$, denoted by $\lambda_k$ and $|\lambda_k\rangle$, $k = 1 - 5$, can be obtained analytically. In particular, there exists one null eigenvalue (denoted $\lambda_1$) with its eigenvector given by

$$|\lambda_1\rangle = \frac{1}{N_1} [\Omega_{SB}, 0, -\Omega_P \Omega_{B4}, \Omega_P \Omega_{B3}, 0]^T,$$

(2)

where $\Omega_{SB} \equiv (\Omega_{S3} \Omega_{B4} - \Omega_{S4} \Omega_{B3})$. Other eigenvalues of $\mathcal{H}_r$ are given by

$$\lambda_k = \frac{1}{2} \left( \Omega_M^2 \pm \sqrt{\Omega_M^4 - 4(\Omega_{SB}^2 + \Omega_{B3}^2 + \Omega_{B4}^2)} \right),$$

(3)

where $k = 2 - 5$, and $\Omega_M^2$ represents the sum of the squares of all the five Rabi frequencies. The associated eigenvectors are given by

$$|\lambda_k\rangle = \frac{1}{N_k} \begin{bmatrix} \Omega_P (\Omega_{B3}^2 - \Omega_{B4}^2 - \Omega_{B4}^2) \\ \lambda_k (\Omega_{B3}^2 - \Omega_{B4}^2 - \Omega_{B4}^2) \\ \Omega_{S3} \Omega_{B3}^2 - \Omega_{B4} \Omega_{SB} \\ \Omega_{S4} \Omega_{B4}^2 + \Omega_{B3} \Omega_{SB} \\ \lambda_k (\Omega_{B3} \Omega_{S3} + \Omega_{B4} \Omega_{S4}) \end{bmatrix}, k = 2 - 5,$$

(4)

where $N_k$ is the normalization factor. Note that $|\lambda_1\rangle$ has a node on state $|2\rangle$, can fully correlate with the initial and final states, and can be far away from $|\lambda_k\rangle$ ($k = 2 - 5$). In the absence of $\mathcal{H}_f$, $|\lambda_1\rangle$ is the key eigenstate for adiabatic passage $\mathcal{H}$ without populating the intermediate state, and the associated population transfer branching ratio between the two degenerate target states $|3\rangle$ and $|4\rangle$ is given by $B = \Omega_{B4}^2 / \Omega_{B3}^2$. Interestingly, $|\lambda_1\rangle$ [see Eq. (2)] also has zero overlap with the branch state, so it survives in the presence of $\mathcal{H}_f$. However, the exact forms of the other eigenvalues and eigenvectors of $\mathcal{H}$ are too complicated to be useful. Below we use various perturbation theory techniques to reveal the interesting consequences for the system of introducing $\mathcal{H}_f$.

Here we consider the case of strong system-probe interaction, i.e., $\Gamma \gg \Omega$. Then the system is dominated by the measurement and the laser-induced couplings can be regarded as a perturbation. In particular, $\mathcal{H}$ can be written as $\mathcal{H} = (\mathcal{H} - \mathcal{V}_B) + \mathcal{V}_B$, where

$$\langle k | \mathcal{V}_B | j \rangle = \Omega_{B3} (\delta_{k3} \delta_{5j} + \delta_{j3} \delta_{5k}) + \Omega_{B4} (\delta_{k4} \delta_{5j} + \delta_{j4} \delta_{5k}).$$

(5)

The eigenvalue-eigenvector structure of $(\mathcal{H} - \mathcal{V}_B)$ can be easily obtained since state $|5\rangle$ therein is decoupled by construction. However, because $(\mathcal{H} - \mathcal{V}_B)$ has two (degenerate) null eigenvalues, a naive perturbation treatment is bound to fail. Our strategy is to first make a special superposition of the two null eigenstates of $(\mathcal{H} - \mathcal{V}_B)$ to construct the eigenstate $|\lambda_1\rangle$ that is known to exist in the presence of $\mathcal{V}_B$. Then second-order perturbation theory is applied to the subspace that is orthogonal to $|\lambda_1\rangle$. We obtain three complex eigenvalues and one purely imaginary eigenvalue (denoted $\lambda_2'$) that lies closest to $\lambda_1$. As such, for the consideration of nonadiabatic effects below, only the coupling between $|\lambda_1\rangle$ and the eigenvector associated with $\lambda_2'$ (denoted $|\lambda_2\rangle$) is important. Specifically,

$$\lambda_2' = -i \left[ \Omega_P (\Omega_{B3}^2 + \Omega_{B4}^2 + \Omega_{SB}^2) / |\Gamma(\lambda_2')^2| \right];$$

(6)

$$|\lambda_2\rangle = \frac{1}{N_2} \begin{bmatrix} \Omega_{SB} \Omega_{B4} + \Omega_{SB} \Omega_{B3} \\ 0 \\ \Omega_{S3} \Omega_{B4} + \Omega_{SB} (\Omega_{B4}^2 + \Omega_{S4}^2) \\ \Omega_{S4} \Omega_{B3} + \Omega_{SB} (\Omega_{B3}^2 + \Omega_{B4}^2) \\ i \left[ \Omega_{B3}^2 (\Omega_{B3}^2 + \Omega_{B4}^2 + \Omega_{SB}^2) / \Gamma \right] \end{bmatrix},$$

(7)

where $N_2$ is the normalization factor. Equation (6) shows that the peak value of $i \lambda_2'$ is of the order of $\Omega_2^2 / \Gamma$. Hence, in effect, the continuous measurement of the population of the branch state with a large strength modifies the spectrum of $\mathcal{H}_r$ such that an eigenstate ($|\lambda_2\rangle$)
that lies close to $|\lambda_1\rangle$ is created and the spacing between them ($|\lambda_1 - \lambda_2\rangle$) becomes tunable. Equation (7) shows that $|\lambda_2\rangle$ also has a node on the intermediate state but does not overlap with the initial state at early times, and that the (final) $B$ associated with $|\lambda_2\rangle$ is given by $B_2 = \tilde{\Omega}_{B3}^2/\tilde{\Omega}_{B4}^2 = 1/B_1$.

Let $C_1(\xi)$ and $C_2(\xi)$ represent the quantum amplitudes on the adiabatic states $|\lambda_1\rangle$ and $|\lambda_2\rangle$, where $\xi \equiv t/T$. With all other eigenstates of $H$ neglected the quantum dynamics reduces to that of a two-level system,

\begin{align}
\frac{dC_1(\xi)}{d\xi} &= O_{21}(\xi)C_2(\xi), \\
\frac{dC_2(\xi)}{d\xi} &= -i\lambda_2^T C_2(\xi) - O_{21}(\xi)C_1(\xi),
\end{align}

where $O_{21}(\xi) = \langle \lambda_1 | d\lambda_2^T / d\xi \rangle$ describes the nonadiabatic coupling between $|\lambda_1\rangle$ and $|\lambda_2\rangle$. Using Eqs. (8) and (9) one finds

\begin{equation}
O_{21}(\xi) = -2\Omega P_3 \Omega_{SB}(\Omega_{S3} \Omega_{B3} + \Omega_{S4} \Omega_{B4})/(N_1 N_2^*). \tag{10}
\end{equation}

Consider then three different regimes of $\Gamma$. First, in the adiabatic limit, i.e., $(\tilde{\Omega}T)^2 \gg T\Gamma$, the decay term $-i\lambda_2^T T$ in Eq. (9) dominates such that $\tilde{C}_2$ is always negligible and so is the population loss from $|\lambda_1\rangle$. This gives $B \approx B_1$. Second, in the quantum Zeno limit, i.e., $(\tilde{\Omega}T)^2 \ll T\Gamma$, $-i\lambda_2^T T$ is negligible and $|\lambda_1\rangle$ and $|\lambda_2\rangle$ become essentially degenerate, resulting in strong nonadiabatic effects that are beyond our control. Indeed, in this case the branch state is observed too vigorously: any transition to it is frozen and so it becomes useless for modulating control. The associated $B$ then approaches $\tilde{\Omega}_{S3}^2/\tilde{\Omega}_{S4}^2$, a result inherent to the four-level system obtained by discarding state [5]. The third regime, i.e., $(\tilde{\Omega}T)^2 \sim T\Gamma$, is of most significance. Denoting $\tilde{C}_1$ and $\tilde{C}_2$ as the final values of $C_1(\xi)$ and $C_2(\xi)$ obtained from Eqs. (9), (10), (11) and (12), and using Eqs. (2) and (7) one obtains

\begin{equation}
B = \frac{\tilde{C}_1^2 \tilde{\Omega}_{B4}^2 + \tilde{C}_2^2 \tilde{\Omega}_{B3}^2 + (\tilde{C}_1 \tilde{C}_2^* + \tilde{C}_1^* \tilde{C}_2) \tilde{\Omega}_{B3} \tilde{\Omega}_{B4}^2}{|\tilde{C}_1|^2 \tilde{\Omega}_{B3}^2 + |\tilde{C}_2|^2 \tilde{\Omega}_{B4}^2 - (\tilde{C}_1^2 \tilde{C}_2^* + \tilde{C}_1 \tilde{C}_2^* \tilde{\Omega}_{B3} \tilde{\Omega}_{B4})}. \tag{11}
\end{equation}

Clearly, the value of $B$ predicted by Eq. (11) is not a simple mixture of the two branching ratios $B_1$ and $B_2$ associated with states $|\lambda_1\rangle$ and $|\lambda_2\rangle$. Rather, due to their constructive or destructive quantum interference $B$ can be zero or infinity. That is, by varying $\Gamma$ and therefore $\tilde{C}_1$ and $\tilde{C}_2$, different superpositions of the two adiabatic states $|\lambda_1\rangle$ and $|\lambda_2\rangle$ can be realized and it becomes possible to completely suppress population transfer to one of the two degenerate target states. Detailed conditions for $B = 0$ or $B = \infty$ will be discussed elsewhere [13].

III. EXAMPLES

Figure 2 shows two typical computational examples of (strong) measurement assisted control of $B$. As seen from Fig. 2 the theoretical results predicted by Eq. (11) are in excellent agreement with those obtained by directly solving the Schrödinger equation. The effect of a continuous measurement of the population of the branch state is profound. In particular, in case (a) the yield of state $|3\rangle$ (denoted $P_3$) is essentially turned off for $\Gamma T \sim 750$ whereas the yield of state $|4\rangle$ (denoted $P_4$) is about 22%; in case (b) $P_3$ is totally suppressed for $\Gamma T \sim 900$ whereas $P_4$ is as large as 33%. From Fig. 2 it is also seen that even though state $|4\rangle$ is coupled more strongly with the measured branch state than state $|3\rangle$, $P_4$ may, counterintuitively, be less affected by the measurement than $P_3$. We stress that the significant control shown in Fig. 2 is achieved without populating the intermediate state. This is the case because the entire two-dimensional subspace spanned by $|\lambda_1\rangle$ and $|\lambda_2\rangle$ has a node on state $|2\rangle$, and is effectively decoupled from other adiabatic states. Remarkably, our further calculations show that one may also achieve $B \approx 0$ or $B \approx \infty$ even when the natural lifetimes of the product states are much shorter ($e.g., T/5$) than the pulse duration $\Gamma$.

FIG. 2: The final population in degenerate states $|3\rangle$ and $|4\rangle$ (represented by $P_3$ and $P_4$, $B = P_3/P_4$) as a function of the measurement strength characterized by $\Gamma$. $\tilde{\Omega}_B T = 10$, $\tilde{\Omega}_{B3} T = 30$, $\tilde{\Omega}_{B4} T = 50$. In case (a) $\tilde{\Omega}_{S3} T = 30$, $\tilde{\Omega}_{S4} T = 70$ and in case (b) $\tilde{\Omega}_{S3} T = 60$, $\tilde{\Omega}_{S4} T = 40$. Solid and dashed lines represent the theoretical results from Eq. (11), and discrete points represent the results obtained by directly solving the Schrödinger equation.

As an aside we note that $H_T$ can be thought of as an “imaginary detuning” from the branch state. Thus, the above formalism with slight modifications ($e.g.,$ with a real $\lambda_2$) seems to suggest that the quantum interference between states $|\lambda_1\rangle$ and $|\lambda_2\rangle$ may also be manipulated if we detune the branching pulse by a very large amount. However, a large detuning often induces resonant or nearly resonant transitions to other states that
are not included in the five-level system. Moreover, due to the different nature of the associated nonadiabatic dynamics, the complete suppression of one product channel based on detuning is found to be much less common (e.g., it does not occur in cases (a) or (b) in Fig. 2), and if obtained has a far more limited tolerance to variation of the natural lifetimes of the product states than that achieved by a strong measurement.

IV. WEAK MEASUREMENT LIMIT

We now turn to the case of weak system-probe interaction, i.e., $\Gamma << \Omega$. Here $H_T$ can be treated as a perturbation to $H_r$. The null eigenvalue $\lambda_1$ and the null eigenvector $|\lambda_1\rangle$ still exist. Let the other eigenvalues and eigenvectors be $\lambda''_k$ and $|\lambda''_k\rangle$, $k = 2 - 5$. To the zeroth order of $H_T$ one has $|\lambda''_k\rangle = |\lambda_k\rangle$. This yields, to the first order of $H_r$,

$$R(\lambda''_k) = R(\lambda_k);$$
$$\Im(\lambda''_k) = -\Gamma \lambda''_k^2(\Omega_{B3}\Omega_{S3} + \Omega_{B4}\Omega_{S4})^2/N_k^2.$$

The above perturbative treatment gives $|\lambda''_k - \lambda_1| \approx |\lambda_k - \lambda_1|$, so the coherent population transfer can adiabatically follow $|\lambda_1\rangle$. $B$ therefore equals $B_1$, and the measurement at first glance seems to play no role. Nevertheless, the imaginary part of $\lambda''_k$ suggests that even if the undesired adiabatic states $|\lambda''_k\rangle$ become populated due to some uncontrollable factors, such as the instability in laser phases or energy level fluctuations, they may still be absorbed away by the measurement which however keeps the population in the null eigenstate intact. More significantly, we find a strong correlation between $\Im(\lambda''_k)$ and $D_B$, where $D_B$ represents the difference between $B_1$ and the time-evolving branching ratio given by $|\lambda''_k\rangle$. Using Eq. (13) one finds

$$D_B = \frac{(\lambda''_k^2\Omega_{S3} + \Omega_{B4}\Omega_{SB})^2}{(\lambda''_k^2\Omega_{S4} + \Omega_{B3}\Omega_{SB})^2} = \frac{\Omega_{B4}^2}{\Omega_{B3}^2}.$$

Comparing the above result with Eq. (13) one sees that, in general, states $|\lambda''_k\rangle$ with a larger $\lambda''_k$ will give a worse $B$ but will be absorbed by the weak measurement more quickly [14]. Interestingly, if $\Omega_{S3}\Omega_{B3} + \Omega_{S4}\Omega_{B4} = 0$, then $\Im(\lambda''_k) = 0$ at all times for $k = 2 - 5$. But this presents no difficulty since Eq. (14) will give $D_B = 0$ as well. That is, in the cases where states $|\lambda''_k\rangle$ are unaffected by the weak measurement of the population of the branch state, they necessarily give the right $B$. Clearly, then, a weak continuous measurement of the population of the branch state can serve as a convenient and effective “error correction” tool in realizing adiabatic passage.

V. EXAMPLE: SELECTIVE POPULATION TRANSFER IN THE PRESENCE OF STRONG DEPHASING

We now apply the finding of the previous section to selective population transfer in the presence of strong dephasing [15, 16, 17], where the dephasing (caused by, e.g., the coupling with other degrees of freedom, bimolecular collisions, or solvent effects on a solute molecule) is simulated by stochastic Gaussian fluctuations $\delta\omega_k$ ($k = 1 - 5$) associated with each of the five levels. The degeneracy between states (3) and (4) is assumed to be maintained, i.e., $\delta\omega_3 = \delta\omega_4$. The mean properties of $\delta\omega_k$ are chosen to be $\langle \delta\omega_k \rangle = 0$ and $\langle \delta\omega_k(t)\delta\omega_k(t') \rangle = \delta\omega_k\Delta^2\exp[-|t - t'|/\tau]$, $k, k' = 1 - 3, 5$. A computational example is shown in Fig. 3a, where $\Delta T = 15$ (a value that represents extremely strong dephasing) and $\tau = 0.02T$ (a value that is comparable to $1/\Omega$ to further enhance the dephasing-induced nonadiabatic effects [16, 17]). The goal in this example is to achieve $B = 25.0$ and it is assumed that there indeed exists a branch state that meets this goal, i.e., $B_1 = 25.0$. As is seen in Fig. 3b, the value of $B$ without the measurement is terribly degraded by dephasing and is as small as 2.6. However, upon introducing a weak measurement of the population of the branch state, we obtain a dramatic increase to $B = 24.0$ for $\Gamma T = 3$ (Fig. 3c), $B = 24.9$ for $\Gamma T = 6$ (Fig. 3d) and for $\Gamma T = 9$ (Fig. 3e). As seen in Fig. 3 this almost perfect recovery of the desired value of $B$ is attained with a considerable total yield of the products and with a wide range of the (weak) measurement strength. We have obtained similar results in numerous other cases, such as those with different $\tau$, $B_1$, $\Omega_{S3}/\Omega_{S4}$, or different timing and duration of the branching pulse.

VI. CONCLUDING REMARKS

It is important to note that although the measurement of the population of the branch state absorbs away some population by, for example, breaking up some molecules from an ensemble of molecules that are subject to the control fields, our purpose in introducing it is to generate desired quantum interference effects. In the strong measurement case considered in Secs. II and III, the measurement creates a second adiabatic state that can be significantly populated during the population transfer and thereby induces quantum interference effects that are absent in the unmeasured five-level STIRAP system. In the weak measurement case considered in Secs. IV and V, the measurement of the population of the branch state enhances the robustness of the quantum interference effects inherent in the unmeasured five-level STIRAP system. That is, during the population transfer those molecules that are broken up by the weak measurement have the potential to generate a wrong branching ratio, and those that survive the weak measurement carry the desired quantum interference induced by the
FIG. 3: Measurement-assisted recovery of a desired branching ratio \((B_3 = 25.0)\) in the presence of strong dephasing. Shown here is the time dependence of the population in states \([3]\) and \([4]\) (represented by \(P_3\) and \(P_4\)) without (case a) measurement, or with measurement for (b) \(\Gamma T = 3\), (c) \(\Gamma T = 6\), and (d) \(\Gamma T = 9\). \(\Omega_P T = 20\), \(\Omega_S T = 50\), \(\Omega_S T = 40\), \(\bar{\Omega}_B T = 15\), \(\bar{\Omega}_S T = 75\). The results are obtained by averaging over 1000 realizations of the stochastic energy level fluctuations.

Hence, while a measurement on a quantum system subject to coherent control necessarily introduces decoherence to the system, it can still be beneficial for coherent control, with the price that the total yield of the product states is less than 100%. Nevertheless, one should never let the best be the enemy of the good. This price is acceptable, particularly when the main objective of coherent control is to alter at will the branching ratio between two product states. The results of our study can also be regarded as an extension of our previous work \([17]\), where we have shown that the decay of a target state or measuring the population of the target state can greatly improve the performance of a three-level STIRAP system in the presence of strong dephasing \([15, 18, 19]\).

In conclusion, we find that the population transfer branching ratio between degenerate product states may be significantly altered by observing the system. Our results suggest that coherent control can be even more powerful than previously thought if we combine quantum interference effects with measurement effects. The effects we have described depend on the character of the influences induced when the population of the branch state is measured, and are different from the kind of final state branching ratio that develops as the result of incoherent kinetic competition between parallel pathways. Potential applications of this work include control of molecular chirality, control of photodissociation, and control of isomerization reactions in solution.

VII. ACKNOWLEDGMENTS

This work was supported by the National Science Foundation.

[1] S.A. Rice and M. Zhao, Optical Control of Molecular Dynamics (John Wiley, New York, 2000).
[2] S.A. Rice, Nature 409, 422 (2001).
[3] M. Shapiro and P. Brumer, Principles of the Quantum Control of Molecular Processes (John Wiley, New York, 2003).
[4] K. Bergmann, H. Theuer, and B.W. Shore, Rev. Mod. Phys. 70, 1003 (1998).
[5] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, Science 288, 824 (2000).
[6] V. Frerichs and A. Schenzle, Phys. Rev. A 44, 1962 (1991).
[7] L.S. Schulman, Phys. Rev. A 57, 1509 (1998).
[8] A. Luis, Phys. Rev. Lett. 76, 4340 (1996); Phys. Rev. A 67, 062113 (2003).
[9] P. Facchi and S. Pascazio, Fortschr. Phys. 49, 941 (2001); Phys. Rev. Lett. 89, 080401 (2002).
[10] M.N. Kobrak and S.A. Rice, Phys. Rev. A 57, 2885 (1998); J. Chem. Phys. 109, 1 (1998).
[11] V. Kurkal and S.A. Rice, J. Phys. Chem. B 105, 6488 (2001).
[12] It is exactly the resonant laser-molecule coupling that makes it possible to describe a molecular system in terms of a few energy levels. For example, Ref. \([11]\) has shown that the Kobrak-Rice five-level model works well in the presence of nonresonant coupling with a large number of background states.
[13] J. Gong and S.A. Rice, unpublished.
[14] Although measuring the intermediate state \([2]\) will also keep \(\ket{\lambda_1}\) intact and introduce nonzero \(\Re(\lambda''_\nu|D_B)\), it is not useful since the strong correlation between \(D_B\) and \(\Re(\lambda''_\nu)\) no longer exists.
[15] M. Demirplak and S.A. Rice, J. Chem. Phys. 116, 8028 (2002).
[16] M. Demirplak and S.A. Rice, J. Phys. Chem. A 107, 9937 (2003).
[17] J. Gong and S.A. Rice, J. Chem. Phys. 120, 3777 (2004).
[18] L.P. Yatsenko, V.I. Romanenko, B. W. Shore, and K. Bergmann, Phys. Rev. A 65, 043409 (2002).
[19] Q. Shi and E. Geva, J. Chem. Phys. 119, 11773 (2003).