Alternate schemes for the coherent laser control of chemical reactions

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Several schemes are presented for the coherent laser control of chemical reactions. They are based on the principle of interference between quantum mechanical excitation pathways first proposed by Brumer and Shapiro [Acc. Chem. Res. 22, 407 (1989)]. The conclusion that these schemes may be useful for coherent laser control is based on the fact that, for each of the schemes, the quantum mechanical interference effect has been observed previously in nonlinear optical experiments; however, no attempt to control the interference was attempted in these experiments.

The purpose of this paper is to bridge a gap between ongoing research in a specific area of photochemistry and previous experimental and theoretical research in the area of optical physics. In particular, the general concepts developed by chemists Brumer and Shapiro for the coherent laser control of chemical reactions will be described and it will be shown that there are several alternate light-matter interactions that can be used for controlling reactions. These alternate schemes are specific implementations of the general concepts developed by Brumer and Shapiro and are drawn from the research efforts of many optical physics groups who were studying the interactions for reasons unrelated to controlling chemical reactions. It is hoped that new experiments will be stimulated by the following discussion which tries to emphasize the applicability of the previous work to photochemistry using a consistent language.

Researchers have found in recent years that the radiative control of chemical reactions can be achieved using coherent, multifrequency laser fields. One method for the coherent laser control of reactions, first proposed by Brumer and Shapiro, relies on the principle that two distinct interfering optical excitation pathways can be created in the molecule of interest using a multifrequency laser field. This field populates via both pathways a pure quantum state that is correlated to a linear combination of the possible product states. The control is manifest by adjusting the relative phase and amplitude of the various frequency components that make up the laser field, thereby changing the relative strength of the excitation pathways and hence changing the relative yield of the products. Since this method relies on an interference effect, the relative phase and amplitudes of the laser frequency components must be stable (coherent). Note that the laser field can be a continuous-wave field in contrast to other schemes that require short laser pulses.

The control technique proposed by Brumer and Shapiro is quite general and is well understood theoretically. A specific proposal to experimentally realize the control technique was advanced by Shapiro et al. It involves irradiating the molecule of interest with a laser field that is composed of two frequency components: one at frequency $\omega_1$ and the other at $\omega_2 = 3 \omega_1$. For future reference it will be said that this technique relies on the three-photon-resonant third-harmonic interaction. Chan et al. have shown theoretically that this technique is ideally suited for controlling the relative product yield of ground and excited state Br atoms in the photo dissociation of IBr. These suggestions have succeeded in stimulating experimental investigations. In particular, Gordon and co-workers have demonstrated coherent laser control of the total, resonantly enhanced multiphoton ionization rate of HCl and CO using the proposed technique. The technique has not yet been used to control the relative yield of different products in a reaction, although success in this aspect of the technique may be imminent.

It is also interesting to note that Elliott and co-workers (from the optical physics community) have used the same excitation scheme to control the multiphoton ionization rate of Hg. Their work proceeded independently from the research described above (from the chemical physics community) and their motivation was driven by other interests. However, the underlying mechanisms responsible for the quantum interference effect observed by Elliott and co-workers are exactly the same mechanisms that are the foundation of the control technique proposed by Brumer and Shapiro and implemented by Gordon and co-workers.

An interesting question then arises: Are there additional excitation schemes that have been observed in different contexts that are potentially useful for controlling chemical reactions? The answer is yes, and the purpose of this paper is to describe in a simple manner and reference the various optical physics experiments (and related theories) that have indirectly observed quantum interference effects. In none of these experiments was an attempt made to actively control the quantum interference effect with the exception of the work of Elliott and co-workers. Since the underlying mechanisms are similar, it is hoped that new ideas for the control of chemical reactions will be stimulated by grouping together related research from different areas.

The essence of the principles behind the control technique proposed by Brumer and Shapiro can be understood by considering a pure bound state $|i\rangle$ and a higher lying state $|f\rangle$ (which can be a pure bound or continuum state) that are connected by two different optical excitation pathways denoted by $a$ and $b$, as shown in Fig. 1. The probability for exciting state $|f\rangle$ when only
FIG. 1. Two optical excitation pathways, a and b, interfere when the fields that drive the pathways are coherent. By adjusting the relative phases of the fields, the probability for exciting the state \( |f\rangle \) can be controlled, thus controlling the product channels that are correlated to the state.

pathway \( a(b) \) is active is denoted by \( P_a(P_b) \). The total probability for exciting the final state (which is correlated to the total product yield) when both pathways are active depends on whether the fields exciting the pathways are coherent with respect to each other. Under conditions when the optical fields exciting pathway a are incoherent with respect to the fields exciting pathway b, the total probability for excitation is given by

\[
(P_{1-f})_{\text{incoh}} = P_a + P_b.
\]

The situation is very different when the fields exciting the two pathways are coherent. In this case, the total probability for exciting the final state is given by

\[
(P_{1-f})_{\text{coh}} = P_a + P_b + P_{a b} \cos(\Delta \theta + \delta_f),
\]

where \( \Delta \theta \) is the relative phase difference between the laser fields exciting pathway a and b, and \( \delta_f \) is a phase that depends on the details of the wave functions associated with states \( |i\rangle \) and \( |f\rangle \) and the specific method of inducing the optical excitation pathways. The third term in Eq. (2) is due to the quantum mechanical interference between the pathways and allows for the control of the total product yield. In particular, \( (P_{1-f})_{\text{coh}} \) can be made to vanish by properly adjusting the phase and amplitude of the various frequency components that make up the laser field. Finally, the product branching ratio, rather than the total product yield, can be controlled if there are two final states \( |f\rangle \) and \( |f'\rangle \) that are degenerate in energy, each of which is correlated to different product channels. An equation analogous to Eq. (2) exists for the state \( |i\rangle \). The ratio of the rates into the different product channels can be controlled if the related phases \( \delta_f \) and \( \delta_{f'} \) are different. For example, the rate into the product channel correlated to the state \( |f\rangle \) can be suppressed completely \( (P_{1-f})_{\text{coh}} \approx 0 \) by adjusting the phase and amplitude of the frequency components of the laser field thus favoring the (perhaps weaker) product channel associated with the state \( |f'\rangle \).

The remainder of the paper is devoted to discussing the various optical physics experiments in which quantum interference effects between different optical excitation pathways have been observed. Note that in these experiments, a single frequency laser field is made to propagate through a dense molecular (or atomic) vapor (or solid, or liquid) rather than a multifrequency field. Due to strong nonlinear optical interactions in the vapor, phase coherent fields at new frequencies are generated which copropagate with the original single-frequency input field. Thus molecules that are spatially located far within the vapor will interact with the original input field and with the fields that are generated near the input face of the vapor. Two different quantum mechanical pathways that connect the initial and final states of the molecule are excited by the total field. This is in contrast to the technique for controlling chemical reactions in that: (1) all fields must be input to the vapor, (2) the relative amplitudes and phases of the frequency components of the field must be controlled, and (3) the vapor must be optically thin. The vapor must not be optically dense because nonlinear interactions could modify the phase and amplitude of the field components as they propagate through the vapor thus disrupting interference between the excitation pathways. However, the same underlying mechanisms are involved in both situations.

To keep the following discussion as unencumbered as possible, pictorial descriptions will be used to show how the photons associated with the frequency components of the field act to excite the two different quantum mechanical pathways for the various schemes. A mathematical description of the processes is embodied essentially in Eq. (2) with the probabilities \( P_a, P_{ab}, \) and \( P_{a b} \) and the phase \( \delta_f \) to be determined. A complete mathematical evaluation of these quantities is not given here so as not to distract from the essential concepts of the control schemes, but is presented in the referenced papers. In addition, applications of the three-photon-resonant, third-harmonic interaction to controlling chemical reactions will not be discussed because eloquent descriptions have been reported previously.\(^{6,7}\)

Perhaps the first discussion of interference between different optical pathways is contained in the classic text on nonlinear optics by Bloembergen.\(^{8}\) In particular, he considered the interaction of a monochromatic laser field (frequency \( \omega_1 \)) with a Raman-active medium. As the laser propagates through the medium a Stokes (anti-Stokes) field is generated at frequency \( \omega_2 = \omega_1 - \omega_f \) (\( \omega_3 = \omega_1 + \omega_f \)), where \( \omega_f \) is the \( f \to f \) transition frequency. One quantum mechanical excitation pathway is driven by the laser and Stokes field (pathway a) and the other is driven by the laser and anti-Stokes field (pathway b), as shown in Fig. 2. As the fields propagate through the medium, they adjust their amplitudes and phases via the nonlinear cou-
pling so that there is complete destructive interference between the pathways. The destructive interference is manifest as loss of gain for the Stokes and anti-Stokes fields. In fact, there is no coupling among the waves, and the medium is essentially transparent under conditions of complete destructive interference. The loss of gain in a Raman-active medium has been observed experimentally.\textsuperscript{5,10} However, the effect can be difficult to observe in some Raman media because of extraneous factors due to high molecular number densities that tend to disrupt the relative phase between the waves and hence to disrupt the interference effect.

Using the Raman interaction for controlling a chemical reaction proceeds in a very different manner. In particular, a beam of light that contains all three phase-coherent frequencies ($\omega_1$, $\omega_2$, and $\omega_3$) is made incident on a low number density sample of the molecule whose reaction is to be controlled (the control molecule). Problems associated with changes in the relative phase among the fields as they propagate is circumvented in this case by using an optically thin (low number density) sample. Note that the three-frequency, phase-coherent field could be generated by exploiting the Raman interaction in a separate, high-density cell containing the same control molecule. The fields produced in this generator cell can be made phase coherent by injecting two of the desired frequencies (e.g., $\omega_1$ and $\omega_2$ which are produced by two independent lasers) in the cell. The nonlinear interaction will then ensure that third field at frequency $\omega_3=2\omega_1-\omega_2$ is coherent with respect to the others.

It might appear that the Raman interaction is not very practical for controlling chemical reactions, because the frequencies required for the scheme would be in the vacuum ultraviolet in the case when the state $|i\rangle$ is the ground state of a molecule and the state $|f\rangle$ is a dissociation state. It must be stressed that this is not the case because the state $|i\rangle$ could be a high-lying, long-lived state that is populated by an incoherent mechanism (e.g., electrical discharge, chemical reaction, or optical excitation). Hence, the energy separation between the states could be small and visible laser sources could be used in the scheme.

Quantum interference effects of a different origin occur in the two-photon-resonant, third-harmonic interaction. These effects were discussed theoretically\textsuperscript{11} and observed experimentally\textsuperscript{12} around that same time that researchers were studying the similar effects that occur in the Raman interaction. The scheme has the practical advantage that only two frequencies are required, denoted by $\omega_1$ and $\omega_2$, where $\omega_3=3\omega_2$. It is very similar to the three-photon-resonant, third-harmonic interaction with the exception that one of the pathways (a) is driven by two photons from the $\omega_1$ frequency component and the other (b) is driven by one photon each from the $\omega_1$ and $\omega_2$ frequency components, as shown in Fig. 3. From the figure, it can be seen that $2\omega_1=\omega_f$ and that $\omega_3-\omega_1=\omega_f$. Note that the amplitude of the field at frequency $\omega_2$ (the third-harmonic) must be comparable in strength to the field at frequency $\omega_1$ to obtain strong interference between the two pathways unless there is an auxiliary state of the molecule that resonantly enhances the $b$ pathway.

More recently, destructive interference between optical pathways has been responsible for the suppression of amplified spontaneous emission in the two-photon-resonant, four-wave mixing interaction.\textsuperscript{13} In this case the field contains three frequency components denoted by $\omega_1$, $\omega_2$ and $\omega_3$, where $\omega_3=2\omega_1-\omega_2$. As shown in Fig. 4, pathway a is driven by two photons from the $\omega_1$ frequency component while pathway b is driven by one photon each from the $\omega_2$ and $\omega_3$ frequency components. Note that this control scheme suffers the same complexity as the Raman interaction in that three phase-coherent fields must be generated. Note also that the amplitudes of the frequency components of the field must be comparable in strength to realize complete interference between the pathways unless resonant enhancement from an auxiliary molecular state favors one of the pathways. For example, the strength of the $b$ pathway could be kept fixed as the amplitude of the $\omega_2$ and $\omega_3$ frequency components is decreased so long as the frequencies are adjusted to bring them more into resonance with some additional state of the molecule (while maintaining the relation $\omega_2+\omega_3=\omega_f$). Within the past year, it has been shown theoretically that this scheme can be used to control the molecular photodissociation of Na$_2$.\textsuperscript{14}

The final four-photon interference effect that will be considered is the three-photon-resonant four-wave mixing interaction\textsuperscript{15} which is depicted in Fig. 5. As with the previous interaction, the field contains three components denoted by $\omega_1$, $\omega_2$, and $\omega_3$, where $\omega_3=2\omega_1-\omega_2$. In this case,
FIG. 6. The optical excitation pathways in the two-photon-resonant, second-harmonic interaction. Two photons from the component at frequency $\omega_1$ and one from the component at frequency $\omega_2$ excite optical pathway $a$ and one from frequency component $\omega_3$ excite pathway $b$. However, two photons from the $\omega_1$ frequency component and one from the $\omega_3$ frequency component drive pathway $b$. In previous experiments, all of the frequencies are nearly equal (different by a few transition line widths) which has the advantage that large transition rates can be induced using relatively weak laser fields (perhaps continuous-wave laser fields). The disadvantage of using nearly equal frequency components is that it might be difficult to adjust the relative phase among the fields using traditional techniques. Note that for the case when the frequency difference is only a few gigahertz or less, an acousto-optic cell could be used to generate all three frequency components from a single laser beam, thus reducing the complexity of generating the field and controlling its phase.

All of the schemes described so far involve different combinations of four photons that excite two different optical excitation pathways consistent with the quantum selection rules for optical excitation of molecular states. It is worth pointing out that there are other potentially simpler schemes that involve only three photons. Consider, for example, the two-photon-resonant, second-harmonic interaction shown in Fig. 6 which requires a field that contains two frequencies, $\omega_1$ and $\omega_2$. Pathway $a$ is driven by two photons from the component at frequency $\omega_1$, and pathway $b$ is driven by one photon from the component at frequency $\omega_2$. If pathway $a$ is an allowed two-photon transition, then pathway $b$ is forbidden by the electric-dipole selection rule. Note that (1) it is possible to destroy the selection rule by applying a static electric field which mixes even and odd parity states and, hence, destroys inversion symmetry, and (2) it is possible that states $|f\rangle$ and $|f\rangle$ could be connected by an allowed electric quadrupole moment or an allowed magnetic dipole moment. Both of these possibilities open up a whole new class of molecular transitions that could be accessed by the control technique.

In summary, it has been shown that quantum interference effects arise in several different types of interactions between laser fields and molecular states and that these effects were reported previously by researchers in the optical physics community. In order to bridge the gap between this previous research and ongoing research in photochemistry, it has been stressed that these interactions might be useful for the coherent laser control of chemical reactions even though the original research exploring these effects was not directed toward this application. Also uncovered in this survey was the observation that neither the initial or final molecular states have to be the ground state of the molecule which may be of practical importance when implementing some of the outlined schemes. In addition, it was pointed out that new schemes for controlling chemical reaction can be developed by considering the use of higher-order transition moments and static fields to open up new optical excitation pathways.

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8N. Bloembergen, Nonlinear Optics, Frontiers in Physics Lecture Note Series (Benjamin Cummings, Reading, MA, 1965), Secs. 2-5, 4-5, and 5-10.


