An Analysis of Two Liquid-State Adaptive Feedback Experiments

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Abstract. Adaptive feedback experiments, which provide an engineering oriented approach to optimizing a desired target in a molecular process, have been extensively developed over the past decade. Efforts to extract the control mechanisms that underlie the observed control have, however, only recently begun in earnest. We describe the results of the analyses of two liquid state adaptive feedback experiments, showing that the resultant control takes little advantage of coherent quantum effects.

INTRODUCTION

Current approaches to the quantum control of molecular dynamics can be roughly divided into two distinct philosophies: coherent control and optimal control.[1,2] Although both rely upon the interaction of lasers and matter to introduce controllable interference contributions, they do so in philosophically different ways. Historically, coherent control has endeavored to construct scenarios that explicitly incorporate quantum interference effects in well-defined ways. The result is a clear relationship between the resultant control and the quantum interference contributions. By contrast, optimal control, as currently practiced,[3] takes advantage of engineering tools designed to optimize the system variables so as to maximize the target cross section within specific constraints. The result often calls for complicated laser pulses, and the mechanisms that underlie the resultant control are difficult to discern. This is particularly true in the modern experimental implementation of adaptive feedback control, of which there are many examples.[4,5]

Within the framework of optimal control-adaptive feedback we note an additional distinction, that between formal theoretical/computational studies and experimental implementations. The former assume wide-ranging attributes to the apparatus that creates the incident laser field, i.e., the field is variable over a large range of frequencies and timescales. By contrast, experimental results are limited by practicalities, a situation that imposes serious constraints in optimal control. These experimental limitations are far from trivial, and have considerable consequences, as discussed in specific cases below.

Regardless of the approach, and regardless of the experimental limitations, one would hope that the currently popular adaptive feedback experimental approach would expose underlying mechanisms through which control is operative. Even more significant would be the discovery of a set of simple control scenarios that underlie the effect of the complex pulse shapes. Indeed, such a set of simple scenarios, a "control tool box" if you will, has been developed within the coherent control approach. Scenarios such as bichromatic control, N-photon vs. M-photon control,[1] incoherent interference control, etc., as well as the original Tannor–Rice pump–dump scenario,[6] are sample examples. A thorough analysis of adaptive feedback experiments would, we hope, expose these elementary control steps as part of the overall control scheme.[7]

Of greatest interest to Chemistry is the liquid phase environment. Since the essence of quantum control is to utilize quantum interference effects to manipulate product cross sections, one may expect that such efforts are thwarted by collisional and decoherence effects (which destroy quantum features) when applied to liquid phase

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dynamics. Consequently, efforts have been ongoing since the inception of the quantum control approach to theoretically design scenarios that allow for control in liquids.[8–10] Recently, a number of experiments on adaptive feedback control in liquids[11–14] have been carried out. Two of these experiments are the subject of discussion below. Specifically, we undertook the analysis of two liquid-phase adaptive feedback experiments,[12,13] both of which had the goal of coherently controlling dynamics in the liquid phase, in an effort to extract their underlying mechanisms. In both cases, results were surprising. Specifically, neither of the experimental results seemed to imply control via coherent quantum interference effects, and neither of the experiments required other than simple qualitative explanations. The reasons for this can be traced back to the particular experimental apparatus, and the particular optimization target chosen for the feedback algorithm.

We summarize these results below, along with comments on the simplifications that can emerge from complex environments. Since both studies appear in recent articles,[15–17] we focus solely upon the essential qualitative features learned from these investigations.

TRANS–CIS ISOMERIZATION IN NK88

Vogt and coworkers[12] examined control of trans to cis isomerization of "NK88" (i.e., 3,3′-diethyl-2,2′-thiacyanine iodide) in liquid methanol. Using adaptive feedback, they demonstrated the ability to optimize the yield of the cis product by shaping a 60-nm-wide fs laser source. The process takes place by excitation from the ground state to the excited state, followed by isomerization. Two cases were studied: ("maximizing") pulses that increased the extent of trans–cis isomerization, and ("minimizing") pulses that minimized the amount of trans–cis isomerization. In both cases the resultant optimal pulses[12] consisted of a number of peaks as a function of time, with an overall time width of 4 ps. Further, the minimizing pulse showed a far more complex structure, suggesting[12] complicated coherent dynamics designed to guide the dynamics away from the product cis state.

These seminal results motivated our subsequent study of the dynamics. We were able to successfully model these studies using a simple one-dimensional model representing the cis–trans isomerization reaction coordinate, plus a decoherence term (within a Redfield framework) modeling the remainder of the NK88 degrees of freedom plus the liquid methanol environment. The ability to do so, emphasized later below, can be qualitatively justified from the theory of decoherence, as applied to the case of rapid decoherence.

Our studies showed that the experimental results were remarkably consistent with control exercised through alteration of the probability of excitation, rather than control over the dynamics. That is, in the case of maximization the pulse creates significantly more of the excited state, whereas the minimization pulse aims to decrease the excited population. Thus, although one would have hoped that these results constitute evidence of active control over the coherent motion of the cis to trans process, our results show that the experiment can be explained in a far simpler fashion.

What then of the "tool box" of control scenarios that we anticipate seeing? For example, control of isomerization by pump–dump[6] or by the CW version[18] applied directly to isomerization, seems a "natural" for isomerization control. Why is it not manifest? To examine this issue we performed a second study[15] that showed that the answer relates to the practical restrictions involved in the experiment. In particular, the state-of-the-art laser used[12] had a 60-nm-wide profile. However, in order to successfully carry out pump-and-dump from the trans to cis would have required a laser with a width of at least 30,000 cm^{-1}. In particular, by repeating the optimization computationally with an unrestricted laser width we found that the optimal control scheme was indeed pump-dump, which gave far larger control than that obtained with the pulse of restricted width. Specifically, the unconstrained pulse showed a final cis population of 0.36, as compared to the 0.16 result obtained with the 60-nm-wide pulse. Of some interest is the fact that the decoherence here is sufficiently rapid so as to result in a modified pump–dump scenario wherein the second pulse operates well after the excited wave packet has decohered.

Decoherence, often viewed in Chemistry as arising from a thermal bath, is indeed far more general.[19] Consider, in particular, an N degree-of-freedom (dof) system. If one is interested in a property of only $M < N$ degrees of freedom, i.e., if one ignores the remaining (N–M) dof, then the ignored dof serves to decohere the observed M dof. In the case of the experiment under consideration, one is actually measuring only one degree-of-freedom, i.e., whether the system is cis or trans. This being the case, the remaining degrees of freedom are *correctly* treated, due to the nature of the measurement, as decoherence. Naturally, the fully correct approach would be to compute the full quantum dynamics and then compute the quantity of interest, which would then entail an averaging over the unobserved degrees of freedom. Here, however, we succeed with a master equation approach (i.e., Redfield theory), which essentially pre-averages over the unobserved degrees of freedom. We believe that the results are in good accord with experiment due to the rapid decoherence in the system.

Thus far, the computational results show excellent agreement with the experiment for a variety of targets that we investigated.[20] The fact that one-dimensional-plus-decoherence models can fit the experimental data in complex systems where the target is one-dimensional is significant. Theoretically, it suggests a surprising simplification in cases that would be expected to be highly complex. Experimentally, it motivates measurements in more degrees of freedom (e.g., determining other system properties in conjunction with ascertaining whether the product is cis or trans), which will provide interesting challenges to theoretical modeling of the results.

CONTROLLED STOKES EMISSION VS. VIBRATIONAL EXCITATION IN METHANOL

A series of experiments carried out by the Michigan group considered control of stimulated Raman scattering (SRS) in liquid methanol.[13,21–24] The basic idea was to selectively excite one of two closely-spaced Raman active modes of methanol associated with the symmetric and antisymmetric C–H stretch modes. The Raman modes were driven by a strong pump pulse with 150 fs bandwidth. This bandwidth is larger than the spacing of the excited Raman modes but smaller than the energies of the vibrational states themselves, thus placing the experiment in the non-impulsive, or transient, regime where the molecules have enough time to vibrate during the pulse. By using an adaptive feedback algorithm to shape a strong pump pulse, significant control over the relative peak heights of the two Raman modes in the Stokes emission was demonstrated experimentally. Pulses were found that could selectively enhance the emission from either mode, enhance both modes together, or completely suppress all emission. By assuming that the intensities of the peaks in the Stokes emission were directly proportional to the associated vibrational modes, it was concluded that selective vibrational excitation had been achieved.

In the absence of a firm theoretical footing, these experiments were being touted by many[13,21–29] as an example of quantum or coherent control of mode-selective vibrational excitation in the liquid phase. This view had been temporarily upheld by a proposal for a coherent mechanism of Raman control in a closely related experiment using a double-Gaussian-shaped pump pulse.[13] Unfortunately, this proposed mechanism has been shown to be faulty.[30] We undertook a detailed theoretical analysis of these experiments, including both molecular excitation and nonlinear optical propagation of the pump and Stokes pulses, in order to extract the underlying control mechanisms.

Our studies[16,17] revealed many control mechanisms capable of affecting the relative intensity of two Stokes peaks in the emitted Raman spectrum. All the identified mechanisms are third-order nonlinear optical effects, and include transient stimulated Raman scattering in a collisional environment, saturated Raman scattering, self- and cross-phase modulation, and focused-beam effects. In hindsight this is maybe not surprising since SRS is itself a third-order nonlinear optical effect, and having a pump pulse strong enough to drive SRS is then necessarily strong enough to drive competing third-order nonlinear processes. All mechanisms have the same clear physical interpretation: shaping the pump pulse controls the nonlinear optical response of the medium, which in turn controls the Stokes emission.

With relation to the vibrational excitation, we were able to draw a number of conclusions.[16,17] First, although it was found that the vibrational populations are affected by the same control mechanisms that affect the Stokes spectra, the ratio of the Stokes spectra peak heights does not directly reflect the ratio of the level populations, as was assumed in the experiment. Second, the control was found to be completely incoherent at the molecular level. The reason for the incoherence was that no amplitude at the Stokes wavelengths was present in the initial pump pulse, hence forcing the Stokes mode to build up from noise (spontaneous emission or collisional excitation). These seeding processes are themselves incoherent, and prevented any chance for coherent dynamics. (Note that coherent dynamics could be induced if both the pump and Stokes frequencies have significant amplitude in the initial shaped pulse, suggesting again that bandwidth limitations seriously affected the range of possible solutions available to the adaptive feedback algorithm.) Finally, no coherent quantum interference effects are needed to explain the observed control. Indeed, classical models that treat the vibrational modes as classical oscillators give identical equations of motion for the vibrational excitations and the pump and Stokes fields. Interfering pathways of the type considered in coherent control would only contribute to fifth-order nonlinear optical emission, which contributes negligibly to the emission at the Stokes wavelengths.

Examination of the literature shows that the role of nonlinear effects in considerations of control has generally been neglected. Such effects can, however, be quite significant, as evidenced above (see also refs 31 and 32). Experimentalists can, however, check for these effects by comparing their pulse shapes before and after the laser passes through the medium. Any significant change in the pulse characteristics should signal the need to consider nonlinear optical effects.

OUTLOOK FOR COHERENT CONTROL IN LIQUIDS

In light of the conclusion that no coherent mechanisms

were present in the two liquid-phase experiments considered, one is lead to question the viability of coherent control in liquids. We anticipate, however, that the lack of coherent contributions or of traditional control schemes in the exposed mechanisms is due, in large part, to experimental limitations.[33] That is, the "optimal" solutions found by adaptive feedback loops are not globally optimal, but severely restricted by the limitations of the state-of-the-art experimental apparatus. Although this is a seemingly obvious statement, our studies have shown that these restrictions may in fact exclude from the very start the possibility of accessing traditional coherent control mechanisms, which could be manifest with experimental setups of wider generality.

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