

Molecular Control Spectrometer

YiJing Yan¹, Bern E. Kohler¹, Richard E. Gillilan¹, Robert M. Whitnell¹, Kent R. Wilson¹, and Shaul Mukamel²

¹Department of Chemistry, University of California San Diego, La Jolla, CA
92093-0339 USA

²Department of Chemistry, University of Rochester, Rochester, NY 14627 USA

Abstract: It is now possible to move beyond the observation of ultrafast molecular dynamics to the control of those dynamics. We discuss here some of the theoretical and experimental issues involved in performing molecular dynamic control experiments. The resolution of these issues can provide the basis for a “molecular control spectrometer” which we are now in the process of building, which tightly couples time domain theory and experiment to not only control molecular processes, but also to discover fundamental properties of molecular systems.

There has been a remarkable growth in the application of ultrafast laser technology to the observation and interpretation of ultrafast molecular dynamics. Dynamics in the subpicosecond regime, which in the not too distant past would have seemed to be inaccessible to observation, can now be probed in many cases with commercial off-the-shelf lasers. The result has been, as this series of conferences demonstrates, a deeper and fuller understanding of how chemical processes, in gas phase and in solution, happen on the microscopic level.

While there is still much to be learned by probing and observing molecular dynamics on the femtosecond time scale, there are also new challenges to be met. A considerable body of theoretical work has been created over the past few years in the area of the control of molecular dynamics by light (by, among others, Tannor, Rice and Kosloff[1], Brumer and Shapiro[2], Rice[3], Rabitz[4], Warren[5], and Bandrauk[6]). The fundamental idea behind these studies is that, by driving a molecular system with an appropriately tailored light field, a desired outcome can be obtained, such as molecular rearrangement, an increased probability of dissociation, the preferential breaking of one molecular bond over another, or the preferential formation of a particular product or product state. However, the experimental tests of theoretical control predictions are only beginning to appear. For example, Gordon and co-workers[7] have recently reported experimentally modulating the ionization rate of HCl using the coherent control methodology of Brumer and Shapiro, and Crim and co-workers[8] and Zare and co-workers[9] have used vibrational excitation of a bond to control the products of both photodissociation reactions[8] and bimolecular gas phase reactions[8,9].

The goal now is to meld the existing considerable theoretical knowledge with solutions to the real world problems confronting molecular control experiments. Among the questions central to this undertaking are:

i) What if the molecular systems are not in a pure state? It is often difficult experimentally to create a pure eigenstate of the molecular system. This is especially true if one wishes to examine the possibility of control at finite temperatures or in a liquid solution or other condensed phase system. Pure state molecular dynamics can be described by a single wavefunction ψ , and the corresponding density matrix is given by

$$\rho = |\psi\rangle\langle\psi|. \quad (1)$$

However, the ensemble behavior of dynamic processes (such as dephasing and energy relaxation) can only be transparently implemented in the (Liouville space) density matrix formulation[10-13]. A specific representation of Liouville space (e.g. the Wigner representation) allows a clear semiclassical picture in phase space.

This phase space picture of control can be expressed as follows[14]. Suppose one has an outcome $A(t_f)$ to optimize that can be expressed as an expectation value over an operator \hat{A} :

$$A(t_f) = \text{Tr}[\hat{A}\rho(t_f)]. \quad (2)$$

The outcome depends on the radiation electric field $E(t)$ through the dipole coupling term $-DE(t)$, where D is the transition dipole moment. Now consider a variation, $\delta E(t)$, away from the true radiation field $E(t)$ that optimizes this outcome. From perturbation theory, the first-order change in the outcome is found to be[14]

$$\delta A^{(1)}(t_f) = - \int_{t_0}^{t_f} d\tau \delta E(\tau) K(\tau), \quad (3)$$

where the kernel $K(\tau)$ is given by

$$K(\tau) = 2 \text{Im} \left\{ \text{Tr} \left[\tilde{A}(\tau) D \rho(\tau) \right] \right\}. \quad (4)$$

The quantity $\rho(\tau)$ is calculated by propagating the initial phase space distribution forward from time t_0 while $\tilde{A}(\tau)$ is calculated via backward propagation of \hat{A} from time t_f . In the pure state case, Equation (4) reduces to the control equations used by Rabitz[4] and co-workers and by Rice, Tannor, Kosloff and co-workers[1,15] for optimal molecular control. However, the phase space formulation of the control problem facilitates the treatment of complex systems and allows the theory to be implemented in a unified way using quantum, semiclassical or classical methods.

ii) What if the ensemble of light pulses is also not a pure state? In most experiments, the light pulses created are not in a specified phase relationship with respect to one another. However, most of the theoretical work on molecular control has assumed a fixed phase relationship. While the work of Scherer, Fleming and co-workers[16] and of Fayer and co-workers[17] has demonstrated the ability to create pulses in a fixed phase relationship, such techniques add to the complexity of these experiments. Is such a fixed phase relationship necessary for control? By performing control calculations using an ensemble of pulses[14] with random phase relationships, one can examine the robustness of the control dynamics with respect to pulse phase.

iii) What light pulses are experimentally realizable? The theoretically optimum light to meet an objective does not necessarily correspond to those fields that can be achieved in the laboratory. However, a wider range of fields is becoming available, for example, from very bright higher repetition rate continuum femtosecond sources[18], such as the one we are using, thereby allowing in principle the synthesis of ultrafast light fields containing a wide range of frequencies. In addition, the types and shapes of ultrashort fields that can be created are becoming more varied. One example is the Fourier plane manipulation of Weiner, Heritage,

Nelson and co-workers[19]. However, even though the universe of experimental light fields is becoming larger, theory must still find the best field within that universe. Many examples of molecular control theory consider unrestricted fields $E(t)$. The optimal field is proportional to the optimal control kernel $K(t)$, in the case that the total energy input to the molecular system from the field $E(t)$ is constrained to be constant. The resulting converged field is the optimal field $E(t)$. Such fields are not guaranteed to be experimentally realizable. In order to mesh with experiment, it is convenient to consider a parameterized electric field, $E(\tau; \{\alpha_j\})$ which corresponds to the realizable range of light fields. The parameters, $\{\alpha_j\}$, of such a field may include such quantities as the sub-pulse carrier frequencies, widths and amplitudes as well as the time delays and relative phases between pulses. One then optimizes the parameters of the field rather than the unrestricted field. An example of optimization of parameters can be found in the work of Rice and co-workers on the control of I_2 and HgAr photodissociation[20].

The optimization of parameters turns the problem into one of calculus rather than control. One wishes to find the set of parameters that optimizes the outcome $A(t_f)$. However, the outcome also now depends on the parameters $\{\alpha_j\}$. For any given set of field parameters, Equation (2) can be used to calculate the outcome while Equation (3) can be used to find the first derivative of the outcome with respect to changes in the parameters[14]:

$$\frac{\partial A(t_f; \{\alpha_j\})}{\partial \alpha_i} = - \int_{t_0}^{t_f} d\tau \frac{\partial E(\tau; \{\alpha_j\})}{\partial \alpha_i} K(\tau). \quad (5)$$

Given the values of A and the first derivatives of A with respect to each of the $\{\alpha_j\}$, standard minimization techniques can then be used to calculate an optimized set of parameters that give the best realization of the objective, given the experimental limitations.

iv) How long are we willing to let our computers run? The molecular control calculations described above require a lengthy optimization process in order to find the optimal electric field. As the systems we wish to control become more complex, or as we have to deal with ensembles of light or molecules, the required computational effort will increase. It has been shown that both the spectral and the temporal profiles of the fields are important in the analysis of nonlinear spectroscopy[11,13,21]. These profiles couple in general to different types of motion such as electronic populations and coherences. It may be possible for example under certain conditions to introduce an independent “snapshot spectrum” in which the field can be considered both infinitely short and monochromatic. This limit is physically realizable without violating the Heisenberg energy-time uncertainty[11,13,21]. In this case, the interpretation of pump-probe measurements simplifies considerably. Yan[22] has recently developed a Liouville-space formalism for weak field pump-probe spectroscopy involving the use of a mixed time-frequency, causality preserving representation in which the light-matter coherent interference is transparent. In the case of pump and probe pulses that do not overlap in time, Yan[22] has shown that the probe absorption $S(t_d)$, where t_d is the delay time, is given by

$$S(t_d) = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_0^{\infty} d\tau F(\tau - t_d, \omega', \omega'') M(\tau, \omega', \omega''). \quad (6)$$

In Equation (6), F depends only on light field properties and M depends only on molecular ensemble properties. Thus, this formulation of pump-probe spectroscopy allows the convenient splitting of the molecular calculations and the light field calculations into separate parts. In principle, one would only have to calculate the molecular properties once. The effect on the molecules of a variety of light fields could then be calculated rapidly. Results such as these, as well as the continuing increase in computational speed and algorithmic efficiency, can make increasingly larger systems accessible to molecular control theory and, eventually, to experiment.

What we have described here are some of the issues relevant to the construction of a “molecular control spectrometer,” as discussed by Rabitz and co-workers[4,23], which we are now in the process of building. Such a spectrometer will closely couple theory and experiment in the following iterative manner. First, for a given molecular system, the theoretical side of the spectrometer (a computer) will take the relevant molecular description (potential energy and transition dipole moment surfaces, etc.) and experimental description (the nature of the available universe of light fields) and calculate the light field expected to best achieve a particular objective, for example, the control of the outcome of a chemical reaction. The parameters for this field are then transferred from the theoretical computer to the computer controlling the experimental side of the spectrometer which adjusts the optical system to produce the desired field. The experimental response of the sample (which will not exactly match that predicted by the theoretical computer because the molecular description is only approximate) is fed back into the theoretical computer, which improves the molecular description to reflect this new information, and computes a new test light field designed to minimize the uncertainty in the molecular description. This new light field is sent to the experimental computer, which measures a new molecular response, and so on, iterating to convergence between experiment and theory. Note that such a spectrometer achieves two goals: not only does it provide a way of controlling molecular processes, but in producing that control, it also discovers new information about molecular systems. In particular, the potential energy and transition dipole moment surfaces become increasingly refined so that control can be achieved. This refinement can be done in an efficient manner: The parts of the potential energy surface that are derived most accurately are precisely those that are important in obtaining the desired outcome.

The implementation of ultrafast molecular control in the “molecular control spectrometer” mode requires a close link between theory and experiment that is perhaps unparalleled in chemical physics. The iterative convergence between theory and experiment should in principle then result in both the discovery of the basic nature of molecular systems and the ability to control the dynamics of such systems.

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