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12a. DISTRIBUTION/AVAILABILITY STATEMENT

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13. ABSTRACT *(Maximum 200 words)* This research concerns the development of molecular control theory techniques for designing optical fields capable of manipulating molecular dynamics phenomena. Although it has been long recognized that lasers should be capable of manipulating dynamic events, many frustrating years of intuitively driven laboratory studies only serve to illustrate the point that the task is complex and defies intuition. The principal new component in the present research is the recognition that this problem falls into the category of control theory and its inherent complexities require the use of modern control theory tools largely developed in the engineering disciplines. Thus, the research has initiated a transfer of the control theory concepts to the molecular scale. Although much continued effort will be needed to fully develop these concepts, the research in this grant set forth the basic components of the theory and carried out illustrative studies involving the design of optical fields capable of controlling rotational, vibrational and electronic degrees of freedom. Optimal control within the quantum mechanical molecular realm represents a frontier area with many possible ultimate applications. At this stage, the theoretical tools need to be joined with merging laboratory optical pulse shaping capabilities to illustrate the power of the concepts.

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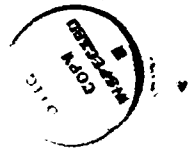
A. Background and Overview

The aim of this research was to introduce optimal control theory into chemical dynamics to establish whether it is feasible in principle as well as in practice to employ optical fields for controlling molecular scale motion. Attempts to achieve control over molecular motion, particularly for site specific chemistry in polyatomic molecules, has been a long sought after goal with virtually no success. Heretofore, experiments and theory aimed at this goal have basically relied on physically inspired intuition for a choice of pumping schemes. Given this background, one could conclude that either the problem of molecular motion control is not soluble or that the solution is far more complex and defies simple guessing at the nature of the optical fields. The mathematical tools of optimal control theory, largely developed in the engineering disciplines, provide a well defined means of settling this issue. Essentially the problem is one of determining the existence of any possible optical field capable of meeting (quantum) mechanical molecular objectives such as local bond excitation or selective bond rupture. Control theory has a long history of being very successful for solving a variety of difficult design problems in the macroscale engineering domain. The basic conclusion of this research summarized in this report clearly shows that control theory is capable of establishing: (a) the feasibility of attaining physically posed molecular dynamics objectives, and (b) in cases deemed feasible actually producing the optimal field designs.

Both practical and fundamental control issues were explored in this research and special emphasis was given to assessing theoretical and experimental limitations for achieving site specific chemistry. Optimal design studies were carried out for the purpose of controlling molecular scale phenomena involving rotational, vibrational and electronic degrees of freedom. Much of this work was executed as an initial exploration of the molecular control theory concepts and to develop the necessary computational software. At this stage, the software is now being redirected to consider realistic applications in

conjunction with current laboratory capabilities. A most important conclusion is that the field designs must be made robust to inherent uncertainties in the molecular Hamiltonian as well as possible laboratory-generated noise, etc. Robustness is expected to play an increasingly important role in future molecular control applications.

The field designs resulting from the research should provide clearly defined targets for the engineering-physics community involved with laser pulse generation. These same optimal pulse design techniques have potential applications in several fields including materials modification. In general controlling phenomena at the molecular scale with precisely designed tools (optical and otherwise) opens up a new field of study for development. If this field follows along the enormously successful history of macroscale applications of control theory, then there are many exciting and rich surprises ahead for the chemical dynamics community. Summarized below in section C are abstracted segments describing the individual research accomplishments achieved during the period of this grant.



B. Participating Scientific Personnel

Dr. J. Beumee, Research Staff

Dr. S. Shi, Research Staff

Dr. D. Neuhauser, Postdoctoral Associate

Dr. M. Dahleh, Ph.D. received 1988

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C. Synopsis of Particular Research Accomplishments

1. Quantum Mechanical Optimal Control of Physical Observables in Microsystems[1]

A quantum mechanical formalism for the optimal control of physical observables of microsystems was developed. The computational procedure for numerical implementation was presented. Three illustrative examples with a model Morse oscillator show that optimal pumping fields can be found to reach the physical objectives: selective excitations, steering a system to a specific state, and breaking a bond.

2. Optimal Design of External Fields for Controlling Molecular Motion: Application to Rotation[2]

A general discussion of quantum controllability leads to the specific focus of this work, namely the use of tailored radiation to excite rotational states, either, specific |JM> states or superposition states which correspond to a high degree of molecular orientation. It was shown that starting form the |00> state it is in principle possible to produce any eigenstate or superposition state given a long enough pulse and specific examples were presented. Highly ordered states, which are useful in a variety of spectroscopic applications, can be prepared by realistic tailored microwave fields.

3. Optimal Control of Uncertain Quantum Systems[3]

The design of optimal final-state controllers of quantum-mechanical systems that are insensitive to errors in the molecular Hamiltonian or to errors in the initial state of the

system was considered. Control arises through the interaction of the system with an external field; the goal was optimal design to modeling errors and other uncertainties in the Hamiltonian functions $H_0(\alpha)$ indexed by the random variable α taking values on a complex set in Euclidean space. Similarly, sensitivity of the optimal control to the initial state was minimized by viewing the initial condition as a Hilbert-space-valued random variable and considering an optimization problem with a cost functional that was averaged over the class of initial conditions. A precise formulation of the control problem was given, and its well-posedness was established. Cost propagators were defined to display the dependence of the performance index on the initial conditions explicitly, which allows analytic averaging of initial conditions. The constrained optimization problem was reduced to an unconstrained optimization problem by the introduction of Lagrange-multiplier operators. Necessary conditions for the unconstrained problem provide the basis for a gradient search for an optimal solution. Finite-difference schemes were utilized to provide a numerical approximation of the optimal control problem. Numerical examples were given for final-state control of a diatomic molecule represented by a Morse potential illustrating design for systems with initial-phase uncertainty and parametric uncertainty. The resultant insensitive controllers execute different strategies depending on the design requirements. The controller designed to be insensitive to errors in the initial phases adopts a strategy of phase imprinting during the initial stages of the control interval to compensate for a lack of knowledge of the initial phases. It was also shown that it is not possible to coerce a system from a state with completely random initial phases to a correlated state using the class of averaged controllers considered here. The controller designed to be insensitive to parametric Hamiltonian errors adopts a strategy of amplitude restraint to prevent the wave packet from taking significant excursions into the regions where the potential is uncertain. The interesting structure exhibited by the controllers in response to the different design requirements, and the superior performance of the insensitive controllers when compared

with controllers designed at nominal phases and parameters, illustrate the usefulness of the cost-averaging technique for design in the presence of uncertainties.

4. Optimal Control of Molecular Motion: Nonlinear Field Effects[4]

This paper was concerned with some of the consequences of strong optical fields and corresponding nonlinear field effects upon the optimal control of molecular motion. It was shown that the presence of nonlinear interactions can give rise of the existence of multiple field solutions to the problem of optimally controlling molecular motion where each of the field produces exactly the same physical effects on the molecule. Secondly, it was argued that nonlinear field interactions may either act as a constraint on the control of molecular motion or an enhancement of that process depending on the circumstances. These various phenomena were illustrated through consideration of control over the motion of harmonic molecules.

5. Optimal Control of Molecular Motion with Robustness and Application to Vinylidene Fluoride[5]

The results of previous research [J.Chem. Phys. **88**, 6870 (1988)] on optimal control of harmonic molecular motion were extended. A closed-form solution for the optimal optical field was derived for a quadratic cost criterion, and an asymptotic form for this field was obtained for large target times. The dynamics of a molecule were shown to be controllable if no normal mode has zero optical absorption intensity. The theoretical formulation yields robustness of the field designs. Therefore the optimal control formalism was extended further to yield optimal fields that exhibit minimal sensitivity of the desired molecular objectives with respect to force constants and dipole derivatives. Examples of

sensitivity minimization were shown, using a linear chain molecule. Finally, optimal control of the molecule vinylidene fluoride was demonstrated.

6. Optimal Control of Bond Selectivity in Unimolecular Reactions[6]

The optimal control theory approach to designing optimal fields for bond-selective unimolecular reactions was presented. A set of equations for determining the optical fields, which will lead to the achievement of the objective of bond-selective dissociation was developed. The numerical procedure given for solving these equations requires the repeated calculation of the time propagator for the system with the time-dependant Hamiltonian. The splitting approximation combined with the fast Fourier transform algorithm was used for computing the short time propagator. As an illustrative example, a model linear triatomic molecule was treated. The model system consisted of two Morse oscillators coupled via kinetic coupling. The magnitude of the dipoles of the two Morse oscillators were the same, the fundamental frequencies were almost the same, but the dissociation energies were different. The rather demanding objective under these conditions was to break the stronger bond while leaving the weaker one intact. It is encouraging that the present computational method efficiently gives rise to the optimal field, which leads to the excellent achievement of the objective of bond selective dissociation.

7. Optimal Control of Molecular Rotation in the Sudden Limit[7]

Optimal control theory was introduced for the control of quantum molecular rotational excitations induced by electric fields. Particular emphasis was given to the case where the electric field pulse was sufficiently short ($\sim$ 1ps) so that the sudden approximation could be made. Consequently, the time evolution of the rotational wave functions could be obtained analytically for general molecular rotations. A hyperbolic curve

was shown to explicitly describe the relationship between the rotational energy and the action integral $x(t) = \int_0^T d\varepsilon(t)dt$ where d is the molecular permanent dipole moment, and $\varepsilon(t)$ is the applied electric filed over time [0,T]. For the case that the control cost functional has the form $Q = F(x(T)) + \beta \int_0^T \varepsilon^2(t)dt$, it was found that the optimal fields were constant in time. The controllability of both rotational energy and transition probability was investigated. A detailed discussion on properties of the optimal fields, as well as the initial and final rotational states, was presented. Numerical calculations were performed for the molecule CsF.

8. Optimal Control of Unimolecular Reactions in the Collisional Regime[8]

The possibility of controlling unimolecular-dissociation processes with multiple laser fields in the collisional regime was examined. Employing the Bloch equations to describe optical excitation and decay processes, optimal control theory was used to design amplitude modulated fields which produce the desired excited-state products. The selectivity of the product distribution of a simple four-state photodissociation system was shown to have a square-root dependence on the relative value of the mean dephasing time T_2 to the pulse length τ, i.e, $(T_2/\tau)^{1/2}$. The equivalence between T_2 decay and phase disruptions occurring in a random-walk fashion was also examined. It was shown that the essential effect of the system temperature was to introduce a Boltzmann population factor in the product selectivity without affecting the nature of the optimal field.

9. Optimal Control of Molecular Motion: Making Molecules Dance[9]

This paper presented an overview of the recent incorporation of formal control theory concepts into molecular physics. The desire to control molecular motion has a long history and the present paper argued that the tools of control theory provide a rigorous foundation for precisely expressing the physical issues as well as providing a practical means of obtaining solutions when they exist. The process involved is one of design and the paper emphasized the choices and flexibility available to the molecular control designer. Illustrative examples were included involving the control of molecular rotation, vibration, and dissociation. The paper attempted to present a synopsis of the current status of the field and where it will likely proceed.

D. Publications Resulting from this Research

1. S. Shi and H. Rabitz, "Quantum Mechanical Optimal Control of Physical Observables in Microsystems", J. Chem. Phys. **92**(1), (1990).

2. R.S. Judson, K.K. Lehmann, H. Rabitz and W.S. Warren, "Optimal design of External Fields for Controlling Molecular Motion: Application to Rotation", J. Mol. Struc. **223**, 425-456 (1990).

3. M. Dahleh, A.P. Peirce and H. Rabitz, "Optimal Control of Uncertain Quantum Systems", Phys. Rev. A **42**(3), 1065-1079 (1990).

4. K. Yao, S. Shi and H. Rabitz, " Optimal Control of Molecular Motion: Nonlinear Field Effects", J. Chem. Phys. **150**, 373-381 (1990).

5. C. Schwieters, J. Beumee and H. Rabitz, "Optical Control of Molecular Motion with Robustness and Application to Vinylidene Flouride", J. Opt. Soc. Am. B **7**, 1737-1747 (1990).

6. S. Shi and H. Rabitz, " Optimal Control of Bond Selectivity in Unimolecular Reactions", Comp. Phys. Comm. **63**, 71-83 (1991).

7. L. Shen and H. Rabitz, "Optimal Control of Molecular Rotation in the Sudden Limit", J. Chem. Phys. **95**, 1047-1053 (1991).

8. P. Gross, D. Neuhauser and H. Rabitz,"Optimal Control of Unimolecular Reactions in the Collisional Regime", J. Chem. Phys. **94**(2) 1158-1166 (1991).

9. H. Rabitz and S. Shi, "Optimal Control of Molecular Motion: Making Molecules Dance", in press.