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TIME DEPENDENT APPROACH TO FEMTOSECOND LASER CHEMISTRY

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Active control of molecular motion is perused using shaped ultrafast laser pulses. The theoretical framework emphasizing the role of interference is presented for a molecule with two electronic surfaces coupled by radiation. The flow of energy and population from one surface to the other is analyzed and compared to the power consumption from the radiation field. The analysis of the flows shows that the phase of the radiation becomes the active control parameter which promotes the transfer of one quantity and stops the transfer of another. The phase relations which are responsible for laser catalysis impulsive excitation and stimulated emission are worked out. An interesting possibility of laser cooling emerges by a process that promotes transfer of energy simultaneously with stopping population transfer.

I. INTRODUCTION

Finding ways to control the temporal evolution of complex molecular systems has recently been motivated by advances in laser technology, molecular spectroscopy and in theoretical insight of molecular dynamics. An important example is control of selection of products of a chemical reaction. Typically, a polyatomic molecule will, for defined initial conditions, react to form several products in different amounts. In most instances one of these products is wanted much more than the others. What is sought is a method for controlling the molecular dynamics actively, in real time, so as to guide the molecule to form the desired product.

The developments in laser technology that have stimulated interest in actively controlling selectivity of product formation in a chemical reaction include methods for the generation of very short pulses, of shaped pulses, of pulses with well-defined phase relationship, of light fields with extraordinary pure frequency, and of light fields with very high intensity. Application of laser technology to molecular spectroscopy has yielded a wealth of information concerning molecular potential energy surfaces. It has also led to an increased awareness that exploitation of interference effects inherent to the quantum mechanical description of a system can be used to guide system evolution; to recognition that the dynamics of a strongly coupled light-matter system can

be influenced by alteration of the temporal and spectral distributions of the light; and to the realization that a polyatomic molecule may have sufficiently few degrees of freedom that it is not impossible to control all of them. The underlying principle of the new approach to controlling product selectivity in a reaction is different from that used in earlier attempts to achieve "bond selective chemistry". The new approach is based on exploitation of quantum interference effects whereas the old approaches are, typically, based on use of a very intense laser field to generate a very high level of local bond excitation and the hope that the rate of bond breakage will then greatly exceed the rate of transfer of energy from the excited bond to the rest of the molecule. Two different ways of using quantum mechanical interference to control product selectivity have been proposed [1-9].

Suppose there are two independent excitation pathways between a specified initial state of a molecule and a specified final state of the products; these might be transitions involving absorption of one and three photons, respectively. Quantum mechanics tells us that the probability of forming the specified product is proportional to the square of a sum of the transition amplitudes for the two pathways; because the amplitudes can have different signs, the magnitude of that probability is determined by the extent of their interference. For example, when one- and three-photon transitions generate the independent pathways between the initial and final states, the extent of interference can be controlled by altering the relative phase of the two excitation sources. The situation is analogous to the formation of a diffraction pattern in a two-slit experiment in that the excited state amplitude in each molecule is the sum of the excitation amplitudes generated by two routes which are not distinguished from each other by measurement. An example of control of the population of a level in HCl with this method has been done [10].

An alternative method of influencing the selectivity of product formation in a reaction is to modulate the product yield via interference between two excitation pulses with a variable time delay between them [6,4]. In the simplest case, when only two electronic potential energy surfaces are involved, the first pulse transfers probability amplitude from the electronic ground state, forming a "replica" of the ground state amplitude on the excited state potential energy surface; that replica then evolves on the excited state potential energy surface during the time interval between pulses. The second pulse of the sequence, whose phase is locked to that of the first one, also creates amplitude in the excited electronic state, which is in superposition with the initial, propagated, amplitude. Such an intramolecular superposition of amplitudes can lead to interference. Whether the interference is constructive or destructive, giving rise to larger or smaller excited state population for a given inter-pulse delay, depends on the optical phase difference between the two pulses and on the detailed nature of the evolution of the initial amplitude. This situation is also

analogous to a two-slit experiment. The method described has been used to control the population of a level of I_2 [5].

In principle, the methods available for guiding the evolution of a quantum system by coupling it to an external field are not restricted to the use of a time-independent field or a simple pulse sequence. If the goal to be achieved is, say, maximization of the amount of a product in a reaction, the design of the external field which accomplishes the goal is an inverse problem: given the goal and the quantum mechanical equations of motion, calculate the guiding field which is required. The solution to this inverse problem is very likely not unique, which for the case under consideration is a strength since it is then plausible that one of the possible guide fields is more easily generated than others.

The methodology used in these calculations is optimal control theory [7]. It is usually found that the optimal guiding field has a complicated spectral and temporal structure. The underlying physical principle that determines the efficiency of the guiding field is, again, interference between the amplitudes associated with its different spectral and temporal components. In the model problems studied to date it is predicted that the use of an optimal guide field can increase the product yield by many orders of magnitude relative to the yield from a two-pulse control field.

To facilitate the understanding of the control strategies of molecular motion it is important to study the control of basic quantities. For example if the object to control is the yield of a chemical species, one has to understand the elementary control of population transfer within an electronic surface and from one surface to the other. If the final objective is to coherently excite or on the contrary cool the motion of the molecule on the ground electronic surface. The elementary step involves the control of energy flow within the molecule. The combination of these elementary controls enables achieving quite elaborate goals including constraints on the dynamics the most important of which is radiation damage control [9,11]. In this overview a time dependent approach to active control is formulated with the purpose of shedding light on the role of interference processes.

II. THE MATTER RADIATION QUANTUM MECHANICAL FORMULATION

To explore the basic possibilities of active control of molecular motion the basic formalism of the interaction of radiation with a molecule has to be revealed. Consider two electronic states of a specific molecule coupled by radiation. The radiation which couples the two surfaces is the means of control. As an explicit example the electronic potential surfaces of a diatomic molecule is shown in figure 1.

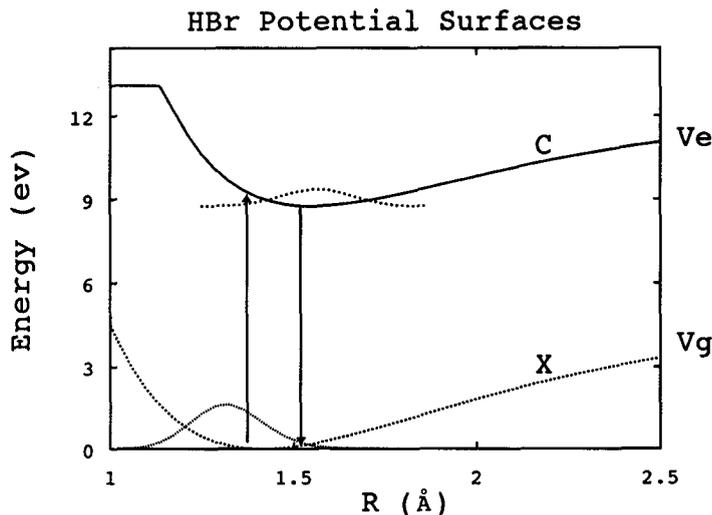


FIG. 1. Ground ($X^1\Sigma^+$) and the ($C^1\Pi$) excited potential energy surfaces of HBr.

The internal state of the molecule is defined by the density operators ρ_l , $l \in g, e$ which are the indexes of the ground and excited surfaces respectively [12]. The combined density operator describing the state of the combined ensemble can be written as:

$$\hat{\rho} = \hat{\rho}_g \otimes \hat{P}_g + \hat{\rho}_e \otimes \hat{P}_e + \hat{\rho}_i \otimes \hat{S}_+ + \hat{\rho}_i^\dagger \otimes \hat{S}_- \quad (1)$$

where the tensor product of the internal space and the surface designation is used. \hat{P}_l are the projection operators on the surface, l and \hat{S}_\pm are the raising and lowering operators from one surface to the other. The first two terms in equation (1) represent the state of the molecules residing on the ground and excited surface. The last two terms represent the electronic coherence induced by the radiation.

The Hamiltonian of the system consists of the sum of internal Hamiltonians and an interaction term

$$\hat{H} = \hat{H}_0 + \hat{V}_i \quad (2)$$

where the zero order Hamiltonian is the sum of the separate parts,

$$\hat{H}_0 = \hat{H}_g \otimes \hat{P}_g + \hat{H}_e \otimes \hat{P}_e = \frac{\hat{P}^2}{2m} \otimes \hat{I} + \hat{V}_g \otimes \hat{P}_g + \hat{V}_e \otimes \hat{P}_e \quad (3)$$

Each surface Hamiltonians \hat{H}_i or surface potential \hat{V}_i is a functions of the internal coordinates. The interaction part controls the transport properties of the between the two electronic manifolds. In this study, it contains only radiative coupling terms:

$$\hat{V}_i = -\hat{\mu} \otimes (\hat{S}_+ \epsilon + \hat{S}_- \epsilon^*) \quad (4)$$

were $\hat{\mu}$ is the transition dipole operator and $\epsilon(t)$ represents a semiclassical time dependent radiation field. The field amplitude $\epsilon(t)$ represents the main control parameter. Experimental methods to shape the field amplitude as well as its phase enable this control.

The evolution of the molecule is generated by the Liouville von Neumann equation [12]:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \mathcal{L}_D(\hat{\rho}) \quad (5)$$

where the first term represents unitary dynamics generated by the Hamiltonian, and the second term represents the dynamics generated by the dissipation. This equation represents the dynamics of an open quantum mechanical system under the restriction of a dynamical semigroup evolution [13–16]. The source of the dissipative term is the reduction of the combined system and bath dynamics to the dynamics of the system only. Within the semigroup approach an explicit form of the dissipative operator exists.

Since the objective is to control observable it is convenient to use the Heisenberg equations of motion to calculate the change in time of an explicitly time dependent operator:

$$\frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + \frac{i}{\hbar} [\hat{H}, \hat{A}] + \mathcal{L}_D^*(\hat{A}) \quad (6)$$

where the first term represents the explicit time dependence of the operator, the second term the Hamiltonian evolution, and the third term the dissipation which is the Heisenberg version of the dissipative superoperator in equation (5).

III. THE TRANSPORT EQUATIONS.

The objective of the control is to change a specific observable. The transport of quantities is the agent of change. Thermodynamic insight can be gained by studying the total change in energy representing the first law of Thermodynamics. Additional insight is gained by considering the population and energy currents from one system to the other. These currents, represent the balance equations. Within the setup of section II, the total energy change becomes:

$$\frac{d \langle E \rangle}{dt} = \left\langle \frac{\partial \hat{H}}{\partial t} \right\rangle + \langle \mathcal{L}_D^*(\hat{H}) \rangle \quad (7)$$

where the second term of equation (6) is zero, since the Hamiltonian commutes with itself. This equation can be interpreted as the time derivative of the first law of thermodynamics [17–19] with the identification of power as:

$$\mathcal{P} = \left\langle \frac{\partial \hat{H}}{\partial t} \right\rangle \quad (8)$$

which is the time derivative of the work. The heat flow is:

$$\dot{Q} = \langle \mathcal{L}_D^*(\hat{H}) \rangle. \quad (9)$$

With these definitions, the power absorbed from the field into the system becomes:

$$\mathcal{P} = - \langle \hat{\mu} \otimes \left(\hat{S}_+ \frac{\partial \epsilon}{\partial t} + \hat{S}_- \frac{\partial \epsilon^*}{\partial t} \right) \rangle = -2 \text{Real} \left(\langle \hat{\mu} \otimes \hat{S}_+ \rangle \cdot \frac{\partial \epsilon}{\partial t} \right) \quad (10)$$

The term $\langle \hat{\mu} \otimes \hat{S}_+ \rangle$ is the main control handle and therefore will reappear in many of the derivations and will be called the instantaneous dipole expectation.

Considering the population balance conditions, the total population is conserved since with only two electronic surfaces the molecule has to reside on one of them therefore:

$$dN_g + dN_e = 0. \quad (11)$$

The flow of population from one electronic surface to the other can be calculated using equation (6):

$$\frac{dN_g}{dt} = \frac{d \langle \hat{P}_g \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{V}_i, \hat{P}_g] \rangle + \langle \mathcal{L}_D^*(\hat{P}_g) \rangle \quad (12)$$

Ignoring nonradiative couplings between the ground and excited surfaces i.e. $\mathcal{L}_D^*(\hat{P}_g) = 0$, the ground surface population change becomes:

$$\frac{dN_g}{dt} = -\frac{i}{\hbar} \langle \hat{\mu} \otimes (\hat{S}_+ \epsilon - \hat{S}_- \epsilon^*) \rangle = \frac{2}{\hbar} \text{Imag} \left(\langle \hat{\mu} \otimes \hat{S}_+ \rangle \epsilon \right) \quad (13)$$

The flow of energy from the ground state can be calculated under the assumptions of small electronic dephasing i.e. $\mathcal{L}_D^*(\hat{P}_g) = 0$ and also pure vibrational dephasing i.e. $\mathcal{L}_D^*(\hat{H}_g) = 0$. Physically these conditions apply when the rate of relaxation to equilibrium is slow compared to the loss of phase ($\tau_1 \gg \tau_2$). Under these conditions:

$$\frac{dE_g}{dt} = \frac{2}{\hbar} \text{Im}ag \left(\langle \hat{\mu} \hat{H}_g \otimes \hat{S}_+ \rangle \epsilon \right) \quad (14)$$

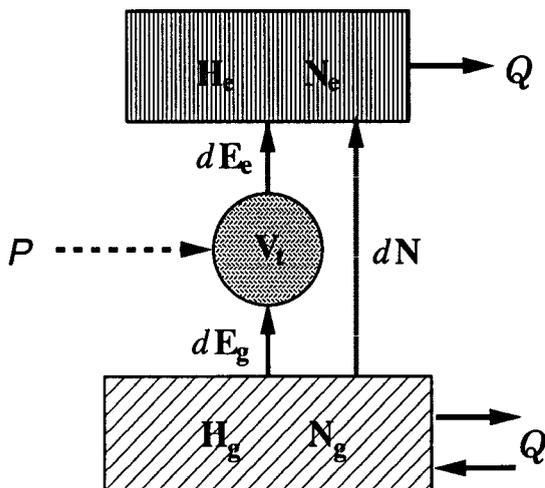


FIG. 2. Schematic diagram of the thermodynamic flows in the radiative quantum mechanical model.

When the total energy balance is considered, the power uptake can be distributed into the "bulk" of ground and excited surfaces as well as into energy stored by the interaction. Since the interaction term is proportional to the field ϵ , for a pulsed field for which $\epsilon = 0$ at $t = \pm\infty$, one can consider the energy flow into the bulk by integrating equation (10) by parts, obtaining:

$$\int_{-\infty}^{\infty} P dt = \int_{-\infty}^{\infty} \frac{\partial \langle \hat{\mu} \rangle}{\partial t} \epsilon dt = \int_{-\infty}^{\infty} \frac{dE_g}{dt} dt + \int_{-\infty}^{\infty} \frac{dE_e}{dt} dt \quad (15)$$

This equation can be interpreted as the energy balance equation. The boundary term $-2\text{Real} \left(\langle \hat{\mu} \otimes \hat{S}_+ \rangle \epsilon(t) \right)$ which goes to zero when deriving equation (15), represents the transient loading of the system. If the loading term becomes small in comparison to the volume terms E_g and E_e then one can omit the integral in equation (15) and obtain:

$$dE = dE_g + dE_e \quad (16)$$

Equation (16) can also be obtained within the limit of weak fields. Such balance equations represent one of the main tools of thermodynamic investigation. A schematic view of the thermodynamic currents can be seen in figure 2.

The spatial derivative of the loading term represents the internal force which the electromagnetic field exerts on the molecule:

$$\vec{F} = -2\text{Real} \left(\langle \nabla_{\vec{r}} \hat{\mu} \otimes \hat{S}_+ \rangle \epsilon \right) \quad (17)$$

where $\nabla_{\vec{r}}$ is the gradient with respect to the internal coordinates. Combined with the conditions imposed in the next section in equation (27); one can apply a directional force on the molecule.

Equations (10), (13), (14) and (17) constitute the transport equations from one surface to the other. It is the objective of control to manipulate these quantities. The next section, describes the control of the transport by manipulating the phase of the transient field ϵ .

IV. TIME DEPENDENT CONTROL OF TRANSPORT.

Molecular transport processes can be promoted either by controlling the field ϵ or its time derivative $\frac{\partial \epsilon}{\partial t}$. This possibility stems from the fact that the transport equations Eq. (13) and Eq. (14) have a similar structure consisting of the real part of a product of a molecular expectation value $\langle \hat{X} \rangle$ by the field ϵ . A similar structure is found in equation (10) where the transport is controlled by the real part of the product of a molecular expectation and the time derivative of the field. This structure can be expressed for equation (13) as:

$$\frac{dN_g}{dt} = \frac{2}{\hbar} \langle \hat{\mu} \otimes \hat{S}_+ \rangle ||\epsilon| \sin(\phi_\mu + \phi_\epsilon) \quad (18)$$

where ϕ_μ is the phase angle of the instantaneous dipole and ϕ_ϵ is the phase angle of the radiation field. The physical interpretation of this angle is the sum of the angle of the induced polarization of the molecule and the angle of the polarization of the light. In a similar way:

$$\mathcal{P} = -2 \langle \hat{\mu} \otimes \hat{S}_+ \rangle ||\frac{\partial \epsilon}{\partial t}| \cos(\phi_\mu + \phi_\epsilon) \quad (19)$$

and

$$\frac{dE_g}{dt} = \frac{2}{\hbar} \langle \hat{\mu} \hat{H}_g \otimes \hat{S}_+ \rangle ||\epsilon| \sin(\phi_{\mu H} + \phi_\epsilon) \quad (20)$$

where $\phi_{\mu H}$ is the phase angle of $\langle \hat{\mu} \hat{H}_g \otimes \hat{S}_+ \rangle$. and

$$\vec{F} = -2 \left| \langle \nabla_{\vec{r}} \hat{\mu} \otimes \hat{S}_+ \rangle \right| |\epsilon| \sin(\phi_{\nabla\mu} + \phi_\epsilon) \quad (21)$$

where $\phi_{\nabla\mu}$ is the phase angle of $\langle \nabla \hat{\mu} \otimes \hat{S}_+ \rangle$. From this description, it is clear that the control parameter of the transport quantities is the phase angle $\phi = \phi_i + \phi_j$. The most simple example is a monochromatic circularly polarized pulse for which $\epsilon(t) = Ae^{-i\omega t}$ where A is a slowly varying envelope function. For this pulse the phase angle of $\frac{\partial \epsilon}{\partial t}$ is 90° rotated from the direction of ϵ , $\phi_{\dot{\epsilon}} = \phi_\epsilon - \pi/2$. Examining equations (18) and (19) one obtains the relation

$$\mathcal{P} = -\hbar\omega \frac{dN_g}{dt} \quad (22)$$

This means that the system behaves as an effective two-level system where the power absorbed is linearly proportional to the population transfer.

For more general pulse shapes, using the above analysis, the control of the transport can be classified as being active or passive. For active control conditions the angle is:

$$\phi_\mu + \phi_\epsilon = \begin{matrix} 0 \\ \pi \end{matrix} \Rightarrow \begin{matrix} \text{maximum energy absorption} \\ \text{maximum energy emission} \end{matrix} \quad (23)$$

$$\phi_\mu + \phi_\epsilon = \begin{matrix} \frac{1}{2}\pi \\ -\frac{1}{2}\pi \end{matrix} \Rightarrow \begin{matrix} \text{maximum positive mass transport} \\ \text{maximum negative mass transport} \end{matrix} \quad (24)$$

$$\phi_{\mu H} + \phi_\epsilon = \begin{matrix} \frac{1}{2}\pi \\ -\frac{1}{2}\pi \end{matrix} \Rightarrow \begin{matrix} \text{maximum energy intake to ground surface} \\ \text{maximum energy disposal from ground surface} \end{matrix} \quad (25)$$

$$\phi_{\nabla\mu} + \phi_\epsilon = \begin{matrix} \frac{1}{2}\pi \\ -\frac{1}{2}\pi \end{matrix} \Rightarrow \begin{matrix} \text{maximum positive force} \\ \text{maximum negative force} \end{matrix} \quad (26)$$

The active control of mass transport using the control relation of equation (24) has been demonstrated experimentally by Sherer et. al. [5]. In this experiment in I_2 the first pulse transfers population from the ground to the excited surface thus creating an instantaneous transition dipole. This dipole function is modulated by the excited surface vibration. At the proper instant when the dipole expectation amplitude is maximized a second pulse is applied. The direction of mass transport was then controlled by changing the relative phase of the second pulse.

Another interesting possibility is the induction of stimulated emission which is obtained when the combined phase angle is π in equation (23). This means

that a pulsed laser can be obtained from an ensemble of molecules without the usual condition of population inversion provided the phase relation is right.

Even more important are passive controls where the transport of a certain quantity is blocked. If the phase angle is

$$\phi_{\mu} + \phi_{\epsilon} = \pm \frac{1}{2}\pi \Rightarrow \text{zero total energy change} \quad (27)$$

$$\phi_{\mu} + \phi_{\epsilon} = 0, \pi \Rightarrow \text{zero mass transport} \quad (28)$$

$$\phi_{\mu H} + \phi_{\epsilon} = 0, \pi \Rightarrow \text{zero change in ground surface energy} \quad (29)$$

$$\phi_{\nabla\mu} + \phi_{\epsilon} = 0, \pi \Rightarrow \text{zero force} \quad (30)$$

On examining the passive control conditions in equation (27),(28),(29),(30) it can be noticed that there are two values of $\phi_i + \phi_j$ for which zero transport conditions apply. This fact can be utilized to simultaneously block the transport of one quantity and to select the direction of the transport of another quantity.

A note of caution is needed at this point because naively it would seem that there is a meaning to the absolute phase of the field and to the phase of the molecular expectation values. But it should be remembered that the phase of the molecular quantity is induced by the radiation in a former time. Therefore all phases have to be related to a previous synchronization pulse which synchronized the molecular clock with the field clock. This is the meaning of quantum mechanical interference between events which are induced in the past propagate and then are used to control transport at a later time.

Figure 3 shows the phase angle conditions leading to different transport quantities.

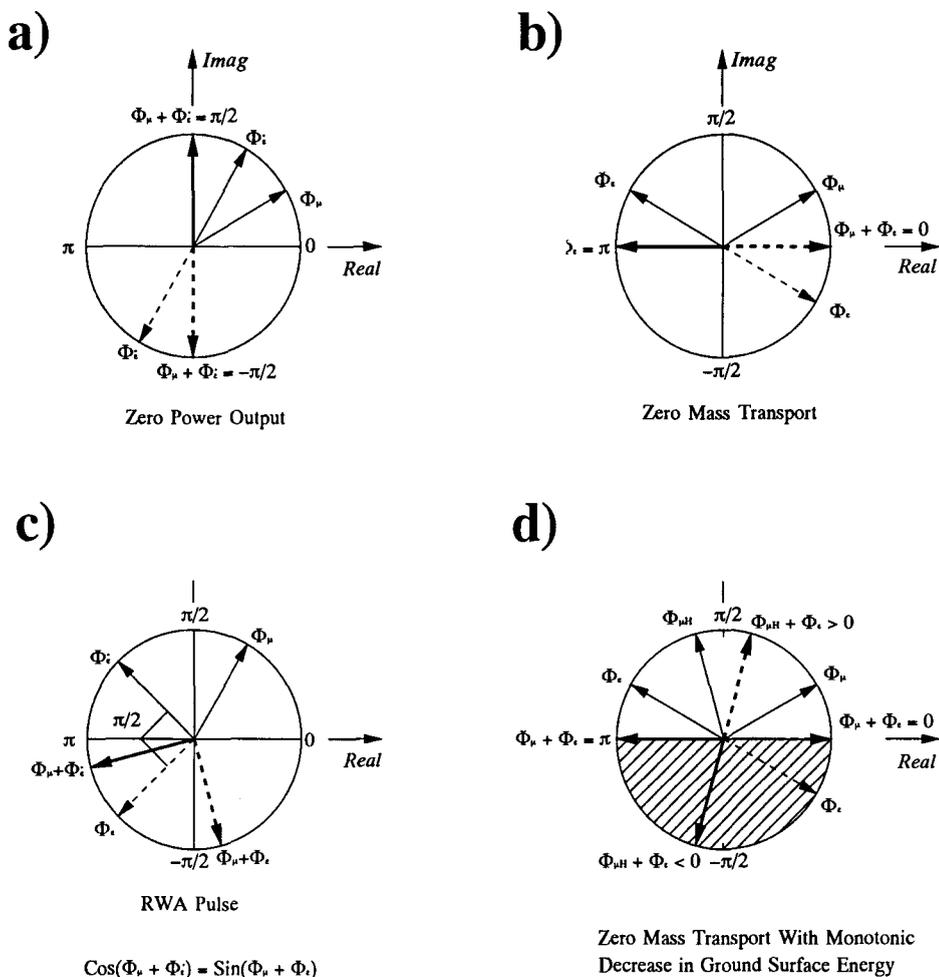


FIG. 3. a) Phase angle diagram for zero power output. b) Phase angle diagram for zero mass transport. c) Phase angle diagram for a RWA pulse. d) phase angle diagram for zero mass transport and for a monotonic decrease in energy. The shaded area represents the region of phase angle of energy decrease in the ground surface.

Figure 3a shows the phase angles for which the total power absorption is zero. Since no energy is absorbed or emitted from the field these conditions define laser catalysis [20]. Figure 2b shows the phase angle relations leading to zero mass transport. Figure 3c is of a RWA pulse corresponding to equation (22), where the mass transport is directed from the ground to the excited surface. Figure 3d shows the phase conditions which stop mass transport while monotonically directing energy out of the ground surface.

V. ENERGY TRANSFER WITH ZERO MASS TRANSPORT.

As an explicit example the local control of energy transport under the constraint of zero mass transport is analysed. The phase relation with null population transfer is obtained when the radiation field has the form:

$$\epsilon = C(t)\Phi (\langle \hat{\mu} \otimes \hat{S}_- \rangle) \tag{31}$$

where $C(t)$ is a real function of time and $\Phi(X) = X/|X| = e^{i\phi}$ is the phase factor. Equation (31) is another formulation of the conditions in equation (28). Active control requires the expectation value of the instantaneous dipole $\langle \hat{\mu} \otimes \hat{S}_+ \rangle$ to be non zero. This means that the present control is related to the instantaneous dipole created in the past.

Under the conditions of zero mass transport, the change of the energy on the ground state becomes:

$$\frac{d \langle E_g \rangle}{dt} = C(t) \frac{2}{\hbar} \text{Imag} (\Phi(\langle \hat{\mu} \otimes \hat{S}_- \rangle) \langle \hat{\mu} \hat{H}_g \otimes \hat{S}_+ \rangle) \tag{32}$$

This means that the sign of the function $C(t)$ determines the direction of the energy transport.

$$C(t) \propto \pm \frac{2}{\hbar} \text{Imag} (\Phi(\langle \hat{\mu} \otimes \hat{S}_- \rangle) \langle \hat{\mu} \hat{H}_g \otimes \hat{S}_+ \rangle) \tag{33}$$

A positive sign will excite the ground surface internal energy. This is the base of an excitation without demolition strategy [9]. Figure 4 shows a monotonic increase in the ground surface energy while maintaining a constant population on the excited surface.

A different excitation strategy has been proposed by Cina and Smith [22] where the excitation is achieved by a double pulse train where the first pulse transfers population to the excited surface and creates an instantaneous dipole. The second pulse is chosen with the inverse phase relation of the first one Cf. (24) transferes all the population back to

the ground surface the net result is an impulsive vibrational excitation.

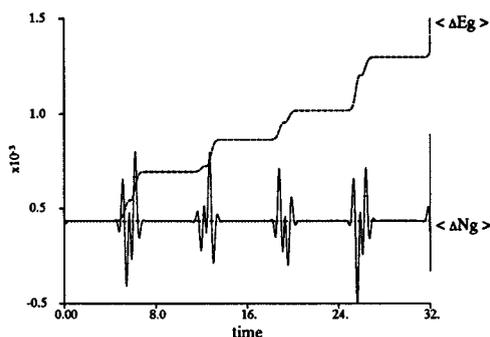


FIG. 4. The change in ground surface energy $\Delta \bar{E}_g$, change in norm $\langle \Delta \hat{N}_g \rangle$ and field amplitude ϵ as a function of time for an excitation pulse. Notice that the field amplitude comes with bursts corresponding to the vibrational period ($\omega = 1$).

A negative sign of $C(t)$ causes a decrease of the ground surface energy. Figure 5, shows a monotonic decrease in energy as a result of a pulse shape calculated according to equation (33).

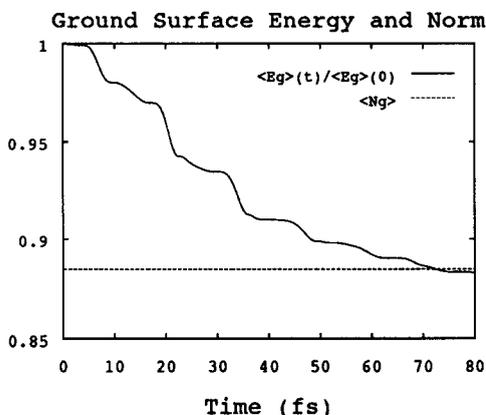


FIG. 5. The ground surface energy \bar{E}_g and norm $\langle \hat{N}_g \rangle$ as a function of time for a cooling pulse, for the HBr molecule starting at a thermal state $T = 5000K$. The energy is normalized to its initial value.

The resulting cooling pulse shape is shown in figures 6. Notice that the pulse

amplitude is modulated by the vibrational period of HBr. The reduction of energy on the ground surface is accompanied by a reduction in entropy while the total entropy of the system increases. Once the system approaches the ground state the it decouples from the radiation in compliance with the third law of thermodynamics.

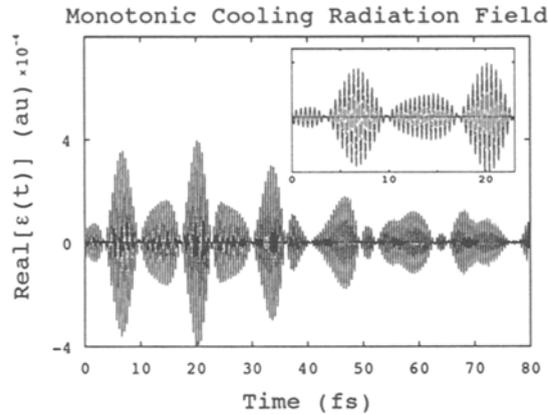


FIG. 6. Real part of the pulse as a function of time for a monotonic decrease in the ground surface energy.

The spectrum of the pulse is shown in figure 7.

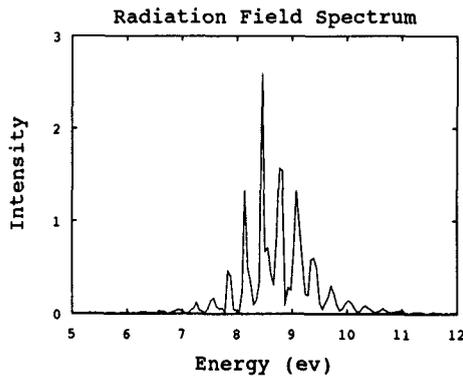


FIG. 7. Spectrum of a cooling pulse for the HBr molecule.

A close analysis shows that the spectrum has its maximum exactly in between the Raman lines of HBr. This decrease in energy can be interpreted as laser cooling [19].

In a similar fashion a force can be applied to the ground surface creating a "squeezed state" with a minimum amount of radiation damage [21].

VI. FROM LOCAL TO GLOBAL CONTROL

The strategy of control using the pulse shape of equation (33), is only one of many possibilities. Therefore the optimal strategy for transporting an observable with minimum power consumption under the restriction of zero mass transport is sought. An optimization solution local in time can be obtained by optimizing the following functional for a ground state quantity $\langle \hat{A}_g \rangle$

$$J = \frac{d \langle \hat{A}_g \otimes \hat{P}_g \rangle}{dt} + W|\epsilon|^2 \quad (34)$$

where W is a penalty function imposed by the power consumption. The variation of J , δJ is with respect to $\delta C(t)$, since the phase is restricted by the zero population transfer condition equation (31). Carrying out the calculation leads to equation (33) with the proportionality constant equal to $1/2W$. This local solution can be replaced with a global one, optimizing the ground surface quantity $J = \langle \hat{A}_g \rangle$ at a specific final time t_f with the minimal cost of external pumping energy $\int_0^{t_f} \mathcal{P} dt$. This problem can be cast into optimal control theory.

The objective is to minimize the ground surface observable $A_g(t_f)$. In the case of cooling the observable is the ground surface energy $E_g(t_f) = \langle \hat{H}_g \rangle$.

The constraints are:

- evolution governed by the Liouville von Neumann equation $\frac{\partial \hat{\rho}}{\partial t} = \mathcal{L}(\hat{\rho})$
- zero mass transport $dN_g = 0$ or other constraints.
- restricted total power consumption $\bar{E} = \int_0^{t_f} |\epsilon|^2 dt$.

The initial state of the system is set as $\hat{\rho}(0)$. By defining the Lagrange multipliers, the objective functional can be minimized subject to the constraints. This leads to the modified objective functional \bar{J} [4]:

$$\bar{J} = \text{tr}(\hat{A}_g \otimes \hat{P}_g \hat{\rho}(t_f)) + \int_0^{t_f} \text{tr} \left(\left(\frac{\partial \hat{\rho}}{\partial t} - \mathcal{L}(\hat{\rho}) \right) \hat{B} + \lambda |\epsilon|^2 \right) dt \quad (35)$$

where \hat{B} , is an operator Lagrange multiplier and λ is a scalar Lagrange multiplier. The variation of \bar{J} is with respect to $\delta \hat{\rho}$ and $\delta |\epsilon|$. The condition $\frac{dN_g}{dt} = 0$ determines the phase of ϵ through equation (28) or (31). It therefore is omitted from the variation. Calculating the variation of equation (35) and integrating by parts leads to the following equations:

- a forward equation for the density operator $\hat{\rho}$

$$\frac{\partial \hat{\rho}}{\partial t} = \mathcal{L}(\hat{\rho}) \quad (36)$$

subject to the initial condition $\hat{\rho}(0)$.

b) a backward equation for the Lagrange operator \hat{B} :

$$-\frac{\partial \hat{B}}{\partial t} = \mathcal{L}^*(\hat{B}) \quad (37)$$

subject to the final condition $\hat{B}(t_f) = \hat{A}_g \otimes \hat{P}_g$. The dissipative part of equation (37) is symmetric in time, meaning that dissipation takes place in the forward as well as backward evolution.

c) and the condition on the field:

$$|\epsilon(t)| = \frac{1}{2\lambda} \text{tr} \left(\frac{\partial \mathcal{L}(\hat{\rho}(t))}{\partial |\epsilon|} \hat{B}(t) \right) = -\frac{1}{2\lambda} \left\langle \frac{\partial \mathcal{L}^*(\hat{B}(t))}{\partial |\epsilon|} \right\rangle \quad (38)$$

Equation (38) can be interpreted as the scalar product of a forward moving density, and of a backward moving time-dependent operator. The optimal field at time t is determined by a time-dependent objective function propagated from the target time t_f backwards to time t . A first order perturbation approach to obtain a similar equation for optimal chemical control in Liouville space has been derived by a different method by Yan et. al. [23].

In dissipative dynamics, the backwards propagating target operator decays into a stationary operator and therefore, its change in time becomes zero $\mathcal{L}^*(B(-\infty)) = 0$. This leads to loss of control, as can be seen in equation (38).

In the cooling process, the target operator is the ground surface operator $\hat{H}_g(t_f)$. In general for weak field excitation, the target operator $\hat{B}(t)$ can be expanded in powers of the field ϵ^k . For the cooling scheme under these conditions the target function becomes time independent and is just the Schrödinger picture operator \hat{H}_g . Inserting the target function into equation (38) one obtains the result of equation (33) with the proportionality constant becoming $1/2\lambda$. As a conclusion the phase and amplitude conditions for cooling suggested in equation (33) are the optimal control solutions for weak fields. They can be used also as a first guess for the optimal field in an iterative solution for strong fields [24].

VII. DISCUSSION

Considering the control processes studied they are all based on the quantum mechanical interference phenomena. Interference is a global phenomena which means that in the context of a time dependent description events created in the past interfere with events created later in time. To unravel the control mechanism, a local in time description is more easy to interpret since one can optimize the transport of the desired quantity which will accumulate to produce the final outcome. The link between the local and global picture is the phase of the molecular expectation the most important of which is the instantaneous dipole $\langle \hat{\mu} \otimes \hat{S}_+ \rangle$. Although the phase is not measurable it links the past events to the present ability to control transport.

The interaction of light with a two electronic surface system, bears close analogies to the thermodynamics of two coupled systems which can transfer mass and energy via external work (figure 2). Versions of the first, second and third law of thermodynamics have been developed [19]. Various processes which transfer energy without mass and mass without energy are identified. An interesting consequence of the analysis is the possibility of a pulsed laser with an active medium without population inversion.

The realization of control scenarios is a matter for the near future. In recent years the techniques of pulse shaping have advanced considerably [32–34]. Methods to shape both the phase and the amplitude of a ultrashort pulse are becoming available. Advances in simulation of quantum dynamics including the solution of the Liouville von Neumann equation methods [25–28] enable the study of molecules under the influence of strong fields and dissipative forces. The third element is the progress in optimal control strategies [24,35].

Finally one has to consider the practicality of using light as a chemical substance. Since the price of photons is high, optical control of chemical reactions is justified only for very expensive materials. Nevertheless the control methods developed have already found their use in new spectroscopic techniques which are based on impulsive excitation of coherent motion [29–31]. It is well known that measurements based on interference effects are of high quality. The control mechanisms can be used to optimize the information content of the experiment. Since in the modern era information is more valuable than materials the effort to seek control is justified.

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