LASER HEATING, COOLING, AND
TRANSPARENCY OF INTERNAL
DEGREES OF FREEDOM OF MOLECULES

D. J. TANNOR*

Department of Chemical Physics
Weizmann Institute of Science
Rehovot Israel

R. KOSLOFF AND A. BARTANA

Department of Physical Chemistry and the
Fritz Haber Research Center
The Hebrew University
Jerusalem Israel

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I. INTRODUCTION

We are in the infancy of a new era in the physical sciences. It is probable that in the coming years we will learn general strategies for manipulating the

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precise quantum states of atoms and molecules using laser light [1–5, 18] (see also S. A. Rice, Perspectives on the Control of Quantum Many-Body Dynamics: Application to Chemical Reactions). The possibilities inherent in manipulation go far beyond simply the excitation of particular quantum states that might otherwise be hard to access but, in addition, to controlling the phase coherence of superposition states in order to achieve desired chemical and physical purposes. This phase coherence can at times be responsible for the most peculiarly quantum effects and at other times for the building of quantum mechanical wavepackets and the recovery of classical-like behavior.

One of the new areas to exploit the assumption of optical phase coherence is quantum computing [6]. The key concept is that in a set of \( N \) two-level systems there are \( 2^N \) basis functions that can be manipulated independently using the laser and that are available for computation, as compared with the \( N \) elements that are up or down in conventional computing. A second new area is laser-induced transparency: An ordinarily opaque material can become transparent in the presence of laser light [7]. Again, the idea is simple: If the laser prepares a coherent superposition of states that connect via opposite signs to the excited state, the net absorption will be zero. This same concept is behind lasing without population inversion and population inversion without lasing [8]. Moreover, the same basic concept of preparing a coherently trapped superposition state underlies one of the most successful methods of atom cooling [9, 10]. Here, a superposition of translational states is created that is dark for \( u = 0 \) and not dark for nonzero \( u \)'s. As atoms get cooled \( u \to 0 \) and then they no longer interact with the light! This cooling mechanism has allowed cooling to 2 \( \mu \)K, below the limit dictated by random recoil from spontaneous emission.

In this brief chapter we discuss two applications of phase tailored pulses to the manipulation of molecules: vibrational heating without demolition and laser cooling of internal molecular degrees of freedom. In both these applications the laser field is used to maintain orthogonality of a lower and upper electronic wavepacket, and as a result there is no absorption. In some sense this work can be viewed as a generalization of the principle of laser-induced transparency and its relatives, discussed in the previous paragraph, from three-level systems to multilevel wavepackets. However, there is a richness in the molecular multilevel case that is absent in the atomic case. The coordinate dependence of the wavepacket in general has a nontrivial spatial dependence that can be manipulated while maintaining the conditions of zero absorption.
II. INSTANTANEOUS DIPOLE MOMENT: GENERALIZED EINSTEIN B COEFFICIENT

The time-dependent Schrödinger equation for a two-electronic-state system with transition dipole moment $\mu$ can be written as

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_g(t) \\ \psi_e(t) \end{pmatrix} = \begin{pmatrix} H_g & -\mu e(t) \\ -\mu e^* (t) & H_e \end{pmatrix} \begin{pmatrix} \psi_g(t) \\ \psi_e(t) \end{pmatrix}$$ \hspace{1cm} (1)

The subscripts $g$ and $e$ refer to the ground and excited electronic state indices, respectively. The term $H_{g/e}$ refers to the Born–Oppenheimer Hamiltonian for the ground/excited electronic state, respectively; $\psi_{g/e}$ is the wave function (wavepacket) associated with the ground/excited Born–Oppenheimer potential-energy surface. The two electronic states are coupled by the transition dipole moment $\mu$, which interacts with the electric field $e(t)$ associated with the laser pulse. Complex values of the field are considered admissible by associating the real and the imaginary parts of the field with the two independent polarizations of the laser light perpendicular to its direction of propagation. It is straightforward to show that Eq. (1) leads to the following equation for the rate of change in excited-electronic-state population:

$$\frac{dN_g}{dt} = \frac{d\langle \psi_g | \psi_g \rangle}{dt} = \frac{2}{\hbar} \text{Im} [\langle \psi_g | \mu | \psi_e \rangle \cdot e(t)]$$ \hspace{1cm} (2)

The quantity $\mu_{eg} = \langle \psi_e | \mu | \psi_g \rangle$ is the instantaneous (complex) transition dipole moment, also called the polarization. It is a generalization of the constant $\mu_{eg}$, which is essentially the Einstein $B$ coefficient. In the standard Einstein treatment the $B$ coefficients for absorption and stimulated emission are identical. In fact, however, $\mu_{eg}$ is complex and not equal to $\mu_{ge}$; moreover, it is time dependent.

An example of the use of Eq. (2) is provided by the wavepacket interferometry experiments of Scherer, Fleming et al. [11]. These workers have demonstrated that the phase of the light can be used to control constructive versus destructive interference of wavepackets in the excited electronic state. An alternative way of interpreting their experiment is that the phase of the second pulse relative to the first determines the direction of population transfer between the two electronic states. In the spirit of the present discussion, absorption versus stimulated emission is being controlled by the choice of phase of the light relative to the instantaneous $\mu_{ge} \neq \mu_{eg}$. Since the direction of population transfer is not determined in this case by population inversion...
alone, it is a short step to consider the possibility of lasing without population inversion and population inversion without lasing using phase-locked laser pulse sequences.

It is possible to view Eq. (2) as a generalization of the third of the optical Bloch equations, that is, the equation for population transfer. This leads us to consider analogies between coherence phenomena in two-level systems and the case where there is a wavepacket on each of two electronic state potential-energy surfaces. Moreover, the Feynman–Vernon–Hellwarth (FVH) geometric picture, which is so useful for two-level systems [12], may be expected to be useful in the wavepacket context as well. In particular, the applications below to heating and cooling can be viewed as wavepacket generalizations of photon locking in two-level systems [13].

III. VIBRATIONAL HEATING USING NONDESTRUCTIVE OPTICAL CYCLING

Several years ago, Nelson posed the following problem [14]: Is it possible to design a pulse sequence, using an impulsive stimulated Raman mechanism, to give large-amplitude vibrational motion on the ground electronic state without creating significant amounts of excited electronic state population? The problem with excited-state population is twofold: It complicates the interpretation of the experimental results, and it is often a precursor to dissociation or ionization. It is simple to see that the condition

$$\epsilon(t) = \langle \psi_e | \mu | \psi_g \rangle C(t)$$

(3)

where $C(t)$ is some real envelope function (positive or negative) guarantees the condition of zero electronic population transfer [19]. The equation for the energy of the wavepacket on the ground state is given by

$$\frac{dE_g}{dt} = -\frac{i}{\hbar \langle \psi_g | \psi_g \rangle} [\langle \psi_g | H_g \mu | \psi_e \rangle \epsilon(t) - \langle \psi_e | \mu H_g | \psi_g \rangle \epsilon^*(t)]$$

(4)

$$= \frac{-2}{\hbar \langle \psi_g | \psi_g \rangle} C(t) \text{Im}((\langle \psi_e | \mu H_g | \psi_g \rangle (\langle \psi_g | \mu | \psi_e \rangle))$$

(5)

The strategy is then to adjust the sign of $C(t)$ in such a way that the vibrational energy on the ground state will monotonically increase. Numerical experiments show that this works beautifully, both for weak fields and strong fields; for strong fields the heating is simply faster (see Figs. 1a–d) [19].

It is interesting to contemplate the possibility of extending these ideas
Figure 1. (a) The FVH diagram illustrating photon locking in two-level system. Pseudopolarization \( r \) vector begins at \( z = -1 \), corresponding to all population in ground state, and precesses about field \( \Omega \) vector (which initially points along \( x \) axis) according to equation \( dr/dt = \Omega \times r \). When \( r \) vector reaches \( x-y \) plane (\( \pi/2 \) pulse), phase of field is changed by \( \pm\pi/2 \). This rotates field vector by \( 90^\circ \), bringing it into alignment with \( r \) vector and making further precession impossible. Physical manifestation of this geometric picture is that although resonant field continues to be applied, there is no further population transferred between two levels. (b) Potential-energy structure of model. Frequencies of ground and excited surfaces are 1.0 and 0.8, respectively. Excited surface shifted by 7.0 units of energy and 3.0 units of distance, which leads to vertical distance of 10.6 units. Dipole operator has slope of 1. Coherent wave function with energy of 1.0 used as initial state on ground surface. Ground and excited absolute values of wave function shown after first exciting pulse (not to scale). (c) Change in population on ground state \( \Delta N_g \) (dotted line), change in ground-state energy \( \Delta E_g \) (dashed line), and real part of field \( \epsilon \) (solid line) as function of time. Note monotonic increase in ground-state energy, coming in bursts at times that pulse is on. This is weak-field case; strong-field case has same qualitative behavior but rise in energy is faster and pulse shapes more sharply modulated. (d) Power spectrum of pulse in (c). Frequency of vertical transition 9; spectrum shows dips at excited-state vibrational resonances, consistent with condition of zero absorption.

to more than two electronic states. For example, if there is a third higher electronic state that is strongly coupled to the second electronic state, is it still possible to apply the excitation without demolition procedure? The answer when there are three states is manifestly yes; if there are many more excited states, the situation is not clear.

IV. NONEVAPORATIVE COOLING

One of the most exciting areas in atomic physics in the last 10 years has been laser cooling of translational motion in atoms to \( 10^{-3}-10^{-9} \) K [9, 10, 15]. Several variations on cooling of atomic translational motion have now been proposed, but the generic scheme is as follows: Two monochromatic laser beams are propagated, one along and one opposite an atomic beam; by tuning the frequency of the laser to the red of resonance with a sharp
Figure 1. (Continued)
electronic transition in the atom, those atoms propagating faster and therefore having a larger Doppler shift absorb light and are slowed down by the momentum imparted by the photon. Slowly shifting the frequency of the light into resonance progressively slows down more and more of the atoms. An added effect comes from a combination of level splitting in the presence of the light, together with a light-induced polarization gradient, leading to a so-called Sisyphus effect [9]. The cooling limit of this process is dictated by the random recoil imparted by the spontaneous emission of the photon; however, even this limit can be overcome by a method of velocity-dependent coherent population trapping [10].

It is generally believed that the same schemes for translational cooling cannot be applied to molecules. The reasons are quickly perceived: molecules, even the smallest of them, have a high density of internal states coming primarily from rotations and vibrations, although also from electronic and spin degrees of freedom. The atomic cooling scheme relies on the validity of a two-level system picture, so that a single frequency red shifted from resonance will cool the entire population. In a molecule with a
congested energy-level spectrum, red shifting from one particular resonance line will cool only those molecules in that one level; then molecules in each level will have to be cooled separately. If there are thousands or millions of internal states occupied, this is quite a challenge. In addition, red shifting away from one level may entail shifting into resonance with another level.

Recently, Bahns et al. [16] suggested a strategy for cooling molecules that involves the progressive cooling of rotations, then translations, and finally vibrations. Probably the most challenging of these stages is the first, the cooling of rotations. The Connecticut group proposes to use the molecule itself to generate the laser light at the characteristic absorption frequencies of the rotational manifolds. When this multitude of frequencies impinges on the rotationally hot molecule, it will lead to optical absorption followed by spontaneous emission. If the frequency corresponding to resonant excitation out of the ground rovibrational state is blocked, the population in this state can only grow, through spontaneous emission, and never diminish. One can imagine a variation on this scheme in which all frequencies are at first blocked and then unblocked from lowest to highest according to some schedule.

An alternative approach to vibrational cooling uses shaped pulses, again based on photon locking [17]. The goal is to cool an initial thermal rotational or vibrational distribution down to 0 K. The strategy, as in the heating scenario, is to use the excited electronic state as an optical lever for cooling without transferring a significant amount of population upstairs. Formally, the biggest difference from the heating is that the equations must be cast in terms of the density operator to describe the absence of coherence in the initial population and the subsequent incomplete coherence. We begin with some defining equations for the operators when there are two coupled potential surfaces. The density operator is given by

$$\rho = \rho_g \otimes P_g + \rho_e \otimes P_e + \rho_i \otimes S_+ + \rho_i^\dagger \otimes S_-$$ (6)

where $P_{g/e}$ are projection operators for the ground- and excited-state surfaces, respectively, and $S_\pm$ are the raising and lowering operators from one surface to another. The Hamiltonian is given by

$$H = H_0 + V(t)$$ (7)

where

$$H_0 = H_g \otimes P_g + H_e \otimes P_e$$ (8)
and the surface Hamiltonians $H_g$ and $H_e$ are functions of the internal coordinates. Moreover,

$$V(t) = -\mu \otimes [S_+ \epsilon(t) + S_- \epsilon^*(t)]$$  \hspace{1cm} (9)

The evolution of the density operator is described by the Liouville–von Neumann equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] + L_D(\rho)$$  \hspace{1cm} (10)

The equation for population change is now given by

$$\frac{dN_g}{dt} = -\frac{i}{\hbar} \langle \mu \otimes (S_+ \epsilon - S_- \epsilon^*) \rangle$$  \hspace{1cm} (11)

$$= \frac{2}{\hbar} \text{Im}(\langle \mu \otimes S_+\rangle \epsilon)$$  \hspace{1cm} (12)

$$= \frac{2}{\hbar} \langle \mu \otimes S_+ \rangle \| \epsilon \| \sin(\phi_\mu + \phi_\epsilon)$$  \hspace{1cm} (13)

where $\phi_\mu$ is the phase of the instantaneous dipole and $\phi_\epsilon$ is the phase angle of the radiation field. Moreover, the equation for the change in ground-state energy is now

$$\frac{dE_g}{dt} = \frac{2}{\hbar} \langle \mu H_g \otimes S_+ \rangle \| \epsilon \| \sin(\phi_{\mu_H} + \phi_\epsilon)$$  \hspace{1cm} (14)

where $\phi_{\mu_H}$ is the phase angle of $\langle \mu H_g \otimes S_+ \rangle$. For zero population transfer, choose $\epsilon = C(t)\Phi(\langle \mu \otimes S_- \rangle)$, where $C(t)$ is a real function of time and $\Phi(X) = X/|X| = e^{i\phi}$ is the phase factor. Under the condition of zero population transfer the change of energy on the ground state becomes

$$\frac{d\langle E_g \rangle}{dt} = C(t) \frac{2}{\hbar} \text{Im}[\Phi(\langle \mu \otimes S_- \rangle)\langle \mu H_g \otimes S_+ \rangle]$$  \hspace{1cm} (15)

The condition on the function $C(t)$ that will lead to a monotonic decrease in energy is
Figure 2. (a) Phase-angle diagram for zero mass transport with monotonic decrease in ground-state energy. Key observation is that zero mass transport condition requires that $\Phi_H + \Phi_e = 0, \pi$; this determines $\Phi_e$ within a sign. Except for pathological case, there will always be one choice of sign that gives $\Phi_H + \Phi_e < 0$, leading to monotonic decrease in ground-state energy; other choice of sign leads to monotonic increase in ground-state energy. (b) Ground surface energy in presence of the cooling pulse as function of time, with and without dissipation. (c) Phase-space density of initial density operator $\rho_0(0)$ (Wigner distribution function in position–momentum phase space). Upper panel: stereoscopic projection. Lower panel: contour map. (d) Phase-space display of final density operator without dissipation $\rho_g(t_f)$. Upper panel: stereoscopic projection. Lower panel: contour map.
Figure 2. (Continued)
The following equations are the density matrix analogues of the heating equations in the previous section. Figures 2a–d (see pages 310–311) show that this strategy is effective in producing monotonic cooling. However, the numerical results indicate that in absolute terms the temperature drop is not dramatic. It turns out that entropy limits the degree of cooling attainable. These entropy considerations, together with alternative laser cooling strategies, will be presented in a separate publication.

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References


DISCUSSION ON THE COMMUNICATION BY D. J. TANNOR
Chairman: M. Quack

D. M. Neumark: We are interested in generating coherent vibrational motion in negative ions, which typically do not have bound excited electronic states. Does your Impulsive Stimulated Raman Scattering (ISRS) scheme work if the excited state is not bound?

D. J. Tannor: I think there is a good chance that the scheme, or some variation, may work even with a dissociative intermediate state. The reason is that the excited-state population is small; in some sense it is "virtual" in the old sense of Raman scattering. Moreover, when strong fields are used, the validity of the original Born–Oppenheimer surfaces as a good zero-order picture generally breaks down. In other words, with strong fields, there is no a priori reason to believe the excited-state dynamics will remain dissociative. It would be very interesting for us to do the calculation.

J. Manz: Prof. D. Tannor has demonstrated the possibility to achieve laser cooling (or heating) of molecules in the electronic ground state. These effects are achieved, however, by laser-induced transitions to and from the electronic excited state. As a consequence, one may end up with an ensemble of molecules where part of them are cooled (or heated) in the electronic ground state, whereas the rest may be found in the electronic excited state with a rather uncontrolled "mixed" distribution of nuclear states. I would like to ask Prof. Tannor to give us some details about the relative fraction of molecules in the excited state, about their distributions of vibrational states, and about their role in view of the original purpose of laser cooling or heating.

D. J. Tannor: In reply to Prof. Manz, I have to emphasize that there are three quantities to examine:

1. Norm (population) in the excited electronic state
2. Energy in the excited electronic state
3. Entropy in the excited electronic state

The scheme guarantees that the norm in the excited state is maintained constant (e.g., at 2%, to avoid sample destruction). The excited-state energy does not necessarily rise; there is no conservation rule that
states the sum of the energy in the ground and excited electronic states must be conserved, since the light can carry away energy. However, the entropy in the ground and excited states is in fact conserved, and hence the entropy in the excited state must increase as the entropy in the ground state decreases (in the cooling scenario). This in fact puts limitations on the ability to cool, depending on the excited-electronic-state density of internal vibrational/rotational states.