

## Excitation without Demolition: Radiative Excitation of Ground-Surface Vibration by Impulsive Stimulated Raman Scattering with Damage Control

Ronnie Kosloff and Audrey Dell Hammerich

*Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel*

David Tanner

*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556*

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A pulse shaping strategy is developed for exciting the ground-surface vibrational motion while minimizing radiation damage. The scheme is based on a resonant impulsive stimulated Raman scattering process where the amount of population transferred to the excited surface is strictly controlled. The scenario begins with an impulsive pulse which creates an instantaneous dipole moment. It follows by a pulse  $180^\circ$  out of phase with the instantaneous dipole which deposits vibrational energy into the ground electronic surface while blocking population transfer to the excited surface.

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Impulsive stimulated Raman scattering (ISRS) [1-4] has been suggested as a mechanism for exciting specific ground-state vibrational modes. The process originates with a short pulse which, by coupling the ground electronic surface to the excited surface, creates an impulsive force on the molecule. The amount of force depends on the strength of the transition which suggests a frequency range close to resonance. Resonance operation conditions create a new difficulty since a strong pulse will induce significant population transfer from the ground to the excited surface. This is followed by further excitations of the excited state ultimately leading to radiation damage either by ionizing or by dissociating the molecule [1]. In this Letter we want to demonstrate how, with the correct control of the amplitude and phase of the radiation, the ground surface of the molecule can be vibrationally excited while minimizing radiation damage.

The dynamics of the process is followed by solving the time-dependent Schrödinger equation for two coupled electronic surfaces

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_g \\ \psi_e \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{H}}_g & -\hat{\mu} \cdot \epsilon \\ -\hat{\mu} \cdot \epsilon^* & \hat{\mathbf{H}}_e \end{pmatrix} \begin{pmatrix} \psi_g \\ \psi_e \end{pmatrix}, \quad (1)$$

where  $\hat{\mathbf{H}}_i = -\frac{\hbar^2}{2m} \nabla_r^2 + \hat{\mathbf{V}}_i(r)$ . The index  $i$  denotes the molecular ground or upper surface field-free Hamiltonian,  $\hat{\mu}(r)$  is the dipole operator, and  $\epsilon(t)$  is the radiation field. A semiclassical dipole field description is used which is appropriate for the strong radiation fields considered here. The change in amplitude on the electronic surfaces  $N_i = \langle \psi_i | \psi_i \rangle$  is to be compared with the change in energy of the system  $E$ . Beginning with the change in amplitude we have

$$\frac{dN_g}{dt} = \left\langle \psi_g \left| \frac{\partial \psi_g}{\partial t} \right. \right\rangle + \left\langle \frac{\partial \psi_g}{\partial t} \left| \psi_g \right. \right\rangle. \quad (2)$$

Then, inserting into the Schrödinger equation and its

conjugate, one obtains

$$\frac{dN_g}{dt} = -\frac{2}{\hbar} \text{Im} [\langle \psi_g | \hat{\mu} | \psi_e \rangle \cdot \epsilon(t)]. \quad (3)$$

Next the total change in energy is considered:

$$\frac{dE}{dt} = \left\langle \frac{\partial \hat{\mathbf{H}}}{\partial t} \right\rangle = -2 \text{Re} \left[ \langle \psi_g | \hat{\mu} | \psi_e \rangle \cdot \frac{\partial \epsilon}{\partial t} \right]. \quad (4)$$

The first equality is the result of commutation of the Hamiltonian with itself while the second equality exists because the only part of the Hamiltonian which is time dependent is the field  $\epsilon(t)$ . To obtain a feeling of the type of field required, a simple excitation pulse is examined:

$$\epsilon(t) = \frac{1}{2} A(t) e^{i\omega t}, \quad (5)$$

where  $A(t)$  is a slowly varying envelope function. For this pulse, the change in energy becomes

$$\frac{dE}{dt} = 2\omega \text{Im} [\langle \psi_g | \hat{\mu} | \psi_e \rangle \cdot \epsilon] - 2 \text{Re} \left[ \langle \psi_g | \hat{\mu} | \psi_e \rangle \cdot \frac{\dot{A}}{A} \epsilon \right]. \quad (6)$$

Now, if  $A$  is a slowly varying envelope function  $\dot{A}/A \ll \omega$ , which is the condition for the pulse to be monochromatic, the second term can be neglected, leading to the result

$$\frac{dE}{dt} \cong -\hbar\omega \frac{dN_g}{dt} \quad (7)$$

in which the equality holds when a monochromatic and circularly polarized light is used. The consequence of this observation is that for a pulse which has this form any change in energy is linearly proportional to the change in population [5]. Since the objective is to pump energy from the field into the system, we conclude that the non-demolition pulse has a different form which will be called anti-RWA. Below we will investigate its shape.

The importance of the phase of the instantaneous tran-

sition moment,  $\langle\psi_g|\mu|\psi_e\rangle$ , in determining the direction of population transfer has been demonstrated experimentally [6]. It was found that if the field were  $\frac{1}{2}\pi$  out of phase with the instantaneous transition moment maximum population transfer from the ground to the excited surfaces is obtained. A  $-\frac{1}{2}\pi$  pulse has the opposite effect. The local control of population transfer has been used as a control mechanism to obtain chemical selectivity [7]. In this work the reverse effect is sought. That is, if  $\epsilon(t)$  is  $\pi$  out of phase with the instantaneous dipole further population transfer will be arrested. As discussed previously this condition applied under the RWA (rotating-wave approximation) pulse form leads to zero energy change. The question then is what are the possibilities of energy change without population transfer?

Starting from the null-population transfer condition, the field which makes the right-hand side of Eq. (3) zero is

$$\epsilon(t) = \langle\psi_e|\hat{\mu}|\psi_g\rangle C(t), \quad (8)$$

where  $C(t)$  is a real quantity. With this choice of pulse shape, the change in energy becomes

$$\frac{dE_g}{dt} = \frac{1}{\langle\psi_g|\psi_g\rangle} \left( \frac{i}{\hbar} \langle\psi_g|\hat{\mathbf{H}}_g\hat{\mu}|\psi_e\rangle\epsilon(t) - \frac{i}{\hbar} \langle\psi_e|\hat{\mu}\hat{\mathbf{H}}_g|\psi_g\rangle\epsilon^*(t) \right) \quad (11)$$

$$= \frac{2}{\hbar\langle\psi_g|\psi_g\rangle} C(t) \text{Im}[\langle\psi_e|\hat{\mu}\hat{\mathbf{H}}_g|\psi_g\rangle\langle\psi_g|\hat{\mu}|\psi_e\rangle]. \quad (12)$$

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. A close study of Eq. (12) reveals that excitation of the ground state under the null-population transfer condition is very difficult if the dipole function is constant or impossible if the ground-state wave function is in an eigenstate of  $\hat{\mathbf{H}}_g$ .

A schematic description of a typical molecular system with two electronic surfaces coupled by a dipole operator is shown in Fig. 1. Initially the molecule is on its ground electronic surface with a small initial vibrational energy. The excitation scenario begins with a short Gaussian pulse on resonance with the electronic transition transferring a small amount of population to the excited surface arbitrarily chosen to be 3%. The purpose of this excitation is to create a nonzero instantaneous transition moment  $\langle\psi_g|\hat{\mu}|\psi_e\rangle$  which is the basis for the next manipulation. A new excitation pulse is now turned on according to the null-population transfer condition [Eq. (8)] where the sign of  $C(t)$  has been adjusted to always increase the energy on the ground surface [Eq. (12)]. Figure 2 displays the pulse shape, the change in population, and the change in ground-state energy as a function of time. Overall the energy has increased by more than a factor of 4 in five vibrational periods while the population has remained constant.

$$\begin{aligned} \frac{dE}{dt} = & -2\dot{C}(t)|\langle\psi_g|\hat{\mu}|\psi_e\rangle|^2 \\ & -2\frac{C(t)}{\hbar} \text{Im}[\langle\psi_g|\hat{\mu}|\psi_e\rangle\langle\psi_e|\hat{\mu}\hat{\mathbf{H}}_g - \hat{\mathbf{H}}_e\hat{\mu}|\psi_g\rangle]. \end{aligned} \quad (9)$$

The first term represents energy absorption which is stored in the field-matter interaction. This fact can be used to ramp up the field to very high values without population changes. The resulting effect is a static Stark force on the molecule. As the energy is stored in the temporary matter-field interaction, it does not serve the objective of vibrational excitation on the ground surface but can be useful for other purposes.

Below it will be seen that the second term, which is proportional to the time derivative of the instantaneous dipole, is associated with vibrational excitation.

Our objective is to increase the average energy on the ground surface:

$$E_g = \frac{\langle\psi_g|\hat{\mathbf{H}}_g|\psi_g\rangle}{\langle\psi_g|\psi_g\rangle}. \quad (10)$$

Since the operation is under the condition of null-population transfer, the change in ground-surface energy becomes

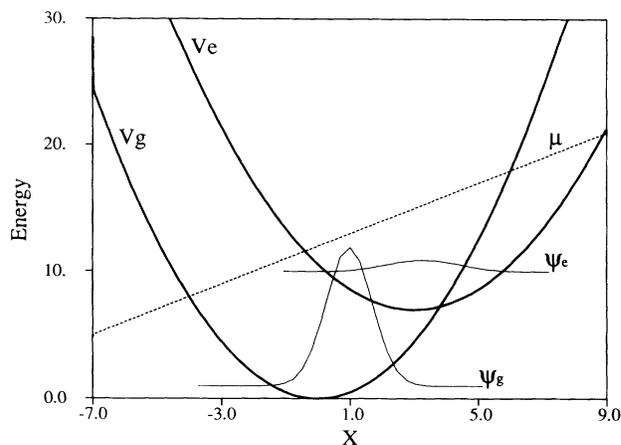


FIG. 1. Potential energy structure of the model. The frequency of the ground and excited surfaces is 1.0 and 0.8, respectively. The excited surface is shifted by 7.0 units of energy and 3.0 units of distance which leads to a vertical energy distance of 10.6 units. The dipole operator has a slope of 1. A grid of 64 points was used with a grid spacing of  $\Delta x = 0.295$ . A coherent wave function with an energy of 1.0 was used as an initial state on the ground surface. The ground and excited absolute values of the wave function after the first exciting pulse are shown (not to scale).

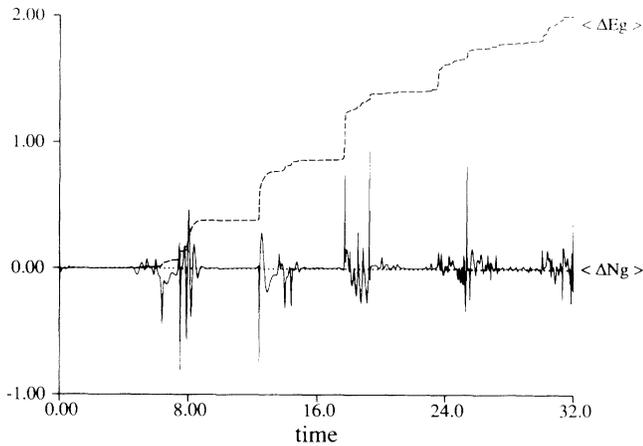


FIG. 2. Change in population on the ground state ( $\Delta N_g$ ) (dotted line), change in ground-state energy ( $\Delta E_g$ ) (dashed line), and the real part of the field  $\epsilon$  (solid line) as a function of time. The strong excitation pulse increases the ground-state energy by a factor of 4 in approximately five vibrational periods. The method of solving the time-dependent Schrödinger equation is similar to the one used in Refs. [5, 7].

The scenario described in this paper can be viewed as an extension of photon locking in a two-level system. The concept of photon locking is most easily grasped geometrically through the Feynman-Vernon-Hellwarth (FVH) picture. A first pulse, which is resonant, leads to a polar precession of the polarization vector about the field vector. In the absence of a field the polarization vector would evolve in time azimuthally with a frequency characteristic of the energy separation of the two levels; this azimuthal evolution can be arrested, however, by instantaneously changing the phase of the field by  $\pm\pi/2$ . This orients the field vector parallel or antiparallel to the polarization vector, "locking" the polarization. In the two-level system the choice of sign in the  $\pi/2$  phase shift is immaterial, as may be seen geometrically. Moreover, in the two-level system, once the populations are locked then so are the energies.

The present work can be viewed as an extension of the concept of photon locking to a two-level system whose energies depend adiabatically on a parameter. Here, the electronic states play the role of the two-level system and the nuclear coordinate plays the role of the adiabatic parameter. As a result of the nuclear coordinate dependence the choice of the sign of the phase shift is now significant: Although both signs lead to zero electronic population transfer, the sign has a profound effect on the vibrational motion, with one sign leading to vibrational heating and one sign leading to cooling. The scenario can be called "lock and rock," since the molecule can be rocked vibrationally while the locking pulse is on.

What are the most important features of the lock-and-rock pulse? Examining Fig. 2, the first feature that draws attention is that the pulse is divided into bursts of inten-

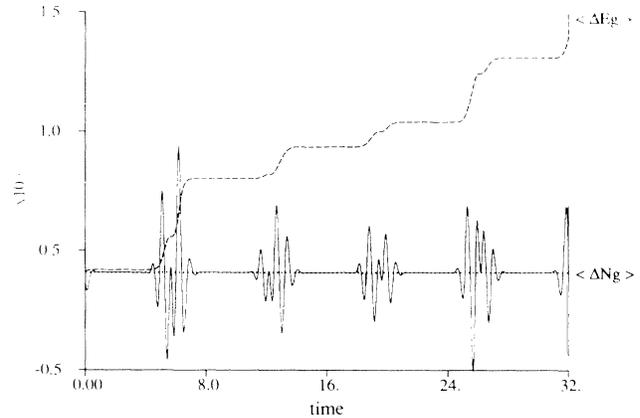


FIG. 3. The same as Fig. 2 for a weak pulse.

sity with dark periods between them. This is a consequence of the fact that only when the ground and excited surface wave functions overlap then  $\langle\psi_g|\hat{\mu}|\psi_e\rangle \neq 0$ , and manipulations can take place. The instantaneous dipole is modulated mainly by the vibrational frequency of the excited surface as the wave packet moves periodically in and out of the Frank-Condon region. This behavior is similar to the modulation of the population transfer found in the work of Sherer *et al.* [6] in the  $I_2$  system and therefore is not peculiar to the locking pulse. Examination of the power spectrum of the pulse in Fig. 2 shows a very broad frequency distribution from which the fundamental frequency of transition is missing. Moreover all the odd harmonics of the fundamental transition are also missing.

The main carrier frequency found is twice the fundamental frequency. In order to gain more insight into the character of the anti-RWA pulse a more gentle excitation was tried. Figure 3 shows the resulting pulse shape in which a series of similar looking subpulses can be identified. This series of pulses can share the image suggested by Nelson of a child gaining amplitude on a swing each time he reaches a turning point [1]. But the pulse sequence designed by Nelson lacks the phase matching property required by the nondemolition condition [4]. Figure 4 shows the power spectrum of the pulse which has much lower frequency components than the pulse of Fig. 2. Again as before, the fundamental frequency is missing. Distributed around the missing point of the spectrum, an almost symmetric progression of lines can be seen where the first peaks are shifted by half the vibrational frequency. They are followed by peaks shifted by the full vibrational frequency. The splitting of the peaks is due to the difference in frequency between the ground and excited surfaces. The power spectrum shows a striking resemblance to the spectrum of Fig. 8b in Ref. [6].

The phase matching conditions of Eq. (8) mean also that the polarization of the pulse has to be modulated in time. To check if the modulation of the polarization is

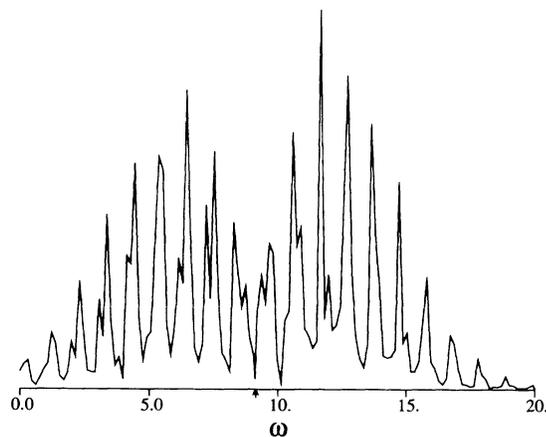


FIG. 4. The power spectrum of the pulse of Fig. 3. The arrow indicates the frequency of the vertical transition.

essential the original pulse was replaced with a linearly polarized pulse. Although the perfect null-population transfer conditions are not fulfilled, the deviations were found to be small and oscillating around the mean value while the vibrational energy increased as before. The amplitude of the oscillations decreased when the ratio between the electronic transition frequency and the vibrational frequency increased.

Considering the possibilities of experimental realization of the scenario developed here, the experiment might have been done in the  $X$  and  $B$  bands of the  $I_2$  system with the phase locked sequence of pulses used in Ref. [6]. The scenario presented here can also be realized by a modification of the experimental setup used by Nelson and co-workers [1, 2, 4]. By incorporating a mask [8] with phase as well as amplitude control the objective of excitation in the null-population transfer condition can be obtained.

A related Raman process with the objective of population transfer which shares the strategy of minimizing the population on an excited energy level has been demonstrated [9]. The scheme could also be used for vibrational excitation on the ground surface by tuning the pump pulse to a transition from the ground vibrational eigenstate to a specific excited vibrational eigenstate and tuning the probe pulse to a transition from the excited-surface vibrational state to a ground-surface excited vibrational state. Damage control is obtained by allowing the probe pulse to precede the pump. This scheme is the opposite extreme to the method described in this work. The scheme of Ref. [9] exploits the concept of adiabatic following and therefore has a cw character which depends on precise frequency tunability. The scheme presented in this work is impulsive on the time scale of the vibrational motion, and depends on the control of phase which is the conjugate variable to frequency.

The nondemolition strategy suggested here is closely related to work on the optimal control of pulses [7, 10]. A local optimization in time of the ground surface excitation with a constraint of total power input and zero population transfer leads to the pulse envelope  $C(t)$  of the form

$$C(t) = \sigma \text{Im}[\langle \psi_e | \hat{\mu} \hat{H}_g | \psi_g \rangle \langle \psi_g | \hat{\mu} | \psi_e \rangle], \quad (13)$$

where  $\sigma$  is a positive constant. For this choice the amount of power delivered by the field is proportional to the rate of ground-surface energy excitation. This pulse shape also has the advantage that the limelight is on only while action takes place on the stage. This choice will minimize the unwanted excitation to highly excited potential surfaces during the dark periods. Several variations of the choice of  $C(t)$  are possible which can be used to maximize the difference  $\bar{E}_g - \bar{E}_e$ . This could be useful in further reducing unwanted excited electronic state excitation. Finally, just by flipping the sign of  $C(t)$  vibrational cooling of the ground electronic state may be achieved. The possibility of cooling the ground surface will be presented separately [11].

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