

LETTERS

Manipulation of Molecular Motions Using Femtosecond Pulse Sequences

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Off-resonant coherent Raman experiments using a femtosecond pulse train have been recently used to selectively excite molecular vibrational modes. We discuss the relevance of this technique to laser-controlled chemistry.

The possible use of multiple laser pulses to attain laser control of molecular motions and reactivity constitutes a longstanding dream which drew considerable experimental and theoretical attention.¹ Most studies had focused on *resonant* excitation, which for short time scales allows the selective excitation of specific modes. Pump-probe spectroscopy is a beautiful example of a resonant technique which manipulates and detects elementary molecular motions.^{2,3}

In a recent report⁴ it was suggested that a femtosecond *off-resonant* coherent Raman experiment using shaped pulses showed the capacity of selective enhancement of vibrational energy in specific modes. Using a terahertz train of femtosecond pulses it was possible to selectively excite a given molecular vibration by adjusting the train interval. An analogy was further made with a child in a swing, which by appropriate timing of repetitive pushes could acquire a large-amplitude motion. In this Letter we discuss the limitations of this analogy for the reported experiment.

Consider a molecule with two electronic states and a single classical harmonic vibrational mode Q . We further assume that the electronic transition dipole matrix element μ depends on the

vibrational coordinate: $\mu = \mu_0(1 + \alpha Q + \dots)$, where α is the non-Condon coefficient which reflects the dependence of the transition dipole on the nuclear coordinate. An off-resonant excitation pulse with electric field envelope $\epsilon(t)$ exerts a time-dependent driving force:

$$f(t) = (2\alpha/\hbar)|\epsilon(t)|^2\mu_0^2[(\omega_{eg} - \Omega)^{-1} + (\omega_{eg} + \Omega)^{-1}] \quad (1)$$

Here Ω is the average pulse frequency and ω_{eg} is the electronic transition frequency. This expression holds when Ω is tuned very far from ω_{eg} so that the molecule is never excited electronically. When a classical oscillator with frequency ω and mass M is driven by this force, it acquires an excess energy

$$\langle E \rangle = \frac{1}{2M} \left| \int_{-\infty}^{\infty} dt \exp(i\omega t) f(t) \right|^2 \quad (2)$$

The oscillator then undergoes a coherent motion, i.e.

$$Q(t) = \left(\frac{2\langle E \rangle}{M\omega^2} \right)^{1/2} \sin(\omega t + \phi) \quad (3)$$

where ϕ is a phase which depends on the driving field, and the Raman signal will be $R(t) \propto |Q(t)|^2 \propto \langle E \rangle$. If we apply a train of N infinitely short pulses with interval T , and vary N by keeping the total pulse train area fixed, we have

$$\langle E(N) \rangle = \langle E(1) \rangle \frac{\sin^2(N\omega T/2)}{N^2 \sin^2(\omega T/2)} \quad (4)$$

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For a large N we can select a mode ω by adjusting the interval $T \approx 2\pi/\omega$. The use of a train of N weak pulses rather than a single strong pulse does not affect the energy of the selected mode with $\omega = 2\pi/T$ but it discriminates against other modes, thus achieving a selectivity in the macroscopic polarization. For the selected mode, the pulse train excites the oscillator in phase, which allows the amplitude to grow. For other modes, the train is out of phase, which results in the discrimination.

For a driven quantum oscillator, the mean energy and the Raman amplitude are given by the same expressions as for the classical oscillator (eqs 2 and 3, respectively). The analogy with a child in a swing is supported by eqs 1–4 and is perfectly valid if we consider oscillator amplitude (coherence) whether the oscillator is classical or quantum mechanical. The situation is very different, however, if we perform a measurement of oscillator energy. For a classical ensemble of oscillators they will all acquire the same energy (eq 2). An ensemble of quantum oscillators will have a very different statistics than the classical ensemble. To see that, we need to consider the wave function of the driven oscillator. Since the reported experiments were conducted on the 104-cm^{-1} mode of α -perylene at 5 K, we assume that the oscillator is initially in the ground vibronic state. The driving force prepares it in the coherent state:

$$|\psi(t)\rangle = e^{-|s|^2/2} \sum_{n=0}^{\infty} \frac{s^n}{(n!)^{1/2}} |n\rangle \quad (5)$$

Here, $s \equiv i(\langle E \rangle / \hbar\omega)^{1/2} \exp[-i(\omega t + \phi)]$ and $|n\rangle$ is the n th quantum level of the oscillator with energy $\hbar\omega(n + 1/2)$. The key quantity here is the parameter $|s|^2$, which is the ratio of the oscillator excess energy to its vibrational energy quantum.

Let us consider the typical value of $|s|^2$ for pulsed Raman scattering experiments in organic molecules. We take $\alpha = 0.1(M\omega/\hbar)^{1/2}$ and μ_0 is 1 D, using a $5\text{-}\mu\text{J}$ laser pulse with beam diameter of 0.1 mm, and detuning $\omega_{\text{eg}} - \Omega = 5000\text{ cm}^{-1}$. We then have $|s|^2 \approx 10^{-4}$ which with eq 3 corresponds to a vibrational amplitude of $\sim 10^{-2}\text{ \AA}$ for an oscillator with $\omega = 100\text{ cm}^{-1}$ and the mass of proton. For such a small value of $|s|^2$, only the $n = 0$ and the $n = 1$ states are populated, with probabilities $1 - |s|^2$ and $|s|^2$, respectively. The probability of exciting other states is of the order of $|s|^4$ or higher and may be neglected. This can be interpreted as follows: For $|s| \ll 1$, the excitation pulse train prepares the oscillator in a coherent superposition of states. The oscillator coordinate undergoes a harmonic motion with an amplitude s related to the coherence among the quantum states. However, if we measure the oscillator energy, we find that only

a fraction $|s|^2$ of the molecules are excited from $n = 0$ to $n = 1$. As long as $|s| \ll 1$ more molecules are excited to the $n = 1$ state as the total pulse area is increased, but the energy of each of the excited molecules does not increase at all! We conclude that the mode selectivity reported in off-resonant coherent Raman experiments using a femtosecond pulse train simply results from the weak excitation of a larger fraction of the molecules. The increased *macroscopic* polarization with increased pulse area is the result of exciting more molecules with the same (small) energy per excited molecule, rather than increasing the vibrational energy of individual molecules, as is necessary for laser-controlled chemistry.

For clarity we have considered here an ensemble of noninteracting molecules. Our analysis and conclusions are, however, valid also for optical phonons in a crystal, as studied in the reported experiments, since the dynamics of individual molecules and their statistics are identical in both cases as long as $|s| \ll 1$. Although the present analysis is for zero temperature, the basic conclusion holds for any temperature. If the oscillator is initially in the n th quantum state, to order $|s|^2$ it can only change to the $n \pm 1$ states. Again, as $|s|^2$ increases, more molecules change their states by a single quantum, but a large vibrational excitation of a single molecule is never attained as long as $|s|^2 \ll 1$.

In summary, coherent Raman experiments using femtosecond pulse shaping do indeed have a *filtering* capacity and they can create a large macroscopic polarization selectively in a given mode. For a classical ensemble of oscillators, all oscillators are equally excited. An increasing macroscopic polarization then necessarily implies that each oscillator acquires a higher energy. For quantum oscillators with excess energy much smaller than the vibrational quantum ($|s|^2 \ll 1$) the picture is very different. The increased macroscopic polarization is related to exciting more molecules by a single vibrational quantum. *Large amplitude of vibrational motion of individual molecules is not achieved in the experiment.* Only when $|s|^2 \gg 1$ will the classical picture hold.

Femtosecond pulse shaping is a very powerful development with numerous potential applications for selectivity and control of chemical dynamics. However, the reported off-resonant Raman measurements show only *macroscopic* selectivity of the total polarization rather than the *microscopic* selectivity required for laser-controlled chemistry.

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