Wave-packet squeezing by iterative pump-dump control in diatomic molecules

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Iterative vibrational wave packet squeezing by a sequence of femtosecond pulses is proposed. Analytic formulas are derived for the harmonic oscillator case, and the practical implementation of the scheme is tested on different electronic transitions in Rb_2.

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Squeezed quantum states are a subject of considerable attention, specially in light. From a fundamental point of view they represent an interesting confrontation to the uncertainty relations. In the molecular frame, increasing the spatial localization of a wave packet (or alternatively, of its velocity) has important consequences in time-dependent spectroscopy. For instance, the detection by femtosecond probing [1] and time-and-frequency resolved fluorescence [2,3] allows the inversion of potential energy data depending on the motion and width of the wave packet. Position and kinetic energy control can be used as well to better specify the desired component of a wave packet obtained after dissociation.

Borrowing ideas from quantum optics, the first schemes for molecular squeezing involved squeezing small vibrational populations in excited electronic states [4,5]. Alternatively, optimal control techniques were applied with excellent, albeit hard to generalize, results [6]. Additionally, work on adiabatic compression in light-induced potentials showed that a wave packet could be frozen and partially squeezed with very strong nonresonant pulses [7]. In all previous work the squeezing was achieved in excited (typically not very stable) states.

In this work we propose a general mechanism that allows maximal squeezing or stretching of the wave packet at the ground or the excited potential. We call it the iterative squeezing-stretching (ISS) scheme. The scheme is based on the properties of free motion of wave packets in harmonic or approximately harmonic potentials and just requires a sequence of ultrafast transform-limited pulses (of area π) which are precisely time delayed. A nonstationary Gaussian wave packet remains Gaussian as it moves in a harmonic potential, with the average position $\langle x(t)\rangle$ and momentum $\langle p(t)\rangle$ following the trajectory of a classical particle, while the width in position $\langle \Delta x(t)\rangle$ oscillates from wide to narrow and vice verse. The frequency of this oscillatory motion (or breathing) is two times the harmonic frequency ω_α, where α labels the electronic state.

In order to induce and increase the amplitude of the oscillatory breathing of the wave packet's width we need to use at least two electronic potentials, which must be approximately harmonic and with different harmonic frequencies. Consider for instance that initially the system is in the ground vibrational state of the fundamental electronic potential $V_1(x)$. If this wave function is promoted to the Franck-Condon region of an excited potential $V_2(x)$, with lower harmonic frequency, the promoted packet will oscillate in $V_2(x)$ and its width, which is initially narrower than the equilibrium one, will stretch. If we then dump it back to $V_1(x)$ when the width is maximal, it will again oscillate and now, since its initial width is wider than the equilibrium one, it will squeeze. This process can be iteratively repeated leading to increasing stretching of the Gaussian wave packet in $V_2(x)$ and squeezing in $V_1(x)$. Figure 1 sketches the idea behind the scheme.

The quantum dynamics of the coupled harmonic oscillators (HO) can be solved analytically, assuming δ pulses of area π that fully transfer the electronic population between the potentials at a negligible time compared to $1/\omega_\alpha$. Using the Gaussian ansatz for the packet's shape in each potential [8–10]

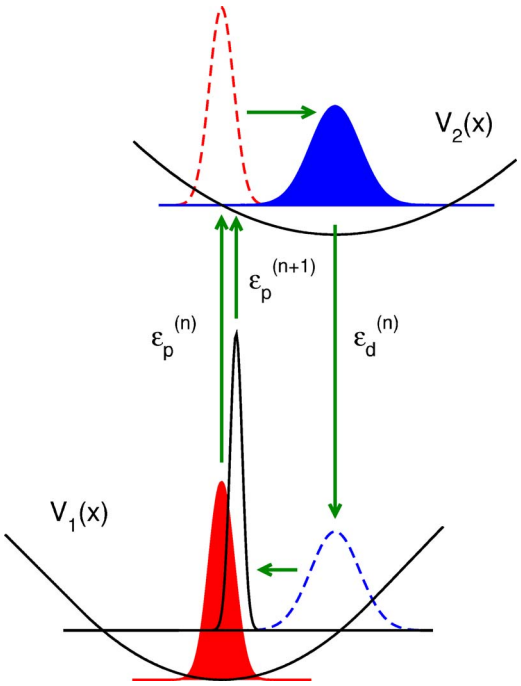

FIG. 1. (Color online) Sketch of the ISS scheme.

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$$\psi_\alpha(x,t) = \exp\Bigg[- \alpha_\alpha(t)[x - \langle x_\alpha(t)\rangle]^2 + \frac{i}{\hbar}\langle p_\alpha(t)\rangle[x - \langle x_\alpha(t)\rangle] + \frac{i}{\hbar}\Gamma_\alpha(t)\Bigg] \tag{1}$$

[where the complex part of $\Gamma_\alpha(t)$ contains the renormalization factor] one obtains for the average position $[\langle x(t)_\alpha\rangle]$, momentum $[\langle p(t)_\alpha\rangle]$ and width $\{\langle \Delta x_\alpha(t)\rangle = 1/\mathrm{Re}[\alpha_\alpha(t)]\}$ at each iteration n [11]

$$\langle x_\alpha^{(n)}(t)\rangle = [\langle x_\alpha^{(n)}(t_s^{(n)})\rangle - x_{\alpha,0}]\cos[\omega_\alpha(t - t_s^{(n)})] + \frac{\langle p_\alpha^{(n)}(t_s^{(n)})\rangle}{m\omega_\alpha}\sin[\omega_\alpha(t - t_s^{(n)})] + x_{\alpha,0}, \tag{2}$$

$$\langle p_\alpha^{(n)}(t)\rangle = -m\omega_\alpha[\langle x_\alpha^{(n)}(t_s^{(n)})\rangle - x_{\alpha,0}]\sin[\omega_\alpha(t - t_s^{(n)})] + \langle p_\alpha^{(n)}(t_s^{(n)})\rangle\cos[\omega_\alpha(t - t_s^{(n)})], \tag{3}$$

$$\langle \Delta x_\alpha^{(n)}(t)\rangle = \left(\beta_\alpha^{(n)} + \left[\frac{1}{\beta_\alpha^{(n)}} - \beta_\alpha^{(n)}\right]\sin^2[\omega_\alpha(t - t_s^{(n)})]\right)^{1/2}\langle \Delta x_\alpha\rangle, \tag{4}$$

where

$$\beta_\alpha^{(n)} = \left(\frac{\langle \Delta x_\alpha^{(n)}(t_s^{(n)})\rangle}{\langle \Delta x_\alpha\rangle}\right)^2, \tag{5}$$

and $x_{\alpha,0}$ is the equilibrium configuration of $V_\alpha(x)$. In Eqs. (2)–(4) the sequence of pulses is decomposed into a series of pump followed by dump pulses, acting at times $t_s^{(n)}$, where s is "p" for the pump pulse and "d" for the dump pulse, and n labels the iteration number. When the pulses are time-delayed a quarter of the oscillator's period, $\tau_2 = t_d^{(n)} - t_p^{(n-1)} = \pi/2\omega_2$ and $\tau_1 = t_p^{(n)} - t_d^{(n)} = \pi/2\omega_1$, the free wave packet motion leads to maximal squeezing in $V_1(x)$ and stretching in $V_2(x)$, given by

$$\langle \Delta x_2^{(n)}\rangle_{max} = \gamma^n\langle \Delta x_1\rangle, \tag{6}$$

and

$$\langle \Delta x_1^{(n)}\rangle_{min} = \gamma^{-n}\langle \Delta x_1\rangle. \tag{7}$$

The physical origin of the squeezing comes from the harmonic frequency ratio between both potentials $\gamma = \omega_1/\omega_2$. Additionally, we need to couple this resource with the free motion in the different potentials, by using short pulses. The average position and momentum of the wave packet at maximal stretching and squeezing are: $\langle x_1^{(n)}\rangle_{min} = d\mathsf{R}_{n-1}/\gamma$, $\langle p_1^{(n)}\rangle_{min} = -m\omega_2 d\gamma\mathsf{Q}_{n-1}$, $\langle x_2^{(n)}\rangle_{max} = d\mathsf{Q}_{n-1}$, and $\langle p_2^{(n)}\rangle_{max} = m\omega_2 d\mathsf{R}_{n-1}$, where $\mathsf{Q}_n(\gamma)$ and $\mathsf{R}_n(\gamma)$ are the geometrical series $\mathsf{Q}_n(\gamma) = 1 - \gamma + \gamma^2 - \cdots + (-\gamma)^n$ and $\mathsf{R}_n(\gamma) = 1 - 1/\gamma + 1/\gamma^2 - \cdots + 1/(-\gamma)^n$. The critical parameters for the motion are the distance between the equilibrium configurations d, and the actual frequency of the potentials (or mass of the molecule). These parameters enter into the physical resources needed for the pulses to operate. For instance, in order to fully transfer the population between the electronic states, the bandwidth of the transform-limited pulses must be approximately given by the electronic absorption spectra, which for the $V_2 \to V_1$ transition are roughly given by the potential energy uncertainty of the promoted wave packets in the Franck-Condon regions [11]. While the equilibrium configurations of the electronic states $V_2(x)$ and $V_1(x)$ are separated by $d \geqslant \langle \Delta x^{(n)}\rangle_{max} = \gamma^n\langle \Delta x_1\rangle$, one obtains

$$\begin{aligned}\Delta\omega_p^{(n)}(\omega) &\sim |V_1(\langle x_2^{(n)}\rangle_{max} + \langle \Delta x_2^{(n)}\rangle_{max}) - V_1(\langle x_2^{(n)}\rangle_{max} - \langle \Delta x_2^{(n)}\rangle_{max})| \\ &= m\omega_1^2|\langle x_2^{(n)}\rangle_{max}|\langle \Delta x_2^{(n)}\rangle_{max}/\hbar \\ &= m\omega_1^2\gamma^n|\mathsf{Q}_{n-1}d|\langle \Delta x_1\rangle/\hbar.\end{aligned} \tag{8}$$

For $d \leqslant \gamma^n\langle \Delta x_1\rangle$ a better approximation is given by

$$\begin{aligned}\Delta\omega_p^{(n)}(\omega) &\sim V_1(\langle x_2^{(n)}\rangle_{max} \pm \langle \Delta x_2^{(n)}\rangle_{max}) - \omega_1/2 \\ &\approx \tfrac{1}{2}m\omega_1^2\langle \Delta x_2^{(n)}\rangle_{max}^2/\hbar = \tfrac{1}{4}\omega_1\gamma^{2n},\end{aligned} \tag{9}$$

where one typically neglects the zero point energy $\omega_1/2$. Therefore, for large n and a given desired final squeezing, one needs pulses with time widths given by ($\mathsf{Q}_n \to \gamma^n/1 + \gamma$, as $n \to \infty$)

$$\sigma_p^{(n)} \sim \frac{2(1+\gamma)}{\beta\omega_1}\frac{\langle \Delta x_1^{(n)}\rangle_{min}^2}{|d|\langle \Delta x_1\rangle}, \tag{10}$$

for large d, and

$$\sigma_p^{(n)} \sim \frac{4}{\beta\omega_1}\frac{\langle \Delta x_1^{(n)}\rangle_{min}^2}{\langle \Delta x_1\rangle^2}, \tag{11}$$

for small d. The parameter β relates the width of the pulse with the approximate pulse bandwidth, given a desired yield of wave packet transfer (e.g., greater than 99%). β can be estimated theoretically [12] but is typically found numerically. From Eqs. (10) and (11) one observes that the physical resources scale more rapidly than the squeezing. The quadratic dependence of the pulse widths on γ basically comes from the need of manipulating wave packets which change width as $\langle \Delta x_2^{(n)}\rangle_{max}/\langle \Delta x_1^{(n)}\rangle_{min} = \gamma^{2n}$ in each iteration. The need of shorter pulses is further stressed when d is large, since $|d| > \langle \Delta x_1\rangle$, and for light molecules, because of the dependence with ω_1^{-1}. Finally, since the photon transitions decouple the oscillatory motions of $\langle x(t)\rangle$ and $\langle \Delta x(t)\rangle$, the Franck-Condon windows change in time, and for a physical implementation of the scheme, one needs to adjust the carrier frequency of the pulses at each transition.

Two are the key problems to physically implement the ISS scheme: the need of very short pulses, and having to deal with the anharmonicity of the vibrational motion. In the harmonic oscillator approximation we can predict the maximal squeezing and stretching and estimate the optimal parameters of the pulses (time delays, time widths, and peak amplitudes) from the analytical results shown previously. When considering realistic potentials, one has to readjust the optimal parameters to take into account the anharmonicity. For instance, the periods of motion and the oscillatory breathing increase, but more importantly, the shape of the wave packet as it propagates freely on the potentials can be severely distorted, so that the maximal squeezing (stretching) can only be estimated numerically.

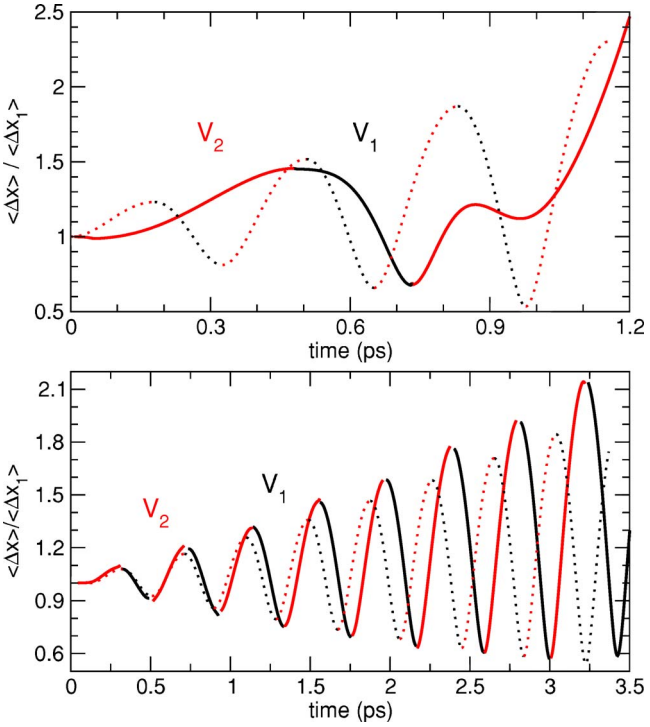

FIG. 2. (Color online) Wave packet breathing dynamics of the ISS in Rb_2 for the $X\ ^1\Sigma_g \rightarrow 1\ ^1\Pi_u$ transition (upper frame) and for the $1\ ^1\Sigma_u \rightarrow 3\ ^1\Pi_g$ transition (lower frame). Dotted lines represent the analytical results in the HO approximation. Gray line refers to the excited (V_2) potential and black line to the ground (V_1) potential.

We have applied the scheme to two different transitions in Rb_2: $X\ ^1\Sigma_g \rightarrow 1\ ^1\Pi_u$ and $1\ ^1\Sigma_u \rightarrow 3\ ^1\Pi_g$. Following the HO approximation, in the first one $\gamma=1.24$, so that according to Eq. (7) the wave packet can be squeezed to one half basically in 1 ps at the third iteration ($n=3$). The equilibrium configurations of the $X\ ^1\Sigma_g$ and $1\ ^1\Pi_u$ states are quite displaced of each other, $d=0.56$ a.u. (approximately 3.6 times the width of the initial wave function $\langle \Delta x_1 \rangle$), so that following Eq. (10) with $\beta=4$, the minimum width pulses needed to achieve the squeezing are of 7.3 fs. On the other hand, in the second transition $\gamma=1.08$, so that more time ($t \sim 3.6$ ps) and iterations ($n=9$) are needed to obtain 50% squeezing of the initial wave function in the HO limit. However, since the equilibrium configurations of $1\ ^1\Sigma_g$ and $3\ ^1\Pi_g$ are practically the same ($d=-0.02$ a.u.), following Eq. (11) (with $\beta=4$) the minimum pulse time width is just 30 fs.

Figure 2 shows the numerical results obtained by solving the time dependent Schrödinger equation (TDSE) for the two-coupled electronic potentials using *ab initio* potential energy curves [13]

$$i\frac{\partial}{\partial t}\begin{pmatrix}\psi_1(t)\\ \psi_2(t)\end{pmatrix} = \begin{pmatrix}\mathsf{T}+V_1(x) & -\mu\mathcal{E}(t)\\ -\mu\mathcal{E}(t) & \mathsf{T}+V_2(x)\end{pmatrix}\begin{pmatrix}\psi_1(t)\\ \psi_2(t)\end{pmatrix}, \quad (12)$$

where T is the kinetic energy operator, and $\mathcal{E}(t)$ is the sequence of Gaussian pulses. We assume the Condon limit (unit dipole moments) but we do not use the rotating wave approximation. The pulse time delays in the sequence are chosen so that the wave packet is at maximum squeezing or stretching in V_1 and V_2, respectively. The resonant carrier frequencies are obtained numerically by evaluating the average energy difference of the wave packet at both potentials. In certain cases the pulses are short enough to overcome the shift from resonance due to the displacement of the Franck-Condon windows. The pulse widths are approximately estimated to ensure more than 99% population transfer at each transition. Finally, the pulse amplitudes are chosen to guarantee a π pulse area. The results of the numerical simulation are compared with the analytical solution of the harmonic oscillator approximation.

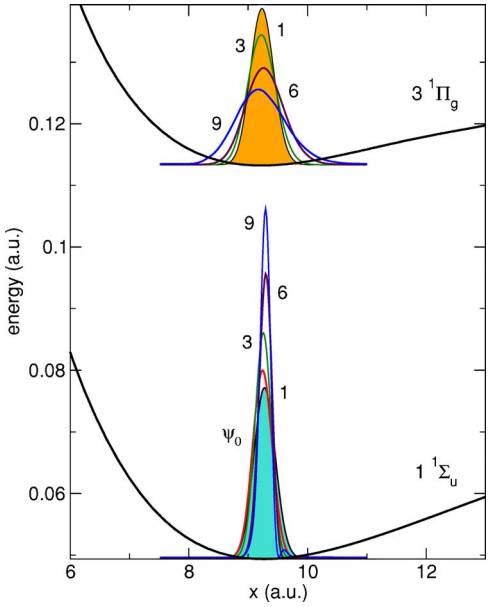

FIG. 3. (Color online) Maximally stretched and squeezed wave packets in the ISS scheme for the $1\ ^1\Sigma_u \rightarrow 3\ ^1\Pi_g$ transition in Rb_2. The numbers label the wave packet at each iteration. The increasing squeezing at consecutive iterations can be seen more clearly from the increasing peak density of the wave packet.

For the $1\ ^1\Sigma_u \rightarrow 3\ ^1\Pi_g$ case we fix the carrier frequency of all the pulses at 710 nm. The width and peak intensity up to $n=3$ is 50 fs and 75 GW/cm^2 respectively, while for the next iterations is 25 fs and 300 GW/cm^2 respectively. Since the displacement between potentials is negligible, the wave packet moves all the time in regions of small anharmonicity and the ISS scheme can work during many iterations, with small deviations from the HO limit. We obtain a maximum squeezing of 43% at $n=7$. In fact, as Fig. 3 shows, the scheme works for several more iterations, but the squeezed packet develops small nodes increasing the standard deviation (the width) quite beyond the value for a Gaussian shape of similar FWHM (full width at half maximum). If a smaller statistical weight is given to the far-off wings of the wave packet (restricting for instance the measure to within five units of the standard deviation around the average position), one can observe that the squeezing continues up to 48% at $n=9$.

In the $X\ ^1\Sigma_g \rightarrow 1\ ^1\Pi_u$ case, the carrier frequencies of the pulses are adjusted so that all transitions are approximately resonant, since the frequency shifts could only be compen-

sated by extremely short pulses. We numerically find for the first pump pulse a carrier frequency of approximately 670 nm and of 650 nm for the second pump, while both dump pulse carrier frequencies are approximately 700 nm. For $n=1$ the width of both pulses is 10 fs (implying 1.2 TW/cm^2 of peak intensity), and for $n=2$ it is 5 fs (7.9 TW/cm^2 of peak intensity). On the other hand, since the Franck-Condon windows for the pump and dump transitions are quite displaced, the kicked vibrational motion occurs in regions of high anharmonicity. Although more squeezing can be achieved at the first iteration compared to the HO model ($\sim$35% vs 19%, respectively), the scheme breaks down at the second iteration, where the packet's width increases during several periods. At this point the packet approaches the collapsed state [8] and the squeezing regime cannot be recovered at least until full revivals occur [14].

For the $1\,^1\Pi_u$ state, assuming a simple anharmonic potential (where the anharmonicity χ_e is obtained by fitting the potential to a Morse curve) the revival time is $T_{rev}=2\pi/\omega_1\chi_e\sim 220$ ps (300 ps for the X state). The collapsed state is a dispersed wave packet whose phase relations mimic an incoherent state [8]. Following Robinett's nomenclature, and assuming a $k=3$ potential [15], $T_{col}=T_{rev}/6\sqrt{\pi}\Delta n$, where Δn is the width of the packet measured in vibrational quanta, that is, the average number of states forming its linear combination. For the second iteration we numerically find $\Delta n \sim 5$ and $T_{col}\sim 4$ ps. Therefore, we should expect the ISS to work for more iterations before the wave packet collapses. In fact, in Fig. 4 we can observe that the failure of the ISS scheme starts when the phase of the wave packet departs from linearity, in disagreement with the Gaussian ansatz [see Eq. (1)]. The parabolic dependence of the phase at $n=2$ implies that the wave packet in the ground potential will no longer squeeze, but keep spreading. On the other hand, phase dispersion can be overcome by frequency chirping, at the expense of reducing the maximal stretch of the wave packet before dumping [16], and therefore the efficiency of the squeezing mechanism. Probably, some optimal balance could be achieved specific of the potential.

In this paper we have proposed a simple method to squeeze (or stretch) vibrational wave packets in the ground (or excited) electronic potential. We have only considered the effect of vibrations. The sequence of π pulses will only switch the population for the set of molecules that are oriented along the laser field. Since the pulses are ultrafast, the orientation of the molecules can be safely considered fixed during the laser action, but only a fraction of molecules will experience the optimal pulse parameters. Alternatively, one could find optimal parameters that squeeze a specifically polarized fraction of the sample. For randomly oriented molecules, the overall efficiency of the scheme will likely be small, particularly after large number of iterations. Possible ways to improve the efficiency would require applying schemes for molecular orientation that minimize the disturbance of the vibrational wave function prior to the vibrational squeezing [17], and the design of a strategy for maintaining the molecular orientation during the ISS procedure [18]. For heavy molecules like Rb_2 we believe that this should be possible, since the rotational period and the rotational dephasing time are much larger than the times required

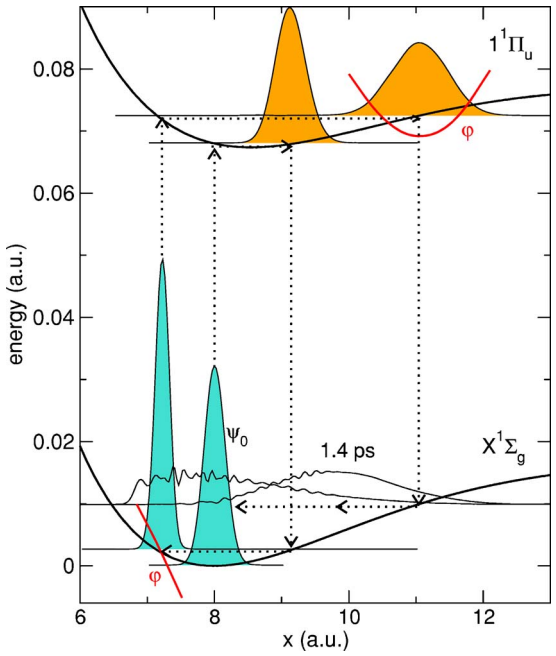

FIG. 4. (Color online) Maximally stretched and squeezed wave packets in the ISS scheme for the $X\,^1\Sigma_g \rightarrow 1\,^1\Pi_u$ transition in Rb_2. The arrows indicate the wave packet motion at the different iterations. After $n=2$ ($t=1.4$ ps) the dumped wave packet on the ground potential disperses. This is due to frequency dispersion. On the plot we also show the packet's phase for two cases. The range of the ordinate axis of the phase varies from $-\pi/2$ to $\pi/2$. Before the onset of dispersion, for instance in the ground wave packet at $n=1$, the phase is linear. However, the parabolic phase of the excited wave packet at $n=2$ implies that the wave packet can not be squeezed later during the time scale of the dynamics.

for squeezing the wave packet in the ISS scheme. Given a fixed (or laser) oriented molecular sample, or a fraction of it, for almost harmonic potentials the scheme is only limited by the pulse bandwidth available. The other physical limitation comes from the effects of anharmonicity on the dynamics. If the equilibrium configurations of the electronic transitions are quite separated, the free wave packet motion occurs in regions of high anharmonicity. We have shown that the squeezing regime can be stopped quite before the onset of the collapsed state. Another nonexplored effect is related to the coordinate dependence of the dipole moment, which can distort the wave packet during the fast vertical $V_2 \rightarrow V_1$ transition. This may induce further squeezing or stretching, depending on the dipole function, or accelerate the onset of the collapsed state. However, there is some freedom in the choice of the Franck-Condon windows [11], so that any detrimental effect could be partially controlled. Finally, we have shown physical systems where we believe that the scheme could be tested.

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