Creation of Intrinsic Localized Modes via Optical Control of Anharmonic Lattices

T. Rössler and J. B. Page

Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504

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The optical creation of intrinsic localized modes in perfect anharmonic lattices with realistic interatomic potentials is demonstrated theoretically, using an efficient optimal control scheme to determine experimentally feasible exciting fields. [S0031-9007(97)02405-8]

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Intrinsic localized modes (ILMs) are novel vibrational excitations in periodic lattices, characterized by displacement patterns which can be highly localized [1]. In contrast to localized impurity modes in harmonic defect crystals, ILMs in perfect lattices result from anharmonicity in the interparticle potentials. Recent studies have obtained ILMs for increasingly realistic models [2,3]. However, beyond a theoretical demonstration that driven ILMs can exist as a steady-state response to an applied spatially homogeneous sinusoidal driving force [4], the key experimental question of how ILMs might be created externally has not been addressed, and ILMs have not yet been verified in the laboratory. Here we describe an avenue for the experimental creation of ILMs. It is shown how ILMs can be produced in a one-dimensional model lattice with realistic potentials by means of laser pulses whose time dependence is designed by an efficient optimal control scheme. Aspects of the experimental feasibility of the approach are discussed.

Owing to their high power densities, lasers are appropriate sources for exciting large-amplitude well-localized ILMs. Recent developments in experimental laser pulse shaping techniques [5,6] provide considerable flexibility in the time dependence of the applied force. Indeed, the use of tailored fields for vibrational excitation has attracted much recent interest, mainly in the context of optical control of dissociation and reactions in molecular chemistry [7], but also for the selective excitation of optical phonons in time-domain spectroscopy [8]. We will focus on two methods for transient optical creation of ILMs: impulsive stimulated Raman scattering (ISRS) excitation [9] by a sequence of femtosecond pulses at THz repetition rates from a laser operating at near visible frequencies, and infrared (IR) excitation by a picosecond far-IR laser pulse. For both mechanisms, the system's dynamical response can be described classically, provided the underlying laser frequency for the ISRS case is well off resonance with vibrational and electronic transitions.

For longitudinal motion in a driven 1D system, the Hamiltonian is

$$H = \sum_n \Big[\frac{p_n^2}{2m_n} + \sum_l V_{n,n-l}(r_n - r_{n-l}) - F_n^{\rm ext}(t) r_n \Big],$$

where particle n has mass m_n, position r_n, and momentum p_n, and interacts with particle $n - l$ via a potential $V_{n,n-l}$. The external force is $F_n^{\rm ext}(t) = \frac{1}{2}\mathcal{P}_n \mathcal{E}^2(t)$ and $F_n^{\rm ext}(t) = q_n \mathcal{E}(t)$ for ISRS and IR excitation, respectively. Here $\mathcal{E}(t)$ is the longitudinally polarized electric field, $\mathcal{P}_n \equiv (\partial \mathcal{P}/\partial r_n)_0$ is the electronic polarizability derivative evaluated at the equilibrium configuration, and q_n is the effective charge.

Our model is a 1D diatomic lattice with masses m and M ($>m$) and nearest-neighbor equilibrium separations R_0^{mM} and R_0^{Mm} ($\neq R_0^{mM}$), where 1st and 2nd neighbors interact via Born-Mayer plus Coulomb and pure Coulomb potentials, respectively. With $\mathcal{P}_n = (-1)^n \mathcal{P}$ and $q_n = (-1)^n q$, the external forces for both excitation methods have equal magnitudes and alternating signs: $\mathcal{F}_n^{\rm ext}(t) = (-1)^n \mathcal{F}(t)$. As a result, the anharmonic version of the optical zone center ($k = 0$) mode (OZCM) is both Raman and IR active. Within our interaction model, an ILM existence criterion based on an interplay between harmonic and anharmonic extended mode properties [10] is satisfied for the OZCM if the curvature of the harmonic optic mode dispersion curve is positive at $k = 0$. The measured transverse phonon branches of ZnS along the (111) direction exhibit this behavior, so we choose potential parameters which approximately match those curves. In the resulting model, the maximum of the phonon gap occurs at the harmonic OZCM frequency ω_0, and ILMs exist with frequencies in the gap. With decreasing amplitude, the ILM displacement patterns spatially broaden, eventually becoming that of the harmonic OZCM. Using a rotating wave approximation (RWA) for the particles' time dependence [1], but generalized to include static and second-harmonic contributions as well as oscillation at the mode's fundamental frequency, we obtain predictions for the undriven ILM and anharmonic OZCM frequencies and displacement patterns over a wide range of amplitudes, together with the OZCM dynamical stability properties. The RWA predictions are verified by direct molecular dynamics (MD) simulations [11].

Designing the time dependence of an external force to steer a dynamical system towards a desired target state is a fundamental problem in engineering. Optimal control theory [12] provides a rigorous mathematical foundation based on the variational minimization of a positive

objective functional. In the realm of atomic dynamics, this approach has recently been successful in the design of external electric fields for selective bond excitation in models of small harmonic lattices [13] and small anharmonic molecules [14]. We apply a similar scheme to the creation of ILMs. The objective functional is a weighted sum of (a) the mean square deviations of the particle positions and momenta from those of a desired target state at a specified final time t_f, and (b) the integral $\int_0^{t_f} dt|\mathcal{F}(t)|^2$. The system's equations of motion are included via time-dependent Lagrange multipliers (see Ref. [13] for details). Optimization can be done for an external force $\mathcal{F}(t)$ whose time dependence is arbitrary or has a prescribed analytic form [13]. In view of the important aspect of experimental feasibility, we discuss the latter approach. For ISRS excitation, the laser frequency is neglected, and we constrain $\mathcal{F}(t)$ to be a sequence of Gaussian pulses whose common width and individual heights and positions are varied. For IR excitation, $\mathcal{F}(t)$ is taken to have a linearly chirped IR frequency under a single Gaussian envelope. Variation of the objective functional with respect to the force parameters leads to nonlinear differential equations describing the coupled time evolution of the particles' driven motion and the Lagrange multipliers, subject to boundary conditions at $t = 0$ and $t = t_f$, respectively. The equations are solved by adapting the 5th-order Gear predictor-corrector MD method [11], within an iterative minimization scheme based on a conjugate gradient technique [15].

Before discussing the creation of ILMs in an infinite lattice, we demonstrate the power of the optimal control scheme by showing results for ISRS excitation of an ILM in a 22-particle system with free ends. At $t = 0$ the particles are at rest at their equilibrium positions. The system is then driven by a sequence of 49 Gaussian pulses over a control interval $[0, t_f = 50T_0]$, where $T_0 \equiv 2\pi/\omega_0$. For the target state at t_f we specify the RWA-predicted displacements of an ILM at frequency $\omega = 0.97\omega_0$. The control algorithm then minimizes the objective functional, yielding the pulse sequence given in the top panel of Fig. 1. The common pulse width is 18 fs (FWHM), and the amplitudes range from zero to 0.13 eV/Å. The bottom panel shows that the application of this rather complex sequence of pulses in MD [16] produces a surprisingly "simple" result, namely the creation of a highly localized excitation which persists almost unchanged well after the applied field ends.

Although the results of Fig. 1 appear promising, they are sensitive to the system's finite size—applying the same pulse sequence to a 42-particle system with free ends yields no localization. As seen in the figure, the system's ends play an essential role by causing vibrational energy to flow towards the center to set up the target ILM. Hence this "direct" ILM excitation method is not suited for crystals, although it may be relevant for the excitation of anharmonic "local modes" in molecules such as benzene (C_6H_6).

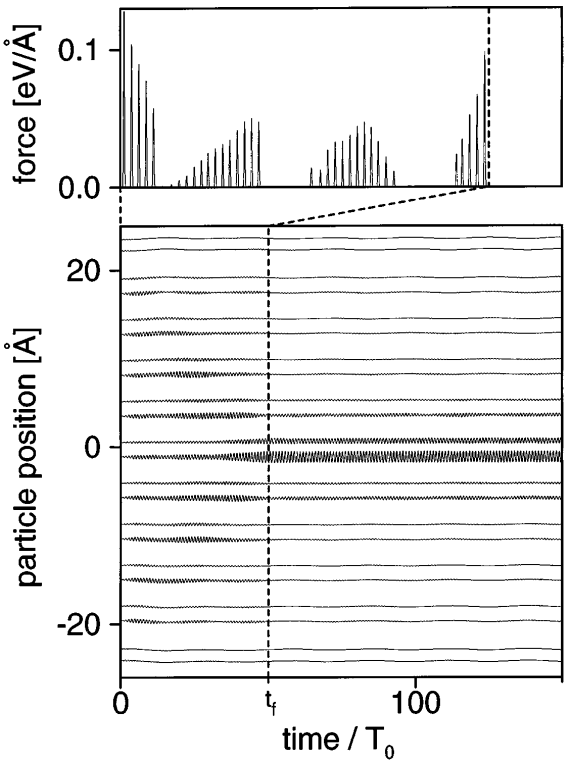

FIG. 1. Top panel: Sequence of Gaussian pulses $\mathcal{F}(t)$ for the direct creation of an ILM in a 22-particle lattice with free ends, via impulsive stimulated Raman scattering. Bottom panel: MD results of applying this sequence, with the particle displacements magnified by a factor 5. The applied field ends at t_f.

For the creation of ILMs in crystal lattices, we exploit previously established connections between ILMs and the dynamical instability of the extended lattice modes into which they spatially broaden with decreasing amplitude [17]. In particular, finite-time MD simulations show that infinitesimal perturbations cause unstable extended modes to decay into localized ILM-like vibrations. Because we have designed our model such that gap ILMs are related to the optically driven OZCM, we can create localized vibrations in the gap "indirectly" by optically driving the unstable OZCM. To illustrate, we again use ISRS excitation. For the optimal control algorithm target state, we specify an OZCM of frequency $\omega = 0.98\omega_0$, in a lattice with periodic boundary conditions (PBCs). The dynamics of the anharmonic OZCM are independent of the size of the PBC supercell, so that the resulting optimal fields apply to an infinite lattice. Starting from rest at $t = 0$, the system is driven with a sequence of 49 Gaussian pulses over a control interval of $50T_0$. In contrast to the pulse sequence given in Fig. 1 for the finite chain, the optimal sequence for OZCM excitation is found to consist of pulses having nearly equal amplitudes. Accordingly, we simplified the control algorithm so as to

vary the pulses' common width, common amplitude, and individual positions in the sequence. The top panel of Fig. 2 shows the resulting $\mathcal{F}(t)$, which consists of pulses of width 32 fs (FWHM) and amplitude 0.013 eV/Å. This is an order of magnitude less than the largest amplitude for the direct ILM excitation in the small lattice of Fig. 1, and the equal amplitudes render this sequence qualitatively simpler. However, the crucial (and somewhat hidden) aspect of the sequence of Fig. 2 is that the spacing between adjacent pulses varies through the sequence in such a way as to maintain resonant impulsive driving of the anharmonic OZCM, whose frequency changes as its amplitude increases over the control interval.

Applying this pulse sequence to a 40-particle PBC lattice in an MD simulation with the system initially at rest, we find that after the field ends at $t_f = 50T_0$ the excited OZCM keeps vibrating with constant amplitude for about $150T_0$ until the perturbation due to accumulated computational round-off error triggers the instability and the OZCM decays into several localized excitations. Instead of showing this behavior, which is computer dependent, the bottom panel of Fig. 2 displays an MD simulation for the same pulse sequence, but with random initial velocities corresponding to a lattice temperature of 5 K. The presence of this perturbation triggers the OZCM decay much sooner. Of course the details of the MD results depend on the specific set of initial velocities, but for 10 sets consistent with 5 K we find the same qualitative results as shown in Fig. 2: The ILM-like localized excitations resulting from the decay of the OZCM persist at fixed locations for several tens of vibrational periods and tend to move slowly through the lattice.

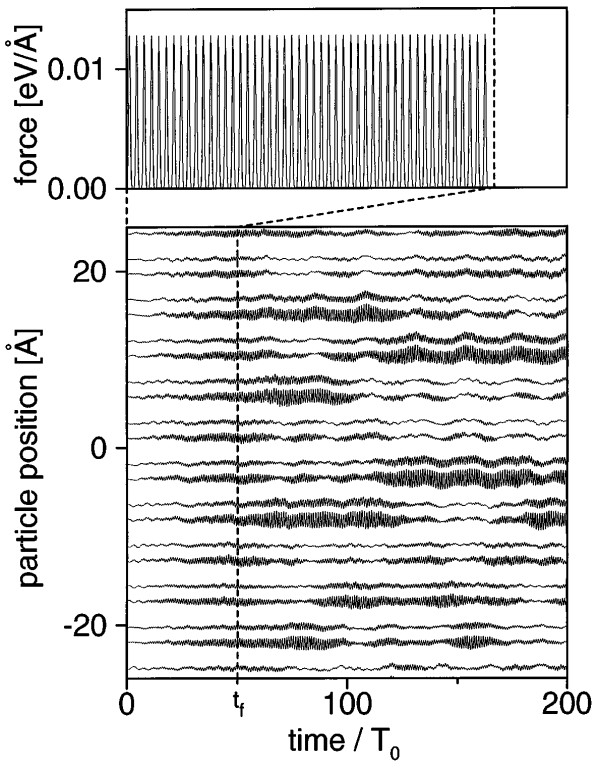

FIG. 2. Top panel: Sequence of Gaussian pulses $\mathcal{F}(t)$ for the indirect creation of ILMs in a 40-particle lattice with periodic boundary conditions, via impulsive stimulated Raman scattering. Bottom panel: Resulting MD simulation, for random initial velocities appropriate to a lattice temperature of 5 K. Displacements are magnified by a factor of 5, and only a portion of the lattice is shown.

We have also studied the indirect ILM creation via OZCM excitation using IR, assuming for $\mathcal{F}(t)$ a single Gaussian pulse of fixed width $33T_0$ (FWHM) and having a linearly chirped far-IR frequency over a control interval of $100T_0$. Varying the pulse position, amplitude, phase, initial frequency, and chirp rate, the control scheme yields an optimal force with pulse amplitude 0.008 eV/Å and chirp rate -2.0×10^{-7} fs^{-2}. Applying this pulse in MD simulations yields results very similar to those for the ISRS excitation of Fig. 2.

Having theoretically demonstrated the creation of ILMs using "designer" external forces, we consider the experimental feasibility of the corresponding fields. For excitation via ISRS, the required pulse widths and field magnitudes do not appear problematic, since visible or near-visible lasers producing ultrashort (18 fs) pulses of very high intensities ($\sim 10^{18}$ W/cm^2) are available [18,19]. The corresponding field magnitudes (~ 270 V/Å) are well above the maximum field strength 0.38 V/Å necessary for the example of Fig. 2, assuming a conservative value $\mathcal{P} = 2.5$ Å^2 for the polarizability derivative [20]. Thus the field magnitudes are likely to be limited only by the damage threshold of the sample. Pulse shaping for ultrashort (13 fs) laser pulses has been demonstrated [21], with complicated final wave forms ranging from 12-pulse sequences with an overall Gaussian envelope and equal spacing to 6-pulse sequences with equal amplitudes and variable spacing. Turning to IR excitation, we note that the maximum force amplitude in the preceding paragraph corresponds to a field strength 0.008 V/Å, assuming that $q = 1e$. Free-electron far-IR lasers produce picosecond pulses with intensities reported up to 4×10^7 W/cm^2 [22], corresponding to a field magnitude of 0.002 V/Å, and their frequency can be chirped at rates of -9×10^{-9} fs^{-2} [6]. These field magnitudes and chirp rates are within a factor of 5 and 20, respectively, of those used for the IR excitation of ILMs described in the preceding paragraph. Thus the fields necessary for the indirect excitation of ILMs via ISRS or IR may be feasible in the near future.

Another important experimental consideration is the robustness of the optimal fields. Although these fields have been obtained assuming that the system is initially at rest, we have seen that for the case of indirect ILM excitation the efficacy of these fields is actually enhanced by the presence of velocity perturbations due

to nonzero initial temperatures, since they trigger the OZCM instability at an earlier time. Considering the experimental limitations on the fidelity of shaped wave forms, we note from Ref. [21] that prespecified pulse amplitudes and widths were reproduced to within 10% and pulse positions to within 10 fs. Randomly perturbing our ISRS pulse parameters for the indirect ILM excitation within these margins reveals that, although the perturbed $\mathcal{F}(t)$ excites the OZCM to a slightly different amplitude in each of the ten cases considered, a decay into localized excitations always occurs.

While our 1D model incorporates some realistic features, such as standard interparticle potentials and the measured harmonic dispersion of ZnS, it is not a model of any real crystal. However, preliminary studies of 3D models of NaCl-structure crystals using standard central potentials between atoms out to 2nd neighbors show that the mapping of the harmonic modes for $\vec{k}$ along [111] onto an effective 1D model involving the collective motion of (111) planes also occurs for the anharmonic OZCM, for certain polarization directions. This suggests that a 1D model with effective anharmonic potentials between planes can yield an approximate representation of the actual motion in some 3D crystals. For such a case, one could again apply the ILM existence criterion of Ref. [10] and combine measured harmonic phonon dispersion data with model calculations for the anharmonic OZCM, to obtain candidate materials for indirect optical excitation of the OZCM's associated ILMs. If the anharmonic properties of the OZCM are qualitatively similar to those for the 1D model used here, some promising materials would be ZnS, ZnSe, copper halides, and nitrides and carbides of Zr and Ti.

In conclusion, our studies demonstrate that suitably tailored laser radiation offers a promising route for the laboratory creation of ILMs. The time dependence of the fields is determined by an efficient optimal control algorithm designed to produce wave forms consistent with the rapidly developing experimental capabilities in laser pulse shaping. Our simulations show that an advantageous means to excite ILMs in crystals is via the decay of an unstable anharmonic extended lattice mode, optically driven to a large amplitude. In addition, the results of Fig. 1 suggest that the approach has considerable potential for the direct optical excitation of local modes in molecules. Indeed, *ab initio* MD simulations for benzene readily yield local modes [23], and the addition of an optimal control scheme could allow the prediction of optical wave forms for their selective creation. Over the last several years, theoretical studies of anharmonic localized vibrational excitations in periodic lattices have revealed a rich variety of interesting phenomena. The emerging picture for the physics of large-amplitude anharmonic lattice dynamics is very different from that for harmonic or weakly anharmonic systems, but experimental support has been lacking. Our studies point to a potentially fruitful avenue for experimentally accessing this regime.

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