

Observation of Intrinsically Localized Modes in a Discrete Low-Dimensional Material

B. I. Swanson,* J. A. Brozik, S. P. Love, G. F. Strouse, and A. P. Shreve*

Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

A. R. Bishop and W.-Z. Wang

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

M. I. Salkola

NHMFL and Department of Physics, Florida State University, Tallahassee, Florida 32310

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We report the experimental observation of intrinsic dynamically localized vibrational states in crystals of the highly nonlinear halide-bridged mixed-valence transition metal complex $\{[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4\}$, where en = ethylenediamine. These states are identified by the distinctive structure and strong redshifts they impose upon the overtone resonance Raman spectra. Quantitative modeling of the observed redshifts is presented based on a nonadiabatic coupled electron-lattice model that self-consistently predicts strong nonlinearity and highly localized multi-quanta bound states. [S0031-9007(99)08915-2]

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Localization of vibrational energy within an extended lattice can impact any condensed matter process that involves high energy densities or transport of energy. Potential examples include deformation, crack propagation, shock phenomena and energy transduction. In this context, solitary nonlinear excitations in low-dimensional solids have been extensively discussed for decades [1–3]. For example, intrinsic localization of vibrational energy to form solitonlike excitations, resulting from anharmonic coupling in a periodic lattice, was proposed by Davydov [2]. More recently, intrinsically localized vibrational modes (ILMs) in lattices have been postulated to occur when both nonlinearity and discreteness are present with appropriate strengths [4]. Despite such intense interest, however, ILMs have largely remained a theoretical construct and unambiguous experimental evidence for their existence has been elusive, although some previous experimental work in acetanilide and its derivatives has been interpreted as being consistent with their presence [5]. The newly recognized importance of both nonlinearity [4,6] and lattice discreteness [7] for the existence and stability of ILMs provides insight into which systems should be probed for their observation *and* what experimental techniques may be useful. We report here ILM (multiphonon bound state) observation in a quasi-one-dimensional (quasi-1D) charge-density wave (CDW) system, the halide-bridged transition metal complex $\{[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4\}$ (en = ethylenediamine), subsequently denoted as PtCl. This highly discrete crystalline material has large nonlinearity provided by very strong coupling between lattice and electronic motions, and with this source of nonlinearity, resonance Raman spectroscopy is indicated as an ideal experimental technique to excite highly energetic vibrational motions. We emphasize that this material offers the opportunity to (a)

distinguish dynamical, intrinsic, localization from familiar disorder-induced localization (present even in linear materials), and (b) self-consistently model the source of the nonlinearity instead of postulating it phenomenologically.

Halogen-bridged transition metal compounds (MX solids) have been studied extensively as model low-dimensional electronic materials where the ground states can be systematically tuned (with chemistry, doping, pressure, and temperature) among different broken symmetry states [8–10]. PtCl (see Fig. 1) is a very strong CDW example with an intervalence charge transfer (IVCT) band edge near 500 nm (≈ 2.5 eV). The material is a well-formed crystal with a homogeneous lattice consisting of quasi-1D chains of chloride-bridged $\text{Pt}(\text{en})_2$ units, with each unit having two associated ClO_4^- counterions [11]. The CDW ground state consists of alternating nominal Pt^{+2} and Pt^{+4} sites with a corresponding distortion of the chloride ions toward the Pt^{+4} site. Resonance Raman (RR) has been used as a probe of both ground and photoexcited states [8,12,13], and RR spectra obtained with excitation into the IVCT band show the fundamental Raman active symmetric Cl-Pt-Cl stretch and a progression of many overtones. At low temperatures, the fundamental exhibits fine structure with up to six discrete, well-resolved modes [13]. Analysis indicates this structure to reflect isotopically (i.e., disorder) induced localization for the component modes ranging from five to one oxidized PtCl_2 unit [13,14].

Here we focus on the evolution of the spectral structure in the overtones of the Raman active fundamental. Raman spectra were obtained using Ar^+ laser illumination at 514 nm of a single crystal of PtCl mounted in a closed-cycle helium cryostat at approximately 12 K. In the isotopically natural abundance material, by the second overtone, the fine structure has evolved to a three

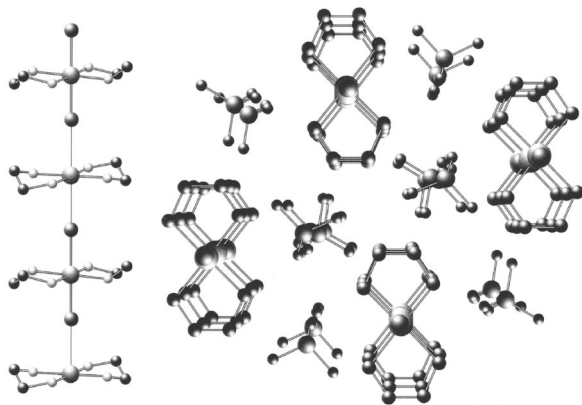


FIG. 1. Structure of $\{[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4\}$ (en = ethylenediamine; H atoms are omitted) [11]. One PtCl chain is shown on the left. Each Pt atom is coordinated by two ethylenediamine units in a near square planar geometry, while Cl^- ions connect the Pt sites along the chain. The packing arrangement of the 1D chains and their ClO_4^- counterions is shown on the right.

peak pattern with an approximate 9.6:6.2:1 ratio (data not shown), as expected for localization of vibrational energy onto a single oxidized PtCl_2 unit with statistical distribution of Cl isotopes [15]. This suggests that in the natural abundance material, by the second overtone the resonance Raman process creates states with localization of vibrational energy onto nearly a single PtCl_2 unit, indicating an *increase in localization from the already somewhat localized fundamental*. These observations strongly indicate the usefulness of examining high overtones in the isotopically pure materials, which are free of isotopic disorder, for evidence of *intrinsic* localization.

The fundamental and overtone spectra observed for the pure ^{35}Cl isotopic sample are shown in Fig. 2, while those for the pure ^{37}Cl spectra are shown in Fig. 3. In both cases, the data are conveniently presented in a stack plot in which each successive trace is offset along the horizontal axis by increasing multiples of the fundamental frequency (312 cm^{-1} in Fig. 2 and 304 cm^{-1} in Fig. 3). Such plots clearly expose the relation of features in the overtone spectrum to multiples of the fundamental peak. The lowest energy dominant feature in each trace (marked by vertical lines), demonstrates a strongly increasing anharmonic redshift. Further, at higher overtones, each of these dominant peaks recurs, offset by the fundamental frequency, in the next trace above. A simple interpretation is that the lowest-energy dominant peaks in the overtone spectra correspond to all quanta of vibrational energy localized in approximately one PtCl_2 unit, while the higher energy peak corresponds to having all quanta but one in a localized PtCl_2 unit combined with one quanta in the more extended fundamental. A related explanation has been previously used to describe structure observed in high overtone direct absorption spectra of isolated molecules in which local modes exist [16]. Other smaller features, for example, the weak symmetric Pt-N

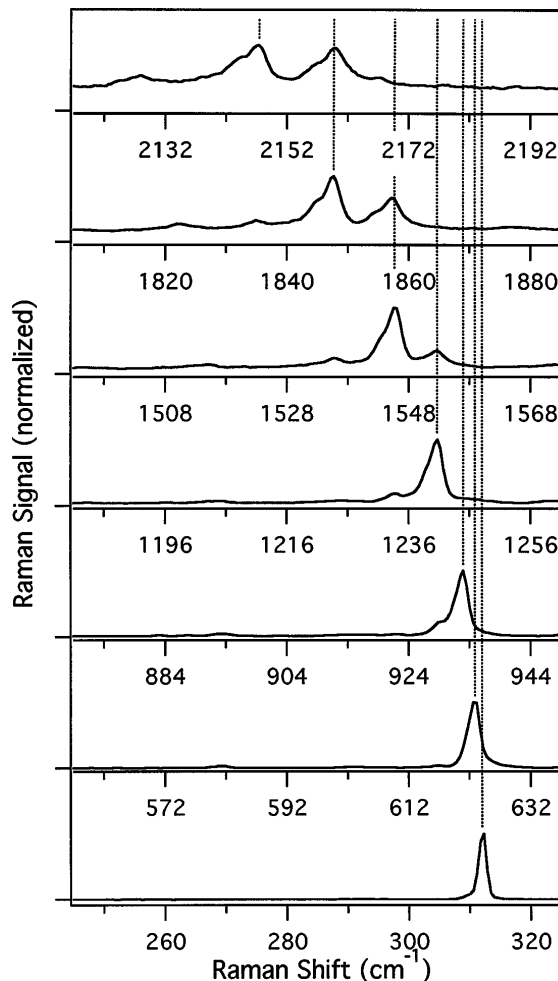


FIG. 2. Fundamental and overtone spectra of isotopically pure Pt^{35}Cl . Moving upward in each panel, each x axis is offset by the appropriate integral multiple of the 312 cm^{-1} fundamental frequency. All spectra have been scaled vertically to equal peak intensities.

stretch near 582 cm^{-1} or the small isotopic impurity feature near 312 cm^{-1} in Fig. 3 can also be assigned [17].

A self-consistent theoretical explanation of multi-quanta bound states must consider both nonlinearity (favoring binding) and quantum tunneling (disfavoring binding). Only if nonlinearity is sufficiently strong will stable bound states localized on a few lattice sites emerge. A characteristic feature of these states will be their large redshifts, resulting from the attractive interaction of Raman phonon quanta located at the same PtCl_2 unit. In addition, each overtone can potentially show peaks at higher energy than the most redshifted feature. These peaks, which arise from combination bands involving states with differing numbers of bound quanta, inherit their energies from combinations of the lower overtones, in a manner easily calculated perturbatively once the redshift associated with localization is accurately predicted.

Thus, in order to explain the unusual evolution of the overtone structure and the energies of the component bands, we have used a fully nonadiabatic model for

a small chain segment to calculate the strong redshift, employing exact diagonalization numerical techniques with large numbers of quanta of the phonon modes [7,18]. The model is based on a Peierls-Hubbard description (i.e., including electron-electron and electron-lattice coupling) employed successfully for many other MX properties [10], and on a realization that PtCl_2 units (analogous to small molecules) are the basic, weakly coupled, building blocks of the extended chain. A strong electron-lattice coupling is used, involving the Raman active mode that dynamically self-generates a highly nonlinear lattice potential relative to the coupling between adjacent units. The nonlinear potential provides an attractive interaction between Raman phonon quanta located at the same PtCl_2 unit. Consequently, the N th overtone has at least $N + 1$ components, each associated with a concomitant redshift. In agreement with the

experimental data, the leading edge of a given overtone is progressively redshifted and many of the remaining components are inherited from the lower overtones, with relative intensities corresponding to the resonance Raman excitation process. The interunit coupling, which is weak compared to the self-generated attractive interaction between phonon quanta at high energies, allows the bound multiphonon quanta to tunnel quantum mechanically to different PtCl_2 units as an entity. This weak tunneling process restores translational symmetry and can be treated perturbatively.

Because the dominant part of the phonon binding is short ranged, it can be reasonably determined within a model involving only a few sites. Specifically, for a simple four-site model, which is as large as can be reasonably handled within the fully nonadiabatic model, the Hamiltonian is

$$H = -t \sum_{i\sigma} (c_{i+1\sigma}^\dagger c_{i\sigma} + \text{H.c.}) + \sum_{i\sigma} \varepsilon_i n_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \hbar \bar{\omega}_R a_R^\dagger a_R + \hbar \bar{\omega}_{\text{IR}} a_{\text{IR}}^\dagger a_{\text{IR}} + \lambda_R (a_R + a_R^\dagger) (n_2 - n_4) + \lambda_{\text{IR}} (a_{\text{IR}} + a_{\text{IR}}^\dagger) (n_2 + n_4). \quad (1)$$

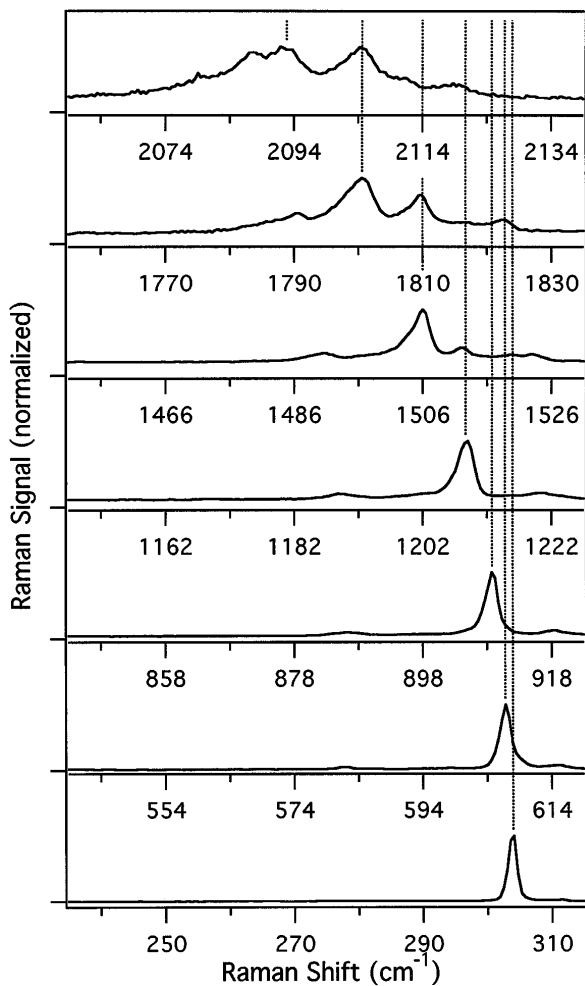


FIG. 3. Fundamental and overtone regions of the isotopically pure Pt^{37}Cl , presented as in Fig. 2, but with 304 cm^{-1} offsets.

In Eq. (1), $c_{i\sigma}$ is the fermion operator for a hole of spin σ at site i , $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, and a_R and a_{IR} are the boson operators for the symmetric (R) and antisymmetric (IR) phonon modes with bare frequencies $\bar{\omega}_R$ and $\bar{\omega}_{\text{IR}}$. The Pt atoms are denoted by the index $i = 2, 4$ and the Cl atoms by $i = 1, 3$. Their site energies can be parametrized by the charge-transfer gap, $\Delta = \varepsilon_1 - \varepsilon_2 (= \varepsilon_3 - \varepsilon_4)$. The electron-electron (Hubbard) interaction U_i is assumed to be smaller than Δ so that the ground state of the Hamiltonian (1) with two holes is a charge-transfer insulator, appropriate for PtCl. For the symmetric modes, the relevant dimensionless parameters quantifying the redshifts are λ_R/Δ and $\bar{\omega}_R/\Delta$, which control the degrees of nonlinearity and nonadiabaticity, respectively. In this model, the nonlinear lattice potential stabilizing ILMs is solely and self-consistently generated through coupling to electronic degrees of freedom. The calculated relative redshift, $r_n = (n\omega_R - \omega_R^{(n)})/\omega_R$, where $\omega_R^{(n)}$ is the observed frequency of the multiphonon state with n quanta in the symmetric phonon mode and $\omega_R = \omega_R^{(1)}$, is successfully compared to experimental data in Fig. 4. We note that calculation of the energies of the combination bands proceeds easily from the most redshifted feature (as noted above), but calculation of the resonance Raman intensities and spectral widths is more complicated and is not addressed here.

In summary, three observations in PtCl strongly suggest intrinsic dynamical localization of vibrational energy. *First*, the evolution of the fine structure observed for the normal isotopic sample indicates that at higher overtones localization occurs beyond that required to model the fundamental region [13,14]. However, to probe intrinsic

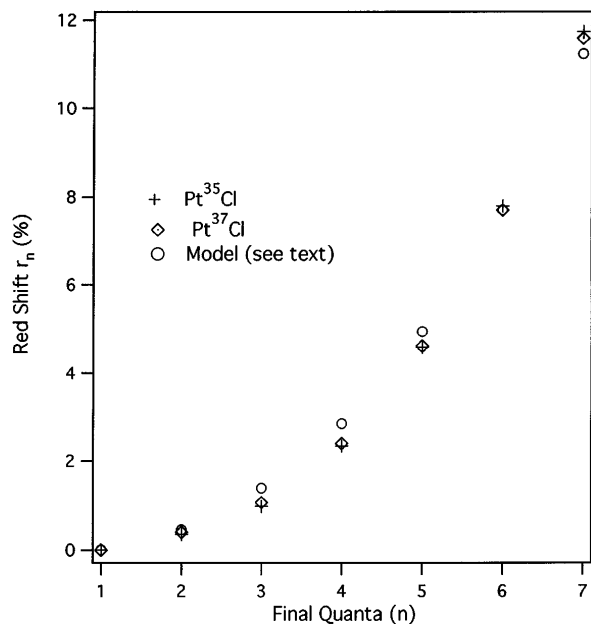


FIG. 4. Redshifts of the lowest-energy peaks (vertical lines in Figs. 2 and 3), normalized by the fundamental frequency, as a function of final quanta of vibrational energy, for the isotopically pure PtCl materials and the model described in the text. Model parameters, which yield vibrational and electronic energies in good agreement with observations for PtCl, were $t = 0.855$ eV, $\Delta/t = 3.125$, $U_i/t = 1.25$ for all i , $\lambda_R/t = 0.186$, $\bar{\omega}_R/t = 0.050$, and $\lambda_{IR}/t = 0$, and the model is solved using periodic boundary conditions.

localization, isotopically pure materials must be considered. *Second*, the observation and modeling of the anharmonicity in isotopically pure materials can be attributed to evolution from an extended (linear) optical phonon mode to a localized vibrational mode, due to high nonlinearity from strong electron-lattice coupling. At higher energies, the increased anharmonicity leads to increased localization because of the larger binding energies. *Third*, the appearance of structure in the pure isotopic samples for high vibrational overtones can be described in terms of different peaks corresponding to varying number of quanta of vibrational energy bound (localized) on approximately a single PtCl₂ unit, in combination with quanta of vibrational energy in more extended, less redshifted, lower order states. Thus, in the isotopically pure material, intrinsic nonlinearity results in the strong redshifts of the higher order scattering, and the corresponding dynamical spatial localization is further supported by analysis of the spectral structure.

These results suggest that MX solids, as a class, are ideal systems to probe and model ILMs and that resonance Raman is an excellent technique to study these multiphonon bound states on the electronic ground state surface. Ground state results for less strongly nonlinear MX cases (e.g., PtBr, PtI [8,9,11]), as well as localized excited state dynamics [18] and competitions with impurity localization, will be considered in future work.

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*Authors to whom correspondence should be addressed.

Electronic addresses: basil@lanl.gov and shreve@lanl.gov

- [1] See *Solitons*, edited by S. E. Trullinger, V. E. Zakharov, and V. Pokrovskii (North-Holland, Amsterdam, 1986).
- [2] A. S. Davydov, Phys. Scr. **20**, 387 (1979); A. S. Davydov, *Biology and Quantum Mechanics* (Pergamon, New York, 1982); A. C. Scott, Phys. Rev. A **26**, 578 (1982).
- [3] J. Ruvalds, Phys. Rev. B **3**, 3556 (1971).
- [4] A. S. Dolgov, Sov. Phys. Solid State **28**, 907 (1986); A. J. Sievers and S. Takeno, Phys. Rev. Lett. **61**, 970 (1988); J. B. Page, Phys. Rev. B **41**, 7835 (1990).
- [5] G. Careri *et al.*, Phys. Rev. B **30**, 4689 (1984); H. Kellouai *et al.*, J. Biol. Phys. **21**, 25 (1995); M. Barthes *et al.*, Physica (Amsterdam) **68D**, 45 (1993); *Davydov's Soliton Revisited: Self-Trapping of Vibrational Energy in Protein*, edited by P. L. Christiansen and A. C. Scott (Plenum Press, New York, 1990), Sec. IV.
- [6] D. Cai, A. R. Bishop, and N. Grønbech-Jensen, Phys. Rev. Lett. **72**, 591 (1994); R. Lai, S. A. Kisilev, and A. J. Sievers, Phys. Rev. B **54**, 12665 (1996).
- [7] S. Flach, K. Kladko, and R. S. MacKay, Phys. Rev. Lett. **78**, 1207 (1997); W.-Z. Wang *et al.*, Phys. Rev. Lett. **76**, 3598 (1996).
- [8] R. J. H. Clark, in *Advances in Infrared and Raman Spectroscopy*, edited by R. J. H. Clark and R. E. Hester (Wiley Heyden, New York, 1984), Vol. 11, p. 95, and references therein.
- [9] H. Okamoto *et al.*, Phys. Rev. Lett. **69**, 2248 (1992); A. Mishima and K. Nasu, Phys. Rev. B **39**, 5758 (1989); **39**, 5763 (1989); F. H. Long *et al.*, Phys. Rev. Lett. **71**, 762 (1993).
- [10] J. T. Gammel *et al.*, Phys. Rev. B **45**, 6408 (1992); S. M. Weber-Milbrodt *et al.*, Phys. Rev. B **45**, 6435 (1992).
- [11] S. C. Hockett *et al.*, Inorg. Chem. **32**, 2137 (1993).
- [12] M. Tanaka and S. Kurita, J. Phys. C **19**, 3019 (1986); R. J. Donohoe, C. D. Tait, and B. I. Swanson, Chem. Mater. **2**, 315 (1990).
- [13] S. P. Love *et al.*, Phys. Rev. B **46**, 813 (1992).
- [14] S. P. Love *et al.*, Phys. Rev. B **47**, 11107 (1993); J. F. Bardeau, A. Bulou, and B. I. Swanson, J. Raman Spectrosc. **26**, 1051 (1995).
- [15] Isotope abundance is 0.7553 for ³⁵Cl and 0.244 for ³⁷Cl, leading to probabilities of 0.570 for ³⁵Cl-Pt-³⁵Cl, 0.368 for the mixed isotope ³⁵Cl-Pt-³⁷Cl and reverse, and 0.0595 for ³⁷Cl-Pt-³⁷Cl, or expected peak area ratios of 9.6:6.2:1. The observed ratios are 8.2:5.7:1.
- [16] For reviews, see K. Lehmann, Annu. Rev. Phys. Chem. **45**, 241 (1994); F. F. Crim, Annu. Rev. Phys. Chem. **44**, 397 (1993); M. S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1 (1984); M. S. Child, Acc. Chem. Res. **18**, 45 (1985).
- [17] The ³⁵Cl isotopic impurity in Pt³⁷Cl is larger than in the reverse case due to the purity of available isotopes.
- [18] W.-Z. Wang *et al.*, Phys. Rev. Lett. **80**, 3284 (1998).