Propagating vibrational excitations in molecular chains

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We investigate quantum dynamics of vibrational excitations in one-dimensional (1D) molecular chain. Our model includes nearest neighbor interaction between identical molecular sites and one impurity atom placed in the middle ($n = 0$). We show that upon exciting the impurity site, its excess energy for relatively long for molecular scales time up to 100 ps is not redistributed uniformly among all other degrees of freedom. On the contrary an excitation propagates along the chain, reflected from the chain ends, and quantum interference of these waves yields to recurrence cycles and echo phenomena. For a critical cycle number k_c, echo components of the neighboring cycles start to overlap, and eventually for $k \gg k_c$ dynamics looks like chaotic one. The critical cycle number k_c depends on the coupling strength $0 \leq C \leq 1$ of the impurity site with its neighbors $n = \pm 1$. k_c achieves the maximum for $C^2 = 1/2$. Our results are in qualitative agreement with experimental data on vibrational excitations in various $(CH_2)_n$ molecular chains, and besides offer a way for loss-free energy transfer between separated in space reaction centers.

The challenging question how energy, released due to certain local chemical reaction propagates almost without dissipation to a distant location (where this energy can trigger a new chemical reaction, and so on) was posed first many years ago by Landau, Tamm, Davydov and some other prominent scientists of their caliber (see discussions and references in the monograph [1], and review paper [2]). However, the identification and understanding of underlying mechanisms responsible for the fast and almost loss-free energy transfer is still very limited. In recent experimental investigations [3–6] were found that excitation of the end group in a linear chain of 18–26 CH_2 fragments, leads to fast (about 2 ps per fragment) and almost ballistic propagation of that vibrational excitation. Reflection of this excitation from the end of the chain yields to re-excitation of the initially excited site (so-called Loschmidt echo phenomenon). Only after a number of these cycles the echo amplitude vanishes, signaling that the initial excitation energy is distributed over many sites of the chain. Another very relevant for biology example provides bacteriorhodopsin molecules, where transformation of the retinal molecule is the primary reaction in vision processes [7]. This chemical reaction is triggered by an optical transition in the reactive center embedded into molecular chain. It is worth to noting also femtosecond spectroscopy experiments in photochromic molecules [8–11]. By analyzing all these data one can extract characteristic time scale 10^{-13}–10^{-11} s, space scale 10–100 Å, and energy scale 0.2–0.3 eV for the excitation energy transfer along mole-

cular chains. Our aim in this work is to build the model (and to solve it) to describe the vibrational excitation propagation in molecular chains.

Our model hamiltonian describes the finite length chain of $2N + 1$ of coupled molecular sites. Each site can be only in the ground and in the first excited states. All higher order excited states are neglected, and the approximation is justified if the energy of these higher excited states is much larger than the inter-molecular coupling energy (vibrational spectrum band width).

$$H = E_0 Q_0^+ Q_0 +$$
$$+ \Omega_0 \sum_n Q_n^+ Q_n + \sum_\pm C(Q_0^+ Q_{\pm 1} + Q_0 Q_{\pm 1}^+) +$$
$$+ \sum_{n \neq 0,\, n \neq -1} J(Q_n^+ Q_{n-1} + Q_n Q_{n-1}^+), \qquad (1)$$

where Q_0^+, Q_0 are creation and annihilation operators of the impurity site excitation $n = 0$, Q_n^+, Q_n for $n \neq 0$ are similar operators for all other molecular sites along the chain, E_0 is the first excited vibrational state of the impurity, Ω_0 determines the chain molecular vibration band center, C, and J are matrix elements for corresponding nearest-neighbor couplings (all the same for a uniform chain).

The hamiltonian (1) is written in the site (space) representation. It can be transformed into the quantum state representation (similar to Wannier basis widely used in solid state physics), keeping separately one impurity $n = 0$ state and standing waves corresponding to two ($n > 0$ and $n < 0$) uniform half-chains. First

let us note that for uniform molecular chain of N sites (one of the two half-chains in our model), its vibrational spectrum looks as

$$E_k = \Omega_0 + 2J \cos \frac{k\pi}{(N+1)^{-1/2}} \ , \ k = 1, 2, ..., N. \quad (2)$$

Eq. (2) represents the unperturbed spectrum of the half-chains (will be termed as reservoir spectrum in what follows). This discrete spectrum (2) is not an equidistant. It becomes denser and denser upon approaching to the spectrum boundaries, however, near the band (2) center the spectrum is almost equidistant with characteristic interlevel spacing on the order of $\Delta_0 \simeq 2\pi J/(N+1)$. Therefore, the characteristic recurrence period T is proportional to the chain length $T \simeq 2(N+1)/J$. In the reservoir state representation the coupling matrix elements C_j are proportional to the amplitudes of the sites $n = \pm 1$ in the j-th state of the unperturbed half-chain. Namely $C_j = C\sqrt{N+1}\cos[\pi j/(N+1)]$. In what follows dynamics behavior is governed by dimensionless parameter $\Gamma \simeq C_j/\Delta_0$ (see below more details and accurate expression for the parameter Γ). The physical meaning of the parameter Γ is quite transparent one, it is a ratio of the transition probability (from the excited vibrational state of the impurity to a reservoir states in the vicinity of the band center). It is worth to remind that for $0 \leq C < 1$ the impurity level lies within the band (2) of the reservoir states.

In the chain of $2N+1$ sites ($n = -N, ..., 0, ..., N$), where the site $n = 0$ is an impurity, the finite difference equations for the site amplitudes ($\tilde{a}_0$, $\{\tilde{b}_n\}$) in the basis of the site wave functions, reads as

$$\begin{aligned}
C\tilde{b}_{-1} + C\tilde{b}_1 &= (\epsilon - E)\tilde{a}_0; \\
\tilde{b}_{-2} + C\tilde{a}_0 &= \epsilon\tilde{b}_1; \\
\tilde{b}_2 + C\tilde{a}_0 &= \epsilon\tilde{b}_1; \\
\tilde{b}_{n-1} + \tilde{b}_{n+1} &= \epsilon\tilde{b}_n, \text{ for } |n| \geq 2; \ \tilde{b}_{\pm(N+1)} = 0.
\end{aligned} \quad (3)$$

From the Eq. (3) we find secular determinant to determine the eigen-values ϵ. We utilize the dimensionless units with $\hbar = 1$, zero energy level chosen as E_0, and all energies (i.e., the impurity state E, and its coupling C to the neighboring sites ± 1) are measured in the units of J. The secular equation derived from the Eqs. (3) is reduced to two equations for antisymmetric and symmetric combinations of the site states

$$D_N = 0 \, ; \ (\epsilon + E)D_N - 2C^2 D_{N-1} = 0, \quad (4)$$

where D_N is $N \times N$ three-diagonal determinant independent of E and C, which is well-known in the Jacobi matrix theory [12–14]

$$D_N = \begin{vmatrix} \epsilon & 1 & 0 & ... & \\ 1 & \epsilon & 0 & 0 & ... \\ 0 & 0 & \epsilon & 1 & ... \\ ... & ... & ... & ... & ... \end{vmatrix} =$$

$$= \frac{\sin(N+1)\kappa}{\sin\kappa} \, ; \ \epsilon = 2\cos\kappa. \quad (5)$$

The roots of the first equation in (4) determine N antisymmetric states

$$\epsilon_k^0 = 2\sin\frac{k\pi}{N+1} \ , \ k = 1, ..., N. \quad (6)$$

The second equation in (4) determines $N + 1$ coupled reservoir-impurity symmetric states

$$F(\kappa) = [E + 2(1 - C^2)\cos\kappa]\sin[(N+1)\kappa] + \\ + 2C^2 \sin\kappa \cos[(N+1)\kappa] = 0. \quad (7)$$

For $C = 0$ the levels of the uncoupled impurity-reservoir (half-chain) are doubly degenerated. For $E = 0$ and odd N values, the impurity level coincides with the reservoir level $\epsilon_{(N+1)/2}^0$. For the sake of simplicity and to have more compact expressions only this case will be consider below. The amplitudes entering Eqs. (3)

$$\tilde{b}_n(\kappa) = A(\kappa)\cos(\kappa n), \quad (8)$$

$$\tilde{b}_{\pm 1}(\kappa) = \frac{\epsilon(\kappa) - E}{\epsilon(\kappa)[\epsilon(\kappa) - E] - 2C^2},$$

$$\tilde{a}_0(\kappa) = \frac{2C}{\epsilon(\kappa)[\epsilon(\kappa) - E] - 2C^2},$$

where the normalization coefficient $A(\kappa)$ is

$$A(\kappa) = \tfrac{1}{2} \times$$

$$\times \left\{ N + \frac{(\epsilon - E)^2 + 2C^2}{[\epsilon(\epsilon - E) - 2C^2]}\left(\frac{\epsilon^2}{2} - 1\right)^2 - \frac{\epsilon^2}{4} \right\}^{1/2} . \quad (9)$$

In our previous papers (see, e.g., [15–17]) we investigated quantum dynamics of the Zwanzig model [18] which would correspond in terms of molecular chain vibrational hamiltonian parameters (1) to the case $E_k = k$, (2), and $C_k = \text{const} = C$. Then the secular equation has a simple form

$$F_Z(\epsilon) = \epsilon - \Gamma_Z \cot(\pi\epsilon), \ \Gamma_Z = \pi C^2. \quad (10)$$

The secular equation (7), we have to solve to describe molecular chain dynamics, can be transformed to the form similar to F_Z (10). Let us consider only let us consider only odd N and $E = 0$. Then the secular equation (7) can be written in the Zwanzig-like form

$$F(\lambda) = f_2(\alpha\lambda)[\lambda - \Gamma f_1(\alpha\lambda)\cot(\pi\lambda)] = 0, \quad (11)$$

where we introduced new variable λ to replace κ by $\kappa = (\pi/2) - \alpha\lambda$, and "corrective" functions

$$f_1(x) = x \cot|x|; \ f_2(x) = \sin x / x. \tag{12}$$

Two parameters entering (11) are defined as

$$\alpha = \frac{\pi}{N+1}; \ \Gamma = \frac{C^2(N+1)}{\pi(1-C^2)}. \tag{13}$$

The roots λ_n of the Eqs. (11) determine the eigenvalues of our hamiltonian

$$\epsilon_n = 2\alpha\lambda_n f_2(\alpha\lambda_n). \tag{14}$$

The transformation performed above map the non-equidistant spectrum ϵ_n of the molecular chain into equidistant in terms of λ_n spectrum. The corrective functions f_2 and f_1 we introduced to describe the deviation of the single impurity molecular chain vibration spectrum from the Zwanzig-like equidistant (the function f_2), and to characterize deviations of the coupling matrix elements C_j from the Zwanzig constant values C (the function f_1). The transformed secular determinant has (besides diagonal terms) one non-zero line and one non-zero column. Applications and analysis of this kind of determinants in multi-level systems have been discussed long time ago by I.M. Lifshitz [19].

With the eigenvalues λ_n in hands we can find now the eigenfunctions. Indeed, for an arbitrary state its wave function $\Phi(t)$ can be represented in the unperturbed basis of the impurity state ϕ_0 uncoupled from the molecular chain states $\{\phi_n\}$

$$\Phi(t) = a_0(t)\phi_0 + \sum_k a_k(t)\phi_k, \tag{15}$$

where the time dependent amplitudes satisfy the Heisenberg dynamic equations

$$i\dot{a}_0 = Ea_0 + \sum_{k=-[N/2]}^{k=+[N/2]} c_k a_k; \ \ i\dot{a}_k = c_k a_0 + \epsilon_k^0 a_k, \tag{16}$$

where $[x]$ stands for an integer part of x, $\epsilon_k^0 \equiv E_k$ is unperturbed molecular vibration spectrum (2). Supplemented by the initial conditions

$$a_0(0) = 1, \ \ a_k(0) = 0 \tag{17}$$

the Eqs. (17) can be solved by some routine algebra and Laplace transformation. For the impurity site amplitude $a_0(t)$

$$a_0(t) = 2 \sum_{k=0}^{+[N/2]} U_k \cos[2t\sin(\alpha\lambda_k)], \tag{18}$$

where

$$U_k = \frac{f_1^2(\lambda_k)}{(1+\pi\Gamma)f_1^2(\lambda_k) + [\alpha^2 + (\pi/\Gamma)]\lambda_k^2}. \tag{19}$$

One comment to avoid confusion is in order here. We are using two representations for stationary Ψ and time dependent Φ wave functions. Site representation is defined by the amplitudes $\tilde{a}_0 \tilde{b}_n$ for Ψ and $a_0(t)$ and $b_n(t)$ for $\Phi(t)$. In the site representation (needed to visualize excitation dynamics), to find eigenstates and eigenfunctions we have to diagonalize Jacobi three-diagonal hamiltonian matrix. We need Wannier like representation (impurity $n = 0$ site coupled to standing waves of two uniform half-chains) to reduce the Jacobi problem to the Hamiltonian matrix in Zwanzig form (non-zero diagonal and one line and one column). Amplitudes in Wannier representation are defined similarly to the site representation by $\tilde{a}_0; \tilde{a}_k$ for Ψ and by $a_0(t)$ and $a_k(t)$ for $\Phi(t)$.

Eq. (18) (with (19)) is formally the exact solution of the Heisenberg equations (16) for $E = 0$. In the limit $\alpha^2\Gamma \ll 1$ the correcting functions $f_1 \simeq f_2 \simeq 1$ and Eq. (18) is reduced to the Zwanzig model solution [15, 17]. The trigonometric series (18) is very poorly converging one, however, the convergence can be considerably improved by noting (see e.g., [20]) that

$$\cos(2t\sin\kappa) = J_0(2t) + 2\sum_{m=1}^{+\infty} J_{2m}(2t)\cos(2m\kappa), \tag{20}$$

where J_{2m} is the corresponding even integer index Bessel functions. From known [21] asymptotic (for large arguments and indexes) of these Bessel functions entering (20) we conclude that the main contribution into $a_0(t)$ comes from the relatively narrow and periodically repeated intervals with characteristic widths w on the order of $w \propto \pi(1-C^2)/C^2$ (for $0 < C^2 \leq 1/2$). Then we can rewrite the series (18) as a sum over recurrence cycles in terms of much faster converging expansion over the Bessel functions

$$a_0(t) = \sum_s a_0^{(s)}(t - Ts), \tag{21}$$

where $a_0^{(s)}$ is the impurity state wave function amplitude for the cycle s. The explicit form of $a_0^{(s)}$ depends on C. For $0 \leq C^2 \leq 1/2$ the summation can be performed by Poisson formulas

$$a_0^{(s)}(\tau_s) = \frac{1}{\pi(1-C^2)} \times$$
$$\times \int_{-\infty}^{+\infty} d\lambda \frac{\exp(i\lambda\tau_s)}{\lambda^2 + \Gamma^2 f_1^2(\lambda)} \left[\frac{\lambda + i\Gamma f_1(\lambda)}{\lambda - i\Gamma f_1(\lambda)}\right]^s f_1(\lambda), \tag{22}$$

where we introduce the local time τ_s of the cycle s

$$\tau_s \equiv t f_2(\lambda) - 2s\pi. \tag{23}$$

In the weak coupling regime $0 < C^2 < 1/2$ the number of the Bessel functions contributing into the partial cycle amplitudes is sufficiently large, the oscillations are effectively suppressed. However upon increasing C (decreasing w) these oscillations increase. For $1/2 < C^2 < 1$ it is sufficient to keep only three Bessel functions in the Eqs. (18), (20) and we end up with

$$a_0^{(s)}(t) \simeq (-1)^s 2\{(1 - C^2)[J_{2s(N+1)-2}(2t) + $$
$$+ J_{2s(N+1)+2}(2t) + J_{2s(N+1)}(2t)\}. \tag{24}$$

We show in the Fig. 1 how dynamic regimes of the impurity site vibrational excitation depend on the coupling strength C. For $C^2 < 1/4$ similar to the Zwanzig model
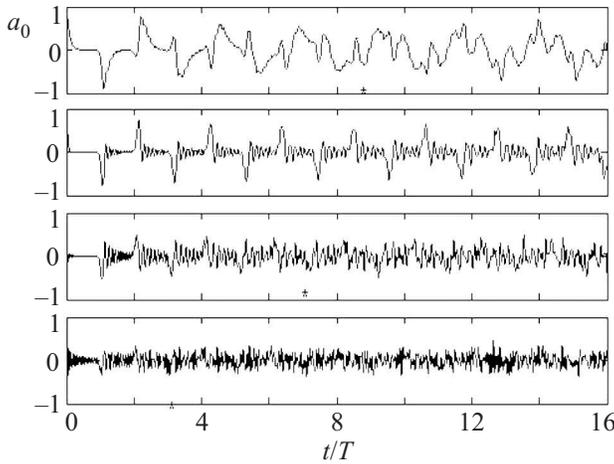

Fig. 1. Impurity site excitation dynamics $a_0(t)$; $N = 49$ and $C^2 = 0.1$, $C^2 = 0.25$, $C^2 = 0.5$, $C^2 = 0.95$ (from the top to the bottom). The critical cycle number s_c is indicated by a star (for $C^2 = 0.25$, $s_c = 23$). The s_c values are found by calculating the maxima of averaged over cycle even $2m$ moments $\langle |a_0^{(s)}(t - sT)|^{2m}\rangle$ and cross-correlation functions $\langle [a_0^{(s)}(t - Ts)]^2 \{a_0^{(s)}[t - (s-1)T]\}^2\rangle$

dynamics [15, 17], the number of the components of the Loschmidt echo and the width of the echo signal increase proportional to the cycle number. The main (most intensive) echo component displaces with the cycle number s towards to the larger time, and for the critical cycle number s_c it achieves the cycle end point. By a simple inspection of the Eq. (22) for the recurrence cycle amplitude, one can estimate the critical cycle number s_c

$$s_c \simeq (N + 1)\frac{C^2}{1 - C^2}; \quad C^2 < 1/4. \tag{25}$$

For $s > s_c$ the main echo component of the cycle s enters into the next recurrence cycle $s+1$, and for larger cycles

$s \gg s_c$, the echo signal includes many components with quasi-irregular extrema and zeros. The main (global) extremum is washed out. This indicates the crossover from the regular to stochastic-like dynamics [15, 16]. For $C^2 \geq 1/4$ (but as we mentioned already to have an impurity state within molecular chain vibration band (2), C^2 has to be < 1) dynamics is qualitatively different from that predicted by the Zwanzig model [15, 17]. Already for the small cycle numbers $s \geq 1$ impurity state population oscillates (instead of exponential decay within the Zwanzig model). Furthermore, the oscillation amplitudes increase upon s increases, whereas the intensity of the main echo component slightly decreases. It signals that dynamics remains regular one up to the limit when the oscillation amplitudes become comparable to the main echo component. Formally, because zeros of the Bessel functions of different indexes are rationally independent, mixing of partial recurrence cycle amplitudes yields to irregular damped oscillations in $a_0(t)$. For the case $1/4 \geq C^2 \leq 1/2$ above defined critical cycle number s_c achieves its maximum for $C^2 \simeq 1/2$ and for larger values of the coupling C, s_c decreases with C. Therefore we see that the thresholds for stochastic like behaviors decreases upon decreasing of the coupling strength in the window $0 \leq C^2 \leq 1/4$ and upon increasing C in the interval $1/2 \leq C^2 < 1$. These two dynamic regimes correspond to two distinct mechanisms of randomization induced by the mixing of echo components. Namely, cycle overlapping and mixing for $0 \leq C^2 \leq 1/4$, and enhancement of quasi-regular oscillation amplitudes for $1/2 \leq C^2 < 1$.

On the same footing of the same Heisenberg equations of motion (16) we can investigate the time evolution for the regular $n \neq 0$ chain sites

$$b_n(t) = \frac{1}{1 - C^2} \sum_{m=0}^{+\infty} J_{2m}(2t) S_{nm}, \tag{26}$$

$$S_{nm} = i\frac{C\Gamma}{\pi} \sum_{k=0}^{+[N/2]} U_k \cos(2m\alpha\lambda_k) \times$$
$$\times \frac{\sin[(N + 1 - n)\alpha\lambda_k]}{\sin[(N + 1)\alpha\lambda_k]}. \tag{27}$$

Note that as one can check by direct calculation the functions $S_{nm} \propto (1 - C^2)$ and, therefore, (26) does not diverge at $C^2 \to 1$. Moreover, the functions S_{nm} are not zero only in a relatively narrow and periodically repeating time intervals. Therefore $b_n(t)$ similar to $a_0(t)$ can be expanded over recurrence cycles

$$b_n(t) = \sum_s b_n^{(s)}(t - sT). \tag{28}$$

Where partial cycle amplitudes are expressed in terms of the Bessel functions with the indexes within the interval $s(N+1) + n(s+1)(N+1) - n$. Since the partial amplitudes depend on the combination $t - n$ this interval determines the arrival $t_{ns}^{(1)}$ and departure $t_{ns}^{(2)}$ times for the n-th site excitation in the cycle s

$$sT + n = t_{ns}^{(1)} \le t \le t_{ns}^{(2)} = (s+1)T + n, \qquad (29)$$

$t_{ns}^{(1)} - t_{ns}^{(2)}$ is the site n excitation duration time, and it decreases with the site number n. Thus we arrived at the conclusion that impurity excitation propagates along the chain with almost constant speed. We present in the Fig. 2 the results of numerical calculation of $|a_0(t)|^2$ and
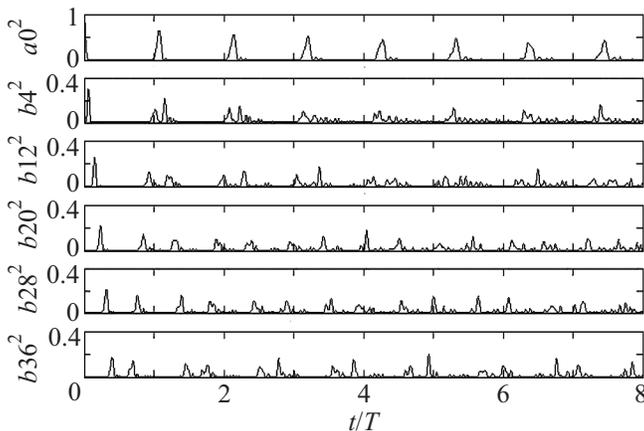

Fig. 2. Impurity site excitation propagation along the chain; $C^2 = 0.5$ and site numbers are indicated in the figures

$|b_n(t)|^2$ time evolution. For small coupling constant in the zero cycle $s = 0$ there are two separate echo signals at the times $t_{ns}^{(1)}$ and $t_{ns}^{(2)}$ when the impurity site excitation passes through the site n. The width of the signal spreads over several sites, and almost independent of the site number n. For larger C values the excitation propagates with the same (as for small C values) speed but the intensity of the signal is reduced considerably. Ultimately at even larger coupling strengths $C^2 \ge 1/2$ the width of the wave packet becomes on the order of the entire cycle duration. We show in the Fig. 3 that for $C^2 > 1/2$ excitation signal (wave packet) acquires considerable width, and therefore the wave propagation is not ballistic anymore. It is worth to noting that in this case $C^2 \ge 1/2$ even for $s < s_c$ the chain sites distant from the impurity site, namely, for $|n| \ge N/2$, are excited irregularly, whereas the impurity site $n = 0$ excitation dynamics remains regular. This means a sort of self-synchronization of forward and backward propagating after reflection from the chain ends waves when they are crossing the impurity site.
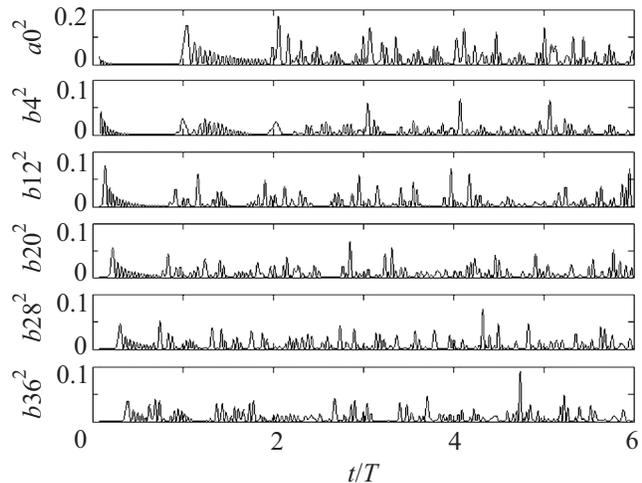

Fig. 3. The same as in the Fig. 2 for $C^2 = 0.75$

To summarize, in this work we found that in the uniform molecular chain coupled to a single impurity site, the impurity vibrational excitation can propagate almost ballistic for relatively long (on molecular scales) times and distances. The number of recurrence cycles with almost regular behavior achieves its maximal value at the intermediate coupling strength $C^2 \simeq 1/2$. For larger couplings excitation dynamics turns into irregular (chaotic-like) oscillations. We identified two mechanisms for this dynamic crossover: cycle overlapping and mixing for small couplings, and enhancement of irregular damped oscillations in the strong coupling limit. Of course the simplified theory presented in our paper is not able to describe all special aspects of ultra fast vibration excitation propagation in molecular chains. For example there are multiple site vibrational excitations (not only single mode). We did not consider conventional phonons. These effects can be included into our model (will be published elsewhere) and do not change qualitatively our main results. Understanding all its limitations, we nevertheless hope that our crude theory captures the essential elements of vibrational excitation propagation in molecular chains. Our approach can be applied to rationalize qualitative features of the experiments, and we anticipate that the effects described in our work are relevant for ultra-fast photo-chemical reactions. One more general message comes out of our work is that an experimental measurement reflects not only the dynamics of a physical system but also how excitations are made and how signals are received.

1. A. S. Davydov, *Solitons in molecular systems*, Kluwer Academic Publishers, Dordrecht, Holland, 1985.

2. A. C. Scott, Phys. Repts. **217**, 67 (1992).

3. A. S. Lagutchev, J. E. Patterson, W. Huang, and D. D. Dlott, J. Phys. Chem. B, **109**, 5033 (2005).

4. Z. Wang, J. A. Carter, A. S. Lagutchev et al., Science **317**, 787 (2007).

5. J. A. Carter, Z. Wang, and D. D. Dlott, Acc. Chem. Res. **42**, 1343 (2009).

6. F. Gai, K. C. Hasson, J. C. McDonald, and P. A. Anfinrud, Science **279**, 1886 (1998).

7. S. Hayashi, E. Tajkhorshid, and K. Shulten, Biophys. J. **85**, 1440 (2003).

8. M. Khalil, N. Demirdoven, and A. Tokmakoff, J. Chem. Phys. **121**, 362 (2004).

9. R. M. Hochstrasser, PNAS **104**, 14190 (2007).

10. I. V. Rubtsov, Acc. Chem. Res. **42**, 1385 (2007).

11. Z. Lin, P. Keiffer, and I. V. Rubtsov, J. Phys. Chem. **115**, 5347 (2011).

12. F. R. Gantmakher and M. G. Krein, *Oscillating matrices and kernels and small vibrations in mechanical Systems* (in Russian), Gostekh-Izdat, Moscow, 1950.

13. C. Domb, Proc. Royal Soc. A **276**, 418 (1963).

14. Z. Lin and B. Li, J. Phys. Soc. Japan **76**, 074003 (2008).

15. V. A. Benderskii, L. A. Falkovsky, and E. I. Kats, JETP Lett. **86**, 311 (2007).

16. V. A. Benderskii, L. N. Gak, and E. I. Kats, JETP, **108**, 159 (2009).

17. V. A. Benderskii and E. I. Kats, Eur. Phys. Journ. E **54**, 597 (2009).

18. R. Zwanzig, Lectures in Theor. Phys. **3**, 106 (1960).

19. I. M. Lifshitz, *Selected papers*, V. 1 (in Russian), Moscow, Nauka, 1987.

20. H. Bateman and A. Erdelyi, *Higher Transcendental Functions*, V. 2, McGraw Hill, N.Y., 1953.

21. F. W. J. Olver, *Asymptotics and Special Functions*, Academic Press, N.Y., 1974.