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Chemical Physics 341 (2007) 189–199

Chemical Physics

www.elsevier.com/locate/chemphys

Anomalous phase behavior and apparent anharmonicity of the pump–probe signal in a two-dimensional harmonic potential system

T. Taneichi [a,b,*], T. Kobayashi [a,b,c,d]

[a] ICORP, JST, Kawaguchi Center Building, 4-1-8, Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

[b] Department of Applied Physics and Chemistry, Institute of Laser Research, The University of Electro-Communications, 1-5-1, Chofugaoka, Chofu, Tokyo 182-8585, Japan

[c] Department of Electrophysics, Advanced Ultrafast Laser Center, National Chiao Tung University, 1001, Ta Hsueh Road, Hsinch 3005, Taiwan

[d] Institute of Laser Engineering, Osaka University, 2-6, Yamada-oka, Suita, Osaka 565-0871, Japan

Received 1 March 2007; accepted 13 July 2007

Available online 10 August 2007

Abstract

Discussion on wavelength dependent "anharmonic" effects in a pump–probe signal for a system of wavepacket on one- and two-dimensional harmonic potentials was given. The Fourier power spectrum of the signal, calculated for a model composed of a three-state electronic system coupled to a set of displaced harmonic oscillators, depends on the pulse duration. Condition under which the wavepacket motion in the harmonic potential substantially deviates from that of the classical point mass is derived. The Fourier power spectrum has enhanced components with frequencies of harmonics even in a system composed of ideally harmonic potentials. Utility of the Fourier analysis of the spectrum for clarification of the squeezed molecular vibrational state is discussed. Calculated oscillatory behavior in phase of a pump–probe signal, as a function of probe frequency, was discussed in terms of a two-dimensional effect on a pump–probe signal.

Keywords: Wavepacket; Molecular vibration; Phonon; Pump–probe spectroscopy; Phase; Fourier power spectrum; Transient spectrum; Molecular dynamics; Vibrational modes; Ultra-fast phenomena

1. Introduction

Pump–probe spectroscopy using a femtosecond laser is a powerful tool for detecting ultra-fast phenomena such as molecular vibrations [1–11], ultra-fast chemical reactions [1–3,12,13], and exciton dynamics [14–16]. The observed results often have been interpreted in terms of a wavepacket picture, by which one can set theoretical bases on the experimental results and predict novel phenomena [17–22]. A classical vibrational motion is obtained as far as the wavepacket is well localized in a vibrational coordinate and vibrational coherence is maintained. An oscillatory structure reflecting the wavepacket motion is obtained in a time-resolved pump–probe signal. A vibrational mode analysis (VMA) is based on the decomposition of the signal into several vibrational modes by the Fourier analysis [23] or the singular-value decomposition [24]. In practice, the signal may not be merely a damped sinusoidal oscillation, but it may follow a complicated dynamics such as a power law due to the process of diffusion [14,15,25–29] and a stretched exponential decay due to distributed decay rates [30]. Even for a system in which such complicated electronic state dynamics are not dominant, they have usually several modes coupled to the electronic excitation. The Fourier power spectrum is formulated and the real-time trace can be analyzed by using the harmonic oscillator model [31]. When a wavepacket is excited in a region near the equilibrium position of a certain excited state, one can approximate the bound-state potential curves under consideration as being harmonic with specified frequencies.

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[*] Corresponding author. Address: ICORP, JST, Kawaguchi Center Building, 4-1-8, Honcho, Kawaguchi-shi, Saitama 332-0012, Japan.
E-mail address: taneichi@ils.uec.ac.jp (T. Taneichi).

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doi:10.1016/j.chemphys.2007.07.047

A common theoretical analysis is to use a harmonic potential as an approximation of a real bound-state potential or those closer to real such as the Morse type [32]. Under the conditions that justify this approximation, however, one needs to consider another issue concerning the excitation process: squeezing of the molecular vibrational wavepacket [33]. It is shown that a substantial difference can be obtained in the Fourier decomposition of experimental spectra for the coherent phonon and the squeezed phonon even for a system containing a realistic amount of electron–phonon coupling [34]. Assume that every mode, which is decomposed either by Fourier decomposition or by SVD, can be well-approximated by a harmonic oscillator. It is discussed that the influences from higher-order components on the VMA are inevitable, that is, there is not always one-to-one correspondence between signals obtained in VMA and vibrational modes of the system under consideration. Focusing on a single vibrational mode, the influence of higher-order components on VMA is quantitatively studied. Intensities of decomposed frequency components vary with change in the probe frequency. It is shown that one can tell, for instance, which peak obtained in VMA is the fundamental frequency component and which ones are the contributions from higher-order components, since decomposed frequency components have different dependences on probe frequency with each other.

In case two vibrational modes are taken into account, wavepacket is considered to move around on a 2D potential surface. Chemical reaction control based on the quantum optimal control simulation using model potential energy surfaces [35–37], and dependence of vibrational distribution on an electronic excited state on the intensity of excitation pulse [38] have been discussed so far. Few reports, however, have aimed at a detailed discussion on the pump–probe signal in such a system. Phase of molecular vibration has been addressed both theoretically and experimentally [31,39]. Pulse width dependent behavior of the phase as a function of probe frequency was observed that shows excellent agreement with theoretical prediction [39]. If the vibrational mode under consideration can be approximated by the harmonic potential, the phase of molecular vibration changes π at the equilibrium position. Strong deviation from this typical behavior in phase was observed in our group [40], in which the phase showed a clear oscillation as a function of the probe frequency. Part of this work is motivated by an idea that the anomalous behavior in phase is due to the wavepacket propagation on 2D potential surfaces, that is, the system is composed of a superposition of two vibrational modes. Calculation of the pump–probe signal for the 2D system is made and, based on the results, phase of molecular vibration is discussed in connection with the observation.

Squeezed molecular vibration was initially discussed as a realization of squeezing of general quantum oscillator in the molecular system. Its generation mechanisms, such as excitation with a chirped optical pulse [41], sudden change in vibrational frequencies during the Franck–Condon transition [42], and superposition of the coherent states in a one dimensional configuration [43], have been proposed. Several proposals were made for the detection of squeezed molecular state [33,41]. In this study, another proposal is made for the detection, based on the Fourier decomposition of the pump–probe signal. It is investigated whether the ratio between the intensity of the fundamental component and that of the higher-order harmonics is valid as a means for the judgment of squeezing.

Effect of the ''apparent anharmonicity'' that emerges in the transient pump–probe signal is discussed, in connection with vibrational scheme of molecule, in Section 2. Squeezing effect in the signal is discussed in detail based on the Fourier analysis. In Section 3, discussion of this anomalous ''apparent anharmonicity'' is extended to the case of two-mode system described by 2D potential surfaces. In an experiment in our group, it was observed that the phase of a pump–probe signal that oscillates with delay-time oscillates with respect to the probe frequency [40]. Two-dimensional effect on a pump–probe signal is discussed concerning this effect, in Section 4.

2. A single mode case

In this chapter, effect of phonon squeezing on the transient spectrum of a system with much smaller coupling strength, which is frequently encountered in real molecular systems is studied. In such a system, the spectra are modified due to squeezed phonons, which are visually less obvious than those discussed in Ref. [33]. We will demonstrate in this paper how the squeezing of phonons substantially influences the Fourier components of the spectrum in such realistic cases. Hereafter the intramolecular vibration is called ''phonon'' for simplicity.

2.1. Phonon statistics

The pump–probe signal obtained in the short-pulse limit has a Gaussian-like dependence on the probe frequency, which does not change its height during the period of molecular vibration, and vibration of the signal along the delay time is sinusoidal at any probe frequency. For a longer pulse, however, the signal changes its shape during the vibrational period, and its vibration is not sinusoidal. With a finite pulse width, therefore, contributions of the second and higher-order components of Fourier decomposition are expected to be more significant than those with the short-pulse limit. In this context, the deviation of the wavepacket formation scheme from the coherent excitation is called ''apparent anharmonicity''. This is due to the deviation of the quantum harmonic system from the classical one.

It was shown that the transient pump–probe spectra obtained for a molecular system is sensitive to the scheme of phonon excitation [33]. The phonon generated through optical excitation, with reciprocal pulse duration, u, in an