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Selective observation of the wave-packet dynamics in the excited states at KBr *F* centers by luminescence experiments

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We investigated temporal evolutions of the luminescence spectra in KBr *F* centers at 5 K using the up-conversion spectroscopy method, and observed damped wave-packet oscillation on the adiabatic potential-energy surface in the excited state. The wave-packet behavior is quite different from that observed through previous pump-probe measurements. The result shows that in the excited state the vacancy trapped electron interacts predominantly with the bulk phonon modes, in contrast to the ground state where it couples mainly to the A_{1g} local mode.

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Time domain ultrafast laser spectroscopy techniques have made it possible to observe atomic motions in free molecules,[1] solvated macromolecules,[2,3] and solids. The most common method applied to solids is the coherent phonon spectroscopy,[4] which probes the bulk phonon spectrum, based on the pump and probe transient absorption/reflection measurements. As for the excitation mechanisms, impulsive stimulated Raman scattering (ISRS) (Ref. 5) and displacive excitation of coherent phonons (DECP) (Ref. 6) are known. In both cases, the excited vibrations are well described as coherent states, which behave as a classical mechanical wave. The obtained information in this case reflects the bulk vibration spectrum of the crystal as the Raman spectroscopy does, because the photoexcitation does not cause appreciable modification of the vibrational properties of the bulk phonons, unless the excitation is intense enough to induce the softening of the phonons.

On the other hand, the vibrational properties of embedded molecules,[7] optical centers,[8] or localized excitons[9–11] largely depend on whether the electronic state is in the ground state or in the excited state, because the coupling of electron with the lattice depends on the size and the symmetry of the relevant electronic wave functions. The lattice dynamics in this case is suitably described in terms of a wave-packet (WP) motion on the adiabatic potential-energy surfaces (APESs), which are defined for the ground and excited states separately. As the pump-probe signals reflect both the ground and excited states in general, the response is rather complicated and difficult to analyze.[8,10] To make the situation more complicated, pump-probe signals contain sometimes the contribution from the transient absorption from the excited state to higher levels.

Luminescence methods have advantages for the purpose of studying the localized states. When the luminescence photon energies are suitably selected to be far from the energy of the absorption band, obtained results are free from the ground-state dynamics.[9,11] Furthermore, complication due to the higher excited states can be avoided, because the participating optical transition is only from the lowest excited state to the ground state.

Kayanuma and Tanaka have theoretically shown that the long-lived temporal oscillation of transmission gains observed in localized systems with the strong electron-phonon interaction in degenerate pump-probe experiments is mainly attributed to the breathing and swinging motions of a spectral hole (negative WP) burned in the ground state rather than a WP (real WP) in the excited state.[12] In order to confirm their argument experimentally, it is indispensable to observe the dynamics in the ground and excited states separately.

In this work, we have chosen the *F* center as a simple optical center with a strong electron-lattice interaction. By using time-resolved luminescence spectroscopy, we observed WP dynamics evidently different from that observed in the pump-probe measurements reported by Nisoli *et al.*[8] This result strongly supports the theoretical predictions.

The *F* center in alkali halides is a prototypical example of a strongly coupled localized electron-phonon system, where an electron is trapped at a negative-ion vacancy. Its electronic ground state is in the 1*s* state and the first excited state is composed of nearly degenerate 2*s* and 2*p* states. It has been shown through a series of electron spin resonance and electron-nuclear double resonance experiments that the vacancy trapped electron is localized mainly within the surrounding octahedron of the six nearest-neighbor alkali ions in the ground state,[13] while in the relaxed excited state, it spreads out to the second-neighbor halide ions.[14] This indicates that the trapped electron can interact with the lattice vibration outside the octahedron more strongly in the excited state than in the ground state, and the real WP will have different modes from the negative WP. Owing to a large Stokes shift (~1 eV) (Ref. 15) it is expected that the excited-state dynamics can be observed separately from the ground-state one, when the detected-photon-energy range is far away from the absorption band and close to the peak of the emission one. Consequently, it will be possible to discriminate between the oscillation of the negative WP and that of the real WP experimentally.

Time evolutions of luminescence spectra were measured by use of the frequency up-conversion technique. Additively colored KBr crystals with *F* centers at a concentration of approximately 7×10^{16} cm^{-3} were cleaved to dimensions of about $3 \times 3 \times 0.3$ mm^3 and kept at 5 K in a He-flow cryostat. The samples were excited by the output beam of an optical parametric amplifier pumped by a mode-locked Ti:sapphire

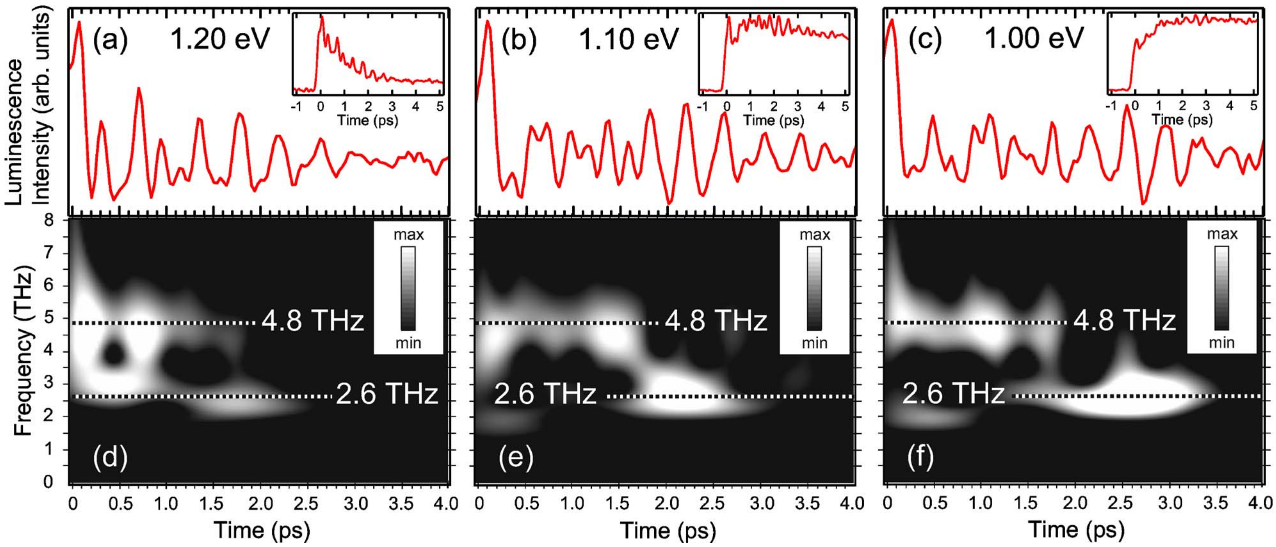

FIG. 1. (Color online) Time dependences of luminescence intensity at various photon energies and their continuous wavelet transforms. (a), (b), (c) The oscillatory components of luminescence intensities in the 0–4 ps delay range at 1.20, 1.10, and 1.00 eV, respectively. Intensities are normalized for clarity. The insets in each figure show the behavior from −1.2 to 5.2 ps. (d), (e), (f) Continuous wavelet transforms of the data in (a), (b), and (c), respectively. The grayscale indicates the signal amplitude, the brighter part having a larger amplitude.

regenerative amplifier with a repetition rate of 200 kHz. The excitation light was polarized parallel to the (100) axis of the KBr crystal and the average excitation power was 1 mW. The excitation photon energy was 2.06 eV so that the resonant excitation condition was satisfied, as the absorption band of KBr *F* centers peaks at 2.064 eV with a FWHM of 0.158 eV at 0 K (Ref. 15). The luminescence photons of the samples were focused onto a nonlinear optical crystal (1-mm-thick $LiIO_3$) and mixed with the time-delayed fundamental laser pulses (gate pulses). The sum frequency light was focused into a double-grating monochromator and detected by a photomultiplier tube with a photon counter. The detected luminescence photon energy range is from 0.85 to 1.20 eV including the peak energy, 0.916 eV at 0 K (Ref. 15). The time origin was determined by cross-correlation signal between the excitation pulse and the gate pulse. The time resolution of the measurement system was about 100 fs.

Figure 1 shows the time dependence of luminescence intensity measured at 1.20, 1.10, and 1.00 eV photon energies, and their continuous wavelet transforms. The insets of (a), (b), and (c) represent the raw data at 1.20, 1.10, and 1.00 eV, respectively. (a), (b), and (c) show the oscillating components extracted from the raw data. Their continuous wavelet transforms are calculated using the Gabor wavelet based on the Gaussian function and shown in (d), (e), and (f), respectively. The luminescence experiences wavelength-dependent time retardation due to the group velocity dispersion of a 1.5-mm-thick optical window of the cryostat. The differences were numerically corrected in each curve in Fig. 1 (Ref. 16). The luminescence intensity at each photon energy is normalized at maxima for a convenient display. As can be seen from the time evolution curves, the luminescence intensity decays faster at higher photon energy (insets), corresponding to the decrease of the oscillation amplitude of WP. The wave forms of the oscillating components are critically dependent on the photon energy. The continuous wavelet transforms indicate that the oscillatory components appear mainly around 2.6 and 4.8 THz, and the lifetime of the former is longer than that of the latter. It is also seen that the 2.6-THz mode survives longer at lower photon energies.

The Fourier transformed (FT) spectrum of the oscillatory component at 1.05 eV between 0.3 and 5 ps was calculated using the Hanning window function (abbreviated as “luminescence FT spectrum”) and is shown in Fig. 2(c) together with the FT spectrum of the result obtained by the pump-probe optical-absorption measurements at room temperature by Nisoli *et al.* (“pump-probe FT spectrum”) cited from the inset of Fig. 2 in Ref. 8 [Fig. 2(a)], the Raman scattering spectrum at 10 K (incident pulse energy, 1.96 eV) from Fig. 7 of Ref. 17 [Fig. 2(b)], and the bulk phonon density of state (DOS) of KBr crystal from Fig. 4 of Ref. 18 [Fig. 2(d)], which is calculated based on the results of the neutron scattering experiments at 90 K (Ref. 19). Prominent structures are peaked at 2.6 and 4.8 THz in the luminescence FT spectrum rather than at 3.3 THz corresponding to the A_{1g} breathing mode of the octahedron of cations surrounding the vacancy. The FT spectra of the oscillatory component at various photon energies have similar features, except for those below 0.95 eV, where the oscillating structure itself cannot be seen well because of a low signal-to-noise (S/N) ratio. In the time evolution of the luminescence intensity near the potential minimum, overtone of the fundamental oscillation is sometimes observed, because the WP passes the minimum point twice in one oscillation period.[11] However, the Fourier component at 4.8 THz, which is close to twice of 2.6 THz, cannot be assigned to the overtone, because the time-frequency analysis in Fig. 1 shows that these oscillation components have clearly different time profiles. Comparing the luminescence FT curve,[19] 2.6- and 4.8-THz modes are

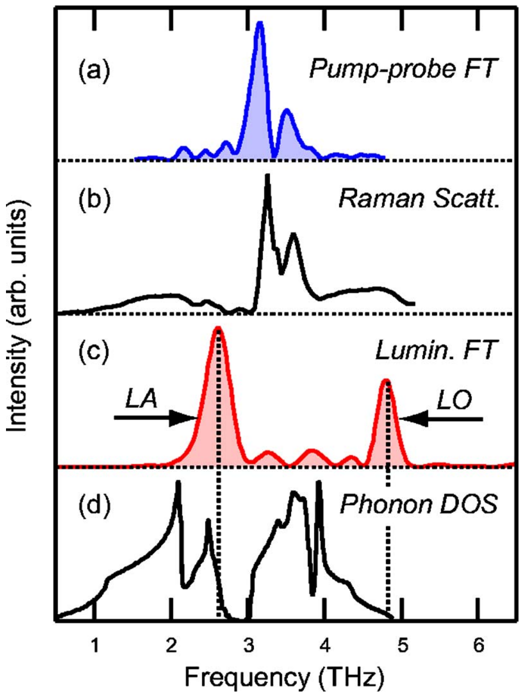

FIG. 2. (Color online) Comparison of Fourier transformed spectrum of the experimental data with various spectra. (a) Fourier transform spectrum of the results of the pump-probe measurements cited from Ref. 8. (b) Raman-scattering spectrum from Ref. 17. (c) Fourier transform spectrum of the oscillatory component extracted from the luminescence intensity at 1.05 eV. (d) Density of state of bulk phonon in KBr crystal from Ref. 18.

attributed to the LA phonons near the singularities in (100) and/or (110) crystal directions, and the LO phonons near the Γ point in the first Brillouin zone, respectively. The A_{1g} mode at 3.3 THz hardly appears in the luminescence FT spectrum, and there is no appreciable amplitude in the continuous wavelet transforms at any time at any photon energy. On the other hand, the peak of the A_{1g} mode is the highest among the structures in the pump-probe FT spectrum and in the Raman spectrum. The small redshift of the former structures relative to the latter's is ascribed to the difference in the measurement temperature.

This striking difference between the luminescence and pump-probe measurements can be understood as follows. Optical pulse excitation makes the negative WP in the ground state[3,12] and the real WP in the excited state. They propagate on each APES independently, and the local vibration around the F center is regarded as the superposition of these vibrations. Our result reflects pure real WP dynamics, because under our experimental conditions the excitation photon energy corresponds to the absorption peak and the detected luminescence energy range covers the emission band far from the absorption one, so that the negative WP cannot be observed. On the other hand, in the previously reported pump-probe measurements the negative WP dynamics is mainly observed, as they were performed under so-called degenerate pump-probe conditions.[12]

We then qualitatively explain the reason why these two WP dynamics differ from each other (Fig. 3). First, we describe the formation of the negative WP in the ground state (lower diagram in Fig. 3). Before the excitation occurs, the trapped electron is localized in the vacancy, and the 1s electronic wave function belongs to the totally symmetric mode as the A_{1g} phonon mode, so that the 1s state is strongly coupled to the A_{1g} mode. Therefore, the configuration coordinate axis for the ground state (axis Q_1) should correspond to the A_{1g} mode. If the excitation pulse energy is set to be off resonant (right case in Fig. 3), the vertical transition in the configuration coordinate space occurs effectively at the off-equilibrium point based on the Franck-Condon principle, where the excitation energy corresponds to the energy difference between the ground- and excited-state APESs. The pulse excitation makes a spectral hole over thermally distributed several vibrational levels on the ground-state APES. This is regarded as the negative WP, which oscillates around the potential minimum of the ground state.[12]

When the negative WP passes the probe window, transmittance increases due to the bleach of the population, and will show the oscillatory structure. Thus, it is suggested that the oscillating transmittance gain in the pump-probe measurements[8] corresponds to the oscillation of the negative WP of A_{1g} vibration in the ground state. It is also supported

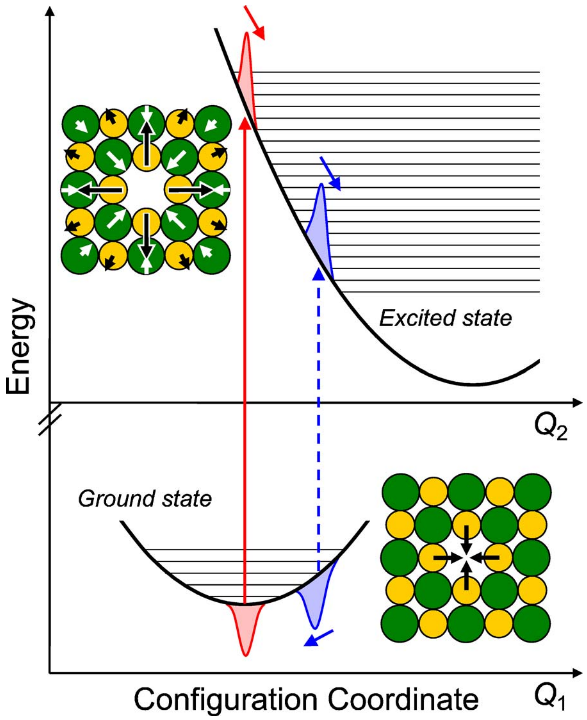

FIG. 3. (Color online) Schematic diagram of the negative WP dynamics in the ground state (lower diagram) and the real WP dynamics in the excited state (upper diagram). The solid and dashed upward arrows connecting two parabolic curves (APESs) show the Franck–Condon transitions due to optical excitations in the luminescence measurement (this work) and the pump-probe one of Ref. 8, respectively. At the right (left) side of the ground-state (excited-state) APES, schematic cross-section drawing of the lattice around the F center is depicted. The larger and smaller circles represent halide ions and alkali ions, respectively. The solid arrows represent the direction of the coherent movements of neighboring ions just after photoexcitation.

from the close resemblance of the FT spectrum of the pump-probe signal to the Raman spectrum, which generally reflects the phonon structures in the ground state. As our experiment has shown that the main oscillation frequency in the excited state is clearly different from the ground-state one, the validity of this interpretation is experimentally proven.

The real WP in the excited state is formed in the following way (see upper diagram in Fig. 3). When the trapped electron is optically excited, its wave function spatially spreads out and the effective negative charge decreases around the center of the vacancy. Coulomb force instantaneously acts on ions in the vicinity of the vacancy and the local vibration of the lattice around the vacancy will be excited coherently. According to Ref. 14, the average radius of the wave function in the relaxed excited state is 6.87 Å, which roughly corresponds to the distance between the center of the vacancy and the second-neighbor halide ions. This means the coupling with the bulk phonons becomes stronger in the excited state. In addition, the bulk phonon modes near the singularities in the Brillouin zone have a high density of state. Therefore, the interaction mode describing the real WP motion in the excited state will be composed mainly of bulk phonon modes near the singularities, LA(ζ00) and/or LA($\zeta\zeta$0) and LO(Γ), rather than the A_{1g} local mode. This interaction mode corresponds to the configuration coordinate axis Q_2 in Fig. 3.

The most important conclusion from our experiment is that we can obtain the information of the WP dynamics on the first excited state, avoiding any ambiguity that might come from the higher excited state or ground state. In this sense, the luminescence method is superior to pump-probe methods, which are widely used in the investigation of the WP dynamics. Much care must be taken in interpreting the obtained results in the latter case, particularly under degenerate pump-probe conditions.

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