Second 2*s*-2*p* level crossing at the *F* center in KCl evidenced by frequency upconversion spectroscopy

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Subpicosecond dynamics of resonant secondary emission from the *F* center in KCl at 5 K is investigated by frequency upconversion method. Detected photon energy range is from 0.65 to 1.55 eV and covers almost all the stationary emission band. The decay time of the luminescence intensity is longer in the low-energy side of emission band than in the high-energy side. A series of transient luminescence spectra shows relatively high intensities in the low-energy side. These two features indicate the existence of the second 2*s*-2*p* level crossing near the relaxed excited state.

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I. INTRODUCTION

Femtosecond laser spectroscopy has directly elucidated atomic and molecular motions in condensed phases such as solutions, biomolecules, and solids.[1] One can observe in real time the particle motions which are coherently excited by a laser-pulse irradiation. Coherent lattice motion at localized systems[2–21] is expected to play a key role in understanding and controlling lattice rearrangement processes such as chemical processes,[22] defect formations,[23] and photoinduced phase transitions.[24]

The localized coherent lattice motion is well described in terms of a vibrational wave packet or nuclear wave packet (NWP). An NWP is a coherent superposition of several vibrational levels on an adiabatic potential-energy surface (APES) along a configuration coordinate. In solids, the configuration coordinate represents the interaction mode consisting of bulk phonon modes as well as local modes[25,26] and, in some cases, it is considered as a reaction axis of the lattice rearrangement processes. During the progress of these phenomena, the NWP will experience a complicated APES which has crossing points and/or large anharmonicity so that it is important to understand the behavior of NWP on such an APES. The *F* center in alkali halides is one of the model systems to study the NWP dynamics on the APESs with level crossings.

The *F* center in alkali halides[27,28] consists of an anion vacancy and a trapped electron. As a prototype of a strongly coupled localized electron-phonon system, the NWP dynamics has been demonstrated in real time by femtosecond laser spectroscopy.[8–13] The ground state is the 1*s* state and the first excited state is composed of the 2*s* and 2*p* states. A configuration coordinate diagram is drawn in Fig. 1. The 2*s* state lies higher than the 2*p* state in the Franck-Condon state (FCS) of absorption[29,30] but is lower in the relaxed excited state (RES).[31] These features show that the 2*s* and 2*p* levels cross each other between the FCS and RES. The crossing point is indicated as the first level crossing (LC) in Fig. 1. Due to the coupling to T_{1u} phonon modes, the RES consists of the 2*s* state slightly admixed with the 2*p* state and is called the 2*s*-like state.[32–34] The upper state of the RES is called the 2*p*-like state.

Intensive studies on the first LC have been performed by measuring luminescences under one-photon and two-photon excitations (e.g., Refs. 35–37). Recently, Akiyama and Muramatsu[38] performed a spectral analysis of hot luminescence in the visible region observed by one- and two-photon excitation measurements with tens of picoseconds resolution. The results indicate that the first LC has the anticrossing nature at the *F* center in KCl, as depicted in the inset of Fig. 1. Very recently, it has been indicated that the anticrossing process also occurs at analogous vacancy centers, the F_A (type II) center in KCl:Li (Ref. 39) and the F_A (type I) center in KCl:Na.[40] A series of these works indicates that the anticrossing picture is conceivable for the first LC. Besides the first LC, the second crossing point has been suggested to exist on the other side of the excited-state APESs (Ref. 38) (represented as the second LC in Fig. 1). However, it has not been proven experimentally.

In the present work, we focus on temporal behaviors of luminescence from the *F* center in KCl, which were obtained for the full range of emission band by using the frequency upconversion method. It is found that the second LC exists, where an anticrossing situation arises.

II. EXPERIMENT

Additively colored KCl crystals (*F*-center concentration: 5×10^{16} cm^{-3} and thickness: 0.3 mm) were mounted in a He-flow cryostat operating at 5 K. The light source was a

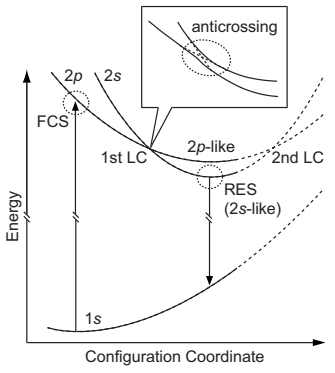

FIG. 1. Schematic of configuration coordinate diagram for the *F* center. The inset indicates an anticrossing in the region around the first LC.

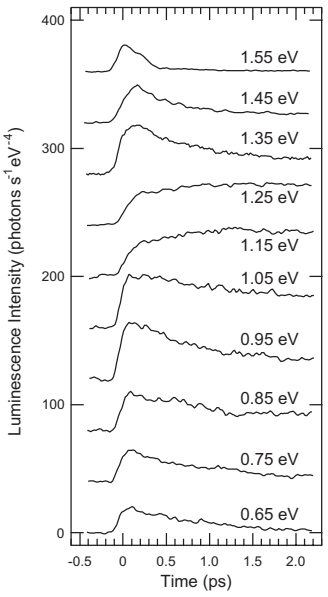

FIG. 2. Time evolutions of luminescence intensities at different photon energies. The ordinate represents a relative luminescence intensity (in the units proportional to photons per unit second per unit energy) divided by the cube of photon energy in order to correct for the probability of spontaneous emission.

home-built noncollinear optical parametric amplifier (NOPA) (repetition rate: 5 kHz, central wavelength: 538 nm, and pulse width: 40 fs). The tuned photon energy corresponds to the absorption peak of sample; the absorption band peaks at 2.313 eV with the full width at half maximum (FWHM) of 0.163 eV.[41] The output of NOPA was divided into excitation and gate pulses. The excitation pulse energy was 200 nJ. Polarization of the excitation pulse was parallel to [100] crystal axis of KCl. The luminescence light passed a low-pass filter (thickness: 20 μm) in order to cut the remnants of the excitation pulses. The sum frequency signal was generated by mixing the luminescence photons with the time-delayed gate pulses in a 0.3-mm-thick beta barium borate crystal (cutting angle: 35.5°). After passing through a high-pass filter and a double-grating monochromator (Jobin Yvon, GEMINI 180), the signal light was detected by a photomultiplier tube (Hamamatsu, R585) with a photon counter (Advantest, TR5822).

The overall time resolution of the measurement system was 60 fs and the spectral resolution was ~0.06 eV. The spectral sensitivity was measured by means of the upconversion signal of a tungsten standard lamp with an output of a continuous-wave diode-pumped $Nd:YVO_4$ laser (wavelength: 532 nm). The luminescence was detected in the photon energy range of 0.65–1.55 eV, covering almost all the stationary emission band, i.e., ordinary luminescence, which peaks at 1.180 eV with the FWHM of 0.294 eV.[41]

III. RESULTS

Figure 2 shows temporal evolutions of luminescence intensities measured at 0.65–1.55 eV. The ordinate represents a relative luminescence intensity divided by the cube of photon energy in order to correct for the probability of spontaneous emission. Then, the scale directly indicates the probability amplitude of the vibrational wave function on APES when the transition matrix is constant. The time origin was defined as the center point of cross-correlation signal between the gate pulse and the excitation pulse scattered at the surface of the sample. As the luminescence passed through a 1.5-mm-thick-fused silica window of the cryostat, each time origin is shifted in this figure to compensate for respective time advances due to the group-velocity dispersion of this window. The radiative lifetime of the RES is 577 ns (Ref. 42) and much larger than the measured time range of 2.2 ps so that the behavior of the radiative decay is not reflected in Fig. 2.

In the high-energy region (1.35 eV and above), which lies in the high-energy tail of the emission band, the luminescence intensities decrease with time. The decay time becomes longer with decrease in photon energy. At 1.15 and 1.25 eV, which are around the emission peak of 1.18 eV, the intensities monotonously increase and approach constant values around 1 ps. In the low-energy region (1.05 eV and below), the luminescence intensities exhibit decreasing behaviors again and the decay time becomes shorter at lower photon energy. The above-mentioned behaviors reflect a convergence of probability amplitude toward the potential minimum due to a damping of NWP toward the RES. In the case that the ground- and excited-state APESs are harmonic and have the same curvature, luminescence wave forms in high- and low-energy sides show similar decay behaviors. However, the difference of decay time between the high- and low-energy sides is clearly found in Fig. 2. For example, comparing the 1.55 and 0.85 eV wave forms (the energies are almost equally separated from the emission peak 1.18 eV), the 0.85 eV wave form exhibits a longer decay.

To further confirm this asymmetric behavior, we look into a series of transient luminescence spectra. The transient spectra at 0.5, 1.0, 1.6, and 2.1 ps are shown by dots with solid lines in Fig. 3. A series of these spectra indicates that the spectral shape becomes narrow in accordance with the convergence of probability amplitude toward the potential minimum associated with the NWP damping. The spectra indicate the asymmetry about the emission peak 1.18 eV. In the low-energy side, the intensity is relatively high and the decay time is long.

IV. DISCUSSION

The asymmetric behavior is explained by considering a motion of NWP on an anharmonic APES with level crossings depicted in Fig. 4(a). The dashed lines indicate the adiabatic potential energies of the $2s$ and $2p$ states [$E_s(Q)$ and $E_p(Q)$] along the normalized configuration coordinate Q, which have been derived by Akiyama and Muramatsu.[38] The potentials are given in the units of eV by

$$E_s(Q) = 1.19(Q - 0.754\,6)^2 + 1.743\,6, \quad (1)$$

$$E_p(Q) = 0.804(Q - 0.816\,4)^2 + 1.777\,1. \quad (2)$$

Here, the potential of the $1s$ ground state is written in the form $E_g(Q) = Q^2$. In Ref. 38, Akiyama and Muramatsu indi-

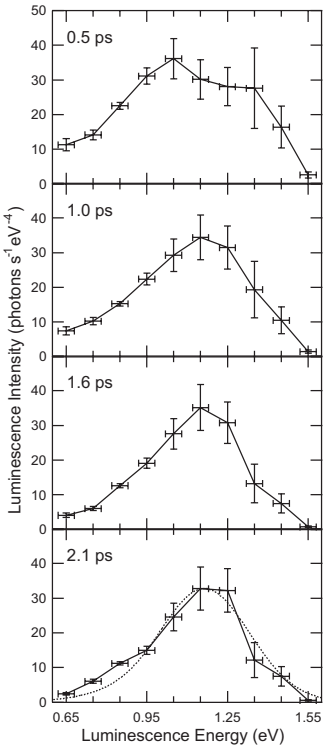

FIG. 3. Transient luminescence spectra at 0.5, 1.0, 1.6, and 2.1 ps. The dots with solid lines indicate the experimental results. The error bars in the ordinate represent the measurement errors due to standard deviations of spectral sensitivities at respective energies. The error bars in the abscissa express the spectral resolution. The dotted line superposed on the 2.1 ps spectrum represents a fitting curve assuming an anharmonic potential (see text).

cated that the anticrossing occurs at $Q_1=0.292\,2$ [corresponding luminescence energy: 1.90 eV; see Fig. 4(b)] and that the coupling constant V_{sp} of the two levels is 0.013 eV. The potentials on the left-hand side in Fig. 4(a) well explain the absorption and emission data,[27,30,31,38,43] and Eqs. (1) and (2) have been reliable expressions of the left-hand side potentials. In contrast, the validity of Eqs. (1) and (2) has been unclear for the right-hand side potentials. Nevertheless, we assume that the potentials on this side are expressed as Eqs. (1) and (2). According to Fig. 4(a), another crossing point lies at $Q_2=0.959\,5$ [corresponding luminescence energy: 0.86 eV; see Fig. 4(b)]. We also assume that the $2s$-$2p$ anticrossing arises at the point with the coupling constant of 0.013 eV. Thus, the $2s$ and $2p$ APESs avoid each other around Q_1 and Q_2 and new nonparabolic APESs are formed as indicated by solid curves in Fig. 4(a).

By referring to Fig. 4, the position of NWP is discussed as follows. We first remind that the oscillation frequency of the NWP is 6 THz (oscillation period 167 fs).[13] At time zero, the NWP is excited in the FCS ($2p$ state) of absorption [the lower APES at $Q=0$], which locates far left from Q_1. Just after this Franck-Condon transition, the luminescence energy is as high as ~2.3 eV [see the lower curve in Fig. 4(b)]. As the NWP slides down along the lower APES, i.e., the center-of-mass position of the NWP moves right, the luminescence energy monotonously decreases. The NWP approaches the crossing point at Q_1 around 20 fs. Figure 4(b) indicates that

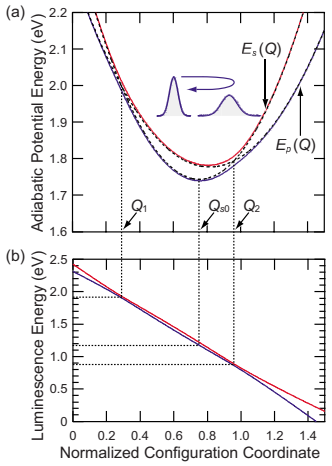

FIG. 4. (Color online) (a) Configuration coordinate diagram for the excited state at the F center in KCl. (b) Correspondence of normalized configuration coordinate with luminescence energy. The upper (lower) curve represents the photon energy of luminescence from the upper (lower) APES in (a).

the energy separation between the upper and lower APES in the energy region of luminescence from 0.65 to 1.55 eV is several tens of meV, which is smaller than the energy resolution of the measurement system (0.06 eV), so that we cannot determine which APES the NWP propagates on. Nevertheless, considering the anticrossing nature,[38] the NWP almost adiabatically passes through the crossing point and propagates on the lower APES. At ~42 fs, the NWP reaches the potential minimum of the lower APES at $Q=0.754\,6$ ($=Q_{s0}$). Beyond the potential minimum, the NWP moves on to the second turning point, which is not accessible in this work but probably to the right of the crossing point at Q_2. When passing around this crossing point at ~50 fs, the NWP almost adiabatically propagates on the lower APES. Once the NWP reaches the turning point around 84 fs, it swings back toward the potential minimum of the lower APES at Q_{s0} and moves on to the first turning point with the oscillation amplitude becoming smaller. Thus, the damped oscillation of NWP proceeds.

Then, we focus our attention on the oscillation amplitude and shape of NWP on the right-hand side. Besides the fact that the curvature of the $2p$ APES is 1.47 times smaller than the $2s$ APES, due to a repulsion of the two APESs, the curvature of the lower APES becomes even smaller in the anticrossing region around Q_2. Namely, a larger anharmonicity is expected in this anticrossing region. Therefore, the NWP swings farther from the potential minimum on the right-hand side in Fig. 4(a) than on the left-hand side, and it becomes wider. As a result, the transient spectra have broader tails in the low-energy side. Since the crossing point Q_2 lies near the RES, the behavior of NWP is influenced by the crossing point even when the oscillation amplitude becomes small.

As the 1.6 and 2.1 ps spectra exhibit a similar shape, the NWP oscillation almost damps by 2.1 ps and a thermalized population is established. The asymmetry in the 2.1 ps spectrum, which has a long tail in the low-energy side, is explained by the thermalized population on the lower APES with anharmonicity. A curve fitting to the 2.1 ps spectrum is

performed by simply assuming the Boltzmann distribution on the lower APES. The result is indicated as the dotted line in Fig. 3. The effective temperature of the distribution is obtained to be 323 K (=27.8 meV). Although the fitting curve reproduces well the experimental data above 0.95 eV, the observed spectrum is more asymmetric, i.e., the intensity below 0.95 eV is larger than the fitting curve. This is qualitatively explained by the increase in the oscillator strength associated with the increase in mixing ratio of the $2p$ state into the lower APES at $Q > \sim Q_2$.

V. CONCLUSION

We studied a dynamics of a nuclear wave packet in the excited state at the F center in KCl at 5 K by frequency upconversion technique. The decay time of luminescence intensity is longer in the low-energy side of emission band than in the high-energy side. Observed transient spectra show a relatively high intensity in the low-energy side. These two features indicate a large anharmonicity of the adiabatic potential-energy surface near the relaxed excited state due to the second $2s$-$2p$ level crossing with the anticrossing nature.

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