Single-Electron Subpicosecond Coherent Dynamics in KBr *F* Centers

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The coherent dynamics of a vibronic wave packet in KBr *F* centers is presented. We observe the temporal evolution of single-electron wave packets following femtosecond laser excitation. Electron dynamics leads to subpicosecond periodic oscillations of the sample transmission. These are monitored in real time by pump-probe techniques yielding directly the vibrational frequencies of the localized modes associated to ground and excited electronic states. These results, complemented by stationary optical characterization, give further insight into the configuration coordinate model for *F* centers. [S0031-9007(96)01432-9]

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Color centers and self-trapped excitons have long been the subject of intense investigations both as model systems for the study of electron-lattice interaction [1,2] and as important systems for the realization of solid-state lasers. In recent years, thanks to subpicosecond spectroscopic techniques, it has become possible to study with unprecedented resolution the dynamics of self-trapped excitons and the formation of color centers by monitoring the lattice relaxation following fundamental electronic excitation [3,4]. These systems, however, offer other exciting possibilities for the study of the coupled dynamics of electron and localized lattice modes. Such phenomena are not easily accessible to ultrafast optical experiments in other much studied solids like semiconductors and semimetals because the observed dynamics is dominated by bulk phonons and many-electron effects.

In this Letter we present the first experimental results on femtosecond dynamics of a single-electron wave packet in the KBr *F* center. This color center consists of an anion vacancy occupied by a single electron. In this system the electronic wave function is localized within few lattice parameters even in the excited state [5]. Consequently, electrons centered on different vacancies can be regarded as independent, even at relatively high densities. This system, therefore, yields the unique opportunity of exploiting femtosecond light pulses to investigate transient dynamics dominated by pure one-electron effects in a solid.

Owing to this small spatial extension, the electron coupling to the lattice is dominated by localized vibrations around the vacancy that were theoretically analyzed by Dominoni and Terzi [6]. This situation is somewhat similar to an electronic transition in a molecule, where the equilibrium distance of the constituents is different in the electronic ground state and in the excited state. The Stokes shift of the corresponding transition can then be interpreted successfully on the basis of a strong coupling of the electron to a molecular vibration. In the case of the color center, the vibration largely responsible for the Stokes shift is the A_{1g} (Γ_1^+) breathing mode of the lattice around the vacancy, dominated by the in-phase movement of the surrounding octahedron of cations [6]. Contrary to small molecules, the vibrational frequency cannot be deduced directly from stationary absorption or photoluminescence measurements, and it is estimated from the temperature dependence of the absorption and photoluminescence linewidth in a rather indirect way [7,8]. The only clear evidence for vibrational symmetries and frequencies was obtained by Raman scattering measurements [9,10].

Our transient pump-probe experiments are based on 10 fs pulses obtained by a newly developed compression technique [11]. Pulses of 140 fs duration, 660 μJ energy, and 1 kHz repetition rate were generated by a Ti:sapphire laser with chirped-pulse amplification. These were focused into a 70-cm-long hollow fiber placed in a high-pressure chamber with quartz windows containing krypton at 2 atm pressure. The broadened spectrum obtained with krypton presents a rather uniform shape, i.e., without the typical deep modulation arising from self-phase modulation effects. Pulse compression was then obtained by a double pass through a couple of quartz prisms. Assuming a sech^2 pulse shape, we derived 10 fs duration at full width at half maximum (FWHM) from the autocorrelation function. The pulse energy is 240 μJ. The pulse spectrum is centered at 1.75 eV with FWHM of 110 meV, corresponding to nearly transform-limited pulses, with a good overlap with the KBr *F* center absorption region (at room temperature absorption peaks at 1.98 eV with FWHM of 0.34 eV). Pump and probe beams are focused onto the sample to a 100-μm-diameter spot. The pump beam is chopped at 400 Hz and the signal is detected using a lock-in amplifier. The probe pulse is frequency filtered after passing through the sample using interference filters with a spectral FWHM of 25 meV.

We studied the transmission variation of thin ($\sim$ 1 mm) additively colored KBr samples with an F center concentration of $\sim 3 \times 10^{16}$ cm^{-3}. Data were recorded as a function of pump-probe delay for a variety of probe frequencies. In Fig. 1, we display room-temperature results for probe wavelength $\lambda_{pr} = 680$ nm in two different delay ranges with pump and probe pulses perpendicularly polarized along two orthogonal axes of the KBr crystal. The transmission exhibits oscillatory behavior with about 15 periods clearly identifiable; a pronounced beating pattern is also observed.

In order to better analyze the oscillatory part, we subtracted the slow decaying part of the signal by fitting it with an exponential (see dashed line in Fig. 1) [12]. Figure 2 shows the extracted oscillating part of the signal for delays larger than 350 fs, together with its spectral analysis (see inset of Fig. 2). The data clearly show that the oscillation pattern results from two distinct frequencies $\nu_1 = 3.2$ THz (period 0.31 ps) and $\nu_2 = 3.5$ THz (period 0.29 ps), with dephasing time of about 1.9 ps. The two peaks in the frequency spectrum were clearly distinguishable and were found unaltered for all probe frequencies studied (range 680–770 nm, data not shown). This shows that the full dynamics of the excited electron is controlled by the excitation of the pump pulse and that different spectral parts of the probe reveal the same oscillation pattern.

The microscopic interpretation of these results is based on the concept of vibronic states for both the s-like ground state and the p-like excited state. Vibronic states result from electron coupling to localized lattice modes, especially the breathing mode. The coherent oscillations of the electronic wave packet in the vibronic potential are responsible for the observed modulation of the transmission.

Using the Fock states of the A_{1g} (Γ_1^+) breathing mode as a basis, we performed a density matrix calculation in order to include coherence and dephasing effects [13]. Our results show that the oscillatory part of the transmission signal is due to off-diagonal elements of the density matrix between consecutive excited and consecutive ground states. These correlations have no equilibrium counterpart and are entirely determined by the inner dynamics of the system after it has been perturbed by the pump pulse. They enter the coupling of the optical transition with the electric field of the probe pulse, giving rise to the oscillatory part of the sample transmission. Contrary to this oscillating part, the slow component of the probe signal is due to transient changes of the occupation number of the vibronic states, appearing as diagonal terms in the density matrix. These transient occupations, in turn, enter the saturation of the optical transition.

The vibrational frequencies measured here are in agreement with resonant Raman data [9,10] but differ significantly from values inferred from continuous wave (cw) measurements by various authors [1,7,9]. The latter values, however, are deduced from the temperature dependence of PL and absorption linewidths or line shapes within the Franck-Condon approach and should be considered model dependent. Additionally, the presence

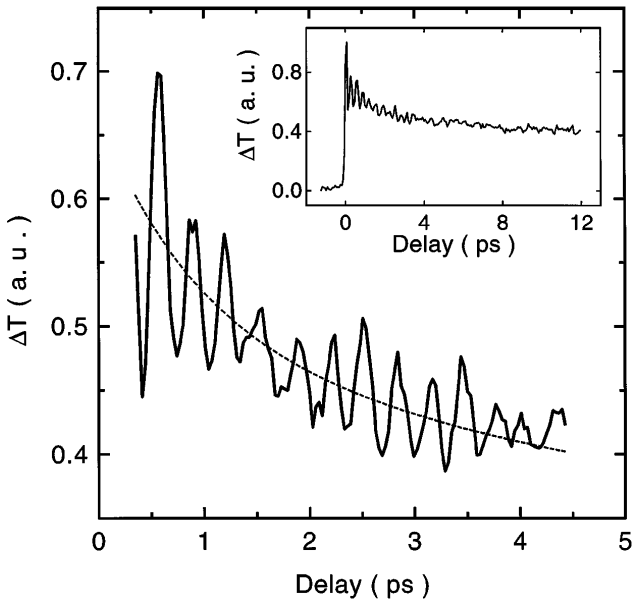

FIG. 1. Transmission change ΔT as a function of time delay between pump and probe pulses at room temperature for delays larger than 0.35 ps. Pump pulse is centered at 1.75 eV and is 10 fs long; transmitted probe pulse is filtered at 1.82 eV (see text). The dashed line is the result of an exponential fit with time constant 2.6 ps. The inset shows the behavior in the -0.6–12 ps delay range.

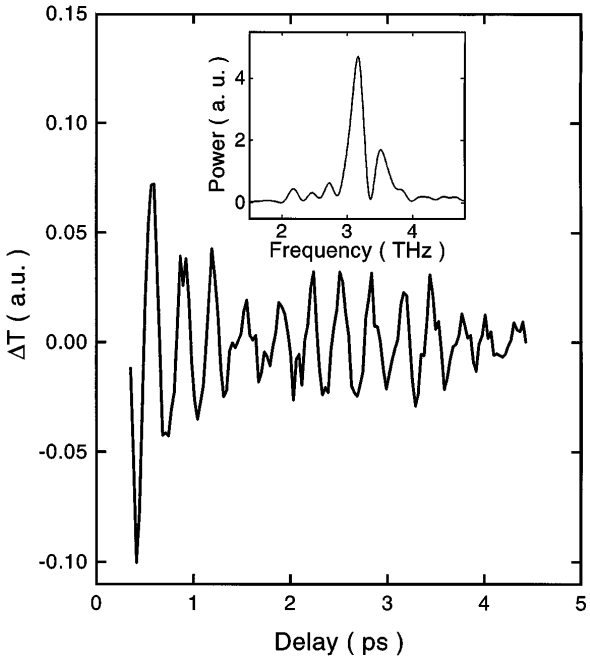

FIG. 2. Oscillatory part of the transmission change as a function of delay for delays larger than 0.35 ps. The curve was obtained by subtraction of the exponential fit in Fig. 1 from the measured data. The inset shows the Fourier power spectrum of the oscillatory part.

of other optically active centers in varying concentrations (e.g., F' and F_2) can influence the accuracy of the cw analysis [14]. From such studies, however, useful information can be derived using the data obtained by ultrafast time-resolved measurements like ours. In fact, by analyzing the temperature dependence of PL and absorption linewidths of our additively colored and quenched samples (see Fig. 3), we were able to unambiguously assign the two measured frequencies to ground ($\nu_g = 3.2$ THz) and excited states ($\nu_e = 3.5$ THz). Furthermore, these data allow us to fully determine the configuration coordinate diagram along the lines of the classical analysis of Russell and Klick [7]. This is achieved by a best-fit procedure to the experimental peak energies and linewidths of PL and absorption at low temperature. Such analysis yields the force constants relative to ground ($k_g \simeq 9.47$ eV/Å^2) and excited states ($k_e \simeq 9.39$ eV/Å^2), the displacement of the equilibrium positions ($\delta = 0.340$ Å), and the energy shift ($\Delta E = 1.51$ eV; see inset of Fig. 3). Thanks to the direct measurement of the vibrational frequencies, it is possible to estimate the masses associated to the vibronic states ($m_{g,e}$) exploiting the classical relation $k_{g,e} = (2\pi\nu_{g,e})^2 m_{g,e}$. In previous studies these were both assumed equal to the mass of the six cations surrounding the F center. We found this value to be appropriate only for the ground state mass, while for the excited state mass we determined a value over 25% smaller.

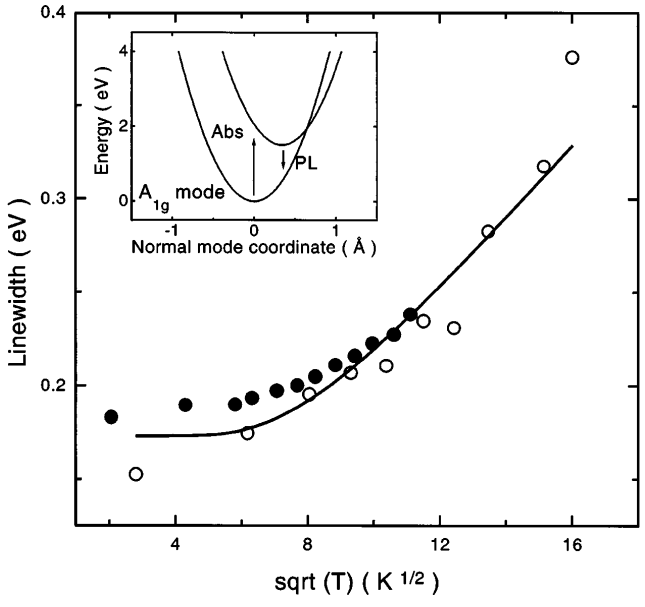

FIG. 3. Stationary linewidth of photoluminescence (full circles, pump energy 1.96 eV) and absorption (hollow circles) as a function of square root of temperature. The continuous line shows the calculated values of the latter derived according to Ref. [7] setting $\nu_g = 3.2$ THz. The inset shows the configuration-coordinate diagram for the A_{1g} breathing mode of KBr F center. Parabolic potentials are defined by $\frac{1}{2}k_g x^2$ and $\frac{1}{2}k_e(x - \delta)^2 + \Delta E$ for ground and excited electronic states, respectively. Force constants are given by $k_{g,e} = (2\pi\nu_{g,e})^2 m_{g,e}$. At 4.2 K experimental absorption and luminescence peak at 2.05 and 0.96 eV, respectively.

This simple picture can reproduce the experimental findings with fair accuracy. Any improvement would require a more complex model. In particular, in addition to effects related to the breathing mode of the cation octahedron, one should take into account that ground and excited states correspond also to different equilibrium values of the configuration coordinate of the E_{1g} (Γ_3^+) stretching mode of the octahedron [1]. The corresponding displacement of the cations is expected to be 1 order of magnitude smaller than for the Γ_1^+ mode [5]. Furthermore, activation of the T_{2g} (Γ_5^+) mode can be expected for appropriate orientation of the pump field whose amplitude, to the best of our knowledge, is not known. In order to analyze the role of these modes we measured the transient transmission change for different orientations of the pump and probe polarizations. Our analysis indeed confirms that the dominating modes have A_{1g} (Γ_1^+) symmetry; i.e., within experimental errors their amplitudes are independent of both pump and probe orientations. We did observe some additional structures at lower frequencies, but a symmetry assignment was hindered by our noise level of about 2% of the maximum transmission change.

In conclusion, we have presented the single-electron coherent dynamics following ultrafast optical excitation in additively colored KBr. This observation is made possible by the strong localization of F center electronic states. Our time-resolved analysis demonstrates the strong coupling of the optical transition of the color center electron to the localized A_{1g} breathing mode of the lattice. By a temperature-dependence absorption and PL study we were able to assign the observed oscillation frequencies to ground and excited vibronic states and obtained the complete determination of the configuration coordinate diagram.

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