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Femtosecond Optical Studies of Intercalated Fullerenes

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Femtosecond pump-probe studies provide a sensitive characterization tool for the study of ultrafast relaxation processes in intercalation compounds, more specifically in the alkali metal intercalated fullerenes K_3C_{60} and Rb_3C_{60}. Films of these materials were excited with femtosecond optical pulses and the induced transient changes in the optical properties were then monitored with a delayed probe pulse, revealing excited state relaxation dynamics occurring on a picosecond or femtosecond time scale. Room temperature measurements with a 20 fs pulse show extremely long-lived coherent phonon oscillations of the *Ag* molecular mode at ~492 cm^{-1}. Information about a highly damped vibrational mode involving an alkali metal cation beating against a C_{60} anion has also been obtained. Low temperature measurements were also performed, yielding new information about the quasi-particle dynamics in the superconducting state and across the normal to superconducting phase transition. These results are discussed in the context of intercalation compounds based on carbon.

Keywords: Ultrafast dynamics; pump-probe; fullerides; superconductivity

INTRODUCTION

Although intercalation compounds based on carbon have been studied for many years, it is only recently that fast optical techniques have become available for the study of fast relaxation processes in this class of materials. Since intercalation compounds exhibit so many unique properties, it is not surprising that their fast optical responses are also unusual.

In this paper we summarize two unusual fast relaxation phenomena in crystalline C_{60} doped with alkali metals. Neither of these phenomena have previously been reported in intercalation compounds. The first involves the coherent excitation of optical phonons and their subsequent decay. The second involves a comparison between the decay of a fast electronic excitation in the normal and superconducting states.

To excite coherent phonons, the excitation pulse duration must be less than half the oscillation period of the phonon. This requirement imposes severe restrictions on observations in graphite where, because the force constants are large and the ion masses are low, the dominant phonons occur at high frequencies, corresponding to short periods. However, the radial breathing mode in fullerenes (C_{60}) has a frequency of $497\,cm^{-1}$, corresponding to a period of 67 fs. Such phonons can be successfully excited by 20 fs pulses produced by a mode-locked Ti:sapphire laser [1]. The A_g symmetry of this mode further promotes its observation [2]. The other phonon in C_{60} with A_g symmetry, i.e., the pentagonal pinch mode, has too high a frequency ($1467\,cm^{-1}$) and too short a period (23 fs) to be studied quantitatively with a 20 fs optical pulse.

RESULTS

Typical pump-probe reflectivity results for K_3C_{60}, obtained with a 20 fs mode locked Ti:sapphire pulse source, operating at 800 nm (1.56 eV) for both pump and probe, are shown in Fig. 1. The signal shows an instantaneous response centered at zero time delay, which we believe is caused by a two-photon absorption. This fast decay is followed by a slower 0.7 ps and 1.0 ps exponential decay for K_3C_{60} (see Fig. 1) and Rb_3C_{60} (not shown), respectively [1]. Superimposed on this decay are tiny coherent phonon oscillations with a $(\Delta R/R)$ modulation amplitude of only $\pm 10^{-7}$. These tiny oscillations are due to coherent excitation of the $A_g(1)$ molecular vibrational mode by the impulsive laser pulse. These oscillations decay very slowly and are still observable at delay times between the probe and pump pulses greater than 10 ps, as shown in the three insets to Fig. 1. The Fourier transform of the pump-probe response for K_3C_{60} is shown in the inset to Fig. 1, and the mode frequency thus obtained ($492.5 \pm 3.5\,cm^{-1}$) is in good agreement with direct measurement of this mode ($497\,cm^{-1}$) by Raman spectroscopy [3]. The results for the coherent phonon frequency, linewidth and decay times for Rb_3C_{60} films are nearly the same as for K_3C_{60} [1].

To analyze the pump-probe data in more detail, we selectively filtered out the oscillatory part of the pump-probe data, by fitting the $\Delta R/R$ data in Fig. 1 with an instantaneous response a modulated by the autocorrelation function $g(t)$, an exponential decay b and a step response c:

$$\Delta R(t)/R = \int_{-t}^{\infty} d\xi g(t+\xi)\,[a\delta(\xi) + b\exp(-\xi/\tau) + c]\,. \qquad (1)$$

The fit thus obtained was then subtracted from the $\Delta R/R$ data, and the remaining oscillatory response was low-pass and high-pass filtered with cut-off frequencies at $250\,cm^{-1}$ and $1000\,cm^{-1}$. The resulting trace was used to extract the amplitude $A(t)$ and phase $\varphi(t)$ of the $A_g(1)$ oscillations $\Delta R(t)/R = A(t)\cos[\omega t - \varphi(t)]$, where ω is the angular frequency of the coherent phonon and the amplitude $A(t)$ and phase $\varphi(t)$ are assumed to vary only slowly with time delay t between the pump and probe pulses. Fits to the data yielded a phonon dephasing time of $\sim$5 ps for both K_3C_{60}

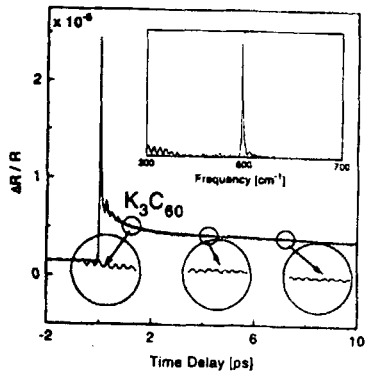

Figure 1: Coherent phonon oscillations in K_3C_{60} at 300K. The pump-probe data were taken in terms of a change in reflectivity ΔR induced by a laser pulse of 20 fs duration. A single laser wavelength (800 nm or 1.56 eV) was used for both the pump and the probe. The three circular insets show the very small oscillations in ΔR superimposed on the decay. The rectangular inset shows the Fourier transform power spectrum for the small oscillatory component, yielding a sharp peak at $492.5 \pm 0.25\,\mathrm{cm}^{-1}$ for K_3C_{60}.

and Rb_3C_{60}, thus allowing us to observe more than 200 oscillations during our observation window. The very slow decay times for the coherent phonon excitations indicate that these $A_g(1)$ radial breathing mode oscillations are almost entirely unaffected by the presence of alkali metal atoms in the intercalation compound, and the results further show only a very weak dependence on the specific alkali metal species that is present.

In addition to the long-lived fast oscillations evident in Fig. 1, the pump-probe data obtained for the K_3C_{60} and Rb_3C_{60} samples in Fig. 2 also show a fast-decay lower frequency component. The traces in Fig. 2 below the pump-probe data for K_3C_{60} and Rb_3C_{60} show the oscillatory response obtained for the first 2.5 ps after the pump excitation pulse. For this lower frequency oscillation, we obtain an approximate frequency of 4.5 ± 1 THz ($150\,\mathrm{cm}^{-1}$) for both K_3C_{60} and Rb_3C_{60}, and dephasing times of 0.25 ps for K_3C_{60} and 0.35 ps for Rb_3C_{60}. The oscillation frequencies for this heavily damped mode cannot be determined more accurately because of the fast decay time for this mode, nor can this mode be detected easily by Raman scattering, because of its very large linewidth. It is believed that vibrational modes involving the alkali-metal and the C_{60} molecule fall in the frequency range from $50\,\mathrm{cm}^{-1}$ to $150\,\mathrm{cm}^{-1}$, and the observed pump-probe response might be due to such a vibration. If the oscillation involves the alkali metal, the higher mass of rubidium ($m_{\mathrm{Rb}} = 85.47$) compared with potassium ($m_{\mathrm{K}} = 39.09$) should result in a lower frequency $\omega_{\mathrm{Rb}}/\omega_{\mathrm{K}} = 0.7$. However, a stronger interaction between the rubidium and the C_{60} due to the larger size of the Rb ion could result in a higher frequency for the Rb_3C_{60} mode than for K_3C_{60}. Furthermore, since the excited electrons are not expected to be strongly localized, the phonon excitation could disperse quickly, resulting in a rapid dephasing of the phonon mode.

Thus fast optics provides a method for probing the strong interaction

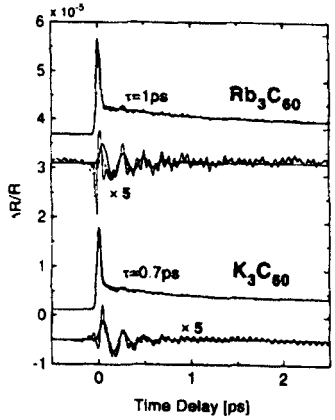

Figure 2: The pump-probe traces obtained for K_3C_{60} and Rb_3C_{60}. The scaled data traces (× 5) below were obtained by subtracting off the δ-function and exponential components from the measured data and then filtering out the $A_g(1)$ mode. Fits to fast decay sinusoids are also shown (thick solid curves).

between the intercalate and host species that is not readily accessible by spectroscopic methods in the frequency domain. For the case of the M_3C_{60} compounds, as well as in alkali metal intercalated graphite, the intercalation process gives rise to a strong electron-phonon coupling, which results in superconducting behavior. Fast optical techniques can provide a powerful probe of the fast dynamical processes in superconducting systems. Because of the low values of T_c in graphite intercalation compounds (GICs), it is not feasible to study fast dynamical processes in GICs across the normal-superconducting transition. However, it is possible to carry out such experiments in K_3C_{60} ($T_c = 18\,\mathrm{K}$) and Rb_3C_{60} ($T_c = 28\,\mathrm{K}$) which have higher T_c values, and the results of such experiments are reported here.

In Fig. 3 we plot the change of the reflectivity $\Delta R/R$ for K_3C_{60} at a series of nominal temperatures above and below the superconducting phase transition of T_c=18 K for pump and probe wavelengths of 775 nm and 2 μm, respectively [2]. The curves are not corrected for the average heating of the lattice by the laser, which is estimated to be on the order of 1 K. A three- to five-fold increase in $(\Delta R/R)$ is observed for both K_3C_{60} and Rb_3C_{60} when the samples are cooled down from room temperature to about 100 K, and this result is consistent with the decreased electronic specific heat at low temperature. The normal state decay time increases by about a factor of two for both K_3C_{60} and Rb_3C_{60} as the temperature is lowered from room temperature to about 50 K. This response is typical for metallic systems in which non-equilibrium carriers are cooled via inelastic collisions with phonons [4].

The $\Delta R/R$ results in Fig. 3 have been analyzed in terms of the relation

$$\Delta R(t)/R = \int_{-t}^{\infty} d\xi g(t+\xi)[1-\exp(-\xi/\tau_R)]\Big[b_1\exp(-\xi/\tau_1) + b_2\exp(-\xi/\tau_2) + c\Big] \quad (2)$$

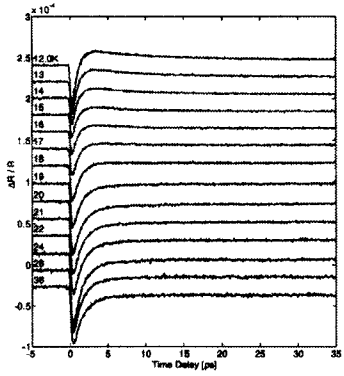

Figure 3: Ultrafast optical $\Delta R/R$ response *versus* time delay between the pump and probe pulses in K_3C_{60} at various nominal temperatures above and below T_c=18 K. Pump and probe wavelengths of 775 nm and 2 μm, respectively, were used for the $\Delta R/R$ measurements. The fitting of the $\Delta R/R$ measurements to Eq. (2) using temperature-dependent parameters is given.

where $g(t)$ is the measured cross-correlation function and the parameters are: (i) A fast exponential decay time (τ_1) on the order of one ps that represents the fast exponential decay associated with the thermal relaxation of the excited electrons via collisions with phonons. This response is observed in both the normal and superconducting phases. (ii) A second slower exponential decay time (τ_2) accounts for the slow decay present only below T_c. (iii) A step function (c) matched to the residual level accounts for long-lived responses ($\tau > 100$ ps). (iv) A rise time (τ_R) models the considerably slower response to the pump pulse around the transition temperature. The δ-function term [see Eq. (1)] observed at room temperature was found to be negligible at low temperatures.

Our pump-probe $\Delta R(t)/R$ results suggest the following picture for the fast dynamics in these intercalation compounds. The pump pulse delivers energy per unit volume ΔE to the sample near its surface by introducing holes relatively deep in the conduction band by interband transitions. The energy is quickly taken up by the conduction electrons, since the lattice cannot respond on the femtosecond time scale of the pump pulse. The electron distribution is raised to a slightly elevated temperature T_E, determined by the electronic specific heat, in a time on the order of a few femtoseconds. The change in electron temperature modifies the dielectric properties of the sample, which results in an impulsive change $\Delta R(0)/R$ in the reflectivity at the probe frequency. As the excess energy is gradually transferred to the lattice through the electron-phonon coupling, $\Delta R(t)/R$ returns to nearly zero in a decay time τ_1 of the order of picoseconds. The return of carriers from higher bands occurs after a longer time.

When the sample becomes superconducting, additional interactions come into play. The energy ΔE delivered to the K_3C_{60} and Rb_3C_{60} samples is almost the same, since the optical properties of K_3C_{60} and Rb_3C_{60} are essentially unchanged at the pump and probe optical frequencies. The electron

temperature T_E is raised by an amount ΔT above the lattice temperature T by the arrival of the pump pulse. The electron system begins to cool down rapidly at a rate determined by the fast relaxation time τ_1. At some point during this process, a Cooper pair bottleneck sets in, trapping excess electrons above the superconducting gap. The electrons continue to cool rapidly via interaction with acoustic phonons until a quasi-equilibrium is reached, in which the electron distribution has returned to nearly the lattice temperature T, but with an excess of normal electrons trapped above the gap, and a quasi Fermi level shifted down in energy because of the missing electron population below the gap. Thereafter, the recombination of electrons to form Cooper pairs continues at a rate determined by the slow relaxation time τ_2, while the entire electron distribution continues to cool toward the lattice temperature T, until true equilibrium is reached, with the disappearance of the excess electron population above the gap, and the return of the Fermi level to its original value.

The fitting parameters b_1 and b_2 in Eq. (2) are, respectively, the fast and slow decay contributions to $\Delta R(t)/R$; while τ_1 and τ_2 are, respectively, the times characterizing electron-phonon cooling and Cooper pair recombination. The small rise time fitting parameter τ_R represents a delay due to Cooper pair bond breaking, or the delay time before the slow component due to the Cooper pairing bottleneck sets in.

The observations for the temperature dependence of the slow decay time $\tau_2(T)$ in K_3C_{60} and Rb_3C_{60} are quite different than for typical BCS superconductors. The reason for this anomalous behavior is not understood.

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