

# Coherent phonons in fullerites with femtosecond laser excitation

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The excitation of coherent phonons in the frequency range 10–400  $\text{cm}^{-1}$ , including ungerade phonons, in a wide spectral probe range  $\hbar\omega_{\text{probe}} = 1.78\text{--}2.34$  eV, was observed by femtosecond laser spectroscopy according to the time-dependent changes in the optical density of a  $\text{C}_{60}$  film. The spectral dependence of the photoinduced response makes it possible to separate selectively the relaxation of electrons in different bands. The possibility of reversible polymerization in the excited state is discussed. © 1995 American Institute of Physics.

Femtosecond laser spectroscopy makes it possible to study the development of different ultrafast processes in solids in real time. This provides a unique possibility to determine the interaction constants directly, to observe the change in the electronic spectrum as new phase arises, and to see other processes (see, for example, Refs. 1 and 2).

In the present work the method of femtosecond laser spectroscopy is used to investigate the nature of the excited state of fullerite and the relaxation of nonequilibrium charge carriers in the femtosecond range. The use of 50-fs excitation and probe pulses made it possible to observe the excitation of coherent phonon vibrations in  $\text{C}_{60}$  according to the evolution of the photoinduced response in the femtosecond time range. Analysis of the spectrum of these vibrations showed that specifically ungerade coherent phonons can be excited. These spectra also show that reversible formation of a new phase in the excited state is possible. The spectral dependence found for the spectrum of the coherent phonons opens up the possibility of selectively separating the relaxation of different groups of excited electrons.

The experimental sample, which consisted of a  $\text{C}_{60}$  film on a quartz substrate, was excited by 50-fs optical pulses with an intensity of  $2.6 \times 10^{12}$   $\text{W}/\text{cm}^2$  at the frequency  $\hbar\omega_{\text{pump}} = 2.58$  eV. The diameter of the excitation spot was equal to 100  $\mu\text{m}$ . The transmission coefficient was investigated with a 50-fs probe pulse in the range 1.78–2.34 eV. The diameter of the probe spot was equal to 50  $\mu\text{m}$ . The repetition frequency of the

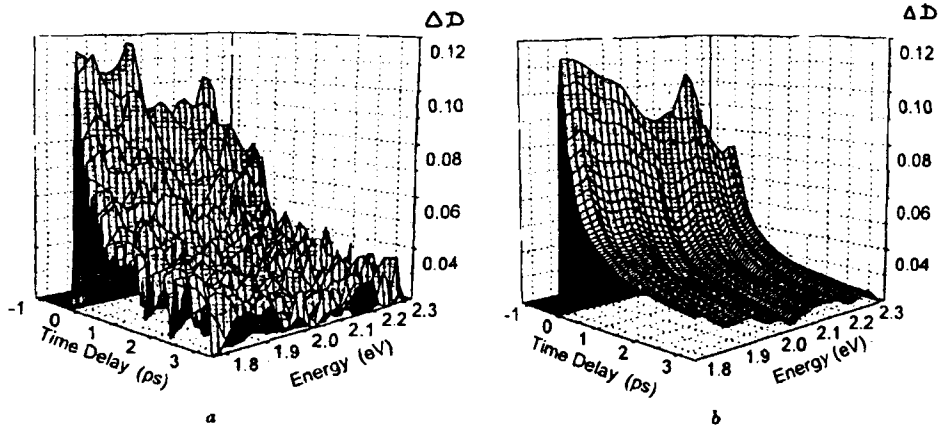


FIG. 1. a—Experimental time dependence of the transmission spectra of a fullerene film; b—time dependence obtained for the transmission spectra by fitting the experimental data.

excitation and probe pulses was  $\approx 1$  Hz. The delay was changed with a step of 27 fs. The maximum delay in the present experiment reached  $\approx 4$  ps. The film quality was monitored in the course of the experiment. No visible irreversible changes were observed in the sample after the experiment.

The temporal dynamics of the measured optical-density spectra  $\Delta D_{\text{exp}}(\omega, t)$  is shown in Fig. 1. The spectral dependences of the relaxation rates  $\tau_1 = 450 \pm 150$  fs and  $\tau_2 \sim 30 \pm 10$  ps of the optical density were determined by fitting the computed curves  $\Delta D_{\text{fit}}(t)$  to the experimental kinetic dependences. It was found that  $\tau_1$  depends on the wavelength of the probe pulse:  $\tau_1 \approx 370 \pm 70$  fs in the range  $1.78 < \hbar\omega < 2.1$  eV and  $\tau_1 = 540 \pm 90$  fs in the range  $2.1 < \hbar\omega < 2.35$  eV. The average value of  $\tau_1$  at low energies agrees well with the value  $\tau_1 \approx 400$  fs obtained in Ref. 3 at the probe frequency  $\hbar\omega = 2$  eV with an excitation pulse with an energy density of  $\sim 100$  mJ/cm<sup>2</sup>.

The use of ultrashort pulses made it possible to observe coherent vibrations which modulate the change in the permittivity and change the intensity of the transmitted or reflected light. The characteristic lattice and intramolecular vibrational frequencies in the frequency range  $10\text{--}400$  cm<sup>-1</sup> were determined with a resolution of approximately  $10$  cm<sup>-1</sup> by Fourier analysis of the time dependence of the change in the optical density [ $\Delta D_{\text{exp}}(t) - \Delta D_{\text{fit}}(t)$ ]. It was found that coherent phonons are excited in the entire spectral range of the probe  $\hbar\omega_{\text{probe}} = 1.78\text{--}2.34$  eV. In addition, the distribution of the intensities of the coherent phonons depended on the probe wavelength (see Fig. 2). For example, vibrations of the fundamental mode  $H_g(1)$  with the frequency  $\approx 270$  cm<sup>-1</sup> are clearly observed in the low-frequency range, while the upper triplet of this mode with frequency  $290$  cm<sup>-1</sup> is observed in the high-frequency range. Moreover, vibrations with the frequency  $105$  cm<sup>-1</sup> are observed only in the high-frequency range. To determine the frequencies of the coherent phonons, which are excited efficiently in the entire spectral range probed in the experiment, we multiplied all Fourier spectra, i.e., we calculated the geometric-mean spectrum of the vibrations (see Fig. 3):

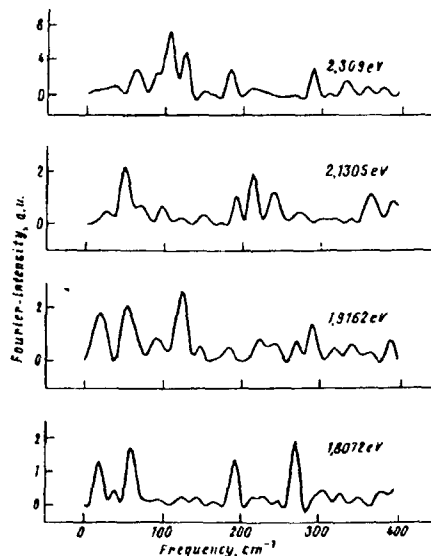


FIG. 2. Fourier spectrum of the coherent vibrations for four different probe frequencies.

$$f_{\text{tot}}(\nu) = \left( \prod_{i=1}^n f(\omega_i, \nu) \right)^{1/n},$$

where  $\omega_i$  is the  $i$ th probe frequency. As a result, it was found that vibrations with the frequencies  $\sim 27, 56, 90, 125, 194, 290,$  and  $357 \text{ cm}^{-1}$  (the dominant frequencies in this spectral range) are excited in the sample. Vibrations with the frequencies  $145, 227, 252, 272, 325,$  and  $386 \text{ cm}^{-1}$  and a number of other modes are observed with lower amplitudes. A characteristic feature of the Fourier spectra is that not only the known (see Refs. 4 and 5 and the literature cited there) lattice and intramolecular phonon modes [27, 56,

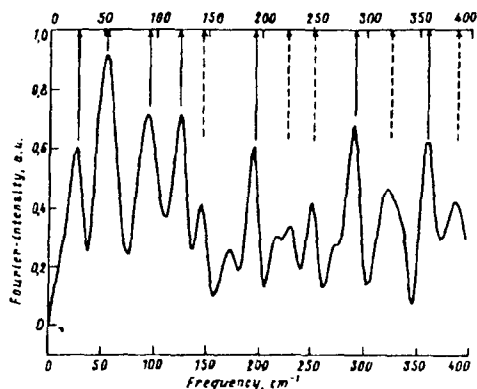


FIG. 3. Geometric-mean Fourier spectrum of the coherent vibrations.

90, and  $145\text{ cm}^{-1}$ —lattice modes; 252, 272, and  $290\text{ cm}^{-1}$ —the split  $H_g(1)$  intramolecular mode] but also the modes characteristic of the dimerized and/or polymerized states<sup>6-8</sup> ( $125$ ,  $227$ ,  $325$ , and  $386\text{ cm}^{-1}$ ) are observed in them.

Under the conditions of the present experiment, the absorption of photons with energy  $\hbar\omega_{\text{pump}} = 2.58\text{ eV}$  corresponds to the transitions  $h_u \rightarrow t_{1u}$  and  $h_u \rightarrow t_{1g}$ . The optical transition  $h_u \rightarrow t_{1u}$  in  $C_{60}$  is dipole-forbidden and absorption is due to vibronic (Herzberg–Teller) mixing of the states. In the solid phase the interaction of the charge carriers with the crystal field makes the mixing of the states even stronger. As a result, in the frequency range  $\hbar\omega = 1.6\text{--}3\text{ eV}$  absorption is stronger in the solid phase than the gas phase.

Absorption in the transition  $h_u \rightarrow t_{1u}$  (to remove the parity forbiddenness) occurs with the emission of ungerade lattice and intramolecular vibrations. These vibrations will be coherent if the duration of the optical excitation pulse is shorter than the half-period of the lattice or intramolecular vibrations. Moreover, the final state is unstable with respect to Jahn–Teller transitions accompanied by the emission of intramolecular phonons with  $H_g$  symmetry. Therefore, coherent  $H_g$ -mode vibrations can also be observed in the present experiment.

An increase in the occupancies of the excited states leads to an increase in the molecular susceptibility, which in turn intensifies the intermolecular attraction. As the intermolecular interaction becomes stronger, the equilibrium distance between the molecules decreases. As a result, the formation of a new nonequilibrium crystalline phase of an orientational-glass type (re-entrant orientational freezing), as well as dimers (lattice of dimers), exciplexes, and even nonequilibrium polymerization of the lattice are possible in the excited state. The emission of low-frequency phonons occurs in the process of a transition to this state: optical lattice phonons and librions in the first case and also vibrations of dimers (polymers) in the second case. The nonequilibrium state can exist only for a very short time, since it is destroyed by the phonons emitted during the relaxation of the charge carriers.

The density of the absorbed photons in the film corresponds to approximately two phonons per molecule. Therefore, the low-frequency phonons which we observed can be associated with both of the above-indicated phases of fullerite in the excited state (we underscore the fact that no irreversible changes of the sample were observed). Since the excitation pulse is absorbed almost completely in the fullerite film, the observed vibrations cannot be associated with processes occurring in the substrate.

The fact that the coherent-phonon and the relaxation time  $\tau_1$  of the charge carriers depend on the probe wavelength indicates that electrons from different groups participate in these processes. It can be assumed on the basis of the band structure of fullerite that coherent vibrations  $h_u$  generated by electrons of the valence band are observed in the spectral range  $\hbar\omega_{\text{probe}} = 1.78\text{--}2\text{ eV}$  and coherent vibrations  $t_{1u}$  generated by electrons of the conduction band are observed in the spectral range  $\hbar\omega_{\text{probe}} = 2\text{--}2.34\text{ eV}$ . This effect makes it possible to investigate the relaxation of charge carriers which are excited in different bands. It also makes it possible to separate the contribution of coherent phonons (and their symmetry) to the relaxation of different groups of electrons and to determine directly the electron-phonon coupling constant in the separated region of the spectrum.

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