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VIBRATIONAL RELAXATION IN CRYSTALLINE BENZENE INVESTGATED BY PICOSECOND CARS

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Time-resolved CARS with picosecond resolution has been utilized to investigate the mechanism of vibrational relaxation of four internal vibrations of benzene crystal.

The method provide values for the total dephasing times T_2 of the vibrational excitations; such a time is related to the pure dephasing time T_2^* and to the population decay time T_1 through

$$(T_2)^{-1} = (2T_1)^{-1} + (T_2^*)^{-1}$$

In T_1 processes the energy is transferred from the excited state to other vibrational levels (with energy and momentum conservation); in pure dephasing T_2^* processes instead the phase of the excitation is randomized without energy exchange.

The pattern of vibrational levels in simple molecular crystals shows in many cases well isolated states, with few decay channel available. This is the case of the four benzene internal modes considered here, for which the interpretation of the relaxation mechanism is relatively simple.

Experimental. Benzene single crystals of good optical quality were grown by very slow cooling (0.2 K per hour) the liquid in a quarz cell.

In the CARS set-up, two dye lasers are pumped by a ML Ar^+ laser, delivering pulses of tunable frequency and duration about 5 ps. Time resolution is achieved by means of an optical delay on the probe beam. The intensity of the output antistokes beam is measured by means of a photon- counting system.

Results. The results at 10 K are consistent with a population decay mechanism: ν_4 and ν_{10}, for which no down-conversion decay channel is available, have much longer dephasing times (95 and 156 ps, respectively) then ν_1 and ν_9 (41 and 33 ps) which fall in a region of non-zero two-phonon density of states.

The temperature dependence of the inverse lifetimes (linewidths) of the four modes allow us to discriminate between the different sources of relaxation. In fact, a linear temperature dependence is characteristic of the three-phonon population relaxation processes; higher order multi-phonon scattering and

pure dephasing mechanisms instead give a T^{2} (or even higher power) dependence of the linewidths.

A well defined linear behavior is observed for ν_1 and ν_6, while a large contribution of higher order processes and, possibly, of pure dephasing, is evident from the results concerning ν_9. The data for ν_{10} are less conclusive, due to the limited temperature range investigated.

In figs. 1 and 2 we show the fit to the experimental data obtained by means of a simple model based on three- and four-phonon scattering mechanism.

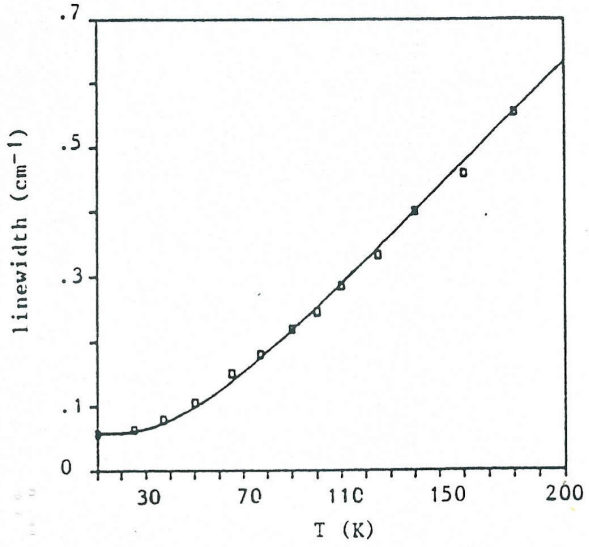

Fig. 1. Linewidth of . The line is a fit assuming Three-phonon mechanism

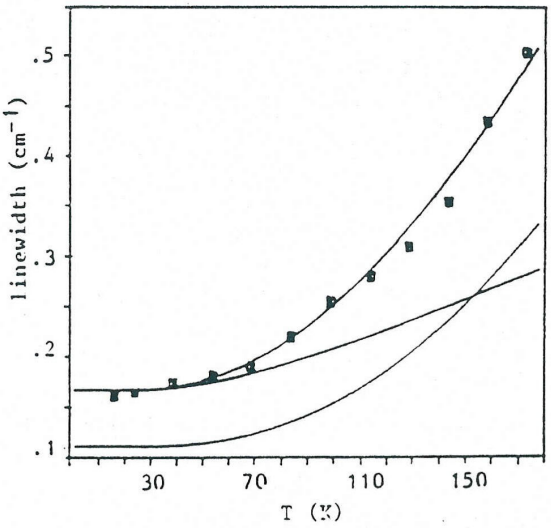

Fig. 2. Linewidth of . The lines show the contributions of three- and four-phonon processes.