Selective Vibrational Mode Excitation in Nanocarbons by Tailored Intense Near-Infrared Pulses and Subsequent Intramolecular Vibrational Energy Redistributions

K. Yamazaki, N. Niitsu, T. Nakamura, M. Kanno, H. Kono

Department of Chemistry, Graduate School of Science, Tohoku University, Japan

k-yamazaki@s.tohoku.ac.jp

Interactions between nanocarbons and intense near-infrared (NIR) pulses with femtosecond pulse length T_p and intensity $I \approx 10^{15}$ W/cm^{-2} induce structural rearrangements and fragmentations. Larrmann *et al.* experimentally showed that tailored NIR pulse trains can optimize the specific fragment yields of fullerene C_{60} [1]. We theoretically showed that selective impulsive Raman excitation of specific vibrational modes with vibrational period T_{vib} in C_{60} can be achieved by setting $T_p \approx T_{vib}/2$ and the fragmentation process depends on the vibrational modes initially excited [2]. These results suggest that intramolecular vibrational energy redistributions (IVR) leading to fragmentations depend on the pulse shape.

We performed the *on-the-fly* trajectory calculations on NIR-pulse-induced vibrational dynamics in C_{60} with various T_p to clarify the effects of the pulse shape on the IVR dynamics. We combined the time-dependent adiabatic state approach [3] and density-functional based tight-binding theory [4] for simulations. We found that exciting different vibrational modes drastically changes the IVR dynamics as in Figs. 1a and 1b even if the total vibrational energy E_{in} acquired remains the same. Exciting the $h_g(1)$ mode ($T_{vib} = 140$ fs) by setting $T_p = 70$ fs leads to the slow IVR in Fig. 1a; fast and complex IVR between the $a_g(1)$ and $h_g(2)$ modes occurs as in Fig. 1b when the $a_g(1)$ mode ($T_{vib} = 60$ fs) is enhanced by setting $T_p = 30$ fs. We will also discuss IVR dynamics in a semiconducting single-wall carbon nanotube [5].
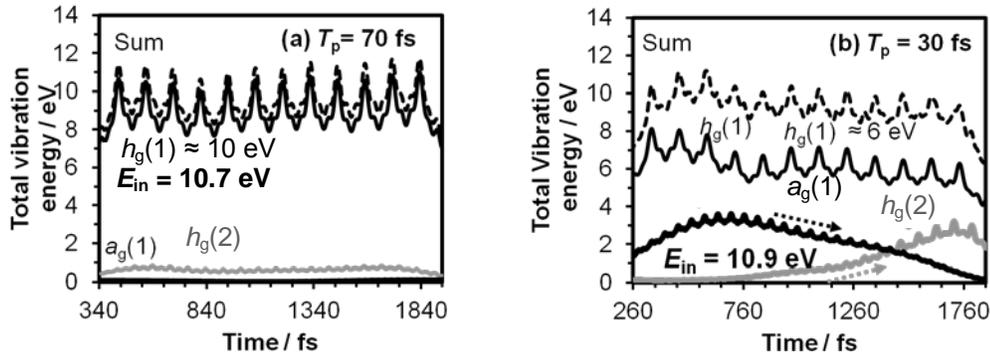
Fig. 1: Temporal change of the vibrational energies in low frequency modes of C_{60} induced by single pulse excitation ($I = 7.0 \times 10^{14}$ W/cm^2, $\lambda = 1800$ nm). (a) $T_p = 70$ fs: the $h_g(1)$ mode ($T_{vib} = 140$ fs) is mainly excited and the IVR is slow. (b) $T_p = 30$ fs: the $a_g(1)$ mode ($T_{vib} = 60$ fs) is relatively enhanced and fast IVR between the $a_g(1)$ and $h_g(2)$ modes is observed.

References: [1] T. Laarmann *et al.*, *Phys. Rev. Lett.*, 98:058302, 2007; [2] N. Niitsu, K. Yamazaki *et al.*, *J. Chem. Phys.*, 136:164304, 2012; [3] Y. Sato, H. Kono *et al.*, *J. Am. Chem. Soc.*, 125:8019-8031, 2003; [4] M. Elstner, *et al.*, *Phys. Rev. B*, 58:7260-7268, 1998; [5] Experiment: J.-H. Kim *et al.*, *Phys. Rev. B*, 86:161415(R), 2012.