Ballistic energy transport via perfluoroalkane linkers

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ABSTRACT

Intramolecular energy transport in a series of perfluoroalkane oligomers with various chain lengths of 3, 5, 7, 9, and 11 carbon atoms terminated by a carboxylic acid moiety on one end and $-CF_2H$ group on another end is studied by relaxation-assisted two-dimensional infrared spectroscopy. Perfluoroalkane oligomers adopt an extended structure with antiperiplanar orientation of the neighboring carbon atoms. The energy transport initiated by exciting the C=O stretching mode of the acid was recorded by measuring a cross-peak amplitude between the C=O stretch and the C–H bending mode as a function of the waiting time between the excitation and probing. A linear dependence of energy transport time vs. chain length is found, which suggests a ballistic energy transport mechanism. The energy transport speed, measured from the chain-length dependence of the half-rise time, $T_{1/2}$, was found to be ca. 1150 m/s, which is close to the longitudinal speed of sound in Teflon polymers.

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1. Introduction

Vibrational energy transport in molecules is important for a variety of fields, including nanotechnology, chemistry, and biochemistry. Detailed understanding of the vibrational energy transport on a molecular level and ability of manipulating its dynamics is essential for a variety of applications such as designing efficient energy transport schematics for energy signaling [1] and controlling chemical reactions [2,3] as well as providing efficient cooling in microscopic and macroscopic molecular systems, such as nanowires [4] and optical limiters.

The energy transport in molecules via linkers lacking periodic structure, and therefore lacking delocalized vibrational states over the linker, is expected to be diffusional governed by intramolecular vibrational energy redistribution (IVR) process. Quantum numbers (i,j,k) of two or more vibrational modes change in an IVR event, e.g. $(i,j,k) \rightarrow (i-1,j+1,k+1)$, which requires anharmonic coupling of the involved modes. The IVR process results in propagation of vibrational energy in the molecule because the modes involved in the exchange have different spatial locations [5]. The energy transport in molecules featuring periodic linker with vibrational states delocalized over the linker may occur ballistically via free-propagating vibrational wavepackets [6].

Both regimes of energy transport have been intensively studied theoretically [4,7–18]. Recent development of time-resolved spectroscopic methods, including two-dimensional infrared (2DIR) [19,20], relaxation-assisted 2DIR (RA 2DIR) [21,22], and combined infrared-Raman [23,24] spectroscopies opened an avenue for studying experimentally the energy transport in molecules. While diffusive energy transport was observed in many molecular systems [21,25–29] and for various amounts of excess energy [30,31], there are only a few reports on ballistic energy transport. The energy transport following electronic relaxation was observed with nearly constant velocity through alkane chains up to 6 carbon atoms [32,33]. A dynamic transition observed in a peptide helix was attributed to a switch between the diffusive and ballistic energy transfer mechanisms [34]. Energy propagation along alkane chains forming a monolayer on a gold surface was found to be ballistic [35].

Very recently, an efficient, constant-speed, long range energy transport was found in the end-labeled polyethylene glycol (PEG) oligomers of different size of 0–12 repeating PEG units [1,36]. The experiments were performed using the dual-frequency thee-pulse RA 2DIR heterodyned photon-echo method. The energy transport was initiated by excitation with IR photons the azido group (the tag, $\sim$2100 cm^{-1}) attached to one end of the compound. C=O stretching modes of succinimide ester attached to another end of the oligomer served as a reporter of the energy transport process. The energy transport towards the reporter results in excitation of the low-frequency modes at the reporter site, which cause a shift of the reporter mode frequency due to their anharmonic coupling to the reporter. The frequency shift of the reporter mode, measured as a tag/reporter cross peak amplitude, is an indicator of the amount of excess energy delivered to the reporter site at different waiting times (T) after excitation. The more excess energy arrives to the reporter site the larger is the shift of the reporter mode frequency. The energy transport time, T_{max}, measured as the waiting time at which the maximal frequency shift of the reporter is observed, was found to depend linearly on the chain

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length, resulting in the transport speed of 550 and 450 m/s in chloroform [1] and CCl$_4$ [36], respectively. An exponential dependence of the amount of energy delivered to the reporter site on the chain length is found with the characteristic decay distance of ca. 15.7 Å [36], which also suggest a ballistic transport mechanism. Although PEG oligomers adopt coiled conformations in solution, the vibrational states of the chain for such conformations, computed for PEG4, were found largely delocalized over ca. 2.6–3.6 PEG units, where the larger delocalization is found for the lower frequency modes. These values correspond to the delocalization lengths of 11–16 Å; notice that the larger number matches the characteristic decay distance of 15.7 Å, suggesting that the lower frequency modes (<600 cm^{-1}) likely facilitate the transport.

In this work we report the first measurements of the energy transport via perfluoroalkane chains. The perfluoroalkane oligomers are known to adopt a rod-like conformation in solution [37,38]. The C=O stretching mode of the carboxylic acid terminating moiety served as a tag while the CH bending mode of another CF$_2$H terminal moiety served as a reporter for RA 2DIR measurements.

2. Experimental details

2.1. Heterodyned dual-frequency 2DIR measurements

Details of the dual-frequency 2DIR setup with heterodyned detection can be found in Refs. [39,40]. Briefly, two in-house-built optical parametric amplifiers followed by difference-frequency generation units were used to generate independently frequency-tunable mid-IR pulses of ca. 150 fs pulse duration. One of the beams was split into two equal parts, each of ca. 1.2 μJ energy, which served as excitation pulses interacting with the sample (k_1 and k_2). A small portion (~4%) was split from the second beam to serve as a local oscillator (LO) for heterodyned detection, while the main part (~1.1 μJ) was used as a third beam (k_3) interacting with the sample. The spectra of the k_1 and k_3 pulses were tuned to ca. 1773 and 1380 cm^{-1}, respectively. A third-order signal generated by the sample was picked at the phase matching direction ($-k_1 + k_2 + k_3$), mixed with the LO, which was delayed by the time delay t, and detected by an MCT detector (Infrared Associates). The delays between the first and the second and the second and the third pulses are referred to as the dephasing time, τ, and the waiting time, T, respectively. Linear-motor translation stages (PI Inc.), equipped with hollow retroreflectors, were used to control the delays between the IR pulses. The positions of all translation stages during the experiments were accurately measured with an external interferometric system based on a continuous-wave HeNe laser [28]. 2DIR spectra were obtained by a double Fourier transformation of the $M(\tau,t)$ data sets.

The waiting time dependences for the relaxation-assisted 2DIR measurements were measured by acquiring 2DIR $F(t,T)$ data sets while keeping the dephasing time (τ) constant at 167 fs. The $F(t,T)$ data sets were then Fourier transformed along the t direction and presented as a set of one-dimensional ω_t spectra at various T values. The experimental conditions for acquiring the $F(t,T)$ data sets were selected so that a single peak along ω_τ, that at ca. 1774 cm^{-1}, dominated the 2DIR spectra. The cross-peak amplitude at each T delay was determined by integrating the ω_t absolute-value peak in the vicinity of its maximum (at ca. 50% level) and subtracting the integrated and normalized background. The resulting cross-peak amplitudes were plotted as a function of the waiting time, T. To suppress completely the C=O diagonal peaks at ca. 1774 cm^{-1}, which were generated due to a tail of the k_3 pulse spectrum, a long-wave-pass filter was used in the k_3 beam to cut off the frequencies above 1550 cm^{-1}.
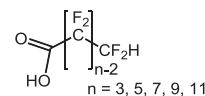
Scheme 1. Structure of Cn compounds.

Table 1
Experimental conditions in 2DIR measurements.

Compound	Concentration, M	Spacer, μm	Temp, °C
C3	0.56	50	23.5 ± 0.6
C5	0.59	50	23.5 ± 0.6
C7	0.29	100	23.5 ± 0.6
C9	0.25	100	34.0 ± 0.5
C11	0.20	100	57.0 ± 0.5
C5	0.59	50	52.0 ± 0.5
C7r (–CF$_3$)	0.29	100	31.0 ± 0.5

2.2. Sample preparation

Perfluoroalkane compounds with chain lengths of 3, 5, 7, 9, and 11 carbon atoms, featuring acetic acid moiety attached to one end of the chain and CF$_2$H group at the other end of the chain were purchased from SynQuest Laboratories Inc. (Scheme 1). The specified compounds, referred here as C3, C5, C7, etc., and the reference compound similar to C7 but terminated with the CF$_3$ group (C7r, SynQuest Laboratories Inc.) instead of CF$_2$H in C7 were dissolved in deuterated chloroform (Cambridge Isotope Laboratories, 99.96%). The infrared spectroscopic measurements were performed in a sample cell made of two CaF$_2$ wafers separated by a Teflon spacer (50 or 100 μm thick). The concentrations of the samples are shown in Table 1. Due to poor solubility of the bulkier compounds, the 100 μm thick spacer was used for the C7, C9, C11, and C7r samples, which allowed using lower concentrations of ca. 0.2 M (Table 1). Additional heating was required to remove clustering of the sample in solution for the C9, C11, and C7r samples (Table 1). The temperature of the sample was set by an electric heating element and measured continuously during the 2DIR measurements by a thermocouple placed in a direct contact with the center of the sample cell window. Interestingly, the clustering was not always apparent by an eye inspection but obvious from the level of the light scattering when placed into the 2DIR apparatus. Disappearing of this additional scattering down to a common, very low level was used as a criterion for setting the temperature. All other experiments were performed at room temperature of 23.5 ± 0.6 °C. A comparison of the waiting time dynamics at room temperature and at elevated temperature of 52.0 ± 0.5 °C was performed for the C5 compound.

2.3. Quantum chemistry calculations

Normal mode harmonic calculations were performed for all Cn compounds using the laboratory cluster and the Gaussian 09 software package [41]. The calculations were done using the density functional theory (DFT) method with B3LYP functional and 6-311+G(d,p) basis sets under vacuum. For the C7 compound the calculations were performed for two conformations: one structure featured a fully ordered chain where all neighboring carbon atoms adopt antiperiplanar orientation, while another structure had two gauche carbon sites in the chain.

3. Results

The DFT calculations with the normal-mode analysis performed on the C7 compound indicated that the C–H bending mode of the